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Reactions of Coordinated Molecules.
XIV. The Substitution Chemistry of the Metallo-Acetylacetonate Complex [*cis*-$(OC)_4Mn(CH_3CO)_2]_3Al$

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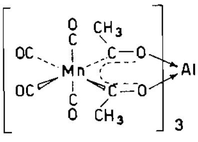
The attempted direct substitution of one carbonyl ligand on each manganese atom of the metallo-acetylacetonate complex [cis-$(OC)_4Mn(CH_3CO)_2]_3$-*Al, by triphenylphosphine, o-phenanthroline, dipyridyl or methyl isocyanide using thermal or photolytic activation led to the degradation of the complex. However, when the substituted acetyl complexes,* cis-$CH_3C(O)Mn(CO)_4(RNC)$*, where R is methyl, cyclohexyl or t-butyl, are prepared and treated with one molar equivalent of methyllithium, the resulting substituted metallo-acetylacetonate anions form neutral,* tris-*chelate complexes with Al(III).*

Introduction

We recently prepared the first example of a complex containing a metallo-β-diketonate ligand, **1**. This complex is essentially isostructural with Al-$(acac)_3$, where the methine groups of the acetylacetonate ligands are replaced formally by the $Mn(CO)_4$ moiety [1]. Several derivatives of this type of complex which contain various chelate-ring substituents with aluminum or gallium as the central coordinating ion, and the $Re(CO)_4$ and η^5-cyclopentadienyl iron carbonyl groups as the metallo moiety have been prepared [2, 3]. In this paper we report the substitution chemistry of complex **1**. This work was undertaken to provide more examples of metallo incorporation into β-diketones and to determine the effect of axial carbonyl substitution on the stability of the aluminum complexes. Such a substitution is expected to alter the degree of intramolecular pi-bonding between the axial carbonyl ligands and the pi-electron system of the metallo-β-diketonate ligand [4].



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Experimental

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C unless otherwise stated. Solvents were distilled from Na/K alloy (P_2O_5 for methylene chloride) before use. Complex **1** [1], $CH_3Mn(CO)_5$ [5], CH_3NC [6] and $(CH_3)_3CNC$ [7] were prepared by literature procedures. All other reagents were purchased.

Infrared spectra were recorded on a Perkin–Elmer 727 spectrometer 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 Jeol MH-100 spectrometer using TMS as an internal reference. Mass spectra were recorded on a LKB 9000 spectrometer.

Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, U.S.A.

Direct Substitution Reactions of Complex 1

Complex 1 *with* Ph_3P

To a solution of 0.108 g (0.14 mmol) of **1** in 60 ml of degassed pentane was added 0.108 g (0.42 mmol) of Ph_3P. The reaction solution was irradiated for 5 hr by a Blak-Ray UV lamp model B-100A at a distance of 30 cm. During this time a yellow solid precipitated from solution and was isolated by filtration affording 0.071 g (81%) of a compound identified as [*trans*-$(Ph_3P)(OC)_4Mn]_2$ by IR, PMR and melting point [8].

Complex 1 *with o-phenanthroline*

To a solution of 0.25 g (0.31 mmol) of **1** in 40 ml of benzene was added 0.50 g (2.77 mmol) of anhydrous *o*-phenanthroline. The reaction solution became cloudy immediately. After stirring for 5 hr the solvent is removed at reduced pressure. The reac-

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tion residue was extracted with 20 ml of methylene chloride. The mixture was filtered and the solvent was removed at reduced pressure. The solid residue was dissolved in a minimum amount of benzene, and this solution was placed onto a benzene–silica gel (60–200 mesh) column (10 cm × 2.5 cm). The column was washed consecutively with 75 ml of benzene and ether, and then the product was eluted with acetone as a deep yellow band. This band was collected and the solvent was removed at reduced pressure affording 0.051 g (15%) of a yellow solid: dec. 130–145 °C; IR(CH_2Cl_2) ν(CO) 2030 (vs), 1937 (vs), 1917 (vs); PMR($CDCl_3$) τ 0.49(2), 1.57(2), 2.10(4), all complex multiplets, 7.83 (singlet, 3, CH_3); mass spec. (P m/e 362, fragments by loss of three CO ligands). Product was identified as *fac*-$(OC)_3Mn(CH_3CO)$(*o*-phen).

