ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 607 (2000) 156–163

Journal of Organometallic Chemistry

Formation and structures of novel polynuclear complexes containing Mo–Mo or Mo–Co bonds with bridging SR or PR_2 group

Ron S. Dickson *, Gary D. Fallon, W. Roy Jackson, Anastasios Polas

Department of Chemistry, Monash University, PO Box 23, Clayton, Victoria 3800, Australia

Received 14 March 2000; received in revised form 9 May 2000; accepted 15 May 2000

Our best wishes to Martin Bennett, a colleague and friend for many years.

Abstract

Four dimolybdenum complexes with bridging thiolato groups, $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}SR)_3Mo(CO)_3$ (**4**; R = Me, Ph, Bn (benzyl), Tol), were formed from $Mo(CO)_3(NCMe)_3$ and $[C_5H_4SR]^-$. The related complex $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}SR)_3Mo(CO)(SR)_2$ (**5**; R = Ph) was obtained when additional $[C_5H_4SR]^-$ was used in the reaction. The molecular structures of **4** (R = Bn) and **5** were determined by X-ray crystallography. A Mo_2Co complex (**6**) was obtained from $(\eta^5\text{-}C_5H_4^-Li^+)(CO)_3MoCo(CO)_4$ and Ph_2PCl. The structure, determined from X-ray diffraction data, reveals some unusual bridging arrangements. Crown Copyright © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Polynuclear compounds; Molybdenum; Cobalt; Thiolato; Phosphido

---

1. Introduction

Organosulfur compounds are versatile ligands in inorganic [1] and organometallic [2] chemistry. They can bind intact as terminal or bridging ligands, or undergo intramolecular modification through S–H, S–C or S–S bond cleavage. The possible relationship of particular complexes to key intermediates in the commercially important hydrodesulfurisation process is a major stimulus for the continued interest in organosulfur–transition metal chemistry [3].

In typical hydrodesulfurisation catalysts, cobalt or nickel is doped into molybdenum sulfide which is supported on alumina [4]. Since the process is heterogeneous and operates at high temperatures (ca. 350°C), little is known about the details of the mechanism of hydrodesulfurisation. In this context, soluble complexes that model typical hydrodesulfurisation sites would provide useful information. Ideally, the models should incorporate an Mo–Co bond supported by bridging sulfur groups with labile ligands such as CO or unsaturated hydrocarbons on the metals. Curtis and co-workers have developed an Mo_2Co_2 sulfido cluster which achieves the hydrodesulfurisation of thiophene at 150°C [5]. A number of groups [3] have used soluble complexes of metals such as iron, ruthenium and iridium which may mimic some steps in the hydrodesulfurisation process.

As an extension of our earlier studies of heterobinuclear homogeneous catalysts [6], we have attempted to design some new heterobinuclear complexes based on the ligand $[C_5H_4SR]^-$. We find that the chemistry is dominated by facile C–S bond cleavage to produce products with independent cyclopentadienyl and thiolato ligands. In this paper, we characterise the products that are formed.

2. Results and discussion

Synthesis of the organosulfido-cyclopentadienyl ligand (**1**)was based on the reactions shown in Eqs. (1) and (2)

---

* Corresponding author. Tel.: + 61-3-9905-4560; fax: + 61-3-9905-9129.

E-mail address: r.dickson@sci.monash.edu.au (R.S. Dickson).

0022-328X/00/$ - see front matter Crown Copyright © 2000 Published by Elsevier Science S.A. All rights reserved.

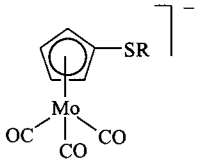
PII: S0022-328X(00)00307-7

$$TlC_5H_5 + RSI \rightarrow C_5H_5SR + TlI \quad (1)$$

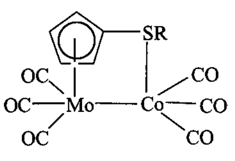
$$C_5H_5SR + NaOBu^t \rightarrow Na^+(C_5H_4SR)^- + HOBu^t \quad (2)$$

This is similar to the procedure used to prepare the related phosphido-ligands $(C_5H_4PR_2)^-$ [7]. The sulfido compound (**1**) was not isolated, but was treated immediately with a slurry of trisacetonitriletricarbonylmolybdenum (one equivalent) in tetrahydrofuran. The target compound from this reaction was **2**, and the plan was to react **2** with $Co(CO)_4I$ to form a heterobinuclear product (**3**).

However, the species isolated from the reaction mixture was the binuclear molybdenum complex (**4**).

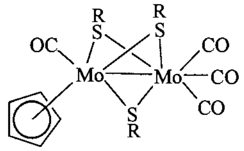


(2)

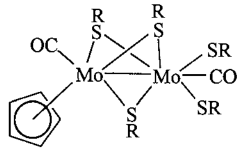


(3)

Four complexes (R = Bn, **4a**; R = Ph, **4b**; R = Me, **4c**; R = Tol, **4d**) were formed in this way, and the isolated yields were generally low (ca. 10%). In all cases a small amount of a second compound was observed. A reaction of trisacetonitriletricarbonylmolybdenum with two equivalents of **1** gave a second binuclear molybdenum compound **5** which was identical with the second compound formed in the equimolar reactions.



