

Improved syntheses of the electronically unsaturated heterobimetallic complexes $[(\eta\text{-C}_5\text{Me}_5)\text{Ni}\cdots\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (M = Mo, W), and their use as cluster building blocks: X-ray structure of the chiral trimetallic cluster $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$

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Abstract – A safer synthesis for the electronically unsaturated complexes $[(\eta\text{-C}_5\text{Me}_5)\text{Ni}\cdots\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (**1a**, M = Mo; **1b**, M = W), which eliminates the use of highly toxic $[\text{Ni}(\text{CO})_4]$, is presented. Complexes **1a** and **1b** are useful as cluster building blocks, and this is illustrated by the high yield synthesis of the chiral mixed-metal clusters $[\text{FeNiM}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ (M = Mo, W). The structure of the FeNiMo cluster **3a** was determined by a single crystal X-ray diffraction study. *To cite this article: P. Braunstein et al., C. R. Chimie 5 (2002) 67–72* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

Chiral clusters / Iron / Mixed-metal clusters / Molybdenum / Nickel / Tungsten

Résumé – Une amélioration significative a été apportée à la synthèse de complexes hétérobimétalliques coordinativement insaturé $[(\eta\text{-C}_5\text{Me}_5)\text{Ni}\cdots\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (**1a**, M = Mo; **1b**, M = W), qui évite de passer par l'utilisation de $[\text{Ni}(\text{CO})_4]$, produit très toxique. Les complexes **1a** et **1b** sont utilisés comme briques élémentaires pour la synthèse rationnelle à haut rendement de clusters mixtes, tels que les clusters chiraux $[\text{FeNiM}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ (M = Mo, W), obtenus par réaction avec $[\text{Fe}_2(\text{CO})_9]$. La structure du cluster FeNiMo **3a** a été déterminée par diffraction des rayons X. *Pour citer cet article: P. Braunstein et al., C. R. Chimie 5 (2002) 67–72* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

clusters chiraux / clusters mixtes / fer / molybdène / nickel / tungstène

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1. Introduction

The increasing and successful use of heterometallic complexes and clusters in reactivity studies and in both homogeneous and heterogeneous catalysis requires these molecules to be accessible in the highest possible yields and as safely as possible. Significant progress towards rational syntheses has been made using appropriate precursor molecules whose reactive sites are predetermined [1–4].

The heterobimetallic complexes $[(\eta\text{-C}_5\text{Me}_5)\text{NiM}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (**1a**, M = Mo, **1b**, M = W) [5] can be considered to contain Ni=Mo or Ni=W double bonds, and are thus electronically unsaturated species. Their rich chemistry, with a wide variety of organic and inorganic ligands, remains under investigation [6,7]. Nevertheless, studies of their reactivity are hampered by the necessity of either using $[\text{Ni}(\text{CO})_4]$ to prepare these species or else purchasing the relatively expensive complex $[\text{Ni}(\mu\text{-CO})(\eta\text{-C}_5\text{Me}_5)]_2$. Here, we present a new synthesis of these complexes that does not require the use of the highly toxic $[\text{Ni}(\text{CO})_4]$. We then illustrate the potential utility of these mixed-metal unsaturated complexes as building blocks in the synthesis of heterometallic clusters by describing the synthesis and X-ray characterization of the chiral mixed metal cluster $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ and of its FeNiW analogue. The advantages that complexes **1a** and **1b** confer over other related heterobimetallic species are described herein.

2. Results and discussion

2.1. Syntheses of complexes **1a** and **1b**

The previously reported synthesis of complexes **1a** and **1b** is outlined below (Fig. 1) [5]. The yields obtained are respectable but the use of $[\text{Ni}(\text{CO})_4]$ to prepare these complexes is a major disadvantage owing to its volatility and extremely high toxicity.