Preparation of the cis-*$(CH_3CO)(RNC)Mn(CO)_4$ Complexes. General Procedure*

To a stirred solution of 1.0 g (4.76 mmol) of $CH_3Mn(CO)_5$ in 50 ml of benzene (pentane was used when R is t-butyl) was added 5.24 mmol of the appropriate isocyanide. The reaction solution was stirred for 18 hr. During this time the solution turned yellow and a peak at 1645 appeared in the IR spectrum. The solvent was removed at reduced pressure and the oily residue was placed onto a 10 cm × 2.5 cm hexane–silica gel (60–200 mesh) column. The column was washed with hexane and the gold-colored product band was eluted with benzene. The solvent was removed at reduced pressure affording a clear deep golden oil of high purity. This oil was dissolved in 5 ml of pentane and was placed at −78 °C. The isolated solid was dried at reduced pressure at 25 °C at which time the product melted to a golden oil. The characterization data for each complex are given below.

cis-$(CH_3CO)(CH_3NC)Mn(CO)_4$, 2: 70%, d = 1.31 g/ml; IR (ether) ν (CN) 2225 (s), ν(CO) 2088 (m), 2010 (s, sh), 1983 (vs), 1970 (s, sh), ν(acyl) 1643(m); PMR(CS_2) τ 7.61 (singlet, 3, CH_3CO), 6.48 (singlet, 3, CH_3NC). *Anal.* Calcd. for $C_8H_6NO_5Mn$: C, 38.27; H, 2.41; N, 5.58. Found: C, 38.37; H, 2.25; N, 5.53%.

cis-$(CH_3CO)(C_6H_{11}NC)Mn(CO)_4$, 3: 68%, d = 1.27 g/ml, IR (ether) ν(CN) 2198 (s), ν(CO) 2080 (m), 2015 (s, sh), 1980 (vs), 1945 (s, sh), ν(acyl) 1645 (m); PMR(CS_2) τ 7.55 (singlet, 3, CH_3CO), 6.05 (broad multiplet, 1, CH), 8.50–8.15 (broad multiplet, 10, $5CH_2$). *Anal.* Calcd. for $C_{13}H_{13}NO_5Mn$: C, 48.91; H, 4.43; N, 4.39. Found: C, 49.91; H, 5.41; N, 4.98%.

cis-(CH_3CO)(t-butyl NC)$Mn(CO)_4$, 4: 95%, d = 1.19 g/ml; IR (ether) ν(CN) 2195 (s), ν(CO) 2070 (m), 2005 (s, sh), 1980 (vs), 1970 (s, sh), ν(acyl) 1645 (m); PMR(CS_2) τ 7.56, 7.67 (two singlets, 3, CH_3CO), 8.41, 8.47 (two singlets, 9, $3CH_3$). *Anal.* Calcd. for $C_{11}H_{12}NO_5Mn$: C, 45.06; H, 4.13; N, 4.78. Found: C, 44.97; H, 4.22; N, 4.90%.

