

Reactions of Terminal Alkynes with Group 6–Group 10 Heterobimetallics

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Reactions of PhC_2H with $\text{NiCp}^*\text{M}(\text{CO})_3\text{Cp}''$ [$\text{Ni}-\text{M}$: $\text{M} = \text{Mo}, \text{W}$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{Cp}'' = \text{Cp} (\eta^5\text{-C}_5\text{H}_5)$ or $\text{Cp}' (\eta^5\text{-C}_5\text{H}_4\text{Me})$] afford metallacyclic species **4**, of formula $\text{NiCp}^*\{\mu\text{-}\eta^3\text{-}(\text{Ni}), \eta^1(1\text{-M})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{O})\}\text{M}(\text{CO})_2\text{Cp}$ ($\text{Ni}-\text{M}$, $\text{M} = \text{Mo}, \text{W}$), as the principal products. These compounds are isomeric to four-membered nickelacycles obtained in similar reactions with disubstituted alkynes and contain five-membered $\text{NiC}(\text{O})\text{C}(\text{H})\text{C}(\text{Ph})\text{M}$ ring systems. Phenylacetylene also affords minor quantities of alkyne bridged complexes with “dimetallatetrahedrane-type” nuclear cores. Alkylation of **4** with $(\text{Me}_3\text{O})^+\text{BF}_4^-$ results in the methylation of the metallacyclic (acyl-like) carbonyl ligand and a structural rearrangement ensues: cationic four-membered molybdena- or tungstenacycles **6** of formula $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-M})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OMe})\}\text{M}(\text{CO})_2\text{Cp}]^+\text{BF}_4^-$ ($\text{Ni}-\text{M}$, $\text{M} = \text{Mo}, \text{W}$) result. An iodide-for-carbonyl substitution reaction on **6** affords the neutral complexes **8** $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-M})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OMe})\}\text{MI}(\text{CO})\text{Cp}]$ ($\text{Ni}-\text{M}$), which maintain the structural core present in **6**. The structure of **8b'**, $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-W})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OMe})\}\text{WI}(\text{CO})\text{Cp}']$ ($\text{Ni}-\text{W}$) was established by X-ray diffraction.

Introduction

The reactions of alkynes with transition metal complexes remains an active research area. The complex nature of many of these reactions and the myriad number of products often isolated is manifested by the large number of publications that regularly document new reactions in this class. Reactions of bimetallic and heterobimetallic complexes with alkynes continue to receive attention by many groups.^{1–18} Our contribu-

tions to this field described the reactions of $\text{Co}_x\text{M}_{4-x}$ ($\text{M} = \text{Mo}, \text{W}$; $x = 1\text{--}3$) clusters with alkynes;¹⁹ other research by our group has detailed the reactions of coordinatively saturated $\text{Ni}-\text{M}$ ($\text{M} = \text{Mo}, \text{W}$) species with alkynes.^{20–23}

Most recently, we have described the chemistry of the mixed-metal *unsaturated* heterobimetallic complexes $\text{NiCp}^*\text{M}(\text{CO})_3\text{Cp}$ ($\text{Ni}-\text{M}$: **1**, $\text{M} = \text{Mo}$; **2**, $\text{M} = \text{W}$) with disubstituted alkynes. The initial products obtained in these reactions are nickelacyclic species in which a carbonyl ligand is coupled with the alkyne as shown in Scheme 1. The resultant $\text{NiC}(\text{R})\text{C}(\text{R}')\text{C}(\text{O})$ metallacycle is π -complexed to the group 6 metal. Further reactions on these species lead to “ring-flip” reactions and to the formation of molybdenacycle or tungstenacycle species which are π -bonded to the nickel atom.²⁴

Terminal alkynes frequently exhibit a chemistry different from that of their disubstituted derivatives, presumably because some or all of the following factors may come into play: (i) the lower steric demands of a *CH* versus a *CR* group; (ii) the lesser electron-donating

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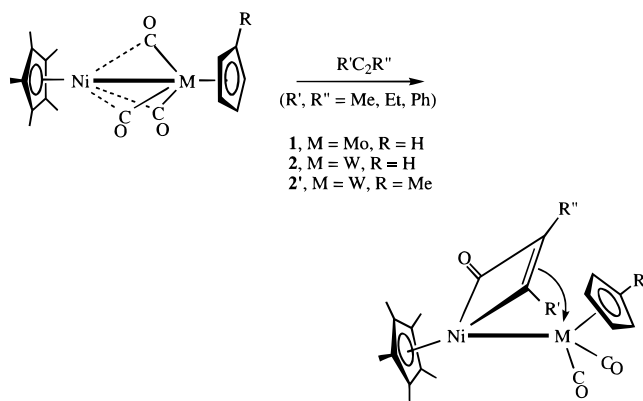
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Scheme 1. Summary of the Reactions of Complexes 1, 2, and 2' with Disubstituted Alkynes

Chart 1

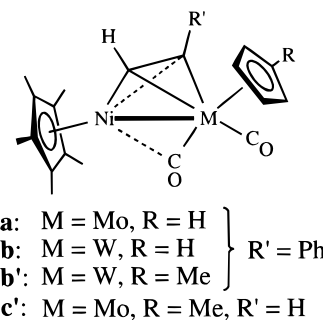
1	NiCp*Mo(CO) ₃ Cp (Ni-Mo)
1'	NiCp*Mo(CO) ₃ Cp' (Ni-Mo)
2	NiCp*W(CO) ₃ Cp (Ni-W)
2'	NiCp*W(CO) ₃ Cp' (Ni-W)
3a	NiCp*(μ-η ² ,η ² -PhC ₂ H)Mo(CO) ₂ Cp (Ni-Mo)
3b	NiCp*(μ-η ² ,η ² -PhC ₂ H)W(CO) ₂ Cp (Ni-W)
3b'	NiCp*(μ-η ² ,η ² -PhC ₂ H)W(CO) ₂ Cp' (Ni-W)
3c'	NiCp*(μ-η ² ,η ² -HC ₂ H)Mo(CO) ₂ Cp' (Ni-Mo)
4a	NiCp*(μ-η ³ (Ni),η ¹ (1-Mo)-C(H)C(Ph)C(O))Mo(CO) ₂ Cp (Ni-Mo)
4b	NiCp*(μ-η ³ (Ni),η ¹ (1-W)-C(H)C(Ph)C(O))W(CO) ₂ Cp (Ni-W)
4b'	NiCp*(μ-η ³ (Ni),η ¹ (1-W)-C(H)C(Ph)C(O))W(CO) ₂ Cp' (Ni-W)
4c'	NiCp*(μ-η ³ (Ni),η ¹ (1-Mo)-C(H)C(H)C(O))Mo(CO) ₂ Cp' (Ni-Mo)
5'	NiCp*(μ-η ² (1,3-Ni),η ² (1,2-W)-C(Ph)C(H)C(O))W(CO) ₂ Cp' (Ni-W)
6a	[NiCp*(μ-η ³ (Ni),η ² (1,3-Mo)-C(H)C(Ph)C(OMe))Mo(CO) ₂ Cp] ⁺ BF ₄ ⁻ (Ni-Mo)
6b'	[NiCp*(μ-η ³ (Ni),η ² (1,3-W)-C(H)C(Ph)C(OMe))W(CO) ₂ Cp] ⁺ BF ₄ ⁻ (Ni-W)
6c'	[NiCp*(μ-η ³ (Ni),η ² (1,3-Mo)-C(H)C(H)C(OMe))Mo(CO) ₂ Cp] ⁺ BF ₄ ⁻ (Ni-Mo)
7	[NiCp*(μ-η ³ (Ni),η ² (1,3-Mo)-C(H)C(Ph)C(OH))Mo(CO) ₂ Cp] ⁺ BF ₄ ⁻ (Ni-Mo)
7'	[NiCp*(μ-η ³ (Ni),η ² (1,3-W)-C(H)C(Ph)C(OH))W(CO) ₂ Cp] ⁺ BF ₄ ⁻ (Ni-W)
8a	NiCp*(μ-η ³ (Ni),η ² (1,3-Mo)-C(H)C(Ph)C(OMe))Mo(CO) ₂ Cp (Ni-Mo)
8b'	NiCp*(μ-η ³ (Ni),η ² (1,3-W)-C(H)C(Ph)C(OMe))W(CO) ₂ Cp' (Ni-W)
8c'	NiCp*(μ-η ³ (Ni),η ² (1,3-Mo)-C(H)C(H)C(OMe))Mo(CO) ₂ Cp' (Ni-Mo)

ability of a C≡CH versus a C≡CR group; (iii) the possibility of C≡CH activation reactions. We were interested in investigating whether the reactions of terminal alkynes with **1** and **2** paralleled the reactions of disubstituted alkynes²⁴ with the same unsaturated heterobimetallic species. Here we describe reactions of the terminal alkynes PhC₂H and HC₂H with **1** and **2**, and with their methylcyclopentadienyl analogs NiCp*M(CO)₃Cp' (Ni-M: **1'**, M = Mo; **2'**, M = W)²⁵ and the structures of the species that result from these ligand transformations.

