ORGANOMETALLICS

Volume 26, Number 16, July 30, 2007

Communications

Metallaboratranes: The M→B Dative Bond as a Ligand Activating Function in the Phosphaboration of Carbon Monosulfide[†]

Ian R. Crossley, Anthony F. Hill,* and Anthony C. Willis

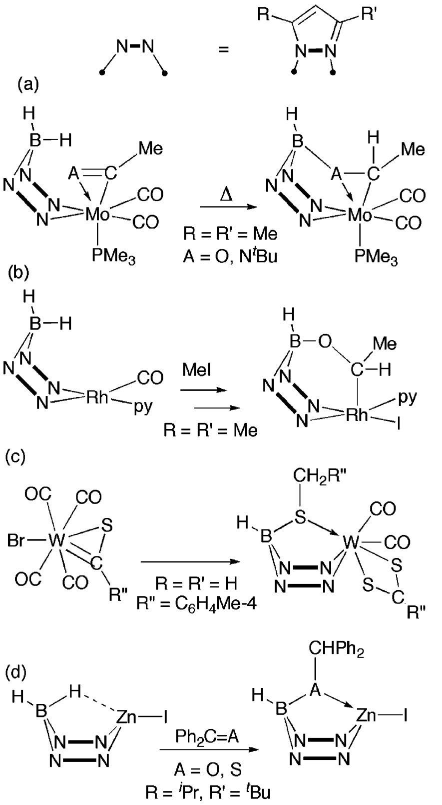
Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory, Australia

Received May 3, 2007

Summary: The reaction of Na[$H_2B(mt)_2$] (mt = methimazolyl) with [RhCl(CO)($PPh_3)_2$] proceeds via simple metathesis to provide the complex [Rh(CO)(PPh_3){$H_2B(mt)_2$}]; however, with [RhCl(CS)($PPh_3)_2$] C,C-phosphaboration of the thiocarbonyl ligand occurs, with formation of the novel cage complex [RhH(PPh_3){η^2(C,S),κ^2S′,S″-SC(PPh_3)BH($mt)_2$}].

Perhaps the most endearing feature of Trofimenko's poly(pyrazolyl)borates[1] is that they can generally be relied upon to do little more than spectate. Thus, while there are scattered examples of the BH_2 group of dihydrobis(pyrazolyl)borates entering into reactions with coligands (vide infra), these remain rare. The most common noninnocent behavior of this ligand involves the formation of *hemilabile* three-center, two-electron B−H−M interactions, which very rarely proceed to B−H activation. Examples of such behavior that have some relevance to the present report include the hydroboration of acyls, iminoacyls, thioacyls, and thioketones. Thus, heating the complexes [Mo(ACMe)(CO)$_2$(PMe$_3$){H$_2$B(pz^{Me2})$_2$}] (A = O, N^{t}Bu; pz^{Me2} = 3,5-dimethylpyrazolyl) provides the internally hydroborated acyl or iminoacyl derivatives [Mo(CO)$_2$(PMe$_3$){η^2(*A,C*),κ^2*N,N′*-MeCHABH(pz^{Me2})$_2$}] (Scheme 1a),[2] while the reaction of [Rh(CO)(py){H$_2$B(pz^{Me2})$_2$}] with iodomethane provides [RhHI-

Scheme 1. Intramolecular Hydroboration of Ligands by Pyrazolylborates



---

* To whom correspondence should be addressed. E-mail: a.hill@anu.edu.au.

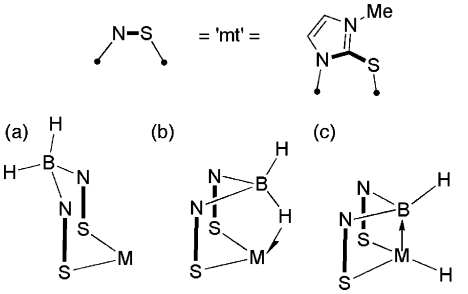
[†] Dedicated to Professor Warren Roper, in recognition of his pioneering, inspirational, and ongoing contributions to the chemistry of transition-metal thiocarbonyls and boryls.

(1) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Poly(pyrazolyl)borate Ligands*; Imperial College Press: London, 1999.

(2) Pizzano, A.; Sánchez, L.; Gutiérrez, E.; Monge, A.; Carmona, E. *Organometallics* **1995**, *14*, 14.