A new synthesis that eliminates the use of $[\text{Ni}(\text{CO})_4]$ was therefore developed. When

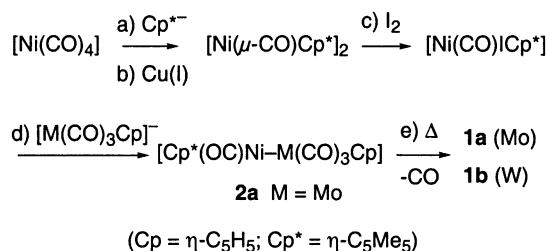


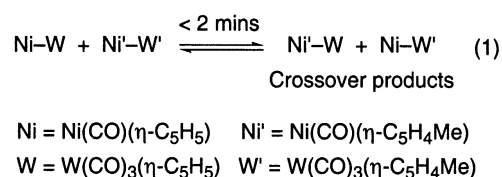
Fig. 1.

$[\text{NiCl}_2\text{-dme}]$ (dme = 1,2-dimethoxyethane) was reacted with $[(\text{C}_5\text{Me}_5)\text{MgCl}]$ [8] at low temperature for 24–36 h, the orange suspension gave way to a dark brown colour and the thermally unstable species $[\text{Ni}(\mu\text{-Cl})(\eta\text{-C}_5\text{Me}_5)]_2$ was formed [9]. When this chloro-complex was treated at low temperature with $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$, the characteristic deep blue colour of the mixed metal complexes **1a** or **1b** appeared. These highly air-sensitive complexes were extracted from the reaction mixture using pentane, as outlined in the experimental section, and isolated in yields ranging from 30–65%.

The advantage that this method offers is clear, no $[\text{Ni}(\text{CO})_4]$ is used, and the unsaturated heterobimetallic complexes are obtained directly, without a decarbonylation step (step ‘e’ in Fig. 1). This new synthetic method is summarized in Fig. 2.

2.2. Use of simple saturated heterobimetallic complexes as cluster building blocks

Simple homo- and heterobimetallic complexes have been used by others and us as cluster building blocks. Many new and otherwise inaccessible clusters can be made this way and the method is useful. However, typical yields are not always high, and often a wide variety of side-products are observed. A major reason why many side-products are obtained is the rapid metal–metal exchange occurring between $\text{L}_n\text{M-M}'\text{L}'_m$ fragments that takes place in solution. We have shown [10] that mixtures of closely related Ni–W heterobimetallic complexes readily scramble when mixed, as shown in equation (1) below. This process, which is general for many simple non-bridged bimetallic complexes, is indeed the basis for the synthesis of many such species [11].



Processes such as this and related ones occur rapidly when two bimetallic species are mixed (in less than 2 min, by ^1H NMR) and lead to crossover mix

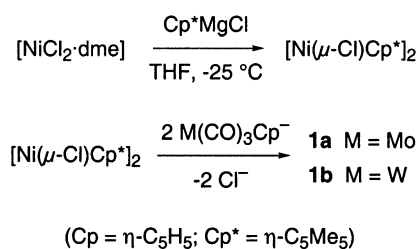
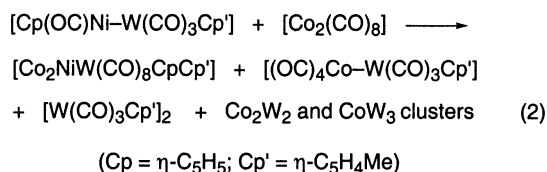


Fig. 2.

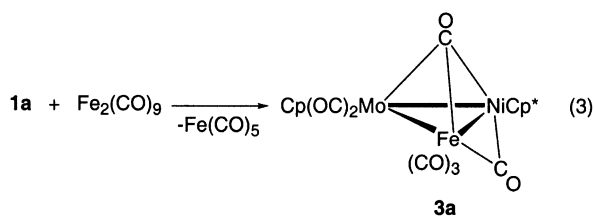
tures. This, in turn, frequently affords unintended products and results in the target cluster that is obtained in moderate to poor yield. For example, the reaction of a saturated analogue of complex **1b** with $[\text{Co}_2(\text{CO})_8]$ was envisaged to produce the Co_2NiW cluster shown in equation (2), by initial CO loss followed by formal addition of a $\text{Co}_2(\text{CO})_6$ unit to an isolobal $(\eta\text{-C}_5\text{H}_5)\text{Ni}-\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$ group. While this species was indeed obtained in moderate yield, other bimetallic complexes and mixed-metal clusters were also formed [12].



