Facile Deprotonation of the Hydrogensulfido Ligand in $[Mn_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(\text{diphosphine})]$ Complexes *

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The unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L\text{–}L)]$ [L–L = $Ph_2PCH_2PPh_2$ (dppm) **1**; or $(EtO)_2POP(OEt)_2$ (tedip) **2**] react with sulfur to yield the hydrogensulfido complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm **3a**; or tedip **3b**). The hydrogen bound to the sulfur atom in **3a** is easily removed by thallium(I) acetylacetonate, generating a species which affords, upon reaction with the appropriate electrophiles, the thiolato complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}SZ)(CO)_6(\mu\text{-dppm})]$ (Z = Me **3c**, $SnMe_3$ **3d**, or $AuPPh_3$ **3e**). The solid-state structure of **3e** has been determined by X-ray methods [monoclinic, space group $P2_1/n$, a = 18.840(4), b = 13.024(2), c = 20.243(4) Å, β = 108.66(2)°, Z = 4].

Hydrogensulfido complexes (M–SH) have received much attention due to the fact that they are assumed to be involved in the formation of metal sulfides in aqueous solution, hydrodesulfurization of petroleum feedstocks and in several biological processes. In particular, the reactivity of the hydrogensulfido group SH has been intensively studied,[1] mainly because proton transfer from it to the organic substrate seems to be a key step in the hydrodesulfurization of organosulfur compounds on metal sulfide surfaces.

We report here the synthesis of binuclear hydrogensulfido complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(\mu\text{-}L\text{–}L)]$ [L–L = $Ph_2PCH_2PPh_2$ (dppm) **3a**; or $(EtO)_2POP(OEt)_2$ (tedip) **3b**], and subsequent easy deprotonation of **3a** with thallium(I) acetylacetonate as the first step in the substitution of the SH hydrogen atom by other groups isolobal with it. The preparation of **3a** has been previously published.[2a]

Results and Discussion

The unsaturated manganese dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L\text{–}L)]$ (L–L = dppm **1**; or tedip **2**)[2] react with S to give the hydrogensulfido complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(\mu\text{-}L\text{–}L)]$ **3a** and **3b** [(*i*) in Scheme 1]. They are obtained as a mixture of two isomers, *syn* and *anti*, which do not interconvert on the NMR time-scale, as their spectroscopic data reveal (Table 1). The presence of two triplets at δ −0.8 and −2.3 for **3a** and at δ −1.3 and −2.4 for **3b** in their ^1H NMR spectra suggests the existence of two different SH groups, which should correspond to the two possible positions of the SH hydrogen atom relative to the diphosphine bridge, either on the same (*syn*) or in the opposite side (*anti*) of the plane defined by the Mn_2S triangle.[3] Moreover, the J[P–H(S)] coupling constants indicate that the predominant species should be the *anti* isomers, which is in agreement with predictions made on steric grounds. The J[P–H(S)] constants are greater for the major than for the minor isomers (20 *versus* 15 for **3a** and 22 *versus* 17 Hz for **3b**), and in accordance with the Karplus-type relationship the coupling constants should be greater for the *anti* (torsion angle close to 150°) than for the *syn* isomer (torsion angle close to 30°). The existence of two isomers is also reflected in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3a**, which shows two peaks at δ 56.6 and 49.1; however the spectrum of **3b** shows only a single broad peak at δ 161.9, thus precluding the observation of the individual resonances.

The insertion of sulfur into a metal–hydrogen bond to yield hydrogensulfido complexes is usually accomplished by the addition of ethylene or propylene sulfide to the appropriate hydride;[4] however, the formation of hydrogensulfides by reaction of hydrido complexes with elemental sulfur is uncommon and few examples have been reported.[1d,f]

The hydrogen attached to the sulfur atom in complex **3a** should keep some acidic character and, in fact, it can be easily removed with thallium(I) acetylacetonate [(*ii*) in Scheme 1]. The resulting unstable orange species, which is soluble in toluene, could not be isolated but its infrared spectrum in solution in the ν(CO) region (2015s, 1988vs, 1935m and 1905vs cm^{-1}) shows a pattern closely related to that of the parent complex **3a**, but shifted to lower wavenumbers, therefore suggesting that it could be $[Mn_2(\mu\text{-}H)(\mu\text{-}STl)(CO)_6(\mu\text{-dppm})]$. In any case, this species reacts with electrophiles such as MeI [(*iii*) in Scheme 1], $SnMe_3Cl$ [(*iv*) in Scheme 1] and $[AuCl(PPh_3)]$ [(*v*) in Scheme 1] to yield the corresponding $[Mn_2(\mu\text{-}H)(\mu\text{-}SZ)(CO)_6(\mu\text{-dppm})]$ (Z = Me **3c**, $SnMe_3$ **3d** or $AuPPh_3$ **3e**). The proposed structures for these complexes are supported by their spectroscopic data (see Table 1).

