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Notes

Polyazolyl Chelate Chemistry. 13. An Osmaboratrane[1]

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Summary: The reaction of [Os(C_6H_5)Cl(CO)(PPh_3)$_2$] with Na[HB(mt)$_3$] (mt = methimazolyl) results in benzene elimination and the formation of the first osmaboratrane [B(mt)$_3$Os(CO)(PPh_3)](Os→B), the crystal structure of which reveals a somewhat long transannular dative bond between osmium(0) and boron(III).

Introduction

Although metal−boron dative bonds have long been postulated,[2,3] the only structurally authenticated example is the ruthenaboratrane [{B(mt)$_3$}Ru(CO)(PPh_3)]-(*Ru*→*B*) (**1a**; mt = methimazolyl).[4] This complex involves a transannular dative bond from ruthenium(0) to the bridgehead boron(III) of a cage structure derived from the hydrotris(methimazolyl)borate ligand, HB-(mt)$_3$. It might therefore be considered isoelectronic with Parshall's archetypal salt Na[H_3BRe(CO)$_5$](*Re*→*B*)[2] with both formally being based on octahedrally coordinated d^8-metal centers. Given the lack of structural data for metal−boron dative bonding other than for **1a**, and the caveat that "simple" ruthenium boryls had not been structurally characterized,[5−7] we have investigated the synthesis of an osmaboratrane. In the interim, a considerable body of structural data for osmium boryls has emerged from the studies of Roper and Wright,[8] and this has now included ruthenium examples. Furthermore, structural data are also available for a range of base-stabilized osmium borylene complexes.[9] Thus the wealth of structural data for 2c-2e Os−B bonding provides a suitable basis for interpreting the structural features.[10]

Results and Discussion

The ruthenaboratrane [B(mt)$_3$Ru(CO)(PPh_3)](*Ru*→*B*) (**1a**) was produced from the reactions of the σ-vinyl complexes [Ru(CH═CHR)Cl(CO)(PPh_3)$_2$] (R = H, Ph, CPh_2OH) with the salt Na[HB(mt)$_3$],[4] and accordingly a similar approach was explored for the preparation of the osmium analogue. Unfortunately, the analogous σ-vinyl complexes of osmium have yet to be isolated via the routes employed for ruthenium: [OsHCl(CO)-(PPh_3)$_3$] fails to hydroosmate alkynes[12] and catalyzes the conversion of bis(*trans*-β-styryl)mercury to ethynyl benzene, diphenylbutadiyne, and styrene and of bis-(phenylethynyl)mercury to diphenylbutadiyne.[12,13] The corresponding σ-phenyl complex [Os(C_6H_5)Cl(CO)(PPh_3)$_2$] (**2**) is however readily obtained from the reaction of [OsHCl(CO)(PPh_3)$_3$] and diphenylmercury[13] and has been shown to serve as a precursor for the introduction of the hydrotris(pyrazolyl)borate ligand (Scheme 1).[14]

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(1) For part 12 see: Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446.

(2) Parshall, G. W. *J. Am. Chem. Soc.* **1964**, *86*, 361.

(3) For a review of metal−boron dative bonding see: Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; 1982; Pergamon: Oxford, Vol. 6, pp 880−886. However, the identity of such complexes has been questioned: Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786.

(4) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.

(5) The boryl complex [Ru{BClBN($SiMe_3$)BClN($SiMe_3$)$_2$}(CO)$_2$(η-C_5H_5)][6] and the diborane(4)yl complex [Ru{B(NMe_2)B(NMe_2)Br}(CO)$_2$-(η-C_5H_5)][7] have been described. In this context when considering unbridged 2c-2e Ru−B bonds, we specifically exclude interstitial boride clusters, ruthenaboranes, ruthenacarbaboranes, and agostic B−H−Ru interactions, wherein delocalized bonding models are appropriate.

(6) Braunschweig, H.; Kollann, C.; Klinkhammer, K. L. *Eur. J. Inorg. Chem.* **1999**, 1523.

(7) Braunschweig, H.; Koster, M.; Wang, R. *Inorg. Chem.* **1999**, *38*, 415.

