(23) B. F. Fieselmann, Ph.D. Thesis, University of Illinois, 1977.
(24) F. R. Japp and E. Cleminshaw, *J. Chem. Soc.*, **51**, 553 (1887); K. Lehmstedt and H. Rolker, *Chem. Ber.*, **76**, 879 (1943).
(25) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
(26) C. G. Barraclough, R. W. Brookes, and R. L. Martin, *Aust. J. Chem.*, **27**, 1843 (1974).

(27) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
(28) W. A. Yager, E. Wasserman, and R. M. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).
(29) J. Reedijk and B. Nieuwenhuijse, *Recl. Trav. Chim. Pays-Bas*, **91**, 533 (1972).
(30) N. D. Chasteen and R. L. Belford, *Inorg. Chem.*, **9**, 169 (1970).

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# Tetrakis(2-methoxy-5-methylphenyl)dichromium

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The title compound has been prepared from $Cr_2(O_2CCH_3)_4$ and 2-methoxy-5-methylphenyllithium. Small single crystals, obtained under special conditions, were used to determine the structure. The solid consists of a van der Waals packing of discrete $Cr_2[C_6H_3Me(OMe)]_4$ molecules, in which the Cr–Cr distance is 1.828 (2) Å. The molecules lie on crystallographic centers of symmetry and have virtual symmetry $C_{2h}$. The extreme insolubility of this compound and the previously reported $Cr_2(C_6H_4OMe)_4$ are evidently due to factors other than polymerization. The crystals belong to the monoclinic system, space group $P2_1/c$, with $a = 8.799$ (2) Å, $b = 14.294$ (3) Å, $c = 11.372$ (2) Å, $\beta = 89.89$ (2)°, $V = 1430.3$ (9) Å$^3$, and $Z = 2$.

## Introduction

We have now reported the preparation and characterization of several compounds containing exceedingly short Cr–Cr quadruple bonds, viz., **1a**,[1] **2**,[2] **3**,[3] and **4a**[4] as well as several of their molybdenum analogues, **1b**[1] and **4b**.[4] We have also



**1a,** M = Cr
**b,** M = Mo

**2**

**3**

**4a,** M = Cr
**b,** M = Mo

**5**

**6**
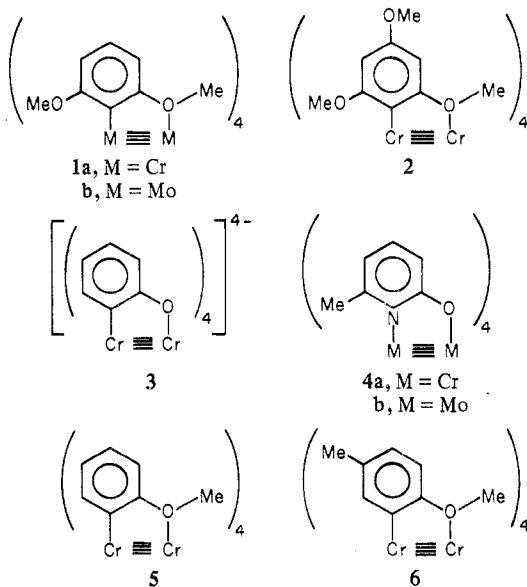
noted that the one earlier compound of this general type, **5**, which has twice been reported[5,6] but never structurally characterized, can indeed be prepared as directed and is so insoluble as to be intractable from the crystallographic point of view. It has been suggested,[6] because of "its extreme insolubility, ...that it is a polymeric species with metal–metal bonds and bridging *o*-anisyl groups." However, those who originally prepared it[5] suggested a binuclear, molecular structure.

Our efforts to resolve this question by means of X-ray crystallography were frustrated by the impossibility of growing crystals. We therefore decided to examine a substance in which a ring substituent was added *in such a way as not to interfere with the type of polymerization previously proposed.* Our rationale in doing this was to try to increase solubility

without destroying the suggested type of polymeric structure, *if there was in fact the suggested type of polymeric structure,* which we doubted. The compound we have made is **6**, in which a methyl group has been placed at the 5-position of the ring, where it does not seem possible that it could interfere with the type of polymerization suggested. The introduction of this substituent does not change the color of the compound nor does it increase its solubility very much, if at all. However, it has been possible to obtain useable single crystals, and we are therefore able to report the structure of **6**, which, we believe, gives a fairly good clue as to the structural nature of **5** as well.

