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Ni→B Interactions in Nickel Phosphino-Alkynyl-Borane Complexes

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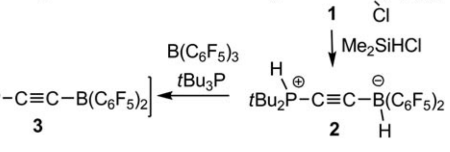
The classical acid–base theory described by Lewis,[1] accounts for much of the chemistry of the main group elements. In addition the interactions of Lewis bases with formally Lewis acidic transition metals is a concept critical to coordination chemistry. However it is the inverse situation, that is the ability of transition metals to act as Lewis bases and form Lewis acid–base adducts with Lewis acidic species that has garnered much interest in the last 10 years.[2] Despite the recent flurry of activity in this area, it was indeed some 30 years ago that Hughes and co-workers[3] first described the species $[\mathrm{CpFe(CO)_2AlPh_3}][\mathrm{NEt_4}]$ containing an Fe→Al dative bond. More recent work on such interactions began in 1999 with the report by Hill et al.[4] of a Ru complex of tris-thioimidazolylborane. The chelating nature of the ligand in this ruthenaboratrane provided the B in close proximity to Ru, affording a Ru→B dative bond. Since then boryl-bridged heterobimetallic complexes[5] have also been shown to incorporate M→B dative interactions. In addition, Piers and co-workers have proposed possible contributions from M→B dative interactions in their metal–borataalkene complexes.[6] The groups of Hill,[4,7] Bourissou,[8] Parkin,[9] and Emslie[10] among others[11] have employed ambiphilic ligands to probe the nature and impact of these unconventional donor–acceptor interactions. Using such ligands, an intramolecular M→B dative interaction can occur thermodynamically facilitated by the chelate effect and without ligand strain or distortion.[12]

In our own work, we have been probing the chemistry of systems incorporating highly electrophilic B centers with basic phosphine fragments in which steric demands preclude P→B dative interactions.[13] Such systems, termed "frustrated Lewis pairs",[14] afford unique reactivity on their own right.[13b,c,15] In addition, they also provide a unique opportunity to examine unusual M→B interactions. To that end, we targeted the synthesis of a strongly polarized phosphino-alkynyl-borane. It is well documented that metal complexation of alkynes results in the "bend-back" of the substituents, consistent with a π-backbonding model involving donation of metal electron density to the π* orbital of the alkyne and reduction of the C≡C bond.[16] Herein, we report that Ni complexation of a phosphino-alkynyl-borane results in the unusual situation in which the boron substituent "bends forward" toward the metal, accommodating a dative Ni→B interaction.

The phosphino-alkyne $t\mathrm{Bu_2PC{\equiv}CH}$[17] was prepared and allowed to react with $\mathrm{ClB(C_6F_5)_2}$[18] at −35 °C to give an off-white product **1** in 72 % isolated yield. Compound **1** exhibits a ^{1}H NMR doublet resonance at $\delta = 5.80$ ppm with a P−H coupling of 469 Hz, indicative of the presence of a PH fragment (^{31}P: $\delta = 25.5$ ppm). It also shows a $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ signal at $\delta = -12.8$ ppm and three ^{19}F resonances at $\delta = -133.1$, -160.5, and 166.1 ppm, consistent with the presence of a four-coordinate borate unit. These data confirm the formulation of **1** as the alkynyl-linked zwitterionic phosphonium borate $t\mathrm{Bu_2PHC{\equiv}CBCl(C_6F_5)_2}$ (Scheme 1). Treatment of **1** with excess $\mathrm{Me_2SiHCl}$ results in the exchange of the B-bound chloride for hydride, affording $t\mathrm{Bu_2PHC{\equiv}CBH(C_6F_5)_2}$ (**2**) as colorless crystals in 79 % yield (Scheme 1). A 1:1:1:1 quartet at $\delta = 3.25$ ppm in the ^{1}H NMR spectrum ($^{1}J_{\mathrm{BH}} = 91$ Hz) confirms the presence of a BH moiety. The acetylenic carbon atom *alpha* to P is observed in the ^{13}C NMR spectrum at $\delta = 64.4$ ppm with a $^{1}J_{\mathrm{CP}}$ of 158 Hz. The resonance for the B-bound acetylenic carbon was not observed, presumably due to quadrupolar broadening. The proposed con-



Scheme 1. Synthesis of **1**–**3**.

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nectivity in **2** was confirmed by X-ray crystallography (Figure 1).[19] Interestingly, viewing the molecule along the BCCP vector in the solid state, it is noted that the substituents on B and P are eclipsed, with the BH and PH occupying the same plane.

