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Seven-coordinate molybdenum complexes containing $SnRCl_2$ and phosphorodithioate. X-Ray structure of $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$

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Abstract

$[Mo(CO)_3(NCMe)_2(SnRCl_2)Cl]$ (**1a**, R = Ph; **1b**, R = Bu) react with ammonium diethyldithiophosphate or with sodium diphenyldithiophosphinate in CH_2Cl_2 to produce $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$ (**2**, R = Ph or Bu; X = OEt or Ph). Upon treatment with an excess of $P(OMe)_3$, complexes **2** undergo substitution of the NCMe and one carbonyl, affording bis(phosphite) complexes $[Mo(CO)_2\{P(OMe)_3\}_2(S_2PX_2)(SnRCl_2)]$ (**3**, R = Ph or Bu; X = OEt or Ph). The same complexes are produced by the reaction of dicarbonyltris(phosphite) complexes $[Mo(CO)_2\{P(OMe)_3\}_3(SnRCl_2)Cl]$ with $NH_4[S_2P(OEt)_2]$ or $Na[S_2PPh_2]$, through substitution of the chloride ion and one phosphite. The structure of the derivative **3c** (R = Bu, X = OEt) has been determined by X-ray crystallography. Complexes **3** are fluxional at room temperature as judged by $^{31}P\{^1H\}$ NMR spectroscopy. At 195 K, the dynamic process is quenched, giving sharp, well resolved spectra, whose assignment is consistent with the solid state structure.

1. Introduction

We have recently reported the preparation of a family of seven-coordinate complexes of molybdenum of formulae $[Mo(CO)_3(NCMe)_2(SnRCl_2)Cl]$ (**1a**, R = Ph; **1b**, R = Bu) [1,2]. Their behaviour towards neutral donors depends markedly on the donor. Thus, the two labile acetonitriles in complexes **1** can be readily replaced by tetramethylthiourea (TMTU), to afford $[Mo(CO)_3(TMTU)_2(SnRCl_2)Cl]$ whereas **1a,b** react with phosphites to give dicarbonyls $[Mo(CO)_2\{P(OMe)_3\}_3(SnRCl_2)Cl]$ through displacement of two acetonitriles and one carbonyl [1,2]. In contrast, upon treatment with the zwitterionic phosphoniodithioformate ligand, S_2CPR_3, **1b** undergoes an incomplete reductive elimination of $SnBuCl_3$, to give $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)(SnBuCl_2)]$ [3]. The reactivity of complexes **1**, containing $SnRCl_2$ groups, is qualitatively different from that reported by Baker *et al.* for the analogue $[Mo(CO)_3(NCMe)_2(SnCl_3)Cl]$ containing trichlorostannate [4–6], as we have discussed previously [1,2]. In this paper, we report the reactions of bis(acetonitrile) complexes **1** with anionic phosphorodithioate.

2. Results and discussion

Addition of ammonium diethyldithiophosphate or sodium diphenyldithiophosphinate to $[Mo(CO)_3(NCMe)_2(SnRCl_2)Cl]$ (**1a**, R = Ph; **1b**, R = Bu) in CH_2Cl_2 solution at room temperature produces the displacement of chloride and one acetonitrile from the molybdenum to give complexes $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$ (**2a–d**, see Scheme 1). Upon addition of hexane to the filtered solutions, the phenyltin derivatives **2a,b** were obtained as yellow, crystalline solids which were fully characterized by analytical and spectroscopic methods (Table 1). In spite of repeated attempts, it was not possible to crystallize the com-

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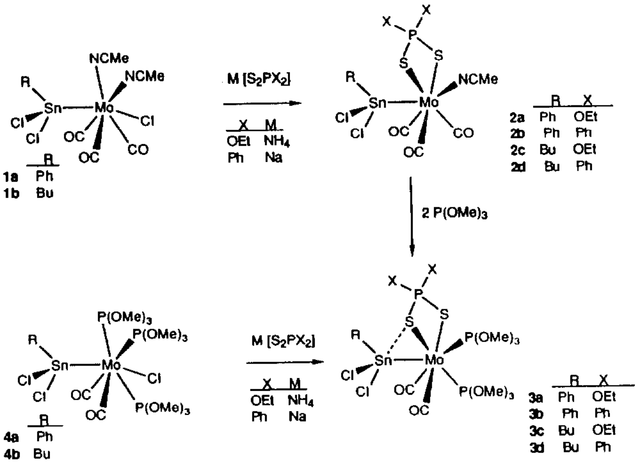

Scheme 1.

plexes containing $SnBuCl_2$ (**2c,d**). Evaporation of the solvents gave yellow oils which were characterized by spectroscopic methods in solution.

