It is probably for this reason that the discrepancies between observed and calculated average M–O bond lengths are, in general, larger for the aqua ligands than for the nitrato ligands.

Calculated strain energy values are also given in Table VII. The negative values are due to the fact that the amount of strain resulting from steric repulsion in the inner coordination sphere is more than compensated for by the numerous long-range attractive van der Waals interactions. Comparisons reveal only small differences in energy for the structural isomers present in Table VII. The NH_4^+ isomer of $La(NO_3)_5(OH_2)_2^{2-}$ is only 2.5 kJ/mol lower in energy than the K^+ isomer. Even smaller differences are observed when calculations are carried out for the same metal ion in the two configurations of $M(NO_3)_3(OH_2)_3$ (the Gd form is 0.4 kJ/mol lower in energy than the Dy form) and in the two configurations of $M(NO_3)_5(OH_2)^{2-}$ (the Nd form is 0.08 kJ/mol lower in energy than the Sm form).

Summary

This study shows how molecular mechanics methodology can be successfully applied to the calculation of structure in high-coordinate metal complexes. A simple method based on the replacement of L–M–L bending interactions with nonbonded interactions between the ligand donor atoms and the use of harmonic M–L stretching potentials yields very reasonable geometric results. The method has been tested by generating 58 known structures of the aqua- and nitratolanthanide(III) complexes. In the majority of cases the discrepancies between observed and calculated M–O bond lengths and O–M–O bond angles are $\leq$0.03 Å ($\leq$1–2%) and $\leq$3°, respectively. Larger discrepancies can be traced to lattice distortions in the observed structures, which are not included in the model.

Although this study has focused on modeling geometries found in high-coordinate metal complexes, the methodology is not limited to the f-block metals. Force fields based on repulsions between ligand donor atoms are suitable models for many of the more common geometries encountered in coordination compounds.[12-16] The MM2 implementation of this type of force field can be used to generate the important tetrahedral, trigonal-bipyramidal, and octahedral geometries found in transition-metal complexes. Square-planar and square-pyramidal geometries can also be obtained.[52] This approach provides a useful alternative to the conventional molecular mechanics force fields that rely upon the definition of strain-free L–M–L bond angles.

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Supplementary Material Available: An example MM2 input file for $Lu(OH_2)_8^{3+}$ (1 page). Ordering information is given on any current masthead page.

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(52) These two geometries can be obtained either by restricting four of the donor atoms to lie in the XY plane or by introducing lone pair(s) in the axial position(s).

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Synthesis and Spectroscopic and X-ray Structural Characterization of the First Homoleptic Transition-Metal Boryloxides $[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$ and $[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$

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The reactions of the metal amides $Mn[N(SiMe_3)_2]_2$ and $Fe[N(SiMe_3)_2]_2$ with the sterically crowded boronous acids $Trip_2BOH$ and Mes_2BOH (Trip = 2,4,6-*i*-$Pr_3C_6H_2$, Mes = 2,4,6-$Me_3C_6H_2$) afford the compounds $[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$ (**1**) and $[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ (**2**), which are the first two examples of homoleptic transition-metal boryloxides. The X-ray crystal structures of compounds **1** and **2** have also been determined. The data show that both **1** and **2** are dimeric with three-coordinate Mn and Fe centers that are bound to one terminal boryloxide ligand and to two bridging boryloxide ligands. The M···M distances (3.094 (5) Å for Mn and 3.057 (5) Å for Fe) are considerably longer than those found in the amide precursors. Surprisingly, the metric features of **1** and **2** are very close to those observed in the closely related bis(aryloxo) complexes $[M(OAr)_2]_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$, M = Mn (**3**), Fe (**4**)). This suggests that the M–O bonding in **1**–**4** is similar: furthermore, it is mainly ionic and little evidence for a π-contribution to the M–O bond could be observed. Compounds **1** and **2** have also been characterized by magnetic measurements. Crystallographic data with Mo Kα radiation (λ = 0.71069 Å) at 130 K: **1**, a = 33.898 (11) Å, b = 16.985 (5) Å, c = 30.861 (11) Å, β = 134.65 (2)°, Z = 4, R = 0.088, space group $C2/c$; **2**, a = 15.004 (5) Å, b = 14.957 (4) Å, c = 16.915 (6) Å, β = 93.86 (3)°, Z = 2, R = 0.074, space group $P2_1/n$.

