

# Some reactions of Ni–Mo and Ni–W propargylic cations with nucleophiles

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## Abstract

Preliminary reactions of the metal stabilized carbocationic species  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\mu\text{-}\eta^2(\text{Ni}),\eta^3(\text{Mo})\text{-HC}_2\text{CMe}_2)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]^+ \text{BF}_4^-$  (Ni–Mo) with nucleophiles are reported. The Ni–Mo cationic propargylic complex undergoes nucleophilic attack by sodium methoxide to regenerate the neutral  $\mu$ -alkyne complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^2\text{-HC}_2\text{CMe}_2(\text{OMe})\}\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–Mo), from which the stabilized carbocation was originally derived by protonation. The new complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–Mo), which exist as an inseparable mixture of 1(c)-1,3- and 2(c)-1,3-cyclopentadienyl isomers, were also obtained. When the Ni–Mo cations were treated with potassium *t*-butoxide, the alkyne isomers with pendant 1(c)-1,3- and 2(c)-1,3-cyclopentadienyl groups are also formed. The  $\mu$ -hydroxyalkyne complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^2\text{-HC}_2\text{CMe}_2(\text{OH})\}\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–Mo) was also isolated concurrently, and presumably arises from nucleophilic attack of fortuitously present hydroxide ions in the  $\text{BuO}^-$  reagent on the Ni–Mo cation. When  $\text{NaBH}_4$  was added to the Ni–Mo propargylic, nucleophilic attack by hydride resulted and the  $\mu\text{-}^i\text{PrC}_2\text{H}$  heterobimetallic complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^2\text{-HC}_2\text{Pr}^i\}\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–Mo) was recovered in good yield. Small quantities of other side-products were isolated and characterized spectroscopically. Some tantalizing differences in reactivity were observed when the corresponding Ni–W stabilized carbocation was reacted with methoxide ions. When the not fully characterized solid formed by protonating  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\mu\text{-}\eta^2,\eta^2\text{-}\{\text{HC}_2\text{CMe}_2\}(\text{OMe}))\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–W) was treated with methoxide ions, regioisomers (1(c)-1,3- and 2(c)-1,3-cyclopentadienyl species) of composition  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$  (Ni–W) were formed. Direct reaction of the pure cation  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}\{\mu\text{-}\eta^2,\eta^3\text{-HC}_2\text{CMe}_2\}\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]^+$  (Ni–W) with methoxide also generated the same 1(c)-1,3- and 2(c)-1,3-cyclopentadiene-substituted alkyne complexes. Unlike the case with the Ni–Mo complexes, the initial  $\mu\text{-HC}_2\text{CMe}_2(\text{OMe})$  species was not regenerated.

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## 1. Introduction

There has been increasing interest in the synthesis and reactivity of metal-stabilized carbocations in which a  $\text{C-CR}_2^+$  is formally bound to, and stabilized on, a dimetal center and the field has been reviewed [1]. Many examples of such species ligated onto Co–Co bonds have been recognized and they are synthetically useful [2–5]. Carbocations (propargylic cations) have also been sta-

bilized over Mo–Mo, and W–W centers. Heterobimetallic examples are also known [6–9], but prior to our recent report [10], all such bimetallic  $\mu\text{-HC}_2\text{CR}'_2$  species had been anchored onto Co–Mo or Co–W centers. To our knowledge no other heterobimetallic combinations have yet been reported.

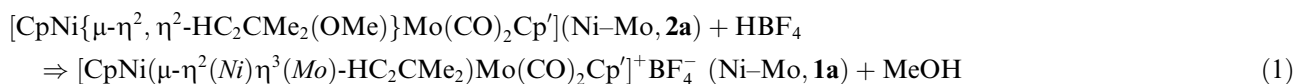
Our recent results described the synthesis and characterization of the di-metal stabilized carbocations  $[\text{CpNi}(\mu\text{-}\eta^2(\text{Ni}),\eta^3(\text{M})\text{-HC}_2\text{CMe}_2)\text{M}(\text{CO})_2\text{Cp}']^+ \text{BF}_4^-$  (Ni–M, **1a**, M = Mo; **1b**, M = W).<sup>1</sup> The bridging

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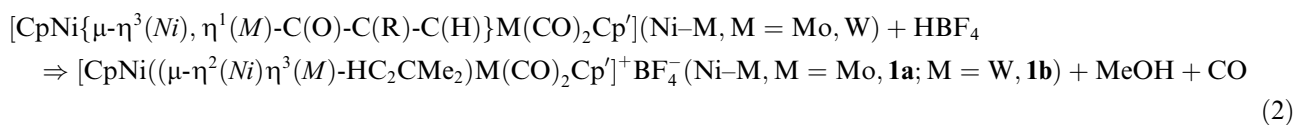
<sup>1</sup> Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; Cp' =  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ .

organic ligand can also be considered to be a cationic  $\mu$ -propargylic (allenyl) species. In these complexes, the carbocation is spanning a Ni–Mo or a Ni–W bond [10]. Complex **1a** was isolated by protonation of the  $\mu$ -alkyne complex **2a** [ $\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2\text{(OMe)}\}\text{Mo(CO)}_2\text{Cp}'$ ] (Ni–Mo) with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , followed by MeOH loss, as shown in Eq. (1)



Curiously, the corresponding Ni–W  $\mu$ -propargylic complex could not be obtained by direct protonation of the Ni–W alkyne complex [ $\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2\text{(OMe)}\}\text{W(CO)}_2\text{Cp}'$ ] (Ni–W), **2b**.