## Procedures

All manipulations were conducted in an atmosphere of nitrogen and solvents were carefully dried and degassed.

**Preparation of 2-Methoxy-5-methylphenyllithium.** 4-Methylanisole (40.0 g, 0.33 mol) and 205 mL of *n*-butyllithium (1.6 M in hexane) were refluxed in 150 mL of diethyl ether for 48 h. The solvent was removed under vacuum and replaced with 100 mL of hexane. After filtration, the solid was washed with 200 mL of hexane to give 25 g of white microcrystalline product. That this product is the one desired is ensured by the work of Letsinger and Schnizer,[7] who showed that lithiation under these conditions is essentially 100% stereospecific. The yield of ca. 60% is far greater than the 16% stated by Wakefield.[8]

**Preparation of Tetrakis(2-methoxy-5-methylphenyl)dichromium.** A solution of 2-methoxy-5-methylphenyllithium (3.0 g, 23.5 mmol) in 100 mL of THF was added to $Cr_2(OAc)_4$ (2.0 g, 5.9 mmol) in 100 mL of THF. An immediate reaction ensued and a yellow microcrystalline compound separated. Filtering and drying under vacuum gave 2.0 g (58% yield) of product.

**Preparation of Crystals of Tetrakis(2-methoxy-5-methylphenyl)dichromium.** Into a flat-bottomed flask containing 1.0 g (2.9 mmol) of $Cr_2(OAc)_4$ was added 50 mL of cold (−78 °C) THF. A solution of 2-methoxy-5-methylphenyllithium (2.0 g, 15.6 mmol) dissolved in 50 mL of cold (−78 °C) THF was gently layered on top of the $Cr_2(OAc)_4$/THF mixture. The flask was then allowed to stand undisturbed at room temperature for 6 days.

**X-ray Structure Determination.** A rectangular crystal with approximate dimensions 0.10 × 0.10 × 0.15 mm was embedded in epoxy cement in a thin-walled glass capillary. Preliminary rotation photographs showed that so small a crystal did not diffract Mo Kα radiation well enough to give sufficient data. It was therefore necessary to use Cu Kα radiation from a more intense source for the intensity data.

The crystal was mounted on a Syntex $P\bar{1}$ diffractometer. General procedures for data collection[9] and interpretation[10] have been described