(4)



(5)

All of the complexes **4** and **5** were fully characterised from elemental analyses and spectroscopic data. The protonated molecular ion $[M+H]^+$ was detected in the positive ion electrospray mass spectrum for all complexes.

Table 1
Summary of crystal structure data for the compounds **4a**, **5** and **6**

	4a	**5**	**6**
Empirical formula	$Mo_2S_3C_{30}H_{26}O_4(C_5H_{12})_{0.4}$	$Mo_2S_5C_{37}H_{30}O_2(C_6H_{14})_{0.25}$	$Mo_2CoP_2C_{42}H_{29}O_8$
Formula weight	767.5	880.4	974.5
Crystal dimensions (mm)	0.26 × 0.10 × 0.10	0.20 × 0.18 × 0.13	0.15 × 0.15 × 0.13
Colour, habit	Dark green, acicular	Brown, prismatic	Red, prismatic
Crystal system	Monoclinic	Monoclinic	Monoclinic
Lattice type	P	P	P
Lattice parameters			
a (Å)	12.1543(2)	13.4462(3)	11.9467(3)
b (Å)	20.4021(4)	29.6989(3)	15.0856(4)
c (Å)	13.8376(2)	19.2092(4)	21.6931(4)
α (°)	90	90	90
β (°)	111.084(1)	93.372(1)	104.943(1)
γ (°)	90	90	90
Space group	$P2_1/C$	$P2_1/C$	$P2_1/c$
Z	4	8	4
μ(Mo–K_α)	10.1	9.6	12.3
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
Radiation (Å)	Mo–K_α ($\lambda = 0.71073$) graphite monochromated	Mo–K_α ($\lambda = 0.71073$) graphite monochromated	Mo–K_α ($\lambda = 0.71073$) graphite monochromated
Temperature (K)	173	123	123
2θ max (°)	55.6	55.7	55.7
Reflections collected	69 013	74 431	52 578
Independent, R_{int}	8114, 0.041	15 068, 0.040	9327, 0.040
Observed $[F > 6\sigma(F)]$	5443	8113	5523
Corrections	Lorentz-polarisation, absorption trans factors 0.808, 0.937	Lorentz-polarisation, absorption trans factors 0.811, 0.586	Lorentz-polarisation, absorption trans factors 0.830, 0.863
Structure solution [13]	TEXSAN	TEXSAN	TEXSAN
Refinement [13], on *F*	TEXSAN	TEXSAN	TEXSAN
Least-squares weights	$[\sigma^{-2}(F)]$	$[\sigma^{-2}(F)]$	$[\sigma^{-2}(F)]$
Variables	372	853	496
Residuals: *R*, wR_2 $[F > 6\sigma(F)]$	0.035, 0.035	0.051, 0.062	0.036, 0.028
R indices (all data)	0.065, 0.036	0.103, 0.070	0.084, 0.030
GOF indicator	2.95	1.96	2.03
Largest difference peak and hole (e Å^{-3})	1.08, −0.59	1.48, −1.80	0.90, 0.78

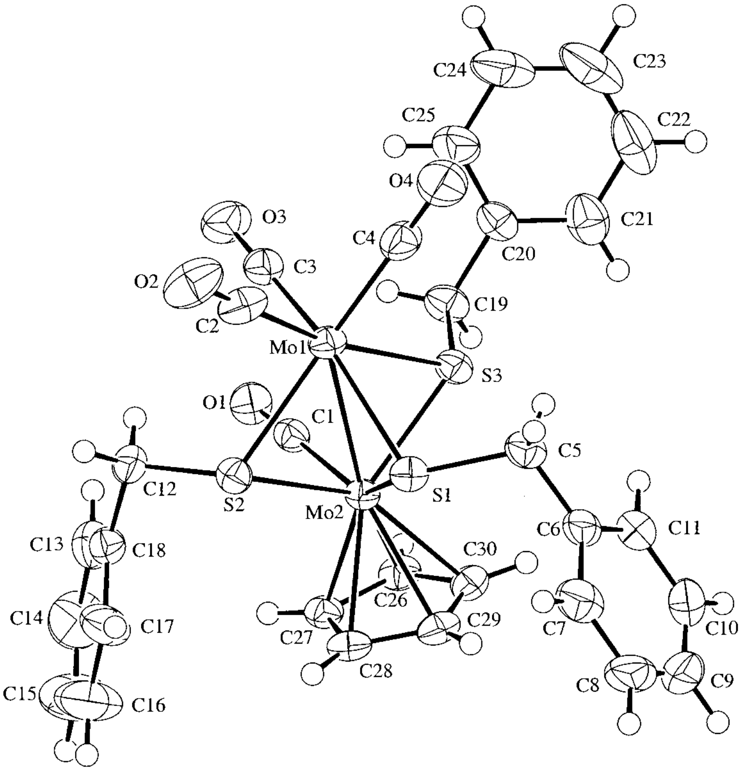


Fig. 1. The molecular structure of **4a**.

