Chemistry of the Metal Carbonyls. Part LXXII.[1] Carbene Complexes of Manganese containing Thiazolidinylidene and Benzothiazolidinylidene Ligands

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N-Methyl-2-chlorobenzothiazolium tetrafluoroborate reacts with the $[(Ph_3P)_2N]^+$ salt of the anion $[Mn(CO)_5]^-$ to afford the cationic carbene complex $[Mn(CO)_5(\overline{C\cdot NMe\cdot C_6H_4\cdot S})][BF_4]$. Treatment of the latter with a mixture of triethylamine, water, and diethyl ether yields the neutral crystalline hydrido-complex $[MnH(CO)_4(\overline{C\cdot NMe\cdot C_6H_4\cdot S})]$. The latter is converted into the halogeno-derivatives $[MnX(CO)_4(\overline{C\cdot NMe\cdot C_6H_4\cdot S})]$ (X = Cl, Br, or I) on treatment with CCl_4, CH_2Br_2, or MeI, respectively. The iodo-complex reacts with triphenylphosphine or 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane to give $[MnI(CO)_3L(\overline{C\cdot NMe\cdot C_6H_4\cdot S})]$ {L = PPh_3 or $P[(OCH_2)_3CMe]$}, and with thallium hexafluoroacetylacetonate to give $[Mn(CO)_3(hfacac)(\overline{C\cdot NMe\cdot C_6H_4\cdot S})]$. Some studies on the hydrido-species $[MnH(CO)_4(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})]$ are also reported.

WE have previously described complexes of manganese $[MnX(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot O})(CO)_4]$ (X = Cl, Br, or I),[2] $[MnI(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})(CO)_4]$,[3] and $[MnI(CO)_4(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})]$ [4] in which a carbene ligand is *cis* to a halide ion within the co-ordination sphere of the metal. In part these complexes were prepared in the hope that they would act as precursors for the synthesis of other species of the type *cis*-[Mn(R)(carbene)$(CO)_4$] which would promote reactions between the carbene ligand and R. Thus, if R were H or alkyl, migration of these substituents to the carbene ligand might occur. However, treatment of *cis*-$[MnI(CO)_4(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})]$ with methyl-lithium led to attack both on the carbonyl groups and on the carbene ring. Reduction with sodium amalgam in tetrahydrofuran gave $[Mn(CO)_5]^-$ rather than the synthetically useful carbene anion $[Mn(CO)_4(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})]^-$. A similar attempt to prepare a carbene anion by reduction of $[Mn_2(CO)_9\{C(OMe)Me\}]$ was also unsuccessful.[5] Moreover, at room temperature there was no reaction between *cis*-$[MnI(CO)_4(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})]$ and tetramethyltin, phenylmercury(II) chloride, or thallium cyclopentadienide. The use of higher temperatures merely resulted in decomposition of the carbene complex to a mixture of $[MnI(CO)_5]$, $[Mn_2I_2(CO)_8]$, and $[Mn_2(CO)_{10}]$. Attempts to prepare an inorganic Grignard reagent $IMg[Mn(CO)_4(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})]$ with magnesium were also unsuccessful. The carbene complex did react with $[Hg(C_5H_5)_2]$ but the product was $[Mn(\eta\text{-}C_5H_5)(CO)_3]$. These results indicated that the carbene ligand is easily displaced from *cis*-$[MnI(CO)_4(\overline{C\cdot O\cdot CH_2\cdot CH_2\cdot CH_2})]$. Studies were therefore carried out with complexes containing the thiazolidinylidene ligands $:\overline{C\cdot NMe\cdot CMe{:}CH\cdot S}$ and $:\overline{C\cdot NMe\cdot C_6H_4\cdot S}$ in the hope that these groups would prove more amenable than the oxacyclopentylidene in this kind of chemistry. Several new complexes were characterised, but no reactions with the co-ordinated carbenes were observed.

