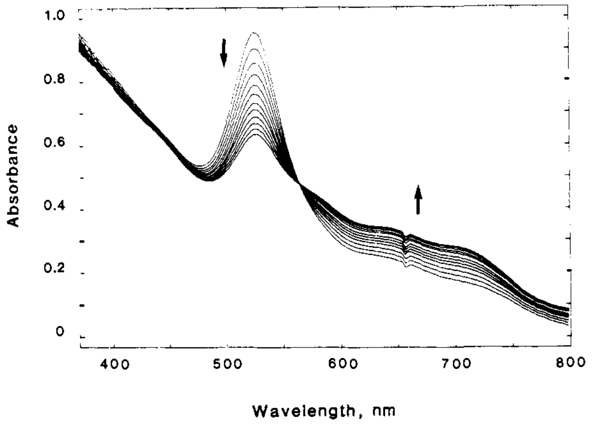

Figure 6. UV-visible changes accompanying the 458-nm photolysis of 2.35×10^{-5} M $[PPN][Os_{18}Hg_3C_2(CO)_{42}]$ (**6**) in deoxygenated CH_2Cl_2 at 293 K. Spectra were recorded at 30-s intervals.

of the in situ generated monoanion **6** to generate **7** led to the complete disappearance of this band and the emergence of a weaker absorption band with its maximum at 570 nm. In the later stages of the photolytic conversion to the product the reaction occurred less cleanly than for the dianion **2**. The photolysis sequences, as e.g. shown in Figure 6, were therefore not carried through to the complete conversion of the starting material in the quantum yield determinations. The quantum yields for the three Ar ion laser lines lie between $\Phi_{cr} = 3.6 \times 10^{-3}$ and 4.6×10^{-3} (Table VII), i.e. slightly below those determined for **2**. Irradiation at 337 nm again led to a competition between metal-ligand dissociation processes and the demercuration, with an observed Φ_{cr} value of 2.0×10^{-4}. Since the oxidized cluster proved to be unstable in the presence of $P(OMe)_3$ and therefore analogous scavenging experiments were not feasible, this quantum yield value can only be regarded as a rough estimate of the photochemical demercuration process.

Conclusions

The aim of this study was the synthesis of systems and the development of methods which allow selective metal core transformations in large mixed-metal clusters. The cluster dianion $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ has been shown to undergo photolytic demercuration to the corresponding dimercury cluster, a reaction that is thermally fully reversible and therefore provides the first example of photochromism in the chemistry of high-nuclearity clusters. The fact that this type of chemistry is feasible for two different oxidation states of the parent compound motivates further investigations into the redox and photochemistry of this and related systems. Such work is currently underway.

Acknowledgment. L.H.G. gratefully acknowledges the award of a Ph.D. scholarship by the Studienstiftung des deutschen Volkes and financial support by ICI Plc. M.McP. thanks the Science and Engineering Research Council (U.K.) for financial support, and A.J.L. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-89ER14039), for support of this work. We are also grateful to Prof. M. E. Starzak (SUNY) for the use of the N_2 laser.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and selected interbond angles (8 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of the Mononuclear Compounds *t*-Bu_2MOAr (M = Al or Ga, Ar = Bulky Aryl Group): Are the Short Al-O and Ga-O Bonds a Consequence of π-Interactions?

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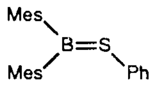
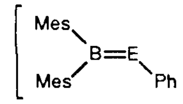
Abstract: The synthesis and characterization of the compounds *t*-Bu_2MOAr (Ar = 2,6-*t*-Bu_2-4-XC_6H_2, M = Al, and X = *t*-Bu, **1**; Me, **2**; H, **3**; X = Me and M = Ga, **4**) are described. They were characterized by X-ray crystallography (**1**, **2**, and **4**) and ^1H NMR and IR spectroscopy. In the crystal, the structures of **1**, **2**, and **4** are monomeric with essentially trigonal planar coordinations at the metals and short Al-O and Ga-O bond lengths that are near 1.71 and 1.82 Å. The structural data together with VT ^1H NMR studies indicate that there is probably little π-character in the M-O bonds. The shortness may be explained on the basis of an ionic bonding contribution and the low coordination number of the metal, with M-O π-interactions playing a relatively minor role. Crystal data with Mo Kα ($\lambda = 0.71069$ Å) at 130 K: **1**, $C_{26}H_{47}AlO$, $a = 11.386$ (10), $b = 29.11$ (2), $c = 24.969$ (16) Å, $\beta = 102.05$ (6)°, monoclinic, space group *Pn*, $Z = 12$ (six molecules per asymmetric unit), $R = 0.105$; **2**, $C_{23}H_{41}AlO$, $a = 8.200$ (2), $b = 17.876$ (4), $c = 15.910$ (4) Å, $\beta = 94.47$ (2)°, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.047$; **4**, $C_{23}H_{41}GaO$, $a = 8.215$ (1), $b = 17.738$ (6), $c = 15.921$ (4) Å, $\beta = 94.73$ (2)°, monoclinic, space group $P2_1/c$, $Z = 4$, $R = 0.051$.