Results and Discussion

When **1** was treated with phenylacetylene, a small amount of the μ-η²,η²-alkyne complex NiCp*(μ-η²,η²-PhC₂H)Mo(CO)₂Cp (Ni-Mo, **3a**) was isolated. Complex

(25) Throughout this manuscript Cp = η⁵-C₅H₅; Cp' = η⁵-C₅H₄Me; Cp* = η⁵-C₅Me₅. All the complexes discussed (Chart 1) have a NiCp* group linked to either a MCp or a MCp' group (M = Mo, W). Primed complexes (e.g., **1'**, NiCp*Mo(CO)₃Cp') contain a MCp' group; unprimed complexes (e.g., **2**, NiCp*W(CO)₃Cp) contain a MCp group.


Figure 1. Structure of the μ-η²,η²-PhC₂H complexes **3**.

3a has a "dimetallatetrahedrane" core; its structure, and those of related species, is shown in Figure 1. Like other bridging alkyne complexes of this type that we^{20–22,24} and others^{11,12} have isolated, this complex has a terminal (semibridging) carbonyl ligand. Terminal (semibridging) carbonyl ligand exchange is presumably prevalent in this molecule, but as this fluxional process cannot give this unsymmetrical molecule effective planar symmetry on the NMR time scale, two carbonyl resonances are observed in its ¹³C NMR spectrum. Four ν(CO) stretches are seen in the IR spectrum of **3a**.

The major product, **4a** comprises 70–80% of the product mixture. Spectroscopic data (Tables 1–3) suggest that phenylacetylene had added to **1** and indicate that the empirical formula of **4a** is NiMoCpCp*(CO)₃(PhC₂H). A plethora of isomers with this empirical formula are possible, but these may be whittled down to a small number of feasible structures by careful spectroscopic analysis.

The IR spectrum of **4a** (Table 3) included a terminal ν(CO) stretch, a *semibridging* ν(CO) stretch (at 1843 cm⁻¹), and a solvent-dependent stretch that appeared at 1690 cm⁻¹; the latter absorption was assigned to a MC(O) group. The downfield chemical shift of the C≡CH proton (7.31 ppm) in the ¹H NMR spectrum of **4a** indicated that an M–C(H) linkage was also present. Four possible isomeric structures for the core structure of **4a** that (i) maintain an 18-electron configuration for each metal, (ii) contain both M–C(O) and M–C(H) [or M'–C(H)] linkages, and (iii) assume an intact C(Ph)–C(H) linkage, are shown in Figure 2. These restrictions still allow possible nickelacycle, molybdenacycle, and dimetallacycle structures for **4a**.

The acyl ν(CO) stretch seen in **4a** is 30–50 cm⁻¹ higher in energy than acyl stretches seen in four-membered nickelacyclic species such as NiCp{μ-η²(1,3-Ni),η²(1,2-Mo)C(Me)C(Me)C(O)}Mo(CO)₂Cp (Figure 1, R = R' = Me),²⁰ whose core geometries adopt structure A (Figure 2). Furthermore the acyl carbon resonance of **4a** appears at 173 ppm in its ¹³C NMR spectrum, a value ~10 ppm upfield from the acyl carbon resonances observed for 2-butyne and 1-phenylpropyne type A metallacycles.²⁴ These data suggest that **4a** is not isostructural to type A metallacycles. Isomer B can be readily dismissed as it requires a fully bridging carbonyl (absent in **4a**) in order to satisfy the 18-electron rule.

Isomers C and D differ in their metal–acyl carbonyl linkage. Isomer C has a Mo–C(O) acyl-type bond as part of a four-membered ring, while D includes a Ni–C(O) linkage within a five-membered ring. While **4a** is believed to have the structure of C or D, the available spectroscopic data for **4a** did not allow us to distinguish between these two options. Nickel–tungsten analogs

Table 1. ^1H NMR Data for the New Complexes^a

complex	Cp*	Cp or Cp'	OMe	H/Ph	H
3a	1.53	5.12		7.19–7.33	5.43
3b	1.52	5.15		7.13–7.31	5.10
3b'	1.50	4.99–5.30, 1.98		7.17–7.34	5.25
3c'	1.78	5.13, ^b 5.23, ^b 2.12		5.39	5.39
4a	1.78	5.35		6.96–7.19	7.31
4b	1.69	5.32		7.00–7.29	6.99
4b'	1.67	5.07, 5.15, 5.18, 5.21, 2.06		7.06, 7.16, 7.31	6.89
4b'^c	1.73	5.50 (2H), 5.62, 5.71, 2.13		6.98, 7.10, 7.21	7.36 ^e
4c'	1.77	5.20, 5.26 (2H), 5.29, 2.06		3.63 ^e	6.73 ^h
5'	1.55	4.79, 4.98, 5.21, 5.51, 1.75 ^d		7.24, 7.36, 7.56	3.27
6a	1.73	5.39	3.80	7.40, 7.65	6.92
6b'^c	1.77	5.50–5.78, 2.03	3.82	7.51, 7.78	6.68 ^f
6c'^c	2.04	5.44–5.56, 1.94	3.72	6.42 ⁱ	6.30 ⁱ
7'	1.70	5.45–5.51, 5.16–5.23, 2.00	9.77 (OH)	7.62, 7.42	6.21 ^g
8a	1.70	4.98	3.64	7.38, 7.64	7.67
8b'	1.69	4.56, 4.81, 4.84, 5.18, 2.01	3.59	7.31–7.42, 7.64	7.24
8c'^c	1.93	4.73(2H), 4.89, 5.18, 1.96	3.57	6.90 ^j	6.19 ^j

^a In CDCl_3 , with CHCl_3 set at 7.26 ppm. δ in ppm; coupling constants in hertz. Cp' and Ph aromatic signals are multiplets: the multiplet center or range is given, followed (for Cp') by the Me signal. Cp' aromatic groups exhibit ABCD-type patterns. ^b AA'BB' multiplet. ^c In acetone- d_6 with $\text{CHD}_2\text{C}(\text{O})\text{CD}_3$ set at 2.04 ppm. ^d Aromatic signals broad, down to -30°C . $J_{\text{WH}} = 2.9$; ^e 4.1. ^f 3.9. ^g $J_{\text{HH}} = 3.9$; ^h 3.8; ⁱ 3.7. ^j

