Supporting Information for the Paper "Structural Elucidation of a Nickel Boryl Complex. A Recyclable Borylation Ni(II) Reagent of Bromobenzene"

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Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere.[1] Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column.[2] Diethyl ether was dried by passage through a column of activated alumina.[2] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into collection flask before being transferred into a dry box. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. Li(PNP) (PNP = $N[2\text{-}P(CHMe_2)_2\text{-}4\text{-methylphenyl}]_2^-$)[3] was prepared according to the literature. All other chemicals were used as received. ^1H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm and 128.0 ppm respectively). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (aqueous solution, δ 0.0 ppm). ^{11}B NMR chemical shifts are reported with respect to external $BF_3.OEt_2$ (δ 0.0 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures.[4]

Synthesis of (PNP)Ni[B(catechol)] (2).

In a vial (PNP)NiH (**1**) (100 mg, 0.205 mmol) was dissolved in 5 mL of benzene and a solution of catecholborane (25 mg, 0.205 mmol) in benzene was added dropwise. The reaction mixture was stirred for 12 hours and then dried in vacuo. The yellow-brown material was extracted with diethyl ether, filtered, and the filtrate reduced in volume. The solution was then cooled to − 35 °C to afford **2** as yellow colored crystals (101 mg, 0.166 mmol, 81% yield). ^{1}H NMR (25 ^{o}C, 399.8 MHz, C_6D_6): δ 7.86 (d, 2H, C_6*H_3*), 7.24 (m, 2H, C_6*H_4*), 6.91 (br, 4H, overlap of aromatic resonances), 6.84 (m, 2H, C_6*H_3*), 2.28-2.21 (br, 10H, methyl and isopropyl methine resonances overlapped), 1.08 (dd, 12H, CH*Me_2*), 1.00 (dd, 12H, CH*Me_2*). ^{13}C NMR (25 ^{o}C, 100.6 MHz, C_6D_6): δ 161.3 (aryl), 150.2 (aryl), 132.7 (aryl), 132.5 (aryl), 128.4 (aryl), 124.0 (aryl), 121.6 (aryl), 114.8 (aryl), 111.4 (aryl), 23.5 (*C*HMe$_2$), 20.6 (*Me*Ar), 18.5 (CH*Me*$_2$), 17.6 (CH*Me*$_2$). ^{31}P NMR (25 ^{o}C, 121.5 MHz, C_6D_6) δ 51.2. ^{11}B NMR (25 ^{o}C, 160.6 MHz, C_6D_6) δ 46.9. MS-CI, $[M+H]^+$: calcd: 605.2288, found: 605.2290. m. p. 172 ^{o}C. UV-vis (hexane, 24 ^{o}C): 413 nm (ε = 4042 $M^{-1}\cdot cm^{-1}$).

Synthesis of (PNP)NiBr (3).

In a thick wall reaction vessel anhydrous $NiBr_2$ (200 mg, 0.915 mmol) was suspended 10 ml of benzene and a benzene solution of (PNP)H (393 mg, 0.915 mmol) was added dropwise. The reaction mixture was heated to 90 ^{o}C for 21 hours upon which 5 drops of NEt_3 was added. The mixture was filtered through a plug of celite and silica gel. The filtrate was dried under vacuo, extracted with diethyl ether and the solution was cooled to − 35 °C to afford dark green crystals of **3** (171.6 mg, 0.302 mmol, 65% yield). ^{1}H NMR (25 ^{o}C, 399.8 MHz, C_6D_6): δ 7.52 (d, 2H, C_6*H_3*), 6.92 (s, 2H C_6*H_3*), 6.73 (d, 2H, C_6*H_3*), 2.33 (m, 4H, C*H*Me$_2$), 2.12 (s, 6H, *Me*Ar), 1.53 (dd, 12H, CH*Me_2*), 1.24 (dd, 12H, CH*Me_2*). ^{13}C NMR (25 ^{o}C, 75.5 MHz, C_6D_6): δ 162.13 (aryl), 132.42 (aryl), 131.95 (aryl), 125.60 (aryl), 120.97 (aryl), 116.85 (aryl), 24.57 (*C*HMe$_2$), 20.46 (*Me*Ar), 18.84 (CH*Me*$_2$), 17.90 (CH*Me*$_2$). ^{31}P NMR (25 ^{o}C, 121.5 MHz, C_6D_6): δ 37.54. MS-CI, $[M+H]^+$: calcd: 565.1167, found: 565.1160. m.p. 168 ^{o}C.