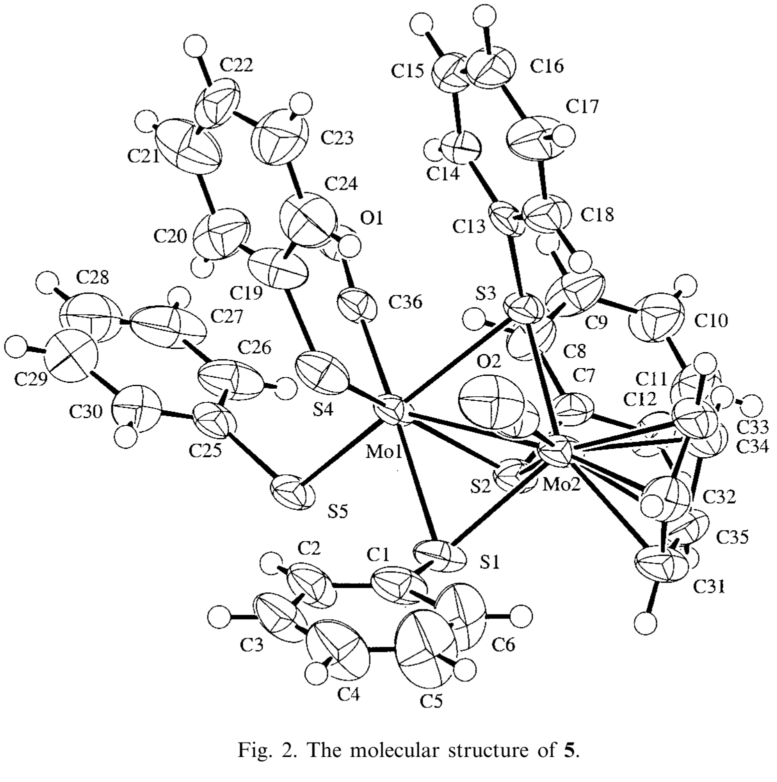


Fig. 2. The molecular structure of **5**.

Molecular structures were determined from X-ray diffraction data for the two complexes **4a** (R = Bn) and **5**. The crystal structure data are summarised in Table 1, drawings of the molecular structures of the complexes are shown in Figs. 1 and 2, and selected bond distances and angles are compared in Table 2.

The core of each structure is a Mo–Mo bond supported by three bridging thiolato groups. Replacement

Table 2
Selected bond distances (Å) and angles (°) for **4a** and **5**

	4a	**5**
Mo(1)–Mo(2)	2.7791(4)	2.8040(9)
Mo(1)–S(1)	2.577(1)	2.537(2)
Mo(1)–S(2)	2.488(1)	2.510(2)
Mo(1)–S(3)	2.4986(9)	2.516(2)
Mo(2)–S(1)	2.5135(9)	2.424(2)
Mo(2)–S(2)	2.4186(9)	2.500(2)
Mo(2)–S(3)	2.4106(9)	2.402(2)
Mo(1)–CO	1.99(ave)	1.978(7)
Mo(2)–CO	1.997(4)	2.02(1)
Mo(1)–S(4)		2.304(3)
Mo(1)–S(5)		2.380(2)
Mo(2)–Mo(1)–C(2/36)	136.2(1)	128.8(2)
Mo(2)–Mo(1)–C(3)	106.6(1)	
Mo(2)–Mo(1)–C(4)	134.0(1)	
C(2)–Mo(1)–C(3)	87.4(1)	
C(2)–Mo(1)–C(4)	85.6(2)	
C(3)–Mo(1)–C(4)	90.5(2)	
Mo(2)–Mo(1)–S(4)		100.3(6)
Mo(2)–Mo(1)–S(5)		131.90(6)
S(4)–Mo(1)–C(36)		95.4(2)
S(5)–Mo(1)–C(36)		87.4(2)
S(4)–Mo(1)–S(5)		107.12(9)
Mo(1)–Mo(2)–CO	82.4(1)	86.5(2)
Mo(1)–S(br)–Mo(2)	68.0(ave)	68.8(ave)

of two terminal carbonyls on Mo(1) in complex **4** by two terminal thiolato groups in **5** has little effect on the main geometric features. There are no unusual bond parameters in these structures. In particular the Mo–S bond distances fall within the range of those quoted for metal thiolate carbonyl complexes with bridging and terminal thiolato groups [8].

The IR and NMR results for **4c** (R = Me) are typical and are briefly discussed, together with those for **5**. Four carbonyl absorptions are observed in the IR spectrum of **4c**. One is at significantly lower wavenumber (1847 cm^{-1}) than the other three (1997, 1969 and 1937 cm^{-1}). Although it is tempting to assign this to the lone carbonyl on the molybdenum which also bears a cyclopentadienyl ligand, it is noted that this low frequency absorption is absent in **5**. Four major carbonyl environments were indicated in the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum shows three separate methyl resonances, and a C_5H_5 singlet. However, a few low intensity signals were observed in both the C_5H_5 and methyl regions of the spectrum, indicating the possible existence of further stereoisomers based on different orientations of the SR groups. Such stereoisomerism has been previously observed in dinuclear complexes with bridging SR groups [9]. A variable temperature ^{1}H-NMR study showed that two of the methyl signals of the predominant stereoisomer broadened at elevated temperature and coalesced at 100°C.

