

Synthesis of asymmetric heterotrimetallic gold clusters containing Mo, W, and Mn

Mei Wang,^a Daniel Miguel,^{*b} Eva M. López,^c Julio Pérez,^c Víctor Riera,^c Claudette Bois^d and Yves Jeannin^d

^a State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Road 158-46, Dalian 116012, P. R. China

^b Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Cl Prado de la Magdalena s/n, E-47071 Valladolid, Spain

^c Departamento de Química Orgánica e Inorgánica I. U. Q. O. E. M. - Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

^d Laboratoire de Chimie des Métaux de Transition, UA-CNRS 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

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A series of new heterotrimetallic gold clusters, $[(OC)_3M(\mu-S_2CPR_3)(\mu-AuPPh_3)Mo(CO)_3]$ ($M = Mn, R = Cy, \mathbf{3a}$; $R = Pr^i, \mathbf{3b}$; $M = Re, R = Cy, \mathbf{3c}$; $R = Pr^i, \mathbf{3d}$) and $[(L)(OC)_2Mo(\mu-S_2CPCy_3)(\mu-AuPPh_3)M'(CO)_3]$ ($M' = Mo, L = \eta^3\text{-allyl}, \mathbf{6a}$; $L = NO, \mathbf{6b}$; $M' = W, L = \eta^3\text{-allyl}, \mathbf{6c}$; $L = NO, \mathbf{6d}$), have been synthesized in good yields by the reactions of $ClAuPPh_3$ with the corresponding homo- or heterobinuclear anions, $[(OC)_3M(\mu-S_2CPR_3)Mo(CO)_3]^-$ and $[(L)(OC)_2Mo(\mu-S_2CPCy_3)M'(CO)_3]^-$, formed respectively by the reduction of the complexes $[(OC)_3M(\mu-Br)(\mu-S_2CPR_3)Mo(CO)_3]$ and $[(L)(OC)_2Mo(\mu-Br)(\mu-S_2CPR_3)M'(CO)_3]$ with Na/Hg . The new complexes have been characterized spectroscopically and the molecular structures of $\mathbf{3a}$, $\mathbf{6a}$, and $\mathbf{6c}$ have been determined by X-ray crystallography, revealing remarkable structural differences between the trimetallic cores.

Introduction

The synthesis of clusters containing metals with disparate properties remains challenging.¹ In recent years a variety of transition-metal gold clusters has been prepared and structurally characterized,² including trinuclear clusters with triangular cores $[M_2Au]$,³ trimetallic gold clusters with a μ_3 -bridging hydride,⁴ and polynuclear transition-metal gold clusters containing metal cores $[M_nAu_m]$.⁵ The catalytic activity of some of these clusters has been studied.⁶ Most reported trimetallic gold clusters have a symmetric triangular skeleton which contains two atoms of the same transition element, while heterotrimetallic gold clusters containing more than one type of transition-metal atoms are scarce.⁷ This is not surprising since heterobinuclear anions, usually employed as precursors, are quite limited in number.⁸ We have found a convenient way to prepare heterobinuclear anions which can be used *in situ* to obtain neutral complexes,^{9,10} and here we report the application of this methodology to the synthesis of asymmetric gold clusters.

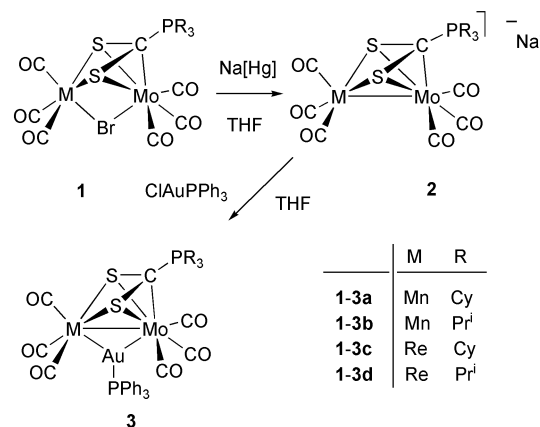
Results and discussion

Synthesis and characterization of heterotrimetallic gold clusters $[(OC)_3M(\mu-S_2CPR_3)(\mu-AuPPh_3)Mo(CO)_3]$, $\mathbf{3a-d}$

A solution of the anionic species $[(OC)_3M(\mu-S_2CPR_3)Mo(CO)_3]^-$ ($M = Mn, R = Cy, \mathbf{2a}$; $R = Pr^i, \mathbf{2b}$; $M = Re, R = Cy, \mathbf{2c}$; $R = Pr^i, \mathbf{2d}$) in THF was reacted with equimolar amounts of $ClAuPPh_3$ to afford trimetallic complexes $\mathbf{3a-d}$ as red crystalline solids (Scheme 1). IR and $^{31}P\{^1H\}$ NMR spectra of the crude reaction showed complexes $\mathbf{3a-d}$ to be the only detectable product in each reaction.

Analytical and spectroscopic data (Tables 1 and 2) are consistent with the molecular structures of $\mathbf{3a-d}$ proposed in Scheme 1.

The structure of $\mathbf{3a}$, characterized by a single-crystal X-ray determination (see Fig. 1 and Tables 3 and 4), consists of the



Scheme 1

$Mn(CO)_3$ and $Mo(CO)_3$ fragments bridged by $AuPPh_3$ and S_2CPCy_3 ligands, the latter acting as an $\eta^2-(S,S')$ chelate toward Mn, and as an $\eta^3-(S,C,S')$ pseudoallyl to Mo.

