Title: A Ni⁰ σ-Borane Complex Bearing a Rigid Bidentate Borane/Phosphine Ligand: Boryl Complex Formation by Oxidative Dehydrochloroborylation and Catalytic Activity for Ethylene Polymerization

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Abstract: While of interest, synthetically feasible access to boryl ligands and complexes remains limited, meaning such complexes remain underexploited in catalysis. For bidentate boryl ligands, oxidative addition of boranes to low valent Ir(I) or Pt(0) are the only examples yet reported. As part of our interest in developing improved group 10 ethylene polymerization catalysts, we present here an optimized synthesis of a novel, rigid borane/phosphine ligand and its Ni(0) σ-borane complex. From the latter, an unprecedented oxidative dehydrochloroborylation, to give a Ni(II) boryl complex, was achieved. Furthermore, this new B/P ligand allowed the nickel catalyzed polymerization of ethylene, which suggests that Ni(0) σ-hydroborane complexes act as masked Ni(II) boryl hydride reagents.
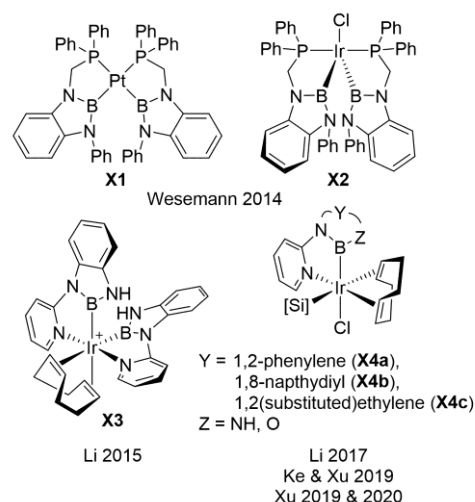
Introduction

Bidentate ligands employing two non-equivalent donor motifs offer stereoelectronic control within their corresponding organometallic complexes due to the differing stability of the isomers formed. This makes them attractive ligands for use in catalysis, as the catalyst can then be tuned to selectively favor preferred reaction pathways.[1] Rigid chelation of the donors allows the use of functional groups that would otherwise be too reactive,[2] such as the extremely σ-donating boryl anion.[3, 4] However due to associated synthetic and practical difficulties, only a few simple and flexible boryl/phosphine (**X1/X2**)[5] or boryl/pyridine type (**X3/X4a-c**)[3] ligands and their corresponding Pt and Ir complexes, have been reported (Figure 1a).

We recently reported a new class of rigid bidentate NHC/phenolate (IzQO) ligands, whose nickel and palladium complexes excelled in the coordination-insertion copolymerization of ethylene and propylene with polar, functionalized olefins.[6] Key to their success was the combination of a strongly σ-donating NHC with a weakly donating phenolate donor. We have since been curious as to whether it would be possible to exchange the NHC function of the IzQO ligand with a yet stronger σ-donating boryl donor, and if so, what the effect would be (Figure 1b). Still to test this hypothesis, we were faced with significant synthetic challenges:

The first synthetic challenge is that current synthetic routes towards boryl complexes remain limited to five approaches (Figure 2a). Transmetalation of a boryl anion[7] with metal salts is a straight forward pathway. Boryl lithium reagents are highly

reducing, however, and thus often act as a reductant rather than transmetalating reagent of the boryl functionality - except for some d⁰, d⁵ or d¹⁰ metal precursors.[8] , The reducing nature of lithium boryls can be avoided via an elegant, albeit indirect, route, in which a metal acylboryl species is formed, followed by decarbonylative boryl ligand migration.[9] Nonetheless in both of these approaches the generation of these boryl anions is practical only if the other parts of the ligand precursor tolerate the harsh conditions for the reduction of boron bromide with lithium metal.[10, 11] Displacement of a boron halide bond by a nucleophilic metal anion is an alternative pathway, but the availability of nucleophilic metals are rather limited.[12] Therefore it is of no surprise that the two most commonly employed routes towards boryl complexes are oxidative addition of a B-R fragment and σ-bond metathesis.[13]

a) Known bidentate boryl ligands and their complexes

b) Motivation: IzQO and the proposed boryl/phosphine ligand
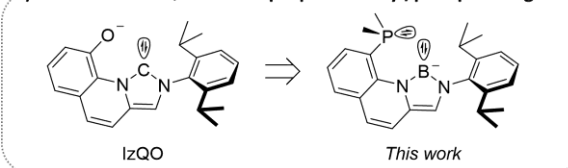
Figure 1. a) Previously reported complexes with bidentate boryl ligands. b) IzQO and the newly proposed boryl/phosphine ligand

In fact, the isolated bidentate boryl complexes shown in Figure 1a originate from the oxidative addition of weak B-H, B-B or B-Si bonds to low-valent Ir(I) or Pt(0).[14]
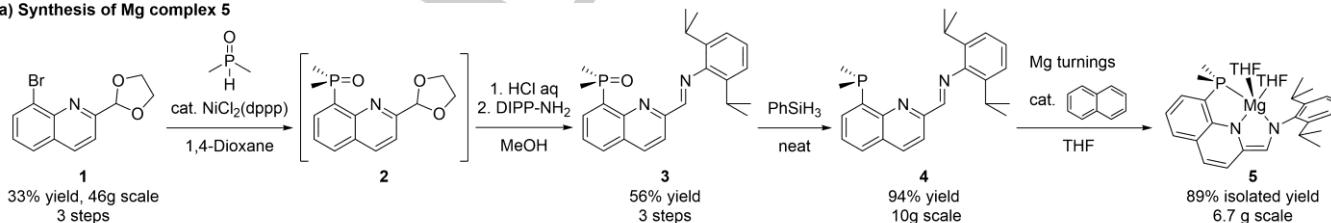
A second synthetic challenge specific to nickel is that the few reported examples of boryl complexes were all accessed via σ-bond metathesis of hydroboranes.[15, 16] Yet the direct oxidative addition of hydroboranes to Ni(0), to yield Ni(II) boryls, has never been reported.[17] The reductive elimination from a nickel boryl hydrido complex, however, was reported: Addition of 1,5-COD to NiH(PBP) led to formal reductive elimination and formation of a σ-borane complex, followed by extrusion of the hydroborane ligand and Ni(cod)₂ (Figure 2b).[15e, 19] Thus based on these literature precedents and our group's understanding of Ni/Pd catalyzed olefin (co)polymerization reactions, we designed our boryl IzQO analogue (Figure 1b right).