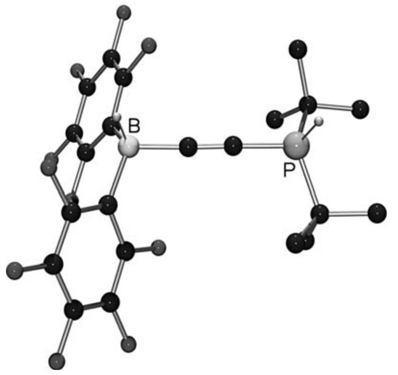


Figure 1. POV-ray drawing of **2**. All hydrogen atoms except PH and BH are omitted for clarity. Selected bond lengths [Å] and angles [°] in the PCCB fragment: P–C 1.716(3), B–C 1.598(4), C–C 1.208(4); C-C-P 175.7(3), C-C-B 177.9(3).

The synthetic strategy for the formation of **1** is related to the recently demonstrated reactivity of PhC≡CH with the frustrated Lewis pair, $B(C_6F_5)_3$ and P*t*Bu$_3$, which yields the salt [HP*t*Bu$_3$][PhC≡CB$(C_6F_5)_3$].[15b] Bestmann and co-workers[20] have previously reported a related species Ph$_2$MePC≡CBR$_3$ (R = Ph, CH$_2$Ph) prepared in a more conventional fashion via generation of Ph$_2$PC≡CLi, reaction with borane and methylation with MeI.

Treatment of **2** with *t*Bu$_3$P and $B(C_6F_5)_3$ generates the neutral phosphino-alkynyl-borane *t*Bu$_2$PC≡CB$(C_6F_5)_2$ (**3**) and the known salt [*t*Bu$_3$PH][HB$(C_6F_5)_3$].[13b] This reaction results from the greater basicity and acidity of *t*Bu$_3$P and B$(C_6F_5)_3$, respectively. The formation of **3** was confirmed by NMR analysis of the reaction mixture. Although no assignable ^{11}B signal was observed, broad ^{19}F resonances at $\delta = 129.0, -147.9$, and -162.3 ppm suggest a neutral three-coordinate borane unit, while a singlet ^{31}P signal at $\delta = 17.6$ ppm indicates a neutral phosphine moiety. Hence, **3** is believed to exist in the monomeric form in solution despite the highly acidic B and basic P centers. A related compound, Ph$_2$PC≡CBMes$_2$ (Mes = 2,4,6-trimethylphenyl), was reported by Marder and co-workers.[21]

Although attempts to isolate the neutral species **3** from solution resulted in unidentified decomposition products, reaction of **3** generated in situ with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) in the presence of excess cod led to the formation of a new species **4**. The broad ^{11}B signal observed at $\delta = 7.0$ ppm along with the ^{19}F signals at $\delta = -129.3, -154.9$, and -163.1 ppm indicate the presence of a B center that is not three-coordinate. A signal in the ^{13}C NMR spectrum at $\delta = 120.7$ ppm exhibiting a C–P coupling of 57 Hz was attributed to the alkynyl carbon atom *alpha* to P. ^{1}H NMR data revealed a COD:PCCB-fragment ratio of 1:1, prompting the formulation of **4** as (*t*Bu$_2$PC≡CB$(C_6F_5)_2$)Ni(cod). Crystallographic data on the structure of **4** (Figure 2)[19] confirmed that Ni adopts a pseudo-square-planar coordination geometry comprising a bidentate cod ligand, an alkynyl fragment, and a coordinated B center. The elongated alkynyl C–C bond length of 1.254(4) Å is consistent with a weakened triple bond. This is also evident from the decrease in C≡C stretching frequency from 2125 cm^{-1} in **2** to 1881 cm^{-1} in **4**.

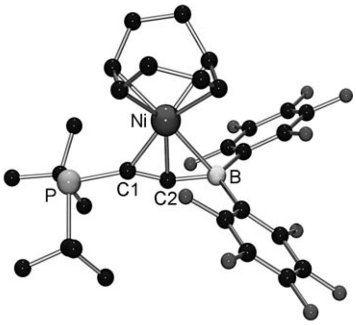
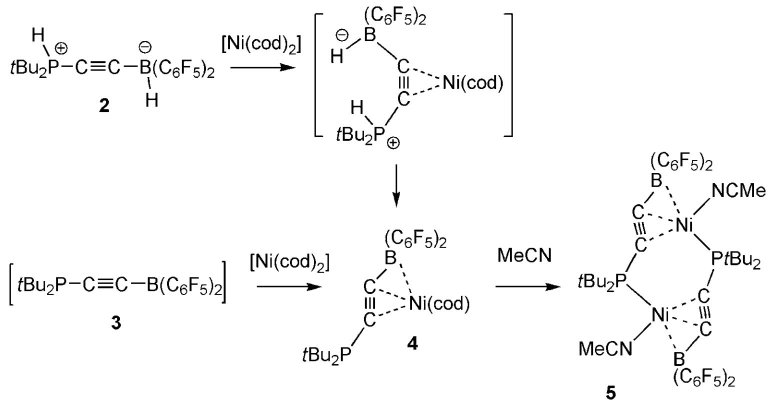


