is probably obscured. We are exploring alternative routes to pyridine complexes of low-valent platinum.

Acknowledgment. We thank Imperial College (ORS Awards) and Austausch-Stipendium, ETH, Zürich, Switzerland, for financial support (to S.E.H.). We are also grateful to Dr. Judith Challis and John Bilton of this Department and to Drs. Graham Taylor, John Williams, and David Watson of the Royal Postgraduate Medical School, Hammersmith Hospital, for GC–MS measurements. We are additionally indebted to Dick Sheppard and Sue Johnson for high-field NMR and to Johnson-Matthey Ltd. for continued support through generous loans of platinum. Equipment grants by the University of London Central Research Fund and the Royal Society, in partial support of this work, are also gratefully acknowledged.

Registry No. 1, 116840-52-9; 2, 64827-25-4; 3, 116840-53-0; Mg(4-$C_6H_4CMe_3$)Br, 63488-10-8; (cod)$PtCl_2$, 12080-32-9; (cod)Pt(4-$C_6H_4CMe_3$)$_2$, 57110-64-2; Hg(4-$C_6H_4CMe_3$)$_2$, 20657-25-4; *m*-bromo-*tert*-butylbenzene, 3972-64-3; *p*-amino-*m*-bromo-*tert*-butylbenzene, 103273-01-4.

Chemistry of the Complexes NiM(CO)$_4$(η^5-C_5H_5)(η^5-C_5H_4Me) (M = Mo, W): Evidence for an Associative Pathway in Their Reactions with Alkynes

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Received February 2, 1988

Mechanistic aspects of reactions of the complexes NiM(CO)$_4$CpCp′ (M = Mo, W; Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me) with alkynes are presented. The nickel–tungsten complexes react with alkynes to yield bridging alkyne species; nickel–molybdenum complexes in addition afford nickelacyclobutenone species (Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298–2306). Benzene solutions of the complexes (η^5-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me) (**1**) and (η^5-C_5H_4Me)(CO)Ni–W(CO)$_3$(η^5-C_5H_5) (**2**) undergo metal–metal bond cleavage, forming a statistical equilibrium mixture of the four heterodinuclear complexes **1**, **2**, (η^5-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_5) (**3**), and (η^5-C_5H_4Me)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me) (**4**) when trace impurities are present. High-purity samples of **1** and **2** do not undergo metal–metal bond metathesis. Crossover experiments demonstrate that phenylacetylene reacts with a heterodinuclear species. The reaction rate of **1** with alkynes decreases in the order phenylacetylene > 2-butyne ≫ diphenylacetylene. Competition studies indicate rate-determining alkyne attack is at the nickel atom. Kinetic studies of the reactions of **1** and **3** with phenylacetylene exhibited a first-order rate dependence on both the mixed-metal complex *and* the phenylacetylene concentrations for moderate concentrations of alkyne and metal complex. The reaction of **1** with phenylacetylene was also monitored under high phenylacetylene concentrations. Pseudo-first-order behavior was observed, suggesting the formation of a transient intermediate, possibly the η^3 species (η^3-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me). The nickel–molybdenum complexes (η^5-C_5H_5)(CO)Ni–Mo(CO)$_3$(η^5-C_5H_4R) (**5**, R = Me; **6**, R = H) form bridging alkyne complexes primarily via the pathway observed in the nickel–tungsten case. Kinetic and mechanistic experiments indicate that alkyne-bridged and nickelacyclobutenone species are formed from common intermediates. Decarbonylation of the nickelacyclobutenone complex (η^5-C_5H_5)Ni{μ-C(O)C(H)C(Ph)}Mo(CO)$_2$(η^5-C_5H_4Me) (**9**) to (η^5-C_5H_5)Ni(μ-PhC_2H)Mo(CO)$_2$(η^5-C_5H_4Me) (**5a**) produces less than 5% of **5a** over a 3-h period, indicating that decomposition of intermediate metallacyclic species is not the major pathway to the nickel–molybdenum alkyne-bridged complexes.

Introduction

Heterodimetallic complexes have been implicated in catalysis and studies of their syntheses and reactivity are underway in several laboratories.[1] In comparison to their homonuclear analogues, mixed-metal species frequently exhibit enhanced reactivity and distinctly different chemistry;[2] synergistic effects may be partly explained by the polarity of many heteronuclear metal–metal bonds. Despite current attention focused on these complexes, their kinetic and mechanistic behavior has been a relatively neglected area. Most mechanistic work on heterodimetallic species has centered on simple metal carbonyl complexes, in which the metals are closely related and has been undertaken in conjunction with homometallic studies. The mixed-metal complex MnRe(CO)$_{10}$,[3] for example, has

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Table I. Numbering Scheme

1	$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_4Me)$	**1a**	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^2\text{-}C_5H_4Me)$
2	$(\eta^5\text{-}C_5H_4Me)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_5)$	**2a**	$(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_5)$
3	$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_5)$	**3a**	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_5)$
		3b	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}MeC_2Me)W(CO)_2(\eta^5\text{-}C_5H_5)$
		3c	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2Ph)W(CO)_2(\eta^5\text{-}C_5H_5)$
4	$(\eta^5\text{-}C_5H_4Me)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_4Me)$	**4a**	$(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_4Me)$
5	$(\eta^5\text{-}C_5H_5)(CO)Ni–Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$	**5a**	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$
6	$(\eta^5\text{-}C_5H_5)(CO)Ni–Mo(CO)_3(\eta^5\text{-}C_5H_5)$	**6a**	$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)Mo(CO)_2(\eta^5\text{-}C_5H_5)$
7	$(\eta^5\text{-}C_5H_4Me)(CO)Ni–Mo(CO)_3(\eta^5\text{-}C_5H_5)$	**7a**	$(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)Mo(CO)_2(\eta^5\text{-}C_5H_5)$
8	$(\eta^5\text{-}C_5H_4Me)(CO)Ni–Mo(CO)_3(\eta\text{-}C_5H_4Me)$		
9	$(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$		
10	$(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2(\eta^5\text{-}C_5H_5)$		
11	$(\eta^5\text{-}C_5H_4Me)Ni\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$		

provided a vital key to carbonyl substitution mechanisms in $M_2(CO)_{10}$ (M = Mn, Re) complexes.[4]

Mechanistic studies of alkyne reactions with dinuclear species have been reported and multiple reaction pathways are not unusual.[5] Dicobalt octacarbonyl and some of its derivatives[6] react via multiple mechanistic routes, one of which depends on the incombing alkyne concentration. Reactions of the dinuclear complexes $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$[7] and $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$[8] with diphenylacetylene have been investigated. The molybdenum complex follows a carbonyl dissociation pathway; a secondary mechanism is first order in the alkyne concentration. The major substitution pathway of $[Ni(\mu\text{-}CO)(\eta\text{-}C_5H_5)]_2$ is alkyne concentration dependent.