Introduction

The synthesis and structural characterization of compounds that have multiple bonding involving the heavier main group elements has been one of the major developments in inorganic/organometallic chemistry in recent years.[1] Much of this effort has concerned members of the phosphorus[2] or silicon groups.[3] The elements of the aluminum group have received much less attention in spite of the fact that their lighter congener boron is known to form multiple bonds to heavier main group elements such as sulfur,[4] phosphorus,[5] and arsenic[6] as illustrated.





E = P or As

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(1) For example, (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, *261* (Sn-Sn double bonds). (b) West, R.; Fink, M. J.; Michl, T. *Science (Washington, D.C.)* **1981**, *1343* (Si-Si double bonds). (c) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587 (P-P double bonds).

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In these compounds, coordinatively unsaturated boron is bonded to S, P, or As atoms bearing lone pair orbitals. Multiple bonding may then occur by delocalization of a lone pair onto boron. The barriers to rotation around the B–E bond (E = S, P, or As) in these compounds are in the range 18–22 kcal mol^{-1}.[4-6]

Aluminum and gallium are, in theory at least, capable of forming similar multiple bonds. This view has received support from recent calculations[7] which have led to the idea that π-symmetry interactions between the oxygen pairs and the aluminum accounts for the observed short Al–O distance in both three- and four-coordinate aluminum alkoxides. The synthesis of compounds wherein three-coordinate aluminum or gallium is bound to terminal alkoxide or thiolate groups has proven to be a formidable problem owing to the larger size of Al and Ga and their greater tendency to achieve higher coordination numbers. The increased difficulty in their synthesis may be gauged from the lack of structurally characterized monomeric examples of species such as R$_2$MER′ (R, R′ = alkyl or aryl, M = Al or Ga, E = O, S, Se)[8] or R$_2$MER$_2$′ (M = Al or Ga, E = N or P)[9] which might display some multiple bonding. The most relevant prior work in the area has involved the structures of the compounds MeAl[O(2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$)]$_2$,[10] Al[N(SiMe$_3$)$_2$]$_3$,[11] and [{MeAlN(2,6-*i*-Pr$_2$C$_6$H$_3$)}$_3$][12] and the heavier species Ga(AsMes$_2$)$_3$,[13] Ga[PH(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$,[14] (η^1-C$_5$Me$_5$)$_2$GaAs(SiMe$_3$)$_2$,[15] and M(SAr)$_3$[16] (M = Al or Ga, Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$). To date, there has been no irrefutable proof for multiple bonding in any of these species, although π-interactions have been mentioned in bonding discussions.[11,12] In many of the compounds, the division of the proposed π-interaction between two or three bonds makes detection of the consequences of π-bonding (bond rotation barriers and shortening) more difficult. In addition, in the case of the derivatives of P and As, the high inversion barrier normally observed at the pnictide does not encourage multiple bonding since planarity is required at P or As to maximize π-overlap. This paper describes the synthesis of some mononuclear main group III metal monoaryl oxides and the study of the possible π-interaction of the Al–O and Ga–O bonds by X-ray crystallography and VT ^{1}H NMR and IR spectroscopy. It is concluded from these data that the primary arbiters of M–O bond shortening are the low coordination number at the metal and the ionic (or resonance) contribution to the M–O bond.

Experimental Section

General Procedures. All experiments were performed either by using modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox under nitrogen. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. ^{1}H NMR spectra were recorded in C$_6$D$_6$ or C$_7$D$_8$ solutions using a General Electric E-300 spectrometer. Infrared spectra were recorded as a Nujol mull between CsI plates by using a Perkin-Elmer PE-1430 spectrometer. The phenols HOC$_6$H$_2$-2,6-*t*-Bu$_2$-4-R (R = H, Me, or *t*-Bu) were purified by recrystallization from hexane or sublimation under reduced pressure. *t*-Bu$_2$AlH[17] and *t*-Bu$_2$GaCl[18] were synthesized by literature procedures.

