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Seven-coordinate molybdenum–tin and tungsten–tin complexes containing phosphites and tetramethylthiourea: X-ray structure of $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$

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Abstract

$[M(CO)_3(nitrile)_3]$ react with $SnRCl_3$ (R = Bu or Ph) to produce $[M(CO)_3(nitrile)_2(SnRCl_2)Cl]$ (1; M = Mo, nitrile = NCMe; M = W, nitrile = NCEt). These complexes react further with three equivalents of phosphite $P(OR')_3$ (R' = Me or Et) at room temperature giving dicarbonyl tris(phosphite) complexes $[M(CO)_2\{P(OR')_3\}_3/(SnRCl_2)Cl]$ (2; M = Mo or W; R = Bu or Ph; R' = Me or Et) through displacement of the two nitriles and one CO. The dicarbonyl tris(phosphite) complexes are produced even when only two equivalents of phosphite are added to the reaction mixture. In contrast, when the tricarbonyl bis(nitrile) compounds 1 react with an excess of tretramethylthiourea (TMTU), only the two nitriles are replaced, leading to tricarbonyls $[M(CO)_3(TMTU)_2(SnRCl_2)Cl]$ (3, M = Mo or W; R = Bu or Ph).

1. Introduction

There has been a resurgant interest in recent times in the chemistry of seven-coordinate complexes of Mo and W, mainly due to their involvement in catalytic processes such as the ring-opening polymerization of norbornene [1] or the hydrostannation of alkenes [2].

Very recently, Baker and co-workers reported the oxidation of $[M(CO)_3(NCMe)_3]$ with $SnCl_4$ to give seven-coordinate bis(nitrile) complexes $[M(CO)_3(NCMe)_2(SnCl_3)Cl]$ in which the labile acetonitrile groups can be easily replaced by other ligands [3–5]. This method opened the way to the preparation of seven-coordinate complexes of Mo or W which were not available by other routes. In fact, oxidative addition reactions of halotin(IV) derivatives to M^0 (M = Mo or W) complexes to give seven-coordinate M^{II} compounds containing M–Sn bonds have been known for more than twenty years [6–14]. Usually, these reactions were performed by reacting SnR_nX_{4-n} with a substituted M^0 compound such as $[Mo(CO)_4(L-L)]$ or $[Mo(CO)_3(L-L)(PR'_3)]$ to give seven-coordinate $[M(CO)_3(L-L)(SnR_nX_{3-n})X]$ or $[Mo(CO)_2(L-L)(PR'_3)(SnR_nX_{3-n})X]$, where L–L are bidentate ligands containing nitrogen [6–11], phosphorus [12], or sulfur donors [13,14]. The range of compounds available by these reactions is limited by the fact that the ligands L–L and PR'_3 must have electronic properties enabling the starting M^0 compound to undergo oxidative addition, and the attempts to extend the range of compounds by displacement reactions on the $[M(CO)_3(L-L)(SnR_nX_{3-n})X]$ complexes by other ligands L' led in some cases to the reductive elimination of the SnR_nX_{4-n} group [10].

We have explored the reactions of $[M(CO)_3(nitrile)_3]$ with haloalkyltin derivatives SnR_nCl_{4-n} as a general route to seven-coordinate complexes of Mo and W containing haloalkylstannate, SnR_nCl_{3-n}, and we wish to report here a facile synthesis for dicarbonyl tris(phosphite) and tricarbonyl bis(tetramethylthiourea) * seven-coordinate complexes of Mo and W

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* Throughout this paper tetramethylthiourea = TMTU.

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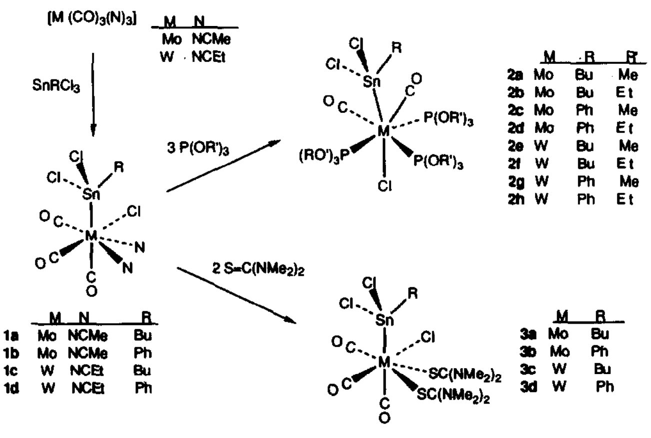

Scheme 1.

containing $SnRCl_2$, and the X-ray crystal structure of one of these derivatives. A preliminary account of part of this work has been published [15].

