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Synthesis, Spectral Properties, and Reactions of Manganese and Rhenium Pentacarbonyl Phosphine and Phosphite Cation Derivatives and Related Complexes[1]

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The synthesis of a variety of monosubstituted manganese and rhenium carbonyl cationic species of the form $[M(CO)_5L][PF_6]$ is reported, where L = group 5A ligands. Preparation of these derivatives was accomplished either through the reaction of $[LM(CO)_4]^-$ with $C_2H_5O_2CCl$ followed by treatment with HBF_4 (or BF_3) or by thermal replacement of CH_3CN in the $M(CO)_5(CH_3CN)^+$ derivative. The latter procedure was shown to be the method of choice. The reaction of these pentacarbonyl derivatives with CH_3NH_2 to form *cis*-$[Mn(CO)_4(L)C(O)NHCH_3]$ is discussed in relation to other nucleophilic reactions at the carbonyl carbon atom. Displacement of CO ligands from the $Mn(CO)_5(CH_3CN)^+$ species in solution by pyridine, phosphines, and CH_3CN is also reported. In some of these multisubstituted species, exchange of the bound CH_3CN ligands was observed. The CO stretching force constants were calculated for all the cationic species prepared. In the pentacarbonylmanganese phosphine derivatives the axial CO force constant, k_1, was quite similar to the equatorial CO force constant, k_2. This result is discussed in terms of a direct donation of phosphorus σ electrons into the π orbitals of the equatorial CO ligands.

Introduction

The extreme sensitivity of the carbonyl ligand in low-valent transition metal complexes toward subtle changes in electronic and steric environment may be monitored both spectroscopically and chemically. For studies defining the nature and magnitude of these effects the preparation of metal carbonyl derivatives, $L_xM(CO)_y$, where L encompasses a range of ligands of varying electronic and steric properties is a necessity.[3-5] Preparations of neutral mononuclear metal carbonyl derivatives generally involve straightforward substitution processes, utilizing either light or thermal energy for the initial M–C bond cleavage in the parent $M(CO)_{x+y}$. Preparations of charged analogs are however considerably more difficult.

The preparation of cationic manganese carbonyl derivatives of the type $Mn(CO)_5L^+$ (L = a Lewis base), which are isoelectronic with $Cr(CO)_5L$ species, has received little attention. Kruck and Hofler[6] have reported the preparation of a limited number of mono- and disubstituted cationic manganese carbonyl derivatives according to the high-pressure synthesis

$$Mn(CO)_{5-n}L_nCl + AlCl_3 \xrightarrow[CO]{250\ atm} [Mn(CO)_{6-n}L_n][AlCl_4] \qquad (1)$$

where L = PPh_3, $P(c\text{-}C_6H_{11})_3$, and *o*-phenanthroline.

We wish to report the preparation of an extensive series of $Mn(CO)_5L^+$ derivatives (L = $P(OPh)_3$, PPh_3, $P(p\text{-}MeC_6H_4)_3$, PMe_2Ph, diphos, NC_5H_5, CH_3CN) as well as products derived from further CO substitution in these $Mn(CO)_5L^+$ species. The preparation of a few rhenium analogs is also reported. In addition, this synthetic capability has allowed us to carry out several interesting spectral and reactivity investigations.

Experimental Section

Material and Equipment. Tetrahydrofuran was purified by distillation from sodium benzophenone dianion under N_2. All other solvents and reagents were reagent grade and used without further treatment. $Mn_2(CO)_{10}$ was generously supplied by Professor G. R. Dobson. Dimethylphenylphosphine was the generous gift of M and T Chemicals Co. All other phosphines were purchased from Strem Chemical Co. Nitrosyl hexafluorophosphate ($NOPF_6$) was obtained from Alfa Inorganics, Inc.

Melting points were taken in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 521 grating spectrophotometer which was calibrated above 2000 cm^{-1} with gaseous CO and below 2000 cm^{-1} with water vapor. The NMR spectra were obtained on a JEOLCO MH-100 instrument.

Preparations. $[LMn(CO)_4]_2$ complexes were prepared from $Mn_2(CO)_{10}$ and ligand (L) using a modified procedure of that previously published by Wawersik and Basolo[7] for the thermal preparation of $[Ph_3PMn(CO)_4]_2$.

$[Ph_3PMn(CO)_4]_2$. $Mn_2(CO)_{10}$ (1.0 g, 2.6 mmol) and 1.33 g (5.2 mmol) of Ph_3P in 20 ml of 1-butanol were refluxed at 120–130° under nitrogen for 2 hr. The initial red solution slowly changed to orange and the orange product precipitated during the heating period. Upon cooling the product was isolated by filtration, washed with pentane, and then recrystallized as orange needles from benzene–heptane. The yield was 1.37 g or 62.5% (mp 133–136° dec and ν(CO) (in $CHCl_3$) 1985 (w) and 1955 (vs) cm^{-1}).

$[(PhO)_3PMn(CO)_4]_2$. $Mn_2(CO)_{10}$ (1.0 g, 2.6 mmol) and 1.6 g (5.2 mmol) of $(PhO)_3P$ in 20 ml of 1-butanol were refluxed at 120–130° under nitrogen for 6 hr. As the solution was cooled to room temperature, a yellow crystalline solid precipitated out. The product was filtered off and recrystallized from CH_2Cl_2–hexane at −78°. The yield was 1.56 g or 65% (mp 136–140° and ν(CO) (in $CHCl_3$) 2003.3 (w, sh) and 1977.8 (vs) cm^{-1}).

$[(CH_3)_2PhPMn(CO)_4]_2$. This previously unreported dimer was prepared in much the same manner as those above from 2.0 g (5.2 mmol) of $Mn_2(CO)_{10}$ and 1.45 g (10.4 mmol) of $(CH_3)_2PhP$ in 20 ml of 1-butanol at 120–130° for 2 hr. Cooling the solution to 0° caused an orange crystalline solid to precipitate. The product was filtered off and recrystallized from benzene–heptane as orange crystals. The yield was 1.62 g or 52% (mp 173–179° and ν(CO) (in $CHCl_3$) 2049.5 (vs), 1980.3 (w), and 1947.3 (vs) cm^{-1}). Anal. Calcd for $C_{24}H_{22}O_8P_2Mn_2$: C, 47.2; H, 3.62; mol wt 610. Found: C, 47.5; H, 3.75; mol wt 586 (determined osmometrically in benzene).

