these compounds are similar stereochemically containing, besides the π-cyclopentadienyl ligand, four monodentate ligands of three different types. In both compounds one isomer exhibits a singlet π-cyclopentadienyl resonance and the other isomer a doublet (J = 3 cps) π-cyclopentadienyl resonance. In the latter case the doublet arises by coupling of the ^{31}P nucleus ($I = {}^1/_2$) of the tricovalent phosphorus ligand with the π-cyclopentadienyl protons.

The complex obtained from $[C_5H_5Mo(NO)I_2]_2$ and 2,2′-bipyridyl is different from the other $C_5H_5Mo(NO)I_2L$ complexes in being completely insoluble in organic solvents including acetone and dichloromethane. This insolubility suggests that this dipyridyl compound, although possessing the composition $C_5H_5Mo(NO)I_2L$, has a different structure. The most likely possibility may be an ionic formulation VI analogous to the ionic compound $[C_5H_5CoIN_2C_{10}H_8]I$ obtained from $C_5H_5Co(CO)I_2$ and 2,2′-bipyridyl.[9,10]

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1,1,1,5,5,5-Hexafluoropentane-2,4-dionato Complexes of Manganese(I) Containing Various Monodentate Ligands[1]

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1,1,1,5,5,5-Hexafluoropentane-2,4-dionatotetracarbonylmanganese(I) reacts readily with several phosphites and tertiary phosphines (L) to yield the dicarbonyl derivatives $Mn(CO)_2L_2(CF_3C(O)CHC(O)CF_3)$. It is inferred from the infrared and proton magnetic resonance spectra that the carbonyl groups are *cis* and the phosphorus-containing ligands are *trans* in these complexes. With L being pyridine, 4-methylpyridine, triphenylarsine, and tricyclohexylphosphine, only the tricarbonyls *cis*-$Mn(CO)_3L(CF_3C(O)CHC(O)CF_3)$ are obtained. No substitution is effected by diethyl sulfide, thiourea, and triphenylstibine. These replacement reactions are discussed in terms of π bonding, base strength, and steric requirements of the ligands, both entering and those already present in the complex. Several of the above compounds, plus the unusual pyridine tricarbonyl $Mn(CO)_3(C_5H_5N)_2(CF_3C(O)C{=}C(OH)CF_3)$, can be prepared by the interaction of $Mn(CO)_3L_2Cl$ or $Mn(CO)_4LCl$ with thallium(I) 1,1,1,5,5,5-hexafluoropentane-2,4-dionate. The metal carbonyl stretching frequencies and the chemical shifts of the ring proton in various derivatives are tabulated and discussed. The latter appear to depend, *inter alia*, on the basicity of L and on the presence of phenyl groups attached to the phosphorus-donor atoms.

Introduction

The synthesis of hexafluoroacetylacetonatotetracarbonylmanganese(I), $Mn(CO)_4(hfac)$, was reported recently.[2] This complex represents the first example of a neutral manganese(I) tetracarbonyl which contains two "hard"[3] donor atoms coordinated to the metal. All previous attempts at the preparation of such derivatives had been unsuccessful; for example, $Mn(CO)_5Cl$ reacts rapidly with a number of organic amines to yield compounds of the type *cis*-$Mn(CO)_3L_2Cl$ (L = amine), no $Mn(CO)_4LCl$ having been detected.[4]

The presence of two equivalent "hard" oxygens in conjunction with the "soft" carbonyls in $Mn(CO)_4(hfac)$ raises an interesting question with regard to the ease of replacement of the CO's by various monodentate ligands as well as to the composition and the stereochemistry of the resultant derivatives.

To elucidate this problem a study was undertaken on reactions of $Mn(CO)_4(hfac)$ with several nucleophiles having phosphorus, nitrogen, sulfur, arsenic, or antimony as the donor atom. Reported here are the results of this investigation.

Experimental Section

Materials.—Trimethyl phosphite, tri-*n*-butyl phosphite, triphenyl phosphite, triphenylstibine, thiourea, and diethyl sulfide were purchased from Matheson Coleman and Bell, whereas triphenylarsine and 4-methylpyridine were obtained from Eastman Organic Chemicals. They were not purified further. Triphenylphosphine and tri-*n*-butylphosphine were supplied by Metal and Thermit Co. The former was recrystallized from ethanol. 1,1,1,5,5,5-Hexafluoropentane-2,4-dione was obtained from Columbia Organic Chemicals Co. It was washed with twice its volume of concentrated sulfuric acid and distilled immediately before use. The phosphines $P(C_6H_5)(CH_3)_2$ and $P(C_6H_5)_2(CH_3)$ were prepared as described in the literature.[5] Tricyclohexylphosphine was a gift from Professor F. Basolo of Northwestern University. Other chemicals and solvents used were reagent grade, except low-boiling (30–60°) petroleum ether and hexane. Woelm alumina (neutral), Florisil (60–100 mesh), and cellulose powder (Whatman, 200 mesh) were employed in chromatographic separations and/or purifications.

The complexes $Mn(CO)_4[P(C_6H_5)_3]Cl$ and $Mn(CO)_4[As-$

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[1] Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug–Sept 1965.

[2] M. Kilner and A. Wojcicki, *Inorg. Chem.*, **4**, 591 (1965). The anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione will be referred to henceforth as hexafluoroacetylacetonate (hfac).

[3] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[4] R. J. Angelici and F. Basolo, *ibid.*, **84**, 2495 (1962).

[5] J. Meisenheimer, *et al.*, *Ann.*, **449**, 213 (1926).

