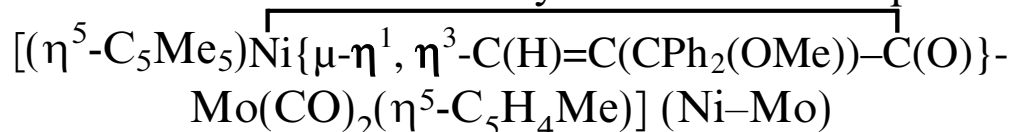


Note

Reactions of nickel-group 6 complexes with a bulky terminal alkyne to afford alkyne–carbonyl coupled products: X-ray structure of the heterobimetallic nickelacyclobutenone complex



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Abstract

The nickel–molybdenum complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}=\text{Mo(CO)}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  can be considered to contain a partially dative nickel–molybdenum double bond. This complex reacts with the bulky terminal alkyne  $\text{HC}\equiv\text{CCPh}_2(\text{OMe})$  (DPMP) to afford the alkyne–carbonyl coupled metallacyclic product  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}\{\mu\text{-CH=CR-C(O)}\}\text{Mo(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  (**3c**, R = CPh<sub>2</sub>(OMe), Ni–Mo) regioselectively and exclusively. No traces of a nickel–molybdenum  $\mu$ -alkyne complex, analogous to similar complexes isolated with less bulky alkynes, were observed. The structure of complex **3c** was established via a single crystal X-ray diffraction study. It exhibits the same connectivity as that observed with a related complex formed with the smaller but-2-yne, but some significant differences are observed between the two structures. Reactions of the nickel–molybdenum and -tungsten species  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}=\text{M(CO)}_3(\eta^5\text{-C}_5\text{H}_5)]$  (M = Mo, W) with DPMP proceeded analogously and afforded similar products.  
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**Keywords:** Alkyne; Heterobimetallic; Metallacycle; Carbon–carbon coupling

1. Introduction

Many research groups have been interested in alkyne reactions with mixed metal complexes, in particular those that involve carbon–carbon coupling [1–6]. We share these interests and have been studying the reactions of  $[\text{Cp}^{\text{a}}\text{-Ni(CO)-M(CO)}_3\text{Cp}^{\text{b}}]$  (M = Cr, Mo, W; Cp<sup>a</sup> = Cp, Cp\*<sup>+</sup>; Cp<sup>b</sup> = Cp, Cp')<sup>1</sup> and, more recently, of the unsaturated tri-

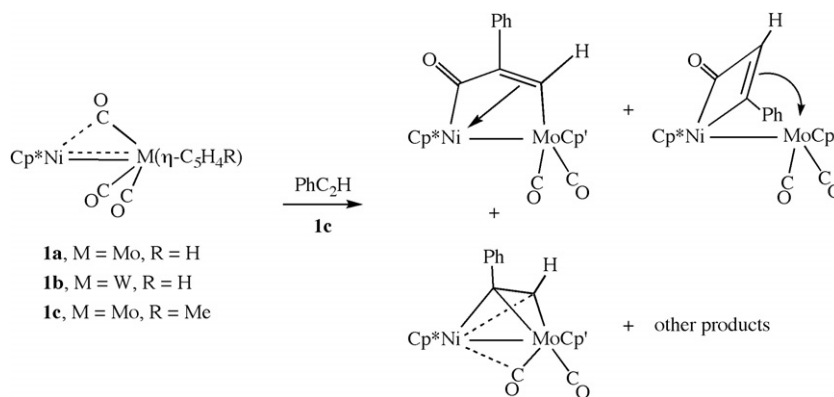
carbonyl complexes **1**  $[\text{Cp}^{\text{a}}\text{Ni}=\text{M(CO)}_3\text{Cp}^{\text{b}}]$  (Cp<sup>a</sup> = Cp, Cp'; M = Mo, W) [7] with alkynes [8–16]. (Complexes **1** are represented with Ni=M double bonds but the real situation is more complex; a better representation is shown in Scheme 1. The metal–metal bond is partially dative). The major products isolated from reactions of nickel–(group 6 metal) complexes with alkynes are nickelacyclobutenone species, in which the alkyne has coupled with a carbonyl group ligand, and this unit is bonded to the group 6 metal [8,9,13,14].

