学位論文

Synthesis, Structure and Properties of Sandwich-Type Fullerene-Transition Metal Complexes

（サンドイッチ型フラーレン-遷移金属錯体の合成，構造および性質）

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Chapter 1   General Introduction

Fullerene[1]-transition metal complexes have received much attention, since these complexes could have the advantages of both fullerene and transition metal moieties and could act as functional molecules. Such interests are mainly based on the bulky spherical structure[2] of fullerene, the catalytic activities[3] of transition metal moieties, and the electronic and magnetic properties[4] of both fullerene and transition metal units. For these reasons, many fullerene-transition metal complexes have been synthesized.[5] These complexes consist mainly of three types of structures as shown below (Figure 1-3).

[1] (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

[2] Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160.

[3] (a) Ivanova, V. N. *J. Struct. Chem.* **2000**, *41*, 135. (b) Goldshleger, N. F. *Fullerene Sci. Technol.* **2001**, *9*, 255. (c) Fukuzumi, S.; Ohtsu, H.; Ohkubo, Kei.; Itoh, S.; Imahori, H. *Coord. Chem. Rev.* **2002**, *226*, 71. (d) Meijer, M. D.; van Klink, G. P. M.; van Koten, G. *Coord. Chem. Rev.* **2002**, *230*, 141.

[4] (a) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075. (b) Rosseinsky, M. J. *Chem. Mater.* **1998**, *10*, 2665.
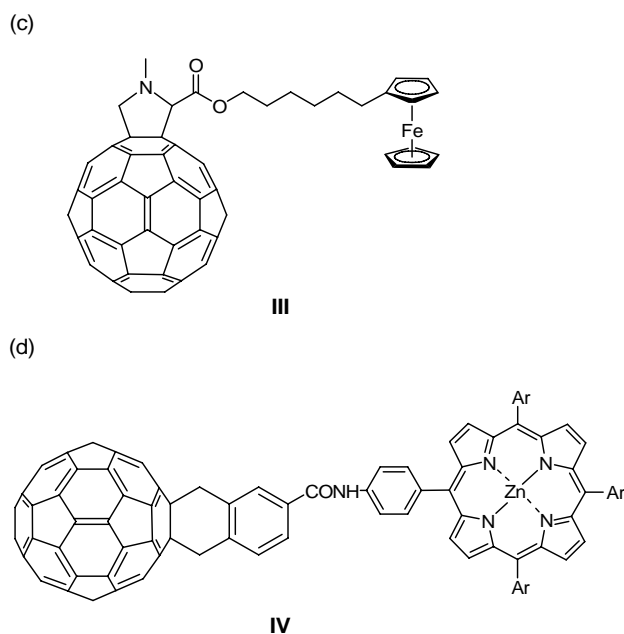
[5] (a) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123. (b) Mathur, P.; Mavunkal, I. J.; Umbarkar, S. B. *J. Clust, Sci.* **1998**, *9*, 393.

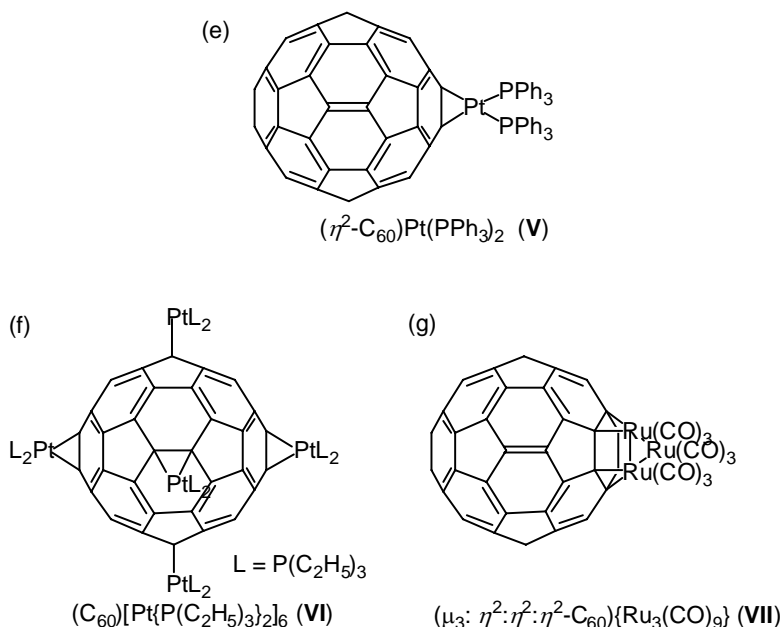1. Cocrystals between fullerene and transition metal complexes.
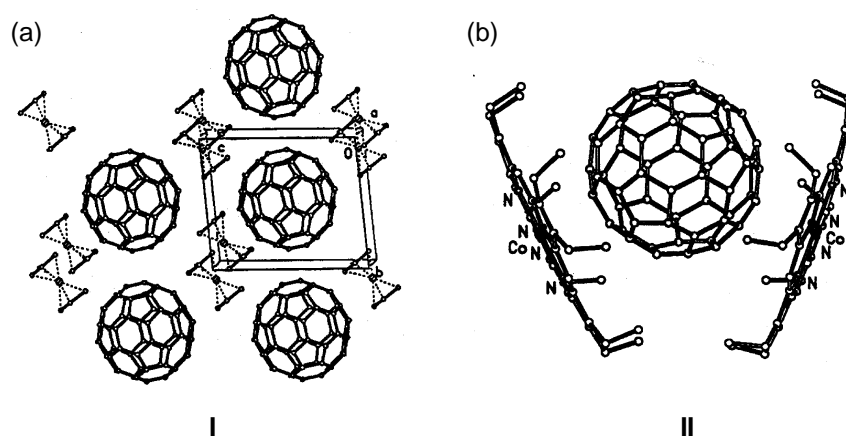
Figure 1. (a) Cocrystals of fullerene C_{60} and ferrocene. (b) Cocrystals of fullerene C_{60} and cobalt(II) octaethylporphyrin.

2. Complexes with tethers to connect fullerene and transition metal units.

Figure 2. (c) Fullerene-linkage-ferrocene complex. (d) Fullerene-linkage-porphyrin complex.

3. Fullerene-metal complexes with direct connections between fullerene and transition metal moieties.

(e)

$(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ (**V**)

(f)

$L = P(C_2H_5)_3$

$(C_{60})[Pt\{P(C_2H_5)_3\}_2]_6$ (**VI**)

(g)

$(\mu_3\text{: }\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})\{Ru_3(CO)_9\}$ (**VII**)

Figure 3. (e) Mono-nuclear platinum complex. (f) Hexa-nuclear platinum complex. (g) Tri-nuclear ruthenium cluster complex.

In view of its oxidation potential, ferrocene is incapable of reducing C_{60} to the corresponding anion. By recrystallization of C_{60} and ferrocene, cocrystals $C_{60} \cdot 2(FeCp_2)$ (**I**)[6] can be obtained (Figure 1). While cocrystals $C_{60} \cdot 2(FeCp_2)$ (**I**) have van der Waals contact between ferrocene and fullerene, there is no electronic communication between C_{60} and ferrocene as expected. By mixing C_{60} and cobalt(II) octaethylporphyrin ($Co^{II}(OEP)$) in solution, cocrystalline

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[6] Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1764.

precipitates $C_{60} \cdot \{Co^{II}(OEP)\} \cdot CHCl_3$ (**II**) [7] were obtained (Figure 1). X-ray crystallographic studies revealed that the cobalt atom is not coordinated to any part of the fullerene molecule. Namely, the distances between the cobalt atoms and adjacent carbon atoms are in a range of 2.7-2.9 Å, which is too long to represent any chemical bonding between the cobalt atoms and adjacent carbon atoms of fullerene. However, it is possible that there is some charge transfer between the two components.

As the example in Figure 2 (**III**[8] and **IV**[9]), there are fullerene-transition metal complexes bearing a tether to connect fullerene and a transition metal. In the fullerene-linkage-ferrocene type molecule **III**, the lifetime of photoinduced charge separation is 2.5 μs. Complex **IV** was synthesized as an artificial photosynthetic model. It was found that the rate of charge recombination of **IV** caused by photoinduced charge separation became smaller than that of the corresponding quinone-linkage-porphyrin molecule.

Fullerene can coordinate in an η^2-fashion to a metal atom [Figure 3, complexes $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ (**V**) [10], $(C_{60})[Pt\{P(C_2H_5)_3\}_2]_6$ (**VI**) [11] and

[7] Costa, D. A.; Olmstead, M. M.; Balch, A. L. Unpublished results.

[8] Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974.

[9] (a) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771. (b) Imahori, H.; Hagiwara, K.; Akiyama, T.; Taniguchi, S.; Okada, T.; Sakata, Y. *Chem. Lett.* **1995**, 265.

[10] (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. (c) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807. (d)

(μ^3-η^2,η^2,η^2-C_{60})$Ru_3(CO)_9$ (**VII**)[12]]. By mixing of C_{60} and $(Ph_3P)_2Pt(\eta^2$-$C_2H_4)$ in solution, (η^2-C_{60})$Pt(PPh_3)_2$ (**V**) formed. This was the first example of the η^2-fullerene-transition metal complex. Multiple coordination of metal atoms to C_{60} has been examined for the reaction of $Pt(PEt_3)_4$ with C_{60}. With an excess of $Pt(PEt_3)_4$, a hexaaddition product $(C_{60})[Pt\{P(C_2H_5)_3\}_2]_6$ (**VI**) was obtained. The six platinum atoms coordinated to C-C bonds at 6:6 ring junction are arranged in an octahedral manner around the fullerene core. A tri-nuclear ruthenium complex (μ^3-η^2,η^2,η^2-C_{60})$Ru_3(CO)_9$ (**VII**), which was obtained in 4% yield by heating of C_{60} and $Ru_3(CO)_{12}$, reveals a hexahapto coordination mode of the fullerene. The ruthenium atoms are attached to the 6:6 ring junctions. These complexes [(η^2-C_{60})$Pt(PPh_3)_2$ (**V**), $(C_{60})[Pt\{P(C_2H_5)_3\}_2]_6$ (**VI**) and (μ^3-η^2,η^2,η^2-C_{60})$Ru_3(CO)_9$ (**VII**)] are stabilized by the back-donation from electron-rich transition metal moieties to C_{60}. Whereas there are some electronic communications between transition metals and fullerene moiety, these η^2-complexes have several problems. One is the difficulty of synthesizing fullerene-transition metal complexes with high valent transition metals because of the weakness of the back-donation from transition metal moieties to

Fagan, P. J.; Calabrese, J. C.; Malone, B. In *Fullerenes, Synthesis, Properties and Chemistry of Large Carbon Clusters*; Hammond, G. S.; Kuck, V. J. Eds.; ACS symposium Series 481; American Chemical Society: Washington DC. **1992**, 177.

[11] (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. (b) Chase, B.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 2252. (c) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807.

[12] (a) Hsu, H. –F.; Shapley, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 9192. (b) Lee, K.; Has, H. –F.; Shapley, J. R. *Organometallics* **1997**, *16*, 3876.

fullerenes. The other problem is that the reaction gives many products (regioisomers or compounds with different numbers of transition metal moieties). This problem causes difficulty in separation and low yields.

One of the most important organometallic compounds is ferrocene,[13] which was discovered half a century ago. The discovery of ferrocene brought about remarkable development of organometallic chemistry.[14] Ferrocene has sandwich-type structure and is stable to air and to redox conditions.

Many people who work on fullerene chemistry must have thought that they can synthesize a dream molecule "bucky ferrocene" $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60})$ (**VIII**), in which ferrocene is constructed on the fullerene sphere (Figure 4).[15] However, nobody succeeded in the synthesis of "bucky ferrocene" $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60})$ (**VIII**). The formation of a hybrid molecule $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60})$ (**VIII**), which may be formed by direct combining of ferrocene and C_{60}, are expected to be difficult by theoretical calculations.[16] One of the reasons for its difficulty is that hybrid

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[13] (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632. (c) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125. (d) Fischer, E. O.; Pfab, W. Z. Z. *Naturforsch* **1952**, *7B*, 377.

[14] (a) Togni, A.; Hayashi, T. *Ferrocenes: homogeneous catalysis, organic synthesis, material science* (Wiley-VCH, Weinheim, 1995). (b) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry: the synthesis, reactions, and structures of organometallic compounds*, Pergamon: New York, 1982. (c) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II: a review of the literature 1982-1994*, Pergamon: New York, 1995.

[15] (a) Chistyakov, A. L.; Stankevich, I. V. *Russ. Chem. Bull.* **1999**, *48*, 1636. (b) Chistyakov, A. L.; Stankevich, I. V. *Mol. Matel.* **2000**, *13*, 311. (c) Gal'pern, E. G.; Stankevich, I. V.; Chistyakov, A. L. *Phys. Solid State* **2001**, *43*, 989. (d) Chistyakov, A. L.; Stankevich, I. V. *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 770.

[16] Jemmis, E. D.; Manoharan, M.; Sharma, P. K. *Organometallics* **2000**, *19*, 1879.

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molecule $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60})$ (**VIII**) has open-shell structure; total electrons of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60})$ (**VIII**) are odd number.


VIII
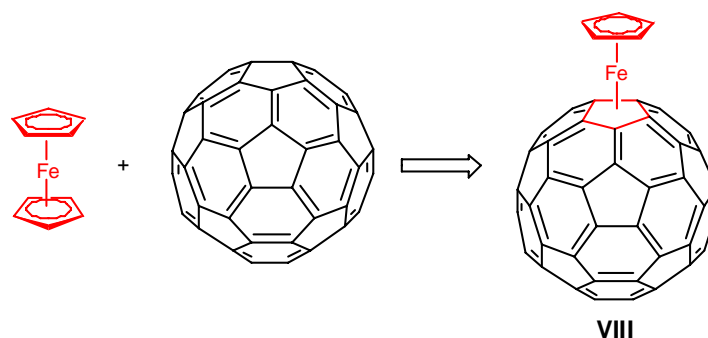
Figure 4. "Bucky ferrocene". Direct combination of ferrocene and fullerene.

If appropriate number of substituted groups could be introduced on the fullerene sphere, hybrid molecule of ferrocene and fullerene (bucky ferrocene) must be synthesizable because of its closed-shell structure. Our group already reported the quantitative and regioselective syntheses of pentaorgano fullerene derivatives $C_{60}R_5H$ (R = Me, Ph, etc.; Figure 5).[17] These compounds have five substituted groups around one of the five-membered rings of C_{60}, and a deprotonated compound can act as a cyclopentadienyl ligand. In these compounds, a transition metal can be introduced into only one position of C_{60}.

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[17] (a) Sawamura M.; Iikura H.; Nakamura E. *J. Am. Chem. Soc.* **1996**, *118,* 12850. (b) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599,* 32. (c) Sawamura, M.; Toganoh M.; Kuninobu Y.; Kato S.; Nakamura E. *Chem. Lett.* **2000,** 270.
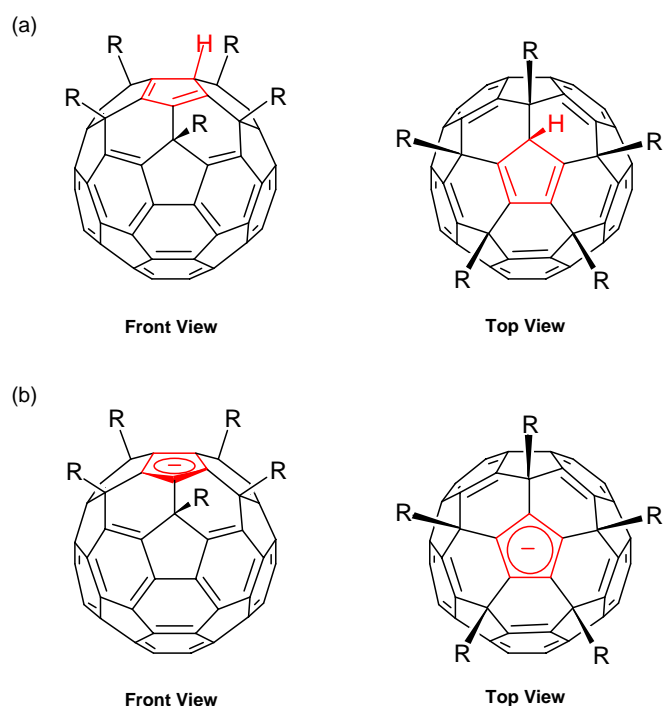
Figure 5. Pentaorgano-fullerene derivatives. (a) Fullerene-cyclopentadiene. (b) Fullerene-cyclopentadienyl ligands.

I succeeded in the synthesis of the bucky ferrocenes by the use of a pentaorgano fullerene derivative $C_{60}R_5$[17] as an η^5-cyclopentadienyl ligands. One of the reasons why bucky ferrocenes could be obtained is that I achieved an even number of the total electrons in bucky ferrocene molecules. I describe the synthesis, structure, stability, redox properties and chemical functionalizations of bucky ferrocenes. The study shows that the ferrocene core is stable and that the iron atom is electronically communicated with the fullerene core. These

results indicate that bucky ferrocenes could be used as functional molecules. I also mention the synthesis, structure and some properties of π-allyl nickel, palladium and platinum complexes as other examples of sandwich molecules. In particular, protection effect of the bulky $C_{60}Ph_5$ ligand was observed in these complexes.

Chapter 2   Nickel, Palladium and Platinum Complexes of η^5-Cyclopentadienide $C_{60}R_5$ Ligands. Stabilization Effect of $C_{60}Ph_5$ Ligand

2-1. Introduction

Electronic structure of ligand is the major factor that controls the reactivity and stability of transition metal complexes: An illustrative example is the 18-electron sandwich complex of iron(II), ferrocene, where a pair of the 6π-electron cyclopentadienide endow extremely high stability of the complex.[13] The sandwich structure may not be enough for the stability, since ferrocene's immediate neighbor, 20-electron nickelocene, is relatively unstable and susceptible to oxidation by molecular oxygen.[18] The 18-electron π-allylcyclopentadienyl nickel complex $Ni(\eta^3$-allyl$)(\eta^5$-Cp$)$ is even more unstable to oxygen and immediately decompose upon exposure to air.[19,20] The physical structure of the ligand is another controlling factor. Suitably designed bulky ligands are known to stabilize coordinatively unsaturated metal complexes by

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[18] Wilke, G.; Jolly, P. W., *The Organic Chemistry of Nickel, vol. I, Organonickel Complexes*, Academic Press, New York and London, **1974**, pp 422.

[19] (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry, vol. 6*, Pergamon, New York, **1982**. (b) Abel, E. W. ; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II*, *vol. 9*, Pergamon: New York, **1995**.

[20] (a) Fischer, E. O.; Bürger, G. *Chem. Ber.* **1961**, *94*, 2409. (b) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.

screening the approaches of extra ligand molecules. Isopropyl-substituted

tris(pyrazolyl)borate is a recent member of such ligands.[21]

I and others in the Nakamura group previously reported the synthesis of a

series of η^5-metal compounds that bear a $C_{60}R_5$ cyclopentadienyl ligand (denoted

generically FCp ligands):[17] $Re(\eta^5\text{-}C_{60}R_5)(CO)_3$,[22] $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{60}Me_5)$,[23]

$Ru(\eta^5\text{-}C_{60}Me_5)L_n$[24, 25] and $Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2$[26] ($C_{60}Me_5$ is abbreviated as

MeFCp). I have so far synthesized MeFCp complexes or, in a case, FCp ligands

bearing hydrogen atoms instead of the methyl groups. Though the Nakamura

group reported the synthesis of a $C_{60}Ph_5$ ligand (PhFCp) already in 1996 as the

first report in the series,[17a] the group members have not been able to synthesize

PhFCp transition metal complexes very likely because of steric congestion

imposed by the five phenyl groups surrounding the cyclopentadienide moiety.

This observation in turn suggested me that the PhFCp ligand may act to stabilize

otherwise unstable transition metal complex by steric protection. In this chapter,

I report the first synthesis of PhFCp transition metal complexes (as well as

MeFCp complexes) for Group 10 triad, and show that the PhFCp ligand allows

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[21] (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (c) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press, London, **1999**.

[22] Toganoh, M.; Matsuo, Y.; Nakamura, E. *Angew. Chem. Int. Ed.* **2003**, *42*, 3530.

[23] Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002,** *124,* 9354.

[24] Matsuo, Y.; Nakamura, E. *Organometallics* **2003**, *22*, 2554.

[25] Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* in press.

[26] Sawamura M.; Kuninobu Y.; Nakamura E. *J. Am. Chem. Soc.* **2000,** *122*, 12407.

the preparation of the first stable nickel π-allyl complex, which is stable against heat, water and molecular oxygen (at 80 °C). Palladium and platinum complexes, Pd(η^3-allylic)(η^5-C$_{60}$R$_5$) (allylic = allyl, methallyl, crotyl; R = Me, Ph) and Pt(η^3-methallyl)(η^5-C$_{60}$R$_5$) (R = Me, Ph), have also been synthesized. Palladium complexes were studied for their electrochemical properties.

2-2. Synthesis of the Nickel Complexes

The parent π-allyl nickel complex, Ni(η^3-allyl)(η^5-Cp), is a sensitive compound; namely, it can be handled at ambient temperature, is stable to water, but immediately decomposes upon exposure to air.[27] I first examined if I can synthesize the FCp analogues to see if the FCp ligand can stabilize the π-allyl nickel complex. Because of the electronegative fullerene core, the FCp cyclopentadienes (both MeFCp and PhFCp) are more acidic than water,[28] and hence the corresponding cyclopentadienides are more electron-deficient than C$_5$H$_5$ anion. Between MeFCp and PhFCp, the latter is markedly congested

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[27] In our reexamination of the synthesis and properties of Ni(η^3-allyl)(η^5-Cp), this complex is very stable to water, reacted with air (probably, O$_2$) to give light yellow solid. This solid seems to be Ni(I) or Ni(II) salt. Since the molecular ion peak of allylcyclopentadiene was detected by GC-MS measurements, decomposed mechanisms of Ni(η^3-allyl)(η^5-Cp) are oxidation of nickel atom and reductive elimination of allylcyclopentadiene.

[28] (a) Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; Zhou, S. –Q.; Chu, B. *Chem. Lett.* **2000**, 1098. (b) Zhou, S. –Q.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; *Science* **2001**, *291*, 1944.
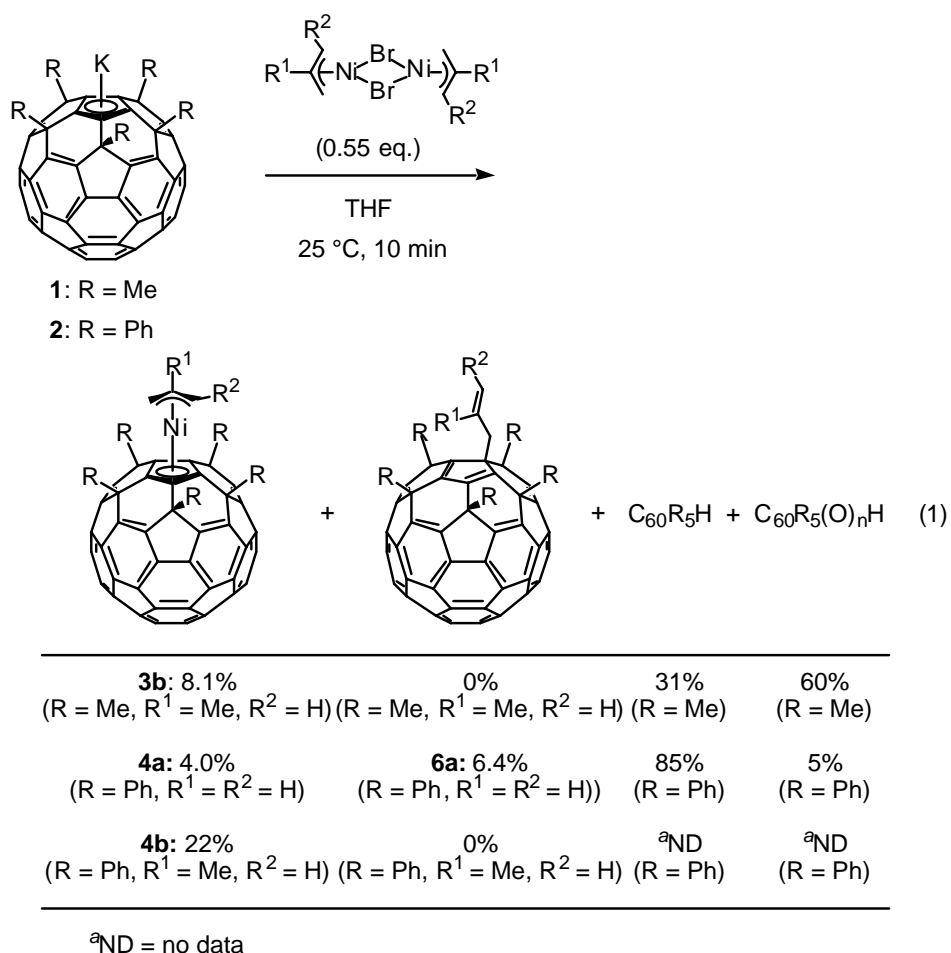
sterically (vide infra). I synthesized the π-allyl nickel complexes of MeFCp and PhFCp.

The standard metathesis method could be carried out reasonably well for the synthesis. The reactions of $K(\eta^5\text{-RFCp})$ ($\mathbf{1}^{17c}$: R = Me; $\mathbf{2}^{17a}$: R = Ph) with [NiBr(allylic)]$_2$ (allylic = allyl and methallyl) [29] provided the desired fullerene-nickel complexes Ni(η^3-allylic)(η^5-RFCp) (**3b**: allylic = methallyl, R = Me; **4a**: allylic = allyl, R = Ph; **4b**: allylic = methallyl, R = Ph) (eq 1). After purification by preparative HPLC separation, fullerene-nickel complexes Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) were obtained in 4.0 to 22% isolated yield. Attempted synthesis of Ni(η^3-allyl)(η^5-MeFCp) resulted in exclusive formation of an allylated product $C_{60}Me_5(CH_2CH=CH_2)$ (**5a**) in 22% yield. In the synthesis of the PhFCp complex Ni(η^3-allyl)(η^5-PhFCp) (**4a**), allyl compound $C_{60}Ph_5(CH_2CH=CH_2)$ (**6a**) was also obtained as a side product in 6% yield. The remainder of the material balance was largely the starting material $C_{60}Me_5H$ (31%) or $C_{60}Ph_5H$ (85%) and its oxidation products (R = Me: 60%; R = Ph: 5%) that were formed during workup. Since nickel complex Ni(η^3-allyl)(η^5-PhFCp) (**4a**) does not decompose to give the allyl compound $C_{60}Ph_5(CH_2CH=CH_2)$ (**6a**) under the reaction condition, allyl compound $C_{60}Ph_5(CH_2CH=CH_2)$ (**6a**) must

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[29] (a) π-Allylnickel halide: United States Patent Office 3422128 (Jan. 14th. 1969). (b) π-Allylnickel halide: German Published Patent Application 1194417 (Aug. 10th. 1963), Studiengesellschaft Kohle.

be formed some how independently of the pathway leading the π-allyl complex.

3b: 8.1%	0%	31%	60%
(R = Me, R^1 = Me, R^2 = H)	(R = Me, R^1 = Me, R^2 = H)	(R = Me)	(R = Me)
4a: 4.0%	**6a:** 6.4%	85%	5%
(R = Ph, R^1 = R^2 = H)	(R = Ph, R^1 = R^2 = H))	(R = Ph)	(R = Ph)
4b: 22%	0%	[a]ND	[a]ND
(R = Ph, R^1 = Me, R^2 = H)	(R = Ph, R^1 = Me, R^2 = H)	(R = Ph)	(R = Ph)

[a]ND = no data

Structure assignment was achieved by the standard physical methods. High resolution APCI-TOF-MS (+) data were consistent with the assigned structures. The ^{1}H and ^{13}C NMR measurements of nickel complexes Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) indicated that the FCp moieties have C_{5v}

symmetry. These results show that the rotation rates of the FCp moieties around the Ni-FCp axis are faster than the relaxation time of NMR spectra.

All FCp nickel complexes Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) were found to be far stable than the parent π-allyl complex, which decomposes in 1 min upon exposure to air. Thus, the methallyl MeFCp complex Ni(η^3-methallyl)(η^5-MeFCp) (**3b**) in toluene decompose very slowly in air at 25 °C, leaving 30% of the material even after 5 days. The π-allyl PhFCp complex Ni(η^3-allyl)(η^5-PhFCp) (**4a**) is extremely stable: In toluene exposed to air at 80 °C, it was completely recovered after 15 h, and the π-methallyl PhFCp complex Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) in toluene was also recovered completely after 15 h at 80 °C.

2-3. Synthesis of the Palladium and Platinum Complexes

On the basis of the method to synthesize fullerene-nickel complexes, I synthesized fullerene-palladium and platinum complexes. Palladium and platinum complexes, Pd(η^3-allylic)(η^5-RFCp) (**7a**: allylic = allyl, R = Me; **7b**: allylic = methallyl, R = Me; **7c**: allylic = crotyl, R = Me; **8a**: allylic = allyl, R = Ph; **8b**: allylic = methallyl, R = Ph; **8c**: allylic = crotyl, R = Ph) and Pt(η^3-methallyl)(η^5-RFCp) (**9**: R = Me; **10**: R = Ph), could be synthesized by transmetalation of a potassium salt K(η^5-MeFCp) (**1**) or K(η^5-PhFCp) (**2**) with
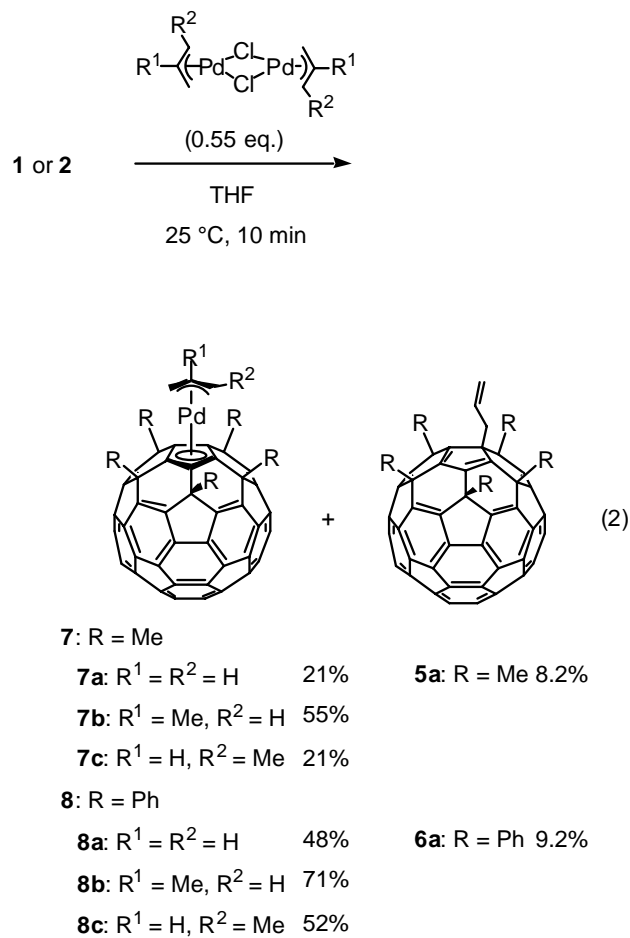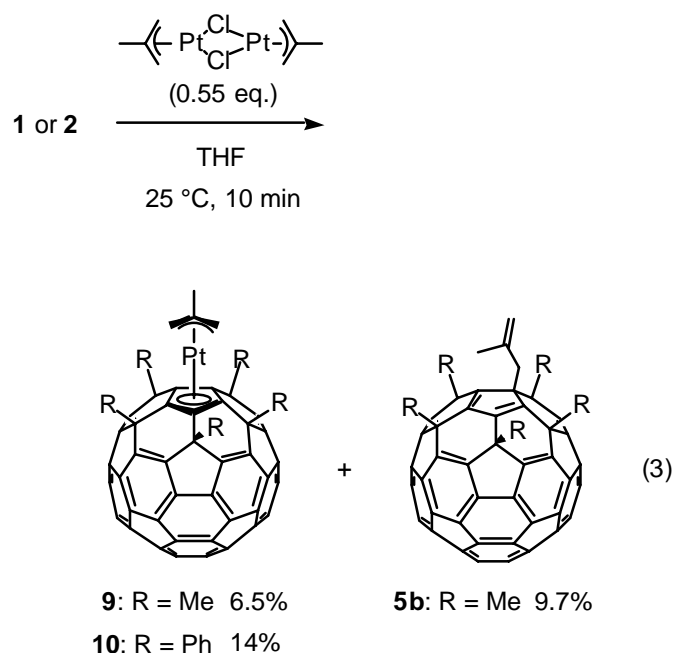
[PdCl(η^3-allylic)]$_2$ (allylic = allyl, methallyl and crotyl) [30] or [PtCl(η^3-methallyl)]$_2$[31] (eqs 2 and 3). The reaction affording the palladium complexes Pd(η^3-allyl)(η^5-MeFCp) (**7a**), Pd(η^3-allyl)(η^5-PhFCp) (**8a**) and platinum complex Pt(η^3-methallyl)(η^5-MeFCp) (**9**) also gave allylated and methallylated side products, C$_{60}$Me$_5$(CH$_2$CH=CH$_2$) (**5a**), C$_{60}$Ph$_5$(CH$_2$CH=CH$_2$) (**6a**) and C$_{60}$Me$_5$(CH$_2$C(Me)=CH$_2$) (**5b**) in 8 to 10% yield. Palladium complexes Pd(η^3-allyl)(η^5-MeFCp) (**7a**), Pd(η^3-allyl)(η^5-PhFCp) (**8a**) and platinum complex Pt(η^3-methallyl)(η^5-MeFCp) (**9**) do not decompose into allylic compounds C$_{60}$Me$_5$(CH$_2$CH=CH$_2$) (**5a**), C$_{60}$Ph$_5$(CH$_2$CH=CH$_2$) (**6a**) and C$_{60}$Me$_5$(CH$_2$C(Me)=CH$_2$) (**5b**) in the reaction conditions, indicating that allylic compounds C$_{60}$Me$_5$(CH$_2$CH=CH$_2$) (**5a**), C$_{60}$Ph$_5$(CH$_2$CH=CH$_2$) (**6a**) and C$_{60}$Me$_5$(CH$_2$C(Me)=CH$_2$) (**5b**) must be formed by the nucleophilic attack of anions MeFCp$^-$ or PhFCp$^-$ to the allylic palladium or platinum species, not by the reductive elimination of palladium or platinum complexes Pd(η^3-allyl)(η^5-MeFCp) (**7a**), Pd(η^3-allyl)(η^5-PhFCp) (**8a**) and platinum complex Pt(η^3-methallyl)(η^5-MeFCp) (**9**). After purification by preparative HPLC separation, fullerene-palladium and platinum complexes Pd(η^3-allylic)(η^5-RFCp) (**7a**: allylic = allyl, R = Me; **7b**: allylic = methallyl, R = Me; **7c**: allylic = crotyl, R = Me; **8a**: allylic = allyl, R = Ph; **8b**: allylic = methallyl,

[30] (a) Shaw, B. L. *Proc. Chem. Soc.* **1960,** 247. (b) Parker, G.; Werner, H. *Helv. Chim. Acta,* **1973**, *56,* 2819. (c) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H, -J.; Kruger, C. *Organometallics* **1983,** *2,* 1369. (d) Powell, J.; Dowling, N. I. *Organometallics* **1983**, 2, 1742.

