Synthesis of Zirconocene Phosphinidenes and Phosphides via P–H Activation

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Summary: In the reaction of Cp_2ZrCl_2 with Mg and $(2,4,6\text{-}Me_3C_6H_2)PH_2$, the mono(phosphinidene)-bridged species $(Cp_2ZrCl)_2(\mu^2\text{-}P(2,4,6\text{-}Me_3C_6H_2))$ (**1**) was isolated and crystallographically characterized. In the related reaction of Cp_2ZrCl_2 with Mg in the presence of $CyPH_2$, the Zr(III) phosphide-bridged zirconocene dimer $[Cp_2Zr(\mu^2\text{-}PCyH)]_2$ (**2**) was isolated. The structure of **2** has been confirmed crystallographically. Preliminary mechanistic information obtained from the analogous reaction employing $Cp^*{}_2ZrCl_2$ suggests the formation of the hydride-phosphide $Cp^*{}_2Zr(PHCy)H$ and the terminal phosphinidene intermediate $Cp^*{}_2Zr{=}PCy$.

The wide-ranging interest and applications of chemistry derived from metal–carbon, –oxygen, and –nitrogen ligand multiple bonds[1] have spawned recent interest in phosphinidene chemistry.[2,3] The primary synthetic route to known phosphinidene species involves the reactions of metal complex anions, generally carbonylate anions, with dihalophosphines.[2] Alternatively, thermal degradation of complexes of specially designed phosphinidene precursors affords transient[3] or isolable[2b] phosphinidene compounds. Such synthetic routes are not applicable to early, high-valent metals, as Ti, Zr, and Hf do not readily form carbonylate anions.[4] Furthermore, these metals coordinate only the most basic of phosphines, thus precluding synthetic routes that proceed by degradation of a coordinated phosphinidene precursor. A potential route to early-metal phosphinidenes involves the oxidative addition of P–H bonds to Zr(II). Herein we show that such reactions provide a new and facile synthetic route to phosphinidene complexes. Further, we characterize the first phosphinidene complex of the group 4 metals. Preliminary mechanistic information reveals that steric factors alter the reaction course and afford a new route to primary phosphide species.

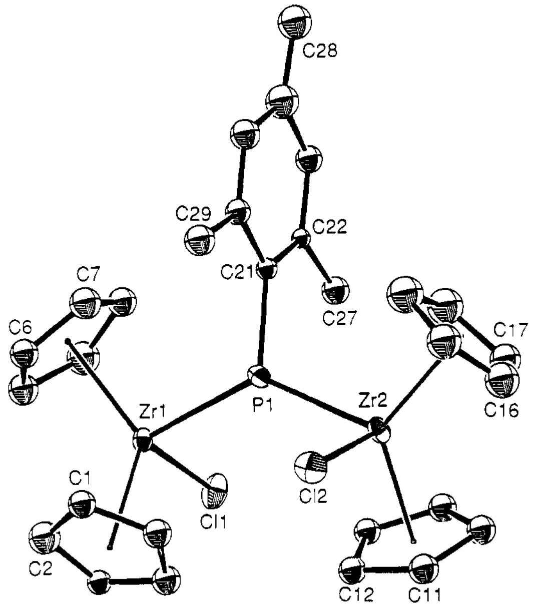

Figure 1. ORTEP drawing of molecule 1 (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg) are as follows: Zr1–P1 = 2.597 (6), Zr2–P1 = 2.637 (6), P1–C21 = 1.84 (2); Zr1–P1–Zr2 = 134.7 (2), Zr1–P1–C21 = 113.7 (6), Zr1–P1–Cl1 = 98.5 (2), Zr2–P1–C21 = 111.0 (6), Zr2–P1–Cl2 = 98.1 (2).