RESULTS AND DISCUSSION

Treatment of the salt [4] $[Mn(CO)_5(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})][BF_4]$ with triethylamine in diethyl ether–water (3 : 1) afforded a red oil. Although the latter resisted conversion to a crystalline complex, it was formulated as the hydrido-species $[MnH(CO)_4(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})]$, (I), on the basis of its spectroscopic properties. The i.r. spectrum showed four terminal carbonyl-stretching bands (2 059m, 1 978s, 1 963vs, and 1 948s cm^{-1}) in accord with the formation of a *cis* di-substituted octahedral complex. No band characteristic of the Mn–H group was observed in the i.r. spectrum, but the ^1H n.m.r. spectrum (C_6D_6) showed the presence of the hydrido-ligand by a signal at τ 17.13 (1 H). The n.m.r. spectrum also showed bands corresponding to the carbene ligand at τ 3.47(1 H, C*H*), 4.63(3H, NCH_3), and 7.43(3 H, CCH_3). In order to establish by a chemical means that the red oil corresponded to a hydrido-species its reactions with methyl iodide and dibromomethane were examined. The former reagent afforded the known [4] complex *cis*-$[MnI(CO)_4(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})]$, while the latter gave *cis*-$[MnBr(CO)_4(\overline{C\cdot NMe\cdot CMe{:}CH\cdot S})]$, (II).

Because of the difficulty encountered in obtaining a

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[1] Part LXXI, M. Green, M. Underhill, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 939.

[2] D. H. Bowen, M. Green, D. M. Grove, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 1189.

[3] C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 351.

[4] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 760.

[5] E. O. Fischer and E. Offhaus, *Chem. Ber.*, 1969, **102**, 2449.

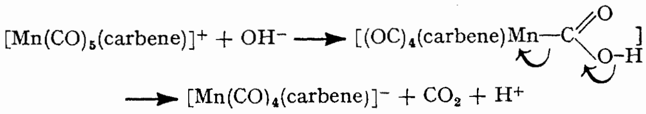
crystalline sample of (I) the carbene ligand was changed to *N*-methylbenzothiazolidinylidene. A number of palladium and platinum complexes containing the ligand $:C{\cdot}NMe{\cdot}C_6H_4{\cdot}S$ have previously been prepared using an electron-rich olefin as precursor.[6] Treatment of 2-chlorobenzothiazole with trimethyloxonium tetrafluoroborate afforded the salt $[Cl{\cdot}C{\cdot}NMe{\cdot}C_6H_4{\cdot}S][BF_4]$, (III). Reaction of this salt with $[(Ph_3P)_2N][Mn(CO)_5]$ [7] afforded air-stable $[Mn(CO)_5(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)][BF_4]$, (IV), in good yield. The ^1H n.m.r. spectrum of (IV) showed a broad multiplet at τ 2.30 and a broad singlet at τ 5.65, corresponding to C_6H_4 and NCH_3, respectively. Attempts to prepare an *N*-isopropyl analogue of (IV) were unsuccessful, perhaps due to steric effects. Complex (IV) did not react with lithium or tetraethylammonium iodides in a manner similar to

$$[Mn(CO)_5(C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S)][BF_4],$$

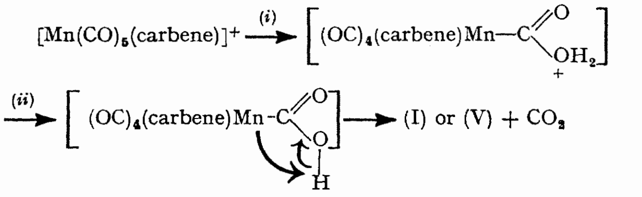
i.e. to give a neutral complex $[MnI(CO)_4(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$.

Complex (IV) reacted with triethylamine in water–diethyl ether to give the air-stable red crystalline hydrido-complex *cis*-$[MnH(CO)_4(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$, (V). This complex showed a parent ion in its mass spectrum followed by stepwise loss of hydrogen and four carbonyl ligands before the carbene was removed. The i.r. spectrum of (V) showed four terminal carbonyl-stretching bands (hexane, 2 063m, 1 984s, 1 969vs, and 1 952s cm^{-1}) as expected for the formulation proposed. As in the spectrum of (I) there was no band for (V) assignable to Mn–H. A deuterido-analogue of (V) was prepared using a D_2O–Et_2O mixture. Examination of the i.r. spectrum of this complex in the range 1 200—1 350 cm^{-1} failed to reveal any new band attributable to ν(Mn–D). Evidently the metal–hydride stretches were too weak to be observed. The presence of the hydrido-ligand in (V) was, however, clearly revealed in the ^1H n.m.r. spectrum by a high-field signal at τ 16.83. Other bands occurred at τ 3.73(4 H, m, C_6H_4) and 7.03(3 H, s, NCH_3) and are virtually identical with those found[1] in $[OsH(CO)_4(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)][BF_4]$. The hydride (V) is thermally stable and heating failed to bring about insertion of the carbene into the manganese–hydride bond. An attempt to prepare a methyl analogue of (V), *i.e.* *cis*-$[MnMe(CO)_4(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$ by treating (IV) with dimethyl sulphate, water, diethyl ether, and triethylamine failed. The only product isolated was (V).

The mechanism of formation of the hydrido-complexes (I) and (V) is of some interest. Some years ago Muetterties[8] showed that the oxygen atoms in $[Re(CO)_6]^+$ undergo exchange with those in water and proposed intermediates $[Re(CO_2H)(CO)_5]$ and $[Re\{C(OH)_2\}(CO)_5]^+$ formed by attack of $[OH]^-$ or H_2O on a co-ordinated carbonyl ligand. Hydrolysis of $[Mn(CO)_6]^+$ affords $[MnH(CO)_5]$ and ultimately $[Mn_2(CO)_{10}]$. Mechanisms proposed[9] for this reaction also involve a carboxylate intermediate $[Mn(CO_2H)(CO)_5]$, it being suggested that subsequent decomposition to the anion $[Mn(CO)_5]^-$ occurs. The last step of the reaction is then abstraction of a proton from a water molecule to give $[MnH(CO)_5]$. Formation of (I) and (V) could be envisaged as occurring in a similar way (Scheme 1). However, this would necessitate as the final step abstraction of a proton from a water molecule to give the hydrides, an unlikely process in the presence of excess of triethylamine. An alternative process which avoids this difficulty is to assume that a co-ordinated carbonyl group in the cations is attacked by a water molecule, rather than a hydroxyl, and that the amine assists formation of the carboxylate which subsequently releases carbon dioxide by an intramolecular β elimination (Scheme 2).



SCHEME 1



SCHEME 2 (*i*), H_2O; (*ii*), NEt_3

As anticipated complex (V) reacts with carbon tetrachloride, dibromomethane, and methyl iodide to give $[MnX(CO)_4(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$, (VI; X = Cl, Br, or I). These are yellow to orange air-stable crystalline solids, their colour intensity and ease of preparation increasing in the order Cl<Br<I. The ^1H n.m.r. spectra confirmed the presence of the carbene ligand. Complex (VI; X = I) reacted with PPh_3 or $P[(OCH_2)_3CMe]$ in benzene to give $[MnI(CO)_3L(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$ {VII; L = PPh_3 or $P[(OCH_2)_3CMe]$}. The i.r. spectra of both complexes showed three terminal carbonyl bands, those of {VII; L = $P[(OCH_2)_3CMe]$} being of equal intensity suggesting that it existed only as the *fac* isomer. The spectrum of (VII; L = PPh_3) consisted of one very strong broad band as well as two weaker ones, perhaps indicating a mixture of *fac* and *mer* isomers. Again the ^1H n.m.r. spectra confirmed the presence of the carbene ligand in the two complexes.

The reaction of thallium cyclopentadienide and

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[6] B. Cetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, 1827; D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *ibid.*, 1973, 514.

[7] J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, 1974, **15**, 84.

[8] E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 1841.

[9] T. Kruck, M. Höfler, and M. Noack, *Chem. Ber.*, 1966, **99**, 1153.

(VI; X = I) was also investigated but no carbene complex was isolated, the stable complex [Mn(CO)$_3$(η-C$_5$H$_5$)] being detected spectroscopically. Unsuccessful attempts were also made to replace the iodo-ligand in (VI) by methyl using methyl-lithium; however, decomposition was observed. Complex (VI; X = I) reacted with thallium hexafluoroacetylacetonate to give the complex [Mn(CO)$_4$(hfacac)($\overline{\mathrm{C{\cdot}NMe{\cdot}C_6H_4{\cdot}S}}$)] [VIII; hfacac = O·C(CF$_3$)·CH·C(CF$_3$)·O]; the ^{1}H n.m.r. spectrum was in agreement with the formulation proposed.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian T60 and HA100 spectrometers. I.r. spectra were measured with Perkin-Elmer 257 and 457 spectrophotometers, and mass spectra with an A.E.I. MS 902 spectrometer operating at 70 eV ionisation potential.* Solvents were dried and distilled under nitrogen before use and all reactions were carried out under oxygen-free nitrogen. The salt [(Ph$_3$P)$_2$N][Mn(CO)$_5$] was prepared by the literature method,[7,10] as was [Cl·$\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$][BF$_4$].[4]

2-Chloro-3-methylbenzothiazolium Tetrafluoroborate, (III).—This salt, m.p. 183—187 °C, was obtained (90%) (Found: C, 34.8; H, 2.6; N, 4.9. C$_8$H$_7$BClF$_4$NS requires C, 35.3; H, 2.6; N, 5.2%) by treating 2-chlorobenzothiazole in methylene chloride–acetonitrile (3 : 1) with trimethyloxonium tetrafluoroborate.

Synthesis of the Complexes cis-[MnX(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$)] (X = H, I, *or* Br).—Treatment of [Mn(CO)$_5$($\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$)][BF$_4$] [4] (0.40 g, 1.0 mmol) at room temperature for 1 h with triethylamine (2 cm^3) in diethyl ether–water (3 : 1, 40 cm^3) gave, after separation of the ether layer, drying over sodium sulphate, and removal of solvent, a red *oil*, [MnH(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$)] (I), which proved impossible to crystallise, $\nu_{\text{max.}}$ (CO) (in hexane) at 2 059m, 1 978s, 1 963vs, and 1 948s cm^{-1}, $\nu_{\text{max.}}$ (thin film) 3 030w, 2 988w, 2 938m, 2 866w, 1 642s, 1 481w, 1 447s, 1 431m, 1 393w, 1 344s, 1 325m, 1 200m, 1 074s, 1 058w, 1 013w, 933s, 867w, 820w, 779s, 725s, 668s, 627s, 571w, and 499m cm^{-1}, ^{1}H n.m.r. resonances (C$_6$D$_6$) τ 3.47(s,br, 1H, CH), 4.63(s,br, 3H, NCH_3), 7.43(s,br, 3H, CCH_3), and 17.13(s, 1H, MnH).

The red oil (I) (0.20 g, 0.71 mmol) was stirred in dibromomethane (10 cm^3) at room temperature for 18 h. Removal of excess of solvent gave an oily solid which was dissolved in dichloromethane. Chromatography (silica gel, eluting with CH$_2$Cl$_2$) afforded a solution which was concentrated. Addition of light petroleum yielded orange *crystals*, [MnBr(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$)] (II) (0.23g, 88%), m.p. 134—136 °C (decomp.) (Found: C, 30.4; H, 2.2; N, 3.6. C$_9$H$_7$BrMnNO$_4$S requires C, 30.0; H, 2.0; N, 3.9%), $\nu_{\text{max.}}$ (CO) (in CH$_2$Cl$_2$) at 2 092m, 2 010s, and 1 949 cm^{-1}, $\nu_{\text{max.}}$ (Nujol) 1 544m, 1 193m, 1 134w, 1 072w, 1 048w, 1 009w, 936m, 865w, 778s, 731w, 673s, 656s, 640s, 628s, 577w, 564w, 546w, 480w, 457s, 439w, and 425w cm^{-1}, ^{1}H n.m.r. resonances (CDCl$_3$) τ 2.80(s, 1H, CH), 5.78(s, 3H, NCH_3), and 7.50(s, 3H, CCH_3).