[31] Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc. Dalton Trans.* **1977**, 294.

R = Ph; **8c**: allylic = crotyl, R = Ph) and Pt(η^3-methallyl)(η^5-RFCp) (**9**: R = Me; **10**: R = Ph) were obtained in 21 to 71% (palladium complexes) or 6.5 to 14% (platinum complexes) isolated yield.
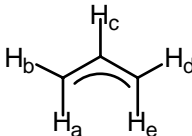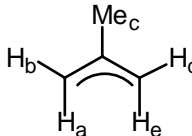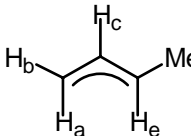

7: R = Me

  7a: $R^1 = R^2 = H$ 21%   **5a**: R = Me 8.2%

  7b: $R^1 = Me, R^2 = H$ 55%

  7c: $R^1 = H, R^2 = Me$ 21%

8: R = Ph

  8a: $R^1 = R^2 = H$ 48%   **6a**: R = Ph 9.2%

  8b: $R^1 = Me, R^2 = H$ 71%

  8c: $R^1 = H, R^2 = Me$ 52%

$$\text{1 or 2} \xrightarrow[\substack{\text{THF} \\ 25\ °C,\ 10\ \text{min}}]{\substack{\text{(0.55 eq.)}}}$$

9: R = Me 6.5%
10: R = Ph 14%

5b: R = Me 9.7%

(3)

Identification of these palladium and platinum complexes, Pd(η^3-allylic)(η^5-RFCp) (**7a**: allylic = allyl, R = Me; **7b**: allylic = methallyl, R = Me; **7c**: allylic = crotyl, R = Me; **8a**: allylic = allyl, R = Ph; **8b**: allylic = methallyl, R = Ph; **8c**: allylic = crotyl, R = Ph) and Pt(η^3-methallyl)(η^5-RFCp) (**9**: R = Me; **10**: R = Ph) were achieved by the high-resolution APCI-TOF-MS (+) and the ^{1}H and ^{13}C NMR measurements. In the ^{1}H NMR spectra of the platinum complexes Pt(η^3-methallyl)(η^5-MeFCp) (**9**) and Pt(η^3-methallyl)(η^5-PhFCp) (**10**), platinum-hydrogen spin-spin couplings [Pt(η^3-methallyl)(η^5-MeFCp) (**9**): J = 27.2, 111.6, 63.6 Hz; Pt(η^3-methallyl)(η^5-PhFCp) (**10**): J = 32.1, 117.8, 64.6 Hz] were observed. These coupling constants in platinum complexes Pt(η^3-methallyl)(η^5-MeFCp) (**9**) and Pt(η^3-methallyl)(η^5-PhFCp) (**10**) are in good

agreement with those in Pt(η^3-methallyl)(η^5-Cp)[32] (J = 34, 111, 61 Hz). The

allylic protons in the Pd-PhFCp complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic

= allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) were observed at higher

magnetic field (δ 2.09, 3.08, and 4.70 ppm) than those of the Pd-C_5Ph_5 ones (δ

2.66, 3.65, and 5.30 ppm) (Table 1).[30d] The reason for this observation is that five

phenyl groups of the Pd-PhFCp complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic

= allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) surround π-allylic palladium

moieties and the protons of allylic moieties receive therefore the shielding

effects of five phenyl groups in Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**:

allylic = methallyl; **8c**: allylic = crotyl). Note that proton signals of π-allyl moiety

of the C_5Me_5 palladium complex Pd(η^3-allyl)(η^5-C_5Me_5)[30c] are observed at

higher magnetic fields (1.91, 2.96, and 4.75 ppm) than those of the C_5Ph_5

palladium complex Pd(η^3-allyl)(η^5-C_5Ph_5)[30d] (Table 1). The differences between

the chemical shift values of C_5Me_5 and C_5Ph_5 complexes are due to the electron

donating or withdrawing nature of C_5Me_5 or C_5Ph_5 ligands. If the same effect

persists in the fullerene palladium complexes, proton signals of π-allyl moiety

of the methylated fullerene-palladium complexes Pd(η^3-allylic)(η^5-MeFCp) (**7a**:

allylic = allyl; **7b**: allylic = methallyl; **7c**: allylic = crotyl) must be observed at

higher magnetic fields than those of the phenylated fullerene-palladium

complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**:

allylic = crotyl). However, the fact is exactly the opposite (Table 1). Namely, in

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[32] Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. (A)* **1971**, 3536.

the ^{1}H NMR spectra, proton signals of Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) were observed at higher magnetic field than those of Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl; **7c**: allylic = crotyl) in spite of the electron withdrawing nature of the PhFCp ligand that is stronger than that of the MeFCp one. These results indicated that the shielding effects of five phenyl groups of the PhFCp moiety to allylic protons are larger than the effect of electron donating or withdrawing nature of the RFCp ligands. These shielding effects must be due to the structure of the PhFCp ligand that will be discussed in the next, X-ray analysis section.

Table 1. Comparison of ^{1}H NMR Chemical Shifts (ppm) between π-Allylic Ligands of Palladium Complexes **7a-c** and **8a-c**

H_c Me_c H_c
H_b H_d H_b H_d H_b Me_d
H_a H_e H_a H_e H_a H_e

7a, **8a** (η^3-allyl)   **7b**, **8b** (η^3-methallyl)   **7c**, **8c** (η^3-crotyl)

	H_a	H_b	H_c	H_d	H_e	Me_c	Me_d
7a	2.99	4.32	5.51	(= H_b)	(= H_a)		
7b	2.94	4.25		(= H_b)	(= H_a)	2.36	
7c	2.81	4.10	5.41		4.06		2.02
8a	2.09	3.08	4.70	(= H_b)	(= H_a)		
8b	1.95	2.99		(= H_b)	(= H_a)	1.63	
8c	1.73	2.67	4.66		3.08		0.51
Pd(η^3-allyl)(η^5-C$_5$Me$_5$)	1.91	2.96	4.75				
Pd(η^3-allyl)(η^5-C$_5$Ph$_5$)	2.66	3.65	5.30				

2-4. X-ray Crystal Structure Analysis

Dark red single crystals of palladium complexes Pd(η^3-allylic)(η^5-RFCp) (**7a**: allylic = allyl, R = Me; **7b**: allylic = methallyl, R = Me; **7c**: allylic = crotyl, R = Me; **8a**: allylic = allyl, R = Ph; **8b**: allylic = methallyl, R = Ph; **8c**: allylic = crotyl, R = Ph) could be obtained by recrystallization from CS_2/EtOH. X-ray crystal structure analyses of these complexes were performed (Figures 6 and 7). The FCp ligands coordinate to the palladium atom in an η^5-fashion. The FCp and the π-allylic moieties form sandwich-type structure. Hydrogen atoms on the π-allylic ligands in palladium complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) are located in the space surrounded by five phenyl groups. These results correspond to the fact that allylic protons of palladium complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) are subjected to the shielding effect of the phenyl groups. The average bond lengths of the five Pd-C(FCp) bonds of fullerene-palladium complexes Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) (2.34 and 2.36 Å) and Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) (2.37, 2.37 and 2.40 Å) are slightly longer than that of Pd(η^3-allyl)(η^5-Cp)[33] (2.26 Å) (Table 2). The bond lengths between palladium atom and three carbon atoms on π-allylic moieties of fullerene-palladium complexes Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) (**7a**: 2.15, 2.09, 2.18 Å; **7b**: 2.13, 2.11, 2.13 Å) and

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[33] Minasyants M. Kh.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 481.

Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) (**8a**: 2.13, 2.08, 2.15 Å; **8b**: 2.13, 2.13, 2.14 Å; **8c**: 2.18, 2.10, 2.16 Å) are also slightly longer than those of Pd(η^3-allyl)(η^5-Cp)[33] (2.10, 2.04, 2.07 Å) (Table 2). These bond lengths of pentaphenylated fullerene complexes Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl) and pentamethylated fullerene complexes Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) are almost the same within the standard deviation. This observation indicates that there is no steric hindrance between the allylic moieties and the five methyl or the phenyl groups of the RFCp ligands. In fact, the closest C-H and H-H bond lengths among the Pd-PhFCp complexes are 2.89-3.28 Å [between carbon atoms of the five phenyl groups and hydrogen atoms of the methallyl ligand, in Pd(η^3-methallyl)(η^5-PhFCp) (**8b**)] and 2.43-3.04 Å [between hydrogen atoms of the five phenyl groups and those of the methallyl ligand, in Pd(η^3-methallyl)(η^5-PhFCp) (**8b**)], respectively, the values of which are longer than known van der Waals contacts (H-C = 2.90 Å; H-H = 2.40 Å).[34]
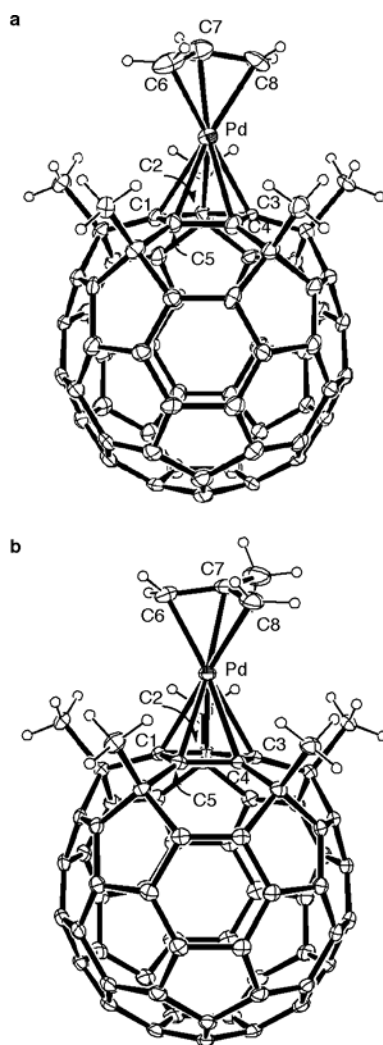

[34] Pauling, L. *The nature of the chemical bond, Third Ed.*, Cornell University Press, New York, **1960**.

Table 2. Selected Bond Lengths (Å) of Fullerene-Palladium Complexes **7a-b** and **8a-c**

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	7a	7b	8a	8b	8c	Pd(π-allyl)Cp
Pd-C(FCp)(averaged)	2.337(9)	2.357(3)	2.370(3)	2.367(5)	2.398(6)	2.26
Pd-C(6)	2.153(12)	2.131(4)	2.134(5)	2.126(6)	2.18(2)	2.10
Pd-C(7)	2.090(12)	2.05(4)	2.076(5)	2.130(7)	2.10(2)	2.04
Pd-C(8)	2.179(1)	2.31(5)	2.148(5)	2.143(8)	2.16(2)	2.07

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Figure 6. Molecular structures of the Pd-MeFCp complexes with 30% probability level ellipsoids. The solvent molecules in the unit cell are omitted for clarity. (a) Pd(η^3-allyl)(η^5-MeFCp) (**7a**) ·CS$_2$. (b) Pd(η^3-methallyl)(η^5-MeFCp) (**7b**) ·(CS$_2$)$_{1.5}$.
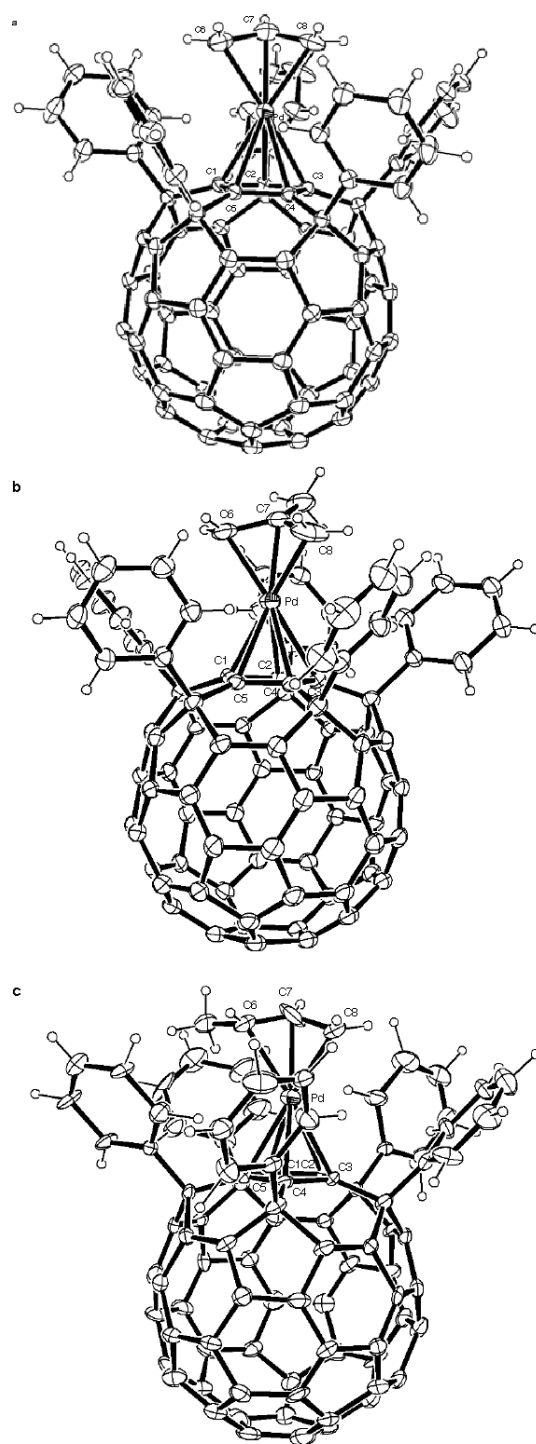
Figure 7. Molecular structures of the Pd-PhFCp complexes with 30% probability level ellipsoids. The solvent molecules in the unit cell are omitted for clarity. (a)

Pd(η^3-allyl)(η^5-PhFCp) (**8a**) ·(CS$_2$)$_{2.5}$. (b) Pd(η^3-methallyl)(η^5-PhFCp) (**8b**) ·(CS$_2$)$_{0.25}$. (c) Pd(η^3-crotyl)(η^5-PhFCp) (**8c**) ·(CHCl$_3$)$_2$.

2-5. Electrochemical Investigations

I and the Nakamura group members already reported the electrochemical investigations of fullerene transition metal complexes Fe(η^5-Cp)(η^5-MeFCp),[23] Ru(η^5-MeFCp)(CH$_3$)(CO)$_2$[24] and Rh(η^5-MeFCp)(CO)$_2$.[26] In these complexes, metal-fullerene bonds are stable under oxidation and reduction conditions. I here examined the redox behavior of π-allyl palladium complexes Pd(η^3-allyl)(η^5-MeFCp) (**7a**) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) (Figure 8, Table 3). A scan from 0.82 to –2.87 V (scan rate: 100 mV/s) revealed that the palladium complexes Pd(η^3-allyl)(η^5-MeFCp) (**7a**) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) were not oxidized but were reduced irreversibly, likewise palladium η^2-fullerene complexes (Figure 8a,c). [35] Pentamethylated fullerene-palladium complex Pd(η^3-allyl)(η^5-MeFCp) (**7a**) is stable in first one electron reduction, but unstable in second one electron reduction (Figure 8a,b; Scheme 1). In the case of pentaphenylated fullerene-palladium complex Pd(η^3-allyl)(η^5-MeFCp) (**8a**), decomposition of the complex is observed in one electron reduction step (Figure 8c,d; Scheme 2). The reduction potentials of Pd(η^3-allyl)(η^5-MeFCp) (**7a**) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) are comparable to those of

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[35] Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807.

Fe(η^5-Cp)(η^5-MeFCp),[23] Ru(η^5-MeFCp)(CH$_3$)(CO)$_2$,[24] Rh(η^5-MeFCp)(CO)$_2$[26] and

C$_{60}$Ph$_5$H.[36] Reversible and irreversible reductions of Pd(η^3-allyl)(η^5-MeFCp)

(**7a**) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) could be considered to occur in the

fullerene moieties. The difference of the reduction potentials between

Pd(η^3-allyl)(η^5-MeFCp) (**7a**) (-1.47 V) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) (-1.40 V)

likely arises from the fact that reduction of the PhFCp ligand is much easier

than that of the MeFCp ligand.

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[36] Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912.
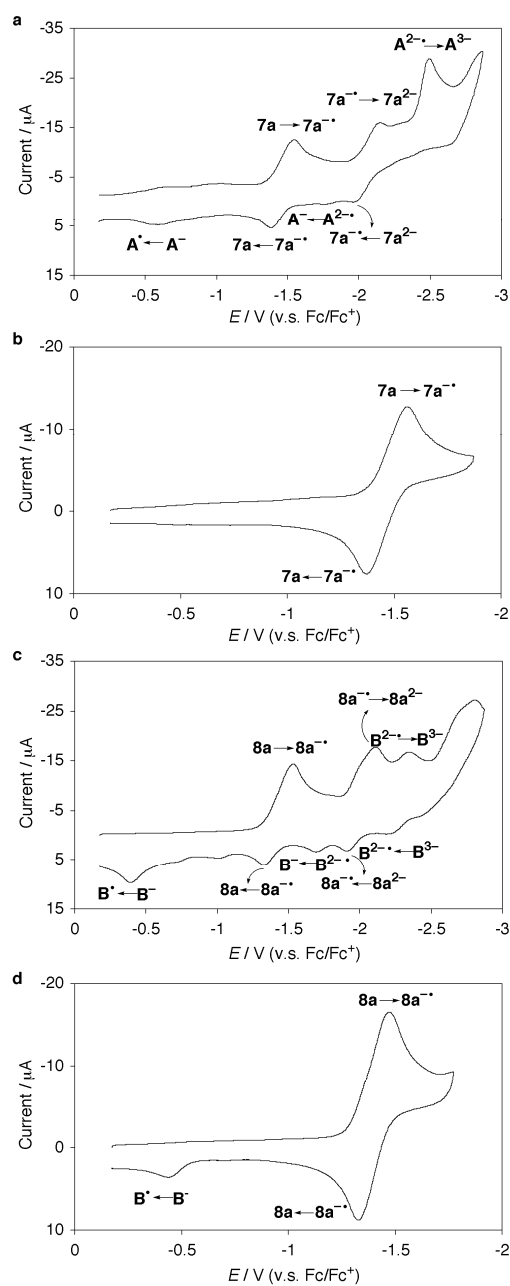
Figure 8. Cyclic voltammograms of Pd(η^3-allyl)(η^5-MeFCp) (**7a**) (a and b) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**) (c and d) (0.10 M [Bu$_4$N][ClO$_4$] in THF, 1.0 mM, glassy carbon working electrode, 0.10 V/s, 25 °C).

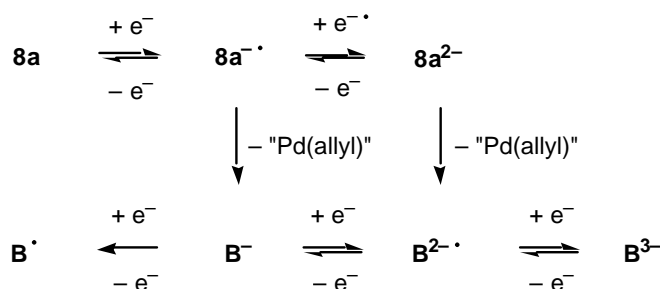**Table 3.** Reduction Potentials for Palladium Complexes and Fullerene Derivatives [a]

	$E_{1/2}^{red1}$ (V)	$E_{1/2}^{red2}$ (V)
Pd(η^3-allyl)(η^5-MeFCp) (**7a**)	-1.47	-2.06 [b]
Fe(η^5-Cp)(η^5-MeFCp)	-1.46	-2.06 [c]
Ru(η^5-MeFCp)(CH$_3$)(CO)$_2$	-1.34	-1.94
Rh(η^5-MeFCp)(CO)$_2$	-1.35	-1.94
C$_{60}$Me$_5$H	-1.48	-2.07
Pd(η^3-allyl)(η^5-PhFCp) (**8a**)	-1.40	-1.99 [b]
C$_{60}$Ph$_5$H	-1.38	-1.98

[a] V vs. ferrocene/ferrocenium couple. 25 °C. [b] Irreversible reduction. [c] Peak top potential.

Scheme 1. Electrochemical behavior of methylated fullerene-palladium complex Pd(η^3-allyl)(η^5-MeFCp) (**7a**).

$$\mathbf{7a} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{7a^{-\bullet}} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{7a^{2-}}$$

$$\downarrow -\text{"Pd(allyl)"}$$

$$\mathbf{A^{\bullet}} \;\overset{+\,e^-}{\underset{-\,e^-}{\longleftarrow}}\; \mathbf{A^-} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{A^{2-\bullet}} \;(\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}})\; \mathbf{A^{3-}}$$
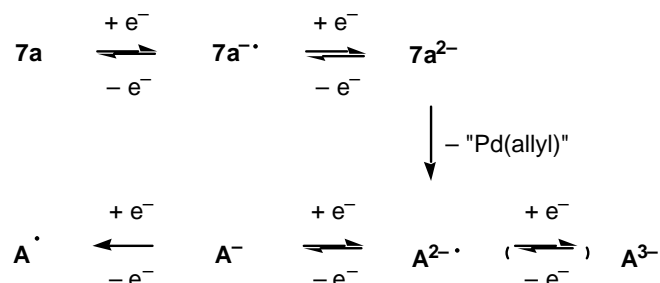
Scheme 2. Electrochemical behavior of phenylated fullerene-palladium complex Pd(η^3-allyl)(η^5-PhFCp) (**8a**).

$$\mathbf{8a} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{8a^{-\bullet}} \;\underset{-\,e^-}{\overset{+\,e^{-\bullet}}{\rightleftharpoons}}\; \mathbf{8a^{2-}}$$

$$\downarrow -\text{"Pd(allyl)"} \qquad \downarrow -\text{"Pd(allyl)"}$$

$$\mathbf{B^{\bullet}} \;\overset{+\,e^-}{\underset{-\,e^-}{\longleftarrow}}\; \mathbf{B^-} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{B^{2-\bullet}} \;\underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}}\; \mathbf{B^{3-}}$$

In the course of the two electron reductions, anion **A⁻**, anion **B⁻** (in Figure 8a,c, and Schemes 1 and 2) and those redox products were formed together with reduced palladium complexes, **7a⁻**, **7a²⁻**, **8a⁻**, and **8a²⁻**. In view of the Nakamura group member's previous result,[36] these anions **A⁻** and **B⁻** can be assigned to the anions MeFCp⁻ and PhFCp⁻. This result shows that Pd-MeFCp and Pd-PhFCp bonds were cleaved by the reductions. One of the explanations why Pd-MeFCp and Pd-PhFCp bonds were cleaved by the reductions is that Pd⁰ (palladium metal) formed, followed by the reduction of the fullerene part of

Pd(η^3-allyl)(η^5-MeFCp) (**7a**) and Pd(η^3-allyl)(η^5-PhFCp) (**8a**). This strongly indicates that there are electronic interactions between the palladium atom and the RFCp ligands like bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp)[23] and the other transition metal-FCp complexes.[24,25,26]

2-6. Stabilization Effect of the FCp Ligand

Present nickel-FCp-allyl complexes Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) are stable upon exposure to air even at high temperature, while the parent nickel-Cp-allyl complexes decompose by molecular oxygen. I thought about two reasons for the stability of Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**). One is an electronic reason; since the electron density of nickel atoms is reduced by the electron withdrawing nature of fullerene moieties, the compounds Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), Ni(η^3-allyl)(η^5-PhFCp) (**4a**) and Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) become difficult to oxidize by air. The other reason is that O_2 molecules might not approach to the nickel atoms because of the sterically hindering five methyl or phenyl groups on the fullerene moiety. Compared with the MeFCp ligand, PhFCp ligand can stabilize nickel complexes more effectively. This result consistent both with the degree of electron withdrawing nature and with the protection effect of the RFCp ligands. Although I can not conclusively determined whether electron withdrawing nature of the ligands or steric

protection reason contribute much more effectively to stabilization of reactive metal center, the FCp ligands, in particular the PhFCp ligand, obviously bring both thermodynamic and kinetic stability of the compounds.

From the point of view of stabilizing effect concerning with the shape of the molecule, I can clearly imagine sterically hindered hydrotris(pyrazolyl)borate (Tp) ligand.[21,37,38,39] The Tp ligands are the six electron donor ones with –I valent and the isoelectronic with cyclopentadienide ones. Thus, many kinds of metal complexes with the Tp ligands have been synthesized.[21] It is well known that the Tp ligands containing sterically bulky substituent can protect metal centers and stabilize kinetically unstable intermediates.[40,41] For example, copper carbonyl complex $HB(3,5-Me_2pz)_3CuCO$[42] is much more stable than $HB(pz)_3CuCO$.[40,42] The stabilization effect was also observed in the fullerene complexes. Thus present FCp ligand may be used extensively as ancillary ligands by changing of substituents of the fullerene ligands.

[37] (a) Akita, M. ; Shirasawa, N.; Hikichi, S.; Moro-oka, Y. Chem. Commun. **1998**, 973. (b) Shirasawa, N.; Nguyet, T. T.; Hikichi, S.; Moro-oka, Y.; Akita M. *Organometallics* **2001**, *20*, 3582.

[38] Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561.

[39] Jewson, J. D.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1999**, *18*, 300.

[40] Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

[41] Akita, M.; Hikichi, S.; Moro-oka, Y. *J. Synth. Org. Chem., Jpn.* **1999**, *57*, 67.

[42] (a) Bruce, M. I.; Ostazewski, A. P. P. **1973**, 2433. (b) Abu Salah, O. M.; Bruce, M. I.; Hameister, C. *Inorg. Synth.* **1982**, *21*, 107.

2-7. Conclusion

In the present study, I have succeeded in the first synthesis and characterizations of pentamethylated and pentaphenylated fullerene-nickel, palladium and platinum complexes. These complexes represent the second sandwich-type complexes bearing the pentasubstituted fullerene ligands ever synthesized. In the nickel complexes, the stabilization effect of the RFCp (R = Me, Ph) ligands to air was observed because of the electron withdrawing nature or steric protection effect of the RFCp moieties. The PhFCp ligand can stabilize nickel complexes much more effectively than the MeFCp ligand, since five phenyl groups surround nickel atom and allylic ligand. In view of the wide field of the Cp and Tp ligands, I thus anticipate that the steric protection effect of FCp ligand plays a unique role in development of new materials and isolation of important unstable compounds.

2-8. Experimental

General Procedure. All manipulations were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. THF was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. $C_{60}Me_5H$ and $C_{60}Ph_5H$ were prepared according to the literature.[17] THF solution of t-BuOK was purchased from Sigma-Aldrich Co. and used as received. Complexes [NiBr(η^3-allyl)]$_2$,[29a] [NiBr(η^3-methallyl)]$_2$,[29b] [PdCl(η^3-allyl)]$_2$,[30] [PdCl(η^3-methallyl)]$_2$,[30] [PdCl(η^3-crotyl)]$_2$[30] and [PtCl(η^3-methallyl)]$_2$[31] were

prepared as reported in the literature. Preparative HPLC separations were performed by use of Bucky Prep. column (Nakalai Tesque Co., 20 mm x 250 mm). The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using JEOL EX-400 spectrometer. Proton chemical shift are reported relative to Me$_4$Si (CDCl$_3$) at δ 0.00 ppm or residual solvent peaks (CDCl$_3$ at δ 7.26 ppm; THF-d_8 at δ 1.73 and 3.58 ppm). Carbon chemical shifts are reported relative to CDCl$_3$ at δ 77.00 ppm or THF-d_8 at δ 25.20 and 67.40 ppm. Other spectra were recorded on the following instruments: IR, JASCO IR-420 and ReactIR 1000; UV/vis spectra, HITACHI U3500 and Shimadzu SPD-6A; Mass spectra, Shimadzu LCMS-QP8000, JEOL Accu TOF (JMS-T100LC) and JEOL GCMS (JMS-GCMATE II). Elemental Analyses were performed at organic elemental analysis laboratory in this department.

Ni(η^3-methallyl)(η^5-MeFCp) (3b). To a suspension of MeFCpH (50.0 mg, 62.7 μmol) in THF (5.0 mL) was added a solution of ^{t}BuOK (1.0 M, 69.0 μL, 69.0 μmol) in THF. To the resulting dark reddish orange solution, [NiBr(η^3-methallyl)]$_2$ (13.4 mg, 34.5 μmol) was added. The reaction mixture was stirred at 25 °C for 10 min before quenched by addition of saturated aqueous NH$_4$Cl (1.0 mL). The mixture was diluted with toluene and washed with water. The organic layer was dried with MgSO$_4$, and was concentrated under reduced pressure. Preparative HPLC separations [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm)] afforded Ni(η^3-methallyl)(η^5-MeFCp) (3b) (4.0 mg, 7.0% yield)

as dark red fine crystals. Ni(η^3-methallyl)(η^5-MeFCp) (**3b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.29 (s, 3H), 2.30 (s, 15H), 2.54 (s, 2H), 3.61 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.79 (1C), 30.08 (5C), 44.20 (2C), 51.01 (5C), 100.51 (1C), 111.88 (5C), 143.30 (10C), 145.05 (10C), 146.39 (5C), 147.55 (10C), 148.29 (5C), 154.19 (10C); IR (powder, cm^{-1}) ν 2959 (m), 2918 (m), 2854 (m), 1723 (m), 1441 (s), 1368 (m), 1286 (m), 1264 (m), 1236 (w), 1213 (w), 1200 (w), 1156 (w), 1115 (w), 1071 (w), 1018 (w), 902 (m), 802 (m), 752 (s), 728 (s), 685 (s), 666 (m), 658 (m); UV-vis (toluene/2-propanol = 7/3) λ$_{max}$ 286, 348 (shoulder), 395, 480 (shoulder); HR-APCI-MS (-) m/z; found: 908.1081; calcd for **3b**: 908.1075.

Ni(η^3-allyl)(η^5-PhFCp) (4a). Complex Ni(η^3-allyl)(η^5-PhFCp) (**4a**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: PhFCpH (50.0 mg, 45.2 μmol), ^{t}BuOK (1.0 M, 49.7 μL, 49.7 μmol) in THF, [NiBr(η^3-methallyl)]$_2$ (8.93 mg, 24.8 μmol), THF (1.0 mL). Yield: Ni(η^3-allyl)(η^5-PhFCp) (**4a**): 2.2 mg (4.0%), C$_{60}$Ph$_5$(allyl) (**6a**): 3.3 mg (6.4%). Ni(η^3-allyl)(η^5-PhFCp) (**4a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.18 (d, ^3J = 11.8 Hz, 2H), 2.27 (d, ^3J = 6.4 Hz, 2H), 4.99 (tt, ^3J = 11.8 Hz, ^3J = 6.4 Hz, 1H), 7.19-7.23 (m, 15H), 7.71 (d, ^3J = 7.4 Hz, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.00 (2C), 58.74 (5C), 98.46 (1C), 112.71 (5C), 127.48 (5C), 127.96 (10C), 128.40 (10C), 142.69 (5C), 143.55 (10C), 145.27 (10C), 146.95 (5C), 147.89 (10C), 148.74 (5C), 152.30 (10C); UV-vis (toluene/2-propanol = 7/3) λ$_{max}$ 287, 355 (shoulder), 396, 470 (shoulder);

HR-APCI-MS (-) m/z; found: 1204.1628; calcd for Ni(η^3-allyl)(η^5-PhFCp) (**4a**): 1204.1701.

$C_{60}Ph_5$(allyl) (**6a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.24 (d, ^3J = 6.8 Hz, 2H), 4.64 (dd, ^3J = 19.2 Hz, ^3J = 2.0 Hz, 1H), 5.10 (dd, ^3J = 12.4 Hz, ^3J = 2.0 Hz, 1H), 5.96 (ddt, ^3J = 19.2 Hz, ^3J = 12.4 Hz, ^3J = 6.8 Hz, 1H), 7.16-7.19 (m, 4H), 7.30-7.43 (m, 13H), 7.75-7.78 (m, 4H), 7.87-7.90 (m, 4H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 2.18 (d, ^3J = 6.8 Hz, 2H), 4.58 (d, ^3J = 17.2 Hz, 2H), 5.02 (d, ^3J = 10.0 Hz, 2H), 5.89 (ddt, ^3J = 17.2 Hz, ^3J = 10.0 Hz, ^3J = 6.8 Hz, 1H), 7.09-7.11 (m, 4H), 7.22-7.32 (m, 13H), 7.67-7.69 (m, 4H), 7.77-7.79 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 43.81 (1C), 58.26 (2C), 60.80 (1C), 62.86 (1C), 64.81 (2C), 118.91 (1C), 126.77 (1C), 127.34 (2C), 127.47 (2C), 127.73 (2C), 127.85 (4C), 128.05 (4C), 128.41 (4C), 128.52 (4C), 130.23 (2C), 133.56 (2C), 137.97 (2C), 139.40 (1C), 142.01 (1C), 142.36 (2C), 143.13 (2C), 143.30 (2C), 143.50 (2C), 143.68 (2C), 143.76 (2C), 143.83 (2C), 143.95 (2C), 144.08 (2C), 144.19 (2C), 144.89 (2C), 145.01 (2C), 146.68 (1C), 146.87 (2C), 146.92 (2C), 147.06 (2C), 147.43 (1C), 147.66 (2C), 147.80 (2C), 147.89 (2C), 148.05 (2C), 148.19 (2C), 148.32 (2C), 148.39 (2C), 150.85 (2C), 152.48 (2C), 155.85 (2C), 156.25 (2C); IR (powder, cm^{-1}) ν 3056 (w), 3023 (w), 2956 (w), 2920 (m), 2851 (m), 1961 (w), 1943 (w), 1724 (brm), 1597 (m), 1491 (m), 1462 (m), 1445 (m), 1419 (w), 1376 (w), 1288 (w), 1260 (m), 1237 (w), 1203 (w), 1183 (w), 1156 (w), 1069 (m), 1029 (s), 1003 (m), 910 (m), 896 (w), 837 (w), 799 (m), 758 (m), 742 (m), 733 (m), 693 (s), 683 (m), 671 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 260 (81800, shoulder), 272 (75100, shoulder), 354 (22300,

shoulder), 395 (11800, shoulder), 474 (4310, shoulder); APCI-MS (±) m/z = 1147 ([M+H]$^+$), 1146 (M$^-$); Anal Calcd for $C_{60}Ph_5$(allyl) (**6a**) ·0.5CS$_2$: C, 94.74; H, 2.55. Found: C, 94.60; H, 3.02.