$[CH_3CNMn(CO)_5][PF_6]$. $Mn_2(CO)_{10}$ (7.7 mmol) dissolved in 90 ml of CH_3CN was stirred under N_2 and 1 molar excess (~5 g) of $NOPF_6$ was added to the solution.[8-11] A vigorous reaction occurred immediately with evolution of NO gas. After stirring of the reaction solution for an additional 5 min the volume of the solution was reduced to 30 ml and the product precipitated by the addition of 100 ml of diethyl ether. The product was isolated by filtration and recrystallized from acetone–Et_2O. The yield was 3.46 g or 61.2% of a white powder (mp 160° dec).

[$(CH_3)_2PhPMn(CO)_5$][BF_4]. Method A. [$(CH_3)_2PhPMn(CO)_4$]$_2$ (0.50 g, 0.82 mmol) dissolved in 10 ml of THF was reduced under N_2 with an excess of sodium amalgam. After stirring for 30 min the yellow solution was filtered under N_2 into 4 ml of ethyl chloroformate and the solution was stirred for an additional 45 min. The cloudy orange solution was filtered to remove the NaCl precipitate. BF_3 was slowly bubbled into the filtrate for 5 min causing a white crystalline precipitate to form. The product was filtered, washed with THF, and vacuum-dried. The yield was 0.20 g or 29%. Anal. Calcd for $C_{13}H_{11}O_5F_4PBMn$: C, 37.2; H, 2.62. Found: C, 37.2; H, 2.73.

Method B. To a suspension of 1.0 g of [$Mn(CO)_5CH_3CN$][PF_6] in 50 ml of $CHCl_3$ stirred under N_2 was added 2.0 ml of $(CH_3)_2PhP$. The mixture was heated at 60° for 10 hr. The product which had precipitated during this heating period was filtered off, washed with 40 ml of $CHCl_3$, and dried under vacuum to yield 1.04 g (82.5%) of white microcrystals (mp 149–151° dec).

[$Ph_3PMn(CO)_5$][BF_4]. Method A. [$Ph_3PMn(CO)_4$]$_2$ (0.5 g, 0.58 mmol) in 10 ml of THF was added to an excess of sodium amalgam under N_2. After stirring for 30 min the solution was filtered into 6 ml of ethyl chloroformate and stirred for an additional 2 hr. A 10-ml sample of 50% HBF_4 (aqueous solution) was then added with stirring. After 10 min 25 ml of H_2O was added and the solution was reduced in volume until solid formed. The product was isolated by filtration, washed repeatedly with benzene, and finally recrystallized from acetone–heptane as white crystals. The yield was 0.20 g or 31.5%. In an additional preparation as described above employing BF_3 instead of HBF_4 a 14% yield of [$Ph_3PMn(CO)_5$][BF_4] was obtained. The benzene wash solution was found to contain 0.12 g of $FMn(CO)_3(PPh_3)_2$. Anal. Calcd for $C_{39}H_{30}P_2O_3FMn$: C, 68.6; H, 4.30; F, 2.78. Found: C, 67.3; H, 4.46; F, 1.98. ν(CO) spectrum in $CHCl_3$: 2036.5 (w), 1951.3 (s), and 1917 (m) cm^{-1}. This is the fluoride analog of the complexes $Mn(CO)_3(PPh_3)_2X$ (X = Cl, Br, I) previously prepared by Abel and Wilkinson.[12]

Method B. [$Mn(CO)_5(CH_3CN)$][PF_6] (0.45 g, 1.23 mmol) and 1.70 g of Ph_3P dissolved in 40 ml of acetone were stirred under nitrogen at 30° for 18 hr. The volume of the solution was reduced to 10 ml. Addition of 40 ml of Et_2O resulted in precipitation of a white solid which was isolated by filtration. The product was washed repeatedly with Et_2O to give 0.67 g (93% yield) of the pure compound [$Mn(CO)_5PPh_3$][PF_6].

[$(PhO)_3PMn(CO)_5$][BF_4]. We have thus far only been able to prepare the phosphite derivative by method A. [$Mn(CO)_5(CH_3CN)$][PF_6] was found not to react with $(PhO)_3P$ under reflux conditions in $CHCl_3$, hexane, and acetone solvents, as well as in warm pure $(PhO)_3P$ solution. [$(PhO)_3PMn(CO)_4$]$_2$ (1.4 g, 1.5 mmol) in 20 ml of THF was reduced under nitrogen with an excess of sodium amalgam. After stirring of the reaction mixture for 1 hr the green solution was filtered under N_2 into 6 ml of ethyl chloroformate. This solution was stirred for an additional 2 hr to yield a cloudy red solution which was filtered to remove NaCl. BF_3 was bubbled slowly into the filtrate for approximately 1 hr during which the solution turned orange but no precipitate formed. A 50-ml amount of distilled water was added and the solution reduced in volume until a yellow solid crystallized. The solid was filtered, washed with benzene, and recrystallized from CH_2Cl_2–hexane as white crystals. The yield was 0.20 g (11.2%) of slightly impure product. Anal. Calcd for $C_{23}H_{15}O_8F_4PBMn$: C, 46.7; H, 2.55. Found: C, 43.0; H, 2.70.

[$(p\text{-}MeC_6H_4)_3PMn(CO)_5$][$PF_6$]. Method B. A solution containing 1.0 g of [$Mn(CO)_5(CH_3CN)$][PF_6] (2.72 mmol) and 1.5 g of $(p\text{-tol})_3P$ in 50 ml of acetone was stirred under nitrogen for 24 hr. Hexane was added to the solution until it became cloudy, and the product crystallized out of solution upon standing cold (~0°) overnight. Filtration followed by vacuum drying gave 0.92 g (53% yield) of yellow crystals (mp 163° dec). Anal. Calcd for $C_{26}H_{21}O_5P_2F_6Mn$: C, 41.5; H, 2.90. Found: C, 41.6; H, 3.03.

{[$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$]$Mn(CO)_5$}{$PF_6$}. Method B. A 0.75-g sample of [$Mn(CO)_5(CH_3CN)$][PF_6] and 1.30 g of diphos in 50 ml of acetone were stirred under nitrogen at 50° for 5 hr. The solvent was removed under vacuum and the residue washed repeatedly with Et_2O. Recrystallization from THF–Et_2O afforded 0.62 g (41% yield) of light yellow powder (mp >208° dec).

