Boryl Complexes

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# Cobalt Boryl Complexes: Enabling and Exploiting Migratory Insertion in Base-Metal-Mediated Borylation**

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***Abstract:*** *Cobalt boryl complexes, which have only been sporadically reported, can be accessed systematically with remarkable (but controllable) variation in the nature of the M–B bond. Complexes incorporating a very strong trans σ-donor display unparalleled inertness, reflected in retention of the M–B bond even in the presence of extremely strong acid. By contrast, the use of the strong π-acceptor CO in the trans position, results in significant Co–B elongation and to labilization of the boryl ligand via unprecedented CO migratory insertion. Such chemistry provides a pathway for the generation of coordinative unsaturation, thereby enabling ligand substitution and/or substrate assimilation. Alkene functionalization by boryl transfer, a well-known reaction for noble metals such as Rh or Pt, can thus be effected by an 18-electron base-metal complex.*

Organoboron reagents occupy a pivotal position in organic synthesis, which is in part due to the ready conversion of C–B bonds into a range of key C–E linkages (E = C, O, halogen).[1–3] When combined with the direct metal-catalyzed borylation of unactivated C–H bonds,[4] such methods facilitate hitherto inaccessible C–H to C–E transformations. A number of these processes involve metal-mediated transfer of the boryl ($-BR_2$) fragment (typically using Rh, Ir, Pd, or Pt), and so the fundamental patterns of reactivity of complexes of the type $L_nMBR_2$ are of key importance.[5–8] Recently, nucleophilic boryllithium reagents[9–12] have opened up routes to classes of M–B bond which cannot be accessed by established procedures employing boron electrophiles or oxidative addition chemistry.[13–27] However, exploitation of such reagents in the synthesis of transition-metal complexes with $d^n$ configurations ($n \neq 0$, 10) is hampered by their tendency to effect reduction chemistry rather than salt metathesis.[28] Very recently, however, we reported an approach which mitigates such redox problems: $(THF)_2Li\{B(NDippCH)_2\}$ (**1**; Dipp = 2,6-diisopropylphenyl) reacts with organometallic esters $[L_nM\{C(O)OR\}]$, to give novel bora-acyl complexes $[L_nM\{C(O)B(NDippCH)_2\}]$, which rearrange under thermal or photolytic conditions to give $[L_nM\{B(NDippCH)_2\}]$ and CO. This approach not only shows that classical CO extrusion from metal acyl species can be extended to the boryl ligand class,[29] but also provides access to a rare example of a cobalt boryl complex, namely $[(Ph_3P)Co(CO)_3\{B(NDippCH)_2\}]$ (**5**).[28]

Carbon monoxide insertion/de-insertion into metal–alkyl bonds is known to be reversible, and is a key mechanistic step in catalytic processes such as hydroformylation. Formal CO insertion via metal-to-carbonyl migration of an alkyl group is therefore a widely precedented pathway for generating coordinative unsaturation at a metal center. Bora-acyl species, by contrast, irreversibly evolve CO to generate metal boryl complexes, and the reverse reaction, that is, net insertion of carbon monoxide into a M–B bond, has no precedent.[22] The greater intrinsic strength of M–B (over M–C) bonds is presumably a factor in these contrasting observations,[30] but the implication of other M–B insertion processes in noble-metal-catalyzed hydro/diboration reactions,[4,8,31–44] for example, encouraged us to target complexes capable of CO insertion. In this way we hoped to facilitate the borylation of external substrates by freeing up a coordination site through (reversible) shuttling of a boryl ligand to an ancillary CO donor. Reasoning that a weaker M–B bond should facilitate boryl migration, and that the strength of M–B bonds falls with d-orbital contraction, we concentrated on complexes of the later 3d transition metals. Furthermore, given the potential of boryl ligands to act as π-acids (albeit relatively weakly), we hypothesized that the use of a competing strong π-acceptor *trans* to the M–B bond might also labilize the M–B bond. Thus, complexes of the type $[LCo(CO)_3(boryl)]$ (L = CO, $P(OR)_3$) were targeted, notwithstanding the fact that (unlike rhodium and iridium complexes) reliable routes to cobalt boryl systems were not widely available at the outset.[28,45–50]

