Organometallics **1998,** *17,* 4869−4874

Crystal Structure of $Os(Bcat)Cl(CO)(PPh_3)_2$ and the Syntheses and Structural Studies of Derived Cationic and Neutral Osmium Boryl Complexes

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Received June 22, 1998

Treatment of $Os(Bcat)Cl(CO)(PPh_3)_2$ (**1**; Bcat = B-1,2-$O_2C_6H_4$) with $AgSbF_6$ in THF removes chloride and gives a cationic boryl complex formulated as $[Os(Bcat)(CO)(THF)_2(PPh_3)_2]SbF_6$. This in turn when treated in situ with NCMe gives $[Os(Bcat)(CO)(NCMe)_2(PPh_3)_2]SbF_6$ (**2**). Complex **2** reacts with CO or CN-*p*-tolyl with displacement of the acetonitrile ligand trans to boryl to give $[Os(Bcat)(CO)(MeCN)L(PPh_3)_2]SbF_6$, (L = CO (**3**), CN-*p*-tolyl (**4**)). Complex **1** also reacts directly with the anionic ligands formate, nitrite, and diethyldithiocarbamate to give the corresponding neutral 6-coordinate complexes $Os(Bcat)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**5**), $Os(Bcat)(\eta^2\text{-}O_2N)(CO)(PPh_3)_2$ (**6**), and $Os(Bcat)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**7**). The crystal structures of **1**, **2**, **4**, and **7** have been determined.

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Introduction

The chemistry of transition-metal boryl complexes, $L_nM{-}BR_2$, originated in the 1960s with the first studies by Nöth and Schmid.[1] Interest in these compounds increased markedly in the mid-1980s with the recognition that compounds of this type are involved in metal-catalyzed hydroboration reactions.[2] Numerous studies since this time have addressed the mechanism of these processes, especially the question of whether insertion of alkenes/alkynes is into M−B or M−H bonds.[3] Structural studies of many stable metal boryl complexes, prepared either by reaction between metal anions and boron halides or through oxidative-addition processes involving breaking of B−B or B−B bonds, have been reported.[4a,b] Recently, the activation of hydrocarbons by M−B bonds has been described.[5a,b]

In contrast with the large number of neutral metal−boryl complexes which have been described, cationic metal−boryl complexes are very rare and to our knowledge only one structurally characterized example, involving iridium(IV), has been reported.[6] Os(Bcat)Cl-(CO)$(PPh_3)_2$ (**1**), which we have previously reported,[77] is a useful synthon because of the lability of the chloride ligand and the coordinatively unsaturated nature of the metal center. Any derived cationic complexes would be expected to show enhanced electrophilicity at the boron atom and would in addition offer the possibility of reintroducing a wide range of anionic ligands, perhaps including alkyl or aryl ligands, to the metal. In this paper we report the crystal structure of the five-coordinate osmium boryl $Os(Bcat)Cl(CO)(PPh_3)_2$ and the syntheses and structural studies of a number of derived cationic and neutral boryl-containing complexes.

Results and Discussion

Cationic Boryl Complexes. Abstraction of the chloride ligand from complex **1** proceeds readily with $AgSbF_6$ in THF at room temperature, to form a solution containing a product which was not characterized but which is likely to be the cationic bis(tetrahydrofuran) complex $[Os(Bcat)(CO)(THF)_2(PPh_3)_2]SbF_6$. Addition of acetonitrile to the solution formed as above gives the bis(acetonitrile) complex **2** (see Scheme 1). Spectral data (IR, ^1H NMR, and ^{13}C NMR) for **2** and all other new compounds reported in this paper are presented in Tables 1−3.

Complex **2** reacts rapidly in dichloromethane with either carbon monoxide or *p*-tolyl isocyanide, effecting displacement of only the acetonitrile trans to the Bcat ligand and thus forming the corresponding complexes $[Os(Bcat)(CO)(MeCN)L(PPh_3)_2]SbF_6$ (L = CO (**3**), CN-*p*-tolyl (**4**)). This observation suggests that the Bcat ligand has a stronger *trans* effect than the carbonyl ligand.

Displacement of Chloride by Bidentate Anionic Ligands. The lability of the chloride ligand in the five-coordinate complex **1** is further demonstrated by its displacement reactions with the potentially bidentate ligands formate, nitrite, and dithiocarbamate to form the corresponding octahedral complexes **5**, **6**, and **7**

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10.1021/om980524w CCC: \$15.00 © 1998 American Chemical Society
Publication on Web 10/08/1998

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Published on October 8, 1998 on http://pubs.acs.org | doi: 10.1021/om980524w

Table 1. Infrared Data (cm^{-1})[a] for Osmium Boryl Complexes

complex	ν(C=O)	ν(C=N)	other bands[c]
$[Os(Bcat)(CO)(NCMe)_2(PPh_3)_2]SbF_6$ (**2**)	1941 m, 1925 vs		1233 m, 1151 w, 1117 m, 1104 m, 1093 m, 1027 w, 811 w
$[Os(Bcat)(CO)_2(NCMe)(PPh_3)_2]SbF_6$ (**3**)	2052 m,[b] 2040 m, 1983 vs		1231 m, 1157 m, 1115 m, 1093 m, 812 w
$[Os(Bcat)(CO)(CN\text{-}p\text{-tolyl})(NCMe)(PPh_3)_2]SbF_6$ (**4**)	1978 vs	2149 s	1236 m, 1144 m, 1111 sh s, 1101 s, 1024 m, 817 m
$Os(Bcat)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**5**)	1925 vs		1552 m,[d] 1234 m, 1144 w, 1105 m, 1096 m, 1021 w, 809 m
$Os(Bcat)(\eta^2\text{-}O_2N)(CO)(PPh_3)_2$ (**6**)	1928 vs		1233 m, 1146 w, 1109 m, 1097 m, 1024 w, 809 w
$Os(Bcat)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**7**)	1913 vs		1235 m, 1147 w, 1082 s, 808 w