Synthesis of (PNP)NiH (1) from (3) and $NaBH_4$.

In a vial **3** (100 mg, 0.176 mmol) was dissolved in 10 ml of THF and a suspension of $NaBH_4$ (66.7 mg, 17.6 mmol) in THF was added. The reaction mixture was stirred for 3 hours and filtered. The filtrate was then dried under vacuo, extracted with pentane and the solution cooled to −35 °C to afford brown colored crystals of **1** (53.36 mg, 0.109 mmol, 62 % yield). The characterizations of **1** was confirmed by ^{1}H and ^{31}P NMR spectra of independently prepared sample reported in the literature.[5]

Separation of 3 and Phenyl Boronic Ester Using preparatory Thin Layer Chromatography.

The product phenyl boronic ester was separated from **3** by a preparatory thin layer chromatography plate coated with silica. After loading the sample, the plate was eluted with 3:7 ethyl acetate, hexane solution. The phenyl boronic ester and **3** were collected in 68% and 88% respectively. Isolation of the boronic ester must be performed quickly since this product decomposes slowly in contact with silica. The phenyl boronic ester was synthesized independently by refluxing $PhB(OH)_2$ and catechol in benzene for 2 hours (in air), then removing water azeotropically by dint of a Dean-Stark apparatus.[6] The crude product was dissolved in toluene and cooled to −20 °C to afford pure ester. Although this product has been reported in the literature,[6] no ^{1}H NMR spectrum was documented. ^{1}H NMR (25 °C, 399.8 MHz, C_6D_6): δ 8.12 (m, aryl), 7.18 (m, aryl, overlapping resonances), 7.06 (m, aryl), 6.81 (m, aryl). ^{11}B NMR (25 °C, 160.6 MHz, C_6D_6) δ 32.

Selected References

(1) For a general description of the equipment and techniques used in carrying out this chemistry see: B. J. Burger; J. E. Bercaw, In *Experimental Organometallic Chemistry*; A. L. Wayda; M. Y. Darensbourg, Edx.; ACS Symposium Series 357; American Chemical Society; Washington D. C., 1987; pp 79-98.

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Computational details

All calculations have been carried out using Density Functional Theory as implemented in the Jaguar 5.5 suite[1] of ab initio quantum chemistry programs. Geometry optimizations have been performed with the

B3LYP [2-5] functional and 6-31G** basis set. Transition metal Ni has been represented using the Los Alamos LACVP** basis [6-7] that includes relativistic effective core potentials. A modified version of the LACVP**, designated as LACV3P** has been used where the exponents are documented to match the effective core potential with the triple-ξ. A simplified model (where the isopropyl groups of phosphorus have been reduced to methyls and methyls of the aromatic ring have been reduced to hydrogens) has been used to obtain Mayer's bond order[8-11] from NBO 5.0[12] implemented in Jaguar 5.5 suite.

Natural Bond Order of important bonds

Ni-B 0.84

B-O 0.80

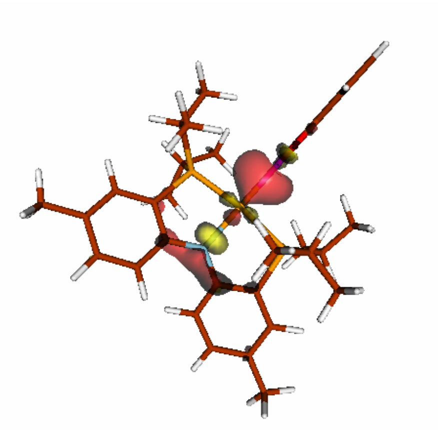

Fig. S1. HOMO-8, to show the Ni-B σ-bond which is a combination of Ni d(x^2-y^2) and B p(x) orbital. The orbital has been drawn with isodensity = 0.05 au.