10.1021/om700433q CCC: $37.00 © 2007 American Chemical Society
Publication on Web 07/04/2007

Chart 1. Coordination Possibilities for the $H_2B(mt)_2$ Ligand: (a) κ^2S,S′; (b) κ^3H,S,S′; (c) κ^3B,S,S′ (Metallaboratrane)



$(py)\{\kappa^3 C,N,N'$-CMeOBH$(pz^{Me2})_2\}]$, which evolves on gentle heating to the isomeric $[RhI(py)\{\kappa^3 C,N,N'$-CHMeOBH$(pz^{Me2})_2\}]$ (Scheme 1b).[3] The sequential reaction of $[W(\equiv CR)Br(CO)_4]$ ($R = C_6H_4Me$) with sulfur and $K[H_2B(pz)_2]$ (pz = pyrazolyl) provides the heteroscorpionate complex $[W(S_2CR)(CO)_2\{\kappa^3 N,N',S$-$RCH_2SBH(pz)_2\}]$ (Scheme 1c),[4] and it was subsequently shown that a related thiolatobis(pyrazolyl)borate ligand could be obtained via the reaction of $[ZnI\{H_2B(pz^{tBuiPr})_2\}]$ with thiobenzophenone (Scheme 1d).[5] These transformations (Scheme 1) have in common that the B−H bond of the borate (ultimately) adds across the carbon−heteroatom linkage, delivering one hydrogen atom to the carbon with the boron binding to the heteroatom—the regiochemistry typical of the hydroboration of polar C−heteroatom multiple bonds in the absence of metals.

Metallaboratranes are complexes that feature a metal−boron dative bond, housed within a cage structure,[6−10] generally supported by methimazolyl (mt) buttresses. With few exceptions,[8,10] these are all derived from intermediate complexes of hydrotris(methimazolyl)- or dihydrobis(methimazolyl)borates[6] or their N-substituted derivatives.[7,9] One such metallaboratrane is the complex $[IrH(CO)(PPh_3)\{BH(mt)_2\}]$$(Ir{\rightarrow}B)^8$ (**1a**),[6f,11] which provided the first example where only two methimazolyl groups buttress the M→B dative bond. All previous examples had involved three mt groups, with the attendant possibility that the M−B association might simply be a corollary of cage geometry. Thus, one might envisage a bis(methimazolyl)borane chemistry that parallels that of the more extensively explored tris(methimazolyl)borane complexes. The iridaboratrane **1a** arises from the reaction of Vaska's complex with $Na[H_2B(mt)_2]$, presumably via the undetected intermediate complex $[Ir(CO)(PPh_3)\{H_2B(mt)_2\}]$ (**2a**), which subsequently undergoes insertion of the iridium center into one B−H bond. In contrast, we have recently reported the complexes $[RhL_2\{H_2B(mt)_2\}]$ (L_2 = cod, L = CO, CNR),[12] in which the B−H bond remains intact, albeit in agostic association with the rhodium center. Thus, there

---

(3) Yeston, J. S.; Bergman, R. G. *Organometallics* **2000**, *19*, 2947.

(4) Hill, A. F.; Malget, J. M. *J. Chem. Soc., Dalton Trans.* **1997**, 2003

(5) Ghosh, P.; Parkin, G. *Chem. Commun.* **1998**, 413.

(6) (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759. (b) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446. (c) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913. (d) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221. (e) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083. (f) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (g) Crossley, I. R.; Hill, A. F. *Organometallic* **2004**, *23*, 5656. (h) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289.

(7) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626.

(8) (a) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611. (b) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 12056.

(9) (a) Landry, V.; Melnick, J. G.; Buccella, D.; Pang, K.; Ulichny, J. C.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 2588. (b) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056.

(10) Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350.

(11) We recommend that line formulas for metallaboratranes be appended with the notation $(M{\rightarrow}B)^n$, where *n* is the total number of electrons initially associated with the metal d orbitals, including the pair assigned to the dative M→B bond: Hill, A. F. *Organometallics* **2006**, 25, 4741.

(12) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Smith, E. R. *Organometallics* **2006**, *25, 2242*.