The Mn–Mo distance (2.982(2) Å) is somewhat longer than in the related complexes, $[(OC)_3Mn(\mu-S_2CPPR^i_3)Mo(CO)_3-(SnPh_3)]$ (2.877(1) Å),^{9b} and $[(OC)_2Mn(\mu-S_2CPPR^i_3)(\mu-PPh_2)Mo(CO)_2]$ (2.726(2) Å).^{9a} As far as we know, the only MnMoAu compound structurally characterized is $[CpMoMn(\mu-PPh_2)-\{\mu-\sigma:\eta^4-CH(Me)CHCHAu(PMe_2Ph)\}(CO)_4]$ in which the gold atom is bonded to Mn and the C(1) atom of the allyl bridge, but not to Mo.¹¹ Therefore, $\mathbf{3a}$ is the first example of a MnMoAu triangle, the closest precedent being the silver-bridging complex $[(OC)_4Mn(\mu-PPh_2)(\mu-AgPPh_3)Mo(CO)_2(\eta^5-C_5H_5)]$ for which a Mn–Mo bond distance of 3.190(2) Å has been reported.¹² The $AuPPh_3$ bridge can be considered as a one-electron donor to form 3-center–2-electron bonds with Mn and Mo atoms, as the isolobal H bridge does. The Mn–Au (2.772(2) Å) and Mo–Au (2.768(1) Å) distances are within the range of previously reported values (Mn–Au, 2.665–2.845; Mo–Au, 2.698–2.914 Å,^{3c,f,g,5f} and Mn and Mo attain 18-electron configurations. The

Table 1 IR and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the novel gold-bridging trinuclear clusters

No.	Compd.	IR (THF)/ cm^{-1}		$^{31}\text{P}\{^1\text{H}\}$ NMR, δ (ppm) ^a	
		$\nu(\text{CO})$	$\nu(\text{NO})$	S_2CP	AuPPh_3
3a	$[(\text{OC})_3\text{Mn}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1988 m, 1941 vs, 1884 s, 1832 m		33.23	67.23
3b	$[(\text{OC})_3\text{Mn}(\mu\text{-S}_2\text{CPr}^i_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1987 m, 1940 s, 1896 s, 1839 m		43.28	93.95
3c	$[(\text{OC})_3\text{Re}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1997 m, 1951 s, 1901 s, 1882 s, 1836 m		43.20	80.16
3d	$[(\text{OC})_3\text{Re}(\mu\text{-S}_2\text{CPr}^i_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1997 m, 1953 s, 1904 s, 1881 s, 1843 m		54.04	79.90
6a	$[(\eta^3\text{-C}_3\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1943 w(sh), 1916 vs, 1869 m, 1830 s		35.23	61.86
6b	$[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$	1997 m, 1948 s, 1919 s, 1882 m, 1839 m	1633 m	37.72	72.43 (br)
6c	$[(\eta^3\text{-C}_3\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{W}(\text{CO})_3]$	1943 w(sh), 1916 vs, 1863 s, 1823 s		34.54	67.73
6d	$[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{W}(\text{CO})_3]$	2000 m, 1946 vs, 1923 s, 1874 s, 1831 m	1629 m	35.94 ^b	77.67 (br)

^a Measured in CD_2Cl_2 solution unless otherwise stated. ^b In CDCl_3 .

Table 2 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for the novel gold-bridging trinuclear clusters^a

Compd.	^1H NMR, δ (ppm)	$^{13}\text{C}\{^1\text{H}\}$ NMR, δ (ppm)
3a ^b	7.63–7.22 [m, 15 H, Ph], 2.50 [m, 3 H, CH of Cy], 2.17–1.30 [m, 30 H, CH ₂ of Cy]	238.7 [s, MoCO], 235.3 [s, MnCO], 135.0 [d(15), CH of Ph], 133.4 [d(41), ipso-C of Ph], 131.2 [s, CH of Ph], 34.1 [d(41), CH of Cy], 28.1 [s, CH ₂ of Cy], 27.4 [d(11), CH ₂ of Cy], 26.2 [s, CH ₂ of Cy]
3b ^c	7.60–7.30 [m, 15 H, Ph], 2.81 [m, 3 H, CH of Pr ⁱ], 1.45 [m, 18 H, CH ₃ of Pr ⁱ]	
3c ^c	7.61–7.19 [m, 3 H, Ph], 2.52 [m, 3 H, CH of Cy], 2.17–1.23 [m, 30 H, CH ₂ of Cy]	
3d	7.60–7.20 [m, 15 H, Ph], 2.83 [m, 3 H, CH of Pr ⁱ], 1.47 [m, 18 H, CH ₃ of Pr ⁱ]	236.6 [s, MoCO], 196.7 [s, ReCO], 134.3 [d(15), CH of Ph], 132.7 [d(41), ipso-C of Ph], 130.5 [s, CH of Ph], 128.8 [d(10), CH of Ph], 84.9 [d(48), S ₂ CP], 23.2 [d(43), CH of Pr ⁱ], 17.8 [d(2), CH ₃ of Pr ⁱ]
6a	7.68–7.44 [m, 15 H, Ph], 3.53 [m, 3 H, CH and H syn of allyl], 2.52 [m, 3 H, CH of Cy], 2.11–1.28 [m, 32 H, CH ₂ of Cy and H anti of allyl]	234.7 [s, Mo ⁰ CO], 234.5 [s, Mo ^I CO], 134.6 [d(15), CH of Ph], 133.3 [d(43), ipso-C of Ph], 130.9 [s, CH of Ph], 129.1 [d(10), CH of Ph], 83.2 [s, CH of allyl], 80.1 [d(50), S ₂ CP], 48.1 [s, CH ₂ of allyl], 34.2 [d(42), CH of Cy], 27.9 [d(3), CH of Cy], 27.2 [d(12), CH ₂ of Cy], 26.0 [s, CH ₂ of Cy]
6b	7.61–7.48 [m, 15 H, Ph], 2.62 [m, 3 H, CH of Cy], 2.06–1.27 [m, 30 H, CH ₂ of Cy]	237.5 [s, Mo ⁰ CO], 227.3 [s, Mo ^I CO], 134.3 [d(15), CH of Ph], 132.2 [d(40), ipso-C of Ph], 130.6 [s, CH of Ph], 128.9 [d(10), CH of Ph], 102.3 [d(43), S ₂ CP], 33.6 [d(42), CH of Cy], 27.5 [s, CH ₂ of Cy], 26.8 [d(12), CH ₂ of Cy], 25.5 [s, CH ₂ of Cy]
6c	7.68–7.44 [m, 15 H, Ph], 3.58 [m, 3 H, CH and H syn of allyl], 2.48 [m, 3 H, CH of Cy], 2.08–1.28 [m, 32 H, CH ₂ of Cy and H anti of allyl]	233.1 [s, MoCO], 227.4 [s, WCO], 134.7 [d(15), CH of Ph], 133.4 [d(43), ipso-C of Ph], 130.9 [s, CH of Ph], 129.1 [d(11), CH of Ph], 81.8 [s, CH of allyl], 76.5 [d(49), S ₂ CP], 48.0 [s, CH ₂ of allyl], 34.1 [d(42), CH of Cy], 28.1 [s, CH ₂ of Cy], 27.1 [d(12), CH ₂ of Cy], 26.0 [s, CH ₂ of Cy]
6d	7.62–7.44 [m, 15 H, Ph], 2.55 [m, 3 H, CH of Cy], 2.08–1.28 [m, 30 H, CH ₂ of Cy]	230.6 [s, WCO], 226.1 [s, MoCO], 134.3 [d(16), CH of Ph], 132.1 [d(40), ipso-C of Ph], 130.6 [s, CH of Ph], 128.9 [d(10), CH of Ph], 90.6 [d(48), S ₂ CP], 33.6 [d(42), CH of Cy], 27.6 [s, CH ₂ of Cy], 26.7 [d(11), CH ₂ of Cy], 25.5 [s, CH ₂ of Cy]