We here present an optimized synthesis of a novel type of bidentate borane/phosphine ligand, which enforces a rigid chelate through its conjugated [1,3,2]diazaborolo-[1,5-a]quinoline scaffold. We also show that the arrested oxidative addition of a σ-borane complex to Ni(0) can be overcome by a new type of oxidative dehydrochloroborylation, to form true Ni(II) boryl complexes (Figure 2c). Finally, we disclose the results of catalytic trials using our newly designed B/P ligand in the nickel catalyzed polymerization of ethylene, which suggest that Ni(0) σ-hydroborane complexes can act as masked Ni(II) boryl hydride species.
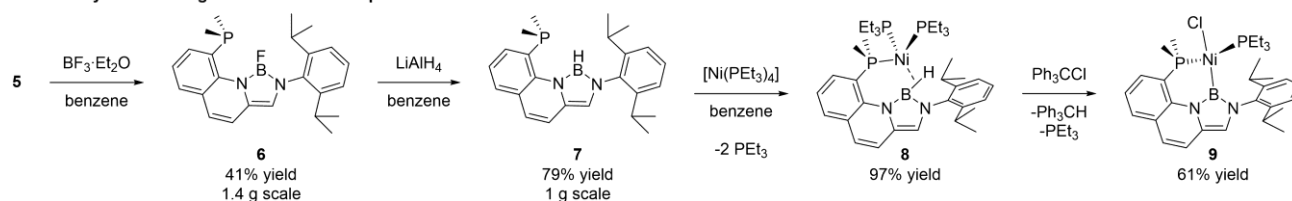
Results and Discussion

To introduce a boron functionality into our target ligand **7**, we established a robust protocol for a dianionic Mg synthon **5** (Scheme 1a). A large scale Doebner-Miller synthesis of 8-bromoquinoline,[18] followed by benzylic oxidation with selenium dioxide and acetal formation gave **1** in 33% yield over three steps. The Ni catalyzed cross-coupling of **1** with dimethylphosphine oxide (safely prepared via a route reported by Hays),[19] furnished the phosphine oxide intermediate **2**,[20, 21] and subsequent imine condensation gave **3**. Successive selective reductions, first of the phosphine oxide (by heating **3** in neat phenylsilane to give **4** in 94% yield)[22] followed by the iminoquinoline in **4** (using Mg turnings with a catalytic amount of naphthalene) gave the dianionic synthon **5** in 89% yield on a multigram scale.[23] [In the absence of naphthalene, the reduction of **4** with Mg metal stopped at an unidentified brown colored radical intermediate (Figure S103)].[24] ScXRD analysis of **5** shows a distorted square pyramidal magnesium center (Sum of angles around Mg (P/N1/N2/O1) = 354.16°),

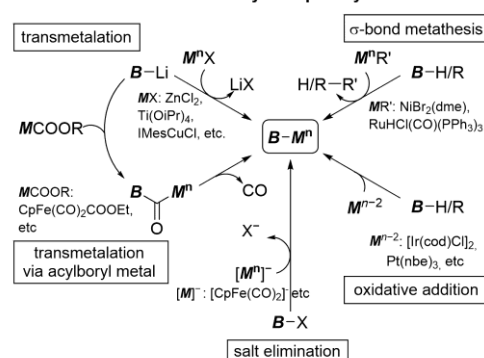**Figure 2.** a) Reported routes towards boryl complexes. b) Formal reductive elimination of hydroborane from PBP-Ni-H complex. c) This work: Oxidative dehydrochloroborylation of hydroborane at Ni(0).

coordinated to the P/N/N motif of the ligand with two THF molecules (one equatorial and one axial; see Figure 3).[25] De-aromatization of the ligand core took place upon reduction, as evidenced by the distinct alternating single/double bond length pattern (e.g. the ylidene displays a short C1−C2 bond of 1.368(3) Å). The aromatic signals of the quinolinylidene core in **5** are shifted upfield to between 5.37 and 6.44 ppm in the resulting ¹H-NMR spectrum (Figure S36). A Mg−P bond of 2.7404(8) Å is observed, most likely due to the rigid pincer manifold.

Addition of **5** to an excess of BF₃·Et₂O in benzene, followed by extraction and recrystallization from hexane, gave fluoroborane **6** in 41% yield.[26] **6** gives crystals containing the enantiopure compound as indicated by the space group P2₁2₁2₁ (Flack parameter: 0.07(6); see Figure S1), with a helical chirality in the quinolinylidene backbone induced by steric repulsion (Pauli repulsion) between the fluoride and phosphine moieties (F−P

a) Synthesis of Mg complex 5

1
33% yield, 46g scale
3 steps

2

3
56% yield
3 steps

4
94% yield
10 g scale

5
89% isolated yield
6.7 g scale

b) Synthesis of hydroborane ligand 7 and its Ni complexes 8 and 9

6
41% yield
1.4 g scale

7
79% yield
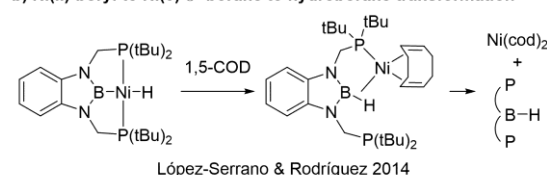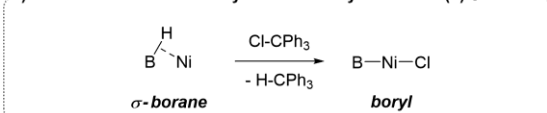1 g scale