In initial studies, the reactions of *trans*-$[LCo(CO)_3\{C(O)OEt\}]$ (L = CO (**2**), $P(OPh)_3$ (**3**)) with boryllithium **1** were studied (Scheme 1). Although tetra-carbonyl-supported cobalt ester **2** quantitatively yields the hydroborane $HB(NDippCH)_2$, phosphite-ligated **3** gives boryl complex **4** and free $P(OPh)_3$. The synthetic balance is therefore a fine one, with the more oxidizing nature of **2** presumably reflecting the greater π-acceptor properties of CO over $(PhO)_3P$. Samples of **4** generated in this fashion

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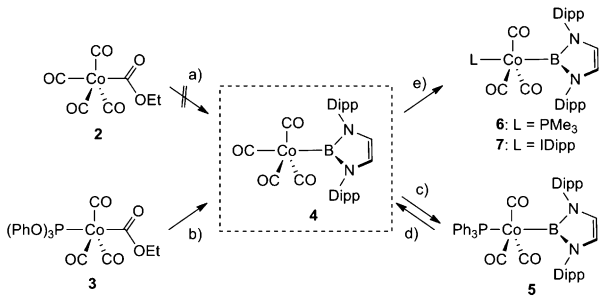



***Scheme 1.*** Reactions of cobalt esters **2** and **3** with boryllithium **1**. Key reagents/conditions: a) **1**, THF, room temperature or −78 °C, 30 min; b) **1**, THF, room temperature, 30 min; c) $PPh_3$, THF, room temp, 24 h; d) $[Cu(MeCN)_4]BF_4$, CO (1 atm.), *hν*, MeCN, room temperature, 4 h; e) for **6**: $PMe_3$, toluene, room temperature, 24 h, for **7**: IDipp (IDipp = $C(NDippCH)_2$), $C_6D_6$, room temperature, 2 weeks.

prove difficult to obtain analytically pure, and unlike recently reported d-block $B(NDippCH)_2$ complexes,[28] **4** does not survive column chromatography. The related triphenylphosphine complex **5**, however, is more robust, tolerates exposure to silica and is obtained quantitatively on addition of $PPh_3$ to **4**. Moreover, post-chromatography, **5** can be re-converted into **4** (also in essentially quantitative yield) by exposure to CO under photolytic conditions, using a $Cu^I$ reagent to trap the eliminated $PPh_3$. This approach provides analytically pure samples of **4**, and structural authentication by X-ray crystallography could also be obtained (Figure 1).

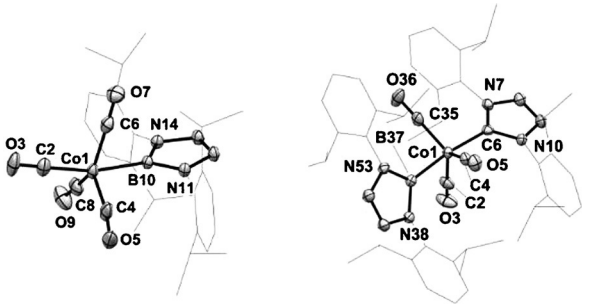
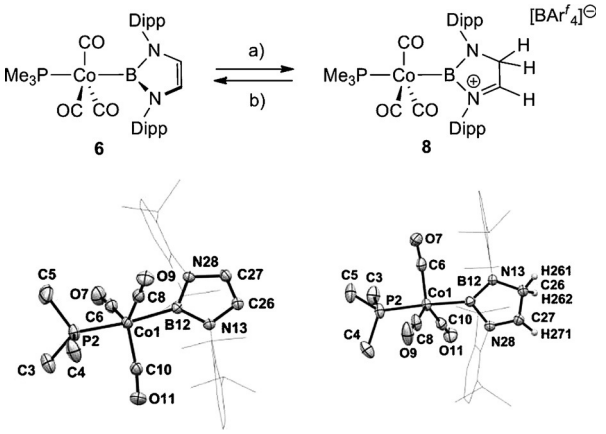