Table 2. ^{13}C NMR Data for New Complexes^a

complex	CO	C(O)M or C(OMe)	Cp*	Cp or Cp'	C(H)/C(Ph), C(H)	Ph
3a	230.3, 240.9		8.4, 100.7	92.2	75.8, 99.1	126.6, 127.9, 130.6, 140.7
3b'^b	222.4, 228.6		8.8, 100.1	14.0, 88.4, 90.2, 90.8, 91.3, 109.2	68.7, 86.6 ^c	127.3, 128.8, 132.0, 141.6
4a	231.6, 232.4	172.9	9.0, 102.3	91.9	67.4, 127.9	123.4, 125.4, 128.3, 139.2
4b	219.2, 219.3	176.9	9.0, 101.7	89.7	53.4, 113.0	124.5, 125.7, 127.9, 138.0
4b'	220.3, 220.6	175.9	8.7, 101.5	13.8, 86.8, 88.8, 88.9, 91.3, 107.8	53.6, 114.0	124.5, 125.6, 127.6, 137.5
5'	222.6, 228.1	183.8	8.2, 103.3	13.5, 82.7, 86.1, 91.0, 95.2, 124.	59.7, 151.8	126.7, 127.5, 128.2, 158.3
6a	220.0	63.3, 177.9	8.8, 105.5	91.0	115.6, 127.1	128.6, 129.1, 130.8, ***
6b'	209.9 ^d 225.9 214.5 ^e	64.0, 164.0 ^f	8.5, 104.9	13.9, 83.5, 85.4, 89.0, 91.7, 110.4	99.6, ^g 129.7 ^h	128.1, 128.8, 130.0, 130.4
6c'^b	223.1, 226.6	63.5, 187.0	9.0, 106.8	14.3, 87.7, 89.1, 92.3, 94.6, 113.1	109.8, 128.5	
7'	207.0, 213.5	160.1	8.2, 104.2	13.9, 83.2, 85.2, 88.4, 91.9, 110.1	98.6, 129.8	128.5, 129.8, 130.3
8a	245.1	60.4, 182.2	9.3, 102.2	90.8	120.7, 130.9	127.8, 128.4, 128.9, 130.3
8b'	238.4	60.7, 168.3	9.1, 101.5	14.6, 82.9, 84.4, 91.9, 94.6, 104.4	119.6, ⁱ 123.0	127.3, 128.1, 128.5, 133.2 ^j
8c'	244.1	59.9, 187.7	9.4, 102.0	14.7, 85.9, 87.3, 94.4, 94.6, 106.2	138.4, 90.8	

^a In chloroform- d_1 ; δ (ppm) referenced to the CDCl_3 signal set at 77.0 ppm. Unobserved signals denoted ***. Cp', Cp* and Ph, signals given in the following order: Me, other aromatic carbon atoms, *ipso* carbon. Coupling constants in hertz. ^b In acetone- d_6 [(CD_3) $_2\text{CO}$ set at 29.8 ppm]. $J_{\text{WC}} = 26.5$; ^c 148.1; ^d 135.2; ^e 64.2; ^f 51.3; ^g 6.8; ^h 59.4; ⁱ 8.6. ^j

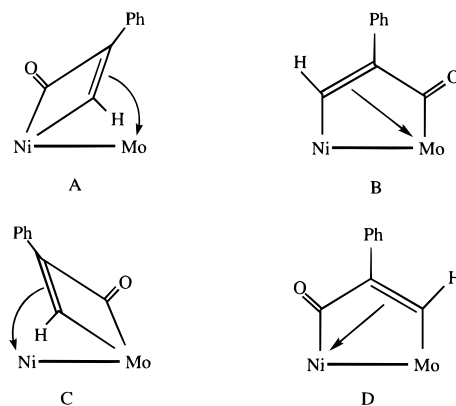
Table 3. IR $\nu(\text{CO})$ Data (cm^{-1}) for New Complexes^a

3a	1935(s), 1904(m), 1866(w), 1809(m)	5'	1970(s), 1899(s), 1653(s)
	1950(s), ^b 1910(m), 1873(w), 1821(m)	6a^d	2020(s), 1965(s)
3b^b	1948(s), 1913(w), 1876(m), 1816(s)	6b'^d	2013(s), 1952(s)
3b'^b	1946(s), 1909(m), 1872(w), 1810(m)	6c'^d	2018(s), 1963(s)
3c'	1910(s), 1829(m)	7	2012(s), 1962(s)
4a	1953(s), 1842(s), 1690(m)	7^d	2013(s), 1952(s)
	1948(s), ^d 1841(s), 1670(m)	8a	1902(s)
4b^c	1933(s), 1831(s), 1671(m)	8b'^d	1885(s)
4b'	1946(s), 1835(s), 1685(m)	8c'	1900(s)
4c'^d	1951(s), 1837(s), 1670(m)		

^a In THF unless otherwise stated. ^b In hexanes. ^c Nujol Mull. ^d In dichloromethane.

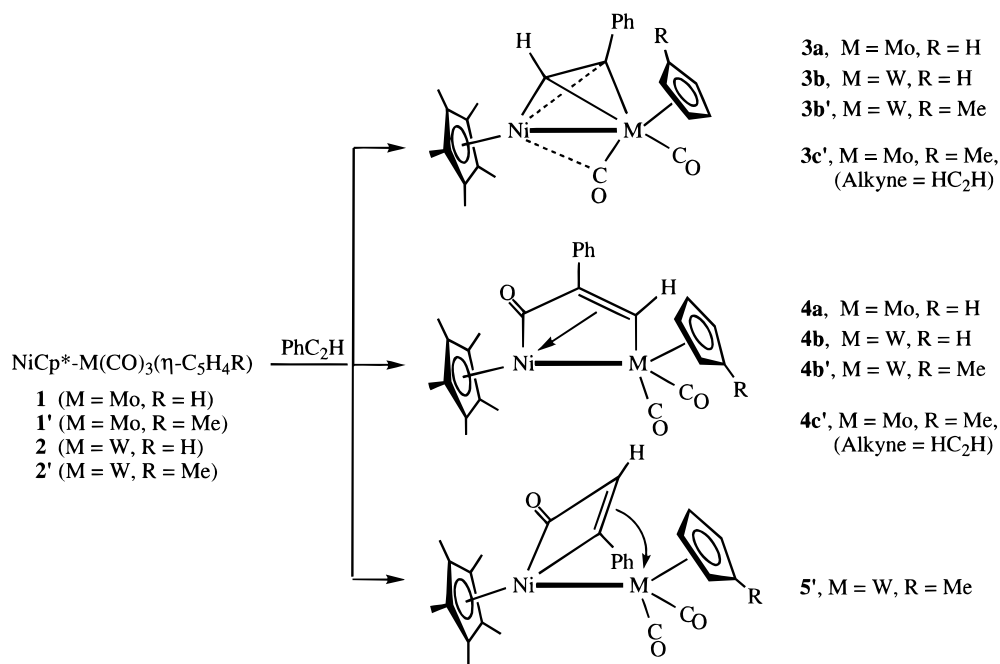
of **4a** were therefore prepared with the hope of obtaining good ^{13}C NMR data. The observation of ^{183}W – ^{13}C couplings in the ^{13}C NMR spectra of the Ni–W analog, and an assessment of their magnitude, would allow us to differentiate between options C and D.

When PhC_2H was reacted with the complexes $\text{NiCp}^*\text{W}(\text{CO})_3\text{Cp}''$ (Ni–W: **2**, $\text{Cp}'' = \text{Cp}$; **2'**, $\text{Cp}'' = \text{Cp}'$), the μ - η^2 , η^2 -alkyne complexes $\text{NiCp}^*(\mu$ - η^2 , η^2 - $\text{PhC}_2\text{H})$ - $\text{W}(\text{CO})_2\text{Cp}''$ (Ni–W: **3b**, $\text{Cp}'' = \text{Cp}$; **3b'**, $\text{Cp}'' = \text{Cp}'$) were isolated as minor reaction products (~ 20 – 30% of the product mixture). Spectroscopic properties of **3b** and **3b'** mirror those of **3a**. The only noteworthy observation

**Figure 2.** Some isomeric cores possible for complex **4a**.

is the fact that the ^1H NMR resonances of complex **3b'** are concentration dependent. Different concentrations of chloroform- d_1 solutions of **3b'** exhibit chemical shift differences up to 0.17 ppm for the PhC_2H proton resonances. The Cp' and Ph aromatic resonances also show (smaller) concentration-dependent chemical shifts. Higher concentrations of **3b'** led to a upfield chemical shift for the PhC_2H resonance.

The major reaction products in the reactions of **2** and **2'** with PhC_2H (complexes **4b** and **4b'**, respectively)

Scheme 2. Reactions of 1, 1', 2, and 2' with Terminal Alkynes and the Probable Structures of the Products

featured semibridging carbonyl ligands and a methine carbon–metal [M–C(H)] linkage. The data indicate that these species are isostructural with **4a**. If these metallacycles were of isomeric form C, a large ¹⁸³W–¹³C coupling to the acyl carbon would be expected, and a comparably large coupling to the methine carbon should also be visible. Were isomer D the actual structure of these species, ¹⁸³W–¹³C coupling to the acyl carbon would be observed.