2. Results and discussion

$[M(CO)_3(nitrile)_3]$ reacts with $SnRCl_3$ (see Scheme 1) to give $[M(CO)_3(nitrile)_2(SnRCl_2)Cl]$ (**1a–1d** in Scheme 1) which can be obtained in virtually quantitative yields as yellow, air-sensitive solids upon evaporation of the solvent. IR spectra of **1a** and **1b** show ν(CO) and ν(CN) frequencies close to those reported for their analogues with $SnCl_3$ [3].

Treatment of **1a–1d** with three equivalents of phosphite leads to the formation in high yield of $[M(CO)_2\{P(OR')_3\}_3(SnRCl_2)Cl]$ (**2a–2h** in Scheme 1) which have been fully characterized by analytical (see experimental section) and spectroscopic methods (see Table 1).

An X-ray study was carried out on a crystal of **2a** to confirm the formulation proposed in Scheme 1. Crystal data, and refinement details are given in Table 2, atomic coordinates in Table 3, and selected bond lengths and angles in Table 4. The molybdenum atom lies in a seven-coordinate environment which can be best described as intermediate between a distorted capped trigonal prism, CTP, [with Cl(3) in the capping position], and a distorted capped octahedron, CO, [with either C(1) or Sn in the capping position]. Due to the different spatial requirements of the ligands, the angles around Mo(1) deviate from the values expected for the ideal CTP and CO geometries [16,17].

A common feature of the structures reported for related complexes such as $[Mo(CO)_3(bipy)(SnCH_3Cl_2)Cl]$ [8], $[W(CO)_3\{CH_3S(CH_2)_2SCH_3\}(SnCH_3Cl_2)Cl]$ [13] and $[Mo(CO)_3\{CH_3S(CH_2)_2SCH_3\}(SnCl_3)Cl]$ [14], is the presence of a chlorine atom bridging the Mo–Sn (or W–Sn) bond. In contrast, in the structure of **2a**, the chlorine atom bonded to Mo is very far from the Sn atom; Sn, Mo, and Cl(3) form a nearly *trans* arrangement [angle 142.0(1)°]. On the other hand, the carbon atom of one carbonyl ligand, C(1), is near the tin. The distance C(1)...Sn of 2.646(13) Å is too long for any significant bonding, but is short enough to be considered as a contact. Accordingly, although the linear geometry of the carbonyl ligand is not altered [angle Mo–C(1)–O(1) of 173.7(12)°], the tetrahedral coordination around the tin atom is somewhat distorted to accomodate the C(1) atom. However, this arrangement may be induced by packing requirements rather than by electronic effects.

The $^{31}P\{^1H\}$ NMR spectra of all dicarbonyls **2a–2h** (see Table 2) show only one signal, instead of three different signals expected for the three non-equivalent phosphorus atoms in the structure of **2a**. This reveals the existence of fluxional processes in solution at room temperature. The spectra of the molybdenum compounds **2a–2d**, at 295 K, exhibit one set of Sn satellites (approximate relative intensities 1:10:1), the different couplings $^{31}P–^{117}Sn$ and $^{31}P–^{119}Sn$ being unresolved. For the tungsten compounds **2e–2h** the behaviour is different, depending on the substituent R attached to the tin atom. Thus, for the butyldichlorostannyl derivatives, **2e** and **2f**, only one set of broad satellites was observed, instead of the expected two (one for $^{31}P–^{117-119}Sn$ and other for $^{31}P–^{183}W$); this suggests that the coupling constants have about the same value, the observed satellites therefore being the envelope of the two expected sets. The relative intensities of the signals are consistent with this assignment. In contrast, for the phenyldichlorostannyl complexes, **2g** and **2h**, the two sets of satellites are resolved, thus enabling the assignment of the values of the coupling constants J(P–Sn) and J(P–W).

