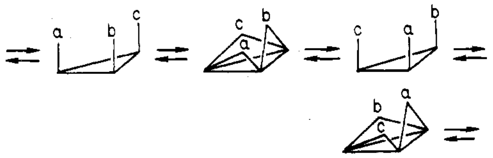
former case and the nonbridged form being the more stable in the latter.



(4)

There is no reason, in principle, such cyclic scrambling processes may not occur in cases where even larger numbers, x, of metal atoms constitute the fixed skeleton around which the x, $2x$, or other $>x$ CO groups move cyclically. Nor is there any requirement that the set of x metal atoms and/or the set of CO groups be geometrically planar. There is only the topological requirement that the set be continuous and closed. It should also be stressed that the existence of such a continuous, closed loop is only a necessary condition but not a sufficient condition for cyclic scrambling to occur.

All processes in this general class share the characteristic that as they proceed they can continuously maintain the electronic population of each metal atom at its optimum value. This is basically because both terminal and bridging CO ligands contribute two electrons to the metal atoms, and in all these processes the breaking of some CO bonds and formation of new ones always occur in a compensatory way.

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Registry No. **1**, 65255-73-4; **2**, 65255-85-8; ^{13}C, 14762-74-4.

Supplementary Material Available: A table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

An Exceedingly Short Metal–Metal Bond in a Bis(*o*-alkoxyphenyl)dicarboxylatodichromium Compound

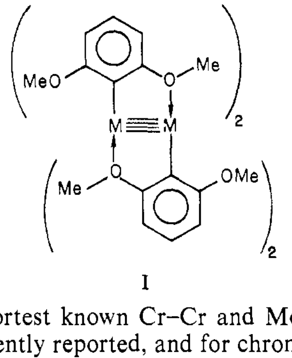
F. ALBERT COTTON* and MICHELLE MILLAR

Received December 7, 1977

To gain more information on the ability of *o*-oxyphenyl type ligands to promote the formation of exceedingly short metal–metal bonds, a compound containing only two such ligands, viz., *o-tert*-butoxyphenyl, together with two acetato groups, has been synthesized and structurally characterized by X-ray crystallography. The molecule, $Cr_2(o\text{-}Bu^tOC_6H_4)_2(O_2CCH_3)_2$, has virtual C_{2h} symmetry, the mirror plane coinciding with the mean plane of the o-OC_6H_4 ligands. The molecule has a rigorous crystallographic inversion center. Even with only two *o*-oxyphenyl type ligands, the Cr–Cr quadruple bond is still extremely short, 1.862 (1) Å, though slightly (~0.02 Å) longer than those found in compounds containing only *o*-oxyphenyl type ligands. The basic crystallographic data are as follows: space group $P2_1/c$, $a = 8.917$ (2) Å, $b = 18.926$ (4) Å, $c = 8.232$ (2) Å, $\beta = 116.32$ (1)°, $V = 1245.2$ (5) Å^3, $Z = 2$. A total of 1814 independent observations with $I > 3\sigma(I)$ has been used to refine the structure to $R_1 = 0.056$ and $R_2 = 0.090$. Other important dimensions are Cr–C = 2.064 (3) Å, Cr–OBu^t = 2.118 (2) Å, Cr–O(acetate) = 1.995 (2) and 1.996 (2) Å, and ∠Cr–Cr–C = 90.5 (1)°.