**Table I.** Positional and Thermal Parameters for $Cr_2(2\text{-MeO-5-MeC}_6H_3)_4$[a,b]

| | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr(1) | 0.0569 (2) | 0.0033 (1) | 0.0671 (1) | 0.0110 (2) | 0.00444 (8) | 0.0070 (1) | −0.0011 (3) | −0.0021 (3) | 0.0001 (3) |
| O(1) | 0.2656 (8) | 0.0554 (6) | −0.0003 (6) | 0.012 (1) | 0.0078 (5) | 0.0074 (7) | −0.005 (1) | −0.002 (1) | 0.0028 (10) |
| O(2) | −0.0231 (8) | −0.1437 (5) | −0.1195 (6) | 0.015 (1) | 0.0045 (4) | 0.0082 (6) | 0.001 (1) | −0.006 (1) | −0.0017 (9) |
| C(11) | 0.124 (1) | 0.0384 (8) | −0.1695 (11) | 0.012 (2) | 0.0051 (6) | 0.0096 (11) | 0.002 (2) | 0.001 (2) | −0.001 (1) |
| C(12) | 0.263 (1) | 0.0659 (8) | −0.1218 (9) | 0.014 (2) | 0.0064 (7) | 0.0063 (9) | −0.000 (2) | −0.003 (2) | 0.001 (1) |
| C(13) | 0.388 (1) | 0.0982 (9) | −0.1841 (10) | 0.016 (2) | 0.0078 (8) | 0.0092 (11) | −0.003 (2) | 0.004 (2) | 0.004 (2) |
| C(14) | 0.373 (1) | 0.1056 (9) | −0.3053 (11) | 0.014 (2) | 0.0077 (9) | 0.0122 (13) | −0.002 (2) | 0.002 (3) | 0.001 (2) |
| C(15) | 0.237 (1) | 0.0796 (8) | −0.3619 (10) | 0.021 (2) | 0.0056 (7) | 0.0085 (11) | 0.000 (2) | 0.006 (3) | 0.002 (2) |
| C(16) | 0.114 (1) | 0.0472 (8) | −0.2947 (9) | 0.019 (2) | 0.0052 (6) | 0.0063 (9) | 0.002 (2) | 0.004 (2) | 0.002 (1) |
| C(17) | 0.216 (2) | 0.0912 (10) | −0.4979 (10) | 0.027 (3) | 0.0086 (9) | 0.0068 (11) | −0.003 (3) | 0.002 (3) | 0.001 (2) |
| C(18) | 0.384 (1) | 0.1041 (10) | 0.0677 (11) | 0.013 (2) | 0.0105 (10) | 0.0110 (12) | −0.008 (2) | −0.005 (2) | −0.004 (2) |
| C(21) | 0.129 (1) | −0.1328 (7) | 0.0456 (9) | 0.011 (1) | 0.0047 (6) | 0.0079 (9) | −0.001 (2) | 0.001 (2) | −0.000 (1) |
| C(22) | 0.084 (1) | −0.1877 (8) | −0.0472 (9) | 0.012 (1) | 0.0052 (6) | 0.0079 (9) | 0.000 (2) | 0.000 (2) | −0.000 (1) |
| C(23) | 0.132 (1) | −0.2795 (8) | −0.0719 (11) | 0.017 (2) | 0.0053 (7) | 0.0125 (13) | 0.003 (2) | 0.001 (3) | 0.002 (2) |
| C(24) | 0.237 (1) | −0.3200 (9) | 0.0083 (10) | 0.016 (2) | 0.0075 (8) | 0.0103 (12) | 0.003 (2) | −0.001 (3) | 0.000 (2) |
| C(25) | 0.287 (1) | −0.2675 (8) | 0.1066 (11) | 0.010 (1) | 0.0069 (8) | 0.0117 (12) | −0.000 (2) | 0.000 (2) | 0.004 (2) |
| C(26) | 0.235 (1) | −0.1759 (8) | 0.1260 (9) | 0.011 (1) | 0.0050 (6) | 0.0096 (10) | −0.001 (2) | 0.002 (2) | 0.002 (1) |
| C(27) | 0.396 (1) | −0.3163 (9) | 0.1949 (12) | 0.022 (2) | 0.0067 (8) | 0.0139 (13) | 0.005 (2) | −0.013 (3) | 0.006 (2) |
| C(28) | −0.062 (1) | −0.1838 (9) | −0.2289 (10) | 0.021 (2) | 0.0072 (8) | 0.0080 (10) | 0.004 (2) | −0.005 (3) | −0.005 (2) |

[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] Figures in parentheses are esd's occurring in the least significant digit.
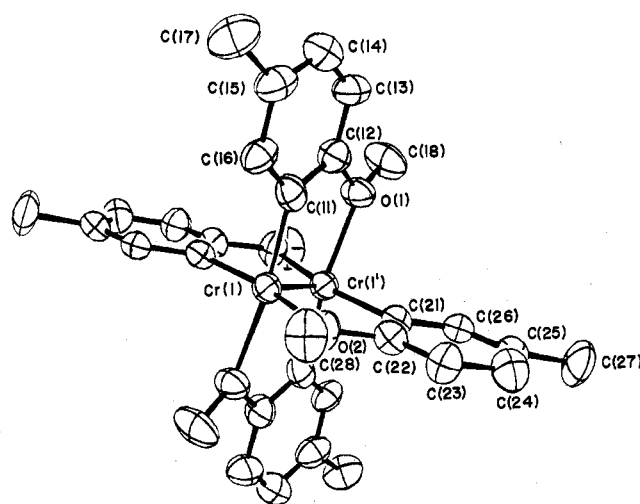


**Figure 1.** An ORTEP drawing of the molecular structure. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of its electron density. The atom numbering scheme is defined; each unlabeled atom is related by an inversion center to a labeled one and will bear the same number primed.

elsewhere. The photographs previously made with Mo radiation had indicated a monoclinic space group with $\beta$ close to 90°. Cell parameters obtained by centering 15 reflections in the range $41 < 2\theta_{Cu\,K_\alpha} < 66°$ confirmed the monoclinic symmetry and gave $a = 8.799$ (2) Å, $b = 14.294$ (3) Å, $c = 11.372$ (2) Å, and $\beta = 89.89$ (2)°. The volume of 1430.3 (9) Å³ is consistent with the presence of two dinuclear molecules in the unit cell. Data were then collected at 4 °C using Cu K$\alpha$ radiation (1.541 84 Å) with the $\theta/2\theta$ scan technique.