The structure of complex **3e** has been further confirmed by an X-ray diffraction study, and it is shown in Fig. 1. The separation between the manganese atoms is 2.919(3) Å, 0.22 Å longer than that found in the unsaturated parent compound **1**,[2a] but inside the range of Mn–Mn single bond distances[5] (see Table 3). The manganese and the sulfur atoms display distorted octahedral and tetrahedral environments respectively, the Mn–S–Mn angle of 76.1(1)° being widely different from a regular tetrahedral angle (109°). The ligand $SAuPPh_3$ is almost linear (S–Au–P 174.2(1)°], symmetrically bound to both metal centres [Mn(1)–S 2.368(4), Mn(2)–S 2.369(5) Å] and located, with regard to the diphosphine bridge, on the other side of the plane defined by the metal centres and the sulfur atom (see Fig. 2), corresponding, therefore, to the *anti* isomer, which could have been anticipated on steric grounds.

Experimental

All reactions were carried out under a nitrogen atmosphere. Light petroleum refers to that fraction distilling in the range 60–65 °C. The reagents were purchased from Aldrich and used

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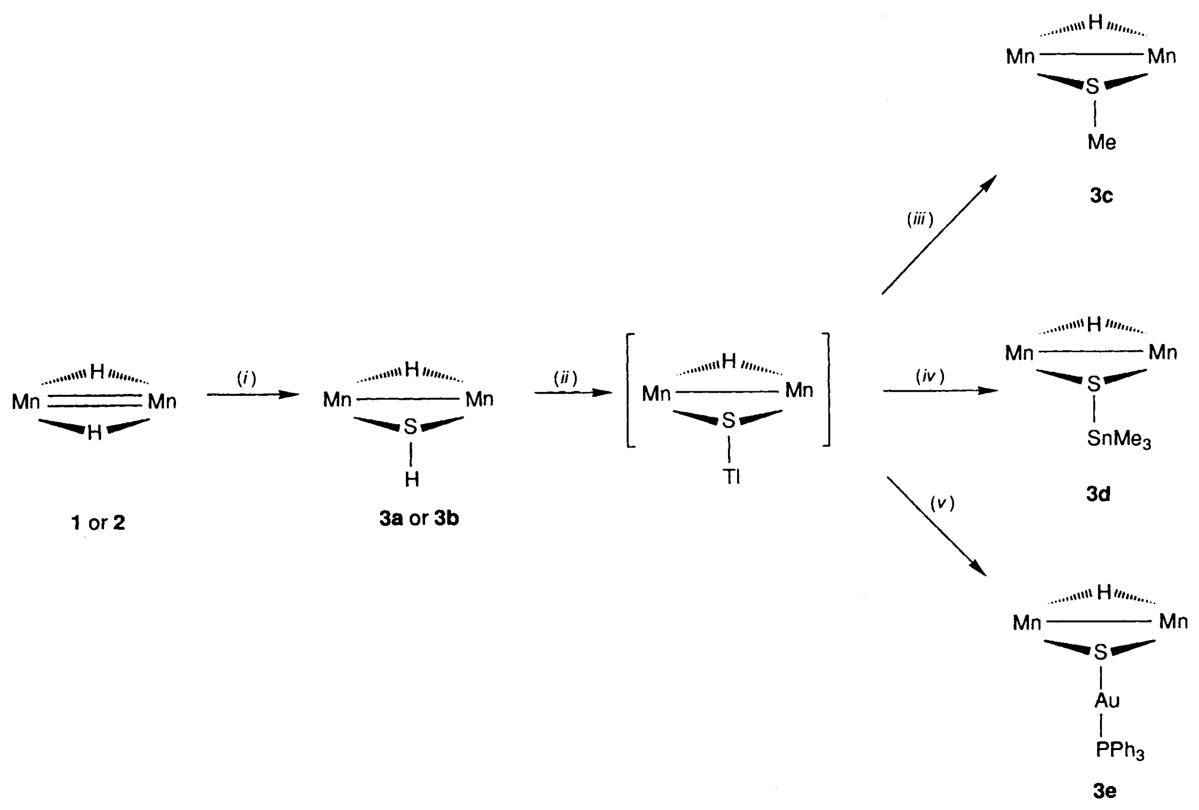
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) S_8; (*ii*) Tl(acac); (*iii*) MeI; (*iv*) $SnMe_3Cl$; (*v*) $[AuCl(PPh_3)]$

