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Synthesis and Spectroscopic and Structural Characterization of Derivatives of the Quasi-Alkoxide Ligand $[OBMes_2]^-$ (Mes = $2,4,6\text{-}Me_3C_6H_2$)

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Treatment of Mes_2BOH (**1**) with *n*-BuLi in hexane/ether affords a suspension of $LiOBMes_2$, which can be crystallized from THF solution as the dimer $[\{Li(THF)OBMes_2\}_2]$ (**2**). Treatment of a slurry of anhydrous $CoCl_2$ in THF with 2 equiv of **2** gives the complex $[Co\{OBMes_2\}_2Li(THF)_2Cl_2Li(THF)_2]$ (**3**) in good yield. The X-ray crystal structures of **1**–**3** are also reported. The structure of **1** is the first for a diorganoboronous acid, and it exists in the solid state as hydrogen-bonded tetramers. The lithium derivative **2** is the first structurally characterized example of a metal salt of a boronous acid, and it possesses a dimeric structure previously seen only with very bulky $-OC(t\text{-}Bu)_3$ and $-OC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me$ salts. The complex **3** has cobalt pseudotetrahedrally bound to two $-OBMes_2$ and Cl^- ligands, which also form bridges to two Li^+ ions. Each Li^+ is also pseudotetrahedrally coordinated, with two THF donors as the remaining ligands in each case. Crystallographic data with Mo Kα radiation ($\lambda = 0.71069$ Å) at 130 K: **1**, $OC_{18}BH_{23}$, M_r 266.19, monoclinic, $C2/c$, $a = 22.934$ (12) Å, $b = 15.248$ (9) Å, $c = 21.993$ (11) Å, $\beta = 125.53$ (3)°, $R = 0.052$; **2**, at 293 K, $O_4C_{44}B_2Li_2H_{60}$, M_r 688.48, monoclinic, $C2/c$, $a = 18.039$ (12) Å, $b = 14.573$ (8) Å, $c = 16.572$ (8) Å, $\beta = 99.86$ (5)°, $R = 0.063$; **3**, $CoCl_2O_6C_{52}B_2Li_2H_{76}$, at 130 K, M_r 962.53, monoclinic, $C2/c$, $a = 20.806$ (7) Å, $b = 12.785$ (3) Å, $c = 19.982$ (4) Å, $\beta = 102.37$ (2)°, $R = 0.042$.

Alkoxide and aryloxide ligands are gradually assuming an important role in inorganic and organometallic chemistry.[2] For example, they have been shown to be extremely useful in the isolation of complexes containing metal–metal multiple bonds[3] as well as valuable supporting ligands for alkene[4] and alkyne metathesis catalysts.[5] Their involvement in catalytic asymmetric epoxidation[6] and their use as bulky ligands[7–9] to obtain unusual coordination numbers and induce reactions involving C–H activation and other reactions[10] has given an added impetus to their study. Interest in this laboratory has focused on structural aspects of alkoxide chemistry. Use of the very bulky groups $-OC(t\text{-}Bu)_3$,[8,11–13] $-OCPh_3$,[14] and $-OC(C_6H_{11})_3$[14] with or without various coligands such as amides[14] or other donors has allowed the isolation of several interesting novel complexes with low coordination number. Recent work by Schrock and co-workers, using the fluoroalkoxide ligands $-OCH(CF_3)_2$ or $-OCMe(CF_3)_2$,[15,16] has shown that the π-donor properties of an alkoxide can be changed by the electron-withdrawing effect of the CF_3 substituent. In a different manner, the π-donor ability of an alkoxide ligand may also be affected by using a substituent at oxygen which has low-lying empty orbitals that can accept electron density from the oxygen lone pairs. Two possible ligands of this type are the boroxide $-OBR_2$ and siloxide $-OSiR_3$, which are not, strictly speaking, alkoxides and may be designated rather as quasi-alkoxide ligands. Diorganoboroxides should be less effective π-electron donors than siloxides since the empty 2p orbital on boron is probably more energetically accessible to the oxygen lone pairs than the 3d orbital on silicon. The oxygen lone pairs should thereby be less available for participation in bonding to the metal. Recent reports by Wolczanski and co-workers have shown that the tri-*tert*-butylsiloxide ligand is capable of supporting unusual bonding in niobium and tantalum complexes.[17]

In this paper we report a facile synthetic route to diorganoboroxide complexes of the interesting $[OBMes_2]^-$ ligand. This ligand was chosen because there is now a considerable body of data which indicates that two mesityl substituents afford the boron center considerable protection from further reaction. This property was recognized early[18] and has been exploited by Wilson[19] and Pelter[20] and more recently by this laboratory.[21] Our object in this preliminary report is to show that metal boroxide complexes can be easily synthesized.

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres HE 43-2 drybox. Solvents were freshly distilled from drying agents and degassed twice before use. Mes_2BF was synthesized by the method of Pelter[22] and Mes_2BOH (**1**) was obtained using the literature procedure.[23] Anhydrous $CoCl_2$ (Alfa) was used as purchased. Electronic spectra were obtained by using a Hewlett-Packard 8450A UV/vis spectrometer. All complexes gave satisfactory C and H analyses.

$[\{Li(THF)(OBMes_2)\}_2]$ (2). Mes_2BOH (1.3 g, 4.8 mmol) in Et_2O (25 mL) cooled in an ice bath was treated dropwise with *n*-BuLi (3.0 mL of a 1.6 M *n*-hexane solution). The resultant white precipitate was redissolved by warming the solution to room temperature and adding THF (5 mL). The addition of *n*-hexane (2 mL) and slow cooling to −20 °C overnight afforded white, well-formed crystals of **2** (1.1 g, 89% yield), mp 155 °C dec.

$[Co(OBMes_2)_2Li(THF)_2Cl_2Li(THF)_2]$ (3). A suspension of $CoCl_2$ (0.27 g, 2.1 mmol) in THF (20 mL) was treated dropwise with a solution of lithiated Mes_2BOH in THF (25 mL) and stirred for 1 h. Cooling

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Table I. Crystal Data and Summary of Data Collection and Refinement[a]

	1	2	3
formula	$OC_{18}BH_{23}$	$O_4C_{44}B_2Li_2H_{60}$	$CoCl_2O_6C_{52}B_2Li_2H_{76}$
fw	266.19	688.48	962.53
cryst system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
conditions	hkl, $h + k = 2n$ $h0l$, $l = 2n$	hkl, $h + k = 2n$ $h0l$, $l = 2n$	hkl, $h + k = 2n$ $h0l$, $l = 2n$
cryst dimens, mm	0.24 × 0.26 × 0.31	0.33 × 0.33 × 0.5	0.35 × 0.37 × 0.50
cryst color and habit	colorless parallelepipeds	colorless parallelpipeds	blue prismatic
temp, K	130	293	130
a, Å	22.934 (12)	18.039 (12)	20.806 (7)
b, Å	15.248 (9)	14.573 (8)	12.785 (3)
c, Å	21.993 (11)	16.572 (8)	19.982 (4)
α, deg			
β, deg	125.53 (3)	99.86 (5)	102.37 (2)
γ, deg			
V, Å^3	6260 (6)	4292 (4)	5192 (2)
Z	16 (4 tetramers)	4	4
d_{calcd}, g/cm^3	1.13	1.06	1.23
linear abs coeff, cm^{-1}	0.62	0.60	4.9
scan speed, deg min^{-1}	8	15	15
scan width, deg	1.0	1.0	1.0
max 2θ, deg	45	50	50
ω offset for bkgd, deg	1.0	1.0	1.0
range of abs factors	1.13–1.23	1.02–1.03	1.15–1.23
octants	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of variables	397	255	313
data/variable ratio	6.88	6.58	11.54
no. of check reflcns	2; (137), $(22\bar{9})$; no decay	2; (004), (021); no decay	3; $(6\bar{2}\bar{3})$, (026), $(8\bar{4}1)$; no decay
no. of reflcns collcd	4165	4077	5011
R(merge)	0.016	0.024	0.005
no. of unique data	3889	3792	4578
no. of data used in refinement	2733 $I > 2.5\sigma(I)$	1678 $I > 2.5\sigma(I)$	3613 $I > 2.0\sigma(I)$
$R(F)$	0.052	0.063	0.042
$R_w(F)$	0.057	0.067	0.045
weighting scheme	$[\sigma^2(F_o) + 0.0024F_c^2]^{-1}$	$[\sigma^2(F_o) + 0.0006F_c^2]^{-1}$	$[\sigma^2(F_o)]^{-1}$
largest Δ/σ	0.017 for overall scale	0.019 for rotation of H on C(8)	0.017 for U_{23} of C(16)
largest feature in final diff map, e Å^{-3}	0.33 in vicinity of O(2), probably H unable to refine	0.16 in vicinity of THF	0.25 near C(10)

[a] All data was taken with Mo Kα radiation with λ = 0.710 69 Å using a ω-scan technique. $R = \sum||F_o| - |F_c||/|F_o$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_ow^{1/2}|$ with weighting scheme as listed above.

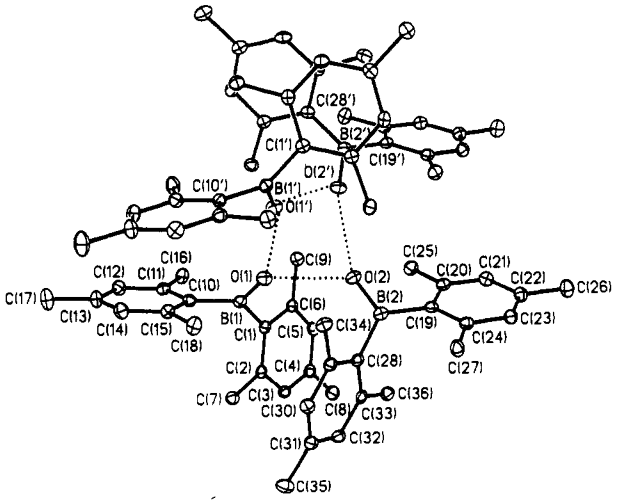

Figure 1. Computer-generated thermal ellipsoid plot of **1** showing tetrameric structure. The H atoms are omitted for clarity.

overnight to −20 °C afforded blue crystals of the product **3** (0.88 g, yield (not optimized) 44%), mp 125 °C (dec). UV/vis spectrum in THF (nm, ε values in parentheses): 542 (138), 568 (154), 626 (247), 656 (256).

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified low-temperature device. Calculations were carried out on a Data General Eclipse computer using SHELXTL version 4 programs. The atomic form factors including anomalous scattering were taken from ref 24. Colorless crystals of **1** and **2** and blue crystals of **3** were grown as described. In each case, after removal from the Schlenk tube, the crystals were protected from air contamination by covering them with a hydrocarbon oil. For compounds **1** and **3** a crystal of each complex was selected under the microscope, attached to a glass fiber on a mounting pin with silicon grease and immediately placed in the cold N_2 stream of the diffractometer. Due to shattering at low temperature the data collection for **2** was at room temperature (293 K). A single crystal was coated and mounted with epoxy on the glass fiber. Table I summarizes the experimental details for each compound. Additional details are given below. In each of the structure determinations, the systematic absences were consistent with the space groups *Cc* or *C*2/*c*. All three were successfully solved and refined in the centrosymmetric space group *C*2/*c*, and there were no disorder problems to indicate that *Cc* should be used. Atom coordinates for **1**–**3** are provided in Table II.

Mes$_2$BOH (1). The structure was solved by direct methods. All non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms on the mesityl rings were included using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter. The hydroxyl hydrogen appeared on the difference map with an electron density of ~0.33e but could not be refined.

[{Li(THF)OBMes$_2$}$_2$] (2). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogens were included by using the riding model described for **1**. The rotation observed in the methyl groups and the large thermal parameters for the THF carbons are probably due to greater motion at the higher (room) temperature used for data collection.

[Co{OBMes$_2$}$_2$Li(THF)$_2$Cl$_2$Li(THF)$_2$] (3). The structure was solved by the Patterson method. An absorption correction was applied by use of the program XABS.[25] All non-hydrogen atoms were refined anisotropically. Hydrogens were added by the riding model described for **1**.

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(24) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(25) Hope, H.; Moezzi, B. The program obtains an absorption tensor from $F_o - F_c$ differences.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3 Å^2)