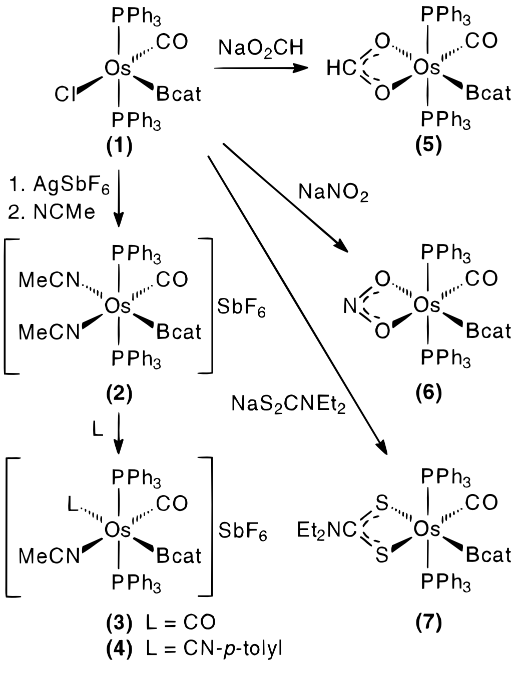
[a] Spectra recorded as Nujol mulls between KBr plates. [b] Solid-state splitting. [c] Bands associated with boryl ligand unless denoted otherwise. [d] Formate.

Table 2. ^1H NMR Data[a] for Osmium Boryl Complexes

complex	δ (ppm)
$[Os(Bcat)(CO)(NCMe)_2(PPh_3)_2]SbF_6$ (**2**)	1.55 (s, 3H, NCMe), 1.79 (s, 3H, NCMe), 6.83 (s, 4H, Bcat), 7.35 (m, 18H, PPh_3), 7.45 (m, 12H, PPh_3)
$[Os(Bcat)(CO)_2(NCMe) (PPh_3)_2]SbF_6$ (**3**)	1.78 (s, 3H, NCMe), 6.87 (m, 4H, Bcat), 7.35−7.45 (m, 30H, PPh_3)
$[Os(Bcat)(CO)(CN\text{-}p\text{-tolyl})(NCMe)(PPh_3)_2]SbF_6$ (**4**)	1.69 (s, 3H, NCMe), 2.32 (s, 3H, CNC_6H_4Me), 6.66 (d, $J = 8.2$ Hz, 2H, CNC_6H_4Me), 6.87 (s, 4H, Bcat), 7.08 (d, $J = 8.2$ Hz, 2H, CNC_6H_4Me), 7.32 (m, 18H, PPh_3), 7.46 (m, 12H, PPh_3)
$Os(Bcat)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2$ (**5**)	6.63 (m, 2H, Bcat), 6.75 (m, 2H, Bcat), 7.31 (m, 18H, PPh_3), 7.50 (m, 12H, PPh_3), 8.01 (t, $J(HP) = 1.7$ Hz, 1H, O_2CH)
$Os(Bcat)(\eta^2\text{-}O_2N)(CO)(PPh_3)_2$ (**6**)	6.65 (m, 2H, Bcat), 6.74 (m, 2H, Bcat), 7.30 (m, 18H, PPh_3), 7.44 (m, 12H, PPh_3)
$Os(Bcat)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$ (**7**)	0.59 (t, $J = 7.2$ Hz, 3H, $S_2CN(CH_2Me)_2$), 0.70 (t, $J = 7.1$ Hz, 3H, $S_2CN(CH_2Me)_2$), 2.66 (q, $J = 7.2$ Hz, 2H, $S_2CN(CH_2Me)_2$), 2.81 (q, $J = 7.2$ Hz, 2H, $S_2CN(CH_2Me)_2$), 6.63 (m, 2H, Bcat), 6.76 (m, 2H, Bcat), 7.17 (m, 18H, PPh_3), 7.61 (m, 12H, PPh_3)

[a] Spectra recorded in $CDCl_3$ at 25 °C. Chemical shifts are referenced to Me_4Si (δ 0.00). Splitting patterns and line shapes are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.

Scheme 1



(Scheme 1). This ligand exchange proceeds readily at room temperature in dichloromethane−ethanol solution to give the colorless products. Alternatively, **5** can be prepared by addition of sodium formate/formic acid to a solution of **2**. The ^1H and ^{13}C NMR spectra of the dithiocarbamate complex **7** show separate environments for the ethyl groups, indicating that there is no rotation about the C−N bond at room temperature in this complex. Complex **7** could be crystallized from benzene−hexane to give transparent crystals suitable for X-ray diffraction.

