presumably because of the facile loss of H_2.

An examination of the synthetic utility of P-H activation in these and related systems is underway. In particular, efforts to stablize and utilize transient terminal phosphinidene complexes are in progress.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged. The University of Windsor is acknowledged for the award of a Research Professorship to D.W.S.

Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, and bond distances and angles (10 pages); listings giving values of $10F_o$ and $10F_c$ (30 pages). Ordering information is given on any current masthead page.

Coupling of Methylene–Carbonyl and Methylene–Allene Groups at a Dimetal Center: Formation of a Bridging Trimethylenemethane Species That Exhibits Remarkable Dynamic Behavior

Michael J. Chetcuti,[*,†] Phillip E. Fanwick,[‡] and Brian E. Grant[†]
Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

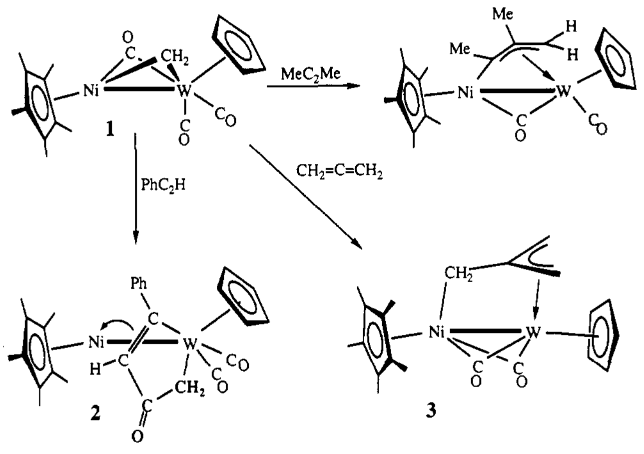
Received May 22, 1991

Summary: The bridging methylene complex $Cp^*Ni(\mu\text{-}CH_2)(\mu\text{-}CO)W(CO)_2Cp$ (Ni-W) (**1**) affords a tungstenacyclopentenone species when treated with PhC_2H, which ensues from a novel $Ph\mathit{C}_2H\text{-}\mathit{C}O\text{-}\mathit{C}H_2$ coupling reaction. Allene formally inserts into the Ni-CH_2 bond of **1** to yield a trimethylenemethane species that exhibits remarkable dynamic behavior on the ^1H NMR time scale.

We recently reported the synthesis of the first nickel methylene species, the complex $Cp^*Ni(\mu\text{-}CH_2)(\mu\text{-}CO)W(CO)_2Cp$ (Ni-W) (1).[1,2] In this species, the angle subtended by the Ni-W-C(H_2) and Ni-W-μ-C(O) planes is only 108°. The proximity of the μ-CO and μ-CH_2 groups indicated that CH_2–CO coupling, a critical step in Fischer–Tropsch chemistry,[3] might be feasible. The first example of a CH_2–CO linkage resulting from such a coupling is reported here.[4] We also describe the *formal* allene insertion into the W-CH_2 bond of 1 to yield a μ-trimethylenemethane complex.

A μ-1-nickelallyl species is formed when 1 reacts with MeC_2Me (Scheme I).[2,5] Treatment of 1[6] with PhC_2H affords a complex (2) whose IR (ν(CO) at 1608 cm^{-1}) and other spectral data[7] are incompatible with such a species. Its structure was established by an X-ray diffraction study.[8] These data revealed (Figure 1) that 2 contains a $\overline{CH_2\text{—}C(O)\text{—}C(H)\text{=}C(Ph)\text{—}W}(CO)_2Cp$ tungstenacyclopentenone ring that is linked to a Cp*Ni group via the olefin group and a Ni—W bond. It adopts an envelope conformation with the η^3 nickel bound -*W*—*C*(Ph)—*C*(H)- pseudo-allylic atoms defining the ring's fold. The $PhC_2H\text{—}CO\text{—}CH_2$ coupling[9] observed in 2 may proceed via alkyne–carbonyl linkage followed by CH_2 insertion into the $\overline{M\text{—}C(Ph)\text{—}C(H)\text{—}C}(O)$ unit formed.[10]

Scheme I



[†] University of Notre Dame.

[‡] Purdue University.

(1) Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5.

(2) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345.

(3) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, G. R. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 653. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *24*, 228.

(4) We are unaware of CH_2–CO ligand coupling reactions that afford species containing intact CH_2–CO groups. Ketenylidene groups, possibly arising via formation of transient complexes containing this linkage, have been reported: Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133.

(5) Reaction of $Me_2C{=}C{=}CH_2$ with Cp(CO)Ni—$W(CO)_3Cp'$ yields a similar species: Chetcuti, M. J.; Fanwick, P. E.; McDonald, S. R.; Rath, N. P. *Organometallics* **1991**, *10*, 1551.

