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CIS–TRANS ISOMERIC INFLUENCE ON THE REACTIVITY OF $BrMn(CO)_2dppmP(OPh)_3$ TOWARDS DIALKYLTHIOETHERS

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Abstract—*Trans*-[$BrMn(CO)_2(dppm)P(OPh)_3$] reacts with SR_2; R = C_2H_5 and C_3H_7 to give the cationic complexes *trans*-[$Mn(CO)_2(dppm)P(OPh)_3(SR_2)$]$PF_6$ while from the reaction of *cis,cis*-[$BrMn(CO)_2(dppm)P(OPh)_3$] with the thioether ligands the unaltered dicarbonyl manganese complex was isolated. The new cationic complexes were characterized by elemental analysis, IR, ^{1}H-NMR, ^{31}P-NMR and UV-visible spectroscopic methods. The different reactivity between the *cis* and *trans* isomers is discussed in terms of Mn—Br bond strength and steric factors.

Carbonyl complexes of manganese(I) of the general type [$XMn(CO)_{5-n}L_n$] X = Br, SCN, CN exhibit interesting redox and isomeric features.[1–4] For example the complex [$BrMn(CO)_2(dppm)P(OPh)_3$]; (dppm = Ph_2PCH_2-PPh_2) exists in both *cis* and *trans* isomeric forms, the latter being prepared by an oxidation–reduction process from the *cis* isomer.[2]

Replacement of the bromo-ligand in either *cis,cis*- or *trans*-$MnBr(CO)_2$(L-L)L using $TIPF_6$ in the presence of N or P donor ligands, results in the formation of the respective cationic *cis,cis*- or *trans*-[$Mn(CO)_2$(L-L)LL′]PF_6 complexes.[2–5] When L′ was the metal containing ligand CpFe(dppe)CN the respective heterobinuclear cyanide bridged complexes were obtained.[6]

However no complexes with sulphur donor ligands have been reported. Some authors have previously noted the scarcity of manganese–sulphur compounds.[7–9]

In this paper we report on the reactions of *cis,cis*- and *trans*-$MnBr(CO)_2(dppm)P(OPh)_3$ with the alkyl sulphide compounds SR_2 (R = C_2H_5 and C_3H_7). The synthesis and characterization of the cationic complexes *trans*-[$MnBr(CO)_2$(dppm) $P(OPh)_3SR_2$]PF_6 is described.

RESULTS AND DISCUSSION

Reaction of the *trans*-$MnBr(CO)_2dppmP(OPh)_3$ with SR_2 in CH_2Cl_2 and in presence of $TIPF_6$ affords the orange solids *trans*-[$MnBr(CO)_2$(dppm) $P(OPh)_3(SR_2)$]PF_6 (see Scheme 1). The IR spectra of the compounds exhibited a strong υ(CO) absorption near 1930 cm^{-1} (Table 1) and a very weak one at higher frequency. This pattern is characteristic of an octahedral *trans* dicarbonyl.[2] A band in the IR, at 840 cm^{-1} showed the presence of the anion PF_6^-. Intense bands between 1600 and 700 cm^{-1} corresponding to coordinated dppm and $P(OPh)_3$ ligands also confirm the presence of the $Mn(CO)_2(dppm)P(OPh)_3$ moiety.[10]

The ^{1}H-NMR spectra of the complexes showed in addition to the expected signal of coordinated dppe (phenyl and methylene protons) and $P(OPh)_3$ (phenyl protons), the signals of $S(C_3H_7)_2$ and $S(C_2H_5)_2$ modified by coordination effects. Data are shown in Table 1.

On the other hand the ^{31}P-NMR spectra of cationic complexes show (see Table 2) the signals corresponding to $P(OPh)_3$ and dppm modified by coordination effects. For comparison the data for the neutral precursor *cis*- and *trans*-[$BrMn(CO)_2(dppm)P(OPh)_3$] are also included in Table 2. The spectra of cationic complexes at room temperature showed three sets of sharp multiplets.

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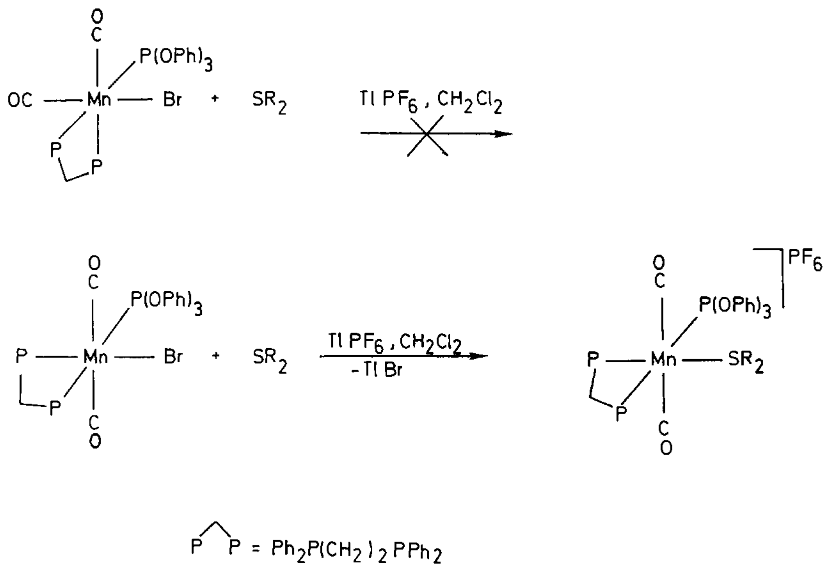


Scheme 1.

An approximate first-order analysis of the spectra[11] (AMX system) yielded the chemical shifts and coupling constants shown in Table 2. Assignments of the chemical shifts were made by taking account of the *trans* influences of the ligands.[12] Thus the chemical shift corresponding to the lowest frequency was assigned to the P(2) phosphorus which is the one *trans* to the $P(OPh)_3$ ligand.

It is interesting to note the changes of the resonance signals of dppm in going from the neutral bromo derivative to the cationic complex. The P(1) decreases while P(2) increases. A similar tendency was observed in comparing $[BrMn(CO)_2(dppm)P(OPh)_3]$ with the cationic $[Mn(CO)_2(dppm)P(OPh)_3(CNCH_3)]PF_6$.[11] The decreasing of the P(1) chemical shift agrees with the *trans* influence of the thioether ligands.[8,12]

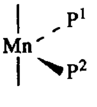
The visible absorption spectra of the complexes confirm the *trans* nature of the $[Mn(CO)_2(dppm)P(OPh)_3]$ moiety. In fact the spectra show one band around 490 nm and a shoulder near 370 nm, as shown in Fig. 1 for $[Mn(CO)_2(dppm)P(OPh)_3(SEt_2)]PF_6$. The lowest absorption band can be assigned to a metal centred

Table 1. Selected spectral data for $[Mn(CO)_2(dppm)P(OPh)_3(SR_2)]PF_6$ complexes

	IR			^{1}H-NMR[c]			Visible[d]
	ν(CO)[a]		$\nu(PF_6)$[b]	SR_2	$P\text{-}C_6H_5$	$P(CH_2)_2$	λ_{max} (log ε)
$[Mn(CO)_2(dppm)P(OPh)_3$	2013	1928	832	2.32 (q,2H)	7.8–6.7	4.5	488 (2.6)
$(SEt_2)]PF_6$				1.26 (t,3H)			369 sh
SEt_2				2.57 (q,2H)			
				1.25 (t,3H)			
$[Mn(CO)_2(dppm)P(OPh)_3$	2013	1929	841	2.26 (t,2H)	7.5–6.8	4.6	492 (2.4)
$(SPr_2)]PF_6$				1.39 (m,2H)			372 sh
				0.79 (t,3H)			
SPr_2				2.52 (t,2H)			
				1.65 (m,2H)			
				1.02 (t,3H)			

[a] In CH_2Cl_2 solution, ν in cm^{-1}.
[b] KBr solid.
[c] In $CDCl_3$ solution.
[d] In CH_2Cl_2 solution, λ in nm.
sh: shoulder.

Table 2. ^{31}P-NMR Data for the complexes containing the fragment *cis*- and *trans*- $Mn(CO)_2(dppm)P(OPh)_3$[a]



Compounds	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{12}	J_{13}	J_{23}
Cis-$[BrMn(CO)_2(dppm)P(OPh)_3]$	7.6	23.8	166.2	43	77	140
Trans-$[BrMn(CO)_2(dppm)P(OPh)_3]$	58	14.18	173.3	30	60	66
Trans-$[Mn(CO)_2(dppm)P(OPh)_3(SEt_2)]PF_6$[b]	40.4	17.8	167.5	36.4	60.7	36.5
Trans-$[Mn(CO)_2(dppm)P(OPh)_3(SPr_2)]PF_6$[c]	40.3	17.9	167.7	37	60.8	50

[a] Proton decoupled. Measured in $CDCl_3$ solution at room temperature to high frequency of external 85% H_3PO_4 δ in ppm $J(PP)$ in Hz.

[b] $\delta(PF_6)$ heptuplet at 144 ppm.

[c] $\delta(PF_6)$ heptuplet at 144.1 ppm.

$d_{xy} \rightarrow d_{z^2}$ transition[13] shifted to higher energy compared with the neutral precursor *trans*-$[BrMn(CO)_2(dppm)P(OPh)_3]$. This effect has been also found in going from neutral CpFe(dppe)X to cationic $[CpFe(dppe)L]PF_6$ complexes[14] and is in agreement with the variation of Δ_o with the charge in the spectrochemical series.

The next lowest energy absorption band can be attributed to a d_{xz}, $d_{yz} \rightarrow d_{z^2}$ transition, and is also shifted to a higher energy respect to that found in the neutral precursor.

Reactions between complex *cis,cis*-$[BrMn(CO)_2(dppm)P(OPh)_3]$ and SR_2 ($R = C_2H_5$ and C_3H_7) in presence of $TlPF_6$ were found to be more complex than the corresponding ones of the *trans*-isomer. The solid yellow products isolated from the reactions had no PF_6^- as revealed by the absence of the $\nu(PF_6)$ band in the IR spectra at 840 cm^{-1} as well as by the absence of the septuplet around −150 ppm in the ^{31}P-NMR spectra.

Thus in addition to the peaks at 23 and 7 ppm corresponding to unchanged *cis,cis*-$[BrMn(CO)_2(dppm)P(OPh)_3]$, two small unidentified peaks at 128 and 63 ppm were also observed.

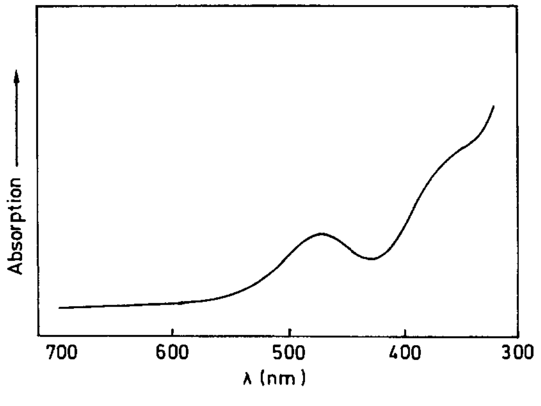


Fig. 1. UV–vis absorption spectrum of the complex *trans*-$[Mn(CO)_2dppmP(OPh)_3SEt_2]PF_6$ in CH_2Cl_2 solution at room temperature.

The IR solution spectra in the ν(CO) region exhibited the two carbonyl bands at 1830 and 1960 cm^{-1} corresponding to unchanged *cis,cis*-$[MnBr(CO)_2(dppm)P(OPh)_3]$. In addition a shoulder at *ca* 1974 cm^{-1} to the weak band at 1918 cm^{-1} was also observed. This suggests the formation of the respective cationic complex *cis*, *cis*-$[Mn(CO)_2(dppm)P(OPh)_3(SR)_2]PF_6$.

The lesser reactivity of the *cis,cis* isomer with respect to the *trans* isomer has been previously noted[6] but not discussed. Considering that it is commonly accepted that substitution reactions in octahedral complexes occurs through an SN_1 dissociative mechanism, then the rupture of the Mn—Br bond is rate determining. In fact we have found a higher Mn—Br force constant for the *cis,cis*-$[BrMn(CO)_2(dppm)P(OPh)_3]$ than the *trans* isomer[10] which suggests a more easy breaking of the Mn—Br bond for the *trans* isomer compared with the *cis* isomer. Steric factors can be also involved because the fragment *cis,cis*-$[Mn(CO)_2(dppm)P(OPh)_3]^3$ is more bulky than the *trans* isomer.

EXPERIMENTAL

Infrared spectra were recorded on Perkin–Elmer 621 and FT-IR Perkin–Elmer 2000 spectrophotometers. NMR spectra were recorded on a Bruker AMX 300 instrument. Chemical shift are given in δ relative to TMS (^{1}H) or 85% H_3PO_4 (^{31}P proton decoupled) downfield positive to the reference; J values are given in Hertz. Visible absortion spectra were measured on a Varian DMS-90 spectrophotometer in 1 cm lengh cuvettes. Elemental analyses were performed with a Perkin–Elmer 240 microanalyser.

All reactions were carried out under N_2. Diethylsuphide and di-propyl sulphide (Aldrich) were used without additional purification. Solvents were purified using standard procedure. The compounds *cis*, *cis*- and *trans*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] were prepared by the published methods.[2] All the reactions were carried out in flasks shielded from the light by aluminium foil.

Trans-[Mn(CO)$_2$(dppm)P(OPh)$_3$(SEt$_2$)]PF$_6$

To 0.1 g (0.14 mmol) of *trans*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] in CH_2Cl_2 was added 0.08 g (0.23 mmol) of $TlPF_6$ (excess) and 0.84 g (9.28 mmol) SEt_2 and the mixture stirred for 18–20 h. After 10 h the red solution changed to orange. The solution was filtered through Kieselghur and concentrated to *ca* 5 cm^3 *in vacuo*. Precipitation with a diethyl ether/*n*-hexane mixture gave an orange solid which was twice washed with a diethyl ether/*n*-hexane mixture and dried *in vacuo*.

Found: C, 57.8; H, 4.4. Calc for $C_{49}H_{47}O_5F_6SP_2Mn$: C, 56.5; H, 4.5%. IR (KBr) 3060 (w), 2930 (w), 2000 (w), 1920 (vst), 1585 (m), 1480 (st), 1430 (m), 1210 (m), 1180 (st), 1155 (m), 1090 (m), 1020 (m), 905 (st), 890 (st, sh), 835 (vst), 762 (m), 720 (m), 685 (st), 620 (st), 555 (st), 522 (st).

Trans-[Mn(CO)$_2$(dppm)P(OPh)$_3$(SPr$_2$)]PF$_6$

To 0.12 g (0.16 mmol) of *trans*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] and 0.1 g (0.28 mmol) of $TlPF_6$ in CH_2Cl_2 was added 0.84 g (7.01 mmol) of SPr_2 and the mixture stirred for 18–20 h. Isolation procedure was similar to the diethyl sulphide complex.

Found: C, 57.1; H, 4.7. Calc for $C_{51}H_{51}O_5F_6SP_2Mn$: C, 57.3; H, 4.8 %. IR (KBr) 3445(w), 2966 (w), 2933 (w), 2010 (w), 1921 (vst), 1589 (st), 1487 (st), 1436 (m), 1213 (m), 1188 (st), 1162 (m), 1094 (m), 912 (m), 841 (vst), 765 (m), 693(m).

Reaction of cis,cis-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] *with thioethers*

To a solution of *cis,cis*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] 0.12 g (0.16 mmol) and the respective thioether 0.837 g (9.28 mmol) of $S(C_2H_5)_2$, 0.84 g (7.1 mmol) of $S(Pr)_2$ in CH_2Cl_2 was added 0.1 g (0.28 mmol) of $TlPF_6$. After stirring for 2 days the solution was filtered through Kiesilghur and concentrated to *ca* 5 cm^3 *in vacuo*. Precipitation with a diethyl ether/*n*-hexane mixture gave a yellow solid wich was washed with a diethyl ether/*n*-hexane mixture and dried *in vacuo*.

The IR spectra of the solids was identical with the starting precursor *cis,cis*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] except a weak band observed at 836 cm^{-1} ($\nu(PF_6)$). On the other hand the ^{31}P-NMR spectra of the isolated solids exhibit similar signals to *cis,cis*-[MnBr(CO)$_2$(dppm)P(OPh)$_3$] and two additional weak signals at 123 and 63 ppm.

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