We have initiated[9] investigations into the chemistry of the heterodinuclear complexes $(\eta^5\text{-}C_5H_4R)(CO)Ni–M(CO)_3(\eta^5\text{-}C_5H_4R)$ (M = Cr, Mo, or W; R = H, Me). Reactions of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ or $[M(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (M = Mo, W) with alkynes [affording $Ni_2(\mu\text{-}RC_2R)(\eta^5\text{-}C_5H_5)_2$[10] or $M_2(CO)_4(\mu\text{-}RC_2R)(\eta^5\text{-}C_5H_5)_2$][11,12] require heating or photolysis; in contrast the nickel–molybdenum and nickel–tungsten complexes react with alkynes at room temperature yielding heterodinuclear alkyne-bridged species. The nickel–molybdenum complexes also yield metallacyclic complexes containing nickelacyclobutenone rings, which decarbonylate to alkyne-bridged species on heating or standing in solution (Scheme I).[13] This paper presents mechanistic and kinetic aspects of reactions of complexes **1**–**6** (Table I) with alkynes.

Table II. Second-Order Rate Constants[a]

metal complex	solv	10^3k ($M^{-1}\ s^{-1}$)
$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1**)	benzene-d_6	2.4 ± 0.5[b]
$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_5)$ (**3**)	benzene-d_6	2.4 ± 0.5[b]
$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_5)$ (**3**)	acetone-d_6	6.6 ± 0.3[b]
$(\eta^5\text{-}C_5H_5)(CO)Ni–Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**5**)	benzene-d_6	2.9 ± 0.4[b]
$(\eta^5\text{-}C_5H_5)(CO)Ni–Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (**6**)	benzene-d_6	4.7 ± 0.9[b]
$(\eta^5\text{-}C_5H_5)(CO)Ni–W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**1**)	benzene-d_6	1.8 ± 0.5[c]

[a] All rate constants were recorded at 20.0 ± 0.5 °C, for a 1:1 ratio of metal complex to alkyne. [b] Phenylacetylene. [c] 2-Butyne.

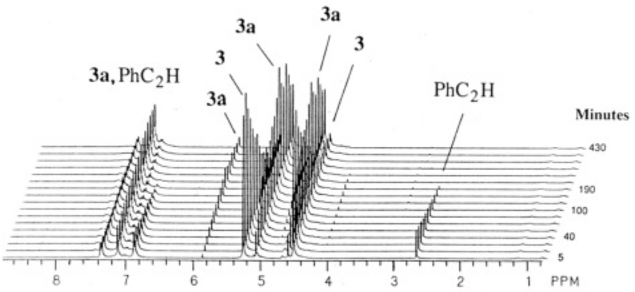

Figure 1. Stacked plot of the time-elapsed ^1H NMR spectra for the reaction of **3** with phenylacetylene showing the decrease in the reactants (**3**, PhC_2H) and increase in **3a** with time.

Results and Discussion

I. Reactions of the Homodinuclear Species. Either one or two pathways to the bridging alkyne products appeared likely, based on our preliminary investigations. All bridging alkyne complexes could be formed through decomposition of intermediate nickelacyclobutenone species, *or* complexes **1**–**6** may react with alkynes via two independent pathways, one of which is inoperative for the nickel–tungsten species.

Radical mechanisms involving homolytic metal–metal bond cleavage appear viable; complexes **1**–**6** were prepared according to eq 1,[9,14] suggesting that a small radical concentration is present at equilibrium. Vahrenkamp and Madach[14] indicate that many 17-electron organometallic fragments formally combine to yield heterodimetallic species in preference to forming their homodinuclear counterparts. UV/vis irradiation of toluene solutions of group 6 and group 10 homonuclear dimers yields the heterodinuclear complexes **1**–**6** over a 1–2 day period (eq 1), implicating metal–metal bond cleavage as a mechanistic

$$[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_4R)]_2 + [M(CO)_3(\eta^5\text{-}C_5H_4R')]_2 \rightleftharpoons 2[(\eta^5\text{-}C_5H_4R)(CO)Ni–M(CO)_3(\eta^5\text{-}C_5H_4R')] \quad (1)$$

$$R, R' = H, Me;\ M = Mo, W$$

pathway. Equimolar solutions of $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ and $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ do not yield **3** when the mixture is

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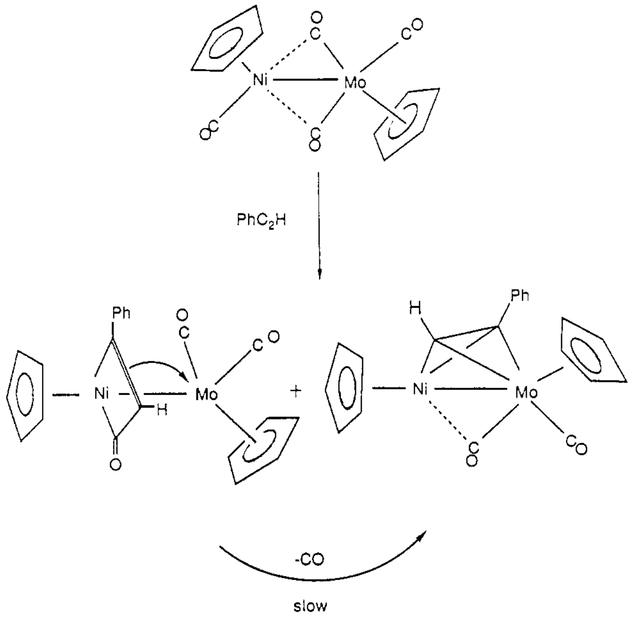
Scheme I. Reaction of (η^5-C_5H_5)(CO)Ni–Mo(CO)$_3$(η^5-C_5H_5) with PhC_2H, Illustrating the Structures of the Bridging Alkyne and the Nickelacyclobutenone Products



kept in the dark or exposed to fluorescent light, indicating that the mixture is kinetically stable in the absence of sunlight or UV irradiation.

Two equivalents of phenylacetylene were added to a 1:1 mixture of $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ and $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ in toluene and stirred for a day under fluorescent light; IR analysis of the solution revealed that no reaction had taken place. When placed near a sunlit window, a color change (red to orange) was evident after 10 h. The major product was $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_5)$ (**3a**), suggesting that phenylacetylene reacts either with photogenerated monometallic radical species or with the heterodimetallic complexes formed on irradiation (eq 1). Complexes **1**–**6** may react similarly. Carbonyl dissociation on the NMR time scale is unlikely in light of the ^{13}C NMR spectrum of **3**, which exhibits a single resonance with ^{183}W satellites for all carbonyl ligands.[15]

II. Kinetics of the Alkyne Reactions. A kinetic study utilizing equimolar concentrations of phenylacetylene and the metal complex was undertaken to establish the reaction order of **1**, **3**, **5**, and **6** with the alkyne. The reaction occurs at a rate conveniently monitored by ^{1}H NMR spectroscopy, and chemical shifts of reactants and products are distinctive. Complexes **1** and **3** yielded **1a** and **3a** respectively; **5** afforded **5a** and **9**; **6** led to **6a** and **10**. No other products were observed. Table II summarizes the kinetic data; Figure 1 shows a stacked plot of the ^{1}H NMR spectra showing the increase of **3a** and the concurrent decrease of **3** with time. Best least-squares linear fits were obtained with plots of [phenylacetylene]$^{-1}$ and [reactant metal complex]$^{-1}$ vs time for 60–70% reactant to product conversion, indicating second-order behavior—first order in both the nickel–molybdenum or nickel–tungsten complex and alkyne concentrations. Very pure samples exhibited no significant rate differences compared to samples of routine purity. Second-order rate constants lie in the range of (2.4–4.7) × 10^{-3} M^{-1} s^{-1}. A kinetic run in acetone-d_6 exhibited a rate constant of 6.6 × 10^{-3} M^{-1} s^{-1}, slightly larger than rate constants obtained in benzene-d_6, suggesting minor differences in ground and transition state polarities.

