Organometallics **1982**, *1*, 1307-1311 1307

Table II. Summary of Thermochemical Results[a]

X^-	$D(Me_2B^+-X^-)$	$D(Me_2Al^+-X^-)$
CH_3^-	250 ± 15	
F^-	238.5 ± 3	228 ± 8
Cl^-	192.5 ± 3	185 ± 5

[a] All data in kcal/mol for the gas phase at 298 K.

$Me_2Al(Me_2O)_2^+$ and $Me_2Al(MeCN)_2^+$ of 1.6 kcal/mol. Ordering of ligands by their binding energies is possible, however. The $Me_2B(L)^+$ ligand-binding energies increase in the order $Me_2S < MeCN < C_6H_5OMe < Me_2O < C_6H_5CN <$ pyridine. For Me_2Al^+ the order is $Me_3Al < Me_2S < C_6H_5OMe < Me_2O < MeCN < Et_2O \approx i\text{-}Pr_2O < C_6H_5CN, Me_3N <$ pyridine.

Comparison of Me_2B^+ and Me_2Al^+ Results. A comparison of the Me_2B^+ ligand order to that obtained for Me_2Al^+ shows one reversal: MeCN binds more strongly to Me_2Al^+ than Me_2O and C_6H_5OMe, whereas with Me_2B^+, MeCN is a weaker ligand than these ethers. It is interesting to compare both scales to the measured ligand binding energies for one-ligand complexes of Al^+, $D(Al^+-L)$.[15] For Al^+ the binding energy order for some relevant ligands is $Me_2S < MeCN < Me_2O < C_6H_5CN < Et_2O$. Thus, Al^+ behaves like Me_2B^+ in that it binds MeCN less strongly than Me_2O. MeCN and other nitriles have been useful and consistent indicators of relative acid softness (in the terminology of hard–soft acid–base theory) in ligand binding energy studies of complexes of Cu^+, Co^+, Ni^+, and $FeBr^+$.[16,17] Thus Me_2Al^+ in binding MeCN relatively more strongly than Me_2B^+ and Al^+ is seen to be a relatively softer acid.

In summary, this study has revealed a number of thermodynamic, structural, and mechanistic similarities and differences between the chemistry of Me_3B and Me_3Al. Fluoride and chloride affinities show about 9 kcal/mol greater stability for Me_2Al^+ compared to Me_2B^+, Table II. Formation of two-ligand complexes with Me_2Al^+ is facile, whereas with Me_2B^+ only one-ligand complexes form. Dehydrochlorination of alkyl chlorides by Me_2Al^+ but not Me_2B^+ may be related since this reaction proceeds through an intermediate in which two ligands, HCl and an alkene, are both bound to Me_2Al^+. Ligand displacement results suggest that Me_2Al^+ is a softer acid than Me_2B^+. Proton transfer from Me_2B^+ giving $MeB{=}CH_2$ and hydride abstraction from Me_3B to give $Me_2B{=}CH_2$ are observed, but the corresponding reactions with Me_2Al^+ and Me_3Al are not. This is consistent with the expectation that boron should more readily form double bonds with carbon than will aluminum.

Registry No. Me_3B, 593-90-8; Me_3Al, 75-24-1; Me_2B^+, 59414-81-2; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; *n*-PrCl, 540-54-5; *i*-PrCl, 75-29-6; EtCl, 75-00-3; CCl_3F, 75-69-4; CCl_2F_2, 75-71-8; CHF_2Cl, 75-45-6; CF_3^+, 18851-76-8; CF_2Cl^+, 40640-71-9; $CHCl_2^+$, 56932-33-3; CHF_2^+, 35398-31-3; $CHFCl^+$, 40640-66-2; $C_2H_5^+$, 14936-94-8; C_6H_5CN, 100-47-0; Me_2O, 115-10-6; C_6H_5OMe, 100-66-3; MeCN, 75-05-8; Me_2S, 75-18-3; C_5H_5N, 110-86-1; Me_3N, 75-50-3; Me_2Al^+, 82614-01-5; Me_3Al^+, 82614-02-6; $C_3H_7^+$, 19252-53-0; $Me_5Al_2^+$, 82614-03-7; $Me_3Al_2Cl_2^+$, 82614-04-8; $C_2H_4Cl_2$, 107-06-2; $CFCl_2^+$, 40640-70-8; $(i\text{-}Pr)_2O$, 108-20-3; Et_2O, 60-29-7; $TiCl_4$, 7550-45-0; MeOH, 67-56-1; MeCHO, 75-07-0; Me_2CO, 67-64-1; $CHFCl_2$, 75-43-4; CH_2Cl^+, 59000-00-9.

