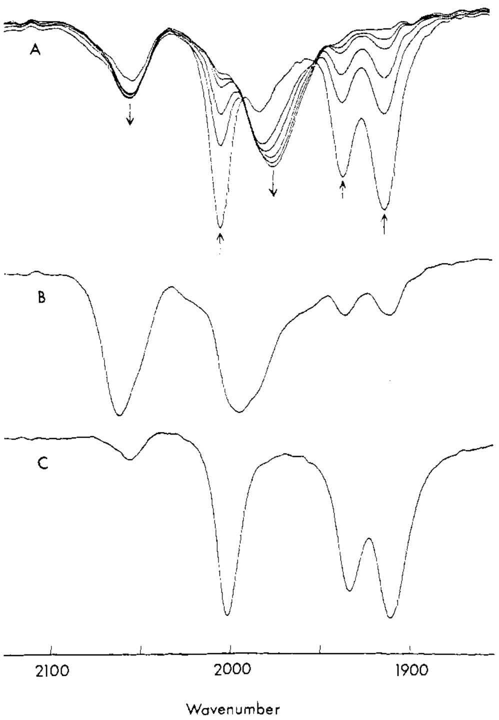

Figure 2. IR spectral changes observed in the stoichiometric reaction of $Ru(dppe)(CO)_3$ with *p*-chloronitrobenzene in *o*-xylene/MeOH: (a) spectral changes during the first 60 m of reaction where the arrows indicate the growth or disappearance of specific absorptions, (b) spectrum after 3 h, and (c) spectrum after heating the solution for 1 h at 95 °C.

could force the migratory insertion of CO into the M-NHAr bond giving a carbamoyl complex that could react with methoxide to form carbamate. Such a competition between CO and MeO^- could be the branch point controlling the observed selectivity of the catalytic reaction.

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Hydroformylation of the $C\equiv C$ Bond of $(C_5H_5)(PMe_3)_2Ru—C\equiv C—CH_3$ by $HRe(CO)_5$ To Give an η^1-Aldehyde Complex of Rhenium

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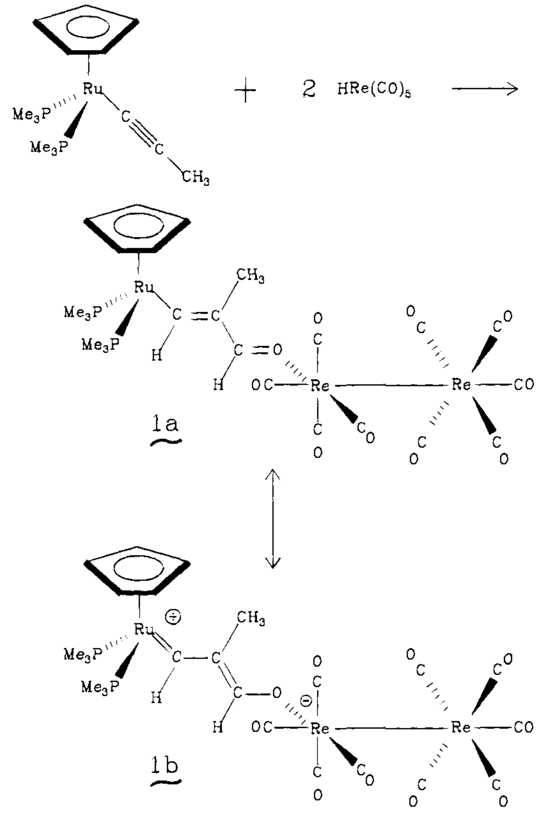
The chemistry of aldehydes bonded to transition metals is not well-developed but has been attracting increasing attention.[1] Most of the previously reported aldehyde complexes exhibit $\eta^2(\pi)$-bonding. We report an unprecedented hydroformylation of the $C\equiv C$ bond of a metal alkynyl complex by a metal carbonyl hydride, which results in an α,β-unsaturated aldehyde $\eta^1(\sigma)$-bonded to $Re_2(CO)_9$.