TABLE I

SYNTHETIC PROCEDURES, REACTION TIMES, COLOR, MELTING POINTS, AND ANALYTICAL DATA FOR HEXAFLUOROACETYLACETONATO MANGANESE(I) CARBONYL COMPLEXES

					Analyses, %							
					Calcd				Found			
Complex	Synthetic procedure[a]	Reaction time, hr	Color	Mp, °C[b]	C	H	P, N, or As	F	C	H	P, N, or As	F
$Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$	A, B, B′	8	Red-brown	159	61.29	3.71	P, 7.35	13.53	61.46	4.05	P, 7.23	13.75
$Mn(CO)_2[P(C_6H_5)_2(CH_3)]_2(hfac)$	A	3	Red-brown	120	55.17	3.79	P, 8.62		55.02	3.84	P, 8.71	
$Mn(CO)_2[P(C_6H_5)(CH_3)_2]_2(hfac)$[c]	A	6	Red-brown	115	46.48	3.90	P, 10.42		46.47	3.63	P, 10.22	
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2(hfac)$	A	3	Red-brown	72	51.52	7.67	P, 8.57	15.78	51.66	7.83	P, 8.49	16.11
$Mn(CO)_2[P(OCH_3)_3]_2(hfac)$	A	14	Purple	40	27.58	3.38	P, 10.94		27.80	3.49	P, 10.59	
$Mn(CO)_2[P(OC_6H_5)_3]_2(hfac)$	A	5	Orange	90	55.02	3.33	P, 6.60		54.90	3.47	P, 6.68	
$Mn(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2(hfac)$[d]	A	20	Orange									
$Mn(CO)_3[P(C_6H_{11})_3](hfac)$	B′	5	Red-brown	128	49.85	5.47	P, 4.94		49.71	5.89	P, 5.21	
$Mn(CO)_3[As(C_6H_5)_3](hfac)$	A, B′	13	Orange	64	47.88	2.47	As, 11.49		47.99	2.48	As, 11.25	
$Mn(CO)_3(C_5H_5N)(hfac)$	A, B[e]	12	Orange	51	36.73	1.42	N, 3.29	26.88	37.05	1.81	N, 3.26	26.68
$Mn(CO)_3(4\text{-}CH_3C_5H_4N)(hfac)$	A	16	Orange	75	38.29	1.84	N, 3.19		38.34	1.80	N, 3.26	

[a] Procedure A = $Mn(CO)_4(hfac)$ + ligand; B = $Mn(CO)_3L_2Cl + Tl(hfac)$; B′ = $Mn(CO)_4LCl + Tl(hfac)$. [b] Determined with a melting-point block and uncorrected. [c] Calculated molecular weight, 594; found, 560. Molar conductivity of a freshly prepared CH_3NO_2 solution = 0.265 $ohm^{-1}\ cm^2$. [d] Obtained as an oil which could not be induced to crystallize; characterized by infrared spectroscopy. [e] Obtained along with the compound $Mn(CO)_3(C_5H_5N)_2(hfac)$; see the Experimental Section.

$(C_6H_5)_3]Cl$ were prepared as described by Angelici and Basolo,[4] whereas *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Cl$ and *cis*-$Mn(CO)_3(C_5H_5N)_2Cl$ were synthesized according to Farona and Wojcicki.[6] The derivative $Mn(CO)_4[P(C_6H_{11})_3]Cl$ was prepared as follows. Chloropentacarbonylmanganese(I) (0.23 g, 1 mmole) and tricyclohexylphosphine (0.28 g, 1 mmole) in chloroform (20 ml) were allowed to react for 15 hr at 27°. The mixture was then filtered and the volume of the filtrate reduced to 4 ml in a stream of nitrogen. Addition of hexane (10 ml) followed by cooling to *ca.* −70° afforded a yellow solid, which was collected on a filter. Recrystallization from a 1:8 (by volume) chloroform–hexane mixture yielded 0.43 g (*ca.* 88%) of the pure product (mp 115°). *Anal.* Calcd for $C_{22}H_{33}O_4PClMn$: C, 54.61; H, 6.82. Found: C, 54.93; H, 7.06. Metal carbonyl stretching frequencies were observed at 2088 (s), 2004 (s), and 1950 (m) cm^{-1} ($CHCl_3$ solution).

The hitherto unreported thallium(I) hexafluoroacetylacetonate was synthesized by the following procedure. Freshly distilled hexafluoroacetylacetone (13.4 g, 0.064 mole) in 15 ml of chloroform was added to a slurry of 10.0 g (0.021 mole) of finely powdered thallium(I) carbonate (Alfa Inorganics) in 10 ml of $CHCl_3$. Evolution of carbon dioxide commenced immediately as the solution turned from colorless to yellow. When the effervescence had subsided, the mixture was heated with stirring at 50° for 15 min. After filtration, petroleum ether (25 ml) was added to the solution. Cooling to *ca.* −70° caused the product to separate as pale yellow needles and platelets. Further purification was effected by sublimation at 45° (~0.1 mm) to give 7.4 g (86%) of the hexafluoroacetylacetonate (mp 119°). *Anal.* Calcd for $TlC_5HF_6O_2$: C, 14.60; H, 0.24; F, 27.71. Found: C, 14.71; H, 0.25; F, 27.68.

Hexafluoroacetylacetonatotetracarbonylmanganese(I) was prepared in much better yields than reported previously[2] by the following procedure. Thallium(I) hexafluoroacetylacetonate (1.90 g, 4.7 mmoles) in 20 ml of chloroform was added dropwise to a solution of 1.29 g (4.7 mmoles) of $Mn(CO)_5Br$[7] in 30 ml of chloroform at 25° and under nitrogen. The mixture was stirred for 4 hr at 25°, and then for 15 min at 50°. Finely dispersed thallium(I) bromide was removed by passing the mixture through a powdered cellulose column (2.5 × 5 cm). The resulting orange solution was concentrated to 15–20 ml in a stream of nitrogen and then chromatographed on a Florisil column (2.5 × 25 cm). A single orange band was eluted with benzene–chloroform (1:1 mixture by volume) and collected under nitrogen. After removal of the solvent at 25° (~20 mm) the residue was purified by sublimation at 55° (~0.1 mm). The yield was 1.1 g (62%).