***Figure 1.*** Molecular structures of **4** (left) and **7** (right), as determined by X-ray crystallography.[56] Ellipsoids are set at 50% probability; H atoms omitted and Dipp groups shown in wireframe format for clarity. Key bond lengths [Å] and angles [°]: For **4**: Co1–B10 2.076(2), Co1–C2 1.808(2), Co1–C4 1.816(2); C2-Co1-B10 166.93(7); For **7**: Co1–B37 2.079(2), Co1–C6 1.998(2), Co1–C35 1.786(2); C6-Co1-B37 172.14(8).

The facile conversion of **4** into **5** suggests marked lability of the carbonyl *trans* to the boryl ligand, in accordance with the strong σ-donor capabilities of this class of ligand.[4,8] With this in mind, further $[LCo(CO)_3\{B(NDippCH)_2\}]$ systems were targeted from **4**, with a view to probing the effect of the *trans* ligand on reactivity patterns. The reactions with $PMe_3$ and IDipp (Scheme 1) can be shown to generate the corresponding *trans* disubstituted complexes $[LCo(CO)_3\{B(NDippCH)_2\}]$ (**6**: L = $PMe_3$; **7**: L = IDipp), which have been characterized by standard spectroscopic/analytic methods and by X-ray crystallography (Figure 1). The nature of L has a profound effect on lability: tetra-carbonyl complex **4** decomposes in the presence of air (or moisture), while mono-substituted systems **5**, **6**, and **7** are indefinitely stable under such conditions. Most remarkably, the Co–B bond in $PMe_3$-ligated **6** proves to be stable even in the presence of the extremely strong acid $[H(OEt_2)_2][BAr^f_4]$ [$Ar^f$ = 3,5-$(CF_3)_2C_6H_3$]. Under such conditions, **4** decomposes rapidly to give the hydroborane $HB(NDippCH)_2$, while **6** undergoes protonation of the boryl ligand heterocycle and retains the Co–B bond (Scheme 2). Moreover, this process is quantitatively reversible, with **8** being deprotonated on silica gel to regenerate **6**.




***Scheme 2.*** Resistance of the Co–B bond in **6** to strong acid. Key reagents/conditions: a) $[H(OEt_2)_2][BAr^f_4]$, $CH_2Cl_2$, room temperature; b) silica gel, $CH_2Cl_2$. Molecular structures of **6** and of the cationic component of **8**, as determined by X-ray crystallography.[56] Ellipsoids are set at 50% probability; anion, toluene, and selected H atoms omitted, and Dipp groups shown in wire-frame format for clarity. Bond lengths [Å]: For **6**: Co1–B12 2.044(2), Co1–P2 2.194(1), Co1–C6 1.764(2); P2-Co1-B12 171.05(6)°; For **8**: Co1–B12 1.982(4), Co1–P2 2.2209(9), Co1–C6 1.790(4), Co1–C8 1.783(4), Co1–C10 1.760(4), C6–O7 1.136(5), C8–O9 1.145(5), C10–C11 1.145(4), B12–N13 1.430(4), B12–N28 1.553(4), N13–C26 1.435(4), N28–C27 1.313(4), C26–C27 1.470(4).