Crystal and Molecular Structure of Tetra-*o*-tolylbis(*μ*-*o*-tolyl)dialuminum and Tri-*o*-tolylaluminum Diethyl Etherate

Maryfrances Barber, David Liptak, and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received March 16, 1982

The crystal and molecular structures of tetra-*o*-tolylbis(*μ*-*o*-tolyl)dialuminum (I) and of tri-*o*-tolylaluminum diethyl etherate (II) have been determined by single-crystal X-ray diffraction techniques. I crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The cell dimensions are $a = 10.319$ (3) Å, $b = 10.201$ (5) Å, $c = 16.544$ (5) Å, and $\beta = 105.84$ (3)°. Full-matrix least-squares refinement for I gave final discrepancy factors of $R_F = 0.038$ and $R_{wF} = 0.052$ for 1634 counter data for which $I \geq 2.5\sigma(I)$. II also crystallizes in the monoclinic system but was solved in the nonconventional space group $P2_1/n$ to bring β closer to 90°. The cell contains four molecules and has dimensions $a = 11.648$ (2) Å, $b = 14.033$ (2) Å, $c = 14.209$ (2) Å, and $\beta = 106.48$ (1)°. Full-matrix least-squares refinement for II gave final discrepancy factors of $R_F = 0.052$ and $R_{wF} = 0.064$ for 2487 counter data for which $I \geq 2.5\sigma(I)$. The structure of I consists of discrete bridged dimeric molecules similar in form to the structures of Al_2Ph_6, $Al_2(c\text{-}C_3H_5)_6$, and Al_2Me_6 with the only unusual feature being the increase in the Al–Al distance from ~2.6 Å commonly observed in bridged dimers to 2.817 (2) Å. The structure of II is similar to other trialkylaluminum adducts with the aluminum bound to three carbon atoms, one from each tolyl ring, and the ether oxygen atom providing a pseudotetrahedral environment for the aluminum atom.

Introduction

The structures of organoaluminum derivatives have been of interest to chemists for many years as a result of their formation of electron-deficient, three-center bridge bonds.[1,2] Our interest in this area has been renewed as a result of the observation that organic groups which contain electron-rich regions tend to form more stable bridged bonds through interaction of these regions and the nonbonding orbitals centered on the metal atoms in a symmetrical fashion. This type of interaction has been invoked to account for the more stable bridge bonds observed in vinyl-,[3] phenyl-,[4] and cyclopropylaluminum[5]

---

(1) Lewis, P. H.; Rundle, R. E. *J. Chem. Phys.* **1953**, *21*, 986.
(2) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235.
(3) Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995.

0276-7333/82/2301-1307$01.25/0 © 1982 American Chemical Society

derivatives. It also was used initially to account for the enhanced stability observed in the ethynyl-bridged species, but this appears to be incorrect since it has been observed, in both the solid[6] and gaseous[7] states, that the ethynyl-bridged systems are bonded unsymmetrically with two significantly different metal–carbon distances, one close to the normal Al–C distance observed in an electron-deficient bridge and the other similar to that observed for a terminal Al–C distance or to the Al–C distance observed in the monomeric, gaseous $AlMe_3$ molecule.[8]

On the basis of these observations, there appear to be two major factors, steric and electronic effects, which lead to destabilization or alteration of the electron-deficient bridged systems. The simplest to understand is that of steric interaction which is exemplified by the decreasing stability of trialkylaluminum dimers with increasing chain length or branching. This has been shown clearly from the molecular weight studies on several of these systems.[9] The electronic effects are less readily observed. Formation of species with nitrogen or oxygen adjacent to the central atom might lead to stabilization of a monomeric species as observed for the amino- or alkoxyboranes, but for aluminum these moieties always appear to form dimeric species because of the increased size around the Al atom and its tendency to achieve higher coordination through formation of the bridged (not electron-deficient) dimer or polymer.[10] Substitution of nitrogen or oxygen, other than in the bridge, usually leads to adduct formation or to other reactions.

