Propargylic Cations Stabilized on Nickel−Molybdenum and Nickel−Tungsten Bonds

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The heterobimetallic complexes [(η-C_5H_5)(OC)Ni−M(CO)$_3$(η-C_5H_4Me)] (Ni−M, M = Mo, W) react with 3-methoxy-3-methyl-1-butyne [HC≡CMe$_2$(OMe)] to afford the enantiomeric μ-alkyne complexes [CpNi(μ-η^2,η^2-HC$_2$R)M(CO)$_2$Cp′] [Ni−M, M = Mo, W; R = CMe$_2$(OMe)], which have chiral dimetalatetrahedrane cores, and the metallacycles [(η-C_5H_5)Ni{μ-η^3(*Ni*),η^1-(*M*)−C(O)−C(R)−C(H)}M(CO)$_2$(η-C_5H_4Me)] [Ni−M, M = Mo, W; R = CMe$_2$(OMe)], formed via highly regioselective alkyne−CO coupling. All complexes react with HBF$_4$·Et$_2$O. The Ni−Mo μ-alkyne complex generated the propargylic cationic species [(η-C_5H_5)Ni(μ-HC$_2$CMe$_2$)-Mo(CO)$_2$(η-C_5H_4Me)]$^+$BF$_4^-$ (Ni−Mo) by protonation, followed by rapid methanol elimination. Attempted protonation of the Ni−W μ-alkyne complex led to intractable products. However cationic Ni−W (μ-HC$_2$CMe$_2$) complexes, and their Ni−Mo analogues, are accessible by direct protonation with HBF$_4$·Et$_2$O of the metallacycles [(η-C_5H_5)Ni{μ-η^3(*Ni*),η^1(*M*)-C(O)−C(R)−C(H)}M(CO)$_2$(η-C_5H_4Me)] [Ni−M, M = Mo, W; R = CMe$_2$(OMe)]. Proton migration and CO and MeOH elimination reactions rapidly follow to generate heterobimetallic μ-HC$_2$CMe$_2$ cationic complexes. An intermediate was isolated from the slower Ni−W reaction. Spectroscopic data suggest that the stabilized HC$_2$CMe$_2^+$ ions are π-coordinated to the group 6 metal atoms and not to the nickel. Differences in dynamic behavior are observed between the Ni−Mo and Ni−W cations: rotation about the C−CMe$_2$ bond occurs at ambient temperature for the Ni−Mo allenyl complex on the ^{1}H NMR time scale, but the Ni−W allenyl species is static.

Introduction

Carbocations have long been successfully stabilized on transition metal atoms and examples of such species are known for mono-[1−3] and polymetallic complexes (Figure 1).[4−11] It is now well established that the positive charge is delocalized on one or more metal centers and that this stabilizes the bound carbocations.[10,12]

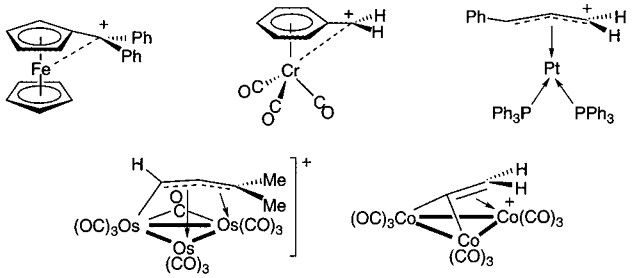

Figure 1. Some examples of metal-bound carbocations.

Bridging propargylic (allenyl) cations of the type μ-RC$_2$CR′R″ were investigated as ligands in the dicobalt cationic species [Co$_2$(CO)$_6$(μ-η^2,η^3-RC$_2$CR′R″)]$^+$ (Co−Co) shown (Figure 2) and have since been the focus of intense interest, both in their own right and in synthetic organic chemistry, since such species benefit from the β-effect of the cobalt atom; nucleophilic attack at the carbocation with a wide range of carbon nucleophiles leads to C−C bond formation in reactions that are often stereo- and diastereoselective.[13−17] Such cations are

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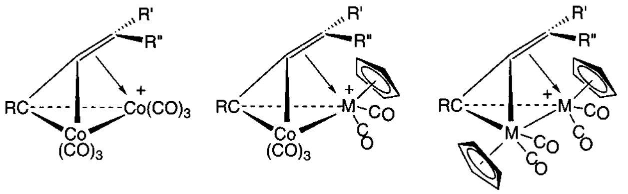

Figure 2. Some examples of bimetallic propargylic (allenyl) cations.

readily prepared from appropriate μ-alkyne complexes by protonation of a pendant hydroxy or alkoxy function on the alkyne, followed by water or alcohol loss, respectively (eq 1).[18]

$$[Co_2(CO)_6\{\mu\text{-}HC_2CR_2(OR')\}]\ (Co{-}Co) + H^+ \Rightarrow [Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC_2CR_2)^+] + R'OH\ (R = H,\ alkyl) \quad (1)$$

Dimolybdenum and ditungsten cations such as $[Mo_2(CO)_4Cp_2(\mu\text{-}\eta^2,\eta^3\text{-}HC_2CH_2)]^+$ (Mo−Mo) [throughout this paper, Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = Cp = η^5-C_5Me_5] and $[W_2(CO)_4Cp_2(\mu\text{-}\eta^2,\eta^3\text{-}HC_2CRR')]^+$ (W−W; R, R′ = H, Me, Figure 2) were prepared similarly or formed by hydride abstraction reactions from μ-allene species.[8,9,19−24] The R′ and/or R″ substituents may even be terpenoid or steroid groups.[17,25]

Heterobimetallic Co−Mo or Co−W examples are also known in which the propargylic cation spans the metal−metal bond, and the stereochemistry and reactivity of these mixed-metal cations have been studied. These heterobimetallic cations are chiral, owing to their tetrahedral μ-MM′C_2 cores (the groups attached to the carbon atoms are different), and for those species with μ-$RC_2CR'R''$ ligands (R′ ≠ R″), the metal-linked carbenium ion carbon leads to diastereomers that are stable to epimerization.