Addition of an excess of $P(OMe)_3$ to dichloromethane solutions of the tricarbonyl-acetonitrile complexes **2a–d**, at room temperature, produces the facile displacement of the acetonitrile and one carbonyl to give dicarbonyl compounds $[Mo(CO)_2\{P(OMe)_3\}_2(S_2PX_2)(SnRCl_2)]$ (**3a–d**, see Scheme 1), which have been isolated as yellow crystalline solids, and fully characterized by analytical and spectroscopic methods. The structure depicted for these complexes in Scheme 1 was confirmed by an X-ray diffraction analysis on a crystal of the derivative **3c** (see below).

Alternatively, complexes **3a–d** can be obtained by reaction of $[Mo(CO)_2\{P(OMe)_3\}_3(SnRCl_2)Cl]$ (**4a,b** in Scheme 1) with ammonium diethyldithiophosphate or sodium diphenyldithiophosphinate in CH_2Cl_2 solution at room temperature. In these reactions, the entering anionic group displaces the chloride anion and one phosphite. Although the procedure does not possess any advantage when compared to the reaction of complexes **2** with phosphite, it serves well to illustrate the dependence of the reactivity of these complexes upon the reagents employed. Thus, no reaction was observed when complexes **4a,b** were treated with neutral S_2CPR_3. All these facts can be rationalized assuming that the driving force of the reaction from **4a,b** to **3a–d** is the precipitation of either NH_4Cl or NaCl to give, initially, a complex containing monodentate $S_2P(OEt)_2$ or S_2PPh_2. The second step (displacement of phosphite) would be favoured by the formation of the chelate $\overline{Mo–S–P–S}$ ring.

The use of halide displacement by dithiophosphate and dithiophosphinate anions to obtain either tin(IV) [7–11] or molybdenum(II) [12–14] mononuclear derivatives is well established. In complexes **1** and **4**, there are two chlorides bonded to tin and one chloride bonded to molybdenum. In both cases, the reactions with dithiophosphate or dithiophosphinate lead selectively to the formation of the product (**2** or **3**, respectively) in which a chloride anion has been displaced from molybdenum.

An X-ray structure determination was carried out on a crystal of **3c**. Crystal data and refinement details are in Table 2, atomic parameters are in Table 3, while selected bond distances and angles are in Table 4. A perspective view of the molecule is depicted in Fig. 1. The molybdenum atom is seven-coordinate, close to the capped-octahedral geometry, with the tin atom in the capping position. The Mo–Sn distance of 2.709(7) Å is within the range expected for a normal Mo–Sn bond. The $S_2P(OEt)_2$ chelates (Mo–S distances of 2.62(1) and 2.65(2) Å). The coordination around the molybdenum is completed by two carbonyls and two phosphites. Coordination around the tin atom is distorted tetrahedral, formed by two chlorides, one carbon from the butyl group, and the molybdenum atom.

An interesting feature of the structure of **3c** is the short distance S(2)–Sn of 3.06(1) Å which, in fact, brings the sulphur atom into the coordination sphere

TABLE 1. Spectroscopic data for the new complexes

	Compound	IR (CH_2Cl_2) ν(CO) (cm^{-1})	$^{31}P\{^1H\}$NMR [a], CD_2Cl_2, δ (ppm)	
			S_2P [b]	Mo-P
2a	$[Mo(CO)_3(NCMe)\{S_2P(OEt)_2\}(SnPhCl_2)]$	2021s, 1946m, 1921s	100.1(105)	
2b	$[Mo(CO)_3(NCMe)(S_2PPh_2)(SnPhCl_2)]$	2018s, 1941m, 1919s	100.9(70)	
2c	$[Mo(CO)_3(NCMe)\{S_2P(OEt)_2\}(SnBuCl_2)]$	2016s, 1941m, 1914s	104.9(73)	
2d	$[Mo(CO)_3(NCMe)(S_2PPh_2)(SnBuCl_2)]$	2014s, 1937m, 1914s	94.0(67)	
3a	$[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnPhCl_2)]$	1942m, 1879s	84.9 (br.)	147 (v.br.)
3b	$[Mo(CO)_2\{P(OMe)_3\}_2(S_2PPh_2)(SnPhCl_2)]$	1937m, 1877s	88.8 (br.)	142 (v.br.)
3c	$[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$	1937m, 1876s	84.8 (br.)	143 (v.br.)
3d	$[Mo(CO)_2\{P(OMe)_3\}_2(S_2PPh_2)(SnBuCl_2)]$	1933m, 1872s	85.9 (br.)	149 (v.br.)

[a] Room temperature spectra. For the low temperature ^{31}P NMR spectra of complexes **3a–d**, see Table 5. [b] J(P–Sn), in Hz, are given in parentheses.