[$C_5H_5NMn(CO)_5$][PF_6]. Pyridine (1.0 ml) was added to a suspension of 1.0 g (2.7 mmol) of [$CH_3CNMn(CO)_5$][PF_6] in 40 ml of chloroform and the mixture was stirred under nitrogen for 15 hr. The product was isolated by filtration and recrystallized from acetone–Et_2O to yield 0.90 g (81%) of light yellow needles (mp >150° dec producing $Mn_2(CO)_{10}$). Anal. Calcd for $C_{10}H_5O_5F_6NPMn$: C, 28.7; H, 1.20. Found: C, 28.8; H, 1.17.

[$CH_3CNRe(CO)_5$][PF_6]. One molar excess of $NOPF_6$ was added to a solution containing 3.0 g of $Re_2(CO)_{10}$ (4.67 mmol) dissolved in 100 ml of acetonitrile.[8] A vigorous reaction results with the expulsion of NO gas. The solution was stirred for an additional 5 min until no further gas was expelled and the product was precipitated from solution upon the addition of 250 ml of diethyl ether. The product was filtered and washed with pentane followed by vacuum-drying to yield 4.03 g (86.7%) of an off-white powder (mp 163–170°). Anal. Calcd for $C_7H_3O_5F_6NPRe$: C, 16.4; H, 0.60. Found: C, 16.3; H, 0.70.

[$(CH_3)_2PhPRe(CO)_5$][PF_6]. A solution containing 0.40 g of [$CH_3CNRe(CO)_5$][PF_6] and 1 ml of $(CH_3)_2PhP$ in 25 ml of acetone was refluxed under nitrogen for 2 hr. After filtration, 100 ml of Et_2O was added and the solution was cooled in an ice bath to yield crystalline product. The product was filtered, washed with diethyl ether, and air-dried to give 0.201 g (53.9% yield) of white needles (mp 154–158°). Anal. Calcd for $C_{13}H_{11}O_5F_6P_2Re$: C, 25.6; H, 1.82. Found: C, 26.7; H, 1.84.

[$(p\text{-}MeC_6H_4)_3PRe(CO)_5$][$PF_6$]. A solution containing 0.50 g of [$(CH_3CN)Re(CO)_5$][PF_6] and 0.60 g of $(p\text{-}MeC_6H_4)_3P$ in 30 ml of acetone was refluxed under nitrogen for 22 hr. A 100-ml amount of Et_2O was added and the solution was filtered. The product was precipitated from the filtrate by the addition of hexane. Recrystallization from $CHCl_3$–heptane yielded 0.230 g (38.8%) of off-white microcrystals which were vacuum-dried (mp 188–193°).

[$(C_5H_5N)_2(CH_3CN)Mn(CO)_3$][$PF_6$]. A solution containing 0.90 g (2.5 mmol) of [$CH_3CNMn(CO)_5$][PF_6] and 3.0 ml of pyridine in 50 ml of CH_3CN was stirred under nitrogen for 48 hr.[10] Addition of 100 ml of water caused a yellow solid to precipitate which was filtered and dried. Recrystallization from acetone–water followed by vacuum-drying gave 0.51 g (43% yield) of fine yellow needles (mp 168° dec). Anal. Calcd for $C_{15}H_{13}O_3N_3F_6PMn$: C, 37.3; H, 2.71. Found: C, 37.2; H, 2.84.

[$(C_5H_5N)_3Mn(CO)_3$][PF_6]. [$CH_3CNMn(CO)_5$][PF_6] (0.50 g) was added to 10 ml of pyridine with stirring under nitrogen. The evolution of CO was rapid and after 10 min excess pyridine was removed under vacuum leaving behind a yellow crystalline solid material. The product was recrystallized from acetone–Et_2O affording 0.45 g (64% yield) of yellow microcrystals (mp 163°). Anal. Calcd for $C_{18}H_{15}O_3N_3F_6PMn$: C, 48.5; H, 3.29. Found: C, 48.7; H, 3.16.

[$(CH_3CN)_3Mn(CO)_3$][PF_6]. A solution containing 1.0 g of [$(CH_3CN)Mn(CO)_5$][PF_6] in 20 ml of CH_3CN was stirred under nitrogen at 50° for 5 hr.[10] The CH_3CN was removed under vacuum to give 0.97 g (91% yield) of yellow-orange microcrystals (mp 130° dec).

[(CH_3CN)(diphos)$Mn(CO)_3$][PF_6]. [$(CH_3CN)Mn(CO)_5$][PF_6] (0.45 g, 1.23 mmol) and 1.45 g (3.64 mmol) of diphos in 40 ml of acetonitrile were stirred under nitrogen at 40° for 4 days. Upon cooling of the solution, most of the excess diphos precipitated and was removed by filtration. Addition of 5 ml of water led to precipitation of the remaining diphos. After filtering, the solvent was removed under vacuum leaving behind a yellow solid which was washed with hexane and Et_2O. Recrystallization from CH_2Cl_2–hexane yielded 0.31 g (36%) of yellow powder (mp 98–108° dec).

Reactions of $MeNH_2$ with [$LMn(CO)_5$][PF_6]. Samples (0.2 g) of [$LMn(CO)_5$][PF_6] (where L = Me_2PhP, Ph_3P, $(p\text{-tol})_3P$, diphos, pyridine, and CH_3CN) were dissolved in 1 ml of $CDCl_3$ and monomethylamine was slowly bubbled into the solutions for approximately 5 min. After degassing of the samples to remove excess CH_3NH_2, ^1H NMR spectra were recorded. The deuteriochloroform solvent was then removed under vacuum and the infrared spectra were obtained on the sample which was redissolved in hexane. Attempts to prepare and isolate crystalline samples of these products were unsuccessful, although infrared and NMR spectra clearly indicated that quantitative reactions had occurred, yielding the expected carbamoyl complexes as sole products.