$^{31}P\{^1H\}$ NMR spectra recorded for **2a**, **2c** and **2e** at −98°C in CD_2Cl_2 exhibit very complex patterns of lines, suggesting that the freezing of the dynamic process leads to more than one isomer at low temperature.

Additionally, when different amounts of free $P(OMe)_3$ are added to a solution of **2a**, the ^{31}P NMR spectra show no displacement of the signals of the compound or of the free phosphite. This is a proof that there is not a dissociation equilibrium of the phosphite ligands in dicarbonyls **2a–2h**. Therefore, the dynamic process which makes the phosphites equivalent in the ^{31}P NMR spectra must consist of an intramolecular concerted motion of the three phosphites.

Since heating $[Mo(CO)_6]$ and $SnRCl_3$ in acetonitrile gives the bis(nitrile) **1a** and **1b**, and the presence of excess acetonitrile does not affect the formation of the dicarbonyls **2a–2d**, these can be prepared in a one-pot

TABLE 1. Spectroscopic data for the new complexes

Compound	IR (CH_2Cl_2), $\nu(CO)$ (cm^{-1})	^1H NMR, $CDCl_3$, δ(ppm)	$^{31}P\{^1H\}$NMR, $CDCl_3$		
			δ(ppm)	J(P–Sn) [a]	J(P–W) [a]
2a $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$	1967m, 1885s	3.81 [m, 27 H, $P(OCH_3)_3$], 1.87, 1.84, and 1.43[m,(2+2+2)H, 3×CH_2 of ^{n}-Bu], 0.94[t, J(H–H) 7Hz, 3H, CH_3 of ^{n}-Bu]	144.1	373	
2b $[Mo(CO)_2\{P(OEt)_3\}_3SnBuCl_2)Cl]$	1961m, 1883s	4.18 [m, 18H, $POCH_2$], 1.90, 1.84, and 1.43 [m, (2+2+2) H, 3×CH_2 of ^{n}-Bu], 1.31 [t, J(H–H) 7Hz, 27 H, $POCH_2CH_3$], 0.93 [t, J(H–H) 7Hz, 3H, CH_3 of ^{n}Bu]	139.6	409	
2c $[Mo(CO)_2\{P(OMe)_3\}_3(SnPhCl_2)Cl]$	1969m, 1890s	7.80 and 7.134 [m, C_6H_5], 3.71 [m, 27 H, $P(OCH_3)_3$]	143.0	422	
2d $[Mo(CO)_2\{P(OEt)_3\}_3(SnPhCl_2)Cl]$	1964m, 1887s	7.91 and 7.34 [m, C_6H_5], 4.17 [m, 18H, $POCH_2$], 1.24 [t, J(H–H) 7Hz, 27 H, $POCH_2CH_3$]	138.0	453	
2e $[W(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$	1954m, 1878s	3.82[m, 27 H, $P(OCH_3)_3$], 1.85, 1.79, and 1.42[m, (2+2+2) H, 3×CH_2 of ^{n}Bu], 0.93[t, J(H–H) 7 Hz, 3H, CH_3 of ^{n}Bu]	123.0	330 [b]	330 [b]
2f $[W(CO)_2\{P(OEt)_3\}_3(SnBuCl_2)Cl]$	1950m, 1873s	4.17 [m, 18H, $POCH_2$], 1.80, 1.77, and 1.42 [m, (2+2+2) H, 3×CH_2 of ^{n}Bu], 1.31 [t, J(H–H) 7Hz, 27 H, $POCH_2CH_3$], 0.92 [t, J(H-H) 7 Hz, 3H, CH_3 of ^{n}Bu]	119.4	327 [b]	327 [b]
2g $[W(CO)_2\{P(OMe)_3\}_3(SnPhCl_2)Cl]$	1958m, 1880s	7.69 and 7.46 [m, C_6H_5], 3.83 [t, J(P–H) 6 Hz, 27H $P(OCH_3)_3$]	121.9	360	327
2h $[W(CO)_2\{P(OEt)_3\}_3(SnPhCl_2)Cl]$	1950m, 1876s	7.86 and 7.34 [m, C_6H_5], 4.16 (m, 18H, $POCH_2$], 1.23 [t, J(H–H) 7 Hz, 27 H, $POCH_2CH_3$],	117.5	377	322
3a $[Mo(CO)_3(TMTU)_2(SnBuCl_2)Cl]$	1986s, 1895s, 1885s	3.23 [s, 24 H, CH_3 of TMTU], 2.03, 1.86, and 1.40 [m, (2+2+2) H, 3×CH_2 of ^{n}Bu], 0.86 [t, J(H–H) 6Hz, 3H, CH_3 of ^{n}Bu]			
3b $[Mo(CO)_3(TMTU)_2(SnPhCl_2)Cl]$	1989s, 1902s, 1893s	8.10 and 7.40 [m, C_6H_5], 3.27 [s, 24 H, CH_3 of TMTU]			
3c $[W(CO)_3(TMTU)_2(SnBuCl_2)Cl]$	1978s, 1887s, 1872s	3.31 [s, 24 H, CH_3 of TMTU], 2.11, 1.92, and 1.44 [m, (2+2+2) H, 3×CH_2 of ^{n}Bu,], 0.93 [t, J(H–H) 6Hz, 3H, CH_3 of ^{n}Bu]			
3d $[W(CO)_3(TMU)_2(SnPhCl_2)Cl]$	1981s, 1890s, 1879s	8.05 and 7.40 [m, C_6H_5], 3.26 [s, 24 H, CH_3 of TMTU]			