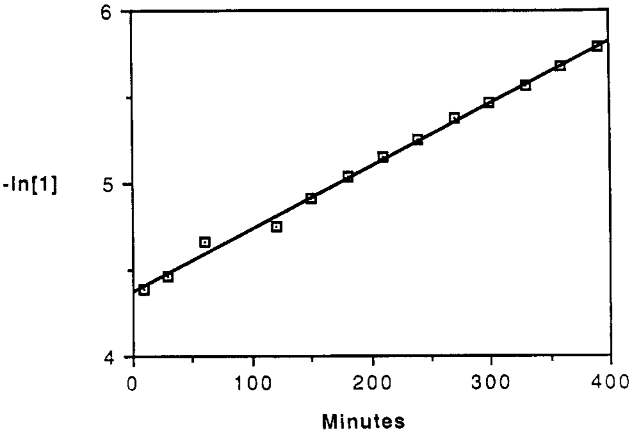


Figure 2. Pseudo-first-order plot of –ln [1] vs time for a 10-fold excess of phenylacetylene.

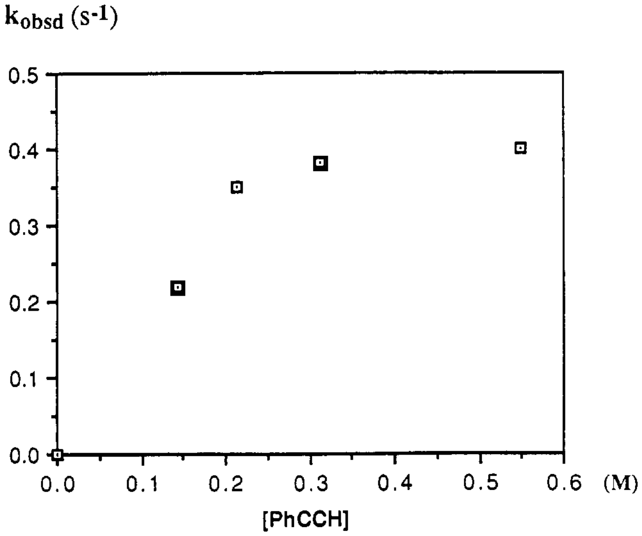


Figure 3. Plot of k_{obsd} (s^{-1}) vs $[PhC_2H]$ (M) for the reaction of **1** with phenylacetylene at varying alkyne concentrations.

The kinetics were also investigated under conditions of excess phenylacetylene. A pseudo-first-order plot of –ln [**1**] vs time for a 10-fold excess of $[PhC_2H]$ is shown in Figure 2. A plot of k_{obsd} vs $[PhC_2H]$, shown in Figure 3, levels off at high alkyne concentrations, indicating pseudo-first-order behavior and implying that the phenylacetylene reacts with a transient intermediate form of the metal complex.

The kinetics of the reaction of **1** with 2-butyne were also investigated. A second-order rate constant of 1.8 × 10^{-3} M^{-1} s^{-1} was obtained which may be compared to a value of 2.4 × 10^{-3} M^{-1} s^{-1} for the analogous reaction with phenylacetylene.

III. Alkyne Competition Experiments. Simultaneous reaction of two alkynes with a nickel–tungsten complex allowed a comparison of relative alkyne reaction rates.[16] Products of competition reactions with **3** and the two alkynes initially in a 1:1:1 molar ratio were analyzed. Alkyne pairs used were (1) 2-butyne, phenylacetylene; (2)

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(15) ^{13}C NMR ($CDCl_3$): δ 90.8, 94.5 [Ni- and W-(η^5-C_5H_5)], 215.9 (CO, J_{W-C} = 118 Hz). The observed J_{W-C} ~75% of typical terminal ^{183}W-^{13}C values [J_{W-C} = 170 Hz for carbonyl ligands in $NiW(CO)_2(\mu\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)_2$,[9] indicating an intramolecular carbonyl exchange process.

(16) In contrast to the more labile $Ni_2(\mu\text{-}RC_2R')(\eta^5\text{-}C_5H_5)_2$ complexes[11a] the nickel–molybdenum and nickel–tungsten alkyne-bridged complexes described are inert to alkyne substitution under a variety of conditions including photolysis and refluxing diglyme. Complexes were recovered with only slight decomposition in all cases (Chetcuti, M. J.; Zakutansky, J., unpublished results).

2-butyne, diphenylacetylene;[17] and (3) phenylacetylene, diphenylacetylene.[17] These afforded the alkyne-bridged products $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}RC_2R')W(CO)_2(\eta^5\text{-}C_5H_5)$ (RC_2R' = PhC_2H, 3a; MeC_2Me, 3b; PhC_2Ph, 3c). Reaction rates with complex 3 decreased in the order: phenylacetylene > 2-butyne ≫ diphenylacetylene.

The competition experiment between phenylacetylene and 2-butyne with complex 1 was also carried out. Relative rates of reaction of 1 with phenylacetylene and 2-butyne obtained in this experiment (~1.8:1) compare favorably, within experimental errors, with the ratio (~1.3:1) obtained from kinetics experiments.

The observed rate dependence on the alkyne may be rationalized primarily on steric grounds with electronic effects contributing to the reaction rates. The slow rate of reaction observed for the diphenylacetylene reactions may be attributed to the steric bulk of that ligand governing the rate. Phenylacetylene is likely to have a less-hindered approach to the metal atom than the two internal alkynes promoting the rate of this reaction. In addition, the electron-withdrawing character of the phenyl group may assist attack at the electron-rich metal center.

IV. Crossover Studies. (a) Without Phenylacetylene. Crossover studies utilizing 1–6 were undertaken to determine whether the species maintained their structural integrity. The metal atoms were labeled with cyclopentadienyl or methylcyclopentadienyl ligands. It was assumed that various ligand combinations did not affect the reactivity of the heterodimetallic species and that the ligands remained attached to the metal to which they were coordinated. The first assumption is not strictly valid; however, reactivity differences between species with coordinated cyclopentadienyl or methylcyclopentadienyl ligands do not affect the experiment's outcome. Metal–cyclopentadienyl or –methylcyclopentadienyl bonds are not activated under the mild reaction conditions.[18]

Equimolar solutions of 1 and 2 were mixed, and the mixture was monitored periodically by ^1H NMR spectroscopy for ca. 13 h. A statistical mixture of the heterodinuclear complexes 1, 2, 3, and 4 formed in a 6-h period; no further changes were observed. Significant crossover occurred within minutes, even in the dark. Complete scrambling did not occur: *homodimetallic species were not observed.* This experiment demonstrated the kinetic lability of the heterodinuclear species compared to their homodinuclear counterparts. Little thermodynamic stability differences exist between cyclopentadienyl and methylcyclopentadienyl species, verifying prior assumptions. Metal–metal metathesis took place when complexes $(\eta^5\text{-}C_5H_5)(CO)Ni\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (5) and $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (7) were mixed: $(\eta^5\text{-}C_5H_5)(CO)Ni\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (6) and $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (8) also were formed.

