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Contribution from the Department of Chemistry,
 Vanderbilt University, Nashville, Tennessee 37235

Reactions of Coordinated Molecules. 6. Preparation of Tris-Chelate Complexes Containing Metallo- β -diketonate Ligands

C. M. LUKEHART,* G. PAULL TORRENCE, and JANE V. ZEILE

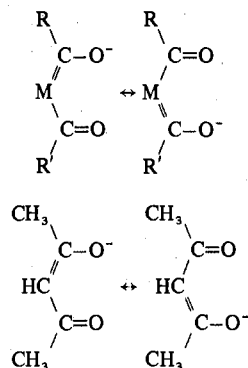
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The nucleophilic addition of a lithium reagent, $R'Li$, to a carbon monoxide ligand of an acyl complex, $RC(O)M(CO)_5$, where M is manganese or rhenium affords a *cis*-diacylmetalate anion, *cis*-(RCO)($R'CO$) $M(CO)_4^-$. These anions are metallo analogues of the enolate anions of 1,3-diketones. This similarity is demonstrated by the coordination of these anions to the central metal ions Al(III) and Ga(III) forming neutral tris-chelate complexes. The preparation of ten such complexes which contain metallo analogues of acetylacetonate, propionylacetonate, isobutyrylacetonate, phenylacetylacetonate, dimethylcarbamylacetonate, valerylacetonate, carboethoxyacetonate, and valerylisobutyrylmethanide as ligands is reported. The solution infrared spectra of these complexes are discussed and the solution proton magnetic resonance spectra indicate *cis*-*trans* isomerization for several of the complexes containing unsymmetrical metallo- β -diketonate ligands.

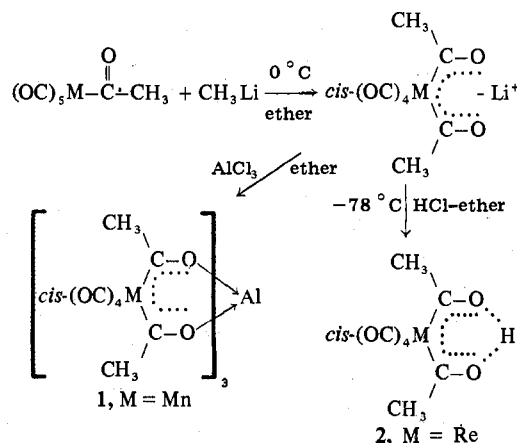
Introduction

During the last 7 years there have been three reports of the preparation of diacylmetalate anions of the type *cis*- $[[RC(O)][R'C(O)]M]^{2-}$, where M is a transition metal atom having ancillary ligands and R and R' are alkyl or aryl groups.¹⁻³ We realized that these anions are isoelectronic with the acetylacetonate anion (where R and R' are methyl), and we initiated an investigation of a possible similarity in reaction chemistry.



Recently we reported such a similarity in both the coordination chemistry⁴ and the acid-base behavior⁵ of the "metalloacetylacetonate" anion to that of the acetylacetonate anion as shown below.

The x-ray crystallographic structure of the tris-chelate complex **1** and of the protonated anion **2** revealed that the "metalloacetylacetonate" anion coordinates to aluminum as a bidentate chelate affording a complex which is essentially isostructural to $Al(acac)_3$ and that the conjugate acid of the "metalloacetylacetonate" anion exists in the solid state as the symmetrical enol tautomer as found for tetraacetyethane.⁶



We wish to report now the synthesis and characterization of several tris-chelate coordination complexes containing solely "metallo- β -diketonate" molecules as ligands. These complexes are formally derivatives of complex **1** where M is Mn or Re, the central metal ion is Al(III) or Ga(III), and either one or both of the methyl substituents are replaced by other groups.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C. Diethyl ether and tetrahydrofuran were dried over Na/K alloy under a nitrogen atmosphere. Other solvents were dried over 4 Å molecular sieves and were purged with nitrogen before use. Manganese and rhenium carbonyl dimers were purchased from Pressure Chemical Co. (Pittsburgh, Pa.). Anhydrous gallium trichloride was purchased from Ventron Corp. and was handled under a nitrogen atmosphere in a glovebag.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as cyclohexane solutions in 0.10-mm sodium chloride cavity cells using

the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1} . Proton NMR spectra were obtained on a Joel MH-100 NMR spectrometer using TMS as an internal reference.

Microanalysis was performed by Galbraith Laboratories, Inc. (Knoxville, Tenn.).