Complex (I) (0.07 g, 0.25 mmol) was stirred with methyl iodide (5 cm^3) at room temperature for 1 h. Removal of excess of MeI gave a red oil which was chromatographed (silica gel, eluting with C$_6$H$_6$). On removing solvent *in vacuo* an orange solid was produced. Recrystallisation (diethyl ether–light petroleum) gave *cis*-[MnI(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}CMe{:}CH{\cdot}S}}$)] (0.06 g, 56%) identified by its i.r. and n.m.r. spectra.[4]

Complexes containing the N-*methylbenzothiazolidinylidene Ligand*.—(a) [Mn(CO)$_5$($\overline{\mathrm{C{\cdot}NMe{\cdot}C_6H_4{\cdot}S}}$)][BF$_4$], (IV). A solution of the complex [(Ph$_3$P)$_2$N][Mn(CO)$_5$] (1.46 g, 2.0 mmol) in methylene chloride (20 cm^3) was stirred at room temperature with (III) (0.54 g, 2.0 mmol) for 20 min. Addition of diethyl ether (20 cm^3) gave a precipitate which was filtered off and washed with ether. White *crystals* of (IV) (0.48 g, 56%) (from acetonitrile–diethyl ether), m.p. 162—163 °C (decomp.), were obtained (Found: C, 36.4; H, 1.6; N, 3.4. C$_{13}$H$_7$BF$_4$MnNO$_5$S requires C, 36.2; H, 1.6; N, 3.3%), $\nu_{\text{max.}}$ (CO) (in MeCN) at 2 145m, and 2 049vs cm^{-1}, $\nu_{\text{max.}}$ (Nujol) 1 338w, 1 309w, 1 292w, 1 279w, 1 179w, 1 065vs, 985w, 910m, 764s, 730m, 701w, 661s, 645s, 607s, 560w, 557w, 534w, 509w, 454s, 433w, and 412w cm^{-1}, ^{1}H n.m.r. resonances (CD$_3$CN) τ 2.30(m, 4H, C$_6H_4$) and 5.65(s,br, 3H, NCH_3).

(b) cis-[MnH(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}C_6H_4{\cdot}S}}$)], (V). A suspension of (IV) (0.43 g, 1.0 mmol) in water–diethyl ether (1 : 3, 40 cm^3) was treated with triethylamine (2 cm^3) at room temperature. After stirring (1h) the red ether layer was separated and dried (Na$_2$[SO$_4$]). Removal of solvent gave a red solid which afforded red *crystals* of (V) (0.25 g, 80%), m.p. 102—104 °C from light petroleum [Found: C, 45.7; H, 2.9; N, 4.6%; *M* 317(mass spec.). C$_{12}$H$_8$MnNO$_4$S requires C, 45.4; H, 2.5; N, 4.4%; *M* 317], $\nu_{\text{max.}}$ (CO) (in hexane) at 2 063m, 1 984s, 1 969vs, and 1 952s cm^{-1}, $\nu_{\text{max.}}$ (Nujol) 1 331w, 1 274w, 1 150w, 1 125w, 1 080m, 910s, 804w, 770s, 727s, 713s, 668s, 640s, 612m, 606m, 566w, 549w, 498m, and 458w cm^{-1}, ^{1}H n.m.r. resonances (C$_6$D$_6$) τ 3.73(m, 4H, C$_6H_4$), 7.03(s, 3H, NCH_3), and 16.83(s, 1H, MnH).

(c) cis-[MnX(CO)$_4$($\overline{\mathrm{C{\cdot}NMe{\cdot}C_6H_4{\cdot}S}}$)], (VI; X = Cl). Complex (V) (0.32 g, 1.0 mmol) was stirred in carbon tetrachloride (10 cm^3) at room temperature for 18 h. Removal of carbon tetrachloride *in vacuo* gave a yellow solid which was extracted with dichloromethane and the solution chromatographed (silica gel, eluting with CH$_2$Cl$_2$). Reducing the volume and adding light petroleum gave yellow *crystals*, (VI; X = Cl) (0.03 g, 9%), m.p. 110 °C (decomp.) (Found: C, 40.7; H, 2.1; N, 4.0. C$_{12}$H$_7$ClMnNO$_4$S requires C, 41.0; H, 2.0; N, 4.0%), $\nu_{\text{max.}}$ (CO) (in CH$_2$Cl$_2$) at 2 093m, 2 016s, and 1 949m cm^{-1}, $\nu_{\text{max.}}$ (Nujol) 1 334w, 1 312w, 1 272w, 1 132w, 1 082w, 1 062m, 708m, 800w, 770s, 758s, 739m, 724w, 672s, 653s, 607m, 569w, 551w, 529w, 489w, 461s, 443w, and 421w cm^{-1}, ^{1}H n.m.r. resonances (CD$_3$NO$_2$) τ 2.80(m, 4H, C$_6H_4$) and 6.05(s, 3H, NCH_3).

(d) (VI; X = Br). A sample (0.32 g, 1.0 mmol) of (V) was stirred in dibromomethane (10 cm^3) for 18 h at room temperature. Removal of excess of solvent yielded a red solid which was dissolved in dichloromethane and chromato-

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* 1 eV ≈ 1.60 × 10^{-19} J.

[10] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1818.

graphed (silica gel, eluting with CH_2Cl_2). Concentration of the eluant and addition of light petroleum gave an orange solid. Orange *crystals*, (VI; X = Br) (0.21 g, 53%), m.p. 148—151 °C (decomp.), were obtained from chloroform–light petroleum (Found: 36.1; H, 1.8; N, 3.7. $C_{12}H_7BrMnNO_4S$ requires C, 36.4; H, 1.8; N, 3.5%), $\nu_{max.}$ (CO) (in CH_2Cl_2) at 2 092m, 2 010s, and 1 949m cm^{-1}, $\nu_{max.}$ (Nujol) 1 333w, 1 310w, 1 274w, 1 171w, 1 083w, 1 053m, 899m, 772s, 739w, 671s, 650s, 606m, 569w, 561w, and 463s cm^{-1}, ^1H n.m.r. resonances ($CDCl_3$) τ 2.40(m, 4 H, C_6H_4) and 5.48 (s, 3 H, NCH_3).

(e) (VI; X = I). In a similar manner (V) (0.25 g, 0.79 mmol) with methyl iodide (10 cm^3) after 18 h gave a yellow solid which was dissolved in benzene and chromatographed (silica gel, eluting with C_6H_6). Concentration and addition of light petroleum afforded orange *crystals*, (VI; X = I) (0.21 g, 60%), m.p. 140 °C (decomp.) [Found: C, 32.0; H, 1.6; N, 3.2%; *M* (mass spec.) 443. $C_{12}H_7IMnNO_4S$ requires C, 32.5; H, 1.6; N, 3.2%; *M* 443], $\nu_{max.}$(CO) (in CH_2Cl_2) at 2 080m, 2 002s, and 1 951m cm^{-1}, $\nu_{max.}$ (Nujol) 1 334w, 1 274w, 1 172w, 1 083w, 1 053m, 904m, 895m, 774s, 741w, 670s, 650s, 607m, 570w, 552w, and 471s cm^{-1}, ^1H n.m.r. resonances ($CDCl_3$) τ 2.47(m, 4 H, C_6H_4) and 5.53(s, 3 H, NCH_3).

(f) $[MnI(CO)_3L(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$, (VII; L = PPh_3). To a solution of (VI; X = I) (0.10 g, 0.23 mmol) in benzene (20 cm^3) was added triphenylphosphine (0.06 g, 0.23 mmol). The solution was stirred (4 d, room temperature) after which solvent was removed and the residue treated with light petroleum. Decantation gave a solid and yellow *crystals*, (VII; L = PPh_3) (0.12 g, 78%), m.p. 137—139 °C (decomp.), were obtained from chloroform–light petroleum (Found: C, 51.1; H, 3.3; N, 1.8. $C_{29}H_{22}IMnNO_3PS$ requires C, 51.4; H, 3.3; N, 2.1%), $\nu_{max.}$ (CO) (in CH_2Cl_2) at 2 028m, 1 946vs, and 1 910w cm^{-1}, $\nu_{max.}$ (Nujol) 1 165w, 1 127w, 1 094w, 886w, 761w, 735m, 706m, 640m, 605w, 552w, and 526m cm^{-1}, ^1H n.m.r. resonances ($CDCl_3$) τ 2.63(m, 19 H, C_6H_4 + C_6H_5) and 5.50(s, 3 H, NCH_3).

(g) fac-{VII; L = $P[(OCH_2)_3CMe]$}. Complex (VI; X = I) (0.24 g, 0.54 mmol) was treated (24 h) with $P[(OCH_2)_3CMe]$ (0.084 g, 0.59 mmol) in benzene (20 cm^3). The orange solution gave an oil from which, using chloroform–light petroleum, yellow *crystals* of {VII; L = $P[(OCH_2)_3CMe]$} (0.28 g, 90%), m.p. 158—160 °C (decomp.), were obtained (Found: C, 34.0; H, 3.2; N, 2.4. $C_{16}H_{16}IMnNO_6PS$ requires C, 34.1; H, 2.9; N, 2.5%), $\nu_{max.}$ (CO) (in CH_2Cl_2) at 2 032s, 1 972s, and 1 926s cm^{-1}, $\nu_{max.}$ (Nujol) 1 331w, 1 185w, 1 080w, 1 027s, 961w, 938m, 889w, 872m, 781s, 765m, 735w, 676w, 665s, 651m, 546w, 525w, and 473w cm^{-1}, ^1H n.m.r. resonances ($CDCl_3$) τ 2.50 (m, 4 H, C_6H_4), 5.57 (s, 3 H, NCH_3), 5.77 [d, 6 H, $POCH_2$, *J*(PH) 4.0 Hz], and 9.20 (s, 3 H, CCH_3].

(h) $[Mn{\cdot}O{\cdot}C(CF_3){\cdot}CH{\cdot}C(CF_3)O(CO)_3(C{\cdot}NMe{\cdot}C_6H_4{\cdot}S)]$, (VIII). A benzene (20 cm^3) solution of (VI; X = I) (0.22 g, 0.50 mmol) was treated with thallium 1,3-bis(trifluoromethyl)propane-1,3-dionate (0.23 g, 0.55 mmol) and stirred for 2 d at room temperature. After filtering and concentrating, the orange solution was chromatographed (silica gel, eluting with C_6H_6). The yellow residue obtained after removal of solvent was crystallised (−78 °C) from light petroleum to give yellow crystals, (VIII) (0.16 g, 65%) (Found: C, 39.9; H, 2.2; N, 2.8. $C_{16}H_8F_6MnNO_5S$ requires C, 38.8; H, 1.6; N, 2.8%), $\nu_{max.}$ (CO) (in hexane) at 2 042s, 1 969s, and 1 931s cm^{-1}, $\nu_{max.}$ (Nujol) 1 628s, 1 601w, 1 555m, 1 331w, 1 263s, 1 239s, 1 219m, 1 210m, 1 164s, 1 086w, 1 051w, 962w, 909m, 826w, 811m, 768s, 738m, 731w, 721w, 691m, 652m, 625m, 607w, 546m, 511w, and 435w cm^{-1}, ^1H n.m.r. resonances ($CDCl_3$) τ 2.40 (m, 4 H, C_6H_4), 4.17 (m, 1 H, CH), and 5.57 (s, 3 H, NCH_3).

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