The reactivity pattern of phenylacetylene, a terminal alkyne, is significantly different from that of internal alkynes, such as 2-butyne. Other reactions, in which multiple

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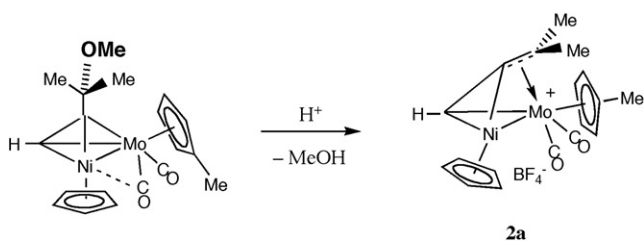
<sup>1</sup> Throughout this manuscript, Cp =  $\eta^5\text{-C}_5\text{H}_5$ , Cp' =  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ , Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ , Cp<sup>+</sup> = Cp or Cp'.

Scheme 1. Complexes **1** and the reaction of phenylacetylene with **1c**.

alkyne–alkyne, alkyne–carbonyl and alkyne–Cp\*H couplings occur, were observed with this alkyne [10,12]. When phenylacetylene was reacted with Ni=Mo and Ni=W complexes **1**, three different metallacycles, were isolated as the major products, as shown in Scheme 1 for complex **1c** [14].

We decided to react complexes **1**, [Cp\*Ni=M(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>4</sub>R)] (**1a**, R = H, M = Mo; **1b**, R = H, M = W; **1c**, R = Me, M = Mo) with the bulky terminal alkyne HC<sub>2</sub>-CPh<sub>2</sub>(OMe) (3,3-diphenyl-3-methoxy-prop-1-yne, DPMP) for two principal reasons. Firstly, we wanted to determine whether a more sterically demanding terminal alkyne would narrow the product distribution from that seen when phenylacetylene reacts with the Ni=Mo heterobimetallic complex **1c**. The presumed structures of the two metallacyclic complexes obtained from the reaction of **1c** with phenylacetylene are shown in Scheme 1. The geometries of these complexes were deduced spectroscopically, but we were keen to confirm the structure of one or more DPMP analogs of these products by an X-ray diffraction study [14].

The second reason for choosing this particular alkyne is related to some of our recent work on metal-stabilized carbocations. The synthesis and some reactions of the carbocationic complexes [CpNi(μ-η<sup>2</sup>, η<sup>2</sup>-HC<sub>2</sub>CMe<sub>2</sub>)M(CO)<sub>2</sub>Cp']<sup>+</sup> (Ni–M: **2a**, M = Mo; **2b**, M = W) were recently described. The nickel–molybdenum cation is formed by the protonation of an alkoxy–alkyne complex; subsequent loss of methanol, as shown in Scheme 2 affords complex **2a** [15].



Scheme 2. Formation of metal-stabilized carbocations by protonation of a μ-alkoxy-alkyne complex.

Complexes **2** are unstable at room temperature and decompose rapidly enough in solution that a <sup>13</sup>C NMR spectrum could not be obtained. We reasoned that we might be able to stabilize these carbocationic complexes (i) by increasing the electron density on the nickel atom and (ii) by stabilizing the cation via resonance delocalization. The electron density could be increased on the nickel atom by replacing the Cp group with a Cp\* ligand and this would help counterbalance the formal positive charge. Replacement of the CMe<sub>2</sub> group in complexes **2** with a CPh<sub>2</sub> group would also allow possible resonance stabilization of the cationic charge. The protonation of such a Cp\* nickel–molybdenum μ-DPMP complex should then result in loss of MeOH to yield a stabilized HC<sub>2</sub>CPh<sub>2</sub><sup>+</sup> carbocation.