$\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$,⁷ $\text{CH}_3\text{C}(\text{O})\text{Re}(\text{CO})_5$,⁸ $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_5$,⁹ $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{Mn}(\text{CO})_5$,¹⁰ $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_5$,⁹ and $(\text{CH}_3)_2\text{CHC}(\text{O})\text{Mn}(\text{CO})_5$ ⁹ were prepared by slight modifications of known procedures using the corresponding pentacarbonylmetalate anion and the appropriate acyl chloride or acid anhydride.

Preparation of Isobutyrylpentacarbonylrhenium. To a stirred solution of 2.14 g (6.13 mmol) of $\text{Na}[\text{Re}(\text{CO})_5]$ in 25 ml of tetrahydrofuran at -78°C was added dropwise 0.64 ml (6.13 mmol) of isobutyryl chloride over a 5-min period. After being stirred at -78°C for 2 h, the reaction solution was allowed to warm to 25°C . The solvent was then removed at reduced pressure affording a bright yellow residue. Extracting the residue with hexane and cooling the extractant to -20°C for 20 h yielded 1.47 g (61%) of the product as bright yellow crystals: mp $65\text{--}67^\circ\text{C}$; ir $\nu(\text{CO})$ 2130 (m), 2050 (m), 2020 (vs), 1990 (s), $\nu(\text{acyl})$ 1620 (m) cm^{-1} ; $^1\text{H NMR}$ (CS_2) τ 9.22 (doublet, 6, 2 CH_3), 7.33 (quintet, 1, methine H). Anal. Calcd for $\text{C}_9\text{H}_7\text{O}_6\text{Re}$: C, 27.21; H, 1.78. Found: C, 27.11; H, 1.80.

General Preparation of the Tris(metallo- β -diketonate) Complexes. To a stirred solution or suspension of 0.3–0.9 g of the acylpentacarbonyl metal complex in 10 ml of solvent (ether or tetrahydrofuran) which was cooled to 0 or -78°C was added 1 molar equiv of the lithium reagent as an ether or tetrahydrofuran solution. The reaction solution changed gradually to a yellow color and any undissolved acyl complex disappeared. The solution was stirred for an additional 20 min and then a solution of either anhydrous aluminum chloride or gallium chloride ($1/3$ molar equiv) in ether or tetrahydrofuran was added dropwise over a 5-min period. The reaction solution was stirred for an additional 2 h at 0°C during which time a white solid precipitated. The solvent was removed under reduced pressure, and the pale yellow residue was extracted with hexane. The manganese compounds were extracted first with methylene chloride followed by the hexane extraction. The hexane extractant was filtered and cooled to either -20 to -78°C for several hours affording the product complexes as white or very pale yellow solids.

Preparation of $\{cis\text{-(OC)}_4\text{Mn}(\text{CH}_3\text{CO})(\text{CH}_3\text{CH}_2\text{CO})\}_3\text{Al}$, 5. To a mixture of 0.41 g (1.6 mmol) of propionylpentacarbonylmanganese in 25 ml of ether was added 0.85 ml (1.7 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.08 g (0.6 mmol) of AlCl_3 affording after crystallization from hexane 0.09 g (21%) of the product as a pale yellow solid: dec pt $95\text{--}200^\circ\text{C}$ (deep brown); ir $\nu(\text{CO})$ 2065 (m), 1985 (s, sh), 1978 (vs), 1960 (s), $\nu(\text{C}\equiv\text{O})$ 1525 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4) τ 9.06 (doublet of triplets, 3, CH_2CH_3), 7.19 (four singlets, 3, CH_3), 6.64 (complex multiplet, 2, CH_2). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_{18}\text{Mn}_3\text{Al}$: C, 39.15; H, 2.92; Al, 3.26. Found: C, 39.43; H, 3.14; Al, 2.92.

Preparation of $\{cis\text{-(OC)}_4\text{Mn}(\text{CH}_3\text{CO})(\text{C}_6\text{H}_5\text{CH}_2\text{CO})\}_3\text{Al}$, 6. To a mixture of 0.86 g (2.7 mmol) of phenacetylpentacarbonylmanganese in 25 ml of ether was added 1.5 ml (3.1 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.14 g (1.1 mmol) of AlCl_3 affording 0.20 g (22%) of the product as a white powder: dec pt $128\text{--}131^\circ\text{C}$; ir $\nu(\text{CO})$ 2065 (m), 1985 (s, sh), 1978 (vs), 1960 (s), $\nu(\text{C}\equiv\text{O})$ 1525 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4) τ 7.37–7.19 (four singlets, 3, CH_3), 5.76 (complex multiplet, 2, CH_2), 2.94 (complex multiplet, 5, C_6H_5). Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{O}_{18}\text{Mn}_3\text{Al}$: C, 49.72; H, 2.98; Al, 2.66. Found: C, 49.36; H, 3.05; Al, 2.50.