8
97% yield

9
61% yield

Scheme 1. a) Large scale synthesis of Mg complex **5**. b) Preparation of borohydride ligand **7** starting from **5**, then stepwise transformation via Ni σ-borane complex **8** to nickel boryl complex **9**.
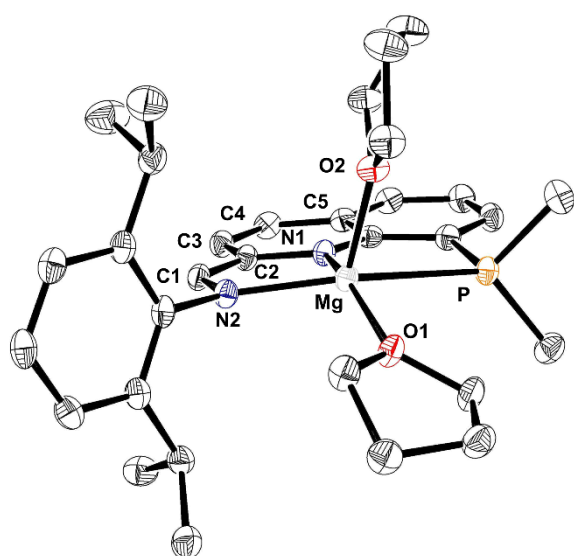
Figure 3. Molecular structure of **5** in the crystal (ORTEP drawn at 50% probability; all H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg−P 2.7404(8), Mg−N1 2.0515(16), Mg−N2 2.0537(16), Mg−O1 2.0562(14), Mg−O2 2.0480(14), C1−C2 1.368(3), C2−C3 1.414(3), C3−C4 1.353(3), C4−C5 1.452(3), P−Mg−N1 74.60(5), P−Mg−O1 92.67(4), P−Mg−O2 87.48(4), N1−Mg−N2 83.23(6), N2−Mg−O1 103.66(6).

distance: 2.881 Å; ^{19}F/^{31}P NMR: $J_{P−F}$ = 252 Hz).[27]

Fluoride-hydride exchange of **6** by $LiAlH_4$ in benzene gave target hydroborane ligand **7** in 79% yield on a 1 g scale.[28] Fully anisotropic Hirshfeld atom refinement (HAR)[29] of a crystallographic dataset reveals that **7** forms an enantiopure helical structure in the crystal as indicated by the space group $P2_12_12_1$ similar to **6** (See Figure 4).[30] The chirality in **7** is likewise induced by Pauli repulsion of the borohydride hydrogen and phosphorus moieties (B−H distance: 1.217(11) Å; H−B−C6−P 45.6(6))°, compared to 51.38(14)° for the analogous dihedral angle in **6**). By IR the hydroborane shows a B−H stretch at 2619 cm^{-1} (Figure S115).

With the hydroborane ligand **7** in hand, we set out to prepare a nickel boryl complex (Scheme 1b, right). Upon mixing of **7** with the zero-valent Ni complex $Ni(PEt_3)_4$, we did not observe the expected oxidative addition product, but instead the displacement of two PEt_3 ligands by **7** to give the σ-borane complex **8** in 97% yield. HAR refinement of an X-ray crystallographic dataset with an isotropic model for the hydrogen atoms shows two symmetry independent molecules of **8** (Figure 5, left) each with a pseudo-tetrahedral arrangement of the ligands around the nickel centers, with τ_4 (0.93 (0.91))[31] and τ_4' (0.93 (0.90))[32] parameters close to 1.[33] The borohydrides are sterically protected by the phosphines and the isopropyl groups of the DIPP moiety, revealing a tilted alignment above the B−Ni bond axis (angles in deg: B−H−Ni 95.6(11) (94.4(11)), sum of angles around B (H/N1/N2): 348.22 (349.95)) and a broad singlet in the ^{1}H-NMR at -3.62 ppm (Figure S62). The B−H bond lengths of 1.288(17) and 1.318(18) Å are elongated by ca. 0.09 Å as compared to **7** (1.217(11) Å), indicative of a weakened bond. NBO analysis[34] (HAR // TPSS-D4/def2-TZVP) using data from the obtained crystal structure reveals a donor-acceptor interaction across the whole σ-borane unit and the nickel center, in which the σ-borane donates into a lone valence on the nickel (18.02 (19.82) kcal mol^{-1}; see Figure 6a). This is approximately half the strength of the Ni-P interactions (32.42 to 34.92 kcal mol^{-1}). Synergistic backdonation, albeit weaker, from the nickel into the antibonding σ-borane NBO of 4.32 (4.71) kcal mol^{-1} is also observed (Figure 6b). Taking the quantum

crystallographic and NBO analyses together, the data are consistent with the coordination of the σ-borane unit to the Ni center as a σ-donor and π-acceptor, in a similar fashion to the Dewar-Chatt-Duncanson model used to describe olefin coordination to metals.[35]