Introduction

The increasing availability of detailed knowledge of the structures and reactivity of molecular transition-metal alkoxides and aryloxides has, with a few important exceptions, been concerned with the early metals.[1-5] For example, if homoleptic alkoxides or aryloxides of formula $[M(OR)_n]$ (n = 2, 3, etc; M = Mn, Fe, Co, Ni, Cu) are considered, only a small number of these or related complexes have been well characterized. Spectroscopic and analytical data have appeared for a few species such as $[LiFe(OR)_4]$, $[Co(OR)_2]_2$ (R = CH(*t*-Bu)$_2$ or 1-adamantyl).[6,7]

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In addition, the structures of the compounds $[Co\{OCR_3\}_2]_2$[8] (R = C_6H_{11} or Ph), $[Co(Cl)\{OC(t\text{-}Bu)_3\}_2Li(THF)_3]$,[9] and $[Co\{N(SiMe_3)_2\}\{OC(t\text{-}Bu)_3\}_2]^-$ with Li^+ or $[Li(THF)_{4.5}]^+$[9] counterions have been determined. No X-ray crystal structural data are available for the homoleptic alkoxides or aryloxides of Ni(II) or Cu(II), and the structure of only one homoleptic Mn(II) complex (the trimer $[Mn\{OCH(t\text{-}Bu)_2\}_2]_3$)[10] has appeared. In addition, the structure of $[Fe\{O(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2]_2$[11] has been described briefly in a review.

A common feature of all these complexes is the presence of large organic substituents at oxygen that prevent extensive association and allow molecular complexes to be more readily characterized. Crystallographic and spectroscopic work in this laboratory has shown that the degree of association can be limited to 2 if bulky groups are employed.[8] With the objective of isolating mononuclear compounds, we have attempted to reduce the bridging tendency in $M(OR)_2$ complexes by using the quasi-alkoxide ligand OBR_2 instead of the OR group. Previous work on the transition metals with this class of ligand had involved the reaction between $CoCl_2$ and 2 equiv of $LiOBMes_2$ to give the bridged compound $[Co\{OBMes_2\}_2Li(THF)_2Cl_2(THF)_2]$.[12] In order to avoid the inclusion of Li^+ or Cl^- ions in the products, we have used the easily purified amides $M[N(SiMe_3)_2]_2$ (M = Mn[13] or Fe[14]) as precursors. Their treatment with the appropriate diarylboronous acid affords the neutral, homoleptic products $[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]$ (**1**) and $[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ (**2**), which are now described in this paper.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or a Vacuum Atmosphere HE43-2 drybox. Solvents were freshly distilled under N_2 from Na/K or sodium/potassium benzophenone ketyl and degassed twice immediately before use. Magnetic moment measurements were performed by using the Evans method.[15] Mes_2BF,[16] $Trip_2BF$,[16] Mes_2BOH,[17] and $Trip_2BOH$[18] were synthesized as previously described. $Mn[N(SiMe_3)_2]_2$[13] was synthesized via a slight modification of the literature method. This involved the reaction of MnI_2 with 2 equiv of $LiN(SiMe_3)_2$ under reflux in Et_2O for 2 h. $Fe[N(SiMe_3)_2]_2$ was isolated as recently described in the literature.[14] Both **1** and **2** gave satisfactory C and H analyses; however, no absorptions were apparent in their UV-vis spectra other than a slight increase in intensity toward higher energy. This behavior is reminiscent of that observed for manganese(II) and iron(II) amides.[11]

$[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$ (1). Addition of toluene (25 mL) to a $Mn[N(SiMe_3)_2]_2$ (0.75 g, 2 mmol) and $Trip_2BOH$ (1.74 g, 4 mmol) mixture at room temperature gave an immediate reaction. After the solution was stirred for 30 min, the volatile byproduct $HN(SiMe_3)_2$ and toluene were removed under reduced pressure. The residue was extracted with hexane (20 mL), and the solution was filtered. The volume was then reduced to ca. 5 mL under reduced pressure. Cooling overnight in a −20 °C freezer gave the product $[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$ (**1**) as pink crystals: yield 1.10 g, 60%; mp 176–178 °C.

$[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ (2). A mixture of $Fe[N(SiMe_3)_2]_2$ (1.51 g, 4 mmol) and Mes_2BOH (2.13 g, 8 mmol) was dissolved in toluene (40 mL) at room temperature. After the solution was stirred for 1 h, the volume was reduced to ca. 15 mL. Slow cooling in a −20 °C freezer gave light brown crystals of the product, **2**: yield 0.47 g, 20%; dec at 120 °C.

