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Seven-coordinate molybdenum–tin complexes containing phosphorodithioato and phosphoniodithioformate. X-Ray structure of $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)] \cdot CH_2Cl_2$

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Abstract

Reactions of $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$ (1) with an excess of S_2CPR_3 afford complexes $[Mo(CO)_2(S_2PX_2)(S_2CPR'_3)(SnRCl_2)]$ (2; R = Ph or Bu; X = OEt or Ph; R′ = Cy or ^iPr). An X-ray structure analysis of $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$ (3a) showed that both sulphur ligands chelate molybdenum. Additionally, one sulphur atom of the S_2CPR_3 group is within bonding distance of the tin atom, and thus bridges molybdenum and tin.

Key words: Molybdenum; Tin; Dithiophosphate; Dithioformate

1. Introduction

In recent papers [1–3], we have shown that the reactivity of bis(acetonitrile) complexes $[Mo(CO)_3(NCMe)_2(SnRCl_2)Cl]$ (1) in substitution reactions depends markedly on the entering ligands, giving rise to different families of complexes, some of them with unusual features. For example, the reaction of 1 with tetramethylthiourea (TMTU), affords tricarbonyls $[Mo(CO)_3(TMTU)_2(SnRCl_2)Cl]$ through replacement of the two labile acetonitriles [2]. When 1 reacts with phosphites (even in less than stoichiometric amount) a carbonyl group is also displaced, to give bis(carbonyl)tris(phosphite) complexes $[Mo(CO)_2\{P(OMe)_3\}_3(SnRCl_2)Cl]$ [1,2]. Anionic sulphur donors such as diethyldithiophosphate or diphenyldithiophosphinate replace one nitrile and the chloride from the molybdenum atom, to give tricarbonyls $[Mo(CO)_3(S_2PX_2)(NCMe)(SnRCl_2)]$ (2; X = OEt or Ph) [3]. These react further with an excess of phosphite, affording bis(carbonyl)bis(phosphite) complexes $[Mo(CO)_2\{P(OMe)_3\}_2(S_2PX_2)(SnRCl_2)]$. An X-Ray analysis of one derivative (X = OEt; R = Bu), showed that one of the sulphur atoms of the dithiophosphate bridges the two metals [3]. In all these reactions, the Mo–Sn bond is maintained. In contrast, upon treatment with the zwitterionic phosphoniodithioformate S_2CPR_3, complex 1 underwent an incomplete reductive elimination of $SnBuCl_3$, to give $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)(SnBuCl_2)]$ [4]. In this complex, the two metal atoms are not directly bonded but held together by a S_2CPR_3 which acts as $\eta^2(S,S')$ chelate towards tin, and as $\eta^3(S,C,S)$ pseudoallyl towards molybdenum. Additionally, one chlorine atom also bridges, forming a normal bond to molybdenum, and a weaker bond to tin. As has been noted before [1,2], 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 [5–7]. Because S_2CPR_3 forms different types of bridges between metal atoms [4,8–17], we have undertaken the study of the reactions of $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$ (2) with S_2CPR_3.

2. Results and discussion

Reaction of $[Mo(CO)_3(NCMe)(S_2PX_2)(SnRCl_2)]$ (**2a–2c** in Scheme 1) [3] with $S_2CPR'_3$ in dichlorometh-

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TABLE 1. Spectroscopic data for the new complexes

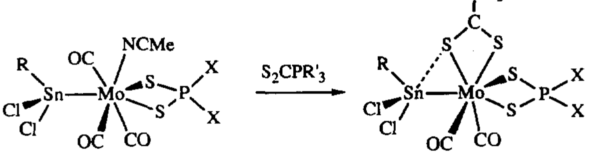
Compound	IR (CH_2Cl_2) ν(CO), cm^{-1}	$^{31}P\{^1H\}$ NMR [a], $CDCl_3$, δ(ppm)	
		S_2CP [a]	S_2P [a]
3a $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$	1948s, 1886vs	24.2(25)	100.3(92)
3b $[Mo(CO)_2(S_2PPh_2)(S_2CPCy_3)(SnPhCl_2)]$	1946s, 1884vs	24.1(23)	87.3(76)
3c $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CP^iPr_3)(SnPhCl_2)]$	1949s, 1888vs	38.6(22)	102.0(82)
3d $[Mo(CO)_2(S_2PPh_2)(S_2CP^iPr_3)(SnPhCl_2)]$	1947s, 1887vs	32.9 [b]	94.4 [b]
3e $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnBuCl_2)]$	1945s, 1881vs	23.6(20)	100.4(99)

