

that tunneling probability should depend on the effective mass along the reaction coordinate and that increased tunnel corrections should steepen the apparent temperature dependences of isotope effects.³⁰ These ideas are not dependent on the details of any

specific model, so the predictions can reasonably be expected to apply in a qualitative sense to any thermally activated slow hydrogen transfers.

Registry No. ¹³C, 14762-74-4; ¹⁴C, 14762-75-5; deuterium, 7782-39-0; tritium, 10028-17-8.

(30) References 11, pp 63-67.

An Unusual C-C Bond Cleavage in a Bulky Metal Alkoxide: Syntheses and X-ray Crystal Structures of Three-Coordinate Mn(II) and Cr(II) Complexes Containing the Di-*tert*-butylmethoxide Ligand

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Abstract: Two multinuclear alkoxides containing the di- or tri-*tert*-butylmethoxide ligand have been characterized by X-ray diffraction. The molecular structures of $[\text{Cr}(\mu\text{-OCH-}t\text{-Bu}_2)(\text{OC-}t\text{-Bu}_3)_2]$ (**1**) and $[\text{Mn}_3(\text{OCH-}t\text{-Bu}_2)_6]$ (**3**) both contain the *t*-Bu₂CHO⁻ group acting as a bridging ligand. The crystal data (Mo K α , $\lambda = 0.71069 \text{ \AA}$) at 140 K are as follows. **1**: $a = 8.151 (2) \text{ \AA}$, $b = 16.520 (4) \text{ \AA}$, $c = 17.434 (4) \text{ \AA}$, $\alpha = 94.46 (2)^\circ$, $\beta = 93.94 (2)^\circ$, $\gamma = 101.01 (2)^\circ$, $Z = 2$ (dimers), space group $P\bar{1}$. **3**: $a = 12.092 (2) \text{ \AA}$, $b = 21.868 (4) \text{ \AA}$, $c = 22.748 (4) \text{ \AA}$, $\beta = 96.57 (2)^\circ$, $Z = 4$, space group $P2_1/c$. For **1**, $R = 0.050$; for **3**, $R = 0.048$. The geometry at the chromium atoms in **1** is distorted trigonal planar. Complex **3** is the first homoleptic manganese(II) alkoxide to be structurally characterized. The nonlinear trimer has a Mn-Mn-Mn angle of 154.0° and does not possess any formal Mn-Mn bonds. Both complexes exhibit very wide M-O-C angles at the terminal alkoxides. In complex **1** the Cr-O-C_{terminal} moiety is essentially linear. The di-*tert*-butylmethoxide ligand in **1** results from an unusual C-C bond cleavage under mild conditions in the complex $[\text{Cr}(\text{OC-}t\text{-Bu}_3)_2\cdot\text{LiCl}(\text{THF})_2]$ (**2**).

Recent years have seen a renewed interest in the synthesis and chemical properties of alkoxide and aryloxo complexes.¹⁻¹¹ Most transition-metal alkoxide and aryloxides containing smaller ligands such as OMe⁻, OEt⁻, or OPh⁻ are oligomeric.⁴ This is due to the excellent bridging ability and lower steric requirements of the alkoxo group compared to isoelectronic amido or alkyl substituents. In sharp contrast, some recent reports have concentrated on the use of bulky aryloxo groups (e.g., 2,6-di-*tert*-butyl-4-methylphenoxide) to achieve low coordination numbers in complexes involving main group, transition, or lanthanoid metals.^{5-9,11} These complexes are in general monomeric and exhibit low coordination (typically three) at the metal.

An interesting consequence of the severe steric requirements imposed by the larger alkoxo groups has been the discovery of

reactions involving C-H bond activation and the formation of benzyne intermediates not seen with the smaller substituents.^{8,9} In addition, work in this laboratory with the large tri-*tert*-butylmethoxide ligand, *t*-Bu₃CO⁻, has allowed the synthesis of the first structurally characterized examples of monomeric alkoxide complexes for Cr(II) and Mn(II).^{1,2}

Recently we reported that the green complex $[\text{Cr}\{\text{OC-}t\text{-Bu}_3\}_2\cdot\text{LiCl}(\text{THF})_2]$ is formed when CrCl₃ is treated with *t*-Bu₃COLi in Et₂O/THF solution.¹ When it is dissolved in warm hexane, LiCl is precipitated and a blue-green crystalline complex is obtained. The complex gave a C, H elemental analysis consistent with the formulation $[\text{Cr}(\text{OC-}t\text{-Bu}_3)_2(\text{THF})_2]$.¹² This composition seemed reasonable since complexes of the type $[\text{Cr}(\text{OR})_2(\text{THF})_2]$ (where OR is 2,6-di-*tert*-butylphenolate or 2,4,6-tri-*tert*-butylphenolate)⁶ and *trans*- $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ had been reported.¹³

However, upon GC/MS analysis of the filtrate we were surprised by the high concentration of C₄H₈ (mostly isobutene) present. In order to explain the origin of C₄H₈ we determined the structure of the blue-green complex.