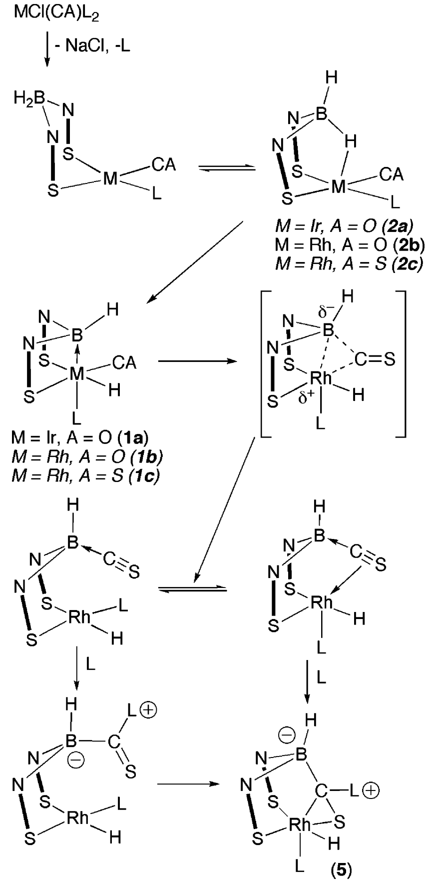
(13) (a) Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680. (b) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *Dalton Trans.* **2000**, 891. (c) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I.; Ortner, K.; Alberto, R. *J. Am. Chem. Soc.* **2000**, *122*, 11240. (d) Garcia, R.; Xing, Y.-H.; Paulo, A.; Domingos, A.; Santos, I. *Dalton Trans.* **2002**, 4236. (e) Philson, L. A.; Alyounes, D. M.; Zakharov, L. N.; Rheingold, A. L.; Rabinovich, D. *Polyhedron* **2003**, *22*, 3461. (f) Alvarez, H. M.; Tanski, J. M.; Rabinovich, D. *Polyhedron* **2004**, *23*, 395. (g) Graham, L. A.; Fout, A. R.; Kuehne, K. R.; White, J. L.; Mookherji, B.; Marks, F. M.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L. Rabinovich, D. *Dalton Trans.* **2005**, 171. (h) Alvarez, H. M.; Krawiec, M.; Donovan-Merkert, B. T.; Fouzi, M.; Rabinovich, D. *Inorg. Chem.* **2001**, *40*, 5736. (i) Kuan, S. L.; Leong, W. K.; Goh, L. Y.; Webster, R. D. *J. Organomet. Chem.* **2006**, *691*, 907. (j) Bailey, P. J.; Lorono-Gonzales, D. J.; McCormack, C.; Parsons, S.; Price, M. *Inorg. Chim. Acta* **2003**, *354*, 61. (k) Wang, Y.-L.; Cao, R.; Bi, W.-H. *Polyhedron* **2005**, *24*, 585. (l) Cammi, R.; Lanfranchi, M.; Marchio, L.; Mora, C.; Paiola, C.; Pellinghelli, M. A. *Inorg. Chem.* **2003**, *42*, 1769. (m) Foreman, M. R. St.-J.; Hill, A. F.; Tshabang, N.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 5593.

(14) (a) Hill, A. F.; Smith, M. K. *Chem. Commun.* **2005**, 1920. (b) Abernethy, R. J.; Hill, A. F.; Neumann, H.; Willis, A. C. *Inorg. Chim. Acta* **2005**, *358*, 1605.

(15) The term oxidative addition is used loosely in this context, since both hydrogen and boron are less electronegative than rhodium.