Discussion

We have developed in this report a means to prepare a whole class of compounds which have previously received little attention, namely, Lewis base monosubstituted products of

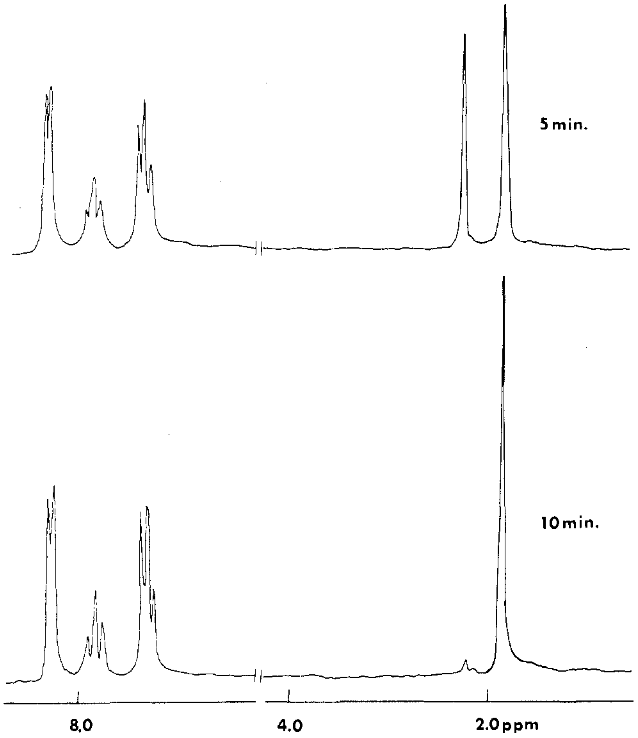


Figure 1. NMR spectra of the exchange process between $(C_5H_5N)_2(CH_3CN)Mn(CO)_3^+$ and free CD_3CN. Peak positions are 7.44 (t), 7.96 (t), 7.96 (t), and 8.39 (d) ppm for the pyridine ligands, and 2.33 (s) ppm for bound CH_3CN (free CH_3CN is noted at 1.92 (s) ppm).

$Mn(CO)_6^+$. These were synthesized under mild reaction conditions employing the two procedures

$$[\mathrm{LMn(CO)_4}]_2 \xrightarrow{\text{Na-Hg}} \mathrm{Na^+[LMn(CO)_4]^-} \xrightarrow{\mathrm{EtO_2CCl}} \xrightarrow[\text{or } \mathrm{BF_3}]{\mathrm{HBF_4}}$$

$$[\mathrm{LMn(CO)_5}][\mathrm{BF_4}] + \mathrm{EtOH} + \mathrm{NaCl} \qquad \text{(A)}$$

$$[\mathrm{Mn(CO)_5(CH_3CN)}][\mathrm{PF_6}] + \mathrm{L} \rightarrow [\mathrm{Mn(CO)_5L}][\mathrm{PF_6}] + \mathrm{CH_3CN} \qquad \text{(B)}$$

The complexes $[LMn(CO)_5][BF_4]$, where L = PPh_3, PMe_2Ph, and $P(OPh)_3$, were prepared by method A in purified yields of about 18% based on the starting material $Mn_2(CO)_{10}$. In addition to a rather poor yield of product, this method of preparation is limited by the availability of the dimer complexes $[LMn(CO)_4]_2$. Therefore, in order to provide a more versatile and efficient synthesis of these complexes, we have investigated the preparation of $Mn(CO)_5L^+$ derivatives employing method B. This procedure resulted in yields in the range of 40–60% based on $Mn_2(CO)_{10}$. Method B was greatly favored by the ease with which $[Mn(CO)_5(CH_3CN)][PF_6]$ could be prepared in large quantities from $Mn_2(CO)_{10}$ and $NOPF_6$ in acetonitrile. The quantitative displacement of acetonitrile from $Mn(CO)_5(CH_3CN)^+$ by the Lewis base (L) was only possible when the reaction was run in a solvent other than acetonitrile. In the presence of excess acetonitrile loss of CO occurs resulting in more highly substituted carbonyl derivatives. This is evidently due to the competition of CH_3CN with the added Lewis base (L) for the vacant site created by the loss of CH_3CN from $Mn(CO)_5(CH_3CN)^+$ in addition to the ability of the CH_3CN ligand to labilize the CO groups. This is illustrated by the preparation of the CO-substituted products $[(C_5H_5N)_2(CH_3CN)Mn(CO)_3][PF_6]$ and $[(diphos)(CH_3CN)Mn(CO)_3][PF_6]$ from $[(CH_3CN)Mn(CO)_5][PF_6]$ and the respective Lewis bases in acetonitrile.

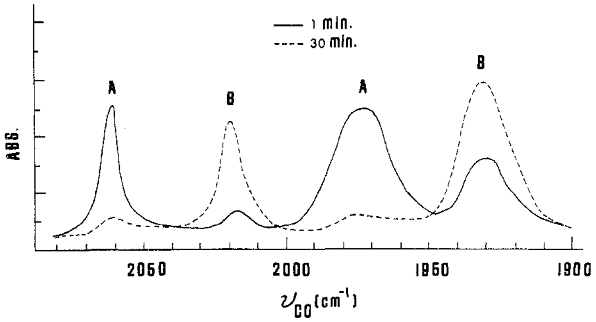


Figure 2. Time dependence of the infrared spectra in the ν(CO) region of $Mn(CO)_3(CH_3CN)_3^+$ in acetone solution: A, $Mn(CO)_3(CH_3CN)_3^+$; B, $Mn(CO)_3((CH_3)_2CO)_3^+$.

The acetonitrile ligands in the tris-substituted derivatives $(C_5H_5N)_2(CH_3CN)Mn(CO)_3^+$ and $(CH_3CN)_3Mn(CO)_3^+$ were observed by NMR to exchange with free CD_3CN in acetonitrile solutions at ambient temperatures. The exchanges were essentially complete in 20 and 40 min (for all three CH_3CN ligands), respectively, for the derivatives $(C_5H_5N)_2(CH_3CN)Mn(CO)_3^+$ and $(CH_3CN)_3Mn(CO)_3^+$. NMR spectra of this exchange process in the bis(pyridine) derivative are depicted in Figure 1. On the other hand, complexes containing the softer Lewis bases CO and $Ph_2PCH_2CH_2PPh_2$, namely, $(diphos)(CH_3CN)Mn(CO)_3^+$ and $(CH_3CN)Mn(CO)_5^+$, exhibited no tendency to exchange the bound acetonitrile ligand with free ligand in acetonitrile solution.