Synthesis of Substituted Hexafluoroactylacetonatomanganese(I) Carbonyl Complexes. $Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$. (a) **From $Mn(CO)_4(hfac)$ and Triphenylphosphine.**—Triphenylphosphine (0.47 g, 1.8 mmoles) in 10 ml of chloroform was added to a solution of $Mn(CO)_4(hfac)$ (0.32 g, 0.86 mmole) in 25 ml of $CHCl_3$ at 30° and under nitrogen. During the initial hour of reaction the color of the solution changed from light orange to deep red. After 8 hr the solvent was removed at 25° (~20 mm) to leave a red oil, which solidified upon cooling to *ca.* −78°. The red-brown solid was then recrystallized from a 1:3 (by volume) chloroform–petroleum ether mixture to give 0.61 g (84% yield) of the product. The analytical data are given in Table I.

When equimolar quantities of $Mn(CO)_4(hfac)$ and triphenylphosphine were allowed to react under similar conditions and then the mixture was chromatographed on grade IV alumina (2.5 × 30 cm column) using benzene eluent, only the dicarbonyl product could be isolated (*ca.* 40% yield).

(b) **From *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Cl$ and Tl(hfac).**—Thallium(I) hexafluoroacetylacetonate (0.15 g, 0.37 mmole) in chloroform (10 ml) was added dropwise to a solution of *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Cl$ (0.24 g, 0.36 mmole) in chloroform (10 ml). A white precipitate formed immediately. After the reaction had proceeded for 8 hr at 30° under nitrogen, the insoluble material was removed by passing the mixture through a small column (2.5 × 5 cm) of cellulose powder. Solvent was then evaporated at 27° (~20 mm), and 0.27 g (89% yield) of the dicarbonyl was isolated in the manner described in part a.

This derivative also can be synthesized from $Mn(CO)_4[P(C_6H_5)_3]Cl$ and Tl(hfac) under the experimental conditions similar to those described above. Chromatography on a grade IV alumina column (2.5 × 30 cm) with benzene eluent, followed by removal of the solvent, affords *ca.* 40% yields of the dicarbonyl.

Other Complexes.—The other hexafluoroacetylacetonato complexes were prepared by analogous methods. Synthetic procedures, reaction times, some physical properties, and analytical data are summarized in Table I. In several cases, it was demonstrated (infrared spectroscopy) that substitution reaches virtual completion in much less than 1 hr; however, solutions were allowed to stand for the periods listed in the table before isolation of the products.

Attempts to prepare the hexafluoroacetylacetonatodicarbonyl derivatives with pyridine and tricyclohexylphosphine were unsuccessful. Refluxing a solution of $Mn(CO)_3(C_5H_5N)(hfac)$ and excess pyridine in chloroform for 10 hr under nitrogen afforded only the starting materials. When a chloroform solution (8 ml) of $Mn(CO)_4(hfac)$ (0.05 g, 0.1 mmole) and tricyclohexylphosphine (0.06 g, 0.2 mmole) was kept at 45° for 15 hr under nitrogen, the original deep red color gradually changed to light yellow. Evaporation of the solvent in a stream of nitrogen yielded $Mn(CO)_4[P(C_6H_{11})_3]Cl$, identified by infrared spectroscopy, and a

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[6] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 1402 (1965).

[7] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

white, noncarbonyl solid which was shown to contain $Mn(hfac)_2 \cdot 2H_2O$ (infrared spectrum[8]).

In another attempt, thallium(I) hexafluoroacetylacetonate (0.60 g, 1.5 mmoles) in chloroform (15 ml) was added slowly to a solution of $Mn(CO)_3(C_5H_5N)_2Cl$ (0.50 g, 1.5 mmoles), also in $CHCl_3$ (20 ml). The reaction mixture was allowed to stand for 4 hr at 30° under nitrogen; then the volume of the solution was reduced to 20 ml at 25° (~20 mm), and the insoluble material was removed as described previously (*vide supra*). Addition of hexane (25 ml) to the clear filtrate afforded light yellow crystals, which were collected on a filter and washed with two 2-ml portions of hexane. The yield was 0.30 g (40%). *Anal.* Calcd for $C_{15}H_{11}O_5N_2F_6Mn$: C, 42.87; H, 2.20; N, 5.55; mol wt, 504. Found: C, 43.19; H, 2.36; N, 5.83; mol wt, 471. The compound decomposes at 153°. Its infrared spectrum exhibits metal carbonyl stretching frequencies at 2041 (s), 1955 (s), and 1919 (s) cm^{-1} ($CHCl_3$ solution); the ketonic carbonyl stretching frequency at 1701 (s) cm^{-1} (KBr pellet); other bands at ~3250 (m, br) cm^{-1} (hexachlorobutadiene mull), 3042 (m), 2990 (w), 2420 (w), 1615 (m), 1545 (m), 1497 (m), 1455 (m), 1426 (m), 1257 (w), 1230 (s), 1155 (s), 1079 (m), 1053 (w), 945 (w), 855 (m), 707 (m), 690 (s), 640 (m), and 533 (w) cm^{-1} (KBr pellet).

The filtrate and the hexane washings were combined and stored for 6–8 hr. The solvent was then removed in a stream of nitrogen, and the residue was sublimed at 45° (0.1 mm) to give 0.26 g (39%) of $Mn(CO)_3(C_5H_5N)(hfac)$.

Attempted Synthesis of Triphenylstibine, Thiourea, and Diethyl Sulfide Complexes.—After triphenylstibine (0.27 g, 0.77 mmole) and $Mn(CO)_4(hfac)$ (0.26 g, 0.69 mmole) in chloroform (25 ml) had been allowed to stand for 15 hr at 27°, only the unreacted materials were detected by infrared spectroscopy. Refluxing $Mn(CO)_4(hfac)$ and a twofold excess of $Sb(C_6H_5)_3$ in $CHCl_3$ for 24 hr under nitrogen yielded a yellow solid which was shown (infrared spectrum) not to contain any carbonyl groups.