Preparation of $(Ph_3P)_2N^+$ [cis-*$(CH_3CO)_2Mn(CO)_4$*]$^-$

A solution of 0.63 mmol of Li^+ [*cis*-$(OC)_4Mn(CH_3CO)_2$]$^-$ in ether was prepared at 0 °C by a literature method [1]. The ether was removed at reduced pressure. The lithium salt was dissolved in 20 ml of THF at 0 °C and 4.0 g (6.4 mmol) of $PPN^+BF_4^-$ was added as a solution in 25 ml of dry acetone. The reaction solution was stirred for 30 min, and then the solvent was removed at reduced pressure. The product was crystallized from methylene chloride/hexane solution (1:1) affording 0.46 g (12%) of a yellow solid: dec. 87–89 °C; IR(CH_2Cl_2) ν(CO) 2050 (m), 1945 (vs, br), 1920 (vs, sh), $\nu(C{\cdots}O)$ 1590 (m); PMR($CDCl_3$) τ 2.36 (complex multiplet, 30, $2Ph_3P$), 7.46 (singlet, 6, $2CH_3$). *Anal.* Calcd. for $C_{44}H_{36}O_6NP_2Mn$: C, 66.59; H, 4.83; N, 1.76; P, 7.80. Found: C, 65.68; H, 4.80; N, 1.64; P, 7.93%.

Preparation of $(Ph_3P)_2N^+$[fac-*$(OC)_3(CH_3NC)Mn(CH_3CO)_2$*]$^-$

To a solution of 0.59 g (2.35 mmol) of 2 in 25 ml of CH_2Cl_2 at 0 °C is added 1.27 ml (2.35 mmol) of a methyllithium solution (1.84 *M* in ether). The solution is stirred for one hr, and then 1.47 g (2.35 mmol) of $PPN^+BF_4^-$ was added as a solution in 8 ml of CH_2Cl_2. The solution was stirred at 0 °C for 2 hr. The reaction solution was concentrated to 4 ml at reduced pressure, and then was filtered. Ether was added until the filtrate became cloudy. The product crystallized from this suspension at −20 °C affording 0.64g (30%) of the salt as the mono-CH_2Cl_2 solvate as yellow crystals: mp 226–228 °C; IR(ether) ν(CN) 2190 (s), ν(CO) 1975 (vs), 1895 (vs) $\nu(C{\cdots}O)$ 1555 (m); PMR($CDCl_3$) τ 2.32 (complex multiplet, 30, $2Ph_3P$) 4.60 (singlet, 2, CH_2Cl_2), 6.46 (singlet, 3, CH_3NC), 7.80 (singlet, 3, CH_3CO). *Anal.* Calcd. for $C_{47}H_{41}O_5N_2P_2MnCl_2$: C, 62.60; H, 4.59; N, 3.11. Found: C, 59.02; H. 4.69; N, 1.93%.

Preparation of the [fac-*$(OC)_3(RNC)Mn(CH_3CO)_2$*]$_3$-*Al Complexes. General Procedure*

To a stirred solution of 0.6–0.8 g of the appropriate acetylisocyanidetetracarbonylmanganese complex in 30 ml ether at 0 °C was added dropwise one molar equivalent of methyllithium as an ether solution. After stirring for 1 hr, an ether solution containing 1/3 molar equivalent of anhydrous aluminum chloride was added over a 5-min period. The reaction solution was stirred at 0 °C for 1 hr, and then it was warmed to 25 °C during which time a white precipitate of LiCl formed. The reaction mixture was filtered immediately, and the solvent was removed from the filtrate at reduced pressure. The yellow residue was extracted with benzene, and the resulting mixture was filtered. The solvent of the filtrate was removed at reduced pressure affording a yellow residue which was washed with pentane. The product was obtained as a bright yellow powder after drying at reduced pressure. These complexes exhibited sufficient thermal instability that repeated attempts at crystallization at –20° and –78 °C were not successful. All spectroscopic data were obtained on freshly prepared material and are given below. The poor elemental analyses reflect the thermal instability of the complexes.

$[\mathrm{fac}\text{-}(OC)_3(CH_3NC)Mn(CH_3CO)_2]_3Al$, **8**

Using 0.66 g of **2** afforded 0.31 g (42%) of the complex as a yellow powder: mp 87–90 °C. IR(ether) ν(CN) 2200 (m), ν(CO) 2020 (vs), 1943 (vs), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ 1519 (m); PMR(CS_2) τ 7.44 (singlet, 18, $6CH_3CO$), 6.52 (singlet, 9, $3CH_3NC$). *Anal.* Calcd. for $C_{27}H_{27}N_3O_{15}Mn_3Al$: C, 39.39; H, 3.31; N, 5.11; Al, 3.28. Found: C, 35.37; H, 3.02; N, 41.8; Al, 1.71%.