Formate complexes can provide a convenient route to metal hydride complexes through thermal elimination of carbon dioxide.[8] Accordingly, when complex **5**, together with 5 equiv of triphenylphosphine, is heated under reflux in benzene for 30 min, $OsH(Bcat)(CO)(PPh_3)_3$ is formed in 80% yield. Further chemistry of this derivative, including a crystal structure determination, will be reported separately.

Likewise, the nitrite ligand has the potential to undergo conversion to a nitrosyl ligand by oxygen transfer to an adjacent or external phosphine.[9] The colorless nature of the nitrite derivative **6** implies six-coordination rather than five-coordination at osmium, and the IR spectral bands observed for **6** are not compatible with an η^1-NO_2 ligand bound through either nitrogen or oxygen. The facile conversion of the η^2-nitrite to η^1-nitrite in complex **6** is brought about by reaction with carbon monoxide to form the *cis*-dicarbonyl $Os(Bcat)(\eta^1\text{-}ONO)(CO)_2(PPh_3)_2$, as evidenced by infrared spectroscopy (ν(CO), 2019 vs and 1955 vs cm^{-1}). Further characterization of this dicarbonyl complex was not possible because the complex slowly loses carbon monoxide and reverts back to the starting material even in the solid state. When complex **6** is heated under reflux in benzene, a deep orange solution is formed which changes to a dark green on cooling. An impure, air-sensitive, green solid can be isolated which shows weak activity in the nitrosyl region of the infrared spectrum. However, attempts to purify this compound were unsuccessful.

Crystal Structure Determinations. Crystal structures were determined for complexes **1**, **2**, **4**, and **7**.

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Table 3. ^{13}C NMR Data[a] for Osmium Boryl Complexes

complex	δ (ppm)
[Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]SbF$_6$ (**2**)	2.29 (NC*Me*), 2.55 (NC*Me*), 110.69 (Bcat), 120.62 (Bcat), 121.78 (N*C*Me), 124.14 (N*C*Me), 128.45 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 130.49 (*p*-PPh$_3$), 131.16 (t′, $^{1,3}J_{CP}$ = 52 Hz, *i*-PPh$_3$), 133.58 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 149.97 (Bcat), 183.41 (CO)
[Os(Bcat)(CO)$_2$(NCMe)(PPh$_3$)$_2$]SbF$_6$ (**3**)	2.56 (NC*Me*), 111.36 (Bcat), 121.42 (Bcat), 124.03 (N*C*Me), 128.91 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 130.72 (t′, $^{1,3}J_{CP}$ = 56 Hz, *i*-PPh$_3$), 131.33 (*p*-PPh$_3$), 133.09 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 149.18 (Bcat), 178.48 (t, J_{CP} = 8 Hz, CO), 179.88 (t, J_{CP} = 8 Hz, CO)
[Os(Bcat)(CO)(CN-*p*-tolyl)-(NCMe)(PPh$_3$)$_2$]SbF$_6$ (**4**)	2.34 (NC*Me*), 21.35 (CNC$_6$H$_4$*Me*), 110.98 (Bcat), 120.87 (Bcat), 122.08 (*q*-CN*C*$_6$H$_4$Me), 123.95 (*q*-N*C*Me), 125.79 (CN*C*$_6$H$_4$Me), 128.60 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 129.98 (CN*C*$_6$H$_4$Me), 130.71 (*p*-PPh$_3$), 131.85 (t′, $^{1,3}J_{CP}$ = 54 Hz, *i*-PPh$_3$), 133.23 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 139.58 (t, J = 9.5 Hz, *C*NC$_6$H$_4$Me), 140.52 (CN*C*$_6$H$_4$Me), 149.76 (Bcat), 182.69 (t, J = 9 Hz, CO)
Os(Bcat)(η^2-O$_2$CH)(CO)(PPh$_3$)$_2$ (**5**)[b]	109.98 (Bcat), 119.63 (Bcat), 128.02 45 (t′, $^{2,4}J_{CP}$ = 9 Hz, *o*-PPh$_3$), 130.05 (*p*-PPh$_3$), 131.36 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.19 (t′, $^{3,5}J_{CP}$ = 11 Hz, *m*-PPh$_3$), 150.03 (Bcat), 173.03 (O$_2$*C*H)
Os(Bcat)(η^2-O$_2$N)(CO)(PPh$_3$)$_2$ (**6**)[b]	110.08 (Bcat), 119.82 (Bcat), 128.14 (t′, $^{2,4}J_{CP}$ = 10 Hz, *o*-PPh$_3$), 130.26 (*p*-PPh$_3$), 131.22 (t′, $^{1,3}J_{CP}$ = 52 Hz, *i*-PPh$_3$), 133.96 (t′, $^{3,5}J_{CP}$ = 12 Hz, *m*-PPh$_3$), 149.88 (Bcat)
Os(Bcat)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (**7**)	11.88 (S$_2$CN(CH$_2$*Me*)$_2$), 12.00 (S$_2$CN(CH$_2$*Me*)$_2$), 42.30 (S$_2$CN(*C*H$_2$Me)$_2$), 43.14 (S$_2$CN(*C*H$_2$Me)$_2$), 109.86 (Bcat), 119.33 (Bcat), 127.06 (t′, $^{2,4}J_{CP}$ = 9 Hz, *o*-PPh$_3$), 128.83 (*p*-PPh$_3$), 133.93 (t′, $^{1,3}J_{CP}$ = 50 Hz, *i*-PPh$_3$), 134.63 (t′, $^{3,5}J_{CP}$ = 10 Hz, *m*-PPh$_3$), 150.69 (Bcat), 186.76 (t, J = 10 Hz, CO), 208.94 (S$_2$*C*N(CH$_2$Me)$_2$)

[a] Spectra recorded in CDCl$_3$ at 25 °C. Chemical shifts are referenced to CDCl$_3$ (δ 77.00). t′ denotes that the signal has apparent multiplicity; $^{m,n}J_{CP}$ is the sum of the two coupling constants $^{m}J_{CP}$ and $^{n}J_{CP}$ as explained in ref 6. [b] Signal for CO ligand not observed because of low solubility.