## 2. Results and discussion

The reaction of DPMP with complex **1a** was relatively slow but after 3 h, the deep blue green color of **1a** had given way to an orange brown solution. Following solution work-up and chromatography on an alumina column (see Section 3.1), red-brown crystals of complex **3a** were isolated as the *only* isolated alkyne-containing product. The nickel–tungsten complex **1b** reacted with DPMP to afford **3b** and the Cp\*Ni=MoCp' complex **1c** afforded **3c**. The spectroscopic data of all three products were similar (see Section 3.1) and indicated that complexes **3** had similar structures. The spectroscopic data of complex **3c** are discussed here and are consistent with the structure [Cp\*Ni{μ-η<sup>1</sup>, η<sup>3</sup>-C(H)=C(R)-C(O)}Mo(CO)<sub>2</sub>Cp'] (Ni–Mo) shown in Fig. 2.

The <sup>1</sup>H NMR data revealed that **3c** contained Cp', Cp\* and DPMP groups in a 1:1:1 ratio. The aromatic Cp' proton resonances exhibited an ABCD type multiplet, indicative of a lack of an effective mirror plane of symmetry in the molecule. The <sup>13</sup>C NMR spectra of solutions of **3c** corroborated these results, and in addition, showed the presence of three CO groups. The IR spectrum of **3c** exhibited three ν(CO) peaks: two corresponded to terminal and semi-bridging metal carbonyl stretches (1951 and

1832 cm<sup>-1</sup>), respectively. [Note that in many systems, a  $\nu(\text{CO})$  absorption below  $\approx 1850$  cm<sup>-1</sup> indicates a  $\mu_2$ -CO ligand. However in this system, with a highly electron rich Cp\*Ni center that significantly weakens the CO bond and lowers its stretching frequency, a semi-bridging CO interaction could easily be observed in the range typical of  $\mu_2$ -CO groups.] A third  $\nu(\text{CO})$  stretch was observed in the metal acyl region of the spectrum (1686 cm<sup>-1</sup>).

All these data are consistent with the presence of a DPMP-CO linked moiety in complex **3c**. Alkyne-carbonyl coupling reactions on bimetallic complexes to form CR-CR'-C(O) moieties have been reported by us and by others. This C<sub>3</sub> chain may either be  $\sigma$ -bonded to a single metal of the bimetallic center, to form a four-membered  $\text{M}-\text{CR}=\text{CR}'-\text{C}(\text{O})$  metallacyclobutenone ring [8,9,17–20], or else  $\sigma$ -bonded to both metals, to  $\text{M}-\text{CR}=\text{CR}'-\text{C}(\text{O})-\text{M}'$  dimetallacyclopentenone ring system [21–26]. (The CR=CR'-C(O) group is also known to bond to a di-metal center in other, non-cyclic bonding modes [27,28]). The two metallacyclic ring systems are not easily distinguished from each other spectroscopically, especially when spin-active metallic nuclei are absent. This proved to be the case with the ligand DPMP: if the DPMP C $\equiv$ C bond is not ruptured, neither the linkage of the alkyne to the CO group [C(O)-CH=CR or C(O)-CR=CH, R = CPh<sub>2</sub>(OMe)], nor the linkage of this framework to the heterobimetallic Ni-Mo center could readily be established spectroscopically. A single crystal

X-ray diffraction study was deemed necessary to establish the structure of the complex.

Key X-ray crystal data and data collection parameters for **3c** are given in Table 1. Lists of key bond-lengths and angles for non-hydrogen atoms of the complex are tabulated in Tables 2 and 3. An ORTEP diagram of complex **3c** is shown in Fig. 1.

The core of complex **3c** [Cp\*Ni{-C(H)=C(R)-C(O)}Mo(CO)<sub>2</sub>Cp'] contains a nickelacyclobutenone Ni-C(H)=C(R)-C(O) ring [R = CPh<sub>2</sub>(OMe)] that is  $\pi$ -coordinated, via the C=C double bond, and via a Ni-Mo single bond, to a Mo(CO)<sub>2</sub>Cp' unit. The nickel atom's coordination sphere is completed by a  $\eta^5$ -bonded Cp\* ligand. The structure is superficially similar to that determined for the complex [CpNi-C(Me)=C(Me)-C(O)}Mo(CO)<sub>2</sub>Cp'] (Ni-Mo, **3d**) in which a similar nickelacyclobutenone ring system is present [8,9]. However, there are some significant structural and geometric differences induced by the presence of the much more sterically demanding CPh<sub>2</sub>(OMe) group, and by the electron rich and sterically demanding Cp\* group present in **3c** that merit discussion. A side-by-side diagram of the structures of **3c** (and of its presumed isostructural analogs **3a** and **3b**) and of complex **3d** is shown in Fig. 2.