TABLE 2. Crystallographic data for $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ (**3c**)

Formula	$C_{16}H_{37}Cl_2MoO_{10}P_3S_2Sn$
F.W.	832.04
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.311(6)
b (Å)	10.231(4)
c (Å)	20.889(6)
β (°)	98.76(3)
V (Å^3)	3234(2)
Z	4
T (K)	293
ρ_{calc} (g cm^{-3})	1.71
F(000)	1664
λ (Mo Kα) (Å)	0.71073
Crystal size (mm); colour	0.16×0.1×0.1, yellow
μ (cm^{-1})	16.32
Method of collection	$\omega-2\theta$ scan
Scan range (°)	$0 \leqslant \theta \leqslant 25$
No. of reflections measured	2328
No. of reflections observed, $I \geqslant 2\sigma(I)$	725
Absorption correction	Empirical (DIFABS)
Correction factors (min, max)	0.975, 1.243
No. of parameters	152
Data to parameters ratio	4.77
Weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
g	0.0006
Residuals R, R_w	0.064, 0.058

of the tin. Although it is long for a covalent S–Sn bond, the distance is similar to those found in tin(IV) complexes such as $[SnMe_2(S_2PR_2)_2]$ (R = Me [7], Et [8] and $[SnPh_2\{S_2P(OEt)_2\}_2]$ [15]). In the latter compound, the diethyldithiophosphate has been described [9] as an anisobidentate chelate, displaying short Sn–S distances [2.49(1) and 2.481(8) Å] assigned to covalent S–Sn bonds associated with long P–S distances [2.03(1) and 2.04(2) Å], and longer Sn–S distances [3.23(1) and 3.20(1) Å] assigned to dative S → Sn bonds associated with shorter P=S distances [1.92(3) and 1.94(1) Å]. Since the S(2)–Sn distance of 3.06(1) Å, found in the structure of **3c**, falls well within the range (2.593–3.947 Å) observed for dative S → Sn bonds [9], it is concluded that the diethyldithiophosphate in **3c** acts as a chelate towards molybdenum and as a bridge, through one sulphur atom, between molybdenum and tin.

Although phosphorodithioates are frequently found acting as bridges between two transition metal atoms, this is not very common in tin complexes [9] and, as far as we know, there is no previous report of a phosphorodithioate bridge between tin and a transition metal. The nearest precedent is the tin(II) derivative $[Sn\{S_2P(OPh)_2\}\{\mu\text{-}S_2P(OPh)_2\}]_2$ [10,11] in which two tin atoms are held together by two bridging diphenyldithiophosphates which act in a severely anisobidentate fashion to one tin atom [distances Sn(1)–S(3) 2.6510(6) and Sn(1)–S(4) 3.3914(6) Å] while, simultaneously, one sulphur acts as a bridge towards the other tin atom [Sn(1′)–S(4) 3.0428(7)] (labels and distances are from ref. 11). In the structure of **3c**, there is small difference between the two Mo–S distances [2.62(1) and 2.65(2) Å], or between the two P–S distances [1.97(2) and 2.02(2) Å], reflecting a high degree of delocalization within the $\overline{\mathrm{Mo{-}S{-}P{-}S}}$ chelate ring.

From Fig. 1 and Table 4, it is clear that the phosphorus atoms of the phosphites are chemically nonequivalent in the solid state structure. Thus P(3) is nearly *trans* to one carbonyl group [angle P(3)–Mo–C(6) 167(1)°] while P(2) is nearly *trans* to one sulphur [angle P(2)–Mo–S(2) 161.7(4)°]. The room temperature $^{31}P\{^1H\}$NMR spectra of complexes **3a–d** (see Fig. 2 and Table 1) display a broad signal in the range δ 84.8 to 88.8 ppm, assignable to the phosphorus of the dithiophosphate or dithiophosphinate, and a very broad

TABLE 3. Atomic coordinates for non-hydrogen atoms in $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ (**3c**)

