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Synthesis and Characterization of 8-Quinolinolato and 1,1,1-Trifluoropentane-2,4-dionato Complexes of Manganese(I)

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Reactions of manganese(I) pentacarbonyl halides with sodium quinolinolate (oxine) and thallium(I) 1,1,1-trifluoropentane-2,4-dionate (tfac) have afforded two new manganese(I) tetracarbonyl complexes, $Mn(CO)_4(oxine)$ *and* $Mn(CO)_4(tfac)$, *respectively, as yellow–orange crystalline solids. These complexes undergo facile substitution of carbon monoxide with various monodentate ligands to yield the tricarbonyls* $Mn(CO)_3L(oxine)$ *and* $Mn(CO)_3L(tfac)$ ($L = C_5H_5N$, $4\text{-}CH_3C_5H_4N$, $p\text{-}CH_3C_6H_4NH_2$, $p\text{-}FC_6H_4NH_2$, $As(C_6H_5)_3$, $P(C_6H_5)_3$, *or* $P(C_6H_{11})_3$) *and the dicarbonyls* $Mn(CO)_2L'_2(oxine)$ *and* $Mn(CO)_2L'_2(tfac)$ ($L' = P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, *or* $P(OC_6H_5)_3$). *The dicarbonyls* $Mn(CO)_2L'_2(oxine)$ *can be also obtained by reaction of* $Mn(CO)_3(C_5H_5N)(oxine)$ *with excess L′. At 25° C, the bidentate ligand 1,2-bis(diphenylphosphino)ethane (diphos) displaces two carbonyl groups from* $Mn(CO)_4(oxine)$ *to yield* $Mn(CO)_2(diphos)(oxine)$, *but there is no reaction between* $Mn(CO)_4(oxine)$ *and o-phenanthroline or 2,2′-bipyridine (bipy). The complexes* $Mn(CO)_3(C_5H_5N)_2(tfac)$ *and* $Mn(CO)_3(bipy)(tfac)$, *each containing a monodentate, carbon-bonded 1,1,1-trifluoropentane-2,4-dionato ligand, were prepared by treatment of* $Mn(CO)_3(C_5H_5N)_2Cl$ *and* $Mn(CO)_3(bipy)Cl$, *respectively, with Tl(tfac). Some spectroscopic (infrared,* ^1H *NMR, mass spectral) and chemical properties of the new complexes are presented and discussed.*

Introduction

Earlier papers from this laboratory reported the synthesis of $Mn(CO)_4(hfac)$[1] and its remarkably facile substitution reactions with several Lewis bases.[2] The observed high reactivity of this tetracarbonyl complex was ascribed to the presence of two "hard" oxygen atoms coordinated to a low-valent (+1) manganese. In an effort to extend the scope of this investigation, and especially to furnish an $Mn(CO)_4(X\text{–}L)$ system (X–L = bidentate, uninegative ligand) which is amenable to a kinetic study of replacement of the carbonyl groups by various monodentate ligands, we have now prepared two related manganese(I) complexes, $Mn(CO)_4(oxine)$[3] and $Mn(CO)_4(tfac)$.[4] Reported herein are the synthesis and characterization of these two tetracarbonyls and of their substituted tricarbonyl and dicarbonyl derivatives. In the accompanying paper[5] we describe a kinetic study of the reaction of $Mn(CO)_4(oxine)$ with several ligands L to yield $Mn(CO)_3L(oxine)$ and of $Mn(CO)_3L'(oxine)$ with L′ to afford $Mn(CO)_2L'_2(oxine)$.

Experimental

Materials and Analyses

Chemicals were obtained from the following sources: dimanganese decacarbonyl (Pressure Chemical Co.); thallium(I) carbonate and 1,2-bis(diphenylphosphino)-ethane (diphos) (Alfa Inorganics); trifluoroacetylacetone (Columbia Organic Chemicals); 8-quinolinol, triphenylstibine, 2,2′-bipyridine (bipy), tri-*n*-butylphosphite, *p*-fluoroaniline, and 1,10-phenanthroline (phen) (Matheson, Coleman and Bell); 4-picoline, *p*-toluidine, and tri-*n*-butylphosphine (Eastman Organic Chemicals); and tricyclohexylphosphine (Orgmet).

Trifluoroacetylacetone was washed twice with an equal volume of concentrated sulfuric acid and distilled immediately before use. Triphenylphosphine was recrystallized from ethanol prior to use. Other ligands were used without further purification. Reagent grade solvents were employed in the preparation of complexes. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use.

Florisil (60–100 mesh) from Fisher Scientific Co. was used as a chromatography support. Whatman (200 mesh) cellulose powder and Zeolite were employed as filtering aids.

Literature methods were used to prepare and purify $Mn(CO)_5Cl$,[6] $Mn(CO)_5Br$,[6] $Mn(CO)_3(C_5H_5N)_2Cl$,[7] $Mn(CO)_3(phen)Cl$,[7] $Mn(CO)_3(bipy)Cl$,[7] and NaC_9H_6NO.[8]

Elemental analyses were carried out by the Galbraith Laboratories, Inc., Knoxville, Tenn., and by the Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Physical Measurements

Infrared spectra were recorded using a Beckman IR–9 spectrophotometer and a Perkin–Elmer Model 337 spectrophotometer with a polystyrene film for calibration. Proton magnetic resonance spectra were measured on Varian Associates A–60 and A–60A spectrometers. Tetramethylsilane was used as an external standard. Molecular weight measurements on $CHCl_3$ solutions were made with a Mechrolab Model 301–A osmometer. Mass spectra were recorded on an A.E.I. MS 12 mass spectrometer in the laboratories of Professor J. Lewis, University College, London, England.[9]

Synthesis of New Manganese(I) Carbonyl Complexes

All of the reactions described below were performed under an atmosphere of nitrogen and the final products were vacuum-dried. Listed in Table I are reaction times, analytical data, and other synthetic information for all tricarbonyl and dicarbonyl derivatives.