Peaks were recorded at scan rates varying from 4 to 24°/min, from 1.0° below K$\alpha_1$ to 1.0° above K$\alpha_2$. In the range $0 < 2\theta \leq 110°$, there were 1108 independent reflections with $I > 3\sigma(I)$ and these were used in the solution and refinement of the structure. The space group $P2_1/c$ was uniquely determined by the systematic absences.

The coordinates of the chromium atom, which occupies a general position, were determined from a Patterson map. All the remaining nonhydrogen atoms were located in two subsequent difference Fourier maps. Refinement to convergence with all atoms treated anisotropically gave final residuals

$$R_1 = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o| = 0.077$$

$$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.108$$

The final difference synthesis showed no features of significance. The largest peaks were small (<0.8 e/Å³) and close to the chromium atom. No effort was made to find the hydrogen atoms.

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

(a) Involving Cr Atoms

| | | | |
|---|---|---|---|
| Cr(1)–Cr(1′) | 1.828 (2) | Cr(1)–C(11) | 2.058 (8) |
| Cr(1)–O(1) | 2.124 (5) | Cr(1)–C(21) | 2.061 (7) |
| Cr(1)–O(2) | 2.115 (5) | | |

| | | | |
|---|---|---|---|
| O(1)–Cr(1)–C(11) | 166.6 (3) | Cr(1)–Cr(1′)–C(21) | 91.3 (2) |
| O(1)–Cr(1)–O(2) | 83.7 (2) | Cr(1)–O(1)–C(12) | 112.3 (5) |
| O(1)–Cr(1)–C(21) | 91.2 (3) | Cr(1)–O(1)–C(18) | 126.1 (5) |
| C(11)–Cr(1)–O(2) | 90.4 (3) | Cr(1)–O(2)–C(22) | 110.8 (4) |
| C(11)–Cr(1)–C(21) | 91.9 (3) | Cr(1)–O(2)–C(28) | 126.8 (5) |
| O(2)–Cr(1)–C(21) | 166.5 (3) | Cr(1)–C(11)–C(12) | 122.6 (6) |
| Cr(1)–Cr(1′)–O(1) | 101.1 (2) | Cr(1)–C(11)–C(16) | 122.7 (6) |
| Cr(1)–Cr(1′)–O(2) | 102.0 (2) | Cr(1)–C(21)–C(22) | 122.7 (6) |
| Cr(1)–Cr(1′)–C(11) | 91.9 (2) | Cr(1)–C(21)–C(26) | 121.9 (6) |

(b) Involving Only Ligand Atoms

| | | | |
|---|---|---|---|
| C(11)–C(12) | 1.40 (1) | C(21)–C(22) | 1.375 (9) |
| C(11)–C(16) | 1.43 (1) | C(21)–C(26) | 1.45 (1) |
| C(12)–O(1) | 1.389 (8) | C(22)–O(2) | 1.403 (8) |
| C(12)–C(13) | 1.39 (1) | C(22)–C(23) | 1.41 (1) |
| C(13)–C(14) | 1.39 (1) | C(23)–C(24) | 1.42 (1) |
| C(14)–C(15) | 1.41 (1) | C(24)–C(25) | 1.42 (1) |
| C(15)–C(16) | 1.41 (1) | C(25)–C(26) | 1.40 (1) |
| C(15)–C(17) | 1.57 (1) | C(25)–C(27) | 1.55 (1) |
| C(18)–O(1) | 1.475 (9) | C(28)–O(2) | 1.412 (8) |
| C(11)–O(1) | 2.31 (1) | C(21)–O(2) | 2.32 (1) |

