Inorg. Chem. **2006**, *45*, 10967–10975

Inorganic Chemistry
Article

Heterometallic Dithiolene Complexes Formed by Stepwise Displacement of Cyclopentadienyl Ligands from Nickelocene with CpMo($S_2C_2Ph_2$)$_2$

Harry Adams, Hannah C. Gardner, Richard A. McRoy, Michael J. Morris,* Jeffrey C. Motley, and Sebastian Torker

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom

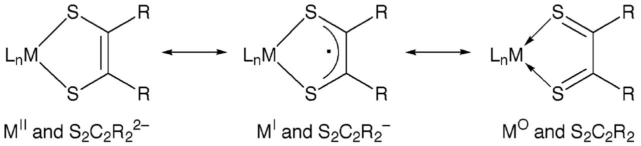
Received April 12, 2006

The dithiolene ligand transfer reaction between Ni($S_2C_2Ph_2$)$_2$ (**1**) and CpMo(CO)$_3$Cl (**2**; Cp $= \eta$-C_5H_5) affords the neutral paramagnetic molybdenum bis(dithiolene) complex CpM($S_2C_2Ph_2$)$_2$ (**3**), which has been structurally characterized. As found in other d^1 complexes of this type, one dithiolene ligand is planar while the other is significantly folded toward the Cp ligand. An unexpected second product of the reaction is the unusual trinuclear species Ni[Mo($S_2C_2Ph_2$)$_2$Cp]$_2$ (**4**), which in the solid state contains three different dithiolene bonding modes (terminal, bridging, and semi-bridging) in the same molecule. Complex **4** can also be synthesized by displacement of the diene ligands in Ni(cod)$_2$ with 2 equiv of **3**. In contrast, the reaction of nickelocene with **3** proceeds by displacement of the Cp ligands in a stepwise manner to give initially the dinuclear species NiMo(μ-$S_2C_2Ph_2$)$_2$Cp$_2$ **5**, which then reacts further with **3** to produce **4**.

Introduction

Since their rise to prominence over 40 years ago, complexes of dithiolene (1,2-enedithiolate) ligands have been recognized as displaying unusual properties.[1] Foremost among these is the existence of multiple accessible redox states, for example, in [Ni($S_2C_2R_2$)$_2$]$^{n-}$ ($n = 0-2$); indeed, one of the main achievements of the 1960s work was the realization that apparently disparate nickel complexes produced in different research laboratories were in fact related by simple redox processes.[2] The redox activity of the dithiolene ligand itself can be described by the existence of three canonical forms separated by the removal or addition of one electron (Scheme 1): a dianionic dithiolate, a radical monoanion, and a neutral dithioglyoxal structure. In this way, the formal oxidation state of the metal in a bis(dithiolene) complex such as Ni($S_2C_2R_2$)$_2$ could be formally regarded as anywhere between +4 and zero. This ambiguity is an archetypal example of what we now recognize as non-innocent behavior.[3] As a result of their redox and optical properties, dithiolene complexes have been investigated for potential applications as nonlinear optical materials, conducting and superconducting solids, and molecular magnets.[4]

Scheme 1. Canonical Forms of Dithiolene Ligand



Dithiolene complexes of molybdenum and tungsten have received particular attention since the discovery that oxidoreductase enzymes containing these metals involve either one or two pterin ligands bound through a dithiolene linkage at the active site.[5] The enzyme systems are thought to cycle between oxidation states M(IV) and M(VI), with M(V) intermediates sometimes observable by EPR spectroscopy.

---

* To whom correspondence should be addressed. E-mail: M.Morris@sheffield.ac.uk.

[1] (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49. (b) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (c) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (d) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, Ch. 16.5. (e) Stiefel, E. I. Dithiolene Chemistry. *Prog. Inorg. Chem.* **2004**, *52*.

[2] Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1963**, *85*, 2029.

[3] Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275.

[4] (a) Robertson, N.; Cronin, L. *Coord. Chem. Rev.* **2002**, *227*, 93. (b) Fourmigué, M. *Acc. Chem. Res.* **2004**, *37*, 179.

[5] (a) Hille, R. *Chem. Rev.* **1996**, *96*, 2757. (b) Johnson, M. K.; Rees, D. C.; Adams, M. W. W. *Chem. Rev.* **1996**, *96*, 2817. (c) Enemark, J. H.; Cooney, J. J. A.; Wang, J.-J.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1175. (d) Sugimoto, H.; Harihara, M.; Shiro, M.; Sugimoto, K.; Tanaka, K.; Miyake, H.; Tsukube, H. *Inorg. Chem.* **2005**, *44*, 6386. (e) Sugimoto, H.; Sakurai, T.; Miyake, H.; Tanaka, K.; Tsukube, H. *Inorg. Chem.* **2005**, *44*, 6927. (f) Wang, J.-J.; Tessier, C.; Holm, R. H. *Inorg. Chem.* **2006**, *45*, 2979.

10.1021/ic0606227 CCC: $33.50

Consequently, the redox properties and EPR parameters of Mo and W dithiolene complexes have been closely studied, even in cases where they do not contain biological co-ligands. These include the bis-cyclopentadienyl compounds $Cp_2M(S_2C_2R_2)$ and dinuclear species such as $Mo_2(\mu\text{-}SCR{=}CRS)_2Cp_2$.[6,7]

Three general methods have been used since the 1960s to prepare dithiolene complexes of virtually all the transition metals:[8] (i) the reaction of metal halides with salts of the free dithiolene ligand, which is limited to those where the free dianions are available such as $S_2C_2(CN)_2^{2-}$ (mnt^{2-}),[9] $S_2C_2H_2$ (edt^{2-}),[10] and $C_3S_5^{2-}$ ($dmit^{2-}$),[11] or those that can be prepared from 1,3-dithiole-2-one heterocycles or the related iminium salts;[12] (ii) reaction of metal carbonyls with the dithiete $(CF_3)_2C_2S_2$, developed by King,[13] which suffers from the fact that this particular dithiete is the only one that is readily available and sufficiently stable; and (iii) reaction of metal halides or carbonyls with the solution derived from the treatment of benzoin or other acyloins with P_2S_5, as developed by Schrauzer and Mayweg.[14] Other less widely applicable methods include the combination of metal sulfido (or di- or polysulfido) complexes with alkynes or of metal alkyne complexes with sulfur.[15] However, one interesting strategy that we felt had been under-used was the transfer of dithiolene ligands from one complex to another. This was also first reported by Schrauzer, who prepared $M(CO)_2(S_2C_2R_2)_2$ (M=Mo, W; R = aryl, alkyl) by the photochemical reaction of $Ni(S_2C_2R_2)_2$ with $M(CO)_6$.[16] This process was later improved by Holm, who found that the reaction proceeded in reasonable yield at room temperature without irradiation when the labile $M(CO)_3(NCMe)_3$ was used as the source of M, leading to typical yields of 30% for Mo and 70% for W.[17] The only other similar reaction was an attempt to transfer an alkylated dithiolene ligand from Ni to $Fe(CO)_5$,[18] until the synthesis of the heterodinuclear complex $(Ph_2C_2S_2)Fe(\mu\text{-}S_2C_2Ph_2)_2RuCp^*$ ($Cp^* = \eta\text{-}C_5Me_5$) by the reaction of $Fe_2(S_2C_2Ph_2)_4$ with $Ru_2(CO)_4Cp^*_2$.[19] Building on the earlier work of Schrauzer and Holm, we have recently reported that dithiolene ligands can be transferred from $Ni(S_2C_2Ph_2)_2$ to the dimolybdenum center of $Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4Cp_2$ to give the alkyne-dithiolene complex $Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}S_2C_2Ph_2)_2Cp_2$.[20] Very recently, the mixed ligand Ni(III) dithiolene complexes $CpNi(S_2C_2R_2)$ (R=Ph, Me) have been efficiently prepared by dithiolene transfer from $Ni(S_2C_2R_2)_2$ to nickelocene with displacement of one Cp ligand.[21]

