Structural elucidation of a nickel boryl complex. A recyclable borylation Ni(II) reagent of bromobenzene†

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The first nickel complex bearing a boryl moiety, (PNP)Ni[B-(catechol)] (PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$), has been prepared, structurally characterized, and analyzed by DFT; this rare species is shown to be a recyclable reagent for the borylation of bromobenzene, *via* an unusual cycle, by applying the ingredients catecholborane and NaBH$_4$.

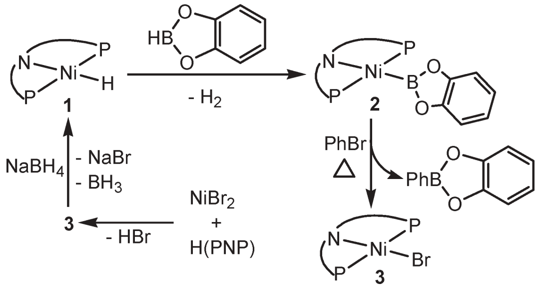
Group-transfer processes involving nickel reagents represent an attractive paradigm given the low cost associated with this element when compared to its heavier congeners. One particular catalytic reaction that has found enormous promise has been the conversion of aromatic and aliphatic hydrocarbons to the corresponding boronic esters[1] since these products can be used as feedstock for a wide variety of cross-coupling reactions[2] as well as substitution chemistries at the C–B linkage.[3] Under this premise, it has been proposed that borylation reactions often proceed *via* reactive M–BR$_2$ intermediates (M = Ir, Rh, Pd and Pt).[4–7] To our surprise, borylation reactions involving Ni as a reagent have not been documented. Arguably, the inability of Ni to emulate the chemistry of its heavier congeners in processes such as borylations might be attributed to lack of stable and isolable systems bearing the prototypical Ni–BR$_2$ linkage, which is in fact the case for this element. The first report of a Ni–BR$_2$ moiety was claimed by Noth and Cundy, but this complex was ill-characterized.[8] Recent studies by Liang and co-workers have revealed that square-planar Ni(II) complexes supported by the pincer ligand N[2-PR-phenyl]$_2^-$ (R = ^{i}Pr, Cy) can activate C–H bonds of benzene when the system is promoted with a Lewis acid such as Al(CH$_3$)$_3$.[9] Inspired by their work, we speculated whether the closely related and robust "(PNP)Ni" surrogate, PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$,[10]could in fact accommodate a boryl group and then transfer such a fragment to haloaromatics.

During the course of our studies involving the Ni(II) complex (PNP)NiH (**1**),[11] we discovered that such a precursor can be converted to the square-planar nickel boryl compound (PNP)Ni[B(catechol)] (**2**). Most notably, compound **2** can transfer the B(catechol) moiety to bromobenzene, and the Ni(II) product can be recycled back to **1** by applying NaBH$_4$. Herein, we present a new borylation cycle of bromobenzene by using the first Ni(II) boryl reagent **2**. This complex has been isolated, structurally elucidated, and theoretically analyzed by DFT.

When complex **1**[11] is treated with catecholborane at room temperature in benzene, the boryl complex **2**‡ and H$_2$ are cleanly formed over a period of 12 h (Scheme 1).† A similar strategy for the synthesis of transition metal boryl complexes has been used by Marder and co-workers.[12] Compound **2** is a yellow colored solid (mp 172 °C) that can be isolated in 81% yield after work-up of the reaction mixture. Diamagnetic **2** evinces a broad ^{11}B NMR resonance at $\sim$47 ppm (J_{B-P} coupling was not resolved even upon cooling the solution to -45 °C), as well as a singlet at 51.2 ppm in the ^{31}P NMR spectrum, the latter being consistent with such a species retaining C_{2v} symmetry in solution. The former chemical shift is comparable to other 3d transition metal boryl complexes reported in the literature.[13,14] To our surprise however, complex **2** is kinetically stable to heat (several days in C$_6$D$_6$ at 155 °C under N$_2$), and even air for brief periods of time ($\sim$30 min).