Table 1 Spectroscopic data for new complexes

Compound	ν(CO)[a]/cm^{-1}	^{1}H NMR[b] (δ)	^{31}P-{^{1}H} NMR[b] (δ)
3a	2032s	7.5–6.9 (m, 4 Ph)	56.5 (major)
	2002s	2.9 (m), 2.7 (m) (CH_2)	49.1 (minor)
	1954m	−0.8 [t, *J*(PH) = 20, SH] (major)	
	1934 (sh)	−2.3 [t, *J*(PH) = 15, SH] (minor)	
	1920vs	−15.3 [t, *J*(PH) = 21, Mn–H–Mn]	
3b	2047s	4.1 (m, CH_2)	161.9 (br)
	2015s	3.9 (m, 2 CH_2)	
	1975m	3.8 (m, CH_2)	
	1955 (sh)	1.3 [t, *J*(HH) = 7, 2 CH_3]	
	1935vs	1.2 [t, *J*(HH) = 7, 2 CH_3]	
		−1.3 [t, *J*(PH) = 22, SH] (major)	
		−2.4 [t, *J*(PH) = 17, SH] (minor)	
		−15.5 [t, *J*(PH) = 26, Mn–H–Mn]	
3c	2022s	7.5–7.0 (m, 4 Ph)	47.8
	2003s	3.1 (m), 2.6 (m) (CH_2)	
	1957m	1.2 (s, CH_3)	
	1936 (sh)	−14.4 [t, *J*(PH) = 18, Mn–H–Mn]	
	1920vs		
3d	2023s	7.8–6.9 (m, 4 Ph)	47.3
	1996s	3.1 (m), 2.7 (m) (CH_2)	
	1944m	0.9 [s, $Sn(CH_3)_3$]	
	1915vs	−14.4 [t, *J*(PH) = 17, Mn–H–Mn]	
3e	2015s	7.6–7.0 (m, 7 Ph)	52.5 (dppm)
	1987s	2.9 (m), 2.2 (m) (CH_2)	34.9 (Au–PPh_3)
	1934m	−14.5 [t, *J*(PH) = 22, Mn–H–Mn]	
	1917 (sh)		
	1904s		

[a] In toluene. [b] In $CDCl_3$, at room temperature, *J* in Hz.

as received. The compound $[AuCl(PPh_3)]$ was prepared according to a literature procedure.[6] Infrared spectra were recorded on a Perkin-Elmer 1720-X Fourier-transform spectrometer, proton and phosphorus-31 NMR spectra on a Bruker AC-300 instrument. Elemental C and H analyses were obtained with a Perkin-Elmer 240B microanalyser.

Preparation of $[Mn_2(\mu\text{-H})(\mu\text{-SH})(CO)_6(\mu\text{-L–L})]$ (L–L = dppm **3a**; *or* tedip **3b**).—To a solution of $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})]\cdot C_6H_5Me$ **1** or $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-tedip})]$ **2** (0.133 mmol) in toluene (20 cm^3) was added elemental sulfur (0.005 g, 0.156 mmol). The solution changed from red-purple to yellow instantaneously or after 2 h respectively. Afterwards the mixture

Table 2 Fractional positional parameters (with estimated standard deviations) for complex **3e**