In complex **3c** both metal carbonyl C-O bond vectors and the metallacyclic C=O bond vector all point in the approximately the same direction (all three CO vectors are going into the plane of the paper, away from the reader). In complex **3d** the metallacyclic C=O vector is directed away from the two Mo-C $\equiv$ O vectors (the metallacyclic C=O vector is directed out towards the reader, while the other metal carbonyl bond vectors are directed into the plane of the paper, away from the reader). This is best appreciated by analysing the torsion angles that the (Mo)-C $\equiv$ O bond vectors make with the metallacyclic C=O group. In complex **3c**, these are: 27.9° for O(2)-C(25)-C(1)-O(1) and 20.7° for O(3)-C(24)-C(1)-O(1). Corresponding values for complex **3d** are 108.9° and 93.5°. The methoxy-group oxygen atom in **3c** is also on the same side of the molecule so that all four oxygen atoms in **3c** are oriented towards the same direction. The steric bulk of the CPh<sub>2</sub>(OMe) group pushes the two diene rings closer together so that the Cp\*<sub>centroid</sub>-Ni-Mo-Cp'<sub>centroid</sub> torsion angle in **3c** = 27.6° as compared to the value of 67.1° for the Cp<sub>centroid</sub>-Ni-Mo-Cp'<sub>centroid</sub> angle in **3d**.

One of the molybdenum-bound carbonyl ligands in **3c** is semi-bridging to the nickel atom, (Mo-C(27)-O(2)) = 166°; Ni...C(27) = 2.386 Å). This semi-bridging interaction probably exists to somewhat relieve the nickel atom's high electron density. It is not observed in **3d**, in which the nickel atom bears a less electron rich Cp (and not a Cp\*) ligand, and so the two carbonyl ligands are strictly terminal in **3d**.

The distances and angles of the NiC<sub>3</sub> rings present in both **3c** and **3d** are virtually identical. This suggests that the bulky Cp\* and CPh<sub>2</sub>(OMe) groups do not have

Table 1  
Crystal data and data collection parameters for **3c**

Formula	C <sub>35</sub> H <sub>36</sub> MoNiO <sub>4</sub>
Formula weight	675.27
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
<i>a</i> (Å)	9.4270(2)
<i>b</i> (Å)	18.8270(4)
<i>c</i> (Å)	17.1270(4)
$\alpha$ (°)	90.00
$\beta$ (°)	94.6400(9)
$\gamma$ (°)	90.00
<i>V</i> (Å <sup>3</sup> )	3029.77(12)
<i>Z</i>	4
Density (g cm <sup>-3</sup> )	1.480
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.073
<i>F</i> (000)	1392
<i>Data collection</i>	
Temperature (K)	173(2)
Theta min-max	1.61–30.03
Dataset [ <i>h</i> , <i>k</i> , <i>l</i> ]	–13/13, 0/26, 0/24
Total, unique data, <i>R</i> <sub>int</sub>	8851, 4839, 0.0000
Observed data	>2 $\sigma$ ( <i>I</i> )
<i>Refinement</i>	
Number of reflections, number of parameters	8851, 370
<i>R</i> <sub>1</sub> , <i>R</i> <sub>2</sub>	0.0547, 0.1316
<i>wR</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.1148, 0.1347
Goodness-of-fit	0.888
Maximum and average shift/error	0.001, 0.000
Minimum, maximum residual density (e Å <sup>-3</sup> )	–0.725, 0.517

Table 2  
Key bond distances (Å) for complex **3c**, with esd's in parenthesis (when available)