(8) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1110. (b) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **1998**, *17*, 4869. (c) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2000**, *19*, 4344. (d) Irvine, G. J.; Roper, W. R.; Wright, L. J. *Organometallics* **1997**, *16*, 2291. (e) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 1714. (f) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *Organometallics* **1997**, *16*, 5499.

(9) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 948. (b) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862.

(10) Since the majority of osmium boryl and borylene chemistry postdates the definitive review of metal boryls,[11] Table S1 in the Supporting Information summarizes salient data (^{11}B NMR chemical shifts and Os−B bond lengths).

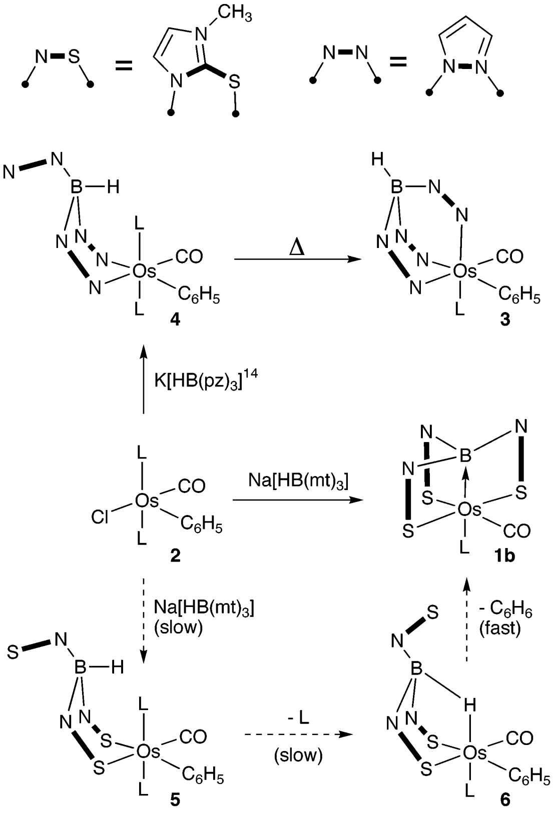
(11) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

(12) Bedford, R. B.; Hill, A. F.; Thompsett, A. R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 1059. (b) Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3501.

(13) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

10.1021/om0306123 CCC: $27.50

Scheme 1. Proposed Mechanism for Osmaboratrane Formation[a]



[a] L = PPh_3.

Notably, in this synthesis of $[Os(C_6H_5)(CO)(PPh_3)\{HB(pz)_3\}]$ (**3**; pz = pyrazolyl), an intermediate complex **4** with a bidentate $HB(pz)_3$ ligand is obtained initially, and this is only slowly converted to the tridentate product in refluxing toluene.

Treating a red dichloromethane solution of **2** [ν(CO) = 1907 cm^{-1}] with $Na[HB(mt)_3]$ results in the rapid formation of a colorless intermediate with ν(CO) = 1934 cm^{-1}. We have not successfully isolated this intermediate because it spontaneously converts at room temperature to a new complex with ν(CO) = 1879 cm^{-1}. By analogy with the formation of **4**, we assume that the intermediate is a complex of the bidentate $HB(mt)_3$ ligand (**5**). Heating the mixture to reflux for 5 min results in complete conversion to the final product, formulated as the desired osmaboratrane $[B(mt)_3Os(CO)(PPh_3)]$ (**1b**). When the reaction was carried out as a diethyl ether suspension, very slow decolorization occurred over 4 days. The isolated solid had two ν(CO) absorptions (ca 1:1 mixture) at 1895 and 1869 cm^{-1}. The latter corresponds to the osmaboratrane (vide infra). The former band relates to an intermediate (**6**), which is however different from that observed in dichloromethane since dissolution of the mixture at ambient temperature results in the immediate conversion to **1b**. Thus the rate-limiting step in the formation of **1b** from **2** would appear to be the conversion of **5** to **6**. Furthermore, phosphine is not liberated in this step, suggesting that the conversion of **5** to **6** involves the displacement of one phosphine ligand, an inference supported by the high temperatures (110 °C) required for the conversion of $[Os(C_6H_5)(CO)(PPh_3)_2\{\kappa^2\text{-}N,N'\text{-}HB(pz)_3\}]$ (**4**) to $[Os(C_6H_5)(CO)(PPh_3)\{\kappa^3\text{-}N,N',N''\text{-}HB(pz)_3\}]$.[14]