Preparation of $\{cis\text{-(OC)}_4\text{Mn}(\text{CH}_3\text{CO})[(\text{CH}_3)_2\text{CHCO}]\}_3\text{Al}$, 7. To a mixture of 0.34 g (1.3 mmol) of isobutyrylpentacarbonylmanganese in 25 ml of ether was added 0.65 ml (1.3 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.07 g (0.5 mmol) of AlCl_3 affording 0.13 g (34%) of product as pale yellow crystals: dec pt $90\text{--}125^\circ\text{C}$; ir $\nu(\text{CO})$ 2065 (m), 1985 (s, sh), 1978 (vs), 1960 (s), $\nu(\text{C}\equiv\text{O})$ 1525 (s) cm^{-1} ; $^1\text{H NMR}$ (CCl_4) τ 9.06 (complex multiplet, 6, 2 CH_3), 7.15 (two singlets, 3, CH_3), 6.28 (complex multiplet, 1, methine proton). Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_{18}\text{Mn}_3\text{Al}$: C, 41.39; H, 3.45; Al, 3.10. Found: C, 41.09; H, 3.49; Al, 2.99.

Preparation of $\{cis\text{-(OC)}_4\text{Mn}(\text{CH}_3\text{CO})[(\text{CH}_3)_2\text{NCO}]\}_3\text{Al}$, 8. To a solution of 1.0 g (4.2 mmol) of acetylpentacarbonylmanganese in 45 ml of tetrahydrofuran at -78°C was added 4.2 mmol of lithium

dimethylamide (prepared from dimethylamine and *n*-butyllithium) in 7 ml of tetrahydrofuran over 1 h. The reaction solution was stirred for an additional 1.5 h, and then 0.19 g (1.4 mmol) of AlCl_3 in 2 ml of tetrahydrofuran was added dropwise over a 5-min period. After being stirred at 0°C for 1 h, the solvent was removed under reduced pressure. The reaction residue was extracted with methylene chloride and the product was crystallized from hexane affording 0.18 g (15%) of a white solid: dec pt ca. 120°C , black at 240°C ; ir $\nu(\text{CO})$ 2075 (m), 1985 (s), 1965 (vs), 1945 (s), $\nu(\text{C}\equiv\text{O})$ 1525 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) τ 7.25 (singlet, 3, CCH_3), 6.77 (singlet, 6, amine CH_3). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_{18}\text{N}_3\text{Mn}_3\text{Al}$: C, 37.13; H, 3.12; N, 4.81; Mn, 18.87; Al, 3.09; O, 32.98. Found: C, 37.48; H, 3.05; N, 4.66; Mn, 18.45; Al, 3.19; O (by difference), 33.17.

Preparation of $\{cis\text{-(OC)}_4\text{Re}(\text{CH}_3\text{CO})_2\}_3\text{Al}$, 12. To a solution of 0.5 g (1.3 mmol) of acetylpentacarbonylrhenium in 10 ml of ether was added 0.66 ml (1.3 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.06 g (0.4 mmol) of AlCl_3 affording 0.29 g (55%) of colorless needles: dec pt $198\text{--}199^\circ\text{C}$; ir $\nu(\text{CO})$ 2050 (s), 1990 (s, sh), 1970 (vs), 1955 (s), $\nu(\text{C}\equiv\text{O})$ 1525 cm^{-1} ; $^1\text{H NMR}$ (CS_2) τ 7.31 (singlet, CH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_{18}\text{Re}_3\text{Al}$: C, 24.43; H, 1.54; Al, 2.29. Found: C, 24.52; H, 1.45; Al, 1.97.

Preparation of $\{cis\text{-(OC)}_4\text{Re}(\text{CH}_3\text{CO})_2\}_3\text{Ga}$, 13. To a solution of 0.5 g (1.3 mmol) of acetylpentacarbonylrhenium in 10 ml of ether was added 0.66 ml (1.3 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.07 g (0.4 mmol) of GaCl_3 affording 0.12 g (24%) of the product as colorless needles: mp $64\text{--}72^\circ\text{C}$; ir $\nu(\text{CO})$ 2090 (m), 2000 (s, sh), 1990 (vs), 1958 (s), $\nu(\text{C}\equiv\text{O})$ 1519 (m) cm^{-1} ; $^1\text{H NMR}$ (CS_2) τ 7.21 (singlet, CH_3). Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_{18}\text{Re}_3\text{Ga}$: C, 23.58; H, 1.48. Found: C, 23.75; H, 1.60. Gallium could not be analyzed in the presence of rhenium.