Table 4. Crystal and Refinement Data for 1, 2, 4, and 7

	1	**2**·CH$_2$Cl$_2$	**4**	**7**·C$_6$H$_6$
empirical formula	C$_{43}$H$_{34}$BClO$_3$OsP$_2$	C$_{48}$H$_{42}$BCl$_2$F$_6$N$_2$O$_3$OsP$_2$Sb	C$_{53}$H$_{44}$BF$_6$N$_2$O$_3$OsP$_2$Sb	C$_{54}$H$_{50}$BNO$_3$OsP$_2$S$_2$
fw	897.10	1264.44	1255.60	1088.02
temp, K	203(2)	203(2)	203(2)	203(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$Pnma$	$P2_1/c$
unit cell dimens				
a, Å	21.8703(2)	11.4600(2)	21.2858(7)	12.0520(2)
b, Å	9.92870(10)	37.74180(10)	15.2408(5)	22.9056(5)
c, Å	18.91350(10)	11.5757(2)	15.8610(6)	18.3323(4)
α, deg	90	90	90	90
β, deg	113.5470(10)	98.2860(10)	90	103.9690(10)
γ, deg	90	90	90	90
V, Å^3	3764.97(5)	4954.47(12)	5145.5(3)	4911.1(2)
Z	4	4	4	4
density (calcd), g cm^{-3}	1.583	1.695	1.621	1.472
abs coeff, mm^{-1}	3.582	3.345	3.120	2.790
$F(000)$	1776	2472	2464	2192
cryst size, mm	0.54 × 0.42 × 0.33	0.49 × 0.39 × 0.33	0.43 × 0.23 × 0.11	0.22 × 0.20 × 0.09
θ range for data collecn, deg	1.02−28.26	1.08−28.26	1.60−28.28	1.45−25.00
index ranges	$-28 \le h \le 26$, $0 \le k \le 12$, $0 \le l \le 24$	$-15 \le h \le 15$, $0 \le k \le 47$, $0 \le l \le 14$	$0 \le h \le 27$, $0 \le k \le 19$, $0 \le l \le 20$	$-15 \le h \le 15$, $0 \le k \le 30$, $0 \le l \le 24$
no. of rflns collected	22 153	29 107	30 942	28 706
no. of indep rflns	8394 (R(int) = 0.0215)	11 008 (R(int) = 0.0229)	6126 (R(int) = 0.0471)	8644 (R(int) = 0.0724)
max and min transmissn	0.3884 and 0.3801	0.4136 and 0.4407	0.7253 and 0.3473	0.8180 and 0.7357
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	8394/3/487	11008/0/597	6126/0/354	8644/36/579
goodness of fit on F^2	1.249	1.283	0.799	0.997
final R indices ($I > 2\sigma(I)$)	R1 = 0.0261, wR2 = 0.0525	R1 = 0.0360, wR2 = 0.0664	R1 = 0.0432, wR2 = 0.1074	R1 = 0.0391, wR2 = 0.0595
R indices (all data)	R1 = 0.0299, wR2 = 0.0537	R1 = 0.0418, wR2 = 0.0683	R1 = 0.0625, wR2 = 0.1270	R1 = 0.0864, wR2 = 0.0711
weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.0018P)^2 + 3.5138P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 10.4000P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0838P)^2 + 42.5926P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole, e Å^{-3}	0.590 and −0.933	1.126 and −1.195	2.019 and −2.029	0.802 and −0.568

Crystal and refinement data are given in Table 4, and selected bond distances and angles for these compounds are presented in Tables 5−8. Bright yellow crystals of **1** that were suitable for X-ray diffraction analysis were obtained by crystallization from dichloromethane−hexane. The molecular structure of **1** is illustrated in Figure 1 and shows a square-based-pyramidal geometry with the boryl ligand, which probably has the strongest *trans* influence, in the apical position. The mutually trans carbonyl and chloride ligands are disordered over the two sites, and the two possible arrangements have been denoted as (a) and (b) in Table 5, which records selected bond distances and angles for **1**. The mutually trans triphenylphosphine ligands are slightly bent away from the boryl ligand, forming a P(1)−Os−P(2) bond angle of 170.46(3)°. The carbonyl ligand is at 90.9(3)° (or 94.6(3)°) to the boryl ligand, but the chloride ligand is much further bent away from the boryl ligand at an

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Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 1