However it, and the Ni–Mo cation **1a**, could be isolated by treating the metallacycles [ $\text{CpNi}\{\mu\text{-}\eta^3(\text{Ni}), \eta^1(\text{M})\text{-C(O)-C(R)-C(H)}\}\text{M(CO)}_2\text{Cp}'$ ] (Ni–M, M = Mo, W) with tetrafluoroboric acid (Eq. (2))



Our previous study reported the synthesis and characterization of cations **1a** and **1b**, in which the  $\text{C-CMe}_2^+$  group is believed to be coordinated to, and stabilized by, the group 6 metal atom. We reported none of their chemistry. Here we report some of the preliminary chemistry of these carbocationic species towards nucleophiles, specifically with sodium methoxide, with potassium butoxide and with sodium borohydride. These reagents are sources, respectively, of  $\text{MeO}^-$ ,  $\text{BuO}^-$  and  $\text{H}^-$ . Minor impurities and co-generated reactants afforded additional, unexpected products.

## 2. Results and discussion

### 2.1. Reaction of methoxide ions with **1a**

Complex **1a**, formed in situ by the protonation of the methoxyalkyne species **2a**, reacted slowly with methoxide ions to generate a mixture of complexes. The reaction is unfortunately a race against time as **1a** spontaneously decomposes in solution at ambient temperatures. Three products (**2a**, **3a** and **4a**, Chart 1) were isolated from this reaction but the yields of all three were low owing to significant decomposition. The  $\mu$ -alkyne complex **2a** was readily characterized by comparison of its spectroscopic data with those of an authentic sample [10]. The addition of methoxide to **1a** to give the  $\mu$ -alkyne complex **2a** is thus, at least partly, reversible. The reaction is depicted in Scheme 1.

Complexes **3a** and **4a** are more intriguing. These two species could not be separated by chromatography, and were isolated as a together as orange-brown oil. They are believed to be the 1(c)-1,3- and 2(c)-1,3-cyclopentadiene isomers of formula [ $\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{Mo(CO)}_2\text{Cp}'$ ] (Ni–Mo) (see Chart 1). The MS for the mixture showed a parent ion that cor-

responded to a  $m/e$  ratio of (**1a** + 65) mass/charge units, i.e., the formal addition of a  $\text{C}_5\text{H}_5$  unit to the cation [ $\text{CpNi}\{\mu\text{-}\eta^2, \eta^3\text{-HC}_2\text{CMe}_2\}\text{Mo(CO)}_2\text{Cp}'$ ]<sup>+</sup> (Ni–Mo). The mixture gave solution IR spectra that were consistent with  $\mu$ -alkyne complexes (experimental section) and the  $^1\text{H}$  NMR spectra (Table 1) of the mixture could be rationalized with their proposed structures. Resonances for two  $\eta\text{-Cp}$  and two  $\eta\text{-Cp}'$  groups as well as over-

lapping multiplets that may be assigned to two sets of  $\text{C}_5\text{H}_5$  vinylic protons were observed. Isomers **3a** and **4a** are always found in a 3:2 ratio in solution at ambient temperature (even when formed in other reactions discussed later), and are likely in equilibrium, but this has not been definitely established. In addition, there is no NMR evidence of the symmetric 5(c)-1,3-cyclopentadiene isomer being formed.

While cyclopentadiene groups attached to metals or metalloids are well known to isomerize and interconvert via metallotropic shifts [11], the equivalent  $\text{C-C}_5\text{H}_5$  shifts seem less likely here, as a stronger  $\text{C}_5\text{H}_5\text{-C}$  bond is present. A similar mixture of cyclopentadienyl isomers is found in a series of indole substituted cyclopentadienyl compounds [12]. The isomers are found in a 1:1 ratio in this work, and as is seen in our work, there is no evidence of the symmetric 2,4-cyclopentadiene species.

It is not obvious how **3a** and **4a** form. Clearly the source of the cyclopentadienyl ligand is the nickel atom. Only cyclopentadienyl addition is seen and no addition of methylcyclopentadienyl groups (bound to the group 6 metal) is ever observed. It is possible that the decomposition of **1a** which is observed concurrently during the course of the reaction, liberates a  $\text{C}_5\text{H}_5^-$  ligand which then nucleophilically attacks complex **1a**. The apparent lability of a Cp ligand bound to nickel is not unprecedented. We have reported several instances of both Cp and Cp\* ligand transfer off a nickel atom [13–16]. Alternatively, the cationic complex **1a** might directly attack a CpNi moiety, present in either another molecule