A heterobimetallic system with multiple metal-bond character could in principle anchor the two metals together and suppress metal-metal bond exchange, just as a heterobimetallic system with bridging ligands binds the two metals together more strongly and favours keeping the bimetallic system intact. In order to test this hypothesis, complexes **1a** and **1b** were reacted with $[\text{Fe}_2(\text{CO})_9]$ and the results were compared with the reaction of the saturated tetracarbonyl analogues of complex **1a** with the same di-iron complex.

2.3. The synthesis of heterotrimetallic FeNiM (M = Mo, W) clusters using Ni-Mo and Ni-W complexes as building blocks

Complex **1a** reacts with $[\text{Fe}_2(\text{CO})_9]$ according to equation (3) to afford a deep green product **3a**.



This species, which is the only product (apart from $[\text{Fe}(\text{CO})_5]$) when the stoichiometry of **1a** to the Fe_2 complex is 1:1, is a FeNiMo cluster. Its IR spectrum is complex and shows the presence of terminal, doubly bridging and even potentially triply bridging CO ligands. The ^1H NMR spectra of **3a** were not very informative but they did show singlets attributed to C_5H_5 and C_5Me_5 groups in a 1:1 ratio (1:3 proton integrated ratio respectively). This suggested that the complex contained both nickel and molybdenum.

The detailed structure of **3a** was established by a single crystal X-ray diffraction study. Complex **3a** is the heterotrimetallic cluster $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$. Key crystal and data

collection parameters, and tables of important bond lengths and angles for **3a** are collected in Tables 1–3, respectively. The structure of **3a** (hydrogen atoms are not shown, for clarity), is shown in Fig. 3.

Complex **3a** crystallizes with two crystallographically independent molecules in the unit cell, but the two clusters are not significantly different from each

Table 1. Selected crystal and data collection parameters for $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ **3a**.

Formula	$\text{C}_{22}\text{H}_{20}\text{FeMoNiO}_7$
<i>Mr</i>	606.88
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	9.479(2)
<i>b</i> (Å)	14.636(3)
<i>c</i> (Å)	16.845(3)
α (°)	103.45(2)
β (°)	94.39(2)
γ (°)	94.92(2)
<i>V</i> (Å ³)	2253.3(8)
<i>Z</i>	4
<i>T</i> (K)	293(2)
ρ (g cm ⁻³)	1.789
λ (Å)	0.710 69
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.060
<i>Rw</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.088
GOF	0.938

Table 2. Selected bond lengths (Å) of $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3a**, with esds between parentheses.

Parameter	Molecule A	Molecule B
Mo–Ni	2.6584(10)	2.6588(9)
Fe–Ni	2.4935(11)	2.4917(14)
Fe–Mo	2.8049(10)	2.8101(10)
Fe–C(μ_3 -CO)	2.220(6)	2.170(7)
Mo–C(μ_3 -CO)	2.177(7)	2.145(6)
Ni–C(μ_3 -CO)	1.967(6)	1.954(6)
Fe–C(μ_2 -CO)	1.881(7)	1.899(7)
Ni–C(μ_2 -CO)	1.958(6)	1.964(7)
C–O(μ_3 -CO)	1.180(6)	1.226(7)
Mo–C(C_5H_5), mean	2.34	2.33
Ni–C(C_5Me_5), mean	2.13	2.14

Table 3. Selected bond angles (°) of $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3a**, with esds between parentheses.

Parameter	Molecule A	Molecule B
Ni–Mo–Fe	54.23(3)	54.12(3)
Ni–Fe–Mo	59.89(3)	59.84(3)
Fe–Ni–Mo	65.88(3)	66.04(3)
Mo–C(μ_3 -CO)–Ni	79.6(2)	80.8(2)
Fe–C(μ_3 -CO)–Mo	79.3(2)	81.3(2)
Fe–C(μ_3 -CO)–Ni	72.80(19)	74.1(2)
Fe–C(μ_3 -CO)–O	127.0(4)	125.8(5)
Mo–C(μ_3 -CO)–O	144.3(5)	143.2(4)
Ni–C(μ_3 -CO)–O	127.6(5)	127.1(5)