Interatomic Distances			
Os−B	2.019(3)	Os−P(2)	2.3585(7)
Os−C(1a)	1.798(8)	C(1a)−O(1a)	1.173(8)
Os−C(1b)	1.808(8)	C(1b)−O(1b)	1.152(8)
Os−Cla	2.406(2)	B−O(2)	1.411(4)
Os−Clb	2.407(2)	B−O(3)	1.406(4)
Os−P(1)	2.3640(7)		
Interatomic Angles			
C(1a)−Os−B	90.9(3)	P(1)−Os−Clb	90.85(5)
C(1a)−Os−Cla	163.9(2)	P(1)−Os−B	94.73(10)
C(1a)−Os−P(1)	88.3(2)	P(2)−Os−Cla	89.95(5)
C(1a)−Os−P(2)	91.4(2)	P(2)−Os−Clb	87.27(5)
C(1b)−Os−B	94.6(3)	P(2)−Os−B	94.81(10)
C(1b)−Os−Clb	164.7(2)	Cla−Os−B	104.97(12)
C(1b)−Os−P(1)	91.1(2)	Clb−Os−B	100.46(12)
C(1b)−Os−P(2)	88.3(2)	O(1a)−C(1a)−Os	175.0(7)
P(1)−Os−P(2)	170.46(3)	O(1b)−C(1b)−Os	174.6(7)
P(1)−Os−Cla	87.73(5)		

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Interatomic Distances			
Os−B	2.094(5)	Os−P(2)	2.3954(9)
Os−C(1)	1.844(4)	C(1)−O(1)	1.158(5)
Os−N(1)	2.168(3)	B−O(2)	1.413(5)
Os−N(2)	2.101(3)	B−O(3)	1.416(5)
Os−P(1)	2.3831(9)		
Interatomic Angles			
C(1)−Os−B	89.2(2)	P(2)−Os−N(2)	86.78(9)
C(1)−Os−N(1)	99.8(2)	P(2)−Os−N(1)	89.56(9)
C(1)−Os−N(2)	171.9(2)	P(2)−Os−B	89.85(12)
C(1)−Os−P(1)	91.59(12)	N(1)−Os−N(2)	88.05(12)
C(1)−Os−P(2)	91.26(12)	N(1)−Os−B	171.0(2)
P(1)−Os−P(2)	177.02(3)	N(2)−Os−B	82.9(2)
P(1)−Os−N(1)	89.10(9)	C(2)−N(1)−Os	179.1(3)
P(1)−Os−N(2)	90.52(9)	C(4)−N(2)−Os	168.0(3)
P(1)−Os−B	91.06(12)	O(1)−C(1)−Os	177.9(4)

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Interatomic Distances			
Os−B	2.135(10)	Os−P(2)	2.3988(14)
Os−C(1)	1.875(8)	C(1)−O(1)	1.150(10)
Os−N(1)	2.078(7)	B−O(2)	1.408(11)
Os−C(4)	2.046(8)	B−O(3)	1.440(11)
Os−P(1)	2.3988(14)		
Interatomic Angles			
C(1)−Os−B	83.4(4)	P(2)−Os−C(4)	89.59(4)
C(1)−Os−C(4)	99.4(3)	P(2)−Os−N(1)	88.52(3)
C(1)−Os−N(1)	169.3(3)	P(2)−Os−B	90.34(4)
C(1)−Os−P(1)	91.53(3)	N(1)−Os−C(4)	91.3(3)
C(1)−Os−P(2)	91.53(3)	N(1)−Os−B	85.9(3)
P(1)−Os−P(2)	176.92(7)	C(4)−Os−B	177.2(3)
P(1)−Os−C(4)	89.59(4)	N(2)−C(4)−Os	178.1(7)
P(1)−Os−N(1)	88.53(3)	C(2)−N(1)−Os	176.6(7)
P(1)−Os−B	90.34(4)	O(1)−C(1)−Os	177.2(8)

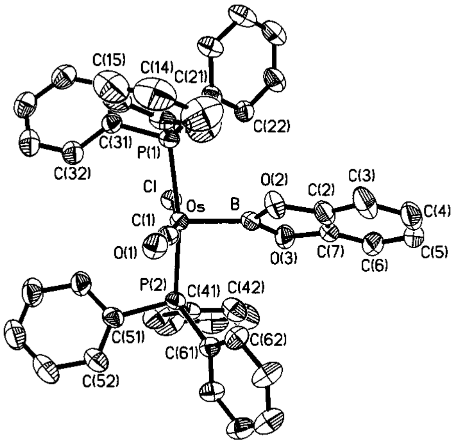

Figure 1. Molecular structure of $Os(Bcat)Cl(CO)(PPh_3)_2$ (**1**) with thermal ellipsoids at the 50% probability level.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complex 7

Interatomic Distances			
Os−B	2.073(7)	S(1)−C(2)	1.715(5)
Os−C(1)	1.847(6)	S(2)−C(2)	1.712(5)
Os−S(1)	2.5209(14)	C(2)−N	1.335(6)
Os−S(2)	2.4709(13)	C(1)−O(1)	1.163(6)
Os−P(1)	2.372(2)	B−O(2)	1.434(6)
Os−P(2)	2.3686(14)	B−O(3)	1.435(8)
Interatomic Angles			
C(1)−Os−B	89.3(2)	P(2)−Os−S(2)	91.92(5)
C(1)−Os−S(1)	105.9(2)	P(2)−Os−B	85.3(2)
C(1)−Os−S(2)	174.5(2)	S(1)−Os−S(2)	70.32(4)
C(1)−Os−P(1)	92.8(2)	S(1)−Os−B	162.9(2)
C(1)−Os−P(2)	91.9(2)	S(2)−Os−B	95.0(2)
P(1)−Os−P(2)	175.04(5)	C(2)−S(1)−Os	87.0(2)
P(1)−Os−S(1)	93.68(5)	C(2)−S(2)−Os	88.7(2)
P(1)−Os−S(2)	83.48(5)	S(1)−C(2)−S(2)	114.0(3)
P(1)−Os−B	93.3(2)	O(1)−C(1)−Os	178.1(5)
P(2)−Os−S(1)	86.48(5)		