Unfortunately, ¹⁸³W–¹³C-coupling data in the ¹³C NMR spectra of both **4b** and **4b'** were of limited utility in distinguishing between possible isomers. For **4b'**, the acyl carbon resonance at $\delta = 176$ ppm was broad and became broader at low temperatures; the methine carbon resonance behaved similarly. This precluded an accurate determination of ¹⁸³W–¹³C coupling to either of these carbon atoms.

More subtle arguments do suggest that isomeric form D is the likely structure for these species. The chemical shifts of the acyl carbonyl resonances for all three complexes are within 3 ppm of each other despite the change in group 6 metal between **4a** (molybdenum) and **4b** and **4b'** (tungsten). Were structure C adopted, a larger chemical shift difference might have been expected between Mo–CO and W–CO resonances in **4a** and **4b**, **4b'**, respectively. Furthermore the chemical shift of the alkyne-derived CH varies significantly from **4a** (67.4 ppm) to **4b** and **4b'** (53.4 and 53.6 ppm, respectively). Based on these chemical shifts data, isomeric form D seems to be the more probable structure for complexes **4**, and this structure was tentatively assigned to them. They may thus be represented as $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^1(1\text{-M})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{O})\}\text{M}(\text{CO})_2\text{Cp}''$ (Ni–M: M = Mo, Cp'' = Cp, **4a**; M = W, Cp'' = Cp, **4b**; Cp'' = Cp', **4b'**). A five-membered NiMC₃ ring is present in the three species.

A third product (**5'**), isolated in low yields (5–15%) from the reaction of **2'** and phenylacetylene, clung tenaciously to a silica gel column and could only be eluted by using methanol as a solvent. The IR spectrum of **5'** revealed the pattern of two terminal and one metal

acyl CO stretches that were familiarly observed for type A (Figure 2) metallacycles. The physical properties of **5'** (its low solubility, very sluggish chromatographic mobility, and orange-brown color) and its spectroscopic features are in accord with **5'** having this structure. However, the upfield chemical shift of the methine proton ($\delta\text{CH} = 3.27$ ppm) suggests that the alkyne-derived CH proton is nested between C(O) and C(Ph) groups (opposite to the linkage that is observed in **4b'**). This compound is therefore assigned the structure $\text{NiCp}^*\{\mu\text{-}\eta^2(1,3\text{-Ni}), \eta^2(1,2\text{-W})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{O})\}\text{W}(\text{CO})_2\text{-Cp}'$ (Ni–W, **5'**). Complex **5'** contains a nickelacyclobutenone ring. Reactions of phenylacetylene with the heterobinuclear complexes and the structures of the products obtained are summarized in Scheme 2.

It is unusual that more than one isomer with organic bridges spanning the same bimetallic framework can be isolated. Previously reported examples of bimetallic metallacycles that incorporate linked alkyne and carbonyl moieties typically show a preference for only one isomer. Earlier work in this laboratory showed that the unsymmetrical alkyne 2-pentyne leads to two metallacycles when reacted with Ni(CO)Cp–MoCp(CO)₃. These products were both characterized as nickelacyclobutenone structures, differing only in their alkyne–carbonyl linkage but not in the bonding mode of the C(R)C(R')C(O) ligand to the metals.²⁰ Similar results were obtained when 2-pentyne was reacted with **1**.²⁶

Previously characterized ditungsten,²⁷ and diiron and diruthenium metallacycles²⁸ with C(R)C(R)C(O) ligands spanning two metal centers have shown a preference for one particular isomer. Furthermore, both the group 6 and the group 8 dinuclear complexes exhibit considerable fluxionality. The ditungsten metallacycle undergoes a fluxional process in which reversible metal–carbon bond cleavage occurs,²⁷ while carbon–carbon

(26) Chetcuti, M. J.; Grant, B. E., unpublished results.

(27) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783–1788.

(28) Dyke, A. F.; Knox, S. A. R.; Morris, N. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

bond breakage is invoked to account for the dynamic behavior of the diiron or diruthenium systems.²⁸

Some dirhodium alkyne complexes have shown greater flexibility. Dickson and co-workers prepared a series of complexes by reacting the coordinatively unsaturated $\text{Rh}_2(\mu\text{-CO})_2\text{Cp}^*_2$ ($\text{Rh}=\text{Rh}$) with a variety of (nonterminal) alkynes.⁵ It was found that the products of these reactions existed in solution as an equilibrium mixture of metallacycle and η^1, η^1 parallel bridging alkyne complex. Moreover, the metallacycles showed further fluxional behavior, independent of this equilibrium, in which the coordination mode of the bridging organic group jumped between the two metal sites by a mechanism similar to that seen in the diruthenium metallacycle. The reaction of the same unsaturated dirhodium complex $\text{Rh}_2(\mu\text{-CO})_2\text{Cp}^*_2$ ($\text{Rh}=\text{Rh}$) with ethyne led to an equilibrium mixture of two metallacycles: both the four-membered metallacycle and five-membered dimetallacycle were characterized with this reaction.²⁹

Our results of the phenylacetylene reaction with **2'** suggest that the different steric and/or electronic demands of the *Ph* and *H* groups of the PhC_2H ligand lead to the formation of the two metallacycles. It is not clear why this occurs. Possible reasons that allow the formation of **4b'** include either the presence of a relatively bulky *Ph* group at C2 or the absence of a sterically demanding group at C1.

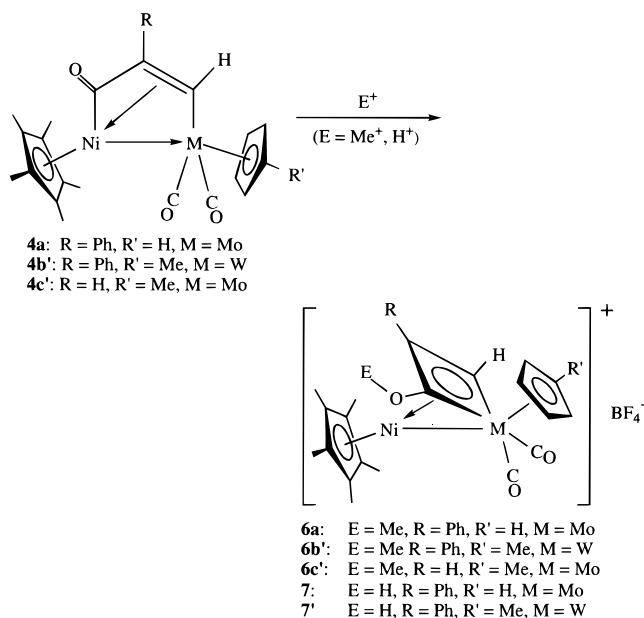
In an attempt to answer why two metallacycles were obtained, **1'** was reacted with ethyne. Methylene chloride solutions of **1'** instantly change from blue to orange when exposed to an ethyne atmosphere at -78°C . Unfortunately, the orange mixture resisted purification, and massive decomposition ensued when chromatography was attempted. No products could be isolated by following this procedure. Vacuum concentration of the crude reaction mixture did afford a brownish oil; ^1H NMR analysis of this oil showed that two main species were present.

The minor product was formulated as the $\mu\text{-}\eta^2, \eta^2$ alkyne complex $\text{NiCp}^*\{\mu\text{-}\eta^2, \eta^2\text{-HC}_2\text{H}\}\text{Mo}(\text{CO})_2\text{Cp}'$ (Ni-Mo , **3c'**). The ^1H NMR and IR spectra of the other product are consistent with a metallacycle of type **4** (a dimetallacyclopenteneone-type species). The major reaction product is thus formulated as $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^1(1\text{-}M)\text{C}(\text{H})\text{C}(\text{O})\}\text{Mo}(\text{CO})_2\text{Cp}'$ (Ni-Mo , **4c'**). The structures of both products are shown in Scheme 2.

The dynamic behavior of the homobimetallic metallacycles referred to earlier^{5,27–29} is mirrored by the broadening of ^{13}C NMR resonances in the spectrum of **4c'**. This complex may also undergo some form of dynamic behavior in solution and suggests that the assignment of a dimetallacyclopenteneone structure to **4c'** and other type **4** complexes may well be simplistic. The failure to obtain low-temperature limiting spectra precluded useful $^{183}\text{W}\text{-}^{13}\text{C}$ coupling information from being obtained from the nickel–tungsten complexes. In order to circumvent this problem and in an attempt to unambiguously distinguish between possible isomeric metallacycles, alkylation of complexes **4** was attempted.