In addition the complex $(CH_3CN)_3Mn(CO)_3^+$ was found to undergo an exchange reaction with acetone in acetone solution. The infrared spectrum in the ν(CO) region of acetone solutions of $[(CH_3CN)_3Mn(CO)_3][PF_6]$ consists initially of two bands at 2062.8 and 1974.3 cm^{-1} of relative intensity 1:2 (A_1 + E). With time these two bands are replaced by two new bands of similar intensity ratio but at significantly lower frequencies (2020.5 and 1931.0 cm^{-1}); see Figure 2. Addition of small amounts of CH_3CN to the acetone solutions results in a quantitative, rapid re-formation of the initial $Mn(CO)_3(CH_3CN)_3^+$ species. Removal of solvent from an acetone solution of $[Mn(CO)_3(CH_3CN)_3][PF_6]$ gave a yellow oil which consisted mainly of the new species, presumably $Mn(CO)_3((CH_3)_2CO)_3^+$, along with a trace of $Mn(CO)_3(CH_3CN)_3^+$. The lack of infrared bands in the metal-coordinated acetonitrile ν(CN) region of concentrated acetone solutions further substantiated the replacement of all three CH_3CN ligands. No intermediate mono- or diacetone-substituted species were noted, indicating rapid displacement of the remaining coordinated CH_3CN ligand in these species. Further confirmation of the $Mn(CO)_3((CH_3)_2CO)_3^+$ species presence is found from the reaction between $Mn_2(CO)_{10}$ and $NOPF_6$ in acetone solution where the same compound is observed to be formed as indicated by its infrared spectrum (reaction 2).

$$\mathrm{Mn_2(CO)_{10}} + 2\mathrm{NOPF_6} \xrightarrow{\text{acetone}} 2[\mathrm{Mn(CO)_3((CH_3)_2CO)_3}][\mathrm{PF_6}] + 2\mathrm{NO} + 4\mathrm{CO} \qquad (2)$$

Since the reaction occurring in acetone solution between $[Mn(CO)_3(CH_3CN)_3][PF_6]$ and acetone was readily reversible in the presence of small quantities of acetonitrile, an attempt was made to determine the overall equilibrium constant (K_{eq}) for reaction 3. Beer's law plots for both the A_1 and E ν(CO)

$$[\mathrm{Mn(CO)_3(CH_3CN)_3}]^+ + 3(\mathrm{CH_3})_2\mathrm{CO} \rightleftarrows [\mathrm{Mn(CO)_3((CH_3)_2CO)_3}]^+ + 3\mathrm{CH_3CN} \qquad (3)$$

$$K_{eq} = \frac{[\mathrm{Mn(CO)_3((CH_3)_2CO)_3^+}]\,[\mathrm{CH_3CN}]^3}{[\mathrm{Mn(CO)_3(CH_3CN)_3^+}]\,[(\mathrm{CH_3})_2\mathrm{CO}]^3} \qquad (4)$$

vibrations in $Mn(CO)_3(CH_3CN)_3^+$, recorded rapidly in acetone solutions at a variety of concentrations, were linear

Table I. Equilibrium Absorbance Values of $Mn(CO)_3(CH_3CN)_3^+$ and $Mn(CO)_3((CH_3)_2CO)_3^+$ [a]

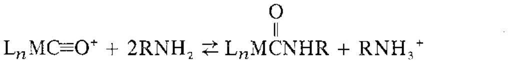
CH_3CN added, ml	$Mn(CO)_3(CH_3CN)_3^+$ [b] A_1	E	$Mn(CO)_3$-$((CH_3)_2CO)_3^+$ [c] A_1	E
0.025	0.455	0.495	0.360	0.510
0.035	0.480	0.530	0.335	0.480
0.050	0.530	0.570	0.265	0.420
0.060	0.590	0.640	0.210	0.365

[a] Determined in acetone solvent in 0.1-mm NaCl cells. [b] ϵ (M^{-1} cm^{-1}): A_1, 2.68 × 10^3; E, 2.89 × 10^3. [c] ϵ (M^{-1} cm^{-1}): A_1, 2.95 × 10^3; E, 3.96 × 10^3.

with zero intercepts. After the solutions were allowed to equilibrate, similar Beer's law plots for the A_1 and E ν(CO) vibrations in the $Mn(CO)_3((CH_3)_2CO)_3^+$ species were obtained. The K_{eq} (eq 4) values for reaction 3 were determined on four solutions having the same initial concentration of $Mn(CO)_3(CH_3CN)_3^+$ (0.0528 g in 5 ml of acetone). Small concentrations of CH_3CN were added to the solutions (0.025–0.060 ml) and 1 hr was allowed for equilibration. The resulting absorbances for reactant and product tricarbonyl species are given in Table I. Using the extinction coefficients of the A_1 modes to determine the concentrations of the two tricarbonyl species at equilibrium, an average K_{eq} value of (1.29 ± 0.45) × 10^{-6} was determined at 25° using the proposed equilibrium reaction 3. It was possible to calculate a Gibbs free energy value for this reaction of +8.04 kcal/mol. Assuming changes in $\Delta S°$ to be small since the reactants and products are quite similar, $\Delta G°$ allows for a qualitative comparison of bond energies for the Mn^I–$NCCH_3$ and Mn^I–$OC(CH_3)_2$ bonds. The average acetonitrile–manganese(I) bond is therefore about 2.7 kcal stronger than the average acetone–manganese(I) bond. It was indeed not possible to isolate and characterize fully the $Mn(CO)_3((CH_3)_2CO)_3^+$ complex. $Mn(CO)_3(CH_3CN)_3^+$ was also observed to exchange acetonitrile ligands with THF in THF solution but at a much slower rate as compared with acetone.

This synthetic capability for preparing $Mn(CO)_5L^+$ compounds has allowed for some interesting extensions of our proposed relationship between reactivity patterns at the carbonyl carbon atom of substituted metal carbonyls with a variety of nucleophiles and infrared spectral parameters, ν(CO) or F(CO).[3] We have already reported our results of addition of benzylmagnesium chloride to $Mn(CO)_5L^+$ species to yield rapidly *cis*-$PhCH_2COMn(CO)_4L$ complexes.[13] In addition, Dobson and his coworkers[14] are currently investigating the addition of other nucleophiles (e.g., organolithium reagents, azide, and halide ions) to these $Mn(CO)_5L^+$ species using stopped-flow techniques. We report here our results on the addition of primary amines to these newly acquired $Mn(CO)_5L^+$ species.

