



This is a repository copy of *Dithiolene transfer to the molybdenum nitrosyl complex [CpMo(CO)₂(NO)]: Formation of bimetallic complexes.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/138788/>

Version: Accepted Version

Article:

Adams, H., Grimes, L., Morris, M.J. orcid.org/0000-0001-8802-9147 et al. (1 more author) (2018) Dithiolene transfer to the molybdenum nitrosyl complex [CpMo(CO)₂(NO)]: Formation of bimetallic complexes. *Journal of Organometallic Chemistry*, 877. pp. 73-79. ISSN 0022-328X

<https://doi.org/10.1016/j.jorganchem.2018.09.021>

Article available under the terms of the CC-BY-NC-ND licence (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Proofs to: Dr. M.J. Morris,
Department of Chemistry,
University of Sheffield,
SHEFFIELD S3 7HF, U.K.

Telephone: 0114 2229363

Fax: 0114 2229346

E-mail M.Morris@sheffield.ac.uk

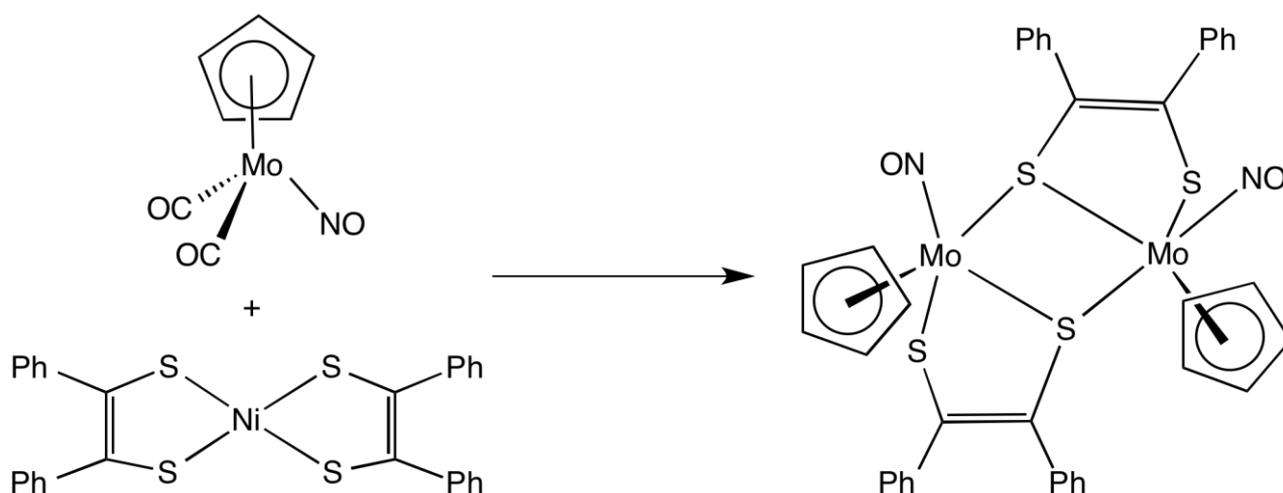
Submitted to J. Organomet. Chem.

**Dithiolene transfer to the molybdenum nitrosyl complex [CpMo(CO)₂(NO)]: formation
of bimetallic complexes**

Harry Adams, Liam Grimes, Michael J. Morris,* Craig C. Robertson

Department of Chemistry, University of Sheffield,
Sheffield S3 7HF, U.K.

Graphical Abstract



The nitrosyl complex $[\text{CpMo}(\text{CO})_2(\text{NO})]$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) reacts with the nickel dithiolene complex $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ to give the expected dimolybdenum complex $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$, but the major product consists of two separable isomers of the tetranuclear complex $[\text{Mo}_2\text{Ni}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2]$, which comprises two $\text{CpMo}(\text{NO})\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2$ units joined through bridging sulfur atoms.

Abstract

The reaction of the nitrosyl complex $[\text{CpMo}(\text{CO})_2(\text{NO})]$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) with the nickel dithiolene complex $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ produces the expected dimolybdenum complex $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$, but only as a minor product (13% yield). The major product (41%) consists of two separable isomers of the tetranuclear complex $[\text{Mo}_2\text{Ni}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2]$, which comprises two $\text{CpMo}(\text{NO})\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2$ units joined through bridging sulfur atoms. The isomers differ in the orientation of one dimeric unit in relation to the other. All three compounds have been structurally characterised.

Keywords

Molybdenum, nickel, nitrosyl, dithiolene, cyclopentadienyl

1. Introduction

Complexes containing dithiolene (1,2-enedithiolate) ligands continue to attract significant research interest [1-5]. Their unusual structural features (e.g. trigonal prismatic coordination in tris-dithiolene complexes)[6] and electronic flexibility (e.g. multiple redox states and the dithiolene ligand's non-innocent character) have led to their investigation for a number of potential applications such as near-IR dyes, conducting solids, molecular magnets, gas separation agents and water-splitting photocatalysts [7-14].

Mononuclear molybdenum and tungsten complexes containing dithiolene ligands have received much research interest as models of the molybdenum cofactor present in a variety of oxygen atom transfer enzymes [15]. More recently the possibility that they might be employed in the chemical separation of ethylene from mixed gas streams by a process involving binding of the alkene to the dithiolene ligands has led to further research on tris-dithiolene complexes of the type $[\text{Mo}(\text{S}_2\text{C}_2\text{R}_2)_3]$ [16]. At the same time, however, a substantial chemistry has developed around dinuclear complexes containing both cyclopentadienyl and dithiolene ligands, exemplified by complexes of the type $[\text{Mo}_2(\mu\text{-S}_2\text{C}_2\text{R}_2)_2\text{Cp}_2]$ [17].