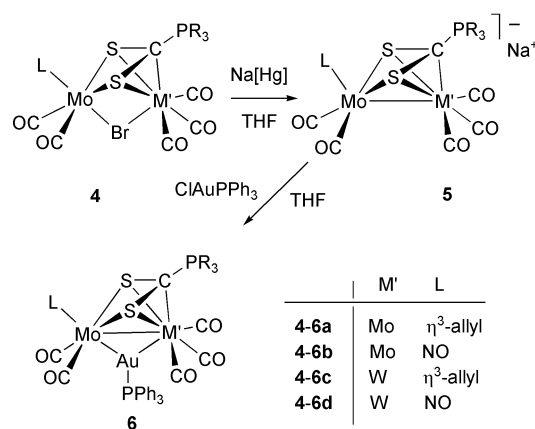
^a In CDCl_3 except **6a**, **6b** and **6c**, which were measured in CD_2Cl_2 . Coupling constants in parentheses are in Hz. ^b The signal for the central carbon of the S_2CPCy_3 ligand was not observed due to the low solubility of **3a**. ^c Owing to the limited solubility of **3b** and **3c**, we were unable to obtain informative ^{13}C NMR spectra for them.

preference of the central carbon of the S_2CPCy_3 ligand in **3a** to bind to Mo instead of Mn agrees with the orbital overlap argument,¹³ and with previous findings in this field.¹⁴

Synthesis and characterization of heterotrimetallic gold-bridging clusters $[(\text{L})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{M}'(\text{CO})_3]$, **6a–d**

Binuclear anions $[(\text{L})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)\text{M}'(\text{CO})_3]^-$ ($\text{M}' = \text{Mo}$, $\text{L} = \eta^3\text{-allyl}$, **5a**; $\text{L} = \text{NO}$, **5b**; $\text{M}' = \text{W}$, $\text{L} = \eta^3\text{-allyl}$, **5c**; $\text{L} = \text{NO}$, **5d**), prepared by Na/Hg reduction of complexes $[(\text{L})(\text{OC})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{M}'(\text{CO})_3]$ ($\text{M}' = \text{Mo}$, W ; $\text{L} = \eta^3\text{-allyl}$, NO), reacted with ClAuPPh_3 to afford deep red solutions from which, after workup, the neutral gold-bridging derivatives $[(\text{L})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{M}'(\text{CO})_3]$ ($\text{M}' = \text{Mo}$, $\text{L} = \eta^3\text{-allyl}$, **6a**; $\text{L} = \text{NO}$, **6b**; $\text{M}' = \text{W}$, $\text{L} = \eta^3\text{-allyl}$, **6c**; $\text{L} = \text{NO}$, **6d**) were obtained as red brown crystals in good yields (Scheme 2).

Complexes **6a–d** have been characterized by spectroscopic (Tables 1 and 2) and analytical data (see Experimental section). Crystals of **6a** and **6c** were subjected to X-ray diffraction studies. Perspective drawings can be seen in Fig. 2 and 3, and selected bond distances and angles are collected in Tables 5 and 6.

**Scheme 2**

Compounds **6a** and **6c** are isostructural, and we will refer to the more accurate results obtained for **6a**. The structures resemble those of compound **3a** (Mn,Mo), although with a remarkable difference: the trimetallic triangle is, for **6a** and **6c**, fairly asymmetric, with a short distance indicating

Table 3 Crystal data and refinement details for $[(\text{CO})_3\text{Mn}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]\cdot\text{H}_2\text{O}$ (**3a**), $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$ (**6a**) and $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{W}(\text{CO})_3]$ (**6c**)

	Compound 3a	Compound 6a	Compound 6c
Formula	$\text{C}_{43}\text{H}_{50}\text{O}_7\text{P}_2\text{S}_2\text{AuMnMo}$	$\text{C}_{45}\text{H}_{53}\text{O}_5\text{P}_2\text{S}_2\text{AuMo}_2$	$\text{C}_{45}\text{H}_{53}\text{O}_5\text{P}_2\text{S}_2\text{AuMoW}$
fw	1152.77	1188.78	1267.7
Crystal system, space group	triclinic, $P\bar{1}$ (No. 2)	triclinic, $P\bar{1}$ (No. 2)	triclinic, $P\bar{1}$ (No. 2)
$a/\text{\AA}$	11.491(9)	12.263(1)	12.213(2)
$b/\text{\AA}$	14.175(8)	12.867(1)	12.867(3)
$c/\text{\AA}$	16.125(7)	15.514(1)	15.503(4)
a/deg	69.10(4)	92.63(1)	92.61(9)
β/deg	73.66(6)	111.33(1)	111.38(9)
γ/deg	78.75(6)	91.07(1)	91.13(2)
$V/\text{\AA}^3$	2341(2)	2267.1(3)	2264(8)
Z	2	2	2
T/K	293	295	293
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.63	1.73	1.87
$F(000)$	1144	1176	1224
$\lambda(\text{Mo K}\alpha)/\text{\AA}$	0.71069	0.71073	0.71069
Crystal size/mm; colour	$0.2 \times 0.2 \times 0.15$; yellow	$0.22 \times 0.13 \times 0.1$; brown	$0.4 \times 0.3 \times 0.2$; brown
μ/cm^{-1}	38.30	39.63	62.82
No. of reflections measured	8238	10393	5311
No. of reflections observed, $I \geq 3\sigma(I)$	5037	4657	2911
Function minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
Weighting scheme	Chebyshev polynomial ^a		
No. of parameters	517	514	230
Residuals $R1, R_w$ ^b	0.061, 0.070	0.0349	0.052, 0.059
$wR2$		0.0597	

^a $w = w'[1 - ((|F_o| - |F_c|)/6\sigma(F_o))^2]$; $w' = 1/\sum_r =_1 A_r T_r(X)$, $X = F_o/F_o(\text{max})$, with three coefficients 4.72, 0.80, and 3.27 for the Chebyshev series.

