Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Dr. Mark Andrews, Dr. Carol Creutz, Dr. Paul Fagan, and Professor Charles Casey for helpful discussions and Professor J. A. Gladysz for a copy of ref 1 prior to publication.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (12 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Isolation of a Tungsten Side-Bound Ketone Complex Containing Eight New Carbon-Carbon Bonds: An Alkyne-Alkyne, Alkyne-Carbonyl, and Alkyne-Pentamethylcyclopentadiene Coupling Reaction

Michael J. Chetcuti* and Brian E. Grant

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

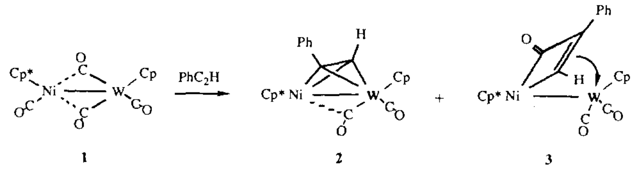
Phillip E. Fanwick

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received October 24, 1988

Reactions of alkynes with polynuclear complexes remain an active field of investigation owing to the large variety of molecules characterized from these reactions.[1] The metals frequently act as templates, promoting carbon-carbon bond formation with high specificity in many cases. In addition to bridging alkyne species,[2] complexes containing two,[3] three,[4] or four[5] linked alkynes have been isolated. Cyclopentadienone,[3d,6] quinone,[7] tropone,[8] and metallacyclic species formed by alkyne-carbonyl linkage reactions[9] have also been observed. The new organic ring or chain can exhibit diverse bonding modes to the metal framework, depending on the particular alkyne/metal combination and the reaction conditions.

Scheme I



Our group has been investigating the chemistry of the complexes $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)$ [M = Mo, W; R = H, Me].[2a,9a,10,11] Dimetallatetrahedrane species are formed when these complexes are treated with alkynes; nickel-molybdenum complexes also yield nickelacyclobutenone species π-coordinated to a molybdenum atom, resulting from alkyne-carbonyl linkage reactions.[2a,9a] As pentamethylcyclopentadienyl (Cp*) complexes exhibit significant reactivity differences from their cyclopentadienyl (Cp) congeners, reactions of analogous Cp* species with alkynes were of interest. This communication presents a remarkable molecule containing eight new carbon-carbon bonds, isolated from the reaction of PhC_2H simultaneously with a nickel and a tungsten species.

$Ni(CO)(\eta^5\text{-}C_5Me_5)I$[12] reacts with $[W(CO)_3(\eta^5\text{-}C_5H_5)]^-$ affording the thermally unstable, pyrophoric species $NiW(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**1**).[13] The nickelacyclobutenone complex $NiW(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2**)[14] and the alkyne species $NiW(CO)_2(\mu\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**3**)[15] were isolated from the reaction of PhC_2H with **1** (see Scheme I). **2** decarbonylates to **3** when heated.[2a,9a]

Treatment of a suspension of $Ni(CO)(\eta^5\text{-}C_5Me_5)I$ and $[W(CO)_3(\eta^5\text{-}C_5H_5)]^-$ with PhC_2H also afforded **2** and **3** but yielded small amounts (<5%) of a purple grey product (**4**). ^1H NMR data indicated that **4** contained an η^5-Cp ligand and four PhC_2H moieties.[16] Five distinct methyl signals suggested that an η^1-Cp* ligand was present. MS of **4** exhibited a parent ion with an isotopic envelope consistent with a monotungsten species. As its structure could not be ascertained, an X-ray diffraction study was carried out on a crystal of **4**.[17] Figure 1 shows a plot of the structure.[18]

4 contains a single tungsten atom embedded in a complex organic framework. Three PhC_2H groups have linked in head-

---

(1) Winter, M. J. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley Interscience: 1985; Vol. 3, p 259.

(2) (a) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298. (b) Chisholm, M. H.; Folting, K.; Hoffmann, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

(3) (a) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1985**, *4*, 1594. (b) Chisholm, M. H.; Hoffmann, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806. (c) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888. (d) Gardner, S. A.; Andrews, P. S.; Rausch, M. D. *Inorg. Chem.* **1973**, *12*, 2396. (e) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* **1980**, 113.

(4) (a) Reference 3c. (b) Brammer, L.; Green, M.; Orpen, A. G.; Paddick, K. E.; Saunders, D. R. *J. Chem. Soc., Dalton Trans.* **1986**, 657. (c) Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333. (d) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 313.