Table I. Crystallographic Data for Compounds **1** and **2**

	1	2
compound	$[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$	$[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$
formula	$C_{120}H_{184}B_4Mn_2O_4 \cdot C_6H_{14}$	$C_{72}H_{88}B_4Fe_2O_4 \cdot 2C_7H_8$
fw	1930.1	1356.7
a, Å	33.898 (11)	15.004 (5)
b, Å	16.985 (5)	14.957 (4)
c, Å	30.861 (11)	16.915 (6)
β, deg	134.65 (2)	93.86 (3)
V, Å^3	12641 (7)	3787 (2)
Z	4	2
space group	*C*2/*c*	*P*2$_1$/*n*
T, K	130	130
λ, Å	0.71069	0.71069
d(calcd), g/cm^3	1.00	1.19
μ(Mo Kα), cm^{-1}	2.3	4.2
range of transn factors	0.93–0.95	0.91–0.94
R	0.088	0.074
R$_w$	0.094	0.075

Table II. Selected Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1** and **2**

	x	*y*	*z*	*U*, Å^2
		1		
Mn	571 (1)	5286 (1)	2714 (1)	21 (1)*
O(1)	1200 (2)	4760 (3)	2979 (2)	24 (4)*
O(2)	252 (2)	5482 (3)	3084 (2)	17 (4)*
B(1)	1565 (4)	4297 (7)	3070 (5)	29 (7)*
B(2)	396 (4)	5820 (6)	3577 (4)	16 (6)*
C(1)	2193 (3)	4208 (5)	3723 (4)	24 (2)
C(16)	1397 (4)	3794 (5)	2514 (4)	30 (2)
C(31)	1022 (3)	5896 (5)	4204 (4)	21 (2)
C(46)	−97 (3)	6138 (5)	3499 (4)	23 (2)
		2		
Fe	4090 (1)	5018 (1)	5355 (2)	27 (1)*
O(1)	3067 (3)	5497 (4)	5694 (3)	27 (2)*
O(2)	5269 (3)	4353 (3)	5470 (3)	23 (2)*
B(1)	2737 (6)	6161 (7)	6134 (5)	24 (3)*
B(2)	5100 (6)	3530 (6)	5770 (5)	22 (3)*
C(1)	3406 (5)	6932 (5)	6430 (5)	23 (2)
C(10)	1718 (5)	6124 (5)	6304 (5)	21 (2)
C(19)	5889 (5)	2855 (5)	6016 (4)	18 (2)
C(28)	4067 (5)	3400 (5)	5893 (4)	22 (2)

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

X-ray Data Collection, Solution, and Refinement of the Structures. The X-ray data for compounds **1** and **2** were collected by using a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 device. All calculations were carried out on a Data General Eclipse Computer using the SHELTXL Version 5 program system. The atomic form factors, including anomalous scattering, were from ref 19. Crystals of **1** and **2** were transferred from the Schlenk tubes under N_2 to Petri dishes and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, mounted on a glass fiber, and immediately placed in a low temperature N_2 stream. Some details of the data collection and refinement are given in Table I. Further details are provided in the supplementary material. All structures were solved by direct methods. An absorption correction was applied using the method described in ref 19b. The atoms Mn, Fe, O, and B were refined anisotropically and all other atoms were refined isotropically due to data constraints. Atom coordinates and isotropic thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. The largest features on the final difference maps were 0.96 and 1.00 for **1** and **2**, respectively. The mean shift/esd were 0.004 and 0.003. In addition, some data for the complexes $[M(OAr)_2]_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$, M = Mn (**3**), Fe (**4**)) along with the corresponding numbers for **1** and **2** is provided in Table IV. The refinement of the data for **1** was marred by the presence of a

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Table III. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