These results can be interpreted as being caused by isomerisation at sulfur with a free energy barrier to inversion of ca. 82 kJ mol^{-1} as calculated using the slow exchange approximation and the Eyring equation. This value is comparable to others reported for inversion at bridging sulfur in a range of metal complexes [10].

Careful examination of the C_5H_5 region of the ^{1}H-NMR spectrum suggested that four diastereoisomers were present. Molecular modelling calculations gave energy values for the four stereoisomers as shown in Fig. 3.

The lowest energy isomer (i) is that characterised in the X-ray crystal structure determination (see Fig. 1). In all cases the two isomers with the C_5H_5 rings at lowest field in the ^{1}H-NMR spectra were present in the smallest amounts and they were tentatively assigned the high energy structures (iii) and (iv). It can be noted that there is eclipsing of the substituent on the non-planar S atom with one of the substituents on a planar S-atom in these structures.

The ^{1}H- and ^{13}C-NMR spectra of **5** in $CDCl_3$ solution showed the presence of a major isomer together with numerous others, as would be expected in a structure with three bridging and two terminal SPh groups. The molecular structure determined by X-ray diffraction showed that the three bridging SPh groups had their Ph substitutents arranged in a geometry similar to that of the minimum energy isomer of **4c** (see (i) Fig. 3). This is the same as the bridging SBn groups in **4a** (see Fig. 1). Although the terminal SPh groups are *syn* in the crystal, this may be due to π–π stacking and is not necessarily indicative of the dominant structure in solution.

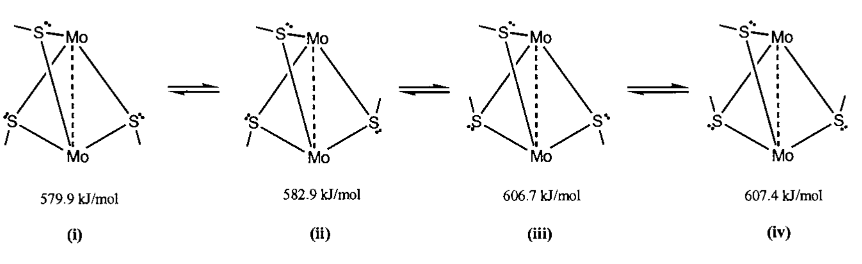


Fig. 3. Calculated energy values for the stereoisomers of **4c**.

In general, all of the compounds **4** were remarkably unreactive, failing to react with a variety of carbonyl–cobalt complexes (e.g. $Co_2(CO)_8$, $Co(CO)_3NO$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$) with attempted thermal or photochemical initiation. In addition, the complexes could be recovered unchanged from treatment with HCl gas (ten equivalents) in ether or heating with thiophene. Even boiling with excess NaOH in ethanol allowed for some recovery of **4**. In contrast, preliminary investigations suggest that **5** is much more reactive and its reactivity is being currently explored.

Failure to form the target compound **3** led us to consider an alternative approach based on the reaction sequence shown in Eqs. (3)–(5), where E in the final step could be S or P.

$$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2 + Co_2(CO)_8$$

$$\rightarrow (\eta^5\text{-}C_5H_5)(OC)_3MoCo(CO)_4 \qquad (3)$$

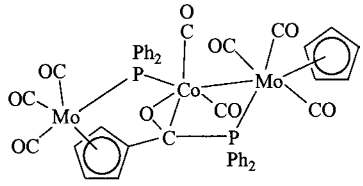
$$(\eta^5\text{-}C_5H_5)(OC)_3MoCo(CO)_4 + LDA$$

$$\rightarrow (C_5H_4^-Li^+)(OC)_3Mo\text{–}Co(CO)_4 \qquad (4)$$

$$(C_5H_4^-Li^+)(OC)_3MoCo(CO)_4 + R_nEX$$

$$\rightarrow (C_5H_4\overline{ER_n)(OC)_3MoC}o(CO)_3 \qquad (5)$$

After completion of the reactions in Eqs. (3) and (4), the final step was attempted with Ph_2PCl. This gave the unexpected Mo_2Co product (**6**) in > 50% yield. Although the microanalytical data were consistent with **6**, the spectroscopic data (see Section 3) were complex and did not enable characterisation of the complex.



(6)

The molecular structure of **6**, as determined from X-ray diffraction data, incorporates some unexpected features (Fig. 4). There is no bond between Mo(1) and Co(1), but the Co(1)–Mo(2) distance (2.902 Å) is consistent with a bonding interaction. The atoms Mo(1) and Co(1), are adjacent and bridged on one side by a diphenylphosphido group. Three terminal carbonyls are attached to Mo(1) and two to Co(1). The Co(1)–Mo(2) bond is not supported by bridging groups. There is an η^5-attached cyclopentadienyl on Mo(2) and a terminal carbonyl. One side of the molecule contains an interesting bridging ligand that spans all three metals. It is formed by condensation of deprotonated-cyclopentadienyl, carbonyl and diphenylphosphido groups. The C_5H_4 and Ph_2P units are attached to Mo(1) and Mo(2) respectively. These two units are linked through a carbon atom which is part of a carbonyl group attached in η^2-manner to Co(1). This bonding of a 'ketonic' carbonyl through both carbon and oxygen to a single metal is most unusual. The overall bonding arrangement creates an assembly of fused three-, four-, and five-membered ring systems. Given this complexity, the