(1)

Reaction of $(C_5H_5)(PMe_3)_2Ru—C\equiv C—CH_3$[2] with excess $HRe(CO)_5$ in CH_3CN (room temperature, 10 min), followed by concentration of the solution, results in precipitation of a bright yellow, air-stable solid in 60% yield. NMR and IR spectra[3] suggested **1a**. The X-ray crystal structure[4] of **1** (Figure 1) confirmed this assignment but also indicated significant contribution from the zwitterionic resonance structure **1b**. In accordance with partial double bond character, the Ru–C distance of **1** (1.986 (9) Å) is shorter than a normal Ru–C single bond[5] but longer than the Ru=C bond in $(C_5H_5)(PMe_3)_2Ru=C=C(CH_3)H^+$ (1.845 (7) Å).[2] The C=O bond length of 1.263 (12) Å is longer than that observed for acrolein[6] (1.208 (3) Å) and may be compared with the 1.228 (31) Å η^1-aldehyde bond of $(PMe_3)(CO)_3(NO)W(O=CHCH=CH_2)^+$.[7] Lewis acid adducts of aromatic aldehydes also exhibit η^1-bonding. The C=O bond length deter-

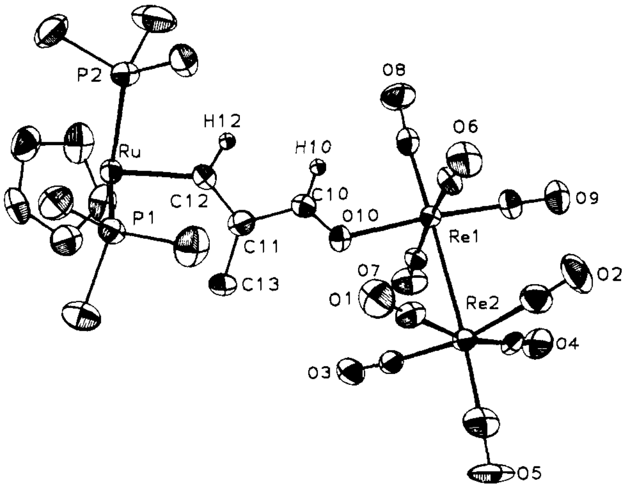


Figure 1. ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level (methyl hydrogens and cyclopentadienyl hydrogens omitted). Selected bond distances (Å) are as follows: Ru–C(12) 1.986 (9); C(12)–C(11) 1.389 (13); C(11)–C(10) 1.436 (12); C(10)–O(10) 1.263 (12), O(10)–Re(1) 2.167 (6); Re(1)–Re(2) 3.019 (1).

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(1) For a recent review, see: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298-303.

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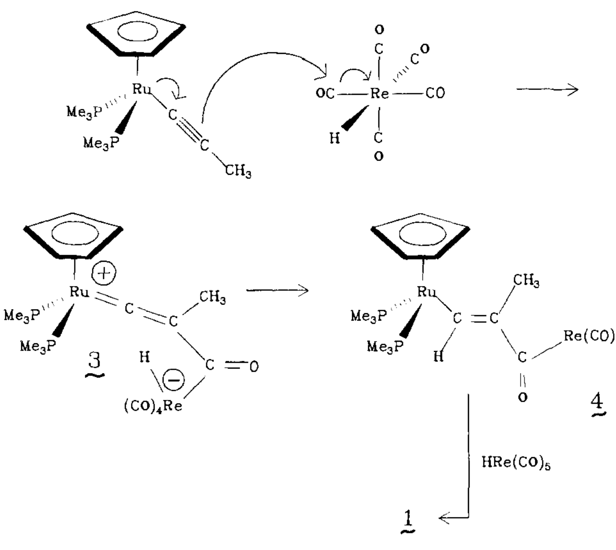
mined for $PhCHO/BF_3$ is 1.244 (5) Å.[8] Note that the modest lengthening (relative to the free aldehyde) of the C=O bond in η^1-aldehyde complexes differs from the case observed for η^2-aldehyde[9] and η^2-ketone[10] complexes, where C=O lengths are typically >1.3 Å.