		Compound **1**			
Mn···Mn	3.094 (5)	Mn–O(1)	1.890 (7)	Mn–O(2)	2.084 (9)
Mn–O(2′)	2.076 (4)	O(2)–Mn′	2.076 (4)	O(1)–B(1)	1.318 (16)
O(2)–B(2)	1.358 (14)	B(1)–C(1)	1.610 (10)	B(1)–C(16)	1.623 (19)
B(2)–C(31)	1.580 (9)	B(2)–C(46)	1.607 (19)		
O(1)–Mn–O(2)	134.7 (3)	O(1)–Mn–O(2′)	139.2 (3)	O(2)–Mn–O(2′)	81.0 (3)
Mn–O(1)–B(1)	168.4 (5)	Mn–O(2)–B(2)	140.1 (6)	Mn–O(2)–Mn′	96.1 (3)
Mn′–O(2)–B(2)	121.6 (7)	O(1)–B(1)–C(1)	122.6 (11)	O(1)–B(1)–C(16)	120.7 (6)
C(1)–B(1)–C(16)	116.7 (10)	C(31)–B(2)–C(46)	121.1 (10)		
		Compound **2**			
Fe···Fe	3.057 (5)	Fe–O(1)	1.821 (5)	Fe–O(2)	2.027 (5)
Fe–O(2′)	1.986 (5)	O(2)–Fe′	1.986 (5)	O(1)–B(1)	1.354 (11)
O(2)–B(2)	1.361 (10)	B(1)–C(1)	1.587 (12)	B(1)–C(10)	1.576 (12)
B(2)–C(19)	1.590 (12)	B(2)–C(28)	1.591 (12)		
O(1)–Fe–O(2)	155.7 (2)	O(1)–Fe–O(2′)	119.6 (2)	O(2)–Fe–O(2′)	80.7 (2)
Fe–O(1)–B(1)	143.9 (5)	Fe–O(2)–B(2)	107.3 (5)	Fe–O(2)–Fe′	99.3 (2)
Fe′–O(2)–B(2)	143.2 (5)	O(1)–B(1)–C(1)	117.3 (7)	O(1)–B(1)–C(10)	118.0 (7)
C(1)–B(1)–C(10)	124.6 (7)	O(2)–B(2)–C(19)	121.2 (7)	O(2)–B(2)–C(28)	111.5 (7)
C(19)–B(2)–C(28)	127.1 (7)				

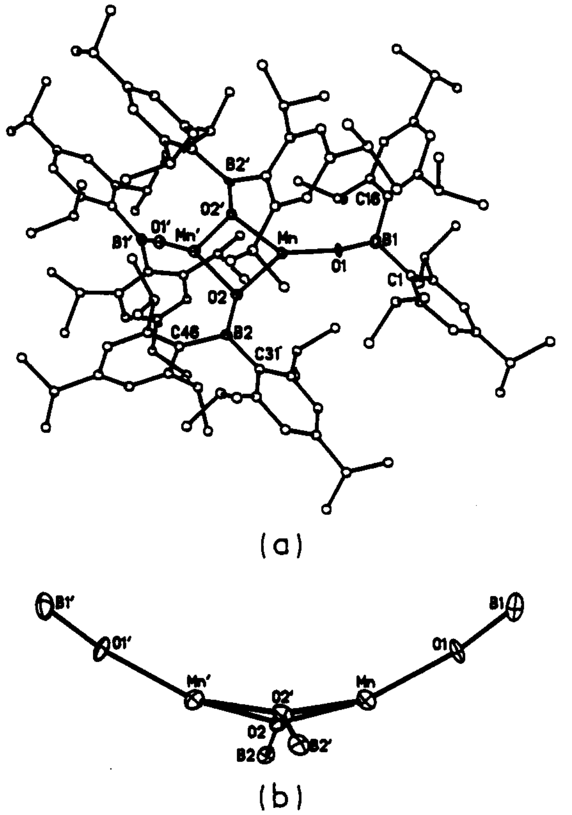

Figure 1. (a) Computer-generated drawing of **1**. (b) Illustration of the core atoms of **1**. H atoms are omitted for clarity.

disordered hexane molecule in the crystal lattice. This molecule could not be modeled satisfactorily. In addition, an *i*-Pr group on a bridging and a terminal OBTrip$_2$ ligand was also disordered.

Results and Discussion

Structural Descriptions. [Mn(OBTrip$_2$)(μ-OBTrip$_2$)]$_2$ (1). The molecular structure of **1** is shown in Figure 1a. It consists of discrete molecules of [Mn(OBTrip$_2$)(μ-OBTrip$_2$)]$_2$ that possess a 2-fold rotation axis perpendicular to the center of the Mn···Mn′ vector. The metals possess a slightly pyramidal coordination ($\sum$° Mn = 354.9°) with wide variation (81.0–134.7°) in the angles from idealized trigonal values. In addition, the bridging O(2) oxygen displays slight deviation from strictly planar coordination and it also has very irregular angles. In the Mn$_2$O$_2$ core the O(2)–Mn–O(2′) and Mn–O(2)–Mn angles are 81.0 (3) and 96.1 (3)°, respectively. The core is slightly folded and the angle between the two MnO(2)O(2)′ planes is 155.8° (see Figure 1b). The terminal Mn–O and the average bridging Mn–O distances are 1.890 (7) and 2.080 (7) Å, respectively. In the terminal boroxide ligand, the O(1)–B(1) distance is 1.318 (16) Å whereas in the bridging ligand the O(2)–B(2) distance is 1.358 (14) Å. The Mn–O(1)–B(1) angle in the terminal ligand is very wide, having a value of 168.4 (5)°. All the boron centers have trigonal planar geometry. The C(1)–B(1)–C(16) angle is 116.7 (11)°. The C(31)–B(2)–C(46) angle is 121.1 (10)°, and the average B–C bond length in the terminal ligand is marginally longer than that