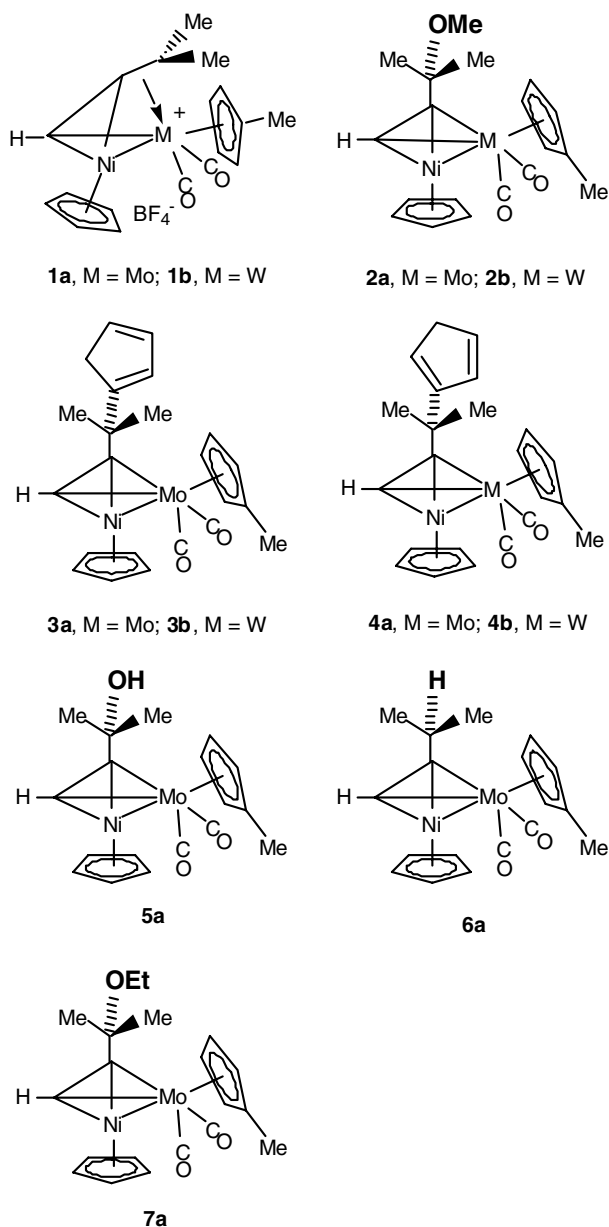


Chart 1.

of **1a** or in one of its decomposition products. Addition of electrophiles such as  $\text{H}^+$  or  $\text{Ph}_3\text{C}^+$  to a Cp group in nickelocene has long been known and would not be novel [17–19].

Following the suggestions of reviewers, we have attempted to prepare complexes **3a** and **4a** by letting a sample of **1a** decompose on its own without the presence of added nucleophiles. This did not lead to detectable quantities of complexes **3a** and **4a**. However, significant yields of **2** were formed when suspensions of the carbocation **1a** were reacted directly with thf solutions of  $\text{Na}^+\text{C}_5\text{H}_5^-$  indicating that **3a** and **4a** can be obtained directly by nucleophilic attack of cyclopentadienide anions.

## 2.2. Reaction of potassium butoxide with **1a**

The reaction of **1a** with potassium <sup>t</sup>butoxide also afforded a mixture of the two cyclopentadiene substituted alkyne complexes **3a** and **4a** (in the same equilibrium 3:2 ratio that was observed in the previously described reaction). Addition of <sup>t</sup>BuO<sup>-</sup> to the cationic complex did not take place. However, small quantities of another species, subsequently identified as the hydroxyalkyne complex  $[\text{CpNi}(\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2\text{OH})\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo, **5a**), were also obtained, as shown in Scheme 2.

The more sterically hindered OBu<sup>-</sup> anion is apparently too bulky to add on to complex **1a**. The isolation of **5a** was surprising, but may be attributed to contamination of the KO<sup>t</sup>Bu with KOH. Nucleophilic attack of OH<sup>-</sup> ions on **1a** would generate **5a**. It is noteworthy that neither <sup>t</sup>BuO<sup>-</sup> nor MeO<sup>-</sup> lead to isolable elimination products. Instead, products that result from direct nucleophilic addition are produced in each case.

## 2.3. Reaction of sodium borohydride with **1a**

Nucleophilic attack of **1a** by hydride ions could in principle lead to attack at the carbocationic center to afford the bimetallic  $\mu$ -isopropyl acetylene complex. Other possible products are complexes which contain 1,1-dimethylallene or its derivatives bound to the di-metal center. Such species have been observed in the reactions of Ni–Mo complexes with 1,1-dimethylallene [14,20].

When the reaction of **1a** with sodium borohydride was attempted in ethanol, the major product obtained was the heterobimetallic  $\mu$ -PrC<sub>2</sub>H species  $[\text{CpNi}(\mu\text{-}\eta^2, \eta^2\text{-Pr}^i\text{C}_2\text{H})\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo, **6a**). This species was fully characterized via MS, HRMS, <sup>1</sup>H NMR and IR spectroscopy. Two other complexes were also isolated in minor yields.

One of these species was the previously described  $\mu$ -hydroxyalkyne complex **5a**. The other complex was spectroscopically characterized as the ethoxyalkyne species  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OEt})\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo, **7a**). All these products result from the addition of various nucleophiles (OH<sup>-</sup>, H<sup>-</sup> or EtO<sup>-</sup>, respectively, for **5a**, **6a** and **7a**) to **1a**. Hydroxide and ethoxide ions likely form via attack of the sodium borohydride on the (wet) ethanol solvent used in this reaction. This reaction is summarized in Scheme 3.

