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STEREOSPECIFIC SYNTHESES OF NEW MANGANESE(I) ISOCYANIDE DERIVATIVES

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Summary

Three series of cationic manganese(I) carbonyls are reported: $[Mn(CO)_{5-n}(CNMe)_n(CNPh)]PF_6$ (n = 1 → 4), $[Mn(CO)_{5-n}(CNMe)(CNPh)_n]PF_6$ (n = 1 → 4), and $[Mn(dpe)(CO)_{4-n}(CNMe)_n]PF_6$ (n = 1 → 4). Most of these compounds were prepared from a substituted metal carbonyl halide by replacement of halide ion by an added ligand (CNR or CO), such reactions requiring an added halide ion acceptor (Ag^+ or $AlCl_3$). The added ligand enters the site of departing halide ion. It was possible to prepare isomers of many compounds reported, taking advantage of this stereospecificity. Structures of the products were defined, often unequivocally, by infrared and nmr spectroscopic data. Cyclic voltammetry showed that these compounds undergo one electron oxidations, the ease of oxidation determined by the nature of the ligand groups and the stereochemistry.

Introduction

Recently, work was reported from our group which showed that replacement of the halide ion in $Mn(CO)_{5-n}(CNR)_nBr$ (R = Me [1], Ph [2]) occurs stereospecifically, placing the substituting group (CO or CNR) in the coordination position previously occupied by bromide. This result permitted the specific, high yield syntheses of fac- and mer- $[Mn(CO)_3(CNR)_3]PF_6$ and cis- and trans- $[Mn(CO)_2(CNR)_4]PF_6$. This reaction was also extended to specific syntheses of cis- and trans- isomers of $[Re(CO)_2(CNtol^p)_4]PF_6$ [3], and used for the syntheses of fac-$[Re(CO)_3L_3]PF_6$ (L = CNMe, $CNtol^p$), cis-$[Re(CO)_2(CNMe)_4]PF_6$ [3], and trans-$[Mn(CO)(CNtol^p)_4L]PF_6$ (L = CNMe, $CNbu^t$, py, NH_2tol^o) [4,5].

In this paper we report the further application of this type of reaction

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TABLE I. INFRARED[a] AND NMR[b] DATA

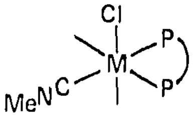
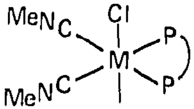
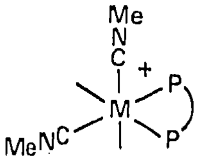
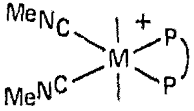
Compound	Geometry	ν(CNPh)	ν(CNMe)	ν(CO)	NMR(δ)[b]
$[Mn(CO)_4(CNMe)(CNPh)]PF_6$	cis	2197m	2256m	2120s,2047vs(br)	3.68s(3),7.59m(5)
$[Mn(CO)_3(CNMe)_2(CNPh)]PF_6$	fac	2181m	2246m(sh),2229m	2066s,2014s	3.65s(6),7.60m(5)
$[Mn(CO)_2(CNMe)_3(CNPh)]PF_6$	mer-cis	2157m	2233w,2202m(sh), 2185s	2016s,1977s	3.57s(9),7.54s(5)
$[Mn(CO)(CNMe)_4(CNPh)]PF_6$	trans	2131m(sh)	2158s	1959m	3.51s(12),7.50s(5)
$[Mn(CO)_3(CNMe)(CNPh)_2]PF_6$	fac	2192,2172m	2240w	2067s,2019s	3.71s(3),7.58m(10)
$[Mn(CO)_2(CNMe)(CNPh)_3]PF_6$	mer-cis	2181w,2150m(sh), 2129s	2227w	2024s,1992s	3.60s(3),7.43s(15)[c]
$[Mn(CO)(CNMe)(CNPh)_4]PF_6$	trans	2170w,2106vs	2217w	1976m	3.58s(3),7.50s(20)[c]
$Mn(CO)_3(CNMe)(CNPh)Br$	fac	2160s	2217s	2039s,1996s, 1946s	3.53s(3),7.40s(5)[c]
$Mn(dpe)(CO)_2(CNMe)Cl$			2161m	1953s,1875s	2.70m(4),3.30s(3), 7.28m(20)[c]
$Mn(dpe)(CO)(CNMe)_2Cl$			2146s,2108s	1850	2.68s(4),3.39s(6), 7.27m(20)[d]
$[Mn(dpe)(CO)_3(CNMe)]PF_6$	fac		2210m	2039s,1976s(br)	2.58s,br(3),3.06d*, J = 17Hz(4),7.49m(20)[e]
$[Mn(dpe)(CO)_3(CNMe)]PF_6$	mer		2196m	2061w,1984s	3.11d*,J = 17Hz(4), 3.60s(3),7.68m(20)[e]
$[Mn(dpe)(CO)_2(CNMe)_2]PF_6$ Isomer 1			2199s,2173s	1987vs,1941vs	2.57t,J = 2Hz(3), 2.91d*,J = 17Hz(4), 3.48d,J = 1.5Hz(3),