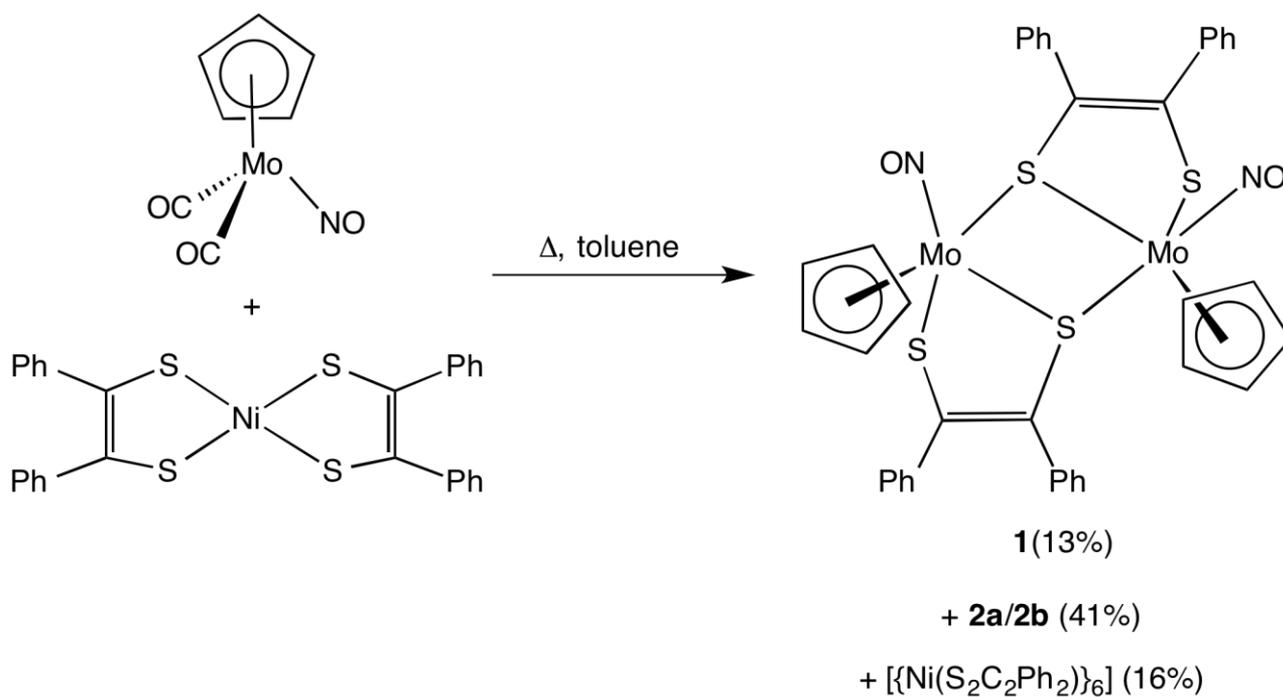
In recent years we have been examining the synthesis of both new and known dithiolene complexes by the intermetallic transfer of the dithiolene ligand, usually from the readily prepared nickel complex $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ to metal centres including molybdenum, tungsten, iron and

ruthenium [18-21]. In the current instance we were drawn to investigate complexes with nitrosyl co-ligands firstly because the NO ligand, like the dithiolene, is a non-innocent variable electron donor ligand; it is also of current interest as a biological signalling molecule. In addition, recent reports of the cleavage of NO in dinuclear metal complexes by Ruiz and co-workers are of relevance to the problem of removal of atmospheric NO_x [22-25].

Relatively few examples of molybdenum nitrosyl dithiolene complexes have been reported previously, and of these the most common structural type is the dinuclear [Mo₂(NO)₂(μ-S₂C₂R₂)₂Cp₂]. For example, the reaction of [CpMo(CO)₂(NO)] with bis(trifluoromethyl)dithiete was shown by King to give [Mo₂(NO)₂{S₂C₂(CF₃)₂}₂Cp₂] in up to 58% yield [26] and the same compound was prepared by McCleverty from [MoI(μ-I)(NO)Cp]₂ and the dithiete [27]. The reaction of [Cp*Mo(CO)₂(NO)] (Cp* = η-C₅Me₅) with sulfur and DMAD (dimethyl acetylenedicarboxylate) gave four complexes in low yield, including [Mo₂(NO)₂{μ-S₂C₂(CO₂Me)₂}₂Cp*₂] (5%) [28]. We therefore considered that the reaction of [CpMo(CO)₂(NO)] with [Ni(S₂C₂Ph₂)₂] might provide a convenient high yield route to a complex such as [Mo₂(NO)₂(μ-S₂C₂Ph₂)₂Cp₂].

2. Results and Discussion

Heating a toluene solution of [CpMo(CO)₂(NO)] with an equimolar amount of [Ni(S₂C₂Ph₂)₂] produced three major new products, all of them brown, of which one was indeed the expected [Mo₂(NO)₂(μ-S₂C₂Ph₂)₂Cp₂] **1** (Scheme 1). The dinuclear formulation was indicated by the mass spectrum, and the complex showed characteristic NO absorptions at 1663 and 1651 cm⁻¹ in its IR spectrum, indicating the loss of all the CO ligands. Its ¹H NMR spectrum showed peaks for phenyl and Cp protons in a 2:1 ratio, with a symmetrical arrangement shown by the latter appearing as a singlet. The ¹³C NMR spectrum contained peaks at δ 157.5 and 123.0 for the dithiolene carbons, indicative of what we term the semi-bridging coordination mode, in which one sulfur atom bridges the two metals and the other is coordinated to only one. For example, in the related complex [Mo₂{μ-C₂(CO₂Me)₂}(μ-S₂C₂Ph₂)₂Cp₂], the corresponding values were δ 163.3 and 116.0. [18]



Scheme 1. Synthesis of complexes **1** and **2**.