## 2.4. Reactions with Ni–W complexes

The reaction of the alkyne complex **2b** with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  has never been shown to produce the cationic complex  $[\text{CpNi}(\mu\text{-}\eta^2, \eta^3\text{-HC}_2\text{CMe}_2)\text{W}(\text{CO})_2\text{Cp}']^+\text{BF}_4^-$  (Ni–W, **1b**). Nevertheless, the insoluble tan solid that formed in this reaction [10] did react slowly with

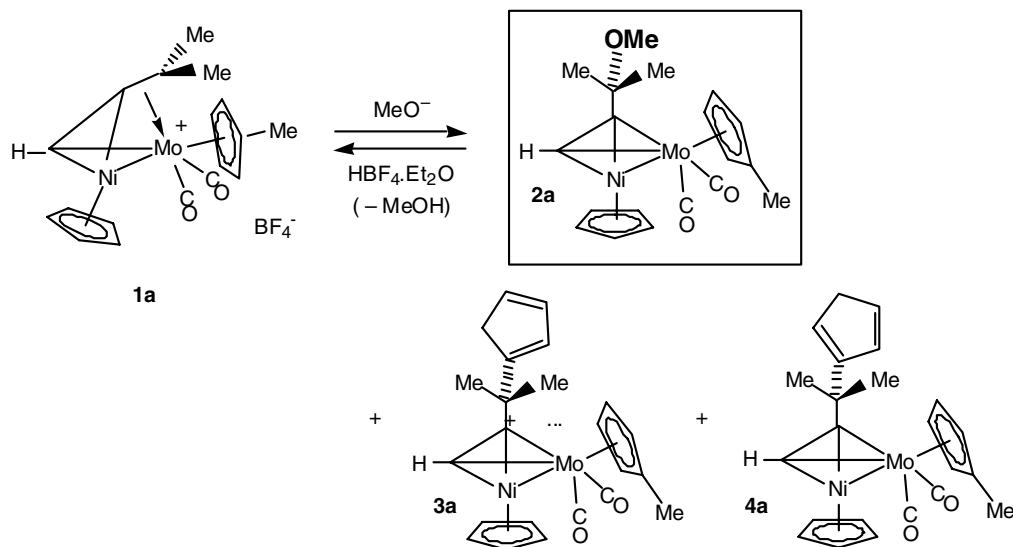
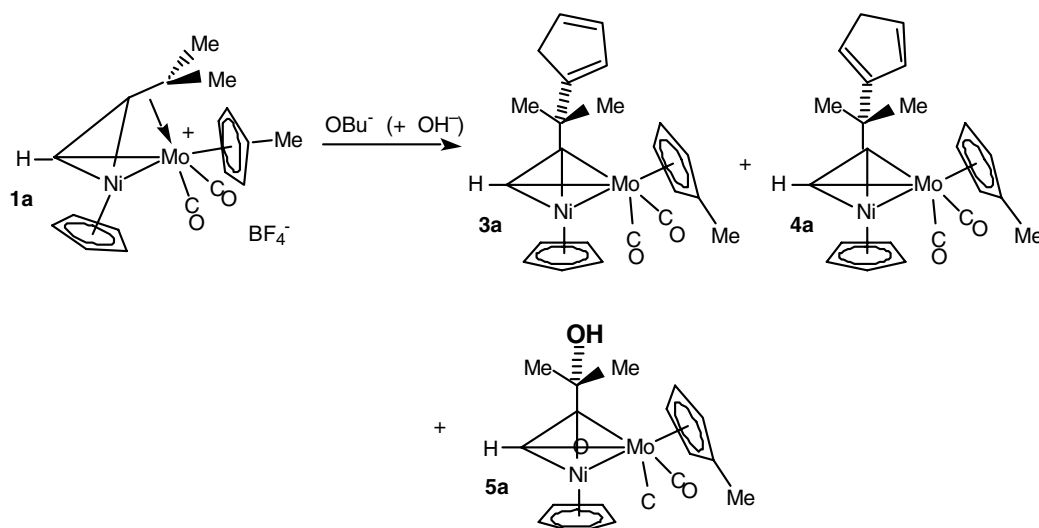
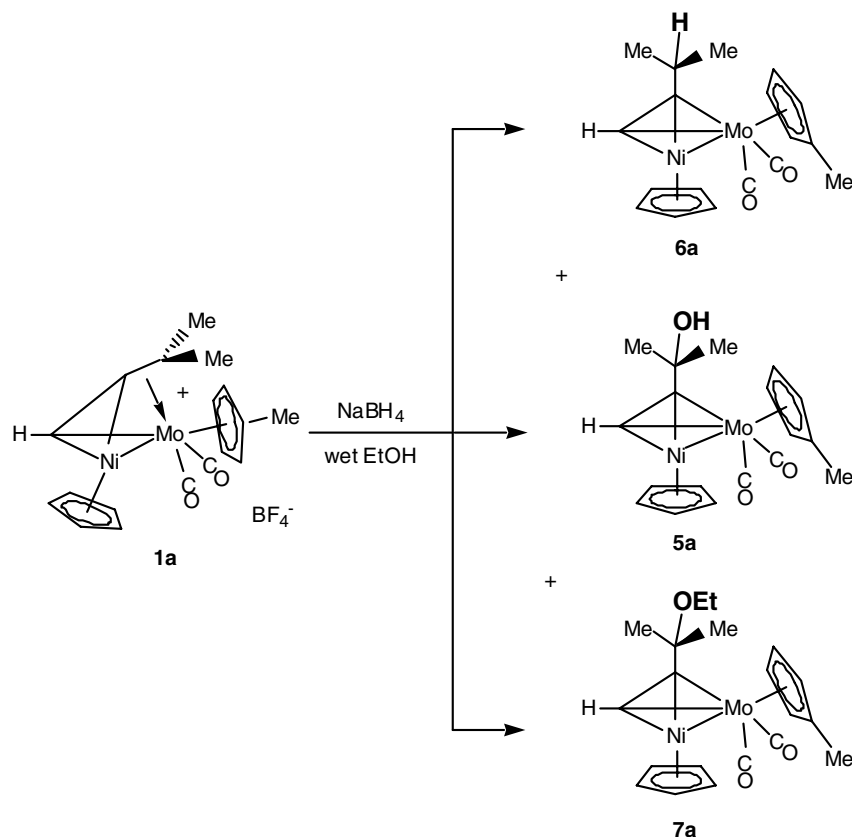
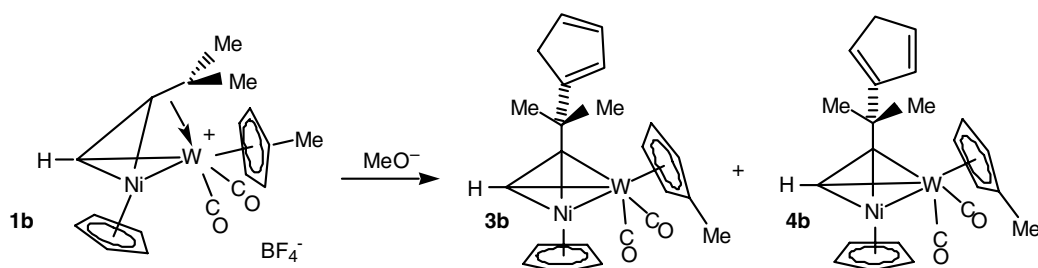
Scheme 1. The reaction of complex **1a** with methoxide ions (only **2a** regenerates **1a** when treated with methoxide).