A number of Co−M (M = Mo, W) propargylic cations of general formula $[Co(CO)_3(\mu\text{-}\eta^2,\eta^3\text{-}RC_2R'R'')M(CO)_2Cp]^+$ (Co−M; M = Mo, W; Cp = Cp, Cp′) were structurally characterized.[10,12,26,27] They all show that the carbocation bends toward the group 6 metal atom (Figure 2). This indicates that the electron density at the α-carbon center is alleviated by it and that it is the $M(CO)_2Cp$ (M = Mo, W) group, and not the $Co(CO)_3$ unit, that better stabilizes these carbocations. Indeed, to our knowledge, no X-ray structures have been reported of $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}RC_2CR'R'')]^+$ (Co−Co) species. But, in addition to the heterobimetallic propargylic complexes referenced earlier, the μ-$CH_2C_2CH_2$ ligand in the dicationic complex $[Mo_2(CO)_4Cp_2(\mu\text{-}CH_2C_2CH_2)]^{2+}$ is sufficiently stabilized by the $CpMo(CO)_2$ groups that it has also been structurally characterized.[28] Many theoretical studies also indicate that such carbocations are stabilized by their interaction with the group 6 metal.[10,12,17,29,30]

We have reported on the chemistry of the alkyne complexes $[Cp^aNi(\mu\text{-}\eta^2,\eta^2\text{-}RC_2R')M(CO)_2Cp^b]$ (Ni−M, M = Cr, Mo, W; Cp^a = Cp, Cp*; Cp^b = Cp, Cp′; R, R′ = H, various alkyl or aryl, not all combinations are known). Complexes formed from asymmetric alkynes exist as enantiomeric mixtures, arising from their NiMCC′ tetrahedral cores. These species are accessible either from reactions of monometallic species with alkynes[31] or by direct combination of the alkyne with the appropriate heterobimetallic complex $[Cp^aNi(CO)_x{-}M(CO)_3Cp^b]$ (Ni−M; x = 0 or 1).[32−36] In view of the isolobal similarity of a CpNi unit with both $Co(CO)_3$ and $M(CO)_2Cp$ (M = Mo, W) groups, the general interest in propargylic cations and the new reactivity patterns sometimes observed with heterobimetallic propargylic species,[26] we decided to synthesize propargylic cations anchored to a Ni−Mo or Ni−W framework. Herein, we describe the preparation of percursor molecules to these complexes and the successful synthesis of cationic species from these precursors.

Results and Discussion

Synthesis of μ-Alkyne and Metallacyclic Complexes 2 and 3. The alkyne HC≡CCMe$_2$(OMe) reacted with the complexes $[CpNi(CO){-}M(CO)_3Cp']$ (Ni−M, **1a**, M = Mo; **1b**, M = W) to afford a mixture of μ-propargyl ether species **2a** (or **2b**) and metallacyclic complexes **3a** (or **3b**, respectively) as shown in Scheme 1. The reaction proceeds analogously to previously reported reactions:[31−36] products are μ-alkyne complexes **2** and smaller quantities of a *single* metallacycle species **3** in each case (the latter being formed via alkyne−CO ligand coupling). Their full characterization is described below.

Characterization and Spectroscopic Properies of the μ-Alkyne Complexes 2. The complexes $[CpNi(\mu\text{-}\eta^2,\eta^2\text{-}HC_2R)M(CO)_2Cp']$ [Ni−M, M = Mo, **2a**; M = W, **2b**; R = CMe$_2$(OMe)] have chiral dimetalatetrahedrane $NiMC_2$ cores,[32,33] and their ^1H, ^{13}C NMR and IR data (Tables 1−3) are consistent with the structures shown in Scheme 1. The molecules have no (C_1) symmetry, so an ABCD type pattern is observed for the C_5H_4Me