[a] Coupling constants in Hz. [b] J(P–Sn) and J(P–W) have about the same value; see text.

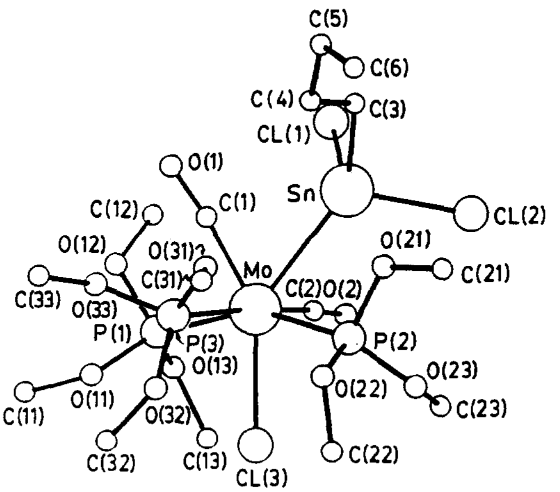

Fig. 1. Perspective view of [Mo(CO)$_2${P(OMe)$_3$}$_3$ (SnBuCl$_2$) Cl] (**2a**) showing the atom numbering.

two-step manner, without isolating the intermediate bis(nitrile) complexes. In contrast, when [W(CO)$_6$] was heated with SnBuCl$_3$ in refluxing propionitrile for a long time, the IR spectra of the reaction mixture showed only the bands of tungsten carbonyl, without any significant amount of the expected bis(nitrile) **1b**, or the intermediate [W(CO)$_3$(NCEt)$_3$] [18].

TABLE 2. Crystallographic data for [Mo(CO$_2${P(OMe)$_3$}$_3$(SnBuCl$_2$)-(Cl)] (**2a**)

Formula	$C_{15}H_{36}Cl_3MoO_{11}P_3Sn$
FW	806.35
Crystal color, size (mm)	pale yellow, 0.3×0.1×0.1
Crystal system	monoclinic
Space group	$P\,2_1/c$
a (Å)	14.714(5)
b (Å)	9.931(6)
c (Å)	21.646(7)
β (°)	91.12(5)
V (Å^3)	3162(3)
Z	4
T (K)	293
ρ_{calc} (g cm^{-3})	1.69
F(0 0 0)	1608
λ (Mo Kα) (Å)	0.71073
μ (cm^{-1})	16.28
Method of collection	$\omega/2\theta$ scan
Scan range (°)	$0 \le \theta \le 25$
Drift corrections (min/max)	1.00, 2.43
No. of reflections measured	5520
No. of reflections observed, $I \ge 3\sigma(I)$	1951
Absorption correction	empirical (psi-scan)
Correction factors (min, max)	0.703, 0.991
No. of parameters	308
Data to parameters ratio	6.33
Weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$
g	0.0001
Residuals R, R_w	0.040, 0.035

TABLE 3. Atomic coordinates for non-hydrogen atoms in [Mo(CO)$_2${P(OMe)$_3$}$_3$(SnBuCl$_2$)(Cl)] (**2a**)

