Reduction of a Tetraaryldialane to Generate Al–Al π-Bonding

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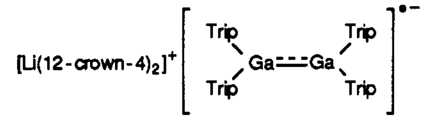
Received March 5, 1993

Recent work[1] has shown that it is possible to effect reduction of the tetraaryldigallium compound $Trip_2GaGaTrip_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) with lithium powder in diethyl ether solution to give the salt $[Li(12\text{-crown-}4)_2]^+[Trip_2GaGaTrip_2]^{\bullet-}$, **1**. This species has a Ga–Ga bond length (2.343(2) Å) which is substantially (0.17 Å) shorter than that in its neutral precursor $Trip_2GaGaTrip_2$, **2** (Ga–Ga = 2.515(3) Å). These data, combined with the observation of low coupling constants between the unpaired electron and the gallium nuclei, are consistent with the formation of a 1-electron Ga–Ga π-bond resulting from the overlap of two Ga 4p-orbitals. This type of reaction can, in principle, be extended to the other heavier main group 3 elements.[2] Gallium was, however, chosen for the initial experiments because it is less electropositive and smaller than the neighboring elements aluminum and indium. Nonetheless, the work of Uhl and co-workers[3–5] has shown that tetraalkyl derivatives (**3a–c**) of all these elements can be readily isolated. It was decided, therefore to synthesize the aluminum analogues of **1** and **2** using the aryl substituent 2,4,6-*i*-$Pr_3C_6H_2$-(Trip).



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$$R_2MMR_2$$

$$M = Al, \mathbf{3a};\ Ga, \mathbf{3b};\ In, \mathbf{3c}$$

$$R = \text{–}CH(SiMe_3)_2$$

The compound $Trip_2AlAlTrip_2$, **4** was isolated[6] by the reduction of $Trip_2AlBr$[7] with potassium in hexane. Its structure[8] features an Al–Al distance of 2.647(3) Å and a torsion angle between the planes at the aluminums of 44.8°. The Al–Al bond length in **4** is marginally shorter than the Al–Al bond length reported for **3a** (2.660(1) Å).[3] Treatment of an ether solution of **4** with excess lithium powder produces, upon the addition of TMEDA (*N,N,N',N'*-tetramethylethylenediamine) or 12-crown-4, dark green, almost black, crystals of **5a** or **5b**. The X-ray crystal structure of **5a**·Et_2O (Figure 1)[8] shows that, upon reduction, the Al–Al bond length decreases to 2.470(2) Å (av) and the torsion angle between the planes at the aluminums decreases to an average of 1.4°. Solutions of **5a** or **5b** display a strong EPR signal due to the presence of the unpaired electron. The spectrum of **5b** in THF (Figure 2) displays an 11-line pattern (*g* = 2.0048(5)) consistent with equal coupling between the unpaired electron and two Al nuclei (^{27}Al, $I = {}^5/_2$). The low value of the coupling

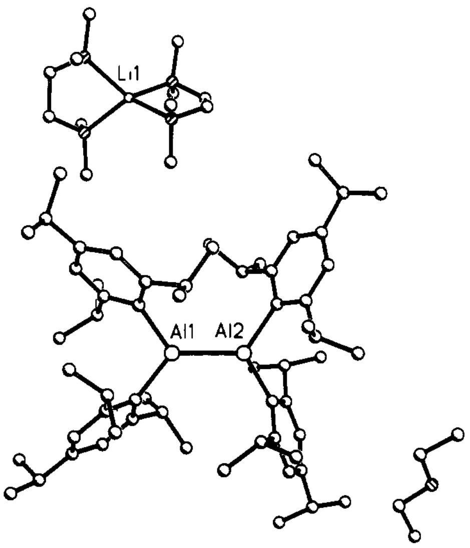
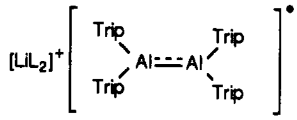


Figure 1. Computer generated drawing of half of the asymmetric unit of **5a**. Important bond distances and angles for **4** and **5a** are given in Table I.