(5) (a) Reppe, W.; Schlichting, O.; Klager, G.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1. (b) Knox, S. A. R.; Stansfield, R. D. F.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221. (c) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 771.

(6) (a) Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* **1977**, *16*, 2354. (b) Davidson, J. L.; Manojlovic-Muir, L.; Muir, K. W.; Keith, A. N. *J. Chem. Soc., Chem. Commun.* **1980**, 749.

(7) (a) Liebeskind, L. S.; Jewell, C. F. *J. Organomet. Chem.* **1985**, *285*, 305. (b) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1981**, *209*, C4.

(8) (a) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358. (b) Weiss, E.; Hübel, W. *Chem. Ber.* **1962**, *95*, 1179.

(9) (a) Azar, M. C.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1984**, *107*, 7209. (b) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 286.

(10) Chetcuti, M. J.; Green, K. A. *Organometallics* **1988**, *7*, 2450.

(11) Chetcuti, M. J.; McDonald, S. R.; Huffman, J. C. *Inorg. Chem.* **1989**, *28*, 238.

(12) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391.

(13) In a representative experiment, 5 mL of a THF solution of $K^+[W(CO)_3(\eta\text{-}C_5H_5)]^-$ (372 mg, 1.00 mmol) was added to a slurry of $Ni(CO)(\eta\text{-}C_5Me_5)I$ (349 mg, 1 mmol) in toluene (10 mL) at −78 °C. The mixture was warmed to 0 °C, solvent was removed, and the residue was extracted with hexane and passed through an alumina pad. Elution with a 3:1 mixture of hexanes/ether and crystallization from hexane at −20 °C deposited crystals of **1** (438 mg, 79%). Spectroscopic data for **1**: ^1H NMR (300 MHz, benzene-d_6, ppm), δ 4.583 (5 H, C_5H_5), 1.810 (15 H, C_5Me_5); ^{13}C NMR (benzene-d_6) 220.50 (CO), 104.45 (C_5Me_5), 90.48 (C_5H_5), 9.60 (C_5Me_5); IR [ν(CO), THF] 1986 (m), 1922 (s), 1852 (br, s), 1805 (w), 1770 (w) cm^{-1}.

(14) PhC_2H (102 mg, 1 mmol) was added to a toluene/THF solution of **1** (277 mg, 0.5 mmol). After stirring for 3 h, the solvent was removed, and the residue was extracted with toluene and filtered through a short alumina pad. Radial chromatography [Stahl, E.; Müller, J. *Chromatographia* **1982**, *15*, 493] on a silica gel plate under nitrogen, using toluene as the eluting solvent, followed by crystallization afforded **2** (66 mg, 21%) and **3** (150 mg, 50%). Spectroscopic data for **2**: ^1H NMR (benzene-d_6), δ 7.00–7.29 (m, 5 H, *Ph*), 6.987 (1 H, C*H*), 5.322 (5 H, C_5H_5), 1.690 (15 H, C_5Me_5); ^{13}C NMR (benzene-d_6) δ 219.28 [W–*C*O], 219.21 [W–*C*O], 176.90 [*C*=O], 137.98 [*C*(1), Ph], 127.89 [2 C, *C*(3), *C*(5) or *C*(2), *C*(6), Ph], 125.72 [*C*(4), Ph], 124.54 [2C, *C*(2), *C*(6) or *C*(3), *C*(5), Ph], 112.98 [*C*(H)], 101.73 (5C, C_5Me_5), 89.74 (5C, C_5H_5), 53.41 [*C*(Ph)], 9.01 (5C, C_5Me_5); IR, [ν(CO), Nujol] 1933 (s), 1831 (s), 1671 (m, C=O) cm^{-1}.

(15) Spectroscopic data for **3**: ^1H NMR (benzene-d_6), δ 7.15–7.35 (m, 5 H, Ph), 5.147 (5 H, C_5H_5), 1.515 (15 H, C_5Me_5); IR [ν(CO), hexanes] 1948 (s), 1913 (w), 1876 (w), 1816 (s) cm^{-1}.

