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Neutral and cationic carbonyl complexes of manganese with tetramethylthiourea. Crystal structure of *cis*-$\{Mn(CO)_4(SC[N(CH_3)_2]_2)_2\}ClO_4$

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Abstract

Tetramethylthiourea (TMTU) reacts with $Mn_2(CO)_{10}$ in hexane under UV irradiation to give axial $Mn_2(CO)_9$(TMTU), with $MnBr(CO)_5$ in CH_2Cl_2 at room temperature to give *cis*-$MnBr(CO)_4$(TMTU), and with $Mn(OClO_3)(CO)_5$ in CH_2Cl_2 to give the cationic tetracarbonyl *cis*-$[Mn(CO)_4(TMTU)_2]ClO_4$. The last complex has been characterized by X-ray diffraction; it reacts with more (TMTU) to give the unstable species *fac*-$[Mn(CO)_3(TMTU)_3]ClO_4$, with pyridine to give *fac*-$[Mn(CO)_3(PY)_2(TMTU)]ClO_4$, and with the bidentate ligands ($L \frown L$) *o*-phenanthroline or bis-diphenylphosphinomethane to give the corresponding cationic *fac*-tricarbonyls *fac*-$[Mn(CO)_3(L \frown L)(TMTU)]ClO_4$. In all the complexes prepared the TMTU ligand is *S*-bonded to the manganese.

Introduction

Transition metal carbonyl complexes containing the potentially ambidentate ligand tetramethylthiourea $SC[N(CH_3)_2]_2$ (TMTU) are rare [1] and, to our knowledge, no manganese carbonyl derivatives with this ligand have been reported. We thus considered it of interest to study the reactions of TMTU with several manganese carbonyl compounds such as $Mn_2(CO)_{10}$, $MnBr(CO)_5$ and $Mn(OClO_3)(CO)_5$ in order to determine the degree of CO substitution that can be achieved, the stereochemistry of the products, and the bonding mode of the ligand.

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Herein we describe the preparation of, inter alia, the cationic tetracarbonyl *cis*-[$Mn(CO)_4(TMTU)_2$]ClO_4, which has been characterized by X-ray diffraction. No cationic tetracarbonyl complexes of manganese had previously been studied crystallographically.

Results and discussion

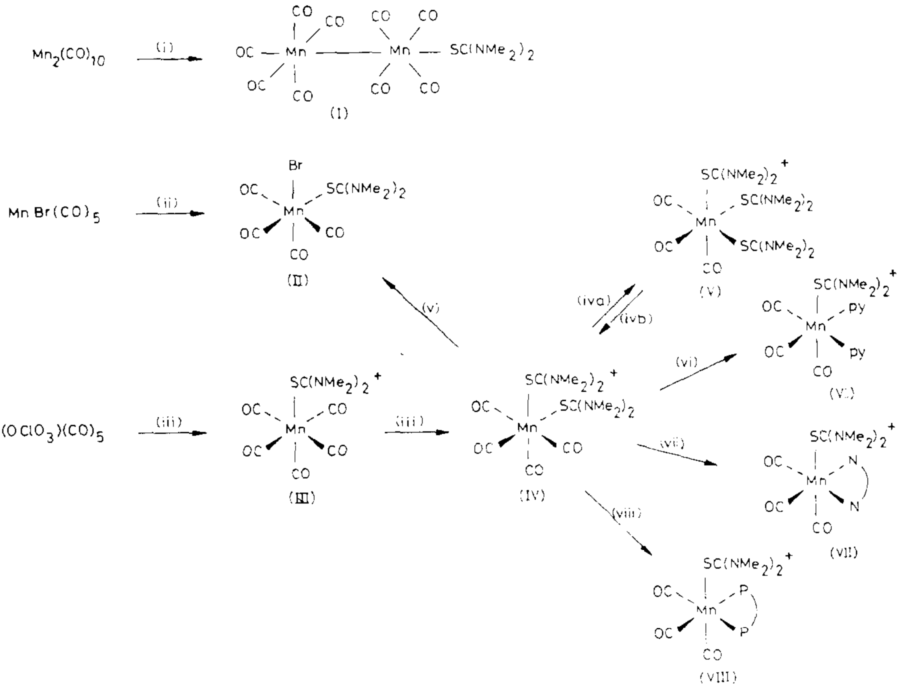
When a 1/1 molar mixture of the carbonyl $Mn_2(CO)_{10}$ and TMTU was irradiated with UV light in hexane (reaction (i) in Scheme 1) an orange crystalline precipitate was obtained and was identified as the neutral compound [$Mn_2(CO)_9$-(TMTU)] (I). The ^1H NMR spectrum showed a sharp singlet at 3.26 ppm, very near to that of the free TMTU (3.10 ppm [1]) indicating that the ligand is *S*-bonded to the manganese. Consistently, the solid-state IR spectrum showed absorptions at 1550, 1375, 1100, 1050, 650 and 625 cm^{-1}, which according to the literature [2], indicates that the TMTU is coordinated through the sulfur atom.