Spectroscopic data for **1b** parallel those reported for the ruthenium analogue.[4] Thus the low frequency of ν(CO) suggests a zerovalent osmium center, while the ^{13}C and ^{1}H NMR data associated with the three mt heterocycles indicate two chemical environments for these. The $^{31}P\{^1H\}$ NMR spectrum comprises a single resonance which is significantly broadened ($\omega_{1/2}$ = 420 Hz), indicating trans disposed phosphorus and quadrupolar boron nuclei. The ^{11}B NMR spectrum consists of a single peak at 12.4 ppm, contrasting with the chemical shifts typically found for osmium boryls, which, with the exception of the coordinatively unsaturated complex $[Os(BO_2C_6H_4)(C_6H_4Me\text{-}2)(CO)(PPh_3)_2]$ (δ_B = 26.5),[8a,c] span the range δ 36–63.[8–10] The move from trigonal to tetrahedral boron coordination is typically accompanied by an upfield shift of the ^{11}B resonance.[15]

The molecular structure of **1b** was confirmed by an X-ray crystallographic study, which showed it to have an overall structure little different from that of the ruthenium analogue **1a** (Figure 1a). The geometry about osmium in **1b** may be described as pseudo-octahedral with angles between the cis ligands falling in the range 81.2(3)–99.99(7)°. The coordination of the phosphine and carbonyl ligands is unremarkable for such ligands bound to osmium(0). The feature of interest is the metallaboratrane cage, the axle of which is provided by the Os→B dative bond, which at 2.171(8) Å, if compared to those observed for conventional 2c-2e Os–B bonds in octahedral boryl complexes [2.073(7)–2.154(7) Å],[10,16] is the longest so far observed. This is perhaps not surprising given both the tetrahedral coordination at boron and the purely σ character of the Os→B bond. The structurally characterized boryl and borylene complexes of osmium[8–10] involve three-coordinate boron with the capacity for a π-component to the Os–B bonding. This is borne out by the observation that for nonmetallacyclic six-coordinate osmium boryls, the shortest Os–B bond is observed for $[Os(BCat)(S_2CNEt_2)(CO)(PPh_3)_2]$ [2.073(7) Å, cat = $OC_6H_4O\text{-}2$], in which the superlatively π-dative dithiocarbamate ligand coordinates trans to the Os–B bond. Furthermore, it is difficult to quantify the impact of the geometric constraints of the inclusion of the Os–B bond within the cage structure of **1b**, given that its retention requires the accommodation of adjacent tetrahedral (B) and octahedral (Os) geometries. The potential strain of such an arrangement is alleviated by a flattening of two of the mt buttresses away from local C_{3v}-$B(mt)_3Os$ symmetry (Figure 1b), such that the boron atom is displaced by 0.348 and 0.243 Å from the mean planes of the heterocycles based on S(1) and S(2), respectively, but only 0.017 Å from the heterocycle bound to S(3). In this respect, an alternative valence-bond description as an osmium(II) base-stabilized boryl complex (Chart 2) would have credence were it not for the effective equivalence of the three B–N bond lengths [1.564(12)–1.572(12) Å] and the remarkably low value of ν(CO).

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[14] Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552.

[15] Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978.

[16] Shorter Os–B bonds are observed in five-coordinate osmium boryls, e.g., $[Os(BCat)Cl(CO)(PPh_3)_2]$, 2.019(3) Å, and $[Os\{B(OEt)_2\}Cl(CO)(PPh_3)_2]$, 2.076(3) Å.[8b]