Neither thiourea nor diethyl sulfide reacted with $Mn(CO)_4(hfac)$ in $CHCl_3$ in 12 and 72 hr, respectively, at 27°.

Infrared Spectral Examination of the Reaction of $Mn(CO)_4(hfac)$ with $P(n\text{-}C_4H_9)_3$ and $P(C_6H_{11})_3$.—A chloroform solution of freshly sublimed $Mn(CO)_4(hfac)$ was added to $P(n\text{-}C_4H_9)_3$, also in chloroform, in an approximate molar ratio of 1:3. The infrared spectra of the mixture were then recorded in the metal carbonyl stretching region at frequent time intervals and at 25°. The first spectrum, taken about 30 sec after mixing of the reagents, showed bands at 2042 (m), 1961 (m), 1933 (vs), and 1852 (s) cm^{-1}. After 5 min, only the absorptions at 1933 (vs) and 1852 (vs) cm^{-1} were discernible.

Examination of the spectrum of a mixture of $Mn(CO)_4(hfac)$ and $P(C_6H_{11})_3$ (1:4 molar ratio) in $CHCl_3$ in the metal carbonyl stretching frequency region about 45 sec after commencement of the reaction at 25° revealed bands at 2038 (vs), 1956 (vs), and 1925 (vs) cm^{-1}. This spectrum did not change with time.

Properties of the Complexes.—The phosphine and phosphite derivatives, except $Mn(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2(hfac)$, which could not be induced to crystallize, are obtained as well-defined orange, purple, or red-brown plates and needles. They are very soluble in a wide range of organic solvents. The solids exhibit considerable stability, but solutions of the complexes in chloroform decompose slowly when exposed to air.

The compounds $Mn(CO)_3(C_5H_5N)(hfac)$ and $Mn(CO)_3(4\text{-}CH_3C_5H_4N)(hfac)$, which can be sublimed at 45° (0.1 mm), are slightly less soluble in organic solvents than the phosphine and phosphite derivatives. The arsine complex has similar solubility properties, whereas $Mn(CO)_3(C_5H_5N)_2(hfac)$ is insoluble in hydrocarbons and only slightly soluble in chloroform. All of these compounds are air stable.

Solutions of $Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$ exhibit a very striking behavior as evidenced by infrared spectral measurements. A freshly prepared solution of the dicarbonyl in $CHCl_3$ shows two intense metal carbonyl stretching frequencies (1947 and 1870 cm^{-1}). On storage (*ca.* 8 min), there appear new bands at 2047 and 1970 cm^{-1} and a shoulder at 1938 cm^{-1}, and the intensities of the original two absorptions decrease. After 3.5 hr the metal carbonyl region of the spectrum consists of four bands: 2047 (m), 1970 (m), 1938 (m), and 1870 (w) cm^{-1}. Evaporation of the solvent at this time yields a red-brown solid (carbonyl bands at 1947 and 1870 cm^{-1}) and a white material which contains the complex $Mn(hfac)_2 \cdot 2H_2O$ (infrared spectrum[8]). Cyclohexane and hexane solutions of the dicarbonyl exhibit the same behavior, but samples of the pure solid remain unchanged after a storage period of 6–8 months.

None of the other derivatives behaved in this manner.

Reaction of $Mn(CO)_3(C_5H_5N)(hfac)$ with Phosphines and Phosphites.—In a typical experiment, to 0.33 g (1 mmole) of $Mn(CO)_3(C_5H_5N)(hfac)$ in 10 ml of chloroform, a solution of the phosphine (2 mmoles) in $CHCl_3$ (10 ml) was added dropwise and under nitrogen at 25°. The initial orange color changed to deep red within a few minutes. After 3 hr the solvent was evaporated, 5–10 ml of absolute ethanol was added to the remaining red oil, and the mixture was allowed to stand for 1–2 hr. The solid which had formed was then collected on a filter, recrystallized from hexane, and identified by infrared spectroscopy as $Mn(CO)_2(PR_3)_2(hfac)$. The yield ranged from 60 to 80% with $P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$, $P(C_6H_5)(CH_3)_2$, $P(n\text{-}C_4H_9)_3$, and $P(OCH_3)_3$.

When tricyclohexylphosphine was employed, only the tricarbonyl, $Mn(CO)_3[P(C_6H_{11})_3](hfac)$, could be isolated.

Infrared Spectra.—Spectra were recorded on a Beckman Model IR-9 spectrophotometer. Solutions were placed in a 0.05-mm KBr cell, a matched reference cell being used at all times. Solids were examined as KBr pellets and hexachlorobutadiene mulls.

Proton Magnetic Resonance Spectra.—Nmr spectra were obtained using a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an external standard.

Electrical Conductivity.—Measurements were made on *ca.* 10^{-3} *M* nitromethane solutions using an Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes.

Molecular Weights.—Measurements were made on 1×10^{-2} to 2×10^{-2} *M* chloroform solutions with a Mechrolab Model 301-A osmometer.

Analyses.—Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Results

Two types of derivatives of $Mn(CO)_4(hfac)$ were prepared in this study: the tricarbonyls $Mn(CO)_3L(hfac)$ and the dicarbonyls $Mn(CO)_2L_2(hfac)$. The former complexes result when L is pyridine, 4-methylpyridine, triphenylarsine, and tricyclohexylphosphine; the latter are formed with L being triphenylphosphine, diphenylmethylphosphine, phenyldimethylphosphine, tri-*n*-butylphosphine, trimethyl phosphite, tri-*n*-butyl phosphite, and triphenyl phosphite. In all of these compounds the hexafluoroacetylacetonate ligand coordinates to the metal through both of its oxygens, as is evidenced by the values of the ketonic carbonyl stretching frequencies, listed in Table II.[8]

There are two possible structures for the tricarbonyls. In one, all three carbonyl groups are *cis;* in the other, two CO's are *trans* and the third is *cis* to the first two. The presence of three metal carbonyl stretching bands of strong intensity in the spectra of these complexes (Table II) lends support to the former structure (Figure 1).[9]

The dicarbonyls exhibit two strong absorptions in the

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[8] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

[9] For a thorough discussion of infrared carbonyl stretching frequencies of such complexes see F. A. Cotton, *ibid.*, **3**, 702 (1964).