[a] J(P–Sn), in Hz, are given in parentheses. [b] Due to the low solubility of complex **3d**, satellites due to the coupling with Sn were not observed.

ane affords new complexes $[Mo(CO)_2(S_2PX_2)(S_2CPR_3)(SnRCl_2)]$ (**3a–3d**, see Scheme). Upon addition of hexane to the filtered solutions, the products were obtained as green, crystalline solids which were fully characterized by analytical and spectroscopic methods (Table 1). Complexes **3a–3e** are only sparingly soluble in CH_2Cl_2, so that it was not possible to obtain ^{13}C NMR data. It is remarkable that the complexes containing diethyldithiophosphate and $SnPhCl_2$ are obtained in reasonably good yields (60% and 54%, respectively), whereas the yields of those containing diphenyldithiophosphinate (**3b** and **3d**) or $SnBuCl_2$ (**3e**) are significantly lower (15–20%).

An X-ray diffraction analysis was carried out on a crystal of $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$ (**3a**). Crystal data, and refinement details are summarized in Table 2. Atomic coordinates are in Table 3, and selected bond lengths and angles in Table 4. Figure 1 shows a schematic view of the molecule of **3a**, with the atom numbering. The molybdenum atom is seven-coordinate surrounded by two carbon, four sulphur, and one tin atoms. The geometry is a severely distorted capped octahedron, with the tin atom in the apical position. The distortion from the ideal geometry is due to the different spatial requirements of the ligands, and the restrictions imposed by the small bite angles of both sulphur donors [S(1)–Mo–S(2) 68.5(1)° and S(3)–Mo–S(4) 76.9(1)°]. The Mo–Sn distance of 2.691(1) Å is well within the range expected for a covalent bond between these metal atoms, being slightly shorter than those found in related dicarbonyl compounds, such as 2.774(1) Å in $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$ [2], or 2.709(1) Å in $[Mo(CO)_2\{P(OMe)_3\}_2\{S_2P(OEt)_2\}(SnBuCl_2)]$ [3].

The most interesting feature of the structure of **3a** is the short Sn–S(1) distance of 2.999(2) Å, which is indicative of a bonding interaction between the two atoms. In fact, a very wide range of distances (*i.e.* 2.5 to 3.9 Å [18]) has been observed for dative S → Sn bonds. In compound **3a**, and in its analogues **3b–3e**, the S_2CPR_3 ligand acts as a bridge, being chelating (*S,S'*) to molybdenum but monodentate (*S*) with tin.



	R	X
2a	Ph	OEt
2b	Ph	Ph
2c	Bu	OEt

	R	X	R'
3a	Ph	OEt	Cy
3b	Ph	Ph	Cy
3c	Ph	OEt	*i*-Pr
3d	Ph	Ph	*i*-Pr
3e	Bu	OEt	Cy

Scheme 1.

TABLE 2. Crystallographic Data for $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$ (**3a**)

formula	$C_{31}H_{48}Cl_2MoO_4P_2S_4Sn \cdot CH_2Cl_2$
fw	1045.37
crystal system	monoclinic
space group	$P2_1/n$
a, Å	15.479(3)
b, Å	16.718(2)
c, Å	17.156(4)
β, deg	95.56(2)
V, Å³	4419(1)
Z	4
T, K	293
ρ_{calc}, g cm^{-3}	1.57
F(000)	2112
λ (Mo Kα), Å	0.71073
crystal size, mm; colour	0.23×0.16×0.16, green
μ, cm^{-1}	13.74
method of collection	$\omega/2\theta$ scan
scan range, deg	$0 \le \theta \le 25$
no. of reflections measured	8335
no. of reflections observed, $I \ge 3\sigma(I)$	4144
absorption correction	empirical (psi-scan)
correction factors (min, max)	0.958, 1.00
no. of parameters	434
data to parameters ratio	9.55
weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
g	0.0007
residuals *R*, R_w	0.039, 0.039

