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Reactions of Mixed-Metal Complexes with Alkynes: Synthesis and Structural Characterization of the Complexes $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)_2]$ and $[NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$

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The mixed-metal complexes $[NiM(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ (M = Cr, R = H; M = Mo, W; R = H, Me) react with a variety of alkynes at ambient conditions affording "dimetallatetrahedrane" type complexes which have been characterized by IR, MS, and ^1H NMR and in some cases by ^{13}C NMR spectroscopy. These complexes exhibit dynamic behavior on the NMR time scale. The structure of $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)_2]$ (**3a**) has been determined through an X-ray diffraction study. **3a** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.224$ (1) Å, $b = 21.151$ (4) Å, $c = 17.629$ (3) Å, $\beta = 90.56$ (1)°, $V = 3066.4$ Å^3, and $Z = 8$. In contrast to the NiCr and all but one reaction involving the NiW starting complexes, the NiMo species $[NiMo(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ (R = H, Me) react with most alkynes yielding, in addition to complexes analogous to **3a**, unusual species containing a nickelacyclobutenone ring π-bonded to the molybdenum. The structure of the complex $[NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**4a′**) was determined through X-ray crystallography. **4a′** forms purple-red monoclinic crystals belonging to space group $P2_1/c$ (No. 14) with lattice dimensions $a = 9.075$ (2) Å, $b = 12.416$ (3) Å, $c = 14.873$ (3) Å, $\beta = 97.72$ (1)°, $V = 1660.6$ Å^3, and $Z = 4$. Thermolysis of **4a′** affords the corresponding alkyne complex $[NiMo(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**2a′**) in quantitative yield.

Introduction

Binuclear mixed-metal complexes are currently under investigation by a number of research groups[1] because of their relevance to heterogeneous catalysis and their potential in activating small organic substrates. Our group has been interested in the chemistry and reactions of binary heteronuclear complexes containing metal–metal bonds. The different electronic and steric requirements of each metal often lead to synergistic activating effects and enhanced reactivity patterns of organic molecules bound to the two metals. The work presented here describes some chemistry of simple heterobimetallic complexes containing a Ni–group 6 metal–metal bond. A preliminary account of some aspects of the work has already appeared.[2]

Results

Reaction of the NiCr complex $[NiCr(CO)_4(\eta\text{-}C_5H_5)_2]$[3] (**1**) with 2-butyne or 2-pentyne afforded the mixed-metal alkyne-bridged complexes $[NiCr(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2R)(\eta\text{-}C_5H_5)_2]$ (**1a**, R = Me; **1b**, R = Et) in high yield as given by eq 1. Complexes **1a** (red) and **1b** (purple) were purified

$$NiCr(CO)_4(\eta\text{-}C_5H_5)_2 + RC{\equiv}CR' \rightarrow NiCr(CO)_2(\mu\text{-}RC{\equiv}CR')(\eta\text{-}C_5H_5)_2 + 2CO\uparrow \quad (1)$$

$$RC_2R' = MeC_2Me,\ MeC_2Et$$

by chromatography on alumina and recrystallized from hexane. The complexes are air-sensitive in solution but are stable in the solid state for a few weeks in air at −20 °C. Both compounds are fairly stable thermally and may be sublimed, with partial decomposition at 80–90 °C and 10^{-3} mmHg. The complexes each show two $\nu(CO)$ stretching bands in the IR at terminal and semibridging frequencies.

Table I. Numbering Scheme Used for Complexes

complex	M Cr	 Mo	 W
$NiM(CO)_4(\eta\text{-}C_5H_5)_2$	1	2	3
$NiM(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$		2′	3′
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)_2$	1a	2a	3a
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$		2a′	3a′
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Et)(\eta\text{-}C_5H_5)_2$	1b	2b	3b
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Et)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$		2b′	3b′
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta\text{-}C_5H_5)_2$		2c	3c
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$		2c′	3c′
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$		2d′	3d′
$NiM(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeCO_2C_2CO_2Me)(\eta\text{-}C_5H_5)_2$			3e
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)_2$		4a	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)$		4a′	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Et)C(O)\}(\eta\text{-}C_5H_5)_2$ (isomer A)		4b	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Et)C(Me)C(O)\}(\eta\text{-}C_5H_5)_2$ (isomer B)		4b	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Et)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)$ (isomer A)		4b′	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Et)C(Me)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)$ (isomer B)		4b′	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(H)C(O)\}(\eta\text{-}C_5H_5)_2$		4c	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(H)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)$		4c′	
$NiM(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)$			5d′

The analogous NiW complexes $[NiW(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ (**3**, R = H; **3′**, R = Me) react similarly with a variety of alkynes yielding complexes analogous to **1a** and **1b**, listed in Table I. The complexes $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}R'C_2R'')(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ [R = H, $R'C_2R''$ = MeC_2Me (**3a**), MeC_2Et (**3b**), PhC_2H (**3c**), PhC_2Ph (**3d**), $MeO_2CC_2CO_2Me$ (**3e**); R = Me, $R'C_2R''$ = MeC_2Me (**3a′**), MeC_2Et (**3b′**), PhC_2H (**3c′**) PhC_2Ph (**3d′**)] are all red to reddish brown and yield observable molecular ions in the

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(1) Some recent examples include (a) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68–74. (b) Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1418–1425. (c) Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1222–1225 references cited therein. (d) Carey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218–1220. (e) Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1980**, *1609*–1614. (f) Chetcuti, M. J.; Green, M.; Jeffery, J. C.; Stone, F. G. A.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, *948*–949. (g) Ashworth, T. V.; Berry, M., Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 45–46. (h) Geoffroy, G. L.; Roberts, D. A. *Comprehensive Organometallic Chemistry*; Pergammon: Oxford, 1982; Vol. 6, Chapter 40, p 763 contains a good review of heterometallic chemistry.

(2) A preliminary communication on some aspects of this work has appeared: Azar, M. C.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7209–7210.

(3) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675–2685.

0276-7333/87/2306-2298$01.50/0

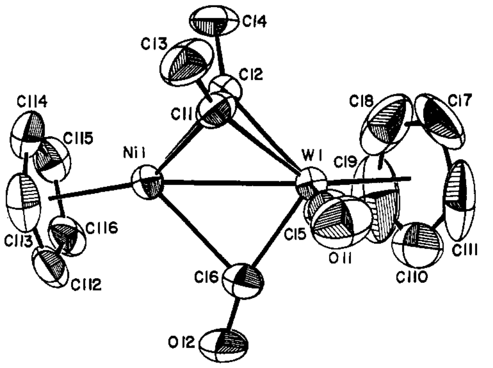

Figure 1. An ORTEP view of $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)_2$ (**3a**) giving the atom numbering scheme used in the tables. The 50% probability level ellipsoids are shown. (Molecule 1, of the two independent molecules, was arbitrarily chosen.)

mass spectrum, with the correct isotopic envelope for the combination of a single nickel atom with a single tungsten atom, together with $(M - CO)^+$, $(M - 2CO)^+$, $(M - R'C_2R'')^+$, and $(M - 2CO - R'C_2R'')^+$ ions.

Reaction of the NiMo complexes $[NiMo(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)]$ (**2**, R = H; **2′**, R = Me) with 2-butyne yielded in each case a varying mixture of two products whose ratio depended in part on the reaction time. One of the two products in each case was the NiMo alkyne-bridged complexes **2a** and **2a′**, analogous to the NiCr and NiW complexes **1a**, **3a**, and **3a′**. IR, NMR, and MS data for complexes **2a** and **2a′** indicated that these compounds were similar to the NiCr and NiW species referred to earlier. In contrast, however, reaction of the NiMo complex **2** with $MeO_2CC_2CO_2Me$ resulted in decomposition—no NiMo alkyne-bridged complex could be obtained with this alkyne.

^1H NMR data for all these alkyne-bridged species exhibited a singlet for the nickel-bound C_5H_5 ring protons and a singlet or multiplet for the group 6 bound C_5H_5 or C_5H_4Me protons. Complexes derived from symmetrical alkynes such as MeC_2Me or PhC_2Ph revealed only one set of alkyne resonances in the ^1H NMR at ambient temperatures. This indicates the existence of an effective mirror plane in the molecule or alkyne rotation about an axis perpendicular to the metal–metal bond.

In order to establish the structure of these complexes, an X-ray diffraction study of $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)_2]$ (**3a**) was undertaken. **3a** crystallizes with two crystallographically independent molecules in the unit cell. The two molecules are similar but not identical. As the molecule is chiral and the space group $P2_1/c$ is not, each complex is present as a racemic mixture in the crystal. An ORTEP diagram of **3a** is shown in Figure 1.

In each molecule the two metal atoms are bridged by the 2-butyne which is positioned perpendicular to the metal–metal vector, resulting in a structure with a "dimetallatetrahedrane" type core. The Ni–W distances of 2.624 (1) and 2.628 (1) Å are close to the values of 2.582 (1) and 2.586 (1) Å found in the molecule $[NiW_2(\eta\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[4] Values averaging 3.10 Å were found[5] in the cluster anion $[Ni_3W_2(CO)_{16}]^{2-}$, but these fairly long distances have been taken to reflect the electron-deficient nature of these bonds.

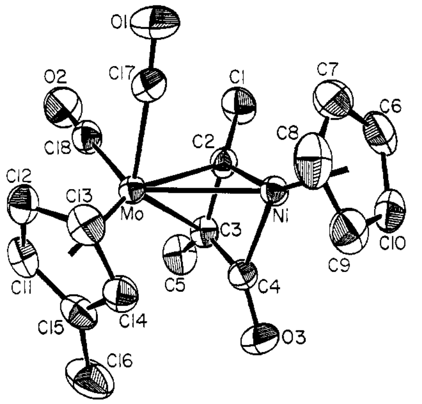

Figure 2. An ORTEP diagram of $NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**4a′**), at the 50% ellipsoid probability level. The view shown is perpendicular to the metal-metal bond and shows the atomic numbering scheme.

Both molecules contain two carbonyl ligands bound to the tungsten atom, one of which (in each case) is semibridging to the nickel atom. The only significant difference between the two molecules lies in bond lengths and angles associated with the semibridging ligand, which in both cases is approximately on the opposite side of the Ni–W bond from the acetylene. While the W(n)–C(n6)–O(n2) angles (n = 1 or 2) are not significantly different, averaging about 163.5°, the Ni(n)–C(n6) distances are 2.266 (8) and 2.357 (7) Å, respectively, a difference of ca. 0.09 Å, well above the estimated standard deviation. This real but minor difference may be the result of intermolecular forces influencing the relatively weak Ni–C interaction.[6] However, the W–C (semibridging CO) distances in the two independent molecules are the same, within experimental error, as are the W–C (acetylenic carbon) distances in both molecules.