^b $R = \Sigma(|\Delta F|)/\Sigma|F_o|$, $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

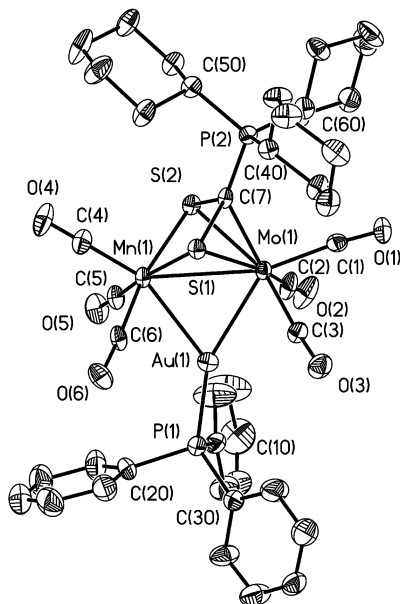


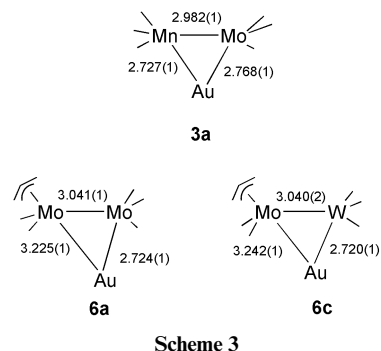
Fig. 1 Perspective view of the molecule of $[(\text{CO})_3\text{Mn}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$ (**3a**) with the atom numbering.

some interaction between the gold atom and one carbonyl ligand.

The geometrical data of the trimetallic core of **3a**, **6a** and **6c** are summarized in Scheme 3. The distance Mo–Mo in **6a** is shorter than in the related complex $[\text{Cp}(\text{OC})_2\text{Mo}(\mu\text{-PPh}_2)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_2\text{Cp}]$,¹⁵ indicating the existence of a direct Mo–Mo bond. While in **3a** the Au atom is approximately equidistant from Mn and Mo, in **6a** and **6c** the distances involving Au (see Scheme 3) differ by more than 0.5 Å, the largest difference between the two metal–gold bond distances in a MM' Au triangle. The Au–M(CO)₃ distances (M = Mo for **6a**, W for **6c**) are similar to those found in other structures with Au–Mo or Au–W bonds. In contrast, the Au atom shifts away from the Mo atom of the Mo(allyl)(CO)₂ fragment, to the limit of the range for a direct Mo–Au or W–Au bond. Therefore, **6a** and **6c** are

Table 4 Selected interatomic distances (Å) and angles (°) in $[(\text{CO})_3\text{Mn}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$ (**3a**)

Au(1)–Mo(1)	2.768(1)	Au(1)–Mn(1)	2.772(2)
Au(1)–P1	2.313(3)	Mo(1)–Mn(1)	2.982(2)
Mo(1)–S(1)	2.501(3)	Mo(1)–S(2)	2.520(2)
Mo(1)–C(1)	1.94(1)	Mo(1)–C(2)	1.92(1)
Mo(1)–C(3)	1.97(1)	Mo(1)–C(7)	2.167(9)
Mn(1)–S(1)	2.316(3)	Mn(1)–S(2)	2.304(3)
Mn(1)–C(5)	1.80(1)	Mn(1)–C(4)	1.80(1)
Mn(1)–C(6)	1.79(1)	S(1)–C(7)	1.770(9)
S(2)–C(7)	1.765(9)	O(1)–C(1)	1.16(1)
O(2)–C(2)	1.18(1)	O(3)–C(3)	1.15(1)
O(4)–C(4)	1.14(1)	O(5)–C(5)	1.14(1)
O(6)–C(6)	1.18(1)		
Mo(1)–Au(1)–Mo(1)	65.13(3)	Mn(1)–Mo(1)–Au(1)	57.50(7)
S(1)–Mo(1)–Au(1)	93.47(6)	S(1)–Mo(1)–Mn(1)	49.01(6)
S(2)–Mo(1)–Au(1)	94.78(6)	S(2)–Mo(1)–Mn(1)	48.62(7)
S(2)–Mo(1)–S(1)	67.85(9)	Mo(1)–Mn(1)–Au(1)	57.36(7)
S(1)–Mn(1)–Au(1)	97.62(8)	S(1)–Mn(1)–Mo(1)	54.60(7)
S(2)–Mn(1)–Au(1)	99.82(8)	S(2)–Mn(1)–Mo(1)	55.17(7)
S(2)–Mn(1)–S(1)	74.7(1)	S(1)–C(7)–S(2)	104.7(4)



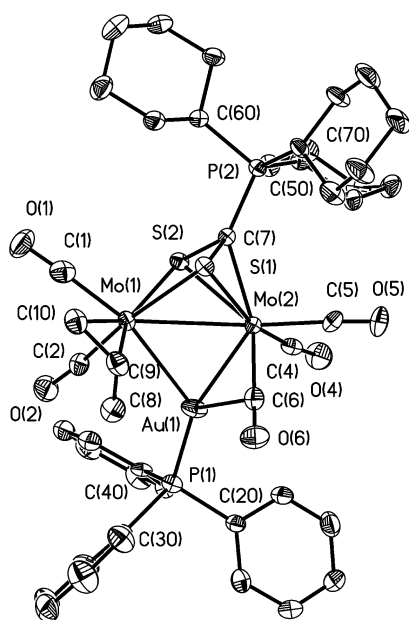
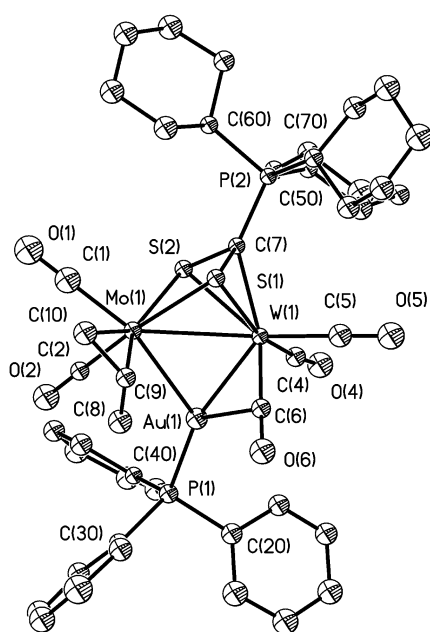
Scheme 3

intermediates between symmetrical triangular clusters and open angular MM' Au chains.