Preparation of $Mn(CO)_4$(oxine)

Sodium 8-quinolinolate (3.7 g, 22 mmol) in 40 ml of THF was added to a solution of $Mn(CO)_5Br$ (6.0 g, 22 mmol) in 150 ml of THF. The mixture was stirred for 26 hr at 25° C. Precipitated NaBr was then removed by filtration and the solvent was stripped from the filtrate (25° C, 20 mm). The residue was washed with water (3 × 5 ml) and air-dried. Further purification was effected by dissolving the solid in a small volume of $CHCl_3$ and adding pentane to yield yellow–orange crystals (5.5 g, 81%), mp (dec) 168° C. *Anal.* Calcd for $C_{13}H_6MnNO_5$: C, 50.20; H, 1.94; N, 4.50. Found: C, 50.25; H, 2.21; N, 4.67.

An attempt was made to prepare $Mn(CO)_4$(oxine) by reaction of $Mn(CO)_5Br$ with 8-quinolinol. A solution of $Mn(CO)_5Br$ (2.1 g, 7.6 mmol) in 70 ml of freshly distilled CH_3CN was treated dropwise with 1.1 g (7.6 mmol) of 8-quinolinol in 120 ml of CH_3CN at 25° C. The mixture was stirred for 2 hr at 50–60° C, cooled to 25° C, and filtered. Solvent was removed from the filtrate (20° C, 20 mm) and the residue was washed with 10 ml of pentane. After several unsuccessful attempts at crystallization from CH_2Cl_2–pentane, solvent was evaporated in a stream of nitrogen to give 1.4 g of $Mn(CO)_3(C_9H_6NOH)_2Br \cdot CH_2Cl_2$ as a

TABLE I. Synthetic Procedures, Color, and Analytical Data for Derivatives of $Mn(CO)_4$(oxine) and $Mn(CO)_4$(tfac).

Complex	Reaction Time, hr[a]	Mole Ratio Complex: Ligand	Yield, %	Color	Analysis, % C Calcd	C Found	H Calcd	H Found
$Mn(CO)_3(C_5H_5N)$(oxine)[b]	2	1:3	91	yellow	56.37	56.24	3.06	3.18
$Mn(CO)_3(4\text{-}CH_3C_5H_4N)$(oxine)	2	1:4	96	yellow	57.46	57.57	3.48	3.21
$Mn(CO)_3(p\text{-}CH_3C_6H_4NH_2)$(oxine)	2	1:2.5	71	yellow	58.47	58.48	3.87	4.05
$Mn(CO)_3(p\text{-}FC_6H_4NH_2)$(oxine)	1	1:3	90	yellow	54.84	54.67	3.07	3.07
$Mn(CO)_3[P(C_6H_5)_3]$(oxine)	<1	1:1.5	95	yellow	66.07	66.19	3.88	3.77
$Mn(CO)_3[As(C_6H_5)_3]$(oxine)	1	1:2	86	yellow–orange	61.14	61.38	3.59	4.25
$Mn(CO)_3[P(C_6H_{11})_3]$(oxine)[c]	1	1:2		orange–red				
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine)	24	1:4	74	red	63.72	63.87	9.17	9.04
$Mn(CO)_2[P(OCH_3)_3]_2$(oxine)	12	1:3	85	orange–red	38.71	38.90	4.58	4.50
$Mn(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2$(oxine)	10	1:3	79	red	55.63	55.56	8.00	7.89
$Mn(CO)_2$(diphos)(oxine)	2	1:1.5	86	red	68.00	68.18	4.63	4.80
$Mn(CO)_2[P(C_6H_5)_3]_2$(oxine)[d]	48	1:20		red				
$Mn(CO)_3(C_5H_5N)$(tfac)[e]	1	1:1.5	90	yellow	42.07	41.94	2.44	2.39
$Mn(CO)_3[P(C_6H_5)_3]$(tfac)	1	1:1	72	yellow	56.33	55.88	3.45	3.40
$Mn(CO)_3[As(C_6H_5)_3]$(tfac)	2	1:1.3	64	yellow	52.22	52.37	3.20	3.31
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(tfac)	1	1:3	52	orange–red	55.68	55.72	8.74	8.80
$Mn(CO)_2[P(C_6H_5)_3]_2$(tfac)	*f*	1:2	85	orange	65.49	65.38	4.35	4.63
$Mn(CO)_3(C_5H_5N)_2$(tfac)[g]			41	yellow	48.01	47.84	3.13	3.07
$Mn(CO)_3$(bipy)(tfac)[h]			82	yellow	48.23	48.19	2.69	2.58

[a] Times listed are for reaction of the appropriate ligand with $Mn(CO)_4$(oxine) or $Mn(CO)_4$(tfac) at 25–27° C as described in Experimental; in many cases the reaction is complete in a shorter time. [b] Calcd N: 7.73. Found: 7.63. Calcd mol wt (soln): 363. Found: 373. [c] Decomposed upon attempt at isolation; characterized by infrared spectroscopy. [d] Large excess of ligand precluded isolation of analytically pure sample; characterized by infrared spectroscopy. [e] Calcd N: 3.77. Found: 3.90. Calcd mol wt (soln): 371. Found: 400. [f] See Experimental. [g] Obtained together with $Mn(CO)_3(C_5H_5N)$(tfac) using another method; see Experimental. [h] Prepared by another method; see Experimental.

glass-like substance which was washed with pentane and vacuum-dried. *Anal.* Calcd for $C_{22}H_{16}MnBrCl_2N_2O_5$: C, 44.45; H, 2.69; N, 4.71. Found: C, 44.41; H, 2.32; N, 4.74.