Atom	x	y	z
Sn	0.3284(2)	0.1140(3)	0.1730(2)
Cl(1)	0.4012(6)	0.217(1)	0.2673(8)
Cl(2)	0.4507(7)	−0.013(1)	0.1514(9)
C(1)	0.252(2)	−0.039(4)	0.205(3)
C(2)	0.289(2)	−0.102(4)	0.263(3)
C(3)	0.220(3)	−0.209(4)	0.281(3)
C(4)	0.259(3)	−0.277(5)	0.339(3)
Mo	0.2639(2)	0.2818(4)	0.0771(3)
S(1)	0.0974(6)	0.328(1)	0.032(1)
S(2)	0.1911(6)	0.327(1)	0.1820(9)
P(1)	0.0796(7)	0.291(1)	0.124(1)
O(11)	0.001(1)	0.376(3)	0.145(2)
C(11)	−0.004(3)	0.511(4)	0.140(3)
C(13)	0.008(3)	0.566(5)	0.206(3)
O(12)	0.055(1)	0.150(2)	0.135(2)
C(12)	−0.014(2)	0.079(4)	0.099(3)
C(14)	−0.004(3)	−0.054(4)	0.103(3)
C(5)	0.391(2)	0.301(4)	0.094(3)
O(5)	0.470(1)	0.301(2)	0.092(2)
C(6)	0.231(2)	0.102(4)	0.048(3)
O(6)	0.208(2)	−0.005(3)	0.031(2)
P(2)	0.2905(7)	0.283(1)	−0.031(1)
O(21)	0.307(1)	0.412(2)	−0.069(2)
C(21)	0.395(2)	0.465(4)	−0.071(2)
O(22)	0.375(2)	0.194(3)	−0.052(2)
C(22)	0.385(3)	0.063(4)	−0.032(3)
O(23)	0.212(2)	0.218(3)	−0.083(3)
C(23)	0.207(3)	0.212(4)	−0.144(3)
P(3)	0.2821(7)	0.527(1)	0.092(1)
O(31)	0.356(2)	0.585(3)	0.053(2)
C(31)	0.384(3)	0.718(4)	0.056(3)
O(32)	0.200(2)	0.624(3)	0.074(2)
C(32)	0.167(3)	0.645(4)	0.010(3)
O(33)	0.304(1)	0.588(3)	0.159(2)
C(33)	0.380(3)	0.541(4)	0.204(3)

TABLE 4. Selected distances (Å) and angles (°) for $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ (**3c**)

Sn–Mo	2.709(7)	Sn–Cl(1)	2.36(2)
Sn–Cl(2)	2.38(1)	Sn–C(1)	2.13(4)
Sn–S(2)	3.06(1)	Mo–S(1)	2.62(1)
Mo–S(2)	2.65(2)	Mo–C(5)	1.94(4)
Mo–C(6)	1.98(4)	Mo–P(2)	2.36(2)
Mo–P(3)	2.53(1)	C(5)–O(5)	1.21(4)
C(6)–O(6)	1.19(4)	S(1)–P(1)	2.02(2)
S(2)–P(1)	1.97(2)	P(1)–O(11)	1.59(3)
P(1)–O(12)	1.52(2)	P(2)–O(21)	1.58(3)
P(2)–O(22)	1.69(3)	P(2)–O(23)	1.63(4)
P(3)–O(31)	1.61(3)	P(3)–O(32)	1.61(3)
P(3)–O(33)	1.53(3)		
Cl(2)–Sn–Cl(1)	96.8(4)	C(1)–Sn–Cl(1)	106(2)
C(1)–Sn–Cl(2)	98(1)	Mo–Sn–Cl(1)	114.1(3)
Mo–Sn–Cl(2)	114.5(5)	Mo–Sn–C(1)	123(1)
S(2)–Sn–Cl(1)	82.6(4)	S(2)–Sn–Cl(2)	166.2(5)
S(2)–Sn–C(1)	95(1)	S(2)–Sn–Mo	54.3(3)
S(1)–Mo–Sn	127.2(4)	S(2)–Mo–Sn	69.6(3)
S(2)–Mo–S(1)	75.9(5)	C(5)–Mo–Sn	72(2)
C(5)–Mo–S(1)	161(2)	C(5)–Mo–S(2)	112(2)
C(6)–Mo–Sn	72(1)	C(6)–Mo–S(1)	82(1)
C(6)–Mo–S(2)	107(2)	C(6)–Mo–C(5)	111(2)
P(2)–Mo–Sn	127.9(3)	P(2)–Mo–S(1)	87.5(6)
P(2)–Mo–S(2)	161.7(4)	P(2)–Mo–C(5)	82(2)
P(2)–Mo–C(6)	78(2)	P(3)–Mo–Sn	121.0(5)
P(3)–Mo–S(1)	87.0(3)	P(3)–Mo–S(2)	77.1(5)
P(3)–Mo–C(5)	78(1)	P(3)–Mo–C(6)	167(1)
P(3)–Mo–P(2)	94.7(6)	O(5)–C(5)–Mo	166(5)
O(6)–C(6)–Mo	178(3)		

signal for the phosphite, in the range δ 142 to 149 ppm. This suggests a dynamic process which renders the two phosphites equivalent at room temperature.

