

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 (–BR₂) fragment (typically using Rh, Ir, Pd, or Pt), and so the fundamental patterns of reactivity of complexes of the type L_nMBR₂ 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 dⁿ configurations (*n* ≠ 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 [(Ph₃P)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]

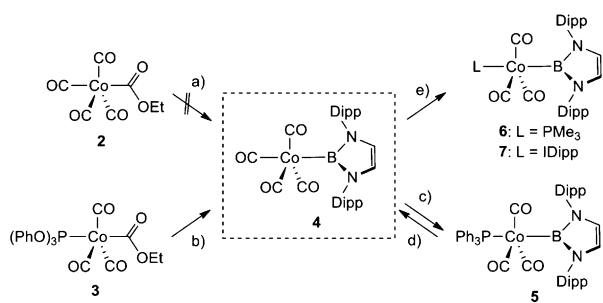
In initial studies, the reactions of *trans*-[LCo(CO)₃{C(O)OEt}] (L = CO (**2**), P(OPh)₃ (**3**)) with boryllithium **1** were studied (Scheme 1). Although tetra-carbonyl-supported cobalt ester **2** quantitatively yields the hydroborane HB(NDippCH)₂, phosphite-ligated **3** gives boryl complex **4** 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) $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$, CO (1 atm.), $h\nu$, MeCN, room temperature, 4 h; e) for **6**: PMe_3 , toluene, room temperature, 24 h, for **7**: IDipp ($\text{IDipp} = \text{C}(\text{NDippCH})_2$), C_6D_6 , room temperature, 2 weeks.

prove difficult to obtain analytically pure, and unlike recently reported d-block $\text{B}(\text{NDippCH})_2$ 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).

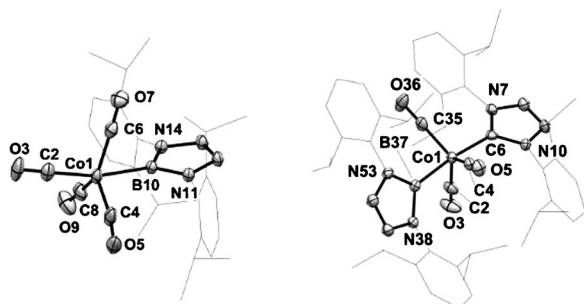
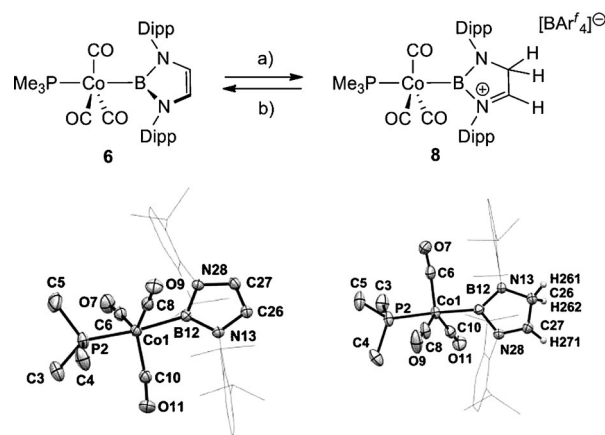


Figure 1. Molecular structures of **4** (left) and **7** (right), as determined by X-ray crystallography.^[56] Ellipsoids are set at 50% probability; H atoms omitted and Dipp groups shown in wireframe format for clarity. Key bond lengths [Å] and angles [$^{\circ}$]: For **4**: Co1–B10 2.076(2), Co1–C2 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 $[\text{LCo}(\text{CO})_3\{\text{B}(\text{NDippCH})_2\}]$ 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 $[\text{LCo}(\text{CO})_3\{\text{B}(\text{NDippCH})_2\}]$ (**6**: $\text{L} = \text{PMe}_3$; **7**: $\text{L} = \text{IDipp}$), 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 $[\text{H}(\text{OEt}_2)_2][\text{BAR}^f_4]$ [$\text{Ar}^f = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$]. Under such conditions, **4** decomposes rapidly to give the hydroborane $\text{HB}(\text{NDippCH})_2$, 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**.



