

parent, then, that substituent effects governing these competitive pathways are complex and studies are underway to further probe the nature of these effects.

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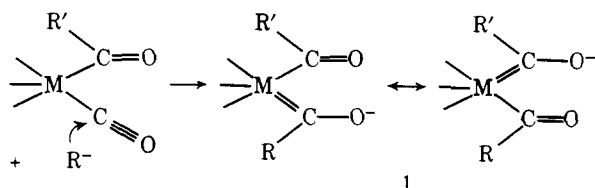
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Reactions on Coordinated Molecules. IV. The Preparation of Tris(*cis*-diacetyltetracarbonylmanganate)aluminum. A Metalloacetylacetonate Complex

Sir:

We wish to report the preparation of a complex which we believe is the first member of an extensive class of coordination compounds. When nucleophilic attack on an acyl complex is directed to a carbonyl ligand which is *cis* to the acyl ligand, the acyl-metalate anion, **1**, produced is electronically equivalent to the acetylacetonate anion.



where M is a transition metal atom.

Anion **1** is similar to the acetylacetonate anion in that the methine group is replaced by the organometallic complex. We report now the preparation of the first example of a "metallo-acac" anion and the complexation of this anion to

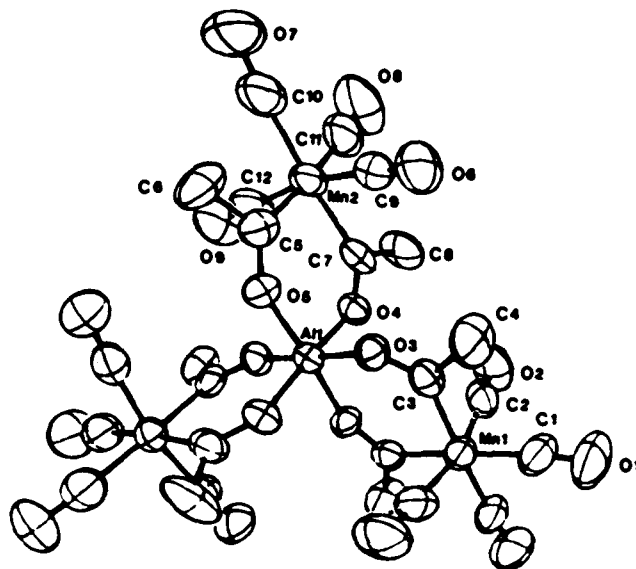
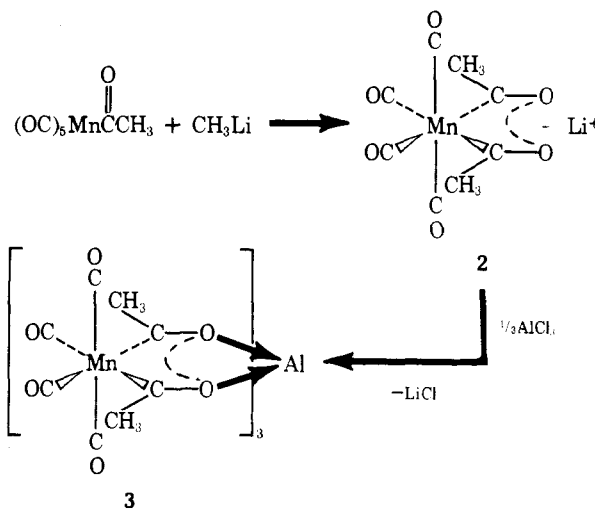


Figure 1. A view of the molecular structure of one of the independent molecules of $\text{Al}[\text{Mn}(\text{CO})_4(\text{COCH}_3)_2]_3$ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and by their perspective view.

an aluminum(III) cation forming a neutral tris-chelate complex.

To a solution of 1.0 g (4.2 mmol) of acetylpentacarbonylmanganese in 15 ml of ether was added 3.0 ml of 1.56 *M* methylolithium solution (4.7 mmol, in ether) at 0° over a 45-min period. During this addition the reaction solution became deep yellow and an infrared spectrum of this solution indicated that the terminal carbon monoxide ligand stretching frequencies of the reactant complex had shifted 70 cm^{-1} to lower frequency, and that the acyl band at 1650 cm^{-1} in the acetyl complex disappeared concomitantly with the appearance of a similar band at 1585 cm^{-1} . These data reflect the formation of the bis(diacetyl)metalate anion, **2**.¹



To this solution is added 0.19 g (1.4 mmol) of anhydrous aluminum chloride in 5 ml of ether over a 5-min period. The reaction solution is stirred for 1.5 hr during which time a light colored solid precipitated. The solution is filtered and the solid is washed with 2 × 4 ml of ether and dried at reduced pressure affording 0.88 g of an off-white powder. This solid is extracted into 30 ml of toluene at room temperature and filtered affording 0.15 g (82%) of a white solid identified as lithium chloride. The yellow filtrate is cooled slowly to -78° affording 0.42 g (38%) of the title compound, **3**, as pale yellow hexagonal needles: mp darkens at

Table I. Bond Distances (Å) and Bond Angles (deg)

Al(1)–O(3)	1.873 (6)	Mn(1)–C(2)	1.818 (10)
C(3)–O(3)	1.248 (9)	Mn(1)–C(1)	1.859 (12)
C(3)–C(4)	1.541 (11)	C(2)–O(2)	1.144 (10)
Mn(1)–C(3)	1.818 (10)	C(1)–O(1)	1.143 (11)
O(3)–Al(1)–O(3)	92.5 (4)	C(2)–Mn(1)–C(2)	165.4 (6)
Al(1)–O(3)–C(3)	139.1 (5)	O(2)–C(2)–Mn(1)	176.5 (9)
Mn(1)–C(3)–O(3)	127.7 (6)	C(1)–Mn(1)–C(1)	85.8 (7)
Mn(1)–C(3)–C(4)	120.1 (7)	O(4)–Al(1)–O(4)	176.2 (4)
C(3)–Mn(1)–C(3)	93.0 (5)	O(3)–Al(1)–O(5)	175.5 (2)