Recrystallized samples of 1 and 2, with no observable impurities by ^1H NMR, exhibited crossover. In one case, repeated purification of 1 and 2 by chromatography resulted in no crossover in a 3-h period, suggesting that trace impurities or oxidation products initiate crossover. Conversely an impure sample of 1 and 2 yielded *complete* scrambling to form all possible homo- and heterodimetallic species. These experiments demonstrate a variable rate and extent of crossover, critically dependent on the purity of 1 and 2, as expected for a radical process.

Table III. Mixed-Metal Complex[a] Competition Experiments

complex A + complex B + PhC_2H

complex A	complex B	ratio of alkyne-bridged products
Ni–W′ (1)	Ni′–W′ (4)	2:1 (**1a**:**4a**)
Ni–W (3)	Ni′–W (2)	3:2 (**3a**:**2a**)
Ni–W′ (1)	Ni–W (3)	7:6 (**1a**:**3a**)
Ni′–W′ (4)	Ni′–W (2)	6:5 (**4a**:**2a**)

[a] Complex A, complex B, and PhC_2H initially present in a 1:1:1 ratio. $(\eta^5\text{-}C_5H_5)M$ and $(\eta^5\text{-}C_5H_4Me)Me$ designated by M and M′, respectively; carbonyl ligands omitted for clarity.

Crossover reactions of 1 and 2 were further investigated by using the radical inhibitors benzoquinone and hydroquinone. Samples were prepared containing a 1:1 mixture of 1 and 2 and 5% benzoquinone or hydroquinone. Metal exchange occurred and no inhibition was noted, indicating that any radical species present were unreactive toward benzoquinone or hydroquinone.

(b) With Phenylacetylene. Equimolar solutions of 1 and 2 were placed sequentially in an NMR tube, rapidly frozen in a liquid nitrogen bath, and treated with 2 equiv of phenylacetylene. The solution was thoroughly mixed as soon as it liquefied and warmed rapidly to 25 °C and the reaction monitored. *The only products observed were the alkyne complexes derived from 1 and 2*, i.e. $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**1a**) and $(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_5)$ (**2a**). The complementary reaction with equimolar solutions of 3 and 4 produced **3a** and $(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**4a**) only. The nickel–molybdenum species **5** and **7** yield complexes **5a** and **7a** together with the metallacyclic complexes **9** and **11** when treated with phenylacetylene.

Equimolar solutions of 1 and 2 were mixed and allowed to stand for approximately 10 min generating observable quantities of 3 and 4. Phenylacetylene was then added and the products analyzed. All four heterodinuclear bridging alkyne complexes were present by ^1H NMR spectroscopy; molecular ions corresponding to *m/e* 485 (**3a**), 499 (**1a**, **2a**), and 513 (**4a**) were observed in the mass spectrum. The major products were **1a** and **2a**, derived from the predominant reactants in solution, 1 and 2; small quantities of **3a** and **4a** were also observed. Ratios of **1a**–**4a** mirrored the molar ratios of complexes 1–4 present in solution when phenylacetylene was added, implying that the alkyne reacts with *heterodimetallic complexes* and not with monometallic radicals.

V. Metal Competition Experiments. Competition experiments between different dimetallic complexes were designed to determine the site of rate-determining alkyne attack. Cyclopentadienyl ligands were altered on one metal atom, leaving ligands on the other metal atom unchanged. Modifying tungsten-bound ligands would have a minimal rate effect if the nickel atom were the site of alkyne attack; modifying ligands on the nickel atom would have a more pronounced effect. The reverse would hold if rate-determining attack occurred on the tungsten atom. Pairs of complexes were reacted with phenylacetylene in a 1:1:1 ratio as outlined in Table III, which describes the notation used. As the alkyne complexes are nonlabile,[16] their relative ratios are a measure of the relative reaction rates of each heterodimetallic precursor.

An overall reactivity order of NiW′ ≈ NiW > Ni′W′ ≈ Ni′W was found. Significant differences in reactivity were observed between nickel–cyclopentadienyl and nickel–methylcyclopentadienyl complexes; nickel–cyclo-

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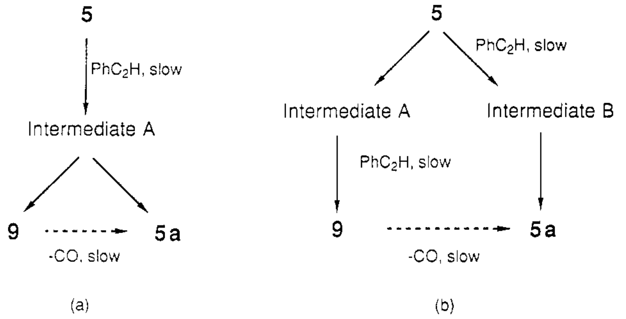
[17] Diphenylacetylene also forms $NiW(CO)_2[\mu\text{-}C(O)C(Ph)C(Ph)](\eta^5\text{-}C_5H_5)_2$.[9] This species is included with 3c in the relative product ratio.

[18] Sealed ^1H NMR solutions of $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{-}W(CO)_3(\eta^5\text{-}C_5H_5)$ do not form $(\eta^5\text{-}C_5H_5)(CO)Ni\text{-}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ over a 24-h period.

Scheme II. (a) The Common Intermediate Pathway to Metallacyclic and Alkyne-Bridged Species and (b) the Pathway in Which the Formation of the Two Complexes Is Not Related



pentadienyl species reacted more rapidly than nickel-methylcyclopentadienyl species as expected for attack at a smaller metal center. Modifying cyclopentadienyl ligands on the tungsten atom has a minimal reactivity effect implying that rate-determining attack occurs at the nickel atom.

VI. Formation and Decarbonylation of 9. (a) Kinetics and Phenylacetylene Concentration Dependence. Reactions of the nickel–molybdenum complexes with phenylacetylene are complicated by metallacycle formation; decarbonylation of this species affords bridging alkyne complexes. We aimed to establish whether nickel–molybdenum alkyne complexes are formed primarily through this pathway or if their major mechanistic route parallels that of the nickel–tungsten complexes.

The decarbonylation of $(\eta^5\text{-}C_5H_5)Ni\{\mu\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**9**) to $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PhC_2H)Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**5a**) was monitored for a 36-h period. The reaction is first order in the concentration of **9**, with a rate constant of 4.5×10^{-6} s^{-1}, too small to account for the amount of **5a** formed by reacting **5** with phenylacetylene for 3 h. Decarbonylation of **9** results in only a 13% conversion to **5a** over an 11-h period, indicating that **9** is not an intermediate in the main pathway to **5a**. A common intermediate may be involved such that rate-determining alkyne attack is the same for both species, *or* **5a** and **9** may be formed independently (Scheme II, pathway a or b). Solutions containing a 1:1 and a 1:10 ratio of **5** and phenylacetylene were prepared and when **5** was entirely consumed the ratio of the products **5a** to **9** was examined. Excess phenylacetylene would not affect the relative formation rate of **5a** and **9** for the common intermediate pathway (Scheme IIa); this would depend on the ratio of the rate constants and not on the alkyne concentration. If the two reactions followed independent pathways (Scheme IIb), reaction with a 10-fold excess of alkyne would yield a higher relative ratio of **5a**; only this rate of formation would depend on the phenylacetylene concentration. Ratios of **5a**:**9** were 2:1 and ~1.5:1.0 for the 1:1 and 1:10 reactions, respectively, a small difference that suggests a common intermediate pathway (Scheme IIa). Relative ratios of **5a**:**9** did not vary during the kinetic experiments, supporting this proposal.