Atom	*x*	*y*	*z*
Au	0.2350(1)	0.0243(1)	0.0292(1)
Mn(1)	0.2846(1)	−0.2595(2)	0.0247(1)
Mn(2)	0.4174(1)	−0.1290(2)	0.0590(1)
P(1)	0.1526(2)	0.1430(3)	−0.0330(2)
P(2)	0.4699(2)	−0.2180(3)	0.1622(2)
P(3)	0.3251(2)	−0.3448(3)	0.1332(2)
S	0.3083(2)	−0.1067(3)	0.0916(2)
C(1)	0.4011(7)	−0.2744(9)	0.1979(6)
O(10)	0.2211(7)	−0.162(1)	−0.1136(6)
O(11)	0.1275(6)	−0.304(1)	0.0111(6)
O(12)	0.3017(7)	−0.433(1)	−0.0609(7)
O(20)	0.3609(7)	−0.024(1)	−0.0771(7)
O(21)	0.4791(7)	0.0662(9)	0.1255(7)
O(22)	0.5480(6)	−0.1836(9)	0.0161(6)
C(10)	0.2479(9)	−0.196(1)	−0.0577(9)
C(11)	0.1916(9)	−0.286(1)	0.0181(7)
C(12)	0.2950(9)	−0.370(1)	−0.0221(8)
C(20)	0.3797(8)	−0.066(1)	−0.0237(8)
C(21)	0.458(1)	−0.008(1)	0.1005(9)
C(22)	0.4965(8)	−0.165(1)	0.0339(7)
C(31)	0.0614(8)	0.083(1)	−0.0670(7)
C(32)	−0.0036(8)	0.124(1)	−0.0622(9)
C(33)	−0.0699(9)	0.070(2)	−0.088(1)
C(34)	−0.073(1)	−0.022(2)	−0.1185(9)
C(35)	−0.008(1)	−0.064(2)	−0.1253(9)
C(36)	0.0578(9)	−0.012(1)	−0.1003(8)
C(41)	0.1739(7)	0.193(1)	−0.1072(7)
C(42)	0.2478(8)	0.208(1)	−0.1056(9)
C(43)	0.268(1)	0.251(1)	−0.158(1)
C(44)	0.212(1)	0.275(2)	−0.218(1)
C(45)	0.138(1)	0.262(1)	−0.2441(9)
C(46)	0.1176(9)	0.220(1)	−0.1701(8)
C(51)	0.1406(7)	0.255(1)	0.0167(7)
C(52)	0.1673(8)	0.253(1)	0.0885(8)
C(53)	0.1567(9)	0.335(1)	0.1281(9)
C(54)	0.1199(9)	0.421(1)	0.0941(9)
C(55)	0.093(1)	0.424(1)	0.023(1)
C(56)	0.1030(8)	0.343(1)	−0.0157(8)
C(61)	0.2589(7)	−0.356(1)	0.1826(7)
C(62)	0.2572(9)	−0.440(1)	0.2228(7)
C(63)	0.210(1)	−0.447(1)	0.2603(7)
C(64)	0.161(1)	−0.363(2)	0.259(1)
C(65)	0.165(1)	−0.275(1)	0.2228(9)
C(66)	0.2131(8)	−0.273(1)	0.1835(8)
C(71)	0.3566(7)	−0.477(1)	0.1340(7)
C(72)	0.315(1)	−0.544(1)	0.083(1)
C(73)	0.338(1)	−0.643(1)	0.078(1)
C(74)	0.404(1)	−0.678(1)	0.125(1)
C(75)	0.445(1)	−0.616(1)	0.178(1)
C(76)	0.4211(8)	−0.515(1)	0.1830(8)
C(81)	0.5306(7)	−0.328(1)	0.1620(7)
C(82)	0.5829(7)	−0.360(1)	0.2254(7)
C(83)	0.6251(8)	−0.450(1)	0.2262(8)
C(84)	0.616(1)	−0.504(1)	0.1657(9)
C(85)	0.5644(9)	−0.474(1)	0.1049(9)
C(86)	0.5214(8)	−0.385(1)	0.1028(8)
C(91)	0.5289(7)	−0.142(1)	0.2350(7)
C(92)	0.512(1)	−0.120(1)	0.2941(8)
C(93)	0.559(1)	−0.061(2)	0.346(1)
C(94)	0.6439(1)	−0.045(1)	0.283(1)
C(95)	0.624(1)	−0.025(2)	0.341(1)
C(96)	0.5958(8)	−0.105(1)	0.2289(9)