In this paper we describe the first structural characterization of (i) a three-coordinate chromium(II) dimer, $[\{\text{Cr}(\mu\text{-OCH-}t\text{-Bu}_2)(\text{OC-}t\text{-Bu}_3)_2\}]$ (**1**), which contains only alkoxide ligands, and (ii) a homoleptic manganese(II) alkoxide trimer, $[\text{Mn}_3\{\text{OCH-}t\text{-Bu}_2\}_6]$. Both of these complexes have the di-*tert*-butylmethoxide group acting as a bridging ligand. The blue-green complex **1** is the result of an unusual solvent dependent C-C cleavage from the compound $[\text{Cr}\{\text{OC-}t\text{-Bu}_3\}_2\cdot\text{LiCl}(\text{THF})_2]$ (**2**).

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Table I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement of 1 and 3

formula	C ₄₄ H ₉₂ O ₄ Cr ₂	C ₅₄ H ₁₁₄ O ₆ Mn ₃
fw, g·mol ⁻¹	789.21	1024.32
cryst system	triclinic	monoclinic
space group	P1	P2 ₁ /c
T, K	140	140
a, Å	8.151 (2)	12.092 (2)
b, Å	16.520 (4)	21.868 (4)
c, Å	17.434 (4)	22.748 (4)
α, deg	94.46 (2)	
β, deg	93.94 (2)	96.57 (2)
γ, deg	101.01 (2)	
V, Å ³	2289.0	5975.7
Z	2 (dimers)	4
d _{calcd} , g·cm ⁻³	1.15	1.14
crystal size, mm	(0.47 × 0.25 × 0.16)	(0.30 × 0.26 × 0.22)
radiation	graphite monochromated Mo Kα (λ = 0.71069 Å)	graphite monochromated Mo Kα (λ = 0.71069 Å)
μ, cm ⁻¹	5.3	7.0
scan type	ω	ω
scan speed, deg·min ⁻¹	20	20
scan range, deg	1.1	0.8
ω background	±1.1	±0.8
offsets, deg		
2θ limits, deg	0–45	0–42
no. of unique data	5983	6420
std rflns (no decay observed)	(1,2,-10)(2,4,4)	(1,1,-6)(0,1,13)
no. of rflns used in L.S. (F > 6σ(F))	3506	4246
no. of parameters	549	700
R	0.050	0.048
R _w (w = 1/σ ² (F))	0.049	0.051
GOF	1.35	1.27

The complex [Mn₃(OCH-*t*-Bu₂)₆] (3) was previously prepared in low yield by Wilkinson and co-workers.³ We have prepared this complex in higher yield by changing the starting materials and reaction conditions.

Experimental Section

General Procedures. All reactions were performed either with modified Schlenk techniques (under N₂) or in a Vacuum Atmosphere HE43-2 drybox (under argon). Solvents were freshly distilled from drying agents and degassed three times immediately before use. Solutions of these metal complexes are extremely air-sensitive and immediately darken to violet or brown if small, controlled amounts of O₂ are added. When excess oxygen is present, these solutions turn black/brown rapidly and deposit solids that are only soluble in concentrated mineral acids. [Cr{OC-*t*-Bu₃LiCl(THF)₂}]₂,¹ [Mn{N(SiMe₃)₂(THF)}]₂,^{14,15} 2,2,4,4-tetramethylpentan-3-ol (*t*-Bu₂CHOH),¹⁶ 2,2,4,4-tetramethyl-3-*tert*-butylpentan-3-ol (*t*-Bu₃COH),¹⁶ [Mn₂{N(SiMe₃)₂}]₄,¹⁵ and lithium bis(trimethylsilyl)amide¹⁷ were prepared by previously described procedures. Melting points were determined in capillaries sealed under argon. Elemental microanalyses were performed at the University of California, Berkeley, and at the University of California, Davis. GC/MS data were obtained on a Finnigan 3200 spectrometer equipped with a 30-m column. Magnetic susceptibility data were obtained at 298 K on a Varian EM-390 spectrometer.