Table 1

<sup>1</sup>H NMR data for the complexes [CpNi{μ-η<sup>2</sup>, η<sup>2</sup>-HC<sub>2</sub>CMe<sub>2</sub>(R)}M(CO)<sub>2</sub>Cp'] (Ni-M, M = Mo, W)<sup>a</sup>

Complex	C <sub>5</sub> H <sub>5</sub>	C <sub>5</sub> H <sub>4</sub> Me	CH	Me	Me	C <sub>5</sub> H <sub>4</sub> Me	R
<b>3a</b> (R = C <sub>5</sub> H <sub>5</sub> )	5.10	5.20–4.98	6.08	1.48	1.47	1.95	6.51(m), 6.32(m), 6.02(m), 2.90(m, CH <sub>2</sub> )
<b>3b</b> (R = C <sub>5</sub> H <sub>5</sub> )	5.14	5.30–4.98	5.85 <sup>b</sup>	1.48	1.46	2.08	6.50(m), 6.33(m), 6.02(m), 2.90(m, CH <sub>2</sub> )
<b>4a</b> (R = C <sub>5</sub> H <sub>5</sub> )	5.11	5.20–4.98	5.96	1.48	1.46	1.97	6.36(m), 6.22(m), 6.19(m), 2.98(m, CHH), 2.68(m, CHH) <sup>c</sup>
<b>4b</b> (R = C <sub>5</sub> H <sub>5</sub> )	5.14	5.30–4.98	5.75 <sup>b</sup>	1.48	1.46	2.11	6.38(m), 6.24(m), 6.18(m), 3.00(m, CHH), 2.72(m, CHH) <sup>c</sup>
<b>5a</b> (R = OH)	5.20	5.33, 5.30, 5.28, 5.27	5.93	1.45	1.30	2.02	1.85
<b>6a</b> (R = H)	5.15	5.24–5.18	5.91(d) <sup>d</sup>	1.24(d) <sup>c</sup>	1.07(d) <sup>c</sup>	1.99	2.75(m)
<b>7a</b> (R = OEt)	5.14	5.37, 5.35, 5.33, 5.23	5.85	1.50	1.27	2.04	3.77 (OCHH), d of q, J <sub>HH</sub> = 8.6, 7.0; 3.44 (OCHH), d of q, J <sub>HH</sub> = 8.6, 7.0; 1.15 (OCH <sub>2</sub> Me), t, J <sub>HH</sub> = 7.0

<sup>a</sup> Spectra recorded on a GE GN-300 spectrometer in chloroform-d; δ, ppm; J in Hz. All C<sub>5</sub>H<sub>4</sub>Me signals are (occasionally overlapping) ABCD type multiplets.<sup>b</sup> J<sub>WH</sub> = 2.1.<sup>c</sup> J<sub>HH(gem)</sub> = 23.<sup>d</sup> J<sub>HH</sub> = 0.8.<sup>e</sup> J<sub>HH</sub> = 6.7.Scheme 2. The reaction of **1a** with wet *t*-butoxide ions.