We decided to investigate the application of the potentially more general dithiolene transfer reaction to the synthesis of mononuclear Cp molybdenum dithiolene complexes since relatively few compounds of the type $[CpM(S_2C_2R_2)_2]^{n-}$ (M=Mo, W; $n = 0$, 1) have been described in the literature. In the 1960s, McCleverty and co-workers prepared $[Ph_4P][CpM(mnt)_2]$ by reaction of $CpMo(CO)_3I$ or $CpW(CO)_3Cl$ with Na_2mnt, in yields of 15 and 35%, respectively. This was, however, accompanied by displacement of the Cp ligand and formation of the tris-dithiolene species $[Ph_4P]_2[M(mnt)_3]$.[22,23] More recently, Fourmigué and Coulon have used a similar route to prepare $[Ph_4P][Cp^*Mo(dmit)_2]$, which was then oxidized by electrocrystallization to neutral $Cp^*Mo(dmit)_2$; the structures of both compounds were determined.[24] The same group has since prepared the tungsten analogue.[25] The only other complexes of this type, $[CpM\{S_2C_2(CF_3)_2\}_2]^{n-}$ (M=W, $n = 0$; M=Mo, $n = 1$), were prepared by treating nitrosyl complexes with the dithiete $S_2C_2(CF_3)_2$.[26,27] A low-yield synthesis of $CpMo\{S_2C_2(CO_2Me)_2\}_2$ by a similar procedure using a combination of sulfur and dimethylacetylene dicarboxylate in place of the dithiete has just been published.[28] We now describe the synthesis of $CpMo(S_2C_2Ph_2)_2$ by dithiolene transfer, together with reactions leading to a family of di- and trinuclear heterometallic dithiolene complexes derived from it.

Results and Discussion

Synthesis of $CpMo(S_2C_2Ph_2)_2$ by Dithiolene Transfer. Treatment of $CpMo(CO)_3Cl$ (**2**) with 1 or 2 molar equiv of $Ni(S_2C_2Ph_2)_2$ (**1**) in refluxing toluene for 2 h produced a dark blue−purple solution that contained two new complexes,

---

(6) Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178−180*, 823.

(7) Rakowski Dubois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmeier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

(8) Rauchfuss, T. B. *Prog. Inorg. Chem.* **2004**, *52*, 1.

(9) Davison, A.; Holm, R. H. *Inorg. Synth.* **1967**, *10*, 8.

(10) (a) Hoyer, E.; Dietzsch, W.; Henning, H.; Schroth, W. *Chem. Ber.* **1969**, *102*, 603. (b) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 3585. (c) King, R. B.; Eggers, C. A. *Inorg. Chem.* **1968**, *7*, 340.

(11) (a) Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215. (b) Pullen, A. E.; Olk, R.-M. *Coord. Chem. Rev.* **1999**, *188*, 211. (c) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115. (d) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99.

(12) (a) Mueller-Westerhoff, U. T.; Sanders, R. W. *Organometallics* **2003**, *22*, 4778. (b) Boyde, S.; Garner, C. D.; Joule, J. A.; Rowe, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 800. (c) Rowe, D. J.; Garner, C. D.; Joule, J. A. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1907.

(13) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587.

(14) (a) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *Inorg. Chem.* **1965**, *4*, 1615. (b) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.

(15) (a) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. (b) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114. (c) Abbott, A.; Bancroft, M. N.; Morris, M. J.; Hogarth, G.; Redmond, S. P. *Chem. Commun.* **1998**, 389.

(16) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 5174.

(17) (a) Lim, B. S.; Donahue, J. P.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 263. (b) Goddard, C. A.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5389.

(18) (a) Schrauzer, G. N.; Kisch, H. *J. Am. Chem. Soc.* **1973**, *95*, 2501. (b) Schrauzer, G. N.; Rabinowitz, H. N.; Frank, J. K.; Paul, I. C. *J. Am. Chem. Soc.* **1970**, *92*, 212.

(19) Kuge, K.; Inomata, S.; Tobita, H.; Ogino, H. *Chem. Lett.* **1999**, 1075.

(20) Adams, H.; Morris, M. J.; Morris, S. A.; Motley, J. C. *J. Organomet. Chem.* **2004**, *689*, 522.

(21) Nomura, M.; Okuyama, R.; Fujita-Takayama, C.; Kajitani, M. *Organometallics* **2005**, *24*, 5110.

(22) (a) Locke, J.; McCleverty, J. A. *Inorg. Chem.* **1966**, *5*, 1157. (b) McCleverty, J. A.; James, T. A.; Wharton, E. J. *Inorg. Chem.* **1969**, *8*, 1340.

(23) Churchill, M. R.; Coake, J. *J. Chem. Soc. A* **1970**, 2046.

(24) Fourmigué, M.; Coulon, C. *Adv. Mater.* **1994**, *6*, 948.

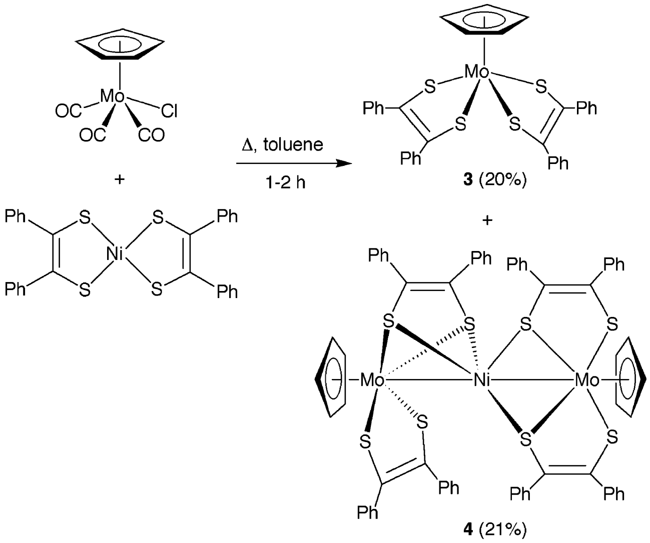
(25) Domercq, B.; Coulon, C.; Feneyrou, P.; Dentan, V.; Robin, P.; Fourmigué, M. *Adv. Funct. Mater.* **2002**, *12*, 359.

(26) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1967**, *6*, 469.

(27) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 3308.

(28) Nomura, M.; Sasaki, S.; Fujita-Takayama, C.; Hoshino, Y.; Kajitani, M. *J. Organomet. Chem.* **2006**, *691*, 3274.

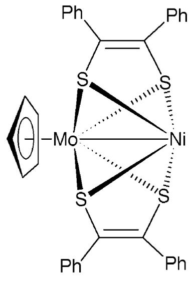
Scheme 2. Dithiolene Transfer from $Ni(S_2C_2Ph_2)_2$ to $CpMo(CO)_3Cl$



dark blue−purple $CpMo(S_2C_2Ph_2)_2$ (**3**) and royal blue trinuclear $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (**4**) (Scheme 2). The two compounds were formed in a combined yield of 35−40%, but their relative isolated yields can vary considerably. This is because during separation of the constituents by column chromatography on silica, **4** gradually decomposes to give more **3**, so to obtain the maximum amount of **4**, the purification should be carried out relatively quickly; if this is done, both compounds can be isolated in yields of around 20%. A further practical consideration is that although unreacted $Ni(S_2C_2Ph_2)_2$ is eluted first from the column, it is rather insoluble; hence, if large amounts remain at the end of the reaction, it can dissolve slowly from the top of the column and contaminate the subsequent bands. Consequently, the use of 1 equiv of the Ni complex in the reaction is recommended. No trace was found of any products arising from displacement of the Cp ring from molybdenum in the current reaction, possibly because it involves only neutral complexes and is carried out in a nonpolar solvent.

There are two possible ways in which the dithiolene ligands might be transferred from nickel to molybdenum: either by release of free dithiobenzil from the nickel center into solution, a process that would essentially be analogous to the reaction of $CpMo(CO)_3Cl$ with the dithiete $S_2C_2(CF_3)_2$ reported earlier; or by the formation of a heterodinuclear NiMo complex followed by transfer of the ligands and release of the Ni in an unspecified form. Additional experiments were carried out to investigate the mechanism of the reaction. First, heating pure $CpMo(S_2C_2Ph_2)_2$ with $Ni(S_2C_2Ph_2)_2$ did not produce **4**, and moreover, **4** did not decompose thermally over the time scale of the reaction to give **3**. Hence, trinuclear **4** does not appear to be an intermediate in the formation of bis(dithiolene) complex **3**. Second, if one postulates the existence of a common dinuclear intermediate complex in the formation of **3** and **4**, such as that illustrated as A (Chart 1), which might either release the Ni to give **3** or react further with **3** to give **4**, we reasoned that if additional **3** was already present in the solution at the start of the reaction, the interception of A might be rendered more effective and the yield of **4** increased. In the event, however, heating equimolar quantities of $CpMo(CO)_3Cl$, $Ni(S_2C_2Ph_2)_2$, and $CpMo(S_2C_2Ph_2)_2$ under similar conditions produced exactly the opposite effect: the yield of **4** dropped to 8%, and the entire reaction was retarded, with much starting material still present after 3 h (81% of the initial Ni complex was reclaimed). However, only 39% of the added molybdenum bis(dithiolene) **3** was recovered, and several new unidentified products were also observed. Clearly, the additional **3** did not react with A to give **4**, and moreover, its presence interfered in some way in the course of the reaction between $CpMo(CO)_3Cl$ and $Ni(S_2C_2Ph_2)_2$.[29] One possibility is that an electron-transfer process is involved during the reaction that might be disrupted by the addition of **3**, which is relatively easily reduced. Despite this outcome, the involvement of a dinuclear complex in the dithiolene transfer process still appears likely given the isolation of heterometallic species in the reaction.

Chart 1. Structure of A, One Possible Intermediate in Dithiolene Transfer Reaction



A

Characterization and Structure of $CpMo(S_2C_2Ph_2)_2$ (3). The nature of $CpMo(S_2C_2Ph_2)_2$ was initially deduced from its mass spectral and analytical data. Formally, **3** contains Mo(V) (d^1 configuration) and, as befits its paramagnetic nature, displays a featureless ^1H NMR spectrum in the δ 0−10 region. On an expanded scale, two broad singlets were observed at δ 15 and −4 ppm, presumably corresponding to the phenyl and Cp protons, respectively. Its X-band EPR spectrum in a toluene/dimethyl formamide (9:1) solution at 220 K displays a peak at $g = 2.0122$ with molybdenum satellites ($A_{Mo} = 9.15$ G). The magnitude of this coupling indicates considerable delocalization of the unpaired electron onto the dithiolene ligands (d^1 molybdenum complexes typically have A_{Mo} of 30−50 G).[30] In a frozen toluene/dimethyl formamide glass (111 K), the compound gives a rhombic spectrum with g values of 2.0275, 2.0074, and 1.9936, all of which display noticeable satellites ($|A_{Mo}| =$ 14, 10.5, and 18 G, respectively). These g values are almost identical to those reported for the single-crystal EPR study of the analogous $Cp^*Mo(dmit)_2$ radical.[24]

The molecular structure of **3** is shown in Figure 1, with selected bond lengths and angles collected in Table 1. The

---

(29) A control reaction was also carried out between **3** and $CpMo(CO)_3Cl$, which showed that these two complexes do react but over a much slower timescale than that of the original reaction.

(30) Cleland, W. E., Jr.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017.

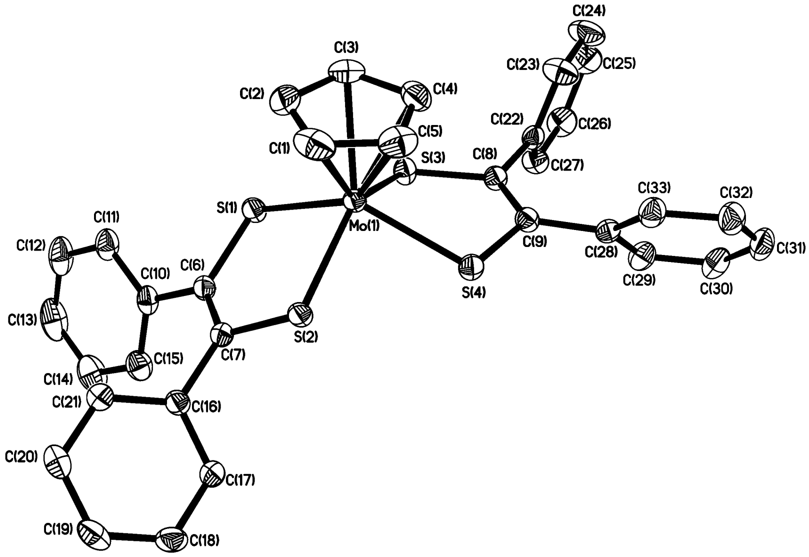


Figure 1. Molecular structure of complex **3** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**

Mo(1)−S(2)	2.3625(6)	Mo(1)−S(3)	2.3668(6)
Mo(1)−S(1)	2.3788(6)	Mo(1)−S(4)	2.3999(7)
S(1)−C(6)	1.732(2)	S(2)−C(7)	1.7362(19)
S(3)−C(8)	1.728(2)	S(4)−C(9)	1.740(2)
C(6)−C(7)	1.366(3)	C(8)−C(9)	1.371(3)
S(2)−Mo(1)−S(3)	132.841(19)	S(2)−Mo(1)−S(1)	80.768(19)
S(3)−Mo(1)−S(1)	78.294(19)	S(2)−Mo(1)−S(4)	84.372(17)
S(3)−Mo(1)−S(4)	80.969(17)	S(1)−Mo(1)−S(4)	134.28(2)
C(6)−S(1)−Mo(1)	110.01(7)	C(7)−S(2)−Mo(1)	110.26(7)
C(8)−S(3)−Mo(1)	105.40(7)	C(9)−S(4)−Mo(1)	104.82(7)