[Cr(μ-OCH-*t*-Bu₂)(OC-*t*-Bu₃)₂] (1). [Cr{OC-*t*-Bu₃LiCl(THF)₂}] (1.00 g) was dissolved in 20 mL of hexane. The green solution was warmed to 60 °C, filtered through a Celite-padded filter funnel (medium porosity) and then cooled to -20 °C to give blue-green crystals in 72% yield. The filtrate was analyzed by GC/MS. The product was multiply recrystallized until the product contained less than 0.1% Cl⁻: mp >157 °C darkens, 196–200 °C decomposes. Anal. Calcd for C₄₄H₉₂O₄Cr₂: C, 67.0; H, 11.8. Found: C, 67.6; H, 11.7.

Table II. Atom Coordinates (×10⁴) for 1

atom	X	Y	Z
Cr(1)	784 (1)	876 (1)	-189 (1)
O(1)	1855 (4)	1939 (2)	-302 (2)
O(2)	697 (4)	164 (2)	664 (2)
C(1)	2706 (7)	2779 (3)	-262 (3)
C(2)	4146 (7)	2887 (3)	448 (3)
C(3)	3428 (7)	2923 (3)	-1089 (3)
C(4)	1281 (7)	3328 (3)	-90 (3)
C(5)	5526 (7)	3677 (4)	493 (3)
C(6)	5039 (7)	2135 (3)	442 (3)
C(7)	3424 (8)	2887 (4)	1248 (3)
C(8)	4056 (8)	3827 (4)	-1252 (3)
C(9)	2155 (8)	2510 (4)	-1776 (3)
C(10)	4926 (8)	2486 (4)	-1198 (4)
C(11)	90 (7)	3383 (4)	-810 (4)
C(12)	1958 (8)	4243 (3)	234 (4)
C(13)	20 (7)	2933 (4)	466 (4)
C(14)	1565 (7)	402 (3)	1409 (3)
C(15)	307 (7)	572 (3)	2013 (3)
C(16)	2875 (7)	-163 (3)	1546 (3)
C(17)	-914 (7)	-195 (4)	2192 (4)
C(18)	-747 (8)	1140 (4)	1660 (4)
C(19)	1223 (8)	1020 (5)	2755 (4)
C(20)	2080 (8)	-1063 (4)	1620 (4)
C(21)	3931 (10)	-157 (4)	865 (4)
C(22)	4052 (9)	151 (5)	2266 (4)
Cr(2)	761 (1)	5916 (1)	5007 (1)
O(3)	1740 (4)	6987 (2)	4904 (2)
O(4)	222 (5)	4904 (2)	4298 (2)
C(23)	2493 (7)	7793 (3)	4754 (3)
C(24)	3694 (7)	8191 (3)	5520 (3)
C(25)	3545 (7)	7668 (3)	4001 (3)
C(26)	950 (7)	8277 (3)	4575 (3)
C(27)	4393 (10)	9141 (4)	5551 (4)
C(28)	2778 (8)	8062 (4)	6262 (3)
C(29)	5193 (9)	7774 (5)	5651 (4)
C(30)	2424 (8)	7377 (4)	3248 (3)
C(31)	4817 (9)	8434 (4)	3834 (4)
C(32)	4525 (8)	6953 (4)	4067 (4)
C(33)	-540 (8)	7702 (5)	4090 (4)
C(34)	1414 (9)	9052 (4)	4145 (4)
C(35)	126 (9)	8533 (5)	5287 (4)
C(36)	794 (7)	4880 (3)	3537 (3)
C(37)	2167 (7)	4349 (4)	3471 (3)
C(38)	-781 (7)	4740 (3)	2944 (3)
C(39)	1508 (8)	3423 (4)	3306 (4)
C(40)	3289 (8)	4509 (4)	4226 (4)
C(41)	3328 (8)	4658 (4)	2838 (4)
C(42)	-2030 (8)	3944 (4)	3013 (4)
C(43)	-1706 (8)	5462 (4)	3105 (4)
C(44)	-319 (8)	4753 (4)	2110 (3)

[Mn₃(OCH-*t*-Bu₂)₆] (3). [Mn{N(SiMe₃)₂(THF)}] (3.00 g) in hexane (45 mL) and benzene (8 mL) was treated with *t*-Bu₂CHOH (1.97 g). The clear pink solution was refluxed for 2 h. The solution was concentrated and then cooled to -30 °C to give pale pink crystals in 61% yield. The trimer can also be prepared from [Mn₂{N(SiMe₃)₂}]₄ in lower yield.³ Since the product is soluble in hexane and benzene it is essential to concentrate the solution in order to obtain a high yield: mp 249–250 °C (does not decompose below 280 °C). Anal. Calcd for C₅₄H₁₁₄O₆Mn₃: C, 63.32; H, 11.22. Found: C, 62.9; H, 11.0.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P₂ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device, using a procedure described earlier.¹⁸ Further details are in Table 1.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors, including anomalous scattering, were from "International Tables of Crystallography".¹⁹