Cp_2ZrCl_2 was reacted with 0.5 equiv of Mg and 1 equiv of $(2,4,6\text{-}Me_3C_6H_2)PH_2$ in THF at 25 °C. The solution gradually becomes dark green, and when it stands, dark green crystals of 1[5] are deposited. The $^{31}P\{^1H\}$ NMR spectrum showed a single resonance at 325.5 ppm. Moreover, the ^{31}P spectrum shows no evidence of P–H coupling, thus suggesting the loss of both hydrogen atoms from the phosphorus atom. The ^1H NMR spectrum shows resonances attributable to cyclopentadienyl, aryl, and methyl protons. These data together with those from combustion analyses suggested the empirical formulation of $(Cp_2ZrCl)_2(\mu^2\text{-}P(2,4,6\text{-}Me_3C_6H_2))$. An X-ray structural study[6] confirmed this formulation of 1 (Figure 1). The most interesting structural feature of 1 is that the Zr_2PC

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[1] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[2] (a) For a recent review see: Huttner, G. *Pure Appl. Chem.* **1986**, *58*, 585. Recent papers on phosphoinidene complexes include: (b) Cowley, A. H.; Pellerin, B. *J. Am. Chem. Soc.* **1990**, *112*, 6734. (c) Cowley, A. H.; Geerts, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 6523. (d) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (e) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Norman, N. C.; Orpen, A. G. *Organometallics* **1987**, *6*, 189. (f) Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1707. (g) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. *Organometallics* **1988**, *7*, 309. (h) Flynn, K. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813. (i) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460. (j) Couret, C.; Escudie, J.; Satge, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280. (k) Lammertsma, K.; Chand, P.; Yang, S.; Hung, J. *Organometallics* **1988**, *7*, 1875.

[3] (a) For a review see: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. (b) Le Floch, P.; Huy, N. H. T.; Mathey, F. *Organometallics* **1988**, *7*, 1293. (c) Huy, N. H. T.; Fischer, J.; Mathey, F. *Organometallics* **1988**, *7*, 240. (d) Huy, N. H. T.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791. (e) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796. (f) Charrier, C.; Maigrot, N.; Mathey, F. *Organometallics* **1987**, *6*, 586. (g) Marinetti, A.; Mathey, F. *Organometallics* **1987**, *6*, 2189.

[4] Carbonylate anions of Ti, Zr, and Hf have been recently prepared; see: Ellis, J. E.; Chi, K.-M. *J. Am. Chem. Soc.* **1990**, *112*, 6022.

[5] Spectral data: 1, ^{31}P NMR (THF, 25 °C) δ 325.5 ppm (relative to 85% H_3PO_4), ^1H NMR (C_6D_6, 25 °C) δ 6.70 (s, Ph), 6.09 (s, Cp), 2.20 (s, 2 CH_3), 2.08 (s, CH_3); **2**, ^1H NMR (C_6D_6, 25 °C) δ 6.21 (s, Cp), 1.2–2.5 (br m, Cy). Satisfactory combustion analyses have been obtained for 1 and **2**.

[6] Crystal data: 1, $C_{29}H_{31}Cl_2PZr_2$, green blocks, monoclinic, space group $P2_1/n$, $a = 19.351$ (8) Å, $b = 7.641$ (3) Å, $c = 19.794$ (7) Å, $\beta = 108.63$ (3)°, $V = 2773$ (4) Å^3, $D_c = 1.59$ g cm^{-3}, $Z = 4$, $\mu = 10.068$ cm^{-1}; **2**, $C_{32}H_{44}P_2Zr_2$, black blocks, triclinic, space group $P\bar{1}$, $a = 11.652$ (7) Å, $b = 13.052$ (10) Å, $c = 11.466$ (12) Å, $\alpha = 102.52$ (9)°, $\beta = 118.45$ (4)°, $\gamma = 94.13$ (7)°, $V = 1465$ (5) Å^3, $D_c = 1.52$ g cm^{-3}, $Z = 2$, $\mu = 8.263$ cm^{-1}. Mo Kα radiation ($\lambda = 0.710\,69$ Å) was used; crystals were sealed in 0.5-mm capillaries under N_2 for crystallographic study. A Rigaku AFC6-S four-circle diffractometer was employed to collect the data (2θ range 4.5–50°) in each case. Three standards were collected every 150 reflections and in each case showed no evidence of crystal decay. The initial solutions for both structures were obtained from the automated Patterson solution portion of SHELXS-86 and the remaining atoms found and refined by employing the TEXSAN software package from MSC running on a VAX 3520 workstation. Refinement: 1, 1505 data with $I > 3\sigma(I)$, 163 variables, $R = 0.0645$, $R_w = 0.0639$, GOF = 1.370; **2**, 2775 data with $I > 3\sigma(I)$, 325 variables, $R = 0.0463$, $R_w = 0.0491$, GOF = 1.335. In each case a final difference map showed residual electron density of no chemical significance. It is also noteworthy that the hydrogen atoms on the P atoms of **2** were located.

