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Ring opening and closing in $(CO)_n(L)Mn^I$ complexes where $L = S_2CPCy_3$ or diphosphine. Novel complexes containing the $Mn(\mu\text{-}L)AuC_6F_5$ entity where $L = S_2CPCy_3$ or dppm

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Abstract

The four-membered $\overline{\text{Mn–S–C–S}}$ ring in complexes containing S_2CPCy_3 chelate ligands are opened very easily when the complexes are treated with phosphites, isocyanides or diphosphines, to give complexes in which the S_2CPCy_3 entity is monodentate. In some cases, the resulting complexes undergo intramolecular displacement of CO by the uncoordinated sulfur with closing of the $\overline{\text{Mn–S–C–S}}$ ring. The uncoordinated sulfur in cationic complexes in which S_2CPCy_3 is monodentate, appears to be a poor nucleophile, and fails to bind a second metal to give four-electron bridges. Treatment of *fac*-$[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ with $[(tht)AuC_6F_5]$, causes opening of the chelate ring of the diphosphine dppm, and simultaneous closing of the ring of the S_2CPCy_3 ligand to give $[(S_2CPCy_3)(CO)_3Mn(\mu\text{-}dppm)Au(C_6F_5)]PF_6$. However, the complex $[(\eta^5\text{-}C_5H_4\text{-}Me)(CO)_2MnSC(PCy_3)SAu(C_6F_5)]$, containing the first example of a $\eta^1(S)$, $\eta^1(S')$, S_2CPCy_3 four-electron bridge between two different metals, can be prepared from $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(SC(S)PCy_3)]$ and $[Au(C_6F_5)(tht)]$.

Introduction

Interest in the chemistry of complexes containing trialkylphosphoniodithiocarboxylato ligands, S_2CPR_3, has led to the preparation of many compounds in which the S_2CPR_3 groups exhibit a wide variety of modes of coordination, usually as monodentate or chelate ligands [1]. However, there have been only a few studies of their reactivity, and these have been centered mainly on the attack of strong nucleophiles (such as H^-, R^-, RO^-, and RS^-) on the central carbon of the S_2CPR_3 ligands [2]. We have recently reported the preparation of a number of compounds containing S_2CPCy_3 groups bonded to manganese as unidentate and chelate ligands [1c,3], and we present here some additional observations that illustrate the ability of the chelate S_2CPCy_3 to undergo ring opening in the presence of other ligands such as phosphites, CN^tBu, and diphosphines. We have also examined the ability of the

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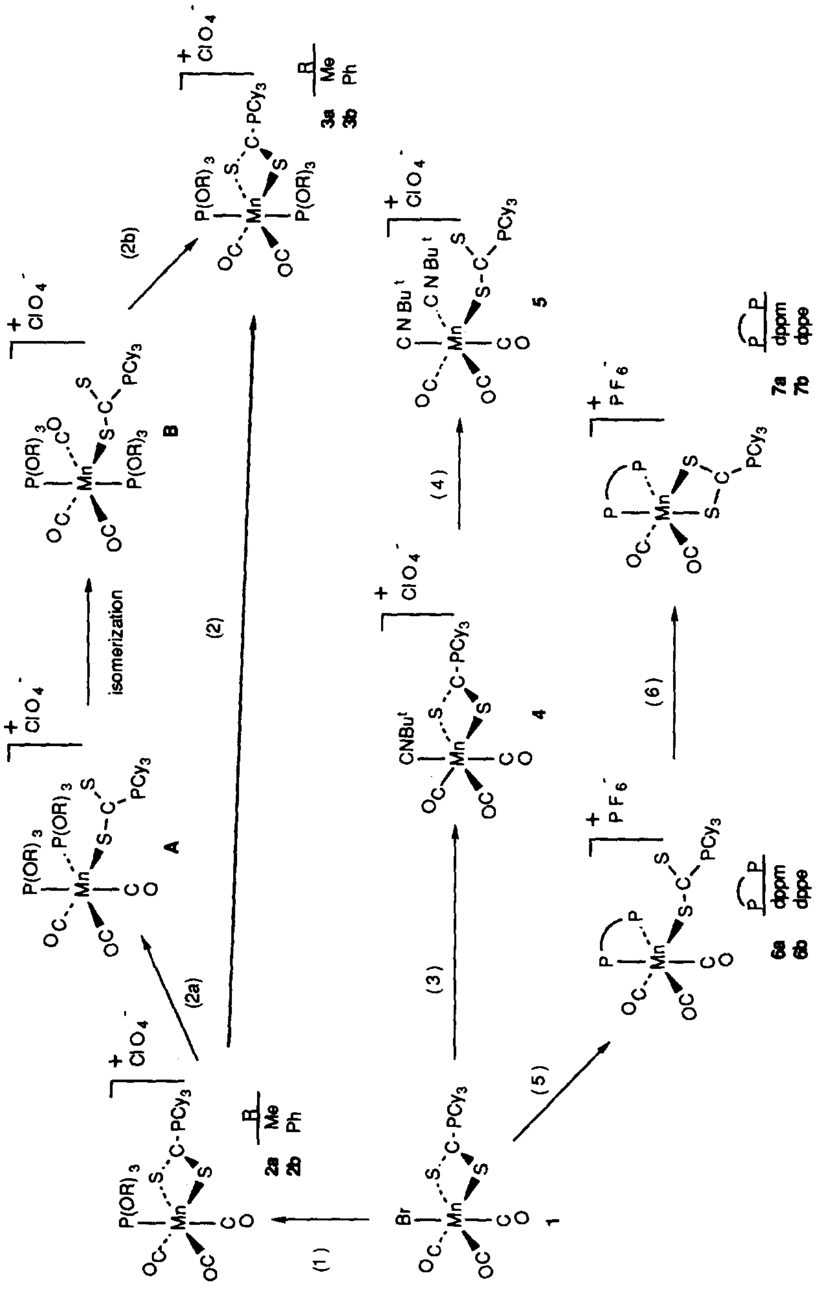
(1)
(2)
(2a)
(2b)
(3)
(4)
(5)
(6)
isomerization
1
2a
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3a
3b
4
5
6a
6b
7a
7b
A
B
R
Me
Ph
dppm
dppe
ClO4⁻
PF6⁻
P(OR)3
CNBu^t
PCy3

Scheme 1

uncoordinated sulfur in manganese(I) complexes containing unidentate S_2CPCy_3 to coordinate a second metal atom.

Results and discussion

Reaction of *fac*-[Mn(CO)$_3${P(OR)$_3$}(S_2CPCy_3)]ClO_4 (**2**) with a molar equivalent of phosphite (reaction 2 in Scheme 1) either under UV irradiation or upon heating in the presence of Me_3NO leads to the substitution of the carbonyl group in *cis* to both sulfur atoms of the chelate S_2CPCy_3 ligand to give the *cis*-dicarbonyl *trans*-bis(phosphite) complexes [Mn(CO)$_2${P(OR)$_3$}$_2$(S_2CPCy_3)]ClO_4 (R = Me (**3a**), Ph (**3b**)). Analytical and spectroscopic (see Tables 1 and 2) data fully support the formulation given for **3a** in Scheme 1. The two ν(CO) absorptions (at 1970s, and 1906s cm^{-1}) are characteristic of a *cis*-arrangement of the two carbonyl ligands, and the $^{31}P\{^1H\}$ shows only one signal (δ 175.4, br) for the two phosphites and a triplet [δ 25.3, ^4J(PP) 15 Hz] for the phosphorus on the S_2CPCy_3 ligand. In the $^{13}C\{^1H\}$ spectrum of **3a**, the signal of the central carbon of the S_2CPCy_3 appears at δ 213.9 and is cleanly resolved into a doublet of triplets due to the coupling to the phosphorus of PCy_3[^1J(PC) 36 Hz] and to two equivalent phosphite ligands [^3J(PC) 3 Hz]. Additionally, the two equivalent carbons of the carbonyl ligands appear as a broad triplet (δ 221.6) due to the coupling to the two phosphites [^2J(PC) 26 Hz]. The $P(OPh)_3$ derivative **3b** has been identified in solution by spectroscopic methods but, in spite of repeated attempts we have not been able to obtain an analytically pure sample.

The new compound *fac*-[Mn(CO)$_3$(S_2CPCy_3)(CN^{t}Bu)]ClO_4 (**4**) can be prepared from **1** by bromide abstraction with $AgClO_4$ and subsequent addition of CN^{t}Bu (reaction 3). Treatment of **4** with an additional equivalent of CN^{t}Bu yields a product which can be unambiguously identified from its analytical and spectroscopic data as *fac*-[Mn(CO)$_3${SC(S)PCy_3}(CN^{t}Bu)$_2$]ClO_4 (**5**). The IR spectrum of **5** in CH_2Cl_2 solution shows three ν(CO) bands (at 2049s, 1983s, and 1962s, cm^{-1}) attributable to a *fac*-arrangement of three carbonyl ligands, and two ν(CN) absorptions (2192m and 2177m cm^{-1}) from two mutually *cis* CN^{t}Bu ligands. The $^{13}C\{^1H\}$ NMR spectrum of **5** shows only one set of signals from the two CN^{t}Bu ligands and two signals from the carbonyl ligands (δ 216.0 and 211.9, approximate ratio 1/2), consistent with the effective symmetry C_s for the cation in **5**. The presence of S_2CPCy_3 acting as a monodentate ligand is shown not only by the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data (Tables 1 and 2) but also by the characteristic absorptions in the region 1000 to 1050 cm^{-1} in the solid state IR spectrum (KBr disc). In reaction 4 the entering CN^{t}Bu ligand displaces one of the sulphur atoms of the chelate S_2CPCy_3 instead of one carbonyl group as in reaction 2. Comparison between reactions 2 and 4 is not straightforward since reaction 2 is made under conditions which promote the loss of CO, whereas reaction 4 is thermally induced. Attempts to carry out reaction 4 under UV irradiation led to extensive decomposition. On the other hand, heating of the phosphite compound **2a** with $P(OMe)_3$ in $CHCl_3$, without a decarbonylating agent, leads ultimately to the same *cis*-dicarbonyl *trans*-bis(phosphite) **3a**, albeit in lower yield than that from reaction 2. IR-monitoring of the thermal reaction between **2a** and $P(OMe)_3$ shows the appearance of ν(CO) bands (2045w, 1977s, and 1937m cm^{-1}) that are tentatively attributed to the formation of a *mer*-tricarbonyl, *trans* bis(phosphite) intermediate *mer-trans-*

Table 1

Infrared and $^{31}P\{^1H\}$ NMR data for the new compounds

Compound	$\nu(CO)$ [a] (cm^{-1})	$^{31}P\{^1H\}$, δ (ppm) [b]	
		S_2C-*P*	other
cis,trans-$[Mn(CO)_2\{P(OMe)_3\}_2(S_2CPCy_3)]ClO_4$ (**3a**)	1970s, 1906s	25.3 t (15)	175.4 br [2 *P*$(OMe)_3$]
cis,trans-$[Mn(CO)_2\{P(OPh)_3\}_2(S_2CPCy_3)]ClO_4$ (**3b**)	1990s, 1927s	26.9 t (15)	159.7 br [2 *P*$(OPh)_3$]
fac-$[Mn(CO)_3(CN^tBu)(S_2CPCy_3)]ClO_4$ [c] (**4**)	2050s, 1996s, 1972s	31.8 s	
fac-$[Mn(CO)_3(CN^tBu)_2\{SC(S)PCy_3\}]ClO_4$ [d] (**5**)	2049s, 1983s, 1962s	34.5 s	
fac-$[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ [e] (**6a**)	2025s, 1961s, 1944s	33.1 t (4)	17.1s, br
fac-$[Mn(CO)_3(dppe)\{SC(S)PCy_3\}]PF_6$ [e] (**6b**)	2024s, 1960s, 1943s	32.4 t (4)	74.3s, br
cis-$[Mn(CO)_2(dppm)(S_2CPCy_3)]PF_6$ [e] (**7a**)	1957s, 1902s	22.1 t (2)	39.13 br. d., and 20.77 br. d.(60)
cis-$[Mn(CO)_2(dppe)(S_2CPCy_3)]PF_6$ [e] (**7b**	1953s, 1895s	23.9 t (11)	79.9 d. of d. (26 and 11), and 94.7 d. of d. (26 and 11)
$[(CO)_3(S_2CPCy_3)Mn(\mu\text{-dppm})Au(C_6F_5)]PF_6$ [e,f] (**8**)	2042s, 1967s, 1937s	31.2 d (10)	29.2 m (Au-*P*) and 47.3 br (Mn-*P*) (μ-dppm)
$[Mn(\eta^5\text{-}C_5H_4\text{-}Me)(CO)_2\{SC(S)PCy_3\}]$ (**9**)	1921s, 1870s	19.21s	
$[(\eta^5\text{-}C_5H_5\text{-}Me)(CO)_2Mn(\mu\text{-}S_2CPCy_3)Au(C_6F_5)]$ [g] (**10**)	1953s, 1908s	35.9s	

[a] CH_2Cl_2 solution. [b] $CDCl_3$ solution; *J*(PP), (Hz) in parentheses. [c] $\nu(CN)$ at 2180m cm^{-1}. [d] $\nu(CN)$ at 2192m, and 2177m, cm^{-1}. [e] $^{31}P\{^1H\}$ NMR spectra of compounds **6a–b**, **7a–b**, and **8** display the signal of the PF_6 anion at ca. δ −144 ppm [septet, *J*(PF) 713 Hz]. [f] $^{19}F\{^1H\}$ NMR [$CDCl_3$, δ (ppm) from CCl_3F] for **8**: −115.3 (m, F^2 and F^6), −158.7 [t, *J*(FF) 20 Hz, F^4], and −162.3 (m, F^3 and F^5). [g] $^{19}F\{^1H\}$ NMR for **10**: −115.0 (m, F^2 and F^6), −160.1 [t, *J*(FF) 20 Hz, F^4], and −163.2 (m, F^3 and F^5).

Table 2

$^{13}C\{^1H\}$ NMR data [a] for the new compounds

Compound	S_2C-P	S_2C-P$(C_6H_{11})_3$	CO	other ligands
3a	213.9 d of t (36 and 3)	30.8 d (38) C^1 26.7 d (12) C^1 and C^6 26.3 d (3) C^2 and C^5 25.4 s, C^4	221.6 t (26)	52.5 s, $P(OCH_3)_3$
5	220.4 d (41)	32.7 d (37) C^1 26.7 d (11) C^1 and C^6 26.5 d (3) C^2 and C^5 25.4 s, C^4	216.0 s (1CO) 211.9 s (2CO)	152.1 s, $CNC(CH_3)_3$ 58.9 s, $CNC(CH_3)_3$ 30.1 s, $CNC(CH_3)_3$
7a	212.5 d of d (32 and 12)	30.3 d (38) C^1 26.6 d (12) C^1 and C^6 26.2 s C^2 and C^5 25.3 s, C^4	226.6 t (15) 220.9 d, br (22)	dppm: 135.1 d of d (38 and 9) 2 C^1 133.7 d of d (27 and 6) 2 C^1 132.8 to 128.4 m 4(C^2 to C^6) 43.9 t (21), PC P
8	227.4 d of d (30 and 8)	30.7 d (36) C^1 26.9 d (10) C^1 and C^6 26.8 s C^2 and C^5 25.6 s, C^4	219.6 d (18) 214.2 s, br	dppm: 135.6 to 128.5 m, 4 (C_6H_5) 43.9 t (21) PCP C_6F_5: 150.4 to 137.6 m
9	202.4 d (51)	32.8 d (41) C^1 26.9 d (12) C^2 and C^6 26.8 d (3) C^3 and C^5 25.7 s, C^4	233.6 s	$C_5H_4CH_3$: 101.6 C^1 82.5, 82.4, C^2 to C^5 13.4, CH_3
10	180.8 d (54)	35.2 d (41) C^1 27.7 C^3 and C^5 27.0 d (10) C^2 and C^6 25.7 s C^4	231.2 s	$C_5H_4CH_3$: 103.6 C^1 85.0, 84.4, C^2 to C^5 13.4, CH_3 C_6F_5: 150.1 to 126.0 m.

[a] $CDCl_3$ solution, δ, ppm, from $SiMe_4$. J(PC) (Hz) in parentheses.

$[Mn(CO)_3(P(OMe)_3)_2\{SC(S)PCy_3\}]ClO_4$ (**B** in Scheme 1) resulting from the displacement (reaction 2a) of one sulfur in the starting compound **2a**, to give the *fac*-tricarbonyl **A**, followed by a rapid *cis*-to-*trans* isomerization of the two phosphite ligands. The intermediate **B** seems to be unstable under the reaction conditions and some decomposition occurs along with the intramolecular displacement (reaction 2b) of CO to give the dicarbonyl **3a**. Thus, reactions 2 and 4 proceed similarly when carried out under thermal conditions. The difference in the final products could arise from the fact that the intramolecular displacement of CO in the bis-isocyanide **5** is more difficult than in the *mer*-tricarbonyl bisphosphite **B** owing to the better donating properties of the isocyanide ligands and also because the two CO ligands *cis* to the sulphur in **B** are mutually *trans*, and therefore labilized.

Ring-opening seems to be a common feature in the reactivity of manganese complexes containing S_2CPCy_3 chelates. Thus, when a mixture of *fac*-$[Mn(CO)_3(S_2CPCy_3)Br]$ (**1**), bis(diphenylphosphino)methane (dppm), KPF_6 and CH_2Cl_2 is stirred at room temperature for 6 h, *fac*-$[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ (**6a**) containing monodentate S_2CPCy_3 is formed. The spectroscopic data for the cation in **6a** are identical to those for the derivative we previously obtained (as the ClO_4^- salt) by displacement of the perchlorato ligand in *fac*-$[Mn(CO)_3(dppm)(OClO_3)]$

[3]. When reaction is carried out with 1,2-bis(diphenylphosphino)ethane (dppe) instead of dppm, the analogous *fac*-$[Mn(CO)_3(dppe)\{SC(S)PCy_3\}]PF_6$ (**6b**) is produced in 3 h. The higher rate of the reaction with dppe probably reflects the better chelating properties of the dppe ligand (to give a 5-membered ring) compared with those of dppm (which gives 4-membered rings).

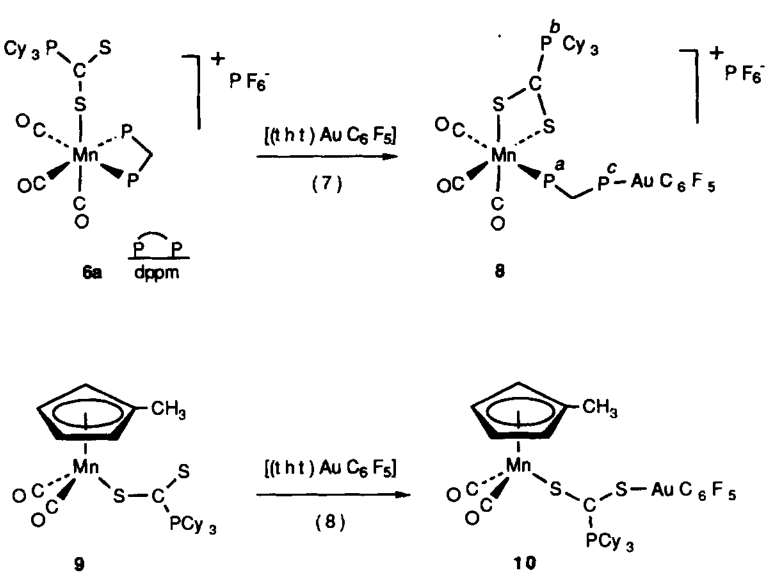
The facile displacement of the bromide ligand from compound **1** by the phosphorus atom of the diphosphines is somewhat unexpected when viewed in the light of the behaviour of other halogeno-carbonyl complexes of manganese(I). It is well known that metal–halide bonds become labilized as the electron density in the metallic fragment increases as a result of progressive replacement of CO groups by less π-acceptor ligands. In the manganese(I) compounds $[Mn(CO)_3(L)_2Br]$ the presence of an efficient halide abstractor such as a silver(I) salt is usually needed to promote the substitution of the halide by a two-electron ligand to give cationic complexes [4]. As far as we know, the direct displacement of halide is possible only in highly-substituted compounds such as $[Mn(CO)(L-L)_2Br]$ [5]. It is therefore remarkable that reaction 5 can be carried out even in the absence of KPF_6, to give compounds **6a**–**b** as unstable bromide salts which can be stabilized by anion exchange with KPF_6 after the substitution of bromide has been completed. This seems to be fairly general, and we have obtained compounds **2** and **4** as hexafluorophosphate salts by stirring **1** with the appropriate ligand $(P(OR)_3$ for **2a**–**b**, CN^tBu for **4**) and KPF_6 in CH_2Cl_2 at room temperature.

The uncoordinated sulphur in complexes **6** can react further and close the chelate ring by intramolecular substitution of CO under appropriate conditions. Thus, UV irradiation of **6a** or **6b** in CH_2Cl_2 gives the purple *cis*-$[Mn(CO)_2(P-P)\{S_2CPCy_3\}]PF_6$ (P–P = dppm (**7a**), dppe (**7b**)), whose identity have been established from analytical and spectroscopic data (Tables 1 and 2).

The presence of a monodentate S_2CPCy_3 ligand in compounds such as **5**, **6a**–**b**, and in others we prepared previously [3], led us to examine the possibility of using the non-coordinated sulfur atom to bind a second metal–ligand fragment and produce homo- or hetero-dinuclear complexes in which the S_2CPCy_3 group acts as a four-electron bridging ligand. Several attempts to obtain homo-dinuclear manganese complexes in this way were unsuccessful: it seems that the nucleophilic character of the non-coordinated sulfur in *fac*-$[Mn(CO)_3(L-L)\{SC(S)PCy_3\}]ClO_4$ (where L–L = 2,2′-bipyridine (bipy), dppm, or dppe) [3] is not strong enough to displace the weakly coordinated perchlorato ligand in *fac*-$[Mn(CO)_3(L-L)(OClO_3)]$ to give the desired dinuclear complexes.

On the other hand, the reaction of the same Mn complexes with $[AuCl(PPh_3)]/TlPF_6$ gave the neutral *fac*-$[Mn(CO)_3(L-L)(OClO_3)]$ together with Au^I species containing the S_2CPCy_3 adducts. This ligand transfer can be regarded as a consequence of the strong demand of electron density in the cationic $MPPh_3^+$ fragment, and therefore use of electron-richer fragments, such as the neutral $Au(C_6F_5)$, would be better for giving the desired manganese–gold complexes.

However, when an orange CH_2Cl_2 solution of *fac*-$[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ (**6a**) was treated with a molar-equivalent of $[Au(tht)(C_6F_5)]$ (tht = tetrahydrothiophene), the colour changed to purple-red and the dinuclear compound $[(S_2CPCy_3)(CO)_3Mn(\mu\text{-dppm})Au(C_6F_5)]PF_6$ (**8**, Scheme 2) could be isolated. The IR spectrum of **8** consist of three bands with a pattern corresponding to a *fac*-tricarbonyl grouping. The $^{31}P\{^1H\}$ NMR spectrum is highly informative: it



Scheme 2

shows three signals; the broad one at higher frequency (47.3 ppm) is attributable to a phosphorus bonded to manganese (P^a in scheme 2) the sharp doublet at 31.2 ppm can be assigned to the phosphorus of the S_2CPCy_3 ligand (P^b) which is coupled to the P^a atom of the diphosphine ($^4J(P^b-P^a)$ 10 Hz), and the third signal, a complex multiplet centered at 29.1 ppm, comes from the remaining P atom of the dppm ligand (P^c) which is bonded to the gold atom and so is coupled to P^a and to the fluorine atoms on the C_6F_5 group. The coordination of P^a to manganese accounts for the broadening of the corresponding signal, and this precludes observation of of the expected multiplet due to the coupling with P^b and P^c. In addition, the $^{13}C\{^1H\}$ NMR spectrum of **8** exhibits the signal corresponding to the central carbon of the S_2CPCy_3 ligand as a doublet of doublets owing the coupling to the P^b atom of PCy_3 ($^1J(PC)$ 30 Hz) and to P^a of the dppm ligand ($^3J(PC)$ 8 Hz). The formation of **8** implies the opening of the dppm chelate ring in the starting compound, promoted by the presence of the $Au(C_6F_5)$ fragment, the final result of the reaction thus reflecting a balance between the chelating and bridging properties of the S_2CPCy_3 and dppm ligands. Two experimental observations indicate that the driving force of the reaction comes from the formation of the phosphorus–gold bond rather than the chelating ability of the S_2CPCy_3 ligand: (a) in reaction 5, discussed above, the chelate S_2CPCy_3 in compound **1** is opened very easily by the dppm ligand to give compound **6a**, thus demonstrating the better chelating properties of dppm compared with S_2CPCy_3, and (b) the non-coordinated sulfur atom on compounds *fac*-$[Mn(CO)_3(L_2)\{SC(S)PCy_3\}]ClO_4$ (L_2 = bipy, dppe, S_2CPCy_3, $2CN^tBu$) fails to displace the weakly coordinated tht ligand in $[Au(C_6F_5)(tht)]$, which reveals the poor nucleophilicity of the uncoordinated sulfur atom in these cationic complexes.

It was thus expected, that the use of compounds containing the monodentate $SC(S)PCy_3$ ligand bonded to an electron-richer fragment would somewhat enhance the nucleophilicity of the non-coordinated S-atom. Thus, the neutral complex

$[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(SC(S)PCy_3)]$ (**9**) was prepared by a method similar to that used for its analogue $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(SC(S)PEt_3)]$ [6]. Treatment of **9** with $[Au(C_6F_5)(tht)]$ in CH_2Cl_2 produces $[(\eta^5\text{-}C_5H_4Me)(CO)_2MnSC(PCy_3)SAu(C_6F_5)]$ (**10**). Analytical and spectroscopic data support the structure depicted for **10** in Scheme 2: the ν(CO) maxima in the IR spectrum of **10** appear at 1955 and 1910 cm^{-1}, shifted to higher frequencies from those of the parent compound **9** (at 1922 and 1869 cm^{-1}), and the $^{31}P\{^1H\}$ NMR spectrum of **10** shows a single peak at δ 35.9 ppm, shifted to higher frequencies when compared to the signal from compound **9** (at δ 19.2). The presence of the $Au(C_6F_5)$ fragment in **10** is confirmed by its $^{19}F\{^1H\}$ NMR spectrum. In addition the $^{13}C\{^1H\}$ NMR spectrum of **10** shows the expected doublet for the central carbon of S_2CPCy_3 at δ 180.8 (^1J(PC) 54 Hz), shifted towards lower frequencies compared with that for the parent compound **9** [δ 202.4 d, ^1J(PC) 51 Hz].

There have been reported a few examples of compounds containing trialkylphosphoniodithiocarboxylato ligands acting as a η^1(S), η^1(S′), four-electron bridges but, as far as we know, all of them are homo-dinuclear complexes of gold [7], silver [8], or molybdenum [9]. Compound **10** thus contains the first example of an S_2CPR_3 group acting as a 4e bridge between two different metals. Unfortunately, despite repeated attempts under different conditions, we could not obtain crystals of **10** suitable for an X-ray analysis.

Experimental

All reactions were carried out in dry solvents under nitrogen. Ligands and other reagents were purchased and used without purification unless otherwise stated. Infrared spectra were recorded on a Perkin–Elmer 298 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$, δ (ppm) to higher frequencies from internal TMS), and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$ solution, δ (ppm) to higher frequencies from external 85% H_3PO_4), were recorded on a Bruker AC-300. $^{19}P\{^1H\}$ NMR spectra [CH_2Cl_2 solution, lock on external D_2O, δ (ppm) positive to higher frequencies from internal $CFCl_3$] were recorded on a Varian FT80-A instrument. Elemental analysis were carried out on a Perkin–Elmer 240-B analyzer.

cis-trans-*$[Mn(CO)_2\{P(OMe)_3\}_2(S_2CPCy_3)]ClO_4$ (3a)*

(a) A mixture of *fac*-$[Mn(CO)_3\{P(OMe)_3\}(S_2CPCy_3)]ClO_4$ (**2a**) [3] (0.214 g; 0.26 mmol), $P(OMe)_3$ (0.04 ml, ca. 0.34 mmol) and Me_3NO (0.022 g, 0.29 mmol) in $CHCl_3$ (25 ml) was heated under reflux for 30 min and then filtered. The solvent was evaporated *in vacuo* to give an oil, which was washed with hexane (3 × 15 ml) to afford a purple solid. Recrystallization was from CH_2Cl_2/hexane. Yield 0.193 g, 80%.

(b) A solution containing **2a** (0.1 g; 0.14 mmol) and $P(OMe)_3$ (0.08 ml, ca. 0.7 mmol) in CH_2Cl_2 (20 ml) was irradiated with UV light for 1.5 h. Work-up was as described for method a. Yield 0.061 g, 53%. Analysis. Found: C, 39.68; H, 6.38. $C_{27}H_{51}ClMnO_{12}P_3S_2$ calc: C, 39.78; H, 6.31%.

Similar reaction between *fac*-$[Mn(CO)_3\{P(OPh)_3\}(S_2CPCy_3)]ClO_4$ (**2b**) and $P(OPh)_3$ afforded *cis-trans*-$[Mn(CO)_2\{P(OPh)_3\}_2(S_2CPCy_3)]ClO_4$ (**3b**) which was identified spectroscopically. However, despite several attempts, we could not obtain a pure sample of **3b**.

fac-*[$Mn(CO)_3(CN^tBu)(S_2CPCy_3)$]$ClO_4$ (4)*

A mixture of **1** [3] (0.5 g, 0.87 mmol) and $AgClO_4$ (0.215, 1.04 mmol) in CH_2Cl_2 (50 ml) was stirred in darkness at room temperature for 1.5 h to give a purple solution of *fac*-[$Mn(CO)_3(S_2CPCy_3)(OClO_3)$][$\nu$(CO) bands at 2030s, 1950s, and 1935s, cm^{-1}]. The mixture was filtered under nitrogen to remove the AgBr and to the solution was added CN^tBu (0.072 g, 0.87 mmol). After 1 h stirring the solvent was evaporated *in vacuo* and the oily residue washed with Et_2O (3 × 15 ml). Recrystallization from CH_2Cl_2/Et_2O at 0 °C gave red-brown crystals of **4** (0.53 g, 90%). Analysis. Found: C, 47.69; H, 6.37; N, 1.93. $C_{27}H_{42}ClMnNO_7PS_2$ calc: C, 47.82; H, 6.24; N, 2.07%.

fac-*[$Mn(CO)_3(CN^tBu)_2\{SC(S)PCy_3\}$]$ClO_4$ (5)*

A mixture of *fac*-[$Mn(CO)_3(CN^tBu)(S_2CPCy_3)$]$ClO_4$ (**4**) (0.4 g, 0.59 mmol) and CN^tBu (0.07 ml, 0.62 mmol) in $CHCl_3$ (20 ml) was heated under reflux for 2 h. The colour of the solution changed from red to yellow. After filtration, the solvent was evaporated *in vacuo*, and the residue washed with hexane (3 × 20 ml) to give a yellow solid. Recrystallization was from CH_2Cl_2/hexane. Yield 0.35 g, 78%. Analysis. Found: C, 50.958; H, 6.90; N, 3.57. $C_{32}H_{51}ClMnN_2O_7PS_2$ calc: C, 50.48; H, 6.75; N, 3.68%.

fac-*[$Mn(CO)_3(dppm)\{SC(S)PCy_3\}$]$PF_6$ (6a)*

A mixture of *fac*-[$Mn(CO)_3(S_2CPCy_3)Br$] (**1**) (0.2 g, 0.347 mmol), dppm (0.113 g, 0.347 mmol) and KPF_6 (0.128 g, 0.694 mmol) in CH_2Cl_2 (15 ml) was stirred in the dark for 6 h. The mixture was then filtered and the solution was concentrated *in vacuo* to ca. 10 ml. Addition of hexane (5 ml) and slow concentration *in vacuo* gave orange-yellow microcrystals of **6a**. Yield 0.267 g, 75%. Analysis. Found: C, 54.40; H, 5.41. $C_{47}H_{55}F_6MnO_3P_4S_2$ calc: C, 55.08; H, 5.41%.

fac-*[$Mn(CO)_3(dppe)\{SC(S)PCy_3\}$]$PF_6$ (6b)*

The procedure was similar to that used for **6a**, starting from *fac*-[$Mn(CO)_3(S_2CPCy_3)Br$] (**1**) (0.2 g, 0.347 mmol), dppe (0.138 g, 0.347 mmol) and KPF_6 (0.128 g, 0.694 mmol). The reaction was complete in 3 h. Yield 0.281 g, 78%. Analysis. Found: C, 55.10; H, 5.46. $C_{48}H_{57}F_6MnO_3P_4S_2$ calc: C, 55.49; H, 5.53%.

cis-*[$Mn(CO)_2(dppm)(S_2CPCy_3)$]$PF_6$ (7a)*

A cooled solution (−10 °C) of *fac*-[$Mn(CO)_3(dppm)\{SC(S)PCy_3\}$]$PF_6$ (**6a**) (0.1 g, 0.098 mmol) in CH_2Cl_2 (15 ml) was irradiated with UV light for 1 h. The colour changed from yellow to deep purple. Evaporation of the solvent gave an oil, which was washed with Et_2O (3 × 15 ml). The solid residue was dissolved in CH_2Cl_2 (10 ml) and the solution was filtered. Addition of hexane (5 ml) and slow evaporation of the solvents *in vacuo* gave deep purple crystals of **7a**. Yield 0.05 g, 52%. Analysis. Found: C, 56.20; H, 5.58. $C_{46}H_{55}F_6MnO_2P_4S_2$ calc: C, 55.42; H, 5.56%.

cis-*[$Mn(CO)_2(dppe)(S_2CPCy_3)$]$PF_6$ (7b)* was obtained as described for **7a**, by irradiation of **6b** (0.1 g, 0.096 mmol) for 1 h at −10 °C. Yield 0.055 g, 56%. Analysis. Found: C, 56.03; H, 5.73. $C_{47}H_{57}F_6MnO_2P_4S_2$ calc: C, 55.84; H, 5.68%.

[(S_2CPCy_3)($CO)_3Mn(\mu$-dppm)$Au(C_6F_5)$]PF_6 (8)

The gold complex [(tht)$Au(C_6H_5)$] [10] (0.046 g, 0.1 mmol) was added to a stirred solution of *fac*-[$Mn(CO)_3(dppm)\{SC(S)PCy_3\}$]$PF_6$ (0.1 g, 0.097 mmol) in CH_2Cl_2

(15 ml). The mixture was stirred for 30 min and the solvent was then evaporated *in vacuo*. The red residue was washed with diethyl ether (2 × 10 ml) and recrystallized from CH_2Cl_2/diethyl ether at 0 °C. Yield 0.11 g, 80%. Analysis. Found: C, 45.96; H, 4.05. $C_{53}H_{55}AuF_{11}MnO_3P_4S_2$ calc: C, 45.83; H, 3.99%.

[Mn(η^5-C_5H_4-Me)(CO)$_2${SC(S)PCy$_3$}] (9) was prepared by the procedure previously described for the PEt_3 derivative [6]. A stirred solution of [Mn(η^5-C_5H_4Me)(CO)$_3$] (0.5 g, 2.29 mol) in tetrahydrofuran (100 ml) was irradiated for 4 h with UV light (at −10 °C, with a slow nitrogen purge) to form [Mn(η^5-C_5H_4Me)(CO)$_2$(THF)]. After this time, S_2CPCy_3 (0.817 g, 2.29 mmol) was added, and the solution turned to deep blue. The solvents were then evaporated *in vacuo* and the resulting oil was dissolved in CH_2Cl_2 and chromatographed in alumina (activity III, 6 × 3 cm column). Hexane eluted a first band consisting mainly of starting compound, and then a mixture of CH_2Cl_2/hexane (1/1) eluted the deep blue band of compound **9**. Evaporation of the solvents *in vacuo* gave a blue solid, which was recrystallized from CH_2Cl_2/hexane. Yield: 0.65 g, 52%. Analysis. Found: C, 60.10; H, 7.13. $C_{27}H_{40}AuMnO_2PS_2$ calc: C, 59.33; H, 7.38%.

[(η^5-C_5H_4-Me)(CO)$_2$MnSC(PCy$_3$)SAu(C_6F_5)] (10)

A mixture of [Mn(η^5-C_5H_4-Me)(CO)$_2${SC(S)PCy$_3$}] (**9**) (0.1 g, 0.183 mmol), [(tht)Au(C_6F_5)] (0.083 g, 0.183 mmol) CH_2Cl_2 (10 ml), and CS_2 (1 ml) was stirred for 30 min. The solvents were then evaporated *in vacuo* and the residue was washed with hexane (2 × 10 ml). Recrystallization from CH_2Cl_2/hexane gave dark blue crystals of **10**. Yield: 0.13 g, 81%. Analysis. Found: C, 41.16; H, 4.24. $C_{33}H_{40}AuF_5MnO_2PS_2 \cdot CH_2Cl_2$ calc: C, 41.03; H, 4.25%.

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