Molybdenum and Tungsten Complexes with Side-on Co-ordinated $SPPh_2$-Ligands. *X*-Ray Crystal Structure Determination of $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2.CH_2Cl_2$

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Summary $M(CO)_3Cl(\eta^5\text{-}C_5H_5)$ and $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) react with $SPPh_2H$ and Et_3N to give $M(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}SPPh_2)$ and $M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$, respectively, an *X*-ray crystal structure determination of $Mo(CO)_2(PPh_3)(SPPh_2)_2$ reveals a 7-co-ordinate pseudo-pentagonal bipyramidal geometry for the molybdenum atom with an almost planar configuration for the sulphur and phosphorus atoms

THE $SPPh_2$-ligand is known to co-ordinate end-on by sulphur in Rh and Ir complexes[1] or to act as bridge between two metal atoms *via* sulphur and phosphorus [2] Recently the first example of a side-on bonded $SPPh_2$-ligand was reported for Rh-complexes [3] We report here the reactions of $SPPh_2H$ with $M(CO)_3Cl(\eta^5\text{-}C_5H_5)$ and $M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) giving complexes with side-on co-ordinated $SPPh_2$-ligands The complexes (**1a**) and (**1b**) were prepared by refluxing $SPPh_2H$ and $M(CO)_3Cl(\eta^5\text{-}C_5H_5)$ (1 : 1) for several hours with an excess of Et_3N in benzene Et_3NHCl was filtered off and the products were precipitated with hexane Analytical data are consistent with the empirical

$M(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}SPPh_2)$
(**1**) **a**; M = Mo
b; M = W

$M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$
(**2**) **a**; M = Mo
b; M = W

TABLE. $^{31}P\{^1H\}$ N.m.r. and i.r. spectra for (**1**) and (**2**)

	$\delta(^{31}P)^a$		$\nu_{CO}{}^b$		$\nu_{P=S}{}^c$	$\nu_{M-S}{}^c$
	SPPh$_2$	PPh$_3$				
(**1a**)	$-46{\cdot}40$	—	1958vs	1873vs	514s	—
(**1b**)	$-10{\cdot}92^d$	—	1942vs	1852vs	520s	—
(**2a**)	$-64{\cdot}46(D)^e$	$-42{\cdot}65(T)^e$	1947m	1871vs	532s	372m
(**2b**)	$-35{\cdot}04^f$	$-24{\cdot}40^g$	1923w	1852vs	530s	384m

[a] In p.p.m. relative to O=P(OMe)$_3$ for compounds in C_6D_6 solution using the solvent as internal lock; upfield shifts are positive. [b] Measured in CH_2Cl_2 solution; ν in cm^{-1}; v = very, s = strong, m = medium, w = weak. [c] Measured in CsI pellets. [d] $^1J(^{183}W-^{31}P)$ = 233·6 Hz. [e] D = doublet, T = triplet: $^2J(P-P)$ = 3·75 Hz. [f] $^1J(^{183}W-^{31}P)$ = 195 Hz. [g] $^1J(^{183}W-^{31}P)$ = 265 Hz.