TABLE II

INFRARED SPECTRA OF HEXAFLUOROACETYLACETONATO MANGANESE(I) CARBONYL COMPLEXES (CM^{-1})

Complex	Metal carbonyl stretches[a]	Hexafluoroacetylacetonato carbonyl stretch[b]	Other bands[b]
$Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$	1947 s, 1870 s	1617 m	1505 w, 1482 m, 1470 m, 1434 m, 1345 w, 1256 s, 1204 s, 1143 s, 1092 m, 1030 w, 1000 w, 951 w, 781 w, 743 m, 695 m, 675 sh, 618 w, 560 w, 518 s
$Mn(CO)_2[P(C_6H_5)_2(CH_3)]_2(hfac)$	1944 s, 1868 s	1616 m	3070 w, 3030 m, 1655 w, 1509 w, 1487 m, 1437 m, 1345 w, 1258 s, 1225 s, 1150 s, 886 m, 699 m, 680 w, 627 w, 565 w, 509 m
$Mn(CO)_2[P(C_6H_5)(CH_3)_2]_2(hfac)$	1939 s, 1869 s	1616 m	3068 m, 3029 w, 1650 w, 1508 w, 1487 m, 1437 m, 1342 w, 1258 s, 1226 s, 1145 s, 884 m, 698 m, 680 w, 627 w, 564 w, 507 m, 436 w
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2(hfac)$	1933 s, 1852 s	1618 m	3025 w, 2965 m, 2935 m, 2875 w, 1650 w, 1510 m, 1466 w, 1342 m, 1259 s, 1225 s, 1149 s, 1105 w, 1095 w, 680 m, 630 m, 570 m
$Mn(CO)_2[P(OCH_3)_3]_2(hfac)$	1970 s, 1893 s	1624 m	3084 m, 3056 m, 3020 m, 2970 m, 1599 s, 1550 w, 1496 s, 1460 m, 1355 w, 1264 s, 1200 s, 1170 s, 1115 s, 1078 m, 1012 w, 965 m, 920 s, 870 s, 830 w, 725 m, 700 s, 634 m, 600 m, 570 m, 505 m
$Mn(CO)_2[P(OC_6H_5)_3]_2(hfac)$	1985 s, 1911 s	1623 m	3083 w, 1590 s, 1488 s, 1475 sh, 1455 w, 1349 w, 1257 s, 1200 s, 1160 m, 1149 m, 1109 w, 1072 w, 1025 m, 1005 w, 915 s, 898 sh, 690 m, 678 w, 625 w, 593 w, 500 w
$Mn(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2(hfac)$[c]	1963 s, 1885 s		
$Mn(CO)_3[P(C_6H_{11})_3](hfac)$	2038 s, 1956 s, 1925 s	1635 m	3020 w, 2935 s, 2860 m, 1656 m, 1510 m, 1482 m, 1450 m, 1350 w, 1260 s, 1151 s, 1112 s, 1009 w, 890 w, 854 w, 680 m, 641 w, 550 w
$Mn(CO)_3[As(C_6H_5)_3](hfac)$	2045 s, 1968 s, 1938 s	1622 m	3050 sh, 3012 s, 1580 w, 1570 w, 1545 m, 1480 m, 1432 m, 1415 s, 1347 w, 1255 s, 1220 s, 1152 s, 1145 s, 1106 m, 1074 m, 1021 w, 995 w, 926 w, 845 w, 780 s, 750 s, 692 s, 632 w, 610 w, 595 w, 530 w, 470 m
$Mn(CO)_3(C_5H_5N)(hfac)$	2048 s, 1962 s, 1937 s	1626 m	1629 m, 1602 m, 1546 m, 1528 w, 1485 w, 1459 s 1440 s, 1350 m, 1260 s, 1218 s, 1142 s, 1105 w, 1063 m, 800 s, 761 s, 697 m, 680 s, 649 w, 633 m, 620 s, 594 m, 530 m, 515 w, 463 w, 440 w
$Mn(CO)_3(4\text{-}CH_3C_5H_4N)(hfac)$	2047 s, 1961 s, 1939 s	1630 m	3036 w, 1600 m, 1551 m, 1514 w, 1506 m, 1479 m, 1433 w, 1378 w, 1351 m, 1336 w, 1262 s, 1245 w, 1205 s, 1159 m, 1150 s, 1103 m, 1067 w, 1030 w, 954 w, 811 s, 801 s, 744 w, 724 w, 681 s, 639 m, 626 m, 598 m, 525 m, 492 m, 465 w
$Mn(CO)_3[P(C_6H_5)_3](hfac)$[d]	2047 s, 1970 s, 1938 s		
$Mn(CO)_3[P(n\text{-}C_4H_9)_3](hfac)$[e]	2042 s, 1961 s, 1933 s		

[a] Chloroform solution. [b] KBr pellet. [c] The compound could not be isolated as a solid. [d] The compound appears to be stable only in solution; see the Experimental Section. [e] The compound was not isolated. The absorption bands listed were detected by examining the spectra of solutions containing $Mn(CO)_4(hfac)$ and the phosphine; see the Experimental Section. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

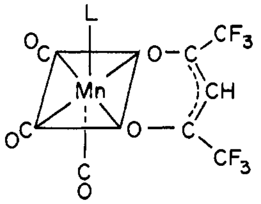

Figure 1.—The structure of $Mn(CO)_3L(hfac)$.