With these arguments in mind and the reports that tri-*o*-tolylaluminum behaved in a manner suggesting lowered stability of the dimeric form,[10,11] we embarked on the determination of the structure of this molecule and of its ether adduct. The intent of these studies is to permit a comparison to be made between the bond distances in the two derivatives and, thus, began to explore the effects of the steric interactions on these bridge-bonded systems.

Experimental Section

The compounds studied are both air and water sensitive so standard drybox, vacuum line, and Schlenk tube techniques were employed for all preparations and for mounting crystals.

The parent aluminum derivative, tri-*o*-tolylaluminum dimer (I), was prepared by the reported reaction[11] of di-*o*-tolylmercury, obtained from reaction of the *o*-tolyl Grignard reagent with $HgBr_2$ in THF, with aluminum powder in a closed system. In our hands the reaction proceeded smoothly under the following conditions. A tall cylindrical reaction vessel equipped with the necessary inlets and stopcocks and magnetic stirring bar was purged thoroughly with argon. Then a large excess of 20–30 mesh aluminum powder, 20 mL of dry xylene, and 4.135 g (10.8 mmol) of $Hg(o\text{-tol})_2$ (*o*-tol = *o*-tolyl) were added. The vessel then was closed off and placed in an oil bath (138 °C) for 5 h with continuous stirring of the reaction mixture. The reaction mixture was worked up by the reported procedure.[11]

Crystals of I suitable for the X-ray structural determination were obtained by recrystallization from a saturated xylene solution by slow removal of solvent on the vacuum system. Crystals of tri-*o*-tolylaluminum diethyl etherate, $(o\text{-tol})_3Al\cdot OEt_2$ (II), were obtained by recrystallizing I from the mixed solvent xylene–diethyl ether in a manner similar to that used to prepare crystals of I. Suitable crystals of each compound were mounted in thin-walled capillary tubes in the drybox under an argon atmosphere and flame sealed.

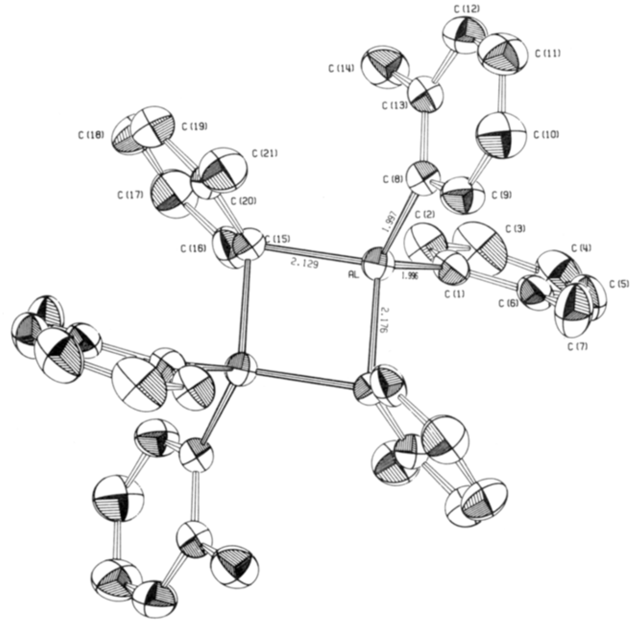

Figure 1. A view of the $Al_2(o\text{-tol})_6$ molecule with the atoms labeled. Hydrogen atoms have been omitted for clarity.

Data Collection. X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer using Mo K$\bar{\alpha}$ radiation diffracted from a highly oriented graphite crystal in the parallel mode. The data were collected for both crystals with the θ–2θ scan in the bisecting condition. The specific conditions, unit cells, and unit-cell dimensions are given in Table I.

Solution and Refinement. For compound I the aluminum atom was located by analysis of a three-dimensional Patterson synthesis.[12] The carbon atoms were located with subsequent Fourier maps. Full-matrix refinement on the positional and anisotropic thermal parameters for the non-hydrogen atoms gave $R = 0.078$, and at this point all 21 hydrogen atoms were represented clearly by peaks on the difference map with intensities ranging from 0.49 to 0.20 e/Å^3. The function $\sum w(|F_o| - |F_c|)^2$ was minimized by least-squares refinement by using the weighting scheme $w = 1/\sigma^2(F_o)^2$. The scattering factors for neutral carbon and aluminum were used.[13] Hydrogen atom positions were refined by use of the Stewart et al. scattering factor.[14] Refinement of the positional parameters for all atoms using isotropic thermal parameters for the hydrogen atoms and anisotropic thermal parameters for the aluminum and carbon atoms converged with final values of $R_F = 0.038$ and $R_{wF} = 0.052$ with maximum shift/error for the cycle equal to 0.019.[15] The residual electron density present in the difference map at this point was 0.26 e/Å^3. Final atomic parameters are given in Table II with pertinent distances and angles in Table III. Thermal parameters and observed and calculated structure factors are available.[16]

---

(4) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646. Malone, J. F.; McDonald, W. S. *Ibid.* **1972**, 2649.