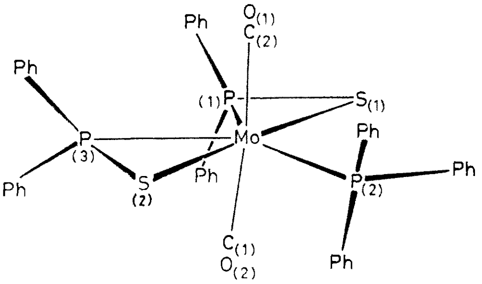

FIGURE. The molecular structure of Mo(CO)$_2$(PPh$_3$)(η^2-SPPh$_2$)$_2$ (**2a**). Selected bond distances and angles: Mo–S(1) 2·613(2), Mo–S(2) 2·630(2), Mo–P(1) 2·401(2), Mo–P(2) 2·542(2), Mo–P(3) 2·382(2), Mo–C(1) 2·007(7), Mo–C(2) 2·027(7), P(1)–S(1) 2·013(2), P(3)–S(2) 2·008(2) Å; P(1)–Mo–P(3) 96·74(6), P(1)–Mo–S(1) 47·11(5), P(2)–Mo–S(1) 87·90(5), P(2)–Mo–S(2) 81·49(5), P(3)–Mo–S(2) 46·91(5), C(1)–Mo–C(2) 176·5(5), Mo–P(1)–S(1) 71·98(7), Mo–P(3)–S(2) 73·04(7), Mo–S(1)–P(1) 60·91(6), Mo–S(2)–P(3) 60·04(7)°.

formula $MC_{19}H_{15}O_2SP$ and the complexes are monomeric in toluene solution. The bis-diphenylphosphine-sulphido-complexes (**2a**) and (**2b**) were prepared by stirring a suspension of M(CO)$_3$(PPh$_3$)$_2$Cl$_2$ with 2 equiv. of SPPh$_2$H in the presence of an excess of Et$_3$N for a few hours. The Et$_3$NHCl was filtered off, the solution evaporated to dryness, and the product recrystallized from CH_2Cl_2–n-hexane. The products are monomeric in CH_2Cl_2 solution and their analytical data are consistent with the empirical formula $MC_{44}H_{35}P_3S_2O_2$. Suitable crystals for *X*-ray analysis of (**2a**) were obtained from CH_2Cl_2–n-hexane (see later).

$^{31}P\{^1H\}$ N.m.r. and i.r. parameters are given in the Table. The ν_{PS} values for these complexes are about 100 cm^{-1} lower than in the free ligand, while in the spectra of (**2a**) and (**2b**) an M–S vibration is observed. The chemical shift of the SPPh$_2$-phosphorus in the $^{31}P\{^1H]$ n.m.r. spectra shows a considerable sensitivity to changes in co-ligands bonded to the central metal. Complex (**2a**) shows P–P coupling between PPh$_3$ and the two equivalent SPPh$_2$-phosphorus atoms, which is not observed in the spectrum of (**2b**).

Crystal data: $C_{44}H_{35}MoP_3S_2O_2.CH_2Cl_2$, triclinic, space group $P\bar{1}$, a = 13·635(2), b = 14·680(2), c = 12·007(2) Å, α = 114·59(2), β = 98·83(2), γ = 82·56(2)°, U = 2153·7 Å^3, Z = 2, D_c = 1·440 g cm^{-3}.

The *X*-ray data were measured on a CAD 4 diffractometer using a θ–2θ scan, with monochromated Mo-K_α radiation. Control reflections showed no indication of crystal decay during the measurements. A total of 24,552 reflections were measured from which 11,963 symmetry-independent reflections remained after averaging, of which 10,186 had $I > 3\sigma(I)$ (σ based on counting statistics). The position of the molybdenum atom was obtained from a Patterson synthesis. The other atoms were found from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares to a final R-value of 0·058. Results of the crystal structure determination are shown in the Figure.† The structure can be considered as a pentagonal bipyramid with a 7-co-ordinate Mo. The two CO-groups are axial and the PPh$_3$ and P and S of both SPPh$_2$-ligands are equatorial. The central Mo obeys the 18-electron rule. It can be considered as in the oxidation state Mo^{II} and the two SPPh$_2$-ligands as uninegative, bidentate, four-electron donors.

It is interesting to note the similarity between (**2a**) and the 18-electron $ML_3(\eta^2\text{-}L')_2$ compounds like IrCl(PPh$_3$)$_2$(η^2-C$_2$H$_4$)$_2$ and IrCl(PPh$_3$)$_2$(η^2-O$_2$)(η^2-C$_2$H$_4$).[4] The P$_3$S$_2$ core is planar and the PS distances found (2·015 Å) are closer to the P=S bond distance (1·95 Å) than P–S (2·18 Å). The great sensitivity of the ^{31}P chemical shift towards the electron density on the central metal is comparable to the well known sensitivity of ^{13}C in η^2-olefin complexes.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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