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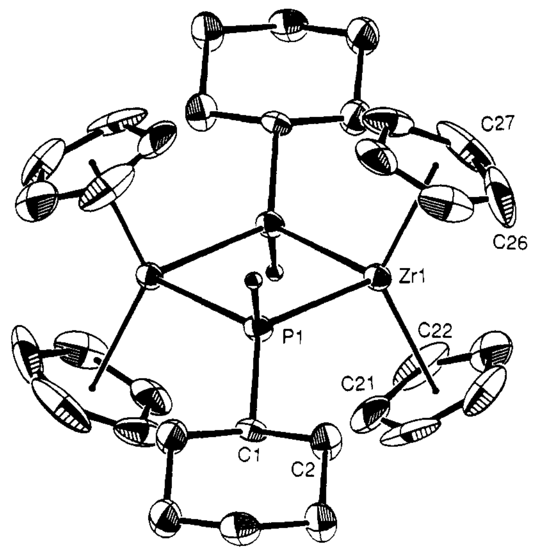
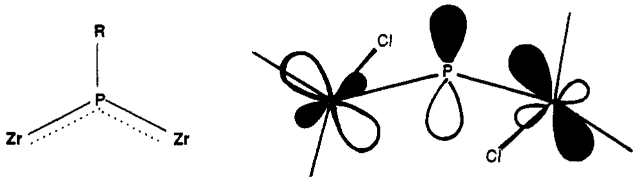


Figure 2. ORTEP drawing of one of the molecules of 2 in the asymmetric unit (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity, with the exception of the hydrogen on phosphorus. Distances (Å) and angles (deg) are as follows: Zr1-P1 = 2.648 (3), Zr1-P1 = 2.643 (4), P1-C1 = 1.872 (8); P1-Zr1-P1 = 94.0 (1), Zr1-P1-Zr1′ = 86.0 (1), Zr1-P1-C1 = 128.0 (3), Zr1′-P1-C1 = 125.9 (3); Zr1···Zr1′ = 3.606 (4).

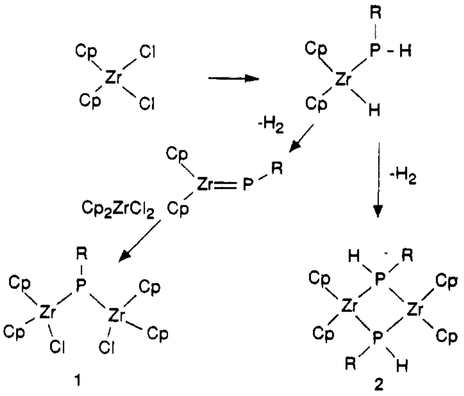
central core is planar with a Zr–P–Zr angle of 134.7 (2°). The Zr–P distances average 2.617 (6) Å, which is shorter than the Zr–P bond distances seen in Cp$_2$Zr(μ-PPh$_2$)$_2$RhH(CO)PPh$_3$.[7] The respective PZrCl planes are canted with respect to each other by 54.92°. These structural features of 1 minimize the steric interactions between the Cp$_2$ZrCl and the aryl ring fragments and at the same time accommodate some degree of Zr–P multiple bonding as in A. The canted orientation of PZrCl planes allows the mixing of the vacant 1a$_1$ orbitals on each Zr atom with the filled p orbital on P.