Table IV. Comparison of Important Bond Distances (Å) and Angles (deg) for Compounds **1**–**3** ([Mn(OAr)(μ-OAr)]$_2$) and **4** ([Fe(OAr)(μ-OAr)]$_2$) (Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$)

	1	**2**	**3**	**4**
M–O(t)	1.890 (7)	1.821 (5)	1.873 (4)	1.822 (6)
M–O(b)	2.080 (7)	2.007 (5)	2.050 (4)	2.016 (6)
M–O–B(or C)	168.4 (5)	143.9 (5)	167.1 (3) 178.8 (3)	156.6 (6)
B–O	1.318 (16) 1.358 (14)	1.354 (11) 1.361 (10)	... ...	... ...
M···M	3.094 (5)	3.057 (5)	3.156 (3)	3.126 (6)
M–O–M	96.1 (3)	99.3 (2)	100.6 (1)	101.7 (3)
O–M–O	81.0 (3)	80.7 (2)	79.3 (1)	78.3 (2)

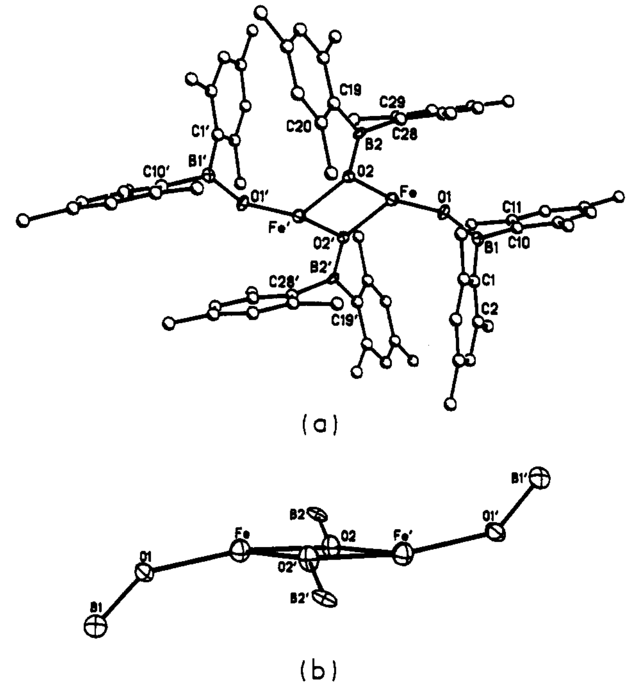

Figure 2. (a) Computer-generated drawing of **2**. (b) Illustration of the core atoms of **2**. H atoms are omitted for clarity.

in the bridging ligand. The distance between two Mn atoms is 3.094 (5) Å.

$[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ (2). The structure of **2** is illustrated in Figure 2a and it consists of well-separated molecules of $[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ dimeric units that possess a crystallographically imposed inversion center. The iron center is not quite planar ($\sum°$ Fe = 356.0°), and it also possesses large angular distortions (80.7–155.7°) from regular trigonal values. Within the planar Fe_2O_2 core, the O(2)–Fe–O(2′) and Fe–O(2)–Fe′ angles are 80.7 (2) and 99.3 (2)°, respectively (see Figure 2b). The distance between two Fe atoms is 3.057 (5) Å. The four central Fe_2O_2 atoms are strictly coplanar (see Figure 2b). The terminal Fe–O and the average bridging Fe–O distances are 1.821 (5) and 2.007 (5) Å, respectively. For the terminal boroxide, the Fe–O(1)–B(1) angle is 143.9 (5)° and the O(1)–B(1) distance is 1.354 (11) Å whereas the O(2)–B(2) distance is 1.361 (10) Å. The boron centers possess trigonal-planar geometry. The C(1)–B(1)–C(10) angle is 124.6 (7)°. The C(19)–B(2)–C(28) angle is 127.1 (7)°.