The Mn/Mo complexes exhibit virtually eclipsed CO groups (see Fig. 4). In contrast, whereas in **1a**, **3a** and **4a**, the bridge, either Br or Au, lies in the pseudo plane of symmetry defined by the two metals and the central carbon of S₂CPR₃ (see Fig. 4), in

Table 5 Selected interatomic distances (Å) and angles (°) in $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$ (**6a**)

Mo(1)–Mo(2)	3.041(1)	Au(1)–Mo(1)	3.225(1)
Au(1)–P(1)	2.291(1)	Au(1)–Mo(2)	2.724(1)
Mo(1)–S(1)	2.447(1)	Mo(1)–S(2)	2.536(1)
Mo(2)–S(1)	2.498(1)	Mo(2)–S(2)	2.545(1)
Mo(1)–C(1)	1.912(8)	Mo(1)–C(2)	1.946(7)
Mo(2)–C(4)	1.958(7)	Mo(2)–C(5)	1.972(8)
Mo(2)–C(6)	1.994(8)	Mo(2)–C(7)	2.194(6)
Mo(1)–C(8)	2.402(6)	Mo(1)–C(9)	2.243(6)
Mo(1)–C(10)	2.328(6)	S(1)–C(7)	1.774(6)
S(2)–C(7)	1.759(6)	P(2)–C(7)	1.791(6)
Mo(1)–Au(1)–Mo(2)	60.794(16)	S(1)–Mo(1)–S(2)	69.49(5)
S(2)–Mo(1)–Au(1)	104.07(4)	Mo(2)–Mo(1)–Au(1)	51.440(14)
S(1)–Mo(1)–Mo(2)	52.80(4)	S(2)–Mo(1)–Mo(2)	53.38(4)
S(1)–Mo(1)–Au(1)	74.77(4)	Au(1)–Mo(2)–Mo(1)	67.766(18)
S(1)–Mo(2)–S(2)	68.57(5)	S(1)–Mo(2)–Au(1)	84.02(4)
S(2)–Mo(2)–Au(1)	119.88(4)	S(1)–Mo(2)–Mo(1)	51.30(4)
S(2)–Mo(2)–Mo(1)	53.10(4)	S(2)–C(7)–S(1)	107.1(3)

**Fig. 2** Perspective view of the molecule of $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{Mo}(\text{CO})_3]$ (**6a**) with the atom numbering.**Fig. 3** Perspective view of the molecule of $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{W}(\text{CO})_3]$ (**6c**) with the atom numbering.**Table 6** Selected interatomic distances (Å) and angles (°) in $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{W}(\text{CO})_3]$ (**6c**)

Au(1)–W(1)	2.720(1)	Au(1)–Mo(1)	3.242(2)
Au(1)–P(1)	2.307(6)	W(1)–Mo(1)	3.040(2)
W(1)–S(2)	2.497(6)	W(1)–S(1)	2.538(6)
Mo(1)–S(2)	2.441(6)	Mo(1)–S(1)	2.539(6)
Mo(1)–C(1)	1.90(3)	Mo(1)–C(2)	1.94(2)
W(1)–C(4)	1.96(2)	W(1)–C(5)	1.92(3)
W(1)–C(6)	1.91(2)	W(1)–C(7)	2.18(2)
Mo(1)–C(8)	2.36(3)	Mo(1)–C(9)	2.25(2)
Mo(1)–C(10)	2.35(3)	S(2)–C(7)	1.77(2)
S(1)–C(7)	1.80(2)	P(2)–C(7)	1.77(2)
W(1)–Au(1)–Mo(1)	60.57(5)	Au(1)–W(1)–Mo(1)	68.23(5)
Au(1)–Mo(1)–W(1)	51.19(4)	Au(1)–Mo(1)–S(2)	74.5(1)
Au(1)–W(1)–S(2)	84.2(1)	Mo(1)–W(1)–S(2)	51.2(1)
Au(1)–W(1)–S(1)	120.5(1)	Mo(1)–W(1)–S(1)	53.2(1)
S(2)–W(1)–S(1)	68.6(2)	Au(1)–W(1)–C(4)	69.0(7)
Au(1)–Mo(1)–W(1)	51.19(4)	Au(1)–Mo(1)–S(2)	74.5(1)
W(1)–Mo(1)–S(2)	52.8(1)	Au(1)–Mo(1)–S(1)	103.7(1)
W(1)–Mo(1)–S(1)	53.2(1)	S(2)–Mo(1)–S(1)	69.5(2)
S(2)–C(7)–S(1)	105.1(11)	C(8)–C(9)–C(10)	122.1(24)