(5) Moore, J. W.; Sanders, D. A.; Scherr, P. A.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1971**, *96*, 1035.

(6) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Erich, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 194.

(7) Almenningen, A.; Fernholt, L.; Haaland, A. *J. Organomet. Chem.* **1978**, *155*, 245.

(8) Smith, M. B. *J. Organomet. Chem.* **1974**, *70*, 13.

(9) Mole, T.; Jeffery, E. A. "Organoaluminum Compounds", Elsevier: Amsterdam, 1972; Chapters 8 and 9.

(10) Stanford, T. B., Jr.; Henold, K. L. *Inorg. Chem.* **1975**, *14*, 2426.

(11) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, 74, 5217.

(12) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) NEWS, W. Schmonsees' program for generation of normalized structure factors; (3) FORDAP, A. Zalkin's Fourier program; (4) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (5) ORTEP, C. K. Johnson's program for drawing crystal models; (6) HFINDR, A. Zalkin's idealized hydrogen program.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(15) Values for the reactors are defined as $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

(16) See the paragraph at the end of the paper regarding supplementary material.

(17) A review of the structure and bonding in bridged organoaluminum compounds has been presented elsewhere; see ref 2.

Table I. Structural Parameters for Tetra-*o*-tolylbis(μ-*o*-tolyl)dialuminum and Tri-*o*-tolylaluminum Diethyl Etherate

	I	II
mol formula	$Al_2(C_7H_7)_6$	$(C_7H_7)_3Al{\cdot}O(C_2H_5)_2$
mol wt	600.8	374.5
cryst size, cm^3	0.02 × 0.02 × 0.03	0.03 × 0.04 × 0.05
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
cell dimens[a]		
a, Å	10.319 (3)	11.648 (2)
b, Å	10.201 (5)	14.033 (2)
c, Å	16.544 (5)	14.290 (2)
β, deg	105.84 (3)	106.48 (1)
V, $Å^3$	1675 (1)	2239.6 (6)
Z	2	4
D_{calcd}, g/cm^3	1.19 g/cm^3	1.11 g/cm^3
radian	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)	
monochromator	graphite	
2θ range	$2\theta \geqslant 45°$	$2\theta \geqslant 55°$
scan type	θ-2θ, moving counter-moving crystal	θ-2θ
scan speed	variable from 0.5-2.0°/min to 2°/min with the time inversely proportional to the intensity of the reflection measured	
scan width, deg	[2θ(Mo Kα_1) − 1.0] to [2θ(Mo Kα_2) + 1.0]	
bkgd measurement	stationary crystal-stationary counter at beginning and end of 2θ, each for one-fourth the time taken for the 2θ scan	
std rflctns	3 measured every 97 reflections; no significant deviation from the mean was observed for either compound	
unique data	2448	5625
unique data with $F_o^2 \geqslant 2.5\sigma(F_o^2)$	1634	2487
abs coeff, μ, cm^{-1}	1.11	0.97
$F_{(000)}$, electrons	640	808
max residual electron density, e/$Å^3$	0.26	0.23
max shift/error	0.019	0.071
discrepancy factor	1.58	1.94
R_F	0.038	0.052
R_{wF}	0.052	0.064

[a] Lattice parameters were obtained with the use of an auto indexing program and a least-squares fit to the setting angles at the unresolved Mo K$\bar{\alpha}$ components of 15 reflections. For compound I these were evenly distributed in the three ranges 2θ < 25°, 25-30°, and >30°; for compound II they were distributed in the range 2θ > 10-45°.