TABLE I continued

$[Mn(dpe)(CO)_2(CNMe)_2]PF_6$ Isomer 2		2180s,2149s	1951vs	2.84d*,J = 17Hz(4), 3.49s(6),7.48m(20)^e
$[Mn(dpe)(CO)(CNMe)_3]PF_6$ Isomer 1	<u>fac</u>	2186s,2143s(br)	1924s	2.49t,J = 2Hz(3), 2.80d*,J = 17Hz(4), 3.46d,J = 2Hz(3), 7.46m(20)^e
$[Mn(dpe)(CO)(CNMe)_3]PF_6$ Isomer 2	<u>mer</u>	2183m,2134vs	1925s	2.47t,J = 2Hz(6), 2.80d*,J = 16Hz(4), 3.44d,J = 2Hz(3), 7.44m(20)^e
$[Mn(dpe)(CNMe)_4]PF_6$	<u>cis</u>	2170m,2108vs(br)		2.45t,J = 2Hz(6), 2.65d*,J = 15Hz(4), 3.41s(6),7.40m(20)^e
$[Mn(dpe)(CNMe)_4](PF_6)_2$		2228m(sh),2194s		--

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a) PE 457 Spectrometer, ± 2 cm^{-1}. CH_2Cl_2 solutions.

b) acetone-d_6 solvent, except as noted. TMS internal standard. Data reported: chemical shift, multiplicity (s singlet, d doublet, d* multiplet pattern with pseudo doublet splitting of 16 ± 1 Hz, t = triplet), coupling constant, (intensity).

c) $CDCl_3$ solvent.

d) CD_2Cl_2 solvent.

e) CD_3CN solvent.

in the specific syntheses of various manganese(I) complexes containing CO, CNMe, CNPh, and/or dpe (dpe = 1,2-bis(diphenylphosphino) ethane). In addition we have run cyclic voltammetry studies on most of these complexes, detecting trends in their ease of oxidation ($E_{1/2}$) as a function of ligand choice.

Experimental

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Beckman IR-10 and Perkin-Elmer 457 spectrophotometers. Proton NMR spectra were recorded on a Jeol MH-100 spectrometer. These data are given in Table I.

Electrochemcial measurements were made using a three-electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled by a Princeton Applied Research Electrochemistry System, Model 169, incorporating compensation for internal resistive potential drop. Dry dichloromethane was used as the solvent with the solution $\sim 5\times10^{-3}$M in substrate. Tetrabutylammonium perchlorate (0.1 m) was employed as base electrolyte. Scan rates were typically 100 to 200 mV/sec. All measurements were made at 25°C.

Molecular weights were determined by vapor pressure osmometry in chloroform (0.05 M) on a Mechrolab Model 301A osmometer on samples previously dried in vacuum at 60° for one hour. Solvent of crystallization in analytical samples, if any, was verified by nmr integrations.

Tetrahydrofuran was dried by distillation from lithium aluminum hydride. Acetonitrile and dichloromethane were dried by reflux and distillation from phosphorus pentoxide. All reactions were carried out under nitrogen.

Preparations of $Mn(CO)_{5-n}(CNPh)_nBr$ (n = 2,3,4) [6], $Mn(CO)_{5-n}(CNMe)_nBr$ (n = 1, 2, 3, 4) [6], $[Mn(CNPh)_5(CNMe)]PF_6$ [4], $[Mn(CO)_{6-n}(CNMe)_n]PF_6$ (n = 4 (cis isomer) [2], n = 6 [6]), and fac-$Mn(CO)_3(dpe)Cl$ [7] were accomplished by methods described in the cited references.

Preparation of Compounds Containing Both CNMe and CNPh Ligands

cis-$[Mn(CO)_4(CNCH_3)(CNC_6H_5)]PF_6$. Samples of $AgPF_6$ (1.35g, 5.3 mmol) and

CNPh (0.41g, 4.0 mmol) are dissolved in 30 ml THF. A solution of 1.15g (4.0 mmol) cis-$Mn(CO)_4(CNCH_3)Br$ in 40 ml THF is added, and the reaction stirred for two hr. Solvent is evaporated, and the residue dissolved in CH_2Cl_2 and filtered. The volume of CH_2Cl_2 is reduced, and this solution filtered through a 1" column of alumina packed with THF. Following removal of solvent, the white product is recrystallized from acetone/ether, mp 134-5° (Yield: 20%).

Found: C, 34.41; N, 6.03; H, 1.75. $C_{13}H_8F_6O_4N_2PMn$ calcd: C, 34.23; N, 6.14; H, 1.77.

fac-$[Mn(CNCH_3)(CNC_6H_5)_2(CO)_3]PF_6$. Prepared similarly from fac-$Mn(CNC_6H_5)_2(CO)_3Br$, methyl isocyanide, and $AgPF_6$. Crystallization proved difficult, but was accomplished from acetone/ether; mp 173-5° (Yield: 78%).