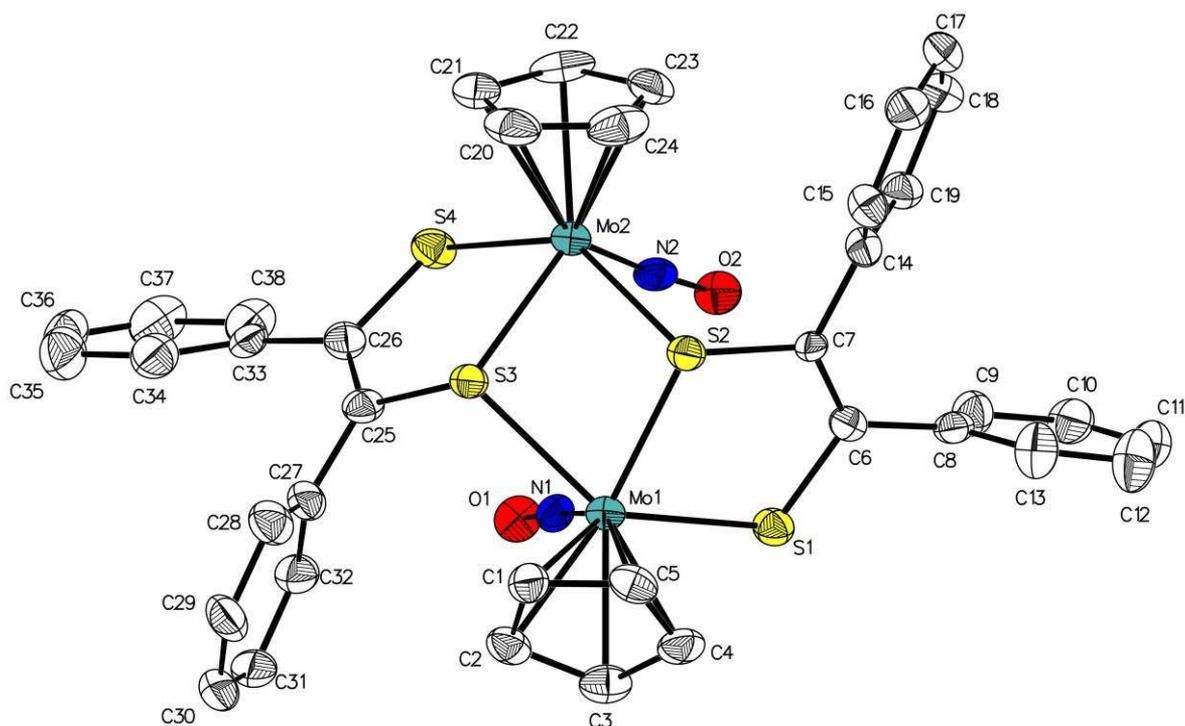


Figure 1. Molecular structure of $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$ **1** in the crystal. Selected bond lengths (Å): Mo(1)–S(1) 2.4628(16); Mo(1)–S(2) 2.4899(15); Mo(1)–S(3) 2.5180(14); Mo(1)–N(1) 1.786(5); N(1)–O(1) 1.193(6); Mo(2)–S(2) 2.5359(15); Mo(2)–S(3) 2.4869(15); Mo(2)–S(4) 2.4544(16); Mo(2)–N(2) 1.800(5); N(2)–O(2) 1.197(7).

Recrystallisation of **1** from dichloromethane and light petroleum gave crystals suitable for X-ray study; the resulting structure is shown in Figure 1 with important bond lengths listed in the caption. Each molybdenum atom is ligated by a Cp ligand and a terminal nitrosyl; the Mo–N–O angles are both virtually linear [175.5(5)° and 174.5(5)°]. The two nitrosyl ligands are disposed in a *cis*-like arrangement. The Mo–Mo distance is 3.692 Å, which is long enough to preclude the existence of significant metal-metal bonding. The dithiolene ligands each chelate one Mo atom to make a planar MoS₂C₂ ring, and in addition one of the sulfur atoms bridges to the other metal. In the chelate rings the Mo to unbridged S bond lengths are shorter than the Mo–μ-S distance, with the bridging Mo–S bond longer still. The structure could therefore be regarded as the dimerisation of two 16e⁻ CpMo(NO)(S₂C₂Ph₂) fragments by coordination of one sulfur to the opposite molybdenum. As might be expected, the structure is very similar to the Cp* analogue prepared by Kajitani [28].

Complex **1** was however not the major component of the product mixture, being formed in only 13% yield. A large brown zone eluted before **1** proved to contain two different species in a 2.3:1 ratio that were readily separable by crystallisation. Both of these complexes showed a highest peak in the mass spectrum at *m/z* 1468.5, which corresponds to a formula of [Mo₂Ni₂(NO)₂(S₂C₂Ph₂)₄Cp₂]. Both isomers **2a** and **2b** were successfully characterised by X-ray crystallography, revealing very similar but subtly different arrangements of the components.