(b) Mechanisms Proposed for Formation of the Metallacycles. A variety of mechanisms have been suggested for alkyne to carbonyl ligand linkage on a metal center, yielding species analogous to **9**. Reactions of $[Rh(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)]_2$ with alkynes[19] afford $Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(R)C(R')(\eta^5\text{-}C_5Me_5)_2$. Mechanistic work is not reported, but cleavage of $[Rh(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)]_2$ into monometallic fragments is unlikely in view of the bridging carbonyl ligands and the formal double bond; an associative mechanism is feasible. A homolytic pathway is postulated[20] for the complex $W_2(CO)_4\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(R)C(R')\}(\eta^5\text{-}C_5H_5)_2$, formed by photolysis of $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ with alkynes. The species $Pt_2\{\mu\text{-}C(O)C(Ph)C(Ph)\}(\eta^5\text{-}C_5H_5)_2$ is proposed[21] to form by trimethylamine *N*-oxide induced carbon monoxide loss, followed by alkyne coordination and subsequent insertion of a coordinated carbonyl ligand into a platinum–carbon bond. The mechanism included an η^5- to η^3-cyclopentadienyl ring slippage. Metal–metal bond retention was proposed[2b] in forming $FeRu(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma,\eta^3\text{-}C(O)C(R)C(R)\}(\eta^5\text{-}C_5H_5)_2$, together with a pathway in which the alkyne "traps" photochemically produced $FeRu(CO)_3(\eta^5\text{-}C_5H_5)_2$. Homolytic cleavage was ruled out as no homodinuclear products were obtained.

As the heterodinuclear alkyne-bridged compounds discussed here are not generally converted to the metallacyclic species under mild conditions,[9] the formation of the nickel–molybdenum metallacycles via the alkyne-bridged compounds is unlikely. The experiments described previously suggest a common intermediate species in the formation of the metallacyclic and alkyne-bridged products. The formation of a carbon–carbon bond between a coordinated carbonyl ligand and an alkyne on a metal center followed by loss of a carbon monoxide ligand seems reasonable.

VII. Comments on Reactions of Complexes 1–6 with Alkynes. Dinuclear carbonyl complexes frequently react via rate-determining carbon monoxide loss,[22] as observed for their mononuclear congeners.[23] Rates generally depend on the metal complex concentrations; incoming nucleophile concentrations may be important, especially for carbonyl cluster species.[24]

Organotransition-metal complexes may also undergo substitution by associative mechanisms if the complexes have ligands available onto which electron density can be delocalized,[25] facilitating nucleophilic attack and avoiding disfavored 20-electron species. Associative mechanisms have been demonstrated for monometallic cyclopentadienyl[26] and indenyl[27] complexes. Basolo et al. have shown[28] that $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ and its derivatives exhibit second-order kinetics in reactions with phosphine ligands and undergo substitution via an associative pathway to yield mono- and disubstituted products. An η^5–η^3 cyclopentadienyl ring shift was proposed, affording a vacant metal orbital for the incoming ligand. Rate enhancements were observed, as expected, in substitution reactions of complexes containing cyclopentadienyl ligands with elec-

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tron-withdrawing substituents. Isolation of related η^1- and η^3-cyclopentadienyl complexes supports the proposed pathway.[29]

Our results under high phenylacetylene concentration indicate pseudo-first-order behavior, which is consistent with alternative reaction pathways. Reversible carbon monoxide dissociation from the mixed-metal complex to yield a vacant coordination site would yield an activated dinuclear species, susceptible to alkyne attack. Equation 2 outlines the process and shows its rate law.

$$\mathrm{NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NiW(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} + \mathrm{CO}$$

$$\mathrm{NiW(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} + \mathrm{PhC_2H} \xrightarrow{k_2} \mathrm{NiW(CO)_2(\mu\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} + \mathrm{CO}$$

$$\text{rate} = \frac{k_1k_2[\mathrm{NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)}][\mathrm{PhC_2H}]}{k_{-1}[\mathrm{CO}] + k_2[\mathrm{PhC_2H}]}$$

A second possible pathway is activation of the metal complex by a process other than carbon monoxide dissociation. For example, slippage of the cyclopentadienyl ring attached to the nickel atom from an η^5- to an η^3-bonding mode would yield an activated form of the mixed-metal complex with a metal localized orbital available for alkyne attack (eq 3).

$$\mathrm{NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{NiW(CO)_4(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)}]^*$$

$$[\mathrm{NiW(CO)_4(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)}]^* + \mathrm{PhC_2H} \xrightarrow{k_2} \mathrm{NiW(CO)_2(\mu\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)} + 2\mathrm{CO}$$

$$\text{rate} = \frac{k_1k_2[\mathrm{NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)}][\mathrm{PhC_2H}]}{k_{-1} + k_2[\mathrm{PhC_2H}]}$$

A third possibility is the formation of an activated species with phenylacetylene coordinated to the metal complex and subsequent rate-determining carbon monoxide dissociation from that species. This is unlikely and will not be discussed further; carbon monoxide dissociation from the sterically congested complex would be expected to be rapid and not rate determining.

Assuming a steady-state concentration of the "activated" species in eq 2 and 3 leads to the rate laws shown. At high concentrations of phenylacetylene both pathways are pseudo-first-order in the mixed-metal complex. The two expressions can be differentiated on the basis of inhibition by carbon monoxide, a factor in the former case but not in the latter. Plots of $-\ln [\mathrm{PhC_2H}]$ vs time exhibited no signs of inhibition despite the buildup of carbon monoxide in the NMR tube. Furthermore, no inhibition was noted when the reaction was monitored under an atmosphere of carbon monoxide favoring the second mechanism (eq 3).

The work presented here indicates that an "activated" form of the nickel–tungsten and nickel–molybdenum complexes reacts with phenylacetylene. The metal competition experiments demonstrated significantly faster reaction rates for the cyclopentadienylnickel compounds as compared to their (methylcyclopentadienyl)nickel analogues. An associative pathway involving the formation of a mixed-metal intermediate through an η^5–η^3 ring slippage mechanism agrees with the metal competition experiments; the metal-substituted cyclopentadienyl ring would be expected to retard the reaction rate on both steric and electronic grounds. The exact nature of the intermediate species is unknown, however, as none could be identified by ^{1}H NMR or IR spectroscopy.

Conclusions

Complexes 1–6 react with alkynes affording only heterodimetallic products. Second-order rate behavior (first-order dependence on the alkyne and the nickel–molybdenum or nickel–tungsten complex concentrations) was observed over a moderate concentration range. Kinetics at higher alkyne concentrations indicate pseudo-first-order behavior; the reaction is apparently not inhibited by the presence of carbon monoxide. Crossover experiments on labeled nickel–molybdenum and nickel–tungsten complexes demonstrate metal–metal bond metathesis readily occurs, apparently triggered by trace impurities or oxidation products. Competition and crossover experiments indicated that phenylacetylene reacts with nickel–molybdenum or nickel–tungsten units rather than with monometallic fragments. Metal competition experiments suggest that rate-determining alkyne attack takes place at the nickel atom. The data are consistent with an associative mechanism possibly involving a transient η^5- to η^3-cyclopentadienyl slipped ring species, followed by alkyne attack at the nickel atom.