Preparation of $Mn(CO)_3(C_5H_5N)$(oxine) and Other $Mn(CO)_3L$(oxine) Complexes

8-Quinolinolatotetracarbonylmanganese(I) (0.15 g, 0.48 mmol) was dissolved in 25 ml of CH_2Cl_2 and to this was added pyridine (0.12 g, 1.5 mmol) in 10 ml of CH_2Cl_2. The solution was stirred for 2 hr at 27° C. Solvent and excess pyridine were removed by a stream of nitrogen. The resulting solid was recrystallized from CH_2Cl_2 by addition of pentane to yield 0.16 g (91%) of yellow crystals, mp 144° C.

Several other tricarbonyl manganese(I) oxine derivatives, $Mn(CO)_3L$(oxine), were prepared in virtually the same manner. Analytical data and synthetic details are presented in Table I.

Preparation of $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine) and Other $Mn(CO)_2L'_2$(oxine) Complexes

To a solution of 0.31 g (1.0 mmol) of $Mn(CO)_4$(oxine) in 10 ml of CH_2Cl_2 was added 0.81 g (4.0 mmol) of $P(n\text{-}C_4H_9)_3$. The mixture immediately became orange-red, deepening to dark red during stirring for 24 hr at 25° C. Solvent and excess ligand were removed under a stream of nitrogen and the resulting solid was washed with methanol and air-dried. Recrystallization from CH_2Cl_2–pentane afforded 0.49 g (74% yield) of red crystals, mp 101° C.

Listed in Table I are other $Mn(CO)_2L'_2$(oxine) complexes which were synthesized in a similar manner. Final yields were dependent upon ease of purification, *i.e.* removal of excess ligand. In all cases the reactions were followed to completion by infrared spectroscopy.

Attempted Synthesis of $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$(oxine) and $Mn(CO)_3[Sb(C_6H_5)_3]$(oxine)

Tri-*n*-butylphosphine (0.10 g, 0.50 mmol) was added to a solution of $Mn(CO)_4$(oxine) (0.15 g, 0.48 mmol) in 20 ml of $CHCl_3$ and the resultant mixture was stirred at 25° C. After 10 min the infrared spectrum showed $Mn(CO)_3[P(n\text{-}C_4H_9)_3]$(oxine) and some unreacted $Mn(CO)_4$(oxine). The solution was then stored for 12 hr, after which time only $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine) was detected by infrared spectroscopy.

A solution of $Mn(CO)_4$(oxine) (0.10 g, 0.32 mmol) and $Sb(C_6H_5)_3$ (0.43 g, 1.2 mmol) in 10 ml of $CHCl_3$ was stirred at 25° C. After 20 min the infrared spectrum indicated only a partial conversion to $Mn(CO)_3[Sb(C_6H_5)_3]$(oxine). A similar result was obtained when $Mn(CO)_4$(oxine) and $Sb(C_6H_5)_3$ were used in a 1:8 mol ratio. Attempts at separation of $Mn(CO)_3[Sb(C_6H_5)_3]$(oxine) and $Mn(CO)_4$(oxine) by chromatography on Florisil with $CHCl_3$ were unsuccessful.

Attempted Reactions of $Mn(CO)_4$(oxine) with o-Phenanthroline and 2,2'-Bipyridine

In a representative experiment $Mn(CO)_4$(oxine) (0.10 g, 0.32 mmol) and *o*-phenanthroline (0.06 g, 0.34 mmol) in 10 ml of $CHCl_3$ were stirred at 25° C for 24 hr. The infrared spectrum of this solution showed no evidence of substitution.

A similar result was obtained by using 2,2′-bipyridine in place of *o*-phenanthroline.

Reaction of $Mn(CO)_3(C_5H_5N)$(oxine) with Phosphines and Phosphites (L′)

In a typical reaction $P(OCH_3)_3$ (0.12 g, 0.97 mmol) was added to $Mn(CO)_3(C_5H_5N)$(oxine) (0.15 g, 0.41 mmol) in 30 ml of $CHCl_3$. Immediately the color changed from yellow to orange–red. The solution was stirred for 12 hr at 25° C, solvent and excess $P(OCH_3)_3$ were removed in a stream of nitrogen, and the resultant $Mn(CO)_2[P(OCH_3)_3]_2$(oxine) was recrystallized from $CHCl_3$–pentane.

Similar reactions were carried out between $Mn(CO)_3(C_5H_5N)$(oxine) and each of $P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_3$, and $P(O\text{-}n\text{-}C_4H_9)_3$ in a 1:3 mol ratio. Yields of $Mn(CO)_2L'_2$(oxine) were 70–75%.

Reaction of $Mn(CO)_3(C_5H_5N)_2Cl$ with NaC_9H_6NO

Sodium 8-quinolinolate (0.17 g, 1.0 mmol) and $Mn(CO)_3(C_5H_5N)_2Cl$ (0.33 g, 1.0 mmol) in 40 ml of THF were stirred at 50° C for 17 hr. The mixture was filtered and the solvent was removed (25° C, 20 mm) from the filtrate. The residue was recrystallized from $CHCl_3$–pentane to afford pure $Mn(CO)_3(C_5H_5N)$(oxine).

Attempted Reaction of $Mn(CO)_3$(phen)Cl with NaC_9H_6NO

A solution of $Mn(CO)_3$(phen)Cl (0.13 g, 0.5 mmol) and NaC_9H_6NO (0.08 g, 0.5 mmol) in 50 ml of THF was stirred for 12 hr at 25° C. No carbonyl complex other than unreacted $Mn(CO)_3$(phen)Cl was detected by infrared spectroscopy.