Preparation of $\{cis\text{-(OC)}_4\text{Re}(\text{CH}_3\text{CO})[(\text{CH}_3)_2\text{CHCO}]\}_3\text{Ga}$, 14. To a solution of 0.5 g (1.2 mmol) of isobutyrylpentacarbonylrhenium in 10 ml of ether was added 0.60 ml (1.2 mmol) of methylolithium solution (2.06 M) followed by the addition of an ether solution of 0.07 (0.4 mmol) of GaCl_3 affording 0.10 g (18%) of the product as colorless needles: mp $38\text{--}40^\circ\text{C}$; ir $\nu(\text{CO})$ 2080 (m), 1980 (s, sh), 1960 (vs), 1958 (s), $\nu(\text{C}\equiv\text{O})$ 1518 cm^{-1} ; $^1\text{H NMR}$ (CS_2) τ 8.98 (doublet, 6, $\text{CH}(\text{CH}_3)_2$, $J_{\text{H-H}} = 7.2$ Hz), 7.17 (singlet, 3, CH_3), 6.71 (quintet, 1, methine H, $J_{\text{H-H}} = 7.2$ Hz). Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_{18}\text{Re}_3\text{Ga}$: C, 27.57; H, 2.31. Found: C, 26.96; H, 2.33. Gallium could not be analyzed in the presence of rhenium.

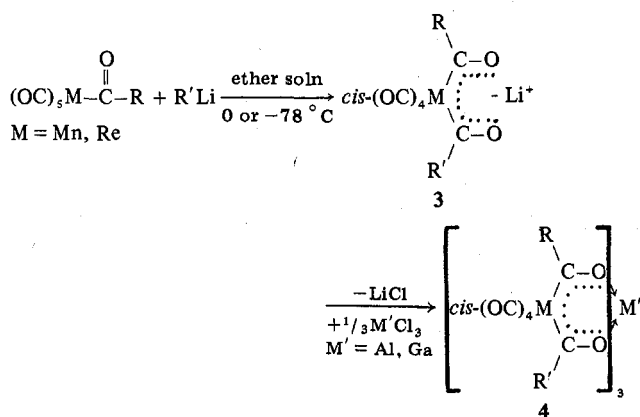
Preparation of Other Tris(metallo- β -diketonate) Complexes. The complexes tris(*cis*-acetylvaleryl)tetra-carbonylmanganate)aluminum, 9, and tris(*cis*-isobutyrylvaleryl)tetra-carbonylmanganate)aluminum, 10, which were prepared from *n*-butyllithium, the corresponding acylpentacarbonylmanganese complex, and tris(*cis*-carboethoxyacetyl)tetra-carbonylmanganate)aluminum, 11, which was prepared from methylolithium and carboethoxypentacarbonylmanganese, were formed in low yield and could not be isolated pure in amounts of more than 2 or 3 mg. These complexes were characterized only by their solution infrared spectra which exhibit the $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{O})$ bands characteristic of the tris(metallo- β -diketonate) complexes.

Results and Discussion

The general preparative procedure for the formation of the tris(metallo- β -diketonate) complexes is shown in Scheme I. The first step of the synthesis is the addition of a lithium reagent to a carbon monoxide ligand of an acyl complex having octahedral coordination geometry. Previous kinetic data^{3,11} and synthetic results^{2,3,12} indicate that nucleophilic addition to a carbon monoxide ligand of a monosubstituted hexacoordinate metal carbonyl complex will occur preferentially at a carbon monoxide ligand which is *cis* to the noncarbonyl ligand. Thus, the *cis*-diacyltetra-carbonylmetalate complex, 3, is formed. These anions are thermally stable in ether solution at 0°C , and they are isoelectronic to β -diketonate anions where the methine group is replaced formally by a $\text{M}(\text{CO})_4$ group.

The metallo- β -diketonate anions, 3, coordinate readily to either aluminum or gallium when treated with an ether solution of the appropriate anhydrous metal chloride affording the tris-chelate complexes, 4. These complexes are air stable in the solid state for at least several hours at 25°C . Complexes

Scheme I



M	R	R'	M'	Compd (from 4)
Mn	CH ₃	CH ₃	Al	1
Mn	CH ₃ CH ₂	CH ₃	Al	5
Mn	C ₆ H ₅ CH ₂	CH ₃	Al	6
Mn	(CH ₃) ₂ CH	CH ₃	Al	7
Mn	CH ₃	(CH ₃) ₂ N	Al	8
Mn	CH ₃	CH ₃ (CH ₂) ₃	Al	9
Mn	(CH ₃) ₂ CH	CH ₃ (CH ₂) ₃	Al	10
Mn	CH ₃ CH ₂ O	CH ₃	Al	11
Re	CH ₃	CH ₃	Al	12
Re	CH ₃	CH ₃	Ga	13
Re	(CH ₃) ₂ CH	CH ₃	Ga	14

9-11 were formed in low yield and were very difficult to purify although the solution infrared spectrum indicated their formation. Complex 11 was obtained as a white solid in very small amounts while compounds 9 and 10 did not crystallize. The aluminum complexes exhibited good thermal stability having decomposition points ranging from 90 to 240 °C. The gallium complexes were slightly less stable thermally and decomposed or melted in air at 38 and 72 °C. The versatility of this synthetic procedure is being explored further utilizing a variety of acyl complexes, nucleophilic reagents, and central coordinating ions to determine how closely the metallo-β-diketonate ligands parallel the coordination chemistry of the nonmetallo analogues. Of particular interest is the coordination chemistry of these metallo ligands when the central metal ion has other types of ancillary ligands.

