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η^2-Alkynyl and Vinylidene Transition Metal Complexes. 8.[1] Synthesis of Bimetallic Tungsten Gold Complexes by Addition of ClAuPPh$_3$ to the Acetylide Li[(η^5-C$_5$H$_5$)(CO)(NO)W(C≡C−R)]

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Tungsten acetylide complexes **1** [R = C(CH$_3$)$_3$; R = C$_6$H$_5$; R = *p*-tolyl] have been found to react in THF at −60 °C with ClAuP(C$_6$H$_5$)$_3$ to yield the bimetallic tungsten gold complexes [(η^5-C$_5$H$_5$)(NO)(μ-CO)(μ-C≡C−R)W−AuP(C$_6$H$_5$)$_3$] [**8a**, R = C(CH$_3$)$_3$; **8b**, R = C$_6$H$_5$; **8c**, R = *p*-tolyl] with semibridging carbonyl and alkynyl ligands. The molecular structure of **8a** was determined by single-crystal X-ray diffraction analysis. Variable-temperature NMR studies of **8a** showed fluxional behavior and at −80 °C the presence of three isomers.

Introduction

Recently we demonstrated that the electrophilic addition to acetylide anion **1** gave rise to a variety of products.[1,2] The use of "hard" electrophiles such as strong acids or alkylating reagents such as methyl triflate led to the formation of vinylidene complex **2**,[2d,e] whereas the addition of "soft" electrophiles such as allyl iodide resulted in the formation of complex **3**,[2c] by the allylation on the metal center. On the other hand, η^2-alkynyl complex **4** is formed by trapping the tungsten acetylide anion **1** with trimethylsilyl chloride as electrophile.[2e]

We could also demonstrate that the formation of η^2-alkynyl complex **4** is the result of a thermal η^1-vinylidene−η^2-alkynyl isomerization reaction and the primary product of the addition of silylating reagent to **1** is a η^1-vinylidene derivative.[3] This process could be demonstrated by refluxing the η^1-vinylidene complex **5** in toluene, which isomerizes to give the η^2-alkynyl complex **6**.[3]

The mechanism of η^1-vinylidene−η^2-alkynyl isomerization in the coordination sphere of a transition metal is subject to recent debate in the literature.[4−7] Two intramolecular mechanisms, the 1,2-hydrogen shift (**A**→**B**→**D** in Scheme 3) and the 1,3-hydrogen shift (**A**→**C**→**D**), are discussed in the literature for this rearrangement. Starting from the η^1-vinylidene species **A**, in the first mechanism a 1,2-hydrogen shift from the β- to α-carbon takes place by forming **B**, followed by a slippage process of the alkyne ligand from **B** to the η^2-alkyne coordination in **D**.[5] Earlier theoretical studies support this mechanism.[7] The second mechanism consists of the 1,3-hydrogen shift from the β-carbon to the metal (**A**→**C**), which undergoes a reductive elimination to form the η^2-alkynyl derivative **D**.[5] In addition to these two mechanisms for the η^2-alkyne→η^1-vinylidene rearrangement, a recent theoretical work discusses an alternative intermolecular process.[6]

To obtain more information for this isomerization, we studied the reaction of tungsten acetylide anion **1** with the gold(I) complex ClAuP(C$_6$H$_5$)$_3$ as an electrophile, since the AuL$^+$ fragment is isolobal to a proton.[8] This paper will focus on the reaction of the tungsten alkynyl complexes **1a**−**c** with ClAuP(C$_6$H$_5$)$_3$ to the η^2(C,Au)-alkynes **8a**−**c**, which resemble the type **B** structure in Scheme 3, the fluxional behavior of the product, and the structural characterization of **8a**.