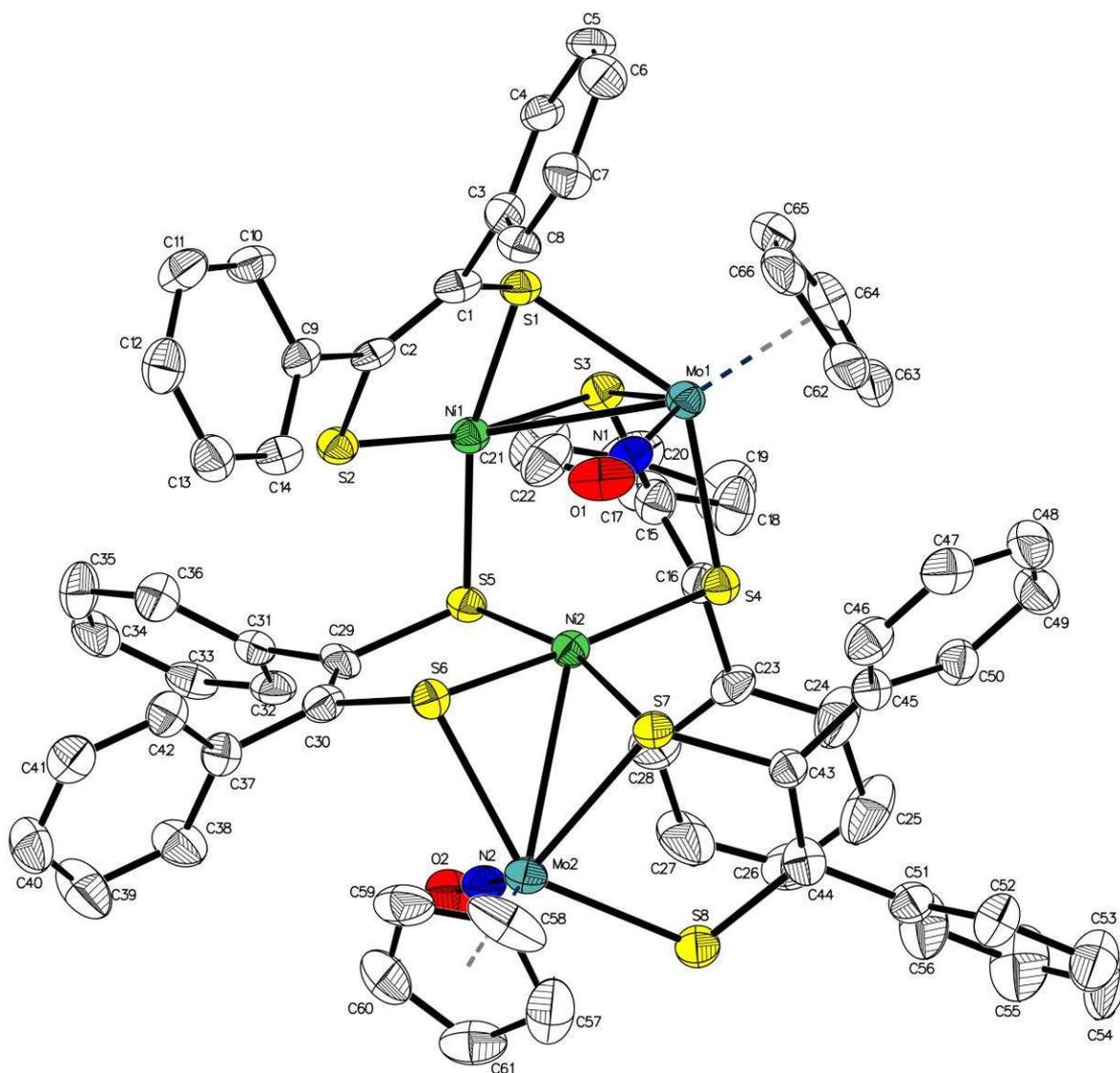


Figure 2. Molecular structure of one of the two independent molecules of the major isomer of $[\text{Mo}_2\text{Ni}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2]$ (**2a**) in the crystal. Selected bond lengths (Å): Mo(1)–S(1) 2.483(2); Ni(1)–S(1) 2.152(2); Ni(1)–S(2) 2.160(2); Mo(1)–S(3) 2.541(2); Ni(1)–S(3) 2.204(2); Mo(1)–S(4) 2.498(2); Ni(2)–S(4) 2.208(2); Ni(1)–S(5) 2.219(2); Ni(2)–S(5) 2.183(2); Mo(2)–S(6) 2.509(2); Ni(2)–S(6) 2.158(2); Mo(2)–S(7) 2.497(2); Ni(2)–S(7) 2.230(2); Mo(2)–S(8) 2.459(2); Mo(1)–N(1) 1.813(8); Mo(2)–N(2) 1.787(8); N(1)–O(1) 1.184(9); N(2)–O(2) 1.199(10).

The major isomer **2a**, which displays peaks for the Cp ligands at δ 5.45 and 5.13 in its ^1H NMR spectrum, has the structure shown in Figure 2. There are two independent molecules in the unit cell with only minor differences between them; the atom connectivities are the same in both.

The molecule is based on two dinuclear MoNi units that are orientated almost perpendicular to each other, joined by sulfur bridges. The existence of any significant metal-metal bonding is again debatable. The Mo(1)–Ni(1) and Mo(3)–Ni(3) distances of 2.871(1) and 2.859(1) Å respectively are shorter than the Mo(2)–Ni(2) and Mo(4)–Ni(4) distances [3.072(1) and 3.129(2) Å]. The Ni–Ni distances are 3.118 and 3.192 Å in the two independent molecules. This can be contrasted with a typical value of 2.6–2.7 Å for a Mo–Ni single bond [29] and 2.4–2.5 Å for a Ni–Ni single bond. However in our previously isolated heterobimetallic complex [Ni{Mo(S₂C₂Ph₂)₂Cp}₂]₂, in which the Mo–Ni bonds are also bridged by dithiolene ligands, the Mo–Ni bond lengths were similarly rather long at 2.7514(5) and 2.8654(5) Å; in the dinuclear complex [MoNi(μ-S₂C₂Ph₂)₂Cp₂] the corresponding distance was slightly shorter at 2.7201(7) Å [19]. It is also known that the Ni–Ni separation in species such as [Ni₂(μ-SR)₂Cp₂], which contain essentially non-bonded nickel atoms bridged by thiolates, is long, typically around 3 Å [30, 31].

Each Mo atom bears a Cp ring and a linear nitrosyl ligand. The four dithiolene ligands all bridge between the metal atoms, but each in a different way. That containing S(1) and S(2) is semibridging, with S(2) bonded only to Ni(1). In the other MoNi unit, the ligand containing S(7) and S(8) is also semibridging, but in the opposite way: S(8) is only bonded to Mo(2). The other two dithiolenes bridge three metal atoms: in the first S(3) bridges between Mo(1) and Ni(1), whereas S(4) bridges between Mo(1) and Ni(2), and in the second S(5) uniquely bridges the two nickel atoms while S(6) bridges Ni(2) and Mo(2). The result is that each molybdenum centre is in a square-based pyramidal environment, with the basal ligands consisting of three sulfurs and the NO, and each nickel adopts a square planar geometry ligated by four sulfurs. It appears that the lack of symmetry in the solid state is retained in solution as the ¹³C NMR spectrum displays a total of 16 peaks for the dithiolene carbons and phenyl *ipso*-carbons.

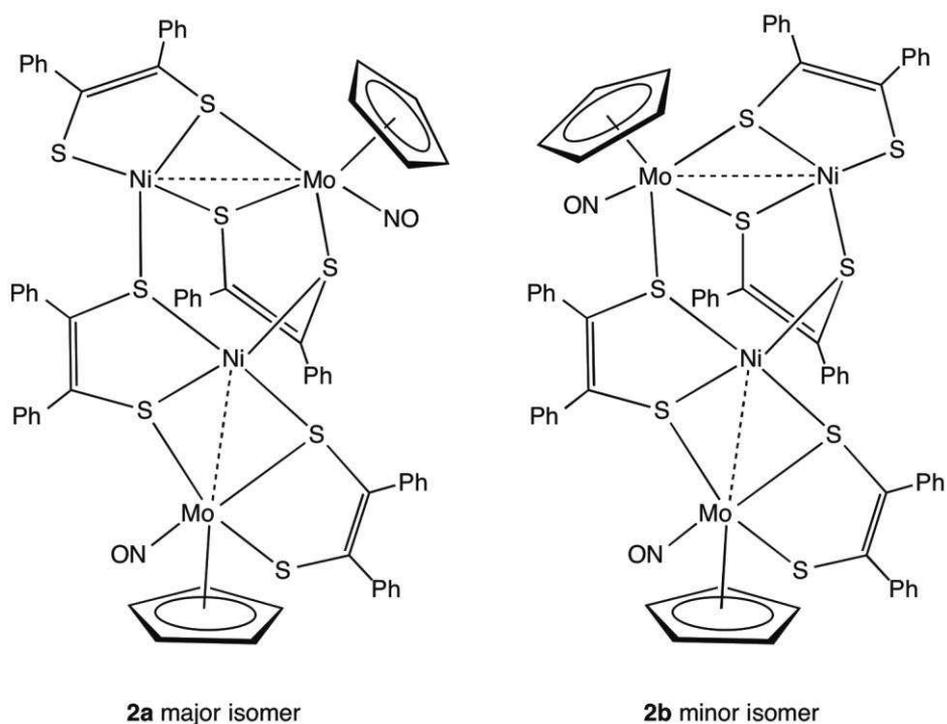


Figure 3. Structural formulae of the two isomers of complex **2**.