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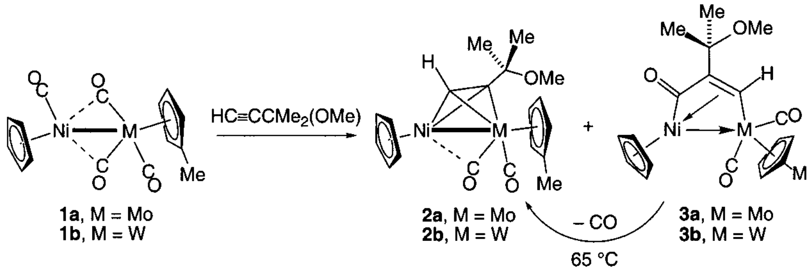
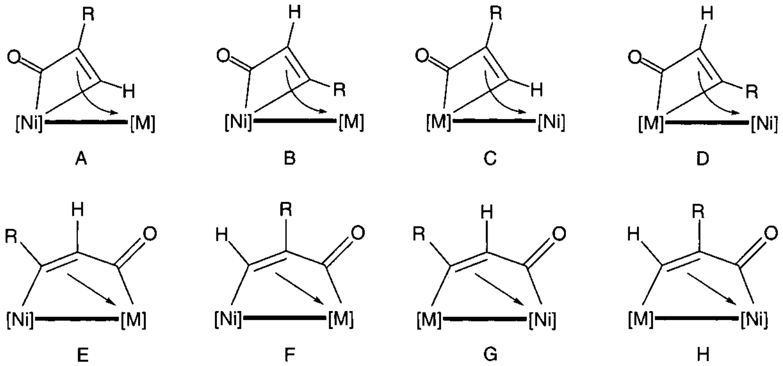
Scheme 1. Reaction of $HC{\equiv}CCMe_2(OMe)$ with the Heterobimetallic Complexes 1



Scheme 2. Possible Structures of Metallacycles 3



aromatic protons. Terminal−semibridging carbonyl ligand exchange is presumably taking place at ambient temperatures in these species, as reported both for Ni−M (M = Mo, W) μ-alkyne systems and in homobinuclear $Mo_2(\mu\text{-alkyne})$ species.[33,37]

MS for **2** showed the M^+ parent ions, with the correct isotopic envelopes for Ni−Mo or Ni−W species, but $[M - CO]^+$ ions did not dominate the spectrum.[33] Instead, the major fragmentation process was MeO^- loss to give $[M - MeO]^+$ ions. This indicated that the generation of cationic propargylic species was feasible and boded well for the envisaged protonation reactions.

Characterization and Spectroscopic Properies of Metallacyclic Complexes 3. IR and NMR spectra and analytical data for **3** (Tables 1−3) are consistent with these species being the metallacycles $[CpNi\{(HC_2R)(CO)\}M(CO)_2Cp']$ [Ni−M, M = Mo, **3a**; M = W, **3b**; R = $CMe_2(OMe)$]. These products are derived from highly regiospecific alkyne−CO coupling, as in each case a *single* metallacycle was produced. Various isomer possibilities exist (Scheme 2); the question is, what is the correct geometry for complexes **3**?

We were unable to grow satisfactory crystals of **3** for an X-ray structural determination. Nevertheless, their similar spectroscopic data indicated that complexes **3a** and **3b** have the same geometry. We believe that their structure is as shown in Scheme 1 (**H** in Scheme 2), as the number of viable candidates may be pared down using the following arguements:

(1) Tungsten-183 coupling is observed *only* for the italicized $\mathit{HC}{\equiv}CCMe_2(OMe)$ proton and carbon atoms, respectively, in the ^1H *and* ^{13}C NMR spectra of **3b**. This suggests that **3b** (and hence **3a**) is probably isomer **C** or **H** (Scheme 2).

(2) NMR data of **3** resemble those of the previously characterized metallacycle complexes $[Cp^*Ni\{\mu\text{-}\eta^3(Ni),\eta^1\text{-}(M)\text{-}C(O){-}C(Ph){-}C(H)\}M(CO)_2Cp']$ (Ni−M, M = Mo, W), which adopt structure **H**. In particular, the $\mathit{HC}{\equiv}CCMe_2(OMe)$ ^1H NMR chemical shifts fall in the $\delta = 7.0 \pm 0.5$ ppm region (**3a**, $\delta = 7.40$ ppm; **3b**, $\delta = 7.14$ ppm), very different from the value of 3.27 found for $[Cp^*Ni\{\mu\text{-}\eta^3(Ni),\eta^1(W)\text{-}C(O){-}C(H){-}C(Ph)\}W(CO)_2Cp']$ (Ni−W), which adopts structure **B**.[36]

These observations suggest that the structures of **3** are based on geometry **H** in Scheme 2 and that these species are $[CpNi\{\mu\text{-}\eta^3(Ni)\eta^1(M)\text{-}C(O){-}C(R){-}C(H)\}M(CO)_2Cp']$ [Ni−M, **3a**, M = Mo; **3b**, M = W. R = $CMe_2(OMe)$], in which both metals form part of the ring. These assignments are consistent with previous results: metallacycles devived from alkyne−CO coupling tend to adopt structures **A** and/or **B** when the alkyne is disubstituted,[32,33,35] but geometry **H** is preferred with terminal alkynes.[36]

When **3** are refluxed in hexane, decarbonylation occurs and the corresponding μ-alkyne complexes **2** are generated (Scheme 1). Facile decarbonylation is also observed in the MS of these compounds: both electron impact and high-resolution MS do not show the parent ions. Instead the peak with the highest *m*/*e* ratio corresponds to the $(M - CO)^+$ signal. However, chemical ionization MS reveal $(M + H)^+$ ions, formed by H^+ transfer to the parent species, for both **3a** and **3b**.