Ni(η^3-methallyl)(η^5-PhFCp) (4b). Complex Ni(η^3-methallyl)(η^5-PhFCp) (**4b**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: PhFCpH (10.0 mg, 9.03 μmol), ^{t}BuOK (1.0 M, 10.0 μL, 10.0 μmol) in THF, [NiBr(η^3-methallyl)]$_2$ (1.92 mg, 4.97 μmol), THF (1.0 mL). Yield: 2.43 mg (22%). Ni(η^3-methallyl)(η^5-PhFCp) (**4b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.12 (s, 2H), 1.59 (s, 3H), 2.17 (s, 2H), 7.25 (t, ^3J = 7.6 Hz, 10H), 7.29 (d, ^3J = 7.6 Hz, 5H), 7.73 (d, ^3J = 7.6 Hz, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.79 (1C), 50.62 (2C), 58.96 (5C), 100.87 (1C), 112.69 (5C), 127.34 (5C), 127.91 (10C), 128.53 (10C), 142.69 (5C), 143.40 (10C), 145.09 (10C), 146.82 (5C), 147.76 (10C), 148.58 (5C), 152.12 (10C); IR (powder, cm^{-1}) ν 2960 (m), 2922 (s), 2851 (m), 1720 (m), 1599 (m), 1492 (m), 1459 (m), 1445 (m), 1418 (w), 1285 (m), 1261 (s), 1238 (m), 1201 (m), 1155 (m), 1105 (m), 1091 (m), 1072 (m), 1030 (s), 1018 (s), 959 (m), 832 (m), 798 (s), 761 (m), 734 (s), 711 (m), 697 (s), 668 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 285, 334 (shoulder), 356 (shoulder), 393, 475 (shoulder); HR-APCI-MS (-): m/z; found: 1218.1968; calcd for Ni(η^3-methallyl)(η^5-PhFCp) (**4b**): 1218.1858.

Synthesis of Pd(η^3-allyl)(η^5-MeFCp) (7a). Complex Pd(η^3-allyl)(η^5-MeFCp) (**7a**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) **(3b)**, using the

following compounds: MeFCpH (100 mg, 125 μmol), ^{t}BuOK (1.0 M, 138 μL, 138 μmol) in THF, [PdCl(η^3-allyl)]$_2$ (25.2 mg, 68.9 μmol), THF (10.0 mL). Yield: Pd(η^3-allyl)(η^5-MeFCp) (**7a**): 25.0 mg (21%), C$_{60}$Me$_5$(allyl) (**5a**): 8.6 mg (8.2%).

Pd(η^3-allyl)(η^5-MeFCp) (**7a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.32 (s, 15H), 2.99 (d, ^3J = 11.2 Hz, 2H), 4.32 (d, ^3J = 6.4 Hz, 2H), 5.51 (tt, ^3J = 11.2 Hz, ^3J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.13 (5C), 47.90 (2C), 51.02 (5C), 95.89 (1C), 119.13 (5C), 143.32 (10C), 145.19 (10C), 146.30 (5C), 147.47 (10C), 148.30 (5C), 154.03 (10C); IR (powder, cm^{-1}) ν 2957 (m), 2913 (m), 2853 (w), 1603 (w), 1579 (w), 1548 (w), 1514 (w), 1494 (m), 1454 (m), 1439 (s), 1416 (m), 1366 (m), 1286 (w), 1265 (m), 1236 (m), 1219 (w), 1200 (m), 1178 (w), 1155 (m), 1136 (m), 1111 (m), 1080 (w), 1009 (m), 951 (w), 904 (m), 728 (s), 695 (m), 684 (s), 657 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 273 (78700), 339 (35300), 356 (30400, shoulder), 395 (13100, shoulder), 472 (3430, shoulder); APCI-MS (+) m/z = 942 (M$^+$), Anal Calcd for Pd(η^3-allyl)(η^5-MeFCp) (**7a**) 0.5CS$_2$: C, 83.83; H, 2.05. Found: C, 83.35; H, 2.23.

C$_{60}$Me$_5$(allyl) (**5a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.24 (s, 6H), 2.27 (s, 6H), 2.40 (s, 3H), 3.27 (d, ^3J = 7.2 Hz, 2H), 5.27 (dd, ^3J = 16.0 Hz, ^3J = 2.0 Hz, 1H), 5.41 (dd, ^3J = 10.0 Hz, ^3J = 2.0 Hz, 1H), 6.19 (ddt, ^3J = 16.0 Hz , ^3J = 10.0 Hz, ^3J = 7.2 Hz, 1H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 2.28 (s, 6H), 2.30 (s, 6H), 2.43 (s, 3H), 3.29 (d, ^3J = 7.2 Hz, 2H), 5.30 (dd, ^3J = 16.0 Hz, ^3J = 2.0 Hz, 1H), 5.41 (dd, ^3J = 10.0 Hz, ^3J = 2.0 Hz, 1H), 6.21 (ddt, ^3J = 16.0 Hz , ^3J = 10.0 Hz, ^3J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 24.31 (2C), 27.16 (2C), 28.92 (1C), 40.02

(1C), 50.31 (2C), 52.40 (2C), 53.40 (1C), 61.80 (1C), 118.66 (1C), 131.48 (1C), 142.49 (2C), 142.98 (2C), 143.59 (2C), 143.61 (2C), 144.00 (2C), 144.04 (2C), 144.08 (2C), 144.39 (2C), 144.42 (2C), 145.05 (2C), 145.54 (2C), 146.25 (2C), 146.44 (2C), 146.46 (2C), 147.37 (2C), 147.49 (2C), 147.56 (1C), 147.65 (2C), 147.86 (2C), 147.97 (2C), 147.99 (1C), 148.06 (2C), 148.20 (2C), 148.91 (2C), 153.23 (2C), 154.34 (2C), 155.21 (2C), 157.30 (2C); IR (powder, cm^{-1}) ν 2957 (m), 2915 (m), 2855 (w), 1636 (w), 1603 (w), 1573 (w), 1545 (w), 1521 (w), 1494 (w), 1458 (m), 1439 (s), 1416 (m), 1370 (m), 1286 (m), 1266 (m), 1238 (m), 1200 (m), 1174 (w), 1160 (w), 1153 (w), 1142 (w), 1129 (m), 1105 (m), 1041 (w), 984 (m), 952 (w), 912 (s), 803 (m), 790 (m), 778 (w), 771 (m), 725 (s), 713 (m), 695 (m), 688 (s), 667 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ_{max} (ε) 255 (66800, shoulder), 348 (21900), 356 (20600, shoulder), 396 (12500), 476 (3450, shoulder); APCI-MS (+) m/z = 837 ([M+H]$^+$); Anal Calcd for C$_{60}$Me$_5$(allyl) (**5a**)·0.5CS$_2$: C, 94.03; H, 2.30. Found: C, 94.31; H, 2.75.

Pd(η^3-methallyl)(η^5-MeFCp) (7b). Complex Pd(η^3-methallyl)(η^5-MeFCp) (**7b**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: MeFCpH (100 mg, 125 µmol), ^{t}BuOK (1.0 M, 138 µL, 138 µmol) in THF, [PdCl(η^3-methallyl)]$_2$ (27.2 mg, 68.9 µmol), THF (10.0 mL). Yield: 66.0 mg (55%). Pd(η^3-methallyl)(η^5-MeFCp) (**7b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.33 (s, 15H), 2.36 (s, 3H), 2.94 (s, 2H), 4.25 (s, 2H); ^{1}H NMR (400 MHz, THF-d_8) δ 2.38 (s, 15H), 2.46 (s, 3H), 3,05 (s, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ

24.52 (1C), 31.90 (5C), 49.17 (5C), 51.08 (2C), 113.41 (1C), 118.94 (5C), 143.31 (10C), 145.24 (10C), 146.29 (5C), 147.46 (10C), 148.31 (5C), 154.14 (10C); ^{13}C NMR (100 MHz, THF-d_8) δ 24.47 (1C), 32.11 (5C), 50.35 (2C), 52.24 (5C), 115.19 (1C), 119.89 (5C), 144.10 (10C), 146.31 (10C), 147.15 (5C), 148.28 (10C), 149.12 (5C), 155.51 (10C); IR (powder, cm^{-1}) ν 2956 (m), 2912 (m), 2852 (w), 1571 (w), 1547 (w), 1514 (w), 1494 (w), 1454 (m), 1440 (s), 1410 (m), 1378 (w), 1365 (m), 1285 (w), 1265 (m), 1230 (m), 1199 (m), 1155 (m), 1136 (m), 1111 (m), 1030 (w), 1020 (m), 986 (w), 951 (w), 923 (w), 830 (s), 806 (w), 789 (w), 767 (w), 726 (s), 692 (m), 685 (s), 669 (m), 657 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 272 (97300), 338 (44500), 358 (34700, shoulder), 391 (15900), 473 (4220, shoulder); APCI-MS (+) m/z = 956 (M$^+$); Anal Calcd for Pd(η^3-methallyl)(η^5-MeFCp) (**7b**): C, 86.57; H, 2.32. Found: C, 86.80; H, 2.60.

Pd(η^3-crotyl)(η^5-MeFCp) (7c). Complex Pd(η^3-crotyl)(η^5-MeFCp) (**7c**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: MeFCpH (100 mg, 125 μmol), ^{t}BuOK (1.0 M, 138 μL, 138 μmol) in THF, [PdCl(η^3-crotyl)]$_2$ (27.2 mg, 68.9 μmol), THF (10.0 mL). Yield: 25.6 mg (21%). Pd(η^3-crotyl)(η^5-MeFCp) (**7c**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.02 (d, ^3J = 6.0 Hz, 3H), 2.34 (s, 15H), 2.81 (d, ^3J = 10.8 Hz, 1H), 4.06 (dq, ^3J = 10.8 Hz, 1H), 4.10 (d, ^3J = 6.4 Hz, 1H), 5.41 (ddd, ^3J = 10.8 Hz, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 22.60 (1C), 31.75 (5C), 44.18 (1C), 51.26 (5C), 71.47 (1C), 97.39 (1C), 119.17 (5C), 143.28 (10C), 145.22 (10C), 146.28 (5C), 147.44 (10C),

148.29 (5C), 154.19 (d, J = 4.1 Hz, 10C); IR (powder, cm^{-1}) ν 2957 (m), 2914 (m), 2854 (w), 1454 (w), 1440 (s), 1417 (w), 1366 (m), 1285 (w), 1265 (m), 1236 (m), 1199 (m), 1156 (m), 1136 (m), 1111 (m), 1019 (m), 984 (w), 962 (w), 877 (w), 831 (w), 727 (m), 694 (w), 685 (s), 657 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ_{max} (ε) 258 (78000, shoulder), 273 (71800, shoulder), 348 (23100, shoulder), 390 (13800, shoulder), 471 (4590, shoulder); APCI-MS (+) m/z = 956 (M$^+$).

Synthesis of Pd(η^3-allyl)(η^5-PhFCp) (8a). Complex Pd(η^3-allyl)(η^5-PhFCp) **(8a)** was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) **(3b)**, using the following compounds: MeFCpH (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, [PdCl(η^3-crotyl)]$_2$ (18.2 mg, 49.7 μmol), THF (10.0 mL). Yield: Pd(η^3-allyl)(η^5-PhFCp) **(8a)**: 54.3 mg (48%), Pd(η^3-allyl)(η^5-PhFCp) **(6a)**: 9.5 mg (9.2%). Pd(η^3-allyl)(η^5-PhFCp) **(8a)**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.09 (d, ^3J = 11.2 Hz, 2H), 3.08 (d, ^3J = 6.4 Hz, 2H), 4.70 (tt, ^3J = 11.2 Hz, ^3J = 6.4 Hz, 1H), 7.16-7.20 (m, 15H), 7.77-7.79 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 57.64 (2C), 59.07 (5C), 100.13 (1C), 120.73 (5C), 127.26 (5C), 127.73 (10C), 128.19 (10C), 143.43 (10C), 143.96 (10C), 145.40 (10C), 146.71 (5C), 147.66 (5C), 148.62 (5C), 152.22 (10C); IR (powder, cm^{-1}) ν 3055 (m), 3027 (m), 2999 (w), 2921 (m), 2855 (m), 2350 (w), 2336 (w), 2216 (w), 2191 (w), 1959 (m), 1942 (m), 1887 (m), 1872 (m), 1798 (m), 1596 (s), 1589 (m), 1575 (m), 1491 (s), 1457 (s), 1444 (s), 1419 (m), 1378 (w), 1346 (w), 1332 (w), 1326 (w), 1284 (m), 1267 (m), 1237 (m), 1218 (m), 1200 (m), 1180 (m), 1156 (m), 1107 (m), 1071 (m), 1053 (m), 1030 (s), 1012 (m), 960

(s), 950 (w), 928 (w), 910 (m), 893 (m), 836 (m), 761 (m), 743 (m), 733 (m), 711 (m), 691 (s), 685 (s), 664 (m); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH_2Cl_2) λ_{max} (ε) 260 (115000), 280 (94600, shoulder), 340 (43400, shoulder), 356 (39000, shoulder), 396 (18200); APCI-MS (+) m/z = 1252 (M$^+$); Anal Calcd for Pd(η^3-allyl)(η^5-PhFCp) (**8a**) 0.5C_7H_8: C, 89.18; H, 2.64. Found: C, 89.28; H, 2.90.

Pd(η^3-methallyl)(η^5-PhFCp) (8b). Complex Pd(η^3-methallyl)(η^5-PhFCp) (**8b**) was synthesized as for Pd(η^3-methallyl)(η^5-PhFCp) (**3b**), using the following compounds: PhFCpH (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, [PdCl(η^3-methallyl)]$_2$ (19.6 mg, 49.7 μmol), THF (10.0 mL). Yield: 81.6 mg (71%). Pd(η^3-methallyl)(η^5-PhFCp) (**8b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.63 (s, 3H), 1.95 (s, 2H), 2.99 (s, 2H), 7.15-7.21 (m, 15H), 7.79-7.81 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.62 (1C), 57.82 (2C), 59.18 (5C), 116.07 (1C), 120.66 (5C), 127.19 (5C), 127,79 (10C), 128.26 (10C), 143.41 (10C), 144.10 (5C), 145.40 (10C), 146.70 (5C), 147.65 (10C), 148,60 (5C), 152.25 (10C); IR (powder, cm^{-1}) ν 3055 (m), 3023 (m), 3002 (w), 2916 (m), 2855 (m), 1958 (m), 1866 (m), 1805 (m), 1596 (m), 1493 (s), 1456 (m), 1445 (m), 1417 (m), 1377 (m), 1284 (m), 1265 (w), 1235 (m), 1202 (m), 1155 (m), 1108 (m), 1081 (w), 1072 (w), 1053 (w), 1031 (m), 1021 (m), 1003 (w), 983 (w), 959 (m), 911 (m), 894 (m), 831 (m), 822 (w), 788 (w), 781 (w), 760 (m), 751 (m), 742 (s), 711 (m), 693 (s), 684 (s), 664 (s); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH_2Cl_2) λ_{max} (ε) 260 (83400), 276 (73400, shoulder), 340 (30900), 358 (27200, shoulder), 395 (12800, shoulder); APCI-MS (+) m/z = 1266 (M$^+$); Anal

Calcd for Pd(η^3-methallyl)(η^5-PhFCp) (**8b**) 0.25CS$_2$: C, 87.98; H, 2.51. Found: C, 87.85; H, 2.72.

Pd(η^3-crotyl)(η^5-PhFCp) (8c). Complex Pd(η^3-crotyl)(η^5-PhFCp) (**8c**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: PhFCpH (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, [PdCl(η^3-crotyl)]$_2$ (19.6 mg, 49.7 μmol), THF (10.0 mL). Yield: 60.0 mg (52%). Pd(η^3-crotyl)(η^5-PhFCp) (**8c**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.51 (d, ^3J = 6.4 Hz, 3H), 1.73 (d, ^3J = 10.8 Hz, 1H), 2.67 (d, ^3J = 6.4 Hz, 1H), 3.08 (dq, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H), 4.66 (td, ^3J = 10.8 Hz, ^3J = 6.4 Hz, 1H), 7.20-7.25 (m, 15H), 7.88-7.90 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 18.31 (1C), 54.31 (1C), 59.13 (5C), 78.36 (1C), 101.32 (1C), 120.20 (5C), 127.14 (5C), 127.82 (10C), 128.30 (10C), 143.35 (10C), 145.30 (10C), 145.50 (5C), 146.68 (5C), 147.62 (10C), 148.59 (5C), 152.10 (10C); IR (powder, cm^{-1}) ν 3055 (m), 3022 (m), 2999 (w), 1949 (m), 1875 (m), 1795 (m), 1596 (m), 1583 (m), 1575 (m), 1491 (s), 1456 (s), 1444 (s), 1417 (m), 1376 (m), 1284 (m), 1264 (m), 1234 (m), 1202 (m), 1179 (m), 1155 (m), 1108 (m), 1070 (w), 1052 (w), 1030 (m), 1002 (w), 980 (w), 959 (m), 910 (m), 893 (m), 836 (m), 821 (w), 741 (m), 727 (s), 710 (m), 692 (s), 685 (s), 664 (s); UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 258 (72600), 278 (77900, shoulder), 338 (34500), 356 (31900, shoulder), 394 (16300, shoulder), 472 (4150, shoulder); HR-APCI-MS (-) m/z; found 1266.1564; calcd for Pd(η^3-crotyl)(η^5-PhFCp) (**8c**): 1266.1567.

Pt(η^3-methallyl)(η^5-MeFCp) (9). Complex Pt(η^3-methallyl)(η^5-MeFCp) (**9**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: MeFCpH (50.4 mg, 63.2 μmol), ^{t}BuOK (1.0 M, 69.6 μL, 69.6 μmol) in THF, [PtCl(η^3-methallyl)]$_2$ (19.9 mg, 34.8 μmol), THF (5.0 mL). Yield: Pt(η^3-methallyl)(η^5-MeFCp) (**9**): 4.3 mg (6.5%), C$_{60}$Me$_5$(methallyl) (**5b**): 5.2 mg (9.7%). Pt(η^3-methallyl)(η^5-MeFCp) (**9**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.38 (s, 15H), 2.66 (s with satellite, J_{pt-H} = 27.2 Hz, 3H), 3.06 (s with satellite, J_{pt-H} = 111.6 Hz, 2H), 4.40 (s with satellite, J_{pt-H} = 63.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 23.52 (1C), 31.35 (satellite, J_{pt-C} = 20.7 Hz, 5C), 33.22 (2C), 52.05 (5C), 92.60 (1C), 118.23 (5C), 144.34 (10C), 146.21 (10C), 147.40 (5C), 148.47 (10C), 149.28 (5C), 155.26 (10C); IR (powder, cm^{-1}) ν 2959 (m), 2916 (m), 2852 (m), 1729 (m), 1454 (m), 1439 (s), 1417 (m), 1378 (w), 1367 (m), 1264 (m), 1237 (m), 1213 (m), 1199 (m), 1156 (m), 1136 (m), 1111 (w), 1074 (w), 1036 (w), 1021 (m), 967 (w), 950 (w), 942 (w), 904 (m), 835 (m), 806 (m), 752 (s), 729 (s), 685 (s), 670 (m), 658 (s); UV-vis (toluene/2-propanol = 7/3) λ$_{max}$ 285, 356 (shoulder), 393, 460 (shoulder); APCI-MS (+) m/z = 1045 (M$^+$); HR-APCI-MS (-) m/z; found: 1045.1314; calcd for Pt(η^3-methallyl)(η^5-MeFCp) (**9**): 1045.1375.

C$_{60}$Me$_5$(methallyl) (**5b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.24 (s, 3H), 2.26 (s, 6H), 2.30 (s. 6H), 2.41 (s, 3H), 3.34 (2, 2H), 4.94 (s, 1H), 5.44 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 25.03 (2C), 26.79 (2C), 26.99 (1C), 29.04 (1C), 44.72 (1C), 50.29 (2C), 52.50 (2C), 53.94 (1C), 62.29 (1C), 118.99 (1C), 139.23 (1C), 142.70 (2C), 143.18 (2C), 143.37 (1C), 143.75 (2C), 143.79 (2C), 144.10 (2C), 144.13

(2C), 144.20 (2C), 144.27 (2C), 144.47 (2C), 145.19 (2C), 145.19 (2C), 145.23 (2C), 145.96 (2C), 146.69 (2C), 147.41 (1C), 147.61 (2C), 147.70 (2C), 147.73 (2C), 147.84 (2C), 148.08 (2C), 148.18 (2C), 148.24 (2C), 148.44 (2C), 149.27 (2C), 153.31 (2C), 154.57 (2C), 155.35 (2C), 157.59 (2C); IR (powder, cm^{-1}) ν 2960 (m), 2918 (m), 2855 (m), 1727 (m), 1444 (s), 1417 (w), 1371 (w), 1286 (w), 1265 (w), 1238 (w), 1200 (w), 1172 (w), 1156 (w), 1130 (w), 1112 (w), 1104 (w), 1036 (w), 889 (m), 727 (s), 690 (m), 684 (s), 671 (m), 660 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 286, 348, 360 (shoulder), 394, 470 (shoulder); HR-APCI-MS (-) m/z; found: 850.1714; calcd for $C_{60}Me_5$(methallyl) (**5b**): 850.1722.

Pt(η^3-methallyl)(η^5-PhFCp) (10). Complex Pt(η^3-methallyl)(η^5-PhFCp) (**10**) was synthesized as for Ni(η^3-methallyl)(η^5-MeFCp) (**3b**), using the following compounds: PhFCpH (50.0 mg, 45.2 μmol), ^{t}BuOK (1.0 M, 49.7 μL, 49.7 μmol) in THF, [PtCl(η^3-methallyl)]$_2$ (14.2 mg, 24.8 μmol), THF (5.0 mL). Yield: 8.6 mg (14%). Pt(η^3-methallyl)(η^5-PhFCp) (**10**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.97 (s with satellite, J_{pt-H} = 32.1 Hz, 3H), 2.02 (s with satellite, J_{Pt-H} = 117.8 Hz, 2H), 3.29 (s with satellite, J_{pt-H} = 64.6 Hz, 2H), 7.19 (m, 15H), 7.79 (d, ^3J = 6.9 Hz, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 29.83 (1C), 41.55 (2C), 58.88 (5C), 101.62 (1C), 120.30 (5C), 127.19 (5C), 127.66 (10C), 128.43 (10C), 142.96 (5C), 143.49 (10C), 145.01 (10C), 146.75 (5C), 147.65 (10C), 148.54 (5C), 151.67 (10C); IR (powder, cm^{-1}) ν 2954 (m), 2922 (s), 2852 (m), 1733 (m), 1596 (m), 1492 (s), 1459 (s), 1445 (s), 1418 (w), 1378 (w), 1285 (w), 1263 (w), 1236 (w), 1202 (w), 1186 (w), 1156 (w), 1107

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(w), 1071 (w), 1031 (m), 1021 (w), 1003 (w), 959 (m), 908 (m), 894 (w), 836 (w), 821 (w), 761 (m), 751 (m), 742 (m), 733 (s), 712 (m), 692 (s), 687 (m), 665 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 285, 320 (shoulder), 357 (shoulder), 390, 460 (shoulder); HR-APCI-MS (-) m/z; found: 1355.2092; calcd for Pt(η^3-methallyl)(η^5-PhFCp) (**10**): 1355.2158.

X-ray Diffraction Study. Crystals of Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) and Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) suitable for the X-ray diffraction study were mounted on a MacScience DIP2030 Imaging Plate diffractometer for data collection using MoKα (graphite monochromated, λ = 0.71069 Å) radiation. Crystal data and data statistics are summarized in Table 4. The structure of the complex Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) and Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) were solved by the directed method (SHELXS-97)[43] and expanded using Fourier techniques (DIRDIF-94).[44] The positional parameter and thermal parameters of non-hydrogen atoms of Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) and Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) were refined using a full-matrix least

[43] Sheldrick, G. M. *Program for the solution of Crystal Structures* **1997**, University of Göttingen, Germany.

[44] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory* **1994**, University of Nijmegan, The Netherlands.

square method. Hydrogen atoms were placed at calculated positions (C-H = 0.95 Å) and kept fixed. All non-hydrogen atoms of Pd(η^3-allylic)(η^5-MeFCp) (**7a**: allylic = allyl; **7b**: allylic = methallyl) and Pd(η^3-allylic)(η^5-PhFCp) (**8a**: allylic = allyl; **8b**: allylic = methallyl; **8c**: allylic = crotyl) were anisotropically refined. In the subsequent refinement, the function $\Sigma\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \Sigma\ (||F_o| - |F_c||)/\Sigma|F_o|$ and $wR2 = [\Sigma\omega\ (F_o^2 - F_c^2)^2/\Sigma\ (\omega F_o^4)]^{1/2}$.

Table 4. Crystal Data and Structure Analysis Results for Complexes **7a-b** and **8a-c**

	7a $\cdot CS_2$	**7b** $\cdot (CS_2)_{1.5}$
formula	$C_{69}H_{20}Pd_1S_2$	$C_{70.50}H_{22}Pd_1S_3$
crystal system	orthorhombic	monoclinic
space group	$P\,c\,a\,21$ (No. 29)	$P\,21/n$ (No. 14)
R, R_w ($I>2\sigma(I)$)	0.0683, 0.0693	0.069, 0.0751
$R1$, $wR2$ (all data)	0.1905, 0.1924	0.1735, 0.1827
GOF on F^2	1.071	1.111
a, Å	17.775(5)	12.2190(5)
b, Å	12.451(5)	19.4580(8)
c, Å	17.726(5)	18.0680(6)
α, deg	90	90
β, deg	90	101.240(3)
γ, deg	90	90
V, Å^3	3923(2)	4213.4(3)
Z	4	4
T, K	153(2)	120(2)
crystal size, mm	0.88, 0.52, 0.12	0.8, 0.42, 0.05
D_{calcd}, g/cm^{-3}	1.726	1.689
$2\theta_{min}$, $2\theta_{max}$, deg	4.58, 51.22	4.18, 51.14
no. refl. measured (unique)	3322	7787
no. refl. measured ($I>2\sigma(I)$)	3225	7008
no. parameters	650	674
Δ, eÅ^{-3}	1.226, -1.751	1.287, -1.584
μ	0.635	0.644
extinction coef.	0.0124(17)	0.051(2)

Table 4. (continued)

	8a $\cdot(CS_2)_{2.5}$	**8b** $\cdot(CS_2)_{0.25}$
formula	$C_{95.50}H_{30}Pd_1S_5$	$C_{94.25}H_{32}Pd_1S_{0.5}$
crystal system	triclinic	triclinic
space group	P -1 (No. 2)	P -1 (No. 2)
R, R_w ($I>2\sigma(I)$)	0.0609, 0.0661	0.0811, 0.1114
$R1$, $wR2$ (all data)	0.1691, 0.1752	0.2118, 0.2541
GOF on F^2	1.025	1.063
a, Å	13.5850(7)	13.4150(11)
b, Å	13.5910(5)	21.3700(12)
c, Å	19.2570(9)	21.1590(16)
α, deg	103.033(3)	65.206(3)
β, deg	95.960(2)	80.338(3)
γ, deg	117.024(2)	78.855(4)
V, Å^3	2997(6)	5377.1(7)
Z	2	4
T, K	120(2)	153(2)
crystal size, mm	0.32, 0.2, 0.12	0.45, 0.18, 0.12
D_{calcd}, g/cm^{-3}	1.6	1.589
$2\theta_{min}$, $2\theta_{max}$, deg	4.32, 51.56	4.26, 51.64
no. refl. measured (unique)	10232	18245
no. refl. measured ($I>2\sigma(I)$)	9162	12391
no. parameters	925	1727
Δ, eÅ^{-3}	1.8, -1.003	1.782, -1.794
μ	0.543	0.426
extinction coef.	0.0097(10)	0.0154(10)

Table 4. (continued)

	8c ·$(CHCl_3)_2$
formula	$C_{96}H_{34}Cl_6Pd_1$
crystal system	triclinic
space group	P -1 (No. 2)
R, R_w ($I>2\sigma(I)$)	0.076
$R1$, $wR2$ (all data)	0.115
GOF on F^2	2.543
a, Å	13.742(2)
b, Å	13.943(2)
c, Å	18.660(3)
α, deg	96.250(5)
β, deg	94.406(5)
γ, deg	116.421(6)
V, Å^3	3151(5)
Z	2
T, K	298
crystal size, mm	0.4, 0.2, 0.1
D_{calcd}, g/cm^{-3}	1.588
$2\theta_{min}$, $2\theta_{max}$, deg	3.0, 55.0
no. refl. measured (unique)	10742
no. refl. measured ($I>2\sigma(I)$)	9366
no. parameters	926
Δ, eÅ^{-3}	2.14, -1.49
μ	0.606
extinction coef.	0.0124(17)

Electrochemical Measurements. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and reference electrode was a Ag/Ag$^+$ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc.

Chapter 3   Bucky Ferrocenes

3-1. Introduction

Ferrocene was discovered about fifty years ago.[13] Ferrocene is the most important and famous organometallic compound because the discovery of ferrocene brought the remarkable development of organometallic chemistry.[45] On the other hand, fullerene[1] has been received much attention because as a new type of carbon allotrope with football shape, it may be possible to apply as functional nano molecules because of its specific steric[46] and electronic[47] structures and light acceptability.[48] Discovery of the method to synthesize large amount of fullerene promoted chemical research of the fullerene chemistry.[49]

Many kinds of fullerene-transition metal complexes have been synthesized and investigated for their properties.[5] We thought that functional molecules with useful properties could be synthesized by combining of ferrocene and

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[45] (a) Togni, A.; Hayashi, T. *Ferrocenes: homogeneous catalysis, organic synthesis, material science* (Wiley-VCH, Weinheim, 1995). (b) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II: a review of the literature 1982-1994; vol. 7,* Pergamon: New York, 1995.

[46] (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (b) Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1764.

[47] (a) Allemend, P. –M.; *J. Am. Chem. Soc.* **1991**, *113*, 1050. (b) Haufler, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (c) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

[48] (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135.

[49] Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

fullerene, because these molecules may have properties of both ferrocene and fullerene. However, the formation of hybrid molecule $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60})$, which will be formed by direct combining of ferrocene and C_{60}, are expected to be difficult by theoretical calculations.[50] One of the reasons of its difficulty is that hybrid molecule $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60})$ has open-shell structure because total electrons of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60})$ are odd number. If an odd number of substituents can be introduced on the fullerene sphere, hybrid molecule of ferrocene and fullerene must be synthesized because of its closed shell structure. We already reported the quantitative and regioselective synthesis of pentaorganofullerene derivatives $C_{60}R_5H$ (R = Me, Ph etc).[17,51] Deprotonated products of these molecules can coordinate as cyclopentadienyl ligands to transition metals.[22,23,24,25,26] On the basis of this knowledge, I synthesized and reported its structure and electrochemical properties of "bucky ferrocene" (a hybrid molecule of ferrocene and fullerene derivatives).[23] These investigations showed that bucky ferrocene is stable to air, heat, light and electrochemical reduction/oxidation. These results supported possibilities of construction of functional molecules by starting with bucky ferrocenes as components. In this thesis work, to examine the properties of bucky ferrocenes, I investigated the syntheses, oxidation, reduction and chemical functionalizations of bucky ferrocenes.

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[50] Jemmis, E. D.; Manoharan, M.; Sharma, P. K. *Organometallics* **2000**, *19*, 1879.
[51] Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285.

It is well known that ferrocene $FeCp_2$ is oxidized reversibly to form ferrocenium cation $FeCp_2^+$. On the other hand, fullerene receive six-step one-electron reductions reversibly.[47] Bucky ferrocene $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60}Me_5)$ (**11**, $C_{60}Me_5$ is abbreviated as MeFCp) is oxidized reversively like ferrocene and is reduced reversively like fullerene.[23] To investigate some properties of oxidation or reduction products of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_{60}Me_5)$ (**11**), I measured UV-vis, EPR, and Mössbauer spectra of these compounds. Since there is an electron spin in those oxidation or reduction products, it is expected that many applications as functional molecules with magnetism or electric conduction must be possible like oxidation or reduction products of ferrocene or fullerene.[52,53]

Numerous studies have been reported on the chemical functionalizations of ferrocenes.[54] One of the other properties of ferrocene is the aromaticity of cyclopentadienyl ligands. Thus, cyclopentadienyl moieties of ferrocene can receive electrophilic substitution reaction, for example, Friedel-Crafts reaction. The ^{1}H NMR measurements indicated that the cyclopentadienyl ligands of bucky ferrocenes also have aromaticity.[55] I thus examined here Friedel-Crafts

[52] Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

[53] Kadish, K. M.; Ruoff, R. S. *Fullerenes: recent advances in the chemistry and physics of fullerenes and related materials*; The Electrochemical Society, Inc.: Pennington, 1994.

[54] (a) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II, Vol. 7*; Elsevier Science Ltd.: Oxford, 1995. (b) Togni, A.; Hayashi, T. *Ferrocenes: homogeneous catalysis, organic synthesis, materials science*; Wiley-VCH: Weinheim, 1995.

[55] Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354.

acylation of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp). Since the cyclopentadienyl moiety of bucky ferrocene can be functionalized, it is expected to do wide variety of applications based on chemical functionalizations of bucky ferrocene.

3-2. Spectroscopic Measurements and Properties of Pentamethylated Bucky Ferrocene Fe(η^5-Cp)(η^5-MeFCp)

The ^{1}H and ^{13}C NMR spectra showed that bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp)[23] (**11**) has C_{5v} symmetry. In INEPT measurement, coupling constant $^1J_{\text{C-H}}$ of C(CH$_3$)-H(CH$_3$) and C(C$_5$H$_5$)-H(C$_5$H$_5$) are 129 and 159 Hz, which are typical values for coupling constant of C(CH$_3$)-H(CH$_3$) and C(C$_5$H$_5$)-H(C$_5$H$_5$). The vertical relaxation (T1) of proton signals are 0.55 s (H(CH_3FCp)) and 1.30 s (H(C_5H_5)), which are typical values as H(CH$_3$) and H(C$_5$H$_5$). Since the hydrogen atoms of the Cp ligand and those of methyl groups in the MeFCp ligand are in van der Waals contact, which was shown by the X-ray crystal structure analysis of Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**), I thought that five hydrogen atoms of the Cp ligand and five methyl groups of the MeFCp one are engaged like cogwheels and the Cp and MeFCp ligands rotate synchronously. Therefore, I measured ^{1}H NMR spectrum of (**11**) at low temperature (0 to –50 °C), but I could not obtain the evidence of synchlonism between five hydrogen atoms of the Cp ligand and five methyl groups of the MeFCp one.