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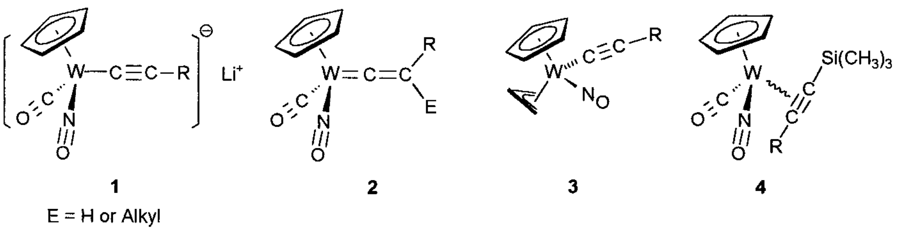
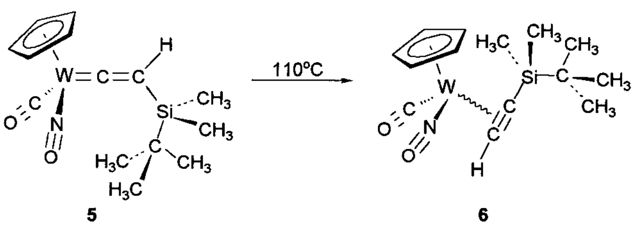
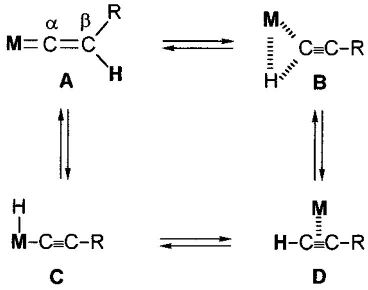
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

Synthesis of Tungsten Gold Complexes 8a–c. The emerald green solutions of tungsten acetylides **1a–c** were generated, as described before, by treatment of the corresponding tungsten vinylidene complexes **7a–c** with 1.0 equiv of *n*-BuLi in THF at −78 °C.[2] After addition of $ClAuP(C_6H_5)_3$ and stirring the mixture for 30 min at −60 °C the solution turned to dark red. Fast removal of the solvent at low temperatures under reduced pressure and crystallization with CH_2Cl_2/pentane at −30 °C leads to the bimetallic tungsten gold complexes **8a–c** in 63–76% yield. The crystals of **8a–c** can be stored under inert gas at −20 °C. The solutions of **8a–c** decompose at room temperature after a few minutes. Complexes **8a–c** are highly soluble in solvents such as CH_2Cl_2 and nearly insoluble in diethyl ether.

Characterization of Binuclear Acetylide Complexes 8a–c. The structures of **8a–c** were characterized by spectroscopic methods and elemental analysis. The structure of **8a** was additionally determined by X-ray crystallography. The binuclear complexes **8a–c** show a fluxional behavior on the NMR time scale. This is demonstrated by variable-temperature NMR spectra of **8a**: The ^1H NMR of **8a** at room temperature contains a broad singlet at 1.23 ppm for the *tert*-butyl protons and also a broad singlet at 5.61 ppm for the cyclopentadienyl (Cp) protons. Below −35 °C the *tert*-butyl and the cyclopentadienyl signal split into three signals, one major and two very minor (Figure 1). At −80 °C the major isomer has a signal for Cp at 5.68 ppm and the *tert*-butyl signal appears at 1.17 ppm. The free energy of activation of this process is estimated by line-shape analysis as $\Delta G^* = 13.3$ kcal/mol.

Due to the fluxional behavior, the ^{13}C NMR spectra of **8a** show no signals for the CO and C≡C group at room temperature. The signal for the cyclopentadienyl ring splits at −80 °C into three well-resolved signals at 94.7 for the main isomer and two very minor isomers at 97.2 and 95.6 ppm. At this temperature the signal for μ-CO and μ-C≡ appears at 246.3 and 162.3 ppm.[9,10] Two weak signals at 230.6 and 87.2 ppm are assigned to the CO group and C_α of the η^2-alkyne complex **9**.[11] Supporting this structure, the signal at 87.2 ppm shows a small phosphorus carbon coupling $^2J_{C-P}$ of 20 Hz.[12] Between 134.6 and 129.2 ppm the ^{13}C NMR spectrum shows also three sets of signals for the aromatic carbon atoms.

At room temperature **8b** shows in the ^{31}P NMR signals at 49.8 ppm for the major isomer and at 43.1 and 42.2 ppm, respectively, for the minor isomers. **8c** has signals at 49.6 (main isomer), 43.1, and 42.3 ppm and **8a** at 45.9 (main isomer) and 42.9 ppm.

The IR spectrum of **8a** in CCl_4 shows three signals for the carbonyl group at 2001, 1944, and 1854 cm $^{-1}$. The major signal at 1854.1 cm^{-1} is significant for a semibridging carbonyl group.[13]

The fluxional behavior of **8a** is consistently explained by the "wiper"-like oscillation process between the semibridged structure and the η^2-alkyne complex **9** (Scheme 3).[14] According to the IR spectra, we assume that the most stable isomer in solution is the semibridged complex **8a**. Whether the third isomer is the vinylidene complex **10**, the η^2-alkyne complex **11**, or a rotamer of **9** cannot be distinguished with certainty due to the low concentration present in the equilibrium mixture.[15]

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[9] μ-CO of **8a** is similar to μ-CO (246 ppm) for $[(\eta^5\text{-}C_5H_5)(CO)_2W(\mu\text{-}C(H)C_6H_4Me\text{-}4)AuPPh_3$: Carriedo, G. A.; Hodgson, D.; Howard, J. A. K.; Marsden, K.; Stone, F. G. A.; Went, M. J.; Wooward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 1006.