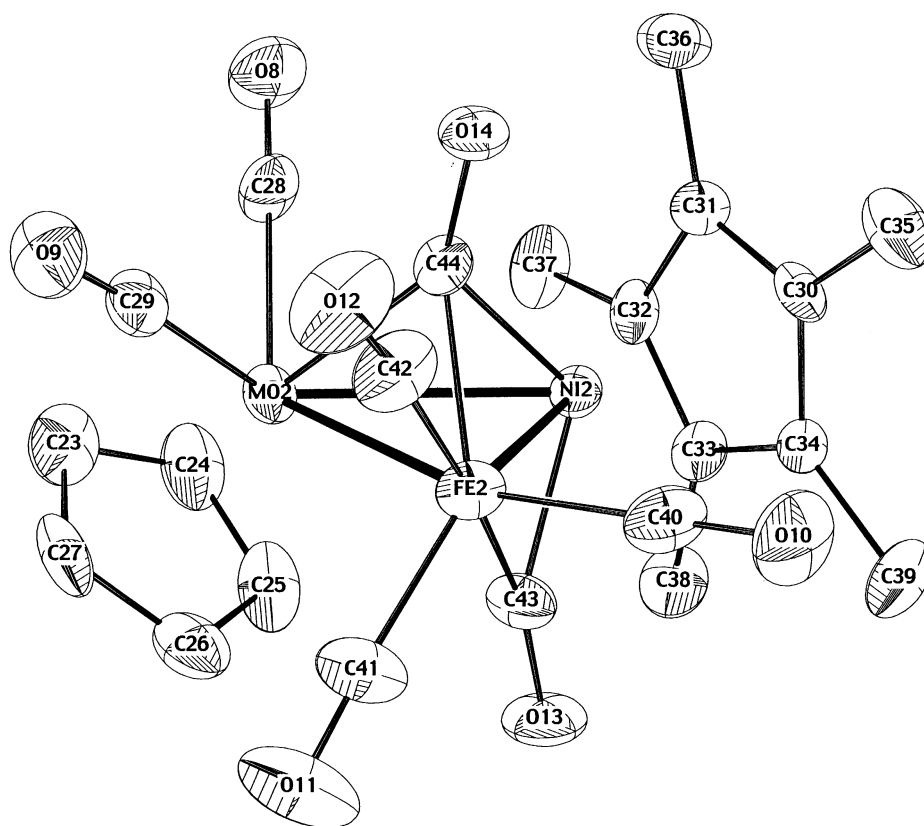


Fig. 3. View of one of the two independent molecules in the unit cell of the cluster $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3a**. Ellipsoids are shown at the 30% probability level; hydrogen atoms are not shown for clarity.

other (Fig. 3 shows molecule B). The trimetal cluster contains a tetrahedral and chiral core as the $\mu_3\text{-CO}$ ligand caps the metal triangle, but both enantiomers of each independent molecule exist in the unit cell as the space group (*PI*) is non-chiral. The $\mu_3\text{-CO}$ ligand does not bridge the three metals symmetrically and is perhaps better described as being semi-bridging to the iron atom. Its semi-bridging character is reflected in the respective $\text{M}-\text{C}(\mu_3)$ bond lengths that are longer for the $\text{Fe}-\text{C}(\mu_3)$ distances (2.20 Å, mean) than for the $\text{Ni}-\text{C}(\mu_3)$ (1.96 Å, mean) or even the $\text{Mo}-\text{C}(\mu_3)$ distances (2.16 Å, mean).

One of the only significant differences between the two independent molecules of **3a** is the length of the C–O bond for the $\mu_3\text{-CO}$ ligand [1.180(6) Å for molecule A; 1.226(7) Å for molecule B]. In addition, the $\text{Fe}(\text{CO})_3$ unit is slightly rotated in one molecule with respect to the other one; but otherwise the two molecules are essentially identical. The centroid of the $\eta\text{-C}_5\text{Me}_5$ group in each case lies close to the trimetal plane, but the molybdenum bound $\eta\text{-C}_5\text{H}_5$ ring lies below this plane, away from the $\text{C}(\mu_3)$ atom in each molecule. Other distances and angles are unremarkable, with all metal–metal distances lying in the usual range.