Atom	x	y	z
Sn	0.33336(6)	0.1358(1)	0.19579(5)
CL(1)	0.2803(3)	−0.0679(4)	0.2438(2)
CL(2)	0.3762(2)	0.2390(4)	0.2916(2)
C(3)	0.461(1)	0.063(2)	0.1638(8)
C(4)	0.482(1)	0.073(2)	0.104(1)
C(5)	0.576(1)	0.038(3)	0.082(1)
C(6)	0.634(2)	0.146(3)	0.070(1)
Mo	0.19026(7)	0.2574(1)	0.13185(6)
CL(3)	0.1005(2)	0.4739(4)	0.1257(2)
C(1)	0.2233(8)	0.079(1)	0.1012(7)
O(1)	0.2376(6)	−0.023(1)	0.0786(4)
C(2)	0.1496(9)	0.227(2)	0.2195(7)
O(2)	0.1233(7)	0.214(1)	0.2687(5)
P(1)	0.0390(2)	0.1553(4)	0.1118(2)
O(11)	−0.0046(5)	0.2047(9)	0.0497(4)
C(11)	−0.0916(9)	0.155(2)	0.0259(7)
O(12)	0.0319(6)	−0.004(1)	0.1031(5)
C(12)	0.049(1)	−0.095(2)	0.1550(8)
O(13)	−0.0389(7)	0.164(1)	0.1621(5)
C(13)	−0.072(1)	0.292(2)	0.1864(8)
P(2)	0.3073(2)	0.4385(4)	0.1456(2)
O(21)	0.4068(5)	0.3760(9)	0.1536(4)
C(21)	0.4868(9)	0.462(2)	0.1648(7)
O(22)	0.3226(6)	0.5359(9)	0.0897(4)
C(22)	0.290(1)	0.672(1)	0.0847(8)
O(23)	0.2987(7)	0.543(1)	0.2002(5)
C(23)	0.245(1)	0.538(2)	0.2516(8)
P(3)	0.2259(2)	0.2969(4)	0.0191(2)
O(31)	0.3320(5)	0.2934(9)	0.0083(4)
C(31)	0.3835(9)	0.369(2)	−0.0340(7)
O(32)	0.1999(6)	0.4327(9)	−0.0170(4)
C(32)	0.108(1)	0.458(2)	−0.0352(8)
O(33)	0.1822(5)	0.1795(8)	−0.0226(4)
C(33)	0.1975(9)	0.170(2)	−0.0888(6)

Addition of only one or two equivalents of phosphite to compounds **1** produces the same dicarbonyl tris(phosphite) complexes **2**, together with unreacted **1**. This behaviour of complexes **1** in substitution reactions contrasts with that reported for their SnCl$_3$ analogues which, when treated with phosphorus donors, replace only the labile nitrile groups, giving tricarbonyl complexes. Thus, it has been reported that the reaction of [Mo(CO)$_3$(NCMe)$_2$(SnCl$_3$)Cl] with two equivalents of Ph$_2$P(CH$_2$)$_2$PPh$_2$ in acetone at room temperature for 24 h gave [Mo(CO)$_3$(dppe)(SnCl$_3$)Cl] and unchanged Ph$_2$P(CH$_2$)$_2$PPh$_2$ [3].

All this may suggest that the change of one Cl for an alkyl group at the tin atom increases the lability of one of the carbonyl ligands in the Mo atom. The behaviour is not general, however, since treatment of tricarbonyls **1a**–**1d** with two molar-equivalents of tetramethylthiourea (TMTU) at room temperature produces the tricarbonyls [Mo(CO)$_3${S=C(NMe$_2$)$_2$}$_2$(SnRCl$_2$)Cl] (**3a**–**3d**) in good yield. IR monitoring of the reaction mix-

TABLE 4. Selected distances (Å) and angles (°) for $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)(Cl)]$ (**2a**)

(a) Distances

Sn–Cl(1)	2.410(4)	Mo–P(2)	2.503(4)
Sn–Cl(2)	2.387(4)	Mo–P(3)	2.536(4)
Sn–C(3)	2.136(14)	C(1)–O(1)	1.151(13)
Sn–Mo	2.774(1)	C(2)–O(2)	1.146(15)
Sn...C(1)	2.646(13)	P(1)–1O(11)	1.557(9)
P(1)–O(12)	1.596(10)	P(1)–O(13)	1.599(11)
P(2)–O(21)	1.597(9)	P(2)–O(22)	1.569(9)
Mo–Cl(3)	2.525(4)	P(2)–O(23)	1.583(11)
Mo–C(1)	1.957(14)	P(3)–O(31)	1.584(8)
Mo–C(2)	2.024(16)	P(3)–O(32)	1.601(9)
Mo–P(1)	2.476(4)	P(3)–O(33)	1.602(9)

