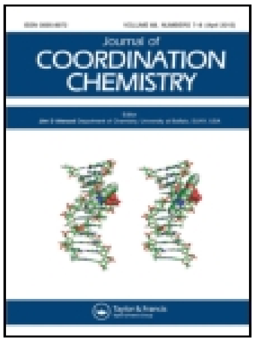

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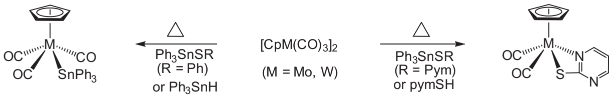

The reactions of $[CpM(CO)_3]_2$ (M = Mo, W) with $PhSSnPh_3$, $pymSSnPh_3$, Ph_3SnH and pymSH have been investigated, leading to Mo/W-Sn bimetallic complexes.

The mixed-metal compounds $CpM(CO)_3(SnPh_3)$ (**1**, M = Mo; **2**, M = W) are obtained as the only isolable products from the reactions of $[CpM(CO)_3]_2$ with $PhSSnPh_3$, whereas similar reactions with $pymSSnPh_3$ (pymS = pyrimidine-2-thiolate) lead to the formation of chelate compounds CpM $(CO)_2(\kappa^2\text{-pymS})$ (**3**, M = Mo; **4**, M = W). Separate experiments show that $CpM(CO)_3(SnPh_3)$ are precursors of $CpM(CO)_2(\kappa^2\text{-pymS})$. $CpM(CO)_3(SnPh_3)$ can also be synthesized in slightly improved yield from the direct reaction between $[CpM(CO)_3]_2$ and Ph_3SnH, while the yield of $CpM(CO)_2(\kappa^2\text{-pymS})$ becomes negligible when $[CpM(CO)_3]_2$ is treated with pymSH.

Keywords: Bimetallic tin compounds; $[CpM(CO)_3]_2$; Triphenyltin; Pyrimidine-2-thiolate; X-ray structures

1. Introduction

Research on bimetallic tin-containing complexes has been driven by the evidence that tin can be used to modify bimetallic catalysts leading to enhanced activity and product selectivity [1–4]. Further, it has recently been found that the oxophilic tin helps the binding of metallic nanoparticles on oxide support in a firm and uniform manner [3–7]. Several methods have been developed in recent years for the incorporation of tin into transition metal

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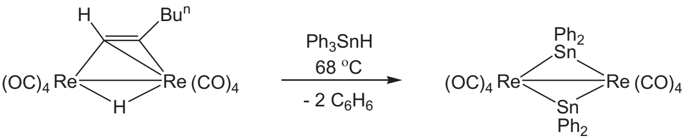
complexes of which oxidative-addition of oraganotin hydride is the most widely used [8–23]. Recently, oxidative-addition of other tin-element bonds has been used which allows inclusion of both tin and a second element into the transition metal complexes [24–29]. Using this latter approach, we have shown that Ph_3SnSR reagents can be used as an excellent source for incorporation of both tin and sulfur into transition metal complexes [27–29].

As shown by Adams and coworkers, reactions of Ph_3SnH with low-valent polynuclear metal carbonyls led to formation of polynuclear complexes containing several Ph_2Sn ligands accompanied by elimination of benzene [16–21]. For example, the dirhenium-tin complex $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$ is obtained from reaction between $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}C(H)C(H)Bu]$ and Ph_3SnH (scheme 1) [12]. With this in mind, we have now investigated the reactions of $[CpM(CO)_3]_2$ (M = Mo, W) with Ph_3SnH and Ph_3SnSR (R = Ph, pymS) and found that neither approach gives the desired dinuclear products, but lead to the formation of mononuclear complexes which are the subject of this article.