Preparation of $Mn(CO)_4$(tfac)

Thallium(I) trifluoroacetylacetonate, employed in this synthesis but as yet unreported, was prepared by the following procedure. Freshly distilled trifluoroacetylacetone (9.9 g, 64 mmol) in 15 ml of $CHCl_3$ was added to a slurry of freshly powdered thallium(I) carbonate (10 g, 21 mmol) in 10 ml of $CHCl_3$. The mixture immediately became yellow, as CO_2 was evolved. After the effervescence had subsided, the mixture was heated with stirring for 15 min at 50° C to ensure completeness of reaction. The mixture was then cooled to 25° C and filtered. Addition of pentane to the filtrate and cooling to –70° C resulted in the precipitation of pale yellow needles (13 g, 91% yield). Further purification was achieved by sublimation (45° C, 0.1 mm) or by crystallization from 1:8 CH_2

Cl_2–pentane, mp 124°C. *Anal.* Calcd for $C_5H_4TlF_3O_2$: C, 16.78; H, 1.13. Found: C, 16.72; H, 1.41.

Thallium(I) trifluoroacetylacetonate (2.3 g, 6.5 mmol) in 40 ml of $CHCl_3$ was added dropwise to 1.5 g (6.5 mmol) of $Mn(CO)_5Cl$ in 20 ml of $CHCl_3$. The mixture was stirred for 18 hr at 25°C and then filtered through a column (5 × 2 cm) of powdered cellulose to remove TlCl. The volume of the filtrate was reduced in a stream of nitrogen and the resulting solution was passed through a Florisil column (20 × 2.5 cm) packed in $CHCl_3$. The single orange band was eluted with 1 : 1 $CHCl_3$–pentane and collected under nitrogen, solvent was removed (25°C, 20 mm), and the residue was purified by sublimation (50°C, 0.1 mm). The yield of yellow–orange crystals, mp 91°C (dec), was 1.3 g (59%). *Anal.* Calcd for $C_9H_4MnF_3O_2$: C, 33.80; H, 1.3. Found: C, 33.79; H, 2.5.

Preparation of $Mn(CO)_3(C_5H_5N)$(tfac) and Other $Mn(CO)_3L$(tfac) Complexes

A solution of 1.2 g (1.5 mmol) of pyridine and 0.32 g (1.0 mmol) of $Mn(CO)_4$(tfac) in 20 ml of $CHCl_3$ was stirred for 1 hr at 25°C. Solvent and excess pyridine were removed in a stream of nitrogen. Sublimation of the residue (45°C, 0.1 mm) afforded 0.34 g (90% yield) of yellow $Mn(CO)_3(C_5H_5N)$(tfac), mp 92°C.

Other $Mn(CO)_3L$(tfac) derivatives were prepared in a similar manner (see Table I), except for purification. The complexes with $L = P(C_6H_5)_3$ and $As(C_6H_5)_3$ were crystallized from CH_2Cl_2–pentane.

Preparation of $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(tfac) and $Mn(CO)_2[P(C_6H_5)_3]_2$(tfac)

Tri-*n*-butylphosphine (0.25 g, 1.2 mmol) was added to a solution of $Mn(CO)_4$(tfac) (0.13 g, 0.41 mmol) in 8 ml of $CHCl_3$. Immediately the color changed from yellow to orange. After 1 hr of stirring at 25°C volatile materials were removed from the orange–red solution in a stream of nitrogen, and the residue was washed with methanol. The complex $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(tfac) was purified by dissolving in a minimum amount of $CHCl_3$, adding pentane, and cooling to 0°C. The yield was 0.14 g (52%).

When $P(C_6H_5)_3$ was used as the ligand in the above reaction, the formation of both $Mn(CO)_3[P(C_6H_5)_3]$(tfac) and $Mn(CO)_2[P(C_6H_5)_3]_2$(tfac) was indicated by infrared spectroscopy upon mixing the reactants. Heating the solution for 1 hr at 48°C and removal of the solvent yielded only the dicarbonyl, $Mn(CO)_2[P(C_6H_5)_3]_2$(tfac) (85%), mp 151°C (dec).

Preparation of $Mn(CO)_3(C_5H_5N)_2$(tfac) and $Mn(CO)_3$(bipy)(tfac)

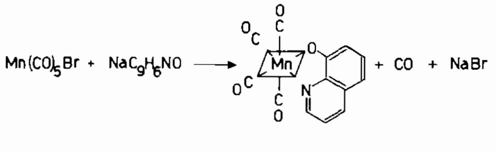
Thallium(I) trifluoroacetylacetonate (0.12 g, 0.29 mmol) in 5 ml of $CHCl_3$ was added to $Mn(CO)_3(C_5H_5N)_2Cl$ (0.10 g, 0.29 mmol) dissolved in 10 ml of CH_2Cl_2. The resulting solution was stirred for 12 hr at 25°C and then filtered through Zeolite to remove thallium(I) chloride. The filtrate was concentrated in a stream of nitrogen and pentane was added to precipitate light yellow crystals of $Mn(CO)_3(C_5H_5N)_2$(tfac). After washing with pentane (2 × 2 ml) and drying the product weighed 0.05 g (41% yield).

The mother liquor and the pentane washings were combined and stored for 24 hr at 25°C; removal of the solvent yielded $Mn(CO)_3(C_5H_5N)$(tfac), identified by infrared spectroscopy.

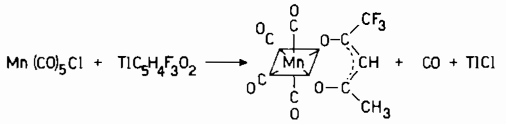
The complex $Mn(CO)_3$(bipy)(tfac) was prepared similarly, with no other carbonyl-containing product being detectable.