The nickelacyclobutenone complexes slowly decarbonylate, affording alkyne complexes. The kinetics of their decomposition were monitored; rate constants obtained show that their decomposition is not the primary pathway to the nickel-molybdenum alkyne complexes.

Experimental Section

General Comments. All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were distilled over sodium–benzophenone ketyl (hexane, diethyl ether, diglyme), sodium (toluene), or $\mathrm{CaH_2}$ (dichloromethane). The dimers $[\mathrm{M(CO)_3(\eta^5\text{-}C_5H_4R)}]_2$ and $[\mathrm{Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_4R)}]_2$ (M = Mo, W; R = H, Me) were prepared by slight modifications of standard methods.[30,31] $\mathrm{Ni(CO)_4}$, $\mathrm{Mo(CO)_6}$ and $\mathrm{W(CO)_6}$ were purchased from Pressure Chemical Co. while alkynes were obtained from Aldrich. $\mathrm{PhC_2H}$ was distilled and stored over molecular sieves; $\mathrm{PhC_2Ph}$ and $\mathrm{MeC_2Me}$ were used as received. Benzoquinone was prepared by standard methods;[32] hydroquinone was purchased from Fisher Scientific. Chromatography was carried out on silica gel or alumina columns under nitrogen. ^{1}H NMR spectra were obtained on a 300-MHz Nicolet NT-300 spectrometer or a 200-MHz Chemagnetics A-200 spectrometer and run in benzene-d_6 unless otherwise stated. IR spectra were obtained on an IBM FT-IR 32 spectrometer.

Complexes 1–6 are highly air-sensitive in solution and moderately so in the solid state. The syntheses and characterization of **1**, **3**, **5**, **6**; the alkyne-bridged species **1a**, **3a**, **3b**, **3c**, **5a**, and **6a** and metallacycles **9** and **10** have been described.[9] Preparations of the complexes $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}W(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**), $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}W(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**4**), $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ (**7**), $(\eta^5\text{-}C_5H_4Me)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ (**8**), $(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_5)$ (**2a**), $(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)W(CO)_2(\eta^5\text{-}C_5H_4Me)$ (**4a**), $(\eta^5\text{-}C_5H_4Me)Ni(\mu\text{-}PhC_2H)Mo(CO)_2(\eta^5\text{-}C_5H_5)$ (**7a**), and $(\eta^5\text{-}C_5H_4Me)Ni\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2(\eta^5\text{-}C_5H_5)$ (**11**) are based on those of the analogous cyclopentadienyl complexes;[9] ^{1}H

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Table IV. ^{1}H NMR Data[a] for the Mixed-Metal Complexes

1[b]	1.57 (s, 3 H, *Me*), 4.51, 4.53 (m, 4 H, C_5H_5Me), 5.34 (s, 5 H, C_5H_5)
1a[b]	1.63 (s, 3 H, *Me*), 4.49, 4.57 (m, 4 H, C_5H_4Me), 5.13 (s, 5 H, C_5H_5), 5.82 (s, 1 H, *H*), 7.01, 7.51 (m, 5 H, *Ph*)
2	1.88 (s, 3 H, *Me*), 4.58 (s, 5 H, C_5H_5), 5.16, 5.26 (m, 4 H, C_5H_4Me)
2a	1.64 (s, 3 H, *Me*), 4.65 (s, 5 H, C_5H_5), 4.96 (m, 4 H, C_5H_4Me), 5.80 (s, 1 H, *H*), 7.06, 7.41 (m, 5 H, *Ph*)
3[b]	4.55 (s, 5 H, W–C_5H_5), 5.30 (s, 5 H, Ni–C_5H_5)
3a[b]	4.63 (s, 5 H, W–C_5H_5), 5.12 (s, 5 H, Ni–C_5H_5), 5.90 (s, 1 H, *H*), 7.00, 7.20, 7.51 (m, 5 H, Ph)
3b[b]	2.46 (s, 6 H, *Me*C_2*Me*), 4.71 (s, 5 H, W–C_5H_5), 5.12 (s, 5 H, Ni–C_5H_5)
3c[b]	4.53 (s, 5 H, W–C_5H_5), 5.06 (s, 5 H, Ni–C_5H_5), 7.15, 7.32, 7.70 (m, 10 H, *Ph*C_2*Ph*)
4	1.60 (s, 3 H, *Me*), 1.92 (s, 3 H, *Me*), 4.55 (m, 4 H, C_5H_4Me), 5.17, 5.29 (m, 4 H, C_5H_4Me)
4a	1.64 (s, 3 H, *Me*), 1.66 (s, 3 H, *Me*), 4.23, 4.53, 4.57, 4.76, 4.95, 4.99, 5.05, 5.07 (m, 8 H, Ni, W–C_5H_4Me), 5.73 (s, 1 H, *H*), 7.05, 7.15, 7.64 (m, 5 H, *Ph*)
5[b]	1.52 (s, 3 H, *Me*), 5.24 (s, 5 H, C_5H_5), 4.54, 4.57 (m, 4 H, C_5H_4Me)
5a[b]	1.55 (s, 3 H, *Me*), 4.58 (m, 4 H, C_5H_4Me), 5.05 (s, 5 H, C_5H_5), 6.00 (s, 1 H, *H*), 7.05, 7.42 (m, 5 H, *Ph*)
6[b]	4.58 (s, 5 H, Mo–C_5H_5), 5.25 (s, 5 H, Ni–C_5H_5)
6a[b]	4.73 (s, 5 H, Mo–C_5H_5), 5.03 (s, 5 H, Ni–C_5H_5), 6.01 (s, 1 H, *H*), 7.02–7.31 (m, 5 H, *Ph*)
7	1.83 (s, 3 H, *Me*), 4.62 (s, 5 H, C_5H_5), 5.11, 5.15 (m, 4 H, C_5H_4Me)
7a	1.59 (s, 3 H, *Me*), 4.72 (s, 5 H, C_5H_5), 5.01–5.22 (m, 4 H, C_5H_4Me), 5.97 (s, 1 H, *H*), 7.00–7.30 (m, 5 H, *Ph*)
8	1.55 (s, 3 H, *Me*), 1.87 (s, 3 H, *Me*), 4.53, 4.55 (m, 4 H, C_5H_4Me), 5.12, 5.16, 5.18 (m, 4 H, C_5H_4Me)
9[b]	1.44 (s, 3 H, *Me*), 5.13 (s, 5 H, Ni–C_5H_5), 4.66–4.72 (m, 4 H, C_5H_4Me), 6.90–7.42 (m, 5 H, *Ph*), 7.15 (s, 1 H, *H*)
10[b]	4.62 (s, 5 H, Mo–C_5H_5), 5.22 (s, 5 H, Ni–C_5H_5), 6.99–7.31 (m, 5 H, *Ph*), 7.8 (s, 1 H, *H*)
11	1.93 (s, 3 H, *Me*), 4.66 (s, 5 H, C_5H_5), 5.00–5.22 (m, 4 H, C_5H_4Me), 7.01–7.29 (m, 5 H, *Ph*), 7.22 (s, 1 H, *H*)

[a] ^{1}H NMR in benzene-d_6 reported in ppm with C_6D_5H set as reference at 7.15 ppm. [b] We have previously reported the syntheses and characterization of these compounds.[9] Spectra have not been previously reported in benzene-d_6 and are included for completeness.