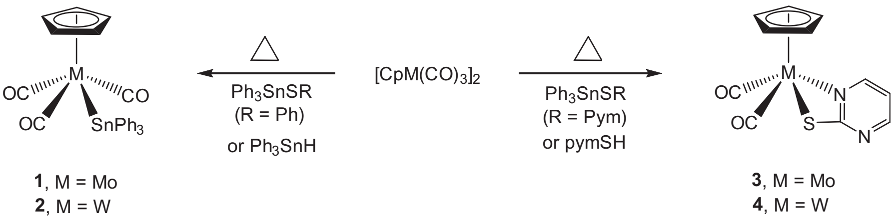
2. Results and discussion

High-temperature reactions between $[CpM(CO)_3]_2$ and $PhSSnPh_3$ afforded the bimetallic compounds $CpM(CO)_3(SnPh_3)$ (**1**, M = Mo, 26%; **2**, M = W, 27%) in moderate yields (scheme 2) which could also be obtained in slightly better yields (34 and 38%, respectively) from the direct reaction between $[CpM(CO)_3]_2$ and Ph_3SnH. Compounds **1** and **2** were previously obtained from the reaction between Ph_3SnCl and $Na[CpMo(CO)_3]$ or $Na[CpW(CO)_3]$ and formulated on basis of spectroscopic data [30, 31]. We have now determined the solid-state molecular structure of **1** by single-crystal X-ray diffraction analysis.

Both **1** and **2** show three absorptions characteristic of $CpMo(CO)_3(SnR_3)$ compounds. The ESI mass spectra of both exhibits $[M + Na]^+$ peak while the ^1H NMR spectrum of each displays resonances for both phenyl and cyclopentadienyl protons. The result of single-crystal X-ray diffraction analysis of **1** is summarized in figure 1 which shows that the



Scheme 1. Preparation of $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$.



Scheme 2. Syntheses of $CpM(CO)_3(SnPh_3)$ and $CpM(CO)_2(\kappa^2\text{-pymS})$ (M = Mo, W).

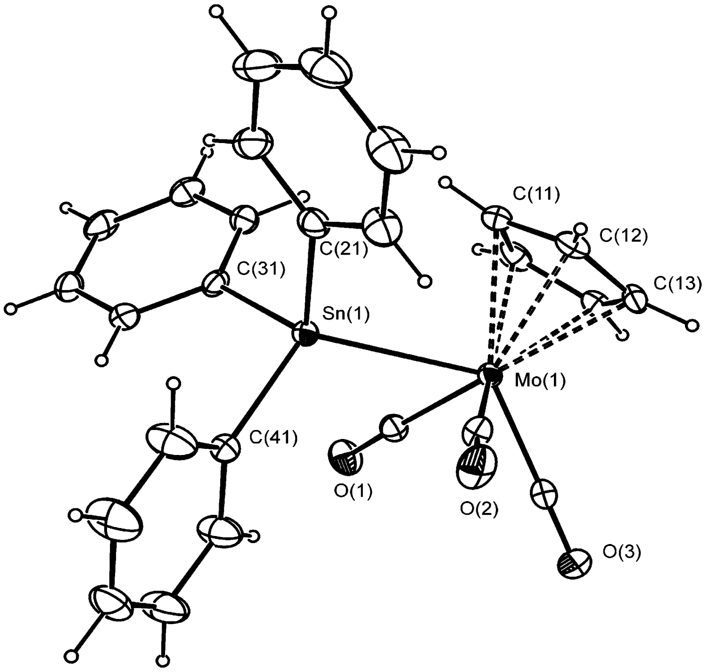


Figure 1. Molecular structure of CpMo(CO)$_3$(SnPh$_3$) (**1**) showing 35% probability thermal ellipsoids. Selected bond distances (Å) and angles (°): Mo(1)–Sn(1) 2.8087(3), av. Mo(1)–CO 1.976(3), av. Mo(1)–C(Cp) 2.338(3), av. Sn(1)–C(Ph) 2.155(3), av. C–O 1.151(4), C(3)–Mo(1)–Sn(1) 127.18(8), C(2)–Mo(1)–Sn(1) 70.73(8), C(1)–Mo(1)–Sn(1) 71.54(8), C(2)–Mo(1)–C(1) 107.65(12), C(3)–Mo(1)–C(1) 78.63(12), C(3)–Mo(1)–C(2) 78.53(12).

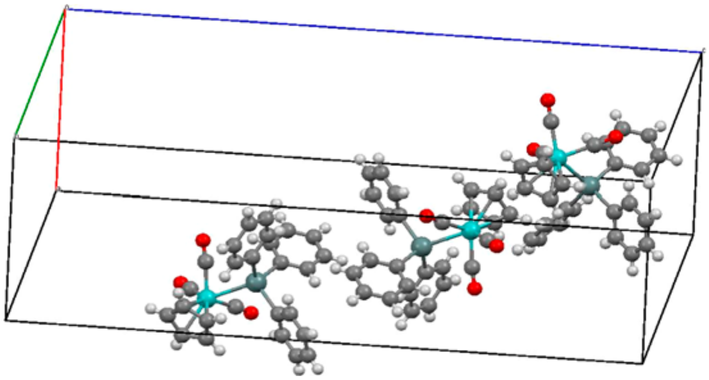


Figure 2. A partial cell-packing diagram of CpMo(CO)$_3$(SnPh$_3$) (**1**) showing the packing motifs: off-set face-to-face interactions between adjacent Cp rings (perpendicular distance 3.13 Å) and sextuple phenyl embraces (cf. Ref. [34]) between adjacent SnPh$_3$ groups (Sn···Sn 8.57 Å).

