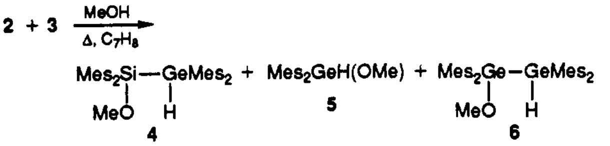
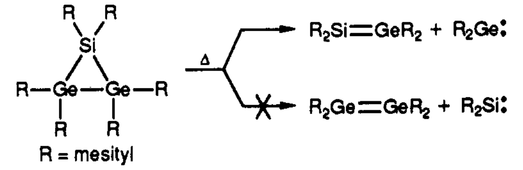
Thermolysis (110 °C) of the siladigermirane/cyclotrigermane mixture (90 mg) in dry toluene (1 mL) for 4 h in the presence of an excess of methanol yielded a mixture of three major compounds: dimesityl(dimesitylmethoxysilyl)germane[18] (**4**), dimesitylmethoxygermane[19] (**5**), and 1,1,2,2-tetramesitylmethoxydigermane[18] (**6**). There was no evidence for the formation of dimesitylmethoxysilane.


$$2 + 3 \xrightarrow[\Delta,\ C_7H_8]{MeOH} \underset{4}{Mes_2Si(OMe){-}GeMes_2H} + \underset{5}{Mes_2GeH(OMe)} + \underset{6}{Mes_2Ge(OMe){-}GeMes_2H} \quad (2)$$

Compound **3** is known to decompose at 80 °C to give dimesitylgermylene and tetramesityldigermene.[20] Thermolysis of **3** in the presence of methanol yields compounds **5** and **6**, apparently from trapping of the germylene and the digermene.[21] Compound **4**, on the other hand, appears to be derived from the addition of methanol to tetramesitylgermasilene, resulting from the thermal decomposition of the siladigermirane. Furthermore, the absence of any trapped *silylene* indicates selective decomposition of the siladigermirane to a germasilene and a germylene and not to a digermene and a silylene:



(3)

In order to confirm the selective decomposition, it is necessary to demonstrate that the sole source of compound **6** is the cyclotrigermane **3**. If the thermolysis temperature is lowered to 60 °C, compound **4** is formed in trace amounts, indicating that the cyclotrigermane is more thermally labile than the siladigermirane. This provides a means of separating **2** from **3**. Thus, thermolysis of the siladigermirane/cyclotrigermane mixture at 80 °C (to obtain a reasonable rate of reaction) in toluene in the presence of methanol for 4 h gave a mixture of compounds **2**, **4**, **5**, and **6**. Compounds **5** and **6** are readily separated from **2** by chromatography, but compound **4** elutes with **2**. Thermolysis of the recovered siladigermirane (containing <10% of **4** as determined by ^{1}H NMR spectroscopy) in toluene with excess methanol yielded only *two* major compounds, **4** and **5**, confirming that the decomposition of **2** occurs regioselectively. Furthermore, the addition of methanol to tetramesitylgermasilene is regioselective, with the alkoxy moiety adding to the silicon end of the double bond and the hydrogen becoming attached to the germanium.

In summary, all the available evidence suggests that we have generated tetramesitylgermasilene by the regioselective thermolysis of hexamesitylsiladigermirane. The germasilene was trapped with methanol in a regioselective manner to give the (methoxysilyl)germane. We are continuing to investigate this novel system.

Acknowledgment. We thank the NSERC (Canada) and the University of Western Ontario for financial support. The assistance of C. Dixon and J. A. Kohls in the preparation of the starting materials is gratefully acknowledged.