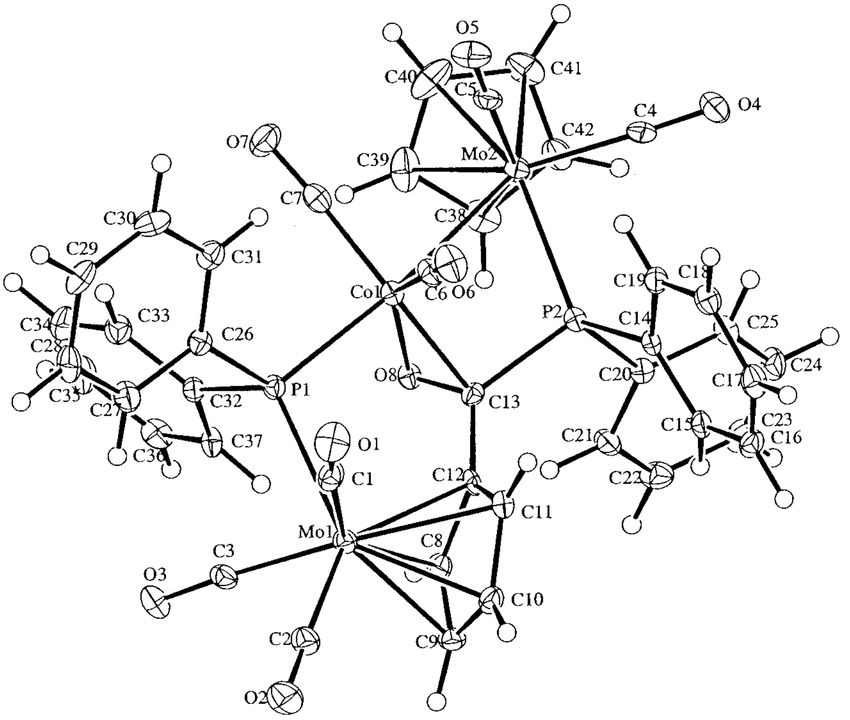


Fig. 4. The molecular structure of **6**.

attachment of the C_5-ring (C_8–C_{12}) to Mo(1) is surprisingly symmetrical and clearly η^5. Within the small ring composed of Co(1), C(13) and O(8), the Co–C and Co–O bond distances are 1.980 and 1.964 Å respectively. The Co–C distance is significantly longer than that for the Co(1) to terminal carbonyl bond (1.800 Å) in which there is undoubtedly significant back bonding. The C(13)–O(8) distance is 1.325 Å, which seems short for a C–O single bond distance.

Formation of the complexes **4**, **5** and **6** could all involve fragmentation of the C_5H_4–ER_n (E = S or P) bond under mild conditions. If this pathway is followed, the metal carbonyl units would collect the bits and reassemble them into remarkably stable polynuclear complexes. However, a referee has pointed out that the formation of **4** and **5** does not necessarily involve $Na^+(C_5H_4SR)^-$ as an intermediate, nor does the formation of **6** necessarily involve the formation of $(C_5H_4\overline{PR_2)(OC)_3MoC}o(CO)_3$ as shown in Eqs. (4) and (5). In the latter case reaction of $(\eta^5\text{-}C_5H_5)(OC)_3$-$MoCo(CO)_4$ could involve attack of the LDA at a carbonyl carbon rather than a proton on the C_5H_5 group, leading to a Fischer carbene intermediate.

3. Experimental

Reactions were carried out under an atmosphere of purified nitrogen in oven-dried Schlenk flasks. Solvents used were freshly distilled over appropriate drying agents prior to use. Purification of products by preparative scale TLC was carried out on 20 × 20 cm glass plates with a 1:1 silica gel GHF_{254} mixture (Type 60, Merck) as adsorbent. Microanalysis was performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Solution IR spectra (KBr windows) were obtained using a Perkin–Elmer 1600 FTIR spectrophotometer. NMR spectra were measured on Bruker AC200 or AM300 spectrometers. Spectroscopic results are reported for the major isomer only.

A Silicon Graphics Indy computer equipped with the Insight II software package [11] was used for molecular modelling.