molecule contains a single molybdenum covalently bonded with a triphenyltin. A cyclopentadienyl and three carbonyl ligands complete the coordination sphere of the molybdenum. The Mo–Sn distance of 2.8087(3) Å in **1** is nearly identical to that found in analogous

$(Me_2NCH_2CH_2C_5H_4)Mo(CO)_3(SnPh_3)$ [2.8152(3) Å] [32] but is slightly contracted (ca. 0.1 Å) compared to those observed in metallostannylene complexes, $CpMo(CO)_3(SnR)$ [33]. The Sn is distorted from its tetrahedral geometry with the *ipso*-C–Sn–*ipso*-C angles ranging from 106.22(11)° to 107.64(10)° and the *ipso*-C–Sn–Mo angles ranging from 109.58(8)° to 114.58(7)°. The Mo–C(Cp) [av. 2.338(3) Å] and Sn–C(Ph) [av. 2.155(3) Å] bond distances are similar to the corresponding bond distances observed in $(Me_2NCH_2CH_2C_5H_4)Mo(CO)_3(SnPh_3)$ [33].

The intermolecular packing is defined by two common motifs (figure 2). There are off-set face-to-face Cp···Cp interactions 3.13 Å apart, 6.5° from parallel. The Ph_3Sn groups are involved in sextuple phenyl embraces about an inversion center of the type that have been more commonly encountered for Ph_3P complexes [34]. These are characterized in **1** by a Sn···Sn distance of 8.57 Å and phenyl-centroid intermolecular distances of 4.9 Å, longer than the corresponding parameters in the phosphorus examples because of the larger radius on tin.

In contrast, similar reactions between $[CpM(CO)_3]_2$ and $pymSSnPh_3$ exclusively gave $CpM(CO)_2(\kappa^2\text{-pymS})$ (**3**, M = Mo, 57%; **4**, M = W, 31%) (scheme 2). The yield of these complexes decreased (ca. 5%) when $[CpM(CO)_3]_2$ was treated with pyrimidine-2-thiol. Both **3** and **4** have been adequately characterized by spectroscopic data together with single-crystal X-ray diffraction analysis for **3**. Figure 3 shows the X-ray structure of **3** with the caption containing selected bond distances and angles. The molecule consists of a single molybdenum ligated by a cyclopentadienyl, two carbonyls, and a chelating pyrimidine-2-thiolate ligand. The molecule is isostructural with $CpM(CO)_2(\kappa^2\text{-pyS})$ [35] with an identical N–Mo–S chelate angle within the experimental error [64.52(5)° in **3** and 64.43(6)° in the