(6) 1 (210 mg, 0.39 mmol) and PhC_2H (45 μL, 0.41 mmol) were stirred in hexane (30 mL) for 24 h. The solution was pumped to dryness, the residue was extracted with ether, and the extract was concentrated. Crystals of **2** (150 mg, 60%) deposited at −20 °C.

(7) Spectroscopic data for **2**: ^1H NMR (chloroform-d_1; J in Hz): ∂ 7.58–7.19 (m, 5 H, Ph), 4.98 (5 H, Cp), 3.69 (H, =C*H*, J_{WH} = 10.2), 2.21 (d, H, CH*H*, J_{HH} = 14.7, J_{WH} = 7.2), 1.52 (15 H, Cp*), 1.44 (d, H, C*H*H, J_{HH} = 14.7) ppm. ^{13}C NMR (chloroform-d_1; J in Hz): ∂ 223.4 and 216.1 (W—CO), 208.5 (C=O), 156.6 and 155.5 (C(1), Ph and =C(Ph)), 128.0, 127.1, and 126.0 (C(2)–C(4), Ph), 103.0 (C_5Me_5), 90.5 (C_5H_5), 89.7 (=*C*H), 13.1 (*C*H_2), 8.2 (*Me*). IR (ν(CO), cm^{-1}; Nujol): 1938 (s), 1880 (s), 1608 (m). MS (*m/e*, amu): 642 ($[M]^+$), 614 ($[M - CO]^+$), 586 ($[M - 2CO]^+$). HRMS: calcd for $NiWC_{27}H_{28}O_3$, 642.0889; found, 642.0884.

(8) $NiWC_{27}H_{28}O_3$ (**2**) at 20 °C belongs to triclinic space group $P\bar{1}$ (No. 2) with a = 9.090 (1) Å, b = 9.560 (1) Å, c = 14.077 (3) Å, α = 79.93 (1)°, β = 79.79 (1)°, γ = 83.330 (9)°, V = 1180.8 (4) Å^3, Z = 2. Lorentz, polarization, and empirical absorption corrections were applied. Of the 3075 unique data, 2807 with $I > 3\sigma(I)$ were used to refine 289 variables. Patterson methods followed by DIRDIF and successive Fourier maps led to a structural solution. Atoms were refined anisotropically. Hydrogen atoms, located and added to F_c listings, were not refined; their thermal parameters were set at 1.3 times the values of their attached carbon atoms: $R(F_o) = 0.022$, $R_w(F_o) = 0.030$.

(9) The coupling of alkynes and CO with either $Fe_2(\mu\text{-}CH_2)$ or $Fe_2(\mu\text{-}C{=}CH_2)$ groups, affording $\overline{\mathit{Fe}\text{—}CO\text{—}R\mathit{C}_2R\text{—}\mathit{C}}H_2$ or $\overline{\mathit{Fe}\text{—}\mathit{C}O\text{—}R\mathit{C}_2R\text{—}C}({=}CH_2)$- ferracyclopentenone rings was reported: (a) Summer, C. E.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (b) Casey, C. P.; Miles, W. H.; Fagan, P. J.; Haller, K. J. *Organometallics* **1985**, *4*, 559.

(10) Reaction of Cp*Ni–WCp carbonyl species with alkynes leads to an alkyne–carbonyl linkage, with retention of the Ni–W bond. Isomeric nickelacyclobutenone and tungstenacycle species both form with PhC_2H. (a) Chetcuti, M. J.; Grant, B. E., unpublished results. Also see: (b) Chetcuti, M. J.; Fanwick, P. E.; Grant, B. E. *J. Am. Chem. Soc.* **1989**, *111*, 2743. (c) Chetcuti, M. J.; DeLiberato, L.; Fanwick, P. E.; Grant, B. E. *Inorg. Chem.* **1990**, *29*, 1295.