Results

The tetracarbonyls $Mn(CO)_4$(oxine) and $Mn(CO)_4$(tfac) were synthesized by the reactions shown in equations (1) and (2). An attempt to prepare $Mn(CO)_4$(oxine) from $Mn(CO)_5Br$ and C_9H_6NOH led to the isolation of *fac*-$Mn(CO)_3(C_9H_6NOH)_2Br$ instead. This reaction is therefore analogous to that of $Mn(CO)_5Br$ with pyridine which yields *fac*-$Mn(CO)_3(C_5H_5N)_2Br$.[7]



(1)



(2)

Both tetracarbonyl complexes are yellow–orange crystalline solids, stable for several months under refrigeration, and soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, and acetone. The compound $Mn(CO)_4$(tfac) sublimes at 45°C (0.1 mm).

The infrared spectra of $Mn(CO)_4$(oxine) and $Mn(CO)_4$(tfac) in the $\nu_{C\equiv O}$ region (see Table II) show four bands – one weak and three strong – which is consistent with the presence of a *cis*-tetracarbonyl moiety.[10] In addition, the spectrum of $Mn(CO)_4$(oxine) contains a strong absorption at 1578 cm^{-1} (KBr pellet), characteristic of the heterocyclic ring of the 8-quinolinolato group.[11,12] For $Mn(CO)_4$(tfac), additional absorptions are observed at 1615 (trifluoroacetylacetonate carbonyl stretching) and 1201 cm^{-1} (C–H in-plane bending) (KBr pellet), thus supporting a bidentate, oxygen-bonded structure.[13,14]

TABLE II. Infrared Spectral Data (cm^{-1}) for 8-Quinolinolato and Trifluoroacetylacetonato Manganese(I) Carbonyl Complexes.

Complex	Metal Carbonyl Stretches, $\nu_{C\equiv O}$ [a]	Trifluoroacetylacetonato Carbonyl Stretch[b]
$Mn(CO)_4$(oxine)	2110w, 2035s, 1931s, 1916s	
$Mn(CO)_3(C_5H_5N)$(oxine)	2030s, 1935s, 1902s	
$Mn(CO)_3(4\text{-}CH_3C_5H_4N)$(oxine)	2039s, 1951s, 1911s	
$Mn(CO)_3(p\text{-}CH_3C_6H_4NH_2)$(oxine)	2033s, 1937s, 1909s	
$Mn(CO)_3(p\text{-}FC_6H_4NH_2)$(oxine)	2036s, 1946s, 1912s	
$Mn(CO)_3[As(C_6H_5)_3]$(oxine)	2033s, 1946s, 1908s	
$Mn(CO)_3[P(C_6H_5)_3]$(oxine)	2034s, 1952s, 1912s	
$Mn(CO)_3[P(C_6H_{11})_3]$(oxine)[c]	2028s, 1940s, 1896s	
$Mn(CO)_3[P(n\text{-}C_4H_9)_3]$(oxine)[c]	2024s, 1935s, 1895s	
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine)	1910s, 1823s	
$Mn(CO)_2[P(C_6H_5)_3]_2$(oxine)	1921s, 1842s	
$Mn(CO)_2[P(OCH_3)_3]_2$(oxine)	1950s, 1865s	
$Mn(CO)_2[P(OC_6H_5)_3]_2$(oxine)	1969s, 1893s	
$Mn(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2$(oxine)	1951s, 1865s	
$Mn(CO)_2$(diphos)(oxine)	1957s, 1840s	
$Mn(CO)_4$(tfac)	2118w, 2047s, 1938s, 1930s	1615m
$Mn(CO)_3(C_5H_5N)$(tfac)	2040s, 1942s, 1920s	1616m
$Mn(CO)_3[As(C_6H_5)_3]$(tfac)	2040s, 1948s, 1920s	1615m
$Mn(CO)_3[P(C_6H_5)_3]$(tfac)	2040s, 1954s, 1916s	1616m
$Mn(CO)_2[P(C_6H_5)_3]_2$(tfac)	1943s, 1855s	1612m
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(tfac)	1919s, 1836s	1611m
$Mn(CO)_3(C_5H_5N)_2$(tfac)	2040s, 1950s, 1914s	1699s
$Mn(CO)_3$(bipy)(tfac)	2040s, 1949s, 1925s	1683s

[a] $CHCl_3$ solution. [b] KBr pellet. [c] Not isolated. Abbreviations: s, strong; m, medium; w, weak.

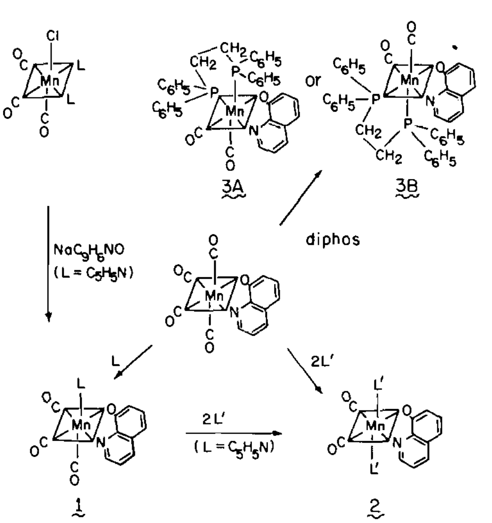
The ^1H NMR spectrum of $Mn(CO)_4$(tfac) in $CDCl_3$ solution shows resonances at τ 7.77 (rel. int. 3) and 4.12 (rel. int. 1), assigned to the CH_3 and ring CH protons, respectively. The positions of these signals are those expected for the proposed O-bonded chelate structure.[14,15] The ^1H NMR spectrum of $Mn(CO)_4$(oxine) exhibits features similar to those found in the spectrum of 8-quinolinol;[16] because of its complexity no attempts was made to employ ^1H NMR spectroscopy in the elucidation of structures of oxine-containing complexes.