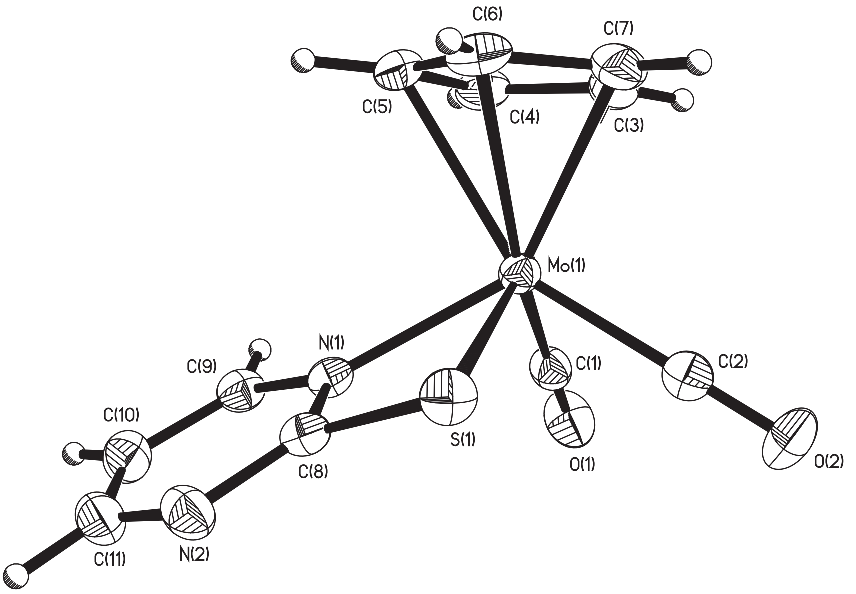
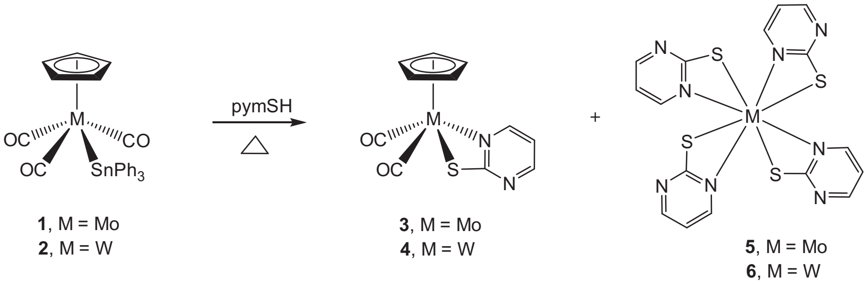


Figure 3. Molecular structure of $CpMo(CO)_2(\kappa^2\text{-pymS})$ (**3**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (°): Mo(1)–S(1) 2.5228(9), Mo(1)–N(1) 2.174(3), Mo(1)–C(1) 1.969(3), Mo(1)–C(2) 1.961(2), av. Mo(1)–C(Cp) 2.333(2), av. C–O 1.156(3), C(1)–Mo(1)–C(2) 75.10(13), C(2)–Mo(1)–S(1) 80.34(9), C(1)–Mo(1)–N(1) 83.91(12), N(1)–Mo(1)–S(1) 64.51(7), C(2)–Mo(1)–N(1) 119.36(12), C(1)–Mo(1)–S(1) 122.34(10).



1, M = Mo
2, M = W

3, M = Mo
4, M = W

5, M = Mo
6, M = W

Scheme 3. Reactions of $CpM(CO)_3(SnPh_3)$ (M = Mo, W) with pymSH.

latter]. The Mo–S [2.5228(9) Å] and Mo–N [2.174(3) Å] bond distances in **3** are also quite similar to those observed in its pyridine-2-thiolate analog [2.5227(9) and 2.183(2) Å, respectively]. The ^1H NMR spectrum of **3** displays two doublets and a triplet in the aromatic region attributed to the heterocyclic ring protons together with a sharp singlet at δ 5.55 ppm for the cyclopentadienyl ring protons and the FAB mass spectrum exhibits a $[M]^+$ ion at *m/z* 328 in accord with the solid-state structure. Akin to **3**, the IR spectrum of **4** displays only two absorption bands in the carbonyl stretching region while the ^1H NMR spectrum displays resonances for both heterocyclic and cyclopentadienyl ring protons. The FAB mass spectrum shows a $[M]^+$ ion at *m/z* 416 consistent with the formulation.

The tin-containing **1** and **2** are the only isolated products from the reactions of $[CpM(CO)_3]_2$ with $PhSSnPh_3$, while the chelate complexes **3** and **4** are exclusively formed in similar reactions with $pymSSnPh_3$. Surprisingly, **1** and **2** were not isolated from reactions with $pymSSnPh_3$. In separate experiments, we showed that **1** and **2** readily react with pyrimidine-2-thiol under similar conditions to give **3** (20%) and **4** (30%) together with the known eight-coordinate compounds $M(\kappa^2\text{-pymS})_4$ [36, 37] (**5**, M = Mo, 13%; **6**, M = W, 16%) (scheme 3). Thus, we assume that **1** and **2** are intermediates in reactions of $[CpM(CO)_3]_2$ with $pymSSnPh_3$ which convert into **3** and **4**, respectively, under the reaction conditions. Attempts to synthesize the known $CpM(CO)_3(\kappa^1\text{-SPh})$ [38, 39] and/or $[CpM(CO)_2(\mu\text{-SPh})]_2$ from the direct reactions between $[CpM(CO)_3]_2$ and PhSH were unsuccessful as these complexes are unstable under the applied reaction conditions.