The boryl species **9** was obtained from the σ-borane **8** through the addition of one equivalent of trityl chloride at 50 °C, which prompted the formation of triphenylmethane, which is indicative of hydride abstraction. By ^{31}P-NMR a new species appeared with a distinct 1:1 set of doublets ($^2J_{P-P}$ = 310 Hz) resembling two inequivalent *cis*-standing phosphines in a square-planar complex (Figure S69). After purification, crystals of **9** were obtained in 61% yield.[36] ScXRD analysis reveals the desired nickel boryl complex to have a distorted seesaw environment at Ni (Figure 5, right; sum of angles around Ni of 367.15°; τ_4 (0.31)[31] and τ_4' (0.28)[32]).[37] The long Ni−Cl bond of 2.2419(4) Å, *trans* to the long Ni−B bond of 1.9589(15) Å, confirms the extremely strong *trans*-influence of the boryl donor (as was previously reported for iridium[15c] and platinum boryl complexes).[4b] Both bonds are elongated in comparison to a reported sp^2-boryl nickel chloride bearing a PBP pincer ligand (t-Bu$_2$P for each P; Ni−B 1.907(2) and Ni−Cl 2.2399(4) Å).[15d] The visible distortion of the ligand plane in **9** is most likely caused by steric repulsion between the triethylphosphine and the diisopropylphenyl (DIPP) group. This results in a twist in the ligand backbone (Ni−B−C6−P1 33.91(8)°) and a bent orientation of the DIPP moiety relative to the quinoline ligand backbone (Ni−N2−C7−C8 56.18(10)°). One DIPP isopropyl group points towards the Ni center and shows a short Ni···H−C contact of 2.4077(3) Å.[38] By ^{1}H-NMR the signals corresponding to the DIPP and dimethylphosphine groups appear heavily broadened at room temperature, but separate at -60 °C (Figure S70). One benzylic DIPP C−H resonance is shifted downfield as a broad singlet at 5.54 ppm due to close contact with the nickel center. Compared to the σ-borane complex **8** (^{11}B-NMR: 28.7 ppm), only a small upfield shift of the boron functionality is seen in **9** (^{11}B-NMR: 26.9 ppm; Figure S67).

The transformation of the nickel (II) σ-borane **8** to the nickel (II) boryl chloride complex **9** brought into question whether this on-metal transformation could act as a new class of convenient transformation towards boryl complexes. From the standpoint of ligand design, the use of borohydrides over haloboranes (Cl, Br,

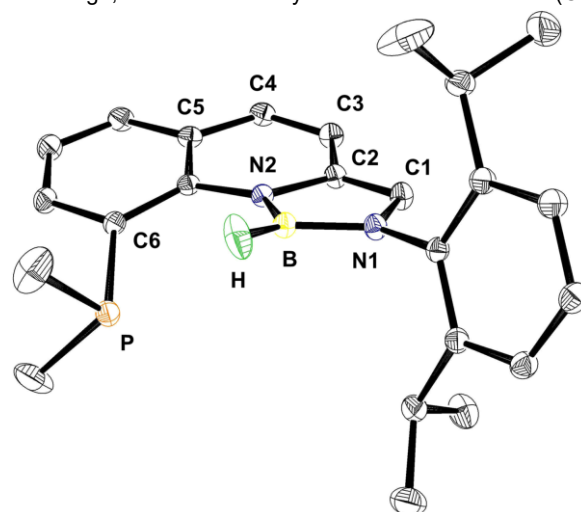**Figure 4.** Molecular structure of **7** (right; HAR-refined structure[29, 39]) in the crystal (ORTEP drawn at 50% probability; all but the hydroborane H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **7**: B−H 1.217(11), B−N1 1.4228(12), B−N2 1.4498(11), C1−C2 1.3618(11), C2−C3 1.4292(11), C3−C4 1.3497(12), C4−C5 1.4517(12), N1−B−N2 105.27(7), H−B−N1 124.6(6), H−B−N2 129.4(6), H−B−C6−P 45.6(6).
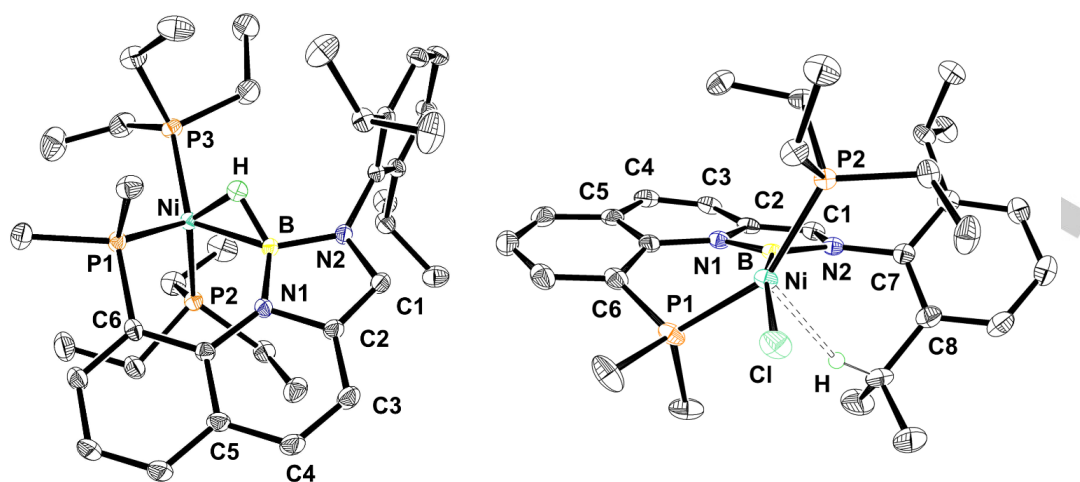
Figure 5. Molecular structure of **8** (left) and **9** (right) in the crystal (ORTEP drawn at 50% probability; For **8**: The structure was HAR refined (BLYP/def2-SVP; isotropic refinement of all H atoms), the position of the σ-borane H was derived from its residual electron density, all other H atoms are omitted; only one of the two symmetry inequivalent molecules of **8** in the unit cell is shown (values in parentheses refer to the second molecule). For **9**: one benzylic proton of the DIPP group with a close contact to Ni is shown, a co-crystallized diethyl ether molecule and all other H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for 8: B−Ni 2.0896(18) (2.0953(18)), B−H 1.288(17) (1.318(18)), Ni−H 1.524(17) (1.531(18)), Ni−P1 2.1783(5) (2.1710(5)), Ni−P2 2.1622(6) (2.1680(6)), Ni−P3 2.1866(5) (2.1923(5)), B−N1 1.485(2) (1.491(2)), B−N2 1.451(2) (1.462(2)), C1−C2 1.361(2) (1.359(3)), C2−C3 1.430(3) (1.427(3)), C3−C4 1.350(3) (1.345(3)), C4−C5 1.447(2) (1.450(2)), B−H−Ni 95.6(11) (94.4(11)), B−Ni−P1 88.32(5) (87.76(5)), B−Ni−P2 99.88(6) (99.86(6)), B−Ni−P3 128.04(6) (132.24(6)), Ni−B−N1 119.61(12) (118.09(12)), Ni−B−N2 135.37(12) (137.43(12)), N1−B−N2 103.12(13) (102.35(13)), Ni−B−C6−P1 35.05(9) (35.09(9)). For 9: Ni−B 1.9589(15), Ni−Cl 2.2419(4), Ni−P1 2.1406(4), Ni−P2 2.1902(4), Ni−H 2.4077(3), B−N1 1.4598(19), B−N2 1.4634(19), C1−C2 1.349(2), C2−C3 1.433(2), C3−C4 1.346(2), C4−C5 1.454(2), B−Ni−P1 83.49(5), B−Ni−P2 92.34(4), Cl−Ni−P1 95.076(15), Cl−Ni−P2 96.241(15), N1−B−N2 102.00(11), Ni−B−C6−P1 33.91(8), Ni−N2−C7−C8 56.18(10).