The Infrared Spectra. The solution infrared spectra of the metallo-β-diketonate tris-chelate complexes are very similar and exhibit a characteristic pattern of $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{O})$ bands. In fact, complexes 1, 5-7, 9, and 10 have superimposable bands in the region 2100-1500 cm^{-1} . Figure 1 is the infrared spectrum of compound 1 in cyclohexane solution for this region.

This spectrum shows that each $\text{M}(\text{CO})_4$ group is independent of the other two identical groups in the same molecule since no dipolar coupling is observed between the carbon monoxide ligands of different $\text{M}(\text{CO})_4$ groups. The local oscillator approximation applies and each $\text{M}(\text{CO})_4$ group can be treated as a cis-disubstituted metal tetracarbonyl complex possessing C_{2v} symmetry. The lower local symmetry, C_s , for the compounds 5-7, 9, and 10 does not noticeably alter the observed pattern of the infrared bands. The qualitative work of Orgel¹⁵ and the quantitative study of Cotton¹⁴ facilitate the assignment of the $\nu(\text{CO})$ stretching vibrations of these complexes.

The $\text{cis-L}_2\text{M}(\text{CO})_4$ spectrum is characterized by four infrared-active carbonyl stretching modes. The two axial carbonyl ligands, which lie out of the L_2M plane, give rise to two bands (A_1 and B_1 symmetry) where the A_1 band is of higher frequency and of much weaker intensity than the B_1 band. The two equatorial carbonyl ligands, which lie in the

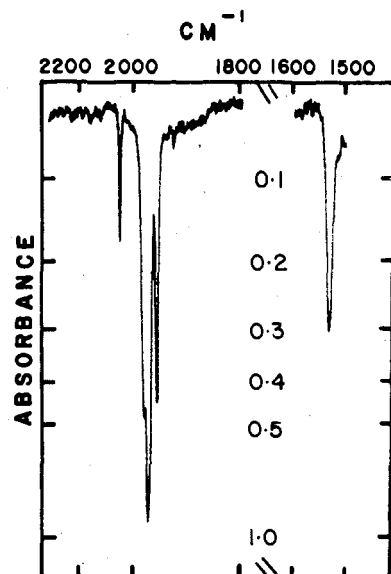


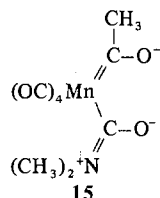
Figure 1. Partial infrared spectrum of $\text{cis-}[(\text{OC})_4\text{Mn}(\text{CH}_3\text{CO})_2]_3\text{-Al}$ as a cyclohexane solution.

L_2M plane, give rise also to two bands (A_1 and B_2 symmetry) where the peaks are of nearly equal intensity. However, the relative positions of these two sets of vibrations cannot be predicted from symmetry considerations alone. The above spectrum, Figure 1, then, is assigned as follows (cm^{-1}): 2065 (A_1 , axial), 1985 (A_1 , equatorial), 1978 (B_1 , axial), 1960 (B_2 , equatorial). This assignment is consistent with that of the manganese carbonyl chloride dimer, $[\text{Mn}(\text{CO})_4\text{Cl}]_2$, if, with the present complex, the two bands derived from the equatorial set of carbonyl ligands fall on opposite sides of the B_1 mode of the axial carbonyl set.

The band at 1525 cm^{-1} is assigned to the $\text{C}\equiv\text{O}$ stretching vibration of the acyl groups which are coordinated to the aluminum ion. This band occurs at 1589 cm^{-1} in $\text{Al}(\text{acac})_3$ ¹⁵ and at 1560 cm^{-1} in $\text{Al}(\text{3-Br-acac})_3$ ¹⁶ which suggests that as the electron deficiency of the methine carbon atom increases the value of the $\text{C}\equiv\text{O}$ stretching frequency decreases. The value of 1525 cm^{-1} of the metallo-β-diketonate complexes is consistent with the expectation that the $\text{Mn}(\text{CO})_4$ group is strongly electron withdrawing. The frequency of this band is characteristic also of the formation of a metallo-β-diketonate complex since its value is nearly independent of the substituents R and R'.