Found: C, 43.06; N, 8.10; H, 2.54. $C_{19}H_{13}F_6N_3O_3PMn$ calcd: C, 42.94; N, 7.91; H, 2.45.

mer-cis-$[(Mn(CNCH_3)(CNC_6H_5)_3(CO)_2]PF_6$. Prepared from mer-cis-$Mn(C_6H_5)_3(CO)_2Br$, methyl isocyanide, and $AgPF_6$; mp 84-7° (Yield: 95%).

Found: C, 49.69; N, 9.12; H, 3.20. $C_{25}H_{18}F_6N_4O_2PMn$ calcd: C, 49.44; N, 9.23; H, 2.99.

trans-$[Mn(CNCH_3)(CNC_6H_5)_4(CO)]PF_6$. Prepared from trans-$Mn(CNC_6H_5)_4(CO)Br$, methyl isocyanide, and $AgPF_6$. Recrystallized by solvent diffusion with Skelly A/acetone; mp 213-5° (Yield: 25%).

Found: C, 54.76; N, 10.27; H, 3.36. $C_{31}H_{23}F_6N_5OMnP$ calcd: C, 54.62; N, 10.28; H, 3.40.

fac-$[Mn(CNC_6H_5)(CNCH_3)_2(CO)_3]PF_6$. Prepared from fac-$Mn(CNCH_3)_2(CO)_3Br$, phenyl isocyanide, and $AgPF_6$; mp 147-8° (Yield: 82%).

Found: C, 35.73; N, 8.98; H, 2.42. $C_{14}H_{11}F_6O_3N_3PMn$ calcd: C, 35.82; N, 8.96; H, 2.35.

mer-cis-$[Mn(CNC_6H_5)(CNCH_3)_3(CO)_2]PF_6$. Prepared from mer-cis-$Mn(CNCH_3)_3(CO)_2Br$, phenyl isocyanide, and $AgPF_6$, mp 130-2°. (Yield: 70%)

Found: C, 37.18; N, 11.61; H, 3.08. $C_{15}H_{14}F_6N_4O_2MnP$ calcd: C, 37.34; N, 11.62; H, 2.93.

trans-$[Mn(CNC_6H_5)(CNCH_3)_4(CO)]PF_6$. Prepared from trans-$Mn(CNCH_3)_4(CO)Br$, phenyl isocyanide, and $AgPF_6$. Recrystallized by solvent diffusion with Skelly A/acetone, mp 179-82°. (Yield: 80%).

Found: C, 38.59; N, 13.97; H, 3.47. $H_{17}C_{16}F_6N_5OMnP$ calcd: C, 38.80; N, 14.14; H, 3.46.

Preparation of *fac*-$Mn(CNC_6H_5)(CNCH_3)(CO)_3Br$. A 0.77g (2.5 mmol) sample of *cis*-$Mn(CO)_4(CNCH_3)Br$ and 0.26g (2.5 mmol) phenyl isocyanide are dissolved in 30 ml THF and stirred for 24 hr. Solvent is removed, and the product recrystallized from dichloromethane/heptane as orange-red crystals; mp 114-6°. (Yield: 40%).

Found: C, 40.03; N, 8.00; H, 2.25. $C_{12}H_8O_3N_2MnBr$ calcd: C, 39.70; N, 7.72; H, 2.22.

Preparation of Compounds Containing Both CNMe and dpe Ligands.

$Mn(dpe)(CO)_2(CNMe)Cl$. A sample of 2.0g (3.5 mmol) of *fac*-$Mn(dpe)(CO)_3Cl$ is dissolved in 20 ml THF, 0.25 ml (4.5 mmol) methyl isocyanide is added, and the solution heated at reflux for 30 hr. Solvent is evaporated, and the residue dissolved in a small amount of CH_2Cl_2 and introduced onto a 6" column of alumina packed with benzene. The starting material elutes first with CH_2Cl_2, and the product then elutes with a mixture of CH_2Cl_2 and acetone (1:1). The yellow-orange compound is recrystallized from acetone/ether as $Mn(dpe)(CO)_2(CNMe)Cl \cdot 0.5$ acetone. The product darkens at 185°C and melts at 201°C. (Yield: 70%).

Found: C, 61.71; N, 2.30; H, 4.77; MW 603. $C_{30}H_{27}O_2P_2NClMn \cdot 0.5\ C_3H_6O$ calcd: C, 61.51; N, 2.28; H, 4.91, MW 586.

$Mn(dpe)(CO)(CNMe)_2Cl$ (II). A sample of 5.5g (9.6 mmol) of *fac*-$Mn(dpe)(CO)_3Cl$ with 250 ml THF is placed in a 500 ml reaction vessel with a water cooled, quartz immersion well and a Hanovia 450 watt mercury arc lamp. The solution is purged with nitrogen for 1.0 hr. Methyl isocyanide (1.1 ml, 20 mmol) is added, and the solution irradiated and stirred for 30 min. The resulting cloudy orange solution is transferred to a nitrogen-filled 250 ml flask with careful exclusion of air and solvent blown off in a stream of nitrogen. The residue is dissolved in a minimum of CH_2Cl_2 and one-fourth of this solution chromatographed on a 6" air-free column of alumina packed with a 1:1 toluene/CH_2Cl_2 solvent mixture. Elution with CH_2Cl_2 gives two separate yellow bands, starting material and

Mn(dpe)(CO)$_2$(CNMe)Cl. A third band elutes with a 15/85 acetone/CH$_2$Cl$_2$ solution. Solvent is blown off in a stream of nitrogen to yield orange Mn(dpe)(CNMe)$_2$(CO)Cl, which is heated under vacuum to drive off trace solvent; mp 201-3°. (Yield: 10%).