Blue-green single crystals of [Cr(μ-OCH-*t*-Bu₂)(OC-*t*-Bu₃)₂] (1) were obtained by cooling a concentrated hexane solution to -30 °C. After the crystals were removed from a Schlenk tube inside the drybox they were protected from air contamination by a layer of epoxy resin. A

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Table III. Atom Coordinates ($\times 10^4$) for 3

atom	X	Y	Z
Mn(1)	1236 (1)	7123 (1)	1520 (1)
Mn(2)	-780 (1)	7889 (1)	1091 (1)
Mn(3)	2604 (1)	5964 (1)	1594 (1)
O(1)	1958 (3)	6536 (2)	2165 (1)
O(2)	3291 (3)	5210 (2)	1566 (2)
O(3)	838 (3)	8034 (2)	1410 (2)
O(4)	-483 (3)	7042 (2)	1418 (2)
O(5)	-1803 (4)	8361 (2)	619 (2)
O(6)	2146 (3)	6598 (2)	973 (1)
C(1)	2303 (5)	6687 (3)	2771 (2)
C(2)	3402 (5)	4627 (3)	1774 (3)
C(3)	1457 (5)	8595 (3)	1507 (3)
C(4)	-1160 (5)	6610 (3)	1687 (2)
C(5)	-2687 (5)	8413 (4)	236 (3)
C(6)	2473 (5)	6696 (2)	387 (2)
C(11)	2072 (5)	6124 (3)	3177 (2)
C(12)	3490 (5)	6987 (3)	2825 (2)
C(21)	2505 (5)	4198 (3)	1454 (3)
C(22)	4644 (5)	4450 (3)	1899 (3)
C(31)	906 (5)	8989 (3)	1973 (3)
C(32)	1729 (5)	8887 (3)	913 (3)
C(42)	-1785 (5)	6202 (3)	1202 (3)
C(41)	-1809 (5)	6931 (3)	2162 (2)
C(51)	-2460 (5)	8361 (3)	-420 (3)
C(52)	-3555 (5)	8877 (3)	427 (3)
C(61)	1594 (5)	6399 (3)	-84 (2)
C(62)	3749 (5)	6571 (3)	371 (2)
C(111)	2325 (10)	6260 (4)	3830 (3)
C(112)	863 (6)	5973 (4)	3077 (5)
C(113)	2657 (8)	5547 (3)	3043 (4)
C(121)	3442 (5)	7484 (3)	2345 (3)
C(122)	3749 (6)	7328 (3)	3417 (3)
C(123)	4445 (5)	6563 (3)	2736 (3)
C(2111)	1384 (6)	4513 (4)	1454 (4)
C(212)	2666 (7)	4137 (4)	800 (3)
C(213)	2431 (10)	3580 (4)	1718 (5)
C(221)	5198 (7)	4373 (5)	1346 (4)
C(222)	5243 (6)	4970 (4)	2250 (4)
C(223)	4827 (8)	3895 (4)	2296 (5)
C(311)	-351 (5)	9052 (3)	1823 (3)
C(312)	1397 (6)	9636 (3)	2061 (3)
C(313)	1128 (6)	8662 (3)	2572 (3)
C(321)	764 (5)	9228 (3)	570 (3)
C(322)	2756 (5)	9304 (3)	1017 (3)
C(323)	2074 (6)	8360 (3)	526 (3)
C(421)	-901 (6)	5774 (3)	995 (3)
C(422)	-2315 (5)	6582 (3)	671 (3)
C(423)	-2688 (5)	5790 (3)	1403 (3)
C(511)	-3375 (7)	8047 (4)	-816 (4)
C(512)	-2101 (8)	8938 (3)	-687 (3)
C(513)	-1472 (7)	7910 (4)	-440 (4)
C(521)	-3031 (8)	9517 (4)	465 (4)
C(522)	-3778 (10)	8739 (5)	1045 (4)
C(523)	-4611 (7)	8959 (5)	1 (4)
C(611)	1378 (5)	5724 (3)	47 (3)
C(612)	513 (5)	6760 (3)	-67 (3)
C(613)	1887 (6)	6448 (3)	-727 (3)
C(622)	4184 (5)	6941 (3)	-129 (3)
C(623)	4052 (5)	5892 (3)	306 (3)
C(411)	-984 (6)	7346 (3)	2528 (3)
C(412)	-2799 (5)	7325 (3)	1893 (3)
C(413)	-2242 (6)	6472 (3)	2600 (3)

crystal was cut to a suitable size, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream (140 K). Final lattice parameters were determined by a least-squares refinement of 20 accurately centered reflections with $25^\circ < 2\theta < 35^\circ$. Intensity data were corrected for Lorentz and polarization effects but not for absorption. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement of the structure. Although the precise stoichiometry was unknown initially the correct composition became readily apparent. The structure was solved by direct methods, phasing difference electron density maps in consecutive steps. All of the 62 H atoms were detected in a difference electron density map; their sites compared well with coordinates calculated according to carbon hybridization. The structure was refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included in the refine-