0002-7863/89/1511-2743$01.50/0

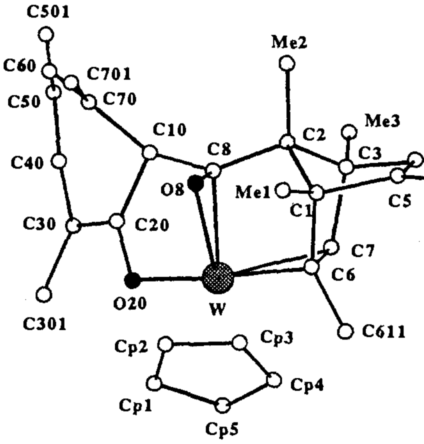


Figure 1. Plot showing the structure of **4**. Only the ipso carbon atoms of the four phenyl groups (C301, C501, C701, and C611) are shown, for clarity. Pertinent bond lengths (Å) and angles (deg) are as follows: W–O(8) = 1.957 (5); W–O(20) = 1.975 (5); W–C(6) = 2.199 (8); W–C(7) = 2.170 (8); W–C(8) = 2.090 (8); C(8)–O(8) = 1.395 (9); C(20)–O(20) = 1.363 (9); C(6)–C(7) = 1.46 (1); O(8)–W–O(20) = 95.1 (2); O(8)–W–C(6) = 107.7 (3); O(8)–W–C(7) = 87.7 (3); O(8)–W–C(8) = 40.2 (2); W–C(8)–O(8) = 64.8 (5); O(20)–W–C(6) = 101.9 (3); O(20)–W–C(7) = 138.3 (3); O(20)–W–C(8) = 78.7 (3); C(8)–W–C(6) = 75.6 (3); C(8)–W–C(7) = 77.1 (3).

to-tail fashion with a CO ligand, forming a triphenyltropone ring that binds in its enol form to the metal, via the oxygen atom. An adjacent carbon in this ring is attached to a CO ligand which is side-bound to the tungsten atom. The carbon atom is also bonded to the 7-carbon of a substituted norbornadiene ligand, derived from a Diels–Alder $4\pi + 2\pi$ cycloaddition of a fourth PhC_2H group to a pentamethylcyclopentadiene group. The PhC_2H derived C=C bond in this ligand is η^2-bonded to the tungsten atom, which is also linked to a η^5-Cp ligand.

The short W–O bonds in **4** [W–O(8) = 1.957 (5) Å; W–O(20) = 1.975 (5) Å] indicate partial oxygen to metal π-bonding[19] and are substantially shorter than the side-bound carbonyl tungsten-carbon bond [W–C(8) = 2.090 (8) Å].[20] C–O distances of 1.395 (9) and 1.363 (9) Å for C(8)–O(8) and C(20)–O(20), respectively, are indicative of single bonds. Carbon–carbon bonds in the seven-membered ring are not delocalized but are single [C–C(mean) = 1.49 Å] or double [C=C (mean) = 1.35 Å]. The C–C bond of the tungsten-coordinated PhC_2H moiety [C(6)–C(7) = 1.46 (1) Å] lies in the range found for coordinated alkenes. Tungsten–carbon bond lengths are 2.199 (8) Å [to C(6)] and 2.170 (8) Å [to C(7)].

Highly unusual features about this molecule include the complex's formation at low to ambient temperatures, the transfer of a Cp* ligand from nickel to tungsten, and the formally 16-electron tungsten at its core. Side-bound ketonic ligands are recognized but are uncommon.[20,21] While tropone derivatives have been observed[8] and Diels–Alder cycloaddition reactions of alkynes with η^1-Cp ligands have been noted,[22] the simultaneous combination of these reactions in the formation of a single molecule is unprecedented.

Our understanding of how **4** forms is primitive. **4** is not formed when **1** is isolated and reacted with PhC_2H. Activation of the Cp* ligand and transfer to the tungsten atom may occur from the complex $Ni(CO)(\eta^5\text{-}C_5Me_5)I$ or from an intermediate species formed in situ. Excess PhC_2H does not increase the yields of **4**. Thermal or photochemical reactions of **1** with PhC_2H afford new species that are currently under investigation; **4** is not formed under these conditions.

A transient η^1-Cp* species may eventually afford **4**. Stable η^1-Cp* complexes are virtually unknown, reflecting the steric demands of such species.[23] Carbonyl insertion into an η^1-Cp*–W bond may well be facile. In an attempt to form a W-acyl species, $W(CO)_3(\eta^5\text{-}C_5H_5)I$ was reacted with Cp*Li under a CO atmosphere. IR evidence suggested that an acyl species was obtained, but the product resisted isolation and was unreactive to PhC_2H. As experiments to date with tungsten species have not generated **4**, the presence of nickel appears necessary to form the tropone unit.[24]

Reactions of $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ [M = Mo, W] with various alkynes do not afford mononuclear species,[9a,10] and other alkynes do not form species analogous to **4** when reacted with **1**. However small amounts of the Mo analogue of **4** were isolated and characterized by ^1H NMR spectroscopy, following parallel synthetic procedures. Further studies aimed at increasing the yield of **4** and understanding the mechanism of its formation are in progress.