Figure 2. POV-ray drawing of **4**. All hydrogen atoms H are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 2.005(3), Ni–C2 1.987(3), Ni–B 2.358(3), P–C1 1.792(3), C2–B 1.486(4), C1–C2 1.254(4), C2-C1-P 155.5(3), C1-C2-B 156.3(3).

The salient structural feature in **4** is the short Ni–B distance of 2.358(3) Å and concomitant unusual *trans* disposition of the P and B groups on the (partially reduced) alkynyl unit. The Ni–B distance is somewhat longer than those previously reported for Ni(triphosphine-borane) (2.1677(16) Å)[8f] and NiX(tris-thioimidazolylborane) (X = Cl, N$_3$, NCS, OAc) (2.079(13)–2.112(3) Å).[9c] This may result from the constraints imposed by the metal–alkyne interaction and the required bending of the B toward Ni (C-C-B angle: 156.3(3)°), as is observed in Emslie's M(η^3-(BCC)-triarylborane) complexes (2.294(4) Å).[10a] The Ni–C$_{cod}$ bonds *trans* to B are significantly longer (Ni–C$_{av}$ 2.138(3) Å) than those *trans* to the alkynyl fragment (Ni–C$_{av}$ 2.088(3) Å), consistent with a dative Ni→B interaction that is known to exert a strong *trans* influence.[22] Despite this interaction, the sum of the C-B-C angles about B is 357.6°. Thus, the dative Ni to B interaction does not lead to significant pyramidalization at boron, consistent with the M to B interaction seen in Rh–boryl compounds.[5] It is also noteworthy that the B–C(2) bond length of 1.486(4) Å in **4** is significantly shorter than in **2** and somewhat shorter than in those alkynylboranes that have been structurally characterized (1.504(6)–1.529(6) Å).[21,23] This suggests some degree of "borato-allene" character in the BCC fragment as in its all-carbon analogues that adopt the η^3-propargyl/allenyl coordination mode.[24]

The species **4** was also generated in the reaction of **2** with [Ni(cod)$_2$]. Monitoring the reaction by NMR spectroscopy revealed the initial formation of a species exhibiting ^{31}P and ^{11}B NMR signals at $\delta = 28.2$ and -24.7 ppm, both of which are doublets with diagnostic $^1J_{PH}$ and $^1J_{BH}$, respectively. Over



Scheme 2. Synthesis of **4** and **5**.

the course of one day these signals are replaced by those attributable to **4**. The observed intermediate is proposed to be a more classical metal–alkyne complex (Scheme 2). The fate of the proton and hydride on P and B is not entirely clear. Evidence of cyclooctene is observed in the reaction mixture although it does not seem to be the only by-product from H_2 transfer. Regardless of the mechanism of loss of H_2, it appears that the Lewis acidity of the resulting free borane drives the rearrangement of the metal-bound fragment to permit the Ni→B dative interaction.

Treatment of **4** with MeCN results in the formation and precipitation of a new product **5**. NMR spectra obtained in $[D_8]$THF showed a ^{31}P resonance at $\delta = 53.2$ ppm, notably shifted downfield from that of **4**. Unfortunately, the ^{1}H NMR spectrum is broad and uninformative, perhaps a result of acetonitrile exchange; however, this could not be confirmed due to the poor solubility at low temperature. Although for **5** no ^{11}B signal was observed, the resemblance of its ^{19}F NMR spectrum to that of **4** suggests a similar B environment. The IR spectrum of **5** in the solid state exhibited a coordinated C≡N stretch at 2269 cm^{-1} and a C≡C stretch at 1838 cm^{-1}, suggesting a more reduced alkynyl group than in **4**. The X-ray structure of **5** (Figure 3)[19] reveals its centrosymmetric dimeric nature in which the B-C-C interaction with Ni is retained. In addition, the formally pendant P is coordinated to a second Ni center. The coordination spheres of the two Ni centers are completed by coordination of NCMe. The Ni–C_{alkyne} bonds were found to be 1.9536(12) and 1.9714(13) Å, while the Ni–B approach is 2.3243(15) Å, slightly shorter than that seen in **4**, presumably as a result of a more electron-rich Ni donor. The six-membered ring formed by the $Ni_2P_2C_2$ core of the dimer is approximately planar with a maximum deviation from the least-squares plane of 0.0805 Å.