A

The analogous reaction mixture of Cp$_2$ZrCl$_2$ with excess magnesium and an equimolar amount of CyPH$_2$ in THF at 25 °C gradually undergoes a color change from colorless to black on stirring overnight. The mixture is filtered to remove the excess magnesium, the solution is concentrated, and gradually, over a 3-day period, black crystals of 2[5] are deposited. This material is only very sparingly soluble in THF or benzene and decomposes in halogenated solvents. This species is diamagnetic at 298 K, and the ^{1}H NMR spectrum shows resonances attributable to cyclopentadienyl and cyclohexyl protons. An X-ray structural study[6] showed 2 to be the dimeric species [Cp$_2$Zr(μ^2-PCyH)]$_2$ (Figure 2). The two pseudotetrahedral Zr atoms are bridged by two primary phosphide groups (PRH$^-$). The equilateral Zr$_2$P$_2$ core is planar with Zr–P distances averaging 2.646 (4) Å. The geometry about P is pyramidal with C1 displaced from the least-squares Zr$_2$P$_2$ plane by 1.067 Å. The Zr···Zr distances are 3.607 (4) and 3.638 (4) Å. The diamagnetic nature of 2 is consistent with strong antiferromagnetic coupling of the unpaired electrons on the Zr centers. We have previously suggested a through-ligand mechanism for such coupling in related Ti species,[8] while others have suggested the presence of "super-long" Zr–Zr bonds.[9]

Scheme I



Preliminary mechanistic information is derived from the slower analogous reaction of Cp*$_2$ZrCl$_2$ with Mg and 1 equiv of CyPH$_2$. Monitoring the reaction by ^{31}P NMR spectroscopy reveals the initial formation of a species which exhibits a resonance at 37.9 ppm with $|J_{P-H}|$ coupling of 198 Hz. This species, formulated as Cp*$_2$Zr(PHCy)H, is presumably derived from the oxidative addition of P–H to the transient Cp*$_2$Zr^{II}. Related hafnium analogues have been isolated by Hillhouse et al.[10] The unstable Cp*$_2$Zr(PHCy)H loses H$_2$, generating a new species which exhibits a singlet resonance in the ^{31}P spectrum at 220.2 ppm with no coupling to protons. Although it is tempting to formulate this compound as the terminal phosphinidene complex Cp*$_2$Zr=PCy,[11] attempts to isolate such intermediates have been frustrated to date by their apparent instability.[12]

In the present reactions of "Cp$_2$Zr", it is clear that once oxidative addition occurs, the subsequent reaction of Cp$_2$ZrH(PRH) can proceed in one of two courses. An intermolecular loss of H$_2$ affords a Zr(III) phosphide-bridged dimer as in 2. Alternatively, an intramolecular loss of H$_2$ generates a terminal phosphinidene complex. In the case of 1, the transient terminal phosphinidene Cp$_2$Zr=P(2,4,6-Me$_3$C$_6$H$_2$) is intercepted by Cp$_2$ZrCl$_2$, which adds across the Zr–P double bond. The course by which H$_2$ is lost appears to be controlled by steric factors. Presumably, the bulk of the mesityl moiety precludes a bimolecular loss of H$_2$ and thus favors the intramolecular phosphinidene route. The two reaction courses are shown in Scheme I. It is noteworthy that, in related M=E systems, dehydrohalogenation has been used to prepare species containing the Zr=S and Zr=O functional groups.[13] Hillhouse et al.[11] previously described attempts to prepare early-metal phosphinidenes via dehydrohalogenation of Cp*$_2$Hf(PCyH)Cl with a variety of bases, but to no avail.[12] The present synthetic route is favorable

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(7) Gelmini, L.; Stephan, D. W. *Organometallics* 1988, 7, 849.