Next, I investigated stabilities of bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**).

Bucky ferrocene $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60}\text{Me}_5)$ (**11**) is stable under heating at 200 °C for 24 h in vacuo. Even in benzene, $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60}\text{Me}_5)$ (**11**) is stable to irradiation of 400 W high pressure mercury lamp. Thus, it is expected that bucky ferrocenes become useful functional molecules stable under harsh condition. C_{60} can be excited from $^1C_{60}$ to $^1C_{60}^*$ by irradiation of light, and $^1C_{60}^*$ then goes to $^3C_{60}^*$.[56] When the energy of $^3C_{60}^*$ is transferred to moleculer oxygen ($^3O_2$), singlet oxygen ($^1O_2$) forms.[57] Thus C_{60} acts as photo-sensitizer (Scheme 3).[58] To elucidate the ability of bucky ferrocene $Fe(\eta^5\text{-Cp})(\eta^5\text{-C}_{60}\text{Me}_5)$ (**11**) as photo-sensitizer, I carried out the experiment as shown in eq 4.

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[56] (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. (c) Foote, C. S. *Top. Curr. Chem.* **1994**, *169*, 347.

[57] (a) Nagano, T.; Arakane, K.; Ryu, A.; Masunaga, T.; Shinmoto, K.; Mashioka, S.; Hirobe, M. *Chem. Pharm. Bull.* **1994**, *42*, 2291. (b) Hamano, T.; Okuda, K.; Mashino, T.; Hirobe, M.; Arakane, K. Ryu, A.; Mashiko, S.; Nagano, T. *Chem. Commun.* **1997**, 21. (c) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073. (d) Hung, R. R.; Grabowski, J. J. *Chem. Phys. Lett.* **1992**, *192*, 249. (e) Anderson, J. L.; An. Y. –Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763. (f) Williams, R. M.; Verhoeven, J. W. *Spectrochem. Acta.* **1994**, *50A*, 251. (g) An, Y. –Z.; Viado, A. L.; Arce, M. –J.; Rubin, Y. *J. Org. Chem.* **1995**, *50*, 8330. (h) Bensasson, R. V.; Bienvenue, E.; Jant J. M.; Leach, S.; Seta, P.; Schuster, D. L. Wilson, S. R.; Zhao, H. *Chem. Phys. Lett.* **1995**, *254*, 566.

[58] (a) Tokuyama, H.; Yamago, S.; Nakamura, E.; Takashi, S.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918. (b) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *54*, 1135.

Scheme 3. Formation of singlet oxygen by irradiation of C_{60}.

$$^1C_{60} \xrightarrow{\;h\nu\;} {}^1C_{60}{}^* \xrightarrow{\;ISC\;} {}^3C_{60}{}^* \xrightarrow{\quad} {}^1C_{60}$$

with $^3O_2 \rightarrow {}^1O_2$

ISC = intersystem crossing

α-terpinene $\xrightarrow[\substack{\text{photo-sensitizer (1.0 mol\%)} \\ \text{toluene (1.3 ml), 40 °C, 1h}}]{\substack{h\nu \text{ (100 W tungsten lamp)} \\ O_2 \text{ (10 ml / 1.5 min)}}}$ ascaridole (4)
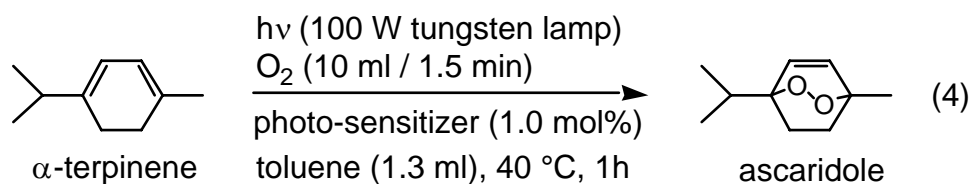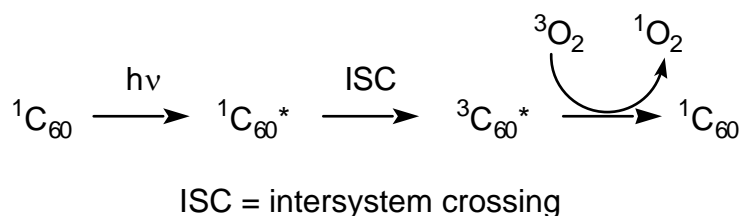
photo-sensitizer	ascaridole*	α-terpinene*
Fe(η^5-Cp)(η^5-MeFCp)	4.6 %	20 %
C_{60}	97 %	0 %

* NMR yield

Oxidation reaction of α-terpinene in toluene was carried out in the presence of Fe(η^5-Cp)(η^5-C_{60}Me$_5$) (**11**) (1.0 mol%) as photo-sensitizer. In this reaction, a solution was irradiated by a 100 W tungsten lamp. As a result, ascaridole was obtained in 4.6% yield. This result showed that bucky ferrocene can act as a photo-sensitizer (ferrocene does not show the ability of photo-sensitizer) although this efficiency is much lower than that of C_{60} (ascaridole: 97% yield). The oxidation reaction did not proceed in the absence of C_{60} or bucky ferrocene Fe(η^5-Cp)(η^5-C_{60}Me$_5$) (**11**). The lower ability of bucky ferrocene

Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) compared with C$_{60}$ indicated that the lifetime of triplet excited state of bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) is shorter than that of C$_{60}$. After the reactions, bucky ferrocene was recovered without trace of other products (HPLC analyses).

3-3. Theoretical Calculations on Pentamethylated Bucky Ferrocene

Bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) may be dissected into three π-conjugated systems (Cp-Fe, the fullerene cyclopentadienide moiety and the bottom C$_{50}$ part). We previously showed that the 50π electron system of C$_{60}$Me$_5^-$ is conjugated with cyclopentadienide moiety using 2π-orbital lobes inside the fullerene core (cf. green circle in Figure 9b)[17].

Molecular orbitals of pentamethylated bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) were calculated by DFT calculations for the geometry of the crystal structure (C_{5v} symmetry) (Figure 9) (in collaboration with Dr. Masahiro Yamanaka).[23] These experimental results suggested that such endohedral homoconjugation is also present in bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) between the C$_{50}$ part and the fullerene cyclopentadienide moiety, and even extends to the Cp-Fe one. The orbital picture in Figure 9 shows a fully extended d-π conjugation system involving iron 3d and carbon 2p-orbitals (Figure 9a). Note the endohedral in-phase interaction between the C$_{50}$ part and the fullerene cyclopentadienide moiety at their juncture (green circle, Figure 9b). The corresponding out-of-phase interaction is found as a higher energy orbital

(HOMO-8, E_1, -6.54 eV).
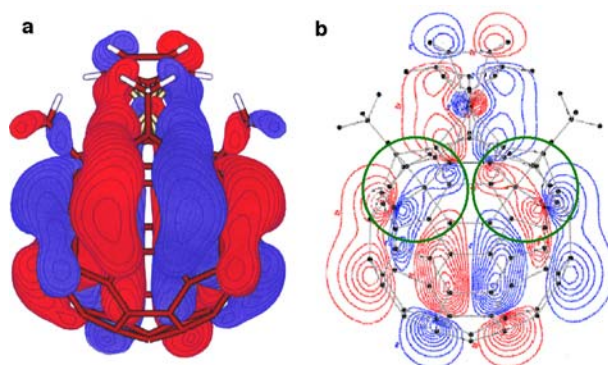
Figure 9. Molecular orbital of Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) obtained by DFT calculations for the geometry of the crystal structure (C_{5v} symmetry). (**a**) 3D Snapshot. (**b**) Contour plot of the HOMO-11 orbital (E_1, -6.88 eV).

Since the ferrocene moiety donates electron to the fullerene moiety, bucky ferrocene is expected to show a large dipole moment, which is calculated to be 5.6 D.

As a result, I have successfully created an entirely new class of d-π conjugate system through face-to-face fusion of ferrocene and fullerene, in which an electron flows through the pentagonal "window" [the fullerene cyclopentadienide moiety in Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**)] shared by the two fragments.

3-4. Acylation of Cyclopentadienide Group of Pentamethylated Bucky Ferrocene

Ferrocene FeCp$_2$ can act as a building block of functional molecules.[54] For this to be achieved, it is important to functionalize the Cp moiety of ferrocene. In fact, many investigations on the derivatization of ferrocene have been reported.[54] The most important is Friedel-Crafts acylation. These reactions are based on the aromatic nature of Cp moiety of ferrocene. Acyl ferrocenes Fe(C$_5$H$_4$COR)Cp are often used as starting materials of various ferrocene derivatives.[59]

The ^{1}H NMR measurement of bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) **11** indicated that the Cp ring of Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) is aromatic.[23] Thus, I examined the acylation of Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**). The reaction of Fe(η^5-Cp)(η^5-C$_{60}$Me$_5$) (**11**) with acyl chloride (acyl = acetyl, benzoyl and cynnamoyl) and anhydrous aluminum chloride took place smoothly in CS$_2$ (38-43% yield) (eq 5). Acetylation of phenyl bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) (see below) did not proceed under the same reaction

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[59] (a) Vogel, H.; Rausch, M. D.; Rosenberg, H. *J. Org. Chem.* **1957**, *22*, 1016. (b) Arimoto, F. S.; Haven, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 6295. (c) Gokel, G.; Ugi, I. *Angew. Chem. Int. Ed.* **1971**, *10*, 191. (d) Ratajczak, A.; Misterkiewicz, B. *J. Organomet. Chem.* **1975**, *91*, 73. (e) Eberle, G.; Ugi, I. *Angew. Chem. Int. Ed.* **1976**, *15*, 492. (f) Stüber, S.; Ugi, I. *Synthesis* **1973**, 309. (g) Allenmark, S. *Tetrahedron Lett.* **1974**, 371. (h) Allenmark, S.; Kalen, K.; Sandblom, A. *Chem. Scr.* **1975**, *7*, 97. (i) Herrmann, R.; Ugi, I. *Angew. Chem. Int. Ed.* **1979**, *18*, 956. (j) Herrmann, R.; Ugi, I. *Tetrahedron* **1981**, *37*, 1001. (k) Misterkiewicz, B. *J. Organomet. Chem.* **1982**, *224*, 43. (l) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1980**, *50*, 2520.

condition probably because of the steric hindrance of the five phenyl groups of bucky ferrocene Fe(η^5-Cp)(η^5-C$_{60}$Ph$_5$) (**12**).

$$ (5) $$

13a: R = Me   38%
13b: R = Ph   41%
13c: R = CH=CHPh   43%
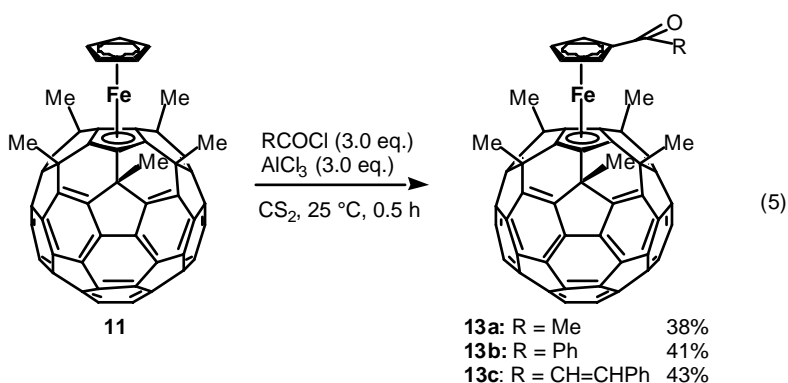
APCI-MS spectra supported the structures of the acyl bucky ferrocenes Fe(η^5-C$_5$H$_4$COR)(η^5-MeFCp) (**13a**: R = Me, **13b**: R = Ph, **13c**: R = CH=CHPh). The ^{1}H and the ^{13}C NMR spectra showed that the acyl cyclopentadienyl moiety is in C_s symmetry and the MeFCp ligand is in C_{5v} symmetry. These results indicated that the rotation rates of acyl group, acyl cyclopentadienyl and FCp moieties around the C(COCH$_3$)-C(Cp) or Fe-Cp or Fe-FCp axis are faster than the relaxation time of NMR measurement. In the acetyl bucky ferrocene Fe(η^5-C$_5$H$_4$COMe)(η^5-MeFCp) (**13a**), the proton signals of the methyl group (acetyl part) (2.62 ppm) and the Cp moiety (5.21, 5.42 ppm) were observed at lower magnetic field that those of Fe(C$_5$H$_4$COMe)Cp (Me: 2.40 ppm; Cp: 4.50, 4.77 ppm),[60,61] suggesting the electron withdrawing nature of the FCp ligand.

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[60] Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416.

In the IR spectra of acyl bucky ferrocenes $Fe(\eta^5\text{-}C_5H_4COMe)(\eta^5\text{-}MeFCp)$ (**13a**) and $Fe(\eta^5\text{-}C_5H_4COPh)(\eta^5\text{-}MeFCp)$ (**13b**), the absorption bands due to the carbonyl group are 1670 and 1640 cm^{-1}, the value are smaller than those of the corresponding acyl ferrocene (1662 [62,63] and 1627 [64,65] cm^{-1}) or acetyl pentamethylferrocene (1664 or 1632 cm^{-1})[66] (Figure 10). A possible explanation of the result is that the electron withdrawing nature of the FCp ligand strengthens the carbonyl bonds. Lower wave number shift, which was caused by the exchange from the acetyl group to the benzoyl one, is due to conjugation between phenyl group and carbonyl one (Figure 10).

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[61] I reexamined the synthesis and ^1H NMR measurement of $Fe(C_5H_4COMe)Cp$ to compare the values of chemical shifts under the same condition.

[62] Rinehart Jr, K. L.; Motz, K. L.; Moon, S. *J. Am. Chem. Soc.* **1957**, *79*, 3416.

[63] I reexamined the synthesis and IR measurement of $Fe(C_5H_4COMe)Cp$ to compare the value of wave number under the same condition.

[64] Weliky, N.; Gould, E. S. *J. Am. Chem. Soc.* **1957**, *79*, 2742.

[65] I reexamined the synthesis and IR measurement of $Fe(C_5H_4COPh)Cp$ to compare the value of wave number under the same condition.

[66] I reexamined the syntheses and IR measurements of $Fe(C_5H_4COR)Cp^*$ (R = Me, Ph) to compare the values of wave number under the same condition.
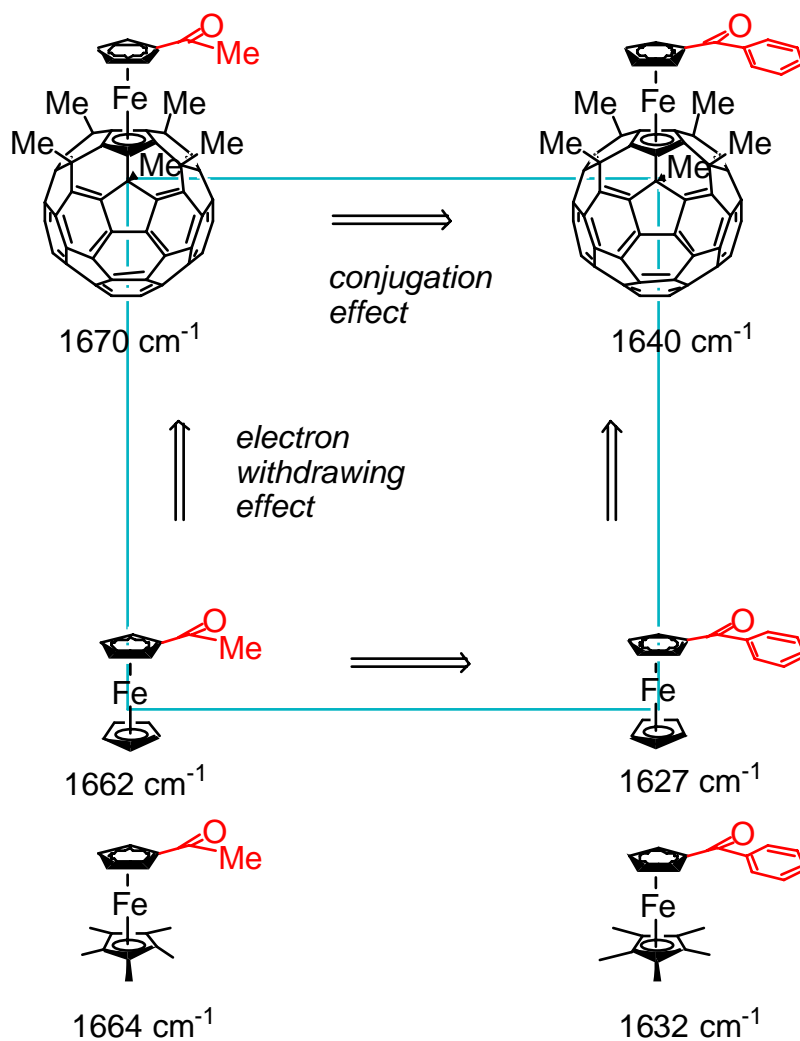
Figure 10. Wave numbers of vibrations of carbonyl groups for acyl bucky ferrocenes, acyl ferrocenes and acyl pentamethylferrocene.

3-5. X-ray Crystal Structure of Acetyl Bucky Ferrocene

Dark red single crystals of acetyl bucky ferrocene Fe(η^5-C$_5$H$_4$COMe)(η^5-MeFCp) (**13a**) were obtained by recrystallization from CS$_2$/EtOH. An X-ray crystal structure analysis of this complex was performed (Figure 11, Table 8).
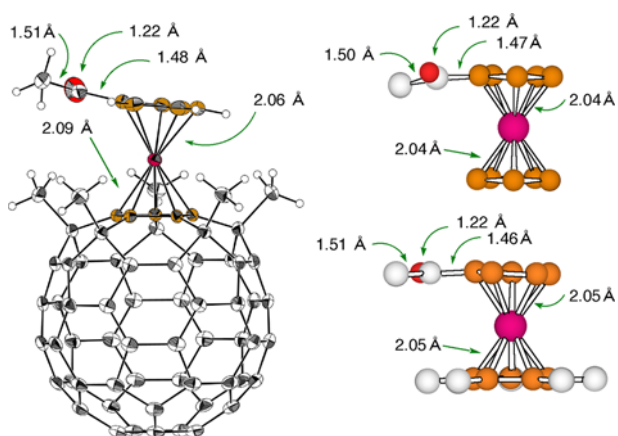
Figure 11. Molecular structure of acetyl bucky ferrocene Fe(η^5-C$_5$H$_4$COMe)(η^5-MeFCp) (**13a**) (30% probability level ellipsoids. The solvent molecule in the unit cell is omitted for clarity). Comparison of the bond lengths with acetyl ferrocene and acetyl pentamethylferrocene.

The FCp ligands coordinate to the iron atom in an η^5-fashion. The Cp and FCp ligands have an eclipsed comformation, which stands in contrast to bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**). Acetyl and Cp groups are tilted against the FCp plain. This result is due to steric repulsion between the acetyl and the methyl groups of the FCp ligand. The bond lengths of the acetyl bucky ferrocene Fe(η^5-C$_5$H$_4$COMe)(η^5-MeFCp) (**13a**) were comparable to those of acetyl ferrocene and acetyl pentamethylferrocene (Figure 11). The bond length of the carbonyl group (1.22 Å) of the acetyl bucky ferrocene Fe(η^5-C$_5$H$_4$COMe)(η^5-MeFCp) (**13a**) is the same as those of acetyl ferrocene and

acetyl pentamethylferrocene. The bond lengths of C(Me)-C(CO) (1.51 Å) and C(CO)-C(Cp) (1.48 Å) of $Fe(\eta^5\text{-}C_5H_4COMe)(\eta^5\text{-MeFCp})$ (**13a**) are also the same as those of acetyl ferrocene and acetyl pentamethylferrocene. The averaged bond lengths between Fe-C(Cp), Fe-C(Cp*) and Fe-C(FCp) are 2.04, 2.05 and 2.09 Å, respectively. These results are in good accordance with the tendency of steric repulsion between acetyl ligand and Cp, Cp* or FCp ones. Another possible reason why the averaged bond length of Fe-C(FCp) is longer than that of Fe-C(Cp) or Fe-C(Cp*) is that the overlap of d orbitals of iron atom and p orbitals of FCp ligand is not effective than those in Fe-C(Cp) or Fe-C(Cp*) bonds because of the spherical shape of FCp ligand.

3-6. Oxidation of Bucky Ferrocenes

It is well known that ferrocene $FeCp_2$ can be transformed reversibly into ferrocenium $[FeCp_2]^+X^-$ (X^- = counter anion) by oxidation.[67] Cyclic voltammetry of bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) indicates that bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) can be oxidized reversibly. Thus, it must be possible to obtain bucky ferroceniums by oxidation of bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) with a proper oxidant.

Preparations of bucky ferrocenium $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})]^+$ and

[67] (a) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559. (b) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

$[Fe(\eta^5\text{-Cp}](\eta^5\text{-PhFCp})]^+$ were performed by the oxidation of $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) with ammoniumyl salt $[(4\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$ (eq 6). The color of the THF solution of bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) changed from light orange to dark orange as oxidizer was added to the THF solution of bucky ferrocenes. At the time, the dark blue color of ammoniumyl salt disappeared immediately.

11: R = Me
12: R = Ph

14: R = Me
15: R = Ph
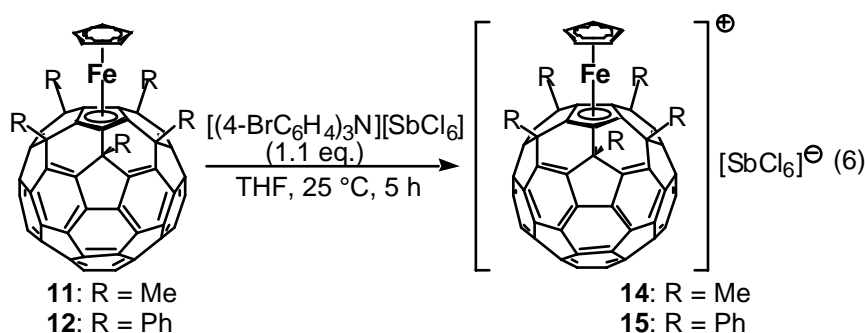
While bucky ferrocenium compounds $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][\text{SbCl}_6]$ (**14**) and $[Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})][\text{SbCl}_6]$ (**15**) are insoluble in non-polar solvents, hexane and carbon disulfide, they are slightly soluble in polar organic solvent, benzonitrile, THF and DMF (however, insoluble in ethanol and acetonitrile).

3-7. UV-vis Spectra of Bucky Ferroceniums

By the oxidation of ferrocene $FeCp_2$, the color changes from yellow to dark blue.[67] This phenomenon is mainly due to ligand-metal charge transfer (LMCT).

To observe the change of color before and after oxidation of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**), I measured the UV-vis spectra.

At the first stage, I measured UV-vis spectrum of bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) under air (Figure 12). This spectrum is very different from that of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**).[23]

Figure 12. UV-vis spectrum of bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) in benzonitrile.

At the next stage, I examined the changes of the UV-vis spectra of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) under oxidation conditions at constant voltage (Figure 13). The UV-vis spectra changed slowly by the oxidition of Fe(η^5-Cp)(η^5-MeFCp) (**11**) at 800 mV (Figure 13 (a)). After 30 min, the UV-vis spectrum became the same as that of bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**). This result shows that bucky ferrocenium

70

can be obtained by both chemical and electrochemical oxidations. After the oxidation, reduction was performed at –600 mV (Figure 13 (b)). The UV-vis spectra changed reversibly, and after 130 min, the spectra became equal to that of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**). This observation shows that bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) is thermally stable under electrochemical conditions.
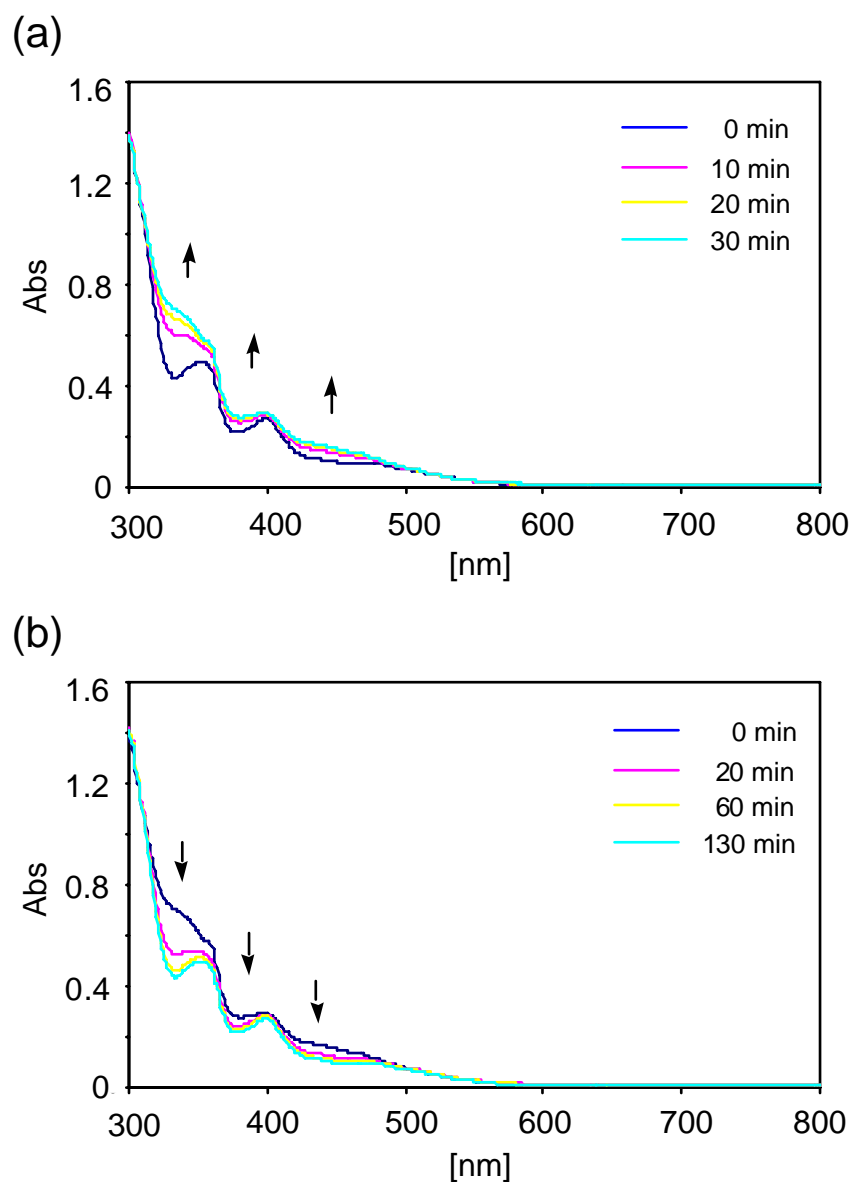
Figure 13. Changes of UV-vis spectra of bucky ferrocene $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)$ (**11**) under oxidation conditions at constant voltage. (a) Oxidation of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)$ (**11**) (PhCN, 800 mV vs Ag/Ag$^+$). (b) Reduction after oxidation of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)$ (**11**) at (a) (benzonitrile, -600 mV vs Ag/Ag$^+$).

While ferrocenium $FeCp_2^+$ has a characteristic absorption at 617 nm,[68] which is assigned as LMCT, such absorption could not be observed in the UV-vis spectrum of bucky ferrocenium $[Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)][SbCl_6]$ (**14**). Two reasons can be suggested; One is that the absorbance of LMCT (in the case of ferrocene $FeCp_2$, ε = 420) in bucky ferrocenium $[Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)][SbCl_6]$ (**14**) is much smaller than that of fullerene core (ε value can be a few thousand to a hundred thousand). The other is that the magnitude of the wavelength of LMCT is too small to observe, as in known for ferrocenes with an electron withdrawing ligand (Table 5).[68]

Table 5. Wave Lengths of LMCT in Some Ferrocenium Ions.

$Fe(C_5H_4CH_3)_2^+$	645 nm
$Fe(C_5H_5)_2^+$	617 nm
$Fe(C_5H_5)(C_5H_4COCH_3)^+$	529 nm

[68] Prince, R. *J. Chem. Soc., Chem. Commun.* **1970**, 280.

3-8. EPR Measurement of Bucky Ferrocenium

Since ferrocenium $FeCp_2^+$ has an open-shell structure, it is EPR active.[69] Cyclic voltammetry and Mössbauer spectrum (described below) of bucky ferroceniums $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) and $[Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})][SbCl_6]$ (**15**) indicated that the oxidations of bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) occurred in its ferrocene moieties. Then $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) and $[Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})][SbCl_6]$ (**15**) must be EPR active like ferrocenium $FeCp_2^+$. I measured EPR spectrum of $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) as solid and solution phases at 4.4 K (Figure 14).
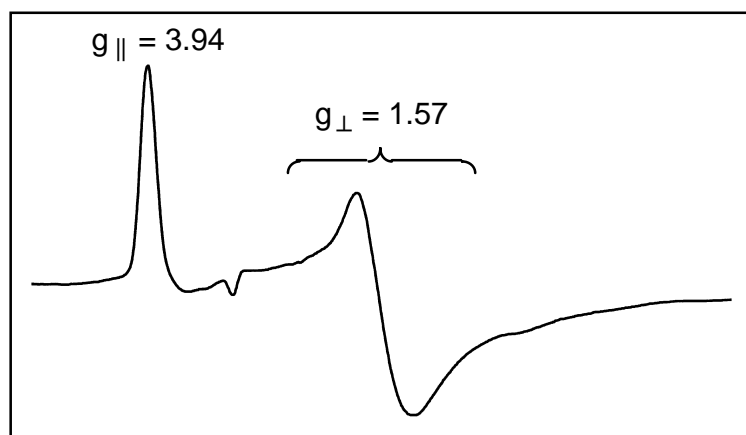
Figure 14. EPR spectrum of bucky ferrocenium $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**).

[69] (a) Prins, R.; Reinders, F. J. *J. Am. Chem. Soc.* **1969**, *91*, 4929. (b) Prins, R.; Kortbeek, A. G. T. G. *J. Organomet. Chem.* **1971**, *33*, C33.

The EPR signals of bucky ferrocenium $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) could not be observed at 25 °C as in the case of ferrocenium $FeCp_2^+$ because spin-lattice relaxation time is very short. The g-values of $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) are 3.94 ($g_{||}$) and 1.57 ($g_\perp$), which are comparable to those in ferroceniums (Table 5).[69]

Table 6. The g-Values of Bucky Ferrocenium $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) and Some Ferroceniums[a,b]

	$g_{||}$	$g_\perp$	Δg
$[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**)[c]	3.94	1.57	2.37
$[FeCp_2^+]$	4.35	1.26	3.09
$[Fe(C_5H_4Me)_2][PF_6]$	4.00	1.92	2.08
$[Fe(C_5H_4Me)_2][TCA]\cdot TCAA$[d]	4.44	1.22	3.22
$[Fe(C_5Me_5)_2][PF_6]$	4.43	1.35	3.08
$[Fe(C_5Me_5)_2][TCA]\cdot 2(TCAA)$[d]	4.37	1.26	3.11

[a] ref 69. [b] 12 K. [c] 4.4 K. [d] TCA = trichloroacetate; TCAA = trichloroacetic acid.

3-9. Mössbauer Spectra of Bucky Ferrocenes and Bucky Ferroceniums

It is well known that ferrocene $FeCp_2$ and ferrocenium $[FeCp_2]^+$ are Mössbauer active.[70] To elucidate the environment around iron center of bucky ferrocenes $Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})$ (**11**) and $Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})$ (**12**) and bucky ferrocenium $[Fe(\eta^5\text{-Cp})(\eta^5\text{-MeFCp})][SbCl_6]$ (**14**) and $[Fe(\eta^5\text{-Cp})(\eta^5\text{-PhFCp})][SbCl_6]$ (**15**), I measured Mössbauer spectra of these complexes (Table 7).

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[70] Birchall, T.; Drummond, I. *Inorg. Chem.* **1971**, *10*, 399.

Table 7. Isomer Shifts and Quadrupole Splitting of Bucky Ferrocenes and Bucky Ferroceniums.[a]

	I.S.[b] (mm/s)	Q.S.[c] (mm/s)
FeCp$_2$	0.537(1)	2.418(1)
Fe(η^5-Cp)(η^5-MeFCp) (**11**)	0.575(4)	2.475(4)
Fe(η^5-Cp)(η^5-PhFCp) (**12**)	0.586(4)	2.471(1)
[Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**)	0.573(7)	0.185(7)
[Fe(η^5-Cp)(η^5-PhFCp)][SbCl$_6$] (**15**)	0.612(9)	0.108(9)

[a] Measurements were performed at 90 K. [b] Isomer shift. [c] Quadrupole splitting.

Mössbauer spectra of bucky ferrocenes Fe(η^5-Cp)(η^5-MeFCp) (**11**) and Fe(η^5-Cp)(η^5-PhFCp) (**12**) and bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) and [Fe(η^5-Cp)(η^5-PhFCp)][SbCl$_6$] (**15**), showed typical ones as ferrocene or ferrocenium. The values of isomer shifts and quadrupole splittings are comparable to those of ferrocene or ferrocenium. The results of both the UV-vis and ESR spectra and the Mössbauer ones indicate that the oxidation of bucky

ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) provides bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) reversively.

3-10. UV-vis Spectra of Bucky Ferrocenates

Electrochemical measurement of the bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) showed that Fe(η^5-Cp)(η^5-MeFCp) (**11**) received first reversible one-electron reduction and second irreversible one-electron one.[23] I thus investigated the reductions of Fe(η^5-Cp)(η^5-MeFCp) (**11**) under constant voltages and measured changes of UV-vis spectra of Fe(η^5-Cp)(η^5-MeFCp) (**11**) (Figure 15).

The UV-vis spectra changed slowly by the reduction of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) at -1650 mV (Figure 15 (a)). After 120 min, the UV-vis spectrum did not change any more. After the reduction, oxidation was performed at 0 mV (Figure 15 (b)). The UV-vis spectra changed reversibly, and after 60 min, the spectra became the same as that of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**). This observation shows that bucky ferrocenate **16** is thermally stable under electrochemical conditions.[71]

Next, I measured UV-vis spectra at –2000 mV (Figure 16). After 70 min, the spectrum did not change at all. The spectrum remained the same after re-oxidation. This observation indicated the decomposition of the bucky ferrocene species.