Introduction

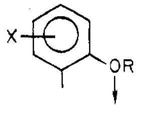
The surprising discovery that the compounds $Cr_2(DMP)_4$ and $Mo_2(DMP)_4$, where DMP represents 2,6-dimethoxyphenyl, which have the qualitatively expected structure I,



I

contain the shortest known Cr–Cr and Mo–Mo quadruple bonds[1] was recently reported, and for chromium, essentially the same Cr–Cr distance was also found[2] in tetrakis(2,4,6-trimethoxyphenyl)dichromium. These two Cr–Cr distances, 1.847 (1) and 1.849 (2) Å, are considerably shorter than the shortest ones accurately known before that, namely, those in $Cr_2(CH_3)_8{}^{4-}$, 1.980 (5) Å,[3] and $Cr_2(C_4H_8)_4{}^{4-}$, 1.975 (5) Å.[4] They are far shorter than those in $Cr_2(O_2CX)_4$ species in which X may be R, Ar, O, or OR, which range from 2.21 to 2.54 Å.[5] More recently, an even shorter Cr–Cr distance, 1.830 (4) Å, was found in $Li_6Br_2(Et_2O)_6[Cr_2(o\text{-}OC_6H_4)_4]$.[6]

Among the many questions prompted by these discoveries, we deal in this paper with that concerning the bond distance which will result when the ligand set consists of a mixture of the *o*-oxyphenyl type ligand and the O_2CX type. We have found a way to synthesize such a molecule and have determined its structure. The synthesis was designed on the principle that for a ligand of type II, the presence of a suf-



II

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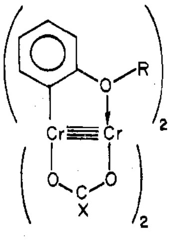
Table I. Positional and Thermal Parameters for $Cr_2(O_2CCH_3)_2(C_6H_4OCMe_3)_2$[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.11614 (7)	0.49731 (3)	0.06159 (7)	0.01013 (8)	0.00189 (2)	0.0112 (1)	−0.00005 (7)	0.0118 (1)	−0.00074 (7)
O(1)	0.1307 (4)	0.5428 (2)	0.2868 (4)	0.0148 (4)	0.00258 (9)	0.0124 (4)	−0.0002 (3)	0.0133 (6)	−0.0023 (3)
O(2)	−0.1463 (3)	0.5437 (2)	0.1453 (3)	0.0149 (4)	0.00264 (9)	0.0148 (4)	0.0003 (3)	0.0197 (6)	−0.0019 (3)
O(3)	−0.1901 (3)	0.4042 (2)	0.0019 (4)	0.0113 (4)	0.00204 (8)	0.0210 (5)	−0.0018 (3)	0.0158 (6)	0.0004 (4)
C(1)	0.1001 (5)	0.3977 (2)	0.1544 (5)	0.0146 (5)	0.0020 (1)	0.0120 (6)	0.0020 (4)	0.0161 (8)	−0.0001 (4)
C(2)	0.2460 (6)	0.3612 (3)	0.2702 (6)	0.0194 (7)	0.0028 (1)	0.0152 (7)	0.0047 (6)	0.0157 (11)	0.0008 (5)
C(3)	0.2379 (7)	0.2940 (3)	0.3400 (7)	0.0280 (9)	0.0030 (2)	0.0175 (9)	0.0079 (6)	0.0180 (13)	0.0010 (6)
C(4)	0.0824 (7)	0.2630 (3)	0.2986 (6)	0.0335 (9)	0.0021 (1)	0.0208 (8)	0.0040 (6)	0.0318 (12)	0.0022 (6)
C(5)	−0.0629 (6)	0.2972 (2)	0.1844 (6)	0.0258 (8)	0.0021 (1)	0.0190 (7)	−0.0010 (5)	0.0277 (11)	−0.0011 (5)
C(6)	−0.0494 (5)	0.3634 (2)	0.1153 (5)	0.0167 (6)	0.0018 (1)	0.0134 (6)	0.0010 (4)	0.0172 (9)	−0.0007 (4)
C(7)	−0.3664 (5)	0.3805 (3)	−0.0811 (6)	0.0128 (6)	0.0028 (1)	0.0254 (9)	−0.0039 (5)	0.0205 (10)	−0.0047 (6)
C(8)	−0.4220 (7)	0.3696 (3)	0.0723 (8)	0.0240 (7)	0.0036 (2)	0.0399 (10)	−0.0018 (6)	0.0477 (11)	−0.0005 (8)
C(9)	−0.3856 (8)	0.3143 (3)	−0.1956 (9)	0.0243 (11)	0.0042 (2)	0.0304 (12)	−0.0042 (8)	0.0172 (18)	−0.0123 (8)
C(10)	−0.4578 (6)	0.4443 (3)	−0.2000 (8)	0.0108 (7)	0.0043 (2)	0.0281 (12)	0.0000 (6)	0.0122 (13)	0.0003 (8)
C(11)	−0.0094 (6)	0.5576 (2)	0.2827 (5)	0.0201 (6)	0.0019 (1)	0.0143 (6)	0.0007 (5)	0.0214 (9)	0.0005 (5)
C(12)	−0.0137 (6)	0.5930 (3)	0.4457 (6)	0.0288 (9)	0.0032 (2)	0.0161 (7)	0.0014 (6)	0.0294 (10)	−0.0033 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's occurring in least significant digits.