molybdenum atom is situated in a four-legged piano-stool environment made up of the Cp ligand and the four sulfur atoms. The Mo(1)−S(2) and Mo(1)−S(3) bonds are shorter than Mo(1)−S(1) and, particularly, Mo(1)−S(4). As noted before for complexes of this type, the C−S bonds in the dithiolene rings are relatively short (av. 1.734 Å), and the C═C bonds relatively long (av. 1.369 Å), indicating a considerable contribution of the radical monoanion resonance structure shown in the center of Scheme 1. The most noticeable feature, however, is the folding of the dithiolene ligands: that containing S(1) and S(2) is almost planar, with the angle between the Mo(1)−S(1)−S(2) plane and the S(1)−C(6)−C(7)−S(2) plane being only 1.1°, whereas the other dithiolene ligand is folded up toward the Cp ligand with a corresponding fold angle of 27.9°. The same phenomenon was observed in the structures of $[Cp^{*}M(dmit)_2]^{n-}$ ($n = 0, 1$): in the neutral complex, one dithiolene was planar and the other folded, as in **3**, whereas in the anion, both were folded toward the Cp ligand.[24,25] It has been shown that in d^2 molecules such as $[CpMo(S_2C_2R_2)_2]^-$, the folding is due to the interaction of both π-donor dithiolenes with the empty d_{z^2} orbital; on oxidation to the d^1 neutral species, one of the dithiolenes begins to bend away from the Cp ligand to interact with the half-filled d_{xy} orbital instead and becomes planar. This trend is continued in d^0 complexes of the type $[CpTi(S_2C_2R_2)_2]^-$, where one dithiolene is folded toward the Cp ring to interact with the d_{z^2} orbital and the other away from it to interact with the d_{xy} orbital.[6]

Characterization and Structure of $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (4). The first indication of the heterometallic nature of **4** came with the observation of a mass ion envelope centered at m/z 1349 in its mass spectrum, and atomic absorption spectroscopy subsequently confirmed the presence of Ni and Mo in a 1:2 ratio. The compound is diamagnetic and displays peaks for phenyl and Cp protons in a 4:1 intensity ratio in its ^1H NMR spectrum. The simplicity of both the ^1H and the ^{13}C NMR spectra indicate the equivalence of the dithiolene ligands in solution, although in the latter, the dithiolene carbon atoms could not be definitively observed.[31] When the ^1H and ^{13}C NMR spectra were recorded at a low temperature (223 K), the phenyl and Cp resonances in both spectra were broadened considerably, indicating the possible operation of a fluxional process.

Complex **4** is air-stable in the solid state, but it decomposes slowly in solution to give **3**, although this decomposition is slower than during the chromatographic purification. Crystallization by diffusion of pentane into a THF solution produced large blue blocks of **4**·THF suitable for X-ray analysis. The unit cell contains two independent molecules with only relatively minor differences between them; the molecular structure of one of these is shown in Figure 2 with selected bond lengths and angles given in Table 2. The core of the molecule consists of a Mo−Ni−Mo axis, which is virtually linear with a Mo(1)−Ni(1)−Mo(2) angle of 174.725(18)°. The Mo(1)−Ni(1) bond [2.7514(5) Å] is considerably shorter than Mo(2)−Ni(1) [2.8654(5) Å], but both of these are quite long when compared to the 2.55−2.65 Å length quoted for typical Ni−Mo single bonds in heterodinuclear compounds.[32] They are, however, very similar to the 2.798(8) Å length found in the trinuclear species $[Ph_4P]_2[Ni(MoS_4)_2]$.[33]

Notwithstanding the solution structure, the molecule exhibits three different bonding modes for the dithiolene

---

(31) In the ^{13}C NMR spectra of **4**, a broad hump was consistently observed at 158.5 ppm, which we tentatively assign to the dithiolene carbons.

(32) (a) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298. (b) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1995**, *14*, 2937. (c) Chetcuti, M. J.; Fanwick, P. E.; McDonald, S. R.; Rath, N. P. *Organometallics* **1991**, *10*, 1551.

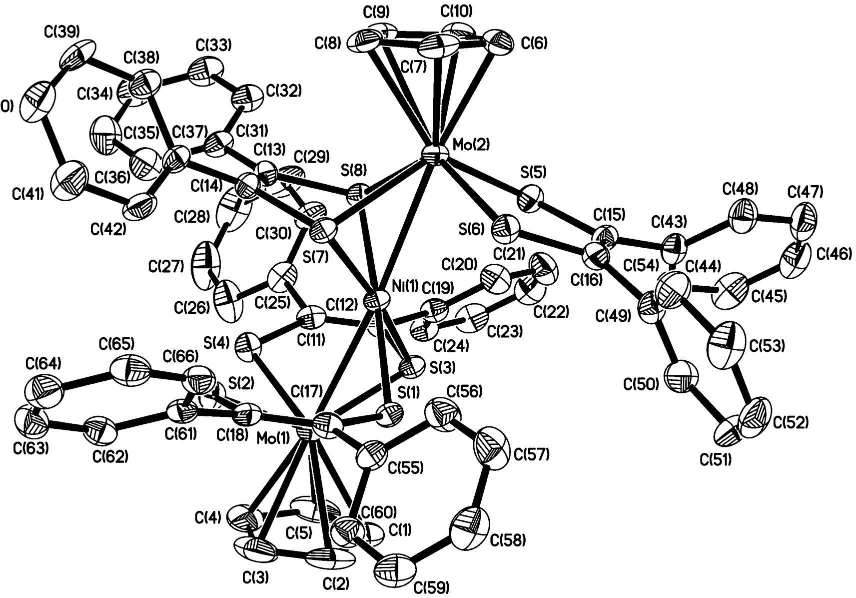


Figure 2. Structure of one of the two independent molecules of complex **4** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms and THF of crystallization have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for One of the Two Independent Molecules of Complex **4**·THF[a] Present in the Unit Cell

Mo(2)−S(5)	2.3262(9)	Mo(2)−S(6)	2.3452(8)
Mo(2)−S(7)	2.4715(8)	Mo(2)−S(8)	2.4807(8)
Mo(2)−Ni(1)	2.8654(5)	Mo(1)−S(1)	2.3861(8)
Mo(1)−S(3)	2.3876(8)	Mo(1)−S(2)	2.3914(8)
Mo(1)−S(4)	2.3923(8)	Mo(1)−Ni(1)	2.7514(5)
Ni(1)−S(8)	2.2286(9)	Ni(1)−S(7)	2.2385(9)
Ni(1)−S(1)	2.2703(9)	Ni(1)−S(3)	2.2733(9)
S(1)−C(17)	1.766(3)	S(2)−C(18)	1.758(3)
S(3)−C(12)	1.765(3)	S(4)−C(11)	1.754(3)
S(5)−C(15)	1.747(3)	S(6)−C(16)	1.750(3)
S(7)−C(14)	1.813(3)	S(8)−C(13)	1.812(3)
C(11)−C(12)	1.358(4)	C(13)−C(14)	1.341(4)
C(15)−C(16)	1.365(4)	C(17)−C(18)	1.370(4)
S(5)−Mo(2)−S(6)	81.31(3)	S(5)−Mo(2)−S(7)	127.20(3)
S(6)−Mo(2)−S(7)	81.70(3)	S(5)−Mo(2)−S(8)	81.65(3)
S(6)−Mo(2)−S(8)	130.38(3)	S(7)−Mo(2)−S(8)	72.63(3)
S(1)−Mo(1)−S(3)	78.37(3)	S(1)−Mo(1)−S(2)	80.94(3)
S(3)−Mo(1)−S(2)	133.06(3)	S(1)−Mo(1)−S(4)	133.16(3)
S(3)−Mo(1)−S(4)	81.30(3)	S(2)−Mo(1)−S(4)	83.05(3)
S(8)−Ni(1)−S(7)	82.07(3)	S(8)−Ni(1)−S(1)	177.06(3)
S(7)−Ni(1)−S(1)	97.90(3)	S(8)−Ni(1)−S(3)	96.47(3)
S(7)−Ni(1)−S(3)	172.78(3)	S(1)−Ni(1)−S(3)	83.19(3)
Mo(1)−Ni(1)−Mo(2)	174.725(18)	Ni(1)−S(1)−Mo(1)	72.39(2)
Ni(1)−S(3)−Mo(1)	72.31(2)	Ni(1)−S(7)−Mo(2)	74.76(2)
Ni(1)−S(8)−Mo(2)	74.74(2)		