On cooling to 195 K, the signals are resolved to a pattern consistent with the arrangement observed in the solid state structure for complex **3c**. The $^{31}P\{^1H\}$ NMR spectrum of **3c** at 195 K is shown in Fig. 2, together with the proposed assignment. As expected for an AMX spin system, the spectrum consists of three signals which appear as doublets of doublets. Although those at higher fields (assigned to P_B and P_C) are only partially resolved, they can be used to obtain a reasonably good estimate of the value of the coupling constant between P_B and P_C. The signal centred at δ 162.15 ppm shows the greatest couplings, and can be assigned to P_A which is nearly *trans* to one sulphur of the dithiophosphate. The signal at δ 133.78 ppm is assigned to P_B which is nearly *trans* to one carbonyl group, and the signal at δ 81.84 can be safely assigned to P_C of the dithiophosphate. The assignment and estimation of the coupling constants are outlined in Fig. 2. Although the satellites due to Sn–P coupling are not resolved, they provide a reasonably good estimate of the values of the *J*(P–Sn) coupling constants, which serve as an additional test of the consistency of the assignment. The low temperature spectra of complexes **3a**, **3b** and **3d** (Table 5) display similar patterns. However, the small coupling between P_B and P_C could not be observed in these cases.

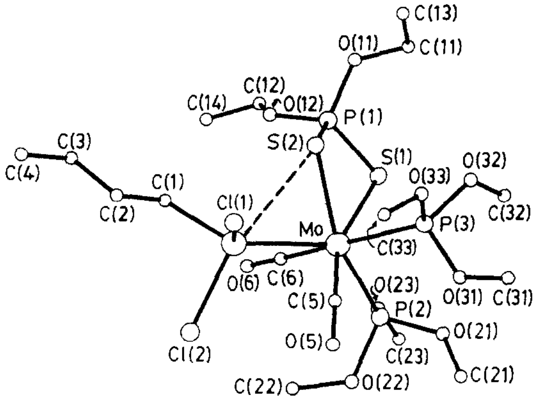

Fig. 1. Perspective view of $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ (**3c**) showing the atom numbering.

3. Experimental details

All reactions were carried out in dry solvents under a nitrogen atmosphere. NaS_2PPh_2 was prepared according to literature procedures [16]. Other materials were purchased and used without purification. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X

TABLE 5. Low temperature (195 K) $^{31}P\{^1H\}$ NMR spectra for complexes **3a–d** [a]

Compound	δ P_A	δ P_B	δ P_C	*J*(P–P) (Hz)			*J* (Sn–P) (Hz)		
				P_A–P_B	P_A–P_C	P_B–P_C	P_A–Sn	P_B–Sn	P_C–Sn
3a	160.42 dd	132.68 d	84.85 d	41	20	[b]	308	147	217
3b	160.07 dd	127.62 d	88.80 d	40	10	[b]	298	162	147
3c	162.15 dd	133.78 dd	81.84 dd	42	16	7	268	137	175
3d	161.34 dd	130.07 d	82.81 d	45	5	[b]	265	141	108

[a] CD_2Cl_2 solutions. [b] Not observed.

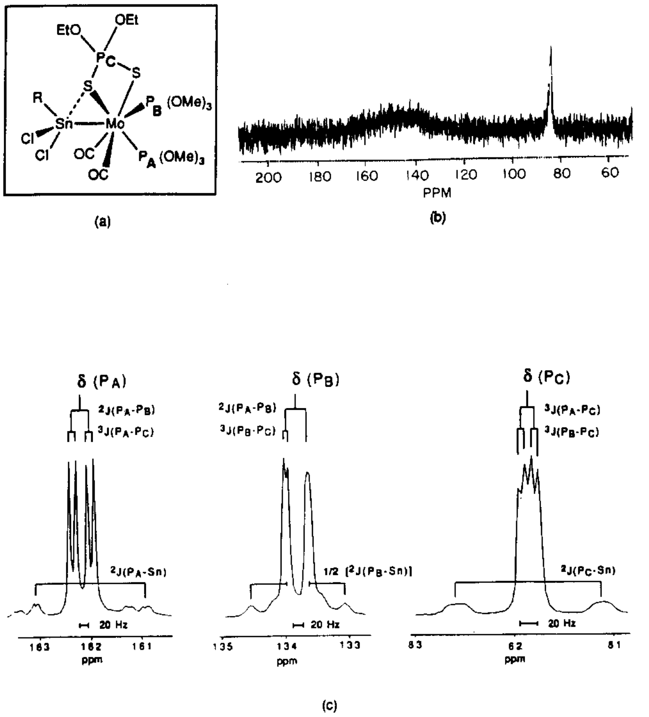

Fig. 2. ^{31}P{^{1}H} NMR spectra of compound **3c**. (a) Schematic drawing showing the assignment of the signals. (b) Room temperature spectrum (295 K). (c) Low temperature spectrum (195 K). The values of chemical shifts and coupling constants for compounds **3a–d** are given in Table 5.

spectrometer. ^{1}H NMR [300.1 MHz, δ(ppm) from internal Si(Me)$_4$], and ^{31}P{^{1}H} NMR (121.5 MHz, δ(ppm) to higher frequencies from external 85% H_3PO_4) were recorded on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240B analyser.