metal carbonyl stretching frequency region, which is consistent with the CO's occupying *cis* positions. The nuclear magnetic resonance spectra of the $P(C_6H_5)(CH_3)_2$, $P(C_6H_5)_2(CH_3)$, and $P(OCH_3)_3$ derivatives show resonances due to the methyl protons as approximate 1:2:1 triplets (Table III), indicating strong coupling of the phosphorus atoms and suggesting *trans* positions for the phosphines and phosphites.[10] All of these data support the structure given in Figure 2 for the three complexes. The same arrangement of ligands is assumed to be present also in the other dicarbonyls.[11]

Attempts to obtain the dicarbonyl complexes containing two tricyclohexylphosphines or pyridines proved unsuccessful. When $Mn(CO)_4(hfac)$ and $P(C_6H_{11})_3$ are allowed to react in chloroform at 45° for 15 hr, the only carbonyl-containing product isolated is Mn-

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[10] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

[11] The only alternative structure (since CO's must be *cis*) involves two L's in *cis* positions. This arrangement of ligands is very unlikely for both steric (when L is $P(C_6H_5)_3$ or $P(OC_6H_5)_3$) and electronic (since now only one CO is *trans* to "hard" oxygen) reasons.

TABLE III

PROTON MAGNETIC RESONANCE SPECTRA OF HEXAFLUOROACETYLACETONATO MANGANESE(I) CARBONYL COMPLEXES

Complex	Chemical shift, τ^a	Rel intens	Assignment
$Mn(CO)_2[P(C_6H_5)_3]_2(hfac)^b$	2.20–2.80 (complex multiplet)	30	C_6H_5
	5.47 (singlet)	1	hfac H
$Mn(CO)_2[P(C_6H_5)_2(CH_3)]_2(hfac)$	2.20–2.65 (complex multiplet)	20	C_6H_5
	4.76 (singlet)	1	hfac H
	7.97 (triplet)^c	~6.8	CH_3
$Mn(CO)_2[P(C_6H_5)(CH_3)_2]_2(hfac)$	2.40–2.70 (complex multiplet)	10	C_6H_5
	4.54 (singlet)	1	hfac H
	8.21 (triplet)^c	12	CH_3
$Mn(CO)_2[P(n\text{-}C_4H_9)_3]_2(hfac)$	4.22 (singlet)	1	hfac H
	7.80–9.00 (complex multiplets)	~55	C_4H_9
$Mn(CO)_2[P(OCH_3)_3]_2(hfac)$	4.02 (singlet)	1	hfac H
	6.20 (triplet)^d	18	CH_3
$Mn(CO)_2[P(OC_6H_5)_3]_2(hfac)$	2.73 (singlet, broad)	30	C_6H_5
	3.84 (singlet)	1	hfac H
$Mn(CO)_3[P(C_6H_{11})_3](hfac)$	5.06 (singlet)	1	hfac H
	8.40–9.90 (complex multiplet)	~35	C_6H_{11}
$Mn(CO)_3[As(C_6H_5)_3](hfac)$	2.76 (singlet)	15	C_6H_5
	4.52 (singlet)	1	hfac H
$Mn(CO)_3(C_5H_5N)(hfac)$	0.82–2.86 (complex pattern)	5	C_5H_5N
	4.05 (singlet)	1	hfac H
$Mn(CO)_3(4\text{-}CH_3C_5H_4N)(hfac)$	1.53 (doublet)^e	2	C_5H_4N 2,6-H
	2.71 (doublet)^e	2	C_5H_4N 3,5-H
	3.99 (singlet)	1	hfac H
	7.53 (singlet)	3	CH_3

[a] $CDCl_3$ solution. [b] Measurements were made immediately after preparation of solution because of decomposition; see the Experimental Section. [c] Approximate intensities of components are 1:2:1. Separation of outer peaks ~8 cps. [d] Approximate intensities of components are 1:2:1. Separation of outer peaks ~12 cps. [e] J ~ 6 cps.

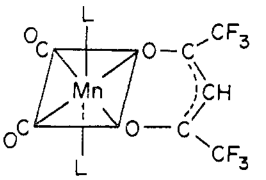

Figure 2.—The structure of $Mn(CO)_2L_2(hfac)$.

$(CO)_4[P(C_6H_{11})_3]Cl$. The fact that a deep red color develops almost immediately after mixing of solutions of the reactants indicates that this reaction proceeds *via* rapid formation of $Mn(CO)_3[P(C_6H_{11})_3](hfac)$. The tricarbonyl must then, more slowly and by an unknown path involving the solvent, lose $CF_3C(O)CHC(O)CF_3$ and undergo chlorination and carbonylation.

It was established that pyridine does not displace CO from $Mn(CO)_3(C_5H_5N)(hfac)$, even in refluxing chloroform. However, when *cis*-$Mn(CO)_3(C_5H_5N)_2Cl$ reacts with Tl(hfac), two products are obtained: $Mn(CO)_3(C_5H_5N)(hfac)$ and $Mn(CO)_3(C_5H_5N)_2(hfac)$, but not the dicarbonyl. The dipyridine derivative changes to the monopyridine complex upon standing in solution. This suggests the over-all reaction scheme

$$Mn(CO)_3(C_5H_5N)_2Cl + Tl(hfac) \longrightarrow Mn(CO)_3(C_5H_5N)_2(hfac) + TlCl \quad (1)$$

$$Mn(CO)_3(C_5H_5N)_2(hfac) \longrightarrow Mn(CO)_3(C_5H_5N)(hfac) + C_5H_5N \quad (2)$$

The infrared spectrum of $Mn(CO)_3(C_5H_5N)_2(hfac)$ exhibits three intense metal carbonyl stretching absorptions, indicating a *cis*-tricarbonyl structure. The hexafluoroacetylacetonato carbonyl band (1701 cm^{-1}), displaced by 66–93 cm^{-1} to higher frequency from the values observed for the dicarbonyl and other tricarbonyl complexes (Table II), and the broad OH stretching absorption centered at *ca.* 3250 cm^{-1} are the other salient spectral features.[12] From these data, the most plausible structure of $Mn(CO)_3(C_5H_5N)_2(hfac)$ is that shown in Figure 3. It thus appears that this derivative represents the first hexafluoroacetylacetonato complex in which the ligand is attached to a metal *via* carbon atom 3. Unfortunately, the insolubility of the compound in common organic solvents has precluded nuclear magnetic resonance measurement to aid in elucidation of the structure. Experiments are now in progress on the deuterated analog possibly to resolve the problem unambiguously. Results of this study and data on other similar compounds will be reported in a forthcoming paper.