6a and **6c**, the Au atom is away from that plane by $33.5(8)^\circ$ as shown in Fig. 4(d). Additionally, the three carbonyl ligands are rotated from the “eclipsed” dispositions which occur in **1a**, **3a** and **4a**. As a consequence, the distances Au–C(6) 2.687(7) Å for **6a** and 2.684(9) Å for **6c** indicate some degree of Au–CO interaction. Both C(6)–O(6) groups can be described as semi-bridging according to the criterion of Curtis *et al.*¹⁶ The asymmetry parameters *a* are 0.34 for **6a** and 0.41 for **6c**, well within the range $0.1 < a < 0.6$. A short Au–C(carbonyl) distance in other transition metal–gold carbonyl clusters^{2b,3a,5a} has often been attributed to packing forces or the steric pressure of the bulky AuPPh₃ fragment.^{2b} Some theoretical analyses have been quoted to indicate a lack of bonding interaction although a full account of such results has not been delivered.¹⁷ In some cases, a slight displacement of the carbonyls away from the gold atom has been observed.^{3h} However, when comparing the structures depicted in Fig. 1–3, it can be seen that the carbonyl group moves towards the Au atom, and this results in a rotation and reorientation of the pyramidal M(CO)₃ fragment which comes closer to AuPPh₃: in **3a** the angle formed by the effective C₃ axis of the Mo(CO)₃ fragment and the Mn(1)–Mo(1) bond is 144.8° , while the corresponding angle in **6a** is 135.9° . Thus the M(CO)₃ fragment turns 8.9° inward (with respect to the Mn–Mo, or Mo–Mo bond) approaching AuPPh₃. This means that the short Au–C(6) distance results from the approaching of the Au atom, which shifts away from the Mo(CO)₂(allyl) fragment, and the carbonyl, which turns inward to meet the Au atom. Thus, the highly asymmetric bridging of the AuPPh₃ ligand is presumably caused by electronic factors rather than steric hindrance or packing forces.

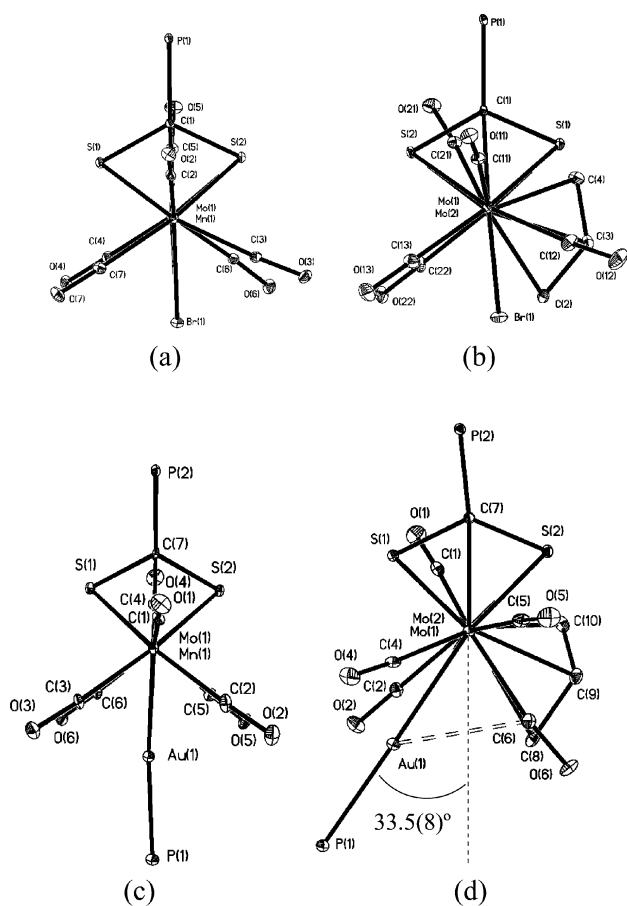
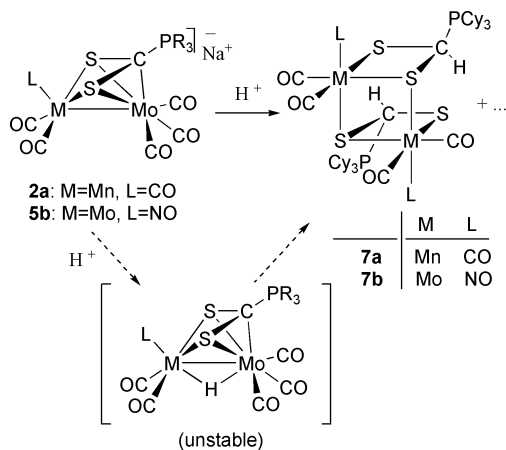


Fig. 4 Perspective views of the molecules down the M–M bond showing the relative dispositions of the carbonyl ligands and the bridging Br or AuPPh₃. (a) [(CO)₃Mn(μ-S₂CPCy₃)(μ-Br)Mo(CO)₃] (**1a**). (b) [(η³-C₃H₅)(CO)₂Mo(μ-S₂CPCy₃)(μ-Br)Mo(CO)₃] (**4a**). (c) [(CO)₃Mn(μ-S₂CPCy₃)(μ-AuPPh₃)Mo(CO)₃] (**3a**). (d) [(η³-C₃H₅)(CO)₂Mo(μ-S₂CPCy₃)(μ-AuPPh₃)Mo(CO)₃] (**6a**).

Attempts to prepare hydrido-bridging binuclear complexes

The interesting reactivity pattern displayed by S₂CPR₃-bridged binuclear complexes (Mn–Mn and Mn–Re) towards hydride addition¹⁸ prompted us to investigate the preparation of hydrogen-bridging binuclear complexes of other metals. Unexpectedly, the reaction of [(L)(OC)₂M(μ-Br)(μ-S₂CPCy₃)Mo(CO)₃] (M = Mn, L = CO, **1a**; M = Mo, L = NO, **4b**) with LiBHET₃ or NaBH₄, or of anionic species [(L)(OC)₂M(μ-S₂CPCy₃)Mo(CO)₃][−] (M = Mn, L = CO, **2a**; M = Mo, L = NO, **5b**) with NH₄PF₆, both at low temperature, gave only the previously known cubic dimer complexes [M₂(CO)₄(L)₂{S₂μ-S'C(H)PCy₃}₂] (M = Mn, L = CO, **7a**; M = Mo, L = NO, **7b**) (Scheme 4), in



Scheme 4

which the hydrogen atom is attached to the central carbon of the S₂CPCy₃ ligand rather than to the metals.¹⁹