Single crystal X-ray analysis of **2**§ unequivocally exposes a square-planar nickel complex bearing the terminal and planar catecholboryl group (Ni–B, 1.9091(18) Å, Fig. 1).† This bond length is within range of other structurally characterized boryl complexes for 3d metals such as Co (1.970(11) Å), Fe (1.973(2) Å), and Mn (2.108(6) Å),[13] but is significantly shorter than that reported for the σ-alkyl borane adduct of Ni(0) (2.172(6) Å).[15] Although square-planar transition metal boryl complexes have been documented, this geometry is rare when weighed against most metal–boryl systems crystallographically characterized.[14] In **2**, the plane composing the O–B–O atoms bisects the imaginary plane defined by the P–Ni–P atoms ($\sim$71.4°); therefore placing the empty p(*y*) orbital of boron virtually along the (PNP)Ni *xy*-plane. Intuitively, the orientation of the boryl fragment with respect to the (PNP)Ni motif is not surprising since the filled d(*xy*) orbital on Ni has the appropriate symmetry to backbond with the empty p(*y*) orbital on boron.

In order to address the geometry in **2** and to ascertain whether the Ni–B linkage enjoyed M→L π-backbonding, we turned our



Scheme 1 Synthesis of complex **2** from **1** using catecholborane, and subsequent borylation of bromobenzene. The preparation of **1** and **3** are also illustrated.

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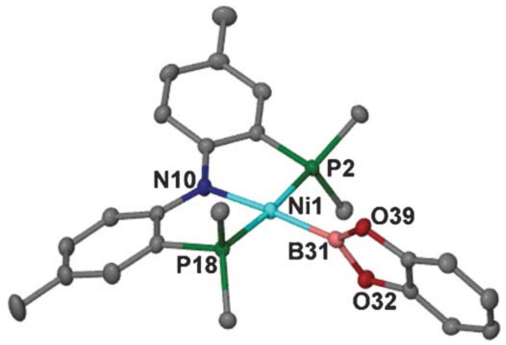

Fig. 1 Molecular structure of **2** omitting H-atoms, Et_2O solvent, and isopropyl methyls on phosphorus for the purpose of clarity. Thermal ellipsoids are displayed at the 50% probability level. Selected metrical parameters (distances in Å, angles in °): Ni1–B31, 1.9091(18); Ni1–P2, 2.1447(4); Ni1–P18, 2.1408(4); Ni1–N10, 1.932(2); B31–O32, 1.419(2); B31–O39, 1.423(2); P2–Ni1–P18, 174.42(7); N10–Ni1–P2, 87.45(4); N10–Ni1–P18, 87.40(4); N10–Ni1–B31, 174.54(7); P2–Ni1–B31, 93.43(5); P18–Ni1–B31, 91.89(5); Ni1–B31–O32, 129.2(2); Ni1–B31–O39, 122.8(2).

attention to high level DFT analysis.† As anticipated for a square planar d^8 system, complex **2** has a filled $d(z^2)$ HOMO-1 orbital and an unoccupied $d(x^2 - y^2)$ LUMO orbital augmented with PNP aryl π^* (Fig. 2). In addition, the HOMO orbital has ligand π^* character with considerable contribution from the PNP nitrogen lone pair (Fig. 2). Upon further analysis of **2**, we observe that backbonding from Ni to B does not take place in this system since the anticipated empty $p(y)$ orbital on boron has been diffused instead to the catechol π-framework thus extricating the Ni $d(xy)$ orbital from any bonding interaction (HOMO-3, Fig. 2). Theoretical calculations by others have demonstrated that the $M–BR_2$ bond strength stems mainly from σ donation of the boryl ligand with minimal contribution from π-backbonding of the transition metal to the vacant p orbital of boron when the R_2 group in question bears a π-donor such as a catechol.[16] As expected for a hard and *trans* influencing ligand,[17] the boryl–Ni σ bond is very low in energy combining a Ni $d(x^2 - y^2)$ and B $p(x)$ orbital (HOMO-8, Fig. S1).† Thence, our orbital analysis and natural bond order calculations (NBO = 0.84)† suggest that complex **2** does not contain multiple bond character between Ni and B. Since NBO calculations do not account for the electrostatic component between Ni and B, and the Ni–B linkage in **2** lacks π overlap, our predicted Mayer bond order is less than one. Hypothetically, this lack of orbital overlap between Ni and B should render the catecholboryl group in **2** amenable to substitution chemistry.