I) is attractive, as the latter are synthetically less accessible and more difficult to handle due to functional group incompatibilities, such as halide displacement by other donors or nucleophiles, as well as their disposition towards hydrolysis. As a proof-of-concept, we applied our strategy to the P(BH)P pincer ligand **10**, for which direct B-H oxidative addition to Ni(0) has never been observed,[15d] and the formation of the corresponding Ni(0) σ-borane complex as supported by NMR analysis, has been reported previously.[40] As expected, the reaction of the P(BH)P ligand **10** with Ni(cod)₂ and trityl chloride in 1:1:1 stoichiometry yielded the desired (PBP)Ni(II)Cl boryl complex **11**, as confirmed by ¹H- and ³¹P-NMR, which was subsequently isolated in the form of orange prisms in 54% yield (Scheme 2). Crystallographic analysis of **11** reveals the expected square-planar PBP nickel chloride pincer complex. The bond lengths in **11** (B-Ni 1.8990(16), Ni-Cl 2.2208(4)) suggest that the PBP ligand exerts a smaller *trans*-influence than that observed in both **9** and the previously reported bis(di-*tert*-butylphosphine) derivative of **11**.[15d] We believe that this new methodology, which allows for a formal oxidative dehydrochloroborylation of a hydroborane at nickel(0) to give boryl nickel(II) chloride complexes under mild conditions, can advance the field of boryl-donor ligands and their complexes, and increase the applications of hydroboranes in catalysis. In contrast to complementary σ-bond metathesis reactions with Ni(II) dihalide salts, this new method bypasses the generation of a stoichiometric amount of protons which can be an issue with sensitive ligand platforms. In comparison to established salt elimination reactions with haloboranes or transmetalation reactions with boryllithium, the use of reactive haloboranes as precursors can be avoided.
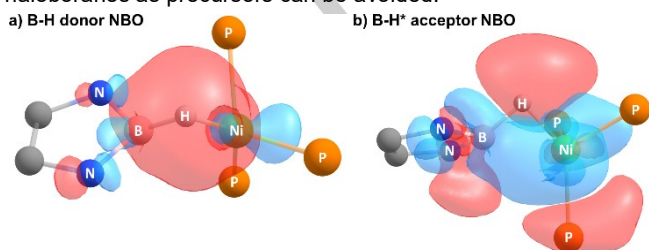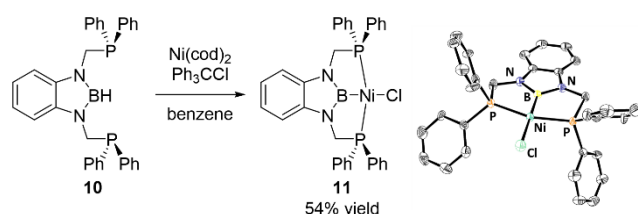
Finally, we turned our attention to investigating the catalytic performance of our complexes in the nickel-catalyzed polymerization of ethylene. When the σ-borane complex **8** was used as a pre-catalyst, only a trace amount of polymeric material was produced (Table 1, entry 1). It is common to other nickel polymerization catalysts that strong coordination of supporting phosphine ligands severely inhibits catalytic activity. This problem is often overcome by the addition of Ni(cod)₂ as a phosphine scavenging reagent.[6b, 41] Furthermore, based on the previous report by López-Serrano & Rodríguez that a PBP nickel hydride pincer complex undergoes reductive elimination of a hydroborane upon addition of the ligand 1,5-COD (Figure 2b), we hypothesized that a "naked", supporting ligand-free nickel species would be required to initiate the polymerization process via the hydrometallation reaction of **8**. Thus, addition of two equivalents of Ni(cod)₂ to **8** as a scavenger for the supporting triethylphosphines increased the polymerization activity six-fold to 0.72 kg mol⁻¹ h⁻¹. SEC analysis of the white polymeric material obtained showed a bimodal peak (M_n of 1.7 kg mol⁻¹ (PDI 2.01) for the major and 20.6 kg mol⁻¹ (PDI 1.24) for the minor component (Table 1, entry 2)). In order to generate a triethylphosphine-free catalyst system *in situ*, we tested 1:1 mixtures of ligand **7** with Wilke's reactive Ni(0) precursors Ni(cod)₂ and Ni(stb)₃.[42] The combination of borohydride ligand **7** and Ni(cod)₂ also gave polyethylene with a bimodal molecular weight distribution and similar PDIs to the catalyst system of **8** and Ni(cod)₂, although with a lower activity of 0.41 kg mol⁻¹ h⁻¹. Yet encouragingly, the major component now consisted of a higher molecular weight polymer with an M_n of 15.2 kg mol⁻¹