Consistent with this coordination around tin is a distorted trigonal bipyramid, with S(1) and Cl(1) in the apical positions [S(1)–Sn–Cl(1) = 167.1(1)°]. The tin atom is 0.618(1) Å away from the equatorial plane defined by Cl(2), C(4) and Mo, which are bent towards S(1). The bridging of S_2CPR_3 in **3a**, which had not been observed before, resembles that found in [Mo(CO)$_2${P(OMe)$_3$}$_2${S$_2$P(OEt)$_2$}(SnBuCl$_2$)], where a

TABLE 3. Atomic coordinates for non-hydrogen atoms in [Mo(CO)$_2${S$_2$P(OEt)$_2$}(S$_2$CPCy$_3$)(SnPhCl$_2$)] (**3a**)

Atom	*x*	*y*	*z*
Mo	0.43675(4)	0.14969(4)	0.13173(4)
Sn	0.27537(3)	0.21126(3)	0.11823(3)
C(4)	0.2440(5)	0.3307(4)	0.1463(4)
C(5)	0.3064(6)	0.3779(5)	0.1884(6)
C(6)	0.2843(8)	0.4545(6)	0.2114(7)
C(7)	0.2020(8)	0.4831(6)	0.1934(7)
C(8)	0.1400(7)	0.4362(7)	0.1572(9)
C(9)	0.1611(6)	0.3598(6)	0.1321(7)
Cl(1)	0.1700(1)	0.1434(1)	0.1880(1)
Cl(2)	0.2021(2)	0.1969(2)	−0.0094(1)
C(2)	0.3540(5)	0.0611(4)	0.1014(5)
O(2)	0.3115(4)	0.0065(3)	0.0849(4)
C(3)	0.4100(5)	0.1727(4)	0.2392(5)
O(3)	0.3963(4)	0.1847(4)	0.3022(3)
S(1)	0.4357(1)	0.2770(1)	0.0566(1)
S(2)	0.4783(1)	0.1272(1)	−0.0057(1)
C(1)	0.4682(4)	0.2267(4)	−0.0193(4)
P(1)	0.4922(1)	0.2739(1)	−0.1098(1)
C(11)	0.4605(5)	0.3784(4)	−0.1048(4)
C(12)	0.3602(5)	0.3932(5)	−0.1081(5)
C(13)	0.3465(6)	0.4819(5)	−0.0871(6)
C(14)	0.3862(6)	0.5371(5)	−0.1439(6)
C(15)	0.4828(6)	0.5200(5)	−0.1450(6)
C(16)	0.4996(6)	0.4324(5)	−0.1645(5)
C(21)	0.6090(4)	0.2729(4)	−0.1141(4)
C(22)	0.6557(5)	0.3189(5)	−0.0451(4)
C(23)	0.7524(5)	0.3226(6)	−0.0513(5)
C(24)	0.7904(6)	0.2395(6)	−0.0545(5)
C(25)	0.7464(5)	0.1928(6)	−0.1224(6)
C(26)	0.6481(5)	0.1880(5)	−0.1177(6)
C(31)	0.4384(5)	0.2153(5)	−0.1897(4)
C(32)	0.4564(6)	0.2450(6)	−0.2714(5)
C(33)	0.4158(7)	0.1876(7)	−0.3336(5)
C(34)	0.3199(6)	0.1769(7)	−0.3279(6)
C(35)	0.3007(6)	0.1505(6)	−0.2481(5)
C(36)	0.3399(5)	0.2054(5)	−0.1853(5)
S(3)	0.5888(1)	0.2068(1)	0.1766(1)
S(4)	0.5197(1)	0.0270(1)	0.1890(1)
P(2)	0.6207(1)	0.0990(1)	0.2188(1)
O(41)	0.6533(4)	0.0969(4)	0.3087(3)
C(42)	0.6047(8)	0.1295(9)	0.3670(7)
C(43)	0.585(1)	0.073(1)	0.421(1)
O(51)	0.7076(3)	0.0668(4)	0.1906(3)
C(52)	0.7138(6)	0.0508(8)	0.1074(6)
C(53)	0.8049(7)	0.0347(9)	0.0961(7)
C(80)	0.0039(8)	0.1020(9)	0.9202(9)
Cl(81)	0.0323(3)	0.1489(3)	0.8337(3)
Cl(82)	−0.0516(3)	0.0152(3)	0.8952(3)