	x	y	z	U^a		x	y	z	U^a
Compound **1**									
O(1)	294 (1)	7104 (1)	2108 (1)	37 (1)	C(17)	−349 (2)	2993 (2)	855 (2)	56 (2)
O(2)	691 (1)	8723 (1)	2711 (1)	37 (1)	C(18)	1016 (2)	5343 (2)	2763 (2)	43 (2)
B(1)	353 (2)	6753 (2)	1574 (2)	28 (2)	C(19)	1439 (2)	10099 (2)	3237 (2)	28 (2)
B(2)	1361 (2)	9083 (3)	3069 (2)	30 (2)	C(20)	960 (2)	10701 (2)	2670 (2)	31 (2)
C(1)	630 (2)	7385 (2)	1224 (2)	27 (2)	C(21)	1035 (2)	11594 (2)	2827 (2)	35 (2)
C(2)	1268 (2)	7198 (2)	1291 (2)	28 (2)	C(22)	1567 (2)	11930 (2)	3519 (2)	35 (2)
C(3)	1521 (2)	7778 (2)	1008 (2)	31 (2)	C(23)	2037 (2)	11342 (2)	4075 (2)	34 (2)
C(4)	1166 (2)	8545 (2)	644 (2)	32 (2)	C(24)	1980 (2)	10442 (2)	3949 (2)	30 (2)
C(5)	534 (2)	8723 (2)	570 (2)	31 (2)	C(25)	374 (2)	10418 (2)	1887 (2)	39 (2)
C(6)	263 (2)	8166 (2)	855 (2)	27 (2)	C(26)	1635 (2)	12910 (2)	3651 (2)	47 (2)
C(7)	1694 (2)	6375 (2)	1678 (2)	34 (2)	C(27)	2496 (2)	9851 (2)	4593 (2)	42 (2)
C(8)	1447 (2)	9156 (2)	335 (2)	45 (2)	C(28)	1985 (2)	8432 (2)	3261 (2)	28 (2)
C(9)	−437 (2)	8407 (2)	730 (2)	35 (2)	C(29)	2126 (2)	7661 (2)	3686 (2)	30 (2)
C(10)	160 (2)	5750 (2)	1378 (2)	29 (2)	C(30)	2654 (2)	7082 (2)	3815 (2)	34 (2)
C(11)	−337 (2)	5465 (2)	632 (2)	32 (2)	C(31)	3056 (2)	7218 (2)	3537 (2)	33 (2)
C(12)	−501 (2)	4580 (2)	479 (2)	38 (2)	C(32)	2924 (2)	7978 (2)	3130 (2)	34 (2)
C(13)	−181 (2)	3947 (2)	1038 (2)	38 (2)	C(33)	2403 (2)	8583 (2)	2991 (2)	30 (2)
C(14)	304 (2)	4228 (2)	1764 (2)	38 (2)	C(34)	1718 (2)	7453 (2)	4020 (2)	37 (2)
C(15)	476 (2)	5108 (2)	1946 (2)	33 (2)	C(35)	3606 (2)	6565 (3)	3663 (2)	46 (2)
C(16)	−727 (2)	6106 (2)	−13 (2)	38 (2)	C(36)	2281 (2)	9380 (2)	2525 (2)	38 (2)
Compound **2**									
O(1)	595 (2)	1342 (2)	1986 (2)	74 (1)	C(9)	−289 (2)	2356 (3)	433 (3)	80 (2)
O(2)	0	−833 (3)	2500	85 (2)	C(10)	1495 (2)	431 (2)	1379 (3)	53 (2)
O(3)	0	3486 (2)	2500	77 (2)	C(11)	1450 (2)	−7 (3)	618 (3)	55 (1)
B	1020 (3)	1347 (3)	1482 (3)	58 (2)	C(12)	1822 (2)	−845 (3)	554 (3)	63 (2)
Li(1)	0	496 (7)	2500	86 (5)	C(13)	2250 (2)	−1252 (3)	1242 (3)	66 (2)
Li(2)	0	2181 (7)	2500	81 (5)	C(14)	2304 (2)	−812 (3)	1969 (3)	68 (2)
C(1)	1130 (2)	2263 (2)	969 (2)	50 (1)	C(15)	1932 (2)	9 (3)	2065 (3)	66 (2)
C(2)	1846 (2)	2657 (3)	978 (2)	51 (2)	C(16)	1003 (2)	395 (3)	−158 (3)	69 (2)
C(3)	1909 (2)	3494 (3)	589 (3)	62 (2)	C(17)	2646 (3)	−2158 (3)	1160 (4)	104 (3)
C(4)	1295 (3)	3959 (3)	162 (3)	69 (2)	C(18)	2034 (3)	434 (4)	2912 (3)	96 (2)
C(5)	602 (2)	3561 (3)	135 (3)	65 (2)	C(19)	−296 (4)	−1411 (3)	3043 (4)	124 (3)
C(6)	507 (2)	2732 (3)	522 (3)	58 (2)	C(20)	−182 (5)	−2321 (4)	2867 (4)	166 (5)