a) B-H donor NBO

b) B-H* acceptor NBO

Figure 6. NBO analyses of the σ-borane/nickel interaction in complex **8**. a) B-H donor NBO. b) B-H* acceptor NBO.

Scheme 2. One-pot synthesis of nickel boryl complex **11** from hydroborane ligand **10**. The crystal structure of **11** is shown on the right.

Table 1. Ethylene polymerization with nickel catalysts.

Entry	Catalyst	Yield[b] [mg]	Activity[c] [kg mol⁻¹ h⁻¹]	M_n[d] (major / minor) [kg mol⁻¹]	M_w[d] (major / minor) [kg mol⁻¹]	PDI[d]
1	**8**	3.4	0.11	nd	nd	nd
2[e]	**8** / Ni(cod)₂	21.7	0.72	1.7 / 20.6	3.6 / 25.6	2.01 / 1.24
3[e]	**7** / Ni(cod)₂	12.2	0.41	15.2 / 0.6	31.4 / 0.9	2.07 / 1.40
4	**7** / Ni(stb)₃	266.9	8.9	5.7	12.7	2.24

[a] A mixture of the respective catalyst mixtures (2.5 µmol each, except for the Ni(cod)₂ additive in entry 2 for which 5.0 mmol (2 equivalents to catalyst) were used) and ethylene (3.0 MPa) in toluene (15 mL) was stirred for 12 h at 80 °C in a stainless-steel autoclave (50 mL) containing a glass-tube. Control experiments under the same conditions employing either ligands **7** or **12**, a mixture of **12**/Ni(stb)₃, or nickel precursors Ni(cod)₂, Ni(stb)₃ or Ni(PEt₃)₄ alone did not lead to noticeable polymer formation. [b] Isolated yields after quenching the reactions with methanol, washing the obtained polymer precipitates with methanol, and drying in vacuo at 100°C for 4 h. [c] Activities are defined as mass of the polymer per mol of catalyst per hour. [d] Molecular weights determined by size-exclusion chromatography with narrow polystyrene standards and corrected by universal calibration. [e] Bimodal GPC peaks were observed for entries 2 and 3, reported as major / minor component. [f] nd: not determined.

(Table 1, entry 3). Upon switching the Ni(0) precursor to Ni(stb)₃, an increase in the activity of the system to 8.9 kg mol⁻¹ h⁻¹ (ca. 80 times that of the σ-borane complex **8** alone) was observed, while GPC analysis of the polymer showed a unimodal peak with an M_n of 5.7 kg mol⁻¹ (Table 1, Entry 4). Quantitative analysis of the polymer by inverse gated decoupled ¹³C-NMR indicated the formation of strictly linear polyethylene with an olefinic chain-end (Figure 7). The latter is indicative of metal catalyzed polymerization with chain-termination via β-hydrogen elimination, but not a radical mechanism. Control experiments confirmed that none of the ligand **7**, Ni(cod)₂, Ni(stb)₃ or Ni(PEt₃)₄ alone showed

polymerization activity under the same conditions. Ethylene polymerization was also not initiated by a B-alkyl bond in butylborane **12** (Scheme S1d),[43] a mixture of **12**/Ni(stb)₃, or a mixture of **9** and 1000 eq. of MMAO (See section 2 in the SI). We then conducted further experiments to better understand the differing activity of our catalyst systems. An NMR experiment of ligand **7** with Ni(stb)₃ revealed the formation of a Ni(0) σ-borane species, which remained the dominant species in solution even after fourteen hours at 75 °C (See Supporting Information 7.2). The corresponding reaction of ligand **7** with Ni(cod)₂ also indicated the initial formation of a Ni(0) σ-borane complex (**SI-6**)
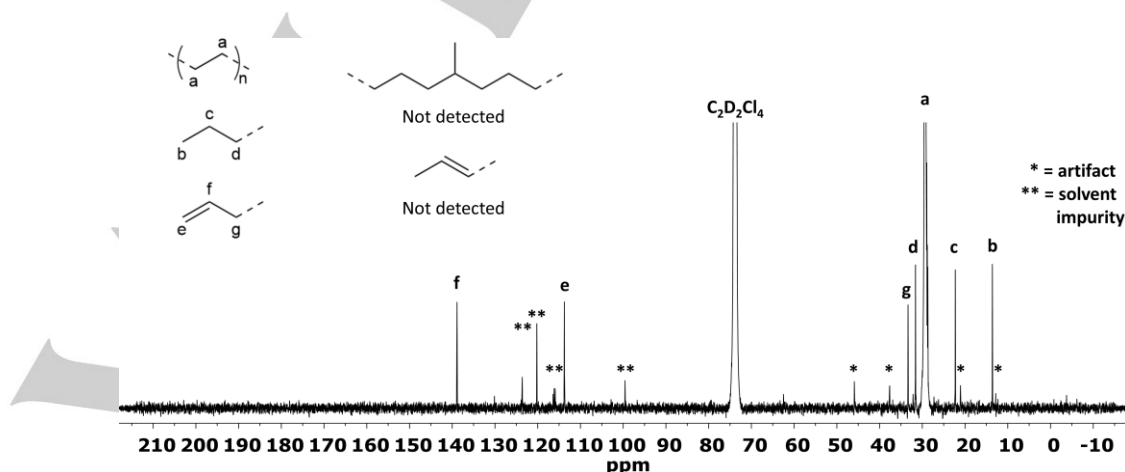
Figure 7. Inverse gated decoupled ¹³C-NMR spectrum of the polyethylene obtained from **7**/Ni(stb)₃ (Table 1, entry 4).