The structure proposed for I (Scheme 1) is also in accord with the ν(CO) IR spectrum in solution (Table 1), which shows the five absorptions corresponding to the $Mn_2(CO)_9L$ species when L occupies an axial position [3], as observed for a variety of ligands L [4].

No further substitution of CO was observed even when an excess of TMTU was used. This fact, and the good yield corresponding to the monosubstituted product I (70%), is not the behaviour normally observed in photochemical reactions of this type [4]. Therefore, if the mechanism involves the fission of the Mn–Mn bond in the starting $Mn_2(CO)_{10}$ [4], it appears that the substituted radical $Mn(CO)_4(TMTU)$ does not undergo further CO substitution and that its dimerisation is unfavourable. It is known, however, that photodissociation of one CO from $Mn_2(CO)_{10}$ without Mn–Mn bond breaking can take place, giving $Mn_2(CO)_9$ [5], and so it is possible that I is formed by interaction of these species with TMTU. On the other hand, the reaction (i) gave no disproportionation products, which indicates that the TMTU is a poorer electron donor ligand than the amines [6].

The reaction of the complex $MnBr(CO)_5$ with TMTU in CH_2Cl_2 at room temperature gave crystalline *cis*-[$MnBr(CO)_4(TMTU)$] (II), data for which are shown in Table 1. The IR (see Experimental section) and ^1H NMR spectra were consistent with *S*-coordination of the TMTU. Use of an excess of the ligand did not bring about further substitution, and under more forcing conditions (refluxing $CHCl_3$ or toluene) much decomposition took place to give insoluble non-carbonyl compounds and a small amount of what appeared to be an unstable *fac*-tricarbonyl; this was not identified but may be *fac*-[$MnBr(CO)_3(TMTU)_2$], analogous to the known *fac*-$MnBr(CO)_3(TU)_2$ (TU = thiourea) [7]. Most frequently the reaction of $MnBr(CO)_5$ with a ligand L gives the disubstituted product $MnBr(CO)_3L_2$, or mixtures of this and the monosubstituted complex $MnBr(CO)_4L$, owing to the facile reaction of the latter with more L [4]. The behaviour of TMTU parallels that of bulky ligands such as PCy_3 [8].

The reaction of TMTU with one equivalent of the complex $Mn(OClO_3)(CO)_5$, which contains the weakly coordinating ligand $OClO_3$ [9], in CH_2Cl_2 at room temperature gave initially the cationic pentacarbonyl [$Mn(CO)_5(TMTU)$]ClO_4 (III) (characterized by its ν(CO) absorptions in the IR spectrum in solution at 2149w, 2059s and 2044sh), which was not isolated because it reacted further with more



Scheme 1. (i) TMTU, $h\nu$, hexane. (ii) TMTU, CH_2Cl_2, r.t. (iii) TMTU, CH_2Cl_2, r.t. (iva) TMTU, refluxing $CHCl_3$. (ivb) decomposition. (v) KBr, CH_2Cl_2, r.t. (vi) py, CH_2Cl_2, r.t. (vii) *o*-phen, CH_2Cl_2, r.t. (viii) dppm, CH_2Cl_2, r.t.

TMTU to give the tetracarbonyl *cis*-$[Mn(CO)_4(TMTU)_2]ClO_4$ (IV). This latter was isolated as a crystalline solid in good yield by using an excess of TMTU (reaction (iii) in Scheme 1). The analytical and spectroscopic data (Table 1) were in accord with the formulation as a cationic *cis*-tetracarbonyl complex, and indicated *S*-coordination of the TMTU. In view of the fact that no cationic tetracarbonyl complex of manganese had been studied crystallographically, we decided to determine the structure of compound IV. The results are summarized in Tables 2 and 3, and the structure of the cation $[Mn(CO)_4(TMTU)_4]^+$ is shown in Fig. 1.

In the cation *, the manganese is in a distorted octahedral coordination in which the major distortion is the angle SMnS (78.6(1)°), which deviates significantly from 90°. The Mn–CO distances are similar to those encountered in other manganese carbonyl derivatives [10], and there is a small difference between the Mn–CO *trans* to another CO (Mn–C(2) 1.880(10) Å) and the Mn–CO *trans* to sulfur (Mn–C(3) 1.793(9) Å). The Mn–S bond length (2.405(3) Å) is identical to that in the complex $Mn(\eta^2\text{-}SCNMe_2)(CO)_3(PPh_3)$ (2.404 Å) [11], and is similar to that in some dithiocarbamato [12] and S_2C complexes [13]. The SCN_2 group of the TMTU ligand is planar, and the manganese atom is 1.744(7) Å out of this plane, with a MnSC bond angle of 112.6(3)°. Those features are usually observed in complexes with *S*-bonded

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* The carbonyl cation is on a two-fold axis parallel to the *b* axis, and the perchlorate anion also lies on a two-fold crystallographic axis parallel to the *c* axis.

Table 1

Melting points, conductivity, analytical and spectroscopic data for the compounds

Compound	M.p. [a] (°C)	Λ [b] (Ω^{-1} cm^2 mol^{-1})	Analyses (Found (calc) (%))			IR [d] (cm^{-1}) ν(CO)	^{1}H NMR [e] δ(CH$_3$)
			C	H	N		
$Mn_2(CO)_9(TMTU)$ (I)	124	1.2	34.0 (34.0)	2.43 (2.44)	5.54 (5.67)	2080w, 2010m, 1982s, 1945sh, 1905w	3.24
cis-$MnBr(CO)_4(TMTU)$ (II)	91	14	28.2 (28.5)	3.18 (3.19)	6.90 (7.38)	2092w, 2015vs, 1994sh, 1942s	3.18
cis-$[Mn(CO)_4(TMTU)_2]ClO_4$ (IV)	124	134	31.5 (31.7)	4.63 (4.56)	10.4 (10.6)	2090m, 2015vs, 1995sh, 1960s	3.28
fac-$[Mn(CO)_3(PY)_2(TMTU)]ClO_4$ (VI)	142	142	40.6 (40.9)	4.23 (4.19)	10.4 [c] (10.6)	2039s, 1932s,br	3.09
fac-$[Mn(CO)_3(phen)(TMTU)]PF_6$ (VIIb)	175	135	40.2 (40.3)	3.48 (3.38)	9.11 (9.39)	2034s, 1947s, 1938s	3.02 [f]
fac-$[Mn(CO)_3(dppm)(TMTU)]ClO_4$ (VIII)	224	130	52.2 (52.5)	4.68 (4.54)	3.80 (3.71)	2024s, 1947s,br	3.00 [g]

[a] With decomposition. [b] In 5×10^{-4} *M* acetone solution. [c] %S: 6.28 (6.06). [d] In CH_2Cl_2 solution. [e] Unless otherwise stated, in $CDCl_3$, in ppm with reference to TMS. [f] In acetone-d_6. [g] $^{31}P\{^1H\}$ NMR signal (in $CDCl_3$ at room temperature) was at 12.6 ppm, to high field of external 85% H_3PO_4.