Mo–Ni	2.6684(7) 2.5859 (2)	Mo···C(1)	2.775(5) 2.661
Mo–C(2)	2.343(4) 2.290(2)	Mo–C(3)	2.104(4) 2.179(2)
Mo–C(24)	1.983(5) 1.985(2)	Mo–C(25)	1.961(4) 1.978(2)
Ni···C(25)	2.387(4) 2.916	Ni–C(1)	1.945(4) 1.927(2)
Ni···C(2)	2.501(4) 2.491	Ni–C(3)	1.912(4) 1.912(2)
C(1)–C(2)	1.466(5) 1.436(2)	C(2)–C(3)	1.435(6) 1.438(2)
O(3)–C(24)	1.152(5) 1.137(2)	O(2)–C(25)	1.171(5) 1.136(2)
O(1)–C(1)	1.198(5) 1.207(2)		
Mo–C <sub>cp</sub> ' (mean)	2.346 2.335	Ni–C <sub>cp</sub> ' (mean)	2.128 2.123
Mo–C <sub>p</sub> centroid	2.013 2.000	Ni–C <sub>p</sub> centroid	1.747 1.755

The second value *in italics* is the equivalent distance in the previously described complex **3d** [8,9].

Table 3  
Key bond distances (Å) for complex **3c**, with esd's in parenthesis

Ni–Mo–C(24)	112.43(13) <i>124.41(5)</i>	Ni–Mo–C(25)	59.78(13) <i>78.18(6)</i>
C(24)–Mo–C(25)	85.74(17) 81.70(8)	C(1)–Ni–C(3)	70.65(17) 69.92(7)
Mo–Ni–C(1)	72.03(13) 70.55(5)	Mo–Ni–C(3)	51.51(13) 55.55(5)
C(1)–C(2)–C(3)	100.5(3) 99.9(1)	C(3)–C(2)–C(4)	127.3(3) 129.3(2)
C(1)–C(2)–C(4)	127.6(4) 127.0(2)	Ni–C(1)–O(1)	130.3(3) 128.8(1)
Mo–C(24)–O(3)	176.3(4) 177.6(2)	Mo–C(25)–O(2)	166.0(4) 176.9(1)
Ni–C(1)–C(2)	93.2(3) 94.4(1)	O(1)–C(1)–C(2)	136.3(4) 133.9(2)
Ni–C(3)–C(2)	95.6(2) 95.1(1)		

The second value, *in italics* is the equivalent angle for the previously described complex **3d** [8,9].

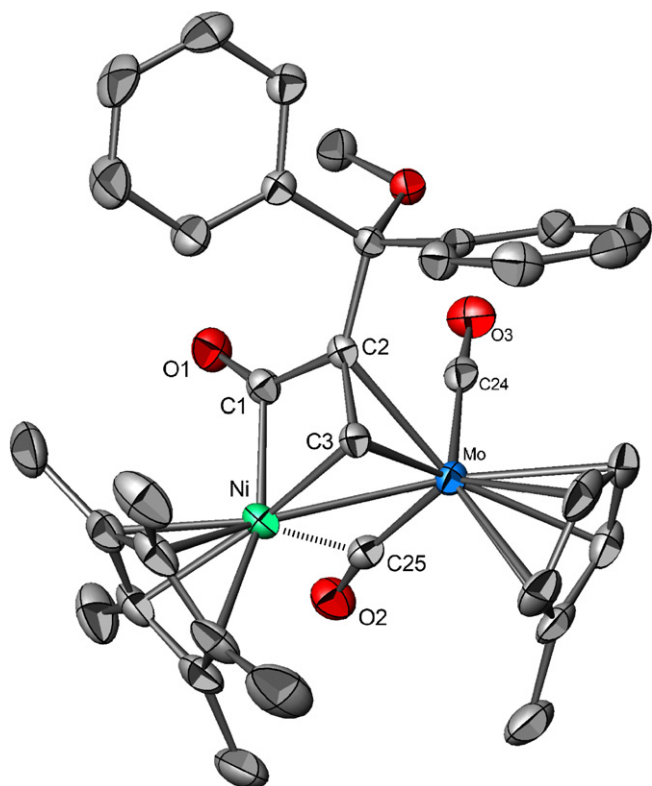


Fig. 1. ORTEP diagram of non-hydrogen atoms of complex **3c**, showing the labeling scheme for key atoms. Ellipsoids are shown at the 50% probability level.