[a] These relate to the molecule shown in Figure 2.

ligands in the solid state. The two ligands that bridge the Mo(1)−Ni(1) bond are both bonded in what we term semi-bridging mode, in which one sulfur atom bridges the two metals but the other is joined solely to Mo. This bonding mode has been frequently encountered before in dimolybdenum chemistry[3,5,34] but is rare in heterodinuclear systems.[19] In contrast, one of the dithiolene ligands bonded to Mo(2) is terminal, and the other is fully bridging, lying effectively perpendicular to the Ni−Mo bond. This unusual arrangement may be a consequence of the steric bulk of the phenyl groups since it allows the two Mo(dithiolene)$_2$ units to lie orthogonal to each other, with the central Ni atom bonded to two *cis*-sulfurs of each [one sulfur atom from each dithiolene attached to Mo(1) and both sulfur atoms of one dithiolene attached to Mo(2)]. The nickel atom thus attains a distorted square planar environment if the metal−metal bonds are disregarded; two of the S−Ni−S angles are approximately 97°, and the other two approximately 83°. This arrangement is reminiscent of that found in the dication $[\mathrm{Cp_2Mo}(\mu\text{-SMe})_2\mathrm{Ni}(\mu\text{-SMe})_2\mathrm{MoCp_2}]^{2+}$, although in this complex the Mo···Ni distance is much longer (3.39 Å), precluding any metal−metal bonding.[35] As expected, the Mo−S bonds in the terminal dithiolene ligand are the shortest (av. 2.336 Å), and those in the bridging dithiolene the longest (av. 2.476 Å), with those involving the semi-bridging dithiolene intermediate in value (av. 2.389 Å).

The structure of **4** is also reminiscent of the products of several recently reported reactions in which mono-dithiolene complexes of the type CpM(S$_2$C$_2$R$_2$) (M═Co, Rh) have been treated with low-valent metal fragments to give the dithiolene-bridged heterotrinuclear species. It is interesting to note that in these products, such as Mo(CO)$_2$[Co(S$_2$C$_6$H$_4$)Cp]$_2$, in which two benzenedithiolate ligands bridge a CoMoCo framework,[36] or Ni[Rh(S$_2$C$_2$B$_{10}$H$_{10}$)(η-C$_5$H$_3{}^t$Bu$_2$)]$_2$, in which

---

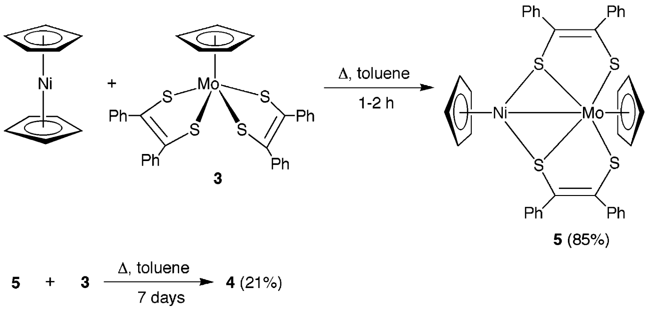
(33) (a) Chetcuti, M. J. *J. Cluster Sci.* **1996**, *7*, 225. (b) Søtofte, I. *Acta Chem. Scand.* **1976**, *30*, 157. (c) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *10*, 934.

(34) (a) Sugiyama, T.; Yamanaka, T.; Shibuya, M.; Nakase, R.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1998**, 501. (b) Shibahara, T.; Tsuboi, M.; Nakaoka, S.; Ide, Y. *Inorg. Chem.* **2003**, *42*, 935. (c) Roesselet, K.; Doan, K. E.; Johnson, S. D.; Nicholls, P.; Miessler, G. L.; Kroeker, R.; Wheeler, S. H. *Organometallics* **1987**, *6*, 480. (d) Miki, Y.; Takagi, H.; Ichimura, A.; Akashi, H.; Shibahara, T. *Chem. Lett.* **2002**, 482.

(35) (a) Prout, K.; Critchley, S. R.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2305. (b) Dias, A. R.; Green, M. L. H. *Chem. Commun.* **1969**, 962. (c) Dias, A. R.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 1951.

(36) (a) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098. (b) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14. (c) Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108.

Scheme 3. Synthesis of NiMo and $NiMo_2$ Complexes from Nickelocene



the dithiolene ligand is incorporated into a carborane unit, the trimetal axis tends to be bent rather than linear, and in the case of the latter compound, the nickel atom adopts a distorted tetrahedral arrangement coordinated by the four sulfurs.[37]

Synthesis of $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$ (5). Consideration of the structure of the $NiMo_2$ complex **4** suggested that it might formally be regarded as two molecules of **3** complexed to a Ni(0) fragment or, alternatively, as two $[CpMo(S_2C_2Ph_2)_2]^-$ anions complexed to a Ni(II) center. Even though the square planar coordination of the four sulfur atoms to the Ni might be considered to favor the latter view, we decided to investigate whether the compound could also be prepared from **3** and a suitable source of Ni(0). Indeed, the reaction of 2 equiv of **3** with $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) in toluene at room temperature was found to produce **4** in 64% yield. Although, as mentioned previously, such reactions have been carried out previously with mono-dithiolene complexes, this appears to be the first of this type involving a bis-(dithiolene) precursor. On the other hand, by heating **4** with elemental sulfur in toluene solution, the Ni atom can be readily abstracted as insoluble nickel sulfide to give **3** in 70% yield.

Since $Ni(cod)_2$ is relatively difficult to make and handle, an alternative source of Ni(0) was then investigated. It is known that nickelocene, which is much easier to prepare, can act as a precursor to complexes of the type $Ni(PR_3)_4$ for use in catalytic reactions; both Cp rings are relatively easily displaced by phosphines.[38] Therefore, the reaction of Cp_2Ni with **3** was attempted. Surprisingly, after 1 h in refluxing toluene, the purple color of the starting solution had changed not to the blue of **4** but to a bright red−purple. Column chromatography allowed the isolation of the dinuclear complex $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$ **5** as an air-stable crystalline solid in 85% yield (Scheme 3). The fate of the displaced Cp ligand is unknown, but it seems likely that it is released as a radical that either dimerizes to fulvalene or abstracts a hydrogen atom to give cyclopentadiene.

The ^1H NMR spectrum of diamagnetic **5** displays phenyl group resonances together with two closely spaced peaks for the Cp ligands at δ 4.80 and 4.77, in a ratio of 4:1:1. This chemical shift is, in our experience, unusually low for a Cp ligand attached to molybdenum. The ^{13}C NMR spectrum contains two peaks for the dithiolene carbons, one of which is at δ 170.2 and the other at 135.1, consistent with the fact that one end of the dithiolene ligand bridges the two metals and the other is attached only to Mo. Two peaks due to the ipso carbons of the phenyl groups are also evident, indicating that the solid state structure is retained in solution. Comparison of the UV−vis spectrum of **5** with that of **4** indicates that the same chromophore is involved in both cases, although assignment of the transitions occurring is problematic.