Alkylation of metal–acyl complexes is a well-known reaction that may lead to heteroatom-stabilized cationic carbene complexes. Reports of electrophilic attack on metallacyclic acyl complexes have appeared in the

Scheme 3. Protonation or Alkylation of the Dimetallacyclic Species^a



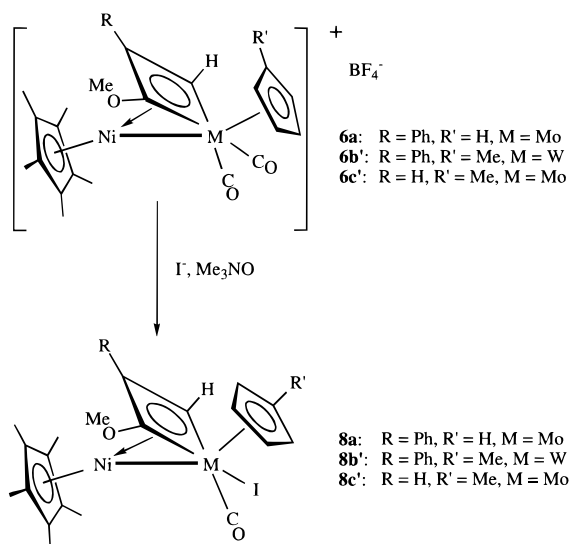
^a The dimetallacycle species are converted to (mono)metallacycles in this reaction.

literature. These include our own recent work²⁴ and other examples that lead to different products. Treatment of the ditungsten metallacyclic species $\text{W}(\text{CO})_2\text{Cp}\{\mu\text{-}\eta^2(1,2)\eta^2(1,3)\text{-C}(\text{R})\text{C}(\text{R}')\text{C}(\text{O})\}\text{W}(\text{CO})_2\text{Cp}$ (W-W) with HBF_4 results in the protonation of the oxygen atom of the acyl group, yielding a compound the authors designate as a hydroxy carbene complex.²⁷ The cationic complex that was isolated exhibited dynamic behavior similar to that observed for the neutral precursor. However, the protonation of diiron metallacyclopentene complexes $\text{Fe}(\text{CO})\text{Cp}\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{R})\text{C}(\text{R}')\text{C}(\text{O})\}\{\mu\text{-CO}\}\text{FeCp}$ (Fe-Fe) follows a very different route. Carbon–carbon bond cleavage occurs here, and the resultant products are μ -alkenyl species.²⁸

Using the same protocol reported earlier,²⁴ the complexes $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-}M)\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OMe})\}\text{Mo}(\text{CO})_2\text{Cp}]^+\text{BF}_4^-$ (Ni-Mo , **6a**) and $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-}M)\text{C}(\text{H})\text{C}(\text{R})\text{C}(\text{OMe})\}\text{M}(\text{CO})_2\text{Cp}]^+\text{BF}_4^-$ (Ni-M , $\text{M} = \text{W}$, $\text{R} = \text{Ph}$, **6b'**; $\text{M} = \text{Mo}$, $\text{R} = \text{H}$, **6c'**) were prepared from their neutral precursors **4a**, **4b'**, and **4c'** by alkylation with $(\text{Me}_3\text{O})^+\text{BF}_4^-$. Two hydroxy complexes, the species $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-}W)\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OH})\}\text{W}(\text{CO})_2\text{Cp}]^+\text{BF}_4^-$ (Ni-W , **7**) and the less well characterized nickel–molybdenum complex $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}), \eta^2(1,3\text{-}M)\text{C}(\text{H})\text{C}(\text{H})\text{C}(\text{OH})\}\text{Mo}(\text{CO})_2\text{Cp}]^+\text{BF}_4^-$ (Ni-Mo , **7**), were also prepared by treatment of **4b'** and **4a**, respectively, with $\text{HBF}_4\cdot\text{Et}_2\text{O}$.

The NMR data, especially $^{183}\text{W}\text{-}^{13}\text{C}$ coupling data gleaned from the ^{13}C NMR spectra for the Ni-W complex **6b'**, suggest that complexes **6** are cationic $\eta^2\text{-}(M)\eta^3(\text{Ni})$ -allylic species ($\text{M} = \text{Mo}$, W). The structures of complexes **6** and **7** are shown in Scheme 3. Alkylation or protonation of complexes **4** thus results in a rearrangement of the organic backbone and to the transformation of what are believed to be dimetallacyclopenteneone species to metallacyclobutenone complexes. Unfortunately, X-ray-quality crystals again could not be obtained for any type **6** complex. Derivatives of complexes **6** were isolated instead.

(29) Herrmann, W. A.; Bauer, C.; Weichmann, J. *J. Organomet. Chem.* **1983**, *243*, C21–C26.

Scheme 4. Iodide-for-Carbonyl Ligand Substitution on Complexes 6^a


^a Structure **8b'** was established by an X-ray diffraction study.

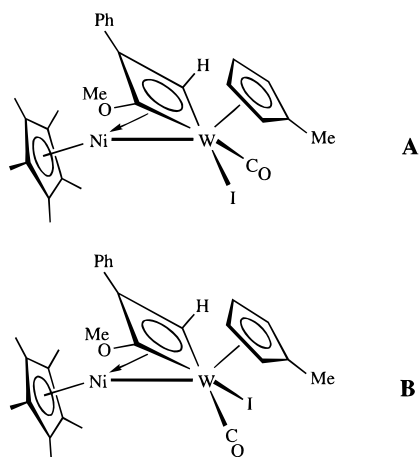


Figure 3. Two possible isomers of complex **8b'**, differing in the relative stereochemistry of the W–I and W–CO bonds relative to the metallacycle ring. B is the correct structure of **8b'**.

Iodide-for-carbonyl ligand substitution on complexes **6a**, **6b'**, and **6c'** was effected by using NBU_4^+I^- as the iodide source and Me_3NO as the carbonyl ligand oxidant. This reaction afforded the neutral iodo complexes **8a**, **8b'**, and **8c'**, respectively, as shown in Scheme 4. The ^{13}C NMR spectra of all iodo compounds exhibited a single downfield chemical shift for the terminal carbonyl ligand; spectroscopic data indicate that they have structures that are similar to their respective cationic precursors **8a**, **8b'**, and **8c'**. These complexes all have relatively low $\nu(\text{CO})$ stretching frequencies for their lone carbonyl ligand (1885–1900 cm^{-1}). They exhibit low-field chemical shift signals for the carbonyl carbon in the ^{13}C NMR of the complexes.

In complexes **8**, the iodide ligand may either be in a *cis* or in a *trans* geometry relative to the C(OMe) group of the metallacycle (Figure 3). Only one of these two possible geometric isomers formed. Similarly, as we reported earlier, only one isomer was observed for the isostructural 2-butyne derivative $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^2(1,3\text{-Mo})\text{C}(\text{Me})\text{C}(\text{Me})\text{C}(\text{OMe})\}\text{MoI}(\text{CO})\text{Cp}$ (Ni–Mo).²⁴ To establish which of these two isomers formed, as well as

to unambiguously determine the structure and geometrical parameters of one of these complexes, a single-crystal X-ray diffraction study was carried out on complex **8b'**. Crystal data and data collection parameters and tables of key bond lengths and bond angles are collected in Tables 4–64, respectively. A labeled ORTEP diagram of **8b'** is shown in Figure 4.

The X-ray study confirms the formulation of complex **8b'** as $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^2(1,3\text{-W})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{OMe})\}\text{WI}(\text{CO})\text{Cp}'$ (Ni–W). The molecule features a tungstenacycle moiety bonded to a Cp^*Ni group via all three carbon atoms and the tungsten atom of the ring. The coordination geometry about the tungsten atom, (ignoring the metal–metal bond) is that of a four-legged piano stool, with the iodide oriented in a *transoid* orientation to the methoxy ring carbon ($\text{C}_{\text{OMe}}\text{-W-I} = 136.4^\circ$) and the carbonyl ligand oriented in a *transoid* orientation to the (alkyne-derived) methine carbon atom, as depicted in Figure 3B.

