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

Xiaoxi Zhao, Edwin Otten, Datong Song, and Douglas W. Stephan*[a]

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 [CpFe(CO)2AlPh3][NEt3] 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, Pieters and co-workers[6] have proposed possible contributions from M→B dative interactions in their metal–borataalkene complexes.[8] The groups of Hill,[4,7] Bourissou,[8] and Emslie[9] among others[10] 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.[11]

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.[12] Such systems, termed “frustrated Lewis pairs”,[14] afford unique reactivity on their own right.[12b,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 alkenes 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 Bu₂PC≡CH[17] was prepared and allowed to react with CI[B(C₆F₅)₃][18] at −35°C to give an off-white product 1 in 72% isolated yield. Compound 1 exhibits a ¹H NMR doublet resonance at δ = 5.80 ppm with a P–H coupling of 469 Hz, indicative of the presence of a PH fragment (¹P: δ = 25.5 ppm). It also shows a ¹¹B[¹H] signal at δ = −12.8 ppm and three ¹³C resonances at δ = −131.1, −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 tBu₂PhCH≡CBH(C₆F₅)₃ (Scheme 1). Treatment of 1 with excess Me₂SiHCl results in the exchange of the B-bound chloride for hydride, affording tBu₂PhCH≡CBH(C₆F₅)₃ (2) as colorless crystals in 79% yield (Scheme 1). A 1:1:1:1 quartet at δ = 3.25 ppm in the ¹H NMR spectrum (J₁BuH = 91 Hz) confirms the presence of a BH moiety. The acetylenic carbon atom alpha to P is observed in the ¹³C NMR spectrum at δ = 64.4 ppm with a ¹3C/¹H coupling of 158 Hz. The resonance for the B-bound acetylenic carbon was not observed, presumably due to quadrupolar broadening. The proposed con-
nectivity in the monomeric form in solution despite the highly acidic nature 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 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)[26] and NiX(tris-thioimidazolylborane) (X = Cl, N3, NCS, OAc) (2.079(13)–2.112(3) Å).[26] 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[η1-(BCC)- triarylborane] complexes (2.294(4) Å).[10a] The Ni–Ccod bonds trans to B are significantly longer (Ni–Ccod 2.138(3) Å) than those trans to the alkynyl fragment (Ni–Caida 2.088(3) Å), consistent with a dative Ni–B interaction that is known to exert a strong trans influence.[25] 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).[21,22] This suggests some degree of “borato-allene” character in the BCC fragment as in its all-carbon analogues that adopt the η1-propargyl/allenyl coordination mode.[24]

Figure 1. POVRay 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).

Figure 2. POVRay drawing of 4. All hydrogen atoms H are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 2.085(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).

**Figure 2.** POVRay drawing of 4. All hydrogen atoms H are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 2.085(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).
Scheme 2. Synthesis of 4 and 5.

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–C1 1.480(2), C1–C2 1.2681(18); C2–C1–P 145.44(11), C1–C2–B 153.50(13).

The coordination sphere of 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–Calkyne 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,P,C,C core of the dimer is approximately planar with a maximum deviation from the least-squares plane of 0.0805 Å.

To probe the nature of the Ni–B interaction, DFT calculations[21] were undertaken. The geometry of 4 was optimized by using the B3PW91 functional and 6-311G** basis set affording 4calc, 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, 4calc 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 4calc not only involves the interaction between the filled Ni d orbital and vacant B p 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 fragment (Figure 4a). The HOMO-1 of 4calc also shows some contribution to the Ni–B–C=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 3calc to 0.36 in the complex 4calc, while that on C(P) also drop by 0.25 from 3calc to 4calc. The NAO Wiberg bond index for 4calc suggests Ni–C(P), Ni–C(al), 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 σ–π; 33 kcal mol−1 for π–π*). Such delocalization is believed to be responsible for the shortening of the B–C(alkyne) distance in 4calc in comparison to that in 3calc, and the retained planarity at the B center of 4.
Nickel Phosphino-Alkynyl-Borane Complexes

COMMUNICATION

Synthesis of [(C6F5)3B(NP(CF3)C(C≡CCH2)C6H5)2] (cod) (4). 1H NMR (C6D6): δ = –154.85 ppm (s, 2F, J2F = 21 Hz, μ-CF3), 163.13 ppm (s, 4F, μ-CF3). 19F NMR (C6D6): δ = 6.86 ppm (s); IR (thin film from CH2Cl2): ν = 1881 cm–1 (ν(C=CF)); elemental analysis calcd (%) for C30H24BF6NiP3C4H4: C 53.54, H 4.71; found: C 53.53, H 5.00.

In summary, the crystallographic and computational data herein illustrate that complexes 4 and 5 contain a dative metal–boron binding mode. The impact of such interactions and the chemistry of highly polarized phosphino-alkynylboranes continue to be subjects of investigation in our laboratories.

Acknowledgements

D.W. is grateful for the financial support of NSERC of Canada. D.W. is grateful for the support of a Canada Research Chair and a Killam Research Fellow ship from the Killam Foundation. X.Z. thanks the Province of Ontario and Digital Specialty Chemicals for an Ontario Graduate Scholarship (OGSS). E.O. is grateful for the support of a Rubicon postdoctoral fellowship from the Netherlands Organisation for Scientific Research (NWO).

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