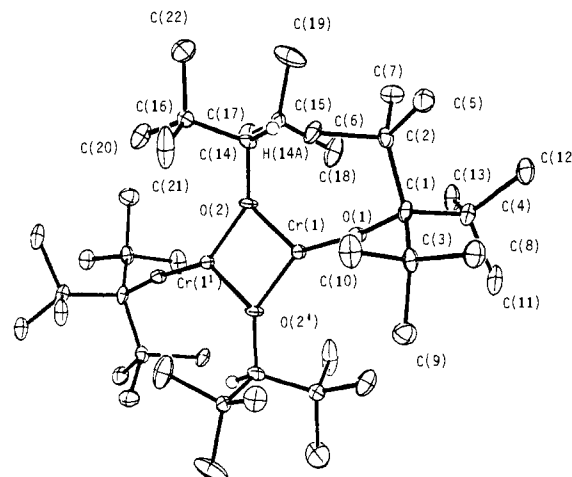


Figure 1. Computer-generated perspective diagram of 1. The H atoms have been omitted for clarity.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 1

(a) Bond Distances			
Cr(1)---Cr(1')	3.075 (1)	Cr(1)-O(1)	1.838 (3)
Cr(1)-O(2)	1.964 (4)	Cr(1)-O(2')	1.986 (3)
O(1)-C(1)	1.421 (6)	O(2)-C(14)	1.426 (6)
C(1)-C(4)	1.634 (8)	C(14)-C(16)	1.564 (8)
(b) Bond Angles			
O(1)-Cr(1)-O(2)	134.1 (1)	O(1)-Cr(1)-O(2')	148.1 (1)
O(2)-Cr(1)-O(2')	77.8 (1)	Cr(1)-O(2)-Cr(1')	102.2 (1)
Cr(1')-O(2)-C(14)	133.1 (3)	Cr(1)-O(1)-C(1)	171.0 (3)
Cr(1)-C(3)-C(8)	116.6 (4)	C(9)-C(3)-C(10)	102.6 (5)
C(15)-C(14)-C(16)	123.0 (4)	C(14)-C(15)-C(19)	111.2 (5)

ment with fixed group geometry, with a C-H distance of 0.96 Å and U 's coupled to U (C). The refinement converged with $R = 0.050$ for the 3506 reflections used. Table II contains the final atomic coordinates for 1.

Pale pink crystals of $[\text{Mn}_3(\text{OCH-}t\text{-Bu}_2)_6]$ (3) were obtained by cooling a concentrated hexane solution to -30°C . The crystals were handled by the procedure described earlier for 1. The space group was uniquely determined as $P2_1/c$ from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $l = 2n + 1$. The structure was solved and refined by the methods used for 1. Of the 114 H atoms 109 were detected in a difference electron density map. The refinement converged with $R = 0.048$ for the 4246 reflections used. Table III contains the final atomic coordinates for 3.

Structural Description

The unit cell of 1 contains two similar centrosymmetric dimers. Although the two dimers are crystallographically independent, an examination of the related bond distances and angles revealed only slight structural differences. The structure of one of the dimers is illustrated in Figure 1. The dimers contain two bridging di-tert-butylmethoxide groups and two terminal tri-tert-butylmethoxide groups. Each dimer has a symmetry required planar central core of two Cr and two O atoms. The three-coordinate chromium atoms are separated by distances of 3.075 (1) and 3.042 (1) Å. These distances are probably too long for any extensive metal-metal bonding. The geometry at the chromium atoms is best described as severely distorted trigonal planar. The methine hydrogen atoms of the $t\text{-Bu}_2\text{CHO}^-$ groups are staggered with respect to each other. Table IV contains some selected bond distances and angles for 1.

The Cr-O-C_(terminal) angles in 1 (171.0 (3)° and 174.9 (3)°) are the widest angles at alkoxide oxygen reported to date. All of the known complexes with bulky alkoxy or aryloxy ligands exhibit characteristically wide M-O-C angles. While some degree of π -bonding between the metal center and the oxygen atom may increase these angles, steric and ligand packing effects are probably much more influential. The terminal C-O distances in 1 do not display any shortening that might support the notion of π -bonding.