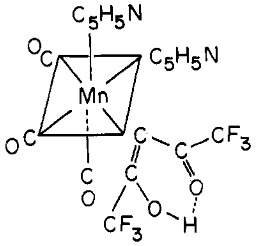

Figure 3.—The proposed structure of $Mn(CO)_3(C_5H_5N)_2(hfac)$.

Infrared spectral examination of the reaction mixture of $Mn(CO)_4(hfac)$ and $P(n\text{-}C_4H_9)_3$ reveals that the replacement of one CO is virtually complete in 45 sec

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(12) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

at 25°. The absorption bands at 2042, 1961, and *ca.* 1933 cm^{-1} (the last one hidden underneath a more intense band of the dicarbonyl) occur at wavenumbers comparable to those observed for the tricarbonyl complexes (Table II) and indicate that the intermediate *cis*-tricarbonyl is present in solution. This compound reacts rapidly, although no so fast as the tetracarbonyl, with excess phosphine to yield the dicarbonyl. Only the latter can be detected in the reaction mixture after about 5 min.

All attempts at the isolation of the tricarbonyl $Mn(CO)_3[P(C_6H_5)_3](hfac)$ have been unsuccessful. From the reactions of equimolar quantities of $Mn(CO)_4(hfac)$ and $P(C_6H_5)_3$ and of $Mn(CO)_4[P(C_6H_5)_3]Cl$ and Tl(hfac), the only carbonyl isolated was $Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$, yet the dicarbonyl in chloroform, cyclohexane, or hexane solutions undergoes transformation to the *cis*-tricarbonyl, as evidenced by the appearance of new infrared bands at 2047, 1970, and 1938 cm^{-1}. Evaporation of the solvent after the CO absorptions of the parent dicarbonyl have virtually disappeared affords $Mn(CO)_2[P(C_6H_5)_3]_2(hfac)$ and $Mn(hfac)_2 \cdot 2H_2O$ as the only detectable hexafluoroacetylacetonate-containing solids. It is not known at present whether the formation of manganese(II) occurs as a result of oxygen being present in the reaction system.[13]

Discussion

One of the most striking properties of $Mn(CO)_4(hfac)$ is the remarkably facile replacement of its carbonyl groups *cis* to hexafluoroacetylacetonate by a variety of bases such as phosphites, phosphines, pyridines, and triphenylarsine. Either one or both the CO's are displaced readily at ambient temperatures. In contrast, however, triphenylstibine, thiourea, and diethyl sulfide do not substitute under similar experimental conditions. Cotton and Zingales[14] suggest, from their infrared spectral study of the compounds $Mo(CO)_3L_3$, where L is a sulfur-donor molecule, and from other literature data,[15] that π-bonding ability of ligands under consideration follows the order $PR_3 > SR_2 > (NH_2)_2CS > C_5H_5N$. Thus the unreactive nature of $(SC_2H_5)_2$ and $(NH_2)CS$ in our investigation cannot be ascribed to the insufficient π-bonding ability of these ligands, since pyridine and 4-methylpyridine do substitute very readily. It is, however, reasonable to postulate that the nucleophile[16] must have a certain minimum basicity in order to replace at least one carbonyl group from $Mn(CO)_4(hfac)$. This would account for the unsuccessful attempt at the substitution not only with $S(C_2H_5)_2$ and $(NH_2)_2CS$, but also with $Sb(C_6H_5)_3$, which is a weaker base than either $P(C_6H_5)_3$ or $As(C_6H_5)_3$.[17]

The results of our investigation complement the data reported recently by Angelici and Graham.[18] These authors observed that the carbonyls $Cr(CO)_4(L\text{-}L)$, where L-L is 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine, undergo relatively rapid substitution reactions with several phosphites to form the complexes *cis*-$Cr(CO)_3[P(OR)_3](L\text{-}L)$. They attribute the enhancement of reactivity in going from $Cr(CO)_6$ to $Cr(CO)_4(L\text{-}L)$ to the presence of the relatively "hard" nitrogen atoms in the bipyridines.

Our study shows that the labilizing effect observed by Angelici and Graham becomes definitely more pronounced when the "harder" oxygen-donor atoms are present and when the formal oxidation state of the metal increases from 0 to +1. Accordingly, not only is the first CO *cis* to $CF_3C(O)CHC(O)CF_3$ replaced very readily but, in a number of reactions, the second *cis*-carbonyl is also substituted rapidly.[19]

Ligands which yield the dicarbonyl complexes, *viz.*, phosphines and phosphites, are noted for their considerable π-bonding ability. Thus, upon replacement of the first CO by one of these molecules, the carbonyl *trans* to it is still sufficiently labile to promote further reaction. However, substitution of the initial CO by a ligand of limited π-bonding capacity such as pyridine or triphenylarsine increases sufficiently the Mn–CO bond strength of the remaining carbonyl *cis* to $CF_3C(O)CHC(O)CF_3$ to render it inert to replacement.

The behavior of tricyclohexylphosphine toward the tetracarbonyl comes as a surprise in that only one CO group can be replaced. That the substitution is arrested at this point cannot be explained readily in terms of the relatively great base strength (or weak π bonding) of the phosphine, since only a slightly weaker base, $P(n\text{-}C_4H_9)_3$,[20] yields the dicarbonyl. Instead, it is more likely that the bulky cyclohexyl groups on the phosphorus cause the hexafluoroacetylacetonate ring and two carbonyls in the equatorial plane to bend downward and away from the $P(C_6H_{11})_3$. This distortion then makes the position *trans* to the tricyclohexylphosphine sterically inaccessible for occupancy by another $P(C_6H_{11})_3$.