Given the isolobal relationship H ↔ AuPR₃,^{3b,f,4a} the isolation of the gold-bridging complexes **3** and **6** suggest that the formation of **7a** and **7b** could proceed through initial protonation (for anions) or hydride addition (for neutral complexes) of the metal centers to form an unstable hydrogen-bridging binuclear intermediate which isomerizes, by hydride transfer to the central carbon of the S₂CPCy₃ ligand, to the observed complexes **7a** and **7b** and some unknown molybdenum species. The products **3** and **6** showed no tendency for such an isomerization even when refluxed in toluene for several hours, which might be explained by the large bulk of the AuPPh₃ ligand. A similar explanation for the transfer of the bridging hydrogen to an adjacent ligand has been proposed by Haupt and co-workers for the generation of [Re₂(CO)₈(μ-PCyH)][−] from [Re₂(CO)₈(μ-H)(μ-PCy)][−].^{3g} This proposition is also supported by the fact that the reaction of the analogous complexes [(OC)₃Mn(μ-S₂CPCy₃)M(CO)₃] (M = Mn, Re) with LiBHET₃ gave hydrogen-bridging binuclear anionic complexes.²⁰

Experimental

General comments

All manipulations were carried out under dinitrogen using Schlenk techniques. Solvents were freshly distilled by standard methods before use. Chromatography employed alumina (activity I, 2 × 15 cm column). ClAuPPh₃²¹ and complexes [(OC)₃M(μ-Br)(μ-S₂CPR₃)Mo(CO)₃] (M = Mn, R = Cy, **1a**; R = Prⁱ, **1b**; M = Re, R = Cy, **1c**; R = Prⁱ, **1d**),^{17b,d} [(η³-C₃H₅)(OC)₂Mo(μ-Br)(μ-S₂CPCy₃)M'(CO)₃] (M' = Mo, **4a**; M' = W, **4c**) and [(ON)(OC)₂Mo(μ-Br)(μ-S₂CPCy₃)M'(CO)₃] (M' = Mo, **4b**; M' = W, **4d**) were prepared by published procedures.^{10,20} The solutions of anions [(OC)₃M(μ-S₂CPR₃)Mo(CO)₃][−] (M = Mn, R = Cy, **2a**; R = Prⁱ, **2b**; M = Re, R = Cy, **2c**; R = Prⁱ, **2d**) were prepared prior to use as in our previous description.^{9b}

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker AC-300 instrument. Elemental analyses were performed on a Perkin-Elmer 240B microanalyser.

Synthesis of [(OC)₃M(μ-S₂CPR₃)(μ-AuPPh₃)Mo(CO)₃] (M = Mn, R = Cy, **3a**; R = Prⁱ, **3b**; M = Re, R = Cy, **3c**; R = Prⁱ, **3d**)

Essentially the same procedures were followed for the syntheses of **3a–3d**, and only the preparation of **3a** will be described. To a THF solution (10 ml) of the anion **2a** (ca. 0.20 mmol) was added ClAuPPh₃ (0.100 g, 0.20 mmol). The color changed instantaneously to red, and IR monitoring showed complete reaction. Solvent was evaporated *in vacuo*, and the red residue was extracted with a minimum amount of CH₂Cl₂ and chromatographed through an alumina column. The filtrate was concentrated to ca. 5 mL, and then hexane (10 mL) was added. Slow diffusion of the solvents at room temperature gave red crystals of **3a**. Yield 0.17 g, 75%. Anal. Calcd. for C₄₃H₄₈AuMnMoO₆S₂P₂: C, 45.50; H, 4.23. Found: C, 45.21; H, 4.09%.

The derivatives (**3b–3d**) were prepared from **2b**, **2c** and **2d** (ca. 0.20 mmol) respectively.

3b. Yield 0.17 g, 84%. Anal. Calcd. for C₃₄H₃₆AuMnMoO₆P₂S₂: C, 40.25; H, 3.57. Found: C, 40.09; H, 3.49%.

3c. Yield 0.207 g, 82%. Anal. Calcd. for C₄₃H₄₈AuMoO₆P₂S₂Re: C, 40.79; H, 3.82. Found: C, 40.98; H, 3.79%.

3d. Yield 0.198 g, 86%. Anal. Calcd. for C₃₄H₃₆AuMoO₆P₂S₂Re: C, 35.64; H, 3.38. Found: C, 35.56; H, 3.16%.

Synthesis of $[(\eta^3\text{-C}_3\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{-M}'(\text{CO})_3]$ ($\text{M}' = \text{Mo}$, **6a**; $\text{M}' = \text{W}$, **6c**)

A THF solution (20 ml) of **4a** (0.202 g, 0.25 mmol) was stirred at room temperature with an excess of 1% Na/Hg until the IR monitoring showed only the bands of anion **5a** (25–30 min). The mixture was allowed to settle, and the supernatant was transferred with a cannula filter to another Schlenk bottle. ClAuPPh_3 (0.124 g, 0.25 mmol) was added to the THF solution of **5a**, and the mixture was stirred for 15 min. Solvent was removed *in vacuo* and the residue was chromatographed through an alumina column. Red brown crystals (**6a**) were isolated in 75% yield (0.223 g) from the brown-reddish band eluted by CH_2Cl_2 after treatment of the filtrate by the procedure applied for **3a**. Anion **5a**, $[(\eta^3\text{-C}_3\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)\text{-Mo}(\text{CO})_3]^-$: IR (THF): $\nu(\text{CO})$ 1916m, 1894vs, 1819m, 1787s, 1745m cm^{-1} . Complex **6a**: Anal. Calcd. for $\text{C}_{45}\text{H}_{53}\text{AuO}_5\text{P}_2\text{-S}_2\text{Mo}_2$: C, 45.45; H, 4.46. Found: C, 45.39; H, 4.47%.

Anion **5c** and complex **6c** were prepared by following the procedure given for **5a** and **6a**, using **4c** (0.225 mg, 0.25 mmol). Anion **5c**, $[(\eta^3\text{-C}_3\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)\text{W}(\text{CO})_3]^-$: IR (THF): $\nu(\text{CO})$ 1917s, 1886vs, 1824s, 1782s, 1737m cm^{-1} . Red brown crystals (**6c**) were isolated in 78% yield (0.249 mg). Anal. Calcd. for $\text{C}_{45}\text{H}_{53}\text{AuMoO}_5\text{P}_2\text{S}_2\text{W}$: C, 42.32; H, 4.19. Found: C, 42.21; H, 4.25%.