TABLE 4. Selected distances (Å) and angles (deg) for [Mo(CO)$_2${S$_2$P(OEt)$_2$}(S$_2$CPCy$_3$)(SnPhCl$_2$)] (**3a**)

Mo–Sn	2.691(1)	Mo–C(2)	1.994(8)
Mo–C(3)	1.967(8)	Mo–S(1)	2.488(2)
Mo–S(2)	2.531(2)	Mo–S(3)	2.588(2)
Mo–S(4)	2.564(2)	Sn–C(4)	2.121(7)
Sn–Cl(1)	2.399(2)	Sn–Cl(2)	2.378(2)
Sn–S(1)	2.999(2)	C(2)–O(2)	1.144(8)
C(3)–O(3)	1.140(9)	S(1)–C(1)	1.669(7)
S(2)–C(1)	1.684(7)	C(1)–P(1)	1.812(7)
P(1)–C(11)	1.818(7)	P(1)–C(21)	1.817(7)
P(1)–C(31)	1.821(7)	S(3)–P(2)	1.986(3)
S(4)–P(2)	2.000(3)	P(2)–O(41)	1.575(6)
P(2)–O(51)	1.568(6)		
C(2)–Mo–Sn	72.2(2)	C(3)–Mo–Sn	74.2(2)
C(3)–Mo–C(2)	101.7(3)	S(1)–Mo–Sn	70.64(6)
S(1)–Mo–C(2)	121.9(2)	S(1)–Mo–C(3)	109.1(2)
S(2)–Mo–Sn	107.1(1)	S(2)–Mo–C(2)	82.0(2)
S(2)–Mo–C(3)	176.3(2)	S(2)–Mo–S(1)	68.5(1)
S(3)–Mo–Sn	134.0(1)	S(3)–Mo–C(2)	153.5(2)
S(3)–Mo–C(3)	85.2(2)	S(3)–Mo–S(1)	78.4(1)
S(3)–Mo–S(2)	91.5(1)	S(4)–Mo–Sn	139.9(1)
S(4)–Mo–C(2)	78.0(2)	S(4)–Mo–C(3)	86.6(2)
S(4)–Mo–S(1)	149.4(1)	S(4)–Mo–S(2)	94.3(1)
S(4)–Mo–S(3)	76.9(1)	C(4)–Sn–Mo	124.8(2)
Cl(1)–Sn–Mo	116.5(1)	Cl(1)–Sn–C(4)	98.6(2)
Cl(2)–Sn–Mo	113.4(1)	Cl(2)–Sn–C(4)	101.8(2)
Cl(2)–Sn–Cl(1)	97.2(1)	S(1)–Sn–Mo	51.53(6)
S(1)–Sn–C(4)	87.1(2)	S(1)–Sn–Cl(1)	167.1(1)
S(1)–Sn–Cl(2)	92.9(1)	O(2)–C(2)–Mo	174.9(6)
O(3)–C(3)–Mo	178.1(7)	Sn–S(1)–Mo	57.9(1)
C(1)–S(1)–Mo	89.1(2)	C(1)–S(1)–Sn	114.3(2)
C(1)–S(2)–Mo	87.4(2)	S(2)–C(1)–S(1)	114.9(4)
P(1)–C(1)–S(1)	123.4(4)	P(1)–C(1)–S(2)	121.7(4)
P(2)–S(3)–Mo	87.7(1)	P(2)–S(4)–Mo	88.1(1)