Complex **2** does in fact transfer the boryl group, inasmuch as treatment with bromobenzene at 120 °C over 18 h afforded PhB(catechol) and (PNP)NiBr (**3**), quantitatively as inferred from ^1H and ^{31}P NMR spectroscopy (Scheme 1). The identity of the former and latter products have been confirmed from independent experiments as well as GC-MS and multinuclear NMR spectra (^1H, ^{11}B, and ^{31}P NMR spectra).† Unfortunately, refluxing **2** in chlorobenzene over 3 days at 120 °C resulted in only $<10\%$ borylation of the arene concurrent with formation of the known precursor (PNP)NiCl (**4**). Our ability to generate the B–C coupled product and **3** from bromobenzene insinuated that this process could be made catalytic since precursors such as **4** have been previously shown to convert to **1** by addition of $NaBH_4$.[11] We therefore prepared **3** independently, from H(PNP) and $NiBr_2$, and found that this system can in fact be converted smoothly to **1** when subjected to $NaBH_4$ (Scheme 1). Pure **1** from **3** and $NaBH_4$ can be isolated in 62% yield by recrystallization.† To our disappointment however, catalysis did not prevail when 10–20 mol% of **3** with HB(catechol) and $NaBH_4$ are mixed in neat bromobenzene for 18 h at 120 °C, since compound **1** reacts at a comparable rate with bromobenzene to generate **3** and benzene. Despite this limitation, we can perform the reaction stoichiometrically with **2** in neat bromobenzene, to afford PhB(catechol) in 68% isolated yield. Separation of PhB(catechol) from **3** was achieved using a preparatory thin layer chromatography plate coated with silica.† Most notably, compound **3** can also be separated from the mixture in 88% and recycled back to **1** with $NaBH_4$ (*vide supra*) thus closing our cycle for the borylation of bromobenzene (Fig. 2).† Isolation of the metal product and its recycling is an improvement over reported cases in the preparation of phenylboronate esters using Co,[18] Rh, or Ir.[19]

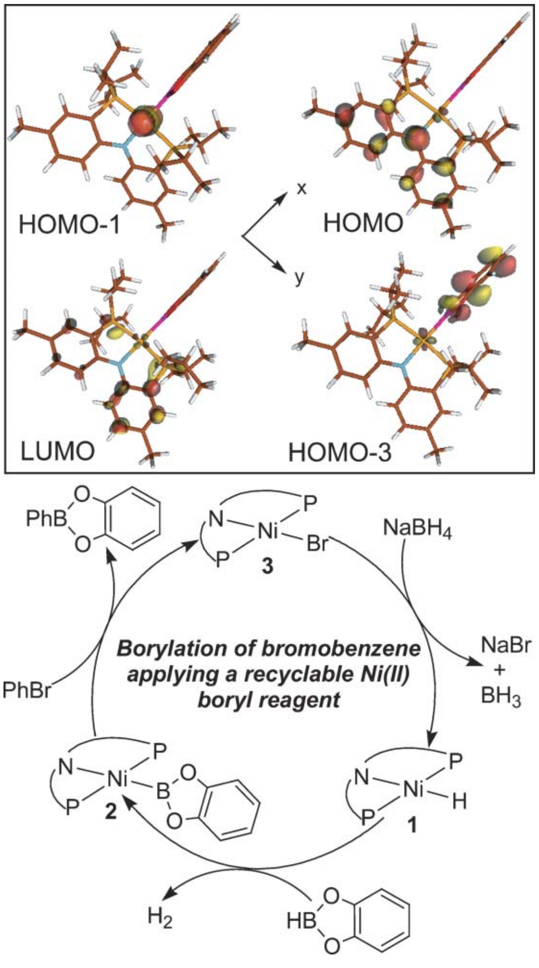

Fig. 2 Some of the most important molecular orbitals of **2** with isodensity = 0.05 au. The bottom scheme depicts a recyclable square-planar Ni(II) reagent applied to borylation of bromobenzene, where the PNP^- cartoon represents the framework $N[2\text{-}P(CHMe_2)_2\text{-}4\text{-methylphenyl}]_2$.