140°; deep brown at 265°; ir (C_6H_{12} in cm^{-1}) $\nu(CO)$ 2065 m, 1985 s, sh, 1978 vs, 1960 s, $\nu(C\equiv O)$ 1525, s; 1H NMR ($CDCl_3$ vs. TMS), τ 7.28 (singlet).⁵ Anal. for $C_{24}H_{18}O_{18}Mn_3Al$: Calcd: C, 36.66; H, 2.31; Mn, 20.96; Al, 3.43. Found: C, 36.50; H, 2.41; Mn, 20.66; Al, 3.45.

Since the formulation of compound **3** as a "metallo-acac" complex would represent the first member of possibly a large series of similar complexes, we obtained, commercially, an x-ray structural determination which was performed as a technical service.⁶

Crystal data: $Al[Mn(CO)_4(COCH_3)_2]_3$; $M = 786.20$, monoclinic; $a = 13.948$ (5) Å, $b = 12.182$ (6) Å, $c = 19.545$ (6) Å; $\alpha = \gamma = 90^\circ$; $\beta = 90.51$ (2)°; $Z = 4$; $d_{calcd} = 1.572$ g/cm³; space group $P2_1/n$. Intensity data were collected on a Syntex P1 computer-controlled diffractometer using $MoK\alpha$ radiation. In the refinement of the structure, 2099 reflections having $F_o^2 > 3 \sigma(F_o^2)$ were used. Anisotropic refinement of all non-hydrogen atoms gave the final agreement factors $R_1 = 0.049$ and $R_2 = 0.070$. An ORTEP view of the molecular structure of **3** is shown in Figure 1 and pertinent bond distances and bond angles are given in Table I. There are two independent molecules per unit cell each having a crystallographic C_2 axis passing through one of the manganese atoms and the aluminum atom. See paragraph at the end of paper regarding supplementary material.

The molecular structure belongs to the symmetry point group D_3 . The chemically interesting structural features of the molecule are: (i) the aluminum and manganese atoms have only slightly distorted octahedral local symmetry; (ii) the "metallo-acac" ligand is symmetrical and essentially planar as expected from the resonance structure of **1**; (iii) the values of the following bond distances (Al–O(3), 1.873 (6) Å; C(3)–O(3), 1.277 (6) Å; C(3)–C(4), 1.541 (11) Å) and the following bond angles (Al–O(3)–C(3), 139.1 (5)°; O(3)–C(3)–Mn(1), 127.7 (6)°; C(3)–Mn(1)–C(3), 93.0 (5)°; O(3)–Al–O(3), 92.5 (4)°) observed within this "metallo-acac" ligand indicate, through comparison with the corresponding values observed in $Al(acac)_3$,⁷ that the 93° angle centered at the Mn atom is compensated by increasing the other intraligand angles so as to maintain an O–Al–O angle of near 90°; and (iv) each of the two carbonyl groups on the manganese atoms which are aligned perpendicular to the "metallo-acac" plane are directed toward an open face of the aluminum coordination octahedral such that the C(2)–Mn(1)–C(2) angle is 165.4 (6)° rather than the expected 180°. Apparently, the aluminum atom is bonded very weakly to these six oxygen atoms through a long range (4.56 Å) Lewis acid–base interaction.

Although complex **3** has a large molecular weight and high thermal stability it dissolves readily in methylene chloride and chloroform and it is moderately soluble in toluene. The number and relative intensities of the $\nu(CO)$ vibrations are consistent with a *cis*- $R_2M(CO)_4$ species.⁸ The values of the chemical shift of the methyl resonance (τ 7.28) and the $C\equiv O$ stretching frequency (1525 cm^{-1}) reported here are lower than the corresponding values observed for $Al(acac)_3$, τ 8.00^{9,10} and 1589¹¹ cm^{-1} , and are closer to those values

observed in $Al(3\text{-bromo-acac})_3$, τ 7.69¹⁰ and 1560¹² cm^{-1} . This similarity is consistent with the expectation of the strong σ -electron withdrawing nature of an $Mn(CO)_4$ group. The influence of the metal group on the ligand π -electron system must await more detailed studies such as introducing a paramagnetic ion in place of the aluminum ion.

Extensive research effort is being applied to extend the preparation of "metallo-acac" complexes using various acyl, carboalkoxy, and carbamyl complexes and diverse organolithium reagents. Substitution of the central coordinating ion and the possible catalytic activity of these complexes are being investigated, also.

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Supplementary Material Available. A listing of data, structure factor amplitudes, refinement procedures, least-squares planes, interatomic bond distances and angles, and positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6903.

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Synthesis, Structure, and Bonding of a Mono(organo)phosphido-Bridged Tetracobalt Carbonyl Cluster, $Co_4(CO)_8(\mu_2-CO)_2(\mu_4-PC_6H_5)_2$, A New Mode of Transition Metal Coordination for a PR Ligand¹

Sir:

We wish to report the isolation and stereochemical characterization of $Co_4(CO)_8(\mu_2-CO)_2(\mu_4-PC_6H_5)_2$ which is unprecedented in its possessing a pentacoordinate phosphorus atom bonded to four transition metal atoms. The structural results are also of interest in relation with other chalcogenido- and phosphido-bridged metal clusters in providing bond-length evidence for the existence of attractive interligand P...P interactions which appear to be considerably stronger than the corresponding interligand S...S interactions. This work was a direct result of our involvement in