L = TMEDA, **5a**
L = 12-crown-4, **5b**

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(1) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.*, in press.

(2) (a) While the work described here was in progress, we were informed that two other groups (those of K. Pörschke and W. Uhl) had succeeded in reducing the tetraalkyldialuminum species R_2AlAlR_2 (R = –CH(SiMe$_3$)$_2$) to give the anion $[R_2AlAlR_2]^-$, which has an Al–Al bond distance of 2.53(1) Å. (b) The EPR spectrum of the $[R_2AlAlR_2]^-$ anion in solution at 60 °C comprises 11 signal groups 11.9 G apart.

(3) Uhl, W. *Z. Naturforsch.* **1988**, *43B*, 1113.

(4) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

(5) Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139.

(6) Under anaerobic and anhydrous conditions, $Trip_2AlBr$ (3.37 g, 6.5 mmol) in hexane (100 mL) and potassium (0.27 g, 7 mmol cut in 3–4-mm pieces) were stirred at room temperature for 24 h. The pale gray-green mixture was then refluxed for 3 h, cooled, and filtered. The fluorescent green-brown filtrate was concentrated to *ca.* 10 mL under reduced pressure. Cooling in a –20 °C freezer for 24 h afforded the product $Trip_2AlAlTrip_2$, **4**, as yellow-green crystals: yield 1.97 g, 70%; mp = 171 °C dec. UV–vis in THF: 420 nm (sh), 395 nm, 322 nm (sh), 292 nm. A solution of $Trip_2AlAlTrip_2$ (0.49 g, 0.54 mol) in diethyl ether (50 mL) was added to lithium powder (*ca.* 50 mg, 7 mmol) at –78 °C. The bright-yellow solution began to darken after *ca.* 15 min. Stirring for 5 h produced a very dark green mixture which was warmed to, and held at, *ca.* –20 °C for 12 h. The solution was then filtered rapidly into a precooled flask containing TMEDA (0.25 g, *ca.* 2 mmol) or 12-crown-4. Concentration of this solution affords the product $[Li(TMEDA)_2]^+[Trip_2AlAlTrip_2]^-\cdot Et_2O$, **5a**, or $[Li(12\text{-crown-}4)_2]^+[Trip_2AlAlTrip_2]^-$, **5b**, as dark green almost black (purple in transmitted light) crystals in *ca.* 50% yield: **5a**, mp 164–166 °C dec; **5b**, mp 181–182 °C dec. UV–vis in THF: 742 nm, 451 nm (sh), 397 (sh).

(7) Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. *Organometallics* **1993**, *12*, 1086.

(8) Crystal data for **4** (Mo Kα, λ = 0.710 69 Å) and **5a** (Cu Kα, λ = 1.541 84 Å) at 130 K: **4**, a = 13.037(4) Å, b = 19.146(6) Å, c = 12.628(4) Å, orthorhombic, space group *Pban*, Z = 2, 1806 ($I > 3\sigma(I)$) data, R = 0.073; **5a**, a = 15.3652(14) Å, b = 19.401(2) Å, c = 28.011(2) Å, α = 71.873(7)°, β = 83.823(7)°, γ = 79.824(7)°, triclinic space group $P\bar{1}$, Z = 4, 14 235 ($I > 2\sigma(I)$) data, R = 0.073. Two crystallographically independent ion pairs of formula $[Li(TMEDA)_2]^+[Trip_2AlAlTrip_2]^-\cdot Et_2O$ are observed in the asymmetric unit.

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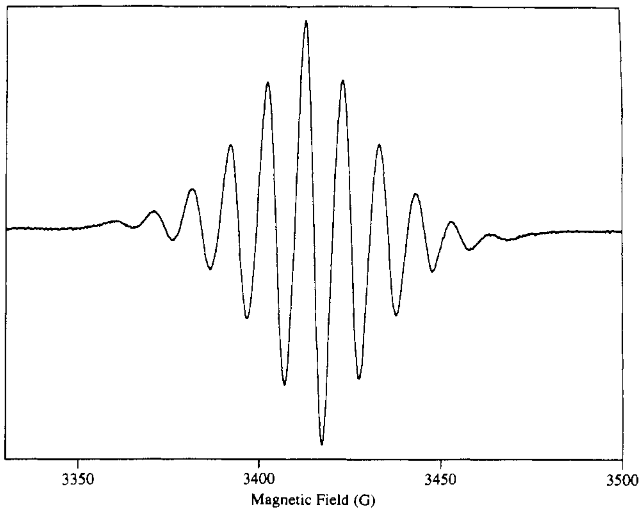

Figure 2. Plot of the EPR spectrum of **5b** in THF at *ca.* 25 °C. The 11-line pattern is due to equal coupling with two ^{27}Al ($I = {}^5/_2$) nuclei.