3. Conclusions

Reactions of $[CpM(CO)_3]_2$ with $PhSSnPh_3$ and $pymSSnPh_3$ lead to isolation of different products i.e. with $PhSSnPh_3$ the bimetallic tin complexes $CpMo(CO)_3(SnPh_3)$ (**1**, M = Mo; **2**, M = W) formed exclusively whereas with $pymSSnPh_3$ the chelate complexes $CpM(CO)_2(\kappa^2\text{-pymS})$ (**3**, M = Mo; **4**, M = W) are the only isolable products. To acknowledge this difference, we carried out separate experiments which show that **1** and **2** are precursors of **3** and **4**. Thus, reactions of **1** and **2** with pymSH gives **3** and **4** as the main products together with small amounts of eight-coordinate $M(\kappa^2\text{-pymS})_4$ [36, 37] (**5**, M = Mo; **6**, M = W). Direct reaction between $[CpM(CO)_3]_2$ and Ph_3SnH slightly improves the yield of the tin compounds (**1** and **2**), while the yield of the chelate compounds (**3** and **4**) decreases dramatically in similar reactions with pymSH. No dinuclear compound has been isolated from this study which we assume is due to the high temperature required for the commencement of these reactions.

4. Experimental

4.1. *General data*

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagent grade solvents were dried using appropriate drying agents and were freshly distilled prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Varian Unity Plus 300 instruments. Mass spectral results are reported as the most intense peak in the isotopic envelope. Elemental analyses were performed by Microanalytical Laboratories, University College London. $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ were purchased from Strem Chemicals Inc. and used without further purification. Ph_3SnCl, PhSH, and pyrimidine-2-thiol were purchased from Aldrich and used as received. $PhSSnPh_3$ and $pymSSnPh_3$ were prepared according to published methods [27, 40].

4.2. *Reaction of $[CpMo(CO)_3]_2$ with $PhSSnPh_3$*

A toluene solution (25 mL) of $[CpMo(CO)_3]_2$ (100 mg, 0.204 mmol) and $PhSSnPh_3$ (95 mg, 0.207 mmol) was heated to reflux for 2 h. The solvent was removed under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7 : 3, v/v) developed two bands. The major band afforded $CpMo(CO)_3(SnPh_3)$ (**1**) (31 mg, 26%) as colorless crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The minor band was unreacted $[CpMo(CO)_3]_2$ (trace). Spectral data for **1**: Anal. Calcd for $C_{26}H_{20}MoO_3Sn$: C, 52.48; H, 3.39. Found: C, 53.04; H, 3.52. IR (ν(CO), CH_2Cl_2): 2003 s, 1931 m, 1901 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.55 (m, 6H), 7.34 (m, 9H), 5.28 (s, 5H). ESI-MS: *m/z* 618.945 $[M + Na]^+$ (Calcd mass: 618.938).

4.3. *Reaction of $[CpW(CO)_3]_2$ with $PhSSnPh_3$*

A xylene solution (25 mL) of $[CpW(CO)_3]_2$ (100 mg, 0.150 mmol) and $PhSSnPh_3$ (72 mg, 0.158 mmol) was heated to reflux for 4 h. A similar workup and chromatographic separation described above developed four bands on TLC plate. The first band was unreacted $[CpW(CO)_3]_2$ (trace) and the second band gave $CpW(CO)_3(SnPh_3)$ (**2**) (28 mg, 27%) as colorless crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The contents of the other bands were too small for characterization. Spectral data for **2**: Anal. Calcd for $C_{26}H_{20}O_3SnW$: C, 45.72; H, 2.95. Found: C, 46.32; H, 3.07. IR (ν(CO), CH_2Cl_2): 1999 s, 1922 m, 1894 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.53 (m, 6H), 7.33 (m, 9H), 5.36 (s, 5H). ESI-MS: *m/z* 704.982 $[M + Na]^+$ (Calcd mass: 704.983).