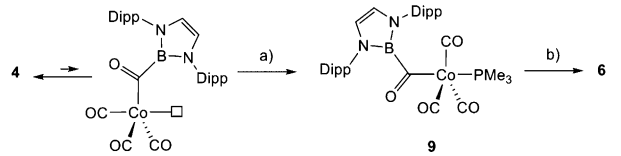
Spectroscopically, the $^{11}B$ NMR signal for **8** is shifted to low field ($\delta(^{11}B)$ = 55.8 ppm cf. 32.8 ppm for **6**), and the $^1H$ NMR spectrum not only reflects the lower symmetry implied by protonation of the heterocycle backbone, but also displays signals at $\delta(^1H)$ = 9.21 (1H) and 5.02 ppm (2H) for the NCH and $NCH_2$ protons. A crystallographic study (Scheme 2) confirms the heavy atom skeleton and the positions of the three backbone hydrogens in the difference Fourier map. The boron-containing heterocycle features a geometry distorted by a change of bond topology compared to the parent complex **6**. Thus, the unsaturated C=C character of the backbone is lost (**8**: $d$(C–C) = 1.470(4) Å, cf 1.345(3) Å for **6**), and one of C–N linkages is shortened, consistent with the generation of an imine function (1.313(4) Å cf. 1.401(3)/1.398(3) for **6**). A consequence of this increased C=N character is a reduced capacity for N28 to engage in π-donation to B12, and the associated B–N distance (1.553(4) Å) is significantly longer than that involving N13 (1.430(4) Å). A description of **8** as a boryl complex bearing

a positively charged nitrogen centre is consistent with the structure proposed for $[Cp^*Fe(CO)_2\{B(NDippCMe)_2CH\}]^+$, with the contraction in the Co–B bond length (1.982(4) Å cf. 2.044(2) Å for **6**) reflecting enhanced Co-to-B back-bonding brought about by diminished N-to-B donation involving N28. Consistently, NBO calculations reveal a stronger Co-to-B π back-bonding interaction in **8**, while NAO analysis indicates that increased 2s/decreased 2p character at boron also contributes to the contraction in the Co–B bond length.[51]

The greater lability of **4** (compared to **6**) in the presence of Brookhart's acid presumably reflects a weaker Co–B bond, which in turn reflects diminished back-bonding to the boryl ligand in the presence of a less-electron-rich metal center. Consistently, **4** possesses a longer Co–B bond than **6** (2.076(2) vs. 2.044(2) Å), and significantly higher CO stretching frequencies (2092, 2030, 2011, 1980 $cm^{-1}$ vs. 2023, 1959, 1928 $cm^{-1}$, respectively).

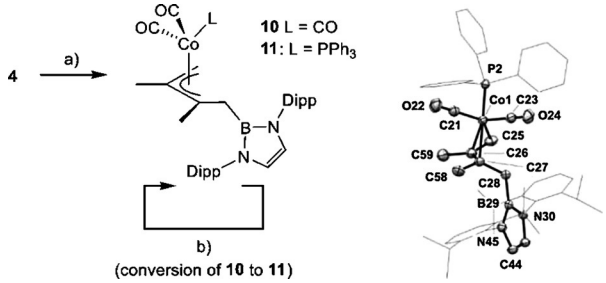
From a mechanistic standpoint, close examination of the substitution of the *trans*-CO ligand in **4** for $PMe_3$ suggests that this transformation does not occur via a simple dissociative pathway (Scheme 3). Thus, an intermediate bora-acyl species **9** (akin to an acyl intermediate in classical organometallic CO migratory insertion)[52] can be isolated at short reaction times and characterized in solution by $^1H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR and IR spectroscopies. In particular, 1) the $^{11}B$ spectrum reveals a shift from $\delta(^{11}B) = 27.3$ ppm to 19.8 ppm for **9**, the latter being typical of bora-acyl species (for example, 19.6 ppm for the $[CpFe(CO)_2\{C(O)B(NDippCH)_2\}]$ complex);[28] 2) the $^{31}P$ NMR resonance ($\delta_P = 13.4$ ppm) is at a very similar position to that measured for *trans*-$[(Me_3P)Co(CO)_3(COMe)]$ ($\delta_P = 10.9$ ppm);[53] and 3) the IR spectrum of **9** shows bands at 2035, 1970, and 1949 $cm^{-1}$ for the carbonyl ligands and a strong absorption at 1655 $cm^{-1}$ for the bora-acyl moiety (cf. 1603 $cm^{-1}$ for the $[CpFe(CO)_2\{C(O)B(NDippCH)_2\}]$ complex). The labile nature of **9** hampers attempts to determine metrical parameters by X-ray crystallography; however the *trans* configuration of the phosphine and bora-acyl ligands can be established by low-temperature $^{13}C$ NMR measurements in $[D_8]$THF. These reveal a broad bora-acyl resonance at $\delta_C =$ 272 ppm and (crucially) a single CO signal at $\delta_C = 198$ ppm with a $^2J_{PC}$ coupling constant (18.9 Hz) diagnostic of a *cis* arrangement of the carbonyl and $PMe_3$ ligands (see the Supporting Information).[54]