$[\mathrm{fac}\text{-}(OC)_3(C_6H_{11}NC)Mn(CH_3CO)_2]_3Al$, **9**

Using 0.75 g of **3** afforded 0.51 g (63%) of the complex as a yellow powder: mp 23–26 °C. IR(ether) ν(CN) 2160 (m), ν(CO) 2010 (vs), 1948 (vs), 1932 (vs, sh), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ 1517 (m); PMR(CS_2) τ 7.33 (singlet, 18, $6CH_3CO$), 6.34 (broad singlet, 3, 3CH), 8.40–8.10 (broad multiplet, 30, $15CH_2$). *Anal.* Calcd. for $C_{42}H_{51}N_3O_{15}Mn_3Al$: C, 48.98; H, 5.00; N, 4.08; Al, 2.62. Found: C, 42.19; H, 5.14; N, 4.48; Al, 1.45%.

$[\mathrm{fac}\text{-}(OC)_3\text{-}t\text{-}butyl\,NC)Mn(CH_3CO)_2]_3Al$, **10**

Using 0.72 g of **4** afforded 0.40 g (52%) of the complex as a yellow powder: mp 50–51 °C; IR(ether) ν(CN) 2155 (m), ν(CO) 2010 (vs), 1945 (vs), 1928 (vs, sh), $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ 1515 (m); PMR (CS_2) τ 7.45–7.26 (4 singlets, 18, $6CH_3$), 8.61–8.54 (2 singlets, 27, 3 t-butyl). *Anal.* Calcd. for $C_{36}H_{45}N_3O_{15}Mn_3Al$: C, 45.43; H. 4.78; N, 4.42; Al, 2.84. Found: C, 39.95; H, 4.91; N, 4.51; Al, 2.24%.

Results and Discussion

The direct substitution of a carbonyl ligand of each manganese atom in complex **1** by Ph_3P, *o*-phenanthroline (*o*-phen) or dipyridyl (bipy) using thermal or photolytic activation led to the degradation of **1** as shown below (1). The fate of the remaining acetyl ligands or the aluminum ion was not determined. The product from the Ph_3P reaction exhibited only one IR band in the carbonyl region as expected for a *trans*-substituted dimer [8]. The thermal reaction of **1** with *o*-phen afforded the substituted acetyl complex as the major manganese-containing product. The IR of this complex showed the relative intensity pattern expected ("A" and split "E" modes) for a facial substitution of an octahedral complex by nonequivalent ligands, $A_2BM(CO)_3$ [9]. The IR spectrum of the analogous bipy complex in the carbonyl region was nearly superimposable with that region of the *o*-phen complex. These spectra were very similar to the reported spectra of the halide complexes, *fac*-$(OC)_3Mn(o\text{-phen})X$ [10]. The acetyl C–O stretching band was not observed due to the overlapping bands of the *o*-phen and bipy ligands.

$$\begin{tikzcd}[column sep=huge] \mathbf{1} \arrow[r, "L = Ph_3P", "h\nu"'] \arrow[d, "\Delta"', "L = o\text{-phen, bipy}"] & {[trans\text{-}(OC)_4LMn]_2} \\ {[fac\text{-}(OC)_3Mn(CH_3CO)(L)]} & \end{tikzcd} \tag{1}$$

When complex **1** is treated with methyl isocyanide in THF at 25 °C for 5 hr, the 1525 cm^{-1} band of **1** disappears completely. This band is the most diagnostic evidence for the presence of a metallo-β-diketonate complex of aluminum [1–3]. The mode of decomposition of **1** is further obscured by the observation that it apparently decomposes completely to $Mn_2(CO)_{10}$ after 18 hr of photolysis in hexane solution at 25 °C in the absence of any external ligand.