The mass spectrum of $Mn(CO)_4$(tfac) shows a weak molecular ion peak at m/e 320, as well as much stronger peaks at m/e 292, 236, and 208, corresponding to sequential (except for $Mn(CO)_2(tfac)^+$) loss of the carbonyl ligands. Peaks due to $Mn(CF_2COCHCOCH_3)^+$ and $Mn(FCOCHCOCH_3)^+$ are also noted; the latter assignment is supported by the appearance of a metastable ion at m/e 120.0 ($Mn(CF_3COCHCOCH_3)^+$–CF_2). Loss of CF_2 fragments in the mass spectra of CF_3-containing organometallic compounds is not unprecedented.[17]

Whereas solutions of $Mn(CO)_4$(oxine) do not readily decompose on storage, solutions of $Mn(CO)_4$(tfac) undergo an unusual change when placed in the beam of the infrared spectrophotometer (Beckman IR–9). This change is reflected in the appearance of new $\nu_{C\equiv O}$ bands at 2009 and 1964 cm^{-1} while the initial absorptions at 1938 and 1930 cm^{-1} decrease and that at 2118 cm^{-1} increases in intensity ($CHCl_3$ solution). The change is noticeable after several minutes and may be reversed by removing the solution from the cell compartment of the spectrophotometer or by evaporating the solvent and redissolving the solid. This phenomenon is currently under further investigation.[18]

Both $Mn(CO)_4$(oxine) and $Mn(CO)_4$(tfac) undergo facile room temperature reactions with various Lewis bases to afford substituted tricarbonyl and dicarbonyl derivatives. These and other reactions leading to the formation of substituted manganese(I) 8-quinolinolato and trifluoroacetylacetonato derivatives are presented in Schemes 1 and 2, respectively.

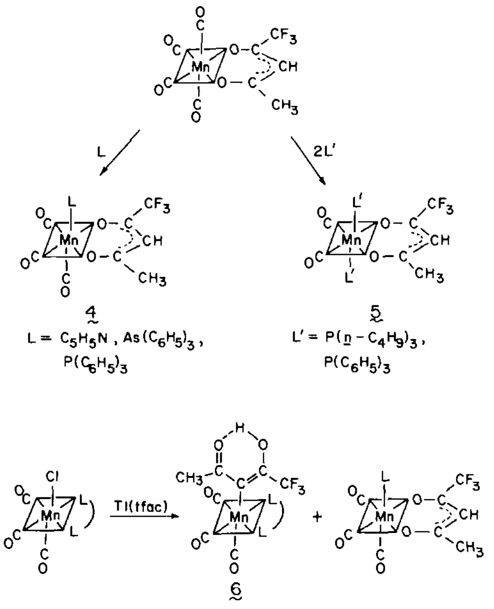
It is to be noted that *N*-donor ligands and $As(C_6H_5)_3$ (L) afford the tricarbonyls $Mn(CO)_3L$(oxine) (**1**) and $Mn(CO)_3L$(tfac) (**4**), whereas *P*-donor ligands (L′) furnish the dicarbonyls $Mn(CO)_2L'_2$(oxine) (**2**) and $Mn(CO)_2L'_2$(tfac) (**5**). Exceptions are provided by $P(C_6H_5)_3$, which affords either the dicarbonyls or the tricarbonyls depending on experimental conditions (see Experimental), and $P(C_6H_{11})_3$, which yields the tricarbonyl $Mn(CO)_3[P(C_6H_{11})_3]$(oxine). Reactions of $Mn(CO)_3(C_5H_5N)$(oxine) with an excess of L′ also provide a convenient route to $Mn(CO)_2L'_2$(oxine).



L = C$_5$H$_5$N, 4-CH$_3$C$_5$H$_4$N, p-CH$_3$C$_6$H$_4$NH$_2$, p-FC$_6$H$_4$NH$_2$, P(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$

L′ = P(n-C$_4$H$_9$)$_3$, P(C$_6$H$_5$)$_3$, P(OCH$_3$)$_3$, P(O-n-C$_4$H$_9$)$_3$

SCHEME 1



L = C$_5$H$_5$N, As(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_3$

L′ = P(n-C$_4$H$_9$)$_3$, P(C$_6$H$_5$)$_3$

L-L = bipy, phen, 2C$_5$H$_5$N

L = C$_5$H$_5$N

SCHEME 2

The substituted complexes are yellow to red crystalline solids, with the dicarbonyl derivatives being more intensely colored; *e.g.*, Mn(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$(oxine) is deep red. They are soluble in polar organic solvents such as CH$_2$Cl$_2$ or CHCl$_3$, but relatively insoluble in nonpolar solvents such as pentane and in water. The dicarbonyls are generally more soluble than the tricarbonyls. Solutions of the oxine complexes are quite stable to air at room temperature, except for Mn(CO)$_3$[P(C$_6$H$_{11}$)$_3$](oxine), which is unstable as noted in Table I. All complexes are stable in the solid under refrigeration. The tricarbonyl Mn(CO)$_3$(C$_5$H$_5$N)(tfac) can be sublimed at 45 °C (0.1 mm).

All substituted trifluoroacetylacetonato complexes obtained by partial replacement of CO in Mn(CO)$_4$(tfac) show infrared carbonyl stretching frequencies of the β-diketonato ligand in the range 1620–1610 cm^{-1}, which is normal for bidentate, O-bonded trifluoroacetylacetonates.[13,14] The infrared spectra of all tricarbonyl complexes display three strong terminal CO stretching frequencies of approximately equal intensity (Table II), thus pointing to a facial structure[19] (see **1** and **4**, Schemes 1 and 2). The dicarbonyls exhibit two $\nu_{C\equiv O}$ bands, indicating one of two structures in which the carbonyl groups are *cis*. The ^{1}H NMR spectrum of Mn(CO)$_2$[P(OCH$_3$)$_3$](oxine) in CDCl$_3$ solution shows a well-resolved 1:2:1 CH$_3$ proton triplet at τ 6.60 in which the separation of the outer peaks is 9 Hz. The appearance of these resonances as "virtually" coupled triplets strongly suggests a structure in which the two P(OCH$_3$)$_3$ ligands are trans.[20,21] Analogous structures are proposed for the other dicarbonyls Mn(CO)$_2$L′$_2$(oxine) and for Mn(CO)$_2$L′$_2$(tfac) (see **2** and **5**, Schemes 1 and 2). This disposition of ligands accords with π-bonding considerations,[2,22] since the second L′ enters a position trans to the first L′, which is a better π acceptor than each of the bidentate ligands.