Angelici and coworkers[15-17] have extensively studied reactions between the cationic species $M(CO)_6^+$ and *trans*-$M(CO)_4L_2^+$ (M = Mn and Re) with a large variety of primary and secondary alkylamines to give carbamoyl compounds according to eq 5. Their results indicate that the rate of the



$$L_nMC{\equiv}O^+ + 2RNH_2 \rightleftarrows L_nM\overset{O}{\overset{\|}{C}}NHR + RNH_3^+ \qquad (5)$$

reaction and the position of equilibrium are indeed consistent with suggestions concerning nucleophilic attack at carbonyl carbon atoms. However their work did not allow for a discrimination between two different types of carbonyl ligands (differing in electronic and steric environment) in a single complex except in the complexes $(CH_3NH_2)M(CO)_5^+$ (M = Mn, Re),[18] where reaction apparently occurred at the CO group with the highest force constant. The reactions of primary amines with $Mn(CO)_5L^+$ derivatives were therefore investigated with this objective in mind.

Table II. Infrared Data on *cis*-$LMn(CO)_4C({=}O)NHCH_3$ Compounds in the ν(CO) Region[a]

L	ν(CO), cm^{-1}			
$(CH_3)_2PhP$	2063.0 m	1992.5 s	1962.0 vs	1955.0 s
Ph_3P	2069.8	2001.0	1966.3, 1959.0	1954.0
diphos	2069.5	2000.0	1960.0	1953.0
$(p\text{-}MeC_6H_4)_3P$	2069.5	2000.0	1960.5	1952.0
NH_2CH_3	2068.8 w	1980.0 vs	1934.0 s	

[a] All spectra were observed in hexane solution.

Table III. NMR Data on *cis*-$LMn(CO)_4C({=}O)NHCH_3$ Compounds[a]

L	Proton	δ, ppm	
$(CH_3)_2PhP$	Ph	7.50	Singlet
	N-H	5.42	Singlet (broad)
	N-CH_3	2.70	Doublet (J_{H-H} = 4.1 Hz)
	P-CH_3	1.89	Doublet (J_{P-H} = 9.0 Hz)
Ph_3P	Ph	7.46	Multiplet
	N-H	5.25	Singlet
	N-CH_3	2.49	Doublet (J_{H-H} = 4.8 Hz)

[a] Measured in deuteriochloroform relative to TMS.

$[LMn(CO)_5][PF_6]$ derivatives, where L = $(CH_3)_2PhP$ or Ph_3P, were found to react with monomethylamine to yield predominantly *cis*-$LMn(CO)_4C({=}O)NHCH_3$ products as indicated by ir and NMR spectral measurements. A small quantity of product resulting from loss of the phosphine ligand, *cis*-$(CH_3NH_2)Mn(CO)_4C({=}O)NHCH_3$, was also formed during these reactions.[18] On the other hand, when $LMn(CO)_5^+$ complexes, where L = C_5H_5N or CH_3CN, were treated with CH_3NH_2, *cis*-$(CH_3NH_2)Mn(CO)_4C({=}O)NHCH_3$ was the only observed product. $LMn(CO)_5^+$ complexes, where L = diphos or $(p\text{-}MeC_6H_4)_3P$ were also found to give *cis*-$LMn(CO)_4C({=}O)NHCH_3$ products upon reaction with NH_2CH_3; however, confirmatory NMR spectral data on these particular derivatives were rather inconclusive.

Infrared spectral measurements in the ν(CO) region of these carbamoyl complexes are given in Table II; NMR spectral properties are given in Table III.

Table IV contains the ν(CO) absorptions and the Cotton–Kraihanzel force constants[19] for the $LM(CO)_5^+$ species (M = Mn and Re) reported in this study. As noted in Table IV the CO stretching force constants in these derivatives are generally greater than 17.0 mdyn/Å. Therefore, the fact that the reactions between CH_3NH_2 and $LMn(CO)_5^+$ derivatives occur rapidly and essentially quantitatively is consistent with our initial proposal[3] as well as with the results reported by Angelici and Blacik.[15] These workers made the observation that CO ligands in manganese and rhenium cationic species with force constants greater than 17.0 readily react to form carboxamide complexes (recall that the higher the CO force constant, supposedly the lower the electron density on carbon), whereas, those with force constant values 17.0–16.0 and below 16.0 gave equilibrium mixtures and no reactions, respectively.

The cis geometry of addition products of $LCr(CO)_5$, the isoelectronic analog of $LMn(CO)_5^+$ species, with RLi or RMgX is always obtained in the absence of excessively large steric requirements for the ligand L.[4,5] This is attributed to electronic effects in that the cis CO ligands have larger force constants as compared with the trans CO ligand. The force constant, k_2, is also slightly greater than k_1 in all the $LMn(CO)_5^+$ cationic derivatives studied except where L = $P(OPh)_3$. However, in the $LMn(CO)_5^+$ derivatives the values of k_2 and k_1 are quite similar, the differences being only on the order of ±0.08 mdyn/Å as compared to ~+0.25 mdyn/Å for the chromium analogs. Nevertheless, addition of all nucleophiles thus far studied leads exclusively to the cis addition products.[13,14]

Table IV. Observed ν(CO) Values and Calculated CO Stretching Force Constants for $M(CO)_5L^+$ and Related Species