Synthesis. The three compounds *t*-Bu$_2$AlO(2,4,6-*t*-Bu$_3$C$_6$H$_2$), **1**, *t*-Bu$_2$AlO(2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$), **2**, and *t*-Bu$_2$AlO(2,6-*t*-Bu$_2$C$_6$H$_3$), **3**, were prepared in an identical manner. The synthesis of **1** is described here. A pentane (10 mL) solution of 2,4,6-*t*-Bu$_3$C$_6$H$_2$OH (0.52 g, 2 mmol) was added dropwise to *t*-Bu$_2$AlH (0.28 g, 2 mmol) in pentane (20 mL). The addition was accompanied by a vigorous evolution of a gas (H$_2$). The colorless solution was stirred for 1 h, whereupon it was pumped down to incipient crystallization. Slow cooling in a −20 °C freezer overnight afforded the product in ~90% yield. **3** was purified by distillation.

t-Bu$_2$AlO(2,4,6-*t*-Bu$_3$C$_6$H$_2$), **1**: mp 72–76 °C; ^{1}H NMR (C$_6$D$_6$) δ 1.08 (AlC(CH$_3$)$_3$), 1.49 (*o*-C(CH$_3$)$_3$), 1.35 (*p*-C(CH$_3$)$_3$), 7.35 (*m*-H); IR 3078 (w), 2900 (br s), 2768 (w), 2735 (w), 2702 (w), 1760 (w), 1595 (w), 1445 (br s), 1382 (s), 1371 (s), 1357 (s), 1293 (m), 1265 (br s), 1240 (s), 1220 (m), 1195 (m), 1120 (m), 1003 (w), 998 (w), 930 (m), 920 (sh), 872 (s), 804 (s), 779 (m), 762 (w), 737 (m), 638 (m), 600 (m), 535 (vw), 482 (w), 470 (w), 424 (w), 393 (m), 362 (w), 340 (w), 298 cm^{-1} (m).

t-Bu$_2$AlO(2,6-*t*-Bu$_2$-4-Me-C$_6$H$_2$), **2**: mp 80–83 °C; ^{1}H NMR (C$_6$D$_6$) δ 1.09 (AlC(CH$_3$)$_3$), 1.45 (*o*-C(CH$_3$)$_3$), 2.24 (*p*-CH$_3$), 7.04 (*m*-H); IR 3060 (w), 2900 (br s), 2768 (w), 2728 (w), 2702 (w), 1738 (w), 1595 (w), 1440 (br s), 1385 (m), 1372 (m), 1358 (m), 1288 (w), 1256 (br s), 1210 (w), 1195 (vw), 1176 (vw), 1153 (w), 1118 (w), 1095 (br w), 1020 (w), 998 (w), 928 (sh), 880 (s), 855 (m), 808 (s), 772 (w), 660 (w), 625 (vw), 600 (m), 572 (w), 523 (w), 465 (vw), 448 (w), 420 (sh), 393 (w), 360 (vw), 342 (vw), 295 cm^{-1} (w).

t-Bu$_2$AlO(2,6-*t*-Bu$_2$C$_6$H$_3$), **3**: bp 98 °C (0.05 Torr); mp 22–25 °C; ^{1}H NMR (C$_6$D$_6$) δ 1.08 (AlC(CH$_3$)$_3$), 1.43 (*o*-C(CH$_3$)$_3$), 6.82 (m, *p*-H), 7.17 (m, *m*-H); IR (neat) 3062 (w), 2900 (br s), 2768 (w), 2735 (w), 2702 (w), 1900 (w), 1842 (w), 1785 (vw), 1690 (vw), 1640 (w), 1578 (m), 1460 (br s), 1420 (br s), 1385 (m), 1358 (m), 1348 (sh), 1255 (br s), 1215 (w), 1192 (w), 1187 (sh), 1120 (m), 1095 (m), 1015 (sh), 1005 (w), 998 (sh), 930 (sh), 898 (br s), 880 (m), 823 (m), 806 (s), 795 (sh), 748 (s), 600 (br s), 553 (w), 523 (w), 490 (w), 452 (w), 423 (w), 393 (m), 363 (w), 325 (sh), 300 cm^{-1} (br m).