Discussion

The compounds **1** and **2** are readily prepared from the reaction of 2 equiv of $Trip_2BOH$ or Mes_2BOH with the corresponding metal amide. The reactions may be represented by

$$Mn[N(SiMe_3)_2]_2 + 2Trip_2BOH \rightarrow \tfrac{1}{2}[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2 + 2HN(SiMe_3)_2$$

$$Fe[N(SiMe_3)_2]_2 + 2Mes_2BOH \rightarrow \tfrac{1}{2}[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2 + 2HN(SiMe_3)_2$$

Species **1** and **2** are the first homoleptic transition-metal derivatives of the quasi-alkoxide ligand OBR_2 to be synthesized and structurally characterized. The work was undertaken because it was thought that the use of the boryl group in place of the more conventional alkyl or aryl substituent should exert considerable influence on the electronic properties of the $[OR]^-$ ligand. In effect, the empty p orbital on boron may accept electron density from one of the oxygen lone pairs, which can greatly reduce the oxygen π-donor properties. This notion has also been applied to the related amide $[NR_2]^-$ ligands. The resulting borylamide ligands e.g. $[NRBMes_2]^-$[11,16] display poor π-donor and bridging characteristics. This property has allowed the synthesis of several new two-coordinate transition-metal complexes for the metals Cr–Ni.[11,16,20] Although the alkoxide and amide ligands are closely related, they differ fundamentally in that the $[OR]^-$ ligand possesses two lone pairs of electrons. In the $[OBR_2]^-$ ligand, one of these pairs may be occupied in bonding to boron. Even though this implies that the remaining lone pair is still available for bridging, it was hoped that the reduction in oxygen electron density and the use of bulky substituents at boron would be sufficient to prevent bridging through oxygen. Previous measurements on the dimeric species $[Co(OCPh_3)_2]_2$ indicated that the energy barrier to the coalescence of the terminal and bridging ligand peaks in the ^1H NMR spectrum was only about 13–14 kcal mol^{-1}. In addition, recent experiments using the $[OB\{CH(SiMe_3)_2\}_2]^-$ ligand had given the monomeric complex $[Li(TMEDA)OB\{CH(SiMe_3)_2\}_2]$, which had an almost linear LiOB moiety and a very short BO distance of 1.308 (8) Å.[21] These metric features suggested that exclusively terminal coordination for $[OBR_2]^-$ ligands might also be possible in its transition-metal derivatives.

Structures. Clearly, in the case of **1** and **2**, the synthesis of mononuclear complexes was not realized. Both **1** and **2** are dimeric with bridging $[OBR_2]$ ligands. Moreover, the metric features observed in **1** and **2** are very similar to those observed in the aryloxide complexes $[M\{O(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2]_2$ (M = Mn (**3**),[22] Fe (**4**)[11,22]). In view of the different bonding properties proposed for the $[OBR_2]^-$ ligand, the closeness of the bond distances and angles in **1** and **2** to those observed in **3** and **4** is surprising. If the oxygen lone pairs are assumed to participate in π-donation in the M–O bond, it follows that the empty boron p orbital may act in competition to a metal d orbital for a share in one of the lone pairs. The close similarity in the bond lengths and angles in **1**–**4** does not support this bonding model. The data may be more simply explained on the basis of a predominantly ionic metal–ligand interaction that is similar to the ionic character of the M–N bonds in borylamides. Attempts to obtain an estimate of the bridge strength in **1** and **2** by ^1H NMR spectroscopy failed owing to the difficulty in observing the signals. Presumably, this is due to their extreme broadness of the peaks as result of the rapid relaxation arising from the presence of unpaired electrons.

Table V. B-O Distances (Å) and M–O–B Angles for Metal–Diorganoboroxides and Related Compounds

compound	B–O	M–O–B (terminal)	ref
$HOBMes_2$	1.367 (6)		12
$\{LiOBMes{\cdot}THF\}_2$	1.317 (6)		12
$LiOB\{CH(SiMe_3)_2\}_2{\cdot}TMED$	1.308 (8)	173.9 (7)	21
$[LiOB\{CH(SiMe_3)_2\}_2]_2$	1.345 (9)		21
$[Mn(OBTrip_2)(\mu\text{-}OBTrip_2)]_2$ (**1**)	1.318 (16) (terminal) 1.358 (14) (bridging)	168.4 (5)	this work
$[Fe(OBMes_2)(\mu\text{-}OBMes_2)]_2$ (**2**)	1.354 (11) (terminal) 1.361 (10) (bridging)	143.9 (5)	this work