Some puzzling features in the NMR spectra of **3b** deserve comment. In contrast to the NMR data observed for **3a**, the aromatic Cp′ resonances and a $HC_2CMe_2(OMe)$ methyl resonance of **3b** are broad at ambient temperature; ^{13}C NMR signals for the C_5H_4Me atoms are also broad. The proton signals sharpen when the spectrum is recorded at or above 40 °C, though decarbonylation to generate **2b** (Scheme 1) commences at 50 °C. Further broadening (including now the $C_5H_4\mathit{Me}$ signal) was observed at −6 °C, but all resonances had

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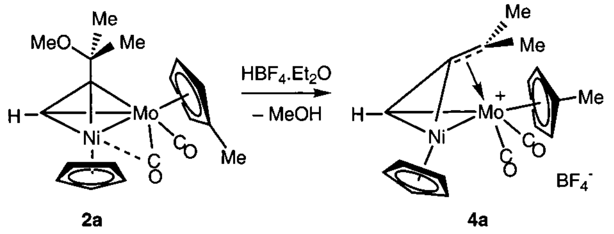
Scheme 3. Protonation of the μ-Alkyne Complex 2a to Give the μ-Propagylic Cation 4a



sharpened at −30 °C and at −55 °C, the C_5H_4Me protons appeared as well-resolved ABCD multiplets. The *Me* proton signal was now also sharp.

One of the alkyne methyl groups may be interferring with Cp′ ligand rotation about the W−Cp′ centroid bond at ambient or low temperature. Thermal energy at or above 40 °C is sufficient to enable this rotation, and time-averaged (but still ABCD type) aromatic signal resonances are now observed. It is not clear why only **3b** exhibits this behavior, since **3a** and **3b** are believed to be isostructural and are otherwise very similar spectroscopically.

Reaction of the μ-Alkyne Complex 2a and 2b with HBF_4. Formation of the Allenyl Cation 4a. As the MS data indicated that methoxide loss from the alkyne complexes was viable, protonation of complexes **2** was attempted. Surprisingly, the reaction did not proceed equally well with the two complexes. In addition, experimental conditions were critical to avoid the formation of intractable oils. An orange-red solid, subsequently identified as the heterobimetallic propargylic cationic complex $[CpNi(\mu\text{-}HC_2CMe_2)Mo(CO)_2Cp']^+BF_4^-$ (Ni−Mo, **4a**) was successfully precipitated when a dilute ethereal solution of $HBF_4\cdot Et_2O$ was slowly added to an ether solution of **2a** (Scheme 3). Surprisingly, the nickel−tungsten μ-allenyl complex could not be made this way. Repeated attempts at protonation at various temperatures, with different concentrations of acid and/or **2b**, gave either intractable oils or else insoluble tan powders which displayed no meaningful ^{1}H resonances. The geometry of **4a** is believed to be as shown in Scheme 3, with the carbocation interacting with the group 6 metal, for reasons that will be discussed shortly.

The cationic product **4a** is highly air-sensitive and not very stable in solution; a ^{13}C NMR spectrum could not be obtained owing to the early appearance of paramagnetic decomposition products. X-ray quality crystals could not be obtained either. Nevertheless, solid **4a** is stable at −20 °C under nitrogen, and the complex is soluble in polar solvents; unlike the dicobalt cations reported by Nicholas,[5] it is not rapidly attacked by acetone.

IR and ^{1}H NMR data were used to characterize **4a**. IR ν(CO) stretching frequencies of this cation (Table 3) are shifted to higher values compared to **2a**. Both Cp and Cp′ (but not MeO) signals were evident in the ^{1}H NMR spectrum **4a** (Table 1), which suggested that the heterobimetallic framework remained intact here. Resonances assignable to the allenyl ligand HC_2CMe_2 protons in **4a** are broad and equivalent at room temperature, indicating that a fluxional process, likely to be rotation about the $C{-}CMe_2$ bond, equivalences the two signals on the ^{1}H NMR time scale. The process is arrested at −30 °C, when two distinct Me signals are observed, at 2.35 and 2.05 ppm. At the coalescence point of 255 K in acetone-d_6, $\Delta G^{\ddagger}$ was calculated to be 11.6 kcal/mol.[38] Rotation about C−C bonds in metal-bound $C{-}CR_2$ (R = H and/or alkyl, ferrocenyl, cymantryl, etc.) allenyl cations species is recognized in both homo- and heterobimetallic complexes; the value found here is in the range commonly found for tertiary cations ligated to a $CpMo(CO)_2$ ligand.[10,29]

Another dynamic process often observed in homobimetallic propargylic cations is antarafacial migration of the $C{-}CMe_2$ group (migration from one metal to another). While antarafacial processes are often of lower energy than C−C bond rotation in Mo_2 complexes,[9,39] the two processes have similar energy barriers in tertiary carbocations.[10,40] We believe that antarafacial rotation on the dimetal framework is unlikely to be a low-energy process here, as the two metals are different and the two "resting states" would not be degenerate. Furthermore, in heterobimetallic Co−Mo propargylic species with secondary carbocations, C−C bond rotation is believed to be the only fluxional process that isomerizes the carbenium ion substituents.[27] Whether this process is active or not here is a moot point, since the two Me signals in **4a** would not become equivalent by this fluxional process alone.