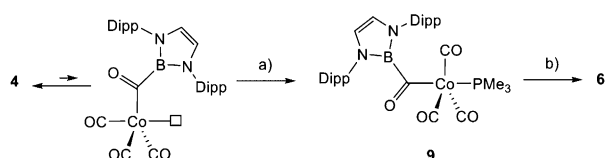
Scheme 2. Resistance of the Co–B bond in **6** to strong acid. Key reagents/conditions: a) $[\text{H}(\text{OEt}_2)_2][\text{BAR}^f_4]$, CH_2Cl_2 , room temperature; b) silica gel, CH_2Cl_2 . Molecular structures of **6** and of the cationic component of **8**, as determined by X-ray crystallography.^[56] 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) $^{\circ}$; 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 ($\delta(^{11}\text{B}) = 55.8$ 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 $\delta(^1\text{H}) = 9.21$ (1 H) and 5.02 ppm (2 H) for the NCH and NCH₂ 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**: $d(\text{C}=\text{C}) = 1.470(4)$ 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 $[\text{Cp}^*\text{Fe}(\text{CO})_2\{\text{B}(\text{NDippCMe})_2\text{CH}\}]^+$, 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 $\delta(^{11}\text{B}) = 27.3$ ppm to 19.8 ppm for **9**, the latter being typical of bora-acyl species (for example, 19.6 ppm for the $[\text{CpFe}(\text{CO})_2\{\text{C}(\text{O})\text{B}(\text{NDippCH})_2\}]$ complex);^[28] 2) the ^{31}P NMR resonance ($\delta_{\text{P}} = 13.4$ ppm) is at a very similar position to that measured for *trans*- $[(\text{Me}_3\text{P})\text{Co}(\text{CO})_3(\text{COMe})]$ ($\delta_{\text{P}} = 10.9$ 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 $[\text{CpFe}(\text{CO})_2\{\text{C}(\text{O})\text{B}(\text{NDippCH})_2\}]$ 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 $[\text{D}_8]\text{THF}$. These reveal a broad bora-acyl resonance at $\delta_{\text{C}} = 272$ ppm and (crucially) a single CO signal at $\delta_{\text{C}} = 198$ ppm with a $^2J_{\text{PC}}$ coupling constant (18.9 Hz) diagnostic of a *cis* arrangement of the carbonyl and PMe_3 ligands (see the Supporting Information).^[54]

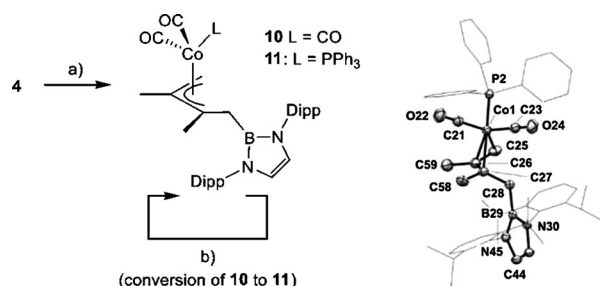


Scheme 3. Conversion of **4** into **6** via migratory insertion and bora-acyl intermediate **9**. Key reagents/conditions: a) PMe_3 , C_6H_6 , room temperature, C_6D_6 , 5 min; b) room temperature, C_6H_6 , 24 h.

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 $[\text{CoCR}_2\text{CR}_2(\text{boryl})]$ 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) η^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 η^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 η^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 $-35^\circ C$ gave colorless crystals of **4** (397 mg, 0.710 mmol, 75 %). 1H NMR (C_6D_6 , 400 MHz): δ = 1.15 (12 H, d, 3J = 6.7 Hz, $CHMe_2$), 1.34 (12 H, d, 3J = 6.7 Hz, $CHMe_2$), 3.23 (4 H, septet, 3J = 6.8 Hz, $CHMe_2$), 6.43 (2 H, s, NCH), 7.13–7.24 ppm (6 H, m, $C_6H_3iPr_2$). ^{13}C NMR (APT, C_6D_6 , 126 MHz): δ = 23.7 (CH_3), 26.9 (CH_3), 28.9 ($CHMe_2$), 124.5 (CH-aryl), 125.2 (NCH), 128.9 (CH-aryl), 139.8 (C-aryl), 147.5 (C-aryl), 196.6 ppm (3 CO). $^{11}B\{^1H\}$ NMR (C_6D_6 , 128 MHz): δ = 27.3 ($\omega_{1/2}$ = 173 Hz). IR (KBr disc): ν_{CO} 2092, 2030, 2011, 1980 cm^{-1} . EI-MS 502.2 ($[M-2CO]^+$, 8 %), 474.2 ppm ($[M-3CO]^+$, 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, β = 98.999(3)°, V = 2937.19(15) Å³, Z = 4, ρ_c = 1.263 g cm⁻³, T = 150 K, λ = 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 [$I > 2\sigma(I)$] 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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- [56] CCDC 1048375 (**4**), 1048376 (**6**), 1048377 (**7**), 1048378 (**8**), and 1048379 (**11**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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