The acyl bands of the Re-Ga complexes 13 and 14 occur at 6-7 cm^{-1} lower frequency than that observed for the Mn-Al complexes and the Re-Al complex 12. This effect may indicate that the rhenium metallo-β-diketonate ligand will coordinate more strongly to the larger gallium ion. The structural studies of compounds 1 and 2 show that the Re-C(CH₃) bond distance is 0.34 Å longer than the corresponding Mn-C(CH₃) bond distance. However, such an interpretation may not be warranted since the $\text{C}\equiv\text{O}$ oscillator will be coupled to the $\text{M}\equiv\text{C}$ and $\nu(\text{CO})$ stretching modes to some extent.

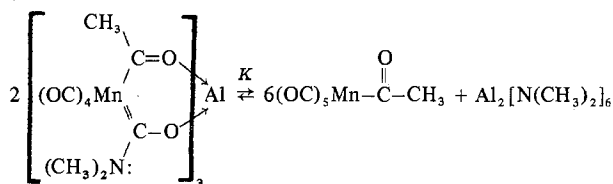
The dimethylcarbonyl complex, 8, exhibits the same $\nu(\text{CO})$ pattern of bands although the infrared frequencies are slightly different from those typical of the dialkyl-substituted metallo-β-diketonate complexes as shown in Figure 1. For this complex the higher frequency A_1 mode is 10 cm^{-1} higher than usual (2075 cm^{-1}) while the other modes (A_1 , B_1 , B_2) are much more separated in frequency since the B_1 and B_2 modes appear 15 cm^{-1} lower than usual. This frequency lowering may be attributed to a contribution to the ground electronic state by resonance structure, 15, through which more electron



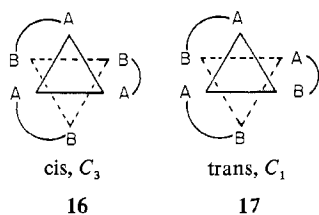
density is introduced into the ligand π -electron system.

After several minutes at 25 °C, the solution infrared and proton NMR spectra of complex **8** indicate detectable decomposition to acetylpentacarbonylmanganese and to some other methyl-containing compound which has proton NMR singlets at τ 7.22 and 7.15 in CDCl_3 solution. Although no further detailed studies of this decomposition were performed, it appears that the reaction reached equilibrium within 30 min and that the amount of decomposition product produced varies with the solvent polarity. More decomposition occurred in chloroform solution than in carbon disulfide.

One explanation is that the dimethylamino group is transferred formally to the Al(III) ion as an anion forming $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$ and an aluminum-amine complex such as $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$. In fact, the proton NMR spectrum of tris(dimethylamino)alane has two singlets of 2:1 relative intensity at τ 7.23 and 7.51 in benzene solution.¹⁷ This suggests the intriguing possibility that metallo- β -diketonate complexes of aluminum could be prepared directly from the organometallic acyl complex and an organoaluminum compound which would act as the alkylating agent, also.



The Proton NMR Spectra. Of the complexes isolated in pure form, compounds **5–8** and **14** should exhibit geometrical and optical isomerization in solution. The two geometrical isomers of unsymmetrical tris-chelate complexes are shown by **16** and **17**. The cis to trans isomerization is observed



usually in the solution proton NMR spectrum, and the characterization of this isomerization as well as the elucidation of the very complex mechanisms enabling the isomerization has been studied extensively. A review of this work has appeared recently.¹⁸

In further support of the similarity of these new compounds to β -diketonate complexes, we wish to establish that such isomerization exists also in several of the tris(metallo- β -diketonate) complexes containing unsymmetrical ligands. The proton NMR spectra of compounds **5–7** in CCl_4 solution at +36 °C are shown in Figure 2. The aromatic resonance of complex **6** is not shown since the methyl groups are the most convenient probes of the isomerization. The methyl resonances of each compound are shown in expanded form as inserts. Our qualitative interpretation of these spectra, which is based upon comparison with published spectra, follows.