The minor isomer, **2b**, displays peaks at δ 5.44 and 4.93 for the Cp ligands in its ^1H NMR spectrum. Its structure is shown in Figure 3, and at first sight is very similar to that of **2a**. The Mo(1)–Ni(1) and Mo(2)–Ni(2) distances are 2.9997(6) Å and 2.8667(6) Å respectively, and the Ni–Ni separation is 3.022 Å. The difference between the two isomers is clear from their structural formulae: the orientation of one of the MoNi subunits is reversed in **2b**.

of complex **1**, possibly indicating that the first mechanism is responsible for the formation of this product. This may take place *via* the $16e^-$ intermediate $CpMo(NO)(S_2C_2Ph_2)$; Nomura and co-workers regarded the formation of some of the co-products of $[Mo_2(NO)_2\{\mu-S_2C_2(CO_2Me)_2\}_2Cp^*_2]$ as evidence for the intermediacy of the analogous $Cp^*Mo(NO)\{S_2C_2(CO_2Me)_2\}$ species [28].

The heterometallic complexes are clearly formed from two dinuclear units of the formula $CpMo(NO)Ni(S_2C_2Ph_2)_2$, which could themselves be formed directly from the two initial reagents, but equally it is possible that if $16e^- CpMo(NO)(S_2C_2Ph_2)$ fragments are produced, they could then combine with the released $Ni(S_2C_2Ph_2)$ moieties to give the dinuclear units that then associate into the two isomers of **2**.

3. Conclusion

The dithiolene transfer reaction between $[Ni(S_2C_2Ph_2)_2]$ and $[CpMo(CO)_2(NO)]$ does give the expected complex, $[Mo_2(NO)_2(\mu-S_2C_2Ph_2)_2Cp_2]$ **1**, but only as a minor product. The formation of heterobimetallic complexes takes precedence in this case, leading to two isomers of the tetranuclear compound $[Mo_2Ni_2(NO)_2(\mu-S_2C_2Ph_2)_4Cp_2]$ **2**. Although the production of heterobimetallic species is common in reactions involving formally unsaturated dithiolene complexes such as $[CpCo(bdt)]$ or $[(\eta-C_6Me_6)Ru(bdt)]$ (bdt = benzene-1,2-dithiolate) [32-35] it is rare in reactions of $[Ni(S_2C_2Ph_2)_2]$ and we are currently investigating further reactions of this type with molybdenum- and tungsten-based substrates.

4. Experimental

4.1 General information

All reactions were performed under an inert atmosphere of argon using Schlenk techniques. Solvents for reactions were purified with a Grubbs-type purification system manufactured by Innovative Technology, Newburyport, MA. Chromatographic separations were carried out on Geduran 60 silica under a positive pressure of nitrogen; columns were initially made up in light petroleum (40-60 °C fraction); polarity was increased by addition of increasing proportions of dichloromethane. The 1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in $CDCl_3$ solution on a Bruker Avance AV400 machine having an automated sample-changer. Chemical shifts are given on the δ scale relative to $SiMe_4$ for 1H and ^{13}C spectra. The $^{13}C\{^1H\}$ NMR spectra

were routinely recorded using an attached proton test technique (JMOD or DEPT pulse sequence). Mass spectra were recorded on a VG AutoSpec instrument operating in electron impact mode or a Waters LCT instrument operating in electrospray mode. Solid state IR spectra were recorded either as KBr disks or neat with a diamond ATR device over the range 4000-400 cm^{-1} , and solution spectra in CH_2Cl_2 solution over the range 2200-1550 cm^{-1} , on a Perkin Elmer Spectrum Two instrument. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

The complexes $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ and $[\text{CpMo}(\text{CO})_2(\text{NO})]$ were prepared by the literature methods [36, 37].

4.2 Synthesis of $[\text{Mo}_2\text{Ni}_2(\text{CO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2]$ and $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$.

A solution of $[\text{CpMo}(\text{CO})_2(\text{NO})]$ (526.1 mg, 2.13 mmol) and $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ (1.1104 g, 2.04 mmol) in toluene (150 cm^3) was heated to reflux for 6 h, during which its colour changed from green to brown. The solvent was removed *in vacuo*, the residue redissolved in dichloromethane and absorbed onto silica, then the silica was loaded onto a chromatography column.

Elution with light petroleum and CH_2Cl_2 (9:1) produced a yellow-orange band of residual $[\text{CpMo}(\text{CO})_2(\text{NO})]$ (120.4 mg, 23% recovery). With a 3:2 mixture of the same solvents a green band of $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$ (204.5 mg, 18% recovery) was obtained, and with an 11:9 mixture a brown band due to $[\{\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)\}_6]$ (97.4 mg, 16%) was eluted. Further elution with a 2:3 mixture of the same solvents produced a large brown band which contains the two isomers of $[\text{Mo}_2\text{Ni}_2(\text{CO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2]$ (combined yield 619 mg, 41%). Finally the eluting solvent was changed to CH_2Cl_2 to elute an orange-brown band of $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$ (123.7 mg, 13%).

Data for $[\text{Mo}_2(\text{NO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_2\text{Cp}_2]$ (**1**)

IR(CH_2Cl_2): $\nu(\text{NO})$ 1663, 1651 cm^{-1} . ^1H NMR: δ 7.28-7.13 (m, 20 H, Ph), 5.36 (s, 10 H, Cp). ^{13}C NMR: δ 157.5 (CPh), 141.2, 140.2 (both C_{ipso}), 131.1-127.2 (m, Ph), 123.0 (CPh), 103.4 (Cp). Mass spectrum m/z 868 ($\text{M}^+ \text{H}^+$). Found: C, 50.67; H, 3.61; N, 3.03; S, 14.05. Calc. for $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_4\text{Mo}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 50.85; H, 3.41; N, 3.08; S, 14.09%. Crystals suitable for X-ray diffraction were grown by diffusion of light petroleum vapour into a dichloromethane solution; they contain two molecules of CH_2Cl_2 , each at one half occupancy, per molecule of **1**. The same crystals

were used for the elemental analysis; on extended drying it appears that one of these solvent molecules is removed.

Data for the major isomer of $\text{Mo}_2\text{Ni}_2(\text{CO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2$ (**2a**)

IR(CH_2Cl_2): $\nu(\text{NO})$ 1650 cm^{-1} . $^1\text{H NMR}$: δ 7.57-6.90 (m, 40 H, Ph), 5.45, 5.13 (both s, 5 H, Cp). $^{13}\text{C NMR}$: δ 160.3, 156.2, 145.8, 143.2, 142.8, 141.8, 141.7, 141.3, 140.0, 139.9, 138.8, 138.3, 138.1, 136.74 (C=C + C_{ipso}), 132.2-125.9 (m, Ph), 125.1, 118.8 (C=C + C_{ipso}) 104.1, 103.9 (Cp). Mass spectrum m/z 1468.5 (M^+). Found: C, 54.74; H, 3.93; N, 1.76; S, 16.75. Calc. for $\text{C}_{66}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_8\text{Mo}_2\text{Ni}_2\cdot\text{C}_5\text{H}_{12}$: C, 55.34; H, 4.05; N, 1.82; S, 16.64.