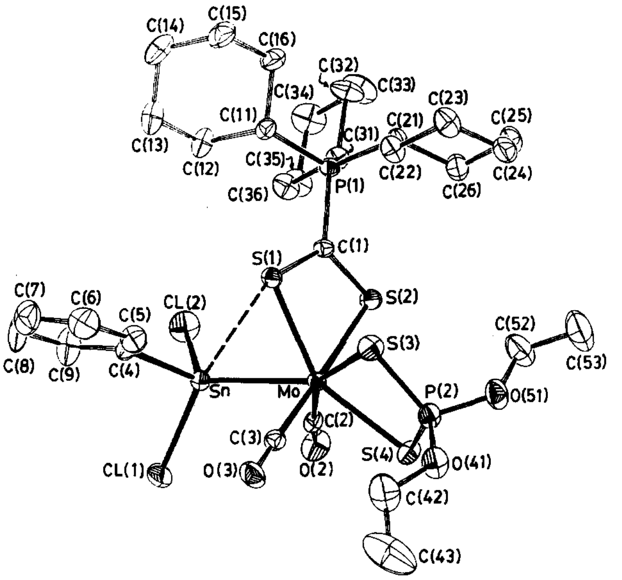


Fig. 1. Perspective view (EUCLID [23]) of the molecule of [Mo(CO)$_2${S$_2$P(OEt)$_2$}(S$_2$CPCy$_3$)(SnPhCl$_2$)] (**3a**) showing the atom numbering scheme.

bridging dithiophosphate chelates Mo and is monodentate [Sn–S = 3.06 (1) Å] to the tin atom [3]. In complex **3a–3e**, the neutral S_2CPR_3 [and not the anionic $S_2P(OEt)_2$] is involved in the bridging situation. The only precedent of a S_2CPR_3 bonded to tin is in complexes $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)(SnBuCl_2)]$ [4], where the S_2CPR_3 bridge is $\eta^3(S,C,S')$ towards molybdenum, and as $\eta^2(S,S')$ towards tin [with distances Sn–S of 2.720(4) and 2.538(4) Å], and there is no direct metal–metal bond.

3. Experimental section

All reactions were carried out in dry solvents under dinitrogen. $Na[S_2PPh_2]$ was prepared according to literature procedures [19]. Other starting materials and donors were purchased and used without purification. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrometer. ^1H NMR [300.1 MHz, δ ppm) from internal $Si(Me)_4$], and $^{31}P\{^1H\}$ NMR (121.5 MHz, δ (ppm) to higher frequencies from external 85% H_3PO_4) were recorded in $CDCl_3$ solutions, on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240 B analyser.

3.1. $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$ (3a)

To a solution of $[Mo(CO)_3(NCMe)\{S_2P(OEt)_2\}(SnPhCl_2)]$ (**2a**) (0.20 g, 0.30 mmol) [3] in CH_2Cl_2 (20 ml) was added S_2CPCy_3 (0.11 g, 0.30 mmol), and the mixture was stirred for 10 min. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 10 ml). The extracts were filtered through Celite. Addition of hexane (20 ml) afforded **2a** as a green solid which was recrystallized twice from CH_2Cl_2/hexane, giving green crystals. Yield 0.17 g, 60%. Analysis. Found: C, 37.1; H, 4.8. $C_{31}H_{48}Cl_2MoO_4P_2S_4Sn.\ CH_2Cl_2$ calc. C, 36.8; H, 4.8% ^1H NMR ($CDCl_3$) δ (ppm) 7.72 [m, 2H, C_6H_5], 7.43 [m, 3H, C_6H_5], 4.21 [m, 4H, $S_2P(OCH_2CH_3)_2$], 2.99 [m, 3H, CH of Cy], 1.81–1.30 [m, 30 H, CH_2 of Cy], 1.36 [t (7 Hz), 6 H, $S_2P(OCH_2CH_3)_2$].

3.1.1. Crystal and refinement data for compound 3a

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 **3a** in CH_2Cl_2 at −20°C. Data were collected on an Enraf-Nonius CAD4 diffractometer, using the $\omega - 2\theta$ scan technique. Mo, Sn, S, and P atoms were located from a Patterson synthesis, and the remaining non-H atoms by DIRDIF [20]. Full-matrix least-squares refinement was made with SHELX76 [21]. After isotropic refinement, an empirical absorption correction was applied with DIFABS [22]. All hydrogen atoms were geometrically positioned. Those on the molecule of **3a** were given a common isotropic factor which was refined. The hydrogen atoms of the CH_2Cl_2 molecule were given a fixed isotropic factor of 0.12 $Å^2$. Full lists of atomic parameters, bond lengths and angles, and anisotropic thermal parameters are available from the Cambridge Crystallographic Data Centre.