A striking feature of the structural data in compounds **1**–**4** is the very wide angles M–O–B and M–O–C observed for the terminal ligands. In addition, the similarity in the angles between **1** and **3** and between **2** and **4** suggest that M–O bonding is little affected by exchanging aryl for boryl substituents. Wide transition-metal M–O–C angles have often been interpreted on the basis of extensive M–O π-bonding that involves overlap of the metal d orbitals and the oxygen lone pairs.[1-3] This phenomenon, however, can often be explained by assuming more ionic bonding. In effect, more polar M–O bonds imply a relaxation of the angular restrictions imposed by orbital overlap or by interelectronic repulsion of the bond pairs. The B–O bonds in **1** and to a lesser extent in **2** also reflect the ionic nature of the bonding. Inspection of the data in Table V shows that the terminal B–O distance in **1** is very similar to those observed in the complexes $[Li(THF)OBMes_2]_2$ or $[Li(TMEDA)OB\{CH(SiMe_3)_2\}_2]$.[21] The B–O bond length in the bridging ligands in **1** and **2** are marginally longer, and this is in line with the higher coordination number at the bridging oxygens. A notable feature of structures **1** and **2** is the more acute terminal M–O–B angles in **2** (see also the M–O–C angles in **3** and **4**). This could be the result of the greater covalent character in the iron complex **2** owing to the smaller size of the Fe^{2+} ion. The greater covalency of the metal oxygen bonding in this complex may impose greater angular constraints as a result of increased orbital overlap. Thus, the directional properties of the hybrid orbitals on oxygen are reflected in the smaller angles observed in **2**. It could also be argued that the narrower angles of **2** could be due to the smaller size of the Mes substituents. However, the similarity in the M–O–B and M–O–C angular differences in the pairs **1** and **2** and **3** and **4** do not support the view that the angle at the terminal oxygen is determined by steric factors.

The M···M distances seen in complexes **1**–**4** are significantly longer (~0.3 Å) than the corresponding distances in the amides $[M\{N(SiMe_3)_2\}_2]_2$, which are 2.811 (1) Å for Mn (**5**) and 2.663 (1) Å for Fe (**6**).[11,23,24] Also, the M···M distances in **1**–**4** display only minor variation upon changing the metal or the ligand whereas the M···M separation in **5** and **6** changes by 0.15 Å when Mn is replaced by Fe. This difference in behavior may be at-

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tributed to the different nature of the ligands. Thus, in the more covalent silylamides **5** and **6**, the four-coordinate bridging nitrogens may impose a more acute bridging angle because of their approximately tetrahedrally disposed orbitals, which may account for the closer approach of the metals. In contrast, the three-coordinate, approximately planar, bridging boryl or aryloxo ligands, are less likely to impose narrow angles at the bridge. This is because a wider MOM angle is expected for the approximately sp^2-hybridized oxygen. More importantly, perhaps, the M–O bonding is more ionic and is less subject to angular restrictions than that generally associated with covalent bonding. In harmony with the longer M···M separations, magnetic studies of **1** and **2** indicate that there is less coupling between the two metal centers. Thus, the μ values measured for **1** and **2** at 300 K are 4.72 and 3.9 μ_B, respectively whereas the values measured for the dimers $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mn or Fe) are 3.26 and 3.52 μ_B, respectively.[14]

Distortions in the structures of **1** and **2** may be attributed, in large part, to the crowding produced by the bulky ligands. For example, in **1** folding of the Mn_2O_2 core as well as deviations from planarity at the bridging oxygen and metal centers are observed, and it is notable that the bridging and terminal ligands are disposed toward opposite sides of the Mn_2O_2 array so as to avoid steric interference. Similarly, in the case of **2**, although the Fe_2O_2 core is planar, both the iron and oxygen centers are slightly pyramidal. In this case, the bridging and terminal ligands are also oriented so as to give the minimum steric interference.

In summary, the first two homoleptic transition-metal boryloxides have been synthesized and structurally characterized. The structural data indicate that the M–O bonding in these cases is mainly ionic rather than covalent. Unexpectedly, the bonding appears to be very similar to that seen in related metal aryloxides. Further studies will be required to determine if this bonding pattern is preserved in other complexes, especially those of the earlier transition metals.

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Supplementary Material Available: Details of the solution of structure 1, full tables of atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates, and figures that include the full numbering of the ligand atoms (17 pages); tables of structure factors (41 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Homoleptic Aryloxides $[M\{O(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2]_2$ (M = Mn, Fe), the Adducts $[Mn(OCPh_3)_2(py)_2]$ and $[Fe(OCPh_3)_2(THF)_2]$, and the Mixed Complex $[Fe\{N(SiMe_3)_2\}\{\mu\text{-}O(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}]_2$: Evidence for Primarily Ionic M–O Bonding