(16) **2b**: a mixture of $[RhCl(CO)(PPh_3)_2]$ (200 mg, 0.29 mmol) and $Na[H_2B(mt)_2]^{13m}$ (75 mg, 0.29 mmol) in CH_2Cl_2 (15 mL) was stirred anaerobically for 2 h, filtered, and concentrated to the onset of crystallization. Dilution with diethyl ether completed precipitation of the crude yellow product, which was recrystallized from a mixture of dichloromethane and hexane. Yield: 0.12 g (65%). IR (KBr): 2376 m (ν_{CO}), 2208 m (ν_{BHRh}), 1970 vs (ν_{CO}), 1383 s, 1190 s, 1111 s, 1094 s cm^{-1}. IR (CH_2Cl_2): 2350, 2338 (ν_{BH}), 1965 cm^{-1} (ν_{CO}). NMR (CD_2Cl_2, 25 °C): ^{1}H, δ_H 3.32 (s br, 6 H, NCH_3), 6.56, 6.78 (d × 2, 2H × 2, NCH═CHN, $^3J_{HH}$ = 2 Hz)), 7.25−7.27, 7.60−7.68 (m × 2, 15 H, C_6H_5); $^{31}P\{^1H\}$, δ_P 44.6 (d, $^1J_{RhP}$ = 151 Hz); $^{11}B\{^1H\}$, δ_B −4.7; $^{13}C\{^1H\}$, δ_C 160.9 (CS), 134.2 (d, J_{PC} = 11, $C^{2,6}$-(C_6H_5)), 132.1 (d, J_{PC} = 8 Hz, $C^{3,5}(C_6H_5)$), 130.0 (s, $C^4(C_6H_5)$), 122.2, 119.6 (NCHCHN), 35.0 (NCH_3), dd for RhCO not observed. ESI$^+$-MS (MeCN): *m/z* (%) 603 (18) $[M - H - CO]^+$. Satisfactory elemental microanalytical data were not obtained, due to the solution instability of the complex preventing successful fractional recrystallization. In solution, the compound slowly evolves to a complex inseparable mixture. **5**: a mixture of $[RhCl(CS)(PPh_3)_2]$ (100 mg, 0.14 mmol; δ_P 31.6, $^1J_{PRh}$ = 143 Hz) and $Na[H_2B(mt)_2]$ (40 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was stirred anaerobically for 2.5 h and then filtered, concentrated under reduced pressure, and diluted with diethyl ether to provide a microcrystalline powder. Yield: 0.065 g (72%). IR (KBr): 2336 m (ν_{BH}), 2177 m (unassigned), 2058 s (ν_{RhH}), 1380 s, 1175 s, 1092, 863 m cm^{-1} (ν_{CS} or ν_{BC}). NMR ($CDCl_3$, 25 °C): ^{1}H, −18.82 (ddd, 1 H, RhH, $^1J_{RhH}$ = 13, $^2J_{PH}$ = 8, $^3J_{PH}$ = 4 Hz), 3.30, 3.43 (s × 2, 3 H × 2, NCH_3), 6.00, 6.11, 6.56, 6.85 (d × 4, 1 H × 4, NCH, $^3J_{HH} \approx 2$ Hz); $^{31}P\{^1H\}$, δ_P 31.6 (s br), 46.6 (dd, $^1J_{RhP}$ = 159, $^3J_{PP}$ = 9 Hz); $^{11}B\{^1H\}$, δ_B −2.2 (hhw = 200 Hz); $^{13}C\{^1H\}$, 158.5, 157.5 (NCS), 134.4 (d, J_{PC} = 13 Hz, $C^{2,6}(C_6H_5)$), 126.8 (s, $C^4(C_6H_5)$), 127.6 (d, J_{PC} = 9 Hz, $C^{3,5}(C_6H_5)$), 123.7, 122.4, 117.9, 117.2 (NCHCHN), 35.5, 34.5 (NCH_3). Two sets of PC_6H_5 resonances are observed, one of which is sharp, while the other displays fluxional broadening (δ_C 135 ($C^{2,6}$), 132.5 (C^4), 128 ($C^{3,5}$)), which also obscures $C^1(C_6H_5)$ for the static phosphine. The η^2(C,S) resonance (expected to be a 32-line quadrupole broadened pattern) was not located. MS (MeOH): (i) accurate mass found *m/z* 909.115 269 (calcd for $[M - H]^+$ 909.111 673); (ii) low resolution *m/z* (%) 959 (11) $[M + CH_3OH + OH]^+$, 909 (42) $[M]^+$, 797 (14) $[M - mt]^+$, 647 (100) $[M - H - PPh_3]^+$. Crystallographic grade crystals were grown from a mixture of CH_2Cl_2 and Et_2O. Crystal data for **5**$\cdot 0.5Et_2O$: $C_{45}H_{42}BN_4P_2RhS_3 \cdot 0.5C_4H_{10}O$, M_w = 947.78, triclinic, $P\bar{1}$ (No. 2), a = 12.8506(5) Å, b = 13.0843(6) Å, c = 13.9351(6) Å, α = 85.869(3)°, β = 83.163(3)°, γ = 75.657(2)°, V = 2251.7(2) Å^3, Z = 2, ρ_{calcd} = 1.40 Mg m^{-3}, μ(Mo Kα) = 0.629 mm^{-1}, T = 200(2) K, orange plate, 7953 independent measured reflections, R1 = 0.034 and wR2 = 0.034 for 5774 independent observed absorption-corrected reflections ($I > 3\sigma(I)$, $2\theta \leq 50°$), 553 parameters, CCDC 603210.