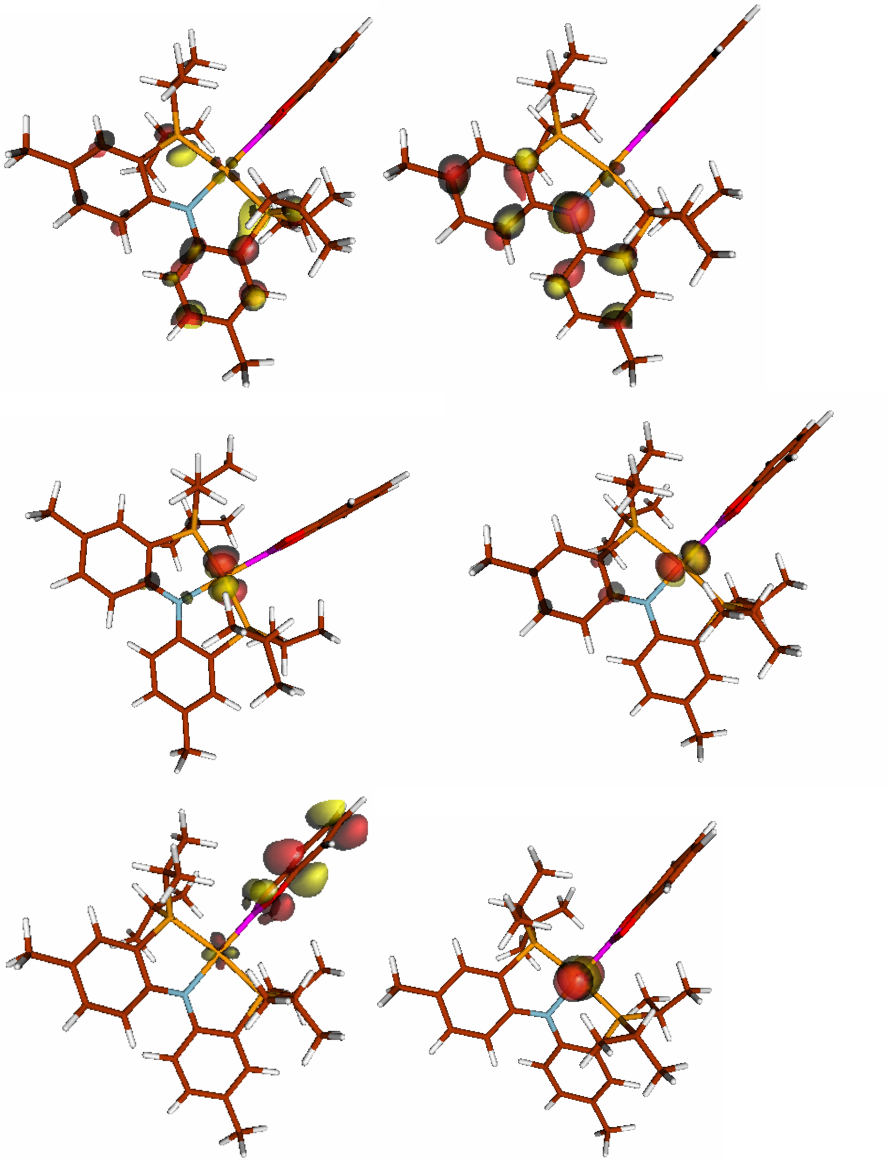

Fig S2. Other important orbitals for compound **2**. From left to right and top to bottom: LUMO, HOMO, HOMO-5, HOMO-4, HOMO-3, HOMO-1.

Selected References for Computational Component

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