angle of 104.97(12)° (or 100.46(12)°). The orientation of the plane of the Bcat ligand is tilted by 38.32(16)° with respect to the plane of best fit through the Os, B, C(1), and Cl atoms. This orientation is different from that observed in the cationic complexes **2** and **4** (see below), where the Bcat ligand is approximately coplanar with this plane. The most interesting feature of this structure is the very short Os−B bond distance of 2.019(3) Å. This is shorter than any of the other Os−B distances reported in this paper, and an important contributing factor to this is undoubtedly the absence of a ligand trans to the Bcat ligand. Additionally we can note that in the closely related five-coordinate boryl complex $Os(B\{OEt\}_2)Cl(CO)(PPh_3)_2$, the Os−B distance is significantly longer at 2.076(3) Å.[10] This observation can be rationalized in terms of a competitive π-donation situation where Os−B π-donation is relatively stronger in the Bcat complex **1** and O−B π-donation is relatively stronger in the $B(OEt)_2$ complex.

Colorless crystals of $[Os(Bcat)(CO)(NCMe)_2(PPh_3)_2]SbF_6$ (**2**) suitable for X-ray diffraction analysis were obtained by crystallization from dichloromethane−hexane and contained one molecule of dichloromethane in the unit cell. The X-ray structure of the cationic part of **2** is shown in Figure 2. The complex has a distorted-octahedral geometry with mutually trans triphenylphosphine ligands and mutually cis acetonitrile ligands. The acetonitrile and the adjacent Bcat ligand form an angle of only 82.9(2)°. The Os−N bond length for the acetonitrile ligand trans to the Bcat ligand, 2.168(3) Å, is longer than the Os−N bond length for the acetonitrile ligand trans to the carbonyl ligand, 2.101(3) Å. This illustrates that the trans influence of the Bcat ligand is greater than that of the carbonyl ligand. The orientation of the plane of the Bcat ligand relative to the plane of best fit through the atoms Os, N(1), N(2), C(1), and B is only 3.74(17)°. The Os−B bond distance is 2.094(5) Å, significantly longer than that of complex **1**. Reasons for this must include the presence of a

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[10] Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. Unpublished results.

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Published on October 8, 1998 on http://pubs.acs.org | doi: 10.1021/om980524w

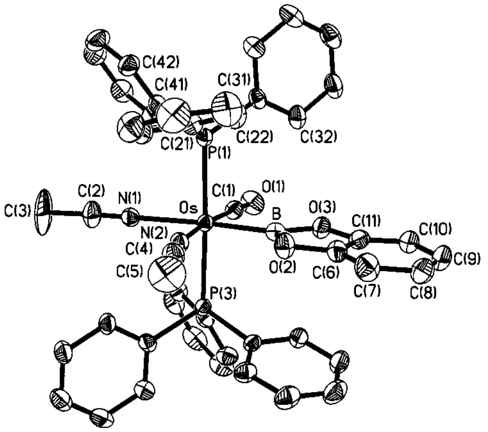

Figure 2. Molecular structure of [Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]SbF$_6$ (**2**) (cation only) with thermal ellipsoids at the 50% probability level.

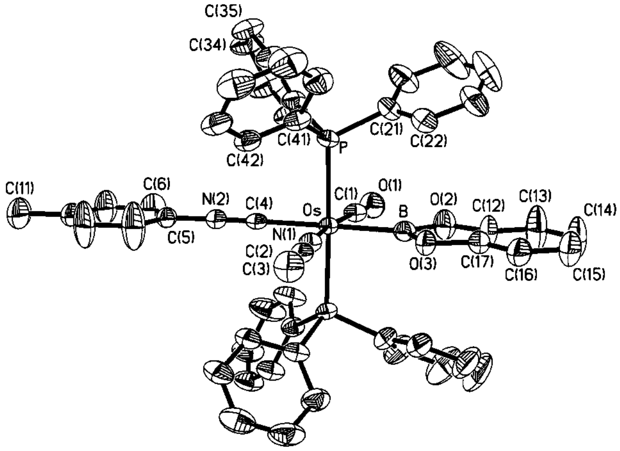

Figure 3. Molecular structure of [Os(Bcat)(CO)(CN-*p*-tolyl)(MeCN)(PPh$_3$)$_2$]SbF$_6$ (**4**) (cation only) with thermal ellipsoids at the 50% probability level.

ligand trans to boron and possibly the effect of an overall positive charge on the complex.

Colorless crystals of [Os(Bcat)(CO)(NCMe)(CN-*p*-tolyl)(PPh$_3$)$_2$]SbF$_6$ (**4**) suitable for X-ray diffraction analysis were obtained by crystallization from dichloromethane−hexane. The structure of the cationic part of **4** is illustrated in Figure 3 and shows a distorted-octahedral structure. The *p*-tolyl isocyanide ligand is trans to the Bcat ligand, and the Os−B bond length is 2.135(10) Å. Because of the large standard deviations for this bond it is not possible to accurately compare the effect of the isocyanide ligand relative to the acetonitrile ligand on the length of the Os−B bond. There is a mirror plane containing the osmium atom and the Bcat, carbonyl, acetonitrile, and isocyanide ligands that is perpendicular to the P−P axis. The carbonyl and acetonitrile ligands are both bent toward the Bcat ligand with angles of 83.4(4) and 85.9(3)°, respectively.

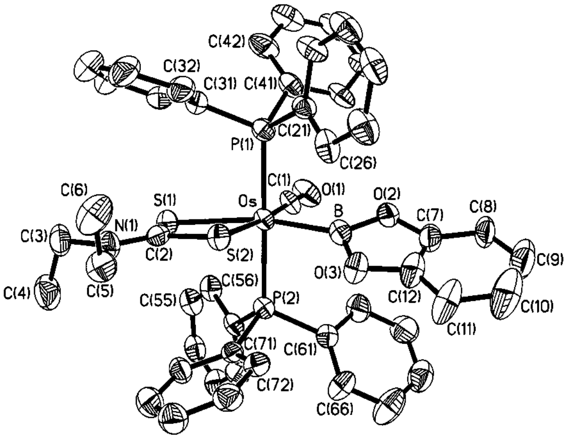

Figure 4. Molecular structure of Os(Bcat)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (**7**) with thermal ellipsoids at the 50% probability level.

Colorless crystals of Os(Bcat)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (**7**) suitable for X-ray diffraction analysis were obtained by crystallization from benzene−hexane. The unit cell contains one molecule of benzene. The structure of **7** is illustrated in Figure 4 and shows a distorted-octahedral geometry. The dithiocarbamate ligand is bidentate and is trans to both the carbonyl and Bcat ligands. The Os−S bond distance trans to the boryl ligand, 2.5209(14) Å, is significantly greater than the Os−S bond distance trans to the carbonyl ligand, 2.4709(13) Å, once again highlighting the strong trans influence of the Bcat ligand. The Os−B bond distance, 2.073(7) Å, is not significantly different from the Os−B distances in the cationic complexes **2** and **4**. However, it is longer than the distance in the neutral, but five-coordinate, complex **1**. The plane of the Bcat ligand is tilted 24.66(19)° with respect to the plane of best fit through the Os, C(1), S(1), S(2), and B atoms.

Summary. Three cationic osmium boryl complexes have been synthesized by chloride abstraction from the five-coordinate complex Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (**1**) followed by the introduction of neutral donor ligands. It is also possible to directly displace the chloride of complex **1** by bidentate formate, nitrite, and dithiocarbamate ligands to give the corresponding neutral six-coordinate complexes. A structural study of **1** shows a square-pyramidal geometry about osmium with the boryl ligand in the apical position and with a short Os−B distance. Structural studies of the cationic complexes **2** and **4** and of the neutral dithiocarbamate complex **7** show an octahedral geometry with Os−B distances significantly longer than those found in **1.** A pronounced trans influence for the Bcat ligand is revealed in the structures of **2** and **7**.

Experimental Section

General Considerations. The general experimental and spectroscopic techniques employed in this work were the same as those described previously.[7,11]

Os(Bcat)Cl(CO)(PPh$_3$)$_2$ was prepared according to the literature method.[7]

[Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]SbF$_6$ (2). Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (205 mg, 0.229 mmol) was dissolved in THF (10 mL) in a Schlenk tube, and a solution of AgSbF$_6$ (95 mg, 0.28 mmol) in THF (5 mL) was added by cannula. After the mixture was stirred for 5 min, acetonitrile (0.5 mL) was added and the resultant gray suspension stirred for 30 min. The suspension was then filtered through Celite and the THF removed from the filtrate in vacuo. Addition of CH$_2$Cl$_2$, followed by filtration through Celite, again gave a colorless solution. Addition of EtOH and removal of the CH$_2$Cl$_2$ in vacuo gave a white suspension, to which *n*-hexane was added to

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(11) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793.

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Published on October 8, 1998 on http://pubs.acs.org | doi: 10.1021/om980524w

complete precipitation of the white solid. This was collected on a sintered-glass crucible and washed with EtOH and *n*-hexane. Recrystallization from CH_2Cl_2-n-hexane afforded colorless crystals of **2,** yield 251 mg (93%). Anal. Calcd for $C_{47}H_{40}BF_6N_2O_3P_2Sb.CH_2Cl_2$: C, 45.59; H, 3.35; N, 2.22. Found: C, 45.32; H, 3.60; N, 2.38.

[Os(Bcat)(CO)$_2$(NCMe)(PPh$_3$)$_2$]SbF$_6$ (3). [Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]SbF$_6$ (**2**; 123 mg, 0.104 mmol) was dissolved in CH_2Cl_2 (15 mL). CO gas was bubbled through the solution for 30 s, and then the volume of the solution was reduced to ca. 0.5 mL in vacuo. Addition of *n*-hexane gave a white solid, which was collected and washed with *n*-hexane. Recrystallization from CH_2Cl_2-n-hexane afforded colorless microcrystals of **3**, yield 0.111 g (91%). ^1H NMR indicated $^1/_4$ equiv of CH_2Cl_2 present as solvate. Anal. Calcd for $C_{46}H_{37}BF_6NO_4OsP_2Sb.0.25\ CH_2Cl_2$: C, 46.77; H, 3.18; N, 1.18. Found: C, 46.90; H, 3.22; N, 1.29.