Protonation of Metallacycle Complexes 3 with HBF_4: Formation of Propargylic and Other Cations and Their Characterization. There are at least two protonation sites in complexes **3**, $[CpNi\{\mu\text{-}\eta^3(Ni)\eta^1\text{-}(M)\text{-}C(O){-}C(R){-}C(H)\}M(CO)_2Cp']$ [Ni−M, M = Mo, W, R = $CMe_2(OMe)$]: the oxygen atoms of the methoxide group or of the metallacyclic carbonyl ligand. When R = Ph or Me, strong acids protonate the metallacyclic carbonyl oxygen and a rearrangement reaction also occurs to yield compounds with four-membered metallacycle rings of types C and D (Scheme 2), as the sole products.[35,36] The methoxide oxygen atom in complexes **3**, not hitherto available, is now a possible alternative protonation site.

Protonation of **3a** with $HBF_4\cdot Et_2O$ led to both methoxide loss (as methanol) *and* to effective decarbonylation of the metallacycle to generate the propargylic (allenyl) species **4a** (Scheme 4). Both processes are rapid and probably simultaneous, as NMR studies of the product reveal no MeO groups or further release of free MeOH. IR spectra of the freshly precipitated solid are identical to those of **4a**.

The reaction of **3b** with $HBF_4\cdot Et_2O$ also eventually afforded the μ-propargyl cation **4b** (which is not accessible directly via protonation of **2b**), but here an intermediate was also characterized. NMR spectral data (Table 1) of the red-brown powder (**5b**) that precipitated following acid addition clearly indicated that protonation had taken place at the metallacyclic oxygen atom. A methoxide resonance was observed in the ^{1}H NMR spectrum of **5b**, and a new signal at δ 9.83 ppm could be assigned to a O*H* group. The metallacyclic ν(C=O)

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Table 1. ^{1}H NMR Data (δ, ppm; J in Hz)[a]

complex	Cp	C_5H_4Me	CH	C_5H_4Me	OMe	Me
2a	5.15	5.38, 5.32,[b] 5.24	5.86	2.04	3.30	1.48, 1.25
2b	5.18	5.43, 5.40, 5.38, 5.28	5.70[c]	2.19	3.28	1.50, 1.24
3a	5.24	5.32, 5.28, 5.23[b]	7.40	2.09	3.25	1.23, 0.70
3b	5.28	5.38,[d] 5.28,[d] 5.22[b,d]	7.14[e]	2.24	3.22	1.21, 0.84[d]
4a[f]	5.64	5.96, 5.81,[b] 5.77	7.04[d]	2.26		2.20[b,d]
4b[f]	5.88	6.01, 5.99, 5.95, 5.79	7.60(m)[g]	2.17		2.18(d),[g] 2.07(d)[g]
5b[h]	5.67	5.41, 5.36, 5.31[b]	6.49[i]	2.15	3.25	1.46, 1.37

[a] Unless otherwise stated, all spectra were collected on a G.E. GN-300 spectrometer in $CDCl_3$; resonances integrate correctly for the protons shown and are singlets unless otherwise stated. All C_5H_4Me resonances are ABCD type multiplets. [b] Resonances coincident. [c] $J_{WH} = 4.0$. [d] Broad. [e] $J_{WH} = 2.9$. [f] Acetone-d_6. [g] $J_{HH} \approx 2.3$. [h] O*H* resonance observed at $\delta = 9.83$. [i] $J_{WH} = 4.5$.

Table 2. $^{13}C\{^1H\}$ NMR Data (δ, ppm; J in Hz)[a]

complex	CO	*C*R[b]	*C*H	Cp	C_5H_4Me	*C*Me₂OMe	OMe	Me	Cp′(Me)
2a	231.2[c]	101.2	84.8	91.7	109.2,[d] 91.0, 90.2, 89.5, 89.4	78.5	50.4	31.2, 29.6	14.3
2b	218.4, 218.2	94.4	78.5	91.1	106.6,[d] 88.9, 87.9, 87.5[c]	−	50.5	31.4, 29.8	14.2
3a	232.3, 231.0, 167.7 (C=O)	−	127.7	94.0	109.6,[d] 93.3, 92.5, 92.1, 91.4	75.1	50.1	24.4[c]	14.2
3b[e]	220.0, 219.4, −	90.7	115.3[f]	93.4	107.3,[d] 91.0, 90.3, 90.0, 89.9	75.6	50.0	24.4[c]	14.1

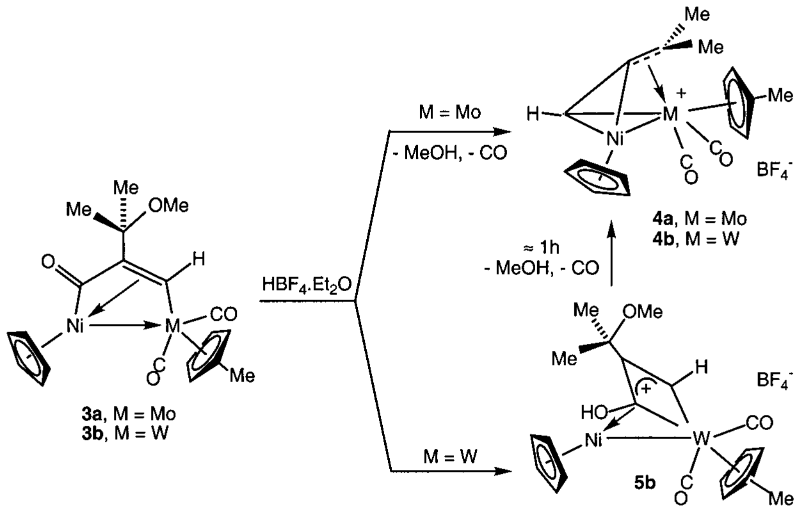
[a] Spectra were collected on a G.E. GN-300 spectrometer in $CDCl_3$; unobserved resonances are denoted by a dash (−). [b] R = $CMe_2(OMe)$. [c] Resonances coincident. [d] Ipso carbon. [e] All aromatic C_5H_4Me and $CMe_2(OMe)$ ligand resonances are broad. [f] $J_{WC} = 4.0$ Hz.