Distances O–C (methyl) in phosphite ligands range from 1.379(15) to 1.473(14)

(b) Angles

Cl(1)–Sn–Cl(2)	93.9(2)	C(1)–Mo–C(2)	105.2(6)
Cl(1)–Sn–C(3)	98.6(5)	Sn–Mo–P(1)	125.4(1)
Cl(2)–Sn–C(3)	102.0(5)	Cl(3)–Mo–P(1)	82.7(1)
Cl(1)–Sn–Mo	109.4(1)	C(1)–Mo–P(1)	78.4(4)
Cl(2)–Sn–Mo	115.6(1)	C(2)–Mo–P(1)	79.7(4)
C(3)–Sn–Mo	130.3(4)	Sn–Mo–P(2)	74.9(1)
Cl(3)–Mo–P(2)	75.7(1)	C(1)–Mo–P(2)	121.0(4)
C(2)–Mo–P(2)	102.2(4)	P(1)–Mo–P(2)	158.2(1)
Sn–Mo–P(3)	112.2(1)	Cl(3)–Mo–P(3)	86.3(1)
C(1)–Mo–P(3)	75.9(4)	Sn–Mo–Cl(3)	142.0(1)
C(2)–Mo–P(3)	174.7(4)	Sn–Mo–C(1)	65.4(4)
P(1)–Mo–P(3)	95.5(1)	Cl(3)–Mo–C(1)	152.4(4)
P(2)–Mo–P(3)	81.3(1)	Sn–Mo–C(2)	72.7(4)
Cl(3)–Mo–C(2)	90.7(4)		

ture showed no indication of displacement of CO to give dicarbonyls analogous to **2a**–**2h**, even when the reaction was conducted with three molar equivalents of TMTU in refluxing CH_2Cl_2 for 3 h. The structure depicted for complexes **3** in Scheme 1 must be considered as tentative on the grounds of the experimental data available. Most of the seven-coordinate complexes of Mo and W containing fragments "$M(CO)_3(SnXCl_2)$" (X=Cl or R) have been described in the literature as having a capped octahedron of ligands around the metal [3–5]. Such arrangement has been confirmed by several structure determinations of tricarbonyl complexes of formulae $[M(CO)_3(L\text{–}L)(SnXCl_2)Cl]$ [8,13,14]. As mentioned above, these complexes contain a bridging chlorine atom between M (Mo or W) and tin. Although the structure of compound **2a** presented in this work shows that the formation of a chlorine bridge is not general, the presence of such a bridge cannot be ruled out for complexes **3a**–**3d**.

3. Experimental section

All reactions were carried out in dry solvents under dinitrogen. Starting materials and ligands 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 spectra (121.5 MHz, δ(ppm) to higher frequencies from external 85% H_3PO_4) were recorded for $CDCl_3$ solutions on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240 B analyser.

3.1. $[Mo(CO)_3(NCMe)_2(SnBuCl_2)Cl]$ (*1a*)

A mixture of $[Mo(CO)_6]$ (0.2 g, 0.758 mmol) and $SnBuCl_3$ (0.127 cm^3, 0.758 mmol) in acetonitrile (20 cm^3) was heated at reflux temperature for 3 h. The solution changed from colourless to orange-yellow. Evaporation of the solvent gave **1a** as a yellow, air sensitive solid. The yield is virtually quantitative. IR (cm^{-1}, CH_2Cl_2 solution): ν(CO) 2014s, 1935(sh), 1916s; ν(CN) 2317w, 2290w. Satisfactory analyses could not be obtained for bis(nitrile) complexes **1a**–**1d** due to their instability and because the solids obtained tend to retain variable amounts of free nitrile, which could not be completely eliminated by prolonged pumping *in vacuo*.