The gallium compound **4** was synthesized by slow addition of a pentane (30 mL) solution of LiOC$_6$H$_2$-2,6-*t*-Bu$_2$-4-Me (prepared from HOC$_6$H$_2$-2,6-*t*-Bu$_2$-4-Me (0.44 g, 2 mmol) and *n*-BuLi (1.6 M, 1.25 mL)) to *t*-Bu$_2$GaCl (0.44 g, 2 mmol) in toluene (10 mL). After stirring for 10 h, all the volatile materials were removed and the residue was dissolved in pentane (30 mL). Filtration and reduction in volume of the filtrate to *ca.* 10 mL and cooling in a −20 °C freezer gave the product **4** as colorless crystals (yield 0.65 g, 81%).

t-Bu$_2$GaO(2,6-*t*-Bu$_2$-4-Me-C$_6$H$_2$), **4**: mp 120–124 °C; ^{1}H NMR (C$_6$D$_6$) δ 1.13 (GaC(CH$_3$)$_3$), 1.50 (*o*-C(CH$_3$)$_3$), 2.30 (*p*-CH$_3$), 7.04 (*m*-H); IR 2905 (br s), 2720 (w), 1738 (w), 1593 (w), 1460 (s), 1424 (sh), 1375 (m), 1361 (w), 1345 (w), 1309 (w), 1256 (w), 1235 (m), 1210 (w), 1195 (vw), 1173 (vw), 1155 (vw), 1115 (w), 1020 (sh), 1010 (w), 939 (w), 915 (vw), 883 (w), 857 (m), 825 (m), 805 (m), 780 (w), 592 (w), 558 (br m), 470 (w), 438 (vw), 412 (w), 387 (w), 335 (vw), 308 cm^{-1} (w).

X-ray Data Collection and the Solution and Refinement of the Structure. X-ray data were collected with a Syntex P2$_1$ (**1** and **4**) or a Siemens R3 m/V (**2**) diffractometer equipped with a graphite monochromator and a locally modified Enraf-Nonius LT apparatus. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system. Neutral atom scattering factors and the correction for anomalous dispersion were from ref 19. Crystals of **1**, **2**, or **4** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N$_2$ stream.[20] The structures of both molecules were solved by direct methods. Compound **1** crystallized in the rarely observed space group *Pn* and had a *Z* value of 12. The structure could not be solved in *P*2/*n*, which is the other possible space group. Compounds **2** and **4** were isomorphous and crystallized in the space group *P*2$_1$/*c*. Details of the data collection and refinement and important atom coordinates and isotropic thermal parameters are given in the supplementary material. Important bond distances and angles for the six crystallographically independent molecules of **1** and those of **2** and **4** are provided in Table I.

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Table I. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, and **4**

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1** (av)	**2**	**4**
M–C[a]	2.056 (12)	1.967 (12)	1.963 (11)	2.024 (12)	1.931 (14)	1.984 (9)	1.987	1.976 (3)	1.979 (4)
M–C′[a]	1.927 (10)	2.009 (12)	1.942 (11)	1.986 (10)	2.063 (14)	2.043 (10)	1.995	1.984 (3)	1.983 (4)
M–O	1.701 (7)	1.687 (7)	1.725 (7)	1.717 (7)	1.728 (7)	1.695 (8)	1.709	1.710 (2)	1.821 (3)
M···H	1.94	2.26	1.99	2.11	2.24	2.08	2.10	2.34	2.41
O–M–C	105.3 (4)	110.7 (4)	110.7 (4)	112.0 (4)	115.1 (4)	110.0 (4)	110.6	110.7 (1)	106.7 (2)
O–M–C′	127.0 (4)	121.0 (5)	129.0 (4)	123.8 (5)	119.3 (5)	120.3 (4)	123.4	123.9 (1)	123.2 (1)
H···M–C	127	121	129	124	119	120	123	104	105
H···M–C′	105	111	111	112	115	110	111	99	97
M–O–C	136.4 (6)	137.1 (6)	130.9 (5)	139.0 (6)	135.1 (6)	132.6 (6)	135.2	129.4 (1)	125.0 (2)
C–M–C′	125.9 (4)	127.7 (5)	118.9 (5)	124.1 (5)	125.3 (5)	128.7 (4)	125.1	125.2 (1)	129.9 (2)
dist (Å) of M from calcd C–C′–O plane									
angle between planes at M and O	8.5	10.9	20.2	17.9	13.0	6.1	12.8	3	1.5
sum of angles at M	358.2	359.4	358.6	359.9	359.7	359.0	359.1	359.8	359.8

[a] Bond lengths M–C and M–C′ involve the *tert*-butyl groups in the *E* and *Z* positions with respect to the aryl group on oxygen, respectively.