In marked contrast to the hydroformylation of alkenes, which has been extensively studied,[11] the hydroformylation of alkynes is not a well-known reaction. Attempted hydroformylations of alkynes have generally resulted in formation of saturated aldehydes or alcohols.[12] While the formation of **1** involves facile hydroformylation of the C≡C bond, it is unlikely that this reaction proceeds by a "normal" hydroformylation mechanism[11] involving loss of CO from the metal carbonyl hydride, coordination of the unsaturated substrate, etc. We propose that instead the initial step of the reaction is nucleophilic attack on a terminal carbonyl of $HRe(CO)_5$ by the β-carbon of the ruthenium complex (Scheme I). Hydride transfer from rhenium to the α-carbon[13] of the zwitterionic intermediate (**3**) then provides a coordinatively unsaturated rhenium acyl intermediate (**4**) which can react with a second equivalent of $HRe(CO)_5$ to produce **1**. Dinuclear eliminations leading to formation of aldehydes have been extensively studied[14] and generally involve reactions of metal hydrides with coordinatively unsaturated metal acyl intermediates. We suggest that η^1-aldehyde complexes are viable intermediates in the formation of aldehydes in dinuclear elimination reactions. Further supporting evidence for this postulate comes from our recent isolation of $Mn_2(CO)_9(\eta^1\text{-aldehyde})$ complexes from the reaction of manganese alkyls with $HMn(CO)_5$.[15]

Scheme I



The reaction of $HRe(CO)_5$ with $(C_5H_5)(PMe_3)_2Ru{-}C{\equiv}C{-}CH_3$ to give **1** is strikingly different from the proton-transfer reaction of the same ruthenium complex with more acidic metal hydrides. We have reported[16] the kinetics of the protonation of $(C_5H_5)(PMe_3)_2Ru{-}C{\equiv}C{-}CH_3$ by $HW(CO)_3(C_5H_5)$ (pK_a = 16.1 in CH_3CN)[17] to give $[(C_5H_5)(PMe)_2Ru{=}C{=}C(H)CH_3]^+[(C_5H_5)(CO)_3W]^-$. The pK_a (in CH_3CN) of $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)CMe_3^+$ (20.8 ± 0.2)[16] is similar to that of $HRe(CO)_5$[17] (21.1 ± 0.3), suggesting that the equilibrium constant for protonation of $(C_5H_5)(PMe_3)_2Ru{-}C{\equiv}C{-}CH_3$ by $HRe(CO)_5$ is approximately unity. It appears that when β-carbon of this ruthenium alkynyl complex is insufficiently basic to rapidly deprotonate a metal hydride, another unusual reaction pathway becomes accessible: nucleophilic attack on a terminal CO ligand.

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(2) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203–2207.

(3) Data for **1**: ^1H NMR (CD_3CN) δ 11.64 (t, $^3J_{PH}$ = 11.0 Hz, 1 H, RuC*H*), 8.64 (s, 1 H, C*H*O), 4.92 (s, 5 H, C_5H_5), 1.79 (s, 3 H, CH_3), 1.35 ("filled-in doublet", separation between outer lines of this pattern = $^2J_{PH} + {}^4J_{PH}$ = 9.1 Hz, 18 H, PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −56 °C, 0.07 M Cr(acac)$_3$) δ 251.3 (t, $^2J_{PC}$ = 15 Hz, Ru*C*), 205.9 (s, $Re(CO)_2$), 196.4 (s, $Re(CO)_4$), 194.8 (s, *C*HO, J_{CH} = 165 Hz in the ^1H coupled ^{13}C NMR), 194.3 (s, Re(CO)), 188.9 (s, Re(CO)), 186.9 (s, Re(CO)); 148.3 (s, RuC*C*(CH_3)), 82.6 (s, C_5H_5), 21.3 (apparent t, observed $J = {}^1J_{PC} + {}^3J_{PC}$ = 15 Hz, PMe_3), 15.1 (s, CH_3); IR (CH_2Cl_2) ν_{CO} 2098 w, 2037 m, 1988 s, 1978 s, 1944 m, 1903 m, 1530 m cm^{-1}. Anal. Calcd for $C_{24}H_{28}O_{10}P_2Re_2Ru$: C, 28.49; H, 2.79. Found: C, 28.64; H, 2.85.