Scheme 3. The reaction of **1a** with ethanolic sodium borohydride.Scheme 4. The reaction of the Ni-W carbocationic complex **1b** with methoxide.

sodium methoxide to give the Ni-W equivalents of complexes **3a** and **4a** [ $\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{W}(\text{CO})_2\text{Cp}'$ ] (Ni-W) **3b** and **4b**. This mixture of isomers was isolated and characterized spectroscopically. Their  $^1\text{H}$  NMR data are very similar to those of the **3a/4a** mixture and indeed the **3b:4b** isomer ratio is also 3:2 at ambient temperatures. However, no  $\mu$ -alkyne species that would have resulted from methoxide addition was ever observed.

The metallacycle [ $\text{CpNi}\{\mu\text{-}\eta^3(\text{Ni}), \eta^1(\text{W})\text{-C}(\text{O})\text{-C}(\text{R})\text{-C}(\text{H})\}\text{W}(\text{CO})_2\text{Cp}'$ ] [Ni-W, R =  $\text{CMe}_2(\text{OMe})$ ] undergoes elimination of methanol and decarbonylation over a 2 h period when treated with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  to afford the Ni-W propargylic cation [ $\text{CpNi}\{\mu\text{-}\eta^2(\text{Ni}), \eta^3(\text{W})\text{-HC}_2\text{CMe}_2\}\text{W}(\text{CO})_2\text{Cp}'$ ] $^+$   $\text{BF}_4^-$  (Ni-W, **1b**) [10]. When

a thf solution of **1b** prepared this way was treated with NaOMe, the only recovered products were the cyclopentadiene-substituted  $\mu$ -alkyne complexes **3b** and **4b** (see Scheme 4). Unlike the corresponding reaction with cation **1a**, the Ni-W  $\mu$ -alkyne complex that would correspond to **2a** was not formed in this reaction. There is thus an interesting difference in behavior between the Ni-Mo and the Ni-W propargylic cations.

### 3. Conclusions

Cationic  $\mu\text{-HC}_2\text{CMe}_2^+$  ions, stabilized on a heterobimetallic Ni-Mo framework, undergo nucleophilic attack to generate  $\mu\text{-HC}_2\text{CMe}_2(\text{Nu})$  (Nu = nucleophile)

complexes with a variety of (sometimes unexpected) nucleophiles. The reaction is slow, and in most cases competes unfavorably with the spontaneous decomposition of the heterobimetallic cations in solution. When the nucleophile is methoxide ( $\text{MeO}^-$ ), the  $\mu\text{-HC}_2\text{CMe}_2(\text{OMe})$  complex  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OMe})\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo) was isolated, but the Ni–W propargyl ether complex was not obtained in corresponding Ni–W reaction with sodium methoxide. An unexpected side-product in reactions of both the Ni–Mo and Ni–W cations was the formation of two probably equilibrating isomers, in each case, of the complexes  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{M}(\text{CO})_2\text{Cp}']$  (Ni–M, M = Mo, W). Decomposition of the bimetallic cations may generate  $\text{Cp}^-$  ions which then nucleophilically attack the cation. Direct electrophilic attack by the cation on a  $\text{CpNi}$  group is also conceivable. The  $\mu\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)$  species were also obtained when the Ni–Mo propargylic cation was treated with  $\text{BuO}^-$ . Traces of KOH in the  $\text{KOBU}^t$  reagent led to the isolation of small quantities of the  $\mu\text{-HC}_2\text{CMe}_2\text{OH}$  complex. When the Ni–Mo propargylic cation was treated with  $\text{NaBH}_4$ , the principal product was the  $\mu\text{-Pr}^i\text{C}_2\text{H}$  complex. Smaller quantities of both  $\mu\text{-HC}_2\text{CMe}_2\text{OEt}$  and  $\mu\text{-HC}_2\text{CMe}_2\text{OH}$  Ni–Mo species, presumably formed by concurrent attack of  $\text{OH}^-$  and  $\text{EtO}^-$  ions generated in the reaction solvent, were also isolated.

Thus, we can conclude that the nickel-molybdenum stabilized carbocation **1a** undergoes nucleophilic addition at the carbocationic carbon atom with small or medium sized nucleophiles such as  $\text{H}^-$ ,  $\text{OH}^-$ ,  $\text{MeO}^-$  and even (effectively)  $\text{C}_5\text{H}_5^-$ . The larger  $\text{BuO}^-$  anion does not add to the complex. The Ni–W cations are more reluctant to undergo nucleophilic addition reactions.

The stability of these cationic  $\mu\text{-HC}_2\text{CMe}_2$  Ni–Mo and Ni–W complexes is greater than that of related Co–Co propargylic cations, but less than that of Co–Mo and Co–W allenyl cations of this type. As cation decomposition is a problem, further studies are underway that are aimed at stabilizing these heterobimetallic Ni–M and Ni–W propargylic cations by using  $\eta\text{-C}_5\text{Me}_5$  and not  $\eta\text{-C}_5\text{H}_5$  ligands ligated to the nickel. The reaction of such species with other nucleophiles will also be explored.