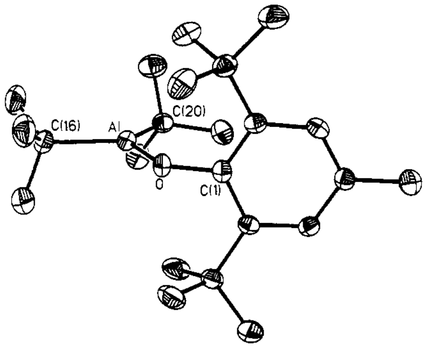

Figure 1. Thermal ellipsoid (40%) plot of **2**. For clarity, H atoms are not shown.

Results and Discussion

Compounds **1**–**4** are, apparently, the first unassociated dialkylaluminum aryl oxides or dialkylgallium aryl oxides to be well characterized. The synthesis of the aluminum compounds **1**–**3**, which proceeded in high yield, involves the use of the hydrogen elimination reaction. The employment of bulky groups at both aluminum and oxygen prevents association of the monomers through Al–O–Al bridging. This may be contrasted to the situation obtained with $Me_2AlO(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$ which exists as part of the equilibrium depicted by the equation[10]

$$Al_2Me_6 + MeAl(OR)_2 \rightleftharpoons Me_2AlOR + Me_5Al_2OR$$

$$R = -O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$$

Replacement of Me groups by *t*-Bu on Al effectively prevents association of the Al centers and allows the isolation of the monomers **1**–**3**. The use of bulky aryl oxide groups in organoaluminum compounds stems from an initial report in the early 1970s,[21] and such compounds have found applications in organic synthesis[22] and polymerization catalysts.[23] The gallium compound **4** was synthesized in good yield by the simple reaction between $t\text{-}Bu_2GaCl$ and $LiO(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$.

Structures. The structures of **1**, **2**, and **4** may be represented by the illustration of **2** in Figure 1. The structure of **1** (which, chronologically, was the first to be determined) has six molecules of the monomer in the asymmetric unit. The six monomers, although chemically equivalent, are crystallographically independent and possess considerable variation in their structural details. The structure of **2** was subsequently undertaken to confirm the correctness of the averaged structural parameters observed in **1**. Inspection of the data in Table I shows that the averaged structure of **1** and the structure of **2**, with the exception of a minor discrepancy (~5°) in the Al–O–C angle, are very close. The Al–C bonds are ~1.99 Å long, and the Al–O bonds are near 1.71 Å. The two O–Al–C angles are asymmetric and differ by about 13°. Moreover, the Al–O–C angles may vary from 129.4 (1)° to 139.2°. In both structures, the Al centers have essentially planar coordination and there is a somewhat close approach (~1.94–2.34 Å) of a hydrogen from one of the *o*-*t*-Bu groups to Al. The minor deviation of the geometry at Al from planarity is such that the Al is always displaced toward the closest hydrogen. In addition, in **1** there is an inverse correlation between the Al···H distance and the amount of asymmetry in the O–Al–C angles. Further, there is a good correlation between individual sets of H–Al–C angles and O–Al–C angles. There is, however, no apparent correlation between the Al–O–C angles and the Al–O bond lengths. The correlation between the Al–O bond length and the angle between the planes at Al and O is not rigorous although there is a tendency for the larger angles to be associated with the longer bonds.

The gallium species **4** has a structure that is very similar to that of **2**. The major difference concerns the Ga–O bond, 1.821 (3) Å, which is significantly longer than the Al–O distance. In contrast, the Al–C and Ga–C distances are very similar. The angles surrounding the gallium and oxygen centers are slightly different from those observed in **2**. The shortest Ga···H approach is 2.41 Å which is considerably longer than the corresponding Al···H distance. In view of the smaller size of Ga in comparison to that of Al (vide infra), the Ga···H interaction is probably very weak.