The molecular structure of **5** in the crystal is shown in Figure 3, with selected bond lengths and angles collected in Table 3. The molecule contains one nickel atom and one molybdenum, each of which bears a Cp ligand. The metals are joined by a bond of length 2.7201(7) Å, which is shorter than either of those in **4**. The bond is spanned by two dithiolene ligands that are bonded in the same semi-bridging mode as those that bridged the Mo(1)−Ni(1) bond in **4**, and the Mo−S and Ni−S bond lengths within this unit are comparable to those in the $NiMo_2$ complex. In fact, the geometry of the $CpMo(dithiolene)_2$ portion of the molecule is also largely unchanged from that in **3**, with the exception that both dithiolene ligands are now folded as a result of the attachment of the CpNi fragment.

Since **5** results from the replacement of one of the Cp ligands in nickelocene by a $CpMo(S_2C_2Ph_2)_2$ fragment, our next step was to see whether the remaining Cp ring could also be replaced to give **4**. In fact, displacement of the second ring is much more difficult in this case. Thus, TLC monitoring of a reaction between equimolar amounts of **5** and **3** showed that the reaction was almost complete after 7 days in refluxing toluene. Column chromatography then produced a 21% yield of **4** (which is difficult to separate from unreacted **5**).

Electrochemistry. Cyclic voltammetry studies of the new complexes were carried out in dichloromethane solution with 0.1 M Bu_4NBF_4 as the supporting electrolyte. The cyclic voltammogram of $CpMo(S_2C_2Ph_2)_2$ shows three reversible processes: a very facile reduction to the monoanion (formally d^2) at −0.134 V (vs Ag/AgCl), a second reduction to a dianion (d^3) at −1.175 V, and an oxidation to a cation (d^0) at +0.447 V. These processes were also investigated spectroelectrochemically in an optically transparent thin layer electrochemical (OTTLE) cell (CH_2Cl_2 solution, −20 °C). The UV−vis/NIR spectrum of neutral **3** shows peaks at 827 and 574 nm, together with much weaker features at 1020 and 1120 nm; in the analogous $Cp^*Mo(dmit)_2$ radical, these features were observed as a strong peak at 941 nm and a weaker one at 1153 nm.[25] On oxidation to the cation $\mathbf{3}^+$, as shown in Figure 4, the stronger peaks shift to higher energy at 725 and 554 nm, retaining their relative intensities, and the weak features disappear. However, on reduction of **3** to the anion $\mathbf{3}^-$, shown in Figure 5, the main peak is somewhat quenched, leading to a broad double-humped feature at 707 and 639 nm, and the weak low-energy peaks again disappear. The appearance of this spectrum is again very similar to that

---

(37) (a) Cai, S.; Wang, J.-Q.; Jin, G.-X. *Organometallics* **2005**, *24*, 4226. (b) Wang, J.-Q.; Hou, X. F.; Weng, L.-H.; Jin, G.-X. *J. Organomet. Chem.* **2005**, *690*, 249. (c) Liu, S.; Wang, X.; Jin, G.-X. *J. Organomet. Chem.* **2006**, *691*, 261.

(38) Leadbeater, N. E. *J. Org. Chem.* **2001**, *66*, 7539.

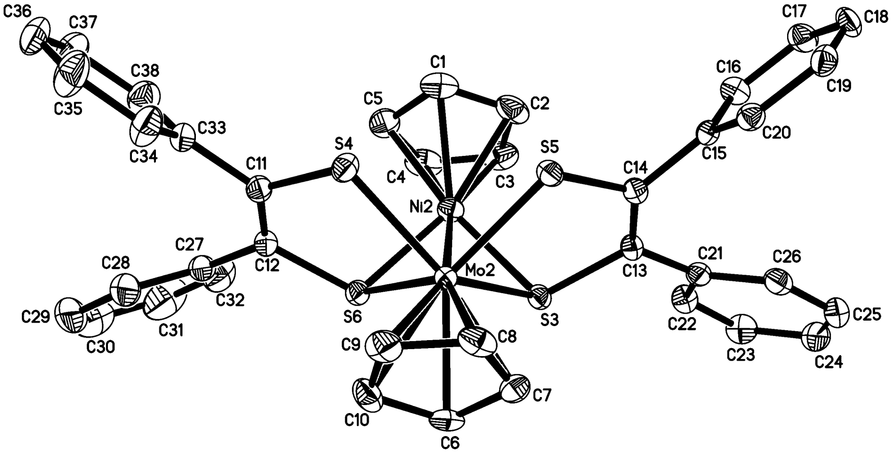


Figure 3. Molecular structure of complex **5** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

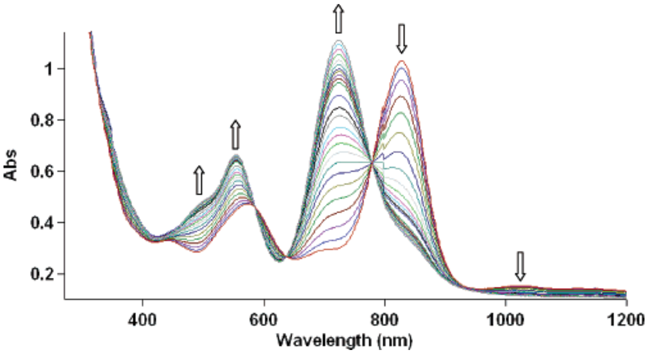


Figure 4. OTTLE plot of redox process occurring on oxidation of 3 to 3^+ (potential held at 0.8 V vs Ag/AgCl).

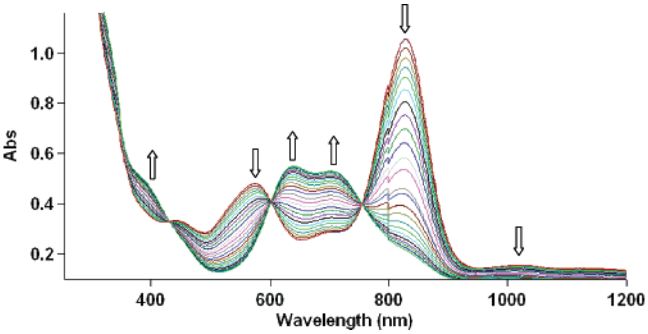


Figure 5. OTTLE plot of redox process occurring on reduction of 3 to 3^- (potential held at −0.5 V vs Ag/AgCl).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Mo(2)−S(6)	2.3814(8)	Mo(2)−S(3)	2.3830(8)
Mo(2)−S(5)	2.4011(8)	Mo(2)−S(4)	2.4098(8)
Mo(2)−Ni(2)	2.7201(7)	Ni(2)−S(6)	2.1990(9)
Ni(2)−S(3)	2.2155(9)	S(3)−C(13)	1.782(3)
S(4)−C(11)	1.753(3)	S(5)−C(14)	1.738(3)
S(6)−C(12)	1.768(3)	C(11)−C(12)	1.354(4)
C(13)−C(14)	1.363(4)		
S(6)−Mo(2)−S(3)	79.76(3)	S(6)−Mo(2)−S(5)	135.33(3)
S(3)−Mo(2)−S(5)	81.58(3)	S(6)−Mo(2)−S(4)	81.72(3)
S(3)−Mo(2)−S(4)	135.03(3)	S(5)−Mo(2)−S(4)	83.57(3)
S(6)−Ni(2)−S(3)	87.58(3)	Ni(2)−S(3)−Mo(2)	72.43(3)
Ni(2)−S(6)−Mo(2)	72.74(3)		

of $[Cp^*Mo(dmit)_2]^-$, in which the peaks have been assigned to transitions from the HOMO (essentially dithiolene π-based) to the LUMO (predominantly the Mo d_{z^2} orbital). Both couples are clearly fully reversible as shown by the occurrence of clear isosbestic points in the spectra. Interestingly, the spectrum of $\mathbf{3}^-$ shows very little further change on reduction to the dianion.