NMR data are listed in Table IV.

Reaction of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ and $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ with PhC_2H. $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (147 mg, 0.48 mmol) and $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ (365 mg, 0.52 mmol) were placed in a round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet. The flask was purged, and toluene (80 mL) and PhC_2H (0.15 mL, 14 mg, 1.36 mmol) were added via syringe. The solution was frozen in liquid nitrogen, evacuated, and warmed to room temperature with stirring. There was no apparent color change after 24 h. IR spectroscopy indicated that only $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ and $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ were present.

The procedure was repeated in sunlight. $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (125 mg, 0.41 mmol), $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ (292 mg, 0.42 mmol), and PhC_2H (55 mL, 51.1 mg, 0.50 mmol) were dissolved in toluene (35 mL). The solution changed from red to orange in 10 h; no further changes were observed. The solution was placed on a silica gel column and eluted with a toluene/hexane (5:1) mixture. The major product, identified by ^{1}H NMR spectroscopy, was **1a**. Trace amounts of other species, eluted with diethyl ether/dichloromethane or methanol, were not characterized.

Crossover Studies. (a) Reaction of 1 and 2. **1** (13.2 mg, 0.026 mmol) and **2** (13.3 mg, 0.027 mmol) were dissolved in benzene-d_6 (0.50 mL), filtered, placed in a degassed ^{1}H NMR tube, sealed, and frozen. The first spectrum obtained 15 min after thawing showed **3** and **4**, with a concurrent decrease in **1** and **2**. Spectra were obtained over 13 h. **3** and **4** increased with time at the expense of **1** and **2**; after 6 h the compounds were present in a 1:1:1:1 (**1**:**2**:**3**:**4**) ratio, and no further changes occurred. The experiment was repeated with samples of **1** and **2** that had been carefully purified by chromatography; no crossover occurred in a 1.5-h period. Anaerobic addition of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ to the sample did not initiate crossover in another 1.5-h period. In a third experiment, **1** and **2** in the presence of unidentified impurities demonstrated complete scrambling after 24 h to yield all possible homo- and heterodimetallic compounds in the ^{1}H NMR.

(b) Reaction of 5 and 7. **5** (0.25 mL of a 0.083 M solution) and 0.25 mL of a 0.081 M solution of **7** in benzene-d_6 were placed in a ^{1}H NMR tube under nitrogen. An initial spectrum, obtained within 15 min, showed resonances for complexes **6** and **8** with a concurrent decrease of **5** and **7**. After 4.5 h, a final spectrum was obtained with a product ratio of 1:1:1:1 (**5**:**6**:**7**:**8**).

(c) Reaction of 3 and 4 with Benzoquinone. **3** (7.0 mg, 0.014 mmol), dissolved in benzene-d_6, was placed into a ^{1}H NMR tube under nitrogen and frozen in liquid nitrogen. Benzene-d_6 solutions of **4** (7.3 mg, 0.014 mmol) and benzoquinone (0.3 mg, 2.5×10^{-3} mmol) were added sequentially; the sample was refrozen after each addition. After warming, the sample was monitored periodically by ^{1}H NMR for 24 h. Resonances assignable to the four heterodinuclear complexes (**1**:**2**:**3**:**4**) were observed in a 1:1:1:1 ratio in the final spectrum.

(d) Reaction of 3 and 4 with Hydroquinone. Following the same procedure, **3** (7.0 mg, 0.014 mmol), **4** (7.3 mg, 0.014 mmol), and hydroquinone (0.3 mg, 2.5×10^{-3} mmol) were placed sequentially into a ^{1}H NMR tube; the sample was refrozen after each addition. The reaction was monitored for 4 h; resonances assignable to **1**, **2**, **3**, and **4** were observed.

(e) Reaction of 1 and 2 with PhC_2H. **1** (5.8 mg, 0.012 mmol) was dissolved in benzene-d_6 placed in a ^{1}H NMR tube, and frozen in liquid nitrogen. **2** (5.8 mg, 0.012 mmol) and PhC_2H (2.6 mL, 2.4 mg, 0.024 mmol) in benzene-d_6 were sequentially added, freezing between the each addition. The sample was warmed rapidly to room temperature with vigorous shaking, and an initial spectrum was obtained within 5 min. After standing for 7 h, a final spectrum was obtained. All resonances were assignable to either **1a** and **2a**. The reaction was repeated by dissolving an equimolar mixture of **1** and **2** in benzene-d_6 and obtaining a preliminary ^{1}H NMR spectrum; resonances from the four heterodimetallic complexes were observed in a ~3:3:1:1 (**1**:**2**:**3**:**4**) ratio. PhC_2H was added under nitrogen and the reaction monitored over a 7.5-h period. The final spectrum showed the ratios of the four products were ~3:2:1:1 (**1a**:**2a**:**3a**:**4a**). Mass spectroscopic analysis yielded molecular ion peaks corresponding to m/e 485 (**1a**), 499 (**2a**, **3a**), and 514 (**4a**).

(f) Reaction of 3 and 4 with PhC_2H. **3** (0.10 mL of 0.080 M solution in benzene-d_6, 0.0080 mmol), **4** (0.10 mL of 0.080 M solution, 0.0080 mmol), and PhC_2H (0.20 mL of 0.080 M solution, 0.016 mmol) were added sequentially to a ^{1}H NMR tube, freezing between reactant addition, and the sample was evacuated and sealed. The solution was then thawed, thoroughly mixed while still cold, and monitored; **3** and **4** were entirely consumed in 6 h. The distribution of **3a** to **4a** was approximately 1:1; no resonances assignable to **1a** and **2a** were observed.

(g) Reaction of 5 and 7 with PhC_2H. Benzene-d_6 solutions of **5** (0.20 mL of a 0.083 M solution, 0.016 mmol), **7** (0.20 mL of a 0.081 M solution; 0.016 mmol), and PhC_2H (0.40 mL of a 0.080 M solution; 0.032 mmol) were placed sequentially into a ^{1}H NMR tube, under nitrogen, freezing the sample in liquid nitrogen between each reactant addition. The sample was warmed and thoroughly mixed upon melting. An initial spectrum was obtained within 5 min of thawing; the final spectrum was obtained after 4.5 h. Resonances were assignable to complexes **5a**, **7a**, **9**, and **11**; there was no evidence of "crossover products".

Alkyne Competition Experiments. (a) MeC_2Me vs PhC_2Ph. MeC_2Me (0.15 mL of a 0.50 M benzene-d_6 solution; 0.075 mmol), PhC_2Ph (0.15 mL of a 0.50 M benzene-d_6 solution; 0.075 mmol), and **3** (0.30 mL of a 0.25 M benzene-d_6 solution; 0.075 mmol) were placed into a degassed ^{1}H NMR tube at 5 °C. After ~24 h, the products were in a 17:1 (**3b**:**3c**) ratio. **(b) PhC_2H vs MeC_2Me.** With use of the same procedure, the final product ratio was ~2:1 (**3a**:**3b**) after ~7 h. **(c) PhC_2H vs PhC_2Ph.** Similarly, the PhC_2H was entirely consumed after ~5 h; the product ratio was ~21:1 (**3a**:**3c**). **(d) PhC_2H vs MeC_2Me with 1.** The procedure was repeated by using complex **1**: a final product ratio of ~1.8:1 (**1a**:**1b**) was obtained.