---

[18] Characterization data for **4**: white solid; IR (thin film) 2024 cm^{-1} (Ge–H); ^{1}H NMR (C_6D_6, δ) 2.07 (s, 6 H, *p*-CH_3), 2.12 (s, 6 H, *p*-CH_3), 2.29 (s, 12 H, *o*-CH_3), 2.38 (s, 12 H, *o*-CH_3), 3.40 (s, 3 H, –OCH_3), 5.57 (s, 1 H, GeH), 6.65 (s, 4 H, Mes H), 6.76 (s, 4 H, Mes H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 20.96, 21.01, 23.30, 24.16 (CH_3), 51.63 (OCH_3), 127.96, 129.00 (Mes CH), 132.07, 135.84, 137.17, 138.84, 143.81, 144.04 (Mes C); ^{29}Si NMR ($CDCl_3$, δ) 0.87 (d of m, *J* = 16 Hz); MS (EI, 70 eV, *m/e* (%)) 610 (<1, M$^+$), 312 (8, Mes_2Ge), 297 (100, Mes_2SiOCH_3), 192 (6, MesGe – 1); high-resolution MS (*m/e*) calcd for $^{74}Ge^{28}SiC_{37}H_{48}O$ 610.26862, found 610.26733. When it stood in solution (C_6D_6) for extended periods of time, compound **4** decomposed. Characterization data for **6**: IR (thin film) 2027 cm^{-1} (Ge–H); ^{1}H NMR (C_6D_6, δ) 2.07 (s, 6 H, *p*-CH_3), 2.10 (s, 6 H, *p*-CH_3), 2.33 (s, 12 H, *o*-CH_3), 2.42 (s, 12 H, *o*-CH_3), 3.57 (s, 3 H, –OCH_3), 5.83 (s, 1 H, GeH), 6.68 (s, 4 H, Mes H), 6.76 (s, 4 H, Mes H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 20.97, 23.12, 24.11 (CH_3), 52.98 (OCH_3), 128.18, 128.82 (Mes CH), 134.68, 135.78, 137.77, 138.44, 143.26, 143.76 (Mes C); MS (EI, *m/e* (%)) 654 (6, M$^+$, $^{74}Ge^{72}Ge$), 431 (5, Mes_3Ge), 343 (100, Mes_2GeOCH_3), 312 (24, Mes_2Ge), 192 (33, MesGe – H), 119 (24, Mes); high-resolution MS (*m/e*) calcd for $^{74}Ge^{72}GeC_{37}H_{48}O$ 654.21376, found 654.21410.

[19] Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Soufiaoui, M. *J. Organomet. Chem.* **1990**, *387*, 1. Characterization data for **5**: ^{1}H NMR (C_6D_6, δ) 2.07 (s, 6 H, *p*-CH_3), 2.45 (s, 12 H, *o*-CH_3), 3.56 (s, 3 H, –OCH_3), 6.67 (s, 1 H, GeH), 6.70 (s, 4 H, Mes H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 21.07, 22.53, 54.54, 128.83, 131.65, 139.52, 143.58. Compound **5** could not be isolated in a pure state from the reaction mixture.

[20] Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

[21] Thermolysis of **3** (prepared as described in ref 13) in the presence of methanol, in xylene at 125 °C, yielded compounds **5** and **6**, as determined by ^{1}H NMR spectroscopy.

Synthesis and Structure of a Tungsten η^3-Enynyl Complex Resulting from Facile Alkynyl–Vinylidene Coupling

Anne K. McMullen, John P. Selegue,* and Jin-Guu Wang
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received June 25, 1991

Summary: Deprotonation of the bis(alkyne) complex $[W(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)_2(Cp^*)][BF_4]$ (**1**) with KH gives the alkynyl/alkyne complex $[W(C{\equiv}CCMe_3)(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp^*)]$ (**2**), methylation of which gives the cationic alkyne/vinylidene complex $[W(C{=}CMeCMe_3)(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp^*)][BF_4]$ (**3**). Deprotonation of **3** with sodium bis(trimethylsilyl)amide under CO gives the crystallographically characterized η^3-enynyl complex $[W(CO)_2(\eta^3\text{-}Me_3CC{\equiv}CC{=}CMeCMe_3)(Cp^*)]$ (**4**) via the facile insertion of a vinylidene ligand into a metal–alkynyl σ-bond.

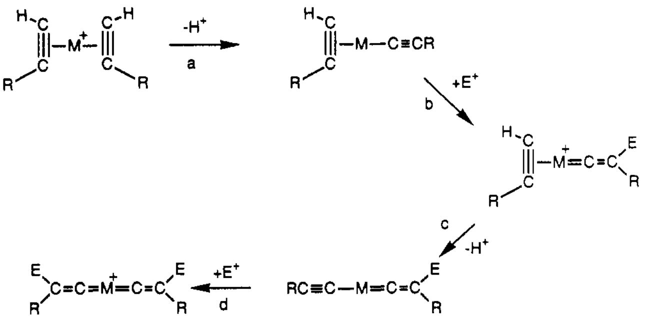
We are interested in preparing complexes with two or more vinylidene ligands bonded to a single transition-metal center, anticipating that the vinylidenes will undergo reductive coupling even more easily than isoelectronic isonitrile[1] and carbonyl ligands.[2] One approach is to start with a bis(1-alkyne) complex, converting each alkyne to

---

[1] Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860 and references cited therein.

[2] (a) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146. (b) Review: Vrtis, R. N.; