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COMPLEXES OF TRIVALENT PHOSPHORUS DERIVATIVES VIII*. TRIS(DIMETHYLAMINO)PHOSPHINE COMPLEXES OF MANGANESE CARBONYL

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SUMMARY

Tris(dimethylamino)phosphine (Tdp) reacts with $Mn_2(CO)_{10}$ in a boiling mixture of 2,2,5-trimethylhexane and toluene to give yellow $[TdpMn(CO)_4]_2$, m.p. 198–199°. Reduction of this compound with dilute sodium amalgam in tetrahydrofuran gives a solution of the sodium salt $Na[Mn(CO)_4Tdp]$ which reacts with alkyl halides to give the stable white *cis*-$RMn(CO)_4Tdp$ (R = methyl or benzyl) derivatives. Reaction of $Na[Mn(CO)_4Tdp]$ with trimethyltin chloride gives white *cis*-$(CH_3)_3SnMn(CO)_4Tdp$ with a manganese–tin σ-bond. Treatment of $[TdpMn(CO)_4]_2$ with the halogens X_2 (X = Br or I) in dichloromethane solution at room temperature gives the yellow halides *cis*-$TdpMn(CO)_4X$ (X = Br or I). The iodide was also obtained from $Na[Mn(CO)_4Tdp]$ and C_3F_7I. Reaction of $Na[Mn(CO)_4Tdp]$ with excess tert-butyl chloride and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) gives the red crystalline carbonyl nitrosyl $TdpMn(CO)_3NO$. Treatment of $[TdpMn(CO)_4]_2$ with excess nitric oxide gives the green volatile unstable trinitrosyl $TdpMn(NO)_3$. The infrared and proton NMR spectra of the new compounds are discussed.

INTRODUCTION

In 1963 reactions of tris(dimethylamino)phosphine (Tdp) with certain carbonyl derivatives of vanadium, chromium, tungsten, iron, cobalt, and nickel were reported[2]. At that time a few preliminary attempts were made to prepare tris(dimethylamino)phosphine derivatives of manganese carbonyl but limitations in the decacarbonyldimanganese supply prevented this work from being carried to completion. Within the last two years, however, decacarbonyldimanganese has become much more readily available owing to the development of a convenient atmosphere pressure synthesis from the inexpensive (methylcyclopentadienyl)tricarbonylmanganese[3]. The Mn_2-

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$(CO)_{10}/[(CH_3)_2N]_3P$ system has therefore been reinvestigated in much greater detail. This has now resulted in the discovery of a convenient and efficient preparation of the disubstituted derivative $[TdpMn(CO)_4]_2$. Furthermore, the presence of a manganese–manganese bond in this new complex makes it a reactive intermediate useful for the preparation of other tris(dimethylamino)phosphine complexes of manganese carbonyl including derivatives containing σ-alkyl, organotin, nitrosyl, and halide ligands. Details of this work are presented in this paper.

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, using the Mechrolab vapor pressure osmometer in benzene solution. Melting points were determined in capillaries and are uncorrected.

Decacarbonyldimanganese was prepared from (methylcyclopentadienyl)tricarbonylmanganese, sodium, and carbon monoxide in diglyme solution at 160°/1 atm[3]. Tris(dimethylamino)phosphine (Tdp) was prepared from phosphorus trichloride and excess dimethylamine[4]. Other reagents and solvents were commercial products. However, the tetrahydrofuran used in this work was purified by redistillation over lithium aluminum hydride.

A nitrogen atmosphere was routinely provided for the following three operations: (*a*) carrying out reactions, (*b*) handling all filtered solutions of metal complexes, (*c*) admission to evacuated vessels.

Preparation of $[TdpMn(CO)_4]_2$

A mixture of 10 g (25.6 mmoles) of $Mn_2(CO)_{10}$, 10 g (62.5 mmoles) of tris(dimethylamino)phosphine, 50 ml of 2,2,5-trimethylhexane, and 75 ml of toluene was boiled under reflux for 17 h with magnetic stirring. During this period of time the original yellow reaction mixture became deep red. After the reaction period was over, the reaction mixture was cooled to room temperature and solvent removed at ~25°/0.5 mm. The remaining bright yellow residue was extracted with 300 ml of acetone in 6 portions. The filtered acetone extracts were cooled 13 h in a −78° bath. Yellow crystals separated. These were removed by filtration and dried at 25°/1 mm to give 9.5 g (62% yield) of yellow $[TdpMn(CO)_4]_2$, m.p. 198–199°. In other similar runs using 5 to 15 g of $Mn_2(CO)_{10}$, the yield of $[TdpMn(CO)_4]_2$ was in the range 62–67%. (Found: C, 36.3; H, 5.6; Mn, 17.2; N, 12.6; O, 19.4; P, 9.0. $C_{20}H_{36}Mn_2N_6O_8P_2$ calcd.: C, 36.4; H, 5.5; Mn, 16.6; N, 12.7; O, 19.4; P, 9.4%.)

Preparation of a solution of $Na[Mn(CO)_4Tdp]$

A dilute sodium amalgam prepared from 4 ml of mercury and 0.3 g (13 mmole) of sodium spheres was stirred vigorously at room temperature with a solution of 1.0 g (1.51 mmoles) of $[TdpMn(CO)_4]_2$ in 50 ml of tetrahydrofuran until the color no longer changed (~1 h). The resulting green-gray solution was assumed to contain 3 mmoles of $Na[Mn(CO)_4Tdp]$ on the basis of the amount of $[TdpMn(CO)_4]_2$ introduced. After removal of the mercury and excess amalgam, this solution was used directly for the experiments described below.

Preparation of $CH_3Mn(CO)_4Tdp$

A solution of 3 mmoles of $Na[Mn(CO)_4Tdp]$ in 50 ml of tetrahydrofuran prepared as described above was stirred for ~12 h at room temperature with excess (4 ml, 9.1 g, 64 mmoles) of methyl iodide. Solvent was then removed at ~25°/35 mm. The residue was extracted with 50 ml of pentane. The filtered pentane extracts were cooled 17 h in a −78° bath. The yellow crystals which separated were removed by filtration and purified finally by sublimation at 70°/0.1 mm to give 0.38 g (37% yield) of pure white crystalline $CH_3Mn(CO)_4Tdp$, m.p. 144–145°. The proton NMR spectrum of this compound exhibited doublet resonances at τ 7.30 (J=9.5 Hz) and τ 10.23 (J=7.7 Hz) in $CHCl_3$ solution arising from the methyl protons bonded to nitrogen and manganese, respectively. (Found: C, 38.4; H, 6.0; N, 12.3; O, 18.4; P, 8.8. $C_{11}H_{21}MnN_3O_4P$ calcd.: C, 38.3; H, 6.1; N, 12.2; O, 18.6; P, 9.0%.)

Preparation of $C_6H_5CH_2Mn(CO)_4Tdp$

A solution of 3 mmoles of $Na[Mn(CO)_4Tdp]$ in 50 ml of tetrahydrofuran prepared as described above was stirred for 24 h at room temperature with 0.4 ml (0.44 g, 3.5 mmoles) of benzyl chloride. Solvent was then removed at ~25°/35 mm. The residue was extracted with 100 ml of pentane in 5 portions. Concentration of the filtered extract to ~15 ml followed by cooling in a −78° bath for 15 h gave pale yellow-brown crystals. These were removed by filtration to give 0.38 g (30% yield) of $C_6H_5CH_2Mn(CO)_4Tdp$, m.p. 73–74°. (Found: C, 48.3; H, 6.0; N, 9.8; O, 15.3; P, 7.2. $C_{17}H_{25}MnN_3O_4P$ calcd.: C, 48.5; H, 6.0; N, 10.0; O, 15.2; P, 7.4%.)

Preparation of $(CH_3)_3SnMn(CO)_4Tdp$

A solution of 3 mmoles of $Na[Mn(CO)_4Tdp]$ in 50 ml of tetrahydrofuran prepared as described above was stirred for 24 h at room temperature with 0.6 g (3.0 mmoles) of $(CH_3)_3SnCl$. Solvent was then removed at ~25°/35 mm. The residue was extracted with 50 ml of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at ~25°/35 mm. The yellow residue was recrystallized twice from pentane and then sublimed at ~70°/0.1 mm to give 0.43 g (29% yield) of pure white $(CH_3)_3SnMn(CO)_4Tdp$, m.p. 98–101°. (Found: C, 30.9; H, 5.3; N, 8.5; O, 12.9; P, 6.1; mol.wt., 480. $C_{13}H_{27}MnN_3O_4PSn$ calcd.: C, 31.6; H, 5.5; N, 8.5; O, 13.0; P, 6.3%; mol.wt., 494.)

Preparation of $TdpMn(CO)_4I$

(a). From $[TdpMn(CO)_4]_2$ and I_2. A mixture of 1.0 g (1.51 mmoles) of $[TdpMn(CO)_4]_2$ and 0.38 g (1.49 mmoles as I_2) of iodine in 60 ml of dichloromethane was stirred for 106 h at room temperature. Solvent was then removed at 25°/30 mm. The dark brown residue was extracted with 25 ml of pentane. The filtered pentane solution was cooled for 12 h in a −78° bath. The yellow crystals which began to separate immediately were removed by filtration to give 0.32 g (23% yield) of $TdpMn(CO)_4I$, m.p. 120–122°. (Found: C, 25.9; H, 4.0; I, 28.2; N, 9.0; O, 13.9. $C_{10}H_{18}IMnN_3O_4P$ calcd.: C, 26.3; H, 4.0; I, 27.8; N, 9.2; O, 14.0; P, 6.8%.)

(b). From $Na[Mn(CO)_4Tdp]$ and $n\text{-}C_3F_7I$. A solution of 3 mmoles of $Na[Mn(CO)_4Tdp]$ in 50 ml of tetrahydrofuran prepared as described above was stirred for 24 h at room temperature with excess (4 ml, 8.4 g, 27 mmoles) of 1-iodoheptafluoropropane. The originally green-gray solution became orange. Solvent was removed at

~25°/35 mm. The residue was extracted with ~100 ml of diethyl ether in several portions. The filtered diethyl ether solution was concentrated to ~6 ml at 35 mm. This concentrated solution was chromatographed on a 2 × 30 cm alumina column. The single yellow band was eluted with diethyl ether. Solvent was removed from the filtered eluate at ~25°/35 mm. A filtered solution of the residue in 20 ml of pentane was cooled for 24 h in a −78° bath. The yellow crystals which separated were removed by filtration to give 0.12 g (8.7% yield) of $TdpMn(CO)_4I$, m.p. 120–122°. (Found: C, 26.9; H, 3.9; I, 28.1; N, 8.5; O, 13.0; P, 6.9%.)

Preparation of $TdpMn(CO)_4Br$

A mixture of 1.0 g (1.51 mmoles) of $[TdpMn(CO)_4]_2$ and 0.24 g (1.5 mmoles as Br_2) of bromine in 60 ml of dichloromethane was stirred for 81 h at room temperature. Solvent was then removed from the filtered reaction mixture at ~25°/35 mm. The red-orange residue was extracted with 20 ml of pentane. The filtered pentane extracts were cooled for 48 h in a −78° bath. The yellow crystals which separated were removed by filtration to give 0.27 g (22% yield) of $TdpMn(CO)_4Br$, m.p. 106–108°. (Found: C, 28.9; H, 4.5; Br, 19.0; N, 9.9; O, 15.0. $C_{10}H_{18}BrMnN_3O_4P$ calcd.: C, 29.3; H, 4.4; Br, 19.5; N, 10.3; O, 15.6%.)

Preparation of $TdpMn(CO)_3NO$

A solution of 3 mmoles of $Na[Mn(CO)_4Tdp]$ in 50 ml of tetrahydrofuran was stirred with 0.65 g (3.0 mmoles) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") and 5 ml (4.2 g, 46 mmoles) of $(CH_3)_3CCl$ at room temperature. Immediate evolution of gas occurred and the reaction mixture turned red-brown. After stirring for 14 h solvent was removed at ~25°/35 mm. The residue was extracted with 100 ml of pentane in five portions. The filtered pentane extracts were concentrated to ~20 ml and then cooled 6 h in a −78° bath. The mixture of red and yellow crystals which separated was removed by filtration*. The pentane filtrate after removal of these crystals was concentrated to ~6 ml and chromatographed on a 2 × 30 cm alumina column. The column was developed with pentane. The single red-orange band was eluted with pentane. The eluate was concentrated to ~10 ml at 30 mm and then cooled in a −78° bath. The red crystals which separated were removed by filtration to give 0.047 g (4.7% yield) of $TdpMn(CO)_3NO$, m.p. 107–108°. This compound could be sublimed at 70°/0.05 mm. (Found: C, 33.0; H, 5.3; N, 16.7; O, 18.9; mol.wt., 306. $C_9H_{18}MnN_4O_4P$ calcd.: C, 32.5; H, 5.5; N, 16.9; O, 19.3%; mol.wt., 332.)

Preparation of $TdpMn(NO)_3$

A solution of 1.0 g (1.51 mmoles) of $[TdpMn(CO)_4]_2$ in 50 ml of tetrahydrofuran was treated for 4 h with nitric oxide which had been purified by passing thru a −78° trap containing molecular sieves. Solvent was then removed from the resulting deep green solution at ~25°/35 mm. The resulting dark green residue was extracted with 40 ml of pentane. The filtered extracts showed strong $\nu(NO)$ frequencies at 1785 and 1690 cm^{-1} and only relatively weak $\nu(CO)$ frequencies indicating $TdpMn(NO)_3$ to be the principal manganese compound present in the solution.

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* The red crystals appeared to be additional $TdpMn(CO)_3NO$, but this could not be readily separated from the yellow material.

Pure green crystalline $TdpMn(NO)_3$ could be isolated by concentrating and cooling the pentane solution in a −78° bath or, less satisfactorily, by sublimation at 0.1 mm. This green compound decomposed appreciably after a few hours at room temperature preventing shipment of a reliable sample to an outside analytical laboratory. The compound was therefore characterized by its mass spectrum.

Mass spectrum of $TdpMn(NO)_3$*. The following ions, *m/e* values, and relative intensities, respectively, were observed: $[(CH_3)_2N]_3PMn(NO)_3^+$, 308, 45; $[(CH_3)_2N]_3PMn(NO)_2^+$, 278, 16; $[(CH_3)_2N]_3PMnNO^+$, 248, 56; $[(CH_3)_2N]_3PMn^+$, 218, 6; $[(CH_3)_2N]_3PO^+$, 179, 9; $[(CH_3)_2N]_2PMnH^+$, 175, 12; $[(CH_3)_2N]_3P^+$, 163, 76; $(CH_3)_2NMnCH_2NCH_3^+$, 142, 13; $(CH_3NCH_2)_2Mn^+$, 141, 8; $[(CH_3)_2N]_2P(H)CH_3^+$, 135, 20; $[(CH_3)_2N]_2P^+$, 119, >2000; $(CH_3)_2NMn^+$, 99, 34; $CH_3NCH_2Mn^+$, 98, 22: $(CH_3)_2NPH^+$, 76, >6000; CH_3NP^+, 60, ~145; Mn^+, 55, 54. Metastable ions: *m/e* 251 ($308^+ \rightarrow 278^+ + 30$), *m/e* 221 ($278^+ \rightarrow 248^+ + 30$), and *m/e* 48.6 ($119^+ \rightarrow 76^+ + 43$).

Carbonylation of $CH_3Mn(CO)_4Tdp$

A solution of ~0.1 g of $CH_3Mn(CO)_4Tdp$ in cyclohexane was treated for several hours with carbon monoxide at room temperature and atmospheric pressure. No reaction occurred. However, when this cyclohexane solution of $CH_3Mn(CO)_4Tdp$ was treated with carbon monoxide at the boiling point (~80°), methylpentacarbonylmanganese, $CH_3Mn(CO)_5$, was slowly formed as indicated by the gradual appearance of new bands at 2108, 2007, and 1994 cm^{-1} in the $\nu(CO)$ region. These correspond closely to the reported[5] values of 2109, 2010, and 1989 cm^{-1} for the A_1^{1b}, E, and A_1^{1a} modes, respectively, of $CH_3Mn(CO)_5$ in cyclohexane solution and to the values obtained from our measurements under identical conditions of the $\nu(CO)$ frequencies of an authentic sample of $CH_3Mn(CO)_5$ prepared from $NaMn(CO)_5$ and methyl iodide[6]. No evidence for the formation of an acetyl derivative was found in this carbonylation study of $CH_3Mn(CO)_4Tdp$ as indicated particularly by the absence of infrared bands around 1600 cm^{-1} which would arise from an acyl carbonyl of the acetyl group. A similar reaction between $Na[Mn(CO)_4Tdp]$ and acetyl chloride failed to yield an acetyl derivative or any crystalline products under conditions similar to those used for the successful reactions of $Na[Mn(CO)_4Tdp]$ described in this pap

DISCUSSION

The reaction of $Mn_2(CO)_{10}$ with tris(dimethylamino)phosphine (TdP) to give a product of stoichiometry $TdpMn(CO)_4$ parallels previously reported[7] reactions of $Mn_2(CO)_{10}$ with tricovalent phosphorus ligands. The product from $Mn_2(CO)_{10}$ and tris(dimethylamino)phosphine is indicated by its relatively low volatility to be the binuclear derivative $[TdpMn(CO)_4]_2$ rather than a corresponding mononuclear derivative. A sample of $[TdpMn(CO)_4]_2$ decomposed extensively upon heating at 140°/0.05 mm with slow sublimation of about 10% of the sample introduced. By contrast the iron complex $TdpFe(CO)_4$[2], shown even by mass spectrometry[8] to be a mononuclear derivative, sublimed readily at 50–60°/0.1 mm with only minor de-

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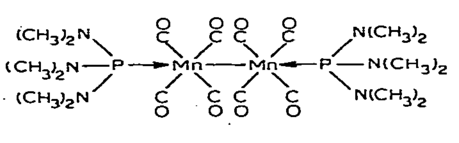
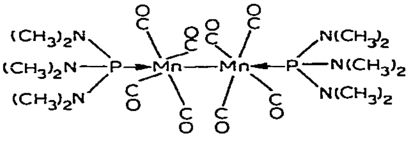
* This mass spectrum was run on a Perkin–Elmer Hitachi RMU-6 mass Spectrometer at 70 eV electron energy and 220° chamber temperature.

composition. Attempted molecular weight determinations of $[TdpMn(CO)_4]_2$ in solution failed because of decomposition. The volatility of $[TdpMn(CO)_4]_2$ proved insufficient to obtain a satisfactory mass spectrum with the available spectrometer. The ESR spectrum of *solid* $[TdpMn(CO)_4]_2$ exhibited a strong resonance possibly arising from some dissociation into free $TdpMn(CO)_4$ radicals. However, no resonances were observed in the ESR spectra of solutions of $[TdpMn(CO)_4]_2$ in accord with its diamagnetism indicated by the NMR spectrum of the Tdp resonance with normal chemical shifts and reasonably sharp lines. This anomalous behavior of $[TdpMn(CO)_4]_2$ in the solid state may relate to the previous confusion[7] concerning the monomeric or dimeric nature of $R_3PMn(CO)_4$ species. In general, the most recent studies[7b,7c] fail to confirm the original[7a] postulations of monomeric $R_3PMn(CO)_4$ compounds.

The infrared spectrum of $[TdpMn(CO)_4]_2$ in the ν(CO) region provides some information on the structure of this complex. Thus the spectrum of $[TdpMn(CO)_4]_2$, like that of $Mn_2(CO)_{10}$, exhibits no bands in the bridging carbonyl region indicating that the halves of $[TdpMn(CO)_4]_2$ are joined solely by a manganese–manganese bond. The only strong ν(CO) frequencies are a closely spaced doublet at 1960 and 1953 cm^{-1} suggestive of a split E mode. The remaining ν(CO) frequencies are weak ones at 1997 and 1985 cm^{-1}. This infrared spectrum can best be explained on the basis of a structure for $[TdpMn(CO)_4]_2$ with the two tris(dimethylamino)phosphine ligands in diaxial positions. [(Ia) or (Ib), respectively]. Thus for structure (Ia) (D_{4h} point group) a strong infrared-active E_u mode and a weak infrared active A_{2u} mode are predicted as well as infrared-inactive and Raman-active A_{1g}, B_{1g}, and E_g modes.



(Ia)



(Ib)

A characteristic chemical property of $[R_3PMn(CO)_4]_2$ compounds is their reduction with sodium amalgam in tetrahydrofuran solution to give sodium salts of the type $Na[Mn(CO)_4PR_3]$[9]. The new tris(dimethylamino)phosphine complex $[TdpMn(CO)_4]_2$ was likewise found to undergo reduction with sodium amalgam in tetrahydrofuran to give a sodium salt $Na[Mn(CO)_4Tdp]$. This sodium salt was characterized by reaction with trimethyltin chloride to form the stable white volatile trimethyltin derivative $(CH_3)_3SnMn(CO)_4Tdp$. Related organotin derivatives of manganese carbonyl with manganese–tin bonds including $(CH_3)_3SnMn(CO)_5$ and $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ have been reported[10,11].

The sodium salt $Na[Mn(CO)_4Tdp]$ was useful for the preparation of alkylmanganese carbonyl derivatives with manganese–carbon σ-bonds and tris(dimethylamino)phosphine ligands. Thus reaction of $Na[Mn(CO)_4Tdp]$ with methyl iodide gave the stable white volatile methyl derivative $CH_3Mn(CO)_4Tdp$. A similar σ-benzyl derivative could be analogously prepared. Reaction of $CH_3Mn(CO)_5$ with tris(dimethylamino)phosphine in boiling benzene also gave the methyl derivative $CH_3Mn(CO)_4Tdp$ identified by comparison of its ν(CO) frequencies with those of material prepared from methyl iodide and $Na[Mn(CO)_4Tdp]$. However, attempts to isolate pure crystalline $CH_3Mn(CO)_4Tdp$ out of the liquid product from the reaction between

$CH_3Mn(CO)_5$ and tris(dimethylamino)phosphine were unsuccessful.

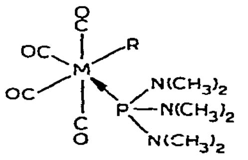
The infrared spectra of the $RMn(CO)_4Tdp$ derivatives in the ν(CO) region exhibited the basic four band pattern expected for a *cis*-$RMn(CO)_4Tdp$ compound of structure (II) (R=methyl or benzyl). The four ν(CO) frequencies of 2055, 1988, 1962, and 1934 cm^{-1} for $CH_3Mn(CO)_4Tdp$ correspond closely to the four ν(CO) frequencies 2055, 1983, 1968, and 1939 cm^{-1} reported by Kraihanzel and Maples[12] for *cis*-$CH_3Mn(CO)_4P(C_6H_5)_3$. However, in both the methyl and benzyl derivatives of the type $RMn(CO)_4Tdp$ one or two of the ν(CO) frequencies are split into doublets (Table 1) in spectra obtained of cyclohexane solutions. The inability for compounds with four carbonyl groups to exhibit more than four ν(CO) frequencies suggests that this doubling of the ν(CO) frequencies must arise from the presence of isomeric *cis*-$CH_3Mn(CO)_4Tdp$ compounds*. The most likely possibility is the occurrence of two conformational isomers similar to those postulated by Jetz and Graham[14] for

TABLE 1

INFRARED SPECTRA OF TRIS(DIMETHYLAMINO)PHOSPHINE COMPLEXES OF MANGANESE CARBONYL[a]

Compound	ν(CO) frequencies[b]			
$[TdpMn(CO)_4]_2$	1997 (w),	1985 (w),	1960 (vs) 1953 (vs)	
$CH_3Mn(CO)_4Tdp$	2055 (m),	1988 (s),	1965 (s) 1960 (s) ,	1938 (s) 1931 (s)
$C_6H_5CH_2Mn(CO)_4Tdp$	2047 (m),	1992 (m),	1967 (vs),	1947 (s) 1938 (s)
$(CH_3)_3SnMn(CO)_4Tdp$		1962 (m),	1946 (s),	1932 (s)
$TdpMn(CO)_4I$	2080 (m),	2017 (m),	2006 (s),	1975 (m) 1968 (m) 1962 (m)
$TdpMn(CO)_4Br$	2076 (m),	2013 (s),	2000 (vs),	1961 (m) 1953 (s) 1946 (s)
$TdpMn(CO)_3NO$	2027 (s),	1971 (s),	1922 (s),	1709 (s)[c]
$TdpMn(NO)_3$			1785 (m)[c]	1690 (s)[c]

[a] These spectra were taken in cyclohexane solutions and recorded on a Perkin-Elmer Model 621 spectrometer. Frequencies are given in cm^{-1}. [b] Bands appearing to result from splitting of a single ν(CO) mode (see text) are grouped together in braces. [c] ν(NO) frequency.



(II)

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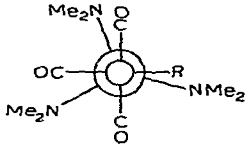
* These "extra" ν(CO) frequencies in the infrared spectra of the *cis*-$RMn(CO)_4Tdp$ derivatives do not correspond to the positions or relative intensities of the frequencies expected for the *trans* isomers. The reported ν(CO) frequencies for the *cis*-*trans* isomer pairs $(C_6H_5)_3PM(CO)_4Br$ (M=Mn or Re)[13a] and $C_6F_5Mn(CO)_4P(C_6H_5)_3$[13b] indicate that the *trans* isomer shows the single strong ν(CO) frequency (*E* mode) predicted from group theory in addition to the very weak A_1 mode. The single strong *E* mode of a hypothetical *trans*-$RMn(CO)_4Tdp$ impurity is not sufficient to account for the observed "extra" ν(CO) frequencies in the *cis*-$RMn(CO)_4Tdp$ compounds.

$C_5H_5Fe(CO)_2SiCl_2CH_3$ and related compounds. Restricted rotation about the manganese–phosphorus bond in the $RMn(CO)_4Tdp$ compounds arising either from partial d_π–d_π double bond character or interference between the dimethylamino groups on the phosphorus and the carbonyl and alkyl groups on the manganese could lead to such conformational isomers. One such possible isomer pair is illustrated schematically in (IIIa) and (IIIb). While it is not yet possible to comment in detail about this apparent conformational isomerism in *cis*-$RMn(CO)_4Tdp$ compounds (II), the following observations have been made:

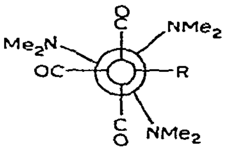
(1) The ratio of the doublets of the two lowest ν(CO) frequencies is approximately the same in the solution spectra of different samples of $CH_3Mn(CO)_4Tdp$ provided that the spectra have been obtained under conditions sufficient for resolution of the doublets.

(2) No definite evidence can be obtained in the NMR spectra for the existence of isomers. This suggests that the two conformational isomers are equilibrating at a rate appreciably faster than the NMR time scale.

Some unsuccessful attempts were also made to prepare the acetyl derivative $CH_3COMn(CO)_4Tdp$. Reaction of $Na[Mn(CO)_4Tdp]$ with acetyl chloride failed to give a crystalline product. Carbon monoxide at 25°/1 atmosphere failed to react with a cyclohexane solution of $CH_3Mn(CO)_4Tdp$. However, carbon monoxide at 80°/1 atmosphere reacted slowly with $CH_3Mn(CO)_4Tdp$ to form $CH_3Mn(CO)_5$ apparently according to the following equation:



(IIIa)



(IIIb)

$$CH_3Mn(CO)_4Tdp + CO \rightarrow CH_3Mn(CO)_5 + Tdp$$

These reactions in cyclohexane solution were followed by measurement of the ν(CO) frequencies.

Manganese carbonyl halides substituted with tris(dimethylamino)phosphine ligands were also investigated. Reaction of $Mn(CO)_5Br$ with tris(dimethylamino)phosphine failed to give a crystalline product. However, bromine and iodine each reacted with $[TdpMn(CO)_4]_2$ in dichloromethane solution to cleave the manganese–manganese bond forming the corresponding $TdpMn(CO)_4X$ (X = Br and I) halides according to the following equation:

$$[TdpMn(CO)_4]_2 + X_2 \rightarrow 2\ TdpMn(CO)_4X$$

The iodide $TdpMn(CO)_4I$ was also prepared from $Na[Mn(CO)_4Tdp]$ and 1-iodoheptafluoropropane according to the following equation:

$$Na[Mn(CO)_4Tdp] + C_3F_7I \rightarrow TdpMn(CO)_4I + NaF + CF_2{=}CFCF_3$$

Perfluoroalkyl iodides have been previously used to convert metal carbonyl anions to the corresponding iodides[1,21].

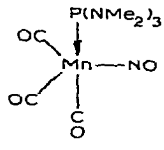
The halides $TdpMn(CO)_4X$ (X = Br or I) are yellow crystalline solids. Their infrared spectra exhibit the four ν(CO) frequencies expected for the *cis*-isomers (II) (R=Br or I). However, in both halides the lowest ν(CO) frequency is split into a triplet in cyclohexane solution probably because of the presence of conformational isomers related to those postulated for the alkyls *cis*-$RMn(CO)_4Tdp$ (R=methyl or benzyl).

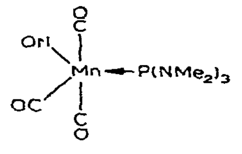
Some tris(dimethylamino)phosphine derivatives of manganese nitrosyls were prepared. Treatment of $Na[Mn(CO)_4Tdp]$ with tert-butyl chloride and Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) gave the red nitrosyl derivative $TdpMn(CO)_3NO$. This preparation parallels that of the unsubstituted $Mn(CO)_4NO$ from $HMn(CO)_5$ and Diazald[16]. However, we were not able to isolate $HMn(CO)_4Tdp$, a presumed intermediate in this $TdpMn(CO)_3NO$ preparation, from the mixture obtained by treatment of $Na[Mn(CO)_4Tdp]$ with tert-butyl chloride. Reaction of $[TdpMn(CO)_4]_2$ with excess nitric oxide gave the green carbonyl-free compound $TdpMn(NO)_3$ apparently according to the following equation:

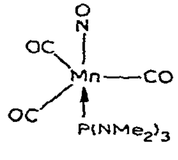
$$[TdpMn(CO)_4]_2 + 6\,NO \rightarrow 2\,TdpMn(NO)_3 + 8\,CO$$

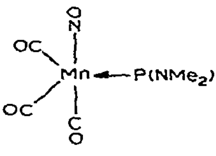
The compound $TdpMn(NO)_3$ soon became brown upon standing. It therefore could not be sent for analysis. Instead it was identified from its ν(NO) frequencies of 1785 and 1690 cm^{-1} characteristic of an $R_3PMn(NO)_3$ derivative[17] and from its mass spectrum (*Experimental Section*) which exhibited the ions $TdpMn(NO)_n^+$ ($n=3,2,1,0$) and other ions expected for $TdpMn(NO)_3$ on the basis of the reported[18] mass spectra of related tris(dimethylamino)phosphine metal complexes.

The infrared spectrum of $TdpMn(CO)_3NO$ in the ν(CO) region exhibited three bands of approximately equal relative intensities. This suggests structure (IVa) [(or IVd)]*. Each of the two structures [(IVa) or (IVb)] has C_s symmetry and would be expected to have three ν(CO) frequencies ($2A'+A''$). However, in structure (IVb) with two axial carbonyl groups the symmetric and antisymmetric stretching modes of these two carbonyl groups involve rather different dipole moment changes and thus are expected to give ν(CO) frequencies of rather different relative intensities. A third possible structure for $TdpMn(CO)_3NO$ with trigonal bipyramidal coordination, (IVc), is excluded from consideration since it has C_{3v} symmetry and thus can have only two ν(CO) frequencies (A_1+E). Square pyramidal structures for $TdpMn(CO)_3NO$ appear unlikely in view of the nearly universal preference of 5-coordinate metal carbonyl derivatives for trigonal bipyramidal structures**. Furthermore, Enemark


(IVa)


(IVb)


(IVc)


(IVd)

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* Structures similar to (IVa), (IVb), and (IVc) but with the tris(dimethylamino)phosphine and nitrosyl ligands interchanged must also be considered. However, the number and relative intensities of the ν(CO) frequencies can only provide unequivocal information on the relative positions of the *carbonyl* groups in $M(CO)_3LL'$ compounds. Therefore these ν(CO) data on $TdpMn(CO)_3NO$ cannot distinguish between (IVa) and (IVd).

** For a review on 5-coordinate derivatives see ref. 18.

and Ibers[19] have found by X-ray crystallography that the manganese atom in the related compound $Mn(NO)(CO)_2[P(C_6H_5)_3]_2$ has a trigonal bipyramidal configuration. Structure (IVa) appears somewhat more likely than structure (IVd) for Tdp-$Mn(CO)_3NO$ since the tertiary phosphine ligands in the related compound $Mn(NO)(CO)_2[P(C_6H_5)_3]_2$ were found[19] to occupy axial rather than equatorial positions.

The new tris(dimethylamino)phosphine complexes of manganese carbonyl have properties similar to those of the previously reported[2] tris(dimethylamino)phosphine complexes of metal carbonyls. The new manganese carbonyl complexes are all relatively soluble in organic solvents making possible a more detailed study of ν(CO) frequencies than with other tricovalent phosphorus derivatives of manganese carbonyl. Many of the new mononuclear manganese carbonyl derivatives of tris(dimethylamino)phosphine are sufficiently volatile to be purified by vacuum sublimation. The proton NMR spectra of the new tris(dimethylamino)phosphine complexes of manganese carbonyl generally exhibit a doublet in the range τ 7.19 to 7.54 ($J = \sim 9$ to ~ 11 Hz) as was previously found for the other tris(dimethylamino)phosphine complexes of metal carbonyls. This resonance arises from the eighteen equivalent protons of the tris(dimethylamino)phosphine ligand being split by the phosphorus nucleus ($J = 0.5$ Hz). The infrared spectra of the new tris(dimethylamino)phosphine complexes of manganese carbonyl exhibit one or more medium to strong bands in the range 940–965 cm^{-1}. These bands have been attributed to the phosphorus–nitrogen bonds in the tris(dimethylamino)phosphine ligand[2]. As in the previous work weaker bands were also observed in the regions 1485–1440, 1275–1255, 1185–1140, and 1070–1050 cm^{-1}.

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