(8) Dick, D. G.; Stephan, D. W. *Can. J. Chem.*, in press.

(9) Rohmer, M. M.; Benard, M. *Organometallics* 1991, *10*, 157.

(10) Vaughan, G. A.; Hillhouse, G. L. *Organometallics* 1989, *8*, 1760.

(11) Solely on the basis of the preliminary ^{31}P NMR data, the possibility of insertion of phosphorus into the Cp* manifold cannot be ruled out.

(12) In reactions in which the dehydrohalogenation of Cp*$_2$HfI(PHPh) was attempted with NaN(SiMe$_3$)$_2$, spectroscopic evidence supported the empirical formation of the species Cp*$_2$Hf(PPh); however, attempts to isolate this product were unsuccessful.[10]

(13) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1990, *112*, 6426.

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.

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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

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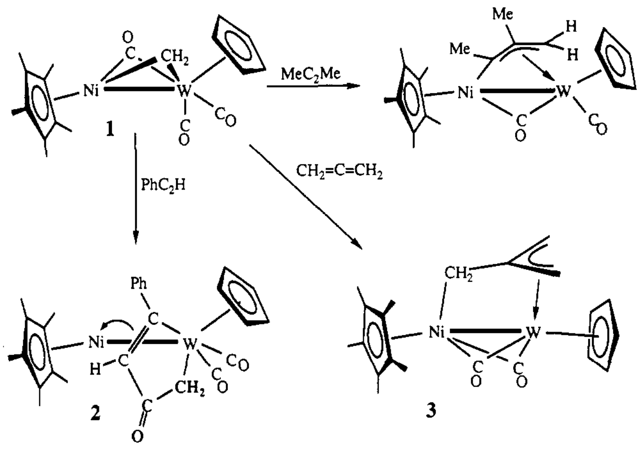
Summary: The bridging methylene complex Cp*Ni(μ-CH_2)(μ-CO)W$(CO)_2$Cp (Ni-W) (**1**) affords a tungstenacyclopentenone species when treated with PhC_2H, which ensues from a novel PhC_2H-CO-$C$$H_2$ coupling reaction. Allene formally inserts into the Ni-CH_2 bond of **1** to yield a trimethylenemethane species that exhibits remarkable dynamic behavior on the ^{1}H NMR time scale.

We recently reported the synthesis of the first nickel methylene species, the complex Cp*Ni(μ-CH_2)(μ-CO)W$(CO)_2$Cp (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 $C$$H_2$—$C$(O)—$C$(H)═$C$(Ph)—$W$$(CO)_2$Cp tungstenacyclopentenone ring that is linked to a Cp*Ni group via the olefin group and a Ni—W bond. It adopts an envelope conformation with the η^3 nickel bound -W—C(Ph)—C(H)- pseudo-allylic atoms defining the ring's fold. The PhC_2H—CO—$C$$H_2$ coupling[9] observed in **2** may proceed via alkyne–carbonyl linkage followed by CH_2 insertion into the M—C(Ph)—C(H)—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$(CO)_3$Cp′ 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**: ^{1}H NMR (chloroform-d_1; J in Hz): ∂ 7.58–7.19 (m, 5 H, Ph), 4.98 (5 H, Cp), 3.69 (H, ═CH, J_{WH} = 10.2), 2.21 (d, H, CHH, J_{HH} = 14.7, J_{WH} = 7.2), 1.52 (15 H, Cp*), 1.44 (d, H, CHH, 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 (═CH), 13.1 ($C$$H_2$), 8.2 ($Me$). IR ($\nu$(CO), cm^{-1}; Nujol): 1938 (s), 1880 (s), 1608 (m). MS (m/e, amu): 642 ($[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 $Fe_2(\mu$-$CH_2)$ or $Fe_2(\mu$-$C{=}CH_2)$ groups, affording Fe—CO—RC_2R—$C$$H_2$ or Fe—CO—RC_2R—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.

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