C(7)	2559 (2)	2209 (3)	1415 (3)	69 (2)	C(21)	630 (3)	4050 (3)	2440 (4)	94 (2)
C(8)	1390 (3)	4876 (3)	−239 (4)	106 (3)	C(22)	347 (3)	5007 (3)	2323 (5)	132 (4)
Compound **3**									
Co	0	7228 (1)	7500	22 (1)	C(13)	1028 (1)	8806 (2)	10091 (1)	28 (1)
Cl	643 (1)	8405 (1)	7071 (1)	33 (1)	C(14)	493 (1)	8141 (2)	907 (1)	26 (1)
O(1)	517 (1)	6134 (1)	8048 (1)	24 (1)	C(15)	483 (1)	7326 (2)	9445 (1)	23 (1)
O(2)	477 (1)	3978 (1)	7053 (1)	32 (1)	C(16)	2157 (1)	7760 (2)	8987 (2)	34 (1)
O(3)	628 (1)	10566 (1)	8068 (1)	31 (1)	C(17)	1032 (2)	9674 (2)	10607 (2)	43 (1)
C(1)	1585 (1)	5362 (2)	8692 (1)	20 (1)	C(18)	−113 (1)	6620 (2)	9316 (1)	27 (1)
C(2)	1951 (1)	5198 (2)	8180 (1)	25 (1)	C(19)	863 (1)	3179 (2)	7473 (1)	33 (1)
C(3)	2421 (1)	4411 (2)	8250 (1)	27 (1)	C(20)	1311 (2)	2696 (3)	7042 (2)	48 (1)
C(4)	2544 (1)	3743 (2)	8816 (1)	24 (1)	C(21)	1247 (2)	3415 (3)	6433 (2)	45 (1)
C(5)	2188 (1)	3903 (2)	9317 (1)	24 (1)	C(22)	559 (2)	3839 (2)	6360 (2)	42 (1)
C(6)	1719 (1)	4701 (2)	9271 (1)	22 (1)	C(23)	1319 (1)	10330 (2)	8218 (2)	38 (1)
C(7)	1846 (2)	5876 (2)	7544 (1)	35 (1)	C(24)	1630 (2)	11141 (3)	8740 (2)	52 (1)
C(8)	3056 (1)	2893 (2)	8881 (2)	30 (1)	C(25)	1080 (2)	11499 (3)	9074 (2)	58 (1)
C(9)	1355 (1)	4822 (2)	9843 (1)	32 (1)	C(26)	484 (2)	10884 (3)	8710 (2)	43 (1)
C(10)	1024 (1)	7156 (2)	9132 (1)	21 (1)	Li(1)	0	9635 (5)	7500	35 (2)
C(11)	1568 (1)	7841 (2)	9317 (1)	25 (1)	Li(2)	0	5035 (5)	7500	27 (2)
C(12)	1559 (1)	8641 (2)	9787 (1)	29 (1)	B	1014 (1)	6224 (2)	8592 (2)	22 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The boronous acid Mes_2BOH (**1**) is readily prepared in good yield from the reaction of Mes_2BF with water as described in the literature.[23] Its structure is depicted in Figure 1. Selected bond distances and angles are given in Table III. So far as we are aware it is the first structural characterization of a organo-substituted boronous acid although two structures of the related boronic acids $PhB(OH)_2$[26] and $4\text{-}BrC_6H_4B(OH)_2$[27] have been reported. The compound crystallizes as tetramers due to hydrogen bonding involving the OH groups. The boron centers remain planar with a rather wide CBC angle of 126.0 (4)°. The mesityl rings are at a mean angle of approximately 55° with respect to the C_2BO plane. This is similar to what is found in other boron mesityl derivatives.[28] The B–C distances have the same value of 1.579 (5) Å, which is in the range normally found for three-coordinate boron.[29] The average B–O bond length is 1.368 (5) Å which is almost identical to the B–O distance expected for three coordinate boron.[29]