ficiently large R should make it difficult if not impossible for four such ligands to fit around one Cr_2 unit because there would not be enough room for two large R groups on the same end of the $Cr_2(C_6H_4OR)_4$ molecule. It should thus be possible to limit the extent to which O_2CX groups are replaced and to obtain a compound of type III, in which only one large R group would be at each end of the molecule. With R = $C(CH_3)_3$, a compound of type III has been made and characterized.



III

Procedure

Preparation. All manipulations were conducted in an atmosphere of nitrogen with dry, degassed solvents. 2-Butoxyphenyllithium was prepared by the reaction of *tert*-butylanisole[7] with *n*-butyllithium.[8]

To a flask containing anhydrous chromium(II) acetate, $Cr_2(O_2CCH_3)_4$ (1.0 g, 2.9 mmol), and 2-butoxyphenyllithium (0.91 g, 5.9 mmol) was added ca. 50 mL of THF. After being stirred for 5 h at room temperature, the reaction mixture was filtered. Repeated extraction of the solid residue with THF gave a yellow-orange crystalline product which was readily recrystallized from THF. The product is extremely air sensitive as a solid and in solution.

Determination of Structure. A crystal with approximate dimensions 0.56 × 0.60 × 0.72 mm was secured in a capillary with epoxy cement and mounted on a Syntex $P\bar{1}$ automated diffractometer. Least-squares refinement of 15 intense reflections in the range $25° < 2\theta < 30°$ gave an orientation matrix for calculation of setting angles and cell parameters. A monoclinic cell, later shown by systematic absences and successful refinement to belong to the space group $P2_1/c$, was used. The cell dimensions are $a = 8.917$ (2) Å, $b = 18.926$ (4) Å, $c = 8.232$ (2) Å, $\beta = 116.32$ (1)°, and $V = 1245.2$ (5) Å^3. For $Z = 2$ and a formula weight of 260.26 the calculated density is 1.388 g/cm^3.

Intensity data were collected using graphite-monochromatized Mo Kα radiation and a θ–2θ scan rate varying from 4 to 24°/min depending upon the intensity of the reflections. Background measurements were made at both limits of each scan. Of the 2428 integrated intensities collected in the range $0° < 2\theta < 50°$, 1814 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected[9] for Lorentz and polarization effects. The standard reflections, measured repeatedly every 100 data points, showed no significant decline in intensity. No absorption correction was made since the linear absorption coefficient, 9.460 cm^{-1}, is small; the ratio of maximum to minimum transmission coefficients would be about 1.16.