Scheme 2. Syntheses and Mechanistic Proposal for the Formation of 2a and 5[a]



[a] L = PPh_3; compounds in italics were not isolated.

appears to be a fine balance between the three possible modes of $H_2B(mt)_2$ coordination depicted in Chart 1 that underpin the mechanistic sequence for metallaboratrane formation.[6f] The κ^3H,S,S' coordination mode appears to be particularly favorable and is often encountered for the $H_2B(mt)_2$ ligand and its N-substituted derivatives.[12−14] Indeed, the complexes $[Ti({=}NCMe_3)\{H_2B(mt)_2\}_2]$ and $[W(CO)\{H_2B(mt)_2\}]$ each feature one bidentate (κ^2S,S') and one tridentate (κ^3H,S,S') coordinated $H_2B(mt)_2$ ligand within the same complex.[14] To better understand the factors that control the degree of B−H activation en route to metallaboratrane formation, we have now investigated the reactions of $Na[H_2B(mt)_2]$ with the complexes $[RhCl(CA)(PPh_3)_2]$ (A = O, S). Both the replacement of iridium by rhodium and the substitution of CO for the strongly π-acidic CS are expected to reduce the propensity of the metal center toward "oxidative" addition.[15] We find that this does indeed allow the observation of the rhodium analogue of the putative intermediate: viz., $[Rh(CO)(PPh_3)\{H_2B(mt)_2\}]$ (**2b**). However, it transpires that in the case of $[RhCl(CS)(PPh_3)_2]$ the reaction proceeds quite differently in an unexpected direction.

We have previously shown that the reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = 1,5-cyclooctadiene) with $Na[H_2B(mt)_2]$ provides $[Rh(cod)\{\kappa^3H,S,S'\text{-}H_2B(mt)_2\}]$ (**3**), low-pressure carbonylation of which affords $[Rh(CO)_2\{\kappa^3H,S,S'\text{-}H_2B(mt)_2\}]$ (**4**). Since neither **3** nor **4** shows any signs of evolving into rhodaboratranes, we expected that complex **2b** might be similarly stable and isolable. This is indeed the case: a smooth reaction ensues between $[RhCl(CO)(PPh_3)_2]$ and $Na[H_2B(mt)_2]$ to provide **2b** in good yields. Spectroscopic data for **2b** are generally unremarkable,[16] other than to confirm the formulation as $[Rh(CO)(PPh_3)\{\kappa^3H,S,S'\text{-}H_2B(mt)_2\}]$ rather than a rhodaboratrane isomer, $[RhH(CO)(PPh_3)\{BH(mt)_2\}](Rh{\rightarrow}B)$[8] (**1b**). Thus, no hydride ligand is indicated by ^1H NMR or IR spectroscopy, the ^{31}P NMR resonance is sharp, indicating no significant interaction with the quadrupolar boron nucleus, and the ν_{CO} IR absorption occurs at a frequency typical of neutral rhodium(I) complexes. Notably, the similar compound $[Rh(CO)(PPh_3)\{HB(taz)_3\}]$ (taz = 4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl) has been described recently by Connelly via sequential treatment of $Na[HB(taz)_3]$ with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$, CO, and PPh_3.[10]

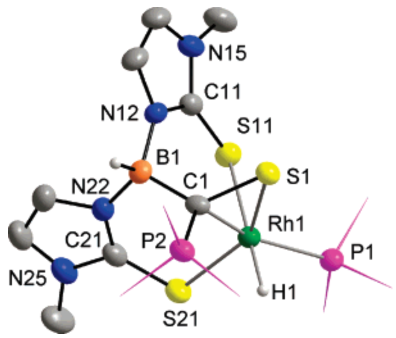


Figure 1. Molecular geometry of **5** in a crystal of **5**$\cdot0.5Et_2O$ (phenyl groups and methimazolyl H atoms omitted, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Rh1−S1 = 2.3345(8), Rh1−S11 = 2.5075(9), Rh1−S21 = 2.3460(9), Rh1−P1 = 2.2733(8), Rh1−C1 = 2.120(3), Rh1−H1 = 1.58(3), S1−C1 = 1.780(3), S11−C11 = 1.692(3), S21−C21 = 1.719(4), P2−C1 = 1.781(3), C1−B1 = 1.614(5); S11−Rh1−S21 = 87.75(3), S1−Rh1−P1 = 112.06(3), S21−Rh1−P1 = 102.16(3), S1−Rh1−C1 = 46.79(8), S21−Rh1−C1 = 99.18(9), Rh1−S1−C1 = 60.26(10), Rh1−S11−C11 = 106.65(12), Rh1−S21−C21 = 103.69(11), S1−C1−P2 = 110.31(18), S1−C1−Rh1 = 72.95(11), P2−C1−Rh1 = 119.70(16), S1−C1−B1 = 125.3(2), P2−C1−B1 = 112.2(2), Rh1−C1−B1 = 111.7(2).