Table 3. IR ν(CO) Data for the Complexes[a]

complex	hexane solution	Nujol mull
2a	1984(s), 1964(w), 1926(s), 1853(w)	1979(s), 1923(s)
2b	1982(s), 1961(w), 1919(s), 1842(w)	1978(s), 1919(s)
3a	1999(s), 1968(w), 1948(s), 1684(w, C=O)	1940(s), 1844(s), 1684(m, C=O)
3b	1997(s), 1962(w), 1941(m), 1929(w), 1681(w, C=O)	1994(s), 1934(s), 1840(m), 1674(m, C=O)
4a[b]	2049(s), 2019(s), 1966(m)	2005(s), 1921(w), 1811(m)
4b[b]	2047(m), 2013(s), 1989(w), 1966(vw)	1989(s), 1810(m)
5b[b]	2034(m), 1979(s)	2037(m), 1977(s)

[a] Data (in cm^{-1}) were collected on an IBM-IR 32 spectrometer. [b] CH_2Cl_2 solution, KBr pellet.

Scheme 4. Reactions of Metallacycles 3 with $HBF_4 \cdot Et_2O$



stretch was now absent in the IR spectrum (Table 3), and only two ν(CO) bands were visible. The $^{183}W-^1H$ coupling to the alkyne *H*C proton and the similarity of spectral data between **5b** and previously reported cationic metallacycles[36] suggest that **5b** is the cationic tungstenacycle $[CpNi(\mu\text{-}\eta^3(Ni),\eta^2(W)\text{-}\overline{C(OH)-C(R)-C(H)\}\text{-}W}(CO)_2Cp']^+BF_4^-$ [Ni−W, R = $Me_2(OMe)$] (structure C, Scheme 2), in which the organic ligand is best regarded as being η^3-allylically bound to the nickel atom as depicted in Scheme 4.

5b is transformed quantitatively into a new species (**4b**) in solution. After 30 min in chloroform-d_1, resonances of **4b** were evident, and after ca. 1 h, the reaction was close to completion. Methanol signals were now also observed. The transformation of **5b** to **4b** is much faster in oxygenated solvents such as acetone or thf, and indeed, when **5b** is dissolved in acetone-d_6, the ^{1}H NMR spectrum only showed resonances of **4b**.

The spectroscopic data indicate that **4b** is the cationic propargylic complex $[CpNi(\mu\text{-}\eta^2(Ni),\eta^3(W)\text{-}HC_2CMe_2)\text{-}W(CO)_2Cp']^+BF_4^-$ (Ni−W), which, as stated earlier, is not accessible in pure form by direct protonation of the alkyne complex **2b**. Proton migration from the OH group to the OMe group in **5b**, followed by loss of both MeO^- (as MeOH) and CO, affords **4b**. Oxygen donor solvents, such as tetrahydrofuran or acetone, facilitate the proton migration and the subsequent ligand eliminations, perhaps by acting as proton carriers. The reactions of complexes **3** with HBF_4 are summarized in Scheme 4.

There are significant differences between the ^1H NMR spectra of **4a** and **4b**. Complex **4b** is not fluxional and two C−C*Me*$_2$ resonances are observed at ambient temperatures. Each appears as a sharp doublet, due to coupling to the alkyne C*H* proton. Unlike **4a**, C−CMe$_2$ bond rotation is clearly arrested in **4b** on the ^1H NMR time scale at this temperature.

These observations are consistent with rotational barriers previously observed in Co−Mo and Co−W cationic allenyl complexes, where higher barriers are seen in the Co−W systems.[29] In general, third-row metals form stronger bonds than second-row metals, and this may partly explain the nonfluxional behavior of **4b**. Proposed mechanisms for rotation about $C-CR_2^+$ bonds involve breakage of the π-interaction to the metal, processes that would be higher in energy for tungsten than for molybdenum, given the normal trend in bond strengths. A stronger metallacyclic M−C(O) bond may also explain why CO elimination and proton transfer in complex **5b** to give **4b** is slower and not spontaneous.

Important structural information can be gleaned from the different rotational energy barriers about the C−CMe$_2$ bond observed in **4a** and **4b**. The large difference between the two complexes strongly suggests that the carbenium ion is ligated to the group 6 metals, as shown in Scheme 4, and not to the nickel atoms. If the C−CMe$_2$ were η^3-coordinated to the nickel atom, changing the group 6 metal atom would not be expected to have such a large effect on the C−CMe$_2$ rotational barrier.