3.1. Preparation of (η⁵-cyclopentadienyl)carbonylmolybdenumtris(μ-thiobenzyl)tricarbonylmolybdenum ***(4a)***

A slurry of thallium cyclopentadienide (1.54 g, 5.72 mmol) in THF (30 ml) was cooled to −78°C in a dry ice–acetone bath and treated with a solution of benzylsulfenyl iodide (1.43 g, 5.72 mmol) in THF (30 ml). The reaction mixture was stirred for 1 h. Sodium tertiary-butoxide (0.43 g, 5.75 mmol) dissolved in a minimum amount of THF was then added via cannula and the mixture was stirred for an additional hour at −78°C. To the reaction mixture a slurry of trisacetonitriletricarbonylmolybdenum (1.73 g, 5.72 mmol) in THF (100 ml) was slowly added via cannula and left to stir at −78°C for a further hour. The mixture was then brought to room temperature and stirred a further 2 h, after which it was filtered through a celite pad to remove any insoluble materials. Solvent removal in vacuo resulted in a dark brown oily residue. This was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (1:2, v/v) separated a green band that was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from pentane resulted in a green microcrystalline solid which was identified spectroscopically as $[(\eta^5\text{-}C_5H_5)(CO)Mo_2(\mu\text{-}SCH_2C_6H_5)_3(CO)_3]$ (183 mg, 13%), m.p. 88–90°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.04 (dd, $J = 22.3$ and 12.9 Hz, 2H, $CH_{2\alpha}$), 3.84 (dd, $J = 17.8$ and 12.8 Hz, 2H, $CH_{2\beta}$), 4.5 (dd, $J = 23.3$ and 12.7 Hz, 2H, $CH_{2\gamma}$), 4.71 (s, 5H, C_5H_5), 6.9–7.6 (m, 15H, C_6H_5). ^{13}C {^{1}H}-NMR (50.3 MHz, $CDCl_3$): δ 27.29, 45.77, 46.00 (Ar–CH_2), 90.80 (C_5H_5), 126.92, 127.30, 127.31 128.34, 128.51, 128.59, 129.02, 129.07, 129.08 (ArCH), 140.38, 140.49, 140.76 (ArC), 220.20, 224.65, 224.67, 230.65 (Mo–CO). IR spectrum (CH_2Cl_2): ν(CO) 2000 s, 1966 s, 1846 m cm^{-1}. MS (electrospray, positive ion): m/z 778.7 (13%, $M^+ + K$), 760.8 (14, $M^+ + Na$), 737.8 (15, $M^+ + H$). Anal. Found: C, 48.8, H 3.5, S, 13.0. Calc. for $C_{30}H_{26}O_4S_3Mo_2$: C, 48.8; H, 3.55; S, 13.0%.

3.2. Preparation of (η⁵-cyclopentadienyl)carbonylmolybdenumtris(μ-thiophenyl)tricarbonylmolybdenum ***(4b)***

A similar preparative procedure was used with thallium cyclopentadienide (1.54 g, 5.72 mmol), phenylsulfenyl iodide (1.35 g, 5.72 mmol), sodium tertiary-butoxide (0.43 g, 5.75 mmol), and trisacetonitriletricarbonylmolybdenum (1.73 g, 5.72 mmol). The resulting brown solution was filtered and solvent removed in vacuo. The residue was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (2:3, v/v) separated a dark green band that was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from dichloromethane–pentane resulted in a green microcrystalline solid which was identified as $[(\eta^5\text{-}C_5H_5)(CO)Mo_2(\mu\text{-}SC_6H_5)_3(CO)_3]$ (92 mg, 7%), m.p. 192–197°C (dec.). ^{1}H-NMR (200 MHz,$CDCl_3$): δ 5.76 (s, 5H, C_5H_5), 7.08–7.46 (m, 15H, C_6H_5). ^{13}C {^{1}H}-NMR (50.3 MHz, $CDCl_3$): δ 93.0 (C_5H_5), 126.4, 127.0, 127.3, 127.9, 128.1, 131.3, 131.6, 135.2 (ArCH), 132.6, 142.8, 144.1 (ArC), 226.0, 224.1 (Mo–CO). IR (CH_2Cl_2): ν(CO) 2010 s, 1985 s, 1952 w, 1862 m cm^{-1}. MS (electrospray, positive ion): *m/z* 739.7 (60%, $M^+ +$ K), 719.8 (30, $M^+ +$ Na), 659.9 ($M^+ +$ K – 3(CO)), 635.8 ($M^+ +$ Na–3(CO), 606.9 ($M^+ +$ Na–4(CO)). Anal. Found: C, 46.5; H 2.9; S, 13.8. Calc. for $C_{27}H_{20}O_4S_3Mo_2$: C, 46.6; H, 2.9; S, 13.8%.

3.3. *Preparation of (η^5-cyclopentadienyl)carbonylmolybdenumtris(μ-thiomethyl)tricarbonylmolybdenum* (**4c**)

A similar preparative procedure was used with thallium cyclopentadienide (1.23 g, 4.56 mmol), methylsulfenyl iodide (0.80 g, 4.56 mmol), sodium tertiary-butoxide (0.35 g, 4.56 mmol), and trisacetonitriletricarbonylmolybdenum (1.38 g, 4.56 mmol). The resulting brown solution was filtered and solvent removed in vacuo. The residue was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (2:3, v/v) separated a dark green band that was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from dichloromethane–pentane resulted in a green microcrystalline solid which was identified as [(η^5-C_5H_5)-(CO)Mo_2(μ-SCH_3)$_3$(CO)$_3$] (87 mg, 11%), m.p. 168–172°C (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.32 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.69 (s, 3H,CH_3), 5.76 (s, 5H, C_5H_5). ^{13}C {^{1}H}-NMR (75 MHz, $CDCl_3$): δ 8.34 (CH_3), 26.52 (CH_3), 26.75 (CH_3), 91.36 (C_5H_5), 220.23, 225.56, 226.24, 230.02 (Mo–CO). IR (CH_2Cl_2): ν(CO) 1997 s, 1969 s, 1937 s, 1847 s cm^{-1}. MS (electrospray, positive ion): *m/z* 524.74 ($M^+ +$ Na), 509.71 ($M^+ +$ H). Anal. Found: C, 28.2; H, 2.7; S, 18.8. Calc. for $C_{12}H_{14}O_4S_3Mo_2$: C, 28.2; H, 2.8; S, 18.9%.