Clusters containing iron, nickel and molybdenum bonded to each other have been reported [13–15], and in addition some sulphur and selenium capped clusters with these three metals are known, including the cluster $[\text{FeNiMo}(\mu_3\text{-S})(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4\text{R})(\text{CO})_5]$ [R = H, C(O)Me, C(O)OMe] and other related species [16–19].

The reaction of the unsaturated nickel–tungsten complex **1b** with $[\text{Fe}_2(\text{CO})_9]$ proceeds similarly and affords the analogous cluster $[\text{FeNiW}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3b**. While **3b** was not structurally characterized, its spectroscopic data are very similar to those of **3a**. In addition the mass spectrum shows a parent ion for this formulation with the correct isotopic envelope for a FeNiW species. The very similar spectroscopic data of **3a** and **3b** strongly suggest that the two species are isostructural. However, **3b** appears to be less stable than **3a** and is obtained in lower overall yields.

The reaction of the saturated analogue of **1a**, the complex $[(\eta\text{-C}_5\text{Me}_5)(\text{OC})\text{Ni}-\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$, **2a** (see Fig. 1) was also attempted with $[\text{Fe}_2(\text{CO})_9]$ to see whether using the unsaturated and formally double-bonded species imparted any advantages to the cluster synthesis described earlier. The reaction proceeded

smoothly, with the green colour of **2a** slowly giving way to an olive green solution. Complex **3a** was indeed isolated as a product from this reaction, but other species including $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$, a little $[\text{Ni}(\mu\text{-CO})(\eta\text{-C}_5\text{Me}_5)]_2$, a green oil that probably contains a nickel–iron cluster, and other unidentified species were also obtained when the reaction mixture was subject to column chromatography. The overall isolated yields of complex **3a** were much lower, clearly showing the advantages of using the formally doubly bonded complexes as building blocks for mixed-metal cluster synthesis.

3. Experimental

3.1. General

Reactions were carried out under nitrogen, in rigorously deoxygenated solvents. The ^1H NMR spectra were recorded on a Bruker AM300 instrument. All resonances are singlets. Chemical shifts (in ppm) were referenced to residual CHCl_3 or C_6HD_5 . IR spectra were recorded on a Bruker IFS66 FT instrument.

3.2. Synthesis of complexes **1a** and **1b**

Both complexes are prepared in a similar fashion. In a typical preparation, $[\text{NiCl}_2\cdot\text{dme}]$ (755 mg, 3.43 mmol) was suspended in 30 ml THF and cooled to -25°C . A solution of $(\text{C}_5\text{Me}_5)\text{MgCl}$ [8] (12.8 ml of a 0.295 M solution, 3.77 mmol) was added dropwise and the solution stirred for 24 h at -25°C . A solution of fresh $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$, prepared by reductive cleavage of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$ (3.43 mmol in 15 ml THF) with 1.0 M KHBet_3 , was then added dropwise to the dark suspension, and the resulting deep blue solution was allowed to warm up to ambient temperature and then pumped down to dryness under vacuum. The dark residue was transferred anaerobically to a filter stick equipped with a pressure equalized side-arm, that was in turn attached to a 50 ml two-necked round bottomed flask with a nitrogen inlet adaptor. When the transfer was complete, a reflux condenser was attached to the top of the filter stick and 30 ml of pentane were added. As the pentane was heated to reflux, the vapours condensed and dripped on the solid residue in a manner similar to a Soxhlet extraction process, dissolving pure **1a**, which concentrated and then started to deposit in the round bottomed flask. After an overnight extraction, the process was complete and **1a** (779 mg, 52% based on $[\text{NiCl}_2\cdot\text{dme}]$) was collected as dark blue-black crystals.