Acknowledgment. The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Notre Dame and the NSF (Grant no. CHE 8615556 for purchase of a Microvax computer and a diffractometer) is gratefully acknowledged.

Supplementary Material Available: An ORTEP plot and tables of data collection parameters, atomic positional parameters for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and bond distances and bond angles for **4** (17 pages); listings of observed and calculated structure factors for **4** (23 pages). Ordering information is given on any current masthead page.

---

(16) PhC_2H (204 mg, 2 mmol) was added to an in situ solution of **1** (0.5 mmol, ref 13) at –78 °C. After warming to room temperature and stirring for 12 h, the solvent was removed, and the residue was dissolved in ether and passed through a short alumina pad. After solvent removal, the residue was dissolved in toluene and subjected to radial silica gel chromatography. Elution with a toluene–ether mixture afforded **2**, **3**, and a purple-grey band containing **4**, which was recrystallized from hexane at –20 °C (19 mg, 4.5%). Spectroscopic data for **4**: ^1H NMR (benzene-d_6), δ 7.75–6.90, (m, 20 H, 4*Ph*), 7.039 (br, 1 H, C*H*), 6.238 (br, 1 H, C*H*), 5.856 (5 H, C_5H_5), 3.386 (br, 1 H, C*H*), 3.089 (br, 1 H, C*H*), 1.520 [q, 3 H, *Me*C=CMe, J_{H-H} = 1.6 Hz], 1.312 (3 H, *Me*), 1.101 (br, 3 H, *Me*), 1.029 [q, 3 H, MeC=C*Me*, J_{H-H} = 1.6 Hz], 0.537 (3 H, *Me*); MS, *m/e* 849 (M^+).

(17) X-ray data at 20 °C: crystals of **4**, $WC_{49}H_{44}O_2$ belong to space group $P2_1/n$ with $a = 14.852$ (2) Å, $b = 16.968$ (2) Å, $c = 15.491$ (2) Å, $\beta = 102.54$ (1)°, $V = 3810$ (2) Å^3, $Z = 4$, $d_{calcd} = 1.479$ g cm^{-3}. Non-hydrogen atoms were independently refined with anisotropic thermal parameters; all hydrogen atoms were located, but they were moved to their idealized locations and constrained to ride on their corresponding carbon atoms in the final cycle, with fixed isotropic thermal parameters and C–H distances set at 0.95 Å. Of the 5153 unique data, 3297 reflections with $F^2 > 3\sigma F^2$ were used in refining the 469 parameters, giving $R = 0.031$, $R_w = 0.036$.

(18) Molecular Editor, Drexel University, 1987.

(19) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(20) In the complex $W(\eta^2\text{-}Ph_2C{=}O)(C_5H_5N)(OCH_2{}^tBu)_4$, W–O and W–C bond distances for the ligated ketonic group are 1.970 (6) and 2.234 (10), respectively: Chisholm, M. H.; Huffman, J. C.; Klang, J., unpublished results, personal communication.

(21) (a) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540. (b) Gauntlett, J. T.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 420. Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360. (c) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. (d) Kreiter, C. G.; Kögler, J.; Sheldrick, W. S.; Nist, K. *J. Organomet. Chem.* **1986**, *311*, 125.

(22) A few recent examples are as follows: (a) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (b) Ibbott, D. G.; Payne, N. C.; Shaver, A. *Inorg. Chem.* **1981**, *20*, 2193. (c) Mercier, R.; Douglade, J.; Amaudrut, J.; Sala-Pala, J.; Guerchais, J. E. *J. Organomet. Chem.* **1983**, *244*, 145. (d) Wright, M. E. *Organometallics* **1983**, *2*, 558.

(23) A tungsten bound η^1-Cp* ligand has been structurally characterized in the species $WO_2(\eta^1\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_5)$: (a) Bercaw, J. E.; Parkin, G. Third Chemical Conference of North America, Toronto, Canada, INOR 94, June 1988. (b) Bercaw, J. E. 196th American Chemical Society National Meeting, Los Angeles, CA, INOR 395, September 1988.

(24) Nickel complexes are well-known cyclooligomerization catalysts of unsaturated hydrocarbons. (a) Jolly, P. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 615. (b) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Wiley: New York, 1975; Vol. 2, p 213.