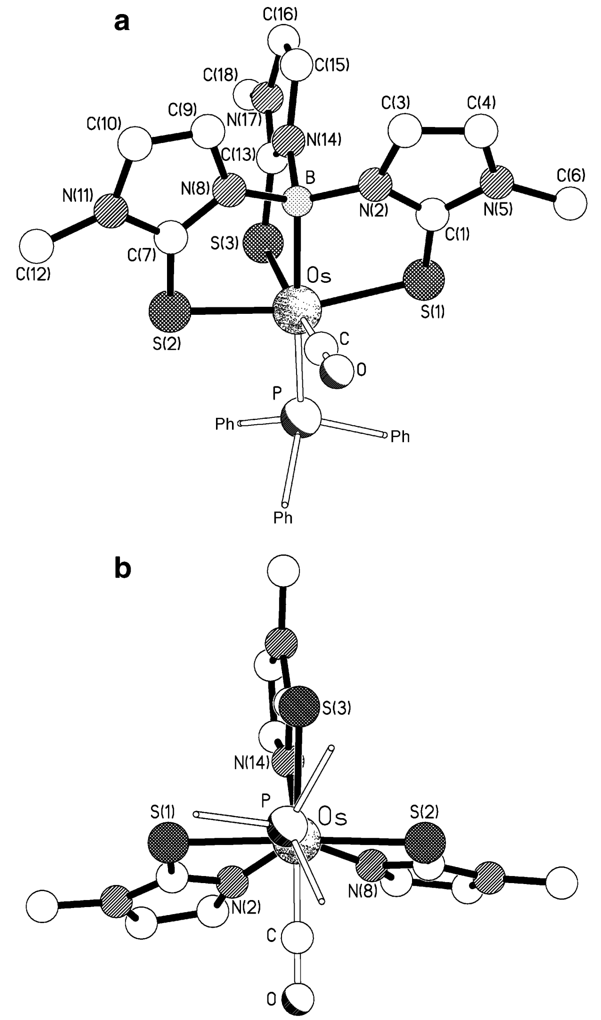


Figure 1. (a) Molecular structure of **1b**. Selected bond distances (Å) and angles (deg): Os−B 2.171(8), Os−C 1.826(8), Os−P 2.403(2), Os−S(1) 2.424(2), Os−S(2) 2.406(2), Os−S(3) 2.493(2), S(1)−C(1) 1.726(9), S(2)−C(7) 1.715(9), S(3)−C(13) 1.720(8), B−N(2) 1.572(12), B−N(8) 1.572(12), B−N(14) 1.564(12), Os−B−N(2) 110.3(5), Os−B−N(8) 111.5(6), Os−B−N(14) 111.6(6), N(2)−B−N(8) 113.0(7), N(2)−B−N(14) 104.6(7), N(8)−B−N(14) 105.6(7). (b) View of the structure of **1b** perpendicular to the {N(2)N(8)N(14)} plane showing the different folding of the mt rings away from local C_3 symmetry.

The disparity between the geometry of the S(3)-based heterocycle and those based on S(1) and S(2) is reflected in the osmium−sulfur bonding with Os−S(1) and Os−S(2) being respectively 44 and 35σ shorter than the Os−S(3) bond length of 2.493(2) Å. This is however not manifest in statistically significant variations in the corresponding C−S thione bond lengths of the heterocycles [1.715(9)−1.726(9) Å].

Conclusions

The structural characterization of the first osmaboratrane reveals an Os−B interaction that is longer than found in octahedral osmium boryls or base-stabilized borylenes for which a degree of Os═B multiple bonding can be inferred. The sp^3 hybridization of boron in boratranes leaves no orbitals of suitable symmetry for π-bonding, and so it may be assumed that the bonding in **1b** is of a purely σ-nature.[17] We are therefore currently investigating the generality of metallaboratrane formation with respect to variations in d-configuration, geometry, and principle quantum number (3d, 4d, and 5d) of the metal.

Chart 1. (a) Hydrotris(methimazolyl)borate and (b) Tris(methimazolyl)borane (metallaboratrane) Coordination

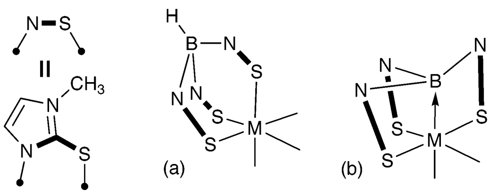
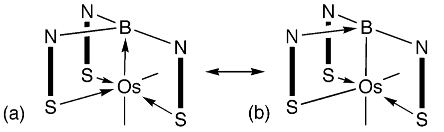


Chart 2. Resonance Forms for (a) Metallaboratrane and (b) Base-Stabilized Boryl Complex



Experimental Section

General Procedures. Conventional Schlenk and vacuum line techniques were employed for the exclusion of air. The salt $Na[HB(mt)_3]$[18] was prepared by heating Hmt and $Na[BH_4]$ in refluxing xylenes according to a published procedure.[4] The complex $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ has been described previously.[13] Elemental microanalytical data were obtained commercially from the University of North London Analytical Service.