Conclusion

The μ-alkyne complexes **2**, [CpNi(μ-η^2,η^2-HC$_2$R)M(CO)$_2$-Cp′] (Ni−M, M = Mo, W; R = CMe$_2$OMe), were prepared by direct reactions of HC≡CR with **1**. The metallacycles **3**, [CpNi{μ-η^3(*Ni*),η^1(*M*)-C(O)−C(R)−C(H)}M(CO)$_2$Cp′] (Ni−M; M = Mo, W; R = CMe$_2$OMe), also formed as side-products in these reactions. Structures of **2** and **3** were established spectroscopically and by analogy with related μ-alkyne and metallacycle species.[35,36]

All four species react with fluoroboric acid, but there are some surprising reactivity differences between the Ni−Mo and Ni−W complexes. The fluxional Ni−Mo allenyl complex **4a** is formed either by protonation of the alkyne complex **2a** (via subsequent rapid MeOH loss) or via protonation of metallacycle **3a** (via rapid MeOH *and* apparently concurrent CO loss). In contrast, the reaction of the Ni−W alkyne complex **2b** with HBF_4 led to intractable products. Complex **4b**, the Ni−W propargylic analogue of **4a**, could be synthesized by reacting **3a** with HBF_4. Intermediate **5b** was also isolated, in which the metallacyclic carbonyl oxygen had been protonated. A spontaneous proton migration reaction, followed by methanol and carbon monoxide loss, then afforded **4b**, which is static on the ^1H NMR time scale.

Our attempts to obtain crystals of the cationic species **4** have failed miserably, owing perhaps to the relative instability of these complexes in solution. Nevertheless, the spectroscopic evidence presented suggests that these propargylic (or allenyl) HC$_2$CMe$_2$ cations are η^3-ligated to the molybdenum (**4a**) or tungsten (**4b**) atoms and not η^3-coordinated to the nickel atom. Studies underway to explore the reactivity of **4** with nucleophiles are promising, but are hampered by the instability of complexes **4**. Our current strategy is to synthesize and stabilize more stable Ni−Mo and Ni−W heterobimetallic cations by (1) using η-C$_5$Me$_5$ instead of η-C$_5$H$_5$ ligands on the nickel atom and (2) using substituents other than R = Me, such as Ph, on the HC$_2$CR$_2$ groups.

Experimental Section

All manipulations were performed under an atmosphere of prepurified nitrogen using standard Schlenk-ware techniques. Solvents were predried and distilled from sodium benzophenone ketyl solutions (diethyl ether, thf, pentane, hexane) or from CaH$_2$ (dichloromethane). Complexes **1** were prepared as described.[33,41] The reagents NaH, HC≡CCMe$_2$OH, MeI, and HBF_4 were purchased from Aldrich. 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. Microanalytical data were obtained by M-H-W Labs of Phoenix, AZ. (Meaningful microanalytical data could not be obtained for the cations due to their inherent instability.) Melting or decomposition points of complexes **2** and **3** were recorded in vacuo on a Büchi melting point apparatus and are uncorrected.

(a) Synthesis of 3-Methoxy-3-methyl-1-butyne, HC≡CCMe$_2$(OMe). This ligand was prepared by alkylation of the propargyl alcohol HC≡CCMe$_2$(OH) in a slightly modified version of the literature method,[42] as described here. A suspension of NaH (4.8 g of a 60% mineral oil solution, 120 mmol) was placed anaerobically in a dried 250 mL two-necked round-bottomed flask, equipped with a magnetic stirrer, a nitrogen inlet, and a pressure-equalized dropping funnel. After rinsing the solid with 3 × 5 mL of hexane to remove the oil, thf (90 mL) was added via syringe, followed by slow dropwise addition of HC≡CCMe$_2$(OH) (11.5 mL, 10.0 g, 119 mmol). After hydrogen evolution had ceased, MeI (20.0 g, 8.8 mL, 141 mmol) was added slowly and the mixture warmed gently. After 30 min, NaI precipitated from the solution. The reaction was then quenched with H$_2$O (30 mL), and pentane (30 mL) was added. After thf was extracted from the mixture by repeated water washings in a separation funnel, the residual pentane solution was dried over anhydrous MgSO$_4$, filtered, and distilled. Following the pentane fore-run, the HC≡CCMe$_2$(OMe) was collected at 73−79 °C in 23% yield (2.72 g). The alkyne was thf free and pure (by ^1H NMR spectroscopy).

(b) Reactions of HC≡CR [R = CMe$_2$(OMe)] with [CpNi(CO)−Mo(CO)$_3$Cp′] (Ni−M, 1a, M = Mo; 1b, M = W): (i) Synthesis of [CpNi{μ-η^2,η^2-HC$_2$R)}Mo(CO)$_2$Cp′] (Ni−Mo, 2a) and [Cp*Ni{μ-η^3(*Ni*),η^1(*Mo*)-C(O)−C(R)−C(H)}Mo(CO)$_2$Cp′] (Ni−Mo, 3a). Complex **1a** (611 mg, 1.50 mmol) was placed in a dried, degassed Schlenk tube, and a 1:1 mixture of hexane and toluene (30 mL solution) was added, followed by HC≡CR (0.14 mL, ≈1.5 mmol). The solution was frozen in liquid nitrogen, evacuated, warmed to room temperature, and stirred for 16 h, during which time the green solution turned orange-brown. Solvents were removed in vacuo, and the residue was subjected to chromatography using a silica gel column. The first band (red-brown) eluted with a 10:1 hexane/Et$_2$O mixture and was subsequently crystallized directly to yield **2a** (172 mg, 26%); the second major band (orange-brown) was collected using pure Et$_2$O and afforded **3a** (107 mg, 15%)

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on concentration and crystallization. **3a** quantitatively decarbonylates to **2a** when refluxed in hexane for ~5 h.