The electrochemistry of the heteronuclear complexes is more complicated. Dinuclear **5** shows one fully reversible reduction at −0.905 V, together with an irreversible oxidation at E_pa = 0.748 V. Trinuclear **4** shows two reductions, the first one being fully reversible at −0.132 V, and the second being irreversible at E_pc = −0.666 V. The similarity of the first reduction potential to that of **3** might indicate that it is localized on the molybdenum dithiolene moieties, while the second has a broader line shape and could be due to a nickel-based reduction. Complex **4** also shows two oxidation waves, the first of which at 0.454 V is broad and partially reversible, whereas the second, at E_pa = 1.032 V, is irreversible. No attempt was made to investigate the spectroelectrochemistry of either **4** or **5**.

Conclusion. The chemistry reported here again demonstrates the utility of the dithiolene ligand transfer reaction, which in this case provides a useful route to the new bis(dithiolene) Mo(V) complex $CpMo(S_2C_2Ph_2)_2$ from the readily available precursors $Ni(S_2C_2Ph_2)_2$ and $CpMo(CO)_3Cl$. The isolation of the unusual Mo_2Ni complex **4** was an unexpected bonus. We have also shown that one of the Cp ligands of nickelocene can be readily displaced by the bis(dithiolene) complex to give an excellent yield of the heterobimetallic dithiolene-bridged compound **5**, whereas the removal of the second ring to give **4** is a much slower process. We are currently investigating the reactions of nickelocene with other suitable dithiolene precursors, and of $CpMo(S_2C_2Ph_2)_2$ with a range of other suitably labile metal−ligand fragments, the results of which will be reported separately.

Experimental Procedures

Materials. General experimental techniques were as described in recent work from this laboratory.[20] All reactions were routinely carried out under an argon or nitrogen atmosphere, although separation procedures were carried out without any special precautions since the products described are all relatively air-stable. Solvents were purified with a Grubbs-type purification system manufactured by Innovative Technology, Newburyport, MA. The complexes $Ni(S_2C_2Ph_2)_2$ and $CpMo(CO)_3Cl$ were prepared by the

Table 4. Summary of Crystallographic Data for Complexes **3**, **4**·THF, and **5**

	3	**4**·THF	**5**
empirical formula	$C_{33}H_{25}MoS_4$	$C_{70}H_{58}Mo_2Ni\ OS_8$	$C_{38}H_{30}MoNiS_4$
Fw	*645.71*	*1422.23*	*769.51*
T (K)	150(2)	150(2)	150(2)
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P21/c$
a (Å)	11.1395(19)	14.4954(8)	15.229(4)
b (Å)	11.408(2)	15.5339(9)	28.544(6)
c (Å)	11.938(2)	28.2119(17)	7.4346(18)
α (deg)	79.504(3)	93.8560(10)	90
β (deg)	81.005(3)	92.7860(10)	92.086(4)
γ (deg)	70.743(3)	104.4510(10)	90
V (Å^3)	1400.7(4)	6123.5(6)	3229.8(13)
Z	2	4	4
density (calcd)/mg m^{-3}	1.531	1.543	1.583
μ (mm^{-1})	0.789	1.026	1.258
F(000)	658	2904	1568
cryst size (mm^3)	0.43 × 0.31 × 0.12	0.48 × 0.48 × 0.40	0.34 × 0.23 × 0.21
θ range for data collection (deg)	1.74−28.32	1.36−27.54	1.34−28.57
reflns collected	8960	51432	37004
independent reflns	6350 [$R_{int} = 0.0237$]	26550 [$R_{int} = 0.0683$]	7686 [$R_{int} = 0.0768$]
data/restraints/params	6350/0/343	26550/0/1477	7686/0/397
GOF on F^2	1.057	0.922	0.926
final R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0314$ $wR_2 = 0.0850$	$R_1 = 0.0411$ $wR_2 = 0.0850$	$R_1 = 0.0364$ $wR_2 = 0.0743$
all data	$R_1 = 0.0339$ $wR_2 = 0.0870$	$R_1 = 0.0723$ $wR_2 = 0.0937$	$R_1 = 0.0643$ $wR_2 = 0.0816$
largest diff. peak and hole (e Å^{-3})	1.104 and −1.253	0.937 and −0.706	0.646 and −0.420

literature procedures.[14,39] All other chemicals were obtained from commercial sources and used as supplied.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 Fourier transform machine with automated sample-changer or on Bruker AMX400 or DRX-500 spectrometers. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm. The $^{13}C\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). IR spectra were recorded on a Perkin-Elmer 1600 FT machine. The EPR spectrum of **3** was recorded at the University of Manchester on a Bruker EMX hybrid spectrometer and simulated with Bruker's Xsophe software. Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with *m*-nitrobenzyl alcohol as a matrix; the figures reported are the highest intensity peak of each isotope envelope. UV−vis absorption spectra were recorded on a Varian Cary 50 instrument in the range of 200−800 nm in dichloromethane solution with a path length of 1 cm. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry with a Perkin-Elmer 2400 analyzer. Cyclic voltammetry was carried out using an EG&G 273A potentiostat. Measurements were carried out under dinitrogen in dry freshly distilled dichloromethane solutions of approximate concentration 1 mM, containing 0.1 M Bu_4NBF_4 as a supporting electrolyte. Potentials were measured relative to a Ag/AgCl electrode. Processes are described as reversible if $\Delta E < 100$ mV and $|I_pa/I_pc| = 1$. UV−vis/NIR spectroelectrochemistry was also carried out in CH_2Cl_2 solution in an OTTLE cell mounted in a Cary 5000 spectrometer, thermostatically held at 253 K.

Synthesis. $CpMo(S_2C_2Ph_2)_2$ (3) and $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (4). The complexes $CpMo(CO)_3Cl$ (244.8 mg, 0.873 mmol) and $Ni(S_2C_2Ph_2)_2$ (474.1 mg, 0.873 mmol) were dissolved in toluene (150 mL), and the solution was refluxed for 2 h. The solvent was removed from the resulting dark solution on the vacuum line. (***Note:*** *We have no evidence for the formation of highly toxic Ni(CO)$_4$ in this reaction, but this possibility should be considered during workup and appropriate precautions taken.*) The solid residue was redissolved in dichloromethane and adsorbed onto 5 g of chromatographic silica, which was then loaded onto a silica column prepared in light petroleum or hexanes. Elution of the column with hexane-dichloromethane (4:1 v/v) produced a green band of unreacted $Ni(S_2C_2Ph_2)_2$ (139.8 mg, 29.5% recovery). A 13:7 mixture of the same solvents was then used to elute a dark blue−purple band of $CpMo(S_2C_2Ph_2)_2$ (**3**) (111.2 mg, 19.8% based on Mo). The eluting solvent was then changed to a 2:3 mixture to elute the royal blue band of $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (**4**) (124.5 mg, 21.1% based on Mo). These yields are for a total chromatography time of 1.5 h; as noted in the text, longer times led to increased amounts of **3** but reduced amounts of **4**.