3.1. [Mo(CO)$_3$(NCMe){S$_2$P(OEt)$_2$}(SnPhCl$_2$)] (**2a**)

A solution of [Mo(CO)$_3$(NCMe)$_2$(Cl)(SnPhCl$_2$)] (**1a**) (*ca.* 0.89 mmol) in CH_2Cl_2 (20 ml) was prepared as previously described [2]. To the solution was added NH$_4$[S$_2$P(OEt)$_2$] (0.18 g, 0.893 mmol), and the mixture was stirred for 30 min. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2 (2 × 15 ml). The extracts were filtered through Celite and then concentrated *in vacuo* to give an orange oil. This was stirred with hexane (20 ml) to produce **2a** as a yellow microcrystalline solid. Yield 0.42 g, 71%. Anal. Found: C, 26.5; H, 2.6; N, 2.1. $C_{15}H_{18}Cl_2MoNO_5PS_2Sn$ calcd.: C, 26.8; H, 2.7; N, 2.1%. ^{1}H NMR (CDCl$_3$): δ 7.86 (m, 2H, C$_6$*H*$_5$); 7.46 (m, 3H, C$_6$*H*$_5$); 3.94 (m, 4H, S$_2$P(OC*H*$_2$CH$_3$)$_2$); 2.33 (s, 3H, NCC*H*$_3$); 1.23 (t (7 Hz), 6H, S$_2$P(OCH$_2$C*H*$_3$)$_2$) ppm.

3.2. [Mo(CO)$_3$(NCMe)(S$_2$PPh$_2$)(SnPhCl$_2$)] (**2b**)

This was prepared as described above from a solution of [Mo(CO)$_3$(NCMe)$_2$(Cl)(SnPhCl$_2$)] (**1a**) (*ca.* 0.53 mmol) in CH_2Cl_2 and Na[S$_2$PPh$_2$] (0.15 g, 0.53 mmol). Yield 0.39 g, 51%. Anal. Found: C, 37.8; H, 2.7; N, 2.1. $C_{23}H_{18}Cl_2MoNO_3PS_2Sn$ calcd.: C, 37.5; H, 2.5; N, 1.9%. ^{1}H NMR (CDCl$_3$): δ 7.79–7.73 (m, 15H, 3 × C$_6$*H*$_5$); 2.04 (s, 3H, NCC*H*$_3$) ppm.

3.3. [Mo(CO)$_3$(NCMe){S$_2$P(OEt)$_2$}(SnBuCl$_2$)] (**2c**)

This was prepared as described above from a solution of [Mo(CO)$_3$(NCMe)$_2$(Cl)(SnBuCl$_2$)] (**1b**) (*ca.* 0.75 mmol) and NH$_4$[S$_2$P(OEt)$_2$] (0.18 g, 0.89 mmol) in CH_2Cl_2 (20 ml). Compound **2c** was obtained as an orange oil which could not be crystallized and therefore it was characterized in solution by spectroscopic methods. ^{1}H NMR (CDCl$_3$): δ 4.20 and 4.11 (m, 2 + 2H, S$_2$P(OC*H*$_2$CH$_3$)$_2$); 2.09 (s, 3H, NCC*H*$_3$); 1.97 (m, 4H, 2 × C*H*$_2$ of ^{n}Bu); 1.48 (m, 2H, C*H*$_2$ of ^{n}Bu); 1.34 (t (7 Hz), 3H, S$_2$P(OCH$_2$C*H*$_3$)$_2$), 1.24 (t (7 Hz), 3H, S$_2$P(OCH$_2$C*H*$_3$)$_2$); 0.94 (t (7 Hz), 3H, C*H*$_3$ of ^{n}Bu) ppm. For IR and ^{31}P NMR data, see Table 1.

3.4. [Mo(CO)$_3$(NCMe)(S$_2$PPh$_2$)(SnBuCl$_2$)] (**2d**)

This was prepared as described above for **2c**, from a solution of [Mo(CO)$_3$(NCMe)$_2$(Cl)(SnBuCl$_2$)] (**1b**) [2] (*ca.* 0.75 mmol) in CH_2Cl_2 and Na[S$_2$PPh$_2$] (0.21 g, 0.75 mmol). As for **2c**, the product could not be obtained as a solid, and was characterized in solution. ^{1}H NMR (CDCl$_3$): δ 7.83 (m, 4H, C$_6$*H*$_5$); 7.42 (m, 6H, C$_6$*H*$_5$); 2.07 (s, 3H, NCC*H*$_3$); 1.92 (m, 4H, 2 × C*H*$_2$ of ^{n}Bu); 1.43 (m, 2H, C*H*$_2$ of ^{n}Bu); 0.90 [t (7 Hz), 3H, C*H*$_3$ of ^{n}Bu) ppm. For IR and ^{31}P NMR data, see Table 1.