Table II. Atomic Coordinates for the Non-Hydrogen Atoms in $Al_2(o\text{-}tol)_6$ Molecule

atom	*x*	*y*	*z*
Al	0.1221 (1)	0.0489 (1)	0.0520 (1)
C(1)	0.1878 (3)	0.2321 (3)	0.0466 (2)
C(2)	0.1280 (4)	0.3449 (3)	0.0696 (2)
C(3)	0.1786 (5)	0.4700 (4)	0.0646 (3)
C(4)	0.2882 (5)	0.4862 (4)	0.0344 (3)
C(5)	0.3512 (4)	0.3787 (4)	0.0135 (2)
C(6)	0.3041 (3)	0.2529 (3)	0.0193 (2)
C(7)	0.3859 (5)	0.1405 (5)	0.0004 (4)
C(8)	0.2611 (3)	−0.0505 (3)	0.1377 (2)
C(9)	0.3423 (3)	−0.1506 (3)	0.1196 (2)
C(10)	0.4463 (4)	−0.2076 (4)	0.1798 (3)
C(11)	0.4761 (4)	−0.1661 (4)	0.2618 (2)
C(12)	0.3995 (3)	−0.0675 (4)	0.2822 (2)
C(13)	0.2935 (3)	−0.0103 (3)	0.2227 (2)
C(14)	0.2155 (5)	0.0968 (5)	0.2509 (3)
C(15)	−0.0708 (3)	0.0313 (3)	0.0743 (2)
C(16)	−0.1350 (3)	0.1547 (3)	0.0720 (2)
C(17)	−0.2072 (4)	0.1896 (5)	0.1271 (3)
C(18)	−0.2181 (5)	0.1018 (6)	0.1874 (3)
C(19)	−0.1567 (4)	−0.0187 (5)	0.1936 (2)
C(20)	−0.0828 (3)	−0.0563 (4)	0.1386 (2)
C(21)	−0.0184 (4)	−0.1895 (4)	0.1493 (3)

Table III. Selected Bond Distances (Å) and Bond Angles (Deg) in $Al_2(o\text{-}tol)_6$ and $(o\text{-}tol)_3Al{\cdot}OEt$

atoms	dist	atoms	angle
	$Al_2(o\text{-}tol)_6$		
Al-C(1)	1.999 (3)	Al-C(15)-Al′	81.9 (1)
Al-C(8)	1.996 (3)	C(15)-Al-C(15)′	98.1 (1)
Al-C(15)	2.128 (3)	C(1)-Al-C(8)	108.7 (1)
Al-Al′[a]	2.817 (2)		
C(15)-C(15)′	3.248 (6)		
	$(o\text{-}tol)_3Al{\cdot}OEt_2$		
Al-C(1)	1.987 (4)	C(1)-Al-C(8)	113.0 (1)
Al-C(8)	1.995 (4)	C(1)-Al-C(15)	114.1 (1)
Al-C(15)	1.989 (4)	C(8)-Al-C(15)	116.2 (2)
Al-O	1.928 (3)	C(1)-Al-O	103.8 (1)
		C(8)-Al-O	100.7 (1)
		C(15)-Al-O	107.0 (1)

[a] Prime indicates relationship through the center of inversion.

Compound II was solved in the nonconventional space group $P2_1/n$ to bring the β angle closer to 90° and minimize calculational errors. The aluminum atoms were located by using the Patterson synthesis in three dimensions. The carbon and oxygen atom positions were then determined from a Fourier map. Adding anisotropic thermal parameters for aluminum the atom lowered the discrepancy factor to R = 0.123. Hydrogen atom positions, visible as peaks on the difference map, compared favorably with those calculated by using HFINDR and were included with fixed thermal parameters. Further refinement on only aluminum, oxygen, and carbon atoms varying the positional and anisotropic thermal parameters and the overall scale factor gave the final values of R_F = 0.052 and R_{wF} = 0.064. Maximum shift/error for the cycle was 0.071, and the maximum residual electron density present was 0.23 e/$Å^3$. Final atomic parameters are given in Table IV with pertinent interatomic distances and angles given in Table III. Thermal parameters and observed and calculated structure factors are available.[16]