4.4. *Reaction of $[CpMo(CO)_3]_2$ with $pymSSnPh_3$*

To a toluene solution (25 mL) of $[CpMo(CO)_3]_2$ (100 mg, 0.204 mmol) was added $pymSSnPh_3$ (95 mg, 0.206 mmol) and the reaction mixture was heated to reflux for 2 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with CH_2Cl_2 developed four bands. The first band was unreacted $[CpMo(CO)_3]_2$ (trace) while the fourth band gave $CpMo(CO)_2(\kappa^2\text{-pymS})$ (**3**) (38 mg, 57%) as red crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The contents of the other bands were too small for characterization. Spectral data for **3**: Anal. Calcd for $C_{11}H_8MoN_2O_2S$: C, 40.26; H, 2.46; N, 8.54. Found: C, 40.67; H, 2.57; N, 8.68. IR (ν(CO), CH_2Cl_2): 1963 s, 1875 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.34 (dd, J = 3.0, 1.5 Hz, 1H), 8.24 (dd, J = 3.0, 1.5 Hz, 1H), 6.73 (t, J = 3.0 Hz, 1H), 5.55 (s, 5H). MS (FAB): *m/z* 328 (M$^+$) (Calcd mass: 327.935).

4.5. *Reaction of [CpW(CO)$_3$]$_2$ with pymSSnPh$_3$*

To a toluene solution (25 mL) of [CpW(CO)$_3$]$_2$ (100 mg, 0.150 mmol) was added pymSSnPh$_3$ (70 mg, 0.152 mmol) and the reaction mixture was heated to reflux for 16 h. A similar workup and chromatographic separation as described above developed four bands on the TLC plate. The first band was unreacted [CpW(CO)$_3$]$_2$ (trace) while the fourth band afforded CpW(CO)$_2$(κ^2-pymS) (**4**) (28 mg, 31%) as red crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. The content of the other two bands were too small for characterization. Spectral data for **4**: Anal. Calcd for $C_{11}H_8N_2O_2SW$: C, 31.75; H, 1.94; N, 6.73. Found: C, 32.04; H, 2.01; N, 6.81. IR (ν(CO), CH_2Cl_2): 1947 s, 1855 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.32 (m, 2H), 6.80 (t, J = 3.0 Hz, 1H), 5.68 (s, 5H). MS (FAB): *m/z* 416 (M$^+$) (Calcd mass: 415.9816).

4.6. *Reaction of [CpMo(CO)$_3$]$_2$ with Ph$_3$SnH*

A toluene solution (25 mL) of [CpMo(CO)$_3$]$_2$ (100 mg, 0.204 mmol) and Ph$_3$SnH (144 mg, 0.410 mmol) was heated to reflux for 45 min. A similar workup and chromatographic separation as described above gave **1** (82 mg, 34%).

4.7. *Reaction of [CpW(CO)$_3$]$_2$ with Ph$_3$SnH*

A xylene solution (25 mL) of [CpW(CO)$_3$]$_2$ (100 mg, 0.150 mmol) and Ph$_3$SnH (106 mg, 0.302 mmol) was heated to reflux for 1 h. A similar workup and chromatographic separation as described above gave **2** (78 mg, 38%).

4.8. *Reaction of [CpMo(CO)$_3$]$_2$ with pyrimidine-2-thiol*

A toluene solution (25 mL) of [CpMo(CO)$_3$]$_2$ (100 mg, 0.204 mmol) and pyrimidine-2-thiol (46 mg, 0.410 mmol) was heated to reflux for 1 h. A similar workup and chromatographic separation as described above gave **3** (8 mg, 5%).

4.9. *Reaction of [CpW(CO)$_3$]$_2$ with pyrimidine-2-thiol*

A toluene solution (25 mL) of [CpW(CO)$_3$]$_2$ (100 mg, 0.150 mmol) and pyrimidine-2-thiol (34 mg, 0.303 mmol) was heated to reflux for 7 h. A similar workup and chromatographic separation as described above gave **4** (6 mg, 5%).

4.10. *Reaction of [CpMo(CO)$_3$(SnPh$_3$)] (1) with pyrimidine-2-thiol*

A toluene solution (25 mL) of **1** (45 mg, 0.076 mmol) and pyrimidine-2-thiol (9 mg, 0.080 mmol) was heated to reflux for 3 h. A similar workup and chromatographic separation as described above developed four bands on the TLC plate. The second band gave **3** (5 mg, 20%) while the fourth band afforded Mo(κ^2-pymS)$_4$ (**5**) [36] (6 mg, 13%) as green crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. The contents of the other two bands were too small for characterization. Spectral data for **5**: Anal. Calcd for $C_{16}H_{12}N_8S_4Mo$: C, 35.55; H, 2.34; N, 20.73. Found: C, 36.01; H, 2.42; N, 20.80. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.26 (dd, $J = 3.0$, 1.5 Hz, 1H), 8.16 (dd, $J = 3.0$, 1.5 Hz, 1H), 6.62 (t, $J = 3.0$ Hz, 1H). MS (FAB): *m/z* 542 (M$^+$) (Calcd monoisotopic mass: 541.9122).