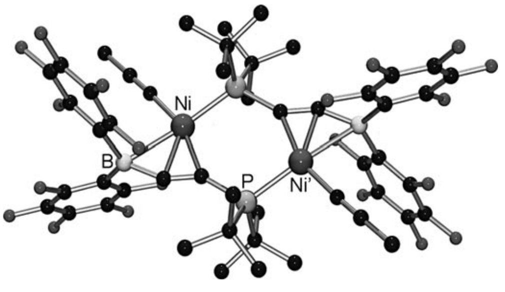


Figure 3. POV-ray drawing of **5**. All hydrogen atoms H are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.9536(12), Ni–C2 1.9714(13), Ni–B 2.3243(15), Ni–P 2.1982(4), Ni–N 1.8674(11), P′–C(1) 1.7877(13), C2–B1 1.486(2), C1–C2 1.2681(18); C2-C1-P′ 145.44(11), C1-C2-B 153.50(13).

To probe the nature of the Ni→B interaction, DFT calculations[25] were undertaken. The geometry of **4** was optimized by using the B3PW91 functional and 6-311G** basis set affording $\mathbf{4}_{calc}$, which was found to be very similar to the crystallographically determined structure. The calculated Ni→B separation was longer than the experimental value by 0.06 Å, while all other pertinent bond lengths differed by less than 0.03 Å. Importantly, $\mathbf{4}_{calc}$ showed B bending towards Ni with an approximately coplanar Ni(BC≡CP) fragment and a B–C≡C angle of 156.5°, almost identical to the experimentally determined value. The HOMO of $\mathbf{4}_{calc}$ not only involves the interaction between the filled Ni d_{xy} orbital and vacant B p_x orbital, but also demonstrates significant contributions from the interaction of Ni with the acetylenic carbon on P ($C_{(P)}$), as well as π-delocalization over the BC≡C fragment (Figure 4a). The HOMO-1 of $\mathbf{4}_{calc}$ also shows some contribution to the Ni–BC≡C interaction, while the HOMO-2, HOMO-13, and HOMO-20 exhibit classical metal–alkyne π-antibonding, π-donating, and σ-donating MOs, respectively. Interestingly, a NBO analysis found a natural bond orbital corresponding to the Ni→B interaction (Figure 4b). This NBO, with an occupancy of 1.63, is highly polarized towards Ni with approximately 80.2 % contribution from the Ni d orbital, signifying the dative nature of the bond. The NPA atomic charge on B shows a rather moderate decrease from 0.66 in the free ligand $\mathbf{3}_{calc}$ to 0.36 in the complex $\mathbf{4}_{calc}$, while that on C(P) also drop by 0.25 from $\mathbf{3}_{calc}$ to $\mathbf{4}_{calc}$. The NAO Wiberg bond index for $\mathbf{4}_{calc}$ suggests Ni–$C_{(P)}$, Ni–$C_{(B)}$ and Ni–B bond orders of 0.40, 0.17, and 0.31, respectively. These data support the notion that there is a moderate degree of Ni→B dative interaction as the electron density is delocalized over the BC≡C moiety affording a hyperconjugation-like stabilization. This is also evidenced by significant delocalization energies provided by second-order NBO interactions between Ni–B σ-orbitals and C≡C π-orbitals (64 kcal mol^{-1} for $\sigma \rightarrow \pi^*$; 33 kcal mol^{-1} for $\pi \rightarrow \sigma^*$). Such delocalization is believed to be responsible for the shortening of the B–C(alkyne) distance in $\mathbf{4}_{calc}$ in comparison to that in $\mathbf{3}_{calc}$, and the retained planarity at the B center of **4**.

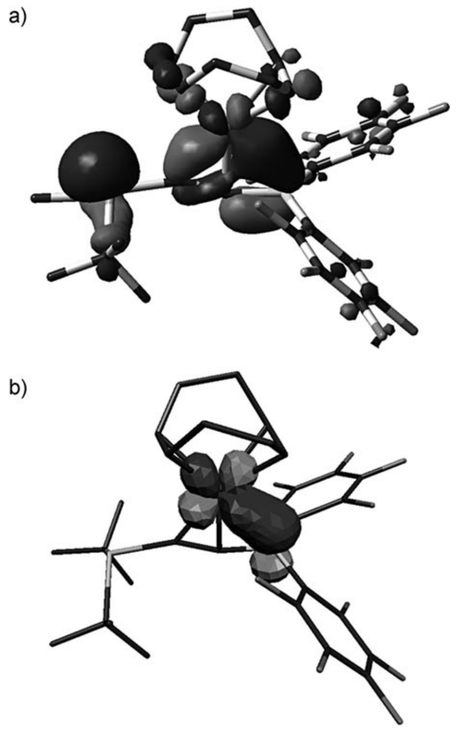


Figure 4. a) Gaussview depiction of the HOMO of **4** (cutoff: 0.04). b) Molekel depiction of the NBO for the Ni→B interaction in **4** (cutoff: 0.05).