Bonding. The major question arising from the structures of **1**, **2**, and **4** concerns the possibility of an M–O p–p π-component in the Al–O and Ga–O bonds. The existence of π-bonding in the corresponding boron species, the R_2BOR' derivatives, has been recognized for a number of years.[24] In the case of **1**, **2**, and **4**, the primary indicators of π-bonding ought to be a bond shorter than the expected M–O distance and restricted rotation around the M–O bond. However, if an ionic bonding model is assumed for the Al–O bonds in **1** and **2**, the Al–O distance is estimated to be 1.65–1.68 Å on the basis of the sum of the extrapolated Shannon–Prewitt radii of a three-coordinate Al^{3+} ion (0.33 Å) and the two-coordinate radii of the OH^- or O^{2-} ions (1.32 and 1.35 Å).[25] In other words, the Al–O bonds in **1** and **2** are slightly longer than predicted. The Al–O bonds in **1** and **2** may also be compared to those seen in the compound $MeAl\{O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)\}_2$, **5**, which is the only other species that has oxygen bound to three-coordinate Al.[10] In this compound, the Al–O bonds average 1.686 (2) Å long (in close agreement with the "ionic" prediction) and the Al–O–C angles are 140.5 (2)° and 146.8 (2)°. A close approach (Al···H = 1.95 Å) of one of the hydrogens of an *o*-*t*-Bu group to the Al center was also observed. It is possible to argue that, if there is a significant π-component present in the

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Al–O bonding in each of the compounds **1**–**3** and **5**, it might be expected that the Al–O distances in the bis(aryl oxide) **5** would be longer than those in **1** and **2**. This is because in **5** the Al p-orbital is shared between two aryl oxides, making for a weaker π-interaction to each oxygen. Support for this prediction comes from VT ^{1}H NMR studies of alkoxyboranes in which it was shown that the dialkoxyboranes had lower (ca. 9 vs 13 kcal mol^{-1}) rotation activation energies than monoalkoxyboranes.[24] In the case of aluminum compounds, however, the Al–O bonds in the bis(aryl oxide) derivative **5** are stronger than those in **1** and **2** which suggests that the π-contribution plays only a minor role in the determination of the Al–O bond strength.

Longer Al–O bonds (1.714 (6)–1.754 (1) Å) are observed in adduct molecules of the type Me$_2$AlO(2,6-t-Bu$_2$-4-MeC$_6$H$_2$)·L, which possess four-coordinate Al.[26] This increase in bond length is expected on the basis of the higher aluminum coordination number. It has been argued in a considerable number of publications[26,27] that a π-interaction between the oxygen p-orbitals and various acceptor orbitals on aluminum may also account for the lengths of the Al–O bonds in four-coordinate species, which are thought to be unusually short.[26,27] It is notable, however, that the formation of strong Lewis base adducts by three-coordinate aluminum alkoxides is, in itself, indicative of low electron density in the nonbonding Al p-orbital. The ready formation of such complexes thus constitutes further evidence of the relative weakness of the Al–O p–p π-interaction.

The structure of the gallium compound **4** generally supports the conclusions drawn from the structures of the Al species **1** and **2**. The most remarkable feature of this structure concerns the length of the Ga–O bond which is 0.11 Å longer than those observed in the Al compounds **1** and **2**. In sharp contrast, the metal–carbon distances in both compounds are practically identical. These observations can be traced to the greater electronegativity of Ga which leads to a lowered ionic character and greater covalency in its bonds. In essence, much smaller differences are observed between bond lengths to gallium and aluminum when the bonds are of low polarity, whereas much greater differences are seen in the more polar bonds (e.g., the M–O bonds) where the ionic contribution is more important.

The possibility of π-bonding in the M–O bonds of **1**–**4** was further investigated by VT ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **1** or **4** in C$_7$D$_8$ at room temperature are consistent with the presence of single species whose structure corresponds to that established by X-ray crystallography. Cooling the solution as low as −100 °C did not result in a splitting of the M(t-Bu)$_2$ signals. Splitting of these might have been expected if a significant M–O p–p π-interaction were present to hinder rotation around the Al–O bond. It may be concluded from this observation that the energy barrier to a dynamic process involving such a rotation is quite low and probably has an upper limit of about 8 kcal mol^{-1}. In effect, the π-contribution to the overall M–O bond strength is probably quite small and is likely to account for not more than about 5% of the overall M–O bond energy. This result is thus in agreement with the structural arguments made above.