Found: C, 62.32; N, 4.77; H, 5.09, MW, 582. $C_{31}H_{30}N_2P_2MnOCl$ calcd: C, 62.21; N, 4.68; H, 5.05; MW 599.

fac-[Mn(dpe)(CO)$_3$(CNMe)]PF$_6$. To 1.3 g (2.26 mmol) of fac-Mn(dpe)(CO)$_3$Cl dissolved in 40 ml of THF, is added a solution of 1.0 g (4.0 mmol) AgPF$_6$ and 0.20 ml (3.6 mmol) methyl isocyanide in 15 ml THF. The reaction is stirred for 1 hr. Solvent is stripped off, the residue dissolved in CH$_2$Cl$_2$ and filtered. The resulting solution is reduced in volume and chromatographed on a 3" column of alumina on CH$_2$Cl$_2$. The yellow starting material elutes with CH$_2$Cl$_2$, and the colorless product elutes with THF. Crystallization of the compound from acetone/ether gives the product with one half molecule of acetone of crystallization, mp 140-2°. (Yield: 40%).

Found: C, 51.59; N, 1.80; H, 4.15. $C_{31}H_{27}F_6O_3P_3NMn \cdot 0.5\ C_3H_6O$ calcd: C, 51.31; N, 1.84; H, 3.94.

mer-[Mn(dpe)(CO)$_3$(CNMe)]PF$_6$. A sample of Mn(dpe)(CO)$_2$(CNMe)Cl (1.0g, 1.8 mmol) is dissolved in 25 ml benzene, 0.60g (4.5 mmol) AlCl$_3$ is added, and CO gas slowly bubbled through the solution for 0.5 hr. Benzene is decanted from the dark blue-green oil that forms, and the oil is taken up in ice water. Addition of excess NH$_4$PF$_6$ produces a white precipitate which is collected, dissolved in acetone, and filtered through anhydrous MgSO$_4$. The white product, recrystallized from acetone/ether, darkens at 200° and melts at 203°. (Yield: 70%).

Found: C, 51.30; N, 1.86; H, 3.82. $C_{31}H_{27}F_6O_3P_3NMn$ calcd: C, 51.45; N, 1.94; H, 3.73.

[Mn(dpe)(CO)$_2$(CNMe)$_2$]PF$_6$ (first isomer). To 1.0g (1.8 mmol) Mn(dpe)(CO)$_2$(CNMe)Cl dissolved in 40 ml THF is added a solution of 0.50g (2.0 mmol) AgPF$_6$ and 0.10 ml (1.8 mmol) methyl isocyanide in 25 ml THF. The immediate formation of white precipitate is observed. After stirring 1.0 hr., solvent is evaporated, and the residue filtered through a 1" column of alumina with THF. Following evaporation of solvent, the material is recrystallized from acetone/ether to give a white product having both acetone and ether of crystallization. These solvents of crystallization were verified in the nmr spectrum of this compound. The compound does not melt cleanly, but froths at ~90°. (Yield: 80%).

Found: C, 52.79; N, 3.44; H, 4.92. $C_{32}H_{30}F_6N_2O_2P_2Mn \cdot 0.4\ C_4H_{10}O + 0.4\ C_3H_6O$ calcd: C, 52.95; N, 3.55; H, 4.65.

[Mn(dpe)(CO)$_2$(CNMe)$_2$]PF$_6$ (second isomer). An 0.50g (0.84 mmol) sample of Mn(dpe)(CO)(CNMe)$_2$Cl is placed in a carbon monoxide-filled flask. 50 ml of a carbon monoxide-saturated solution of 0.30g (2.3 mmol) $AlCl_3$ in benzene is added, and CO bubbled through the stirred reaction mixture for 15 min. Benzene is decanted from the pale yellow oil that forms, and an ethanol solution of NH_4PF_6 added. After stirring briefly, the ethanol is evaporated and the residue washed with H_2O to remove excess NH_4PF_6. The solid material is then dissolved in acetone and filtered through anhydrous $MgSO_4$. Solvent is evaporated and the residue is crystallized from acetone/ether, giving a white product, which contains 0.75 molecule acetone of crystallization. This product does not melt, but froths at 73-5°. (Yield: 65%).

Found: C, 52.48; N, 3.59; H, 4.46. $C_{32}H_{30}F_6N_2O_2P_2Mn \cdot 0.75\ C_3H_6O$ calcd: C, 52.74; N, 3.56; H, 4.64.