3.4. *Preparation of (η^5-cyclopentadienyl)carbonylmolybdenumtris(μ-thio-p-tolyl)tricarbonylmolybdenum* (**4d**)

A similar preparative procedure was used. The reactants were: thallium cyclopentadienide (1.54 g, 5.72 mmol), *p*-tolylsulfenyl iodide (1.43 g, 5.72 mmol), sodium tertiary-butoxide (0.43 g, 5.75 mmol), and trisacetonitriletricarbonylmolybdenum (1.73 g, 5.72 mmol). The resulting brown solution was filtered and solvent removed in vacuo. The residue was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (2:3, v/v) separated a dark green band which was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from dichloromethane–pentane resulted in a green microcrystalline solid which was identified as [(η^5-C_5H_5)-(CO)Mo_2(μ-$SC_6H_4CH_3$)$_3$(CO)$_3$] (44 mg, 3%), m.p. 114–119°C (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 6H, CH_3), 2.32 (s, 3H, CH_3), 5.72 (s, 5H, C_5H_5), 6.8–7.1 (m, 8H, C_6H_4), 7.22 (d, 4H, C_6H_4), 7.35 (d, 2H, C_6H_4). ^{13}C {^{1}H}-NMR (75 MHz, $CDCl_3$): δ 21.03, 21.09, 21.15 (CH_3), 92.98 (C_5H_5), 128.74, 128.76, 128.95, 129.00, 129.21, 129.94, 131.39, 131.47, 131.60, 135.21 (ArCH), 136.47, 137.38, 137.60, 139.52, 140.40, 140.86 (ArC), 219.45, 221.43, 224.73 (Mo–CO). IR (CH_2Cl_2): ν(CO) 2010 s, 1985 s, 1952 w, 1862 m cm^{-1}. MS (electrospray, positive ion): *m/z* 778.7 (30%, $M^+ +$ K), 760.8 (50, $M^+ +$ Na), 737.8 (45, $M^+ +$ H), 676.9 (100, $M^+ +$ H – C_5H_5). Anal. Found: C, 48.7; H 3.6; S, 13.0. Calc. for $C_{30}H_{26}O_4S_3Mo_2$: C, 48.8; H, 3.6; S, 13.0%.

3.5. *Preparation of (η^5-cyclopentadienyl)carbonylmolybdenumtris(μ-thiophenyl)carbonylbisthiophenylmolybdenum* (**5**)

A similar preparative procedure was used with thallium cyclopentadienide (1.54 g, 5.72 mmol), phenylsulfenyl iodide (1.35 g, 5.72 mmol), sodium tertiary-butoxide (0.43 g, 5.75 mmol), and trisacetonitriletricarbonylmolybdenum (0.86 g, 2.86 mmol). The resulting brown solution was filtered and solvent removed in vacuo. The residue was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (2:3, v/v) separated a dark brown band that was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from dichloromethane–pentane resulted in a brown microcrystalline solid which was identified as [(η^5-C_5H_5)-(CO)Mo_2(μ-SC_6H_5)$_3$(CO)(SC_6H_5)$_2$] (120 mg, 12%), m.p. 192–197°C (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.92 (s, 5H, C_5H_5), 6.5–7.9 (m, 25H, C_6H_5). ^{13}C {^{1}H}-NMR (50 MHz, $CDCl_3$): δ 92.52 (C_5H_5), 125.7–134.8 (ArCH), 134.8–155.1 (ArC), 232.82, 225.59 (CO). IR (CH_2Cl_2): ν(CO) 2002 s, 1950 s cm^{-1}. MS (electrospray, positive ion): *m/z* 861.8 ($M^+ +$ H), 692.9 ($M^+ +$ H – 2(CO) – SPh), 660, C($M^+ +$ Na – 2(SPh)). Anal. Found: C, 51.8; H, 3.6; S, 18.8. Calc. for $C_{37}H_{30}O_2S_5Mo_2$: C, 51.8; H, 3.5; S, 18.7%.