In summary, the crystallographic and computational data herein illustrate that complexes **4** and **5** contain a dative Ni→B interaction, which prompts an unconventional *trans* metal–alkyne binding mode. The impact of such interactions and the chemistry of highly polarized phosphino-alkynyl-boranes continue to be subjects of investigation in our laboratories.

Experimental Section

For full experimental and spectroscopic details for all compounds, see the Supporting Information.

Synthesis of [(*t*Bu$_2$PC≡CB(C$_6$F$_5$)$_2$)Ni(cod)]·0.5 C$_7$H$_8$ (4): B(C$_6$F$_5$)$_3$ (99 mg, 0.19 mmol) and P*t*Bu$_3$ (39 mg, 0.19 mmol) were added to **2** in toluene. After the mixture had been stirred for 1 h, hexane was added and the was mixture cooled at −35 °C for 3 h. Follwing filteration, [Ni(cod)$_2$] (50 mg, 0.18 mmol) and 1,5-cyclooctadiene (190 mg, 1.8 mmol) were added to the filtrate. Upon stirring for 6 h, the mixture was filtered and the orange-red product precipitated from the concentrated solution at −35 °C. Yield: 86 mg, 65 %. ^{1}H NMR (C$_6$D$_6$): $\delta = 7.13$ (m, 1.5 H, *o/p*-Ph, toluene), 7.02 (m, 1 H, *m*-Ph, toluene), 5.50 (br, 2 H, =CH, cod), 4.88 (br, 2 H, =CH, cod), 2.11 (s, 1.5 H, CH$_3$, toluene), 1.90 (m, 4 H, CH$_2$, cod), 1.67 (m, 4 H, CH$_2$, cod), 1.22 ppm (d, 18 H, $^3J_{\mathrm{HP}} = 12.3$ Hz, *t*Bu); ^{11}B{^{1}H} NMR (C$_6$D$_6$): $\delta = 6.98$ ppm (br); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 147.89$ (dm, $^1J_{\mathrm{CF}} = 241$ Hz, *o*-C$_6$F$_5$), 140.49 (dm, $^1J_{\mathrm{CF}} = 247$ Hz, *p*-C$_6$F$_5$), 137.96 (dm, $^1J_{\mathrm{CF}} = 250$ Hz, *m*-C$_6$F$_5$), 137.90 (s, *i*-Ph, toluene), 129.34 (s, *o*-Ph, toluene), 128.69 (s, *m*-Ph, toluene), 125.68 (s, *p*-Ph, toluene), 120.70 (d, $^1J_{\mathrm{CP}} =$ 57 Hz, C≡*C*P), 108.62 (d, $^3J_{\mathrm{CP}} = 11.2$ Hz, =CH, cod), 98.70 (s, =CH, cod), 33.03 (d, $^1J_{\mathrm{CP}} = 25$ Hz, quat-*t*Bu), 31.03 (s, CH$_2$, cod), 29.60 (d, $^2J_{\mathrm{CP}} =$ 14 Hz, *t*Bu), 28.31 (s, CH$_2$, cod), 21.42 ppm (s, *C*H$_3$, toluene). C≡*C*B and quat-C$_6$F$_5$ carbons were not observed. ^{19}F NMR (C$_6$D$_6$): $\delta = -129.32$ (m, 4F, *o*-C$_6$F$_5$), −154.85 (t, 2F, $^3J_{\mathrm{FF}} = 21$ Hz, *p*-C$_6$F$_5$), 163.13 ppm (m, 4F, *m*-C$_6$F$_5$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 6.86$ ppm (s); IR (thin film from CH$_2$Cl$_2$): $\tilde{\nu} = 1881$ cm^{-1} (υ(C≡C)); elemental analysis calcd (%) for C$_{30}$H$_{30}$BF$_{10}$PNi·C$_{3.5}$H$_4$: C 55.34, H 4.71; found: C 55.35, H 5.00.

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Keywords: alkyne complexes • boranes • dative metal–boron bonding • nickel • nickel–borane interactions

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