<u>[Mn(dpe)(CO)(CNMe)$_3$]PF$_6$</u>. A sample of Mn(dpe)(CO)(CNMe)$_2$Cl (0.55g, 0.92 mmol) is dissolved in 30 ml of N_2-purged THF. A solution of 0.30g (1.2 mmol) $AgPF_6$ and 0.10 ml (1.8 mmol) methyl isocyanide in deaerated THF is syringed into the first flask. After 0.5 hour, solvent is evaporated and the residue dissolved in acetone and run down a 3" column of alumina. The faint yellow major band contains the product. This material is crystallized from acetone/ether, mp. 195°. (Yield: 90%).

Found: C, 53.07; N, 5.61; H, 4.51. $C_{33}H_{33}F_6P_3N_3OMn$ calcd: C, 52.88; N, 5.64; H, 4.44.

<u>[Mn(dpe)(CO)(CNMe)$_3$]PF$_6$</u>. One gram (1.0g, 2.4 mmol) <u>cis</u>-[Mn(CNMe)$_4$(CO)$_2$]PF$_6$ and 0.95g (2.4 mmol) dpe are ground together with a mortar and pestle and sealed under vacuum in a glass ampule. The ampule is heated at 145° for 24 hr, allowed to cool, and the black residue dissolved in CH_2Cl_2 and placed on a 6" column of alumina packed on a 2:98 acetone/CH_2Cl_2 solvent mixture. Elution with the same solvent mixture gave a faint yellow band containing the product. This

is crystallized from acetone/ether. The pale yellow compound contains 0.3 molecule of acetone of crystallization. mp 237-8°. (Yield 32%.)

Found: C, 53.07; N, 5.74; H, 4.53. $C_{33}H_{33}F_6N_3OP_3Mn$ 0.3 C_3H_6O calcd: C, 53.09; N, 5.48; H, 4.57.

$[Mn(dpe)(CNMe)_4]PF_6$. Solid $[Mn(CNCH_3)_6]PF_6$ (1.0g, 2.2 mmole) and 0.90 g (2.2 mmol) dpe are ground together with mortar and pestle and then sealed under vacuum in a glass ampule. The ampule is heated at 180° overnight, allowed to cool, and the black residue dissolved in CH_2Cl_2 and placed on a 4" column of alumina packed on a 4/100 acetone/CH_2Cl_2 solvent mixture. On elution with this solvent mixture a pale yellow band develops, which is eluted. The product obtained from this fraction is crystallized from acetone/ether. Upon heating, the pale yellow product begins to froth at 97°. (Yield: 26%).

Found: C, 53.40; N, 7.22; H, 4.86. $H_{36}C_{34}F_6N_4P_3Mn$ calcd: C, 53.56; N, 7.35; H, 4.76.

Oxidation of $[Mn(dpe)(CNMe)_4]PF_6$. A sample of $[Mn(dpe)(CNMe)_4]PF_6$ (0.70 g, 0.92 mmol) is dissolved in 50 ml freshly distilled acetone. When 0.30 g (1.2 mmol) $AgPF_6$ is added, the solution immediately turns maroon. After 10 min stirring the solution is reduced in volume, run down a 4" column of alumina, a major red band eluting with acetone. Removal of solvent leaves an oil, which crystallizes upon the addition of 2 ml THF. The dark orange product froths upon heating at 108°, and is only moderately stable (as evidenced by the distinct smell of free isocyanide coming from the crystals). While only a rather poor analysis could be obtained, the color, infrared spectrum, and broad, unresolved nmr spectrum point to formulation of this complex as the paramagnetic $[Mn(dpe)(CNMe)_4](PF_6)_2$.

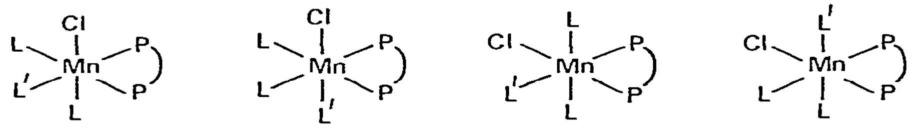
Found: C, 47.57; N, 5.33; H, 5.03; P, 12.26. $H_{36}C_{34}F_{12}N_4P_4Mn$ calcd: C, 45.05; N, 6.17; H, 4.00; P, 13.65.

Results and Discussion

Three uncharged complexes having CNMe and either CNPh or dpe ligands were prepared by carbonyl substitution reactions. Using mild conditions and stoichiometric amounts of CNMe and $Mn(CO)_4(CNPh)Br$ it was possible to make fac-$Mn(CO)_3(CNMe)(CNPh)Br$. From $Mn(CO)_3(dpe)Cl$ and CNMe, one can obtain either $Mn(dpe)(CO)_2(CNMe)Cl$ (THF reflux) or $Mn(dpe)(CO)(CNMe)_2Cl$ (uv irradiation of a THF solution). There was considerable reluctance to the substitution of the second carbonyl group by CNMe, and the latter product was only obtained in low yield in conjunction with the monosubstituted species and starting material. This compound was somewhat air sensitive. The two dpe compounds were used as precursors in subsequent syntheses of cationic complexes.

In earlier work from our group the syntheses of the related compounds $Mn(CO)_3(PPh_3)(CNMe)Br$ and $Mn(CO)_2(PPh_3)(CNMe)_2Br$ were reported [6]. These compou were prepared in reactions of CNMe with $Mn(CO)_4(PPh_3)Br$ and $Mn(CO)_3(PPh_3)_2Br$.