Data for the minor isomer of $\text{Mo}_2\text{Ni}_2(\text{CO})_2(\mu\text{-S}_2\text{C}_2\text{Ph}_2)_4\text{Cp}_2$ (**2b**)

IR(CH_2Cl_2): $\nu(\text{NO})$ 1650 cm^{-1} . $^1\text{H NMR}$: δ 7.78-6.91 (m, 40 H, Ph), 5.44, 4.93 (both s, 5 H, Cp). $^{13}\text{C NMR}$: δ 181.7, 161.2, 154.5, 149.0, 145.4, 142.9, 141.6, 141.3, 141.2, 140.5, 140.0, 139.3, 138.7, 138.7, 138.1, 137.9 (C=C + C_{ipso}), 132.5-126.0 (m, Ph), 127.9, 120.8 (C=C + C_{ipso}), 104.4, 103.0 (Cp). Mass spectrum m/z 1468.5 (M^+). Found: C, 50.80; H, 3.46; N, 1.61; S, 16.01. Calc. for $\text{C}_{66}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_8\text{Mo}_2\text{Ni}_2\cdot 1.5\text{CH}_2\text{Cl}_2$: C, 50.74; H, 3.32; N, 1.75; S, 16.03%.

4.3 X-ray crystallography

Crystal data for the three structures are summarised in Tables 1 and 2. All diffraction data were collected on a Bruker X8 Apex II CCD diffractometer at 100 K (Mo-K α radiation) from crystals mounted in fomblin oil on a MiTiGen microloop and cooled in a stream of cold N_2 . Using OLEX2 [38] structures were solved using the SHELXS [39] or SHELXT [40] programs using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimisation [40]. Hydrogen atoms were constrained to idealised geometries with $C_{\text{aromatic-H}}$ 0.95 Å and $C_{\text{sp}^3\text{-H}}$ 0.99 Å. All H displacement parameters were constrained to be $1.2 \times U_{\text{eq}}$. Compound **1** crystallises with two half occupancy molecules of CH_2Cl_2 per molecule of **1**. Compounds **2a** crystallised with 0.5 CH_2Cl_2 per molecule of **2a**. Complex **2b** crystallised with solvent which was found to be disordered and proved impossible to model satisfactorily. The intensity contribution of the solvent was determined and removed using SQUEEZE [41] implemented in PLATON [42]. The total electron count of solvent in **2b** was 176 e^- per unit cell, corresponding to 4 molecules of CH_2Cl_2 (two molecules per molecule of **2b**) located in a void of 551 Å^3 .

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 1859764 (**1**), 1859764 (**2b**) and 1859766 (**2a**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or from their website at www.ccdc.cam.ac.uk.

Acknowledgements

We thank the University of Sheffield for support. This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

Supplementary Material

Copies of the IR, NMR and mass spectra of complexes **1** and **2** (both isomers) can be downloaded from the online version.

References

1. J. A. McCleverty, Metal 1,2-Dithiolene and Related Complexes, *Prog. Inorg. Chem.* 10 (1969) 49-221.
2. R. Eisenberg, Structural Systematics of 1,1- and 1,2-Dithiolato Chelates, *Prog. Inorg. Chem.* 12 (1970) 295-369.
3. R. P. Burns, C. A. McAuliffe, 1,2-Dithiolene Complexes of Transition Metals, *Adv. Inorg. Chem. Radiochem.* 22 (1979) 303-348.
4. U. T. Mueller-Westerhoff, B. Vance, Dithiolenes and Related Species, in: G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1987, Vol. 2, Chapter 16.5, pp. 595-632.
5. E. I. Stiefel (Ed.), *Dithiolene Chemistry*, *Prog. Inorg. Chem.* 52 (2004) 1-730.
6. S. Sproules, Tris(dithiolene) Chemistry: A Golden Jubilee, *Prog. Inorg. Chem.* 58 (2014) 1-144.
7. U. T. Mueller-Westerhoff, B. Vance, D. I. Yoon, The Synthesis of Dithiolene Dyes with Strong Near-IR Absorption, *Tetrahedron* 47 (1991) 909-932.

8. K. L. Marshall, G. Painter, K. Lotito, A. G. Noto, P. Chang, Transition Metal Dithiolene Near-IR Dyes and Their Applications in Liquid Crystal Devices, *Mol. Cryst. Liq. Cryst.*, 454 (2006) 47-79.
9. N. Robertson, L. Cronin, Metal bis-1,2-dithiolene complexes in conducting or magnetic crystalline assemblies, *Coord. Chem. Rev.* 227 (2002) 93-127.
10. M. Fourmigué, Paramagnetic Cp/Dithiolene Complexes as Molecular Hinges: Interplay of Metal/ Ligand Electronic Delocalization and Solid-State Magnetic Behavior, *Acc. Chem. Res.* 37 (2004) 179-186.
11. K. Wang, E. I. Stiefel, Toward Separation and Purification of Olefins Using Dithiolene Complexes: An Electrochemical Approach, *Science* 291 (2001) 106-109.
12. W. R. McNamara, Z. Han, P. J. Alperin, W. W. Brennessel, P. L. Holland, R. Eisenberg, A Cobalt Dithiolene Complex for the Photocatalytic and Electrocatalytic Reduction of Protons, *J. Am. Chem. Soc.* 133 (2011) 15368-15371.
13. W. R. McNamara, Z. Han, C.-J. Yin, W. W. Brennessel, P. L. Holland, R. Eisenberg, Cobalt-dithiolene complexes for the photocatalytic and electrocatalytic reduction of protons in aqueous solutions, *Proc. Natl. Acad. Sci. USA* 109 (2012) 15594-15599.
14. W. T. Eckenhoff, W. W. Brennessel, R. Eisenberg, Light-Driven Hydrogen Production from Aqueous Protons using Molybdenum Catalysts^[1], *Inorg. Chem.* 53 (2014) 9860-9869.
15. J. H. Enemark, J. J. A. Cooney, J.-J. Wang, R. H. Holm, Synthetic Analogues and Reaction Systems Relevant to the Molybdenum and Tungsten Oxotransferases, *Chem. Rev.* 104 (2004) 1175-1200.
16. D. J. Harrison, A. J. Lough, N. Nguyen, U. Fekl, Push–Pull Molybdenum Trisdithiolenes Allow Rapid Nonconventional Binding of Ethylene at Ligand Sulfur Atoms^[1], *Angew. Chem. Int. Ed.* 46 (2007) 7644-7647.
17. M. Fourmigué, Mixed cyclopentadienyl/dithiolene complexes, *Coord. Chem. Rev.* 178-80 (1998) 823-864.
18. H. Adams, M. J. Morris, S. A. Morris, J. C. Motley, Dithiolene transfer from nickel to a dimolybdenum centre: the first dithiolene alkyne complex, *J. Organomet. Chem.* 689 (2004) 522-527.