structural repercussions on this central core. However, in **3c**, the Ni–Mo bond is significantly longer than in the less sterically demanding complex **3d** [2.6684(7) Å for **3c**; 2.5859(2) Å for **3d**]. Both bonds are in the normal

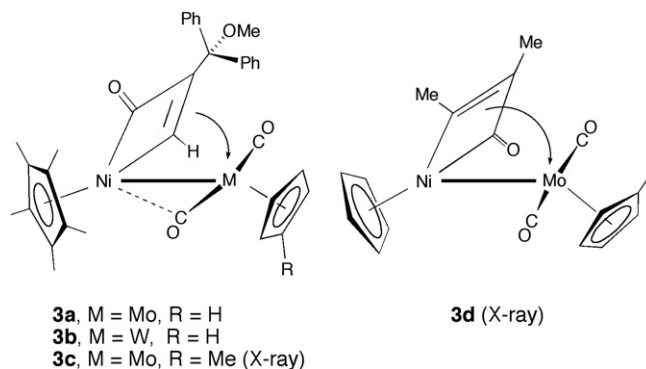


Fig. 2. A side-by-side comparison of the structures of the metallacyclic complexes **3c** and **3d**. The Mo–CO groups are on the same side as the metallacyclic C=O group in **3c**, but not in **3d**.

range of Ni–Mo single bonds observed in the literature [29–34].

No close hydrogen-bonded interactions are seen in this structure. However, a methoxy-group hydrogen atom may interact weakly, in an intramolecular fashion, with the metallacyclic CO oxygen atom [O(1)–H(17A) = 2.213 Å; C(17)–H(17A)–O(1) = 155.6°].

### 3. Conclusion

In previous reactions of the Ni=Mo and Ni=W complexes **1** with PhC≡CH and with other terminal alkynes, mixtures of products, and isomeric metallacycles were observed. However, with the bulky terminal alkyne DPMP, only one alkyne-containing product could be isolated. Yields are modest and substantial decomposition takes place on the chromatography column. It does appear that

if the steric bulk of the alkyne is sufficiently large, as is the case here, the only alkyne-containing products isolated are complexes of type **3**, and formation of the  $\mu$ -alkyne complex is suppressed. The  $\text{Ni}-\text{C}(\text{H})=\text{C}(\text{R})-\text{C}(\text{O})$  [R =  $\text{CPh}_2(\text{OMe})$ ] linkage of the metallacycle obtained in these complexes places the steric bulk of the R group far away from both metals and minimizes severe steric interactions that would be found in the other  $\text{Ni}-\text{C}(\text{R})-\text{C}(\text{H})-\text{C}(\text{O})$  geometries.

It is not clear what factors favor the formation of a four-membered metallacyclic ring as opposed to a five-membered isoelectronic dimetallacyclic ring system. Both ring systems have been observed previously in homo- and in heterobimetallic systems. In our previously reported reactions of complex **1a** with  $\text{PhC}_2\text{H}$ , both complexes were obtained, but in most cases in the literature, there is a preference for one or the other isomer [8,9,17–26]. With the bulky DPMP ligand, a five-membered dimetallacyclopentone ring system might have been expected, but this isomer of complexes **3** is not observed. Factors that lead to the observed metallacycle geometries are subtle and not well understood. Experiments into the protonation of complexes **3** to generate carbocationic complexes are underway and will be reported elsewhere.

### 3.1. Experimental

#### 3.1.1. General

All manipulations were performed under an atmosphere of argon or pre-purified nitrogen, using standard Schlenkware techniques. Solvents were pre-dried and distilled from sodium benzophenone ketyl solutions (diethylether, thf, pentane, toluene).

IR data were collected on a Perkin–Elmer FT-IR spectrometer and were obtained on KBr pellets.  $^1\text{H}$  NMR spectra were recorded on a Bruker GN-300 spectrometer in chloroform- $d_1$ , acetone- $d_6$  or benzene- $d_6$  as noted, and were referenced with respect to the residual protons in these solvents. Chemical shifts are in ppm with coupling constants  $J$  in Hertz. Microanalytical data for complexes **3** were obtained by using the in-house microanalysis laboratory at the Université Louis Pasteur. The ligand DPMP,  $\text{HC}\equiv\text{CCPh}_2(\text{OMe})$  was synthesized via methylation of  $\text{HC}\equiv\text{CCPh}_2(\text{OH})$  (purchased from Aldrich) according to the literature procedure [35]. It was freeze–thaw degassed prior to use. Complexes **1a**, **1b** and **1c** were prepared as previously described [7].