Table I. Comparison of the Bond Distances (Å) and Angles (deg) Surrounding the Metals in $Trip_2MMTrip_2$ and the Anion $[Trip_2MMTrip_2]^{\bullet-}$ (M = Al or Ga)

	$Trip_2MMTrip_2$		$[Trip_2MMTrip_2]^{\bullet-}$	
parameter	M = Al, **4**	M = Ga, **2**	M = Al, **5a**	M = Ga, **1**
M–M	2.647(3)	2.515(3)	2.470(2) (av)	2.343(2)
M–C	1.996(3)	2.008(7)	2.021(1) (av)	2.038(10)
C–M–C	113.7(2)	112.2(4)	107.3(9) (av) 116.8(7) (av)	111.5(5) 117.4(6)
twist angle between planes at the metals	44.8	43.8	1.4	15.5

constant $a^{Al} = 10.4$ G (*cf.* ref 2b) is consistent with the location of the unpaired electron in a π-orbital.

The spectroscopic and structural data thus support the formation of a one-electron π-bond between the aluminums. The average Al–Al distance of 2.470(2) Å in **5a** is the shortest observed to date (*cf.* ref 2a) for any Al–Al bonded system. In Table I important structural parameters for **4** and **5a** and their gallium analogues[1] are provided. These data show that for both the aluminum and gallium compounds a *ca.* 0.17 Å shortening in the M–M distances is produced by the one-electron reduction process. Moreover, slight lengthenings in the M–C distances as well as a large decrease in the torsion angles between the planes at the metals are observed.

A detailed explanation for the magnitude of the M–M bond shortening is not currently available. The large decrease in the metal-metal bond length upon the addition of just one electron is, however, surprising. This is especially true when it is apparent that there are no major changes in σ-hybridization (e.g. $sp^3 \rightarrow sp^2$) contributing to the shortening.[9] Furthermore, the M–M bond contractions in **1** and **5a** are substantially greater than that (*ca.* 0.1 Å) observed for the two-electron reduction of tetraorganodiboron species to give $[R_2BBR_2]^{2-}$ ions. One possible explanation for the large change in bond length in **1** and **5a** involves the charge separations across the M–C and M–M bonds, which result in partial positive and negative charges on the M and C atoms, respectively. In the neutral precursors **2** and **4** this ionic character is expected to increase the M–M and decrease the M–C bond lengths relative to what is predicted from the sum of the radii.[10] The addition of an electron to the bimetallic system, however, tends to cancel these ionic interactions by placing negative charge density in a π-orbital. Thus, in both reduced species, **1** and **5a**, an increase in the M–C distances is observed, as well as the dramatic shortening in the M–M bond which may be, in part, due to the cancellation of the intermetallic δ^+–δ^+ repulsion. In a similar fashion it can be argued that, for the doubly reduced $[R_2BBR_2]^{2-}$ species[11,12] the addition of a second electron to the bonding π-orbital introduces significant Coulombic repulsion between the negative charges. Consequently, the observed shortening is not as dramatic as that seen in **1** and **5a**. It is therefore possible that a structural characterization of a singly reduced $[R_2BBR_2]^{\bullet-}$ [13] will reveal a shorter B–B bond than those found in the doubly reduced species.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. R.J.W. thanks the Deutsche Forschungsgemeinschaft for a fellowship award.

Supplementary Material Available: Tables giving a summary of data collection and refinement, atom coordinates and isotropic thermal parameters bond distances and angles, hydrogen coordinates and anisotropic thermal parameters and ORTEP diagrams (28 pages). Ordering information is given on any current masthead page.

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