Synthesis of $[B(mt)_3Os(CO)(PPh_3)]$ (1b). A mixture of $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ (0.126 g, 0.147 mmol) and $Na[HB(mt)_3]$ (0.060 g, 0.16 mmol) in dichloromethane (20 mL) was stirred for 30 min, by which time the solution had decolorized. The mixture was then heated under reflux for 20 min and then diluted with ethanol (20 mL). The solvent volume was reduced in vacuo to ca. 10 mL, and the colorless crystals that formed were isolated by filtration and washed with ether. Yield: 0.122 g (0.141 mmol, 96%). The complex is air stable both as a solid and in solution. Crystallographic grade crystals were grown by slow vertical diffusion of a dichloromethane solution of the complex through layers of diethyl ether and hexane. IR (CH_2Cl_2): 1879 [ν(CO)]; (Nujol):* 1862vs [ν(CO)], 1562w, 1408w, 1297w, 1280w, 1261w, 1204s, 1018vs cm^{-1}. *Values for samples crystallized from dichloromethane and ethanol. The solid product isolated from carrying out the synthesis in diethyl ether suspension has ν(CO) = 1869 cm^{-1}; however when dissolved in dichloromethane, a ν(CO) value of 1879 cm^{-1} is observed, which is identical to that for samples crystallized from dichloromethane and ethanol, suggesting crystal polymorphism. FAB-MS (nba matrix): *m*/*z* (%) 832(92) $[M]^+$, 804(13) $[M-CO]^+$, 719(19) $[M-mt]^+$, 689(4) $[M-mt-CO]^+$, 570(7) $[M-PPh_3]^+$, 542(100) $[M-PPh_3-CO]^+$. NMR ($CDCl_3$, 25 °C) ^1H: 3.65 (s, 3 H, NCH_3), 3.92 (s br, 6 H, NCH_3), 6.00, 6.42 (s br × 2, 1 H × 2, NCH═CH), 6.50, 6.55 (s × 2, 2 H × 2, NCH═CH), 7.27, 7.36, 7.52 (m × 3, 15 H, C_6H_5) ppm. ^{11}B: 12.4 ppm. $^{31}P\{^1H\}$: 6.14 (s br, $\omega_{1/2}$ = 3.84 ppm, 420 Hz). $^{13}C\{^1H\}$: 133.6 [$C^4(C_6H_5)$], 128.6, 127.6 [$C^{2,3,5,6}(C_6H_5)$], 121.9, 121.4,

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[17] We have ignored the possibility of $(d\pi)\rightarrow(B-N\sigma^*)$ hyperconjugation in the absence of a full molecular orbital treatment.

[18] Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.

117.5, 117.0 (C_3N_2), 33.3 (1C, NCH_3), 32.8 (2C, NCH_3) ppm (quaternary carbon resonances CO, CS, and CP not observed due to low solubility). Anal. Found: C, 44.86; H, 3.73; N, 9.96. Calcd for $C_{31}H_{30}BN_6OOsPS_3$: C, 44.82; H, 3.64; N, 10.12. *Crystal data*: $[C_{31}H_{30}N_6OBPS_3Os]\cdot 2CH_2Cl_2.Et_2O$, $M = 1074.74$, monoclinic, $P2_1/n$ (no. 14), $a = 16.690(2)$ Å, $b = 11.1483(10)$ Å, $c = 24.269(2)$ Å, $\beta = 107.365(9)°$, $V = 4310.0(7)$ Å^3, $Z = 4$, $D_c = 1.656$ g cm^{-3}, μ(Mo Kα) = 3.430 mm^{-1}, $T = 293$ K, pale yellow prisms; 7548 independent measured reflections, F^2 refinement, $R_1 = 0.044$, $wR_2 = 0.086$, 4672 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 460 parameters. CCDC 223925.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure of compound **1b**$\cdot 2CH_2Cl_2\cdot Et_2O$; a table of selected ^{11}B NMR and structural data for boryl and borylene complexes of osmium post-dating ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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