## 4. Experimental

### 4.1. (a) General

All manipulations were performed under an atmosphere of pre-purified nitrogen using standard Schlenkware techniques. Solvents were pre-dried and distilled from sodium benzophenone ketyl solutions (diethylether, thf, hexane). The syntheses of the  $\mu$ -alkyne complexes **2a** and **2b**, the heterobimetallic propargylic

cations **1a** and **1b**, and that of the ligand  $\text{HC}_2\text{CMe}_2(\text{OMe})$  have been described [10]. The reagents  $\text{NaOMe}$ ,  $\text{KOBU}^t$  and  $\text{NaBH}_4$  were purchased from Aldrich and used as received.

IR data were collected on an IBM IR-32 spectrometer in hexanes (unless otherwise noted).  $^1\text{H}$  NMR spectra were recorded on a GE GN-300 spectrometer in chloroform- $d_1$ , and referenced with respect to the residual protons in this solvent. Values are in ppm with coupling constants  $J$  in Hz. All  $\text{C}_5\text{H}_4\text{Me}$  signals are (occasionally overlapping) ABCD type multiplets. Mass spectra were obtained on a Finnegan Matt 8430 spectrometer using electron impact (EI) or chemical ionization (CI) techniques. The appropriate isotopic envelope patterns were observed for the Ni–Mo and Ni–W complexes. HRMS were obtained for all complexes. Microanalytical data for **5a** were obtained by M-H-W labs of Phoenix, AZ. These data were not recorded for the other complexes since they were isolated as oils.

### 4.2. (b) Reaction of **1a**, $[\text{CpNi}\{\mu\text{-}\eta^2(\text{Ni}), \eta^3(\text{Mo})\text{-HC}_2\text{CMe}_2\}\text{Mo}(\text{CO})_2\text{Cp}']^+ \text{BF}_4^-$ (Ni–Mo) with $\text{NaOMe}$ to afford the **3a/4a** isomeric mixture $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{Mo}(\text{CO})_2\text{Cp}']$ (Ni–Mo)

The cationic complex **1a** was generated and reacted immediately. A solution of **2a**,  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OMe})\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo) (100 mg, 0.22 mmol) in  $\text{Et}_2\text{O}$  (30 mL) was treated with a 1% solution of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ . After precipitation of **1a** was complete (ca. 8 mL  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  was used), the solid was rinsed with  $3 \times 5$  mL  $\text{Et}_2\text{O}$  and dried under vacuum. Sodium methoxide (30 mg, 0.56 mmol) was added under and the mixture was dissolved in thf (30 mL). The yellowish solution slowly reddened over a 16 h period. The thf was then removed in vacuo, the residue extracted with a hexane:diethylether mixture (5:1), filtered through a small alumina pad, and then subjected to silica-gel chromatography. The isomeric mixture of  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo) (**3a** and **4a**) eluted first, using a hexane:diethylether mixture (200:1), as an orange band which could be concentrated to a brown oil (10 mg, 9.3%). Complex **2a** followed as an orange brown band using a more polar hexane:diethylether mixture (1:5) and was subsequently recrystallized from this mixture. Yield: 8 mg (8%). IR [ $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ]: 1983(s), 1949(m), 1925(s), 1855(w). HRMS for the **3a:4a** mixture ( $^{60}\text{Ni}$ ,  $^{100}\text{Mo}$ ;  $m/e$ ): 488.017  $\text{C}_{23}\text{H}_{24}\text{MoNiO}_2$  requires 488.018.

### 4.3. (c)

A suspension of **1a** was prepared as described (Section 4.2) starting with **2a** (74 mg, mmol). The suspension of **1a** was dissolved in thf and allowed to stand at room temperature overnight. The solution darkened

progressively and insoluble solids precipitated. The solvent was then removed in vacuo and the residue extracted with toluene to give a light green-brown solution which was concentrated. Chromatography of this toluene solution on a silica-gel column with toluene eluted small quantities of a green eluate. This green product is volatile and paramagnetic, and is probably nickelocene.

#### 4.4. (d)

A suspension of **1a** was prepared as noted in Section 4.2, by starting with **2a** (124 mg, 0.28 mmol). Excess  $\text{NaC}_5\text{H}_5$  (0.85 mL of a 0.72 M solution in thf, 0.61 mmol) was then added to the solid **1a** and the solution stirred overnight. The thf was removed from the reaction mixture in vacuo, and the residue was dissolved in toluene and subjected to chromatography on a silica gel column. Elution with toluene afforded a brown band that was found to contain  $\approx 18$  mg of the **3a:4a** mixture.

#### 4.5. (e) Reaction of **1a** with wet $\text{KOBu}^t$ to afford the **3a/4a** mixture and complex **5a**, $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OH})\}\text{Mo}(\text{CO})_2\text{Cp}']$ (Ni–Mo)

$\text{KOBu}^t$  (44 mg, 0.39 mmol) was added to a sample of **1a** [prepared from **2a** (100 mg, 0.22 mmol) as described in Section 4.2] in thf (15 mL). The solution was stirred for 19 h, after which time the solvent was removed under vacuo and the residue extracted with hexanes and filtered through a Celite pad. Chromatography (using silica gel) led to the isolation of two bands: the **3a/4a** mixture eluted with a hexane:diethylether (200:1), followed by **5a**,  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OH})\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo). This complex eluted with a 1:1 mixture of hexane:diethylether. Yields: **3a/4a**, 15 mg (14%). **5a**, 17 mg (18%). Anal. Calc. for  $\text{C}_{18}\text{H}_{20}\text{MoNiO}_3$ , **5a**: C, 49.25; H, 4.59. Found: C, 49.32, H, 4.74. IR  $[\nu(\text{CO})]$ ,  $\text{cm}^{-1}$ : 1986(s), 1928(s), 1861(w);  $\nu(\text{CO})$  (in mineral oil,  $\text{cm}^{-1}$ ): 1980(s), 1926(s). HRMS for **5a**, ( $^{60}\text{Ni}$ ,  $^{100}\text{Mo}$ ;  $m/e$ ): 439.982.  $\text{C}_{18}\text{H}_{20}\text{MoNiO}_3$  requires 439.981.