Table IV. Atomic Coordinates for the Non-Hydrogen Atoms in the $(o\text{-tolyl})_3Al{\cdot}OEt_2$ Molecule

atom	x	y	z
Al	0.1080 (1)	0.0772 (1)	0.2637 (1)
C(1)	0.0965 (3)	0.1418 (3)	0.3846 (3)
C(2)	0.0558 (4)	0.2357 (3)	0.3849 (3)
C(3)	0.0439 (4)	0.2813 (3)	0.4681 (3)
C(4)	0.0722 (5)	0.2323 (4)	0.5549 (3)
C(5)	0.1103 (4)	0.1391 (4)	0.5578 (3)
C(6)	0.1224 (3)	0.0931 (3)	0.4748 (3)
C(7)	0.1615 (4)	−0.0091 (3)	0.4834 (3)
C(8)	0.2754 (3)	0.0409 (3)	0.2684 (3)
C(9)	0.3640 (3)	0.0566 (3)	0.3568 (3)
C(10)	0.4847 (3)	0.0389 (3)	0.3704 (3)
C(11)	0.5211 (4)	0.0054 (3)	0.2937 (4)
C(12)	0.4384 (4)	−0.0090 (3)	0.2045 (3)
C(13)	0.3165 (4)	0.0074 (3)	0.1915 (3)
C(14)	0.2310 (4)	−0.0115 (3)	0.0916 (3)
C(15)	−0.0171 (3)	−0.0211 (3)	0.2127 (3)
C(16)	0.0203 (4)	−0.1128 (3)	0.2000 (3)
C(17)	−0.0599 (5)	−0.1897 (3)	0.1747 (3)
C(18)	−0.1782 (5)	−0.1758 (4)	0.1598 (3)
C(19)	−0.2206 (4)	−0.0863 (4)	0.1703 (3)
C(20)	−0.1416 (4)	−0.0094 (3)	0.1982 (3)
C(21)	−0.1934 (4)	0.0835 (4)	0.2140 (4)
O	0.0798 (2)	0.1787 (2)	0.1684 (2)
C(22)	−0.0881 (5)	0.2632 (4)	0.0593 (4)
C(23)	−0.0122 (4)	0.1758 (3)	0.0740 (3)
C(24)	0.1670 (4)	0.2576 (3)	0.1822 (3)
C(25)	0.2368 (4)	0.2554 (4)	0.1090 (3)

Table V. Comparison of R Groups

R	Me[a]	▽[b]	Ph[c]	vinyl[d]	o-tol
Al–Al (Å)	2.60	2.618	2.618	2.68	2.817 (2)
Al–C–Al (deg)	74.7	78.2	76.5		81.9 (1)
C–Al–C (deg) (internal)	105.3	96.7	103.5		98.1 (1)

[a] Reference 1. [b] Reference 5. [c] Reference 4. [d] Reference 3. [e] This work.

Results and Discussion

Tri-*o*-tolylaluminum crystallizes in discrete dimeric molecular units as shown in Figure 1, which gives a view of the molecule with labeling. The two bridging *o*-tolyl groups are coplanar as required by symmetry and form a 91.0 (7)° dihedral angle with the least-squares plane obtained from the four-membered Al–C–Al–C ring. The *o*-tolyl methyl groups are in the anti conformation. The planes defined by the terminal *o*-tolyl groups are perpendicular to one another (90.4 (8)°) forming angles of 119.2 (4)° and −53.5 (4)° with the plane of the Al–C–Al–C ring. The methyl group on the two terminal *o*-tolyl groups attached to the same Al atom also are in the anti conformation. Pertinent interatomic distances and angles are given in Table III, with a full listing given in the supplementary material. Figure S-1, which shows the molecular packing, is available in the supplementary material.

A comparison of the structural parameters obtained from this molecule with those observed from other dimeric organoaluminum derivatives is given in Table V. These data show that the gross structural features are the same, especially when compared with the phenyl-bridged derivatives. Both the Al–C terminal and bridge distances are essentially identical with those observed for other derivatives, and the orientation of the bridging groups is the same as that observed for the phenyl species. The most pronouced difference occurs in the elongation of the Al–Al distance which increases from 2.6 Å in Al_2Me_6 to ~2.7 Å in Al_2Ph_6 and in $Al_2(\mu\text{-}CH{=}CHC_6H_{11})_2(i\text{-}Bu)_4$ and finally to 2.817 (2) Å in $Al_2(o\text{-tolyl})_6$. The most likely cause for this observed increase in the Al–Al distance arises from the steric interactions (especially in the *o*-tolyl systems involving the methyl groups) between bridge and terminal groups and across the Al–C–Al–C ring. This increase in the Al–Al separation demonstrates that these interactions are dominant in the *o*-tolyl derivative. The interaction between the π-electron systems of the bridging rings and the nonbonding metal orbitals, which should strengthen the bridge bond, is supported by the observed distortion in the bridging rings. In both the phenyl and *o*-tolyl derivatives, this distortion is seen clearly by examination of the C–C distances between α- and β-carbon atoms (1.42 (1) Å) in both the phenyl and *o*-tolyl derivatives which are significantly greater than the mean of the remaining C–C ring distances (1.38 (1) Å). This distortion is exactly the type of distortion anticipated when the π electrons in the ring interact with the nonbonding metal orbital. From these results, and earlier information concerning the stability of the aromatic bridged systems, we conclude that π-electron interaction is of major importance in stabilizing these systems.