19. H. Adams, H. C. Gardner, R. A. McRoy, M. J. Morris, J. C. Motley, S. Torker, Heterometallic Dithiolene Complexes Formed by Stepwise Displacement of Cyclopentadienyl Ligands from Nickelocene with $\text{CpMo}(\text{S}_2\text{C}_2\text{Ph}_2)_2$, *Inorg. Chem.* 45 (2006) 10967-10975.
20. H. Adams, A. M. Coffey, M. J. Morris, S. A. Morris, Efficient Transfer of Either One or Two Dithiolene Ligands from Nickel to Ruthenium: Synthesis and Crystal Structures of $[\text{Ru}(\text{SCR}=\text{CPhS})_2(\text{PPh}_3)]$ and $[\text{RuCl}_2(\text{SCR}=\text{CPhS})(\text{PPh}_3)_2]$ (R = Ph, H), *Inorg. Chem.* 48 (2009) 11945-11953.
21. H. Adams, M. J. Morris, C. A. Robertson, H. Tunnicliffe, manuscript in preparation.
22. M. A. Alvarez, M. E. Garcia, D. Garcia-Vivo, M. A. Ruiz, A. Toyos, Mild N–O Bond Cleavage Reactions of a Pyramidalized Nitrosyl Ligand Bridging a Dimolybdenum Center^[SEP], *Inorg. Chem.* 54 (2015) 10536-10538.
23. M. A. Alvarez, M. E. Garcia, M. A. Ruiz, A. Toyos, M. F. Vega, Low-Temperature N–O Bond Cleavage and Reversible N–P Bond Formation Processes in the Reactions of the Unsaturated Anions $[\text{M}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ (M = Mo, W) with the Nitrosyl Complex $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{NO})]^+$, *Inorg. Chem.* 52 (2013) 3942-3952.
24. M. E. Garcia, D. Garcia-Vivo, S. Melon, M. A. Ruiz, C. Graiff, A. Tiripicchio, Low-Temperature N-O Bond Cleavage in Nitrosyl Ligands Induced by the Unsaturated Dimolybdenum Anion $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-PPh}_2)(\mu\text{-CO})_2]^-$, *Inorg. Chem.* 48 (2009) 9282-9293.
25. M. E. Garcia, S. Melon, M. A. Ruiz, R. Lopez, T. Sordo, L. Marchio, A. Tiripicchio, Low-Temperature N-O Bond Cleavage of Nitrogen Monoxide in Heterometallic Carbonyl Complexes. An Experimental and Theoretical Study, *Inorg. Chem.* 47 (2008) 10644-10655.
26. R. B. King, M. B. Bisnette, Organosulfur Derivatives of the Metal Carbonyls. IX.^[SEP] Some Transition Metal Derivatives Containing Both ^[SEP] π -Cyclopentadienyl and Bis(trifluoromethyl)ethylene Dithiolate Ligands, *Inorg. Chem.* 6 (1967) 469-479.
27. T. A. James, J. A. McCleverty, Transition-metal Dithiolene Complexes. Part XV. π -Cyclopentadienyl Nitrosyl and Related Molybdenum Complexes, *J. Chem. Soc. (A)* (1970) 3308-3314.

28. M. Nomura, S. Sasaki, C. Fujita-Takayama, Y. Hoshino, M. Kajitani, Formations and electrochemical behavior of mononuclear and binuclear molybdenum dithiolene complexes with nitrosyl ligands: Evidence for the formation of a coordinatively unsaturated species [Cp*Mo(NO)(dithiolene)], *J. Organomet. Chem.* 691 (2006) 3274-3284.
29. S. Clapham, P. Braunstein, N. M. Boag, R. Welter, M. J. Chetcuti, Carbon-Phosphorus Bond Cleavage in Allyldiphenylphosphine by a Heterobimetallic Ni=Mo Complex and Formation of an Electronically Unsaturated NiMo₂ μ -Diphenylphosphido Cluster, *Organometallics* 27 (2008) 1758-1764.
30. G. M. Chambers, T. B. Rauchfuss, F. Arrigoni, G. Zampella, Effect of Pyramidalization of the M₂(SR)₂ Center: The Case of (C₅H₅)₂Ni₂(SR)₂(SEP)₂, *Organometallics* 35 (2016) 836-846.
31. N.-F. Ho, T. C. W. Mak, T.-Y. Luh, Reductive Cleavage of the C–S Bond in [Ni₂(cp)₂(μ -SR)₂] (cp = η -C₅H₅) by LiAlH₄. Crystal Structures of [Ni₂(cp)₂(μ -SPh)₂] and [Ni₂(cp)₂{ μ -*o*-(SCH₂)₂-C₆H₄}], *J. Chem. Soc., Dalton Trans.* (1990) 3591-3595.
32. M. Murata, S. Habe, S. Araki, K. Namiki, T. Yamada, N. Nakagawa, T. Nankawa, M. Nihei, J. Mizutani, M. Kurihara, H. Nishihara, Synthesis of Heterometal Cluster Complexes by the Reaction of Cobaltadichalcogenolato Complexes with Groups 6 and 8 Metal Carbonyls, *Inorg. Chem.* 45 (2006) 1108-1116.
33. N. Nakagawa, T. Yamada, M. Murata, M. Sugimoto, H. Nishihara, Thermochemical Triangular [MCo₂] (M = Rh, Ir, Ru) Clusters Containing a Planar Metalladithiolene Ring in η^3 Coordination, *Inorg. Chem.* 45 (2006) 14-16.
34. T. Sagawa, S. Tsukada, K. Yamamoto, T. Gunji, *Eur. J. Inorg. Chem.* (2017) 3823-3828.
35. T. Sagawa, S. Tsukada, K. Yamamoto, T. Gunji, *Polyhedron* 139 (2018) 196-200.
36. G. N. Schrauzer, V. P. Mayweg, Preparation, Reactions, and Structure of Bisdithio- α -diketone Complexes of Nickel, Palladium, and Platinum, *J. Am. Chem. Soc.* 87 (1965) 1483-1489.
37. T. T. Chin, J. K. Hoyano, P. Legzdins, J. T. Malito, Dicarbonyl (η^5 -Cyclopentadienyl) Nitrosyl Complexes of Chromium, Molybdenum, and Tungsten *Inorg. Synth.* 28 (1990) 196-198.

38. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, , *OLEX2*: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 42 (2009) 339-341.
39. G. M. Sheldrick, A short history of *SHELX*, *Acta Cryst.* A64 (2008) 112-122.
40. G. M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Cryst.* A71 (2015) 3-8.
41. A. L. Spek, *PLATON SQUEEZE*: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Cryst.* C71 (2015) 9-18.
42. A. L. Spek, Structure validation in chemical crystallography, *Acta Cryst.* D65 (2009) 148-155.

Captions for Tables, Figures and Schemes

Table 1. Summary of crystallographic data for complex **1**.CH₂Cl₂.

Table 2. Summary of crystallographic data for complexes **2a** and **2b**.

Scheme 1. Synthesis of complexes **1** and **2**.

Figure 1. Molecular structure of [Mo₂(NO)₂(μ-S₂C₂Ph₂)₂Cp₂] **1** in the crystal. Selected bond lengths (Å): Mo(1)–S(1) 2.4628(16); Mo(1)–S(2) 2.4899(15); Mo(1)–S(3) 2.5180(14); Mo(1)–N(1) 1.786(5); N(1)–O(1) 1.193(6); Mo(2)–S(2) 2.5359(15); Mo(2)–S(3) 2.4869(15); Mo(2)–S(4) 2.4544(16); Mo(2)–N(2) 1.800(5); N(2)–O(2) 1.197(7).

Figure 2. Molecular structure of one of the two independent molecules of the major isomer of [Mo₂Ni₂(NO)₂(S₂C₂Ph₂)₄Cp₂] (**2a**) in the crystal. Selected bond lengths (Å): Mo(1)–S(1) 2.483(2); Ni(1)–S(1) 2.152(2); Ni(1)–S(2) 2.160(2); Mo(1)–S(3) 2.541(2); Ni(1)–S(3) 2.204(2); Mo(1)–S(4) 2.498(2); Ni(2)–S(4) 2.208(2); Ni(1)–S(5) 2.219(2); Ni(2)–S(5) 2.183(2); Mo(2)–S(6) 2.509(2); Ni(2)–S(6) 2.158(2); Mo(2)–S(7) 2.497(2); Ni(2)–S(7) 2.230(2); Mo(2)–S(8) 2.459(2); Mo(1)–N(1) 1.813(8); Mo(2)–N(2) 1.787(8); N(1)–O(1) 1.184(9); N(2)–O(2) 1.199(10).

Figure 3. Structural formulae of the two isomers of complex **2**.

Figure 4. Molecular structure of the minor isomer of [Mo₂Ni₂(NO)₂(S₂C₂Ph₂)₄Cp₂] (**2b**) in the crystal. Selected bond lengths (Å): Mo(1)–S(1) 2.4550(11); Mo(1)–S(2) 2.5110(11); Ni(1)–S(2) 2.2415(12); Mo(1)–S(3) 2.5100(11); Ni(1)–S(3) 2.1728(11); Mo(2)–S(4) 2.5290(10); Ni(1)–S(4) 2.2217(11); Ni(1)–S(5) 2.2186(11); Ni(2)–S(5) 2.1874(11); Mo(2)–S(6) 2.6594(11); Ni(2)–S(6)

2.1439(11); Ni(2)–S(7) 2.1708(12); Mo(2)–S(8) 2.4816(11); Ni(2)–S(8) 2.1555(11); Mo(1)–N(1)
1.792(4); Mo(2)–N(2) 1.782(4); N(1)–O(1) 1.202(5); N(2)–O(2) 1.188(5).

Table 1. Summary of crystallographic data for complex **1**.CH₂Cl₂.

	1
Empirical formula	C ₃₉ H ₃₂ Cl ₂ Mo ₂ N ₂ O ₂ S ₄
Formula weight	951.68
<i>T</i> /K	100
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> /Å	32.5542(6)
<i>b</i> /Å	13.1525(2)
<i>c</i> /Å	19.4346(4)
α /°	90
β /°	114.0330(10)
γ /°	90
<i>V</i> /Å ³	7599.9(2)
<i>Z</i>	8
Density (calcd)/Mgm ⁻³	1.663
μ /mm ⁻¹	1.059
<i>F</i> (000)	3824.0
Crystal size/mm ³	0.42 × 0.21 × 0.08
2 θ range for data collection/°	2.74 to 55.256
Reflections collected	86367
Independent reflections	8816 [<i>R</i> _{int} = 0.0913, <i>R</i> _{sigma} = 0.0522]
Data/restraints/parameters	8816/48/487
Goodness-of-fit on <i>F</i> ²	1.091
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0814, <i>wR</i> ₂ = 0.2161
(all data)	<i>R</i> ₁ = 0.1050, <i>wR</i> ₂ = 0.2516
Largest diff. peak and hole/ e.Å ⁻³	5.30 and -2.42

Table 2. Summary of crystallographic data for complexes **2a** and **2b**.

	2a.0.5CH₂Cl₂	2b
Empirical formula	C _{66.5} H ₅₁ ClM ₀₂ N ₂ Ni ₂ O ₂ S ₈	C ₆₆ H ₅₀ M ₀₂ N ₂ Ni ₂ O ₂ S ₈
Formula weight	1511.32	1468.86
<i>T</i> /K	100	100
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> /Å	15.4936(7)	15.2525(5)
<i>b</i> /Å	16.6458(7)	15.3548(6)
<i>c</i> /Å	25.6210(12)	15.5661(6)
α /°	77.376(2)	66.848(2)
β /°	76.344(2)	86.552(2)
γ /°	75.436(2)	81.095(2)
<i>V</i> /Å ³	6125.0(5)	3311.6(2)
<i>Z</i>	4	2
Density (calcd)/Mgm ⁻³	1.639	1.473
μ /mm ⁻¹	1.370	1.225
<i>F</i> (000)	3060	1488.0
Crystal size/mm ³	0.32 × 0.25 × 0.22	0.5 × 0.38 × 0.28
θ range for data collection/°	1.405 to 27.613	1.351 to 27.796
Reflections collected	124401	88386
Independent reflections	28138 [R(int) = 0.0613]	15579 [R(int) = 0.0529]
Data/restraints/parameters	28138 / 24 / 1504	15579 / 0 / 739
Goodness-of-fit on <i>F</i> ²	1.097	1.200
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0814, <i>wR</i> ₂ = 0.2037	<i>R</i> ₁ = 0.0604, <i>wR</i> ₂ = 0.1523
(all data)	<i>R</i> ₁ = 0.1402, <i>wR</i> ₂ = 0.2479	<i>R</i> ₁ = 0.0721, <i>wR</i> ₂ = 0.1703
Largest diff. peak and hole/ e.Å ⁻³	2.38 and -1.72	1.02 and -1.38