| | | | |
|---|---|---|---|
| C(16)–C(11)–C(12) | 114.6 (7) | C(26)–C(21)–C(22) | 115.4 (7) |
| C(11)–C(12)–O(1) | 111.9 (7) | C(21)–C(22)–O(2) | 112.9 (7) |
| C(11)–C(12)–C(13) | 126.2 (7) | C(21)–C(22)–C(23) | 126.9 (8) |
| O(1)–C(12)–C(13) | 121.9 (7) | O(2)–C(22)–C(23) | 120.2 (7) |
| C(12)–C(13)–C(14) | 117.2 (8) | C(22)–C(23)–C(24) | 116.6 (9) |
| C(13)–C(14)–C(15) | 121.0 (8) | C(23)–C(24)–C(25) | 119.5 (9) |
| C(14)–C(15)–C(16) | 119.6 (8) | C(24)–C(25)–C(26) | 121.2 (8) |
| C(14)–C(15)–C(17) | 121.7 (8) | C(24)–C(25)–C(27) | 117.6 (8) |
| C(17)–C(15)–C(16) | 118.6 (8) | C(27)–C(25)–C(26) | 121.1 (8) |
| C(15)–C(16)–C(11) | 121.4 (8) | C(25)–C(26)–C(21) | 120.5 (8) |
| C(12)–O(1)–C(18) | 118.9 (6) | C(22)–O(2)–C(28) | 119.9 (6) |

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

## Results

The positional and thermal vibration parameters are listed in Table I, and the molecular unit is shown in Figure 1, which also defines the numbering scheme. The bond lengths and angles are presented in Table II, and information on the mean planes of the ligands is given in Table III. The molecule has a rigorous crystallographic center of inversion. In addition, it comes very close to having $C_{2h}$ symmetry.

The crystal packing is shown in Figure 2 where the molecules lying at the corners of the $bc$ face and the molecule at
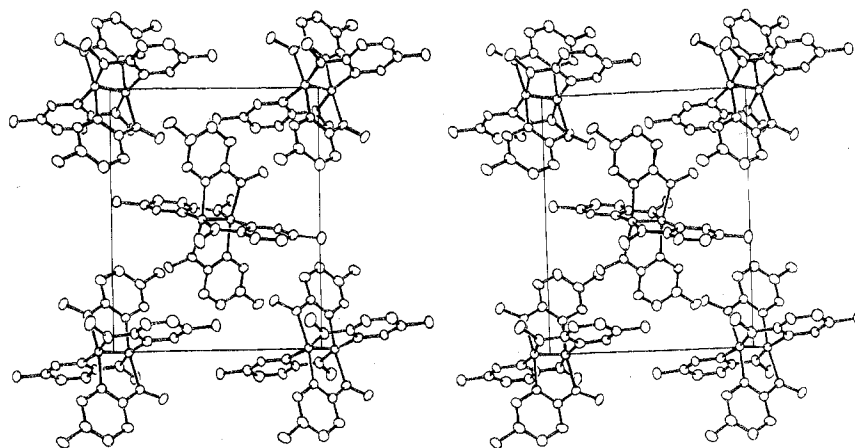
**Figure 2.** A stereographic projection of the five molecules at 000, 010, 001, 011, and 0, $^1/_2$, $^1/_2$ on the *bc* plane. Atoms are represented by ellipsoids of thermal vibration enclosing 25% of their electron density.

**Table III.** Least-Squares Planes for the Ligands

| Atom | Dev, Å | Atom | Dev, Å |
|---|---|---|---|
| Ligand 1: $0.3201x - 0.9416y - 0.1043z = 0$ | | | |
| Cr(1) | 0.037 | C(14) | 0.01 |
| O(1) | 0.00 | C(15) | −0.02 |
| C(11) | 0.03 | C(16) | 0.03 |
| C(12) | 0.00 | C(17) | −0.03 |
| C(13) | −0.01 | C(18)[a] | −0.40 |
| Ligand 2: $0.7672x + 0.3275y - 0.5514z = 0$ | | | |
| Cr(1) | −0.02 | C(24) | 0.05 |
| O(2) | −0.08 | C(25) | 0.02 |
| C(21) | −0.03 | C(26) | 0.02 |
| C(22) | −0.01 | C(27) | −0.03 |
| C(23) | 0.03 | C(28)[a] | 0.16 |

Dihedral Angle between Ligand Planes: 89.7°

[a] Not included in least-squares determination of plane.