The reaction of $Na[H_2B(mt)_2]$ with $[RhCl(CS)(PPh_3)_2]$ also provides a single complex, **5**. The spectroscopic data for **5** are, however, inconsistent with either the simple scorpionate complex $[Rh(CS)(PPh_3)\{H_2B(mt)_2\}]$ (**2c**) or the rhodaboratrane $[RhH(CS)(PPh_3)\{BH(mt)_2\}](Rh{\rightarrow}B)$[8] (**1c**), although an accurate mass determination (ESI^+-MS) confirmed the same elemental composition on the basis of the $[M - H]^+$ peak.[16] The integrity of the terminal thiocarbonyl ligand is clearly lost, as evidenced by the conspicuous absence of characteristic low-field ^{13}C NMR or IR spectroscopic signatures.[17,18] The spectroscopic data indicate that the complex has no molecular element of symmetry, and most remarkably, the $^{31}P\{^1H\}$ NMR spectrum comprises two resonances, one of which is a very slightly broadened singlet, while the other shows coupling to rhodium ($^1J_{RhP}$ = 159 Hz) and weak coupling to phosphorus (9 Hz), suggesting that only one phosphine remains bound directly to rhodium. A hydride resonance is observed (δ_H −18.82) which displays couplings to the rhodium ($^1J_{RhH}$ = 13 Hz) and two phosphorus nuclei ($^2J_{PH}$ = 9, $^3J_{PH}$ = 5 Hz), the latter being lost upon ^{31}P decoupling. Given that neither of the ^{31}P resonances showed significant broadening, direct coordination to boron could be excluded, while the sharply resolved hydride resonance

---

(17) Terminal thiocarbonyl ligands typically give rise to a very intense IR absorption in the range 1150−1400 cm^{-1}: e.g., 1327 cm^{-1} for $[Rh(CS)(PPh_3)_2\{H_2B(bta)_2\}]$[18] and 1309 cm^{-1} for $[RhCl(CS)(PPh_3)_2]$. Although a medium-intensity band occurs in this region for **5** (IR (KBr) 1380 cm^{-1}), it is significantly less intense than expected and corresponds to a similar band observed at 1382 cm^{-1} for **1b** and may therefore be attributed to the methimazolyl heterocycles. For a review of metal thiocarbonyls see: Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

(18) (a) Cartwright, J.; Harman, A.; Hill, A. F. *J. Organomet. Chem.* **1990**, *396*, C31. (b) Anderson, S.; Harman, A.; Hill, A. F. *J. Organomet. Chem.* **1995**, *498*, 251.

pointed toward the absence of any direct metal−boron bond. These data taken together point toward both one phosphine and the boron having migrated to the thiocarbonyl ligand (Scheme 2), a formulation which was confirmed crystallographically.[16] The results of this study are summarized in Figure 1, which reveals that the "RhH(PPh_3)" group is coordinated by a novel zwitterionic phosphonioborate in which the two methimazolyl arms act as conventional σ-thione donors, while the third donor involves η^2(C,S) coordination of the phosphoniothiocarbonyl group. Although this type of ligand is unprecedented, phosphoniothioacyl ($[L_nM_x\{SCR(PR'_3)\}]$; R = H, SMe, Ph)[19] and thiocarbonylphosphine ($[L_nM_x(SCPR'_3)]$)[20] complexes have been previously observed. The C1−S1 separation of 1.780(3) Å lies at the long end of the range observed for π-coordinated thioketones and thioaldehydes (1.70−1.78 Å)[21] and is significantly longer than separations observed for nonconjugated examples of these free molecules (1.57−1.62 Å).[21] The pyramidalization at C1 as a result of π-C=S coordination is modest, with the sum of (non-Rh) angles at C1 being 347.8°. The Rh1−C1 and Rh1−S1 bond lengths fall within the range typical of single bonds between rhodium and these elements.