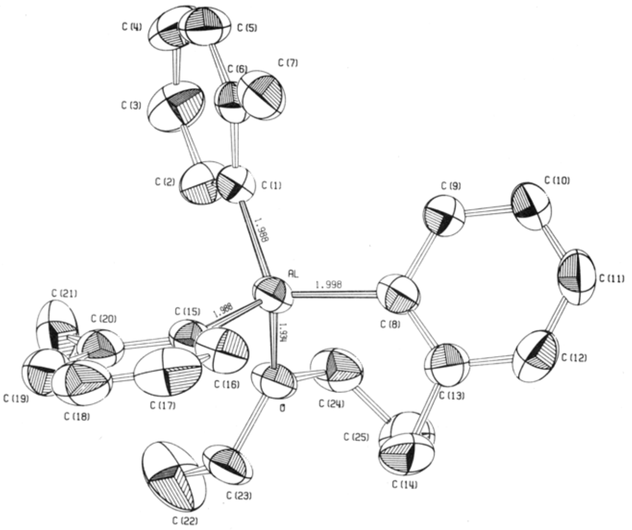

Figure 2. A view of the $(o\text{-tol})_3Al{\cdot}OEt_2$ molecule with all atoms labeled. Hydrogen atoms have been omitted for clarity.

Examination of the structure of the tri-*o*-tolylaluminum–diethyl ether adduct shows that it crystallizes as discrete monomeric units. Figure 2 gives a view of the molecular unit with labeling. The aluminum atom is four-coordinate, bound to three carbon atoms and to the oxygen atom of the ether molecule. Looking down the O–Al axis, the *o*-tolyl groups appear as propellers with the methyl groups skewed with respect to one another. There are no important interactions between molecules. The pertinent interatomic distances and angles are given in Table III. A projection (Figure S-2), which shows the molecular packing, is available in the supplementary material.[16]

A comparison of the structure with others which have been determined in the solid state reveals no unanticipated structural changes. The Al–O distance (1.928 (3) Å) is slightly shorter than that observed in $Me_3Al{\cdot}OMe_2$ (2.014 (24) Å)[18] and in $Me_3Al{\cdot}p$-dioxane (2.02 (2) Å)[19] while the Al–C distance are lengthened slightly. This is in keeping with enhanced ability of the *o*-tolyl group to remove electron density from the aluminum, making it a stronger Lewis acid, and does not indicate a particular steric interference around the four-coordinate Al atoms.

---

(18) Haaland, A.; Samdal, S.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1977**, *134*, 165.

(19) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362.

Acknowledgment is made to the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for support of this research and to Dr. Peter R. W. Corfield for helpful discussions and comments on the manuscript. M.B. was a Wayne State University Graduate Fellow during the period 1980-82.

Registry No. I, 82583-11-7; II, 82583-12-8.

Supplementary Material Available: Projections showing the molecular packing observed in the two molecules, listings of observed and calculated structure amplitudes (×10), and thermal parameters (32 pages). Ordering information is given on any current masthead page.