Data for **3**: Mp 237−240 °C. IR (KBr): 3106 m, 3052 m, 2925 m, 2854 m, 1676s, 1661s, 1594 m, 1448vs (C═C), 1428vs (C═C), 1211s, 1175s, 1164s, 1072w, 1027w, 999w, 875 m (C−S), 865 m (C−S), 816 m cm^{-1}. ^{1}H NMR: δ 15 (br s), −4 (br s). EPR (toluene, 298 K): $g = 2.010$ ($A_{Mo} = 9.6$ G). Anal. Found: C, 61.06; H, 3.95; S, 19.82. Required for $C_{33}H_{25}MoS_4$: C, 61.40; H, 3.88; S, 19.84%. MS: *m*/*z* 647 (M^+). UV−vis spectrum 574 nm ($\epsilon = 5535$ M^{-1} cm^{-1}), 442 nm ($\epsilon = 3560$ M^{-1} cm^{-1}).

Data for **4**: Mp 202−205 °C. ^{1}H NMR: δ 7.15−6.90 (m, 40 H, Ph), 5.04 (s, 10 H, Cp). ^{13}C NMR: 158.5 (br s, possibly C of dithiolene), 141.0 (C_{ipso} of Ph), 129.6, 127.5, 126.8 (Ph), 94.1 (Cp). Anal. Found: C, 59.51; H, 4.08; S, 18.11. Required for **4**·THF $C_{70}H_{58}Mo_2NiOS_8$: C, 59.13; H, 4.08; S, 18.02%. MS: *m*/*z* 1349 (M^+), 1107 $(M-S_2C_2Ph_2)^+$, 647 $[CpMo(S_2C_2Ph_2)_2]^+$. UV−vis spectrum 587 nm ($\epsilon = 13\,230$ M^{-1} cm^{-1}), 358 nm ($\epsilon = 17\,360$ M^{-1} cm^{-1}).

Reaction of $CpMo(CO)_3Cl$ with $Ni(S_2C_2Ph_2)_2$ in the Presence of Additional $CpMo(S_2C_2Ph_2)_2$. A Schlenk tube was charged with $CpMo(CO)_3Cl$ (74.4 mg, 0.27 mmol), $Ni(S_2C_2Ph_2)_2$ (147.8 mg, 0.27 mmol), and $CpMo(S_2C_2Ph_2)_2$ (169.3 mg, 0.26 mmol). The complexes were dissolved in toluene (50 mL), and the solution was

---

(39) Hoffmann, N. W. *Inorg. Chim. Acta* **1984**, *88*, 59. This procedure was modified in that the NaCp solution was treated with $Mo(CO)_6$ in refluxing THF for 24 h; we did not use $Mo(CO)_3(NCMe)_3$ as an intermediate. A detailed description of our procedure has been posted at http://www.mjmorris.staff.shef.ac.uk/preps.html and is also included in the Supporting Information.

heated to reflux for 3 h. Column chromatography as stated previously afforded green $Ni(S_2C_2Ph_2)_2$ (89.8 mg, 81% recovery), purple $CpMo(S_2C_2Ph_2)_2$ (66.4 mg, 39% recovery), and a small amount of blue $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (13.8 mg, 3.7% based on Ni). Several other unidentified minor bands were observed, and much decomposed material remained uneluted.

Reaction of $Ni(cod)_2$ with $CpMo(S_2C_2Ph_2)_2$. In a glove box, $Ni(cod)_2$ (0.260 g, 0.946 mmol) and $CpMo(S_2C_2Ph_2)_2$ (1.172 g, 1.82 mmol) were dissolved in toluene (50 mL). After stirring for 20.5 h, the solution was removed from the glove box and evaporated to dryness. Column chromatography as stated previously produced a purple band of unchanged **3** followed by a blue zone of $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (0.7893 g, 62%).

Reaction of $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ with Sulfur. A solution of $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$ (100.9 mg, 0.074 mmol) and elemental sulfur (5.3 mg, 0.167 mmol) in toluene (20 mL) was heated to reflux for 2.5 h. After removal of the solvent, column chromatography produced $CpMo(S_2C_2Ph_2)_2$ (71.1 mg, 0.11 mmol, 74%). A black insoluble residue remained at the top of the column.

Synthesis of $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$. A solution of Cp_2Ni (30.0 mg, 0.16 mmol) and $CpMo(S_2C_2Ph_2)_2$ (96.5 mg, 0.15 mmol) in toluene (100 mL) was heated to reflux for 1 h. Column chromatography produced two minor bands (yellow and green) followed by a large red zone of $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$ (97.7 mg, 85%). Mp dec at 230 °C. ^1H NMR: δ 7.25−7.15 (m, 20 H, Ph), 4.80 (s, 5 H, Cp), 4.77 (s, 5 H, Cp). ^{13}C NMR: 170.2 (CPh), 143.5 (C_{ipso}), 141.4 (C_{ipso}), 135.1 (CPh), 129.6−126.3 (m, Ph), 95.7 (Cp), 93.3 (Cp). Anal. Found: C, 59.06; H, 3.91; S, 16.49. Required for $C_{38}H_{30}MoNiS_4$: C, 59.38; H, 3.90; S, 16.67%. MS *m*/*z* 770 (M^+), 647 $(M\text{-}NiCp)^+$. UV−vis spectrum 534 nm ($\epsilon = 13\,445$ M^{-1} cm^{-1}), 339 nm ($\epsilon = 17\,772$ M^{-1} cm^{-1}).

Reaction of $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$ with $CpMo(S_2C_2Ph_2)_2$ To Give $Ni[Mo(S_2C_2Ph_2)_2Cp]_2$. A solution of $NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2$ (100.0 mg, 0.13 mmol) and $CpMo(S_2C_2Ph_2)_2$ (85.0 mg, 0.13 mmol) in toluene (20 mL) was heated to reflux for 7 days, during which the solution took on a blue color. Monitoring the solution by TLC revealed the red spot due to **5** gradually being replaced by a blue one. At the end of the reaction, column chromatography produced two minor bands followed by a purple band of residual **3** (18.5 mg, 22% recovery). Careful elution with a 1:1 mixture of hexane−CH_2Cl_2 produced a blue band of **4**, which could not be completely separated from the red band of residual **5** that immediately followed it. The total mass collected was 65 mg, and ^1H NMR integration revealed that this consisted of a 3:1 mixture of **4** and **5**. Hence, the yield of **4** is approximately 21%. Two further minor green bands were eluted subsequently, but these have yet to be identified.

Crystal Structure Determinations. Crystal data for the three structures are summarized in Table 4 . The data were collected at 150 K on a Bruker Smart CCD area detector equipped with an Oxford Systems cryostat and refined with the program package *SHELXTL*[40] implemented on a Viglen Pentium computer. Hydrogen atoms were placed geometrically and refined in riding mode with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom.

Acknowledgment. We thank the EPSRC and the University of Sheffield for support, Prof. M.D. Ward for provision of electrochemical facilities, and Drs. D. Collison and J. Wolowska (University of Manchester) for recording and simulating the EPR spectrum.

Supporting Information Available: Crystallographic information files for structures 3−5 and a detailed preparation of $CpMo(CO)_3Cl$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0606227

---

(40) *SHELXTL*, an integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS Ltd.