(1) Complex **7**, spectrum A, exhibits two methyl resonances of intensity ratio ca. 2:1 and the prochiral methyl groups of

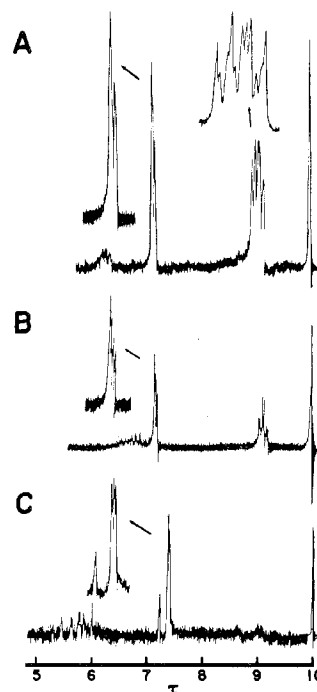


Figure 2. Proton NMR spectra of $\{cis-(\text{OC})_4\text{Mn}(\text{CH}_3\text{CO})[(\text{CH}_3)_2\text{NCHCO}]\}_3\text{Al}$ (A), $\{cis-(\text{OC})_4\text{Mn}(\text{CH}_3\text{CO})(\text{CH}_3\text{CH}_2\text{CO})\}_3\text{Al}$ (B), and $\{cis-(\text{OC})_4\text{Mn}(\text{CH}_3\text{CO})(\text{C}_6\text{H}_5\text{CH}_2\text{CO})\}_3\text{Al}$ (C) in CCl_4 solution at +36 °C recorded at 1080-Hz sweep width. The resonances of the methyl and isopropyl substituents are shown as inserts in expanded scale recorded at 540 and 270 Hz, respectively. The phenyl resonance is not shown in spectrum C.

the isopropyl substituent¹⁹ give an 11-line pattern. These results are consistent with the presence of the trans isomer predominantly. Two of the expected three resonances for the single methyl substituent have accidental degeneracy as is found also for the complex $\text{Co}(\text{mhd})_3$.²⁰ The six nonequivalent methyl groups of the isopropyl substituent should show a 12-line pattern due to coupling to the methine proton. An 11-line pattern is observed and is qualitatively quite similar to the 13-line pattern observed for the isopropyl resonance of $\text{Al}(\text{pmhd})_3$ which contains a small amount of the cis isomer.²¹ Although the presence of a small amount of the cis isomer cannot be excluded for complex **7**, there is no direct evidence suggesting its presence.

(2) Complex **5**, spectrum B, exhibits four distinct singlets for the methyl substituent resonance and a complex splitting pattern for the resonance of the methyl group of the ethyl substituent. The four resonances of the methyl substituent consist of three nearly equally separated singlets with a fourth singlet lying between the two singlets at low field and closer to the lowest field singlet. This pattern is similar to that of the methyl resonance of $\text{Al}(\text{bzac})_3$ where both cis and trans isomers are present.²² The cis isomer should possess only a singlet for the methyl substituent resonance. This fourth singlet is assigned arbitrarily to the cis isomer, and assuming this assignment, the cis isomer is present in a low relative concentration.

(3) Complex **6**, spectrum C, exhibits four singlet resonances for the methyl substituent. Three of these singlets form a pattern similar to that assigned to the trans isomer of the complexes **5**, $\text{Al}(\text{bzac})_3$,²² and $\text{Co}(\text{bzac})_3$.²³ The less intense singlet at 0.18 ppm lower field than any of the other three resonances is present in all samples and is assigned tentatively to the cis isomer. Although the methyl resonance of the cis isomer usually falls between the methyl resonances of the trans isomer, the methyl resonance of the cis isomer of $\text{Co}(\text{bzac})_3$ ²³ lies 0.05 ppm to higher field than any of the methyl singlets

due to the trans isomer. Perhaps the magnetic influence of the benzyl substituent is sufficiently different from that of a phenyl substituent in the cis isomer to account for the opposite pattern observed for the cis and trans methyl resonances of the complexes **6** and $\text{Co}(\text{bzac})_3$. If this assignment is correct, 18.5% of complex **6** is present as the cis isomer at +36 °C at equilibrium.

The prochiral methylene groups of complexes **5** and **6** should contain additional information regarding the geometrical isomerization of these compounds. Unfortunately, the low solubility of these complexes prevents a detailed analysis of these highly split resonances.

The partial solution decomposition of complex **8** prevents any estimate as to geometrical isomerization. Complex **14** exhibits only one singlet for the resonance of the methyl substituent and a single doublet for the resonance of the methyl groups of the isopropyl substituent. This pattern is unexpected and seems to suggest that only the cis isomer is present. A more reasonable explanation is that since the Mn-Al complexes apparently reach cis-trans equilibration rapidly after dissolution at 25 °C, the Re-Ga complex, **14**, may be undergoing such rapid cis-trans isomerization at +36 °C that only the higher symmetry structure of the cis isomer is observed as a time-averaged spectrum. This may be quite probable since $\text{Ga}(\text{pmhd})_3$ undergoes cis-trans isomerization ca. 80 000 times faster than $\text{Al}(\text{pmhd})_3$,¹⁸ and this isomerization is fast on the proton NMR time scale at only +85 °C affording only a single doublet for the methyl groups of the isopropyl substituents.²¹ At present, we have no quantitative information regarding the lability of the metallo- β -diketonate ligand, although, if this explanation is correct, these metallo β -diketonate ligands should be slightly more labile than the nonmetallo β -diketonate ligands.