0276-7333/91/2310-3003$02.50/0

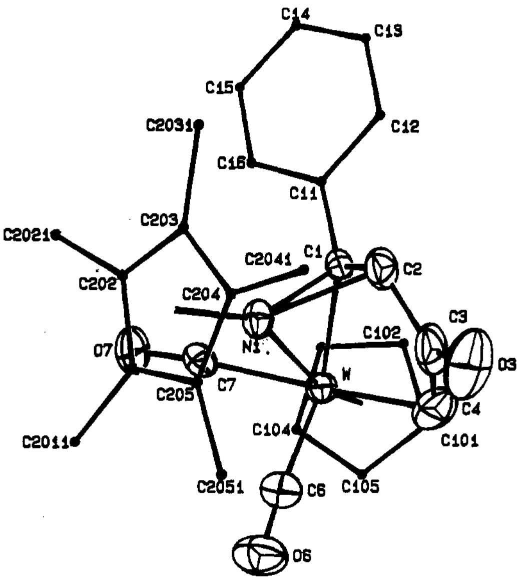


Figure 1. ORTEP diagram of $Cp^*Ni\{\mu\text{-}\eta^2{:}\eta^2\text{-}\overline{CH_2\text{—}C(O)\text{—}C(H)\text{=}C(Ph)}\}W(CO)_2Cp$ (2) with ellipsoids shown at the 50% probability level for the metals, carbonyl ligands, and atoms of the tungstenacycle ring. All other atoms are shown with an arbitrarily small radius. Key bond lengths (Å) and angles (deg) for 2: Ni–W = 2.6888 (6); W–$C1_{CPh}$ = 2.165 (5); W–$C4_{CH_2}$ = 2.264 (6); Ni–C1 = 1.978 (5); Ni–$C2_{CH}$ = 2.002 (5); C3–O3 = 1.243 (7); W–C1–C2 = 113.5 (3); W–C4–C3 = 110.8 (4); C1–C2–C3 = 118.6 95); C2–C3–C4 = 112.1 (4).

Complex 3 forms in high yield when allene reacts with 1.[11] NMR spectra disclose that three CH_2 groups, two of which are related by a molecular mirror plane, are present in 3.[12] The unique group exhibits an alkyl-like ^1H NMR chemical shift of ∂ 0.85 ppm; the lack of J_{WH} or J_{WC} coupling implies a Ni—CH_2 σ-bond. These data, paired with an X-ray diffraction study,[13] establish 3 as the trimethylenemethane species $Cp^*Ni\{\mu\text{-}\eta^1{:}\eta^3\text{-}CH_2C(CH_2)_2\}W(CO)_2Cp$ (Ni–W).[14]

3 is only the second μ-trimethylenemethane species recognized.[15] Figure 2 shows an ORTEP diagram of its geometry. The $\mu\text{-}\eta^1{:}\eta^3\text{-}CH_2C(CH_2)_2$ group is σ-bonded to the nickel atom via atom C(4); C(2), C(3), and C(4) are bound in π-allylic fashion to the tungsten atom and are close to equidistant to it (W–C = 2.309 Å, mean). Two strongly semibridging CO groups (W–C–O = 156.1°, Ni–C = 2.153 Å, mean)[16] and a Ni–W bond anchor the metals together. The metals and the carbonyl and $CH_2C(CH_2)_2$ ligands are bisected by a (noncrystallographically imposed) mirror plane defined by Ni–W–C(2)–C(4).[17] The Ni-bound Cp* and the W-bound Cp rings lie in a cisoid arrangement but are (slightly) twisted so as not to be cleaved by this plane.

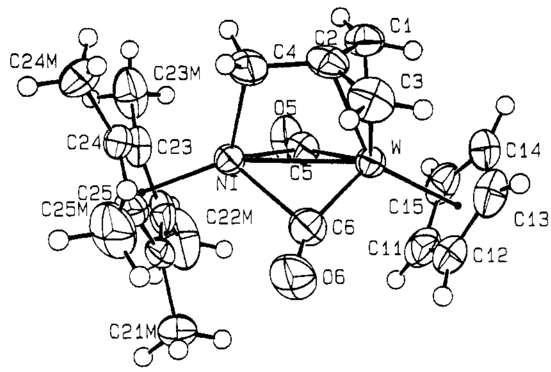


Figure 2. ORTEP diagram of the complex $Cp^*Ni\{\mu\text{-}\eta^1{:}\eta^3\text{-}CH_2C(CH_2)_2\}W(CO)_2Cp$ (3) (50% probability ellipsoids shown for all non-hydrogen atoms). Key bond lengths (Å) and angles (deg) for 3: Ni–W = 2.6839 (7); W–C1 = 2.319 (6); W–C2 = 2.297 (5); W–C3 = 2.312 (6); Ni–C4 = 1.962 (6); Ni–C5 = 2.167 (5); Ni–C6 = 2.138 (6); C1–C2 = 1.419 (8); C2–C3 = 1.412 (9); C2–C4 = 1.471 (9); W–C5–O5 = 156.4 (5); W–C6–O6 = 155.7 (5); Ni–C4–C2 = 105.7 (4); C1–C2–C3 = 115.6 (6); C1–C2–C4 = 120.4 (6); C3–C2–C4 = 121.0 (6).