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[71] I could not measure the UV-vis spectrum of one electron chemical reduction product of **11** because of the oxidation when I prepared UV-vis sample (UV-vis absorption of **11** was observed).
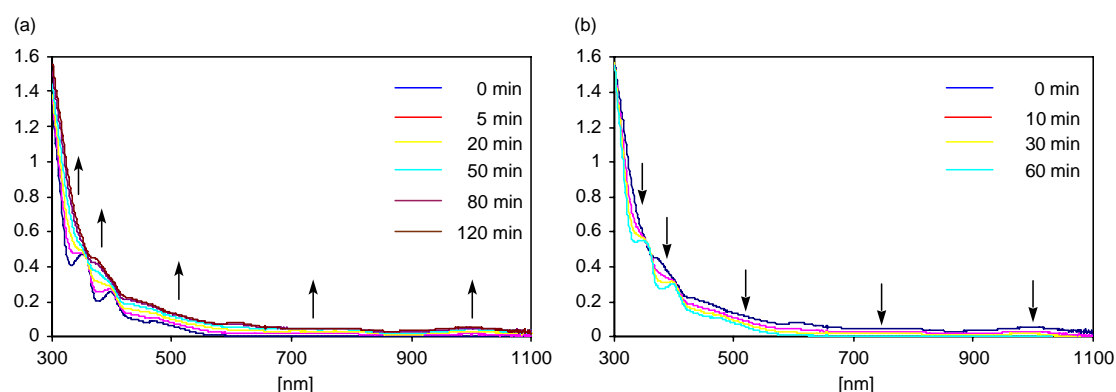
Figure 15. Changes of UV-vis spectra of Fe(η^5-Cp)(η^5-MeFCp) (**11**) in benzonitrile under constant voltage. (a) Reduction of Fe(η^5-Cp)(η^5-MeFCp) (**11**) (-1650 mV vs Ag/Ag$^+$). (b) Oxidation after the reduction (a) (0 mV vs Ag/Ag$^+$) to show the reversibility of the reduction.
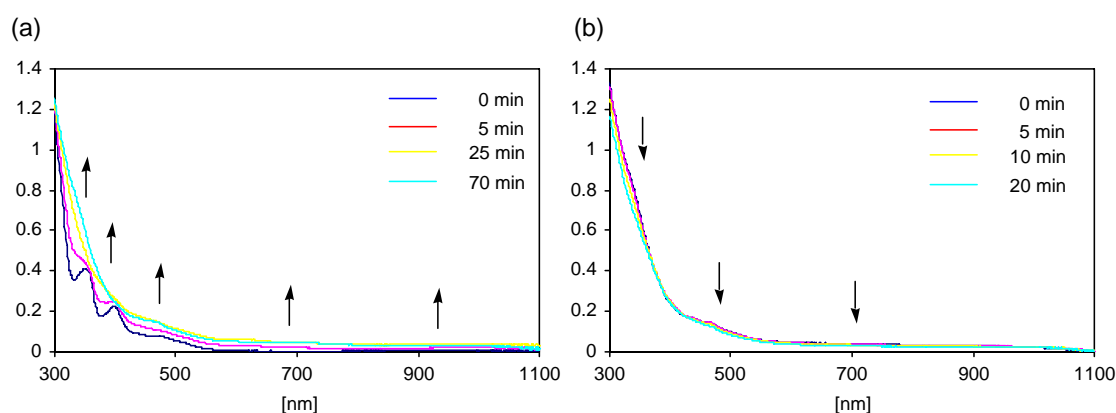
Figure 16. Changes of UV-vis spectra of Fe(η^5-Cp)(η^5-MeFCp) (**11**) in benzonitrile under constant voltage. (a) Reduction of Fe(η^5-Cp)(η^5-MeFCp) (**11**) (-2000 mV vs Ag/Ag$^+$). (b) Oxidation after the reduction at –2000 mV (0 mV vs Ag/Ag$^+$) to show the irreversibility of the two-electron reductions.

3-11. Synthesis of Functionalized Bucky Ferrocenes

Various bucky ferrocenes could be synthesized by the use of ArFCp ligands [Ar = Ph, 4-MeOC$_6$H$_4$, 3-CH$_2$=CHC$_6$H$_4$, 4-CH$_2$=CHC$_6$H$_4$, 3-BrCH$_2$CH(Br)C$_6$H$_4$ and 4-BrCH$_2$CH(Br)C$_6$H$_4$] instead of MeFCp one. Phenyl bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) was synthesized by the procedure similar to that reported for methyl bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) (eq 7). High resolution APCI-TOF-MS (+) data were consistent with the assigned structure. The ^{1}H and ^{13}C NMR measurements of bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) showed that the Cp and FCp moieties have C_{5v} symmetry. These results show that the rotation rates of Cp and FCp moieties around the Fe-Cp and Fe-FCp axis are faster than the relaxation time of NMR measurement.
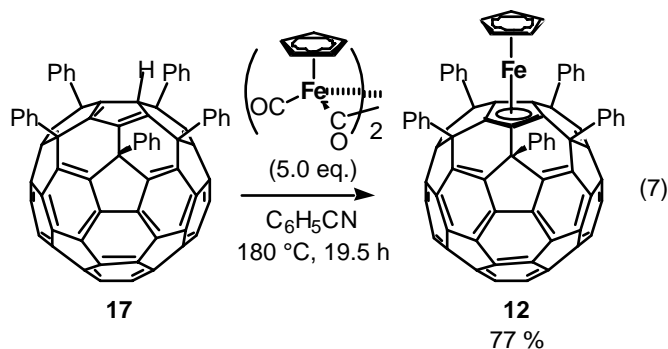
As is the previous experiments, it seemed to be difficult to functionalize phenyl groups of bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**). These difficulties must be due to the low nucleophilicity of aryl groups (fullerene part is an electron withdrawing group) and the difficulty of introducing functional

groups to five aryl groups at the same time. So I tried to synthesize functionalized bucky ferrocenes by constracting ferrocene moiety on five-fold functionalized aryl adducts of C_{60}.

I synthesized 4-methoxyphenyl bucky ferrocene $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**) by the reaction of $C_{60}(4\text{-}MeOC_6H_4)_5H$ (**18**) with $[FeCp(CO)_2]_2$ (eq. 8). After the purification by silica gel short path and recrystalization, bucky ferrocene $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**) was obtained as air- and moisture-stable dark red crystals in 8% isolated yield. Structure assignment of bucky ferrocene $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**) was achieved by the ^1H and ^{13}C NMR and high resolution APCI-TOF-MS measurements.
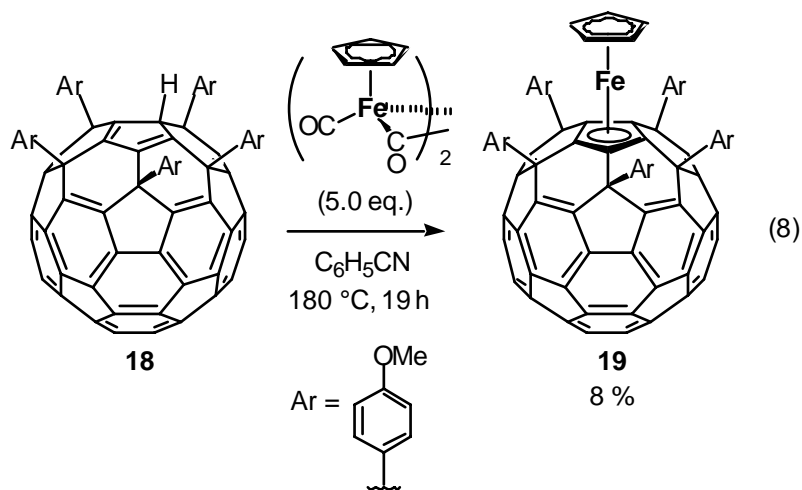
Next, I tried to synthesize 3- or 4-vinylphenyl bucky ferrocenes because vinyl groups of these molecules are expected to be functionalized easily. As

starting materials, I synthesized pentaarylated fullerene derivatives $C_{60}(3-CH_2=CHC_6H_4)_5H$ (**20**) and $C_{60}(4-CH_2=CHC_6H_4)_5H$ (**21**) according to the synthetic method of $C_{60}Ph_5H$. After the purification by silica gel and recrystalization, 3-vinylphenyl and 4-vinylphenyl fullerene derivatives $C_{60}(3-CH_2=CHC_6H_4)_5H$ (**20**) and $C_{60}(4-CH_2=CHC_6H_4)_5H$ (**21**) were obtained as orange powders in 89 and 47% isolated yield (eq 9). High resolution APCI-TOF-MS (+) measurements indicated the formation of $C_{60}(3-CH_2=CHC_6H_4)_5H$ (**20**) and $C_{60}(4-CH_2=CHC_6H_4)_5H$ (**21**). The ^1H and ^{13}C NMR measurements were also consistent with the assigned structures (C_s symmetry). While the solubility of $C_{60}(3-CH_2=CHC_6H_4)_5H$ (**20**) in organic solvent is much better than $C_{60}Ph_5H$, that of $C_{60}(4-CH_2=CHC_6H_4)_5H$ (**21**) is much lower than $C_{60}(3-CH_2=CHC_6H_4)_5H$ (**20**).
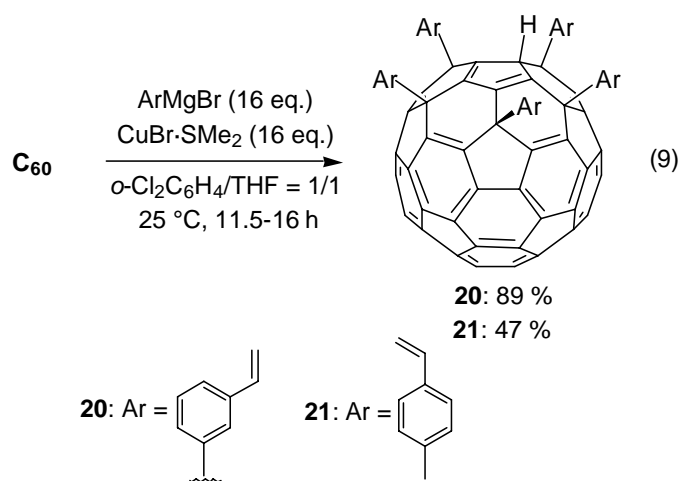
According to the synthetic method of methyl or phenyl bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) or Fe(η^5-Cp)(η^5-PhFCp) (**12**), I synthesized 3-vinylphenyl bucky ferrocene Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) and 4-vinylphenyl bucky ferrocene Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**). After the purification by silica gel short path and recrystalization, bucky ferrocenes Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) and Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) were obtained as air- and moisture-stable dark red crystals in 18 and 8.2% isolated yield (eq. 10).[72] The ^{1}H, ^{13}C NMR measurements and APCI-MS indicated the formation of bucky ferrocene Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) and Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**). ^{1}H and ^{13}C NMR measurements of Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) and Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) showed that the Cp and FCp moieties have C_{5v} symmetry. While bucky ferrocene Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) has good solubility (> 20 mg/CDCl$_3$ 0.6 mL) as compared to phenyl bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**), bucky ferrocene Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) has low solubility (< 9.0 mg /CDCl$_3$ 0.6 mL).

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[72] One of the reasons for low isolated yield was the formation of insoluble solid.

$$[FeCp(CO)_2]_2$$
(2.5 eq.)
20 or **21** $\xrightarrow{}$ PhCN
180 °C, 2-3 h

(10)

22: 18 %
23: 8.2 %

20, **22**: Ar =

21, **23**: Ar =
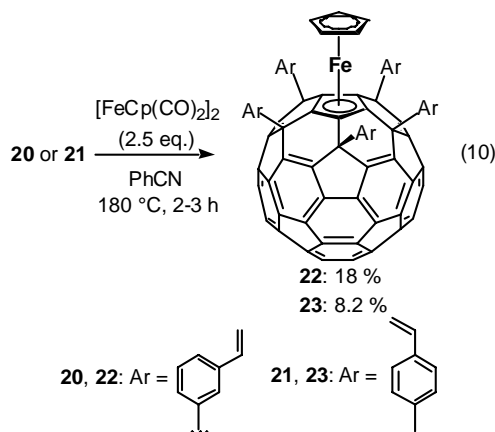
To investigate the easiness of functionalization of vinyl groups of bucky ferrocenes $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(3\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**22**) and $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(4\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**23**), I carried out bromination reactions of $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(3\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**22**) and $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(4\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**23**). The reactions of $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(3\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**22**) and $Fe(\eta^5\text{-Cp})[\eta^5\text{-}(4\text{-CH}_2\text{=CHC}_6\text{H}_4)\text{FCp}]$ (**23**) with bromine gave brominated bucky ferrocenes $Fe(\eta^5\text{-Cp})[\eta^5\text{-}\{3\text{-BrCH}_2\text{CH(Br)C}_6\text{H}_4\}\text{FCp}]$ (**24**) and $Fe(\eta^5\text{-Cp})[\eta^5\text{-}\{4\text{-BrCH}_2\text{CH(Br)C}_6\text{H}_4\}\text{FCp}]$ (**25**) in 59 and 83% isolated yield (eq 11). The ^1H NMR spectra indicated the formation of brominated bucky ferrocenes $Fe(\eta^5\text{-Cp})[\eta^5\text{-}\{3\text{-BrCH}_2\text{CH(Br)C}_6\text{H}_4\}\text{FCp}]$ (**24**) and $Fe(\eta^5\text{-Cp})[\eta^5\text{-}\{4\text{-BrCH}_2\text{CH(Br)C}_6\text{H}_4\}\text{FCp}]$ (**25**) (mixture of isomers).[73] The good yield of the formation of $Fe(\eta^5\text{-Cp})[\eta^5\text{-}\{4\text{-BrCH}_2\text{CH(Br)C}_6\text{H}_4\}\text{FCp}]$ (**25**) indicates

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[73] Since these compounds are the mixture of isomers and there are small amount of compounds, signals in the ^{13}C NMR could not be observed.

that functional groups on bucky ferrocenes could be derivatized effectively to useful functional ones.
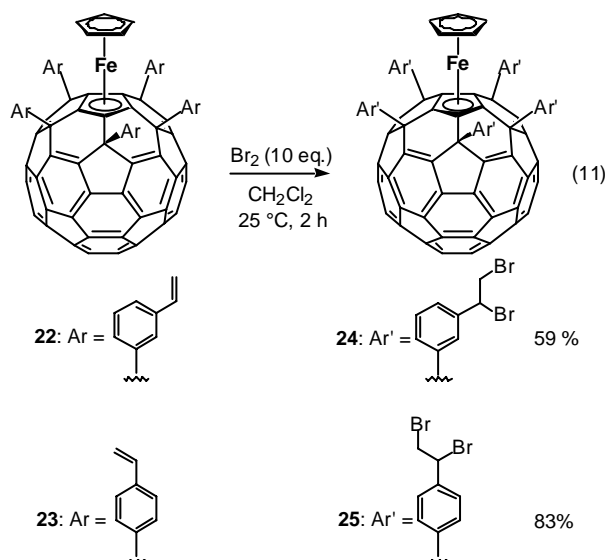
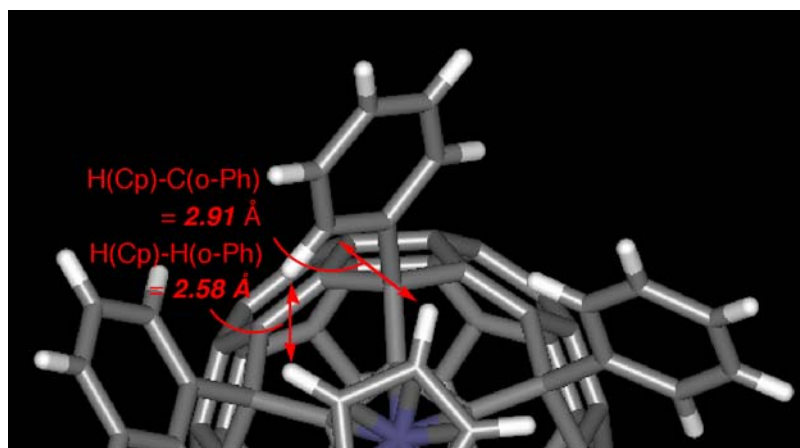## 3-12. X-ray Structures of Functionalized Bucky Ferrocenes

Dark red single crystals of bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) could be obtained by recrystalization from CS_2/EtOH. The structure of Fe(η^5-Cp)(η^5-PhFCp) (**12**) was determined by X-ray analysis (Figure 17, Table 8). While the Cp and FCp ligands of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) are in a staggered conformation with each other,[23] those of bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) are in an inperfect staggered conformation because of the steric repulsion between the Cp ligand and the five phenyl groups of FCp one. The averaged bond lengths of Fe-C(Cp) and Fe-C(FCp) are 2.062(5) and 2.084(4) Å in pentaphenylated bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**).[23] The

bond length of Fe-C(Cp) in bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**) is slightly

longer than that in bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (**11**) (2.033 Å) because

of the steric repulsion between the Cp ligand and five phenyl groups of FCp

ligand. In fact, since the closest C-H distances among bucky ferrocene

Fe(η^5-Cp)(η^5-PhFCp) (**12**) is 2.91 Å (between ortho-position carbon atoms of

phenyl groups and hydrogen atoms of the Cp ligand), the ortho-position carbon

atoms of phenyl groups and hydrogen atoms of the Cp ligand contact each

other by van der Waals manner (C-H = 2.90 Å)[74] (Figure 18).
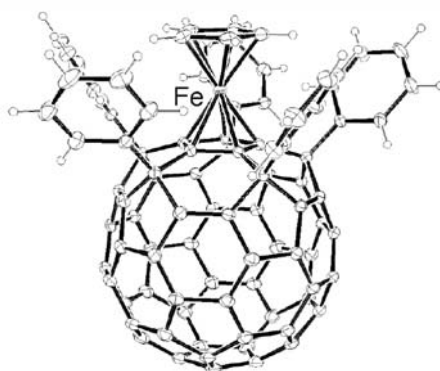
Figure 17. Molecular structure of Fe(η^5-Cp)(η^5-PhFCp) (**12**) (30% probability

level ellipsoid. The solvent molecules in the unit cell are omitted for clarity).

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[74] Pauling, L. *The nature of the chemical bond, Third Ed.,* Cornell University Press, New York, **1960**.

Figure 18. H-C and H-H distances of bucky ferrocene Fe(η^5-Cp)(η^5-PhFCp) (**12**).

Dark red single crystals of bucky ferrocene Fe(η^5-Cp)[η^5-(4-MeOC$_6$H$_4$)FCp] (**19**) could be obtained by recrystallization from CS$_2$/EtOH. Thus X-ray crystal structure analysis of this complex was performed (Figure 19, Table 8). The averaged bond lengths of Fe-C(Cp) and Fe-C(FCp) are 2.061(4) and 2.084(3) Å that are similar to those of Fe(η^5-Cp)(η^5-PhFCp) (Fe-C(Cp) (ave): 2.062(5) Å, Fe-C(FCp) (ave): 2.084(4) Å). The averaged bond lengths of Me-O and O-Ar are 1.427(6) and 1.377(4) Å. These bond lengths are normal distances as the methoxy groups of anisole derivatives.
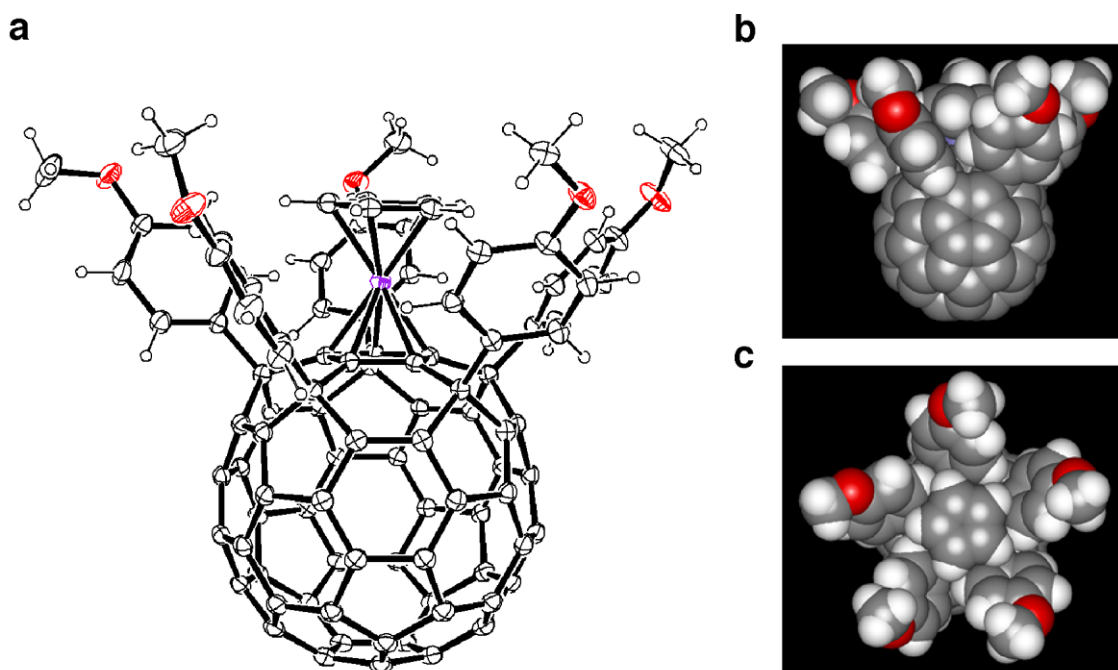
Figure 19. X-ray crystal structure of 4-methoxyphenyl bucky ferrocene Fe(η^5-Cp)[η^5-(4-MeOC$_6$H$_4$)FCp] (**19**). (a) ORTEP drawing (30 % probability level ellipsoid). (b) Front view. (c) Top view.

Dark red single crystals of bucky ferrocenes Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) and Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) could be obtained by recrystallization from CS$_2$/EtOH. Then X-ray crystal structure analyses of these complexes were performed (Figures 20 and 21, Table 8). While the plane of Cp ligand tilts slightly against the plane of FCp one because of steric repulsion between Cp ligand and two vinyl groups in Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**), the planes of Cp and FCp ligands are parallel in Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**). The conformation of five vinyl groups

is various. The averaged bond lengths of Fe-C(Cp), Fe-C(FCp), CH_2=CH- and

=CH_2-Ar are typical distances as Fe-C(Cp), Fe-C(FCp) or vinyl groups of

styrene derivatives.

a

b

c
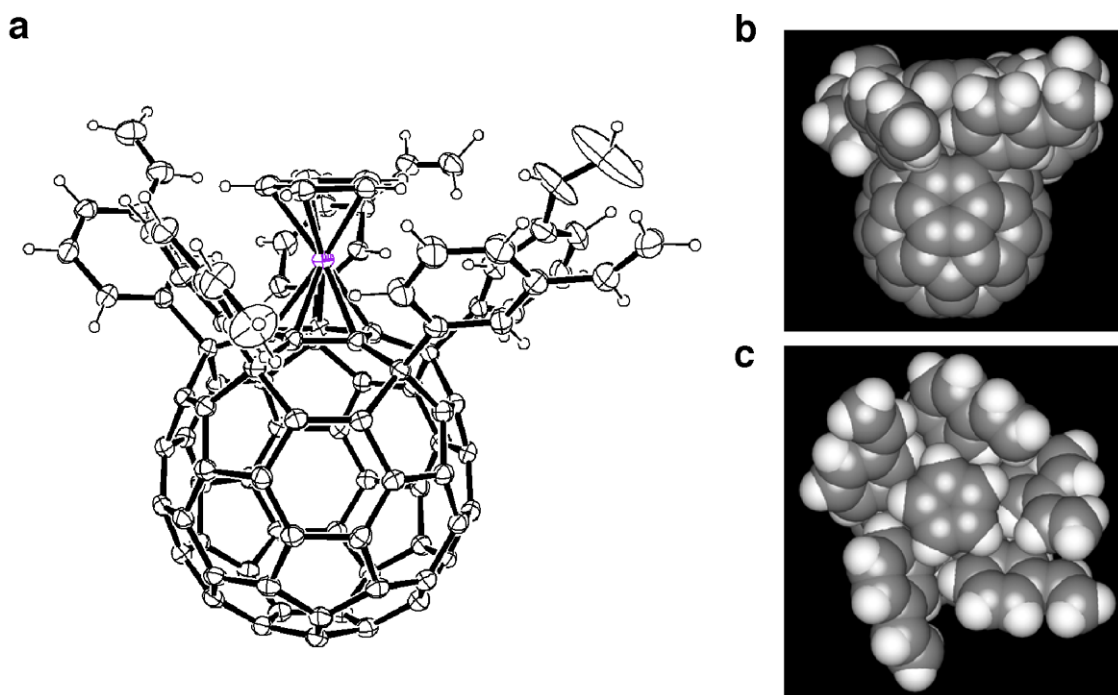
Figure 20. X-ray crystal structure of 3-vinylphenyl bucky ferrocene

Fe(η^5-Cp)[η^5-(3-CH_2=CHC_6H_4)FCp] (**22**). (a) ORTEP drawing (30 % probability

level ellipsoid). (b) Front view. (c) Top view.
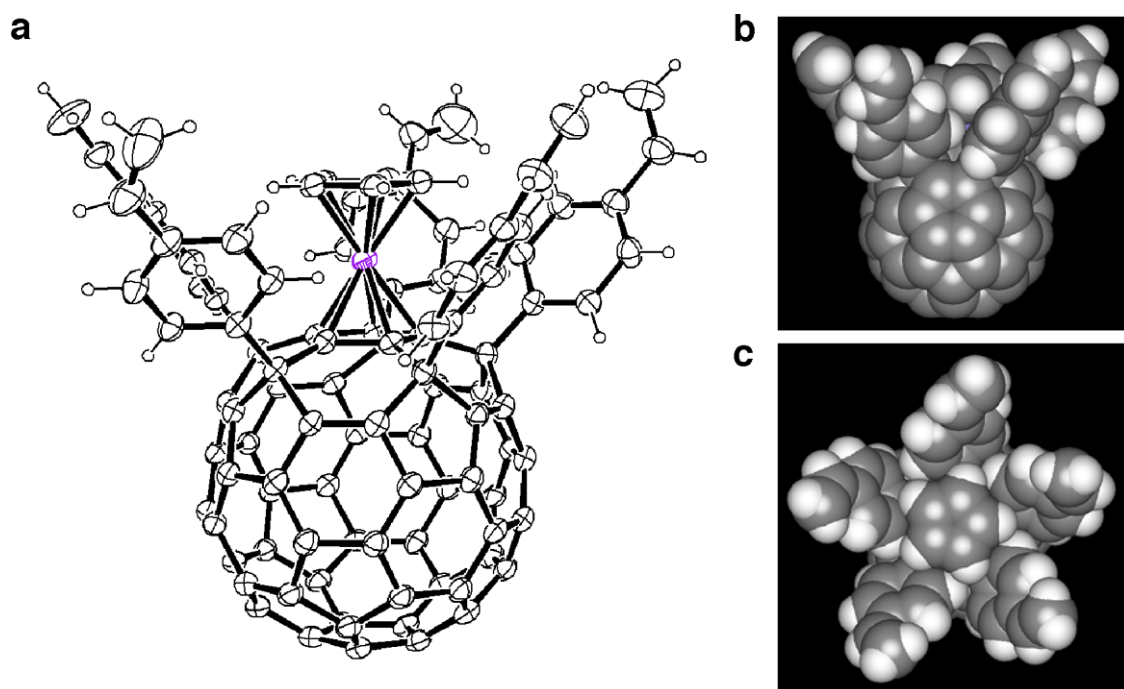
Figure 21. X-ray crystal structure of 4-vinylphenyl bucky ferrocene Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**). (a) ORTEP drawing (30 % probability level ellipsoid). (b) Front view. (c) Top view.

3-13. Conclusion

Bucky ferrocenes are very stable to water, dioxygen, heat and light. Theoretical calculations, IR and electrochemical measurements indicate that there is an electronic communication between fullerene core and Fe-Cp moiety. Bucky ferrocenes can be derivatized by some ways; acylation, oxidation and reduction. Given the versatile electro- and photochemistry of the fullerene group, the flexibility of the synthesis of the FCp ligand,[17] and self-assembly of

the FCp structure,[28,75] I anticipate that these molecules will lead to a new world of carbon clusters in catalysis and materials science.

3-14. Experimental

General Procedure. All manipulations were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. THF was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. Carbon disulfide, 1,2-dichlorobenzene, benzonitrile and dichloromethane were distilled from CaH_2. Acetyl chloride, benzoyl chloride and sinnamoyl chloride were distilled before use. Aluminum trichloride was sublimed before use. $C_{60}(4\text{-}MeOC_6H_4)_5H$[17b] and $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)$[23] were prepared according to the literature. $[FeCp(CO)_2]_2$ and $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$ were purchased from Acros Organics and Sigma-Aldrich Co. and used as received. Br_2 was used as received.

Preparative HPLC separations were performed by use of Bucky Prep. column (Nakalai Tesque Co., 20 mm x 250 mm).

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using JEOL EX-400 spectrometer. Proton chemical shift are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peaks ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. Other spectra

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[75] Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702.

were recorded by the use of the following instruments: IR, JASCO IR-420 and ReactIR 1000; UV/vis spectra, HITACHI U3500 and Shimadzu SPD-6A; Mass spectra, Shimadzu LCMS-QP8000 and JEOL Accu TOF (JMS-T100LC). Elemental Analyses were performed at organic elemental analysis laboratory in this department.

Synthesis of Fe(η^5-Cp)(η^5-PhFCp) (12): A mixture of $C_{60}Ph_5H$ (**17**) (200 mg, 0.181 mmol) and $[FeCp(CO)_2]_2$ (320 mg, 0.900 mmol) in benzonitrile (40.0 mL) was stirred at 180 °C for 19.5 h. After evaporation of the solvent, the crude mixture was diluted with toluene, and the solution was passed through a pad of silica gel. Solvent was removed in vacuo, and the mixture was recrystalized from CS_2/hexane to obtain Fe(η^5-Cp)(η^5-PhFCp) (**12**) as air stable dark red microcrystals (171 mg, 77% yield). Fe(η^5-Cp)(η^5-PhFCp) (**12**): ^1H NMR (400 MHz, $CDCl_3$) δ 3.21 (s, 5H, Cp), 7.33-7.37 (m, 10H, Ph), 7.39-7.40 (m. 5H, Ph), 7.93-7.95 (m, 10H, Ph); ^1H NMR (400 MHz, $CDCl_3$/CS_2 = 1/1) δ 3.16 (s, 5H, Cp), 7.31-7.35 (m, 10H, Ph), 7.37-7.41 (m. 5H, Ph), 7.89-7.91 (m, 10H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$/CS_2 = 1/1) δ 58.23 (5C), 73.20 (5C), 92.47 (s, 5C), 127.41 (5C), 127.47 (10C), 128.97 (10C), 142.82 (5C), 142.92 (10C), 143.66 (10C), 147.03 (5C), 147.81 (10C), 148.06 (5C), 152.14 (10C); IR (CS_2) $\nu_{C-H\,(Cp)}$/cm^{-1} 3101; UV-vis (1.0 x 10^{-5} mol•L^{-1} in CH_2Cl_2) λ_{max} (ε) 260 (84700), 295 (57300, shoulder), 351 (23600), 394 (12200), 475 (4330, shoulder) nm; APCI-MS: m/z = 1226 (M$^+$); HR-APCI-MS (+) m/z ; found: 1226.1708; calcd for Fe(η^5-Cp)(η^5-PhFCp) (**12**): 1226.1701.

Synthesis of Fe(η^5-C$_5$H$_4$COCH$_3$)(η^5-MeFCp) (13a). To a mixture of Fe(η^5-Cp)(η^5-MeFCp) (**11**) (50.1 mg, 54.6 μmol) and AlCl$_3$ (30.0 mg, 225 μmol), a solution of CH$_3$COCl (16.0 μL, 225 μmol) in CS$_2$ (3.0 mL) was added. After stirring at 25 °C for 40 min, the reaction mixrure was quenched with methanol (0.5 mL). The mixture was diluted with toluene and was washed with water. The organic layer was dried with MgSO$_4$ for 30 min and was concentrated under reduced pressure. After preparative HPLC separation [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm), toluene/*i*-PrOH = 7/3, flow rate = 18 mL/min, retention time = 8.5–9.5 min], Fe(η^5-C$_5$H$_4$COCH$_3$)(η^5-MeFCp) (**13a**) (19.7 mg, 38% yield) was obtained as air stable reddish orange microcrystals: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.53 (s, 15H), 2.62 (s, Me), 5.22 (t, ^3J = 2.0 Hz, 2H), 5.44 (t, ^3J = 2.0 Hz, 2H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 2.55 (s, 15H), 2.62 (s, 3H), 5.19 (t, ^3J = 1.8 Hz, 2H), 5.40 (t, ^3J = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 29.25 (5C), 29.90 (1C), 50.27 (5C), 69.95 (2C), 71.33 (2C), 81.92 (1C), 92.65 (5C), 143.04 (10C), 143.57 (10C), 146.68 (5C), 147.73 (10C), 147.94 (5C), 153.79 (10C), 201.94 (1C); IR (KBr, ν(CO)/cm^{-1}) 1670; UV-vis (1.0x10^{-5} mol·L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 239 (61900), 258 (55000, shoulder), 273 (50300, shoulder), 354 (13100, shoulder), 395 (6710) nm; APCI-MS (±) *m/z* = 958 (M$^\pm$); HR-APCI-MS (+) *m/z* ; found: 959.1117; calcd for Fe(η^5-C$_5$H$_4$COCH$_3$)(η^5-MeFCp) (**13a**): 959.1125.

Synthesis of Fe(η^5-C$_5$H$_4$COC$_6$H$_5$)(η^5-MeFCp) (13b). Complex Fe(η^5-C$_5$H$_4$COC$_6$H$_5$)(η^5-MeFCp) (**13b**) was synthesized as for Fe(η^5-C$_5$H$_4$COCH$_3$)(η^5-MeFCp) (**13a**), using the following amounts: Fe(η^5-Cp)(η^5-MeFCp) (**11**) (50.0 mg, 54.5 μmol), AlCl$_3$ (21.8 mg, 164 μmol), PhCOCl (19.0 μL, 164 μmol), CS$_2$ (8.0 mL). Yield: 22.7 mg (41%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.49 (s, 15H), 5.28 (t, ^3J = 2.0 Hz, 2H), 5.61 (t, ^3J = 2.0 Hz, 2H), 7.51-7.65 (m, 3H), 7.98-8.01 (m, 2H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 2.50 (s, 15H), 5.27 (t, ^3J = 2.0 Hz, 2H), 5.58 (t, ^3J = 2.0 Hz, 2H), 7.54 (m, 2H), 7.63 (m, 1H), 7.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 29.02 (5C), 50.22 (5C), 71.04 (2C), 71.76 (2C), 79.59 (1C), 92.67 (5C), 127.98 (2C), 128.74 (2C), 131.31 (1C), 142.98 (10C), 143.58 (10C), 146.63 (5C), 147.68 (10C), 147.88 (5C), 153.86 (10C) [Two signals (1C (Ph) and 1C (CO)) could not be detected because of the low solubility]; IR (KBr, ν(CO)/cm^{-1}) 1640; UV-vis (1.0x10^{-5} mol·L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 257 (55100), 350 (16200, shoulder), 395 (8680), 470 (3170, shoulder) nm; APCI-MS (±) m/z = 1020 (M$^\pm$); HR-APCI-MS (+) m/z ; found: 1021.1233; calcd for Fe(η^5-C$_5$H$_4$COC$_6$H$_5$)(η^5-MeFCp) (**13b**): 1021.1229.