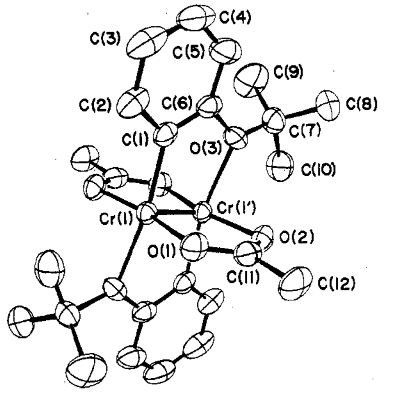


Figure 1. ORTEP drawing of the molecular structure. Each atom is represented by its ellipsoid of thermal vibration, drawn to enclose 50% of the electron density. Unlabeled atoms are related to labeled ones by the center of inversion at the midpoint of the Cr–Cr bond.

Structure Solution and Refinement. The position of the chromium atom was deduced from the three-dimensional Patterson map. A difference Fourier synthesis based on the refined chromium position revealed the three oxygen atoms coordinated to the chromium. These four atoms were refined to give discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.383$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.512$$

All remaining nonhydrogen atoms appeared on the next difference map. Refinement was continued with isotropic thermal parameters to discrepancy indices of $R_1 = 0.113$ and $R_2 = 0.171$. The chromium and then all of the remaining atoms were assigned anisotropic thermal parameters, and further least-squares refinement led to $R_1 = 0.056$ and $R_2 = 0.090$ at convergence; the error in an observation of unit weight was 2.172. No attempt was made to locate the hydrogen atoms. A final difference map had no peaks with intensity greater than 1 e/Å^3.

A table of observed and final calculated structure factors is available as supplementary material.

Results

The product of the reaction was shown by X-ray crystallography to be a molecule of type III, as desired. The atomic positional and thermal parameters are reported in Table I. The interatomic distances and angles are listed in Table II, and the molecule is depicted in Figure 1, where the atomic numbering scheme is defined. Some pertinent least-squares planes are described in Table III.

Discussion

The crystal structure consists of identical, individual molecules, each as shown in Figure 1, packed under the in-

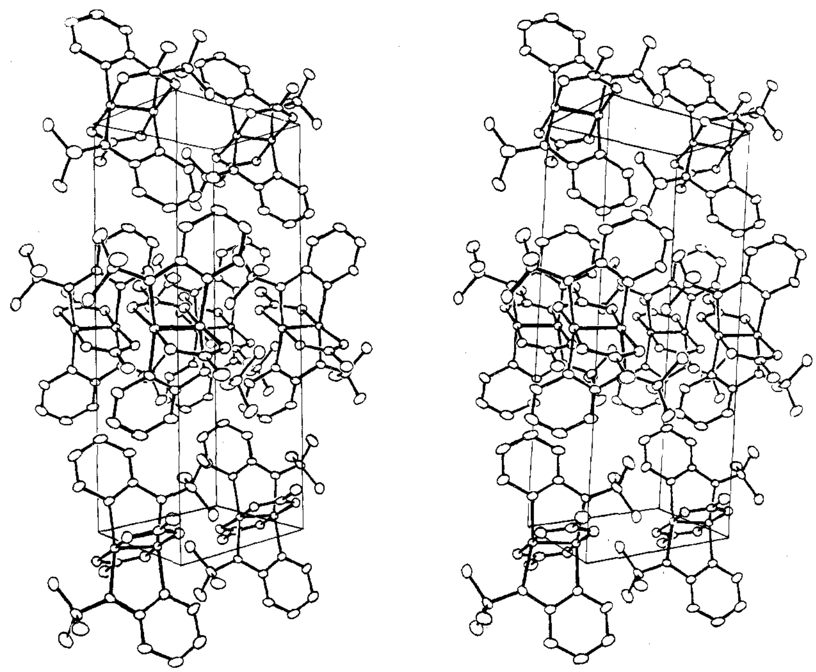


Figure 2. ORTEP stereographic view of the molecular packing. The projection shows one unit cell. The origin is at lower front corner with the *b* axis vertical. Atoms are represented by thermal vibration ellipsoids that enclose 20% of their electron density.