The alkyne lies close to perpendicular to the Ni–W bond, with all Ni–acetylenic carbon atom distances (equal within experimental error) averaging to 1.949 (6) Å.[7] The two acetylenic carbon–tungsten atom distances are distinct for each molecule averaging at 2.156 (7) and 2.088 (7) Å. The cyclopentadienyl group bound to the tungsten atom in one of the molecules is slightly disordered. Other bond lengths and angles in the molecule are unremarkable.

In most cases, for the reactions involving the NiMo complexes **2** and **2′** with alkynes, a second product was also obtained appearing as an orange-brown slow-moving band on the alumina column. The alkynes used with **2** and **2′** were 2-butyne, 2-pentyne, phenylacetylene, and diphenylacetylene. IR studies of hexane solutions or Nujol mulls of solid samples showed three ν(CO) bands in the carbonyl region of the IR spectrum. Two of these bands are indicative of terminal CO stretching frequencies (>1900 cm^{-1}) while the third band was observed at $\sim$1650 cm^{-1}, lower than many bridging and even triply bridging carbonyl bands and ranging in the ketonic and acyl region. Mass spectra of complexes **4a**, **4a′**, **4b**, and **4b′** are almost identical with those of their corresponding alkyne complexes **2a**, **2a′**, **2b**, or **2b′**. However, the ^1H NMR spectrum of these complexes reveals that for the 2-butyne complex **4a** the alkyne methyl protons resonate at δ 1.27 and 2.70.

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(4) Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1981, 763–770.

(5) Ruff, J. K.; White, R. P.; Dahl, L. F. *J. Am. Chem. Soc.* 1971, *93*, 2159–2176.

(6) Atom O(12) experiences four intermolecular contacts less than 4.0 Å, the closest being 3.39 Å, whereas atom O(22) only has two such contacts of 3.66 and 3.99 Å.

(7) Ni–C distances average 1.911 Å in the complex $CoNi(CO)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)$,[8] 1.884 Å in the Ni_2 complex $Ni_2(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2$,[9] and 1.898 Å in the complex $FeNi(CO)_3(\mu\text{-}HC_2PPh_3)(\eta\text{-}C_5H_5)$.[10]

(8) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyres, K. G. *Inorg. Chem.* 1980, *19*, 693–696.

(9) Wang, Y.; Coppens, P. *Inorg. Chem.* 1976, *15*, 1122–1127.

(10) Yasufuku, K.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* 1975, *84*, C28–C30.

Two alkyne methyl resonances are also observed in complex **4a′**. The ^{1}H NMR spectrum reveals that the 2-pentyne derived complex **4b** exists as a mixture of isomers in a ~1:1 ratio. Repeated attempts at separating these isomers by column chromatography or fractional crystallization were unsuccessful: separation was ultimately achieved by centrifugal chromatography. **4b′** also exists as an isomeric mixture in an approximately 2:1 ratio.

As the structure of these complexes was unclear from spectroscopic data, an X-ray diffraction study of **4a′** was undertaken. An ORTEP view is shown in Figure 2.

The molecule contains a Ni–Mo bond[11] of 2.5859 (2) Å bridged by an unusual three carbon chain, *C*(2)Me–*C*(3)-Me–*C*(4)O3. Carbon atoms C(2) and C(4) σ-bond to the nickel atom forming a nickelacyclobutenone ring which can be considered to π-bond to the molybdenum atom using carbon atoms C(2) and C(3). No strong bonding interaction occurs between carbon atom C(4) and the molybdenum atom [Mo···C(4) = 2.661 Å]. Atoms C(2), C(3), C(4), and Ni form a slightly puckered four-membered ring,[14] and the molybdenum atom is positioned in the projection of the triangle defined by Ni, C(2), and C(3) and away from C(4). The Mo–C(2) and Mo–C(3) distances are significantly different [Mo–C(2) = 2.179 (2) Å; Mo–C(3) = 2.290 (2) Å]. As occurs in the three other complexes of this type that have been structurally characterized,[15] the longest M–C(R) π-bond in the C(R)–C(R)–C(O) system is always that to the carbon atom adjacent to the carbonyl group.

Some multiple-bond character is present in the NiC_3 ring. The Ni–C(2) and Ni–C(4) distances are close to equal and average 1.920 (8) Å, in the range found for other Ni–C σ-bonds. However, the C(2)–C(3) and C(3)–C(4) distances are identical within their estimated standard deviations, and their value of 1.437 (2) Å is shorter than a normal C–C single bond length. The substituents on carbon atoms C(2), C(3), and C(4) all bend back out of the NiC_3 plane, away from the molybdenum atom. The two carbonyl ligands on the molybdenum atom are both terminal.

The mixture of isomers constituting **4b** now becomes clear. In one of the isomers, the C(Me) group of the pentyne is bonded to the nickel atom with the C(Et) group linked to the carbonyl group. In the other isomer, the linkage of the alkyne fragment to the CO and nickel atom is reversed.

Initial experiments suggested that only the nickel–molybdenum carbonyl species **2** and **2′** form nickelacyclobutenone complexes typified by **4a**, **4a′**, or the **4b** and **4b′** mixtures. However, reaction of diphenylacetylene with the nickel–tungsten complex **3′** afforded the NiW alkyne complex $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**3d′**) and also the complex $[NiW(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**5d′**) which was characterized by ^{1}H NMR and IR spectroscopy. Reaction of **2** with phenylacetylene afforded **2c** together with **4c**. Only a *single* isomer of **4c** was obtained. **2′** exhibits identical behavior.

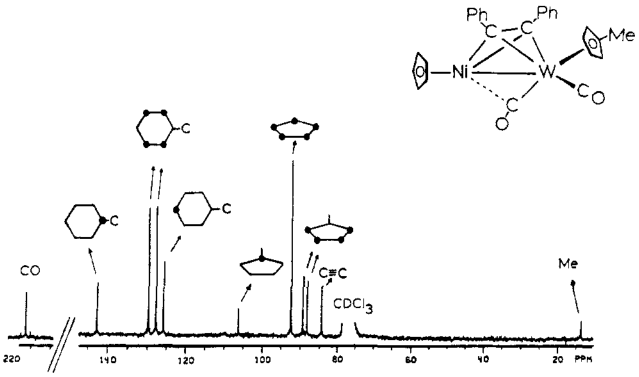

Figure 3. ^{13}C NMR spectrum of $[NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**3d′**) at 25 °C. Note that only one set of resonances is observed for the Ph groups and three resonances, instead of five, are exhibited by the C_5H_4Me ring carbon atoms. The two carbonyl groups and the acetylenic carbons give rise to one resonance each.

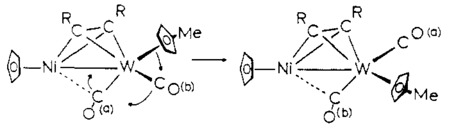

Figure 4. Fluxional process believed to be occurring in the alkyne-bridged molecules, creating an effective mirror plane for species bridged by symmetric alkynes.

All the nickelacyclobutenone complexes isolated slowly lose CO when allowed to stand in solution at ambient temperatures affording CO and their corresponding alkyne complexes. Decomposition also occurs, in the solid state, and becomes rapid at elevated temperatures. Samples of these compounds appear to keep for weeks however, when stored at −20 °C. In only one case is a weak molecular ion observed in the mass spectrometer—for all other species the molecular ion is not seen, and the highest mass peak corresponds to the $(M - CO)^+$ ion.

For all but one of these complexes, CO loss to form the alkyne complex is irreversible. In one case however, loss of CO from complex **4a** to generate **2a** is reversed by bubbling CO through solutions of **2a** in toluene at 25 °C overnight. Attempts to react other alkyne complexes with CO led to no cyclobutenone ring formation. Subtle steric and electronic factors which we do not fully understand appear to govern the formation of the cyclobutenone ring from the alkyne complex. Under our experimental conditions, even the methylcyclopentadienyl complex **2a′** does not react with carbon monoxide.

Discussion

As alluded to earlier, the ^{1}H NMR spectra of complexes containing symmetric alkynes exhibit only one set of resonances for the alkyne substituents and an AA′BB′ or AA′XX′ pattern for aromatic C_5H_4Me resonances, indicating the presence of an effective mirror or alkyne rotation in the molecule at ambient temperatures. For the complex $NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**3a′**), exactly the same spectrum is observed at −95 °C indicating that even at this low temperature, an effective mirror plane is still present. Data from ^{13}C NMR experiments parallel those of ^{1}H NMR. Complex **3d′** for example exhibits only one carbonyl resonance, four (not eight) phenyl resonances, one acetylenic carbon peak and three ring carbon signals

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[11] Ni–Mo = 2.651 and 2.557 Å in the complex $MoNi_2(\mu_3\text{-}CPh)(CO)_2(\eta\text{-}C_5H_5)_3$,[12] 2.622 Å in the related complex $CoMoNi(\mu_3\text{-}CMe)(CO)_5(\eta\text{-}C_5H_5)_2$[12] and 2.616 Å in the alkyne-bridged species $FeMoNi(CO)_5(\mu\text{-}PhC_2CO_2\text{-}i\text{-}Pr)(\eta\text{-}C_5H_5)_2$.[13]

[12] Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409–2422.

[13] Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123–1130.

[14] The angle between the planes defined by Ni, C(2), C(3) and Ni, C(3), C(4) is 171°.

[15] Structurally characterized complexes of this type include $Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2,\eta^2\text{-}C_2(CF_3)_2C(O)\}(\eta\text{-}C_5Me_5)_2$,[16] $W_2(CO)_4\{\mu\text{-}\eta^2,\eta^2\text{-}C_2(CO_2Me)_2C(O)\}(\eta\text{-}C_5H_5)_2$,[17] and the platinum complex $Pt_2\{\mu\text{-}\eta^2,\eta^2\text{-}C_2Ph_2C(O)\}(\eta\text{-}C_5H_5)_2$.[18]

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[17] Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783–1788.

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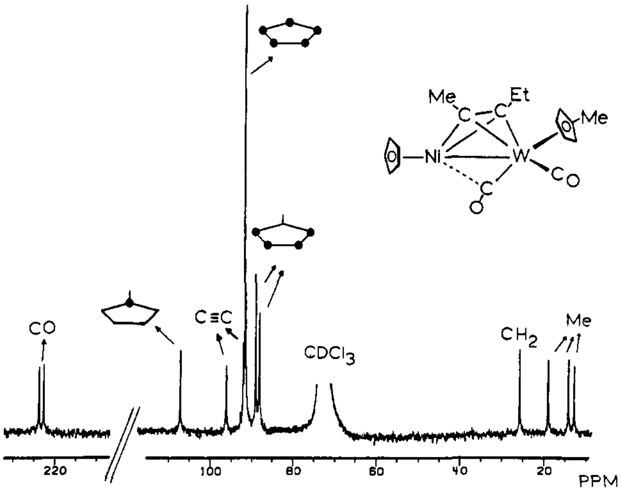

Figure 5. ^{13}C NMR spectrum of [NiW(CO)$_2$(μ-η^2,η^2-MeC$_2$Et)-(η-C$_5$H$_5$)(η-C$_5$H$_4$Me)] (**3b′**). Two CO resonances are observed. Of the five ring carbon resonances for the C$_5$H$_4$Me group, two are fortuitously coincident.

for the methylcyclopentadienyl group at ambient temperatures (see Figure 3).