The fac-geometry was assigned for $Mn(CO)_3(CNMe)(CNPh)Br$ based on the pattern of three strong ν(CO) absorptions in its infrared spectrum. This is the geometry assumed by almost all disubstituted $Mn(CO)_3L_2X$ compounds. The geometries of the two $Mn(dpe)(CO)_{3-n}(CNMe)_nCl$ compounds were assumed to be those arising from equatorial substitution of carbonyls. The same pattern of substitution has been observed in other systems, e.g., in the syntheses of $Mn(CO)_{5-n}(CNR)_nBr$ (R = Me, Ph) [6], and $Mn(CO)_{5-n}[P(OMe)_3]_nBr$ [8]. Infrared data (ν(CO) and ν(CN)) are in accord with these assigned geometries, but are not conclusive evidence. Thus for $Mn(dpe)(CO)_2(CNMe)Cl$ the observation of two ν(CO) absorptions eliminates only one (Ic) of the four possible isomers (Figure I). Similarly two ν(CN) absorptions in $Mn(dpe)(CO)(CNMe)_2Cl$ eliminates only the structure with trans CNMe groups (IIc) leaving a choice between the three remaining geometries. The most conclusive evidence concerning the structures of these compounds comes indirectly from the better defined geometries of cationic compounds derived upon



(a) (b) (c) (d)

I. $Mn(dpe)(CO)_2(CNMe)Cl$ L = CO, L' = CNMe

II. $Mn(dpe)(CO)(CNMe)_2Cl$ L = CNMe, L' = CO

FIGURE I. POSSIBLE GEOMETRIC ISOMERS OF $Mn(dpe)(CO)_{3-n}(CNMe)_nCl$ (n = 1,2) substitution of either CNMe or CO for Cl^- in what are assumed to be stereospecific reactions (vide infra).

One general route by which a metal carbonyl halide can be converted to a cationic complexes involves replacement of the halide ion by a neutral ligand. Such reactions, ordinarily requiring the assistance of a halide acceptor, e.g., $AlCl_3$ or Ag^+, have been used extensively in the syntheses of cationic manganese(I) carbonyl species. We have recently reported syntheses of various members of the series $[Mn(CO)_{6-n}(CNR)_n]^+$ (R = Me [1,6], Ph [9]; n = 1-6) using this synthetic route. It is noted that in the forementioned examples of these reactions, the entering ligand assumes the coordination position previously occupied by the halide ion. This fact has permitted the intentional synthesis of specific isomeric species [1].

The successful application of this route to the specific syntheses of cationic manganese(I) complexes having CO, CNMe, and either 1,2-bis(diphenylphosphino)-ethane or CNPh is reported here. Starting from known [6,9] $Mn(CO)_{5-n}(CNMe)_nBr$ (n = 1-4), CNPh, and $AgPF_6$ one obtains the complexes $[Mn(CO)_{5-n}(CNMe)_n(CNPh)]PF_6$ (n = 1-4). Similarly, from $Mn(CO)_{5-n}(CNPh)_nBr$, CNMe, and $AgPF_6$, it is possible to prepare $[Mn(CO)_{5-n}(CNMe)(CNPh)_n]PF_6$ (n = 2-4). The synthesis of the last member in this series (the compound having n = 5) by this route was reported in a previous paper [4]:

$$Mn(CO)_{5-n}(CNMe)_nBr + AgPF_6 + CNPh \rightarrow [Mn(CO)_{5-n}(CNMe)_n(CNPh)]PF_6 + AgBr\downarrow$$
$$(n = 1 \rightarrow 4)$$

$$Mn(CO)_{5-n}(CNPh)_nBr + AgPF_6 + CNMe \rightarrow [Mn(CO)_{5-n}(CNMe)(CNPh)_n]PF_6 + AgBr\downarrow$$
$$(n = 2 \rightarrow 5)$$

The new compounds are white or pale yellow crystalline solids which are air stable in solid state, and moderately stable in solution.

Infrared and nmr data argue for the stereospecificity of some of these reactions. For example, the compounds $Mn(CO)(L)_4Br$ (L = CNMe, CNPh) are known to have trans configurations because of a single ν(CN) absorption, and for the CNMe compound, a single proton resonance. Upon substitution of L' for Br^-, giving $[Mn(CO)L_4L']^+$ (L,L' = CNMe,CNPh) these spectral characteristics are retained. Likewise, the infrared data on $[Mn(CO)_2(CNMe)_3(CNPh)]^+$ and on $[Mn(CO)_2(CNMe)(CNPh)_3]^+$ are reasonably conclusive for the mer-cis geometry. In each compound two ν(CO) absorptions indicate CO groups in cis positions, and the three ν(CN) absorptions of unequal intensities are more in accord with a mer configuration for the three similar isocyanides than for a fac configuration of these ligands. The mer-cis configurations are those predicted assuming that these reactions are stereospecific.

Unfortunately methyl groups in dissimilar environments in the mer-cis compoun are not differentiated on the basis of chemical shifts. There is, apparently, a fortuitious coincidence of these resonances.

Syntheses of complexes with 1,2-bis-(diphenylphosphino)ethane as a ligand starts with the three known compounds $Mn(dpe)(CO)_{3-n}(CNMe)_nCl$ (n = 0, 1, 2). Treating each member of this series with CNMe and $AgPF_6$ yields the products $[Mn(dpe)(CO)_{3-n}(CNMe)_{n+1}]PF_6$; the same organometallic starting materials with CO and $AlCl_3$, followed by metathesis with PF_6, gives $[Mn(dpe)(CO)_{4-n}(CNMe)_n]PF_6$:

$$Mn(dpe)(CO)_{3-n}(CNMe)_nCl + CNMe + AgPF_6 \rightarrow [Mn(dpe)(CO)_{3-n}(CNMe)_{n+1}]PF_6 + AgCl\downarrow$$

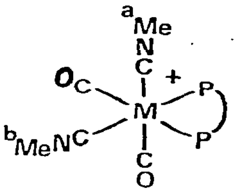
(n = 0,1,2)

$$Mn(dpe)(CO)_{3-n}(CNMe)_nCl + CO + AlCl_3 \xrightarrow{2)PF_6^-} [Mn(dpe)(CO)_{4-n}(CNMe)_n]PF_6$$

A second isomer of $[Mn(dpe)(CO)(CNMe)_3]PF_6$ and the new complex [Mn(dpe)(CNMe) were prepared in reactions of dpe with cis-$[Mn(CO)_2(CNMe)_4]PF_6$ and $[Mn(CNMe)_6]PF_6$ respectively. A similar route to $[Mn(CNBu^t)_5PPh_3]PF_6$ had been reported earlier by King and coworkers [9]. Resembling the other cationic compounds reported earlie these compounds are also white or pale yellow, air stable crystalline species.

All the spectroscopic evidence (ir and nmr) on these new complexes support assignments of structures in which the incoming ligand has assumed the coordinatio position of the departing halide. Most conclusive is the nmr data on these comple Protons of a methyl group in a ligand cis- to dpe occur as triplets (J ~ 2Hz), coupled to equivalent phosphorus atoms, at about δ2.5 vs TMS. Trans to one phospho of the dpe ligand, these protons occurred further downfield, around δ3.5, and when resolved there is coupling to only one phosphorus atom giving rise to a doublet pattern. Supporting these assigned geometries are the infrared patterns which show the expected numbers of ν(CO) and ν(CN) values.

Data on the two sets of isomeric compounds, [Mn(dpe)(CO)$_2$(CNMe)$_2$]PF$_6$ and [Mn(dpe)(CO)(CNMe)$_3$]PF$_6$, illustrating these conclusions, are given in Figure II. It can be seen that the structural assignments based on nmr and ir



Isomer 1

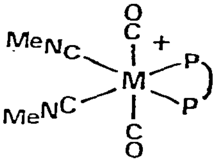
(from Mn(dpe)(CO)$_2$(CNMe)Cl
+ CNMe + AgPF$_6$)

Me^a δ2.57t (int 3)

Me^b δ3.48d (int 3)

ν(CO) 1984,1941 cm^{-1}

ν(CN) 2199,2173 cm^{-1}



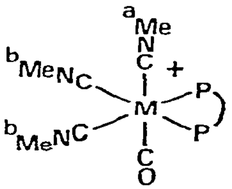
Isomer 2

(from Mn(dpe)(CO)(CNMe)$_2$Cl
+ CO + AlCl$_3$)

Me δ3.49d (int 6)

ν(CO) 1951 cm^{-1}

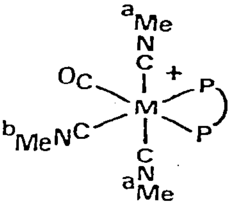
ν(CN) 2180,2149 cm^{-1}



(from Mn(dpe)(CO)(CNMe)$_2$Cl
+ CNMe + AgPF$_6$)

Me^a δ2.49t (int 3)

Me^b δ3.46d (int 6)



(from cis-[Mn(CO)$_2$(CNMe)$_4$]$^+$ + dpe)

Me^a δ2.47t (int 6)

Me^b δ3.44d (int 3)

FIGURE II. STRUCTURES AND SUPPORTING DATA FOR ISOMERS OF [Mn(dpe)(CO)$_n$(CNMe)$_{4-n}$]PF$_6$ (n = 1, 2)