Table II. Interatomic Distances (Å) and Bond Angles (deg)

(a) Chromium Atoms and Acetate Ligand			
Cr(1)-Cr(1′)	1.862 (1)	Cr(1)-O(2)	1.996 (2)
Cr(1)-O(1)	1.995 (2)		
Cr(1′)-Cr(1)-O(1)	94.63 (7)	Cr(1)-O(2)-C(11)	113.5 (2)
Cr(1)-Cr(1′)-O(2)	95.44 (7)	O(1)-Cr(1)-O(2′)	169.41 (9)
Cr(1)-O(1)-C(11)	114.4 (2)		
(b) Chromium Atoms and 2-*tert*-Butoxyphenyl Ligand			
Cr(1)-C(1)	2.064 (3)	Cr(1)-O(3)	2.118 (2)
Cr(1)-Cr(1′)-C(1)	90.49 (9)	Cr(1′)-O(3)-C(6)	111.2 (2)
Cr(1)-Cr(1′)-O(3)	102.12 (7)	Cr(1′)-O(3)-C(7)	122.4 (2)
Cr(1)-C(1)-C(6)	124.0 (2)	C(1)-Cr(1)-O(3′)	167.4 (1)
(c) Acetate Ligand			
C(11)-O(1)	1.266 (4)	C(11)-C(12)	1.515 (4)
C(11)-O(2)	1.271 (4)		
O(1)-C(11)-O(2)	121.7 (3)	O(1)-C(11)-C(12)	119.1 (3)
(d) 2-*tert*-Butylphenyl Ligand			
C(1)-C(2)	1.407 (5)	C(6)-O(3)	1.416 (4)
C(2)-C(3)	1.409 (6)	O(3)-C(7)	1.479 (4)
C(3)-C(4)	1.401 (6)	C(7)-C(8)	1.562 (5)
C(4)-C(5)	1.379 (6)	C(7)-C(9)	1.531 (5)
C(5)-C(6)	1.402 (5)	C(7)-C(10)	1.541 (5)
C(6)-C(1)	1.386 (5)		
C(1)-C(2)-C(3)	121.3 (4)	C(6)-O(3)-C(7)	126.1 (3)
C(2)-C(3)-C(4)	120.2 (4)	O(3)-C(7)-C(8)	108.7 (3)
C(3)-C(4)-C(5)	119.9 (3)	O(3)-C(7)-C(9)	109.8 (3)
C(4)-C(5)-C(6)	118.1 (4)	O(3)-C(7)-C(10)	102.1 (3)
C(5)-C(6)-C(1)	124.8 (3)		
C(6)-C(1)-C(2)	115.7 (3)		
(e) Interligand Angles			
O(1)-Cr(1)-C(1)	92.1 (1)	O(1)-Cr(1)-O(3)	87.2 (1)
O(2)-Cr(1)-C(1)	91.1 (1)	O(2)-Cr(1)-O(3)	87.5 (1)

Table III. Least-Squares Planes for the Ligands[a]

Atom	Dev, Å	Atom	Dev, Å
(a) Acetate Ligands $0.2247x + 0.9049y - 0.3614z = 8.5528$			
O(1)	0.006	C(12)	0.021
O(2)	−0.041	Cr(1)	−0.018
C(11)	−0.007	Cr(1′)	0.038
(b) 2-*tert*-Butoxyphenyl Ligands $0.4452x - 0.4197y - 0.7910z = -3.9463$			
C(1)	0.033	C(6)	0.038
C(2)	0.003	O(3)	0.033
C(3)	0.040	C(7)	0.075
C(4)	−0.044	Cr(1)	−0.002
C(5)	0.019	Cr(1′)	−0.048

[a] Dihedral angles between planes 89.7°.

fluence of van der Waals forces as shown in Figure 2. There is a crystallographic center of symmetry at the midpoint of the Cr–Cr bond. When all of the bond lengths and angles in the molecule are compared, it is evident that the molecule comes very close to having C_{2h} symmetry, so close, indeed, that all discussion of the molecular and electronic structure may safely be based on ideal C_{2h} symmetry.