We believe that CO exchange rather than formal alkyne rotation about an axis perpendicular to the metal–metal bond is occurring. Rotation of the M(CO)$_2$(η-C$_5$H$_4$Me) entity about the M–Ni bond (equivalent to semi-bridge–terminal CO exchange) would result in the molecule having a time-averaged mirror plane (see Figure 4). Dynamic behavior of this type is believed to occur in the homometallic alkyne-bridged species M$_2$(CO)$_4$(μ-R′C$_2$R″)(η-C$_5$R$_5$)$_2$ (M = Mo, W) and is known to be a facile, low-energy process.[19,20]

Alkyne rotation has been predicted to have a high activation energy[21] and experimental evidence[22] for this in related molecules with sterically hindered and electron-withdrawing alkynes suggests that this is indeed the case. Whereas alkyne rotation on its own would not generate mirror symmetry in the molecule, we cannot rule out its occurrence in conjunction with the carbonyl dynamic exchange for symmetrical alkynes.

NMR data on complexes formed from unsymmetrical alkynes at ambient temperatures, however, eliminate alkyne rotation as a component of CO exchange. The ^{1}H NMR spectrum of NiW(CO)$_2$(μ-η^2,η^2-MeC$_2$Et)(η-C$_5$H$_5$)(η-C$_5$H$_4$Me) (**3b′**), for example, exhibits an ABCD type spectrum for the aromatic C$_5$$H_4$Me resonances and an ABX$_3$ type spectrum for the Et group resonances. Similar conclusions can be drawn from the ^{13}C NMR spectrum, where the C_5H$_4$Me group shows five ring carbon resonances. Two carbonyl resonances are now observed (see Figure 5); formal rotation of the W(CO)$_2$(η-C$_5$H$_4$Me) group about the Ni–W vector will never cause the CO groups in the now chiral molecule to become equivalent without concurrent alkyne rotation.

The ^{1}H NMR spectrum of **3b′** has been studied at temperatures of up to +95 °C. No changes in the spectrum are observed suggesting that no alkyne rotation occurs at this temperature on the NMR time scale.

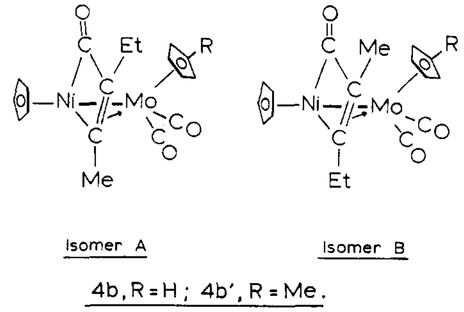

Figure 6. The structure of the mixture of isomers A and B for both **4b** and **4b′**.

In contrast to the dynamic NMR behavior exhibited by the alkyne complexes, the nickelacyclobutenone compounds are not fluxional at ambient temperatures. Two resonances are observed for the alkyne-derived Me protons in complexes **4a** and **4a′** in the ^{1}H NMR spectrum. The two terminal carbonyl groups resonate in the 225–235 ppm range in the ^{13}C NMR spectrum and are always distinct. The metal-bound ring C=O group appears in the δ 170–180 range, typical of an organic ketone, and not of an acyl or a metal carbonyl group. The nondynamic behavior of complexes **4a** and **4a′** contrasts with that shown by the complexes containing a bridging C(O)C(R)C(R) ligand synthesized by Knox and co-workers.[17,23] The complex W$_2$(CO)$_4${μ-η^2,η^2-C(O)C$_2$(CO$_2$Me)$_2$}(η-C$_5$H$_5$)$_2$ exhibits[17] an unusual fluxional process appearing to involve an oscillation of the bridging ligand between the two metals with retention of the alkyne–carbonyl carbon link. The Fe$_2$ and Ru$_2$ species M$_2$(CO)(μ-CO){μ-σ:η^3-C(O)C(R^1)C(R^2)}(η-C$_5$H$_5$)$_2$ which contain *five*-membered MC(O)C(R^1)C(R^2)M rings also are fluxional,[23] undergoing synchronous carbonyl "insertion" into, and elimination from, the dimetallacycle. Both these complexes are homodinuclear. A fluxional process analogous to that occurring in the ditungsten complex W$_2$(CO)$_4${μ-η^2,η^2-C(O)C$_2$(CO$_2$Me)$_2$}(η-C$_5$H$_5$)$_2$ in our system would lead to the bridging ligand being σ-bonded to the molybdenum atom and π-bonded to the nickel atom, and we have never observed any evidence for this isomer.

We do not fully understand the factors that affect the ease of formation and the stability of the nickelacyclobutenone complexes we have synthesized. While the metallacycle complexes do lose CO slowly forming their corresponding alkyne complexes, we do not believe that this is the major pathway to the alkyne species. We[24] are currently investigating the kinetics of the reaction of **2′** and **3′** with alkynes, and it appears that the alkyne complexes and their corresponding metallacycles are formed independently. The rate of decomposition of the metallacycles we have isolated appears to be too slow to account for the quantities of alkyne complexes isolated in the reaction time period. While NiC$_3$ ring systems are formed for both 2-butyne and 2-pentyne only with the NiMo complexes, diphenylacetylene yields these species with *both* the NiMo and the NiW mixed-metal compounds—the only NiW species of this type isolated. The steric effect and the slightly electron-withdrawing effect of the phenyl groups may increase the stability of the metallacycle.[25] For unsymmetrical alkynes steric effects appear to control the relative ratio of isomers obtained for the metallacyclobutenone rings. For 2-pentyne, a ratio close to 1:1 is ob-

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[22] Jaouen, G.; Marinetti, A.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 225–227.

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[24] Chetcuti, M. J.; Green, K. A., to be submitted for publication.

[25] It is interesting that all the hitherto synthesized and structurally characterized complexes of this type are derived from electron-withdrawing alkynes [C$_2$(CF$_3$)$_2$, C$_2$(CO$_2$Me)$_2$, or C$_2$Ph$_2$].

tained for the isomeric mixture **4b** (see Figure 6); the methylcyclopentadienyl complex **4b′** occurs in a 2:1 isomeric mixture. However, only one isomer of **4c′**, derived from phenylacetylene is obtained; spectroscopic data suggest it contains a C(Ph)C(H)C(O) linkage.

It is also unclear to us why the isomeric bonding mode consisting of a molybdenacyclobutenone MoC_3 ring π-bonded to the nickel atom (as opposed to the nickelacyclobutenone complexes π-bonded to the molybdenum atom) is never observed in the complexes we have prepared. A carbonyl group within range to interact and relieve excess electron density on the nickel atom may be required in these molecules, and hence a NiC_3 group rather than a MoC_3 group is formed. In the alkyne complexes, excess electron density on the nickel atom and the absence of a directly bonded CO ligand may lead one of the carbonyl ligands on the molybdenum atom to semibridge to the nickel atom, relieving the metal of some excess electron density.

Conclusion

We have discovered an interesting difference between the chemistry of the molybdenum complexes and the chromium and tungsten complexes in the mixed-metal systems $NiM(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4R)$ and their reactions with alkynes. While all three group 6 metal complexes react to form bridging alkyne species, the nickel–molybdenum species also form nickelacyclobutenone complexes that lose CO (in one case reversibly). Further investigations into the chemistry of these metallacycles are in progress. The dynamic behavior of the alkyne complexes is also being studied in greater depth. Differences in the energy barrier of the dynamic process for the NiW and NiMo complexes appear to exist, with the molybdenum complexes having a higher activation energy, as is found in the homonuclear alkyne-bridged species $M_2(CO)_4(\mu\text{-}R'C_2R'')(\eta\text{-}C_5H_5)_2$ (M = Mo, W).[19]

Experimental Section

X-ray Data Collection. Specific X-ray data collection parameters for complexes **3a** and **4a′** are given in Table II. Other experimental details are outlined here.

Brownish red rectangular plates of **3a** were grown from a hexane solution at −20 °C. A crystal was mounted on a glass fiber with its long axis roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed at 23 ± 1 °C with Mo Kα radiation (λ = 0.71073 Å) on a Enraf-Nonius CAD4.

Cell constants were obtained from least-squares refinement of 25 reflections in the range 25.4° < 2θ < 29.8°, measured by the computer-controlled diagonal slit method of centering. The density of **3a** was measured by flotation in aqueous ZnI_2. From the systematic absences of $0k0$, $k = 2n$, and $h0l$, $l = 2n$, and from subsequent least squares refinement, the space group was determined to be $P2_1/c$ (No. 14).

The intensities of three representative reflections were measured every 60 min of X-ray exposure as a check on crystal and electronic stability. The structure was solved by direct methods[26] and developed with Fourier techniques. Corrections for absorption effects were made by using ψ-scan data.

Scattering factors were taken from Cromer and Waber,[27] and anomalous dispersion effects[28] were included in F_c. Values used were obtained from Cromer.[29] The residuals showed no unusual trends. Positional parameters of all non-hydrogen atoms and bond lengths and angles for each molecule are given in Tables III–V. The numbering of all the atoms in molecule 2 parallels that of molecule 1 except that the first digit of the atoms in molecule 2 is a "2". An ORTEP diagram of one of the two crystallographically distinct molecules (molecule 1) is shown in Figure 1.

Table II. X-ray Data Collection Parameters for 3a and 4a′

	3a	4a′
formula	$C_{16}H_{16}NiO_2W$	$C_{18}H_{18}MoNiO_3$
fw	482.86	436.99
F(000)	1840	880
crystal dimens, mm	0.10 × 0.20 × 0.30	0.20 × 0.30 × 0.40
ω width at half-height, deg	0.20	0.40
space group	$P2_1/c$	$P2_1/n$
a, Å	8.224 (1)	9.075 (2)
b, Å	21.151 (4)	12.416 (3)
c, Å	17.629 (3)	14.873 (3)
β, deg	90.56 (1)	97.72 (1)
V, Å^3	3066.4 (15)	1660.6 (10)
Z	8	4
d(calcd), g/cm^3	2.092 (d(obsd) = 2.092)	1.748 (d(obsd) = 1.701)
μ (Mo Kα), cm^{-1}	88.9	18.9
takeoff angle, deg	3.0	2.8
detector aperture	1.5 mm horizontal, 4.0 mm vertical	4.0 mm horizontal, 4.0 mm vertical
scan type	$\theta/2\theta$	$\theta/2\theta$
scan rate, deg/min (in ω)	2.0–4.0	1.0–4.0
scan width, deg	0.8 + 0.350 tan θ	1.2 + 0.350 tan θ
max 2θ, deg	54.9	63.7
no. of reflctns measd	8043 total, 6995 unique	7299 total, 5677 unique
corrections	linear decay (from 1.000 to 1.028 on I) empirical absorption (0.835–1.000 on I) reflection averaging (for 963 reflections) (agreement on I = 2.7%)	linear decay (from 1.000 to 1.031 on I) empirical absorption (0.89–1.031 on I) reflection averaging (for 731 reflections) (agreement on I = 1.7%)
hydrogen atoms	included as fixed contribution	located and refined isotropically
reflctns included $F(o)^2 > 3.0\sigma(Fo^2)$	4916	4342
parameters refined	361	280
unweighted residual factor	0.031	0.024
weighted residual factor	0.036	0.030
esd of observn of unit weight	1.06	1.30
convergence, largest shift	0.27σ	0.48σ
high peak in final diff map, e/Å^3	0.74 (14)	0.60 (7)

Data collection for **4a′** was carried out by using the same equipment and procedure as for **3a**. Data are tabulated in Table II. A deep purple parallelepiped of **4a′** grown from a saturated hexane solution at −20° was mounted in a random orientation on a glass fiber. A total of 25 reflections in the range 20° < 2θ < 30° were used to obtain the cell constants and orientation matrix. From the systematic absences of $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$, the space group was determined to be $P2_1/n$ (No. 14). Four representative reflections were monitored every 60 min, and a linear decay correction was applied.

ψ scans collected for six reflections between 5 and 24° in θ showed an average I_{min}/I_{max} of 90%. Absorption effects would

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(26) SDP-PLUS Software—see: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsvelt, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland 1978; pp 64–71.

(27) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(28) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(29) Reference 25, Table 2.3.1.

Table III. Positional Parameters and Their Estimated Standard Deviations for Complex 3a[a]

atom	*x*	*y*	*z*	*B*, Å^2
W1	0.08025 (3)	0.05552 (2)	0.77886 (2)	2.666 (5)
W2	−0.37530 (3)	−0.16414 (1)	0.93040 (2)	2.530 (5)
Ni1	0.2488 (1)	−0.02636 (4)	0.68728 (5)	2.57 (2)
Ni2	−0.2797 (1)	−0.27278 (4)	0.98774 (5)	2.64 (2)
O11	0.0765 (7)	−0.0361 (3)	0.9171 (3)	4.9 (1)
O12	0.4546 (6)	0.0736 (3)	0.7832 (3)	4.7 (1)
O21	−0.3788 (9)	−0.2180 (3)	0.7669 (3)	6.6 (2)
O22	−0.0002 (7)	−0.1808 (3)	0.9452 (4)	5.6 (2)
C11	0.0455 (8)	−0.0390 (3)	0.7358 (4)	3.0 (1)
C12	0.0167 (7)	0.0037 (3)	0.6816 (4)	2.8 (1)
C13	−0.011 (1)	−0.1052 (4)	0.7548 (5)	4.6 (2)
C14	−0.0858 (8)	0.0083 (4)	0.6115 (4)	4.1 (2)
C15	0.0848 (9)	−0.0020 (4)	0.8644 (4)	3.4 (2)
C16	0.3193 (8)	0.0578 (4)	0.7744 (4)	3.4 (2)
C21	−0.4853 (8)	−0.2292 (4)	1.0019 (5)	3.5 (1)
C22	−0.4830 (9)	0.2569 (3)	0.9334 (5)	3.7 (2)
C23	−0.593 (1)	−0.2306 (5)	1.0712 (5)	6.7 (2)
C24	−0.587 (1)	−0.3031 (4)	0.8911 (6)	6.5 (3)
C25	−0.370 (1)	−0.1981 (4)	0.8276 (4)	3.9 (2)
C26	−0.1398 (9)	−0.1836 (4)	0.9418 (5)	3.7 (2)
C112	0.4928 (9)	−0.0457 (4)	0.6780 (4)	4.2 (2)
C113	0.394 (1)	−0.0981 (4)	0.6679 (5)	4.7 (2)
C114	0.293 (1)	−0.0859 (4)	0.6042 (5)	4.5 (2)
C115	0.3372 (9)	−0.0275 (4)	0.5731 (4)	4.1 (2)
C116	0.4571 (8)	−0.0020 (4)	0.6185 (4)	2.8 (2)
C17	−0.150 (1)	0.1160 (5)	0.8008 (7)	8.3 (3)
C18	−0.085 (1)	0.1360 (5)	0.7341 (6)	8.6 (3)
C19	0.058 (2)	0.1623 (5)	0.7502 (9)	10.5 (4)
C110	0.086 (1)	0.1586 (8)	0.8250 (8)	10.1 (3)
C111	−0.040 (1)	0.1304 (5)	0.8567 (6)	7.7 (2)
C212	−0.0582 (9)	0.3236 (4)	0.9824 (5)	4.0 (2)
C213	−0.1863 (9)	−0.3645 (4)	0.9654 (5)	3.6 (2)
C214	−0.289 (1)	−0.3654 (4)	1.0302 (5)	4.3 (2)
C215	−0.220 (1)	−0.3279 (4)	1.0858 (5)	4.4 (2)
C216	−0.0779 (9)	−0.3002 (4)	1.0571 (5)	4.1 (2)
C27	−0.575 (1)	−0.0913 (4)	0.9664 (5)	4.5 (2)
C28	−0.526 (1)	−0.0755 (4)	0.8928 (5)	4.2 (2)
C29	−0.360 (1)	−0.0569 (4)	0.8983 (5)	4.4 (2)
C210	−0.310 (1)	−0.0606 (4)	0.9755 (6)	5.3 (2)
C211	−0.445 (1)	−0.0826 (4)	1.0172 (5)	5.1 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as B (Å^2) = $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

lead to variations as high as 17% on I. An empirical absorption correction based on the converged isotropic model was applied, and the intensities of equivalent reflections were averaged.[26]

The structure was solved by using direct methods and worked up from subsequent Fourier syntheses; all atomic positional parameters were refined together with their anisotropic thermal parameters (hydrogen atoms isotropic). The weighing parameter p was set to 0.030. The weighing scheme and other corrections were as in the data collection of **3a**. Refinement using the 4342 reflections with $F_o^2 > 3\sigma(F_o^2)$ included 280 variable parameters and converged at $R = 0.024$ and $R_w = 0.030$. Positional parameters of all non-hydrogen atoms and bond lengths and angles are given in Tables VI–VIII.

Syntheses. All manipulations were performed by using standard Schlenk techniques under prepurified nitrogen. Solvents were distilled over Na–benzophenone ketyl (toluene, hexane, diethyl ether, diglyme) or CaH_2 (dichloromethane). The carbonyl complexes $[Ni(CO)(\eta\text{-}C_5H_5)]_2$ and $M(CO)_6$ (M = Cr, M, W) were purchased from Pressure Chemical Co. The group 6 homonuclear dimers $[M(CO)_3(\eta\text{-}C_5H_4R)]_2$ (M = Cr, R = H; M = Mo, W, R = H, CH_3) were synthesized by using standard methods.[30]

Caution: In our hands, $[Cr(CO)_3(\eta\text{-}C_5H_5)]_2$ *was frequently found to be pyrophoric in powder form. Weighings and manipulations of this complex were carried out in a Vacuum Atmospheres glovebox.*

Table IV. Bond Distances (Å) for 3a[a]

molecule 1			molecule 2		
atom 1	atom 2	dist	atom 1	atom 2	dist
W1	Ni1	2.624 (1)	W2	Ni2	2.628 (1)
W1	C11	2.157 (7)	W2	C22	2.154 (7)
W1	C12	2.096 (7)	W2	C21	2.079 (7)
W1	C15	1.951 (8)	W2	C25	1.950 (8)
W1	C16	1.969 (7)	W2	C26	1.988 (8)
W1	C17	2.320 (9)	W2	C27	2.344 (8)
W1	C18	2.313 (13)	W2	C28	2.341 (7)
W1	C19	2.322 (12)	W2	C29	2.341 (8)
W1	C110	2.327 (11)	W2	C210	2.387 (8)
W1	C111	2.323 (9)	W2	C211	2.379 (8)
Ni1	C11	1.946 (7)	Ni2	C22	1.948 (7)
Ni1	C12	1.958 (6)	Ni2	C21	1.945 (7)
Ni1	C16	2.266 (8)	Ni2	C26	2.357 (7)
Ni1	C112	2.108 (7)	Ni2	C212	2.118 (7)
Ni1	C113	2.128 (8)	Ni2	C213	2.125 (7)
Ni1	C114	2.110 (8)	Ni2	C214	2.099 (7)
Ni1	C115	2.159 (7)	Ni2	C215	2.139 (8)
Ni1	C116	2.129 (7)	Ni2	C216	2.132 (7)
O11	C15	1.164 (9)	O21	C25	1.152 (9)
O12	C16	1.171 (8)	O22	C26	1.151 (9)
C11	C12	1.335 (10)	C21	C22	1.343 (11)
C11	C13	1.511 (10)	C21	C23	1.515 (11)
C12	C14	1.491 (9)	C22	C24	1.491 (11)
C17	C18	1.36 (2)	C27	C28	1.401 (11)
C17	C111	1.36 (2)	C27	C211	1.400 (12)
C18	C19	1.33 (2)	C28	C29	1.426 (12)
C19	C110	1.34 (2)	C29	C210	1.418 (13)
C110	C111	1.32 (2)	C210	C211	1.414 (13)
C112	C113	1.386 (12)	C212	C213	1.394 (11)
C112	C116	1.426 (11)	C212	C216	1.417 (11)
C113	C114	1.410 (12)	C213	C214	1.429 (11)
C114	C115	1.400 (12)	C214	C215	1.381 (12)
C115	C116	1.374 (11)	C215	C216	1.404 (12)
CpW1	W1	2.020	CpW2	W2	2.030
CpNi1	Ni1	1.763	CpNi2	Ni2	1.754

[a] CpW1 refers to the centroid of the cyclopentadienyl group bound to atom W1. The same notation is used for the other cyclopentadienyl groups and atoms in both molecules. Numbers in parentheses are estimated standard deviations in the least significant digits.

All the alkynes were purchased from Aldrich and used as received. Chromatography was carried out on alumina columns under N_2. NMR spectra were obtained on a 200-MHz Magnachem A-200 spectrometer or on a 300-MHz Nicolet NT-300 spectrometer. Unless otherwise stated all ^1H NMR and ^{13}C NMR spectra were recorded by using $CDCl_3$ as the solvent. $Cr(acac)_3$ was added (0.05 M concentrations) as a shiftless relaxation reagent for most reported ^{13}C NMR spectra. FT IR spectra were obtained on an IBM IR 32 spectrometer. IR data are in inverse centimeters. Mass spectra were obtained on an AEI MS 902 instrument. High-resolution mass spectra (HRMS) were obtained on a Finnegan MAT 8430 using PFK as the standard. Molecular ion masses are based on ^{52}Cr, ^{58}Ni, ^{98}Mo, and ^{184}W. Spectroscopic data are given after the representative syntheses listed below.

Preparation of the Mixed-Metal Complexes $[NiM(CO)_4(\eta\text{-}C_5H_5)_2]$ (1, M = Cr; 2, M = Mo; 3, M = W) and $[NiM(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (2′, M = Mo; 3′, M = W). Complexes 1–3 were first prepared by Vahrenkamp.[3] Their synthesis and that of the new compounds **2′** and **3′** are based on some slight modifications of his methods. The preparation of $[NiW(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (**3′**) which is representative is given here.

Preparation of $[NiW(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (3′). In a typical reaction, 250 mL of toluene was added to a degassed Schlenk containing equimolar ratios of $[Ni(CO)(\eta\text{-}C_5H_5)]_2$ (1.53 g, 5.0 mmol) and $[W(CO)_3(\eta\text{-}C_5H_4Me)]_2$ (3.50 g, 5.0 mmol). The solution was magnetically stirred and irradiated for 2 days at room temperature, changing from red to deep green in the process. The toluene was then removed and the residue dried in vacuo, extracted with the minimum quantity of hexane, and filtered through a Celite pad. Concentration and crystallization at −20 °C afforded green crystals of complex **3′** in moderate yield (1.70–2.15 g, 34–43%). **3′**: ^1H NMR δ 1.64 (s, 3 H, C_5H_4*Me*), 4.60, 4.62 (m,

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(30) Birdwhistell, J.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* 1978, *157*, 239–241.

Table V. Bond Angles (deg) for 3a[a]

molecule 1		molecule 2	
C11–W1–C15	72.5 (3)	C22–W2–C25	72.5 (3)
C15–W1–C16	92.0 (3)	C25–W2–C26	89.3 (4)
C11–W1–C16	97.9 (3)	C22–W2–C26	102.1 (3)
C12–W1–C16	102.8 (3)	C21–W2–C26	103.4 (3)
C12–W1–C15	108.5 (3)	C21–W2–C25	109.5 (4)
C11–W1–C12	36.6 (3)	C21–W2–C22	36.9 (3)
C11–Ni1–C16	95.0 (3)	C22–Ni2–C26	96.5 (3)
C11–Ni1–C12	40.0 (3)	C21–Ni2–C22	40.4 (3)
C12–Ni1–C16	97.3 (3)	C21–Ni2–C26	95.3 (3)
C12–C11–C13	137.2 (7)	C21–C22–C24	136.3 (8)
C11–C12–C14	137.0 (7)	C22–C21–C23	136.9 (8)
W1–C15–O11	175.6 (7)	W2–C25–O21	175.2 (8)
W1–C16–O12	161.8 (7)	W2–C26–O22	164.9 (7)
Ni1–C16–O11	121.6 (6)	Ni2–C26–O22	120.8 (6)
C18–C17–C111	107 (1)	C28–C27–C211	109.8 (8)
C17–C18–C19	107 (1)	C27–C28–C29	106.5 (8)
C18–C19–C110	109 (2)	C28–C29–C210	108.5 (8)
C19–C110–C111	108 (1)	C29–C210–C211	107.3 (9)
C17–C111–C110	108 (1)	C27–C211–C210	107.9 (8)
C113–C112–C116	107.8 (7)	C213–C212–C216	108.9 (8)
C112–C113–C114	107.2 (8)	C212–C213–C214	106.8 (7)
C113–C114–C115	108.8 (8)	C213–C214–C215	108.3 (7)
C114–C115–C116	107.7 (8)	C214–C215–C216	108.9 (8)
C112–C116–C115	108.4 (8)	C212–C216–C215	107.0 (8)
CpW1–W1–Ni1	145.8	CpW2–W2–Ni2	147.5
CpNi1–Ni1–W1	167.5	CpNi2–Ni2–W2	165.2
CpW1–W1–C11	144.6	CpW2–W2–C22	138.0
CpW1–W1–C12	117.7	CpW2–W2–C21	113.6
CpW1–W1–C16	114.7	CpW2–W2–C26	116.6
CpW1–W1–C15	117.5	CpW2–W2–C25	121.0
CpNi1–Ni1–C11	138.3	CpNi2–Ni2–C22	139.7
CpNi1–Ni1–C12	137.0	CpNi2–Ni2–C21	140.9
CpNi1–Ni1–C16	121.5	CpNi2–Ni2–C26	118.7

[a] Number in parentheses are estimated standard deviations in the least significant digits. CpW1 refers to the center of the cyclopentadienyl ring bound to W1—likewise the other Cp notation.

Table VI. Positional Parameters and Their Estimated Standard Deviations for 4a′[a]

atom	x	y	z	B, Å^2
Mo	0.48805 (2)	0.28305 (1)	0.67055 (1)	2.014 (2)
Ni	0.72502 (2)	0.20031 (2)	0.61973 (2)	2.200 (4)
O1	0.6332 (2)	0.4868 (2)	0.5979 (1)	5.58 (5)
O2	0.2187 (2)	0.3696 (2)	0.5376 (1)	4.66 (4)
O3	0.6138 (2)	0.0036 (1)	0.6863 (1)	3.87 (3)
C1	0.5109 (3)	0.2477 (2)	0.4461 (1)	3.68 (4)
C2	0.5392 (2)	0.2151 (2)	0.5432 (1)	2.42 (3)
C3	0.4670 (2)	0.1291 (2)	0.5850 (1)	2.49 (3)
C4	0.5915 (2)	0.0866 (2)	0.6443 (1)	2.57 (3)
C5	0.3229 (2)	0.0179 (2)	0.5520 (2)	3.84 (4)
C6	0.9079 (3)	0.2086 (2)	0.5445 (2)	4.08 (5)
C7	0.9061 (3)	0.3054 (2)	0.5939 (2)	4.66 (6)
C8	0.9219 (3)	0.2788 (2)	0.6863 (2)	4.34 (5)
C9	0.9320 (2)	0.1677 (2)	0.6938 (2)	3.94 (5)
C10	0.9241 (2)	0.1236 (2)	0.6056 (2)	3.62 (4)
C11	0.3369 (2)	0.2849 (2)	0.7853 (1)	3.36 (4)
C12	0.4324 (2)	0.3749 (2)	0.7947 (1)	3.25 (4)
C13	0.5805 (2)	0.3363 (2)	0.8146 (1)	3.09 (4)
C14	0.5734 (2)	0.2231 (2)	0.8188 (1)	3.04 (4)
C15	0.4229 (3)	0.1911 (2)	0.8025 (1)	3.25 (4)
C16	0.3637 (3)	0.0800 (2)	0.8097 (2)	5.56 (6)
C17	0.5831 (2)	0.4107 (2)	0.6233 (2)	3.27 (4)
C18	0.3151 (2)	0.3360 (2)	0.5863 (1)	3.02 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as B (Å^2) = $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VII. Bond Distances (Å) for 4a′[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Mo	Ni	2.5859 (2)	Mo	C17	1.978 (2)
Mo	C2	2.179 (2)	Mo	C18	1.985 (2)
Mo	C3	2.290 (2)	O1	C17	1.136 (2)
Ni	C2	1.912 (2)	O2	C18	1.137 (2)
Ni	C3	2.491 (2)	O3	C4	1.207 (2)
Ni	C4	1.927 (2)	Ni	C6	2.125 (2)
Mo	C11	2.329 (2)	Mo	C12	2.284 (2)
Mo	C13	2.291 (2)	Mo	C14	2.357 (2)
Mo	C15	2.412 (2)	Ni	C7	2.172 (2)
Ni	C8	2.155 (2)	Ni	C9	2.086 (2)
Ni	C10	2.078 (2)	C1	C2	1.489 (2)
C2	C3	1.436 (2)	C3	C4	1.438 (2)
C3	C5	1.512 (3)	C6	C7	1.410 (4)
C6	C10	1.388 (3)	C7	C8	1.401 (4)
C8	C9	1.386 (4)	C9	C10	1.414 (3)
C11	C12	1.410 (3)	C11	C15	1.407 (3)
C12	C13	1.420 (3)	C13	C14	1.408 (3)
C14	C15	1.412 (3)	C15	C16	1.489 (3)
Cp′Mo	Mo	2.000	CpNi	Ni	1.755

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Cp′Mo and CpNi refer respectively to the centroids of the methylcyclopentadienyl group bound to the molybdenum atom and the cyclopentadienyl group bound to the nickel atom.

Table VIII. Bond Angles (deg) for 4a′[a]

C2–Mo–C3	37.39 (6)	C2–Mo–C17	81.25 (8)
Ni–Mo–C17	78.18 (6)	C3–Mo–C18	85.74 (7)
C17–Mo–C18	81.70 (8)	Ni–Mo–C18	124.41 (5)
C3–Mo–Ni	61.09 (4)	C2–Mo–Ni	46.35 (4)
C4–Ni–Mo	70.55 (5)	C2–Ni–Mo	55.55 (5)
C3–Mo–C17	118.63 (7)	C2–Mo–C18	79.75 (7)
C3–Ni–C4	35.13 (7)	C2–Ni–C4	69.92 (7)
C2–Ni–C3	35.05 (6)	Mo–C3–C2	67.14 (9)
Mo–C2–Ni	78.09 (6)	Mo–C3–C4	88.0 (1)
Mo–C2–C1	135.1 (1)	Mo–C3–C5	125.2 (1)
Mo–C2–C3	75.47 (9)	Ni–C4–O3	131.1 (2)
Ni–C2–C1	128.8 (1)	Ni–C2–C3	95.1 (1)
Ni–C4–C3	94.4 (1)	C1–C2–C3	126.3 (2)
C2–C3–C5	129.3 (2)	O3–C4–C3	133.9 (2)
C4–C3–C5	127.0 (2)	C2–C3–C4	99.9 (1)
Mo–C18–O2	177.6 (2)	C7–C6–C10	108.3 (2)
C6–C7–C8	107.7 (2)	C7–C8–C9	108.1 (2)
C8–C9–C10	108.4 (2)	C6–C10–C9	107.5 (2)
C12–C11–C15	108.7 (2)	C11–C12–C13	107.7 (2)
C12–C13–C14	107.4 (2)	C13–C14–C15	108.8 (2)
C11–C15–C14	107.3 (2)	C11–C15–C16	125.7 (2)
C14–C15–C16	126.8 (2)	Mo–C17–O1	176.9 (1)
Cp′Mo–Mo–C3	122.0	Cp′Mo–Mo–C2	155.5
Cp′Mo–Mo–C17	117.0	Cp′Mo–Mo–C18	117.3
Cp′Mo–Mo–Ni	118.1	CpNi–Ni–C2	144.1
CpNi–Ni–C4	136.6	CpNi–Ni–Mo	143.5

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Cp′Mo and CpNi refer respectively to the centroids of the methylcyclopentadienyl group bound to the molybdenum atom and the cyclopentadienyl group bound to the nickel atom.

4 H, C_5H_4Me), 5.23 (s, 5 H, C_5H_5); IR ν(CO) (hexane) 1998 (w), 1955 (s), 1893 (s) cm^{-1}.

Synthesis of the Alkyne and Nickelacyclobutenone Complexes. All the complexes were prepared similarly, and a few representative syntheses are listed. Reactions involving phenylacetylene were complete within 30 min and yielded some brown insoluble material and traces of an uncharacterized yellowish compound in addition to the characterized products. The synthesis of $NiW(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}MeO_2CC_2CO_2Me\}(\eta\text{-}C_5H_5)_2$ required reaction times of at least 12 h and also yielded some unidentified decomposition products. The other alkyne reactions proceeded smoothly at 25 °C over a 2–4-h period, yielding the alkyne complexes without appreciable quantities of any byproducts. The NiMo complexes **2** and **2′** also yield the corresponding nickelacyclobutenone products. After chromatography and recrystallization, yields ranged in the 40–75% range for the NiCr and NiW complexes. The nickelacyclobutenone compounds were produced in 10–30% yields, while the NiMo alkyne species formed concurrently were obtained in 35–60% yield. Significantly longer reaction times increased the yield of the NiMo alkyne complexes, at the expense of the nickelacyclobutenone products.

Preparation of $[\mathrm{NiCr(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Me})(\eta\text{-}\mathrm{C_5H_5})_2]$ (1a). 2-Butyne (0.45 mL of a 3.7 M solution in hexane, 2.67 mmol) was syringed into 50 mL of toluene solution of 1 (0.522 g, 1.48 mmol) contained in a Schlenk tube. The solution was frozen in liquid nitrogen, evacuated, and allowed to warm to room temperature in vacuo, while being magnetically stirred. After 2–3 h reaction time, the solvent was removed from the red solution and the residue dissolved in hexane and purified by chromatography on an alumina column. One reddish brown band was eluted with hexane/ether (6:1). Concentration and crystallization from hexane at −20 °C afforded red crystals of **1a** in 55% yield (0.286 g, 0.82 mmol). **1a**: ^{1}H NMR δ 2.55 (s, 6 H, $\mathit{Me}\mathrm{C_2}\mathit{Me}$), 4.75 (s, 5 H, $\mathrm{CrC_5H_5}$), 5.08 (s, 5 H, $\mathrm{NiC_5H_5}$); IR ν(CO) (Nujol) 1900 (s), 1802 (s) cm^{-1}; IR ν(CO) (hexane) 1940 (s), 1845 (s) cm^{-1}; MS, *m/e* 350 M$^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{MeC_2Me})^+$; HRMS calcd for $\mathrm{C_{16}H_{16}CrNiO_2}$ 349.9909, found 349.9908.

Synthesis of $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Et})(\eta\text{-}\mathrm{C_5H_5})_2$ (2b) and $\mathrm{NiMo(CO)_2}\{\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{C(R)C(R')C(O)}\}(\eta\text{-}\mathrm{C_5H_5})_2$ (4b) (R = Me, R′ = Et; R = Et, R′ = Me). 2-Pentyne (0.35 mL, 1.7 mmol) was syringed into a stirred toluene solution of **2** (0.595 g, 1.50 mmol) under nitrogen. The solution slowly turned reddish brown over a 2-h period, and most of the solvent was then removed in vacuo. The remaining solution was passed through an alumina column and eluted with toluene yielding two colored bands. The first band was red and was subsequently recrystallized from hexane and characterized as **2b**. The second product was eluted by using a toluene/ether (1:1) solvent mixture. Recrystallization at −20 °C from hexane afforded the isomeric reddish mixture making up **4b**, containing a 1:1 ratio of the two isomers. Careful centrifugal chromatography using hexane to elute afforded separation of the two isomers.

2b: ^{1}H NMR δ 1.15 (t, 3 H, $\mathrm{CH_2}\mathit{CH_3}$, $J_{\mathrm{HH}} = 7.7$ Hz), 2.58 (s, 3 H, $\mathit{Me}\mathrm{C_2Et}$), 2.85 (m, 2 H, $\mathit{CH_2}\mathrm{CH_3}$), 5.10 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.31 (s, 5 H, $\mathrm{MoC_5H_5}$); ^{13}C NMR (acetone-d_6) δ 14.0, 15.8 (Me and $\mathit{Me}\mathrm{CH_2}$) 25.1 ($\mathrm{CH_2}$), 93.2, 93.9 (Ni- and $\mathrm{MoC_5H_5}$), 102.0, 104.3 ($\mathrm{Me}\mathit{C_2}\mathrm{Et}$), 235.7, 234.5 (CO); IR ν(CO) (methylcyclohexane) 1972 (m), 1940 (s), 1914 (m), 1850 (m) cm^{-1}; HRMS calcd for $\mathrm{C_{17}H_{18}MoNiO_2}$ 409.9714, found 409.9714. **4b**: isomer A (R = Me, R′ = Et), ^{1}H NMR δ 1.15 (s, 3 H, Me), 1.77 (t, 3 H, $\mathrm{CH_2}\mathit{CH_3}$, $J_{\mathrm{HH}} = 7.7$ Hz), 2.46, 2.77 (m, 2 H, $\mathit{CH_2}\mathrm{CH_3}$), 5.23 (s, 5 H, $\mathrm{C_5H_5}$), 5.31 (s, 5 H, $\mathrm{C_5H_5}$); isomer B (R = Et, R′ = Me), ^{1}H NMR δ 0.88 (t, 3 H, $\mathrm{CH_2}\mathit{CH_3}$, $J_{\mathrm{HH}} = 7.7$ Hz), 1.27, 1.61 (m, 2 H, $\mathit{CH_2}\mathrm{CH_3}$), 2.65 (s, 3 H, Me), 5.19 (s, 5 H, $\mathrm{C_5H_5}$), 5.35 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C NMR (mixture isomers A and B) δ 15.2, 17.4, 25.1, 26.8 (Me), 28.1, 33.5 ($\mathrm{CH_2}$), 62.1, 69.4 [$\mathit{C}\mathrm{(R)C(R')C(O)}$], 93.1, 93.7, 93.8, 94.0 ($\mathrm{C_5H_5}$), 151.8, 158.6 [$\mathrm{C(R)}\mathit{C}\mathrm{(R')C(O)}$], 175.9, 178.9 [$\mathrm{C(R)C(R')}\mathit{C}\mathrm{(O)}$], 231.0, 231.2, 232.4, 232.5 (CO); IR ν(CO) (Nujol) 1984 (s), 1931 (s, br), 1927 (sh), 1659 (sh), 1648 (s) cm^{-1}.

Synthesis of $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Me})(\eta\text{-}\mathrm{C_5H_5})_2$ (2a) and $\mathrm{NiMo(CO)_2}\{\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{C(Me)C(Me)C(O)}\}(\eta\text{-}\mathrm{C_5H_5})_2$ (4a). 2-Butyne (0.45 mL, 1.63 mmol) was syringed into a stirred toluene solution (50 mL) of **2** (0.591 g, 1.49 mmol). The solution was frozen in liquid nitrogen and evacuated and the mixture allowed to warm to room temperature. After 2 h the solvent was removed from the red solution in vacuo and the mixture taken up in hexane. Chromatography on alumina afforded two bands. Elution with hexane/ether (6:1) resulted in collection of the first product **2a** (0.314 g, 0.795 mmol, 53%) which was recrystallized from hexane. The second compound **4a** was removed from the column by using ether and also recrystallized from hexane at −20 °C (0.132 g, 0.312 mmol, 21%). **2a**: ^{1}H NMR δ 2.51 (s, 6 H, $\mathit{Me}\mathrm{C_2}\mathit{Me}$), 5.07 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.30 (s, 5 H, $\mathrm{MoC_5H_5}$); IR ν(CO) (Nujol) 1902 (s), 1807 (s) cm^{-1}; MS, *m/e* 396 M$^+$; HRMS calcd for $\mathrm{C_{16}H_{16}MoNiO_2}$ 395.956, found 395.956. **4a**: ^{1}H NMR δ 1.27 (s, 3 H, $\mathrm{C(}\mathit{Me}\mathrm{)C(Me)C(O)}$], 2.70 [s, 3 H, $\mathrm{C(Me)C(}\mathit{Me}\mathrm{)C(O)}$], 5.24 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.37 (s, 5 H, $\mathrm{MoC_5H_5}$); ^{13}C NMR δ 15.3, 25.9 [$\mathrm{C(}\mathit{Me}\mathrm{)C(}\mathit{Me}\mathrm{)}$] 63.1, 149.6 [$\mathit{C}\mathrm{(Me)}\mathit{C}\mathrm{(Me)C(O)}$], 93.1 92.9 ($\mathrm{C_5H_5}$), 179.4 [$\mathrm{C(Me)C(Me)}\mathit{C}\mathrm{(O)}$], 228.4, 229.7 (CO); IR ν(CO) (Nujol) 1983 (s), 1927 (s), 1658 (m) cm^{-1}.

Synthesis of $\mathrm{NiW(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{PhC_2Ph})(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5H_4Me})$ (3d′) and $\mathrm{NiW(CO)_2}\{\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{C(Ph)C(Ph)C(O)}\}(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5H_4Me})$ (5d′). Freshly distilled toluene (20 mL) was syringed into a Schlenk containing **3′** (0.391 g, 0.784 mmol) and diphenylacetylene (0.163 g, 0.915 mmol). The solution was stirred for 4 h, the solvent removed in vacuo, and ca. 5 mL of hexane added to dissolve the residue. Chromatography on an alumina column and elution with ether afforded complex **3d′** which was subsequently recrystallized from hexane. Further elution with ether/dichloromethane (1:1) led to compound **5d′**. **3d′**: ^{1}H NMR δ 2.05 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.06 (m, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 5.07 (s, 5 H, $\mathrm{C_5H_5}$), 7.21 (m, 2 H), 7.26 (m, 4 H), 7.46 (m, 4 H, $\mathit{Ph}\mathrm{C_2}\mathit{Ph}$); ^{13}C NMR δ 13.47 ($\mathrm{C_5H_4}\mathit{Me}$), 84.2 ($\mathrm{Ph}\mathit{C_2}\mathrm{Ph}$), 88.1, 89.2, 106.1 ($\mathit{C_5}\mathrm{H_4Me}$), 92.2 ($\mathrm{C_5H_5}$), 125.7, 127.6, 129.6, 142.5 ($\mathit{Ph}\mathrm{C_2}\mathit{Ph}$), 216.1 (2CO, $J_{\mathrm{WC}} =$ 170 Hz); IR ν(CO) (Nujol) 2024 (s), 1969 (s) cm^{-1}; MS, *m/e* 621 M$^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{PhC_2Ph})^+$; HRMS calcd for $\mathrm{C_{27}H_{22}NiO_2W}$ 620.048, found 620.050. **5d′**: ^{1}H NMR δ 2.06 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.00, 5.11 (m, ABCD type, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 5.08 (s, 5 H, $\mathrm{C_5H_5}$), 7.04, 7.24, 7.32, 7.58 [m, 10 H, $\mathrm{C(}\mathit{Ph}\mathrm{)C(}\mathit{Ph}\mathrm{)C(O)}$]; IR ν(CO) (Nujol) 1988 (s), 1934 (s) 1641 (m) cm^{-1}; IR ν(CO) (chloroform) 1992 (m), 1930 (m), 1644 (w), 1602 (w) cm^{-1}. Anal. Calcd for $\mathrm{C_{28}H_{22}NiO_3W}$: C, 51.82, H, 3.42. Found: C, 51.98, H, 3.70.

Reaction of 2a with CO. A solution of **2a** (0.197 g, 0.499 mmol) in 15 mL of toluene was stirred in a small Schlenk tube, and CO was bubbled through the solution. The reaction was monitored by IR. After 24 h, no ν(CO) peaks of **2a** were observable and only ν(CO) peaks due to **4a** were present.

Attempted Reaction of 2b′ with CO. A solution of **2b′** (0.276 g, 0.676 mmol) in 20 mL of hexane was stirred in a Schlenk, and CO was bubbled through the solution for 24 h. No new ν(CO) peaks were observed during periodic monitoring of the solution by IR, and at the end of that time all of **2b′** was recovered. Attempted irradiation of **2b′** with UV light also led to no change in the appearance of the IR spectrum.

Spectroscopic Data for the Remaining Complexes. 1b, $\mathrm{NiCr(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Et})(\eta\text{-}\mathrm{C_5H_5})_2$: ^{1}H NMR δ 1.13 (t, 3 H, $\mathrm{CH_2}\mathit{CH_3}$, $J_{\mathrm{HH}} = 7$ Hz), 2.68 (s, 3 H, $\mathit{Me}\mathrm{C_2Et}$), 2.73 and 2.99 (m, 2 H, $\mathit{CH_2}\mathrm{CH_3}$), 4.75 (s, 5 H, $\mathrm{CrC_5H_5}$), 5.10 (s, 5 H, $\mathrm{NiC_5H_5}$); IR ν(CO) (Nujol) 1947 (s), 1841 (s) cm^{-1}; MS, *m/e* 364 M$^+$, $(\mathrm{M} - \mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{MeC_2Et})^+$; HRMS calcd for $\mathrm{C_{17}H_{18}CrNiO_2}$ 364.006, found 364.007.

2′, $\mathrm{NiMo(CO)_4}(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5H_4Me})$: ^{1}H NMR δ 2.01 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.14 (m, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 5.44 (s, 5 H, $\mathrm{C_5H_5}$); IR ν(CO) (chloroform) 2003 (w), 1953 (s), 1895 (m) 1843 (m) cm^{-1}.

2a′, $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Me})(\mathrm{C_5H_5})(\mathrm{C_5H_4Me})$: ^{1}H NMR δ 2.01 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.51 (s, 6 H, $\mathit{Me}\mathrm{C_2}\mathit{Me}$), 5.07 (s, 5 H, $\mathrm{C_5H_5}$), 5.23 (m, 4 H, $\mathrm{C_5H_4Me}$); IR ν(CO) (Nujol) 1916 (s) 1818 (m) cm^{-1}; MS, *m/e* 410 M$^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{MeC_2Me})^+$; HRMS calcd for $\mathrm{C_{17}H_{18}MoNiO_2}$ 409.971, found 409.972.

2b′, $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Et})(\mathrm{C_5H_5})(\mathrm{C_5H_4Me})$: ^{1}H NMR (acetone-$d_6$) δ 1.08 (t, 3 H, $\mathrm{CH_2}\mathit{CH_3}$, $J_{\mathrm{HH}} = 7.3$ Hz), 1.74 (s, 3 H, Me), 2.42 (s, 3 H, Me), 2.68 (m, 2 H, $\mathit{CH_2}\mathrm{CH_3}$), 4.70, 4.83 (m, ABCD type, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 5.04 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C NMR δ 13.6, 14.4, 20.3 ($\mathit{C}\mathrm{H_3C_2CH_2}\mathit{C}\mathrm{H_3}$, $\mathrm{C_5H_4}\mathit{Me}$), 27.0 ($\mathrm{CH_2}$), 90.7, 91.9, 93.2, 109.5 ($\mathit{C_5}\mathrm{H_4Me}$), 92.7 ($\mathrm{C_5H_5}$), 100.6, 103.4 ($\mathrm{Me}\mathit{C_2}\mathrm{Et}$), 233.8, 235.2 (CO); IR ν(CO) (methylcyclohexane) 1970 (m), 1958 (m), 1937 (m), 1916 (m), 1850 (m) cm^{-1}; MS, *m/e* 424 M$^+$, $(\mathrm{M} - \mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{MeC_2Et})^+$; HRMS calcd for $\mathrm{C_{18}H_{20}MoNiO_2}$ 423.987, found 423.986.

2c, $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{PhC_2H})(\mathrm{C_5H_5})_2$: ^{1}H NMR δ 5.12 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.26 (s, 5 H, $\mathrm{MoC_5H_5}$), 6.25 (s, 1 H, $\mathrm{PhC_2}\mathit{H}$), 7.26, 7.31, 7.44 (m, 5 H, $\mathit{Ph}\mathrm{C_2H}$); ^{13}C NMR δ 91.2, 98.0 ($\mathrm{Ph}\mathit{C_2}\mathrm{H}$), 91.7, 92.5 (Ni- and $\mathrm{MoC_5H_5}$), 126.0, 127.3, 129.2, 141.1 ($\mathit{Ph}\mathrm{C_2H}$), 229.7, 234.0 (CO); IR ν(CO) (Nujol) 1959 (s), 1854 (s) cm^{-1}; IR ν(CO) (chloroform) 1904 (s), 1804 (m) cm^{-1}; MS, *m/e* 444 M$^+$, $(\mathrm{M} - 2\mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{PhC_2H})^+$; HRMS calcd for $\mathrm{C_{20}H_{16}MoNiO_2}$ 443.956, found 443.958.

2c′, $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{PhC_2H})(\mathrm{C_5H_5})(\mathrm{C_5H_4Me})$: ^{1}H NMR δ 1.95 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.15 (s, 5 H, $\mathrm{C_5H_5}$), 5.15, 5.30 (m, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 6.18 (s, 1 H, $\mathrm{PhC_2}\mathit{H}$), 7.23, 7.45 (m, 5 H, $\mathit{Ph}\mathrm{C_2H}$); ^{13}C NMR δ 19.9 ($\mathrm{C_5H_4}\mathit{Me}$), 84.3 ($\mathrm{C_5H_5}$), 83.1, 83.7, 84.8, 85.4, 101.0 ($\mathit{C_5}\mathrm{H_4Me}$), 84.5, 98.9 ($\mathrm{Ph}\mathit{C_2}\mathrm{H}$), 118.1, 119.3, 121.0, 131.9 ($\mathit{Ph}\mathrm{C_2H}$), 221.8, 224.9 (CO); IR ν(CO) (hexane) 1958 (s), 1918 (m), 1855 (m) cm^{-1}; HRMS calcd for $\mathrm{C_{21}H_{18}MoNiO_2}$ 457.971, found 457.971.

2d′, $\mathrm{NiMo(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{PhC_2Ph})(\mathrm{C_5H_5})(\mathrm{C_5H_4Me})$: ^{1}H NMR δ 2.05 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.07 (s, 5 H, $\mathrm{C_5H_5}$), 5.17, 5.33 (m, 4 H, $\mathrm{C_5}\mathit{H_4}\mathrm{Me}$), 7.24 (m, $\mathit{Ph}\mathrm{C_2}\mathit{Ph}$); IR ν(CO) (hexane) 1959 (s), 1916 (s) cm^{-1}; HRMS calcd for $\mathrm{C_{27}H_{22}MoNiO_2}$ 534.003, found 534.002.

3a, $\mathrm{NiW(CO)_2}(\mu\text{-}\eta^2,\eta^2\text{-}\mathrm{MeC_2Me})(\mathrm{C_5H_5})_2$: ^{1}H NMR δ 2.60 (s, 6 H, $\mathit{Me}\mathrm{C_2}\mathit{Me}$), 5.08 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.33 (s, 5 H, $\mathrm{WC_5H_5}$); IR ν(CO) (Nujol) 1915 (s), 1810 (s) cm^{-1}; MS, *m/e* 482 M$^+$, $(\mathrm{M} - \mathrm{CO})^+$, $(\mathrm{M} - 2\mathrm{CO} - \mathrm{MeC_2Me})^+$; HRMS calcd for $\mathrm{C_{16}H_{16}NiO_2W}$ 482.001, found 482.001.

3a′, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)(C_5H_5)(C_5H_4Me)}$: ^{1}H NMR δ 2.13 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.61 (s, 6 H, $\mathit{Me}\mathrm{C_2}\mathit{Me}$), 5.08 (s, 5 H, $\mathrm{C_5H_5}$), 5.15 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$); ^{13}C NMR δ 7.3 ($\mathrm{C_5H_4}\mathit{Me}$), 12.1 ($\mathit{Me}\mathrm{C_2}\mathit{Me}$), 82.6, 83.7, 100.3 ($\mathit{C}_5\mathrm{H_4Me}$), 84.3 ($\mathrm{Me}\mathit{C}_2\mathrm{Me}$), 85.4 ($\mathrm{NiC_5H_5}$), 216.9 (2CO, J_{WC} = 174 Hz); IR ν(CO) (Nujol) 1914 (s), 1810 (s) cm^{-1}; MS, *m/e* 498 M$^+$, (M – 2CO)$^+$, (M – 2CO – $\mathrm{MeC_2Me}$)$^+$; HRMS calcd for $\mathrm{C_{17}H_{18}NiO_2W}$ 496.0170, found 496.0177.

3b, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Et)(C_5H_5)_2}$: ^{1}H NMR δ 1.13 (t, 3 H, $\mathrm{CH_2}\mathit{CH}_3$, J_{HH} = 7 Hz), 2.69 (s, 3 H, $\mathit{Me}\mathrm{C_2Et}$), 2.85 (m, 2 H, $\mathit{CH}_2\mathrm{CH_3}$), 5.12 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.37 (s, 5 H, $\mathrm{WC_5H_5}$); IR ν(CO) (Nujol) 1918 (s), 1810 (s), 1787 (w) cm^{-1}; MS, *m/e* 496 M$^+$, (M – 2CO)$^+$, (M – 2CO – $\mathrm{MeC_2Et}$)$^+$; HRMS calcd for $\mathrm{C_{17}H_{18}NiO_2W}$ 496.017, found 496.017.

3b′, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Et)(C_5H_5)(C_5H_4Me)}$: ^{1}H NMR (acetone-$d_6$) δ 1.05 (t, 3 H, $\mathrm{CH_2}\mathit{CH}_3$, J_{HH} = 7 Hz), 1.76 (s, 3 H, $\mathit{Me}\mathrm{C_2Et}$), 2.76 (m, 2 H, $\mathit{CH}_2\mathrm{CH_3}$), 4.60, 4.70 (m, ABCD type, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.11 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C NMR δ 12.8 ($\mathrm{C_5H_4}\mathit{Me}$), 14.1, 18.9 ($\mathit{CH}_3\mathrm{C_2CH_2}\mathit{CH}_3$), 25.7 ($\mathrm{CH_2}$), 88.1, 88.2, 89.1 (2 C), 96.1 ($\mathit{C}_5\mathrm{H_4Me}$), 91.7 ($\mathrm{NiC_5H_5}$), 92.1, 96.1 ($\mathrm{Me}\mathit{C}_2\mathrm{Et}$), 222.6, 223.7 (CO); IR ν(CO) (hexane) 1970 (s), 1936 (s), 1907 (s), 1834 (m) cm^{-1}; MS, *m/e* 510 M$^+$, (M – 2CO)$^+$, (M – 2CO – $\mathrm{MeC_2Et}$); HRMS calcd for $\mathrm{C_{18}H_{20}NiO_2W}$ 510.033, found 510.032.

3c, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(C_5H_5)_2}$: ^{1}H NMR δ 5.10 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.33 (s, 5 H, $\mathrm{WC_5H_5}$), 6.10 (s, 1 H, $\mathrm{PhC_2}\mathit{H}$), 7.21 (m, 1 H), 7.30 (m, 2 H), 7.41 (m, 2 H) ($\mathit{Ph}\mathrm{C_2H}$); ^{13}C NMR δ 66.0, 85.2 ($\mathrm{Ph}\mathit{C}_2\mathrm{H}$), 87.0, 89.1 (Ni- and $\mathrm{WC_5H_5}$), 123.1, 124.4, 126.7, 137.8 ($\mathit{Ph}\mathrm{C_2H}$), 214.4, 217.9 (CO); IR ν(CO) (Nujol) 1915 (s), 1807 (m), 1792 (s) cm^{-1}; MS, *m/e* 506 M$^+$, (M – 2CO)$^+$, (M – 2CO – $\mathrm{PhC_2H}$)$^+$; HRMS calcd for $\mathrm{C_{20}H_{16}NiO_2W}$ 530.001, found 530.002.

3c′, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)(C_5H_5)(C_5H_4Me)}$: ^{1}H NMR (benzene-$d_6$) δ 1.62 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 4.56, 4.73 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.10 (s, 5 H, $\mathrm{C_5H_5}$), 5.80 (s, 1 H, $\mathrm{PhC_2}\mathit{H}$), 6.90, 7.13, 7.43 (m, 5 H, $\mathit{Ph}\mathrm{C_2H}$); ^{13}C NMR δ 12.8 ($\mathrm{C_5H_4}\mathit{Me}$), 70.9, 88.8 ($\mathrm{Ph}\mathit{C}_2\mathrm{H}$), 88.7, 89.5, 90.4, 93.5 107.3 ($\mathit{C}_5\mathrm{H_4Me}$), 89.4 ($\mathrm{C_5H_5}$), 126.8, 128.6, 129.3, 140.5 ($\mathit{Ph}\mathrm{C_2H}$), 218.7 (CO, J_{WC} = 169 Hz), 221.2 (CO, J_{WC} = 171 Hz); IR ν(CO) (hexane) 1980 (m), 1954 (s), 1920 (m), 1895 (m), 1843 (m) cm^{-1}; HRMS calcd for $\mathrm{C_{21}H_{18}NiO_2W}$ 544.018, found 544.018.

3e, $\mathrm{NiW(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeO_2CC_2CO_2Me)(C_5H_5)_2}$: ^{1}H NMR δ 3.80 (s, 6 H, $\mathit{Me}\mathrm{O_2CC_2CO_2}\mathit{Me}$), 5.30 (s, 5 H, $\mathrm{C_5H_5}$), 5.49 (s, 5 H, $\mathrm{C_5H_5}$); IR ν(CO) (Nujol) 1968 (s), 1910 (s) 1697 (m), 1653 (m) cm^{-1}; MS, *m/e* 570 M$^+$, (M – 2CO)$^+$; HRMS calcd for $\mathrm{C_{18}H_{16}NiO_6W}$ 569.981, found 569.981.

4a′, $\mathrm{NiMo(CO)_2\{(\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(C_5H_5)(C_5H_4Me)}$: ^{1}H NMR δ 1.19 [s, 3 H, C(Me)C(Me)C(O)], 2.07 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.65 [s, 3 H, C(Me)C($\mathit{Me}$)C(O)], 5.08, 5.10, 5.28, 5.33 (m, ABCD type, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.20 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C NMR δ 12.6, 13.5, 24.9 [C(Me)C(Me)C(O), $\mathrm{C_5H_4}\mathit{Me}$], 61.6, 147.6 [$\mathit{C}(Me)\mathit{C}$(Me)C(O)], 91.0, 91.2, 92.7, 93.8, 108.3 ($\mathit{C}_5\mathrm{H_4Me}$), 92.0 ($\mathrm{C_5H_5}$), 178.3 [C(Me)C(Me)$\mathit{C}$(O)], 227.8, 229.2 (CO); IR ν(CO) (Nujol) 1980 (s), 1941 (s), 1646 (s) cm^{-1}.

4b′, $\mathrm{NiMo(CO)_2\{(\mu\text{-}\eta^2,\eta^2\text{-}C(R)\mathbf{C}(R')C(O)\}(C_5H_5)(C_5H_4Me)}$: isomer A (R = Me, R′ = Et), ^{1}H NMR δ 1.18 [s, 3 H, C(O)C(Et)C(Me)], 2.02 (t, 3 H, $\mathrm{CH_2}\mathit{CH}_3$, J_{HH} = 8 Hz), 2.07 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.51, 2.77 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 5.21 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.10, 5.34 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$); isomer B (R = Et, R′ = Me), ^{1}H NMR δ 0.90 (t, 3 H, $\mathrm{CH_2}\mathit{CH}_3$, J_{HH} = 7 Hz), 1.23, 1.69 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.11 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 2.68 [s, 3 H, C(O)C($\mathit{Me}$)C(Et)], 5.17 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 5.10, 5.34 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$); ^{13}C NMR (mixture isomers A and B) δ 12.9, 13.5 ($\mathrm{C_5H_4}\mathit{Me}$), 14.2, 16.2, 23.6, 25.5 ($\mathrm{CH_2}\mathit{CH}_3$ and $\mathrm{C}\mathit{C}\mathrm{H_3}$), 32.0 ($\mathit{C}\mathrm{H_2CH_3}$), 61.4, 68.5 [$\mathit{C}$(R)C(R′)C(O)], 91.2, 91.5, 91.8, 92.6, 92.7, 94.1 ($\mathit{C}_5\mathrm{H_4Me}$), 92.0, 92.5 ($\mathrm{C_5H_5}$) 108.1, 108.5 ($\mathit{C}_5\mathrm{H_4Me\text{-}C_1}$), 148.3, 155.2 [(C(R)$\mathit{C}$(R′)C(O)], 178.1, 180.2 [(C(R)C(R′)C(O)], 228.3, 228.4, 229.6, 229.8 (CO); IR ν(CO) (hexane) 1984 (s), 1927 (s), 1677 (m) cm^{-1}. Anal. Calcd for $\mathrm{C_{19}H_{20}MoNiO_3}$: C, 50.60; H, 4.47. Found: C, 50.72; H, 4.55.

4c, $\mathrm{NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(H)C(O)\}(C_5H_5)_2}$: ^{1}H NMR δ 5.32 (s, 5 H, $\mathrm{NiC_5H_5}$), 5.40 (s, 5 H, $\mathrm{MoC_5H_5}$), 7.17 (m, 5 H, Ph), 7.45 [s, 1 H, C(Ph)C(H)C(O)]; IR ν(CO) (dichloromethane) 2000 (s), 1965 (s), 1949 (s), 1660 (w) cm^{-1}.

4c′, $\mathrm{NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Ph)C(H)C(O)\}(C_5H_5)(C_5H_4Me)}$: ^{1}H NMR δ 2.00 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.19, 5.31 (m, ABCD type, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.30 (s, 5 H, $\mathrm{C_5H_5}$), 7.50–7.60 (m, 5 H, Ph), 7.45 [s, 1 H, C(Ph)C(H)C(O)]. Anal. Calcd for $\mathrm{C_{22}H_{18}MoNiO_3}$: C, 54.48; H, 3.74. Found: C, 54.26; H, 3.91.

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Registry No. 1, 75339-33-2; **1a**, 110512-04-4; **1b**, 110512-05-5; **2**, 75339-34-3; **2′**, 110512-06-6; **2a**, 99280-71-4; **2a′**, 99280-72-5; **2b**, 99297-95-7; **2b′**, 110512-07-7; **2c**, 110512-08-8; **2c′**, 110512-09-9; **2d′**, 110512-10-2; **3**, 75339-35-4; **3′**, 110512-11-3; **3a**, 110512-12-4; **3a′**, 110512-13-5; **3b**, 110512-14-6; **3b′**, 110512-15-7; **3c**, 110512-16-8; **3c′**, 110512-17-9; **3d′**, 110512-18-0; **3e**, 110512-19-1; **4a**, 99297-96-8; **4a′**, 99308-98-2; **4b** (isomer A), 99297-98-0; **4b** (isomer B), 99297-97-9; **4b′** (isomer A), 110512-20-4; **4b′** (isomer B), 110512-21-5; **4c**, 110512-22-6; **4c′**, 110512-23-7; **5d′**, 110512-24-8; $\mathrm{[Ni(CO)(\eta^5\text{–}C_5H_5)]_2}$, 12170-92-2; $\mathrm{[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2}$, 68111-11-5; $\mathrm{PhC{\equiv}CH}$, 536-74-3; $\mathrm{CH_3C{\equiv}CCH_3}$, 503-17-3; $\mathrm{CH_3C{\equiv}CCH_2CH_3}$, 627-21-4; $\mathrm{PhC{\equiv}CPh}$, 501-65-5; $\mathrm{MeCO_2C_2CO_2Me}$, 762-42-5.

Supplementary Material Available: Tables of calculated hydrogen positions, anisotropic thermal parameters, and least-squares planes for **3a** (Tables IX, X, XIa, XIb) and tables of hydrogen atom positions and their isotopic thermal parameters, anisotropic thermal parameters of non-hydrogen atoms, and least-squares planes for **4a′** (Tables III–V) (13 pages); listings of F_o, F_c, and h,k,l values for **3a** and **4a′** (Tables XII and XVI, respectively) (64 pages). Ordering information is given on any masthead page.