#### 3.1.2. Synthesis of complex **3a**

DPMP (134 mg, 0.60 mmol) was added under argon to a solution of **1a** (264 mg, 0.60 mmol) in thf (15 mL). The initially blue–green mixture gave way to a reddish brown color over 3.5 h. The solvent was then removed under vacuum, and the dark residue was dissolved in toluene and subjected to chromatography on an alumina column. Three bands were eluted: small quantities of the molybde-

num dimer  $\text{Mo}_2(\text{CO})_6\text{Cp}_2$  (Mo–Mo) were eluted with toluene followed by an unidentified tan product. The third product, **3a** eluted with dichloromethane as a reddish brown band. The solution was concentrated and layered with pentane. Crystals of **3c** were obtained from this solvent system at  $-25^\circ\text{C}$ . Yield: 110 mg, 0.166 mmol, 28%. Anal. Calc. (expt.) for  $\text{C}_{34}\text{H}_{34}\text{MoNiO}_4$ : C, 61.76 (61.59); H, 5.18 (5.04). Spectroscopic data for **3a**. IR [KBr,  $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ] 1964 (vs), 1958 (vs) 1829 (m) 1631 (m, br).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.80, 7.68, 7.52, 7.4–7.15, 7.0 (m, 10H, Ph), 6.59 (1H,  $\text{HC}\equiv$ ), 4.65 (5H, Cp), 2.90 (3H, OMe), 1.79 (15H,  $\text{Cp}^*$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ): 230.7 and 230.4 (Mo–CO), 177.4 (C=O), 143.4 and 142.1 [C(1), Ph], 130.5, 130.3, 129.8, 128.7, 128.6, 128.4, 128.1, 127.7, 127.2, 127.1 [C(2)–C(6), Ph], 101.9 ( $\text{C}_5\text{Me}_5$ ), 92.4 (CR), 92.1 ( $\text{C}_5\text{H}_5$ ), 89.7 [CH], 52.8 (OMe), 10.4 ( $\text{C}_5\text{Me}_5$ ).

#### 3.1.3. Synthesis of complex **3b**

DPMP (185 mg, 0.83 mmol) was added under argon to a solution of **1b** (428 mg, 0.81 mmol) in thf (20 mL). The deep blue solution turned reddish brown over a 3 h period. The thf was removed under vacuum, and the dark brown residue was dissolved in toluene and subjected to chromatography on an alumina column. Three bands were eluted: the tungsten dimer  $\text{W}_2(\text{CO})_6\text{Cp}_2$  (W–W) eluted with toluene as a cherry red band, followed by small quantities of an unidentified light brown product. The third product, **3b** eluted slowly with dichloromethane as a dark reddish brown band. The solution was concentrated and crystals of **3b** were obtained by crystallization from a mixed pentane/dichloromethane solvent system at  $-25^\circ\text{C}$ . Yield: 192 mg, 0.256 mmol, 26%. Anal. Calc. (expt.) for  $\text{C}_{34}\text{H}_{34}\text{NiO}_4\text{W}$ : C, 54.51 (54.62); H, 4.57 (4.82). Spectroscopic data for **3b**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.66, 7.55, 7.40, 7.34–7.13, 7.07 (m, 10H, Ph), 6.62 (1H,  $\text{HC}\equiv$ ), 4.73 (5H, Cp), 2.88 (3H, OMe), 1.80 (15H,  $\text{Cp}^*$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ): 216.4 and 215.7 (W–CO), 179.6 (C=O), 143.5 and 141.1 [C(1), Ph], 130.7, 129.3, 128.4, 127.7, 127.5, 127.2, 126.8, 126.7, 127.2, 127.1 [C(2)–C(6), Ph], 119.6 (CR), 101.9 ( $\text{C}_5\text{Me}_5$ ), 90.8 (CH), 92.1 ( $\text{C}_5\text{H}_5$ ), 85.6 [ $\text{CPh}_2(\text{OMe})$ ], 51.9 (OMe), 9.7 ( $\text{C}_5\text{Me}_5$ ).