Compd[a]	ν(CO),[b] cm^{-1}			Force constants, mdyn/Å		
	$A_1^{(2)}$	$A_1^{(1)}$	E	k_1	k_2	k_i
$Mn(CO)_5P(OPh)_3^+$	2153.5 w	2083.5 m	2063.5 vs	17.74	17.65	0.22_2
$Mn(CO)_5PPh_3^+$	2141.8	2063 sh	2052.0	17.37	17.46	0.22_4
$Mn(CO)_5P(p\text{-}CH_3C_6H_4)_3^+$	2141.5	2062 sh	2051.5	17.35	17.45	0.22_5
$Re(CO)_5P(p\text{-}CH_3C_6H_4)_3^+$	2156.5	2055[c]	2048.0	17.26	17.49	0.27_6
$Mn(CO)_5PMe_2Ph^+$	2141.8	2062 sh	2050.3	17.36	17.44	0.22_8
$Re(CO)_5PMe_2Ph^+$	2156.5	2055[c]	2046.8	17.26	17.48	0.27_7
$Mn(CO)_5(diphos)^+$	2140.6	2062 sh	2050.1	17.36	17.43	0.22_6
$Mn(CO)_5NC_5H_5^+$	2153.5	2041.8	2063.3	16.97	17.67	0.23_5
$Mn(CO)_5(CH_3CN)^+$	2161.3	2047.3	2073.5	17.05	17.83	0.23_1
$Re(CO)_5(CH_3CN)^+$	2169.0	2029.8	2059.5			

Compd[a]	ν(CO),[b] cm^{-1}		Force constants, mdyn/Å	
	A_1	E	k	k_i
$Mn(CO)_3(NC_5H_5)_3^+$	2041.0 vs	1947.0 vs	15.81	0.50_4
$Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$	2048.0	1955.3	15.94	0.50_4
$Mn(CO)_3(CH_3CN)_3^+$	2063.0	1973.7	16.21	0.48_5
$Mn(CO)_3(diphos)(CH_3CN)^+$	2040.0	1972.1, 1952.3	15.97	0.41_9
$Mn(CO)_3((CH_3)_2CO)_3^+$	2020.5	1931.0	15.53	0.47_6

[a] All compounds existed as the PF_6^- salt except for $Mn(CO)_5P(OPh)_3^+$ which existed as the BF_4^- salt. [b] All frequencies were determined in acetonitrile solvent except for those of $Mn(CO)_3((CH_3)_2CO)_3^+$ which were determined in acetone solvent. [c] This vibration is grossly buried beneath the E mode vibration and is therefore only a rough estimate. It is, however, slightly higher in energy than the E mode (see text for discussion).

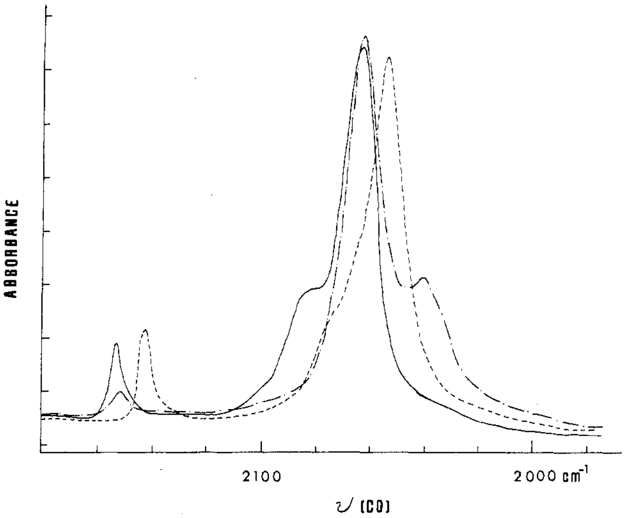


Figure 3. Infrared spectra in the ν(CO) region of $Mn(CO)_5L^+$ species in CH_3CN solution: ——, $(PhO)_3PMn(CO)_5^+$; - - -, $(p\text{-}CH_3C_6H_4)_3PMn(CO)_5^+$; — · —, $(C_5H_5N)Mn(CO)_5^+$.

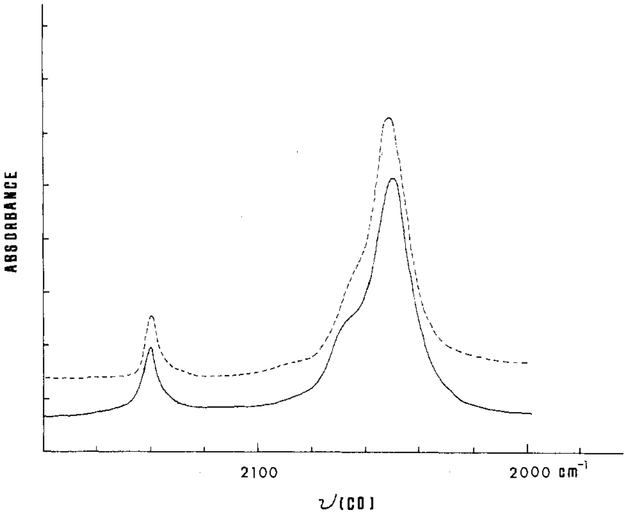


Figure 4. Solvent dependence of the infrared spectra in the ν(CO) region of $Ph_3PMn(CO)_5^+$: - - -, in CH_3CN solution; ——, in acetone solution.

At this point it would be useful to examine carefully the factors which might affect the Cotton–Kraihanzel force constants in $LM(CO)_5^+$ derivatives and their concomitant influence on the electronic charge distribution in these species. Figure 3 contains representative spectra of several $LMn(CO)_5^+$ species in CH_3CN solution. Unfortunately in all phosphine-substituted derivatives the $A_1^{(1)}$ CO stretching vibration (associated primarily with the axial CO ligand and therefore very important in accurately determining k_1) is buried to some extent beneath the E mode CO stretching vibration. However, this vibration does show up as a slight asymmetry on the high-frequency side of the intense E mode absorption in the manganese derivatives (see, e.g., the spectrum of $(p\text{-}CH_3C_6H_4)_3PMn(CO)_5^+$ in Figure 3). It is also clear that in the rhenium analogs the $A_1^{(1)}$ and E ν(CO) vibrations are even more nearly accidentally degenerate when compared with their manganese counterparts. On the other hand, in the triphenyl phosphite, pyridine, and acetonitrile manganese pentacarbonyl derivatives, the $A_1^{(1)}$ vibration is clearly separated as a moderately intense band (see Figure 3). In addition, it was possible in the manganese phosphine derivatives to observe the ν(CO) spectra in acetone as well as CH_3CN with slightly more discernible features showing up in the former solvent (Figure 4). Therefore, assignment of $A_1^{(1)}$ vibration in all the phosphine pentacarbonyl derivatives of manganese to slightly higher frequencies (~10 cm^{-1}) than that of the intense E mode absorption is made with confidence. We hope further to confirm this assignment from detailed Raman studies which are presently under way.[20]