The salient feature of the structure is the exceptionally short Cr–Cr bond, 1.862 (1) Å. As noted in the Introduction, this is very similar to those in the three dichromium compounds in which all four ligands are of the *o*-oxophenyl type.

The general features of the $(o\text{-Bu}^t\text{OC}_6\text{H}_4)_2\text{Cr}_2$ portion of the structure are essentially the same as those previously observed. Thus, this entire unit except, of course, for the atoms of the methyl groups is essentially planar (cf. Table III). The carbon to chromium distance, 2.064 (3) Å, is comparable to those (which range from 2.05 to 2.10 Å) in the previously reported compounds. Similarly, the Cr–O distance, 2.118 (2) Å, is very similar to those (which are in the range 2.130 ± 0.003 Å) in the two previous compounds consisting of neutral molecules, viz., tetrakis(2,6-dimethoxyphenyl)dichromium and tetrakis(2,4,6-trimethoxyphenyl)dichromium. It is also found, once again, that the Cr–Cr–C angle is very close to 90° (90.49 (9)°) and that the excessive "bite" of the ligand is compensated almost entirely by the obtuseness of the Cr–Cr–O angle (102.12 (7)°).

The configuration at the oxygen atom is, again, essentially planar, as shown by the figures in Table III and also by the sum of the three angles about it, namely, 359.7 (7)°. Such a configuration makes it impossible for there to be any intermolecular interactions along the axial directions, as occurs in all known nonsolvated $\text{Cr}_2(\text{O}_2\text{CR})_4$[5a] compounds because the lone pair on the oxygen atom occupies a p orbital perpendicular to the ligand plane and the R group on oxygen is directed so as to afford maximum interference with such an interaction. It is thus understandable that the molecules are packed in such a way (Figure 2) that there are no intermolecular interactions except van der Waals contacts between peripheral portions of the molecules.

The $Cr_2(O_2CCH_3)_2$ unit of the molecule has dimensions entirely typical of those in a host of $Cr_2(O_2CR)_4L_2$[5a,b] except that the Cr–Cr–O angles here, 95 ± 0.5°, are much larger because of the much smaller Cr–Cr distance. This observation provides further support for the point to which we first drew attention years ago,[10] namely, that bridging RCO_2^- ligands of this type merely keep the metal atoms close enough to interact according to their own electronic requirements but allow the actual M–M distance to vary enormously, as those electronic requirements may dictate.

Acknowledgment. We thank Dr. S. A. Koch for his interest and assistance and the National Science Foundation for financial support.

Registry No. $Cr_2(o\text{-}Bu^tOC_6H_4)_2(O_2CCH_3)_2$, 66183-85-5; $Cr_2(O_2CCH_3)_4$, 15020-15-2; 2-butoxyphenyllithium, 66183-92-4.

Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

X-ray Crystallographic Structural Studies of the Quadruply Bonded Octamethylditungsten Anion and a Related Species Containing a Mixture of Chloro and Methyl Ligands

DOUGLAS M. COLLINS, F. ALBERT COTTON,* STEPHEN A. KOCH, MICHELLE MILLAR, and CARLOS A. MURILLO

Received January 6, 1978

Two compounds containing tungsten-to-tungsten quadruple bonds have been studied by X-ray crystallography. These are $Li_4W_2(CH_3)_8{\cdot}4Et_2O$ (**1**) and $Li_4W_2(CH_3)_xCl_{8-x}{\cdot}4THF$ (**2**). In each case the $W_2X_8^{4-}$ ion of idealized D_{4h} symmetry has been found and its structure defined; in **1** all X are CH_3 while in **2** CH_3 and Cl are randomly distributed with 59% of X being CH_3 and 41% being Cl in the crystal studied. The W–W distances are 2.264 (1) and 2.263 (2) Å in **1** and **2**, respectively. For **1** the space group is $C2/c$. The unit cell dimensions are a = 19.319 (3) Å, b = 11.554 (3) Å, c = 18.679 (3) Å, and β = 104.83 (1)°; V = 4031 (2) Å^3, and with Z = 4, d_{calcd} = 1.34 g cm^{-3}. For **2** the space group is $P42_12$ and the cell dimensions are a = 11.403 (8) and c = 11.969 (5) Å; V = 1556 (2) Å^3, and with Z = 2, d_{calcd} = 1.89 g cm^{-3}.