[10] Comparable shifts for μ-C≡C are reported in the following compounds. (i) $\{[(\eta^5\text{-}C_5H_5)\mu\text{-}(CO)(NO)W]\eta^2\text{-}[(\eta^5\text{-}C_5H_5)(CO)_2Fe-C\equiv C\text{-}{}^tBu)]\}$ (162.4 ppm): see ref 2d. (ii) $[(Ph_3P)_2N][Mo_2(\mu\text{-}C_2Ph)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (182.6 ppm): Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171. (iii) Mercer, R. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 567.

[11] (a) For similar chemical shift for the CO group and C_α see ref 10 and: Shiu, C. W.; Su, C. J.; Pin, C. W.; Chi, Y.; Peng, P. S.; Lee, G. *J. Organomet. Chem.* **1997**, *545*, 151.

[12] For similar $^2J_{C-P}$ value see: Naulty, R. H.; Cifuentes, M. P.; Humphrey, M. G.; Houbrechts, S.; Boutton, C.; Persoons, A.; Heath, G. A. Hockless, D. C. R.; Luther-Davies, B.; Samoc, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4167. Gamasa, M. P.; Gimeno, J.; Zhang, L.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1996**, *514*, 287.

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[15] Signals at lower field (>300 pm) which are characteristic for C_α in vinylidenes were not found.

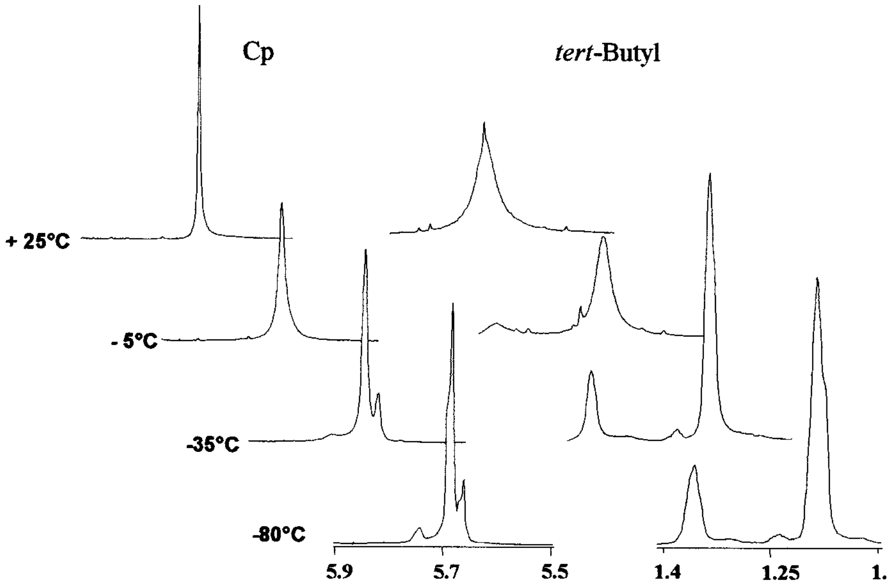
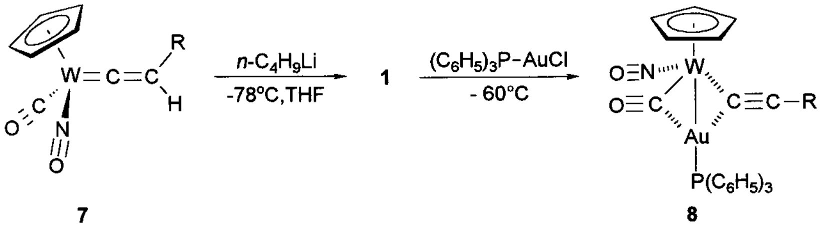


Figure 1. Selected signals of variable-temperature ^{1}H NMR spectra of {(η^5-C_5H_5)(NO)(μ-CO)[μ-C≡C−C(CH_3)$_3$]W−AuP(C_6H_5)$_3$} (**8a**) observed at 400 MHz in CD_2Cl_2.