X-Ray diffraction studies

Compounds 3a and 6c. Suitable crystals were grown by slow diffusion of hexane into a concentrated solution of the complex in THF at -20°C , and measured on a Nonius CAD 4 diffractometer. Relevant crystallographic data are given in Table 3. The structures were solved by direct methods with SHELXS 86²² and subsequent Fourier maps. Least squares refinement were made with CRYSTALS.²³ An absorption correction was made with DIFABS.²⁴ Non-hydrogen atoms were anisotropically refined for **3a**. After refinement a peak was found to correspond to a molecule of adventitious water placed near the inversion center, being hydrogen-bonded to its symmetry related counterpart (distance O–O = 2.82 Å). Due to the low number of reflections, the refinement for **6c** had to be kept isotropic. In both cases hydrogen atoms were geometrically positioned with a common isotropic temperature factor, which was refined.

Compound 6a. A suitable crystal was grown by diffusion of hexane into a concentrated solution of THF at -30°C , and was measured on a Bruker AXS SMART 1000 CCD diffractometer. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6^\circ$. Raw frame data were integrated with the SAINT²⁵ program. Relevant data are given in Table 3. The structure was solved by direct methods with SHELXTL.²⁶ A semi-empirical absorption correction was applied with the program SADABS.²⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Thermal ellipsoid plots in Fig. 1, 2 and 3 were made with XP of SHELXTL.

CCDC reference numbers 195126 (**3a**), 195127 (**6a**) and 195128 (**6c**).

See <http://www.rsc.org/suppdata/dt/b2/b209842c/> for crystallographic data in CIF or other electronic format.

Synthesis of $[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)(\mu\text{-AuPPh}_3)\text{M}'(\text{CO})_3]$ ($\text{M}' = \text{Mo}$, **6b**; $\text{M}' = \text{W}$, **6d**)

A solution of **4b** (0.200 g, 0.25 mmol) in THF (15 ml) was stirred with an excess of 1% Na/Hg at -40°C until IR monitoring showed no presence of the $\nu(\text{CO})$ and $\nu(\text{NO})$ bands of **4b**. With strong stirring the reaction took 5–10 min and the solution changed from brown to deep red (with longer stirring time, even at low temperature, the unstable anion **5b**

decomposed). The supernatant solution was then transferred with cannula to another Schlenk flask containing a pre-cooled (-60°C) solution of ClAuPPh_3 (0.124 g, 0.25 mmol) in THF (5 ml). The mixture was stirred at low temperature for 10 min, allowed to reach room temperature and, when the IR monitoring showed complete reaction (*ca.* 20 min), the solvent was evaporated to dryness *in vacuo*. The red brown residue was extracted with a minimum amount of CH_2Cl_2 and chromatographed through an alumina column. The collected red brown solution was concentrated to *ca.* 10 mL and hexane (10 ml) was added. Slow diffusion at -20°C gave **6b** as red brown crystals in 62% yield (0.195 g). Anion **5b**, $[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]^-$: IR (THF): $\nu(\text{CO})$ 1987s, 1894vs, 1803s, 1753m cm^{-1} ; $\nu(\text{NO})$ 1611s cm^{-1} . Complex **6b**: Anal. Calcd. for $\text{C}_{42}\text{H}_{48}\text{AuMo}_2\text{NO}_6\text{P}_2\text{S}_2\text{-CH}_2\text{Cl}_2$: C, 40.89; H, 3.96; N, 1.11. Found: C, 40.68; H, 3.93; N, 1.16%.

Anion **5d** and complex **6d** were prepared *via* the same procedure as described above for **5b** and **6b**, using **4d** (0.222 g, 0.25 mmol). Anion **5d**, $[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-S}_2\text{CPCy}_3)\text{W}(\text{CO})_3]^-$: IR (THF): $\nu(\text{CO})$ 1989s, 1908s, 1887vs, 1797s, 1747s cm^{-1} ; $\nu(\text{NO})$ 1612s cm^{-1} . Complex **6d** was isolated in 68% yield (0.230 g). Anal. Calcd. for $\text{C}_{42}\text{H}_{48}\text{AuMoNO}_6\text{P}_2\text{S}_2\text{W-CH}_2\text{Cl}_2$: C, 38.22; H, 3.70; N, 1.04. Found: C, 38.16; H, 3.71; N, 1.08%.

Reactions of $[(\text{L})(\text{OC})_2\text{M}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$ with hydride reagents

To a solution of $[(\text{ON})(\text{OC})_2\text{Mo}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$ (0.400 g, 0.5 mmol) in THF (20 ml) at 0°C was added either LiBHET_3 (0.6 ml, 0.6 mmol, 1 M in THF) or solid NaBH_4 (0.038 g, 1.0 mmol). The mixture was stirred at low temperature until IR monitoring showed complete reaction. The solvent was evaporated *in vacuo*, the residue was redissolved in CH_2Cl_2 and chromatographed through alumina with CH_2Cl_2 as eluent. Hexane (10 ml) was added to the collected solution. By slow concentration, complex **7b** was obtained as orange crystalline solid in 48–52% yield (0.270 g). Anal. Calcd. for $\text{C}_{42}\text{H}_{68}\text{Mo}_2\text{N}_2\text{O}_6\text{P}_2\text{S}_4$: C, 46.75; H, 6.35; N, 2.60. Found: C, 46.79; H, 6.41; N, 2.47%.

The reactions of $[(\text{OC})_3\text{Mn}(\mu\text{-Br})(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]$ (0.400 g, 0.53 mmol) with LiBHET_3 (0.65 ml, 0.65 mmol) were as described for **7b**. Complex **7a** was obtained in 45% yield (0.236 g). Anal. Calcd. for $\text{C}_{44}\text{H}_{68}\text{Mn}_2\text{O}_6\text{P}_2\text{S}_4$: C, 53.22; H, 6.90. Found: C, 53.05; H, 6.77%.

Reactions of $[(\text{L})(\text{OC})_2\text{M}(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]^-$ with NH_4PF_6

To a solution of $[(\text{L})(\text{OC})_2\text{M}(\mu\text{-S}_2\text{CPCy}_3)\text{Mo}(\text{CO})_3]^-$ ($\text{M} = \text{Mn}$, $\text{L} = \text{CO}$, **2a**; $\text{M} = \text{Mo}$, $\text{L} = \text{NO}$, **5b**) (*ca.* 0.25 mmol) in THF (15 ml) at 0°C was added NH_4PF_6 (0.050 g, 0.3 mmol). Workup was as described for **7b**. The complexes **7a** and **7b** obtained by this method have correct C, H, N analyses.

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