#### 3.1.4. Synthesis of complex **3c**

DPMP (222 mg, 1.00 mmol) was added under argon to a solution of **1a** (299 mg, 0.66 mmol) in thf (20 mL). The initially blue–green mixture gave way to a reddish brown color over 3 h. Volatile liquids were then removed under vacuum, and the dark residue was dissolved in toluene and subjected to chromatography on an alumina column. Three bands were eluted: the molybdenum dimer  $\text{Mo}_2(\text{CO})_6\text{Cp}_2$  (Mo–Mo) eluted with toluene, followed by small quantities of an unidentified yellow–tan product. The third product, **3c** eluted with dichloromethane as a reddish band. The solution was concentrated and pentane was added. Crystals of **3c** were obtained by crystallization from this mixed pentane/dichloromethane solvent system at  $-25^\circ\text{C}$ . Yield: 192 mg, 0.284 mmol, 43%. Anal. Calc. (expt.) for

$C_{35}H_{36}MoNiO_4$ : C, 62.25 (62.71); H, 5.37 (5.64). Spectroscopic data for **3c**: IR [KBr,  $\nu(CO)$ ,  $cm^{-1}$ ] 1951 (vs) 1832 (s) 1686 (m, br).  $^1H$  NMR ( $CDCl_3$ ): 7.39, 7.31–7.14, 7.0 (m, 10H, Ph), 6.58 (1H,  $HC\equiv$ ), 4.81, 4.55 (2H) and 4.12 (ABCD multiplets,  $C_5H_4Me$ ), 2.90 (3H, OMe), 1.88 ( $C_5H_4Me$ ), 1.77 (15H, Cp\*). Acetone- $d_6$ : 7.60, 7.45, 7.21–6.90, 6.80 (m, 10H, Ph), 6.54 (1H,  $HC\equiv$ ), 4.88, 4.80, 4.62 and 4.41 (ABCD multiplets,  $C_5H_4Me$ ), 2.96 (3H, OMe), 1.88 ( $C_5H_4Me$ ), 1.75 (15H, Cp\*). Benzene- $d_6$ : 7.69, 7.60, 7.39, 7.20–6.96, 6.80 (m, 10H, Ph), 6.70 (1H,  $HC\equiv$ ), 4.58, 4.48, 4.43 and 4.11 (ABCD multiplets,  $C_5H_4Me$ ), 3.15 (3H, OMe), 1.72 (15H, Cp\*), 1.69 ( $C_5H_4Me$ ).  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ ): 233.1 and 232.2, (Mo–CO), 173.8 ( $C=O$ ), 143.8 and 143.2 [ $C(1)$ , Ph], 134.2, 130.4, 129–126 [ $C(2)$ – $C(6)$ , Ph overlap with solvent resonances], 110.1 (CR), 108.1 [ $C(1)$ , Cp'], 101.9 ( $C_5Me_5$ ), 99.2 (CH), 94.8, 92.9, 91.5, 90.0 [ $C(2)$ – $C(5)$ ,  $C_5H_4Me$ ], 85.6 [ $CPh_2(OMe)$ ], 53.2 (OMe), 14.1 (Me, Cp'), 10.1 ( $C_5Me_5$ ).

### 3.1.5. Crystal structure determination of complex **3c**

Crystals suitable for an X-ray diffraction study were obtained from a mixed diethylether/pentane solvent system at  $-25^\circ C$ . Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The complete conditions of data collection (DENZO software) and structure refinements are given in Table 1. The cell parameters were determined from reflections taken from one set of 10 frames ( $1.0^\circ$  steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against  $F^2$  using the SHELXL97 software. The absorption was not corrected empirically. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97 [36,37].

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### Appendix A. Supplementary material

CCDC 644689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.07.020](https://doi.org/10.1016/j.jorganchem.2007.07.020).

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