by displacement of one 1,5-COD ligand (See Supporting Information 7.3). Unlike in the reaction with Ni(stb)$_3$, this species starts to interconvert into a boryl η^3-allyl Ni(II) complex (SI-7) even at room temperature, presumably via hydrometallation of the 1,5-COD ligand, followed by ring-walking via consecutive β-hydrogen elimination and reinsertion events. This process runs to near completion within 15 min at 75 °C, while at the same time decomposition of the sample was observed as seen by the formation of nickel black and 1,3-COD, presumably via a β-hydrogen elimination from the observed η^3-allyl species SI-7. Taken together, these data suggest that the Ni(0) σ-borane complexes investigated here can act as masked Ni(II) boryl hydride reagents to initiate polymerization processes via hydrometallation of an olefin. The pronounced differences in the activities of the reactions using Ni(cod)$_2$ and Ni(stb)$_3$ appear to stem from higher activity of the σ-borane complex formed from Ni(stb)$_3$ as compared to the stable Ni(η^3-allyl) complex from Ni(cod)$_2$.[44]

Conclusion

To conclude, we isolated the Mg diamide complex 5 following the naphthalene-catalyzed reduction of a rigid quinoline-imine precursor 4 using Mg metal. The synthetic versatility of 5 was exemplified by the subsequent reaction with BF$_3$·Et$_2$O, and a follow-up salt metathesis exchange of the B-F functionality with LiAlH$_4$ to give a novel hydroborane/phosphine ligand 7. Complexation with a nickel(0) precursor led to σ-borane coordination (with concomitant phosphorus coordination) of the ligand in complex 8, but not of the oxidative addition product. We demonstrated that nickel(II) boryl chloride complexes (9, and the PBP pincer complex 11) can be conveniently accessed via hydride abstraction from σ-hydroborane complexes. Although no oxidative addition product from 8 was detected, the observation that catalytic systems based on this new B-H/P ligand and nickel allow the polymerization of ethylene to give strictly linear polyethylene strongly suggests that the Ni(0) σ-borane complexes behave as masked Ni(II) boryl hydrides, which undergo hydrometallation reactions of olefins.

We expect that this work will promote the development of more sophisticated ligands that make use of the boryl functionality, as well as increasing the ubiquity of boryl containing pre-catalysts. Specifically, we hope that this work can stimulate the search for novel ligand types in nickel and palladium catalyzed olefin polymerization reactions, which have so far been mostly limited to similar scaffolds based on C/N/O/P donors.

Acknowledgements

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[21] We found that impurities can be conveniently removed from **2** during the following acetal deprotection by a simple acid-base extraction.

[22] An excess of reagent was neccessary to fully dissolve **3**. The reduction if phosphine oxides by phenylsilane in apolar media as the reagent itself proceeds by a concerted mechanism while in more polar media an ionic mechanism takes place, see: O. M. Demchuk, R. Jasiński, K. M. Pietrusiewicz, *Heteroat. Chem.* **2015**, *26*, 441-448. The reduction of imines by phenylsilane is only reported in the presence of an catalyst via ionic mechanisms. Thus under the given conditions the requirements are not given for imine reduction. Nevertheless we found out in preliminary screening experiments with phosphine oxides and imines in neat phenylsilane that depending on the nature of the phosphine oxide reduction of the imine functionalities can take place. Therefore a generality of this method is not given.

[23] Attempted reduction of **4** with Li metal was not clean and the lithium reduced samples had a distinct phosphine smell, indicative of an reductive cleavage of the Ar-PMe$_2$ bond.

[24] We discovered the catalytic influence of naphthalene during initial screening experiments with Rieke Magnesium prepared from MgCl$_2$, Li metal and naphthalene (Rieke, R. D.; Li, P. T.-J.; Burns, T. P.; Uhm, S. T., Preparation of highly reactive metal powders. New procedure for the preparation of highly reactive zinc and magnesium metal powders. *J. Org. Chem.* **1981**, *46*, 4323-4324). Berben and coworkers reported that the reduction of a related iminopyridine with magnesium metal stopped after a one electron reduction to form a dimeric diradical magnesium complex, see: O. T. Summerscales, T. W. Myers, L. A. Berben, *Organometallics* **2012**, *31*, 3463-3465. Attempts by us for the two electron reduction of the same substrate by adding naphthalene under otherwise identical conditons as for Berben and coworkers did nevertheless not lead to a second one electron reduction event. We are aware of one previous publication that used naphthalene to modulate the reduction of dichlorphosphines with magnesium metal to form fleeting phosphinidene species, see: R. C. Smith, S. Shah, J. D. Protasiewicz, *J. Organomet. Chem.* **2002**, *646*, 255-261. The formation of naphthyl magnesium itself has only been reported in liquid ammonia, nevertheless the authors themself note that this is likely due to the exceptional dissolution ability of the reaction medium: C. Ivanoff, P. Markov, *Naturwissenschaften* **1963**, *50*, 688-689.