The interpretation of complex **7** existing in solution as predominantly the trans isomer and complexes **5** and **6** exhibiting some cis isomer is consistent with the larger steric bulk of an isopropyl group compared to either an ethyl or a benzyl group. Apparently the effect of the size of the ring substituents in nonmetallo tris(β -diketonate) complexes is not significant and cis-trans mixtures of nearly statistical proportions are observed.²⁴

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Registry No. **1**, 58034-11-0; **5**, 59839-89-3; *cis*-**6**, 59839-96-2; *trans*-**6**, 59839-85-9; **7**, 59839-92-8; **8**, 59839-91-7; **9**, 59839-94-0; **10**, 59839-95-1; **11**, 59839-90-6; **12**, 59839-87-1; **13**, 59839-88-2; **14**, 59839-93-9; isobutyrylpentacarbonylrhenium, 59831-00-4; propionylpentacarbonylmanganese, 15022-56-7; phenacetyl-pentacarbonylmanganese, 15022-57-8; isobutyrylpentacarbonylmanganese, 15022-36-3; acetyl-pentacarbonylmanganese, 13963-91-2; acetyl-pentacarbonylrhenium, 23319-44-0; carboethoxypentacarbonylmanganese, 28300-66-5.

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Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Electrophilic and Oxidative Addition Reactions of Tungsten Thiocarbonyl Complexes

B. DUANE DOMBEK and ROBERT J. ANGELICI*

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Electrophilic reagents react with tungsten(0) thiocarbonyl complexes to yield products which result from either oxidative addition to the metal atom or electrophilic addition to the thiocarbonyl sulfur atom. Thus, $\text{W}(\text{CO})_5(\text{CS})$ reacts with Br_2 and PPh_3 to yield $\text{W}(\text{CO})_2(\text{CS})(\text{PPh}_3)_2\text{Br}_2$, but it does not undergo Lewis acid adduct formation at the thiocarbonyl sulfur. Proton addition to the metal atom in $\text{W}(\text{CO})(\text{CS})(\text{diphos})_2$ [diphos = ethylenebis(diphenylphosphine)] is observed with $\text{CF}_3\text{SO}_3\text{H}$, to afford $[\text{HW}(\text{CO})(\text{CS})(\text{diphos})_2]\text{CF}_3\text{SO}_3$. However, $[(\text{diphos})_2(\text{CO})\text{W}(\text{CS})\text{HgX}_2]$, $[(\text{diphos})_2(\text{CO})\text{W}(\text{CS})\text{Ag}]\text{BF}_4$, $[(\text{diphos})_2(\text{CO})\text{W}(\text{CS})\text{W}(\text{CO})_5]$, $[(\text{diphos})_2(\text{CO})\text{W}(\text{CSC}_2\text{H}_5)]\text{BF}_4$ result from reactions of Lewis acids (HgX_2 , AgBF_4 , $\text{W}(\text{CO})_5(\text{CH}_3\text{COCH}_3)$, $\text{CH}_3\text{OSO}_2\text{F}$, or $[(\text{C}_2\text{H}_5)_3\text{O}]\text{BF}_4$, respectively) at the thiocarbonyl sulfur atom. Sulfur dioxide is absorbed reversibly by $\text{W}(\text{CO})(\text{CS})(\text{diphos})_2$, and ir evidence suggests that this Lewis acid also coordinates to the thiocarbonyl sulfur atom. The $\text{Bu}_4\text{N}[\text{W}(\text{CO})_4(\text{CS})(\text{I})]$ complex is alkylated at sulfur by $\text{CH}_3\text{OSO}_2\text{F}$ and $[(\text{C}_2\text{H}_5)_3\text{O}]\text{BF}_4$, to afford $\text{W}(\text{CO})_4(\text{I})(\text{CSR})$ products, and is acylated by carboxylic acid anhydrides to give $\text{W}(\text{CO})_4(\text{I})(\text{CSC}(\text{O})\text{R})$ complexes. These reactions of thiocarbonyl complexes are contrasted with those of carbonyl analogues, which give different types of products with many of these reagents.

Introduction

The formal similarity of carbon monosulfide (CS) to CO has stimulated much recent interest in the reactivity of the CS ligand in its metal complexes.¹⁻⁶ Certain electron-rich

metal carbonyl complexes have shown the capability of forming Lewis acid adducts at the oxygen atom of a terminal carbonyl ligand.⁷⁻¹³ It was therefore expected that thiocarbonyl complexes might form sulfur-bound adducts with Lewis acids