The compound **1** readily reacts with *n*-BuLi on hexane/ether to give almost quantitative yields of **2**. Its structure is illustrated

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Table III. Selected Bond Distances (Å) and Angles (deg) for **1**–**3**

	Compound **1**		
B(1)–O(1)	1.367 (6)	O(1)B(1)C(1)	116.7 (3)
B(1)–C(1)	1.579 (6)	O(1)B(1)C(10)	117.4 (4)
B(2)–C(19)	1.579 (5)	C(1)B(1)C(10)	125.9 (4)
B(2)–O(2)	1.369 (4)	C(19)B(2)C(28)	126.1 (3)
B(1)–C(10)	1.581 (5)		
B(2)–C(28)	1.584 (5)		
O(1)···O(1)′	2.737 (6)		
O(2)···O(2)′	2.736 (6)		
O(1)···O(2)	2.699 (6)		
	Compound **2**[a]		
B–O(1)	1.317 (6)	Li(1)O(1)Li(2)	83.2 (3)
Li(1)–O(1)	1.853 (7)	O(1)Li(1)O(1)′	96.6 (5)
Li(1)–O(2)	1.938 (10)	O(1)Li(2)O(1)′	97.1 (5)
Li(2)–O(1)	1.845 (7)	O(1)BC(1)	119.7 (4)
Li(2)–O(3)	1.903 (10)	O(1)BC(10)	119.4 (4)
B–C(1)	1.613 (6)	C(1)BC(10)	120.9 (4)
B–C(10)	1.611 (6)		
	Compound **3**[b]		
Co–Cl	2.297 (1)	O(1)CoO(1)′	88.4 (1)
Co–O(1)	1.951 (2)	ClCoCl′	98.2 (1)
Li(1)–Cl	2.343 (4)	CoClLi(1)	83.1 (1)
Li(1)–O(3)	1.943 (4)	ClLi(1)Cl′	95.6 (2)
Li(2)–O(1)	1.956 (5)	O(3)Li(1)O(3)′	104.4 (3)
Li(2)–O(2)	1.997 (5)	CoO(1)Li(2)	91.8 (1)
B–O(1)	1.336 (3)	O(1)Li(2)O(1)′	88.1 (3)
B–C(1)	1.602 (4)	O(2)Li(2)O(2)′	94.8 (3)
B–C(10)	1.605 (4)	CoO(1)B	129.2 (2)
		Li(2)O(1)B	139.0 (2)
		C(1)BC(10)	121.6 (2)
		O(1)BC(1)	117.8 (2)
		O(1)BC(10)	120.5 (2)

[a] Average angle between the Mes and OBC_2 plane is 55°. [b] Average angle between the Mes and OBC_2 plane is 57°.

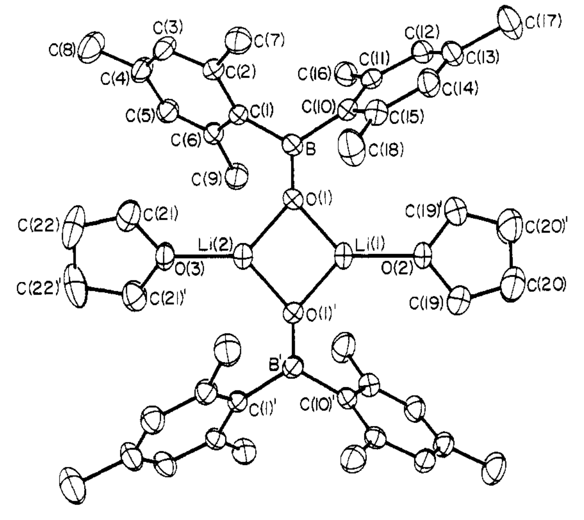

Figure 2. Computer-generated thermal ellipsoid plot of **2**. The H atoms are omitted for clarity.

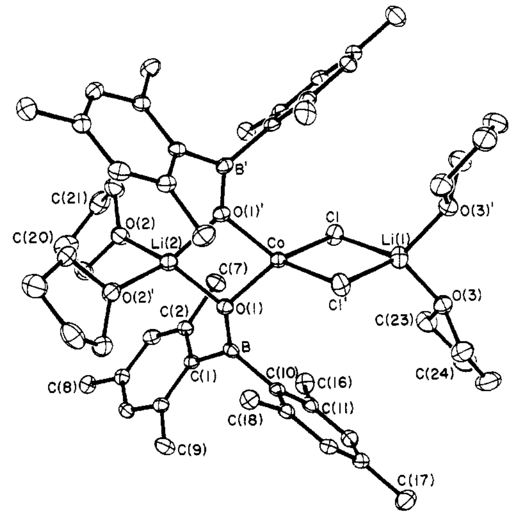

Figure 3. Computer-generated thermal ellipsoid plot of **3**. The H atoms are omitted for clarity.

in Figure 2. It crystallizes as a dimer from a THF/Et_2O/hexane solution and has two $[OBMes_2]^-$ groups bridged by two lithium ions to form an Li_2O_2 core. Each Li^+ is also coordinated to a THF molecule. There is a crystallographically imposed 2-fold rotation axis through the Li(1)···Li(2) vector. Selected bond distances and angles are given in Table III. The angles at boron are quite regular, but the B–C(1), B–C(10) and B–O(1) bond lengths show interesting changes from those found in the parent ligand **1**. The mean B–C distance in **2** is 1.612 (6) Å whereas in **1** it is 1.58 Å. In **2** the B–O distance is 1.317 (6) Å whereas in **1** it is 1.368 (5) Å. The longer B–C and shorter B–O bonds in **2** may be explained in a number of ways. In valence bond terms, the planar nature of the oxygen in **2** involves three bond pairs at oxygen bonding to two lithium ions and boron. The remaining lone pair is in an essentially 2p orbital, which can overlap effectively with the empty 2p orbital on boron. In ionic terms there is a greater electron density on the O(1) atom owing to a greater charge separation in the more ionic **2** relative to that in Mes_2BOH. This affords greater electron density at oxygen, which in turn results in a stronger and shorter B–O bond due to increased electron availability. The trend in the B–C bond lengths supports this argument. The B–C distances in **2** are significantly longer because any interaction between the π-electrons on the aromatic rings and the 2p orbital on boron is reduced due to the increase in the B–O interaction. A further effect of the multiple B–O bond is apparent in comparing the CBC angles. In **1** the average value is 126.0 (4)° whereas in **2** it is reduced to 120.9 (4)°.