Nevertheless it is realistic to include some uncertainty (±5 cm^{-1}) in the determination of the position of the $A_1^{(1)}$ ν(CO) absorptions in the phosphine pentacarbonyl derivatives. The calculated value of the CO stretching force constant, k_1, taking this limitation into account in the manganese pentacarbonyl phosphine derivatives is 17.36 ± 0.09 while k_2 is essentially unchanged from the value listed in Table IV.[21,22] Similarly, for the rhenium pentacarbonyl phosphine derivatives, a value of $k_1 = 17.26 \pm 0.09$ is obtained for an $A_1^{(1)}$ ν(CO) assignment of 2055 ± 5 cm^{-1}. Therefore it is quite clear that after due consideration of the various factors affecting the calculated values of the CO stretching force constants in $Mn(CO)_5L^+$ trivalent phosphorus derivatives, the k_1 and k_2 values are very similar to each other.[23] This result is contrary to the usual order observed in all neutral $Mn(CO)_5L$ derivatives[24] as well as isoelectronic $Cr(CO)_5L$ derivatives, where k_2 is significantly greater than k_1. However in the rhenium phosphine analogs k_2 is considerably larger than k_1, the difference being on the order of that observed in the neutral isoelectronic group 6 derivatives, e.g., $W(CO)_5PPh_3$.[4]

These observations taken together may indeed be indicative of direct donation of electron density into the π^* orbitals of the equatorial CO ligands by phosphorus ligands in $M(CO)_5L^+$ derivatives.[25,26] It would be expected that in going from Cr to Mn the direct donation would increase, whereas in going from Mn to Re the direct donation would decrease.[27]

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Registry No. $[CH_3CNMn(CO)_5][PF_6]$, 55029-96-4; $[(CH_3)_2PhPMn(CO)_5][BF_4]$, 54039-48-4; $[(CH_3)_2PhPMn(CO)_5][PF_6]$, 54039-52-0; $[Ph_3PMn(CO)_5][BF_4]$, 54039-46-2; $[Ph_3PMn(CO)_5][PF_6]$, 54039-57-5; $[(PhO)_3PMn(CO)_5][BF_4]$, 54039-50-8; $[(p\text{-}MeC_6H_4)_3PMn(CO)_5][PF_6]$, 54039-59-7; $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Mn(CO)_5\}\{PF_6\}$, 54039-56-4; $[C_5H_5NMn(CO)_5][PF_6]$, 54039-54-2; $[CH_3CNRe(CO)_5][PF_6]$, 55057-83-5; $[(CH_3)_2PhPRe(CO)_5][PF_6]$, 55057-85-7; $[(p\text{-}MeC_6H_4)_3PRe(CO)_5][PF_6]$, 55029-93-1; $[(C_5H_5N)_2(CH_3CN)Mn(CO)_3][PF_6]$, 55029-80-6; $[(C_5H_5N)_3Mn(CO)_3][PF_6]$, 55029-82-8; $[(CH_3CN)_3Mn(CO)_3][PF_6]$, 55029-84-0; $[(CH_3CN)(\text{diphos})Mn(CO)_3][PF_6]$, 55029-86-2; $Mn(CO)_3((CH_3)_2CO)_3^+$, 55029-87-3; $FMn(CO)_3(PPh_3)_2$, 55029-88-4; *cis*-$((CH_3)_2PPh)Mn(CO)_4C(=O)NHCH_3$, 54064-21-0; *cis*-$(Ph_3P)Mn(CO)_4C(=O)NHCH_3$, 55029-89-5; *cis*-$(\text{diphos})Mn(CO)_4C(=O)NHCH_3$, 55029-90-8; *cis*-$((p\text{-}MeC_6H_4)_3P)Mn(CO)_4C(=O)NHCH_3$, 55029-91-9; *cis*-$(CH_3NH_2)Mn(CO)_4C(=O)NHCH_3$, 18973-77-8; $[Ph_3PMn(CO)_4]_2$, 10170-70-4; $[(PhO)_3PMn(CO)_4]_2$, 15529-62-1; $[(CH_3)_2PhPMn(CO)_4]_2$, 55029-78-2; $Mn_2(CO)_{10}$, 10170-69-1; Ph_3P, 603-35-0; $(PhO)_3P$, 101-02-0; $Re_2(CO)_{10}$, 14285-68-8; C_5H_5N, 110-86-1; CH_3CN, 75-05-8; CH_3NH_2, 74-89-5.

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Kinetics of Complexation of Silver(I) with Thiosulfate Ion in Aqueous Solution

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A specific rate constant for the rapid complexation of Ag^+ ion by thiosulfate ion in aqueous solution was determined using the recently developed laser optical–acoustic technique for sound absorption measurements. In aqueous solution the predominant complexed species is the 1:2 ion $Ag(S_2O_3)_2^{3-}$. Over the 15–230-MHz frequency range of the measurements two relaxations were observed. Both relaxations have been attributed to the stepwise mutual approach of $AgS_2O_3^-$ and $S_2O_3^{2-}$, with the elimination of coordinated water to form the 1:2 complex ion, i.e., to the second association step in the complete reaction. At 25° the specific rate constant k_3 for this association reaction is 3.5×10^9 M^{-1} sec^{-1}. The result is compared with the theoretical value assuming diffusion control, with the theoretical value for the preceding step, and with a previously published value for Ag^+ complexation by *o*-phenanthroline.

Introduction

The kinetics of metal complexation reactions in which the central metal is a univalent ion have attracted comparatively little attention[2a] until the recent appearance of a flurry of kinetic studies of alkali metal ion complexation by antibiotics, crown ethers, and related ligands.[2b] Apart from Tl^+ complexation,[3] which is a relatively slow process, the rates of univalent ion complexation reactions are very rapid requiring access to sophisticated relaxation kinetic methods. Interpreting the mechanisms of chelation processes involving multidentate ligands with multivalent ions has been the objective of the great majority of the kinetic studies of metal complexation reactions.[2a,4] Although we do not propose a systematic study of univalent ion complexation reactions, these should not be excluded entirely from such investigations.

So far as its first coordination sphere is concerned, Ag^+ is generally believed to be predominantly two-coordinate because of the sp-hybridized coordination orbitals on the ion.[4] Thus,