Other indications of weak π-bonding are the apparently readily distorted angles between the substituent atom planes Al and O as exemplified by **1**. In addition, the relatively narrow M–O–C angles in **1**, **2**, and **4** do not strongly support significant π-bonding.[7] Moreover, correlation between the Al···H distance and the asymmetry in the O–Al–C angles in **1** suggests that the relatively weak Al···H interaction is capable of exerting considerable influence on the position of the oxygen ligand in the coordination sphere of the Al. These observations are consistent with considerable ionic character in the Al–O bond. There is evidence of some asymmetry in the M–C bonds which could be interpreted on the basis of an in-plane π-overlap.[7] Equally probable, however, is that the different steric crowding at opposite sides of the M–O axis results in a slight asymmetry in the M–C bonds, and the different O–M–C angles, in the configuration seen in the X-ray structure.

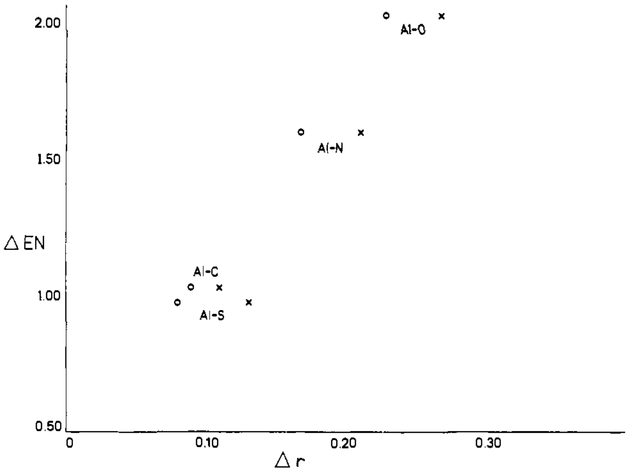

Figure 2. A graphical illustration of the relationship between the EN differences (Allred–Rochow) and the observed (x) and calculated (o)[34] bond shortening (Δr, Å) in three-coordinate Al compounds.

Collectively, the data in this paper indicate that the Al–O or Ga–O bonds have little π-character. Although there is undoubtedly some π-contribution, the observed M–O bond lengths can be largely accounted for in terms of the low coordination number and a strong ionic contribution to the bond strength.

A Comment on the Bonding in Three-Coordinate Aluminum and Gallium. In the context of the compounds in this paper, it should be borne in mind that, in general, experimental bond lengths in Al and Ga compounds can differ markedly from those predicted from tables of atomic radii.[28] Current values of the radii of Al and Ga are 1.3 and 1.2 Å.[28] These are slightly shorter than those calculated from the recently reported structures of the compounds R$_2$MMR$_2$ (R = –CH(SiMe$_3$)$_2$, M = Al (**6**), Al–Al = 2.660 (1) Å[29]; M = Ga (**7**), Ga–Ga = 2.541 (1) Å[30]), Al and Ga radii 1.33 and 1.27 Å. The latter values, however, may be elongated somewhat owing to the large size of the R groups. Accepting for the moment the validity of the numbers 1.3 Å for Al and 1.2 Å for Ga, it is obvious that the use of these radii results in bond lengths that are much longer than those measured experimentally. For example, in the case of Al compounds, if the normally accepted sp^3 carbon radius (0.77 Å) is added to 1.3 Å, a bond length of 2.07 Å is obtained, whereas in most three-coordinate Al compounds the Al–C distances are less than 2 Å. Similarly, the addition of the normal radii for N (0.73 Å)[31], O (0.7 Å), or S (1.02 Å) to an Al radius of 1.3 Å leads to predicted Al–N, Al–O, and Al–S bond lengths of 2.03, 2.0, and 2.32 Å whereas the Al–N, Al–O, and Al–S bonds in three-coordinate Al compounds can be as short as 1.78,[11,12] 1.68,[10] and 2.19 Å.[16]

Obviously, there are large discrepancies between experimental and predicted (on the basis of simple covalent radii) bond lengths in three-coordinate Al compounds. Moreover, significant differences are observed even when there is no obvious mechanism for strong Al–ligand p–p π-bonding as exemplified by the shorter than predicted Al–C bond lengths. The bonding in these compounds may be largely explained by the presence of a large ionic

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(31) A slightly smaller value (0.7 Å) for the radius of sp^2-hybridized nitrogen, which takes into account its planar coordination, may also be used. This gives a predicted Al–N distance of 2.0 Å. This revised figure does not, of course, change the arguments made in the discussion. For further information, see the following reference: Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528. It is also possible to use a similarly revised oxygen radius of 0.66 Å without affecting the argument.