The average of the terminal Cr-O distances is 1.83 (1) Å. This is shorter than the Cr-O distance of 1.881 (4) Å found in 2 but

Table V. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances			
Mn(1)–Mn(2)	3.026 (1)	Mn(1)–Mn(3)	3.020 (1)
Mn(1)–O(3)	2.058 (3)	Mn(1)–O(6)	2.095 (4)
Mn(2)–O(4)	2.013 (4)	Mn(3)–L(6)	2.012 (3)
Mn(2)–O(5)	1.856 (4)	O(1)–C(1)	1.432 (6)
O(5)–C(5)	1.304 (7)	O(2)–C(2)	1.360 (7)
C(6)–C(61)	1.562 (7)	C(2)–C(21)	1.550 (8)
(b) Bond Angles			
Mn(1)–O(1)–Mn(3)	95.2 (1)	O(1)–Mn(1)–O(3)	139.6 (1)
O(3)–Mn(1)–O(6)	126.1 (1)	O(3)–Mn(1)–O(4)	81.5 (1)
O(3)–Mn(2)–O(5)	132.1 (2)	O(4)–Mn(2)–O(5)	143.5 (2)
O(1)–Mn(3)–O(2)	141.3 (2)	Mn(1)–O(3)–C(3)	134.1 (3)
Mn(2)–O(3)–C(3)	130.5 (3)	Mn(2)–O(5)–C(5)	151.2 (5)
Mn(3)–O(2)–C(2)	148.2 (4)	C(61)–C(6)–C(62)	120.3 (5)
C(21)–C(2)–C(22)	123.2 (5)	C(511)–C(51)–C(513)	101.9 (6)

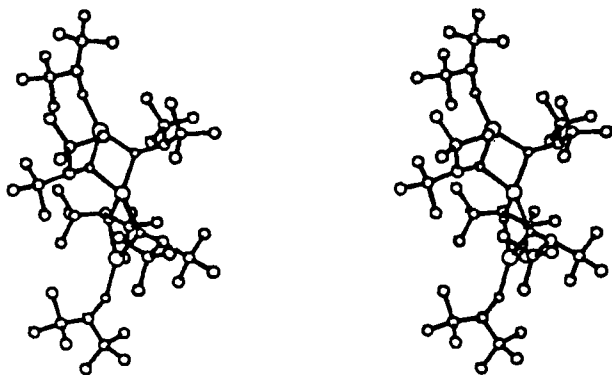


Figure 2. Stereoview of 3. The H atoms have been omitted for clarity.

is similar to those in $[\text{LiCr}(\text{OCH-}t\text{-Bu}_2)_4(\text{THF})]$ (1.82 (1) Å) and longer than those in $[\text{Cr}(\text{OCH-}t\text{-Bu}_2)_4]$ (1.77 (1) Å).^{1,3} The average bridging Cr–O distance of 1.97 (1) Å is similar to those found in **2** and $[\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-Ot-Bu})\}_2]$.¹⁰ This suggests that metal-to-metal bonding which occurs in the *tert*-butoxide bridged dimer does not greatly affect the Cr–O distance in these bridging alkoxides.

The structure determination of **3** is the first X-ray structural characterization of a homoleptic manganese(II) alkoxide. The molecule is a nonlinear trimer containing two terminal and four bridging alkoxy groups (see Figures 2 and 3). The central manganese atom has a distorted tetrahedral geometry while the terminal manganese atoms display distorted trigonal planar coordination. The deviations from the plane defined by the three nearest oxygens are 0.091 (3) and 0.009 (3) Å for Mn(2) and Mn(3), respectively. The dihedral angle formed by the two planes is 93.6°. The average Mn···Mn distance of 3.023 (4) Å is too long for any extensive metal bonding, although the magnetic susceptibility of 5.2 μ_B (298 K, toluene) supports a very minor magnetic interaction. The Mn(2)–Mn(1)–Mn(3) angle is 154.0 (1)°.

The Mn–O distances in **3** range from 1.852 (4) to 2.095 (4) Å, with the terminal Mn–O distances the shortest and the central Mn–O distances the longest. Thus, the bonding mode and coordination number affect the Mn–O distance. The terminal alkoxides display shortened C–O distances compared to the bridging C–O distances. The terminal distances may be reduced slightly due to the higher thermal motion of the terminal alkoxy groups. The *t*-Bu–C–*t*-Bu angles in the terminal groups are wider than in the bridging ligands. This can be attributed to increased crowding near the center of the trimer.