[Os(Bcat)(CO)(NCMe)(CN-*p*-tolyl)(PPh$_3$)$_2$]SbF$_6$ (4). [Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]SbF$_6$ (**2**; 175 mg, 0.148 mmol) was dissolved in CH_2Cl_2 (15 mL). *p*-Tolyl isocyanide (25 mg, 0.213 mmol) was added to the solution, and the mixture was stirred for 15 min. The volume of the solution was reduced to ca. 0.5 mL in vacuo, and *n*-hexane was added to give a white solid, which was collected and washed with *n*-hexane. Recrystallization from CH_2Cl_2-n-hexane afforded colorless crystals of **4**, yield 179 mg (96%). Anal. Calcd for $C_{53}H_{44}BF_6N_2O_3OsP_2Sb$: C, 50.70; H, 3.53; N, 2.23. Found: C, 50.56; H, 3.41; N, 2.05.

Os(Bcat)(η^2-O$_2$CH)(CO)(PPh$_3$)$_2$ (5). Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (150 mg, 0.167 mmol) and NaO_2CH (100 mg, 1.47 mmol) were stirred in a mixture of CH_2Cl_2 (15 mL) and EtOH (5 mL) for 20 min. During this time the mixture changed from yellow to colorless. The sodium salts were removed by filtration and washed with CH_2Cl_2. The filtrate and washings were combined, and the CH_2Cl_2 was removed from the resulting colorless solution in vacuo to give a white suspension. The solid was collected and washed with EtOH and *n*-hexane. This material was recrystallized from CH_2Cl_2-n-hexane to give **5**, yield 136 mg (90%). ^1H NMR indicated $^1/_3$ equiv of CH_2Cl_2 present as solvate. Anal. Calcd for $C_{44}H_{35}BO_5OsP_2\cdot 0.33CH_2Cl_2$: C, 56.95; H, 3.85. Found: C, 56.89; H, 3.71.

Os(Bcat)(η^2-NO$_2$)(CO)(PPh$_3$)$_2$ (6). Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (150 mg, 0.167 mmol) and $NaNO_2$ (100 mg, 1.45 mmol) were stirred in a mixture of CH_2Cl_2 (15 mL) and EtOH (5 mL) for 20 min, the mixture changing color from yellow to colorless. The sodium salts were removed by filtration and washed with CH_2Cl_2. The filtrate and washings were combined, and the CH_2Cl_2 was removed from the resulting colorless solution in vacuo to give a white suspension. The solid was collected and washed with EtOH and *n*-hexane. This material was recrystallized from CH_2Cl_2-n-hexane to give **6**, yield 131 mg (89%). Anal. Calcd for $C_{43}H_{34}BNO_5OsP_2$: C, 56.90; H, 3.78; N, 1.54. Found: C, 56.90; H, 3.58; N, 1.50.

Os(Bcat)(η^2-S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$ (7). Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (125 mg, 0.139 mmol) was dissolved in CH_2Cl_2 (10 mL). A solution of $NaS_2CNEt_2\cdot 3H_2O$ (62 mg, 0.278 mmol) in EtOH (5 mL) was then added to the yellow solution. The mixture was stirred for 15 min, the color changing from yellow to colorless. The CH_2Cl_2 was removed in vacuo to give a white suspension. The solid was collected and washed with EtOH and *n*-hexane. Recrystallization from benzene$-n$-hexane afforded colorless crystals of **7**, yield 115 mg (82%). Anal. Calcd for $C_{48}H_{44}BNO_3OsP_2S_2\cdot C_6H_6$: C, 59.61; H, 4.63; N, 1.29. Found: C, 60.20; H, 4.75; N, 1.27.

X-ray Diffraction Study of 1, 2, 4, and 7. Accurate intensity data were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters were determined by automated matrix determination. Data were collected over a [hemisphere/sphere] of reciprocal space and were corrected for Lorentz and polarization effects by empirical absorption correction (SADABS program, Siemens Area Detector ABSorption correction).

Structure solution was by direct methods/super-sharp Patterson and difference Fourier methods. Refinement was by full-matrix least squares on F^2 with scattering curves taken from the International Tables for Crystallography. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located either by a difference map or included in calculated positions. Hydrogen positions were at fixed lengths with the temperature factor riding on that of the atom to which they were bonded (1.5 times for methyl hydrogens, 1.2 times for all others).

Programs used for structure solution were SHELXS-86 (G. M. Sheldrick, University of Gottingen, 1986), XS (Siemens SHELXTL package, 1995), or SHELXS-97 (G. M. Sheldrick, University of Gottingen, 1997). SHELXL-93 (G. M. Sheldrick, University of Gottingen, 1993), XL (Siemens SHELXTL package, 1995) or SHELXL-97 (G. M. Sheldrick, University of Gottingen, 1997) and were run on a Silicon Graphics INDY work station. Diagrams were produced by the XP program (Siemens SHELXTL package, 1995).

Acknowledgment. We thank the Marsden Fund for supporting this work.

Supporting Information Available: Tables of crystal data and collection and refinement parameters, positional and anisotropic displacement parameters, and bond distances and angles for **1**, **2·CH$_2$Cl$_2$**, **4**, and **7·C$_6$H$_6$** (35 pages). Ordering information is given on any current masthead page.

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