Direct and Indirect Electrochemical Oxidation of (Benzene)tricarbonylchromium and Its Derivatives in *N*,*N*-Dimethylformamide

Chantal Degrand,* Anne Radecki-Sudre, and Jack Besançon

Laboratoire de Synthèse et d'Electrosynthèse Organométallique Associé au CNRS (LA 33), Faculté des Sciences, 21100 Dijon, France

Received July 19, 1982

In *N*,*N*-dimethylformamide, benchrotrenyl, $XC_6H_5Cr(CO)_3$ (X = H, $COCH_3$, $N(CH_3)_2$), complexes exhibit a three-electron irreversible oxidation at the glassy carbon electrode. It is suggested that the first electron loss is followed by a fast decomposition of the intermediate Cr(I) complex, with the further formation of Cr(III). The electrooxidation can be carried out indirectly, by homogeneous redox catalysis, by means of catalyst redox couples whose oxidized forms are active. They include ferrocenes, tetrathiafulvalenes (TTF), and an aromatic amine. A quantitative study in cyclic voltammetry shows that the catalytic process corresponds to the limiting case of a kinetic control by the follow-up chemical reaction with the homogeneous electron transfer as a preequilibrium. It is shown that the presence of an electron-donating substituent on the benzene ring does not improve the stability of the intermediate Cr(I) species. When benchrotrenyl and catalyst groups belong to the same molecule, the induced oxidation of the former by the latter can occur in certain conditions which are filled for the chalcones $R_1COCH{=}C(CH_3)R_2$ (R_1 = TTF, R_2 = $C_6H_5Cr(CO)_3$; R_1 = $C_6H_5Cr(CO)_3$, R_2 = TTF).

In a recent study of the electrochemical redox properties of mixed chalcones derived from tetrathiafulvalene (TTF) and metallocenes, we have reported the abnormal behavior of the chalcones **1** and **2** in cyclic voltammetry performed

$R_1(C{=}O)CH{=}C(CH_3)R_2$
1, R_1 = TTF, R_2 = $C_6H_5Cr(CO)_3$
2, R_1 = $C_6H_5Cr(CO)_3$, R_2 = TTF
$XC_6H_5Cr(CO)_3$
3, X = H
4, X = $COCH_3$
5, X = $N(CH_3)_2$

at platinum electrode in *N*,*N*-dimethylformamide (DMF).[1] Despite the electron-withdrawing power of the C=CH-C=O group contained in these molecules, the oxidation of the benchrotrenyl unit occurs at potentials less positive than in (benzene)tricarbonylchromium (**3**); the respective values of the anodic peak potential, E_{pa}, of **1**, **2**, and **3** are 0.68, 0.75, and 0.83 V vs. SCE, respectively, when the scan rate is 0.1 V s^{-1}.

We now report on the direct and indirect electrochemical oxidations, through homogeneous redox catalysis,[2] of (benzene)tricarbonylchromium (**3**) and its derivatives **4** and **5**, in DMF as solvent. Furthermore, it is shown that, in **1** and **2**, the abnormal behavior observed in cyclic voltammetry results from the induced oxidation of the benchrotrenyl unit by the TTF group contained in the same molecule.

Table I. Half-Wave Potential ($E_{1/2}$) and Limit Current (i_l) of the Waves of **3**-**5** and of *N*,*N*-Dimethylaniline[a]

	anodic wave		cathodic wave	
substrate	$E_{1/2}$, V	i_l, μA	$E_{1/2}$, V	i_l, μA
3	0.82	224	−2.35	144[b]
4	0.87	242	−1.65	80[c]
			−2.51	75[c]
5	0.55	208	−2.50	140
	0.85	144		
N,*N*-dimethylaniline	0.83	150		

[a] Substrate concentration = 2 × 10^{-3} M°, angular velocity of the RDE = 115 s^{-1}. [b] Two-electron process; see ref 11. [c] One-electron processes; see ref 8-10.

We have applied several electrochemical techniques including voltammetry at stationary (SDE) and rotating disk electrodes (RDE), coulometry, and preparative electrolyses at a controlled potential. In order to prevent the electrode coating which is observed on platinum and which causes the appearance of a new anodic wave,[1] we have performed the voltammetric experiments with use of a glassy carbon electrode and the electrolyses and coulometric experiments with use of a glassy carbon cloth as the anode.

Prior to this report, the electrochemical oxidation of (arene)tricarbonylchromium complexes has been studied at the rotating Pt electrode in acetonitrile (MeCN)[3] and methylene chloride.[4] In the case of **3** in MeCN, a single

---

(1) Besançon, J.; Radecki-Sudre, A.; Degrand, C.; Tirouflet, J. *C. R. Hebd. Seances Acad. Sci.* **1981**, *293*, 365.

(2) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39.

(3) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

(4) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Malcom Jones, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1768.

0276-7333/82/2301-1311$01.25/0 © 1982 American Chemical Society