The mechanism by which **5** forms calls for some comment. We may assume by analogy with the isolation of **2b** herein and of **1a** previously that the hypothetical rhodaboratrane **2c** is an intermediate. We are unaware of any previous reports of the migration of PPh_3 to a thiocarbonyl ligand, despite a plethora of complexes in which both these ligands coexist bound to metals from groups 6−10 in a range of oxidation states, complex charges, and degrees of coordinative (un)saturation. Furthermore, intermolecular nucleophilic attack by phosphine is unlikely for CS bound to an electron-rich center. We therefore suspect that the key step involves insertion of the thiocarbonyl ligand into the dative Rh→B bond. Nothing is known at present concerning the nature of the M→B dative bond with regard to insertion chemistry. Indeed, no reactions of M→B bonds have been reported, other than the oxidative cleavage of the Fe→B bond of a ferraboratrane by halocarbons or peroxides.[9b] However, the insertion of CS into the M−B (M = Ru, Os) bond of σ-boryl ligands has been briefly mentioned.[22] The thiocarbonylborane intermediate might exist in one of two tautomeric forms, depending on the degree of association of the CS group with rhodium, and the preferred coordination mode remains open to conjecture. However, the form that would appear most susceptible to nucleophilic attack (by PPh_3 liberated in the first step) would involve a dissociated CS group. Although the thiocarbonylboranes $R_3B\leftarrow CS$ do not appear to have been considered in the literature, $H_3B\leftarrow CO$ is well documented,[23] including the activation of the CO "ligand" toward nucleophiles: e.g., amines.[24] The final step involving coordination of the thione group to rhodium could in principle occur in a σ-S or (as observed) π-C,S manner.[20] The latter is disfavored in the case of the methimazolyl donors, not only due to attendant cage strain but also because the C−S multiple bonding is already mesomerically reduced through conjugation into the heterocyclic π-system. However, these factors do not operate for the phosphonioborane thione such that the adoption of the π-C,S mode of coordination presumably reflects the strong π-basicity of the Rh(I) center, which is otherwise devoid of π-acidic ligands.

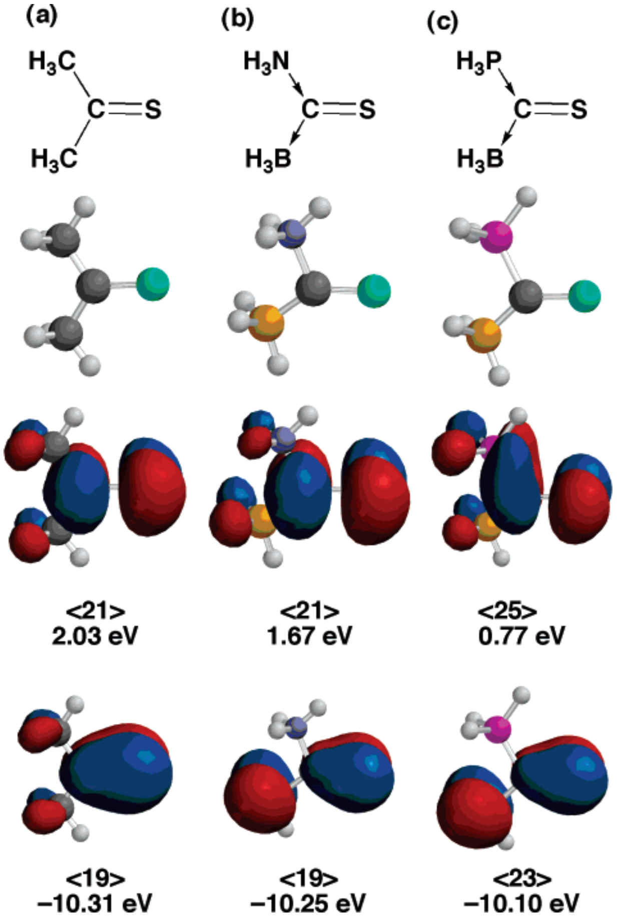


Figure 2. Optimized geometries (MP2, 6-31G*) and π-HOMO and π-LUMO topologies for the molecules (a) $S{=}C(CH_3)_2$, (b) $S{=}C(NH_3)(BH_3)$, and (c) $S{=}C(PH_3)(BH_3)$.