The overall structure and stoichiometry in **2** is very similar to that seen in the complexes $[\{Li(THF)OC(t\text{-}Bu)_3\}_2]$[8] (**4**) and $[\{Li(Et_2O)OC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}R\}_2]$ (R = Me (**5**),[30] H (**6**)[31]). The Li–O distances in all three complexes are very similar. However, an interesting indication of the degree of B–O multiple bonding in **2** may be found by comparison of the distance 1.317 (6) Å with the much longer mean C–O distance of 1.39 Å in **4** even though boron has a radius almost 0.1 Å greater than carbon. Also noteworthy is the fact that **4**–**6** are almost certainly dimeric, rather than more highly aggregated, due to steric effects. However, molecular models show that $-OBMes_2$ is not as crowding as either the $OC\text{-}t\text{-}Bu_3$ or $OC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me$ groups so that a higher degree of aggregation of solvation might be predicted for **2**. One explanation for the dimeric nature of **2** is that the lower electron density at the oxygens reduces their ability to achieve higher coordination numbers. Thus, the stoichiometry of **2** may be regarded as further evidence of the different electronic properties of the $[OBMes_2]^-$ group.

The lithium salt **2** reacts smoothly with $CoCl_2$ in THF to give complex **3**, which is shown in Figure 3. The cobalt(II) ion is in a distorted tetrahedral environment of two Cl^- and two $[OBMes_2]^-$ ligands. Both the chlorides and the boroxides also bridge to two lithium ions. Each lithium ion is pseudotetrahedrally coordinated due to the coordination of each to two THF donors. Prominent bond distances and angles are given in Table III.

The cobalt center is the main feature of interest in the context of the ligand behavior of $[OBMes_2]^-$. The Co–O distance is 1.951 (2) Å, which has to be considered in the light of other four-coordinate Co(II)–O(alkoxide) bond lengths. Perhaps the most relevant compound is $Co(OCPh_3)_2(THF)_2$,[14] which also has cobalt in a distorted tetrahedral configuration. The $Co\text{-}OCPh_3$ bond is 1.872 (2) Å, much shorter than the 1.951 (2) Å for the $Co\text{-}OBMes_2$ distance in **3**. Since $OBMes_2$ is a bridging moiety, a longer Co–O distance may be expected, making it difficult to draw accurate conclusions. However, it is notable that in the three-coordinate cobalt alkoxides $Co(OC\text{-}t\text{-}Bu_3)_2Cl(THF)_3$ and $Co(OC\text{-}t\text{-}Bu_3)_2N(SiMe_3)_2Li$ there is little difference in the Co–O bond lengths whether or not the alkoxide forms a bridge to lithium.

Therefore the Co–O lengths in these cobalt alkoxides suggest that the Co–O distance in **3** is rather long. This lends further support to the view that the $[OBMes_2]^-$ ligand is a less effective π-donor than alkoxides. The preservation of the short B–O distance is also good evidence for the multiple nature of the B–O bond. This fact, in combination with the suggestion of reduction in π-donor character in the cobalt complex above, indicates that the $[OBMes_2]^-$ will prove a useful ligand in other systems. The syntheses of earlier transition-metal complexes where the changes in M–O distances should be more clear-cut are underway.

The UV/vis absorption spectrum of **3** in THF is fully consistent with the X-ray structural data. The ^4F ground state for a Co^{2+} ion in a tetrahedral field is split into three states, $^4A_2$, $^4T_2$, and $^4T_1$, so that two absorptions may be expected. The imposition of a lowered C_{2v} symmetry on the basic T_d configuration splits the two T states, giving the observed total of four absorptions.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (11 pages); tables of structure factors (49 pages). Ordering information is given on any current masthead page.