Results and Discussion

The complex **1** is formed by an elimination reaction. The first step in hexane may be the loss of LiCl and THF. This produces a low-coordinate Cr(II) center having two electronegative substituents.

The next step in the reaction may involve the association of two $[\text{Cr}(\text{OC-}t\text{-Bu}_2)_2]$ fragments followed by the loss of C_4H_8 . This pathway allows the highly electron-deficient metal centers to

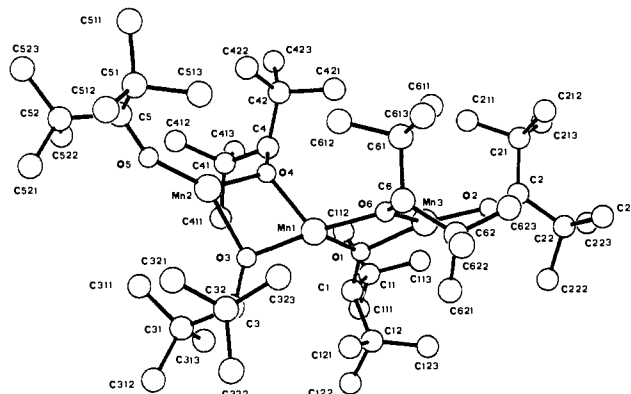


Figure 3. Computer-generated perspective diagram of 3. The H atoms have been omitted for clarity.

become more saturated. Another possibility is an intramolecular metal promoted C–C bond cleavage in a $[\text{Cr}(\text{OC-}t\text{-Bu}_2)_2]$ unit. Upon elimination of C_4H_8 , two $[\text{Cr}(\text{OC-}t\text{-Bu}_2)(\text{OCH-}t\text{-Bu}_2)]$ units can dimerize through the less sterically hindered *t*-Bu₂CHO[−] group. The latter mechanism is supported by the fact that bending at the Cr–O–C–*t*-Bu₃ bonds allows the carbon atoms α and γ to the oxygen to come very close to the metal upon free rotation (1.8–3.0 Å). There are many examples of C–H and C–C bond activation when organic groups are allowed to approach coordinately unsaturated metal centers.^{8,9,20,21} The fact that these reactions are known does not preclude a radical mechanism.

The drive to form the new Cr–O and C–H bonds is assisted by the increased entropy of the products and the ease with which the volatile C_4H_8 can be removed. Another contributing factor is the relief in internal strain that accompanies the loss of C_4H_8 . The large difference in C–C(*t*-Bu) bond distances for the *t*-Bu₃CO[−] and *t*-Bu₂CHO[−] groups (1.63 (1) Å vs. 1.56 (1) Å) provides strong evidence for this.

The fact that **3** is trimeric is worthy of discussion. While trimers of rhenium are quite common, there are only a few homonuclear manganese trimers known.^{22–28} These complexes exhibit a wide range of coordination numbers (3–7) and geometries at the metals. Linear,^{23–25} triangular,²⁶ oxo-centered,²⁷ and bent²⁸ Mn₃ configurations are known. The linear configuration is the most prevalent for manganese.

Floriani has recently reported the structure of the deep maroon colored trinuclear complex $[\text{Mn}_3(\text{mesityl})_6]$.²³ This linear trimer has two Mn···Mn distances of 2.851 (3) Å. Two other examples of linear Mn₃ complexes are $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$ ²⁴ and $[\text{Mn}_3(3\text{-CH}_3\text{C}_5\text{H}_4)_4]$.²⁵ The nonlinear trimer **3** and the complex $[\text{CH}_3\text{N}_2][\text{Mn}(\text{CO})_4]_3$ ²⁸ (**4**) are the only bent Mn trimers known. The nonlinearity in **4** is due to the CH_3N_2 group. The nonlinearity in **3** may be the result of packing effects in the crystal lattice.

Packing effects and the steric bulk of the ligands employed have a profound effect on the formation of homonuclear chains of metal ions. The complex dineopentylmanganese exists as a linear tetramer while the similar neophyl and trimethylsilylmethyl compounds are dimeric and polymeric.²⁹ Similar steric control has

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been reported by us and other workers.^{1,3,4,29}

The magnetic susceptibility of $5.2 \mu_B$ for **3** (Evans method)^{30,31} is higher than the values reported for similar Mn(II) systems ($3.0\text{--}3.9 \mu_B$).^{15,23,29} This is probably due to the longer Mn–Mn distances in **3**. For example, $\text{Mn}_3(\text{mesityl})_6$ has a magnetic moment of $3.65 \mu_B$ at 299 K.²³ The complex $\text{Mn}_2\{\text{N}(\text{SiMe}_3)_2\}_4$ has a Mn–Mn distance of 2.811 (1) Å at 140 K (2.841 (1) Å at room temperature) and has a magnetic moment of $3.34 \mu_B$.^{15,32}

In summary, the $t\text{-Bu}_2\text{CHO}^-$ group can be employed as a bridging group to permit the stabilization of low-coordinate multinuclear metal complexes. The ligand can be introduced into metal complexes by (i) treating the lithium alkoxide with metal

halides, (ii) by exchange with metal amides, or (iii) by the conversion of $t\text{-Bu}_3\text{CO}^-$ into $t\text{-Bu}_2\text{CHO}^-$ via the cleavage of a C–C bond and subsequent production of C_4H_8 .