The question remains as to why the putative thiocarbonyl rhodaboratrane **2c** evolves into **5**, while the carbonyl analogue **2b** does not. This may be answered in part by a consideration of the hypothetical molecules $H_3N\rightarrow C({=}A)\rightarrow BH_3$ (A = O (**6**), S (**7**)) and $H_3P\rightarrow C({=}S)\rightarrow BH_3$ (**8**), which are isoelectronic with $A{=}C(CH_3)_2$. The optimized geometries and associated frontier orbitals (MP2, 6-31G*)[25] for **7** and **8** are shown in Figure 2, with energies not dissimilar to those obtained for thiopropanone by the same method. In the case of **6**, however, optimization leads to dissociation of ammonia and generation of $H_3B\leftarrow CO$. Similarly, optimization of the imino analogue (A = NCH_3) results in dissociation to the isonitrile−borane adduct $H_3B\leftarrow CNMe$. Thus, for the molecules $H_3B\leftarrow CA$ the degenerate

---

[19] (a) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *J. Organomet. Chem.* **1984**, *270*, 251. (b) Li, J.; Miguel, D.; Morales, D.; Riera, V.; Aguirre-Perez, A.; Garcia-Granda, S. *Dalton Trans.* **2003**, 3264. (c) Kreissl, F. R.; Ullrich, N.; Wirsing. A.; Thewalt, U. *Organometallics* **1991**, *10*, 3275. (d) Alvarez, B.; Garcia-Granda, S.; Jeannin, Y.; Miguel, D.; Miguel, J. A.; Riera, V. *Organometallics* **1991**, *10*, 3005. (e) Ferguson, G.; Gallagher, J. F.; Jennings, M. C.; Coughan, S.; Spalding, T. R.; Kennedy, J. D.; Fontaine, X. L. R. *J. Chem. Soc., Chem. Commun.* **1994**, 1595.

[20] (a) Miguel, D.; Morales, D.; Riera, V.; Garcia-Granda, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3034. (b) Miguel, D.; Li, J.; Morales, D.; Riera, V.; Garcia-Granda, S. *Organometallics* **2001**, *20*, 3063. (c) Klein, H.-F.; Schmidt, A.; Florke, U.; Haupt, H.-J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2385.

[21] Cambridge Crystallographic Data Centre January 2006 Release, Conquest Version 1.8. (b) Fischer, H.; Stumpf, R.; Roth, G. *Adv. Organomet. Chem*. **1998**, *43*, 125.

[22] Irvine, G. J. Ph.D. Thesis, University of Auckland. Referred to in: Irvine, G. J.; Lesley, M. J.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

[23] (a) Fehlner, T. P.; Koski, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 409. (b) Fu, Y.-C.; Hill, G. R. *J. Am. Chem. Soc.* **1962**, *84*, 353.

[24] Parry, R. W.; Nordman, C. E.; Carter, J. C.; Terhaar, G. *Adv. Chem. Ser.* **1964**, *No. 42*, 302.

[25] SPARTAN 04, Macintosh, Version 1.0.3, Wavefunction Inc.

LUMOs associated with the C═A π-bond (MP2, 6-31G*)[25] are significantly lower in energy for A = S (0.89 eV) than for E = O (2.74 eV), NCH_3 (4.12 eV), pointing toward enhanced electrophilicity for $H_3B \leftarrow CS$, with respect to assuming a π-acidic η^2(C,S) role.

To conclude, it has been demonstrated that the fine balance between the formation of bis(methimazolyl)borate and metallaboratrane complexes may be dependent on the nature of the metal (4d vs 5d), with all other things being equal, allowing the isolation of $[Rh(CO)(PPh_3)\{\kappa^3 H,S,S'\text{-}H_2B(mt)_2\}]$ and $[IrH(CO)(PPh_3)\{BH(mt)_2\}](Ir\rightarrow B)$[8]. Furthermore, the M→B bond has been shown to not be inert but, rather, a functionality capable of activating a coligand. While the thiocarbonyl ligand is a somewhat exotic case, this principle of two-site substrate activation has considerable scope for investigation with other more conventional ligands. The hypothetical stability of $S{=}C(NH_3)(BH_3)$ and instability of $O{=}C(NH_3)(BH_3)$ provides an unusual inverse of the defunct double-bond rule, wherein the presence of multiple bonding between carbon and a heavier element actually contributes to increased stability relative to the lighter element analogue.

Acknowledgment. We thank the Australian Research Council (ARC) for financial support (Grant No. DP034270). We are grateful to Professor Peter Gill for helpful discussions and advice.

Supporting Information Available: A CIF file giving full details of the crystal structure determination of **5**·$0.5Et_2O$ (CCDC 603210). This material is available free of charge via the Internet at http://pubs.acs.org.

OM700433Q