3.6. *Preparation of (η^5-$C_5H_4C(O)PPh_2(CO)_3Mo$-(μ-PPh_2)$Co(CO)_2Mo(CO)_2$(η^5-C_5H_5)* (**6**)

(η^5-C_5H_5)(CO)$_3$MoCo(CO)$_4$ (0.25 g, 0.60 mmol), prepared as described by Abrahamson et al. [12] was dissolved in THF (30 ml) with stirring and cooled to – 78°C. The red solution was treated with a 1.3 molar excess of lithium diisopropylamine in THF producing an immediate colour change to deep orange. Stirring was continued for a further 30 min after which chlorodiphenylphosphine (0.17 g, 0.78 mmol) was added. After a further 30 min the reaction mixture was slowly brought to room temperature. The solvent was removed in vacuo and the residue dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC. Elution with hexane–dichloromethane (2:3, v/v) separated a major crimson–purple band that was extracted with dichloromethane. Evaporation of the solvent followed by recrystallisation from dichloromethane–pentane resulted in a purple microcrystalline solid which was identified as

$(\eta^5\text{-}C_5H_4C(O)PPh_2)(CO)_3Mo(\mu\text{-}PPh_2)Co(CO)_2\text{-}$

$Mo(CO)_2(\eta^5\text{-}C_5H_5)$ (**6**)

(166 mg, 56%), m.p. 192–197°C (dec.). ^{1}H-NMR (300 MHz, C_6D_6): δ 3.86 (q, 1H, C_5H_4), 4.14 (q, 1H, C_5H_4), 4.28 (q, 1H, C_5H_4), 4.77 (s, 5H, C_5H_5), 6.13 (q, 1H, C_5H_4), 6.8–7.15 (m, 12H, C_6H_5), 7.3–8.0 (m, 8H, C_5H_5). ^{13}C {^{1}H}-NMR (50 MHz, C_6D_6): δ 82.33 (C1), 87.44 (C2), 92.39 (C_5H_5), 94.35 (C3), 99.10 (C4), 101.85 (C5), 133.33–134.60 (ArCH), 137.48–137.88 (ArC). ^{31}P {^{13}C}-NMR (75 MHz, C_6D_6): δ 73.5 (s, br), 104.7 (d, $J = 26$ Hz). IR(CH_2Cl_2): ν(CO) 2028 s, 1999 m, 1955 s(br), 1944 s(sh), 1933 s(sh), 1910 s, 1845 w, 1839 w cm^{-1}. MS (electrospray, positive ion): m/z 988.9 (12%, $M^+ + K - CO$), 904.8 ($M^+ + K - 4CO$), 888.9 ($M^+ + Na - 4CO$), 832.5 ($M^+ + Na - 6CO$). Anal. Found: C, 51.6; H, 2.9; P, 6.4. Calc. for $C_{42}H_{29}O_8P_2CoMo_2$: C, 51.8; H, 3.0; P, 6.4%.

4. Supplementary material

Tables of fractional atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles and observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-141071–141072. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This project has been supported by funds from the ARC large grants scheme. We thank the Australian Government for an Australian Postgraduate Award (to A.P.).

References

[1] Recent reviews include: (a) I. Dance, K. Fisher, Prog. Inorg. Chem. 41 (1994) 637. (b) E.I. Stiefel (Ed.), Transition Metal Sulfur Chemistry, American Chemical Society, Washington, DC, 1996.

[2] See, for example: L. Linford, H.G. Raubenheimer, Adv. Organomet. Chem. 32 (1991) 1.

[3] Some recent references include: (a) W.D. Jones, R.M. Chin, C.L. Hoaglin, Organometallics 18 (1999) 1786. (b) M.A. Reynolds, I.A. Guzei, B.C. Logsdon, L.M. Thomas, R.A. Jacobson, R.J. Angelici, Organometallics 18 (1999) 4075. (c) C. Bianchini, A. Meli, S. Moneti, F. Vizza, Organometallics 17 (1998) 2636.

[4] H. Topse, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, Springer-Verlag, Berlin, 1996.

[5] (a) M.D. Curtis, S. Druber, J. Am. Chem. Soc. 119 (1997) 1027. (b) U. Riaz, O. Curnow, M.D. Curtis, J. Am. Chem. Soc. 113 (1991) 1416.

[6] (a) R.S. Dickson, T. DeSimone, E.M. Campi, W.R. Jackson, Inorg. Chim. Acta 220 (1994) 187. (b) K.J. Coutinho, R.S. Dickson, G.D. Fallon, W.R. Jackson, T. DeSimone, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1997) 3193. (c) R.S. Dickson, J. Bowen, E.M. Campi, W.R. Jackson, C.A.M. Jonasson, F.J. McGrath, D.J. Paslow, A. Polas, P. Renton, S. Gladiali, J. Mol. Catal. A: Chem. 150 (1999) 133.

[7] C.P. Casey, R.M. Bullock, W.C. Fulz, A.L. Rheingold, Organometallics 1 (1982) 1591.

[8] S. Woodward, in: E.A. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 5, J.A. Labinger, M.J. Winter (Eds.), Pergamon, Oxford, 1995, Chapter 4, p. 266 and refs. cited therein.

[9] K.-B. Shiu, S.-L. Wang, F.-L. Liao, M.Y. Chiang, S.-M. Peng, G.-H. Lee, J.-C. Wang, L.-S. Liou, Organometallics 17 (1998) 1790 and refs. cited therein.

[10] C.J. Ruffing, T.B. Rauchfuss, Organometallics 4 (1985) 524 and refs. cited therein.

[11] Insight II, MSI, San Diego, CA.

[12] B. Abrahamson, M.S. Wrighton, Inorg. Chem. 17 (1978) 103.

[13] TEXSAN, Crystal structure analysis package, Molecular Structure Corporation, 1985 and 1992.