Data for 2a. Anal. Calcd for $C_{19}H_{22}MoNiO_3$: C, 50.38; H, 4.90. Found: C, 50.20; H, 5.00. EIMS (*m*/*e*): 454 (M^+), 426 (M − CO)$^+$, and 423 (M − MeO), overlapping envelopes, 367 (M − MeO − 2 CO)$^+$. HRMS (^{60}Ni, ^{100}Mo; *m*/*e*): 453.997. $C_{19}H_{22}MoNiO_3$ requires 453.998. Mp: 124 °C.

Data for 3a. Anal. Calcd for $C_{20}H_{22}MoNiO_4$: C, 50.09; H, 4.61. Found: C, 49.94; H, 4.87. EIMS (*m*/*e*): 454 (M − CO)$^+$, 426 (M − 2CO)$^+$, and 423 (M − CO − MeO)$^+$, overlapping envelopes. CIMS (*m*/*e*): 471 (MH^+). Mp: 74 °C (dec).

(ii) Synthesis of [CpNi{*μ*-*η*^{2},*η*^{2}-HC$_2$R)}W(CO)$_2$Cp′] (Ni−W, 2b) and [CpNi{*μ*-*η*^{3}(*Ni*),*η*^{1}(*W*)-C(O)−C(R)−C(H)}W-(CO)$_2$Cp′] (Ni−W, 3b). Complexes **2b** and **3b** are formed in a fashion similar to their Ni−Mo analogues, but **3b** is less soluble than **3a** and is also immobile on a chromatography column. Hence after reaction, the mixture of **2b** and **3b** was chilled to −20 °C overnight. The solution, which contained mainly **2b**, was removed by syringe and the complex was purified by chromatography, using a 10:1 hexane/Et_2O mixture as eluate, and crystallized to afford pure **2b** (151 mg, 27%). The residual solid was dissolved in Et_2O, filtered through a Celite pad, concentrated, and recrystallized from this solvent to yield **3b** (36 mg, 7%).

Data for 2b. Anal. Calcd for $C_{19}H_{22}NiO_3W$: C, 42.19; H, 4.10. Found: C, 42.20; H, 4.33. EIMS (*m*/*e*): 540 (M^+), 512 (M − CO)$^+$, and 509 (M − MeO), overlapping envelopes, 453 (M − MeO − 2CO)$^+$. HRMS (^{60}Ni, ^{184}W; *m*/*e*): 540.041. $C_{19}H_{22}NiOW_3$ requires 540.042. Mp: 146 °C (with dec).

Data for 3b. Anal. Calcd for $C_{20}H_{22}NiO_4W$: C, 42.22; H, 3.90. Found: C, 42.43; H. 4.10. EIMS (*m*/*e*): 540 (M − CO)$^+$, 512 (M − 2CO)$^+$, and 509 (M − CO − MeO)$^+$, overlapping envelopes. CIMS (*m*/*e*): 569 (MH^+). Mp: 98 °C (dec).

(c) Synthesis of the Cationic Complexes. (i) Formation of 4a by Protonation of 2a. Complex **2a** (92 mg, 0.203 mmol) was placed in a dried Schlenk tube under nitrogen, and Et_2O (10 mL) was added. A 1% solution of $HBF_4{\cdot}Et_2O$ was slowly added dropwise to the stirred solution of the alkyne and resulted in immediate precipitation of **4a**, [CpNi(*μ*-*η*^{2}(*Ni*),*η*^{3}(*Mo*)-HC$_2$CMe$_2$)Mo(CO)$_2$Cp′]$^+$BF$_4^-$ (Ni−Mo), as a fine orange-red powder. Addition was continued until precipitation was complete (≈2 mL). The pale orange solution was then removed via syringe, and **4a** was washed with Et_2O (2 × 5 mL) and dried in vacuo. All attempts at further purification of this species by recrystallization resulted in decomposition. Yield of **4a**: 96 mg, 93%.

(ii) Protonation of Complex 2b. The protonation of **2b** was performed in a manner similar to **2a**, and a tan powder was obtained. However, this species was intractable and insoluble in organic solvents and could not be characterized further.

(iii) Protonation of Complexes 3a and 3b. The procedures followed were identical to those reported for the protonation of complex **3a**. The yield of complex **4a** obtained by protonation of **3a** was 82% (the finely divided product in this case was pyrophoric). For **3b**, 94% of the protonated cationic species [CpNi(*μ*-*η*^{2}(*W*)*η*^{3}(*Ni*)-C(OH)−C(R)−C(H)}W(CO)$_2$Cp′]$^+$ BF$_4^-$ [Ni−W, R = CMe$_2$(OMe)], **5b**, was obtained. **5b** converted spontaneously to the cationic species **4b**, [CpNi(*μ*-*η*^{2}(*Ni*),*η*^{3}(*W*)-HC$_2$CMe$_2$)W(CO)$_2$Cp′]$^+$BF$_4^-$ (Ni−W), when allowed to stand in solution for ~1 h in dichloromethane or chloroform-*d*$_1$; the transformation was virtually instantaneous in acetone.

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