Synthesis of Fe(η^5-C$_5$H$_4$COCH=CHC$_6$H$_5$)(η^5-MeFCp) (13c). Complex Fe(η^5-C$_5$H$_4$COCH=CHC$_6$H$_5$)(η^5-MeFCp) (**13c**) was synthesized as for Fe(η^5-C$_5$H$_4$COCH$_3$)(η^5-MeFCp) (**13a**), using the following amounts: Fe(η^5-Cp)(η^5-MeFCp) (**11**) (29.7 mg, 32.4 μmol), AlCl$_3$ (13.1 mg, 97.2 μmol), C$_6$H$_5$CH=CHCOCl (16.3 mg, 97.2 μmol), CS$_2$ (4.8 mL). Yield: 14.6 mg (43%). ^{1}H

NMR (400 MHz, CDCl$_3$) δ 2.55 (s, 15H), 5.29 (t, ^3J = 2.0 Hz, 2H), 5.61 (t, ^3J = 2.0 Hz, 2H), 7.41 (d, ^3J = 15.6 Hz, 1H), 7.44-7.47 (m, 3H), 7.69-7.71 (m, 2H), 7.90 (d, ^3J = 15.6 Hz, 1H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 2.53 (s, 15H), 5.25 (t, ^3J = 2.0 Hz, 2H), 5.56 (t, ^3J = 2.0 Hz, 2H), 7.39 (d, ^3J = 15.6 Hz, 1H), 7.41-7.44 (m, 3H), 7.64-7.66 (m, 2H), 7.84 (d, ^3J = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 29.16 (5C), 50.32 (5C), 69.67 (2C), 71.17 (2C), 83.09 (1C), 92.73 (5C), 122.88 (1C), 128.15 (2C), 128.87 (2C), 130.34 (1C), 134.53 (1C), 137.32 (1C), 142.98 (10C), 143.56 (10C), 146.62 (5C), 147.68 (10C), 147.87 (5C), 153.81 (10C), 192 68 (1C); IR (KBr, ν(CO)/cm^{-1}) 1633; UV-vis (1.0x10^{-5} mol·L^{-1} in CH$_2$Cl$_2$) λ$_{max}$ (ε) 257 (124000), 269 (121000), 290 (104000, shoulder), 355 (40900, shoulder), 394 (20900), 435 (9560, shoulder), 470 (7270, shoulder) nm; APCI-MS (±) m/z = 1046 (M$^\pm$); HR-APCI-MS (+) m/z ; found: 1047.1411; calcd for Fe(η^5-C$_5$H$_4$COCH=CHC$_6$H$_5$)(η^5-MeFCp) (**13c**): 1047.1411.

Preparation of [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (14). To a solution of Fe(η^5-Cp)(η^5-MeFCp) (**11**) (151 mg, 164 μmol) in THF (300 mL), [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] (147 mg, 181 μmol) was added. After stirring at 25 °C for 5 h, the solvent was removed in vacuo. The solid was washed several times with CHCl$_3$, EtOH, H$_2$O, EtOH and Et$_2$O. After the solid was dried in vacuo, bucky ferrocenium [Fe(η^5-Cp)(η^5-MeFCp)][SbCl$_6$] (**14**) (170 mg, 83%) was obtained as reddish brown solid. IR (powder, cm^{-1}) ν 2968 (m), 2921 (m), 2865 (w), 1544 (w), 1509 (w), 1457 (m), 1443 (s), 1418 (m), 1374 (m), 1338 (w), 1266 (w),

1239 (m), 1200 (m), 1154 (m), 1136 (m), 1113 (w), 1077 (w), 1007 (w), 951 (w), 855 (s), 754 (w), 683 (s), 658 (s); UV-vis ([Fe(η^5-Cp)(η^5-MeFCp)][ClO$_4$], 1.0 x 10^{-5} mol•L^{-1} in PhCN) λ_{max} (ε) 341 (67500, shoulder), 358 (57000, shoulder), 403 (29400), 462 (13600) nm.

Preparation of [Fe(η^5-Cp)(η^5-PhFCp)][SbCl$_6$] (15). To a solution of Fe(η^5-Cp)(η^5-PhFCp) (**12**) (99.2 mg, 80.8 μmol) in THF (70.0 mL), [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] (72.6 mg, 88.9 μmol) was added. After stirring at 25 °C for 5 h, the solvent was removed in vacuo. The solid was washed several times with CHCl$_3$, EtOH, H$_2$O, EtOH and Et$_2$O. After the solid was dried in vacuo, bucky ferrocenium [Fe(η^5-Cp)(η^5-PhFCp)][SbCl$_6$] (**15**) (62.2 mg, 49%) was obtained as reddish brown solid.

UV-vis spectrum of [Bu$_4$N][Fe(η^5-Cp)(η^5-MeFCp)]. UV-vis (1.0 x 10^{-5} mol•L^{-1} in PhCN) λ_{max} (ε) 357 (39300, shoulder), 401 (22800, shoulder), 475 (9660, shoulder).

UV-vis spectrum of [Bu$_4$N]$_2$[Fe(η^5-Cp)(η^5-MeFCp)]. UV-vis (1.0 x 10^{-5} mol•L^{-1} in PhCN) λ_{max} (ε) 472 (15200, shoulder), 734 (4140, shoulder) nm.

Synthesis of Fe(η^5-Cp)[η^5-(4-MeOC$_6$H$_4$)FCp] (19). A mixture of C$_{60}$(4-MeOC$_6$H$_4$)$_5$H (**18**) (21.6 mg, 17.2 μmol) and [FeCp(CO)$_2$]$_2$ (30.4 mg, 42.9

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μmol) in benzonitrile (4.0 ml) was stirred at 180 °C for 19 h. After evaporation of the solvent, the crude mixture was diluted with toluene, and the solution was passed through a pad of silica gel. Solvent was removed in vacuo. After preparative HPLC separation [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm)], $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**) was obtained as air stable orange microcrystals (1.9 mg, 8.0% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 3.32 (s, 5H, Cp), 3.88 (s, 15H, O*Me*), 6.89 (d, ^3J = 8.8 Hz, 10H, Ar), 7.85 (d, ^3J = 9.2 Hz, 10H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.56 (5C), 57.86 (5C), 73.14 (5C, Cp), 93.01 (5C, FCp), 113.11 (5C, Ar), 130.29 (10C, Ar), 135.68 (5C, Ar), 143.07 (10C), 144.01 (10C), 147.30 (5C), 148.06 (10C), 148.29 (5C), 152.74 (10C), 158.93 (10C); IR (powder, cm^{-1}) ν 1684 (w), 1653 (w), 1606 (m), 1559 (m), 1508 (s), 1459 (m), 1437 (w), 1294 (w), 1253 (s), 1179 (s), 1114 (w), 1030 (m), 1004 (w), 962 (w), 900 (w), 844 (m), 822 (m), 793 (m), 729 (s), 696 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 287, 303 (shoulder), 354, 407 (shoulder), 487 (shoulder); APCI-MS: m/z = 1377 ([M+H]$^+$), 1376 ([M]$^-$); HR-APCI-MS (+) m/z ; found: 1376.2162; calcd for $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**): 1376.2229.

Synthesis of $C_{60}(3\text{-}CH_2\text{=}CHC_6H_4)_5H$ (20). To a suspension of CuBr•SMe$_2$ (9.13 g, 44.4 mmol) in THF (55.6 mL) was added a THF solution of $3\text{-}CH_2\text{=}CHC_6H_4MgBr$ (1.0 M, 44.4 mL, 44.4 mmol) at 25 °C and stirring continued for 20 min at this temperature. To the resulting dark yellowish orange solution was added a solution of C_{60} (2.00 g, 2.78 mmol) in

1,2-dichlorobenzene (100 mL). The mixture was stirred for 16 h at 25 °C and quenched with saturated aqueous NH_4Cl solution. The crude mixture was diluted with toluene and was passed through a pad of silica gel. The organic phase was concentrated in vacuo and was recrystalized by the addition of hexane. The precipitate was filtered and was dried in vacuo. $C_{60}(3\text{-}CH_2\text{=}CHC_6H_4)_5H$ (**20**) (3.06 g, 89% yield) was obtained as an air stable orange solid; [^1]H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, ^3J = 11.2 Hz, 1H, CH_2=CH-), 5.05 (d, ^3J = 11.2 Hz, 2H, CH_2=CH-), 5.11 (d, ^3J = 10.8 Hz, 2H, CH_2=CH-), 5.16 (d, ^3J = 17.6 Hz, 1H, CH_2=CH-), 5.28 (d, ^3J = 17.6 Hz, 2H, CH_2=CH-), 5.36 (d, ^3J = 18.0 Hz, 2H, CH_2=CH-), 5.38 (s, 1H, FCpH), 6.31 (dd, ^3J = 16.6 Hz, ^3J = 11.0 Hz, 1H, CH_2=CH-), 6.35 (dd, ^3J = 17.6 Hz, ^3J = 10.8 Hz, 2H, CH_2=CH-), 6.49 (dd, ^3J = 17.6 Hz, ^3J = 10.8 Hz, 2H, CH_2=CH-), 7.17-7.72 (m, 20H, Ar); [^1]H NMR (500 MHz, $CDCl_3/CS_2$ = 1/3) δ 4.94 (d, ^3J = 11.0 Hz, 1H, CH_2=CH-), 4.98 (d, ^3J = 10.5 Hz, 2H, CH_2=CH-), 5.05 (d, ^3J = 11.0 Hz, 2H, CH_2=CH-), 5.09 (d, ^3J = 17.5 Hz, 1H, CH_2=CH-), 5.21 (d, ^3J = 17.0 Hz, 2H, CH_2=CH-), 5.26 (s, 1H, FCpH), 5.33 (d, ^3J = 17.0 Hz, 2H, CH_2=CH-), 6.22 (dd, ^3J = 18.0 Hz, ^3J = 11.0 Hz, 1H, CH_2=CH-), 6.26 (dd, ^3J = 18.0 Hz, ^3J = 11.0 Hz, 2H, CH_2=CH-), 6.42 (dd, ^3J = 18.0 Hz, ^3J = 11.0 Hz, 2H, CH_2=CH-), 7.08-7.11 (m, 3H, Ar), 7.15-7.16 (m, 1H, Ar), 7.20-7.25 (m, 4H, Ar), 7.29-7.31 (m, 2H, Ar), 7.33-7.34 (m, 2H, Ar), 7.43-7.45 (m, 4H, Ar), 7.61-7.63 (m, 4H, Ar); [^13]C NMR (125 MHz, $CDCl_3/CS_2$ = 1/3) δ 58.52 (2C), 58.53 (1C), 60.61 (2C), 62.88 (1C), 114.43 (2C), 114.60 (1C), 114.66 (2C), 124.98 (2C), 125.03 (2C), 125.28 (2C), 125.87 (2C), 125.90 (2C), 126.05 (2C), 126.49 (1C), 126.95 (2C), 127.10

(2C), 127.34 (1C), 128.76 (2C), 129.03 (2C), 130.26 (1C), 135.59 (1C), 135.77 (2C), 135.80 (2C), 138.08 (2C), 138.35 (1C), 138.37 (2C), 139.77 (1C), 139.87 (1C), 143.02 (2C), 143.34 (2C), 143.92 (2C), 144.02 (3C), 144.08 (2C), 144.10 (2C), 144.22 (2C), 145.03 (2C), 145.32 (2C), 145.54 (4C), 145.57 (2C), 146.63 (1C), 146.82 (2C), 146.90 (2C), 147.32 (2C), 147.50 (2C), 147.83 (2C), 148.00 (2C), 148.14 (2C), 148.42 (2C), 148.48 (2C), 148.52 (2C), 151.13 (2C), 151.78 (2C), 152.29 (2C), 155.45 (2C); IR (powder, cm^{-1}) ν 3089 (w), 3043 (m), 2935 (m), 2881 (w), 2377 (m), 2368 (m), 2342 (m), 2331 (m), 2314 (m), 1600 (m), 1580 (m), 1486 (m), 1461 (w), 1416 (w), 1399 (w), 1289 (w), 1235 (w), 1198 (w), 1171 (w), 1098 (w), 1036 (w), 988 (m), 915 (s), 893 (m), 795 (s), 778 (m), 754 (m), 708 (s), 660 (m); UV-vis (toluene/2-propanol = 7/3) λ$_{max}$ 284, 353, 396, 471; APCI-MS (-): m/z = 1236 ([M]$^-$); HR-APCI-MS (+) m/z ; found: 1236.2766; calcd for C$_{60}$(3-CH$_2$=CHC$_6$H$_4$)$_5$H (**20**): 1236.2817.

Synthesis of C$_{60}$(4-CH$_2$=CHC$_6$H$_4$)$_5$H (21). To a suspension of CuBr•SMe$_2$ (2.28 g, 11.1 mmol) in THF (38.9 mL) was added a THF solution of 3-CH$_2$=CHC$_6$H$_4$MgBr (1.0 M, 11.1 mL, 11.1 mmol) at 25 °C and stirring continued for 20 min at this temperature. To the resulting yellowish brown suspension was added a solution of C$_{60}$ (500 mg, 694 μmol) in 1,2-dichlorobenzene (50.0 mL). The mixture was stirred for 11.5 h at 25 °C and quenched with saturated aqueous NH$_4$Cl solution. The crude mixture was diluted with toluene and was passed through a pad of silica gel. The organic phase was concentrated in vacuo and was recrystalized by the addition of

hexane. The precipitate was filtered and was dried in vacuo. $C_{60}(4\text{-}CH_2=CHC_6H_4)_5H$ (**21**) (405 mg, 47% yield) was obtained as an air stable orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 5.24 (d, ^3J = 11.2 Hz, 1H, CH_2=CH-), 5.26 (d, ^3J = 11.2 Hz, 2H, CH_2=CH-), 5.28 (s, 1H, FCpH), 5.31 (d, ^3J = 11.6 Hz, 2H, CH_2=CH-), 5.70 (d, ^3J = 17.6 Hz, 1H, CH_2=CH-), 5.73 (d, ^3J = 17.6 Hz, 2H, CH_2=CH-), 5.79 (d, ^3J = 17.6 Hz, 2H, CH_2=CH-), 6.61-6.79 (m, 5H, CH_2=CH-), 7.23 (d, ^3J = 10.0 Hz, 4H, Ar), 7.37 (d, ^3J = 8.0 Hz, 2H, Ar), 7.39 (d, ^3J = 8.0 Hz, 4H, Ar), 7.45 (d, ^3J = 10.0 Hz, 2H, Ar), 7.56 (d, ^3J = 8.0 Hz, 4H, Ar), 7.74 (d, ^3J = 8.4 Hz, 4H, Ar); ^1H NMR (400 MHz, $CDCl_3/CS_2$ = 1/3) δ 5.18 (d, ^3J = 11.6 Hz, 1H, CH_2=CH-), 5.19 (s, 1H, FCpH), 5.21 (d, ^3J = 11.6 Hz, 2H, CH_2=CH-), 5.26 (d, ^3J = 11.6 Hz, 2H, CH_2=CH-), 5.64 (d, ^3J = 17.6 Hz, 1H, CH_2=CH-), 5.67 (d, ^3J = 16.8 Hz, 2H, CH_2=CH-), 5.74 (d, ^3J = 17.6 Hz, 2H, CH_2=CH-), 6.54-6.73 (m, 5H, CH_2=CH-), 7.12 (d, ^3J = 8.4 Hz, 2H, Ar), 7.17 (d, ^3J = 8.4 Hz, 4H, Ar), 7.26 (d, ^3J = 8.0 Hz, 2H, Ar), 7.33 (d, ^3J = 8.4 Hz, 4H, Ar), 7.46 (d, ^3J = 8.0 Hz, 4H, Ar), 7.67 (d, ^3J = 8.4 Hz, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/3) δ 58.27 (1C), 58.37 (2C), 60.37 (1C), 62.73 (2C), 114.03 (2C), 114.14 (1C), 114.20 (2C), 126.29 (4C), 126.53 (2C), 126.60 (4C), 127.55 (2C), 127.82 (4C), 128.00 (4C), 135.69 (2C), 135.86 (6C), 136.28 (1C), 136.55 (2C), 136.82 (1C), 138.51 (1C), 138.58 (2C), 142.99 (2C), 143.31 (2C), 143.89 (2C), 143.96 (2C), 144.05 (2C), 144.10 (2C), 144.18 (2C), 144.52 (2C), 144.98 (2C), 145.00 (1C), 145.28 (2C), 145.46 (2C), 145.67 (2C), 146.59 (1C), 146.78 (2C), 146.87 (2C), 147.23 (2C), 147.46 (2C), 147.80 (2C), 147.96 (2C), 148.10 (2C), 148.38 (2C), 148.44 (2C), 148.48 (2C), 150.91 (2C), 151.71 (2C), 152.03 (2C), 155.57 (2C);

IR (powder, cm^{-1}) ν 1630 (m), 1607 (m), 1507 (s), 1461 (m), 1418 (w), 1403 (m), 1287 (w), 1237 (w), 1210 (w), 1192 (w), 1119 (w), 1017 (m), 986 (s), 901 (s), 888 (m), 839 (s), 822 (s), 770 (w), 760 (m), 741 (w), 702 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 285, 355, 397, 484 (shoulder); APCI-MS: m/z = 1236 (M$^-$); HR-APCI-MS (+) m/z ; found: 1236.2818; calcd for C$_{60}$(4-CH$_2$=CHC$_6$H$_4$)$_5$H (**21**): 1236.2817.

Synthesis of Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (22). A mixture of C$_{60}$(3-CH$_2$=CHC$_6$H$_4$)$_5$H (**20**) (100 mg, 80.8 μmol) and [FeCp(CO)$_2$]$_2$ (71.5 mg, 202 mol) in benzonitrile (20.0 mL) was stirred at 180 °C for 3 h. After evaporation of solvent, the crude mixture was diluted with toluene, and solution was passed through a pad of silica gel. Solvent was removed in vacuo and preparative HPLC separations [Bucky Prep. (Nakalai Tesque Co., 20 mm x 250 mm), toluene/i-PrOH = 7/3, flow rate = 18 mL/min, retention time = 7.5-8.5 min] afforded Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) (20.0 mg, 18% yield) as reddish orange solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.36 (s, 5H, Cp), 5.14 (d, ^3J = 11.2 Hz, 5H, CH_2=CH-), 5.45 (d, ^3J = 17.2 Hz, 5H, CH_2=CH-), 6.44 (dd, ^3J = 17.8 Hz, ^3J = 11.2 Hz, 5H, CH$_2$=CH-), 7.35 (t, ^3J = 7.8 Hz, 5H, Ar), 7.51 (d, ^3J = 8.0 Hz, 5H, Ar), 7.85 (d, ^3J = 8.4 Hz, 5H, Ar), 7.95 (s, 5H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 58.43 (5C, sp^3), 73.16 (5C, Cp), 92.80 (5C, FCp), 114.94 (5C, olefin), 124.93 (5C), 127.96 (5C), 127.99 (5C), 128.31 (5C), 135.98 (5C), 137.80 (5C), 143.10 (10C), 143.59 (5C), 143.90 (10C), 147.29 (5C), 148.06 (10C), 148.29 (5C), 152.36

(10C); UV-vis (toluene/2-propanol = 7/3) λ_{max} 285, 309 (shoulder), 352, 396, 472; APCI-MS: m/z = 1357 ([M+H]$^+$), 1356 (M$^-$); HR-APCI-MS (+) m/z ; found: 1356.2465; calcd for Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**): 1356.2484.

Synthesis of Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (23). A mixture of C$_{60}$(4-CH$_2$=CHC$_6$H$_4$)$_5$H (**21**) (100 mg, 80.8 μmol) and [FeCp(CO)$_2$]$_2$ (71.5 mg, 202 μmol) in benzonitrile (20.0 mL) was stirred at 180 °C for 2 h. After evaporation of solvent, the crude mixture was diluted with toluene, and solution was passed through a pad of silica gel. Solvent was removed in vacuo and preparative HPLC separations [Bucky Prep. (Nakalai Tesque Co., 20 mm x 250 mm), toluene/hexane = 1/1, flow rate = 18 mL/min, retention time = 13.5-15.0 min] afforded Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) (9.0 mg, 8.2% yield) as reddish orange solid; Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.33 (s, 5H, Cp), 5.34 (d, ^3J = 11.6 Hz, 5H, C*H*$_2$=CH-), 5.84 (d, ^3J = 17.2 Hz, 5H, C*H*$_2$=CH-), 6.80 (dd, ^3J = 17.4 Hz, ^3J = 11.0 Hz, 5H, CH$_2$=C*H*-), 7.42 (d, ^3J = 8.4 Hz, 10H, Ar), 7.90 (d, ^3J = 8.0 Hz, 10H, Ar); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 3.29 (s, 5H, Cp), 5.33 (d, ^3J = 11.6 Hz, 5H, C*H*$_2$=CH-), 5.83 (d, ^3J = 17.6 Hz, 5H, C*H*$_2$=CH-), 6.78 (dd, ^3J = 17.4 Hz, ^3J = 11.6 Hz, 5H, CH$_2$=C*H*-), 7.39 (d, ^3J = 8.4 Hz, 10H, Ar), 7.86 (d, ^3J = 8.0 Hz, 10H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 58.07 (5C, sp^3), 73.25 (5C, Cp), 92.26 (5C, FCp), 114.22 (5C, olefin), 125.47 (10C, Ar), 129.08 (10C, Ar), 135.83 (5C), 136.69 (5C), 142.22 (5C), 142.95 (10C), 143.64 (10C), 147.04 (5C), 147.84 (10C), 148.10 (5C), 152.08 (10C);

UV-vis (toluene/2-propanol = 7/3) λ_{max} 285, 310 (shoulder), 355, 398, 482 (shoulder); APCI-MS: m/z = 1356 (M$^{\pm}$); HR-APCI-MS (+) m/z ; found: 1356.2587; calcd for Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**): 1356.2484.

Synthesis of Fe(η^5-Cp)[η^5-(3-BrCH$_2$CH(Br)C$_6$H$_4$)FCp] (24). To an orange suspension of Fe(η^5-Cp)[η^5-(3-CH$_2$=CHC$_6$H$_4$)FCp] (**22**) (18.2 mg, 13.4 μmol) in CH$_2$Cl$_2$ (5.0 mL), 2.0% CH$_2$Cl$_2$ solution of Br$_2$ (6.88 mL, 134 μmol) was added. After stirring at 25 °C for 2 h, the solvent and Br$_2$ was evaporated in vacuo. Preparative HPLC separations [Bucky Prep. (Nakalai Tesque Co., 20 mm x 250 mm), toluene/hexane = 1/1, flow rate = 20 mL/min, retention time = 12.0-13.0 min] afforded Fe(η^5-Cp)[η^5-(3-BrCH$_2$CH(Br)C$_6$H$_4$)FCp] (**24**) (16.9 mg, 59% yield) as reddish orange solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.56 (s, 5H, Cp), 4.02 (m, 10H, BrC*H*$_2$CH(Br)-), 4.67 (m, 5H, BrCH$_2$C*H*(Br)-), 7.58 (m, 5H, Ar), 7.68 (m, 5H, Ar), 7.87 (s, 5H, Ar), 7.97 (m, 5H, Ar); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 3.40-3.43 (m, 5H), 3.93-3.97 (m, 10H), 4.56-4.61 (m, 5H), 7.49-7.51 (m, 5H, Ar), 7.57-7.66 (m, 5H, Ar), 7.78-7.79 (m, 5H, Ar), 7.87-7.89 (m, 5H, Ar); IR (powder, cm^{-1}) ν 2958 (w), 2921 (m), 2852 (w), 1723 (m), 1713 (w), 1600 (w), 1584 (m), 1486 (m), 1463 (m), 1441 (m), 1416 (m), 1285 (w), 1262 (m), 1239 (w), 1216 (w), 1202 (w), 1177 (w), 1158 (m), 1109 (m), 1007 (m), 901 (w), 874 (w), 822 (m), 797 (s), 754 (m), 699 (s), 666 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 286, 313 (shoulder), 351, 395, 471.

Synthesis of Fe(η^5-Cp)[η^5-(4-BrCH$_2$CH(Br)C$_6$H$_4$)FCp] (25). To an orange solution of Fe(η^5-Cp)[η^5-(4-CH$_2$=CHC$_6$H$_4$)FCp] (**23**) (3.4 mg, 2.50 μmol) in CH$_2$Cl$_2$ (2.0 mL), 2.0% CH$_2$Cl$_2$ solution of Br$_2$ (1.29 mL, 25.0 μmol) was added. After stirring at 25 °C for 2 h, the solvent and Br$_2$ were evaporated in vacuo. Preparative HPLC separations [Bucky Prep. (Nakalai Tesque Co., 20 mm x 250 mm), toluene/hexane = 1/1, flow rate = 20 mL/min, retention time = 18.0-19.5 min] afforded Fe(η^5-Cp)[η^5-(4-BrCH$_2$CH(Br)C$_6$H$_4$)FCp] (**25**) (4.5 mg, 83% yield) as reddish orange solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.16 (s, 5H, Cp), 4.05-4.17 (m, 10H, BrCH_2CH(Br)-), 5.20 (m, 5H, BrCH$_2$CH(Br)-), 7.40 (m, 10H, Ar), 7.91 (d, ^3J = 8.0 Hz, 10H, Ar); ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 3.08-3.09 (m, 5H), 4.02-4.03 (m, 5H), 4.10-4.11 (m, 5H), 5.12-5.13 (m, 5H), 7.34-7.35 (m, 10H, Ar), 7.83-7.84 (m, 10H, Ar); IR (powder, cm^{-1}) ν 2952 (w), 2925 (m), 2850 (w), 1727 (w), 1605 (w), 1511 (w), 1414 (m), 1287 (m), 1264 (w), 1235 (m), 1200 (m), 1160 (w), 1131 (m), 1109 (m), 1019 (w), 1007 (w), 961 (w), 911 (m), 899 (s), 847 (m), 830 (m), 820 (s), 764 (w), 739 (m), 710 (m); UV-vis (toluene/2-propanol = 7/3) λ$_{max}$ 286, 313 (shoulder), 351, 395, 463 (shoulder).

Theoretical calculations of bucky ferrocene Fe(η^5-Cp)(η^5-MeFCp) (11). Calculations were performed by the hybrid DFT method (B3LYP) with the GAUSSIAN 98 program package (Frisch, M. J. *et al.*: Gaussian Inc., Pittsburgh, Pennsylvania, 1998). To obtain the molecular orbital (Kohn-Sham orbital), the molecular geometry including the carbon and iron atoms was fixed at an

average crystallographic structure of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}MeFCp)$ (**11**) (C_{5v}), and the positions of the hydrogen atoms were first optimised under C_{5v} symmetry using the Ahlrichs-TZV all-electron basis set for the Fe atom[76] and the 6-31G(d) basis set for the C and H atoms.

X-ray Diffraction. Crystals of acetyl bucky ferrocene $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}PhFCp)$ (**12**), $Fe(\eta^5\text{-}C_5H_4COCH_3)(\eta^5\text{-}MeFCp)$ (**13a**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(3\text{-}CH_2=CHC_6H_4)FCp]$ (**22**) and $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}CH_2=CHC_6H_4)FCp]$ (**23**) suitable for the X-ray diffraction study were mounted on a MacScience DIP2030 Imaging Plate diffractometer for data collection using MoKα (graphite monochromated, λ = 0.71069 Å) radiation. Crystal data and data statistics are summarized in Table 8. The structures of the complexes $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}PhFCp)$ (**12**), $Fe(\eta^5\text{-}C_5H_4COCH_3)(\eta^5\text{-}MeFCp)$ (**13a**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(3\text{-}CH_2=CHC_6H_4)FCp]$ (**22**) and $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}CH_2=CHC_6H_4)FCp]$ (**23**) were solved by the directed method (SHELXS-97)[43] and expanded using Fourier techniques (DIRDIF-94).[44] The positional parameters and thermal parameters of non-hydrogen atoms of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}PhFCp)$ (**12**), $Fe(\eta^5\text{-}C_5H_4COCH_3)(\eta^5\text{-}MeFCp)$ (**13a**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(3\text{-}CH_2=CHC_6H_4)FCp]$ (**22**) and $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}CH_2=CHC_6H_4)FCp]$ (**23**) were refined using a full-matrix least square method. Hydrogen atoms were placed at calculated positions (C-H

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[76] Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

= 0.95 Å) and kept fixed. All non-hydrogen atoms of $Fe(\eta^5\text{-}Cp)(\eta^5\text{-}PhFCp)$ (**12**), $Fe(\eta^5\text{-}C_5H_4COCH_3)(\eta^5\text{-}MeFCp)$ (**13a**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}MeOC_6H_4)FCp]$ (**19**), $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(3\text{-}CH_2{=}CHC_6H_4)FCp]$ (**22**) and $Fe(\eta^5\text{-}Cp)[\eta^5\text{-}(4\text{-}CH_2{=}CHC_6H_4)FCp]$ (**23**) were anisotropically refined. In the subsequent refinement, the function $\Sigma\omega(F_o{}^2 - F_c{}^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \Sigma\ (||F_o| - |F_c||)/\Sigma|F_o|$ and $wR2 = [\Sigma\omega\ (F_o{}^2{-}F_c{}^2)^2/\Sigma\ (\omega F_o{}^4)]^{1/2}$.

Table 8. Crystal Data and Structure Analysis Results for Bucky Ferrocenes 12, 13a, 19, 22 and 23.

	12 $\cdot CS_2$	**13a**
formula	$C_{96}H_{30}Fe_1S_2$	$C_{72}H_{22}Fe_1O_1$
crystal system	triclinic	monoclinic
space group	P 21 21 21 (No. 19)	P 21/n (No. 14)
R, R_w ($I>2\sigma(I)$)	0.0536, 0.0619	0.056, 0.099
$R1, wR2$ (all data)	0.1373, 0.1445	—, —
GOF on F^2	1.03	—
a, Å	15.188(5)	11.7620(5)
b, Å	17.395(5)	16.7030(6)
c, Å	20.561(5)	20.5620(9)
α, deg	90	90
β, deg	90	95.519(3)
γ, deg	90	90
V, Å^3	5432(3)	4020.9(5)
Z	4	4
T, K	150(2)	298
crystal size, mm	0.52, 0.18, 0.12	0.20, 0.20, 0.05
D_{calcd}, g/cm^{-3}	1.593	1.19
$2\theta_{min}, 2\theta_{max}$, deg	4.6, 51.18	—, 49.60
no. refl. measured (Unique)	9394	7883
no. refl. measured ($I>2\sigma(I)$)	8207	5325
no. parameters	893	679
Δ, eÅ^{-3}	0.313, -0.685	11.08, -0.69
μ	0.418	—
extinction coef.	0.0068(6)	—

Table 8. (Continued)

	19 ·(CS$_2$)$_2$	**22** ·CS$_2$
formula	C$_{102}$H$_{40}$Fe$_1$O$_5$S$_4$	C$_{107}$H$_{45}$Fe$_1$S$_4$
crystal system	monoclinic	orthorhombic
space group	$P\,21/n$ (No. 14)	$P\,b\,c\,a$ (No. 61)
R, R_w (I>2σ(I))	0.0718, 0.0939	0.094, 0.1209
$R1$, $wR2$ (all data)	0.1987, 0.2223	0.2485, 0.2865
GOF on F^2	1.031	1.126
a, Å	18.8260(9)	15.6020(4)
b, Å	17.2670(10)	23.2820(16)
c, Å	21.4060(12)	36.332(3)
$α$, deg	90	90
$β$, deg	103.633(3)	90
$γ$, deg	90	90
V, Å^3	6762.4(6)	13197.4(13)
Z	4	8
T, K	153(2)	153(2)
crystal size, mm	0.46, 0.21, 0.08	0.46, 0.28, 0.21
D_{calcd}, g/cm^{-3}	1.502	1.519
$2θ_{min}$, $2θ_{max}$, deg	4.58, 51.56	4.90, 51.54
no. refl. measured (Unique)	12814	10265
no. refl. measured (I>2σ(I))	9522	7088
no. parameters	1010	1019
$Δ$, eÅ^{-3}	1.462, -0.961	1.322, -0.808
$μ$	0.413	0.417
extinction coef.	0.0101(8)	0.0075(7)

Table 8. (Continued)

	$23 \cdot (CS_2)_2$
formula	$C_{107}H_{45}Fe_1S_4$
crystal system	triclinic
space group	P -1 (No. 2)
R, R_w ($I>2\sigma(I)$)	0.0938, 0.1379
$R1$, $wR2$ (all data)	0.2486, 0.2919
GOF on F^2	1.04
a, Å	14.9480(15)
b, Å	15.389(2)
c, Å	17.003(2)
α, deg	113.096(7)
β, deg	94.910(8)
γ, deg	108.131(8)
V, Å^3	3321.3(7)
Z	2
T, K	120(2)
crystal size, mm	0.52, 0.32, 0.05
D_{calcd}, g/cm^{-3}	1.509
$2\theta_{min}$, $2\theta_{max}$, deg	4.72, 51.60
no. refl. measured (Unique)	11387
no. refl. measured ($I>2\sigma(I)$)	7201
no. parameters	1010
Δ, eÅ^{-3}	1.581, -0.976
μ	0.414
extinction coef.	0.0075(7)

Electrochemical Measurements. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and reference electrode was a Ag/Ag$^+$ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc$^+$.

Chapter 4 Synthesis of Fullerene-Transition Metal Complexes by the Use of Fullerene Halide

4-1. Introduction

I and the Nakamura group already reported the syntheses of pentaorgano fullerene[17,36]-transition metal complexes by transmetalation,[23,25,26] the reactions via C-H bond activation[23] and hydrometallation reaction.[22] In these complexes, pentaorgano fullerene ligand acts as a cyclopentadienide. As the standard synthetic methods of cyclopentadienyl-transition metal complexes, not only transmetalation or the reactions via C-H bond activation reaction but also the reactions between cyclopentadienyl halides with transition metal ate complexes or oxidative addition reactions of cyclopentadienyl halides with low valent transition metal complexes, are well known. As fullerene halides $C_{60}R_5X$ (X = halide), $C_{60}Me_5Cl$ (**28b**)[77] and $C_{60}Ph_5Cl$ (**29b**)[78] were already reported. The chloride $C_{60}Me_5Cl$ (**28b**) was isolated in 4.5% yield by silica gel column chromatography and HPLC separations of the many products obtained by the reaction of $C_{60}Cl_6$[79] with methyllithium. The Friedel-Crafts reaction of $C_{60}Cl_6$[79] with benzene in the presence of $FeCl_3$ gave (**29b**) in 68% yield. The problems of

[77] Al-Matar, H.; Abdul-Sada, A. K.; Avent, A. G.; Fowler, P. W.; Hitchcock, P. B.; Rogers, K. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 53.