0, $^1/_2$, $^1/_2$ are shown in projection on a 100 plane. It is clear that there are no axial bonds to the chromium atoms and that the molecules are packed according to the usual van der Waals forces. The mean volume per atom is 18.8 Å³ which is at, or slightly below, the normal value of ca. 20 Å³.

**Discussion**

It is ironic that, in all liklihood, the compound we have studied is probably no more convenient or tractable than the original anisyl compound, $Cr_2(C_6H_4OMe)_4$, itself. At any rate, our compound is also very insoluble and the way in which crystals (albeit very small ones) were obtained does not depend on its solubility and might well have succeeded with $Cr_2$-$(C_6H_4OMe)_4$ as well. That method is to allow the reactants to meet at the interface of two liquid phases so that, after initial turbulence subsided, product was formed slowly under diffusion control.

The structure of the new compound and its general physical and chemical resemblance to the unsubstituted compound strongly suggest that they must be structurally similar, that is, both polymeric or neither polymeric. Thus, we suggest that $Cr_2(C_6H_4OMe)_4$ has a molecular and not a polymeric structure. These compounds, certainly the new one, provide further examples of the fact that unexpectedly low solubility is *not* a reliable indication that a compound is nonmolecular in its crystal packing.

The $Cr_2(2\text{-MeO-5-MeC}_6H_3)_4$ molecule has a structure entirely in keeping with those previously found in **1a**, **2**, and

3. The paddle wheel arrangement of essentially planar ligands, making nearly 90° dihedral angles, is such that each Cr–C bond is trans to a Cr–O bond. As in all other cases, the Cr–Cr–C angles are very nearly right angles (91.6 ± 0.3°), while the Cr–Cr–O angles are markedly obtuse (101.5 ± 0.5°). The Cr–C and Cr–O bond lengths averaging 2.060 (7) and 2.120 (5) Å are essentially the same as those in **1a** and **2**.

The Cr–Cr distance, 1.828 (2) Å, is the shortest such bond length ever reported, though it is not significantly, in a statistical sense, shorter than that in **3**, which is 1.830 (4) Å.

The crystal packing, as is evident from Figure 2, is such that only van der Waals contacts between peripheral atoms occur. In particular, there is not the slightest indication of any intermolecular donor interaction to the Cr atoms. It appears that no such interaction is possible for several reasons. The hydrogen atoms at the 6-positions of the phenyl rings partly block the axial positions, while the methyl groups on the oxygen atoms do so even more effectively. It is to be noted that the three bonds about each oxygen atom are essentially coplanar, the sums of the bond angles being 357.3 (16) and 357.5 (15)° at the two crystallographically independent oxygen atoms. Thus, the methyl groups are placed directly over the axial positions and the lone pair on oxygen is forced to occupy an essentially pure pπ orbital, so oriented as to make it inaccessible to any neighboring acceptor even if the latter had no steric problems of its own.

**Supplementary Material Available:** A listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

**References and Notes**

(1) F. A. Cotton, S. Koch, and M. Millar, *J. Am. Chem. Soc.*, **99**, 7273 (1977).
(2) F. A. Cotton and M. Millar, *Inorg. Chim. Acta*, **25**, L105 (1977).
(3) F. A. Cotton and S. Koch, *Inorg. Chem.*, **17**, 2021 (1978).
(4) F. A. Cotton, P. E. Fanwick, R. H. Niswander and J. C. Sekutowski, *J. Am. Chem. Soc.*, in press.
(5) F. Hein and D. Tille, *Z. Anorg. Allg. Chem.*, **329**, 72 (1964).
(6) R. P. A. Sneeden and H. H. Zeiss, *J. Organomet. Chem.*, **47**, 125 (1973).
(7) R. L. Letsinger and A. W. Schnizer, *J. Org. Chem.*, **16**, 869 (1951).
(8) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York, N.Y., 1974, p 42.
(9) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).
(10) The Enraf-Nonius structure determination package was used on the PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas.