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Reduction reactions of binuclear manganese–molybdenum complexes containing S_2CPR_3 and bidentate *P*-donor bridges. X-Ray structure of $[MnMo(SnPh_3)(CO)_4(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]$

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Abstract

The reduction of the substituted derivatives $[MnMo(CO)_5(\mu\text{-Br})(\mu\text{-L—L})(\mu\text{-}S_2CPR_3)]$ (**1**, L—L = dmpm or tedip), with NaHg produces anions (**2**) that, upon reaction with $ClSnPh_3$, give neutral tetracarbonyls $[MnMo(SnPh_3)(CO)_4(\mu\text{-L—L})(\mu\text{-}S_2CPR_3)]$ (**3**). An X-ray structure determination of **3a** (L—L = tedip, R = Cy) demonstrates the addition of $SnPh_3$ to Mo and migration of the central carbon atom of the S_2CPR_3 from Mo to Mn. Simultaneous loss of one carbonyl group from the manganese atom allows a change of coordination of S_2CPR_3 from $\eta^1;\eta^3$ (in **1**) to $\eta^3;\eta^2$ (in **3**). The tetracarbonyls **3** can also be prepared by reaction of the triphenylstannylhexacarbonyl derivatives $[MnMo(CO)_6(SnPh_3)(\mu\text{-}S_2CPR_3)]$ with bidentate donors L—L (dmpm or tedip), through substitution of one CO group on each metal.

Keywords: Manganese; Molybdenum; Trialkylphosphoniodithioformate bridges; X-ray structure

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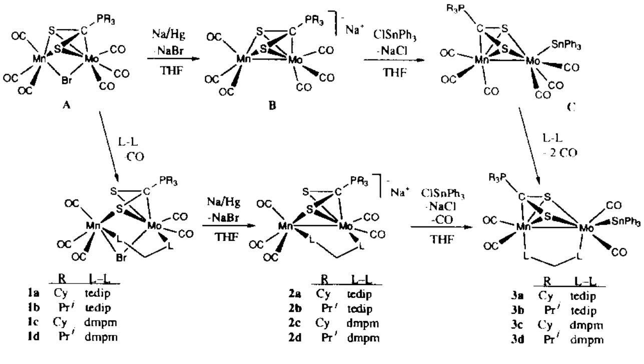
1. Introduction

Trialkylphosphoniodithioformates S_2CPR_3, are capable of forming very stable bridges when coordinated η^2(S, S′);η^3(S, C, S′) in binuclear complexes, such as the hexacarbonyls $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ which contain an Mn–Mn bond [1]. These hexacarbonyl complexes undergo reduction and hydride-addition reactions, affording μ-hydrido compounds containing phosphoniodithioformate esters [2] or phosphonioethenetrithiolate [3]. All these facts have stimulated our interest in finding rational methods to prepare similar complexes of other metals and we have recently reported a convenient method for obtaining heterodinuclear complexes containing manganese and molybdenum. The metal atoms, which are not directly bonded, are bridged by a halide and an S_2CPR_3 which acts as an (*S*, *S*′) chelate (to Mn) and as η^3(S, C, S′) pseudoallyl (to Mo) [4]. As an extension, we have found recently that the reduction of hexacarbonyls $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**A** in Scheme 1) with sodium amalgam in THF produces very reactive heterobinuclear anions **B** which react with $ClSnPh_3$ to afford neutral $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPR_3)]$ (**C** in Scheme 1) [5].

The formation of intermediate heterodinuclear carbonyl anions such as **B** is of great interest due to the lack of such kind of species as recently pointed out [6]. Additionally, the reactions leading from **A** to **C** had



Scheme 1.

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two special features: first, regiospecific addition of the triphenylstannyl group to the molybdenum atom, suggesting that it is Mo which carries most of the negative charge in the heterobinuclear anions **B** and second the rearrangement of the S_2CPR_3 which includes migration of the central carbon from Mo to Mn. The additional bridges play an important role in the kind of bonding by 1,1-dithiolate [7,8]. Since the pentacarbonyls $[MnMo(CO)_5(\mu\text{-Br})(\mu\text{-L—L})(\mu\text{-}S_2CPR_3)]$ (**1a–d** in Scheme 1) which contain bidentate *P*-donor bridges were available from previous work [4], they were chosen to test the scope of the reduction reactions and the generality of the rearrangement. We report here the application of the reduction/stannylation sequence to obtain derivatives containing diphosphine and diphosphite bridges.

2. Results and discussion

Treatment of $[MnMo(CO)_5(\mu\text{-Br})(\mu\text{-L—L})(\mu\text{-}S_2CPR_3)]$ (**1a–d** in Scheme 1) [4] with NaHg in THF at room temperature affords highly reactive anions which are formulated as $[MnMo(CO)_5(\mu\text{-P—P})(\mu\text{-}S_2CPR_3)]^-$ (**2a–d**). Subsequent reaction with $ClSnPh_3$ produced neutral, stable derivatives of formula $[MnMo(SnPh_3)(CO)_4(\mu\text{-P—P})(\mu\text{-}S_2CPR_3)]$ (**3a–d** in Scheme 1).

An X-ray determination was carried out on **3a**. The crystallographic data are presented in Table 1 (the perspective view being given in Fig. 1), Table 2 (atomic parameters) and Table 3 (selected bond distances and angles). The Mn—Mo distance of 2.937(8) Å, although slightly longer than that in the related hexacarbonyl $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CP^iPr_3)]$ (2.877(1) Å [5]) is consistent with the existence of a direct bond between manganese and molybdenum. In contrast, the structure of **3a** indicates the regiospecific addition of the triphenyltin group to the molybdenum atom and the migration of the central carbon of the S_2CCy_3 from molybdenum to manganese. This shows that the P—P bridges in **3a–d** do not modify either the regiochemistry of the addition of $SnPPh_3$ or the factors governing the rearrangement of the central carbon atom of S_2CPCy_3 from one of the metals to the other.

However, there is a remarkable difference between reaction sequence **1** → **2** → **3** and **A** → **B** → **C**. In **3a**, both sulphur atoms of the S_2CPCy_3 are coordinated to both metals, whereas in the starting complex **1a** one sulphur was coordinated to molybdenum but not to manganese [4]. Apart from rearranging the carbon–metal bond in the reaction sequence from **1** to **3** (through the intermediate anions **2**), the S_2CPR_3 has regained the $\eta^2(S, S');\eta^3(S, C, S')$ bonding mode by expelling one of the carbonyl groups bonded to manganese. The loss of the CO occurs either in the first step (reduction with sodium amalgam) or after incorporation of the triphenyltin group. Due to the instability of anions **2**, it has not been possible to obtain reliable spectroscopic information apart from their IR spectra (see Experimental details).

Table 1
Crystal data and refinement details for $[MnMo(SnPh_3)(CO)_4(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]\cdot CH_2Cl_2$ (**3a**)

Empirical formula	$C_{49}H_{68}MnMoO_9P_3S_2Sn\cdot CH_2Cl_2$
M	1312.61
Crystal system, space group	triclinic, $P\bar{1}$
a (Å)	12.911(5)
b (Å)	19.909(6)
c (Å)	13.243(5)
α (°)	89.96(3)
β (°)	116.85(3)
γ (°)	91.18(3)
U (Å^3)	3036(2)
Z	2
T(K)	293
D (g cm^{-3})	1.44
F(000)	1340
λ(Mo Kα) (Å)	0.71073
Crystal size (mm)	0.10×0.07×0.07
Crystal colour	red
μ(cm^{-1})	10.84
Method of collection	$\omega-2\theta$ scan
Scan range (°)	$0 \le \theta \le 25$
Drift corrections: max, min	1.128, 0.995
No. of reflections measured	11204
No. of reflections observed $I \ge 3\sigma(I)$	1712
Absorption correction factors: max, min	DIFABS 0.740, 1.135
No. of parameters	326
Weighting scheme	$w = [\sigma^2(F) + g(F^2)]^{-1}$
g	0.0015
Final residuals R, R_w	0.074, 0.074

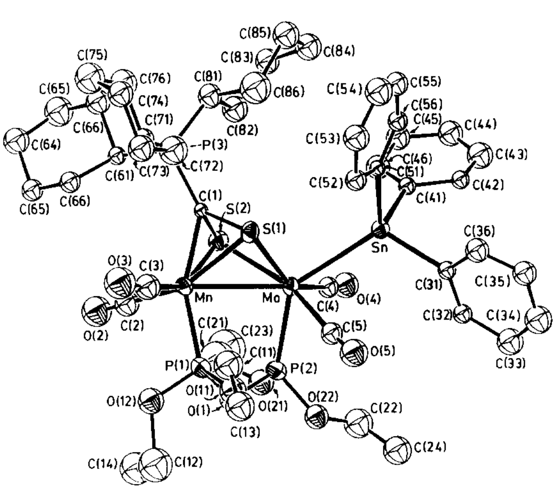

Fig. 1. Perspective view (EUCLID package) [12] of the core of $[MnMo(SnPh_3)(CO)_4(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]$ (**3a**), showing the atom numbering.

Table 2
Fractional coordinates and equivalent isotropic displacement coefficients [a] ($Å^2 \times 10^2$) for $[MnMo(SnPh_3)(CO)_4(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]$ **(3a)**

Atom	x	y	z	U_{iso} (× 100)
Mn	0.3416(6)	0.8222(3)	1.0229(6)	4.2(4)
Mo	0.2155(4)	0.6931(2)	0.9467(3)	3.6(2)
Sn	0.1227(3)	0.6090(2)	0.7554(3)	3.7(2)
S(1)	0.260(1)	0.7770(6)	0.836(1)	4.4(6)
S(2)	0.424(1)	0.7170(6)	1.034(1)	4.5(6)
P(1)	0.213(1)	0.8342(7)	1.084(1)	5.6(8)
P(2)	0.182(1)	0.6986(6)	1.107(1)	5.4(8)
P(3)	0.524(1)	0.7979(6)	0.895(1)	4.2(6)
C(1)	0.409(3)	0.781(2)	0.930(3)	2.0(1)
C(2)	0.457(5)	0.846(2)	1.165(5)	7.0(2)
O(2)	0.527(4)	0.853(2)	1.248(3)	10.0(1)
C(3)	0.331(4)	0.906(3)	0.985(4)	7.0(2)
O(3)	0.337(3)	0.962(2)	0.963(3)	12.0(1)
C(4)	0.234(4)	0.601(2)	0.998(4)	5.0(1)
O(4)	0.258(3)	0.547(2)	1.035(3)	7.0(1)
C(5)	0.040(4)	0.710(2)	0.880(4)	6.0(2)
O(5)	−0.052(3)	0.721(2)	0.834(3)	9.0(1)
O(1)	0.186(2)	0.773(1)	1.152(2)	6.0(9)
O(11)	0.086(3)	0.848(2)	1.010(3)	8.0(1)
C(11)	0.067(5)	0.887(3)	0.919(5)	10.0 [b]
C(13)	−0.042(5)	0.919(2)	0.899(4)	10.0 [b]
O(12)	0.254(3)	0.888(2)	1.182(3)	8.0(1)
C(12)	0.172(6)	0.902(3)	1.247(5)	14.0(3)
C(14)	0.254(5)	0.880(3)	1.341(5)	13.0(3)
O(21)	0.264(3)	0.662(2)	1.227(3)	8.0(1)
C(21)	0.385(6)	0.679(3)	1.283(6)	16.0(3)
C(23)	0.440(6)	0.625(3)	1.330(6)	18.0(3)
O(22)	0.060(3)	0.678(2)	1.104(2)	7.0(1)
C(22)	0.023(5)	0.614(3)	1.106(5)	10.0(2)
C(24)	−0.099(4)	0.609(2)	1.052(4)	9.0(2)
C(31)	−0.050(4)	0.575(2)	0.694(4)	4.0(1)
C(32)	−0.100(4)	0.554(2)	0.754(4)	4.0(1)
C(33)	−0.217(5)	0.526(2)	0.714(4)	8.0(2)
C(34)	−0.281(5)	0.529(2)	0.601(5)	9.0(2)
C(35)	−0.233(4)	0.548(2)	0.534(4)	7.0(2)
C(36)	−0.123(4)	0.578(2)	0.577(4)	6.0(2)
C(41)	0.206(4)	0.516(2)	0.770(3)	3.0(1)
C(42)	0.141(4)	0.458(2)	0.712(3)	4.0(1)
C(43)	0.188(5)	0.397(3)	0.722(4)	8.0(2)
C(44)	0.300(5)	0.388(2)	0.782(4)	7.0(2)
C(45)	0.369(4)	0.443(2)	0.840(4)	7.0(2)
C(46)	0.316(4)	0.507(2)	0.835(4)	7.0(2)
C(51)	0.127(3)	0.647(2)	0.608(3)	3.0(1)
C(52)	0.090(4)	0.712(2)	0.577(4)	5.0(1)
C(53)	0.088(4)	0.738(3)	0.469(4)	8.0(2)
C(54)	0.112(5)	0.700(3)	0.400(5)	9.0(2)
C(55)	0.149(4)	0.640(2)	0.438(4)	6.0(2)
C(56)	0.152(4)	0.614(2)	0.535(4)	5.0(1)
C(61)	0.657(3)	0.805(2)	1.035(3)	4.0(1)
C(62)	0.775(4)	0.788(2)	1.030(4)	7.0(2)
C(63)	0.874(5)	0.791(3)	1.146(4)	10.0(2)
C(64)	0.882(4)	0.856(2)	1.198(4)	8.0(2)
C(65)	0.771(4)	0.876(2)	1.198(3)	5.0(1)
C(66)	0.672(4)	0.875(2)	1.085(3)	5.0(1)
C(71)	0.498(4)	0.877(2)	0.819(4)	5.0(1)
C(72)	0.386(5)	0.891(3)	0.731(5)	9.0(2)
C(73)	0.379(4)	0.964(2)	0.695(4)	8.0(2)
C(74)	0.467(5)	0.974(2)	0.651(4)	7.0(2)
C(75)	0.584(5)	0.960(3)	0.733(5)	11.0(2)
C(76)	0.587(5)	0.886(2)	0.774(4)	9.0(2)
C(81)	0.542(4)	0.730(2)	0.813(4)	7.0(2)
C(82)	0.555(4)	0.662(2)	0.879(4)	8.0(2)
C(83)	0.578(4)	0.605(2)	0.811(4)	7.0(2)
C(84)	0.481(4)	0.599(2)	0.688(4)	8.0(2)
C(85)	0.470(5)	0.659(2)	0.631(4)	8.0(2)
C(86)	0.433(5)	0.721(3)	0.692(5)	11.0(2)
C(90)	0.764(9)	0.743(4)	1.559(6)	5.0(4) [c]
Cl(91)	0.685(9)	0.804(4)	1.590(6)	14.0(2) [c]
Cl(92)	0.771(9)	0.754(4)	1.430(6)	18.0(3) [c]
C(93)	0.97(1)	0.896(6)	1.58(2)	4.0(1) [d]
Cl(94)	0.84(1)	0.852(6)	1.54(2)	13.0(4) [d]
Cl(95)	0.96(1)	0.984(6)	1.59(2)	19.0(7) [d]

[a] U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.
[b] Fixed U_{iso}.
[c] Occupancy factor 0.35.
[d] Occupancy factor 0.15.

In the reduction of the bromo derivatives **A** to give the anions **B**, the mean value of the ν(CO) frequencies is decreased by ca. 90 cm^{-1} and, in the subsequent addition of the triphenylstannyl group to the anions **B** to give complexes **C**, the mean value of the ν(CO) increases by ca. 90 cm^{-1} [1]. In the reaction sequence $\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{3}$, a decrease of ca. 90 cm^{-1} was observed during reduction, while the addition of the $SnPh_3$ was accompanied by an increase of only 50 cm^{-1}. From these data it seems that the step from **2** to **3** involves both the addition of $SnPh_3$ and the loss of CO. Since the M—CO bonds in the electron-rich anions **2** would be strengthened by back-donation from the metals, it is reasonable to assume that the loss of CO occurs after incorporation of $SnPh_3$. It is apparent from the structures depicted in Scheme 1 that the triphenyltin derivatives **C** and **3** are more closely related, than their bromo precursors **A** and **1**, in which the S_2CPR_3 exhibits different coordination modes. As previously reported, the reaction of **A** with the bidentate phosphorus L—L produced the pentacarbonyls **1** through substitution of one CO group of molybdenum and cleavage of one Mn—S bond [4]. Complexes **3** can be considered as resulting from the substitution of two carbonyl groups (one from each metal) in the hexacarbonyls **C** by the P atoms of the bidentate L—L. Treatment of complexes **C** with dmpm in refluxing toluene for a short time produces derivatives **3c,d**, which can be isolated in moderate yields. The analogous reactions with tedip require longer refluxing times and this leads to extensive decomposition. IR and ^{31}P NMR monitoring of the crude reaction mixtures confirms the production of the tetracarbonyls **3a,b** in low yield, accompanied by decomposition products.

The reaction conditions necessary to achieve the carbonyl substitutions leading from **C** to **3** are significantly more extreme (refluxing toluene) than those required to transform **A** into **1** (−78°C for dmpm, r.t. for tedip) [4].

There is a close structural relationship between the triphenyltin complexes **C** and **3**, as can be seen from a comparison of **3a** with **C** (R = ^{i}Pr) [5]. Due to the low accuracy in the structural determination of **3a**, this comparison must be limited to the central part of the molecules which contain the heaviest atoms and lower thermal parameters. The distances between homologous pairs of atoms in the cores of structure differ by less than 5%. The main differences in geometry concerns to the relative orientations of the substituents on the Mo atom compared with those in Mn. Fig. 2 shows a projection of the core of the molecules on to a plane perpendicular to the Mn—Mo bond. The $S_2C(P)$-$Mn(CO)_3$ groups of both molecules are nearly superimposable, whereas the substituents of the molybdenum atom rotate in going from **C** to **3a** in order to accommodate the additional P—P bridge. This is reminiscent of the relative geometry of [$Mn_2(CO)_6(\mu$-$S_2CPCy_3)$] and [$Mn_2(CO)_4(\mu$-$S_2CPCy_3)(\mu$-dppm)] [1b], although in the present case the distortion produced by substitution of two carbonyl groups by tedip is smaller than that found in the dimanganese compounds. This may be due to the lower steric requirement of tedip when compared to the dppm present in the dimanganese complex.

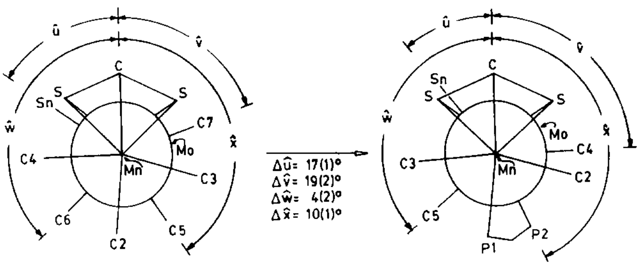

Fig. 2. Schematic view of molecules of [$MnMo(SnPh_3)(CO)_6(\mu$-$S_2CP^iPr_3)$] (**C**) and **3a** projected on to the plane perpendicular to the Mn—Mo bond. The differences in the torsion angles $\Delta\hat{u},\Delta\hat{v},\Delta\hat{w},\Delta\hat{x}$ have been taken as absolute values, i.e. $\Delta u = ||\hat{u}(C)|-|\hat{u}(3a)||$.

Table 3
Selected bond lengths (Å) and angles (°) for [$MnMo(SnPh_3)(CO)_4$-(μ-tedip)(μ-S_2CPCy_3)] (**3a**)

Mn–Mo	2.937(8)	Mn–S(1)	2.38(1)
Mn–S(2)	2.34(1)	Mn–P(1)	2.16(2)
Mn–C(1)	1.99(4)	Mn–C(2)	1.85(6)
Mn–C(3)	1.74(5)	Mo–Sn	2.799(5)
Mo–S(1)	2.45(1)	Mo–S(2)	2.44(1)
Mo–P(2)	2.35(1)	Mo–C(4)	1.93(5)
Mo–C(5)	2.06(5)	Sn–C(31)	2.09(4)
Sn–C(41)	2.12(4)	Sn–C(51)	2.12(4)
S(1)–C(1)	1.76(4)	S(2)–C(1)	1.81(4)
C(2)–O(2)	1.07(5)	C(3)–O(3)	1.15(5)
C(4)–O(4)	1.17(4)	C(5)–O(5)	1.08(5)
P(3)–C(1)	1.77(4)		
S(1)–Mn–Mo	53.6(3)	S(2)–Mn–Mo	53.5(3)
S(2)–Mn–S(1)	72.8(4)	P(1)–Mn–Mo	80.7(4)
P(1)–Mn–S(1)	112.4(6)	P(1)–Mn–S(2)	119.6(6)
C(1)–Mn–Mo	76.(1)	C(1)–Mn–S(1)	47(1)
C(1)–Mn–S(2)	49.(1)	C(1)–Mn–P(1)	155.(1)
C(2)–Mn–Mo	129.(2)	C(2)–Mn–S(1)	157.(2)
C(2)–Mn–S(2)	92.(2)	C(2)–Mn–P(1)	89.(2)
C(2)–Mn–C(1)	111.(2)	C(3)–Mn–Mo	141.(2)
C(3)–Mn–S(1)	97.(2)	C(3)–Mn–S(2)	150.(2)
C(3)–Mn–P(1)	91.(2)	C(3)–Mn–C(1)	104.(2)
C(3)–Mn–C(2)	89.(2)	Sn–Mo–Mn	139.9(2)
S(1)–Mo–Mn	51.4(3)	S(1)–Mo–Sn	88.8(3)
S(2)–Mo–Mn	50.6(3)	S(2)–Mo–Sn	117.4(3)
S(2)–Mo–S(1)	70.0(4)	P(2)–Mo–Mn	86.8(4)
P(2)–Mo–Sn	131.9(4)	P(2)–Mo–S(1)	133.9(4)
P(2)–Mo–S(2)	100.3(5)	C(4)–Mo–Mn	138.(1)
C(4)–Mo–Sn	72.(1)	C(4)–Mo–S(1)	146.(1)
C(4)–Mo–S(2)	94.(1)	C(4)–Mo–P(2)	77.(1)
C(5)–Mo–Mn	108.(1)	C(5)–Mo–Sn	78.(1)
C(5)–Mo–S(1)	97.(1)	C(5)–Mo–S(2)	159.(1)
C(5)–Mo–P(2)	76.(1)	C(5)–Mo–C(4)	105.(2)
C(31)–Sn–Mo	118.(1)	C(41)–Sn–Mo	116.(1)
C(41)–Sn–C(31)	100.(2)	C(51)–Sn–Mo	116.(1)
C(51)–Sn–C(31)	103.(2)	C(51)–Sn–C(41)	100.(2)
S(1)–C(1)–Mn	78.(2)	S(2)–C(1)–Mn	76.(1)
S(2)–C(1)–S(1)	103.(2)	P(3)–C(1)–Mn	138.(2)
P(3)–C(1)–S(1)	127.(2)	P(3)–C(1)–S(2)	121.(2)
O(2)–C(2)–Mn	172.(5)	O(3)–C(3)–Mn	172.(5)
O(4)–C(4)–Mo	172.(4)	O(5)–C(5)–Mo	172.(4)

3. Experimental details

All reactions were carried out in dry solvents under dinitrogen. Literature procedures for the preparation of starting materials are quoted in each case. Donors and other reagents were purchased and used without purification unless otherwise stated.

3.1. [$MnMo(SnPh_3)(CO)_4(\mu$-tedip)(μ-S_2CPCy_3)] (3a)

A solution of [$MnMo(CO)_5(\mu$-Br)(μ-tedip)(μ-S_2CPCy_3)] (**1a**) [4] (0.197 g, 0.20 mmol) in THF (15 cm^3) was stirred with an excess of 1% NaHg (10 g) until IR monitoring showed exclusively ν(CO) bands of [$MnMo(CO)_5(\mu$-tedip)(μ-S_2CPCy_3)]$^-$ (**2a**) at 1912 m, 1888 (s), 1811 (s) and 1753 (m) (cm^{-1}). This took about 40–50 min with a change from red to yellow. The mixture was allowed to settle for several minutes and the supernatant solution was then transferred to another flask containing solid $ClSnPh_3$ (0.077 g, 0.20 mmol). The colour changed instantaneously to red and IR monitoring showed completed reaction. The solvent was evaporated in vacuo, the red residue extracted with CH_2Cl_2 and the extract filtered through alumina (activity III, 2 × 15 cm column). To the filtrate (ca. 35 cm^3) was added hexane (15 cm^3). Careful concentration in vacuo gave **3a** as a red microcrystalline solid. Yield, 0.17 g, 68%. (Anal. Found: C, 47.63; H 5.40%. $C_{49}H_{68}MnMoO_9P_3S_2Sn$ requires: C, 47.94; H, 5.58%).

Table 4
IR and $^{31}P\{^1H\}$ NMR data for new complexes

Compound	IR (THF) $\nu(CO)$ (cm^{-1})	$^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ(ppm) [a]					
		S_2CP^1	Mn–P^2	Mo–P^3	$J(P^1-P^2)$	$J(P^2-P^3)$	$J(P^1-Sn)$
3a $[MnMo(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-tedip})(SnPh_3)]$	1935 (s), 1907 (s), 1870 (s), 1844 (s)	33.10	179.01 (d)	174.54 (d)	[b]	51	153
3b $[MnMo(CO)_4(\mu\text{-}S_2CP^iPr_3)(\mu\text{-tedip})(SnPh_3)]$	1937 (s), 1906 (s), 1872 (s), 1842 (s)	43.12	179.47 (d)	173.41 (d)	[b]	50	153
3c $[MnMo(CO)_4(\mu\text{-}S_2CPCy_3)(\mu\text{-dmpm})(SnPh_3)]$	1909 (s), 1879 (s), 1844 (s), 1800 (s)	32.09 (d)	22.54 (dd)	26.35 (d)	3	48	141
3d $[MnMo(CO)_4(\mu\text{-}S_2CP^iPr_3)(\mu\text{-dmpm})(SnPh_3)]$	1908 (s), 1879 (s), 1841 (s), 1808 (s)	42.00 (d)	21.91, (dd)	25.17 (d)	3	49	138

[a] Coupling constants in Hz.

[b] Not observed.

3.1.1. Structure determination of ***3a***

Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into concentrated solutions of the compounds in CH_2Cl_2. Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least-squares refinement of a set of 25 centred reflections. Three reflections were measured every 1 h as orientation and intensity control. Significant decay was not observed. Heavy atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms by DIRDIF [9]. Full matrix least-squares refinements for both structures were made with SHELX76 [10]. After isotropic refinement, an absorption correction was applied with DIFABS [11]. A molecule of CH_2Cl_2 was found to be disordered and was refined with fixed geometries in two positions (occupancy factors 0.35 and 0.15). Due to the poor quality of the crystal, and in order to keep an aceptable data-to-parameter ratio, only the heavier atoms (Sn, Mo, Mn, S and P) were refined anisotropically. The remaining non-hydrogen atoms were refined isotropically. The carbon atoms of one ethyl group of the tedip ligand [C(11) and C(13)] showed some degree of thermal disorder. They were refined with fixed temperature factors of 0.10 Å^2. Hydrogen atoms were geometrically positioned and were given a common isotropic temperature factor which was refined. Full lists of structural data have been deposited at the Cambridge Crystallographic Data Centre.

*3.2. [MnMo(SnPh$_3$)(CO)$_4$(μ-tedip)(μ-S$_2$CP^{i}Pr$_3$)] (**3b**)*

Compound **3b** was prepared as described above for **3a** from [MnMo(CO)$_5$(μ-Br)(μ-tedip)(μ-S$_2$CP^{i}Pr$_3$)] (**1b**) [4] (0.173 g, 0.20 mmol), NaHg (1%, 10 g, an excess) and $ClSnPh_3$ (0.077 g, 0.20 mmol). The intermediate anion [MnMo(CO)$_5$(μ-tedip)(μ-S$_2$CP^{i}Pr$_3$)]$^-$ (**2b**) exhibited ν(CO) bands at 1913 (m), 1889 (s), 1812 (s) and 1753 (m) (cm^{-1}). Similar work-up afforded **3b** as yellow needles. Yield, 0.14 g, 64%. (Anal. Found: C, 43.12; H, 5.23%. $C_{40}H_{56}MnMoO_9P_3S_2Sn$ requires: C, 43.38; H, 5.10%.)

*3.3. [MnMo(SnPh$_3$)(CO)$_4$(μ-dmpm)(μ-S$_2$CPCy$_3$)] (**3c**)*

Method A

Compound **3c** was prepared as described above for **3a** from [MnMo(CO)$_5$(μ-Br)(μ-dmpm)(μ-S$_2$CPCy$_3$)] (**1c**) [4] (0.172 g, 0.20 mmol), NaHg (1%, 10 g, an excess) and $ClSnPh_3$ (0.077 g, 0.20 mmol). The intermediate anion [MnMo(CO)$_5$(μ-dmpm)(μ-S$_2$CPCy$_3$)]$^-$ (**2c**) exhibited ν(CO) bands at 1895 (m), 1863 (s), 1788 (s) and 1728 (m) (cm^{-1}). Compound **3c** was obtained as deep red crystals. Yield, 0.13 g, 60%. (Anal. Found: C,

Table 5
^{1}H and ^{13}C{^{1}H} NMR data for new complexes [a]

Compound	^{1}H NMR δ (ppm)	^{13}C{^{1}H} NMR δ (ppm)
3a	7.75, 7.25 [m, 15H, Sn(C_6H_5)$_3$]; 4.19, 3.92 [m, 8H, 2 CH_2 of tedip]; 2.31 [m, 3H, CH of Cy]; 1.95–1.19 [m, br, 30H, CH_2 of Cy]; 1.39 [t(7), 6H, 2 CH_3 of tedip]; 1.20 [t(7), 6H, 2 CH_3 of tedip]	232.9 [d(35), Mo*C*O]; 228.7 [d(33), 2 Mn*C*O]; 146.7 [s, *J*(C–Sn) = 362 Hz, C^1 of SnPh]; 137.5 [s, *J*(C–Sn) = 36 Hz, C^3 and C^5 of SnPh]; 128.0 [s, *J*(C–Sn) = 42 Hz, C^2 and C^6 of SnPh]; 127.8 [s, C^4 of SnPh]; 86.6 [d(49), S$_2$*C*P]; 62.11 [dd(12 and 5), *C*H$_2$ of tedip]; 34.4 [d(40), C^1 of Cy]; 27.6 [s, C^2 and C^6 of Cy]; 27.1 [d(12), C^3 and C^5 of Cy]; 25.5 [s, C^4 of Cy]; 16.4 [m, CH_3 of tedip]
3b	7.74, 7.27 [m, 15H, Sn(C_6H_5)$_3$]; 4.24, 3.85 [m, 8H, 2 CH_2 of tedip]; 2.58 [m, 3H, CH of ^{i}Pr]; 1.44 [t(7), 6H, 2 CH_3 of tedip]; 1.32–1.25 [m, 24 H, 8 CH_3 of ^{i}Pr and tedip]	231.9 [d(34), *J*(C–Sn) = 362 Hz, 2 Mo*C*O]; 227.2 [d(32), 2 Mn*C*O]; 146.5 [s, *J*(C–Sn) = 334 Hz, C^1 of SnPh]; 137.2 [s, *J*(C–Sn) = 36 Hz, C^3 and C^5 of SnPh]; 127.6 [s, *J*(C–Sn) = 42 Hz, C^2 and C^6 of SnPh]; 127.4 [s, C^4 of SnPh]; 86.6 [d(51), S$_2$*C*P]; 61.7 [dd(8 and 5), *C*H$_2$ of tedip]; 23.6 [d(44), *C*H of ^{i}Pr]; 17.7 [d(2), *C*H$_3$ of ^{i}Pr]; 15.1 [m, *C*H$_3$ of tedip]
3c	7.69, 7.26 [m, 15H, Sn(C_6H_5)$_3$]; 3.71 [m, 2H, CH_2 of dmpm]; 2.27 [m, 3H, CH of Cy]; 2.06–1.04 [m, a, 30H, CH_2 of Cy]; 1.90 [d(8), 6H, 2 CH_3 of dmpm]; 1.61 [d(9), 6H, 2 CH_3 of dmpm]	236.3 [d(25), 2 Mo*C*O]; 232.3 [d(22), 2 Mn*C*O]; 147.4 [s, C^1 of SnPh]; 137.1 [s, *J*(C–Sn) = 36 Hz, C^3 and C^5 of SnPh]; 127.4 [s, *J*(C–Sn) = 41 Hz, C^2 and C^6 of SnPh]; 127.0 [s, C^4 of SnPh]; 85.7 [d(51), S$_2$*C*P]; 57.9; 34.0 [d(42), C^1 of Cy]; 27.6 [s, C^2 and C^6 of Cy]; 26.8 [d(12), C^3 and C^5 of Cy]; 25.3 [s, C^4 of Cy]; 24.1 [dd(30 and 5), *C*H$_3$ of dmpm]; 18.8 [dd(30 and 5), *C*H$_3$ of dmpm]
3d	7.67, 7.24 [m, 15H, Sn(C_6H_5)$_3$]; 3.65 [m, 2H, CH_2 of dmpm]; 2.50 [m, 3H, CH of ^{i}Pr]; 1.91 [d(8), 6H, 2 CH_3 of dmpm]; 1.60 [d(9), 6H, 2 CH_3 of dmpm]	236.0 [d(24), 2 Mo*C*O]; 232.0 [d(22), 2 Mn*C*O]; 147.4 [s, *J*(C–Sn) = 362 Hz, C^1 of SnPh]; 137.2 [s, *J*(C–Sn) = 36 Hz, C^3 and C^5 of SnPh]; 127.5 [s, *J*(C–Sn) = 41 Hz, C^2 and C^6 of SnPh]; 127.1 [s, C^4 of SnPh]; 84.7 [d(51), S$_2$*C*P]; 56.8 [dd(26 and 21), *C*H$_2$ of dmpm]; 24.6–23.5 [m, *C*H$_3$ of dmpm and *C*H of ^{i}Pr]; 18.5 [dd(10 and 5), *C*H$_3$ of dmpm]; 17.7 [d(2), *C*H$_3$ of ^{i}Pr]

[a] From CD_2Cl_2 solutions.

50.32; H, 5.60%. $C_{46}H_{62}MnMoO_4P_3S_2Sn$ requires: C, 49.97; H, 5.65%.)

Method B

A mixture of [MnMo(SnPh$_3$)(CO)$_6$(μ-S$_2$CPCy$_3$)] [5] (0.21 g, 0.20 mmol) and dmpm (0.032 cm^3, 0.2 mmol) was heated under reflux in toluene (15 cm^3) for 20 min. The solvent was removed in vacuo, the residue extracted with a minimum amount of a mixture of CH_2Cl_2/hexane (1 : 1, vol : vol) and filtered through alumina. The filtrate was concentrated in vacuo and stored at −20°C for several days, to give red crystals of **3c**. Yield, 0.093 g, 42%. (Anal. Found: C, 50.26; H, 5.48%. $C_{46}H_{62}MnMoO_4P_3S_2Sn$ requires: C, 49.97; H, 5.65%.)

3.4. [MnMo(SnPh$_3$)(CO)$_4$(μ-dmpm)(μ-S$_2$CP^{i}Pr$_3$)] (3d)

Method A

Compound **3d** was prepared as described above for **3a** from [MnMo(CO)$_5$(μ-Br)(μ-dmpm)(μ-S$_2$CP^{i}Pr$_3$)] (**1d**) [4] (0.149 g, 0.20 mmol), NaHg (1%, 10 g, an excess) and ClSnPh$_3$ (0.077 g, 0.20 mmol). The intermediate anion [MnMo(CO)$_5$(μ-dmpm)(μ-S$_2$CP^{i}Pr$_3$)]$^-$ (**2d**) exhibited ν(CO) bands at 1894 (m), 1865 (s), 1790 (m) and 1730 (m)(cm^{-1}). Compound **3d** was obtained as deep red crystals. Yield, 0.11 g, 56%. (Anal. Found: C, 44.93; H, 5.02%. $C_{37}H_{50}MnMoO_4P_3S_2Sn$ requires: C, 45.10; H, 5.11%.)

Method B

Compound **3d** was prepared as **3c** (Method B) above by heating a mixture of [MnMo(SnPh$_3$)(CO)$_6$(μ-S$_2$C^{i}Pr$_3$)] [5] (0.18 g, 0.20 mmol) and dmpm (0.032 cm^3, 0.2 mmol) in toluene (15 cm^3) for 20 min under reflux. The work-up was as described for **3c**. Yield, 0.095 g, 48%. (Anal. Found: C, 44.87; H, 4.78%. $C_{37}H_{50}MnMoO_4P_3S_2Sn$ requires: C, 45.01; H, 5.11%.)

The relevant IR and $^{31}P\{^1H\}$ NMR data for complexes **3a–d** are listed in Table 4 while the corresponding ^1H and $^{13}C\{^1H\}$ NMR data are listed in Table 5.

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