4.11. *Reaction of [CpW(CO)$_3$(SnPh$_3$)] (2) with pyrimidine-2-thiol*

A xylene solution (25 mL) of **2** (22 mg, 0.032 mmol) and pyrimidine-2-thiol (4 mg, 0.036 mmol) was heated to reflux for 1.5 h. A similar workup and chromatographic separation as as described above developed four bands on the TLC plate. The second band gave **4** (4 mg, 30%) while the fourth band afforded W(κ^2-pymS)$_4$ (**6**) [37] (3 mg, 16%) as green crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. The contents of the other two bands were too small for characterization. Spectral data for **6**: Anal. Calcd for $C_{16}H_{12}N_8S_4$ W: C, 30.58; H, 1.93; N, 17.83. Found: C, 30.93; H, 1.98; N, 17.91. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.22 (dd, $J = 3.0$, 1.5 Hz, 1H), 8.13 (dd, $J = 3.0$, 1.5 Hz, 1H), 6.67 (t, $J = 3.0$ Hz, 1H). MS (FAB): *m/z* 628 (M$^+$) (Calcd mass: 627.9577).

Table 1. Crystallographic data and structure refinement for **1** and **3**.

	1	**3**
Empirical formula	$C_{26}H_{20}MoO_3Sn$	$C_{11}H_8MoN_2O_2S$
Formula weight (Å)	595.05	328.19
Temperature (K)	90(2)	150(2)
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	$P2_12_12_1$
Unit-cell dimensions		
a (Å)	12.7538(2)	6.5460(14)
b (Å)	11.0097(1)	12.666(3)
c (Å)	32.9594(4)	14.085(3)
α (°)	90	90
β (°)	97.817(1)	90
γ (°)	90	90
Volume (Å^3)	4585.0(1)	1167.8(4)
Z	8	4
Density (calculated) (Mg m^{-3})	1.724	1.867
Absorption coefficient (mm^{-1})	1.661	1.291
F(0 0 0)	2336	648
Crystal size (mm)	0.26 × 0.16 × 0.14	0.24 × 0.14 × 0.06
θ Range for data collection (°)	2.45–27.88	2.89–28.25
Index ranges	$-16 \leq h \geq 16$ $-13 \leq k \geq 14$ $-43 \leq l \geq 43$	$-8 \leq h \geq 8$ $-16 \leq k \geq 16$ $-17 \leq l \geq 18$
Reflections collected	28,150	9509
Independent reflections	5406 [$R_{int} = 0.0217$]	2727 [$R_{int} = 0.0419$]
Max. and min. transmission	0.8008 and 0.6720	0.9266 and 0.7470
Data/restraints/parameters	5406/0/280	2727/0/186
Goodness of fit on F^2	1.250	1.038
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0270$, $wR_2 = 0.0607$	$R_1 = 0.0222$, $wR_2 = 0.0480$
R indices (all data)	$R_1 = 0.0289$, $wR_2 = 0.0614$	$R_1 = 0.0233$, $wR_2 = 0.0486$
Largest diff. peak and hole (e Å^{-3})	0.761 and −0.852	0.70 and −0.30

4.12. *X-ray structure determinations*

Single crystals of **1** and **3** suitable for X-ray structure analysis were grown by slow diffusion of hexane into a dichloromethane solution at 4 °C. Single crystals were mounted on fibers and diffraction data collected at 90 K (for **1**) or 150 K (for **3**) on a Bruker SMART APEX diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å). Data collection, indexing, and initial cell refinements were all done using SMART software [41]. Data reduction was accomplished with SAINT [42] software and SADABS [43] programs were used to apply empirical absorption corrections. The structures were solved by direct methods or Patterson methods and refined by full-matrix least-squares (SHELXL) [44]. The refinement of **3** was as a racemic twin [0.56(4)/0.44(4)]. All non-hydrogen atoms were refined anisotropically and hydrogens were included using a riding model for **1**, but were located and refined for **3**. Additional details of data collection and structure refinement are given in table 1.

Supplementary material

Electronic supplementary information (ESI) contains the mass spectra of **5** and **6** and selected IR spectra. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 954006 for **1** and 954007 for **3**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1FZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk, or on the Web at http://www.ccdc.ac.uk).

Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1033411].

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