Formation of **3** from **2** and bromobenzene as well as the conversion of **2** from **1** with HB(catechol) might involve Ni(II)/Ni(IV) redox couples, but we have not identified other intermediates than the ones previously mentioned. Our proposed mechanism contrasts with Masuda's palladium-catalyzed borylation of Ar–X (X = Br, I, OTf) to arylboronates in terms of oxidation states as well as the order of intermediates formed during the cycle. For example, the oxidative addition of an Ar–X bond to Pd(0) differs from our proposed oxidative addition to a Ni(II) center.[20,21] Likewise, the formation of a Pd–B bond is assumed to occur in the last step of the catalytic cycle, while in our case a Ni–B bond must precede the oxidative addition step of the Ar–X. Our recycling diagram depicted in Fig. 2 is interesting for four reasons: (1) three key intermediates along the borylation process can be readily isolated and characterized, which includes the first Ni–boryl complex **2**, (2) the process uses fairly stable Ni(II) reagents such as **1**–**3**, which can be prepared readily and recycled, (3) our borylation cycle bypasses the use of the more common, but expensive biscatecholdiborane reagent by applying HB(catechol) as an alternate boryl source, and (4) our unique mechanism scenario most likely involves a Ni(II)/Ni(IV) redox couple whereby a Ni(II) boryl undergoes oxidative addition of Ar–Br.

Based on these results, we have demonstrated that a Ni–boryl complex can be prepared, characterized spectroscopically and structurally in conjunction with theoretical analysis of its geometry and bonding scheme. Such species is capable of transferring the boryl fragment to bromobenzene to form PhB(catechol) and the corresponding nickel(II) bromide. The new borylation cycle presented here can be accomplished using relatively stable Ni(II) reactants by applying cheaper reagents such as HB(catechol) and $NaBH_4$ as a means to borylate and recycle, respectively, the (PNP)Ni(II) scaffold. Our proposed cycle differs from other group 10 catalytic borylation processes and could offer a new, selective entry to this type of transformation.

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Notes and references

‡ Synthesis of (PNP)Ni[B(catechol)] (**2**): in a vial, (PNP)NiH (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 h and then dried *in vacuo*. The yellow-brown materials were 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). ^1H NMR (25 °C, 399.8 MHz, C_6D_6): δ 7.86 (d, 2H, $C_6\mathit{H_3}$), 7.24 (m, 2H, $C_6\mathit{H_4}$), 6.91 (br, 4H, overlap of aromatic resonances), 6.84 (m, 2H, $C_6\mathit{H_3}$), 2.28–2.21 (br, 10H, methyl and isopropyl methine resonances overlapped), 1.08 (dd, 12H, $CH\mathit{Me_2}$), 1.00 (dd, 12H, $CH\mathit{Me_2}$). ^{13}C NMR (25 °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 ($\mathit{C}HMe_2$), 20.6 ($\mathit{Me}Ar$), 18.5 ($CH\mathit{Me_2}$), 17.6 ($CH\mathit{Me_2}$). ^{31}P NMR (25 °C, 121.5 MHz, C_6D_6) δ 51.2. ^{11}B NMR (25 °C, 160.6 MHz, C_6D_6) δ 46.9. MS-CI, $[M + H]^+$: calcd 605.2288, found 605.2290. Mp 172 °C. UV-vis (hexane, 24 °C): 413 nm (ε = 4042 M^{-1} cm^{-1}).

§ Crystal data for **2**: $C_{32}H_{44}BNNiO_2P_2\cdot Et_2O$, M_r = 680.26; triclinic; $P\bar{1}$; a = 9.6521(7), b = 12.1376(9), c = 15.950(1) Å, α = 94.662(2), β = 91.022(2), γ = 100.029(2)°, V = 1833.0(2) Å^3; Z = 2; D_c = 1.233 g cm^{-3}; $R1$ = 0.0473, w$R2$ = 0.0765 ($I > 2\sigma(I)$); $R1$ = 0.0304, w$R2$ = 0.0842 (all data) and GoF = 0.975. Inert atmosphere techniques were used to place a yellow needle of approximate dimensions 0.25 × 0.25 × 0.15 mm onto the tip of a 0.1 mm diameter glass fiber. A total of 55 063 reflections ($-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-20 \leqslant l \leqslant 20$) were collected at T = 132(2) K in the θ range of 2.05 to 27.56°, of which 8459 were independent, and 6455 were observed (R_{int} = 0.0730); MoKα radiation (λ = 0.71073 Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. CCDC 652070 (**2**). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b709832d

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