The behaviour of the dicarbonyl Mn(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$(tfac) deserves comment. A freshly prepared CHCl$_3$ solution of this complex shows $\nu_{C\equiv O}$ bands at 1943 and 1855 cm^{-1}. After 40 min, three additional $\nu_{C\equiv O}$ absorptions are discernible at 2040, 1954, and 1916 cm^{-1}; they are identical with the ones recorded for the isolable tricarbonyl Mn(CO)$_3$[P(C$_6$H$_5$)$_3$](tfac). Longer storage results in an increase in intensity of the latter three bands at the expense of the former two. Similarly, the ^{1}H NMR spectrum of Mn(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$(tfac) in CDCl$_3$ solution changes with time. Originally, the CH$_3$ and CH proton signals are observed at τ 9.08 and 5.83, respectively; on storage, resonances due to Mn(CO)$_3$[P(C$_6$H$_5$)$_3$](tfac) become discernible and grow at τ 8.0 (CH$_3$) and 4.98 (CH). None of the other dicarbonyl complexes isolated manifested this kind of behavior.

Attempts at isolation of the tricarbonyls Mn(CO)$_3$L(oxine) (L = Sb(C$_6$H$_5$)$_3$ and P(*n*-C$_4$H$_9$)$_3$) from Mn(CO)$_4$(oxine) and L were unsuccessful. The reaction with L = Sb(C$_6$H$_5$)$_3$ yielded some of the desired tricarbonyl in solution; however, this product could not be isolated. Similarly, Mn(CO)$_3$[P(*n*-C$_4$H$_9$)$_3$](oxine) forms in solution upon reaction of Mn(CO)$_4$(oxine) with one equivalent of P(*n*-C$_4$H$_9$)$_3$. This tricarbonyl undergoes conversion to the isolable

$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine) upon storage in solution.

Reaction of $Mn(CO)_4$(oxine) with the bidentate $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (diphos) affords $Mn(CO)_2$(diphos)(oxine). The infrared spectrum of this complex contains two $\nu_{C\equiv O}$ absorptions to indicate that the carbonyls are *cis*. Two structures may be proposed which are compatible with this spectral datum; they are depicted in Scheme 1 (**3A** and **3B**).[23] Although structure **3A**, containing one oxine oxygen trans to a CO, appears to be the preferred arrangement of ligands on electronic grounds, we can rule out neither structure **3B** nor the possibility of a mixture of the two.

In contrast to its reaction with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, $Mn(CO)_4$(oxine) is unaffected by *o*-phenanthroline or 2,2′-bipyridine. This observed inertness may be ascribed to the apparent inability of the *N*-donor ligands to replace more than one CO in $Mn(CO)_4$(oxine) and to the reluctance of *o*-phenanthroline and 2,2′-bipyridine to bond as monodentate ligands.

In order to circumvent the above difficulties an attempt was made to synthesize $Mn(CO)_2$(phen)(oxine) by allowing $Mn(CO)_3$(phen)Cl to interact with NaC_9H_6NO. However, no reaction was observed in THF at 25°C within 12 hr. A similar experiment with $Mn(CO)_3(C_5H_5N)_2Cl$ in place of $Mn(CO)_3$(phen)Cl resulted in the replacement of the chlorine and one pyridine by the oxine to give $Mn(CO)_3(C_5H_5N)$(oxine).

In contrast to the aforementioned lack of reactivity of $Mn(CO)_3$(phen)Cl toward NaC_9H_6NO, $Mn(CO)_3$(bipy)Cl undergoes metathetical reaction with Tl(tfac) to furnish $Mn(CO)_3$(bipy)(tfac). The complex $Mn(CO)_3(C_5H_5N)_2Cl$ also reacts with Tl(tfac), to yield $Mn(CO)_3(C_5H_5N)_2$(tfac) as well as $Mn(CO)_3(C_5H_5N)$(tfac). The derivatives $Mn(CO)_3$(bipy)(tfac) and $Mn(CO)_3(C_5H_5N)_2$(tfac) are yellow solids, sparingly soluble in $CHCl_3$ and insoluble in pentane and similar nonpolar solvents. Their infrared spectra show three $\nu_{C\equiv O}$ bands of equal intensity (Table II) and a carbonyl stretching absorption of the trifluoroacetylacetonato ligand at 1699–1683 cm^{-1}. The position of the last-mentioned band is appreciably higher than that for the bidentate, *O*-bonded trifluoroacetylacetonates. From the above data, and by analogy with the corresponding hexafluoroacetylacetonato complexes $Mn(CO)_3(C_5H_5N)_2$(hfac),[2] $Mn(CO)_3$(bipy)(hfac),[24] and $Mn(CO)_3$(phen)(hfac)[24] investigated earlier,[25] structure **6**, shown in Scheme 2, is proposed for these derivatives.