3.2. $[Mo(CO)_3(NCMe)_2(SnPhCl_2)Cl]$ (*1b*)

The procedure was similar to that used for **1a**, starting from $[Mo(CO)_6]$ (0.2 g, 0.758 mmol) and $SnPhCl_3$ (0.124 cm^3, 0.758 mmol). IR (cm^{-1}, CH_2Cl_2 solution): ν(CO) 2017s, 1930(sh), 1920s; ν(CN) 2317w, 2290w.

3.3. $[W(CO)_3(NCEt)_2(SnBuCl_2)Cl]$ (*1c*)

To a solution of $[W(CO)_3(NCEt)_3]$ [18] (0.215g, 0.5 mmol) in CH_2Cl_2 (20 cm^3) was added $SnBuCl_3$ (0.083 cm^3, 0.5 mmol). The colour changed from yellow to orange. Evaporation of the solvent *in vacuo* gave **1c** as an air-sensitive solid. IR (cm^{-1}, CH_2Cl_2 solution): ν(CO) 2006s, 1915(sh), 1904s; ν(CN) 2320w, 2292w.

3.4. $[W(CO)_3(NCEt)_2(SnCl_2Ph)Cl]$ (*1d*)

Compound **1d** was prepared as described above for **1c**, from $[W(CO)_3(NCEt)_3]$ [18] (0.215 g, 0.5 mmol) and $SnCl_3Ph$ (0.082 cm^3, 0.5 mmol). IR (cm^{-1}, CH_2Cl_2 solution): ν(CO) 2009s, 1920(sh), 1909s; ν(CN) 2305w, 2288w.

3.5. $[Mo(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$ (*2a*)

To a solution containing *ca.* 0.75 mmol of **1a** in acetonitrile, prepared as described above, was added $P(OMe)_3$ (0.268 cm^3, 2.27 mmol). The mixture was stirred for 30 min. and then filtered. Evaporation of the solvent *in vacuo* gave yellow microcrystals of **2a** which were washed with hexane (2 × 5 cm^3) and dried *in vacuo*. Yield 0.562 g, 92%. Crystals suitable for

X-ray analysis were grown by slow diffusion of hexane into a concentrated solution of the compound in CH_2Cl_2 at −20°C. (Found: C, 22.08; H, 4.51. Calc. for $C_{15}H_{36}Cl_3MoO_{11}P_3Sn$: C, 22.34; H, 4.50).

*3.5.1. Crystal and refinement data for compound **2a***

Crystal data and relevant refinement details are collected in Table 2. Intensities were collected on an Enraf-Nonius CAD4 diffractometer, using the $\omega-2\theta$ scan technique. Profile analysis was applied for all reflections [19]. Drift, Lorentz, and polarization corrections were applied. Mo and Sn 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 non-H atoms were anisotropically refined. H atoms were geometrically positioned with a fixed overall isotropic factor of 0.08 Å^2.

3.6. $[Mo(CO)_2\{P(OEt)_3\}_3(SnBuCl_2)Cl]$ *(**2b**)*

The preparation was as described for **2a** from a solution of **1a** (0.75 mmol) and $P(OEt)_3$ (0.490 cm^3, 2.82 mmol). Yield 0.636 g, 90%. (Found: C, 30.53; H, 5.82. Calc. for $C_{24}H_{54}Cl_3MoO_{11}P_3Sn$: C, 30.91; H, 5.84).

3.7. $[Mo(CO)_2\{P(OMe)_3\}_3(SnPhCl_2)Cl]$ *(**2c**).*

2c was prepared as described for **2a** from a solution of **1b** (0.75 mmol) and $P(OMe)_3$ (0.268 cm^3, 2.27 mmol). Yield 0.57 g, 92%. (Found: C, 24.87; H, 3.84. Calc. for $C_{17}H_{32}Cl_3MoO_{11}P_3Sn$: C, 24.71; H, 3.90).

3.8. $[Mo(CO)_2\{P(OEt)_3\}_3(SnPhCl_2)Cl]$ *(**2d**)*

2d was prepared as described for **2a** from a solution of **1b** (0.75 mmol) and $P(OEt)_3$ (0.490 cm^3, 2.82 mmol). Yield 0.607 g, 85%. (Found: C, 32.49; H, 5.21. Calc. for $C_{26}H_{50}Cl_3MoO_{11}P_3Sn$: C, 32.78; H, 5.29).