3.5. [Mo(CO)$_2${P(OMe)$_3$}$_2${S$_2$P(OEt)$_2$}(SnPhCl$_2$)] (**3a**)

(a) A mixture of **2a** (0.186 g, 0.33 mmol) and P(OMe)$_3$ (120 μl, 1 mmol) in CH_2Cl_2 (15 ml) was stirred for 30 min. The solvent was evaporated to dryness *in vacuo*. The brown residue was extracted with CH_2Cl_2 (2 × 15 ml) and filtered. Hexane (20 ml) was added to the filtrate, and the mixture was concentrated *in vacuo* to *ca.* 10 ml. Overnight cooling in a fridge (−20°C) produced yellow crystals of complex **3a**. Yield 0.19 g, 68%.

(b) To a solution of [Mo(CO)$_2${P(OMe)$_3$}$_3$Cl(SnPhCl$_2$)] [2] (0.143 g, 0.17 mmol) in CH_2Cl_2 (15 ml) was added NH$_4$[S$_2$P(OEt)$_2$] (0.035 g, 0.17 mmol), and the mixture was stirred for 3 h. The work-up was as described in (a), to yield **3a** as yellow crystals. Yield 0.09 g, 62%. Anal. Found: C, 25.0; H, 3.9. $C_{18}H_{33}Cl_2MoO_{10}P_3S_2Sn$ calcd.: C, 25.4; H, 3.9%. ^{1}H NMR (CDCl$_3$): δ 7.90 (m, 2H, C$_6$*H*$_5$); 7.43 (m, 3H, C$_6$*H*$_5$), 3.89 (m, 4H, $S_2P(OCH_2CH_3)_2$); 3.73 (d (11 Hz), 18H, $2 \times P(OCH_3)_3$); 2.05 (m, 2H, CH_2 of ^{n}Bu); 1.86 (m, 2H, CH_2 of ^{n}Bu); 1.45 [m, 2H, CH_2 of ^{n}Bu); 1.16 (t (7 Hz), 6H, $S_2P(OCH_2CH_3)_2$) ppm.

3.6. $[Mo(CO)_2\{P(OMe)_3\}_2(S_2PPh_2)(SnPhCl_2)]$ (3b)

(a) A mixture of **2b** (0.39 g, 0.53 mmol) and $P(OMe)_3$ (187 μl, 1.59 mmol) in CH_2Cl_2 (20 ml) was stirred for 30 min. The work-up was as for **3a**, to afford orange crystals of **3b**. Yield 0.26 g, 53%.

(b) $[Mo(CO)_2\{P(OMe)_3\}_3(SnPhCl_2)Cl]$ [2] (0.21 g, 0.25 mmol) and $Na[S_2PPh_2]$ (0.07 g, 0.25 mmol) were stirred in CH_2Cl_2 (15 ml) for 3 h. Yield 0.15 g, 66%. Anal. Found: C, 34.4; H, 3.8. $C_{26}H_{33}Cl_2MoO_8P_3S_2Sn$ calcd.: C, 34.1; H, 3.6%. ^1H NMR ($CDCl_3$): δ 7.66–7.26 (m, 15H, $3 \times C_6H_5$); 3.70 (d (11 Hz), 18H, $2 \times P(OCH_3)_3$) ppm.

3.7. $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ (3c)

(a) To a solution of **2c** (*ca.* 0.75 mmol), prepared as described above, was added $P(OMe)_3$ (266 μl, 2.25 mmol). After stirring for 30 min, the solvent was evaporated to dryness. The brown residue was extracted with CH_2Cl_2 (2 × 10 ml), and the combined extracts were filtered. The filtrate was concentrated *in vacuo* to give an oil which was stirred with hexane (20 ml) to afford a yellow-orange solid. After washing with hexane (2 × 10 ml), the solid was dissolved in CH_2Cl_2 (5 ml). Hexane (10 ml) was added, and the solution was concentrated *in vacuo* to *ca.* 10 ml. Overnight cooling in a fridge (−20°C) afforded yellow crystals of **3c**. Yield 0.51 g, 67%. Anal. Found: C, 23.4; H, 4.8. $C_{16}H_{37}Cl_2MoO_{10}P_3S_2Sn$ calcd.: C, 23.1; H, 4.5%. ^1H NMR ($CDCl_3$): δ 4.15 (m, 4H, $S_2P(OCH_2CH_3)_2$); 3.71 (d (11 Hz), 18H, $2 \times P(OCH_3)_3$); 2.05 (m, 2H, CH_2 of ^{n}Bu); 1.86 (m, 2H, CH_2 of ^{n}Bu); 1.45 (m, 2H, CH_2 of ^{n}Bu); 1.35 (t (7 Hz), 6H, $S_2P(OCH_2CH_3)_2$); 0.95 (t (7 Hz), 3H, CH_3 of ^{n}Bu) ppm.