Discussion

Three manganese(I) tetracarbonyl complexes of the type $Mn(CO)_4$(X–L) where both X and L are "hard" donor atoms have been now prepared and investigated with respect to ligand substitution reactions. They are $Mn(CO)_4$(hfac),[1,2] $Mn(CO)_4$(tfac), and $Mn(CO)_4$(oxine). All three undergo carbon monoxide replacement at a rate which is considerably faster than that in $Mn(CO)_5Cl$.[26] Thus the additional "hard" donor atom of $Mn(CO)_4$(X–L) markedly labilizes the coordinated carbonyl groups therein; this has been already discussed in some detail earlier.[2,27,28]

A comparison of the infrared terminal CO stretching frequencies for the three tetracarbonyl complexes reveals the order $Mn(CO)_4$(oxine) < $Mn(CO)_4$(tfac) < $Mn(CO)_4$(hfac). A strictly parallel trend is found among the substituted tricarbonyl and dicarbonyl derivatives; *e.g.*, $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(oxine) (1910, 1823 cm^{-1}) < $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(tfac) (1919, 1836 cm^{-1}) < $Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2$(hfac) (1933, 1852 cm^{-1}).[2] These variations are consistent with the ability of the 8-quinolinolato ligand to release charge to the metal more effectively than do the β-diketonates. The observed differences between trifluoroacetylacetonato and hexafluoroacetylacetonato complexes may be ascribed to their different degrees of fluorination, with the more fluorinated ligand functioning as a poorer electron donor to the manganese. Similar observations have been made for the $\nu_{C\equiv O}$ bands of $Rh(CO)_2$(X–L) containing these same bidentate ligands.[12,14]

Substitution reactions of each of $Mn(CO)_4$(hfac), $Mn(CO)_4$(tfac), and $Mn(CO)_4$(oxine) furnish derivatives whose composition depends on the entering ligand. Thus *N*-donor, amine ligands, as well as $As(C_6H_5)_3$ and $P(C_6H_{11})_3$, all give the tricarbonyls; in contrast, tertiary phosphines and phosphites yield the dicarbonyls. The only ligand which manifests observable differences in its behavior toward the three tetracarbonyls is triphenylphosphine. With $Mn(CO)_4$(oxine), it yields $Mn(CO)_3[P(C_6H_5)_3]$(oxine) and, more slowly when present in large excess, $Mn(CO)_2[P(C_6H_5)_3]_2$(oxine), both compounds being isolable and stable in solution. With $Mn(CO)_4$(tfac), it affords both $Mn(CO)_3[P(C_6H_5)_3]$(tfac) and $Mn(CO)_2[P(C_6H_5)_3]_2$(tfac), the formation of the latter complex requiring higher temperatures. Both products can be isolated, with the dicarbonyl converting to the tricarbonyl in solution in the absence of triphenylphosphine. Reactions of $Mn(CO)_4$(hfac) with $P(C_6H_5)_3$ lead to the isolation of $Mn(CO)_2[P(C_6H_5)_3]_2$(hfac) only; in solution this complex gradually changes to the tricarbonyl which, however, could not be isolated.[2]

The foregoing observations indicate that these triphenylphosphine-containing dicarbonyls are generally more stable in the solid than in solution. Furthermore, the relative stability of the dicarbonyl with respect to the corresponding tricarbonyl increases as a function of the bidentate ligand X–L in the order oxine < tfac < hfac. Since the electron withdrawing ability of X–L increases in this same order, and since steric effects are expected to be neither different nor dominant, it appears that the above trend is governed by electronic factors.

The difference in the observed limit to substitution of CO in $Mn(CO)_4(X–L)$ by the *N*-donor and *P*-donor ligands is of considerable interest. The formation of the dicarbonyls with the latter ligands indicates that the phosphorus, unlike the amine nitrogen, labilizes the CO *trans* to it. This labilization may result either from the π-acceptor ability of phosphorus to weaken the Mn=CO bond, or from strong σ-electron release by phosphorus to weaken the Mn–CO σ bond, or from both. Additionally, a much better π-acceptor ability of the *P*-donor ligands as compared to the *N*-donor ligands is expected to influence Lewis acidity of the metal.[22] The metal will be a better acid, and hence more susceptible to further substitution, in the phosphine and phosphite complexes than in the amine complexes. We cannot readily differentiate among these various possible explanations.

Finally, it is noteworthy that the two acetylacetonato ligands tfac and hfac can bond to the manganese in a monodentate fashion, whereas oxine does not appear to do so. This behavior is quite strikingly illustrated by the metathetical reactions of $Mn(CO)_3(C_5H_5N)_2Cl$ with each of Tl(hfac),[2] Tl(tfac), and NaC_9H_6NO. The β-diketonates yield $Mn(CO)_3(C_5H_5N)_2(hfac)$ and $Mn(CO)_3(C_5H_5N)_2(tfac)$ in which the acetylacetonato groups are monodentate, in addition to $Mn(CO)_3(C_5H_5N)(hfac)$ and $Mn(CO)_3(C_5H_5N)(tfac)$ containing bidentate, *O*-bonded hexafluoroacetylacetonate and trifluoroacetylacetonate, respectively. In contrast, NaC_9H_6NO furnishes only $Mn(CO)_3(C_5H_5N)(oxine)$ in which the oxine is bidentate. As a further illustration of this behavior, $Mn(CO)_3(L–L)Cl$ (L–L = phen or bipy) reacts with Tl(hfac) and Tl(tfac) to afford the complexes $Mn(CO)_3(L–L)(hfac)$[2] and $Mn(CO)_3(L–L)(tfac)$, respectively, which similarly contain monodentate β-diketonato groups. However, no reaction was observed between $Mn(CO)_3(phen)Cl$ and NaC_9H_6NO.

The above-described behavior is actually not unexpected. Monodentate coordination of acetylacetonates to metals is well documented, and examples have been reported of rearrangements from a bidentate to a monodentate structure for these ligands.[14,29,30] In contrast, as far as we know, the 8-quinolinolato ion coordinates only in a bidentate fashion.[31]

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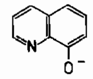
3 *Oxine* stands for 8-quinolinolate, 

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