Scheme 4



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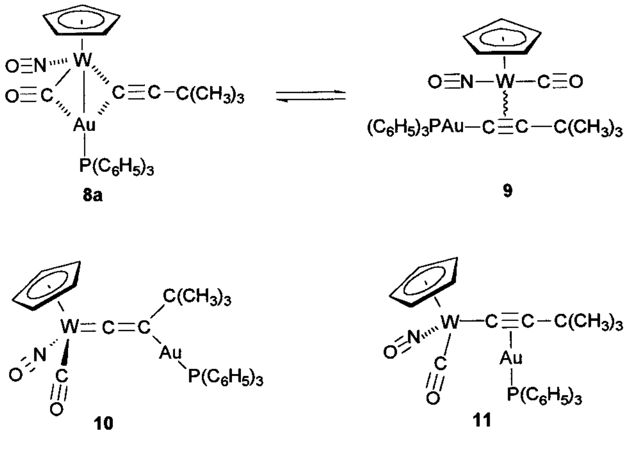
	R
a	$C(CH_3)_3$
b	C_6H_5
c	p-CH_3-C_6H_4

Scheme 5



Molecular Structure of 8a. Suitable single crystals of **8a** are grown from a dichloromethane solution by slow diffusion of pentane at ambient temperature. The crystal parameters, data collection parameters, and conditions for structure refinement are summarized in Table 1. Selected bonds distances and angles are given in Table 2. A view of the molecule **8a** is shown in Figure 2.

The most notable features of the structure are the following: The W−Au bond distance of 2.803 Å is short and similar to those reported for a single bond in the literature (2.698−2.824 Å).[16] The CO group is in a semibridging mode and is characterized by different bond distances and angles to tungsten and gold [W−C(7) = 1.97 Å, Au−C(7) = 2.51 Å, W−C(7)−O(2) = 164° and Au−C(7)−O(2) = 119°].[17] Due to the semibridging character of the carbonyl ligand with 1.17 Å the C(7)−O(2) bond is longer than expected for a terminal CO.[18] Also the W−C(1)−C(2) angle of 172.6° is nearly linear, and with an Au−C(1)−C(2) angle of 107.8° and distances of 2.12 Å for W−C(1) and 2.26 Å for Au−C(1) the acetylenic group [C(1)−C(2) bond length = 1.21 Å] is a semibridging group and not a side-on bonded group.[13b]

Experimental Section

General Procedures. All operations were carried out under argon. All solvents were purified by standard tech-

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[17] (a) Miller, Th. F., III; Strout, D. L.; Hall, M. B. *Organometallics* **1998**, *17*, 4164. (b) Reference 13b.

[18] For the terminal CO group in [HB(pz)$_3$]−(CO)$_2$(CS)W−AuPPh$_3$ a bond length of 1.14 Å is reported in ref 13c.

Table 1. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 8a

formula	$C_{30}H_{29}AuNO_2PW$
cryst size/mm	0.15 × 0.19 × 0.30
fw	847.33
color	red, transparent
cryst syst	monoclinic
space group	$P2_1/a$ (No. 14)
cell params	$a = 10.0955(7)$ Å, $\alpha = 90°$ $b = 26.700(2)$ Å, $\beta = 103.413(9)°$ $c = 10.7924(8)$ Å, $\gamma = 90°$
V/Å^3	2829.7
Z	4
d_{calc}/g · cm^{-3}	1.99
μ/cm^{-1}	93.2
diffractometer	Image Plate Diffractometer System (STOE)
radiation	Mo Kα
monochromator	graphite
2θ/deg	$4.9 \leq 2\theta \leq 52.0$
h,k,l range	$-12 \leq h \leq 12, -32 \leq k \leq 32, -13 \leq k \leq 13$
no. of reflns measd	20 515
no. of indep rflns	5519
R_{int}	0.0561
reflns with $F_o > 4\sigma(F_o)$	4622
temperature/K	293
applied corrections	Lorentz and polarization coefficients
structure determination and refinement	W, Au, and P positional params from direct methods (SHELXS-97);[a] further atoms from ΔF synthesis (SHELXL-97),[b] refinement by anisotropic full-matrix least-squares procedure for all non-hydrogens; hydrogen position refinement by riding model
refined params	326
wR2	0.079
R1	0.0379
R1 [$F_o > 4\sigma(F_o)$]	0.0295
max and min in $\Delta\sigma$ (e Å^{-3})	1.84, −1.50

[a] Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures; Universität Göttingen, 1997. [b] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen, 1997.