The nickel–allylic carbon bond distances differ significantly in length, ranging from 1.967(5) Å for the Ni–C(H) bond, to 2.042(6) Å for the Ni–C(Ph) bond and 2.021(6) Å for the Ni–C(OMe) bond. Significant variations in metal–carbon bond lengths between the C_1 , C_2 , and C_3 carbon atoms of the allyl ligand are not unusual. In the cationic complex $[\text{Ni}(\eta^3,\eta^2,\eta^2\text{-C}_{12}\text{H}_{19})]^+$ for example, Ni– C_{allyl} bond lengths range from 2.018(4) to 2.116(4) Å.³⁰

The Ni–W distance of 2.6359(8) Å is consistent with that of a Ni–W single bond.²² The W– C_{CO} distance of 1.945(7) Å is somewhat shorter than a normal W–carbonyl distance, perhaps reflecting the increased $d\pi\text{-}p\pi$ backbonding, due to the factors outlined above. All the atoms in the tungsten metallacycle are essentially coplanar (Σ angles inside the WC_3 quadrilateral = 357.6°), tallying with the treatment of the C_3 unit in the metallacycle as an allylic ligand. The MeO atom and the *ipso* carbon atom of the phenyl ring are also practically coplanar with the C_3 ligand as expected for allylic ligand substituents [Σ angles around $\text{C}_2 = 358.2^\circ$; Σ angles around $\text{C}_3 = 360.1^\circ$]. The MeO and the other phenyl carbon atoms, and the Cp^* group carbon atoms are essentially in the same plane as the WC_3 ring. Finally, the Cp' and Cp^* ligands are in a slightly distorted *trans* orientation ($\text{Cp}'_{\text{centroid}}\text{-W-Ni-Cp}^*_{\text{centroid}}$ torsion angle = 154.3°).

The overall structure of **8b'** (and, presumably, those of the other iodo complexes and their cationic precursors) can be viewed as a 1,3-tungsten substituted allyl species. Alternatively, the WC_3 unit as a whole can also be viewed as an η^4 -coordinated tungstenacyclobutadiene group bonded to a Cp^*Ni fragment. Parallels can be drawn by considering the reaction of alkynes with bimetallic bridging alkyldiyne complexes. Stone and co-workers have synthesized many $\mu\text{-}\eta^2,\eta^3$ -allyl complexes, whose $\text{MM}'\text{C}(\text{R})\text{C}(\text{R}')\text{C}(\text{R}'')$ cores mirror those observed for complexes **6–8**. An alkoxy-substituted $\mu\text{-}\eta^2,\eta^3$ -allyl complex has also been reported by Mathieu and co-workers. The species $\text{Fe}(\text{CO})_3\{\mu\text{-}\eta^2,\eta^3\text{-C}(\text{R})\text{C}(\text{R}')\text{C}(\text{OEt})\}\{\mu\text{-}\eta^2,\eta^2\text{-PhC}_2\text{Ph}\}\text{Fe}(\text{CO})_3$ (Fe–Fe) was obtained through

(30) Taube, R.; Wache, S.; Sieler, S.; Kempe, R. *J. Organomet. Chem.* **1993**, *456*, 131–136.

Table 4. Crystal Data and Data Collection Parameters for $\text{NiCp}^*\{\mu\text{-}\eta^2(\text{W})\eta^3(\text{Ni})\text{-C(H)C(Ph)C(OMe)}\}\text{WI(CO)Cp}'$ (Ni–W, **8b).**

parameter	value	parameter	value
formula	$\text{NiWC}_{27}\text{H}_{31}\text{IO}_2$	formula wt	757.01
space group	$P2_1/c$ (No. 14)	<i>a</i> , Å	9.3131(5)
<i>b</i> , Å	14.953(2)	<i>c</i> , Å	18.617(2)
β , °	103.126(5)	<i>V</i> , Å ³	2524.8(8)
<i>Z</i>	4	<i>d</i> _{calc} , g cm ⁻³	1.991
cryst dimens, mm	0.35 × 0.31 × 0.28	temp, °C	20
radiation, λ (Å)	Mo Ka, 0.71073	monochromator	graphite
abs coeff μ, cm ⁻¹	66.33	abs corr applied	empirical
transm factors	0.74, 1.00	diffractometer	Enraf-Nonius CAD4
scan method	ω -2 θ	2 θ range, deg	4.00–45.00
<i>h,k,l</i> limits	–10 to 9, 0–16, 0–20	scan width, deg	0.82 + 0.35 tan θ
takeoff angle, deg	2.95	programs used	Enraf-Nonius SDP
<i>F</i> ₀₀₀	1456.0	weighing <i>p</i> -factor	0.040
no. of data collected	3426	no. of unique data	3425
no. of data with <i>I</i> > 3.0σ(<i>I</i>)	2660	no. of variables	289
<i>R</i> ^a	0.021	<i>R</i> _w ^b	0.027
goodness of fit	0.910	max. shift/esd in final cycle	0.18

^a $R = \sum |F_o - F_c| / \sum F_o$. ^b $R_w = [\sum w(|F_o - F_c|)^2 / \sum wF_o^2]^{1/2}$.

Table 5. Key Bond Distances (Å) of $\text{NiCp}^*\{\mu\text{-}\eta^2(\text{Mo})\eta^3(\text{Ni})\text{-C(H)C(Ph)C(OMe)}\}\text{WI(CO)Cp}'$ (Ni–W, **8b)^a**

atoms	distance	atoms	distance
W–I	2.8423(5)	W–Ni	2.6359(8)
W–C(1)	1.945(7)	W–C(2)	2.136(6)
W–C(4)	2.131(6)	Ni–C(2)	2.021(6)
Ni–C(3)	2.042(6)	Ni–C(4)	1.967(5)
O(1)–C(1)	1.173(8)	O(21)–C(2)	1.362(7)
O(21)–C(22)	1.431(8)	C(2)–C(3)	1.434(8)
C(3)–C(4)	1.417(8)		

^a ESD's in parentheses.

Table 6. Key Bond Angles (deg) in $\text{NiCp}^*\{\mu\text{-}\eta^2(\text{Mo})\eta^3(\text{Ni})\text{-C(H)C(Ph)C(OMe)}\}\text{WI(CO)Cp}'$ (Ni–W, **8b)^a**

atoms	angle	atoms	angle
I–W–Ni	89.37(2)	Ni–W–C(1)	81.1(2)
I–W–C(1)	88.7(2)	Ni–W–C(4)	47.3(1)
I–W–C(2)	136.3(2)	C(2)–W–C(4)	60.6(2)
I–W–C(4)	82.9(2)	C(1)–W–C(4)	127.5(2)
Ni–W–C(2)	48.8(2)	C(1)–W–C(2)	95.1(2)
C(2)–Ni–C(3)	41.3(2)	C(2)–Ni–C(4)	65.3(2)
C(3)–Ni–C(4)	41.4(2)	W–Ni–C(2)	52.6(2)
W–Ni–C(3)	70.8(2)	W–Ni–C(4)	52.8(2)
C(2)–O(21)–C(22)	116.6(5)	W–C(1)–O(1)	174.3(6)
W–C(2)–Ni	78.6(2)	W–C(2)–O(21)	139.4(4)
W–C(2)–C(3)	99.1(4)	Ni–C(2)–O(21)	123.5(4)
Ni–C(2)–C(3)	70.1(3)	O(21)–C(2)–C(3)	119.7(5)
Ni–C(3)–C(2)	68.6(3)	Ni–C(3)–C(4)	66.5(3)
Ni–C(3)–C(31)	125.5(4)	C(2)–C(3)–C(4)	98.1(5)
C(2)–C(3)–C(31)	132.7(5)	C(4)–C(3)–C(31)	129.3(5)
W–C(4)–Ni	79.9(2)	W–C(4)–C(3)	99.8(4)
Ni–C(4)–C(3)	72.2(3)		

^a ESDs in parentheses.

the reaction of a the bridging methoxycarbonyl diiron complex $\text{Fe(CO)}_3\{\mu\text{-C(OEt)}\}\{\mu\text{-}\eta^2,\eta^2\text{-PhC}_2\text{Ph}\}\text{Fe(CO)}_3$ with alkynes.³¹