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A Novel Case of Metal–Metal Bond Mobility. Structure and Fluxional Behavior of $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2][BPh_4]$ and Related Compounds

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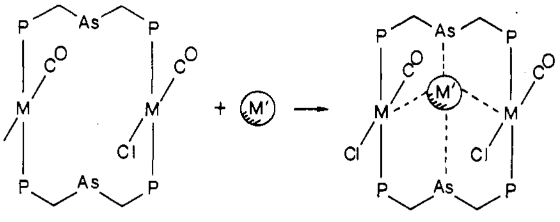
Treatment of the metallamacrocycle $Rh_2(CO)_2Cl_2(\mu\text{-dpma})_2$ (dpma is bis((diphenylphosphino)methyl)phenylarsine) with bis(benzonitrile)palladium(II) chloride results in the introduction of palladium into the center of the macrocycle to form $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-dpma})_2]^+$, which has been isolated as the tetraphenylborate salt. The corresponding bromide and iodide complexes have been prepared by metathesis. An analogous iridium complex, $[Ir_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-dpma})_2]^+$, has been prepared. Red parallelepipeds of $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-dpma})_2][BPh_4]\cdot 2CH_2Cl_2\cdot(C_2H_5)_2O$ were grown by diffusion of ethyl ether into a dichloromethane solution of **5**. They belong to the monoclinic space group $P2_1/n$ (No. 14) with $a = 20.354$ (3) Å, $b = 14.494$ (3) Å, $c = 32.987$ (5) Å, and $\beta = 104.65$ (1)° at 140 K, $Z = 4$, and $R = 0.071$ for 11 021 reflections with $I > 2\sigma(I)$ and 535 parameters. The cation contains a palladium at the center of the original macrocycle. The palladium is bound to two trans arsines, a bridging chloride, and Rh(2). A Pd–Cl bond has oxidatively added to Rh(2), which has as ligands two trans phosphines, two chloride ligands, a terminal carbon monoxide, and the palladium ion (Pd–Rh(2), 2.699 (1) Å). Rh(1) has as ligands two trans phosphines, a terminal carbonyl, and a bridging chloride. ^{31}P and ^{13}C NMR data in solution indicate that a fluxional process renders the two ends of $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-dpma})_2]^+$ equivalent through a process that must relocate the chloride ligands and the Rh–Pd bond. The mechanism of this process is discussed in the context of experimental observations.

Introduction

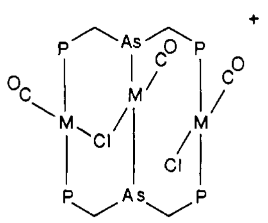
The metallamacrocycles $Rh_2(CO)_2Cl_2(\mu\text{-dpma})_2$ (**1**) and $Ir_2(CO)_2Cl_2(\mu\text{-dpma})_2$ (**2**) (dpma is bis((diphenylphosphino)methyl)phenylarsine) have central cavities that are capable of binding a variety of metal ions, as shown schematically in eq 1.[1,2]



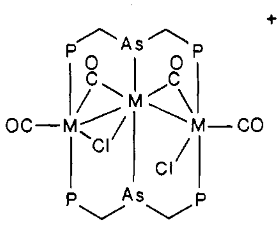
(1)

1, M = Rh
2, M = Ir

We have reported on the systematic synthesis of a series of complexes, **3** and **4**, with nearly linear Rh_3, RhIrRh, IrRhIr, and Ir_3



3



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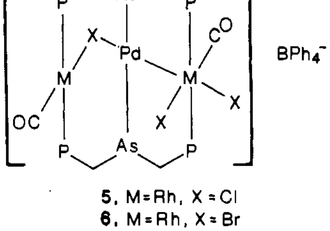
chains.[2] In solution these cations, and an analogous Rh_3 chain involving the corresponding triphosphine, bis((diphenylphosphino)methyl)phenylphosphine (=dpmp), undergo facile bridge/terminal halide exchange, which renders the two end metal environments equivalent.[3,4] The insertions of palladium(II) into **1** and **2** have also been briefly described.[1] Here we report details of this reaction, structural characterization of the products, and delineation of the fluxional behavior of these mixed-metal species.

Results

Synthetic Studies. Treatment of **1** with bis(benzonitrile)palladium(II) chloride in dichloromethane solution yields a deep red solution from which red crystals of $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-dpma})_2][BPh_4]$ (**5**) are obtained in 75% yield upon precipitation with a methanol solution of sodium tetraphenylborate. Because a change in the halide ligand produces significant structural changes in complexes of the $[M_3(\mu\text{-dpmp})_2(CO)_3X_2]^+$ or $[M_3(\mu\text{-dpma})_2(CO)_3X_2]^+$ type,[3] the effect of exchanging chloride for



5, M = Rh, X = Cl
6, M = Rh, X = Br
7, M = Rh, X = I
8, M = Ir, X = I
9, M = Ir, X = Cl

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