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Registry No. **1**, 93684-91-4; **3**, 93684-92-5; $[\text{Cr}\{\text{OC-}t\text{-Bu}_3\}_2\text{LiCl}(\text{THF})_2]$, 89189-87-7; $[\text{Mn}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})]$, 69900-28-3; $\text{HOC-}t\text{-Bu}_3$, 41902-42-5.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and calculated positional and thermal parameters for **1** and **3** (56 pages). Ordering information is given on any current masthead page.

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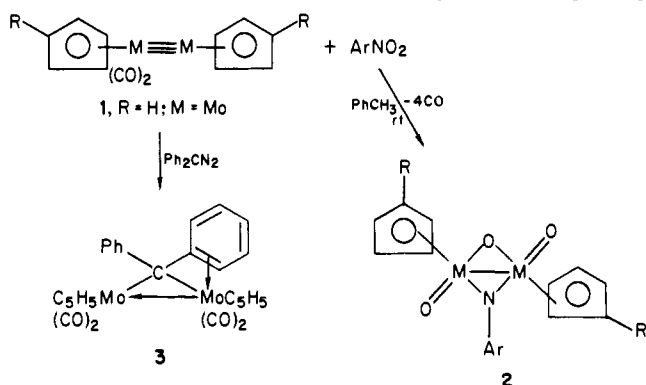
Novel Organosulfur Metal Complexes Derived from Dithioesters

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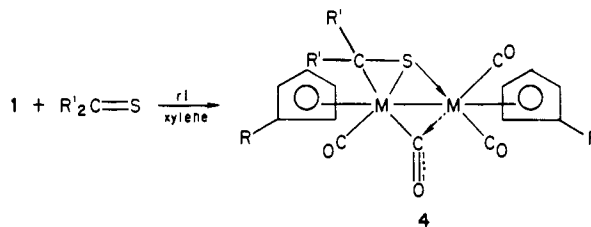
Abstract: Dithioesters react with complexes containing a metal–metal triple bond, in refluxing toluene or xylene, to give a novel class of organosulfur complexes. A single-crystal X-ray analysis of one such complex $[(\text{CH}_3\text{C}_3\text{H}_4)_2\text{Mo}_2(\text{CO})_2(\text{SCC-H}_3)(\text{SC}_2\text{H}_5)]$ confirms the presence of a symmetrically bridging thioacyl function, a bridging thioalkyl group, and a molybdenum–molybdenum single-bond distance of 2.806 (1) Å. When the reaction was effected at room temperature, a complex with a retained dithioester unit was obtained. As established by an X-ray analysis of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{CH}_3\text{C}(\text{S})\text{SC}_2\text{H}_5)]$, the thiocarbonyl group is bonded to one molybdenum atom with the sulfur atom also donor bound to the other metal atom. A semibringing carbonyl group is also present.

One of the most exciting areas of research in inorganic chemistry is the chemistry of compounds containing metal–metal multiple bonds.² Significant work has been done on the reactivity of cyclopentadienylmolybdenum dicarbonyl dimer [**1**, R = H; M = Mo] and related complexes containing a metal–metal triple bond.^{3,4} Interesting reactions have been observed on treatment of **1** with organonitrogen and sulfur compounds. Regarding



affording complexes **2** in a high-oxidation state.⁵ Diazo compounds undergo several types of reactions,^{6–10} including the loss of nitrogen with the formation of **3** (from diphenyldiazomethane) which contains a formal metal–metal donor bond.⁶

Treatment of thioketones with **1** at room temperature results in the isolation of complexes **4** with the thione function bonded to one metal atom, the sulfur donor bound to the other metal atom, and a semibringing carbonyl group.¹¹ Thioesters and thiolactones ($\text{RC}(=\text{S})\text{OR}'$) form complexes formally of the same type as **4**, but with interesting differences in structural details. There is no evidence for participation of the oxygen atom in bonding to a metal atom.¹²



nitrogen-containing substrates, nitro compounds react with **1**

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