Conclusions

The reaction of nickel–molybdenum and nickel–tungsten complexes with alkynes leads to two main classes of products: $\mu\text{-}\eta^2,\eta^2$ -alkyne complexes (with dimetallatetrahedrane cores) and metallacyclic products in which alkyne–carbonyl ligand coupling has occurred. The metallacyclic species are generally obtained in

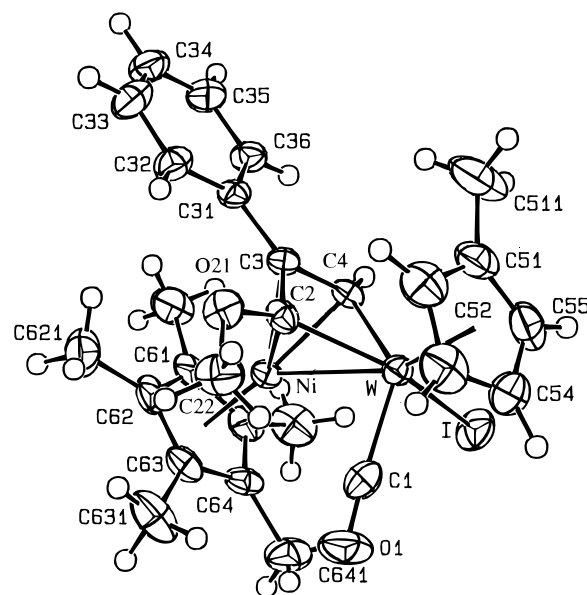


Figure 4. ORTEP diagram of $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^2(1,3\text{-W})\text{-C(H)C(Ph)C(OMe)}\}\text{WI(CO)Cp}'$ (**8b**′, Ni–W). All non-hydrogen atoms are shown as ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

higher yields than the alkyne species. The nature of the metallacycle (four-membered or five-membered ring, nickelacycle or molybdena- or tungstenacycle, depends on the particular alkyne and the metallacyclic substituents. Disubstituted alkynes lead to nickelacyclic products, as described earlier. These species rearrange to four-membered molybdenacycle or tungstenacycle complexes when alkylated or protonated.

A more complex mixture of products is obtained with terminal alkynes. The principal products are five-membered dimetallacycles in which the C(H)C(R)C(O) unit is bound to the nickel via the C(H) carbon atom, and ligated to the group 6 metal in a η^1,η^2 -fashion [via the C(O) and the C(H)C(R) atoms]. Alkylation or protonation of these dimetallacycles leads to a rearrangement and affords four-membered molybdenacycle or tungstenacycle cationic complexes analogous to those observed with disubstituted alkynes. These cationic species undergo “iodide-for-carbonyl” substitution reactions to yield neutral complexes; the iodide ligand resides on the group 6 metal.

(31) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087.

The diversity of molecular frameworks one sees with C(R)C(R)C(O) ligands attached to Ni–Mo and Ni–W frameworks is surprising. The structure of the product depends on the nature of R and R' and on whether the C(O) group is alkylated or protonated. The energy differences between the neutral metallacycle isomers must not be large; which particular isomer obtained is influenced by steric and electronic factors of the alkyne. Alkylation or protonation of the C(O) group clearly favors the molybdenacycle or tungstenacycle isomer over nickelacycle species, irrespective of the nature of the alkyne, but we are unable to come up with a convincing explanation why this is so. However, some comments on the rearrangement process are in order.

Complexes of type **5'** and those formed by disubstituted alkynes [NiCp* $\{\mu\text{-}\eta^2(1,3\text{-}N\eta), \eta^2(1,2\text{-}M)C(R)C(R')C(O)\}M(CO)_2Cp'$] (Ni–M), whose cores contain NiC(R)C(R')C(O) metallacycles π -complexed to the group 6 metal, can be considered to be *nido*-octahedra with the NiC₃ ring forming the basal plane and group 6 metal in the apical position. The molybdena- or tungstenacycle species of types **6**–**8** can also be regarded as *nido*-octahedral species with the nickel atom now in the apical position. The rearrangement of the *nido*-octahedral species C₅H₅⁺ has been predicted to take place via a C_{4v} → C_s → C_{2v} → C_s → C_{4v} pathway.³² In fact this mechanism has been proposed to occur in various metal alkyne cluster species with M₃C₂ cores.³³ Indeed, the complex OsW₂(CO)₇(μ -PhC₂Ph)Cp₂ has been crystallized with either a tungsten atom or the osmium atom as the capping apical metal,³⁴ the orientation of the alkyne C₂ fragment relative to the OsW₂ triangle has been the subject of an extended Hückel MO investigation.³⁵

The rearrangements on the alkylation or protonation of nickelacycle species observed here and seen earlier²⁴ are topologically similar to those discussed above but involve M₂C₃, and not M₃C₂, core structures. Complexes of type **4** can be considered to be intermediates in the rearrangement of a group 6 metal capped *nido*-core octahedral geometry to a similar *nido*-octahedral core structure the nickel atom in the apical position.³⁶

Experimental Section

(a) General Techniques. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk tube techniques and flame-dried glassware. Reagent grade chemicals were used. Solvents were purified as follows: toluene, hexanes, tetrahydrofuran (THF), and diethyl ether were distilled from blue or purple Na/benzophenone ketyl solutions; methylene chloride was distilled over CaH₂ under a nitrogen atmosphere, and reagent grade acetone was stored over 4 Å molecular sieves and deoxygenated by bubbling nitrogen through it immediately prior to use. Deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere and were subjected to three freeze/thaw degassing cycles prior to use.

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The heterodinuclear species NiCp*M(CO)₃(C₅H₄R) (Ni–M) were prepared according to published procedures.³⁷ The alkynes PhC₂H and HC₂H were purchased from Aldrich and were used as received. Trimethylxonium tetrafluoroborate (Aldrich) was stored in an oven-dried Schlenk tube under an atmosphere of nitrogen and was rinsed with several portions of dry CH₂Cl₂ immediately prior to use.

(b) Spectroscopic Measurements. IR spectra were obtained on an IBM IR-32 FT spectrometer: the solvent-subtract function for solution spectra. Mass spectra were obtained on JEOL JMS-AX505 HA or Finnegan-Matt mass spectrometers. Low-resolution spectra were obtained using chemical ionization (CI), with isobutane as the ionization source; high-resolution spectra employed electron impact (EI) ionization and PFK as a standard. All low-resolution spectra were compared with calculated isotopomer patterns. The ¹H and ¹³C NMR spectra were recorded on a G.E. GN-300 instrument at 300 and 75 MHz, respectively, in chloroform-*d*₁; Cr(acac)₃ (~0.01 M) was added to the ¹³C NMR samples as a shiftless relaxation agent.

(c) Syntheses of Complexes NiCp*($\mu\text{-}\eta^2, \eta^2\text{-PhC}_2\text{H}$)M(CO)₂Cp' (3**) and NiCp*($\mu\text{-}\eta^1, \eta^3\text{-C(O)C(Ph)C(H)}$)M(CO)₂Cp' (**4**).** The preparation of the Ni–Mo derivatives (**3a**, **4a**) and Ni–W derivatives (**3b**, **3b'** and **4b**, **4b'**) followed similar methods. The preparation of **3b'** and **4b'** is given as a typical example. Complex **2'** (~200 mg, 0.37 mmol) was dissolved in CH₂Cl₂ (15 mL), and the solution was cooled to –78 °C. Phenylacetylene (0.05 mL, 0.45 mmol) was added, and the reaction mixture was allowed to warm to room temperature over a 2 h period. The mixture was then separated by chromatography. Complex NiCp*($\mu\text{-}\eta^2, \eta^2\text{-PhC}_2\text{H}$)W(CO)₂Cp' (Ni–W, **3b'**) eluted with a hexane/diethyl ether (14:1) mixture and was isolated as an orange-brown solid (41 mg, ~17%). The metallacyclic species NiCp*($\mu\text{-}\eta^3(N\eta), \eta^1(1\text{-}W)C(H)C(Ph)C(O)$)-W(CO)₂Cp' (Ni–W, **4b'**) eluted with a hexane/ether (5:1) mixture and was isolated as dark brown crystals (90 mg, ~37%). Elution with MeOH gave a third band. After removal of most of the methanol, addition of diethyl ether and filtration afforded NiCp*($\mu\text{-}\eta^2(1,3\text{-}N\eta), \eta^2(1,2\text{-}W)C(Ph)C(H)C(O)$)-W(CO)₂Cp' (Ni–W, **5'**) as a brown powder (18 mg, ~7%). Analogs to complex **5'** were not observed with the Cp derivatives **1** or **2**.