Table 2. Selected Distances (Å) and Bond Angles (deg) for 8a

Distances			
Au−W	2.803(3)	W−C(1)	2.120(6)
Au−C(1)	2.262(5)	W−C(7)	1.971(6)
Au−C(7)	2.514(6)		
Au−P	2.265(14)	C(7)−O(2)	1.166(7)
C(1)−C(2)	1.215(8)	C(2)−C(3)	1.483(8)
Angles			
P−Au−W	168.8(1)	W−C(1)−Au	79.5(2)
P−Au−C(1)	142.3(1)	W−C(7)−Au	76.3(2)
P−Au−C(7)	126.6(1)	W−C(7)−O(2)	164.2(5)
Au−W−C(1)	52.5(1)	W−N−O(1)	172.8(4)
Au−W−C(7)	60.6(2)	W−C(1)−C(2)	172.6(5)
Au−C(1)−C(2)	107.7(4)	C(1)−C(2)−C(3)	171.8(6)
Au−C(7)−O(2)	119.5(4)		

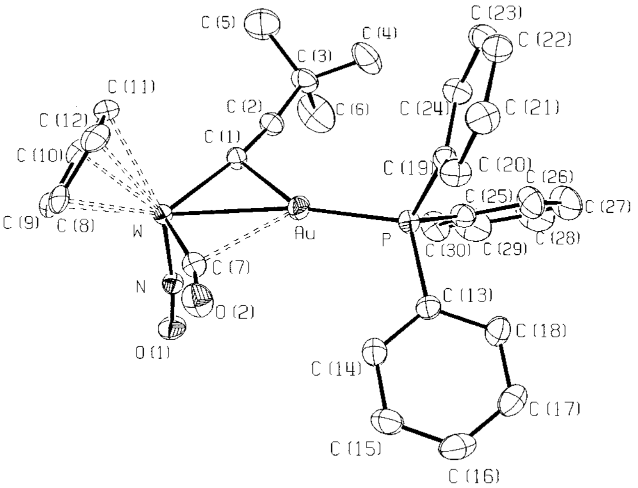

Figure 2. Molecular structure and atom-numbering scheme for $\{(\eta^5\text{-}C_5H_5)(NO)(\mu\text{-}CO)[\mu\text{-}C{\equiv}C{-}C(CH_3)_3]W{-}AuP(C_6H_5)_3\}$ (**8a**). Thermal ellipsoids are shown at the 30% probability level.

niques. Literature methods were used to prepare **1**, the vinylidenes, and $ClAu{-}P(C_6H_5)_3$. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. ^1H NMR were meassured at 400 MHz, ^{13}C NMR were meassured at 100 MHz, and ^{31}P NMR were measured at 162 MHz with H_3PO_4 as external standard. Proton and carbon chemical shifts are referred to TMS. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo-Erba 1104 elemental analyzer.