TABLE II. ELECTROCHEMICAL DATA

Compound	Geometry	$1/2[E_{p,c}+E_{p,a}]^a$	$E_{p,c}-E_{p,a}$
$[Mn(CO)_4(CNMe)(CNPh)]PF_6$	*cis*	2.22	0.250
$[Mn(CO)_3(CNMe)_2(CNPh)]PF_6$	*fac*	1.98	0.184
$[Mn(CO)_2(CNMe)_3(CNPh)]PF_6$	*mer-cis*	1.52	0.184
$[Mn(CO)(CNMe)_4(CNPh)]PF_6$	*trans*	0.95	0.166
$[Mn(CO)_3(CNMe)(CNPh)_2]PF_6$	*fac*	2.08	0.264
$[Mn(CO)_2(CNMe)(CNPh)_3]PF_6$	*mer-cis*	1.65	0.267
$[Mn(CO)(CNMe)(CNPh)_4]PF_6$	*trans*	1.23	0.166
$[Mn(CNMe)(CNPh)_5]PF_6{}^c$		$0.92,(1.88)^b$	0.192,(0.208)
$[Mn(dpe)(CO)_3(CNMe)]PF_6$	*fac*	1.97	0.218
$[Mn(dpe)(CO)_3(CNMe)]PF_6$	*mer*	1.75	0.196
$[Mn(dpe)(CO)_2(CNMe)_2]PF_6$ Isomer 1		1.42	0.170
$[Mn(dpe)(CO)_2(CNMe)_2]PF_6$ Isomer 2		1.16	0.175
$[Mn(dpe)(CO)(CNMe)_3]PF_6$ Isomer 1	*fac*	0.83	0.224
$[Mn(dpe)(CO)(CNMe)_3]PF_6$ Isomer 2	*mer*	0.91	0.268
$[Mn(dpe)(CNMe)_4]PF_6$	*cis*	$0.46,(1.43)^b$	0.186,(0.160)

a) Cathodic and anodic peak potentials, volts vs. SCE. First oxidation potentials are for the process +1 → +2.

b) E_2 is the second oxidation potential, +2 → +3.

c) Ref. 4.

evidence are unambiguous. Isomer 1 of the first compound has non-equivalent CNMe groups according to nmr, and must have the given structure; supporting this is the infrared spectrum showing two ν(CO) and two ν(CN) absorptions. Isomer 2 is one of two possible isomers having equivalent CNMe groups. Predicted for this geometry, and found, is a doublet splitting of the methyl proton resonances, two ν(CN) absorptions and one ν(CO) absorption. The only other isomer of this formula would be trans CNMe and cis CO groups; for this isomer a triplet splitting for the methyl protons, two ν(CO), and one ν(CN) absorptions are predicted. It would be interesting to make this isomer to test this prediction. For the compound $[Mn(dpe)(CO)(CNMe)_3]PF_6$ only two isomers can exist. One (Isomer 1) has two CNMe groups trans and one CNMe group cis to dpe; this gives rise, respectively, to doublet and triplet patterns of relative intensities six and three. In Isomer 2 there are two CNMe groups cis to dpe for which the nmr spectrum shows a triplet (intensity = 6) and one CNMe trans to a phosphorous atom giving one doublet nmr resonance of intensity 3.

The structures of the $[Mn(dpe)(CO)_3(CNMe)]PF_6$ isomer are assigned based on the chemical shifts of the methyl protons. The fac isomer has an nmr resonance at δ2.58, while the mer isomer shows a resonance at δ3.60. Both values correspond with chemical shifts seen for methyl protons in these environments in other compounds. Unfortunately the coupling to phosphorus in these compounds, which would unequivocally define stereochemistry, could not be resolved.

A significant point is that these data argue for the assigned geometries of the precursors $Mn(dpe)(CO)_{3-n}(CNMe)_nCl$ (n = 1, 2). One starts with knowledge of the precise structures of the product species. Assuming a stereochemical pathway involving substitution of an incoming ligand into the site occupied by halide, which is now known to have considerable precedence [1,2], we can conclude that our assumptions of the geometries of $Mn(dpe)(CO)_{3-n}(CNMe)_nCl$ are most likely correct.

Electrochemical data on all the compounds described here are reported. Only one electrochemical process, a one electron oxidation, is observed for each compound, with the potential required for this oxidation decreasing with a decreasing carbonyl content. Isomers of the compounds $[Mn(dpe)(CO)_{4-n}(CNMe)_n]PF_6$ (n = 1, 2, 3) exhibit $E_{1/2}$ values differing by about 0.1-0.3v. This is not surprising, considering earlier published work on $[Mn(CO)_{6-n}(CNR)_n]PF_6$ (R = Me, Ph), and presumably there is a similar explanation based on relative stabilizations of the metal 3d orbitals by different ligand [1,2].

It is interesting to note the regular variation of $E_{1/2}$ values in the series fac-$[Mn(CO)_3(CNMe)_{3-n}(CNPh)_n]PF_6$ ($n = 0 \rightarrow 3$). The $E_{1/2}$ values are, in order, 1.90 [1], 1.98v, 2.08v, 2.12v [9]. Similar variations are seen for the series, cis-$[Mn(CO)_2(CNMe)_{4-n}(CNPh)_n]PF_6$ (in order from n = 0 to n = 4: 1.44v, 1.52, – , 1.65v, 1.70v). Note here that the series is not complete; none of the isomers of cis-$[Mn(CO)_2(CNMe)_2(CNPh)_2]PF_6$ have yet been made, as yet we do not know of a unique route which would lead to such a species. Similar sequences of $E_{1/2}$ values are also seen for other partial series of related compounds. The synthesis some of the missing isomeric species represent an interesting future challenge.

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