For the Ni–Mo complexes **3a** and **4a**, less of the bridging alkyne compound **3a** was obtained (**3a**:**4a** = 1:8). To obtain sufficient quantities of **3a** for characterization, **4a** (100 mg) was dissolved in THF (20 mL) and the solution was brought to reflux. After 5 h, the solvent was removed under reduced pressure, and the product was chromatographed. A single orange band was eluted with a hexanes/ether (5:1) mixture. Crystallization from a concentrated hexanes solution at –20 °C afforded orange needles of (54 mg, 59%). Anal. Found (Calcd) for **4a**, NiMoC₂₆H₂₆O₃: C, 57.71 (57.67); H, 4.84 (4.98). MS data. **3a**: 514 (M⁺), 486 (M – CO)⁺, 458 (M – 2CO)⁺, 356 (M – 2CO – PhC₂H)⁺. HRMS: calcd for NiMoC₂₅H₂₆O₂, 514.0340; found, 514.0333. **3b**: 600 (M⁺), 572 (M – CO)⁺, 544 (M – 2CO)⁺, 442 (M – 2CO – PhC₂H)⁺. HRMS: calcd for NiWC₂₅H₂₆O₂, 600.0795; found, 600.0789. **3b'**: Anal. Found (Calcd) for NiWC₂₆H₂₈O₂: C, 50.81 (50.77); H, 4.59 (4.59). **4a**: 514 (M – CO)⁺, 486 (M – 2CO)⁺, 458 (M – 3CO)⁺.

Synthesis of NiCp*($\mu\text{-}\eta^3(N\eta), \eta^1(1\text{-}Mo)C(H)C(H)C(O)$)-Mo(CO)₂Cp' (Ni–Mo, **4c).** **1'** (~250 mg, ~0.55 mmol) was dissolved in CH₂Cl₂ (15 mL) and chilled to –78 °C. The cold Schlenk tube was evacuated, and an atmosphere of ethyne was introduced. The reaction mixture was allowed to stir at this temperature for 30 min and then slowly warmed to 0 °C. The solvent was removed under reduced pressure at this temperature leaving **4c'** as dark brown oily solid. Analysis of the crude mixture by ¹H NMR spectroscopy showed that, within the experiment's detection limits, **4c'** was the only product detected from this reaction (>90%). Anal. Found (Calcd) for NiMoC₂₁H₂₄O₃: C, 52.50 (52.65); H, 5.05 (5.03).

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Alkylation of Metallacycles. Synthesis of $[\text{NiCp}^*\{\mu\text{-}\eta^2\text{-}\eta^3\text{-C(OMe)C(R)C(R')}\}\text{M(CO)}_2\text{Cp}']^+\text{BF}_4^-$ (Complexes 6). Methylation of the metallacycles with $\text{Me}_3\text{O}^+\text{BF}_4^-$ followed similar methods used to prepare $[\text{NiCp}^*\{\mu\text{-}\eta^2\text{-}\eta^3\text{-C(OMe)C(R)C(R')}\}\text{M(CO)}_2\text{Cp}']^+\text{BF}_4^-$ ²⁴ and proceed in virtually quantitative yield. By using 2–3 equiv of the alkylating agent, the reaction time can be reduced to 2–3 h from the normal 5 h. However, this necessitates a filtration step to remove unreacted $\text{Me}_3\text{O}^+\text{BF}_4^-$. MS data, (*m/e*): **6a**, 458 ($\text{M} - 2\text{CO} - \text{MeO}$)⁺, 356 ($\text{M} - 2\text{CO} - \text{MeO} - \text{PhC}_2\text{H}$)⁺. **6c'** (CI, with isobutane): 496 (M^+ and $\text{M} + \text{H}^+$).

Protonation of Synthesis of $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^1(1\text{-W})\text{C(H)C(Ph)C(OH)}\}\text{W(CO)}_2\text{Cp}']^+\text{BF}_4^-$ (Ni–W, 7) and $[\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^1(1\text{-Mo})\text{C(H)C(Ph)C(OH)}\}\text{Mo(CO)}_2\text{Cp}']^+\text{BF}_4^-$ (Ni–Mo, 7). Both 7' and 7 were prepared similarly. The synthesis of the better characterized 7' is given here. **4b'** (150 mg, 0.23 mmol) was dissolved in ether (30 mL) and cooled to 0 °C. An excess of HBF_4 (~3–4 equiv) was added via a pipet, prompting immediate and complete precipitation of a dark red solid. After allowing the precipitate to settle, the (colorless) solvent was removed via syringe. Sequential rinsings with ether (3 × 5 mL) were also colorless. Residual ether was evaporated under reduced pressure, leaving a red-black powder. The ¹H NMR analysis of the product showed exclusive (>95%) formation of 7'.

Synthesis of $\text{NiCp}^*\{\mu\text{-}\eta^2(1,3\text{-Ni}),\eta^3(\text{W})\text{C(OMe)C(R)C(R')}\}\text{MI(CO)Cp}''$ (Ni–M, Complexes 8). The preparation of **8a**, **8b'**, and **8c'** followed similar procedures, and the synthesis of **8a** is given as a typical example. A Schlenk tube was charged with **6a** (105 mg, 0.18 mmol), ⁿBu₄N⁺I[−] (67 mg, 0.18 mmol), and Me₃NO (17 mg, 0.22 mmol). The mixture was dissolved in 30 mL of CH₂Cl₂, and the solution was allowed to stir at reflux temperature for 30 min, during which time the color of the solution changed from brown to red. The solution was concentrated and the mixture was filtered and subjected to chromatography. Elution with hexane/CH₂Cl₂ (2:1) gave a single, slow-moving red band. Concentrating the solution and cooling to −20 °C gave **8a** as reddish-black crystals (yield after crystallization 90 mg, 82%). Yields of **8b'** and **8c'** were similar, with brownish-red **8b'** (W) differing in color from the red Mo derivatives. Crystals of **8b'** suitable for an X-ray diffraction study were grown from a CH₂Cl₂/hexane mixture at −20 °C. MS Data for **8c'** (CI using isobutane, *m/e*): 795 and 794 ($\text{M} + \text{H}^+$, M^+) (peaks overlap), 566 ($\text{M} - \text{CO}$)⁺.

(d) X-ray Diffraction Study of $\text{NiCp}^*\{\mu\text{-}\eta^3(\text{Ni}),\eta^2(1,3\text{-W})\text{C(H)C(Ph)C(OMe)}\}\text{W(CO)ICp}'$ (Ni–W, **8b').** A cube of **8b'** was mounted in a glass capillary tube in a random orientation on a Enraf Nonius CAD4 computer controlled κ

axis diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $21 < \theta < 23^\circ$. Systematic absences of $h0l$, $l = 2n$ and $0k0$, $k = 2n$ and the subsequent successful refinement indicated that the space group was $P2_1/c$ (No. 14). Lorentz, polarization corrections, and an empirical absorption correction³⁸ were applied.

The structure was solved using the SHELX-86 structure solution package. Remaining atoms were located in succeeding Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The structure was refined by using full-matrix least squares: the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w was defined as per the Killean and Lawrence method, with terms of 0.020 and 1.0.³⁹

Scattering factors were from Cromer and Waber.⁴⁰ Anomalous dispersion effects were included in F_c ;⁴¹ values for $\delta f'$ and $\delta f''$ were those of Cromer.⁴² The highest peak in the final difference Fourier had a height of 0.52 e/Å³, with an estimated error based on δF of 0.09.⁴³ All calculations were performed on a VAX computer using SDP/VAX software.⁴⁴

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Supporting Information Available: An ORTEP diagram and tables of structural data, positional parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and bond angles for all non-hydrogen atoms for **8b'** (14 pages). Ordering information is given on any current masthead page. Calculated and observed structure factor listings are available from the authors on request.

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