These results indicated that a better approach would be the preparation of a substituted metallo-β-diketonate anion as the initial step. This anion might then coordinate to the aluminum ion. The isocyanide ligand was chosen because of its electronic similarity to the carbonyl ligand [11]. Three acetyl-isocyanide complexes were prepared by the "CO-insertion" reaction of $CH_3Mn(CO)_5$, as shown below (2),

$$CH_3Mn(CO)_5 + RNC \xrightarrow[25\,^\circ C]{RH} cis\text{-}(CH_3CO)(RNC)Mn(CO)_4 \tag{2}$$

$$R = CH_3, \mathbf{2};\ C_6H_{11}, \mathbf{3};\ (CH_3)_3C, \mathbf{4}$$

where R is methyl, **2**, cyclohexyl, **3**, or t-butyl, **4**. Although phenylisocyanide does not effect "CO-insertion" with $CH_3Mn(CO)_5$ [12], this reaction proceeds smoothly and in high yield with the three alkyl isocyanides reported here. Apparently, this is the first report of this facile reaction [11].

The complexes **2**–**4** are yellow oils which are thermally stable at room temperature. The infrared spectra indicate a terminally coordinated isocyanide ligand and the four-band pattern expected for a *cis*-substituted $Mn(CO)_4$ octahedral complex [13]. The PMR spectra show the expected frequencies for acetyl and isocyanide ligands [14, 15].

The PMR spectrum of complex **4** reveals *two* singlets for both the acetyl and t-butyl methyl resonances. These resonances appear as two sets of unequal relative intensity. The set at lower field (2.44 and 1.59δ) comprise 78% of the total intensity, while the set at higher field (2.33 and 1.53δ) account for the remaining 22% of the intensity. Presumably there are two isomers of this complex in solution. Perhaps the large steric bulk of the t-butyl group has led to restricted rotation about the acetyl carbon–manganese bond. There are two different environments possible for the acetyl and t-butyl methyl groups for such an isomerism.

When the complexes **2–4** are treated with one molar equivalent of methyllithium, the substituted metallo-β-diketonate anions, **5–7**, are formed. These anions formed neutral *tris*-chelate complexes with aluminum when treated with anhydrous $AlCl_3$ like all previously reported metallo-β-diketonate anions, as shown below (3) [1–3].

$$\underset{\mathbf{2\text{–}4}}{cis\text{-}(CH_3CO)(RNC)Mn(CO)_4} + CH_3Li \xrightarrow[0\,°C]{} \underset{\mathbf{5\text{–}7}}{fac\text{-}(OC)_3(RNC)Mn(CH_3CO)_2^-Li^+}$$

$$\xrightarrow[0\,°C]{1/3\ AlCl_3} \underset{\mathbf{8\text{–}10}}{[fac\text{-}(OC)_3(RNC)Mn(CH_3CO)_2]_3\,Al} + LiCl \qquad (3)$$

R	*Compound*
CH_3	**2, 5, 8**
C_6H_{11}	**3, 6, 9**
t-butyl	**4, 7, 10**

The overall reaction is followed easily by IR. The formation of the anions **5–7** is characterized by a shift of both the C≡N and C≡O bands to lower frequency. The isocyanide C≡N band drops in frequency by *ca.* 40 cm^{-1} while the four-band pattern of the carbonyl ligands of the complexes **2–4** becomes a two-band pattern at lower energy for the anions. These peaks appear at *ca.* 1987 and 1917 cm^{-1} and have the relative intensity and shape expected for a facial isomer of the type $L_3M(CO)_3$. The meridional isomer is never observed [16]. Also, the acyl C–O stretch of the anions occurs at *ca.* 1575 cm^{-1} which is nearly 70 cm^{-1} lower than the corresponding stretch of the complexes, **2–4**. These shifts parallel the changes observed in the same reaction of the unsubstituted complex [1].