***Scheme 3.*** Conversion of **4** into **6** via migratory insertion and bora-acyl intermediate **9**. Key reagents/conditions: a) $PMe_3$, $C_6H_6$, room temperature, $C_6D_6$, 5 min; b) room temperature, $C_6H_6$, 24 h.

The formation of **9** from **4** takes 5 min at room temperature, and **9** itself can be manipulated for ca. 10 min in $C_6D_6$ before significant decarbonylation to boryl complex **6** is observed.[55] The onward conversion of bora-acyl species **9** into boryl complex **6** follows a first-order rate law with a half-life of circa 1 h in $C_6D_6$. It is therefore proposed that **4** undergoes boryl migration to generate a 16-electron bora-acyl complex (possessing a vacant coordination site), which is rapidly trapped by $PMe_3$ to give **9** (Scheme 3). While such a mechanism would necessarily generate a *cis* isomer of **9**,[52] it is proposed that rapid isomerization (to give the observed *trans* intermediate) is driven by the steric requirements of the phosphine and bora-acyl ligands. Subsequent extrusion of CO from **9** to generate **6** is clearly slower than seen previously for 3d metal bora-acyl complexes featuring all-carbonyl ligand sets (such that **9** can be observed spectroscopically),[28] presumably as a result of enhanced metal-to-CO back bonding in the presence of a $PMe_3$ co-ligand.

The formation of bora-acyl species **9** from **4** represents, to our knowledge, the first example of carbonyl migratory insertion into an electron-precise M–B single bond. With this in mind, boryl migration to other unsaturated cobalt-bound ligands was targeted. The insertion of C–C multiple bonds into M–B linkages is known to be a key mechanistic step in a number of borylation procedures utilizing noble-metal catalysts. Thus, we targeted alkene insertion into Co–B bonds to generate a $[CoCR_2CR_2(boryl)]$ function. Given the propensity of cobalt-bound alkyl groups themselves to undergo CO insertion, however, we employed a 1,3-diene in the hope of generating a more tractable (less labile) $\eta^3$-allyl product. Accordingly, the reaction of **4** with 2,3-dimethyl-1,3-butadiene proceeds via insertion of the diene into the Co–B bond (with accompanying loss of CO) and leads to the formation of the $\eta^3$-allyl species **10** (Scheme 4). Since **10** is an orange oil, the corresponding triphenylphosphine complex, **11**, was formed (by reaction with $PPh_3$) to allow structural authentication by X-ray crystallography (Scheme 4). The structural metrics of **11** are largely in line with related $Co^I$ $\eta^3$-allyl complexes; its formation, however, provides further evidence of the unprecedented lability of the 18-electron boryl complex **4** towards the insertion of unsaturated substrates under thermal conditions.




***Scheme 4.*** Alkene insertion into the Co-B bond of **4**. Key reagents/conditions: a) 2,3-dimethylbutadiene, $C_6H_6$, 55 °C, 60 h; b) $PPh_3$, $C_6H_6$, room temperature, 1 h. Molecular structure of **11** as determined by X-ray crystallography.[56] Ellipsoids are set at 50% probability; solvate and H atoms omitted, and phenyl/Dipp groups shown in wireframe format for clarity. Bond lengths [Å] and angles [°]: Co1–P2 2.1737(6), Co1–C23 1.769(2), Co1–C25 2.109(2), Co1–C26 2.037(2), Co1–C27 2.129(3), C25–C26 1.397(4), C26–C27 1.409(4), C27–C28 1.525(3), C28–B29 1.584(3); C25-C26-C27-C28 40.41(7).