[25] Deposition Number 2025415 (for **4**), 2025445 (for **5**), 2025419 (for **6**), 2057506 (for **7**, ShelXL), 2025403 (for **7**, HAR), 2027507 (For **8**, ShelXL), 2025704 (for **8**, HAR), 2034571 (for **9**), 2086787 (for **11**), 2025417 (for **SI-5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

[26] An excess of BF$_3$·Et$_2$O was required due to formation of magnesium tetrafluoroborate salts, whose reaction with **5** only proceeded sluggishly. BF$_3$ is known to only form weakly bound adducts with phosphines: J. Burt, J. W. Emsley, W. Levason, G. Reid, I. S. Tinkler, *Inorg. Chem.* **2016**, *55*, 8852-8864. The reagent was therefore essential to prevent strong borane adduct formation with the phosphine moiety.

[27] The chirality is not stable in solution for **6** and **7** as indicated by single set of signals for the diisopropylphenyl groups in the ^{1}H NMR. A reviewer mentioned that the aforementioned repulsion could also stem from repulsion of the H/F moiety with the phosphine lone pair. The

authors think that steric repulsion as a consequence of Pauli repulsion includes this phenomenon.

[28] The formation of highly coloured byproducts was observed when the reaction was conducted in coordinating solvents such as Et_2O or THF, or if the lithium aluminium hydride contained traces of Et_2O from its extractive purification. This transformation was previously exploited for the preparation of structurally related hydroborane compound: L. Weber, M. Schnieder, R. Boese, D. Bläser, *J. Chem. Soc., Dalton Trans.* **2001**, 378-382.

[29] S. C. Capelli, H.-B. Burgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, *IUCrJ* **2014**, *1*, 361-379.

[30] The reader here is advised against a direct comparison of bond lengths of light atoms between ShelXL and HAR refined structures, as the former typically incorrectly captures the positions of light atoms such as hydrogen due to polarization of the limited electron density of the element into the bonds. HAR refines atomic positions and anisotropy on the basis of density- or wave functional theory-based electron densities, which correctly describe e.g. these polarization effects. Therefore, HAR refinement correctly captures e.g. the position of hydrogen atoms on the basis of X-ray crystallography with an accuracy rivalling neutron diffraction experiments, thus allowing quantitative discussions on its basis. For a quantitative discussion see: Woińska, M.; Grabowsky, S.; Dominiak, P. M.; Woźniak, K.; Jayatilaka, D., Hydrogen atoms can be located accurately and precisely by x-ray crystallography. *Sci. Adv.* **2016**, *2*, e1600192.

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[33] For the calculation of the τ_4 and $\tau_4{'}$ parameters a dummy atom was placed in the center of the BH-donor unit. The respective xyz coordinates are given in the SI.

[34] NBO 7.0 (**2018**): E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P.

Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI

[35] This has been previously described for σ-boranes in the literature, see: Z. Lin, in *Contemporary Metal Boron Chemistry I: Borylenes, Boryls, Borane σ-Complexes, and Borohydrides* (Eds.: T. B. Marder, Z. Lin), Springer Berlin Heidelberg, Berlin, Heidelberg, **2008**, pp. 123-148.

[36] It should be noted that heating of ligand itself with trityl chloride only led to formation of untraceable decomposition products.

[37] τ_4 and $\tau_4{'}$ values for a perfect seesaw structure are ca. 0.43 and 0.24 respectively, while a perfect square-planar geometry would show 0 for each.

[38] NBO analysis (ShelXL structure, hydrogen positions reoptimized by BP86-D4/def2-TZVP // BP86-D4/def2-TZVP) reveals the donation from two Ni d-orbital derived NBOs to the close C-H* acceptor NBO (stabilized by 0.71 and 0.61 kcal mol^{-1}).

[39] M. Woińska, S. Grabowsky, P. M. Dominiak, K. Woźniak, D. Jayatilaka, *Sci. Adv.* **2016**, *2*, e1600192.

[40] The authors strongly suspect that a dimerization of two sigma-borane complexes leads to formation of the dimeric Ni(I) boryl species under concomitant dihydrogen elimination as observed by Lin and Peters.

[41] Y. Konishi, W.-j. Tao, H. Yasuda, S. Ito, Y. Oishi, H. Ohtaki, A. Tanna, T. Tayano, K. Nozaki, *ACS Macro Lett.* **2018**, *7*, 213-217.

[42] G. Wilke, E. W. Müller, M. Kröner, P. Heimbach, H. Breil, Studiengesellschaft Kohle m.b.H., **1960**, German patent DE1191375B.

[43] As by NMR consumption of half an equivalent of butylborane was observed with concomitant formation of some grey insolubles, but not formation of butane, the reaction likely proceeds via a nucleophilic displacement of the hydroborane by the alkyl zinc species but not via a σ-metathesis type reaction.

[44] a) S. Noda, T. Kochi, K. Nozaki, *Organometallics* **2009**, *28*, 656-658; b) J. Jung, H. Yasuda, K. Nozaki, *Macromolecules* **2020**, *53*, 2547-2556.

Entry for the Table of Contents
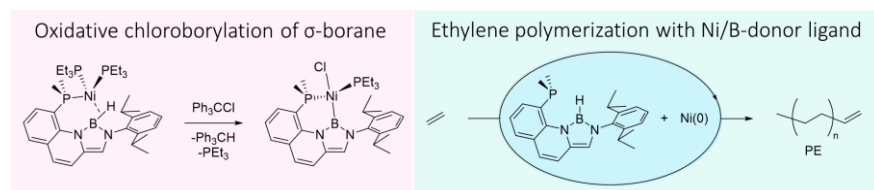
The synthesis of a rigid bidentate borane/phosphine ligand was explored within the background of statistical olefin copolymerization with group 10 metals. During this work, a mild oxidative dehydrochloroborylation reaction was found to convert different Ni(0) σ-borane complexes into Ni(II) boryl chloride complexes. This new ligand also allows the nickel catalyzed polymerization of ethylene, a first for a B-donor in group 10 olefin polymerization.

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