Due to the thermal instability of the aluminum complexes, **8–10**, the *bis*(triphenylphosphine)iminium (PPN) salt of the anion, **5**, was isolated and characterized. The PPN salt of the unsubstituted anion, *cis*-$(OC)_4Mn(CH_3CO)_2^-$, was isolated, also. The substituted anion, **5**, has slightly lower carbonyl stretching frequencies, and the PMR resonance of the acyl-methyl groups occurs at slightly higher field. These data are consistent with a slightly larger negative charge residing on the manganese atom of anion **5** than in the unsubstituted anion.

The aluminum complexes, **8–10**, are prepared by the addition of an ether solution of anhydrous aluminum chloride to a solution containing the substituted anions, **5–7**. This reaction can be followed by IR, also. Upon addition of the aluminum chloride, the spectrum of the anion disappears with the concomitant appearance of the spectrum of the neutral, *tris*-chelate complex. The isocyanide C≡N stretch of the aluminum complex appears at *ca.* 10 cm^{-1} to higher frequency than in the corresponding anion. Also, the "A" and "split-E" modes of the carbonyl ligands of the aluminum complex appear at *ca.* 30 cm^{-1} above the same modes of the anion. These shifts in frequency place these stretching modes at frequencies nearly intermediate between the C≡O and C≡N vibrations of the corresponding neutral acetyl complexes and the anionic intermediates, **5–7**. No evidence for the meridional isomer was observed [16]. The lowering of the acyl C–O stretching vibration of the anions by *ca.* 35 cm^{-1} to 1516–1519 cm^{-1} for the aluminum complexes strongly supports the formation of the metallo-β-diketonate complexes [1, 2].

The aluminum complexes, **8–10**, were considerably less stable thermally than the unsubstituted analogue, **1**. These complexes decomposed or melted at less than 90 °C while complex **1** decomposes rapidly only at 265 °C. This thermal instability thwarted repeated crystallization attempts, and even extensive washing of the complexes led to partial decomposition. The best elemental analyses are provided above.

PMR spectra of the aluminum complexes could be obtained on freshly prepared material although some degree of decomposition was always observed. The resonance of the methyl groups of the chelate ring of compounds **8** and **9** appeared as singlets at 2.56 and 2.67δ, respectively. The corresponding resonance of complex **1** appears at 2.72δ. The resonances of the alkyl groups of the isocyanide ligands appeared at the expected frequencies [15].

The PMR spectrum of complex **10** revealed possible isomerism. The chelate-ring methyl groups show a four-line pattern. Three closely spaced singlets appear at 2.74, 2.70 and 2.65δ while another singlet appears at 10 Hz to higher field, 2.55δ. This pattern indicates a *cis–trans* isomerization about the aluminum atom. The three isocyanide ligands can be either on the same *(cis)* or opposite *(trans)* sides of a hypothetical σ_h plane defined by the manganese and aluminum atoms. This type of isomerism has been detected similarly before [2, 3]. Although the t-butyl region is partially obscured by an impurity peak at 1.58δ, there are two singlets, 1.46 and 1.39δ, observed for the t-butyl groups. The three closely spaced methyl singlets are assigned to the *trans* isomer, and the single resonance at slightly higher field is assigned to the *cis* isomer. Integration of these resonances provides a *cis* to *trans* ratio of 0.35. The statistical value is one-third. Apparently, the larger bulk of the t-butyl groups permits the detection of this isomerism only for complex **10**.

Recently, a theoretical model describing a possible mode of intramolecular stabilization of complex **1** was reported [4]. It was shown that the two axial carbonyl ligands on each manganese atom of complex **1** could π-bond synergistically to the π-electron system of the metallo-β-diketonate ligand. In complexes **8–10**, the facial geometry about each manganese atom requires that the isocyanide ligand occupy one of these axial sites. If the isocyanide ligand has lower lying filled π-molecular orbitals and higher lying unoccupied π-molecular orbitals than does a carbonyl ligand [11], then this intramolecular stabilization of the complexes **8–10** is greatly reduced relative to that of complex **1**. This reduction may facilitate the thermal decomposition of these substituted metallo-β-diketonate complexes.

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