[78] Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463.

[79] Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1230.
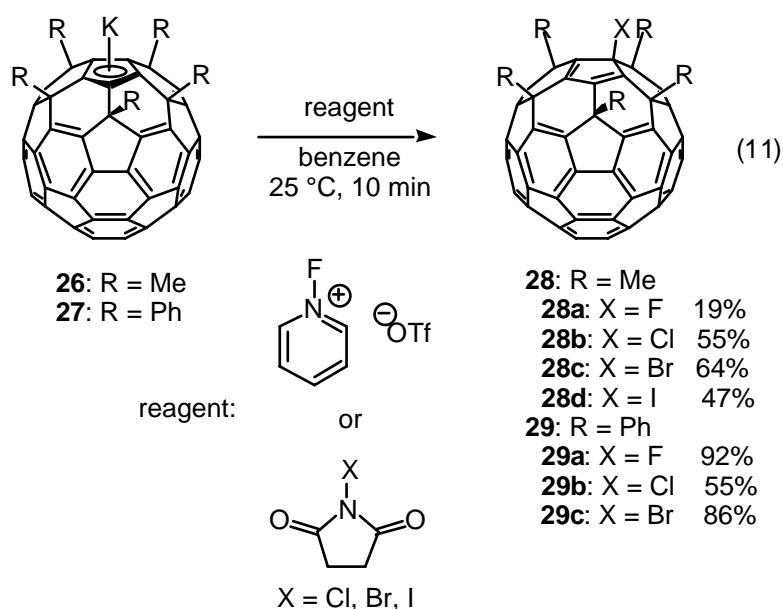
these synthetic reactions are low yield or limitation that only chlorides can be synthesized. These fullerene chlorides have not been used as starting materials of the synthesis of fullerene-transition metal complexes. In this thesis, I prepared fullerene halides $C_{60}R_5X$ (**28a**: R = Me, X = F; **28b**: R = Me, X = Cl; **28c**: R = Me, X = Br; **28d**: R = Me, X = I; **29a**: R = Ph, X = F; **29b**: R = Ph, X = Cl; **29c**: R = Ph, X = Br) and synthesized fullerene-transition metal complexes $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**), $FeBr(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**32**) and $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**) by use of fullerene bromide $C_{60}Me_5Br$ (**28c**). These reactions are the first example of the synthesis of pentaorgano fullerene-metal complexes by the reactions between fullerene halides and transition metal complexes. It is expected that many kinds of fullerene-transition metal complexes could be obtained by use of not only transmetalation or C-H bond activation reaction or hydrometallation reaction but also the reactions between fullerene halides and transition metal complexes.

4-2. Synthesis and Characterization of Fullerene Halides

Fullerene halides $C_{60}R_5X$ (**28a**: R = Me, X = F; **28b**: R = Me, X = Cl; **28c**: R = Me, X = Br; **28d**: R = Me, X = I; **29a**: R = Ph, X = F; **29b**: R = Ph, X = Cl, **29c**: R = Ph, X = Br) could be synthesized by the reaction of $K(\eta^5\text{-}C_{60}R_5)$ (**26**: R = Me; **27**: R = Ph)[17] ($C_{60}R_5$ is abbreviated as RFCp) with *N*-fluoropyridinium triflate, *N*-chloro, *N*-bromo and *N*-iodo succinimide (eq 11). These reactions proceeded smoothly in benzene at 25 °C. However, iodide $C_{60}Ph_5I$ could not be obtained.

In the synthesis of fluoride $C_{60}Me_5F$ (**28a**), $C_{60}Me_5$(pyridyl) (**30**) was obtained as a side product. While fluoride $C_{60}Me_5F$ (**28a**), $C_{60}Ph_5F$ (**29a**), chloride $C_{60}Me_5Cl$ (**28b**), $C_{60}Ph_5Cl$ (**29b**) and bromide $C_{60}Me_5Br$ (**28c**), $C_{60}Ph_5Br$ (**29c**) are air and moisture stable reddish orange solid, iodide $C_{60}Me_5I$ (**28d**) is sensitive to air and decompose to oxidation products of $C_{60}Me_5H$.


26: R = Me
27: R = Ph

reagent:

F–N$^{\oplus}$ $^{\ominus}$OTf

or

X = Cl, Br, I

28: R = Me
  28a: X = F   19%
  28b: X = Cl 55%
  28c: X = Br 64%
  28d: X = I   47%
29: R = Ph
  29a: X = F   92%
  29b: X = Cl 55%
  29c: X = Br 86%

reagent
benzene
25 °C, 10 min

(11)

APCI-MS spectra of products in these reactions indicated the formation of fullerene halides **28a-c** and **29a-c**. In the ^{1}H NMR spectra of pentamethylated fullerene halides $C_{60}Me_5F$ (**28a**), $C_{60}Me_5Cl$ (**28b**) and $C_{60}Me_5Br$ (**28c**), three singlet proton signals assigned as methyl groups were observed in the ratio 2 : 2 : 1. These observations show C_s symmetry of **28a-c**. The ^{1}H and ^{13}C NMR spectra of fullerene halides $C_{60}Ph_5F$ (**29a**), $C_{60}Ph_5Cl$ (**29b**) and $C_{60}Ph_5Br$ (**29c**) indicated that **29a-c** also have C_s symmetry. In the ^{1}H NMR spectrum of iodide

$C_{60}Me_5I$ (**28d**), only one singlet signal, corresponded to protons of methyl groups, was observed. These observations show that $C_{60}Me_5I$ (**28d**) has C_{5v} symmetry. A possible explanation for this observation is that since ion radius of iodide ion is large, there is no covalent bond between iodo atom and one carbon atom of FCp moiety. This observation is contranst to an η^1-coordination of Cp*I.[80]

To conclusively determine the structure of pentamethyl[60]fullerene bromide $C_{60}Me_5Br$ (**28c**), a single crystal X-ray diffraction study was performed (Figure 22, Table 9). Recrystallization of $C_{60}Me_5Br$ (**28c**) from CS_2/ethanol gave red single crystals composed of a 1:1 mixture of $C_{60}Me_5Br$ (**28c**) and CS_2. Bromo atom combines with one carbon atom of cyclopentadiene moiety of $C_{60}Me_5$.

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[80] Jutzi, P.; Schwartzen, K.-H.; Mix, A. *Chem. Ber.* **1990**, *123*, 837.
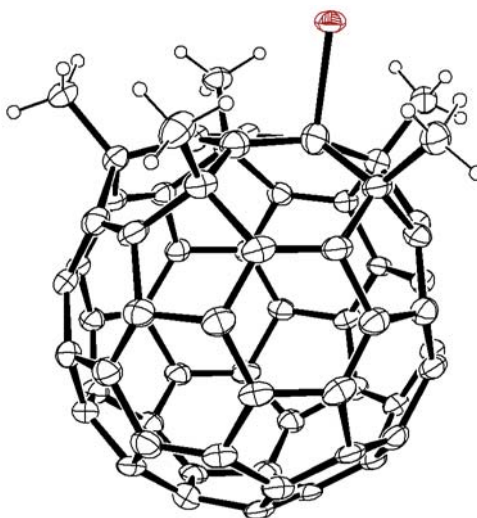
Figure 22. Molecular structure of fullerene bromide $C_{60}Me_5Br$ (**28c**) with 30% probability level ellipsoids. The CS_2 molecule found in the unit cell is omitted for clarity.

4-3. Electrochemical Measurement of Fullerene Halides

The electrochemical properties of fullerene halides $C_{60}Me_5Cl$ (**28b**) and $C_{60}Me_5Br$ (**28c**) were examined (Figure 23). While fullerene chloride $C_{60}Me_5Cl$ (**28b**) and bromide $C_{60}Me_5Br$ (**28c**) were not oxidized, could be reduced irreversively. After the reductions, $C_{60}Me_5^-$ and its redox species were observed. These results show that the C-X (X = Cl, Br) bonds of fullerene halides are cleaved by reduction. The fact that the first step is two-electrons reduction indicates that radical species $C_{60}Me_5^\bullet$ (**A$^\bullet$**), which forms by the cleavage of the C-X bonds, is reduced immediately to form anion $C_{60}Me_5^-$ (**A$^-$**). After the

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reduction, the anion A^- was oxidized to radical $A^\bullet$ and recombined with radicals $Cl^\bullet$ or $Br^\bullet$ to form $C_{60}Me_5Cl$ (**28b**) and $C_{60}Me_5Br$ (**28c**) again (Scheme 3). These results are similar to the reduction of $C_{60}Ph_5Cl$.[78] Reduction potentials of $C_{60}Me_5Cl$ (**28b**) and $C_{60}Me_5Br$ (**28c**) are –1.35 and –1.14 V, the values of which are larger than that of $C_{60}Me_5H$ ($E_{1/2}$ = -1.48 V).[17c] This result shows that halide anions can be removed easily from fullerene core.
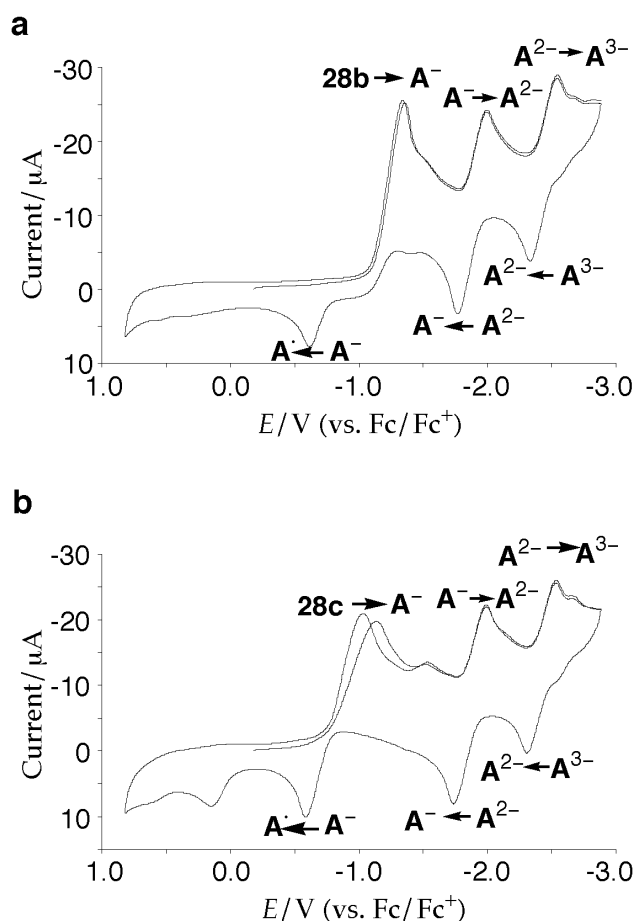
Figure 23. Cyclic voltammograms of chloride $C_{60}Me_5Cl$ (**28b**) (a) and bromide $C_{60}Me_5Br$ (**28c**) (b) (0.10 M [Bu$_4$N][ClO$_4$] in THF, 1.0 mM, glassy carbon working electrode, 0.10 V/s, 25 °C).

Scheme 3. Proposed mechanism of redox behavior of $C_{60}Me_5Cl$ (**28b**) and $C_{60}Me_5Br$ (**28c**).

28b: X = Cl
28c: X = Br

A·   **A⁻**   **A²⁻**   **A³⁻**
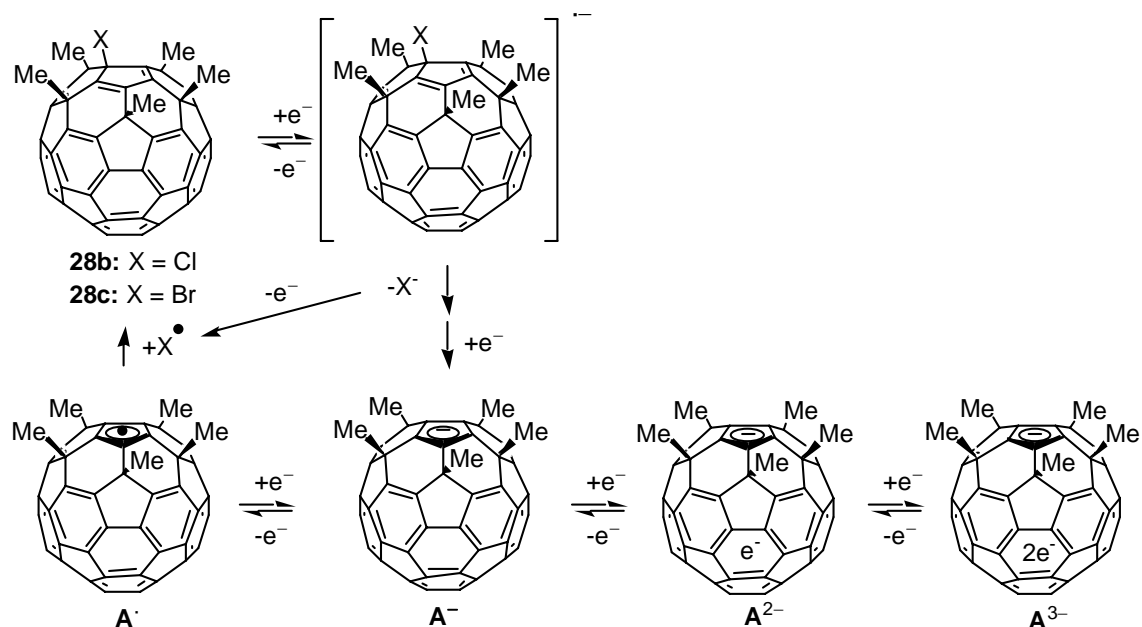
4-4. Synthesis of Fullerene-Transition Metal Complexes

By the reactions of the fullerene bromide $C_{60}Me_5Br$ (**28c**) with some low valent transition metal species, we succeeded in the syntheses of fullerene-transition metal complexes (eq 12-14). Rhenium tricarbonyl complex $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**) was obtained by the reaction of fullerene bromide $C_{60}Me_5Br$ (**28c**) with ate-type rhenium complex $Na[Re(CO)_5]$ (eq 12). The fullerene bromide $C_{60}Me_5Br$ (**28c**) was consumed completely after this reaction. APCI-MS spectrum indicated the formation of rhenium complex $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**). The ^1H and ^{13}C NMR spectra showed C_{5v} symmetry of the MeFCp moiety. In the ^{13}C NMR spectrum, only one signal assigned to

carbonyl groups was observed. The IR spectrum showed that there are two absorptions at 2022 and 1932 cm^{-1}, which correspond to stretching vibrations of three carbonyl groups [Re(η^5-C$_{60}$Bn$_2$PhH$_2$)(CO)$_3$[22]: 2024, 1939 cm^{-1}; ReCp(CO)$_3$[81]: 2019, 1897 cm^{-1}; Re(η^5-C$_{20}$H$_{17}$)(CO)$_3$ (C$_{20}$H$_{17}$ = partially hydrogenated coranulene)[82]: 2009, 1896 cm^{-1}]. These bond strengths of carbonyl groups are reflected by the electron withdrawing or donating nature of the MeFCp or Cp or C$_{20}$H$_{17}$ ligands. These results showed that three carbonyl groups are equal and coordinate to rhenium center as a piano-stool shape.

(12)
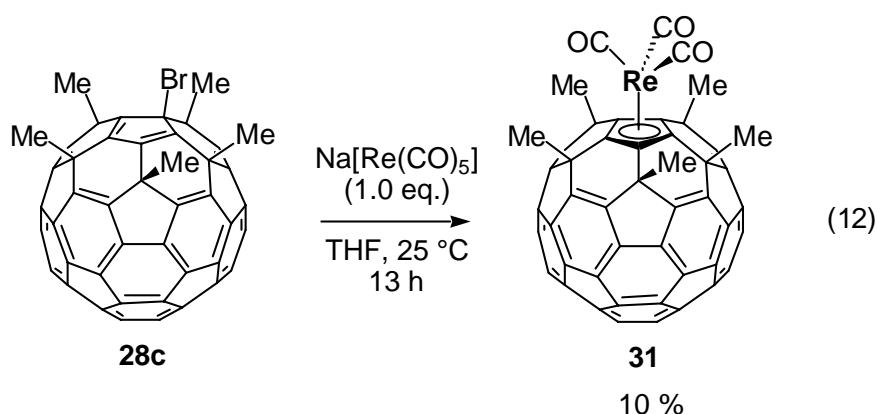
Next, I examined to synthesize iron bromodicarbonyl complex FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**). The oxidative addition of the fullerene bromide C$_{60}$Me$_5$Br (**28c**) with Fe(CO)$_5$ in 1,2-dichlorobenzene at 25 °C to give FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**) in 95% yield (eq 13). The iron carbonyl complex

[81] Tellers, D. M.; Skoog, S. J.; Bergmann, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428.

[82] Chin, R. M.; Caird, B.; Jarosh, M.; Rassman, J.; Barry, B. *Organometallics* **2003**, ASAP.

FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**) in solution is sensitive to air and light and decomposes to C$_{60}$Me$_5$H and its oxidation products. The chemical shifts of the ^{1}H and ^{13}C NMR spectra of iron complex FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**) are comparable to those of ruthenium halodicarbonyl complexes RuCl(η^5-C$_{60}$Me$_5$)(CO)$_2$[24] and RuBr(η^5-C$_{60}$Me$_5$)(CO)$_2$[25] (eq 13). This observation strongly supports the formation of FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**). In the IR spectrum, two absorption signals, which were assigned to symmetric and asymmetric stretching vibrations of carbonyl groups, were observed at 2037 and 1996 cm^{-1} (FeBrCp(CO)$_2$[83]: 2048, 2002 cm^{-1}).

28c → **32** (13)

95 %
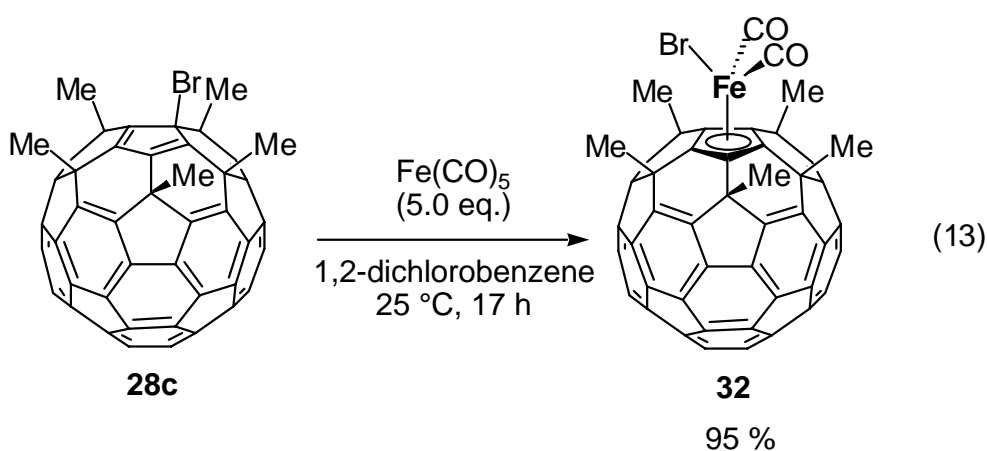
The reaction of the fullerene bromide C$_{60}$Me$_5$Br (**28c**) with cobalt complex Na[Co(CO)$_4$] gave cobalt dicarbonyl complex Co(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**33**) (eq 14). In this reaction, C$_{60}$Me$_5$H was formed as a side product. Since the cobalt complex Co(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**33**) was very sensitive to air, we could not

[83] Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1976**, *110*, 331.

succeeded in the isolation of this complex. The ^{1}H and ^{13}C NMR spectra show that MeFCp moiety of cobalt complex $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**) has C_{5v} symmetry. The chemical sifts of cobalt complex $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**) are similar to those of rhodium dicarbonyl complex $Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2$.[26] In the FAB-MS spectrum, molecular ion signal (m/z = 910) of cobalt complex $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**) was observed. These results support the formation of $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**).

$$(14)$$
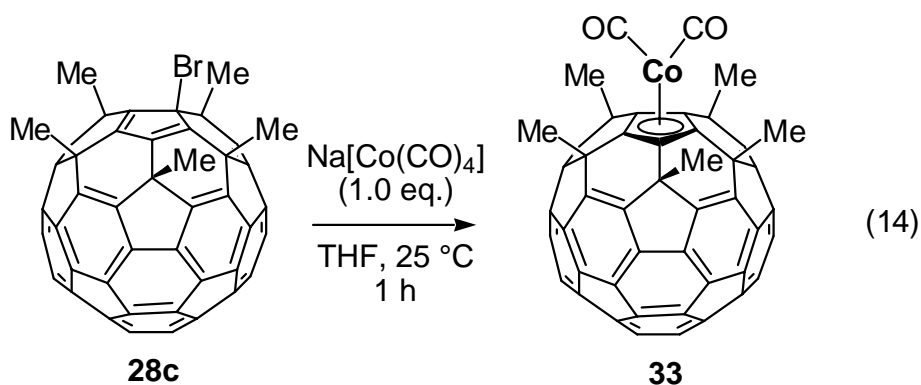
The proposed formation mechanisms of these fullerene-transition metal complexes $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**), $FeBr(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**32**) and $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**33**) are as follows. The bromide ion comes apart from fullerene bromide $C_{60}Me_5Br$ (**28c**), followed by the single electron transfer from low valent transition metal complexes to fullerene bromide $C_{60}Me_5Br$ (**28c**). The radical $C_{60}Me_5^{\bullet}$ or anion $C_{60}Me_5^-$, and bromide ion combine with transition metal species to give fullerene-transition metal complexes $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$

(**31**), FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**) and Co(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**33**).

4-5. X-ray Crystal Structure Analysis of Rhenium Complex

The red single crystals suitable for X-ray diffraction were obtained by recrystalization from CS$_2$/ethanol. The conclusive structure of rhenium complex Re(η^5-C$_{60}$Me$_5$)(CO)$_3$ (**31**) was determined by X-ray analysis (Figure 24). The MeFCp ligand coordinates to rhenium atom in an η^5 fashion. The averaged bond length of five Re-C(FCp) bonds is 2.327(11) Å, which is similar to those of Re(η^5-C$_{60}$Bn$_2$PhH$_2$)(CO)$_3$[22] (2.334(8) Å) and Re(η^5-C$_{20}$H$_{17}$)(CO)$_3$[82] (2.340(5) Å). The averaged bond lengths of Re-C(CO) (1.911(18) Å) and C(CO)-O(CO) (1.159(19) Å) are almost the same as those of Re(η^5-C$_{60}$Bn$_2$PhH$_2$)(CO)$_3$[22] (1.909(12) and 1.165(15) Å) and Re(η^5-C$_{20}$H$_{17}$)(CO)$_3$[82] (1.907(7) and 1.154(9) Å).
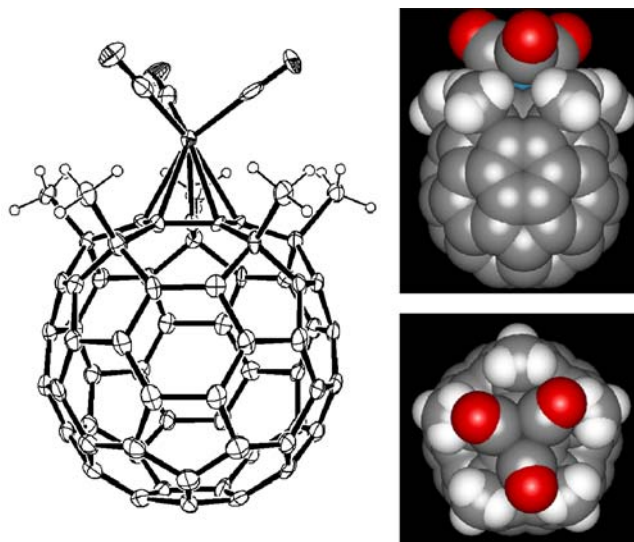
Figure 24. Molecular structure of rhenium tricarbonyl complex Re(η^5-C$_{60}$Me$_5$)(CO)$_3$ (**31**) with 30% probability level ellipsoids. The CS$_2$ molecule in the unit cell is omitted for clarity.

4-6. Electrochemical Measurement of Rhenium Complex

To elucidate the electrochemical properties of the rhenium tricarbonyl complex Re(η^5-C$_{60}$Me$_5$)(CO)$_3$ (**31**), electrochemical measurements were performed (Figure 25). Complex Re(η^5-C$_{60}$Me$_5$)(CO)$_3$ (**31**) could not be oxidized, but could be reduced reversibly in two step-one electron reductions. Since these reduction potentials are –1.33 and –1.94 V, which are similar to those of fullerene transition metal complexes,[23,24,25,26] the reductions must occur in the 50π electron system of C$_{60}$.
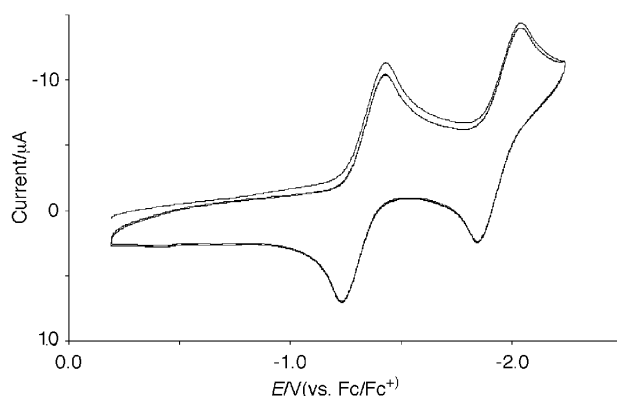
Figure 25. Cyclic voltammogram of rhenium complex $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**).

4-7. Derivatization of Iron Chlorodicarbonyl Complex

The iron dicarbonyl complex $FeBr(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**32**) could be derivatized into bucky ferrocene $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{60}Me_5)$ (**11**)[23] by the method similar to synthesize bucky ruthenocene $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{60}Me_5)$[24] (Scheme 4) (in collaboration with Ms. Ayako Muramatsu). The iron complex $FeBr(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**32**) could also be derivatized into $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**34**), $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**35**) and $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**) by the similar method of the syntheses of $FeCp(CO)_2R$[84] or $Ru(\eta^5\text{-}C_{60}Me_5)(CO)_2R$[24] (Scheme 4).

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[84] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

Scheme 4. Derivatization of FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**32**) into some iron complexes.
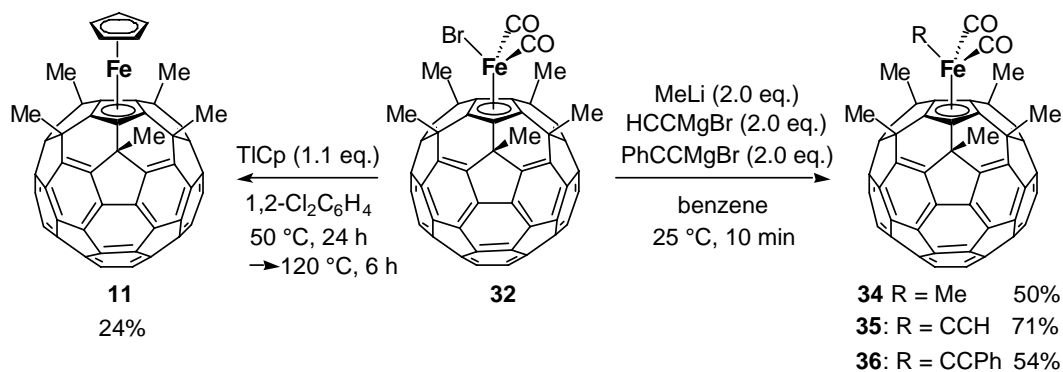
The complex Fe(η^5-C$_5$H$_5$)(η^5-C$_{60}$Me$_5$) (**11**) could be assigned as bucky ferrocene Fe(η^5-C$_5$H$_5$)(η^5-C$_{60}$Me$_5$) because the chemical shifts of the ^{1}H and ^{13}C NMR spectra of Fe(η^5-C$_5$H$_5$)(η^5-C$_{60}$Me$_5$) (**11**) are the same as those of bucky ferrocene Fe(η^5-C$_5$H$_5$)(η^5-C$_{60}$Me$_5$).[23] The ^{1}H and ^{13}C NMR and IR spectra of iron complex Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$Me (**34**), Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCH) (**35**) and Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCPh) (**36**), were similar to those of the corresponding ruthenium complexes Ru(η^5-C$_{60}$Me$_5$)(CO)$_2$Me, Ru(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCH) and Ru(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCPh).[24] The ^{1}H and ^{13}C NMR of Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$Me (**34**), Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCH) (**35**) and Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCPh) (**36**) indicated that MeFCp moieties of these iron complexes have C_{5v} symmetry. This results show that the rotation rates of MeFCp moieties around the Fe-MeFCp axis are faster than the relaxation time of NMR spectra. Carbon signal due to methyl group of Fe(Me)(η^5-C$_{60}$Me$_5$)(CO)$_2$ (**34**) was observed at –20.82 ppm,

which is similar to that of $FeCp(CO)_2Me$ (-23.5 ppm).[84] IR spectra of $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**34**), $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**35**) and $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**) showed two signals, which are assigned to stretching vibrations of carbonyl groups, at 2004, 1953 cm^{-1} [$Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**34**)], 2035, 1991 cm^{-1} [$Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**35**)] and 2035, 1990 cm^{-1} [$Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**)]. These wave numbers are similar to those of the corresponding iron carbonyl complexes $FeCp(CO)_2Me$[84] (2010, 1955 cm^{-1}), $FeCp(CO)_2(CCH)$[85] (2050, 1998 cm^{-1}) and $FeCp(CO)_2(CCPh)$[86] (2045, 2000 cm^{-1}). The stretching vibrations of phenylethynyl complex $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**) were observed at 2107 (CC), 2035 and 1990 cm^{-1} (CO), which are higher wave numbers than those of the corresponding phenylethynyl complex $FeCp^*(CO)_2(CCPh)$ (CC: 2094 cm^{-1}; CO: 2006, 1966 cm^{-1}).[86] These observations reflect the electron withdrawing nature of the MeFCp ligand.

While $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**34**), $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**35**) and $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**) are unstable in degassed solution, [87] $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**34**), $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**35**) and $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**36**) did not decompose under shading condition even in air or water for a few days. These results indicate that

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[85] Kim, P. J. Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem.Lett.* **1970**, *6*, 181.

[86] (a) Bruce, M. I. Harbourne, D. A.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. (A)* **1968**, 356. (b) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404.

[87] $C_{60}Me_5H$ was formed as a decomposition product.

Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$Me (**34**), Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCH) (**35**) and

Fe(η^5-C$_{60}$Me$_5$)(CO)$_2$(CCPh) (**36**) are sensitive to light and decompose into

C$_{60}$Me$_5$H.

4-8. Conclusion

I succeeded in the syntheses of fullerene halides RFCpX (R = Me, Ph; X = F,

Cl, Br, I) by the reaction of C$_{60}$R$_5$K with halogenation reagents. The reactions

between fullerene halides and low valent transition metal compounds gave

fullerene-rhenium, iron and cobalt complexes, Re(η^5-C$_{60}$Me$_5$)(CO)$_3$,

FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ and Co(η^5-C$_{60}$Me$_5$)(CO)$_2$. I could derivatize

FeBr(η^5-C$_{60}$Me$_5$)(CO)$_2$ into some iron complexes. The synthetic methods not

only transmetalation or the reactions via C-H activation or hydrometallation

reaction but also the reactions between fullerene halides and transition metal

compounds are expected to give many kinds of fullerene-transition metal

complexes. These complexes will bring wide varieties of development of

fullerene-organometallic chemistry,[88,89,90,91] catalytic reactions[92,93,94] and

[88] (a) Herberhold, M.; Biersack, M. *J. Organomet. Chem.* **1990**, *381*, 379. (b) Herberhold, M.; Biersack, M. *J. Organomet. Chem.* **1993**, *443*, 1. (c) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614.

[89] Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (b) Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. (c) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (d) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

materials science.

4-9. Experimental

General Procedure. All manipulations were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. THF was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. Benzene was distilled from calcium hydride. $C_{60}Me_5H$ and $C_{60}Ph_5H$ were prepared according to the literature.[17] THF solution of *t*-BuOK, MeLi, HCCMgBr and PhCCMgBr were purchased from Sigma-Aldrich Co. and used as received. *N*-Fluoropyridinium triflate, *N*-Chlorosuccinimide, *N*-Bromosuccinimide and *N*-Iodosuccinimide were purchased from Tokyo Kasei Co. and were recrystallized from benzene.

Preparative HPLC separations were performed by use of Bucky Prep. column (Nakalai Tesque Co., 20 mm x 250 mm).

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using JEOL EX-400 spectrometer. Proton chemical shifts are reported relative to Me_4Si

90 Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1.
91 King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* **1973**, *56*, 345.
92 (a) Chen, H.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **1999**, *38*, 3391. (b) Nishiyama, Y.; Kazushou, F.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2779.
93 (a) Fusi, A.; Cesaarotti, E.; Ugo, R. *J. Mol. Cat.* **1981**, *10*, 213. (b) Colombo, L.; Ulgheri, F.; Prati, L. *Tetrahedron Lett.* **1989**, *30*, 6435. (c) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 3543.
94 (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 215. (c) Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Eng.* **1984**, *23*, 539.

(CDCl$_3$) at δ 0.00 ppm or residual solvent peaks (CDCl$_3$ at δ 7.26 ppm; THF-d_8 at δ 1.73 and 3.58 ppm). Carbon chemical shifts are reported relative to CDCl$_3$ at δ 77.00 ppm or THF-d_8 at δ 25.20 and 67.40 ppm. Other spectra were recorded on the following instruments: IR, JASCO IR-420 and ReactIR 1000; UV/vis spectra, HITACHI U3500 and Shimadzu SPD-6A; Mass spectra, Shimadzu LCMS-QP8000 and JEOL Accu TOF (JMS-T100LC). Elemental Analyses were performed at organic elemental analysis laboratory in this department.