3.9. $[W(CO)_2\{P(OMe)_3\}_3(SnBuCl_2)Cl]$ *(**2e**)*

To a solution of **1c** (*ca.* 0.5 mmol) in CH_2Cl_2 (20 cm^3) was added $P(OMe)_3$ (0.195 cm^3, 1.65 mmol). The mixture was stirred for 30 min and then filtered. Workup was as described for **2a**, giving pale yellow microcrystals of **2e**. Yield 0.331 g, 74%. (Found: C, 20.27; H, 3.95. Calc. for $C_{15}H_{36}Cl_3O_{11}P_3SnW$: C, 20.15; H, 4.06).

3.10. $[W(CO_2\{P(OEt)_3\}_3(SnBuCl_2)Cl]$ *(**2f**)*

The preparation was as described for **2e** from a solution of **1c** (0.5 mmol) and $P(OEt)_3$ (0.309 cm^3, 1.8 mmol). Yield 0.358 g, 70%. (Found: C, 27.94; H, 5.34. Calc. For $C_{24}H_{54}Cl_3O_{11}P_3SnW$: C, 28.25; H, 5.33).

3.11. $[W(CO)_2\{P(OMe)_3\}_3(SnPhCl_2)Cl]$ *(**2g**)*

Compound **2g** was prepared as described above for **2e** from a solution of **1d** (0.5 mmol) and $P(OMe)_3$ (0.195 cm^3, 1.65 mmol). Yield 0.393 g, 86%. (Found: C, 22.46; H, 3.30. Calc. for $C_{17}H_{32}Cl_3O_{11}P_3SnW$: C, 22.33; H, 3.53).

3.12. $[W(CO)_2\{P(OEt)_3\}_3(SnPhCl_2)Cl]$ *(**2h**)*

Compound **2h** was prepared as described above for **2e** from a solution of **1d** (0.5 mmol) and $P(OEt)_3$ (0.309 cm^3, 1.8 mmol). Yield 0.415 g, 80%. (Found: C, 30.12; H, 4.70. Calc. for $C_{26}H_{50}Cl_3O_{11}P_3SnW$: C, 30.01; H, 4.84).

3.13. $[Mo(CO)_3(TMTU)_2(SnBuCl_2)Cl]$ *(**3a**)*

To a solution of compound **1a** (1 mmol) in CH_2Cl_2 (20 cm^3) was added TMTU (0.265 g, 2 mmol). The mixture was stirred for 30 min and then filtered. Addition of hexane (20 cm^3) followed by slow concentration *in vacuo* gave **3a** as an air-sensitive yellow solid which was recrystallized from CH_2Cl_2/hexane. Yield 0.538 g, 74%. (Found: C, 27.85; H, 4.32; N, 7.57. Calc. for $C_{17}H_{33}Cl_3MoN_4O_3S_2Sn$: C, 28.10; H, 4.58; N, 7.71).

3.14. $[Mo(CO)_3(TMTU)_2(SnPhCl_2)Cl]$ *(**3b**)*

Compound **3b** was prepared as described for **3a** from **1b** (1 mmol) and TMTU (0.265 g, 2 mmol). Yield 0.612 g, 82%. (Found: C, 30.05; H, 3.84; N, 7.33. Calc. for $C_{19}H_{29}Cl_3MoN_4O_3S_2Sn$: C, 30.57; H, 3.91; N, 7.50).

3.15. $[W(CO)_3(TMTU)_2(SnBuCl_2)Cl]$ *(**3c**).*

Compound **3c** was prepared as described for **3a** from **1c** (0.5 mmol) and TMTU (0.132 g, 1 mmol). Yield 0.265 g, 65%. (Found: C, 24.78; H, 3.91; N, 6.65. Calc. for $C_{17}H_{33}Cl_3N_4O_3S_2SnW$: C, 25.07; H, 4.08; N, 6.88).

3.16. $[W(CO)_3(TMTU)_2(SnPhCl_2)Cl]$ *(**3d**)*

Compound **3d** was prepared as described for **3a** from **1c** (0.5 mmol) and TMTU (0.132 g, 1 mmol). Yield 0.317 g, 76%. (Found: C, 27.18; H, 3.45; N, 6.59. Calc. for $C_{19}H_{29}Cl_3N_4O_3S_2SnW$: C, 27.35; H, 3.50; N, 6.71).

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