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The characterization of several aryloxide and alkoxide derivatives of manganese and iron is reported. They were synthesized by treatment of the amides $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mn, Fe) with the appropriate alcohol or phenol, in the presence or absence of donor molecules, to give the title compounds. Thus, the reaction of $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mn, Fe) with 2 equiv of HOMes* (Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$) gave $[Mn(OMes^*)_2]_2$ (**1**) or $[Fe(OMes^*)_2]_2$ (**2**). The intermediate species $[Fe\{N(SiMe_3)_2\}(\mu\text{-}OMes^*)]_2$ (**3**) was isolated by using 1 equiv of HOMes*. The base adducts $Mn(OCPh_3)_2(py)_2$ (**4**) (py = pyridine) and $Fe(OCPh_3)_2(THF)_2$ (**5**) were isolated by treatment of the amide with 2 equiv of $HOCPh_3$ in the presence of the base. The X-ray crystal structures of **1**–**3** show them to be dimers with aryloxide bridging. They were further characterized by IR spectroscopy. Variable-temperature ^1H NMR spectroscopy shows that the bridging is quite strong and in the case of **2** is >15 kcal mol^{-1}. The structures of **4** and **5** have very distorted 4-fold coordination at the metals. In all compounds the M–O bonding appears to be primarily ionic with little evidence for a strong M–O π interaction. Crystal data with Mo Kα (λ = 0.71069 Å) at 130 K: **1**, a = 14.201 (6) Å, b = 28.677 (11) Å, c = 18.515 (8) Å, β = 103.30 (3)°, Z = 4, space group $P2_1/c$, 6851 data with $I > 2\sigma(I)$, R = 0.07; **2**, a = 14.343 (6) Å, b = 27.110 (9)°, c = 21.121 (8) Å, β = 101.51 (3)°, Z = 4, space group $P2_1/c$, 5035 data with $I > 2.5\sigma(I)$, R = 0.77; **3**, a = 10.194 (3) Å, b = 12.376 (6) Å, c = 12.558 (3) Å, α = 74.73 (3)°, β = 65.93 (2)°, γ = 84.61 (3)°, Z = 1 (dimer), space group $P\bar{1}$, 5308 data with $I > 2\sigma(I)$, R = 0.040; **4**, a = 9.613 (3) Å, b = 10.614 (3) Å, c = 21.543 (5) Å, α = 79.88 (2)°, β = 78.70 (2)°, γ = 62.86 (2)°, Z = 2, space group $P\bar{1}$, 4103 data with $I > 2\sigma(I)$, R = 0.077; **5**, a = 19.078 (4) Å, b = 9.562 (3) Å, c = 23.454 (3) Å, β = 119.06 (1)°, Z = 4, space group $C2/c$, 2936 data with $I > 3\sigma(I)$, R = 0.039.

Homoleptic, alkoxide and aryloxide (both designated as –OR) derivatives of the later transition metals have been less intensively studied than their early-metal counterparts.[1-4] While it is true that some alkoxide derivatives of almost every later transition metal have been reported, they are often more difficult to study owing to their extensive association and lower solubility in hydrocarbon solvents.[1] Until recently there were very few structural reports for –OR derivatives of the metals Mn → Cu. The use of sterically crowding hydrocarbon substituents, to reduce the extent of alkoxide bridging, is effecting a rapid change in this interesting area. An early paper[5] showed that the degree of association in $Mn(OR)_2$ derivatives was greatly reduced by using large hydrocarbon groups such as 1-adamantyl (1-Ad), $-CPh_3$, or $2,4,6\text{-}t\text{-}Bu_3C_6H_2$ (Mes*). Similarly, the use of the ligand $-OCH(t\text{-}Bu)_2$ allowed the isolation of compounds such as $[Co(OR)_2]_2$ or $[Mn(OR)_2]_3$ and the structural characterization of the salt $[ROH{\cdot}LiFe(OR)_4]$ (R = $CH(t\text{-}Bu)_2$).[6] In addition, ligands such as $-OC(t\text{-}Bu)_3$, $-OCPh_3$, and $-OC(C_6H_{11})_3$ have afforded the mononuclear salts $[Li_2(THF)_2MnBr_2\{OC(t\text{-}Bu)_3\}_2]$,[7] $[LiMn\{OC(t\text{-}Bu)_3\}_2\{N(SiMe_3)_2\}]$,[7] $[Li(THF)_3Co(Cl)\{OC(t\text{-}Bu)_3\}_2]$,[8] $[Li(THF)_{4,5}][Co\{OC(t\text{-}Bu)_3\}_2\{N(SiMe_3)_2\}]$,[8] and $[LiCo\{OC(t\text{-}Bu)_3\}_2\{N(SiMe_3)_2\}]$,[8] the neutral

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