3.3. Synthesis and spectroscopic data for the complexes $[\text{FeNiMo}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3a** and $[\text{FeNiW}(\mu_3\text{-CO})(\mu_2\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$, **3b**

The synthesis of **3b** is representative and is given here. Complex **3b** (327 mg, 0.62 mmol) was dissolved in 25 ml Et_2O and $[\text{Fe}_2(\text{CO})_9]$ (226 mg, 0.62 mmol) was added. The solution was stirred magnetically until all the $[\text{Fe}_2(\text{CO})_9]$ was consumed (ca 1 h) and then pumped down to dryness in vacuo to remove any $[\text{Fe}(\text{CO})_5]$. The residue was redissolved in toluene, to give a deep green solution, and this was filtered through a short (5 cm) Al_2O_3 pad. After the toluene solution was concentrated and layered with pentane, dark green crystals of **3b** (353 mg, 82%) deposited at -20°C . The product was contaminated with traces of red crystals of $[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$, which could easily be removed manually. A purer crop of **3b** was obtained in somewhat reduced yield (typically 50–70%) by column chromatography on Al_2O_3 : traces of $[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$ were readily separated from the only other band, cluster **3b**.

3.3.1. Spectroscopic data for **3a**

^1H NMR [ppm, CDCl_3]: 5.17 (5H, C_5H_5), 1.65 (15H, C_5Me_5). [ppm, C_6D_6]: 5.27 (5H, C_5H_5), 1.64 (15H, C_5Me_5). IR [$\nu(\text{CO})$, pentane, cm^{-1}]: 2047(s), 2028(w), 1996(m), 1984(s), 1966(m), 1936(m), 1784(w). Anal: expt. (calculated) for $\text{C}_{22}\text{H}_{20}\text{FeMoNiO}_7$: C, 43.49 (43.60); H, 2.96 (2.99)%.

3.3.2. Spectroscopic data for **3b**

^1H NMR [ppm, CDCl_3]: 5.24 (5H, C_5H_5), 1.68 (15H, C_5Me_5). IR [$\nu(\text{CO})$, pentane, cm^{-1}]: 2048(s), 2028(w), 2004(w), 1995(s), 1984(vs), 1965(m), 1936(s), 1920(sh), 1871(m), 1789(w). Anal: expt. (calculated) for $\text{C}_{22}\text{H}_{20}\text{FeNiWO}_7$: C, 38.37 (38.03); H, 2.67 (2.90)%. MS (FABS, m/e): 694 (M^+), 666 (M-CO^+).

3.4. Reaction of $[(\eta\text{-C}_5\text{Me}_5)(\text{OC})\text{Ni-Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ **2a** with $[\text{Fe}_2(\text{CO})_9]$

The saturated complex **2a** (306 mg, 0.66 mmol) was reacted with $[\text{Fe}_2(\text{CO})_9]$ (240 mg, 0.66 mmol) in THF. The solution darkened as the mixture was stirred for 2 h. It was then pumped down to dryness in vacuo, dissolved in ca 4 ml toluene and subjected to chromatography on an Al_2O_3 column. Two red bands eluted with toluene (respectively $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$ and $[\text{Ni}(\mu\text{-CO})(\eta\text{-C}_5\text{Me}_5)]_2$), followed by a non-characterized green band, **4a**. Complex **3a** eluted next using a toluene: Et_2O mixture followed by small quantities of a light brown band, and then a lighter red-brown band that decomposed on the column and was

not eluted. Complex **3a** was recrystallized from toluene:pentane mixtures and collected in 28% yield (109 mg, 0.18 mmol).

3.5. X-ray data collection

A dark green–black crystal of **3a**, of dimensions $0.10 \times 0.08 \times 0.05$ mm, that was grown from a toluene/pentane mixture, was selected and mounted on a Kappa CCD diffractometer. Data were collected using phi-scans and the structure was solved using direct methods and refined against F^2 using SHELX 97 software [20–21]. No absorption correction was used. A total of 10 169 reflections was collected with

$1.44^\circ < \theta < 27.43^\circ$, of which 4799 unique reflections had intensities $I > 2 \sigma(I)$. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C-H} = 0.95 \text{ \AA}$, $U_{11} = 0.04$). Full data collection parameters, and structural data are available as supplementary material.

• Supplementary material

The supplementary material has been sent in electronic format to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as cif file No. CCDC 166551, and can be obtained by contacting the CCDC.

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