It is also noteworthy that $Mn(CO)_3(C_5H_5N)(hfac)$ undergoes facile replacement of the pyridine by various phosphines and phosphites. This behavior reflects a powerful labilizing effect of carbon monoxide in tricarbonyl complexes containing three ligands of limited or no π-bonding capacity and located *trans* to the CO's.

Inspection of the nmr data, listed in Table III, reveals that the position of the resonance due to the proton on carbon atom 3 of the hexafluoroacetylacetonate ring varies markedly with the nature of the ligands

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[13] No attempt has yet been made to exclude *very rigorously* oxygen and water from the reaction mixture. Complete removal of water from these systems is extremely difficult.

[14] F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962).

[15] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

[16] The word *nucleophile* is not to be interpreted as suggesting that these reactions proceed by an SN2 path. The mechanism of substitution has not yet been elucidated.

[17] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

[18] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).

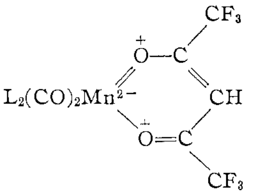
[19] Other examples of such disubstitution have been reported. Thus, the compounds *cis*-$Fe(CO)_4X_2$ containing two relatively "hard" bromines or chlorines react readily with several ligands (L) and afford $Fe(CO)_2L_2X_2$. See I. A. Cohen and F. Basolo, *J. Inorg. Nucl. Chem.*, **28**, 511 (1966); R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, **3**, 584 (1964), and references therein.

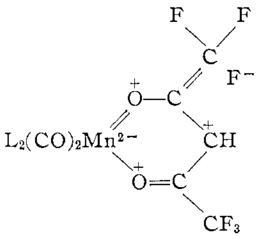
[20] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

in the complex. Moreover, the signal occurs between τ 3.84 and 5.47, spanning a range of 1.63 ppm. In order to discuss this variation, it is convenient to treat the dicarbonyls and the tricarbonyls separately.

Among the complexes $Mn(CO)_2L_2$(hfac) the resonance moves upfield in the order $L = CO \sim P(OC_6H_5)_3 < P(OCH_3)_3 < P(n\text{-}C_4H_9)_3 < P(C_6H_5)(CH_3)_2 < P(C_6H_5)_2(CH_3) < P(C_6H_5)_3$. It thus appears that the better π-bonding ligands, *viz.*, CO and phosphites, give rise to signals at lower fieds than the more basic and poorer π-bonding phosphines.[21] Furthermore, triphenyl phosphite, which π bonds better than trimethyl phosphite in $Mn(CO)_2L_2$(hfac), causes a larger downfield displacement of the proton resonance.

The positions of these signals suggest that the deshielding of the hexafluoroacetylacetonate hydrogen might result from a drift of π electrons from the ring toward the manganese. This drift would involve acceptance of π electrons from the ring oxygens by the metal[22] and might be expected to increase with an increase in π-bonding capacity of the phosphite (or other neutral ligand). Two of the important contributing resonance structures are depicted in Ia, b.


Ia


Ib

Of interest, of course, in this connection would be to examine the Mn–O stretching frequencies. However, the complexity of the infrared spectra of the derivatives has precluded an unambiguous assignment of absorption bands in this region.

Surprisingly, the chemical shifts of the ring proton in the phosphine complexes follow the order which is exactly the reverse of that expected from π-bonding abilities of PR_3.[21] Since displacement of the signal to higher fields increases with progressive substitution of alkyl moieties by the phenyl groups on the phosphorus, it is reasonable to postulate that long-range shielding of the proton in question by the aromatic rings[23] influences primarily the prevailing trend. In accordance with this, when the phenyl groups are placed farther away from the hexafluoroacetylacetonate ring, as is the case in $Mn(CO)_2[P(OC_6H_5)_3]_2$(hfac), the shielding effect no longer appears to be important.

The resonance of the chelate proton in $Mn(CO)_3L$-(hfac) moves to higher fields as L changes in the order $4\text{-}CH_3C_5H_4N < C_5H_5N < As(C_6H_5)_3 < P(C_6H_{11})_3$. The chemical shifts in the pyridine and arsine complexes are not unexpected; however, the position of the signal in the tricyclohexylphosphine complex comes as a surprise. This unusually large upfield shift is not understood at present, but it may result from distortion of the ring caused by steric requirements of the bulky phosphine.

Acknowledgment.—Financial support of this investigation by the National Science Foundation is gratefully acknowledged. We also wish to thank P. J. Pollick for assistance in obtaining the nmr spectra.

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[21] The relative π-bonding abilities of the phosphines and phosphites are reflected in the positions of the metal carbonyl stretching bands for these complexes, listed in Table II.

[22] That some ligands can function as π donors in metal carbonyl complexes has been already postulated.[9]

[23] See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 125, 126.

Contribution from the CSIRO, Division of Applied Chemistry, High Pressure Unit,
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Pressure in Coordination Chemistry. I. Nickel(II) Salicylaldimines and Aminotroponeimineates

By A. H. EWALD and E. SINN

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The anomalous magnetic and spectroscopic behavior of a number of N-substituted Ni(II) salicylaldimine and aminotroponeimine complexes in solution has been examined over a range of pressures. The susceptibility of the aminotroponeimineates is found to decrease with pressure, indicating that the planar, diamagnetic form of the complex has a smaller volume in solution than the tetrahedral form. The susceptibility of the salicylaldimine complexes, on the other hand, is found to increase with pressure indicating that the associated complexes are formed with a decrease in volume. For *n*-alkyl but not *sec*-alkyl salicylaldimines the contribution of a planar–tetrahedral equilibrium to the pressure dependence is negligible.

Introduction

In recent years many coordination compounds have been shown to deviate, in the solid state and in solution, from the Curie and Curie–Weiss laws for magnetic susceptibility. The mechanisms giving rise to these deviations may be divided into four main types.