$\{(\eta^5\text{-}C_5H_5)(NO)(\mu\text{-}CO)[\mu\text{-}C{\equiv}C{-}C(CH_3)_3]W{-}AuPPh_3\}$ (8a). To 389 mg (1 mmol) of the tungsten vinylidene **7a** in 30 mL of THF at −78 °C was added 0.7 mL (1 mmol) of *n*-BuLi to give a green solution of the tungsten acetylide **1a**. To the green solution 495 mg (1 mmol) of $ClAuPPh_3$ was added at −60 °C. The solution was stirred for 30 min at −60 °C while the color of the solution turned to red. To avoid decomposition, the solvent was removed fast to three-fourths under reduced pressure at 0 °C. After adding ca. 10 mL of cooled (−60 °C) Et_2O an orange-red precipitate was obtained, which was filtered at −30 °C and washed several times with small amounts of cooled Et_2O (−60 °C). From the precipitate, the product was extracted with cooled (−60 °C) CH_2Cl_2. Crystallization from CH_2Cl_2/pentane at −30 °C yielded 650 mg (76%) of **8a** as red crystals (mp 125−127 °C dec). Anal. Calcd for $C_{30}H_{29}AuNO_2PW$: C 42.52; H 3.44; N 1.65. Found: C 42.45; H 3.16; N 2.06. ^1H NMR ($CDCl_3$, RT): δ 7.67−7.39 (Ph), 5.61 (br, Cp), 1.23 (br, ^{t}Bu). ^{13}C NMR (CD_2Cl_2, RT): δ 134.5 (d, 14 Hz $^2J_{PC}$, o-Ph); 131.6 (br, p-Ph); 129.4 (d, 10 Hz $^3J_{PC}$, m-Ph); 94.6 (br, Cp), 33.2, (br, $C\mathit{CH}_3$), 32.4($\mathit{C}CH_3$). ^{13}C NMR (CD_2Cl_2, −80 °C): δ 246.3 (μ-CO) 230.5 (CO), 162.3 (μ-$C{\equiv}$), 134.6 [d, $^2J_{C-P} = 13$ Hz, C_6H_5 (ortho)], 134.2 [d, $^2J_{C-P} = 15$ Hz, C_6H_5 (ortho)]; 132.2 (^{t}Bu-$C{\equiv}$), 132.0 [C_6H_5 (para)] 131.9 [C_6H_5 (para)], 131.7 (^{t}Bu-$C{\equiv}$), 131.6 [C_6H_5 (para)], 130.1 [C_6H_5 (ipso)], 129.6 [d, $^3J_{C-P} = 10$ Hz, C_6H_5 (meta)], 129.3 [d, $^3J_{C-P} = 12$ Hz, C_6H_5 (meta)], 97.2 (Cp), 95.6 (Cp), 94.7 (Cp); 87.2 (d, $^2J_{C-P} = 20$ Hz, Au-$C{\equiv}$); 37.7, 35.8, 31.3 (C-CH_3); 32.9, 32.8, 31.6 (CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2, RT): δ 45.9 (br), 42.9. IR (CCl_4; cm^{-1}): 2001, 1944 (small), 1854 (μ-CO), 1612 (NO).

$\{(\eta^5\text{-}C_5H_5)(NO)(\mu\text{-}CO)(\mu\text{-}C{\equiv}C{-}C_6H_5)W{-}AuPPh_3\}$ (8b). Preparation was similar to that for **8a** with 409 mg (1 mmol) of vinylidene **7b** and 495 mg (1 mmol) of $ClAuPPh_3$. After removing the solvent and adding Et_2O (−60 °C) a red precipitate was obtained, which was washed and purified analogously to **8a**. Crystallization from CH_2Cl_2/pentane at −30 °C yielded 543 mg (63%) of **8b** as red crystals (mp 129−131 °C dec). Anal. Calcd for $C_{32}H_{25}AuNO_2PW$: C 44.27; H 2.89; N 1.61. Found: C 43.75; H 2.68; N 2.01. ^1H NMR ($CDCl_3$, RT): δ 7.7−7.03 (m, C_6H_5), 5.72 (br, s, Cp). ^{13}C NMR (CD_2Cl_2, RT): δ 240.4 (μ-CO), 184.7, 149.3, 135.1−125.9 (C_6H_5), 104.2, 94.9 (br, Cp). ^{31}P NMR (CD_2Cl_2, RT): δ 49.8, 43.1, 42.2. IR (CCl_4; cm^{-1}): 2023, 1957 (small), 1859 (CO), 1600 (NO).

{(η^5-C_5H_5)(NO)(μ-CO)(μ-C≡C−C_6H_4-CH_3)W−AuPPh$_3$} (8c). Preparation was analogous to that for **8a** and **8b** with 423 mg (1 mmol) of vinylidene **7c** and 495 mg (1 mmol) of ClAuPPh$_3$ to give 649 mg (74%) of red crystals (mp 130−132 °C dec). Anal. Calcd for $C_{33}H_{27}AuNO_2PW$: C 44.97; H 3.11; N 1.58. Found: C 44.57; H 2.90; N 2.39. ^{1}H NMR ($CDCl_3$, RT): δ 7.8−6.9 (m, C_6H_5), 5.7 (s, br, Cp), 2.35 (s, CH_3). ^{13}C NMR (CD_2Cl_2, RT): δ 241.0 (μ-CO); 234.4; 149.6; 134.6−128.9 (C_6H_5) 94.5 (br, Cp); 21.4 (CH_3). ^{31}P NMR (CD_2Cl_2, RT): δ 49.6, 43.1, 42.3. IR (CCl_4; cm^{-1}): 2007, 1957 (small), 1858 (μ-CO), 1620 (NO).

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Supporting Information Available: Data of crystal structure determination and refinement, tables of atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters of compounds **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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