Complex 3 exhibits remarkable dynamic behavior. The three sets of $CH_2C(CH_2)_2$ ^1H NMR signals broaden and collapse as the temperature is raised above –20 °C. At 95 °C, a new resonance appears at approximately the mean chemical shift of these peaks.[18] We believe that $C(CH_2)_3$ ligand rotation about an axis perpendicular to its plane, in a helicopter-like motion, equivalences the CH_2 groups.[19]

While MeC_2Me and PhC_2H react diversely with 1, in each case the Ni–CH_2 bond is ruptured and products effectively retain a W–CH_2 bond. In contrast allene *formally* inserts into the W–CH_2 bond. However, the fluxionality of 3[20] may transiently require the $C(CH_2)_3$ group to be η^3-bonded to the nickel and η^1-coordinated to the tungsten atom; thus, the allene reaction may proceed via initial *Ni*–CH_2 insertion.

Acknowledgment. We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from the Reilly Foundation for a fellowship (B.E.G.), and from the Jesse H. Jones Faculty Research Fund.

Supplementary Material Available: Tables of data collection parameters, bond lengths, angles, positional parameters, and thermal parameters for 2 and 3 (30 pages); listings of calculated and experimental structure factors (22 pages). Ordering information is given on any current masthead page.

---

[11] 1 (150 mg, 0.28 mmol) in hexane (20 mL) was stirred under allene; a precipitate formed slowly. After 12 h, the hexane was removed, the residue extracted with CH_2Cl_2, and the extract filtered. Crystals of 3 (115 mg, 74%) were harvested from a CH_2Cl_2/hexane mixture.

[12] Spectroscopic data for 3: ^1H NMR (acetone-d_6, –30 °C, *J* in Hz): ∂ 5.22 (5 H, *Cp*), 2.25 (2 H, CH*H* syn), 1.87 (d, 2 H, CH*H* anti, J_{HH} = 2.4), 1.52 (15 H, *Cp**), 0.85 (d, 2 H, Ni–C*H*$_2$, J_{HH} = 2.4). ^1H NMR (toluene-d_8, 95 °C): 1.59 (v br, 6 H, C(C*H*$_2$)$_3$) replaces C*H*$_2$C(C*H*$_2$)$_2$ signals seen at 0 °C. ^{13}C NMR (chloroform-d_6, *J* in Hz): ∂ 249.0 (*C*O), 111.9 (CH$_2$*C*(CH$_2$)$_2$), 104.7 (*C*$_5$Me$_5$), 90.0 (*Cp*), 37.0 (CH$_2$C(*C*H$_2$)$_2$, J_{WC} = 16), 16.4 (Ni–*C*H$_2$), 9.09 (C$_5$*Me*$_5$). IR (ν(CO), hexane, cm^{-1}): 1809 (w), 1778 (s). MS (*m/e*, amu): 552 ($[M]^+$), 524 ($[M - CO]^+$), 496 ($[M - 2CO]^+$), 442 ($[M - 2CO - C(CH_2)_3]^+$). HRMS: calcd for $NiWC_{21}H_{26}O_2$, 552.0787; found, 552.0769.

[13] $NiWC_{21}H_{26}O_2$ (3) belongs to the triclinic space group $P\bar{1}$ (No. 2) at 20 °C with a = 8.266 (1) Å, b = 10.106 (1) Å, c = 13.631 (1) Å, α = 69.943 (7)°, β = 73.84 (1)°, γ = 65.66 (1)°, V = 962.0 (1) Å^3, and Z = 2. A total of 226 variables were refined with 2257 of the 2502 unique data with $I > 3\sigma(I)$. Other details are as for 2 (DIRDIF was not used). Refinement converged to $R(F_o) = 0.018$, $R_w(F_o) = 0.024$.

[14] For a review of trimethylenemethane complexes see: Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279.

[15] Fildes, M. J.; Knox, S. A. R.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1680.

[16] These are best considered as two half-bridges; each ligand effectively donates one electron to the nickel atom.

[17] Bond lengths and angles of mirror-related parameters lie within experimental errors.

[18] This chemical shift is very close to that of the Cp* protons.

[19] $C(CH_2)_3$ ligands occasionally rotate in monometallic complexes,[14] but the only other example of a $\mu\text{-}\eta^1{:}\eta^3\text{-}CH_2C(CH_2)_2$ group is nondynamic on the ^1H NMR time scale.

[20] This may involve rotation about C(2), to afford a $\mu\text{-}\eta^2(\sigma){:}\eta^2(\pi)\text{-}(CH_2)_2C{=}CH_2$ intermediate in which the ligand is σ-coordinated to nickel via two CH_2 groups and π-bonded to the tungsten atom. Alternatively, ligand rotation coupled with a sliding of the C_4 plane toward the nickel atom may lead to a $\mu\text{-}\eta^1(\sigma){:}\eta^3(\pi)\text{-}(CH_2)C(CH_2)_2$ intermediate in which the ligand is η^3-bound to the nickel and σ-bonded to the tungsten atom. In each case, CO ligand rocking between semibridging (to nickel) and terminal (to tungsten) geometries maintains the metals' electronic requirements. Further studies to clarify this process are underway.