Table II. Relationship between EN Differences and Bond Length in Three-Coordinate Al Compounds

	Al–C[a]	Al–N[b]	Al–O[c]	Al–S[d]
bond length (Å)	1.96	1.79	1.69	2.19
predicted bond length (Å)[e]	2.07	2.0	1.96	2.32
Δr (Å)	0.11	0.21	0.27	0.13
Δr (Å) calcd[f,g]	0.08	0.14	0.2	0.08
Δr (Å) calcd[h,g]	0.09	0.17	0.23	0.08
ΔEN[f]	0.94	1.43	1.83	0.97
ΔEN[h]	1.03	1.6	2.03	0.97

[a] The mean of known Al (three-coordinate)–C distances. [b] References 11, 12, and 36. [c] The average of values in ref 10 and this work. [d] Reference 16. [e] Based on a radius of 1.3 Å for Al, 0.77 Å for C, 0.7 Å for sp^2-hybridized N,[31,33] and 0.66 Å for O[33]. [f] Pauling electronegativities. [g] Δr (Å) calculated from the formula[34] $\Delta r = 0.085(\mathrm{EN_A} - \mathrm{EN_B})^{1.4}$. [h] Allred–Rochow electronegativities.

component in Al–ligand bonds. The relationship between the ionic character (as expressed by EN differences) and bond shortening (as expressed by differences between measured and predicted bond lengths) in a range of three-coordinate Al compounds is illustrated in Table II and Figure 2. Correlations of this type have, of course, been known for a long time[32] and have undergone considerable refinement.[33,34] The data in Table II, which include calculated shortenings on the basis of the Schomaker–Stevenson formula[32] (as modified by Haaland),[34] show that these principles can be successfully applied to Al compounds. Presumably, this was not done previously owing to the lack of structural data for a sufficiently extensive series of three-coordinate Al species. Clearly, there is a fair agreement between the discrepancies in the bond length (Δr, Å) and the shortening that is expected by the modified Schomaker–Stevenson formula, especially where Allred–Rochow electronegativities are used. For example, in the case of the Al–O bond the use of this formula[34] predicts a discrepancy of 0.23 Å, whereas the difference between the observed and predicted Al–O bond lengths for compounds **1** or **2** is 0.25 Å (1.96 Å, predicted from the sum of the radii, less the measured value, 1.71 Å). It should be added that this quasi-empirical method of predicting bond lengths, which makes allowances for ionic character, does not preclude the existence of π-bonding in these compounds. It does, however, suggest that π-bonding is of minor significance in determining the bond distances.

Correlations, similar to those in Table II and Figure 2, are less easily made for three-coordinate Ga compounds owing to the scarcity of available data. Currently, the structure of **4** is the sole example that has bonding between oxygen and three-coordinate Ga. No structures of compounds that have bonding between three-coordinate Ga and nitrogen have been reported. In addition, estimates of EN values for Ga display wide variation.[35] These factors do not permit a useful correlation similar to that in Table II to be made at present. Nonetheless, the apparent smaller size and greater electronegativity of this element suggest that π-bonding might be more easily observed in its compounds than in more polar Al species.

Note Added in Proof. Calculation of the adiabatic barrier to rotation around the Al–O bond in the model compound H_2AlOH with a hierarchy of basis sets (STO-36, 6-31G*, 6-31G**) at the Hartree–Fock level gives relatively low values, 6.7, 3.5, and 2.4 kcal mol^{-1}, consistent with a weak π-interaction. The ground-state HOMO is characterized as contributing to the Al–H bonds with some O in-plane p-orbital participation. The LUMO, which is quite low-lying in energy, is an almost pure Al p-orbital perpendicular to the molecular plane. At the level of a single determinant wave function there is little evidence for Al–O π-bonding. Further work, which involves more sophisticated handling of resonance forms than is permitted by a single determinant wave function, is in progress.

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Registry No. 1, 136237-92-8; **2**, 136237-93-9; **3**, 136237-94-0; **4**, 136237-95-1; 2,4,6-*t*-$Bu_3C_6H_2OH$, 732-26-3; *t*-Bu_2AlH, 70776-29-3; HOC_6H_2-2,6-*t*-Bu_2-4-Me, 128-37-0; 2,6-*t*-Bu_2CH_3OH, 128-39-2; *t*-Bu_2GaCl, 56309-98-9.

Supplementary Material Available: Full tables of data collection parameters, atomic coordinates, bond distances and angles, hydrogen coordinates, and anisotropic parameters (29 pages); listing of observed and calculated structure factors (66 pages). Ordering information is given on any current masthead page.

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