C$_{60}$Me$_5$F (28a). To a suspension of C$_{60}$Me$_5$H (202 mg, 251 μmol) in THF (10.0 mL) was added a solution of ^{t}BuOK (1.0 M, 0.28 mL, 280 μmol) in THF. After stirring for 1.5 h, *N*-fluoropyridinium triflate (93.1 mg, 377 μmol) was added. The mixture was stirred for 0.5h. After dilution with toluene, the mixture was washed with water. The organic phase was concentrated in vacuo. After preparative HPLC separation [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm), toluene/2-propanol = 7/3, flow rate = 18 mL/min, retention time = 7.5 - 9.0 min])] afforded C$_{60}$Me$_5$F (**28a**) (37.9 mg, 19% yield) and C$_{60}$Me$_5$(2-pyridyl) (**30**) (32.2 mg, 15%) as air stable reddish orange solids. C$_{60}$Me$_5$F (**28a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.24 (s, 6H), 2.34 (s, 6H), 2.36 (s, 3H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$) δ 2.21 (s, 6H), 2.29 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$) δ 24.97 (d, J_{F-C} = 1.7 Hz, 2C, C(Me)), 26.37 (d, J_{F-C} = 1.7 Hz, 2C, C(Me)), 26.57 (d, $^3J_{F-C}$ = 19.0 Hz, 1C, C(Me)), 50.27 (d, $^3J_{F-C}$ = 1.7 Hz, 2C, C(α)), 51.61 (2C, C(α)), 53.49 (d, $^2J_{F-C}$ = 27.3 Hz, 1C, C(α)), 82.18 (d, $^1J_{F-C}$ = 338 Hz, 1C,

C(α)), 142.47 (2C), 142.72 (2C), 143.43 (2C), 143.63 (2C), 143.66 (2C), 143.74 (2C), 144.04 (2C), 144.19 (2C), 144.51 (2C), 145.24 (2C), 146.35 (1C), 146.37 (2C), 146.43 (2C), 146.44 (2C), 147.12 (2C), 147.44 (2C), 147.50 (2C), 147.55 (1C), 147.88 (2C), 147.96 (2C), 147.99 (2C), 148.16 (2C), 148.18 (2C), 148.35 (1C), 151.15 (2C), 151.17 (2C), 152.78 (2C), 156.12 (2C); ^{19}F NMR (376.4 MHz, CDCl$_3$/CS$_2$) δ 47.05 (q, $^4J_{F-H}$ = 9.0 Hz, 1F); IR (KBr) ν/cm^{-1} 2962 (m), 2920 (m), 2859 (w), 1513 (s), 1445 (s), 1417 (w), 1373 (w), 1288 (w), 1266 (w), 1239 (w), 1201 (w), 1179 (w), 1127 (w), 1104 (w), 1063 (w), 1028 (w), 1010 (w), 998 (w), 982 (m), 955 (w), 685 (m), 660 (w), 656 (w), 576 (w), 569 (w), 555 (m), 545 (m), 528 (m), 521 (m), 509 (w), 499 (m), 461 (w); UV-vis (1.0x10^{-5} mol·L^{-1} in CH$_2$Cl$_2$) λ_{max} ( ) 258 (76600), 271 (74900), 355 (21600, shoulder), 393 (12500), 470 (3830, shoulder) nm; APCI-MS (+) m/z = 814 (M$^+$), (-) m/z = 795 ([M-F]$^-$). HR-APCI-MS (+) m/z ; found: 814.1100; calcd for C$_{60}$Me$_5$F (**28a**): 814.1158.

C$_{60}$Me$_5$(2-pyridyl) (**30**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.08 (s, 3H), 2.21 (s, 6H), 2.52 (s, 6H), 7.37 (dd, $^3J_{C-H}$ = 7.6 Hz, $^3J_{C-H}$ = 4.4 Hz, 1H), 7.82 (td, $^3J_{C-H}$ = 7.6 Hz, $^4J_{C-H}$ = 2.0 Hz, 1H), 7.91 (d, $^3J_{C-H}$ = 7.6 Hz, 1H), 8.81 (dt, $^3J_{C-H}$ = 4.4 Hz, $^4J_{C-H}$ = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 26.57 (2C, C(Me)), 27.23 (2C, C(Me)), 32.36 (1C, C(Me)), 50.68 (2C, C(α)), 53.56 (2C, C(α)), 54.71 (1C, C(α)), 71.71 (1C, C(α)), 119.73 (1C, pyridyl), 121.88 (1C, pyridyl), 136.67 (1C, pyridyl), 142.70 (2C), 143.22 (2C), 143.78 (2C), 143.87 (2C), 143.92 (1C), 143.99 (2C), 144.09 (2C), 144.49 (2C), 144.90 (2C), 145.19 (2C), 145.53 (2C), 146.24 (2C), 146.62 (2C), 146.80 (2C), 146.90 (2C), 147.29 (1C, pyridyl), 147.61 (1C), 147.78 (2C), 147.82 (2C), 147.95

(2C), 148.21 (2C), 148.26 (2C), 148.28 (2C), 148 51 (2C), 149.24 (2C), 152.12 (2C), 153.57 (2C), 155.70 (1C, pyridyl), 156.98 (2C), 158.69 (2C); IR (KBr) ν/cm^{-1} 2960 (m), 2919 (m), 2859 (w), 1581 (m), 1515 (m), 1458 (m), 1447 (m), 1428 (m), 1417 (w), 1370 (w), 1287 (w), 1266 (w), 1239 (w), 1200 (w), 1127 (w), 1093 (w), 1051 (w), 997 (w), 924 (w), 879 (w), 795 (w), 782 (w), 747 (w), 729 (w), 694 (w), 686 (m), 655 (w), 577 (w), 569 (w), 561 (w), 552 (m), 541 (m), 527 (m), 519 (m); UV-vis (1.0x10^{-5} mol ·L^{-1} in CH$_2$Cl$_2$) λ_{max} (ε) 260 (72000), 270 (71500), 347 (21500), 355 (20700, shoulder), 393 (12200), 470 (3860, shoulder) nm; APCI-MS (+) m/z = 874 ([M+H]$^+$), (-) m/z = 873 ([M]$^-$). HR-APCI-MS (+) m/z ; found: 873.1509; calcd for C$_{60}$Me$_5$(2-pyridyl) (**30**): 873.1518.

C$_{60}$Me$_5$Cl (28b). To a suspension of C$_{60}$Me$_5$H (501 mg, 628 μmol) in benzene (20.0 mL) was added a solution of ^{t}BuOK (1.0 M, 0.75 mL, 750 μmol) in THF. After stirring for 5.5 h, *N*-chlorosuccinimide (109 mg, 816 μmol) was added. The mixture was stirred for 10 min. After the mixture was diluted with toluene, the mixture was washed with water. The organic phase was concentrated in vacuo. After preparative HPLC separation [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm), toluene/2-propanol = 7/3, flow rate = 18 mL/min, retention time = 7.0 - 8.0 min])], C$_{60}$Me$_5$Cl (**28b**) (285 mg, 55% yield) was obtained as an air stable reddish orange solid. C$_{60}$Me$_5$Cl (**28b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.33 (s, 6H), 2.35 (s, 6H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 24.55 (2C, C(Me)), 26.53 (2C, C(Me)), 33.58 (1C, C(Me)), 50.65 (2C, C(α)), 52.49 (2C, C(α)), 54.25 (1C,

C(α)), 77.64 (1C, C(α)), 142.79 (2C), 142.99 (2C), 143.20 (2C), 143.58 (2C), 143.87 (2C), 144.15 (2C), 144.24 (2C), 144.37 (2C), 144.41 (2C), 145.12 (2C), 145.13 (2C), 146.74 (2C), 146.80 (2C), 147.70 (2C), 147.86 (2C), 147.94 (2C), 148.13 (2C), 148.27 (2C), 148.28 (2C), 148.30 (2C), 148.31 (2C), 148.52 (2C), 152.40 (2C), 153.41 (2C), 154.63 (2C), 156.92 (2C); [Two sp^2 (1C) signals could not be detected because of the low solubility of $C_{60}Me_5Cl$ (**28b**)] ; IR (KBr) ν/cm^{-1} 2963 (m), 2920 (m), 2859 (m), 1444 (s), 1417 (w), 1373 (w), 1287 (w), 1265 (w), 1238 (w), 1201 (w), 1129 (w), 815 (m), 797 (m), 686 (m), 656 (w), 576 (w), 553 (m), 543 (m), 526 (m); UV-vis (1.0x10^{-5} mol·L^{-1} in CH_2Cl_2) λ_{max} (ϵ) 258 (110000), 272 (105000), 338 (33900), 354 (30600), 394 (17400), 475 (5020, shoulder) nm; APCI-MS (+) m/z = 830; HR-APCI-MS (+) m/z ; found: 830.0864; calcd for $C_{60}Me_5Cl$ (**28b**): 830.0862.

$C_{60}Me_5Br$ (28c). Bromide $C_{60}Me_5Br$ (**28c**) was synthesized as for $C_{60}Me_5Cl$ (**28b**), using the following amounts: $C_{60}Me_5H$ (1004 mg, 1.26 mmol), ^tBuOK (1.0 M, 1.50 mL, 1.50 mmol) in THF (1.0 M, 1.50 mL), N-bromosuccinimide (289 mg, 1.62 mmol), benzene (40.0 mL). Yield: 707 mg (64% yield). $C_{60}Me_5Br$ (**28c**): ^1H NMR (400 MHz, CDCl$_3$) δ 2.31 (s, 6H), 2.43 (s, 6H), 2.67 (s, 3H); ^1H NMR (400 MHz, CDCl$_3$/CS$_2$) δ 2.29 (s, 6H), 2.41 (s, 6H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 24.68 (2C, C(Me)), 26.37 (2C, C(Me)), 37.73 (1C, C(Me)), 50.60 (2C, C(α)), 52.73 (2C, C(α)), 54.10 (1C, C(α)), 69.54 (1C, C(α)), 141.91 (2C), 142.76 (2C), 143.05 (2C), 143.52 (2C), 143.82 (2C), 143.87 (2C), 144.19 (5C), 144.35 (2C), 144.42 (2C), 145.16 (4C), 146.71 (2C), 146.76 (2C), 147.64 (2C), 147.87 (2C), 147.95 (1C),

148.06 (2C), 148.28 (6C), 148.51 (2C), 148.58 (2C), 152.00 (2C), 153.34 (2C), 155.18 (2C), 157.15 (2C); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 24.52 (2C, C(Me)), 26.22 (2C, C(Me)), 37.52 (1C, C(Me)), 50.26 (2C, C(α)), 52.39 (2C, C(α)), 53.83 (1C, C(α)), 69.43 (1C, C(α)), 141.57 (2C), 142.63 (2C), 142.75 (2C), 143.20 (2C), 143.68 (2C), 143.73 (2C), 143.89 (2C), 144.04 (2C), 144.12 (2C), 144.20 (2C), 144.35 (1C), 144.77 (2C), 144.86 (2C), 146.44 (2C), 146.48 (2C), 147.39 (2C), 147.62 (2C), 147.72 (1C), 147.83 (2C), 148.05 (6C), 148.19 (2C), 148.25 (2C), 151.64 (2C), 152.96 (2C), 154.84 (2C), 156.78 (2C); IR (KBr) ν/cm^{-1} 2963 (m), 2920 (m), 2859 (m), 1443 (s), 1417 (w), 1372 (w), 1287 (w), 1264 (w), 1238 (w), 1200 (w), 1129 (w), 806 (w), 782 (m), 756 (w), 685 (m), 656 (w), 576 (w), 552 (m), 541 (m), 526 (m); UV-vis (1.0x10^{-5} mol·L^{-1} in CH_2Cl_2) λ$_{max}$ (ε) 259 (104000), 271 (100000), 340 (32500), 354 (29600), 393 (17300), 475 (4880, shoulder) nm; FAB-MS (+) m/z = 874 (M$^+$); APCI-MS (+) m/z = 874 (M$^+$); HR-APCI-MS (+) m/z ; found: 874.0371; calcd for $C_{60}Me_5Br$ (**28c**): 874.0357.

$C_{60}Me_5I$ (28d). Iodide $C_{60}Me_5I$ (**28d**) was synthesized as for $C_{60}Me_5Cl$ (**28b**), using the following amounts: $C_{60}Me_5H$ (50.0 mg, 62.7 μmol), ^tBuOK (1.0 M, 69.0 μL, 69.0 μmol) in THF, N-iodosuccinimide (16.9 mg, 75.2 μmol), benzene (2.5 mL). Yield: 27.3 mg (47%). $C_{60}Me_5I$ (**28d**): ^1H NMR (400 MHz, $CDCl_3$) δ 2.49 (brs, 15H); ^1H NMR (400 MHz, THF-d_8) δ 2.52 (brs, 15H); ^1H NMR (400 MHz, C_6D_6) δ 2.20 (brs, 15H); ^{13}C NMR (100 MHz, THF-d_8) δ 24.39 (5C, C(Me)), 48.42 (5C, C(α)), 128.91 (5C, C(Cp)),144.52 (10C), 145.25 (5C), 147.56 (10C), 148.88 (10C),

149.05 (10C), 149.27 (5C); IR (powder) ν/cm^{-1} 2962, (m), 2920 (w), 2859 (w), 1669 (m), 1656 (m), 1626 (s), 1569 (w), 1444 (m), 1336 (m), 1289 (m), 1245 (s), 1236 (s), 1153 (m), 1091 (s), 1016 (s), 874 (m), 800 (s), 668 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 286, 342, 357 (shoulder), 391, 472 (shoulder) nm; APCI-MS (+) m/z = 796 ([M-I+H]$^+$), 828 ([M-I+2O-H]$^+$), (-) m/z = 795 ([M-I]$^-$).

C$_{60}$Ph$_5$F (29a). Fluoride C$_{60}$Ph$_5$F (**29a**) was synthesized as for C$_{60}$Ph$_5$F (**29a**), using the following amounts: C$_{60}$Ph$_5$H (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, N-fluoropyridinium triflate (26.8 mg, 108 μmol), THF (5.0 mL). Yield: 93.1 mg (92%). C$_{60}$Ph$_5$F (**29a**): ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 7.01-7.19 (m, 11H), 7.31-7.38 (m, 6H), 7.49-7.51 (m, 4H), 7.84-7.87 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 58.21 (2C, sp^3), 60.28 (2C, sp^3), 61.93 (1C, sp^3), 67.75 (1C, sp^3), 127.16 (1C, C(Ph)), 127.59 (2C, C(Ph)), 127.73 (2C, C(Ph)), 127.84 (4C, C(Ph)), 127.90 (2C, C(Ph)), 127.96 (2C, C(Ph)), 127.99 (4C, C(Ph)), 128.65 (4C, C(Ph)), 128.90 (4C, C(Ph)), 130.10 (2C, C(Ph)), 137.73 (2C, C(Ph)), 137.92 (1C, C(Ph)), 142.72 (2C), 143.10 (2C), 144.01 (1C), 144.10 (2C), 144.11 (2C), 144.16 (2C), 144.40 (2C), 144.58 (2C), 144.64 (2C), 145.07 (2C), 145.15 (2C), 145.58 (2C), 147.09 (2C), 147.11 (2C), 147.22 (2C), 147.36 (2C), 147.39 (2C), 147.58 (2C), 147.82 (2C), 147.98 (1C), 148.06 (2C), 148.46 (2C), 148.49 (2C), 148.53 (2C), 148.57 (2C), 148.61 (2C), 151.45 (2C), 155.62 (2C); IR (powder, cm^{-1}) ν 1598 (w), 1492 (m), 1463 (w), 1447 (m), 1419 (w), 1261 (m), 1237 (w), 1158 (w), 1069 (w), 1031 (m), 1012 (m), 964 (w), 943 (w), 910 (w), 889 (w), 735 (m), 692 (s), 668

(m), 656 (m); UV-vis (toluene/2-propanol = 7/3) λ_{max} 287, 340, 354 (shoulder), 394, 470 nm; APCI-MS (±) m/z = 1124 (M±).

C$_{60}$Ph$_5$Cl (29b). Chloride C$_{60}$Ph$_5$Cl (**29b**) was synthesized as for C$_{60}$Me$_5$Cl (**28b**), using the following amounts: C$_{60}$Ph$_5$H (201 mg, 181 μmol), ^{t}BuOK in THF (1.0 M, 0.22 mL), *N*-chlorosuccinimide (31.4 mg, 235 μmol), benzene (8.0 mL). Yield: 114 mg (55%). C$_{60}$Ph$_5$Cl (**29b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10-7.40 (m, 17H), 7.64-7.69 (m, 4H), 7.93-7.98 (m, 4H); ^{1}H NMR (400 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 7.04-7.30 (m, 17H), 7.59-7.61 (m, 4H), 7.89-7.90 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 58.25 (2C, sp^3), 60.89 (2C, sp^3), 63.47 (1C, sp^3), 127.19 (1C, C(Ph)), 127.72 (4C, C(Ph)), 127.82 (2C, C(Ph)), 128.45 (4C, C(Ph)), 128.49 (4C, C(Ph)), 128.68 (4C, C(Ph)), 128.69 (4C, C(Ph)), 130.03 (2C, C(Ph)), 137.10 (2C, C(Ph)), 138.60 (2C, C(Ph)), 142.78 (2C), 143.28 (2C), 143.47 (1C, C(Ph)), 143.53 (2C), 143.62 (2C), 143.74 (2C), 143.89 (2C), 144.07 (2C), 144.18 (2C), 144.29 (2C), 144.43 (2C), 145.21 (2C), 145.25 (2C), 146.66 (2C), 147.18 (2C), 147.30 (2C), 147.75 (2C), 148.06 (2C), 148.18 (2C), 148.40 (2C), 148.56 (2C), 148.62 (2C), 148.69 (2C), 150.22 (2C), 151.09 (2C), 153.61 (2C), 156.63 (2C) [One sp3 (1C) signal and two sp^2 (1C) signals could not be detected because of the low solubility of C$_{60}$Ph$_5$Cl (**29b**)]; ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$ = 1/1) δ 57.95 (2C, sp^3), 60.63 (2C, sp^3), 63.21 (1C, sp^3), 76.13 (1C, sp^3), 127.00 (1C, C(Ph)), 127.57(4C, C(Ph)), 127.62 (2C, C(Ph)), 128.25 (4C, C(Ph)), 128.33 (4C, C(Ph)), 128.49 (4C, C(Ph)), 128.55 (4C, C(Ph)), 129.83 (2C, C(Ph)), 136.75 (2C, C(Ph)), 138.26 (2C, C(Ph)), 142.65 (2C),

143.03 (2C+1C(Ph)),143.23 (2C), 143.37 (2C), 143.44 (2C), 143.66 (2C), 143.94 (2C), 144.04 (2C), 144.11 (2C), 144.30 (2C), 144.94 (2C), 145.01 (2C), 146.37 (2C), 146.94 (2C+1C), 147.07 (2C), 147.54 (2C), 147.83 (1C), 147.97 (2C), 148.16 (2C), 148.35 (6C), 148.46 (2C), 149.96 (2C), 150.77 (2C), 153.29 (2C), 156.33 (2C); IR (KBr) ν/cm^{-1}; 3058 (w), 3028 (w), 2924 (w), 1599 (m), 1493 (s), 1462 (w), 1446 (m), 1418 (w), 1288 (w), 1263 (w), 1236 (w), 1204 (w), 1185 (w), 1157 (w), 1109 (w), 1070 (w), 1032 (m), 1003 (w), 911 (w), 837 (w), 788 (w), 735 (m), 694 (s), 666 (w), 584 (m), 565 (m), 543 (s), 479 (w); UV-vis (1.0x10^{-5} mol·L^{-1} in CH$_2$Cl$_2$) λ_{max} (ε) 260 (106000), 273 (96300, shoulder), 339 (32300), 356 (28300, shoulder), 390 (14600), 475 (4850, shoulder) nm; APCI-MS (+) m/z = 1140 (M$^+$); HR-APCI-MS (+) m/z ; found: 1140.1745; calcd for C$_{60}$Ph$_5$Cl (**29b**): 1140.1645.

C$_{60}$Ph$_5$Br (29c). Bromide C$_{60}$Ph$_5$Br (**29c**) was synthesized as for C$_{60}$Me$_5$Cl (**28b**), using the following amounts: C$_{60}$Ph$_5$H (100 mg, 90.3 μmol), ^{t}BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, N-bromosuccinimide (19.2 mg, 108 μmol), benzene (5.0 mL). Yield: 91.8 mg (86%). C$_{60}$Ph$_5$Br (**29c**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10-7.42 (m, 17H), 7.66-7.73 (m, 4H), 7.94-8.03 (m, 4H); ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 7.03-7.27 (m, 17H), 7.57-7.58 (m, 4H), 7.88 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$/CS$_2$ = 1/3) δ 57.69 (2C, sp^3), 60.60 (2C, sp^3), 67.62 (1C, sp^3), 69.45 (1C, sp^3), 127.51 (1C, C(Ph)), 127.60 (2C, C(Ph)), 128.35 (4C, C(Ph)), 128.67 (12C, C(Ph)), 128.29 (2C, C(Ph)), 129.49 (2C, C(Ph)), 136.83 (1C, C(Ph)), 138.48 (2C, C(Ph)), 141.90 (2C), 142.64 (2C), 142.99(2C), 143.21 (2C), 143.33 (2C), 143.64

(2C), 144.06 (4C), 144.33 (2C), 145.04 (2C), 145.78 (1C), 146.75 (2C), 146.95 (6C), 147.08 (2C), 147.54 (2C), 147.89 (1C), 148.04 (2C), 148.10 (2C), 148.18 (2C), 148.45 (6C), 149.94 (2C), 150.68 (2C), 153.93 (2C), 156.60 (2C); IR (KBr) ν/cm^{-1} 3058 (w), 3028 (w), 2960 (m), 2924 (w), 1599 (m), 1493 (s), 1462 (m), 1446 (m), 1418 (w), 1288 (w), 1260 (s), 1236 (w), 1204 (w), 1185 (w), 1156 (w), 1094 (brs), 1030 (brs), 910 (w), 863 (w), 804 (s), 735 (m), 695 (s), 666 (w), 584 (m), 565 (w), 554 (w), 541 (m), 478 (w); UV-vis (1.0x10^{-5} mol·L^{-1} in CH_2Cl_2) λ_{max} (ε) 260 (122000), 350 (35500), 395 (18300), 475 (6230, shoulder) nm; APCI-MS (+) m/z = 1184.

Re(η^5-MeFCp)(CO)$_3$ (31). To a solution of $C_{60}Me_5Br$ (**28c**) (10.0 mg, 11.4 μmol) in THF (4.0 mL) was added a solution of Na[Re(CO)$_5$] (3.98 mg, 11.4 mmol) in THF (46.6 μL). After the mixture was stirred for 13 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (0.50 mL). The mixture was diluted with toluene and washed with water. The organic layer was dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. Preparative HPLC separations [Bucky Prep. (Nacalai Tesque Co., 20 mm x 250 mm), toluene/2-propanol = 7/3, flow rate = 14 mL/min, retention time = 115 - 12.5 min] afforded Re(η^5-MeFCp)(CO)$_3$ (**31**) (1.2 mg, 10%) as dark reddish orange microcrystals. Re(η^5-MeFCp)(CO)$_3$ (**31**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.41 (s, 15H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.11 (5C, Me), 50.96 (5C, C(α)), 110.80 (5C, C(Cp)), 143.65 (10C), 143.87 (10C), 146.72 (5C), 147.86 (10C), 148.47 (5C), 152.39 (10C), 193.40 (3C, CO); IR (KBr) ν_{CO}/cm^{-1} 2022, 1932; UV-vis

(toluene/2-propanol = 7/3) λ_{max} 285, 355, 395, 468 nm; APCI-MS (±) m/z = 1064 (M±); HR-APCI-MS (+) m/z ; found: 1064.0602; calcd for Re(η^5-MeFCp)(CO)$_3$ (**31**): 1064.0551.

FeBr(η^5-MeFCp)(CO)$_2$ (32). To a suspension of C$_{60}$Me$_5$Br (**28c**) (660 mg, 754 μmol) in 1,2-dichlorobenzene (11.0 mL) was added Fe(CO)$_5$ (500 μL, 3.80 mmol). After stirring for 17 h at 25 °C, dark orange precipitate was formed. Degassed hexane (40 mL) was added to a reaction mixture, then the precipitate was filtered and washed with hexane. After the solid was dried under reduced pressure, FeBr(η^5-MeFCp)(CO)$_2$ (**32**) (707 mg, 95%) was obtained as reddish orange solid. FeBr(η^5-MeFCp)(CO)$_2$ (**32**): ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.23 (s, 15H); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 28.70 (5C, C(Me)), 51.11 (5C, C(α)), 105.89 (5C, C(Cp)), 143.62 (10C), 144.10 (10C), 147.38 (5C), 148.59 (10C), 148.86 (5C), 152.33 (10C), 214.06 (2C, C(CO)): IR (KBr, ν/cm^{-1}) 2037, 1996; UV-vis (toluene/2-propanol = 7/3) λ_{max} 288, 336 (shoulder), 356 (shoulder), 394, 466 (shoulder) nm.

Co(η^5-MeFCp)(CO)$_2$ (33). To a solution of C$_{60}$Me$_5$Br (**28c**) (20.1 mg, 23.0 μmol) in THF (5.0 mL), Na[Co(CO)$_4$] (4.45 mg, 22.9 μmol) in THF (0.97 mL) was added. After the mixture was stirred for 1 h, the solvent was removed in vacuo. Co(η^5-MeFCp)(CO)$_2$ (**33**): ^{1}H NMR (400 MHz, THF-d_8) δ 2.43 (s, 15H); ^{13}C NMR (100 MHz, THF-d_8) δ 32.78 (5C, Me), 51.25 (5C, C(α)), 108.90 (5C, C(Cp)), 144.32

(5C), 145.23 (10C), 145.36 (10C), 147.54 (10C), 148.71 (10C), 154.11 (5C), [Carbonyl (2C) signal could not be detected because of the low solubility of **33**]; FAB-MS (+) m/z = 910 (M$^+$).

Fe(η^5-MeFCp)(CO)$_2$Me (34). To a solution of FeBr(η^5-MeFCp)(CO)$_2$ (**32**) (47.6 mg, 48.1 μmol) in benzene (8.4 mL) was added 1.14 M solution of MeLi in ether (84.5 mL, 96.2 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel and was concentrated in vacuo (ca. 5 mL). By the addition of methanol into the mixture, iron-methyl complex Fe(η^5-MeFCp)(CO)$_2$Me (**34**) (22.3 mg, 50%) was obtained as orange solid. MeMgBr in THF also gave Fe(η^5-MeFCp)(CO)$_2$Me (**34**). Fe(η^5-MeFCp)(CO)$_2$Me (**34**): ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 0.99 (s, 3H), 2.10 (s, 15H); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ -20.83 (1C, Fe-*Me*), 28.18 (5C, C(Me)), 50.95 (5C, C(α)), 106.59 (5C, C(Cp)), 144.04 (10C), 144.22 (10C), 147.39 (5C), 148.55 (10C), 148.93 (5C), 153.11 (10C), 218.13 (2C, C(CO)): IR (KBr, ν/cm^{-1}) 2004, 1953.

Fe(η^5-MeFCp)(CO)$_2$(CCH) (35). To a solution of FeBr(η^5-MeFCp)(CO)$_2$ (**32**) (108 mg, 110 μmol) in benzene (19.2 mL) was added 0.95 M solution of HCCMgBr in THF (217 μL, 206 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel and was concentrated in vacuo (ca. 10 mL). By the addition of methanol into the mixture, iron-ethynyl complex Fe(η^5-MeFCp)(CO)$_2$(CCH) (**35**) (74.3 mg, 71%) was obtained as orange

microcrystals. Fe(η^5-MeFCp)(CO)$_2$(CCH) (**35**): ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.72 (s, 1H), 2.34 (s, 15H); ^{1}H NMR (400 MHz, THF-d_8/CS$_2$ = 1/1) δ 1.80 (s, 1H), 2.57 (s, 15H); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 28.72 (5C, C(Me)), 50.72 (5C, C(α)), 107.02 (5C, C(Cp)), 107.76 (1C, CCH), 128.80 (1C, CCH), 143.99 (10C), 144.12 (10C), 147.39 (5C), 148.59 (10C), 148.93 (5C), 152.79 (10C), 213.66 (2C, C(CO)).

Fe(η^5-MeFCp)(CO)$_2$(CCPh) (36). To a solution of FeBr(η^5-MeFCp)(CO)$_2$ (**32**) (102 mg, 103 μmol) in benzene (18.0 mL) was added 0.95 M solution of PhCCMgBr in THF (217 μL, 206 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel and was concentrated in vacuo (ca. 10 mL). Methanol was added to the mixture, iron-phenylethynyl complex Fe(η^5-MeFCp)(CO)$_2$(CCPh) (**36**) (55.8 mg, 54%) was obtained as orange microcrystals. Fe(η^5-MeFCp)(CO)$_2$(CCPh) (**36**): ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.25 (s, 15H), 7.34 (m, 5H, Ph), 7.67 (m, 10H, Ph);[95] ^{1}H NMR (400 MHz, THF-d_8/CS$_2$ = 1/1) δ 2.60 (s, 15H), 7.10 (m, 5H, Ph), 7.21 (m, 10H, Ph), 7.33 (m, 10H, Ph); ^{13}C NMR (100 MHz, THF-d_8/CS$_2$ = 1/1) δ 28.73 (5C, C(Me)), 50.74 (5C, C(α)), 82.98 (1C, CCPh), 107.24 (5C, C(Cp)), 126.18 (5C, Ph), 128.58 (10C), 128.84 (5C), 128.95 (1C, CCPh), 131.69 (10C, Ph), 144.34 (10C), 144.36 (10C), 147.54 (5C), 148.74 (10C), 149.04 (5C), 153.25 (10C), 213.37 (2C, C(CO)); IR (KBr, ν/cm^{-1}) 2035, 1991.

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[95] A proton signal of phenyl groups (10H) could not be assigned because of the overlapping with the residual proton signals of benzene-d_6.

X-ray Diffraction. Crystals of $C_{60}Me_5Br$ (**28c**) and $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**) suitable for the X-ray diffraction study were mounted on a MacScience DIP2030 Imaging Plate diffractometer for data collection using MoKα (graphite monochromated, λ = 0.71069 Å) radiation. Crystal data and data statistics are summarized in Table 9. The structure of the complex $C_{60}Me_5Br$ (**28c**) and $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**) were solved by the directed method (SHELXS-97)[43] and expanded using Fourier techniques (DIRDIF-94).[44] The positional parameter and thermal parameters of non-hydrogen atoms of $C_{60}Me_5Br$ (**28c**) and $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**) were refined using a full-matrix least square method. Hydrogen atoms were placed at calculated positions (C-H = 0.95 Å) and kept fixed. All non-hydrogen atoms of $C_{60}Me_5Br$ (**28c**) and $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**31**) were anisotropically refined. In the subsequent refinement, the function $\Sigma\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$.

We could put three points as to bromo atom in $C_{60}Me_5Br$ (**28c**) because of its disorder. Each ratios of the existences are 52, 24 and 12%. The bond length between bromo atom (52%) and carbon atom of $C_{60}Me_5$ moiety is 2.12 Å. However, these data have low confidence because of the disorder of bromo atom.

Table 9. Crystal Data and Structure Analysis Results for Complexes $C_{60}Me_5Br$ (28c) and $Re(\eta^5$-$C_{60}Me_5)(CO)_3$ (31).

	28c ·CS$_2$	31 ·CS$_2$
formula	$C_{66}H_{15}Br_1S_2$	$C_{69}H_{15}O_3Re_1S_2$
crystal system	monoclinic	monoclinic
space group	$P\,21/n$ (No. 14)	$C\,2/c$ (No. 15)
R, R_w ($I>2\sigma(I)$)	0.1921, 0.204	0.0863, 0.09
$R1$, $wR2$ (all data)	0.4899, 0.4983	0.2523, 0.2565
GOF on F^2	2.265	1.067
a, Å	13.6920(12)	32.9090(10)
b, Å	18.5770(12)	14.7480(7)
c, Å	14.5360(12)	19.4810(6)
α, deg	90	90
β, deg	90.663(4)	122.842(2)
γ, deg	90	90
V, Å^3	3697.1(5)	7943.8(5)
Z	4	8
T, K	153(2)	153(2)
crystal size, mm	0.42, 0.32, 0.1	0.70, 0.20, 0.10
D_{calcd}, g/cm^{-3}	1.71	1.91
$2\theta_{min}$, $2\theta_{max}$, deg	4.12, 51.66	4.46, 51.12
no. refl. measured (Unique)	6934	6790
no. refl. measured ($I>2\sigma(I)$)	5748	6251
no. parameters	649	677
D, eÅ^{-3}	2.008, -1.226	3.826, -3.711
m	1.28	3.229
extinction coef.	0.17(2)	0.0023 (2)

Electrochemical Measurements. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and reference electrode was a Ag/Ag$^+$ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc$^+$.

Chapter 5   Conclusion

For the development of functional materials based on fullerenes, I studied the synthesis, structure and properties of fullerene cyclopentadienyl-transition metal complexes.

In Chapter 2, I reported the synthesis of π-allyl nickel, palladium and platinum complexes. In particular, the results that π-allyl nickel complexes are stable to air are opposite to the fact that low valent nickel complexes are sensitive to air. These results are specific in $C_{60}Ph_5$-nickel complexes than $C_{60}Me_5$ ones. This result indicated that fullerene ligands $C_{60}R_5$ have a steric protection effect owing to the steric environment made by five substituents..

In Chapter 3, I reported the synthesis of bucky ferrocenes, which are hybrid molecules of ferrocene and fullerene. As the discovery of ferrocene brought wide variety of development of organometallic chemistry, it is expected that the discovery of bucky ferrrocenes will bring development of organometallic chemistry of fullerene. Bucky ferrocenes are very stable to heat, light, water and dioxigen like ferrocene $FeCp_2$. Cyclic voltammetry showed that bucky ferrocenes show a reversible oxidation and reduction behavior like ferrocene and fullerene, and there is electron communication between the ferrocene and the fullerene parts, which was also supported by the theoretical calculations. These results may bring the new properties, for example, redox active nano-devices. The ^{1}H NMR spectra of bucky ferrocenes showed that Cp ligands

of bucky ferrocenes have aromatic nature like that of ferrocene. Thus Friedel-Crafts acylation of bucky ferrocene gave corresponding acyl bucky ferrocenes. With appropriate functionalizations, bucky ferrocene could be used as building blocks of functional molecules.

In Chapter 4, I reported the syntheses of pentasubstituted fullerene halides, and rhenium, iron and cobalt fullerene complexes by the reaction of fullerene bromide with low valent transition metal complexes. As a result, many kinds of penta-substituted fullerene-transition metal complexes could be synthesized not only by transmetalation or reactions via C-H bond activation, but also by the reaction between fullerene halides and low valent transition metal complexes.

Based on the data reported in this thesis, it is expected that fullerene-transition metal complexes and their substituted derivatives could be utilized for catalysts and functional materials in the future.