Metal Competition Experiments. All of the experiments were carried out as detailed below. Initial ^{1}H NMR spectra were obtained within 5 min of mixing; samples were kept at 20 °C.

(a) 1 vs 4. 1 (0.15 mL of a 0.081 M solution in benzene-d_6; 0.012 mmol) was placed into a degassed ^1H NMR tube and frozen in a liquid-nitrogen bath. 4 (0.15 mL of a 0.080 M solution in benzene-d_6, 0.012 mmol) and PhC_2H (0.15 mL of a 0.081 M solution in benzene-d_6, 0.012 mmol) were added sequentially, keeping the mixture frozen between each reactant's addition. The sample was then vigorously shaken and warmed to room temperature, and an initial spectrum was obtained. After 7 h at room temperature, the final ^1H NMR spectrum was recorded. Procedures for **(b) 3** vs **2**, **(c) 2** vs **4**, and **(d) 1** vs **3** were similar; product ratios are tabulated in Table III.

Kinetics. (a) Alkyne Reactions. Each experiment followed the procedure outlined below. Solids were rapidly weighed in air to ±0.2 mg on a CAHN 50T analytical balance and dissolved in benzene-d_6 to give simple concentrations of 0.025–0.190 M. Acetone-d_6 was used in one case to investigate solvent effects. Most kinetic data was obtained by using 1:1 molar ratios of the metal complex and PhC_2H. The alkyne was added to a frozen solution of the complex; the ^1H NMR tube walls were rinsed with solvent, evacuated, sealed, and kept frozen in liquid nitrogen until data collection when the samples were thawed, vigorously mixed while still cold, and placed in the ^1H NMR spectrometer probe and the temperature was maintained at 20.0 ± 0.5 °C. Spectra were obtained on a Nicolet NT-300 spectrometer using the KINET program. For each reaction, 10–25 data points were obtained. Intervals were initially 15 min, increasing to 60 min as the reaction neared completion. Reactant concentrations were determined from integral areas and/or peak heights. (Differences were <10% when both methods were used.)

Plots of [concentration] vs time, −ln [concentration] vs time, and $[\text{concentration}]^{-1}$ vs time were obtained. Curvature was observed in the natural log plots; reciprocal plots were linear and yielded correlation coefficients ranging from 0.97 to 0.99 for 60–70% of reactant to product conversion. Rate constants (Table II) are average values for two to three experiments. Maximum errors are estimated at ±20% for the kinetic experiments, attributed mainly to sample transfer, oxidation, temperature variations, and integration errors. A representative experiment is detailed below.

(b) Kinetics of the Reaction of 3 with PhC_2H. 3 (47.3 mg, 0.098 mmol) was dissolved in 0.25 mL of benzene-d_6, filtered, and transferred to a ^1H NMR tube under nitrogen. After the solution was frozen in liquid nitrogen, PhC_2H (10.7 mL, 9.9 mg, 0.098 mmol) was added via microsyringe. The inside of the NMR tube was rinsed with 0.25 mL of benzene-d_6; the sample was refrozen, evacuated, and sealed. The sample was then thawed and vigorously mixed, and ^1H NMR spectra were recorded until the PhC_2H was consumed (3 h).

(c) Decarbonylation of 9. 9 (2.9 mg, 0.0060 mmol) was placed into a nitrogen-purged vial. The sample was dissolved in 0.50 mL of benzene-d_6, filtered, transferred to a ^1H NMR tube, and sealed in vacuo. A spectrum was obtained immediately on warming to room temperature. A plot of −ln [9] vs time was linear, yielding a first-order rate constant of $(4.5 \pm 0.5) \times 10^{-6}\ s^{-1}$.

(d) Pseudo-First-Order Kinetics. All reactions were monitored in toluene-d_8 at 5.0 ± 0.5 °C, partially compensating for the faster rates observed with higher alkyne concentrations. Samples were quickly thawed and thoroughly mixed before placement into the ^1H NMR spectrometer. Spectra were obtained at 10- or 15-min intervals, increasing to 20 or 30 min as the reaction proceeded. Plots of −ln [1] vs time yielded linear plots with good correlation for 60–70% reaction; no deviations from first-order behavior were observed as the reactions progressed. A representative experiment is detailed below.

1 (9.4 mg, 0.019 mmol) was placed into a vial and dissolved in toluene-d_8 (1.20 mL) under nitrogen. A 0.50-mL portion was removed, placed in an NMR tube, and frozen in liquid nitrogen. Phenylacetylene (17 μL, 0.16 mmol, 0.31 M, 20-fold excess) was added to the frozen solution. The mixture was thawed, mixed while still cold, and placed in the ^1H NMR spectrometer probe and the reaction monitored. A plot of −ln [1] vs time yielded a pseudo-first-order rate constant of $0.38\ s^{-1}$.

The following concentrations of phenylacetylene yielded the pseudo-first-order rate shown: [PhCCH] = 0.14 M (10-fold excess), $k_{obsd} = 0.22\ s^{-1}$; [PhCCH] = 0.21 M (15-fold excess), $k_{obsd} = 0.35\ s^{-1}$; [PhCCH] = 0.55 M (35-fold excess), $k_{obsd} = 0.40\ s^{-1}$.

(e) Investigation of Inhibition by Carbon Monoxide. 1 (3.4 mg, 0.0068 mmol) was placed into a degassed vial, dissolved in toluene-d_8 (0.6 mL), and placed into an ^1H NMR tube. The sample was freeze–thaw–degassed with carbon monoxide and frozen in liquid nitrogen, and phenylacetylene (7.5 μL, 0.068 mmol) was added. With use of the procedure outlined above, a pseudo-first-order rate constant of $0.16\ s^{-1}$ was obtained. No apparent inhibition by carbon monoxide was observed.

Investigation of the Possibility of a Common Intermediate. 5 (8.3 mg, 0.020 mmol) in benzene-d_6 (0.25 mL) was syringed into a ^1H NMR tube and frozen in liquid nitrogen. PhC_2H (2.2 mL, 2.0 mg, 0.020 mmol) in benzene-d_6 (0.25 mL) was added and the mixture kept frozen until the first spectrum was taken. A final spectrum, obtained after 8 h, showed a **5a** to **9** ratio of 2:1. The procedure was repeated by using a 10-fold excess of PhC_2H; reaction was complete within 10 min. The ratio of the two products was 1.5:1 (**5a**:**9**). (Errors in this measurement are large as reaction with a 10-fold excess of PhC_2H was measured at completion; the equimolar reaction takes longer and decarbonylation of **9** to **5a** becomes significant.)

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Dr. A. G. Lappin of the University of Notre Dame for helpful discussions.

Registry No. 1, 110512-11-3; **1a**, 110512-17-9; **2**, 116970-02-6; **2a**, 116996-67-9; **3**, 75339-35-4; **3a**, 110512-16-8; **3b**, 110512-12-4; **3c**, 116996-68-0; **4**, 116970-03-7; **4a**, 116996-69-1; **5**, 110512-06-6; **5a**, 110512-09-9; **6**, 75339-34-3; **6a**, 110512-08-8; **7**, 116970-04-8; **7a**, 116996-70-4; **8**, 116970-05-9; **9**, 110512-23-7; **10**, 110512-22-6; **11**, 116970-06-0; Ni, 7440-02-0; W, 7440-33-7; Mo, 7439-98-7.