(b) A mixture of $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$ [2] (0.2 g, 0.25 mmol) and $NH_4[S_2P(OEt)_2]$ (0.05 g, 0.25 mmol) was stirred in CH_2Cl_2 (20 ml) for 2 h. Work-up was as described for **3a**. Yield 0.13 g, 62%.

3.8. $[Mo(CO)_2\{P(OMe)_3\}_2(S_2PPh_2)(SnBuCl_2)]$ (3d)

(a) A solution of **2d** (*ca.* 0.75 mmol), prepared as described above, was stirred with $P(OMe)_3$ (266 μl, 2.25 mmol) for 30 min. The work-up was as described for **3c**, to afford orange-yellow crystals of **3d**. Yield 0.48 g, 72%. Anal. Found: C, 32.5; H, 4.2. $C_{24}H_{37}Cl_2MoO_8P_3S_2Sn$ calcd.: C, 32.2; H, 4.2%. ^1H NMR ($CDCl_3$): δ 7.85 (m, 4H, C_6H_5); 7.53 (m, 6H, C_6H_5); 3.69 (d (11 Hz), 18H, $2 \times P(OCH_3)_3$); 1.57 (m, 2 + 2H, $2 \times CH_2$ of ^{n}Bu); 1.22 (m, 2H, CH_2 of ^{n}Bu); 0.83 (t (7 Hz), 3H, CH_3 of ^{n}Bu) ppm.

(b) A mixture of $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$ [2] (0.2 g, 0.25 mmol) and $Na[S_2PPh_2]$ (0.07 g, 0.25 mmol) was stirred in CH_2Cl_2 (20 ml) for 2 h. Work-up was as described for **3a**. Yield 0.16 g, 72%.

3.9. Crystal and refinement data for compound 3c

Crystal data and relevant refinement details are collected in Table 2. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a concentrated solution of compound **3c** in CH_2Cl_2 at −20°C. Intensities were collected on an Enraf-Nonius CAD4 diffractometer, using the ω–2θ scan technique. Mo and Sn atoms were located from a Patterson synthesis, and the remaining non-H atoms by DIRDIF [17]. Full-matrix least-squares refinement was made with SHELX76 [18]. After isotropic refinement, an empirical absorption correction was applied with DIFABS [19]. Due to the low number of observed reflections, only Mo and Sn atoms were refined anisotropically. H atoms were geometrically positioned with a fixed overall isotropic factor of 0.10 Å². The full list of atomic parameters, bond lengths and angles, and anisotropic thermal parameters is available from the Cambridge Crystallographic Data Centre.

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References

1 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Polyhedron, 10* (1991) 1717.
2 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem., 455* (1993) 121.
3 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Angew. Chem. Int. Ed. Engl., 31* (1992) 76.
4 P.K. Baker and A. Bury, *J. Organomet. Chem., 359* (1989) 189.
5 P.K. Baker and A.J. Quinlan, *Inorg. Chim. Acta, 162* (1989) 179.
6 P.K. Baker and A. Bury, *Polyhedron, 8* (1989) 917.
7 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and F.P. Mullins, *Inorg. Chem., 20* (1981) 2172.
8 C. Silvestru, I. Haiduc, S. Klima, U. Thewalt, M. Gielen and J.J. Zuckerman, *J. Organomet. Chem., 327* (1987) 181.
9 K.C. Molloy and J.J. Zuckerman, *Acc. Chem. Res., 16* (1983) 386.
10 J.L. Lafferts, M.B. Hossain, K.C. Molloy, D. van der Helm and J.J. Zuckerman, *Angew. Chem., Int. Ed. Engl., 19* (1980) 309.
11 J.L. Lafferts, M.B. Hossain, K.C. Molloy, D. van der Helm and J.J. Zuckerman, *Inorg. Chem., 21* (1982) 1410.
12 G.J.-J. Cheng, R.O. Yelton and J.W. McDonald, *Inorg. Chim. Acta, 22* (1977) 249.
13 C.Y. Chou and E.A. Maatta, *Inorg. Chem., 23* (1984) 2912.

14 J.W. McDonald, J.L. Corbin and W.E. Newton, *J. Am. Chem. Soc., 97* (1975) 1970.

15 B.W. Liebich and M. Tomassini, *Acta Crystallogr., Sect. B, 34* (1978) 944.

16 W.A. Higgins, P.W. Vogel and W.G. Craig, *J. Am. Chem. Soc., 77* (1955) 1864; R.G. Cavell, W. Byers and E.D. Day, *Inorg. Chem., 10* (1971) 2710.

17 P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M. Smits and C. Smykalla, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

18 G.M. Sheldrick, SHELX76, *Program for Crystal Structure Determinations*, University of Cambridge, 1976.

19 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A, 39* (1983) 158.