3.2. $[Mo(CO)_2(S_2PPh_2)(S_2CPCy_3)(SnPhCl_2)]$ (3b)

Compound **3b** was prepared as described for **3a** above, from $[Mo(CO)_3(NCMe)(S_2PPh_2)(SnPhCl_2)]$ (**2b**) (0.26 g, 0.35 mmol) [3] and S_2CPCy_3 (0.13 g, 0.35 mmol). Yield 0.07 g, 20%. Analysis. Found: C, 43.5; H, 4.7. $C_{39}H_{48}Cl_2MoO_2P_2S_4Sn.CH_2Cl_2$ calc. C, 43.3; H, 4.5% ^1H NMR ($CDCl_3$) δ(ppm) 7.79–7.26 [m, 15H, SnC_6H_5 and $S_2P(C_6H_5)_2$], 2.69 [m, 3H, CH of Cy], 1.88–1.27 [m, 30H, CH_2 of Cy].

3.3. $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CP^iPr_3)(SnPhCl_2)]$ (3c)

Compound **3c** was prepared as described for **3a** above, from **2a** (0.24 g, 0.35 mmol) [3], P^iPr_3 (63 μl, 0.39 mmol), and CS_2 (1 ml, excess) in CH_2Cl_2 (20 ml). Yield 0.16 g, 54%. Analysis. Found: C, 29.5; H, 3.8. $C_{22}H_{36}Cl_2MoO_4P_2S_4Sn.CH_2Cl_2$ calc. C, 29.9; H, 4.1% ^1H NMR ($CDCl_3$) δ(ppm) 8.07–7.39 [m, 5H, SnC_6H_5], 4.17 [m, 4H, $P(OCH_2)$], 3.33 [m, 3H, CH of ^{i}Pr], 1.49 [m, 18H, CH_3 of ^{i}Pr].

3.4. $[Mo(CO)_2(S_2PPh_2)(S_2CP^iPr_3)(SnPhCl_2)]$ (3d)

A mixture of **2b** (0.18 g, 0.24 mmol) [3], P^iPr_3 (43 μl, 0.27 mmol), and CS_2 (1 ml, excess) was stirred in CH_2Cl_2 (20 ml) for 15 min. Compound **3d** precipitated as a green solid, which was washed with a mixture of CH_2Cl_2/hexane (1 : 1, 3 × 5 ml). Yield 0.04 g, 15%. Analysis. Found: C, 37.1; H, 3.9. $C_{30}H_{36}Cl_2MoO_2P_2S_4Sn.CH_2Cl_2$ calc. C, 37.6; H, 3.9% ^1H NMR ($CDCl_3$) δ (ppm) 7.79–7.26 [m, 15H, SnC_6H_5 and $S_2P(C_6H_5)_2$], 2.90 [m, 3H, CH of ^{i}Pr], 1.28 [m, 18H, CH_3 of ^{i}Pr].

3.5. $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnBuCl_2)]$ (3e)

To a solution of $[Mo(CO)_3(NCMe)\{S_2P(OEt)_2\}(SnBuCl_2)]$ (**2c**) (0.30 g, 0.46 mmol) [3] in CH_2Cl_2 (20 ml) was added S_2CPCy_3 (0.16 g, 0.46 mmol), and the mixture was stirred for 2 h. The workup, as described above for **3a**, gave compound **3e** as green crystals. Yield 0.09 g, 20%. Analysis. Found: C, 35.5; H, 5.4. $C_{29}H_{52}Cl_2MoO_4P_2S_4Sn.CH_2Cl_2$ calc. C, 35.1; H, 5.4% ^1H NMR ($CDCl_3$) δ (ppm) 4.16 [m, 4H, $S_2P(OCH_2CH_3)_2$], 2.78 [m, 3H, CH of Cy], 1.96–1.35 [m, 42H, 15 × CH_2 of Cy, 3 × CH_2 of ^{n}Bu, and $S_2P(OCH_2CH_3)_2$], 0.93 [t (7 Hz), 3 H, CH_3 of ^{n}Bu].

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