In conclusion, cobalt boryl complexes are shown not only to be systematically accessible, but to possess chemical lability that is highly dependent on the nature of the *trans* substituent. While more electron-rich systems give rise to Co–B bonds, which will survive exposure even to very strong acid, a carbonyl-only ancillary ligand set gives rise to a much more reactive metal–ligand bond. The boryl fragment in $[(OC)_4Co\{B(NDippCH)_2\}]$ undergoes unprecedented migratory insertion reactivity with CO, thereby opening up a new pathway for substitution processes. Moreover, when combined with an alkene substrate, crystallographic evidence of C=C insertion can be obtained, thereby demonstrating a key step in a number of metal-mediated borylation processes typically the preserve of noble metals.

## Experimental Section

Synthetic and characterization details for compound **4** are given below. The corresponding data for all other new compounds, details of the DFT calculations, and all CIFs can be found in the Supporting Information.

$[Co(CO)_4\{B(NDippCH)_2\}]$ (**4**): **5** (750 mg, 0.947 mmol) and $[Cu(MeCN)_4]BF_4$ (460 mg, 1.46 mmol) were dissolved in acetonitrile (25 mL) under an atmosphere of CO and UV-irradiated with stirring at room temperature. After 4 h, volatiles were removed from the yellow solution in vacuo, and the solid residue was extracted with pentane (3 × 5 mL). The volume of the filtered solution was decreased (ca. 0.5 mL); cooling to −35 °C gave colorless crystals of **4** (397 mg, 0.710 mmol, 75 %). $^1$H NMR ($C_6D_6$, 400 MHz): $\delta = 1.15$ (12 H, d, $^3J =$ 6.7 Hz, CH*Me*$_2$), 1.34 (12 H, d, $^3J = 6.7$ Hz, CH*Me*$_2$), 3.23 (4 H, septet, $^3J = 6.8$ Hz, C*H*Me$_2$), 6.43 (2 H, s, NCH), 7.13–7.24 ppm (6 H, m, $C_6H_3i$Pr$_2$). $^{13}$C NMR (APT, $C_6D_6$, 126 MHz): $\delta = 23.7$ ($CH_3$), 26.9 ($CH_3$), 28.9 (*C*HMe$_2$), 124.5 (CH-aryl), 125.2 (NCH), 128.9 (CH-aryl), 139.8 (C-aryl), 147.5 (C-aryl), 196.6 ppm (3 CO). $^{11}$B{$^1$H} NMR ($C_6D_6$, 128 MHz): $\delta = 27.3$ ($\omega_{1/2} = 173$ Hz). IR (KBr disc): $\nu_{CO}$ 2092, 2030, 2011, 1980 cm$^{-1}$. EI-MS 502.2 ([M−2 CO]$^+$, 8 %), 474.2 ppm ([M−3 CO]$^+$, 6 %). Elemental analysis calcd (%) for $C_{30}H_{36}BCoN_2O_4$: C 64.53, H 6.50, N 5.02 %; found: C 65.08, H 6.64, N 4.88 %. Crystallography: $C_{30}H_{36}BCoN_2O_4$, $M_r = 558.37$, monoclinic, $P2_1/c$, $a = 16.9460(5)$, $b = 9.4661(3)$, $c = 18.5384(5)$ Å, $\beta = 98.999(3)°$, $V = 2937.19(15)$ Å$^3$, $Z = 4$, $\rho_c = 1.263$ g cm$^{-3}$, $T = 150$ K, $\lambda =$ 1.54180 Å, 16252 reflns collected, 6081 independent [$R$(int) = 0.032], which were used in calculations. $R_1 = 0.0344$, $wR_2 = 0.0837$ for observed unique reflns [I > 2σ(I)] and $R_1 = 0.0379$, $wR_2 = 0.0860$ for all unique reflns. Max. and min. residual electron densities 0.32 and −0.41 e Å$^{-3}$.

**Keywords:** boron · boryl ligands · carbonyl ligands · cobalt · insertion reactions

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