#### 4.6. (f) Reaction of **1a** with $\text{NaBH}_4$ in wet ethanol to afford **5a**, complex **6a** $[\text{CpNi}(\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{Pr}^i)\text{Mo}(\text{CO})_2\text{Cp}']$ (Ni–Mo), and complex **7a**, $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OEt})\}\text{Mo}(\text{CO})_2\text{Cp}']$ (Ni–Mo)

$\text{NaBH}_4$  (18 mg, mmol) was added to a **1a**, [prepared from **2a** (103 mg, 0.23 mmol) as described in Section 4.2], in ethanol (20 mL). The cation was slightly soluble in this solvent and dissolved with effervescence as it reacted. After 1 h, the now reddish brown solution was pumped down to dryness in vacuum, and subjected to chromatography on a silica-gel column. The major product was  $\mu\text{-PrC}_2\text{H}$  complex **6a**  $[\text{CpNi}(\mu\text{-}\eta^2, \eta^2\text{-Pr}^i\text{C}_2\text{H})\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo), which eluted as a red-brown band with a hexane: diethylether mixture (200:1).

A slightly more polar solvent mixture of hexane: diethylether (50:1) eluted the brown ethoxyalkyne complex **7a**  $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{OEt})\}\text{Mo}(\text{CO})_2\text{Cp}']$  (Ni–Mo), while **5a** was eluted using a 10:1 ether:hexane mixture. All three complexes were isolated as oils. Yields: **5a**; 8 mg, 8%. **6a**; 50 mg, 52%. **7a**; 12 mg, 11%.

IR (**6a**),  $[\nu(\text{CO})]$ ,  $\text{cm}^{-1}$ : 1970(s), 1947(m), 1909(s), 1874(m), 1858(m). HRMS for **6a**, ( $^{60}\text{Ni}$ ,  $^{100}\text{Mo}$ ;  $m/e$ ): 423.985  $\text{C}_{18}\text{H}_{20}\text{MoNiO}_2$  requires 423.986.

IR (**7a**),  $[\nu(\text{CO})]$ ,  $\text{cm}^{-1}$ : 1983(s), 1961(m), 1925(s), 1853(m). HRMS for **7a**, ( $^{60}\text{Ni}$ ,  $^{100}\text{Mo}$ ;  $m/e$ ): 468.011.  $\text{C}_{20}\text{H}_{24}\text{MoNiO}_3$  requires 468.012.

#### 4.7. (g) Reaction of **2b** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ followed by $\text{NaOMe}$ to afford the **3b**, **4b** isomeric mixture $[\text{CpNi}\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{CMe}_2(\text{C}_5\text{H}_5)\}\text{W}(\text{CO})_2\text{Cp}']$ (Ni–W)

The reaction of the Ni–W complex mirrored that of the Ni–Mo (Section 4.2). Complex **2b** (100 mg, 0.18 mmol) was reacted with 1%  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  and then treated with  $\text{NaOMe}$  (22 mg, 0.41 mmol) in thf (20 mL) for 18 h. The mixture turned from yellow-brown to red-brown. After solvents were removed in vacuum, the residue was dissolved in a hexane–ether mixture and subjected to chromatography on a silica-gel. A single brown band eluted and yielded the **3b:4b** as an oily mixture when concentrated. Yield: 10 mg (9%). HRMS for the **3b:4b** mixture ( $^{60}\text{Ni}$ ,  $^{184}\text{W}$ ;  $m/e$ ): 574.062.  $\text{C}_{23}\text{H}_{24}\text{NiO}_2\text{W}$  requires 574.063.

#### 4.8. (h) Reaction of $[\text{CpNi}(\mu\text{-}\eta^2(\text{Ni}), \eta^3(\text{W})\text{-HC}_2\text{CMe}_2)\text{W}(\text{CO})_2\text{Cp}']^+ \text{BF}_4^-$ (Ni–Mo, **1b**) with $\text{NaOMe}$ to afford the **3b/4b** mixture

The cationic metallacyclic complex  $[\text{CpNi}\{\mu\text{-}\eta^3(\text{Ni}), \eta^1(\text{M})\text{-C}(\text{OH})\text{-C}(\text{Me}_2(\text{OMe})\text{-C}(\text{H}))\}\text{W}(\text{CO})_2\text{Cp}']^+ \text{BF}_4^-$  (Ni–W) (48 mg, 0.073 mmol) was stirred in thf (10 mL) and monitored by IR till the complex had completely transformed into **1b** (2.5 h).  $\text{NaOMe}$  (17 mg, 0.31 mmol) was then added and the solution stirred for 18 h. The solution was then passed through an alumina pad and concentrated to give a dark brown oil of the **3b:4b** mixture. Yield: 17 mg (40%).

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