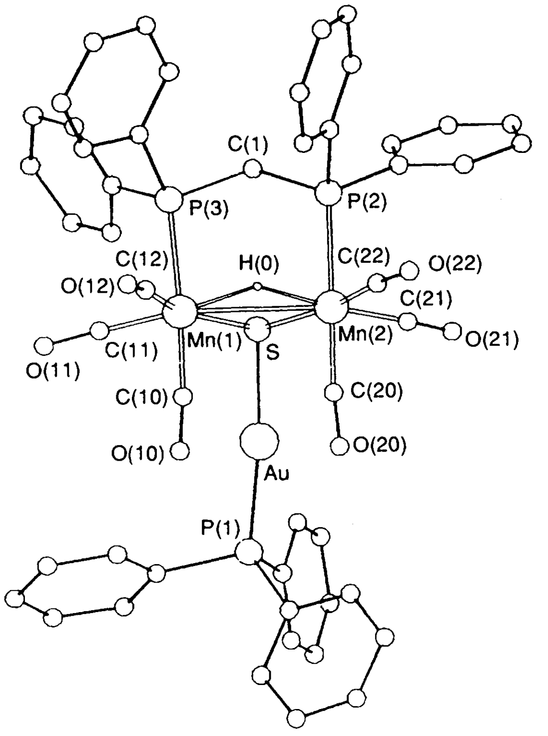


Fig. 1 View of the molecular structure of $[Mn_2(\mu\text{-}H)(\mu\text{-}SAuPPh_3)(CO)_6(\mu\text{-}dppm)]$ **3e**. Hydrogen atoms have been omitted for clarity

was filtered through Celite. The resulting solution was evaporated to dryness yielding the hydrogensulfido complex **3a** or **3b** as a yellow solid. Yields: **3a**, 56% (Found: C, 53.70; H, 3.55. $C_{31}H_{24}Mn_2O_6P_2S$ requires C, 53.45; H, 3.45%); **3b**, 63% (Found: C, 29.65; H, 3.80. $C_{14}H_{22}Mn_2O_{11}P_2S$ requires C, 29.50; H, 3.90%).

Table 3 Selected bond lengths (Å) and angles (°) in complex **3e**

Au–P(1)	2.267(3)	Mn(1)–Mn(2)	2.919(3)
Au–S	2.301(3)	Mn(2)–P(2)	2.317(4)
Mn(1)–P(3)	2.360(4)	Mn(2)–S	2.369(5)
Mn(1)–S	2.368(4)	Mn(2)–C(20)	1.79(2)
Mn(1)–C(10)	1.79(2)	Mn(2)–C(21)	1.83(2)
Mn(1)–C(11)	1.85(2)	Mn(2)–C(22)	1.79(2)
Mn(1)–C(12)	1.76(2)		
P(1)–Au–S	174.2(1)	P(2)–Mn(2)–C(20)	176.3(6)
P(3)–Mn(1)–S	85.3(1)	S–Mn(2)–C(20)	94.8(6)
P(3)–Mn(1)–C(10)	176.4(6)	P(2)–Mn(2)–C(21)	91.2(5)
S–Mn(1)–C(10)	95.3(5)	S–Mn(2)–C(21)	92.0(6)
P(3)–Mn(1)–C(11)	89.7(5)	C(20)–Mn(2)–C(21)	90.9(7)
S–Mn(1)–C(11)	102.2(5)	P(2)–Mn(2)–C(22)	88.3(5)
C(10)–Mn(1)–C(11)	86.7(7)	S–Mn(2)–C(22)	171.6(5)
P(3)–Mn(1)–C(12)	93.3(5)	C(20)–Mn(2)–C(22)	88.5(7)
S–Mn(1)–C(12)	163.2(6)	C(21)–Mn(2)–C(22)	95.7(8)
C(10)–Mn(1)–C(12)	87.2(8)	Au(1)–S–Mn(1)	109.8(1)
C(11)–Mn(1)–C(12)	94.4(8)	Au(1)–S–Mn(2)	111.1(2)
P(2)–Mn(2)–S	88.2(2)	Mn(1)–S–Mn(2)	76.1(1)

Preparation of $[Mn_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_6(\mu\text{-}dppm)]$ **3c**.—To a solution of the hydrogensulfide **3a** (0.060 g, 0.086 mmol) in toluene (20 cm^3) was added freshly prepared thallium(I) acetylacetonate (0.026 g, 0.086 mmol). The solution turned deep orange then orange and became cloudy. The subsequent addition of an excess of methyl iodide caused the precipitation of thallium(I) iodide, and the solution became yellow. After filtration through Celite the solvent was removed *in vacuo*, affording complex **3c** as a yellow solid (52%) (Found: C, 54.20; H, 3.80. $C_{32}H_{26}Mn_2O_6P_2S$ requires C, 54.10: H, 3.70%).

The complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}SSnMe_3)(CO)_6(\mu\text{-}dppm)]$ **3d** and $[Mn_2(\mu\text{-}H)(\mu\text{-}SAuPPh_3)(CO)_6(\mu\text{-}dppm)]$ **3e** were prepared following the same procedure and appropriate amounts of

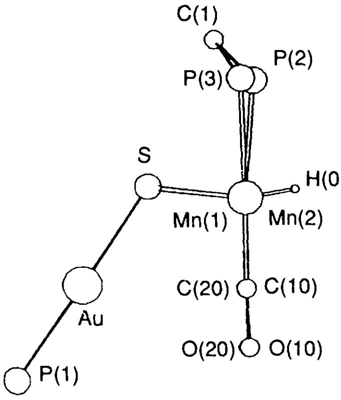


Fig. 2 Partial view of complex **3e**, showing the *anti* disposition of the $SAuPPh_3$ ligand

$SnMe_3Cl$ or $[AuCl(PPh_3)]$ respectively. Complexes **3d** and **3e** were recrystallized from methylene chloride–light petrolum and toluene–light petroleum respectively. Yields: **3d**, 58% (Found: C, 47.75; H, 3.80. $C_{34}H_{32}Mn_2O_6P_2SSn$ requires C, 47.55; H, 3.75%); **3e**, 59% (Found: C, 51.15; H, 3.45. $C_{49}H_{38}AuMn_2O_6P_3S$ requires C, 50.95; H, 3.30%).

Crystal Structure Determination of Complex **3e**.—*Crystal data.* $C_{49}H_{38}AuMn_2O_6P_3S$, $M = 1154.66$, monoclinic, space group $P2_1/n$, $a = 18.840(4)$, $b = 13.024(2)$, $c = 20.243(4)$ Å, $\beta = 108.66(2)^\circ$, $U = 4706(3)$ Å^3, $Z = 4$, $D_c = 1.63$ Mg m^{-3}, $F(000) = 2280$, μ(Mo-Kα) = 38.01 cm^{-1}, orange crystal dimensions 0.23 × 0.13 × 0.13 mm.

Data collection and processing. Enraf-Nonius CAD4 diffractometer. The intensities of 8866 reflections ($0 \leqslant \theta \leqslant 25^\circ$, $-22 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 24$, ω–2θ scan mode, Mo-Kα radiation, graphite monochromator) were collected. Three standard reflections were measured every 60 min, final drift correction factors between 1.00 and 1.58. A semiempirical absorption correction was applied using ψ scans;[7] maximum and minimum correction factors 0.84 and 1.00. Some doubly measured reflections were averaged, $R_{int} = 0.046$, resulting in 3952 observed with $I \geqslant 3\sigma(I)$.

Structure solution and refinement. Patterson methods, using SHELX 86[8] to locate all heavy atoms; the rest of the structure was revealed using DIRDIF.[9] Least-squares refinement in two blocks (567 parameters) using SHELX.[10] After the isotropic refinement an absorption correction using DIFABS[11] was applied with maximum and minimum values of 1.18 and 0.66, respectively. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. Most hydrogen atoms were geometrically placed and refined riding on their parent atom. The μ-H, H(0), was located from a Fourier difference synthesis and its coordinates freely refined. All hydrogen atoms were refined with a common isotropic thermal parameter. The average shift/e.s.d. was 0.46 in the last cycle of refinement. A final difference map showed no peaks higher than 2.00 e Å^{-3} (minimum −2.00 e Å^{-3}) the maximum electronic density being located near to the Au atom. Final R and R' values were 0.050 and 0.049, the function minimized being $\Sigma w(F_o - F_c)^2$ where $w = 1/[\sigma^2(F_o) + 0.000\,60F_o^2]$. Final fractional coordinates are shown in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Dirección General de Investigación Científica y Tecnológica (Spain) (PB88–0467) for financial support.

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Received 8*th August* 1991; *Paper* 1/04151G