(4) Crystal data: $(C_5H_5)(PMe_3)_2RuCHC(CH_3)CHORe_2(CO)_9{\cdot}CH_3CN$; crystal size: 0.058 × 0.152 × 0.228 mm; yellow flat plates grown from CH_3CN at −20 °C, triclinic; $P\bar{1}$ (No. 2); a = 12.942 (2) Å, b = 14.570 (4) Å, c = 9.443 (1) Å, α = 105.39 (1)°, β = 96.28 (1)°, γ = 85.69 (2)°, V = 1704 (1) Å^3, Z = 2, ρ(calcd) = 2.051 g cm^{-3} at 200 K. Enraf-Nonius Cad-4 diffractometer, μ = 181.4 cm^{-1} (Cu Kα) (absorption corrected, max and min transmission coefficient, 0.4222 and 0.0945; $2\theta_{max}$ = 140°; N_{refl} = 6940; 5403 reflections used ($F_o > 3\sigma(F_o)$). $R(F)$ = 0.051; $R_w(F)$ = 0.070. Direct method solution and full-matrix least-squares refinement (SHELX-76), all non-hydrogen atoms with anisotropic thermal parameters, hydrogen atoms at calculated positions (C–H = 0.95 Å).

(5) A typical Ru–C(sp^2) bond length is about 2.07 Å. Tables of Ru–C bond lengths may be found in the following: (a) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, *100*, 115–123. (b) Bruce, M. J. *Pure Appl. Chem.* **1986**, *58*, 553–560.

(6) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1967**, *1*, 463–479.

(7) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293–5296.

(8) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405–2408.

(9) (a) Fernández, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268–8270. (b) Creswick, M. W.; Bernal, I. *Inorg. Chim. Acta* **1983**, *71*, 41–48. (c) Birk, R.; Berke, H.; Hund, H.-U.; Evertz, K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1988**, *342*, 67–75. (d) Kaiser, J.; Sieler, J.; Walther, D.; Dinjus, E.; Golic, L. *Acta Crystallogr.* **1982**, *B38*, 1584–1586. (e) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956–965. (f) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335–360. (g) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360–1361. (h) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109, and references therein. (i) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362. (j) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425–2433; *J. Am. Chem. Soc.* **1983**, *105*, 1690–1691; *J. Am. Chem. Soc.* **1985**, *107*, 2985–2986. (k) Schröder, W.; Pörschke, K. R.; Tsay, Y.-H.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 919–921.

(10) (a) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227. (b) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311–2317. (c) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213–7214. (d) Countryman, R.; Penfold, B. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1598–1599. (e) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668–676.

(11) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; Chapter 1. (b) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 43–231. (c) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1–60. (d) Pruett, R. L. *J. Chem. Educ.* **1986**, *63*, 196–198. (e) Orchin, M.; Rupilius, W. *Catal. Rev.* **1972**, *6*, 85–131.

(12) (a) Brown, C. K.; Georgiou, D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3120–3127. (b) Jardine, F. H.; Osborn, J. A.; Wilkinson, G.; Young, J. F. *Chem. Ind.* **1965**, 560. (c) Greenfield, H.; Wotiz, J. H.; Wender, I. *J. Org. Chem.* **1957**, *22*, 542–546. (d) Botteghi, C.; Salomon, C. *Tetrahedron Lett.* **1974**, 4285–4288. (e) Fell, B.; Beutler, M. *Tetrahedron Lett.* **1972**, 3455–3456.

(13) Substantial precedent exists for the nucleophilicity of C_β of metal alkynyl complexes as well as for addition of hydride and other nucleophiles to the α-carbon of metal vinylidenes: (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455–2456 and **1978**, *100*, 7763–7765. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59–128, and references therein. For a theoretical treatment, see: Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974–982.

(14) (a) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33–39. (b) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150–2160. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34–41. (d) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338. (e) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415–4423. (f) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447–5449. (g) Alemdaroğlu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1153–1165. (h) Barborak, J. C.; Cann, K. *Organometallics* **1982**, *1*, 1726–1728. (i) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 209–215.

(15) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G., Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261–263.

(16) Bullock, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 8087–8089.

(17) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.

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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

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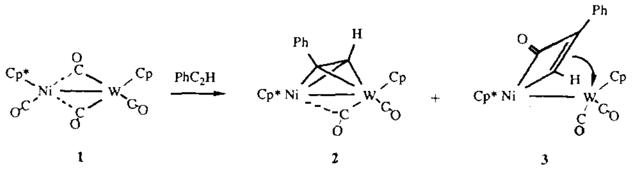
Reactions of alkynes with polynuclear complexes remain an active field of investigation owing to the large variety of molecules characterized from these reactions.[1] The metals frequently act as templates, promoting carbon-carbon bond formation with high specificity in many cases. In addition to bridging 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-

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(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}.

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