Table 2

Atomic coordinates (× 10000) for compound IV

Atom	x	y	z	B_{eq} [a]
Mn	7500	1698(2)	2500	2.34(8)
S(2)	8041(1)	3454(2)	2951(3)	3.10(11)
C(1)	8657(3)	2998(8)	3044(10)	2.49(35)
N(11)	8970(3)	3623(7)	2078(9)	3.20(36)
C(12)	8836(4)	4292(10)	537(12)	4.28(51)
C(13)	9479(3)	3858(10)	2615(13)	3.92(44)
N(14)	8815(2)	2136(7)	4080(9)	2.87(33)
C(15)	8584(4)	1845(9)	5733(11)	3.65(44)
C(16)	9242(3)	1287(10)	3668(15)	4.49(52)
C(2)	7689(3)	1808(10)	−9760(14)	3.72(47)
O(2)	7820(3)	1859(9)	−1071(9)	6.28(47)
C(3)	7046(3)	503(9)	2165(11)	3.14(42)
O(3)	6779(3)	−329(7)	2059(9)	4.89(40)
Cl	0	2500	8014(4)	3.84(17)
O(4)	−234(3)	3420(9)	6990(13)	7.30(57)
O(5)	360(3)	3092(8)	9037(10)	6.26(47)

[a] $B_{eq} = \frac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

TMTU [14–16] and also in compounds with thiourea and other substituted thioureas, although there are variations in the metal to SCN_2 plane distances and in the MSC angles. It has been suggested that these differences may arise from changes in the hybridisation (sp^2–sp^3) of the sulfur atom [17]. As already found for other TMTU complexes [14] (and also for thiourea and substituted thiourea complexes [17]), the changes in the dimensions of the ligand upon coordination are small. The S–C bond length (1.752(8) Å) is, however significantly larger than that in the free ligand (1.68 Å), and is closer to the values expected for a C–S single bond (1.79–1.86 Å) than for the C=S double bond (1.55–1.56 Å) [11]. The SC–N distance (mean 1.317(11) Å) is slightly shorter than in the free ligand (1.37 Å) and is near the value corresponding to a C=N double bond [11]. As in cases previous studied [14], the small angles C(12)N(11)C(13) (113.4(7)°) and C(15)N(14)C(16) (113.3(7)°) may be due to packing forces. The dihedral angles between the plane SCN_2 and those defined by the atoms N(14)C(15)C(16) and N(11)C(13)C(12) (31.7(7) and 27.0(7)°, respectively) are also commonly observed in TMTU complexes [14–16]. In solution, however, the four methyl groups give only one signal in the ^{1}H NMR spectrum at room temperature, because of free rotation around the SC–N thioamide bond [18].

The cationic tetracarbonyl IV reacts with more TMTU in refluxing chloroform (reaction (iva) in Scheme 1) to give one *fac*-tricarbonyl with two bands in the ν(CO) IR spectrum (2009s, 1912s,br) that could be the tris-tetramethylthiourea species *fac*-$[Mn(CO)_3(TMTU)_3]ClO_4$ (V) *, although because of the low value of the ν(CO) frequencies other possibilities involving *N*-bonded TMTU cannot be ruled out. Our attempts to isolate this compound resulted in decomposition, with formation of IV (reaction (ivb) in Scheme 1). It thus appears that the behaviour of the TMTU towards the complex $Mn(OClO_3)(CO)_5$ contrasts with that observed for

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* The known tris-ethylene-thiourea (ETU) analogue has ν(CO) absorptions at 2020s, 1925s cm^{-1} [23c].

Table 3

Bond lengths (Å) and bond angles (°) for compound IV [a]

S–Mn	2.405(3)	S–Mn–S′	78.6(2)
C(2)–Mn	1.880(10)	C(2)–Mn–S	85.8(3)
C(3)–Mn	1.793(9)	C(2)′–Mn–S	88.7(3)
C(1)–S	1.752(8)	C(2)′–Mn–C(2)	172.9(4)
N(11)–C(1)	1.328(11)	C(3)–Mn–S	174.2(3)
N(14)–C(1)	1.306(10)	C(3)–Mn–S′	95.7(3)
C(12)–N(11)	1.466(11)	C(3)–Mn–C(2)	95.2(4)
C(13)–N(11)	1.476(10)	C(3)–Mn–C(2)′	89.9(4)
C(15)–N(14)	1.495(11)	C(3)′–Mn–S′	174.2(3)
C(16)–N(14)	1.508(11)	C(3)–Mn–C(3)′	90.0(4)
O(2)–C(2)	1.108(11)	C(1)–S–Mn	112.6(3)
O(3)–C(3)	1.148(10)	N(11)–C(1)–S	117.1(6)
O(4)–Cl	1.423(8)	N(14)–C(1)–S	122.5(6)
O(5)–Cl	1.424(8)	N(14)–C(1)–N(11)	120.2(7)
		C(12)–N(11)–C(1)	124.6(7)
		C(13)–N(11)–C(1)	121.4(7)
		C(13)–N(11)–C(12)	113.4(7)
		C(15)–N(14)–C(1)	124.3(7)
		C(16)–N(14)–C(1)	122.4(7)
		C(16)–N(14)–C(15)	113.3(7)
		O(2)–C(2)–Mn	176.8(9)
		O(3)–C(3)–Mn	173.6(8)
		C(3)–Mn–C(3)	90.0(6)
		O(5)–Cl–O(4)	109.7(5)
		O(4)–Cl–O(4)″	110.0(9)
		O(5)–Cl–O(5)″	110.1(7)

[a] ′ is 1.5 − x; y 0.5 − x, ″ is − x, 0.5 − y, z.

many other ligands L, which readily give the *fac*-tricarbonyls $[Mn(CO)_3L_3]^+$, and no tetracarbonyl species are formed [9,19]. More recently, however, it has been reported that the reaction of $[Mn(CO)_5(NCMe)]PF_6$ with PPh_3 gives mixtures of $[Mn(CO)_5(PPh_3)]PF_6$ and *cis*-$[Mn(CO)_4(PPh_3)_2]PF_6$ [20].

The reaction of IV with other ligands resulted in replacement of one TMTU, or one CO and one TMTU. Thus, with KBr in CH_2Cl_2 at room temperature, complex II was formed quantitatively (reaction (v) in Scheme 1), and with pyridine (PY) the cationic tricarbonyl *fac*-$[Mn(CO)_3(PY)_2(TMTU)]ClO_4$ (IV) was obtained in good yield (reaction (vi) in Scheme 1). Similarly, the bidentate ligands *ortho*-phenanthroline (phen) and bis-diphenylphosphinomethane (dppm) reacted with IV (reactions (vii) and (viii) in Scheme 1) to give respectively *fac*-$[Mn(CO)_3(phen)(TMTU)]ClO_4$ (VIIa) and *fac*-$[Mn(CO)_3(dppm)(TMTU)]ClO_4$ (VIII). The complexes VIIa and VIII were also prepared from the corresponding perchlorate species *fac*-$[Mn(OClO_3)(CO)_3(L^\frown L)]$ ($L^\frown L$ = phen or dppm) and TMTU in CH_2Cl_2, and the salt *fac*-$[Mn(CO)_3(phen)(TMTU)]PF_6$ (VIIb) was obtained by treating *fac*-$[MnBr(CO)_3(phen)]$ with TMTU in CH_2Cl_2 in the presence of $TlPF_6$. In these complexes, the NMR and IR data again supported the *S*-coordination of the TMTU, although some IR absorptions of this ligand were obscured by those of the other ligands and of the counterion.

The replacement of the remaining TMTU in VII and VIII by ligands such as $P(OPh)_3$ was difficult; decomposition occurred in the case of VIII, and the known

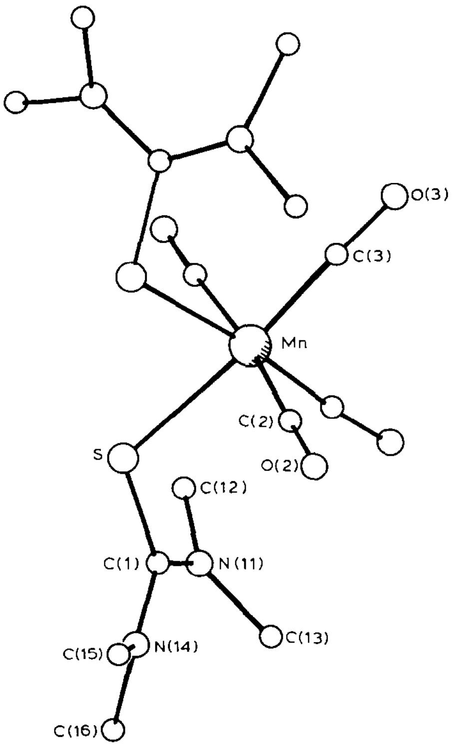

Fig. 1. Structure of the cation $[Mn(CO)_4(TMTU)_2]^+$ with the atom numbering.

cis,trans-$\{Mn(CO)_2(phen)[P(OPh)_3]_2\}ClO_4$ [21] was formed very slowly in the case of VIIa. The *cis,trans* cationic dicarbonyl was also formed when the neutral complex $[MnI(CO)_2(phen)[P(OPh)_3]]$ [22] was treated in CH_2Cl_2 with TMTU and $TlPF_6$.

The partial replacement of TMTU from IV is reminiscent of the outcome of reactions of salts of the cation *fac*-$[Mn(CO)_3(NCMe)_3]^+$ with monodentate or bidentate ligands; these give $[Mn(CO)_3(NCMe)_2L]^+$, $[Mn(CO)_3(NCMe)L_2]^+$ or $[Mn(CO)_2(NCMe)_2L_2]^+$ [23], showing that it is difficult to replace all the NCMe ligands.

Experimental

All reactions were carried out under dry argon. The complexes $Mn(OClO_3)(CO)_5$ [9], *fac*-$Mn(OClO_3)(CO)_3(phen)$ [21] and *fac*-$Mn(OClO_3)(CO)_3(dppm)$ [24] were prepared by published methods. The IR spectra were recorded with a Perkin–Elmer 298 spectrometer and calibrated against the 1601 cm^{-1} polystyrene absorption. The NMR spectra were measured on a Varian FT 80A spectrometer.

$Mn_2(CO)_9(TMTU)$ (I)

To a solution of $Mn_2(CO)_{10}$ (0.10 g, 0.27 mmol) in hexane (30 ml) was added TMTU (0.16 g, 1.24 mmol), and the mixture was irradiated with UV light for 4 h. The orange precipitate formed was filtered off and crystallized from diethyl ether as orange crystals (0.09 g, 70%).

IR (KBr): 1550m, 1490w, 1455m, 1405w, 1375m, 1265w, 1155w, 1110–1100m, 1050w, 870vw, 665sh, 645vs, 615s cm^{-1}.

MnBr(CO)$_4$(TMTU) (II)

A mixture of MnBr(CO)$_5$ (0.10 g, 0.36 mmol) and TMTU (0.07 g, 0.55 mmol) in CH_2Cl_2 (25 ml) was stirred at room temperature for 48 h. Addition of hexane and partial evaporation of the solvents gave an orange precipitate, which was recrystallized from CH_2Cl_2/hexane to give orange crystals (0.09 g, 65%).

IR (Nujol): 1552s, 1500m, 1465–1452s, 1405vw, 1390sh, 1378s, 1250m, 1210w, 1160m, 1140w, 1112m, 1095m, 1055w, 878w, 665s, 655m, 635s, 610s cm^{-1}.

cis-[Mn(CO)$_4$(TMTU)$_2$]ClO$_4$ (IV)

To a solution of Mn(OClO$_3$)(CO)$_5$ (0.54 g, 1.84 mmol) in CH_2Cl_2 (40 ml) was added TMTU (0.49 g, 3.68 mmol). The mixture was stirred at room temperature for 4.5 h in the absence of light and then addition of hexane gave a yellow precipitate, which was recrystallized from CH_2Cl_2/hexane to give yellow crystals (0.69 g, 71%).

IR (Nujol): 1565s, 1505w, 1460s, 1415w, 1400sh, 1385s, 1265m, 1210w, 1165m, 1150w, 1095vs (ClO_4), 1085sh, 880w, 670w, 660w, 640sh, 625s cm^{-1}.

fac-[Mn(CO)$_3$(PY)$_2$(TMTU)]ClO$_4$ (VI)

Pyridine (0.03 g, 0.38 mmol) was added to a solution of IV (0.1 g, 0.19 mmol) in CH_2Cl_2 (30 ml), and the mixture was stirred at room temperature for 30 min. After addition of hexane, partial evaporation of the solvent gave VI as an orange solid (0.09 g, 90%).

IR (KBr): 1595w, 1550m, 1435m, 1375m, 1260w, 1220w, 1160w, 1090vs,br (ClO_4), 1060sh, 765–755m, 695m, 630w, 620s cm^{-1}.

fac-[Mn(CO)$_3$(phen)(TMTU)]PF$_6$ (VIIb)

To a solution of *fac*-MnBr(CO)$_3$(phen) (0.10 g, 0.24 mmol) in CH_2Cl_2 (25 ml) was added TlPF$_6$ (0.12 g, 0.36 mmol) and TMTU (0.04 g, 0.32 mmol). The mixture was stirred for 1.5 h in the absence of light and filtered. Addition of hexane to the filtrate gave an orange precipitate of VIIb, which was recrystallized from CH_2Cl_2/diethyl ether (0.11 g, 75%).

IR (KBr): 1552m, 1510w, 1490w, 1460w, 1420w, 1375w, 1260w, 1155w, 1105m, 1050w, 835s (PF_6), 720m, 675m, 630m, 620sh, 500m cm^{-1}.

fac-[Mn(CO)$_3$(dppm)(TMTU)]ClO$_4$ (VIII)

To a solution of *fac*-Mn(OClO$_3$)(CO)$_3$(dppm) (0.17 g, 0.28 mmol) in CH_2Cl_2 (25 ml) was added TMTU (0.04 g, 0.32 mmol). The mixture was stirred in the absence of light at room temperature for 45 h then addition of hexane gave a solid, which was recrystallized from CH_2Cl_2/ethanol to give pale yellow needles (0.14 g, 68%).

IR (Nujol): 1550m, 1455s, 1435sh, 1375s, 1260w, 1095sbr (ClO_4), 750w, 730s, 710w, 670w, 660w, 620s cm^{-1}.

Crystal structure determination of compound IV

Crystal data: $C_{14}H_{24}N_4O_4S_2Mn \cdot ClO_4$. *FW* = 530.9, orthorhombic. Space group *Pnnb* *, *a* 27.328(4), *b* 10.602(3), *c* 7.980(2) Å, *V* 2312 Å^3, D_x 1.525 g cm^{-3}, $Z = 4$.

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* This is a non-standard setting of *Pnna* (Nr. 52).

$F(000) = 1096$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, μ 6.98 cm^{-1}, 288 K. A prismatic crystal ($0.1 \times 0.1 \times 0.15$ mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-K_α radiation, using the ω-scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}. 1198 independent reflections were measured in the range $2 \leqslant \theta \leqslant 25°$; 1053 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz-polarization, but not absorption, corrections were made.

The structure was solved by direct methods, using the MULTAN84 system of computer programs [25] and refined by full-matrix least-squares, using the SHELX76 program [26].

The function minimized was $\Sigma w \| F_0 | - | F_c \|^2$, where $w = (\sigma^2(F_0) + 0.014 | F_0 |^2)^{-1}$. The final R values were 0.065 ($wR = 0.072$) for all observed reflections.

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