Introduction

The first reports of compounds for which there was good evidence of the presence of quadruple W–W bonds appeared only recently.[1,2] The principal compounds described were two containing the octamethylditungsten anion, $W_2(CH_3)_8^{4-}$, and another in which the ligand set was a mixture of CH_3 and Cl in about a 5/3 ratio. Only for this last compound had it been possible to obtain crystallographic data up to the time of our earlier report,[1] and this has been reported in a preliminary note.[2] The compounds containing only methyl groups proved very difficult to crystallize in forms suitable for single-crystal X-ray structure analysis. However, we have recently succeeded in obtaining some acceptable crystals of one of them. We are, therefore, reporting fully on our structural studies of the compounds $Li_4W_2(CH_8){\cdot}4Et_2O$ (**1**) and $Li_4W_2(CH_3)_xCl_{8-x}{\cdot}4THF$ (**2**).

Experimental Section

Compounds **1** and **2** were prepared by procedures previously described.[2] We also prepared, crystallized, and examined by X-ray diffraction the compound $Li_4W_2(CH_3)_8{\cdot}4THF$. We never succeeded in obtaining fully satisfactory crystals of this substance. X-ray data were collected on several, and a partial structure, showing a $W_2(CH_3)_8$ unit, was obtained and refined to give imprecise but reasonable W–W and W–C distances. However, no entirely satisfactory refinement was ever obtained and we shall not discuss the crystallography of this compound further.

Crystal Mounting Procedure for Pyrophoric, Thermally Unstable Crystals. The extreme reactivity of these compounds precludes normal crystal mounting procedures. The crystals were suspended in a matrix of cold, dry, degassed mineral oil which served to protect them from attack by air or moisture. The crystals were examined and mounted while working in a cold room whose temperature was maintained at −25 to −30 °C. Potential single crystals were transferred by pipet into Nujol-filled capillaries which had already been glued to metal mounting pins. The open end of the capillary was then sealed with epoxy cement, and the crystal was transported over a pool of liquid nitrogen to a Syntex $P\bar{1}$ diffractometer equipped with a Syntex LT-1 low-temperature attachment,[3] where the capillary was placed directly into the cold nitrogen steam. The crystal was held in place by the frozen mineral oil. If the cold stream flowing over the crystal was interrupted even momentarily, the crystal decomposed.

Structure Determination[4] for $Li_4W_2(CH_3)_8{\cdot}4Et_2O$ (1). The actual crystal used in data collection was chosen from a batch of crystals which was shown analytically to be free of chloride. A crystal of approximate dimensions 0.3 × 0.3 × 0.35 mm was mounted using the techniques described above. Crystal examination and data collection were done at −70 ± 2 °C. Cell constants and axial photographs showed that the crystal had monoclinic symmetry with cell parameters a = 19.319 (3) Å, b = 11.554 (3) Å, c = 18.679 (3) Å, β = 104.83 (1)°, and V = 4031 (2) Å^3. For a formula weight of 812.23 and Z = 4 the calculated density is 1.34 g cm^{-3}. Data were collected with Mo Kα radiation monochromated by a graphite crystal in the incident beam, using the θ–2θ scan technique with a variable scan rate 4.0 to 24.0°/min. In the range $\theta < 2\theta \leq 55°$, 2556 independent reflections with $I > 3\sigma(I)$ were observed, reduced to $|F_o^2|$,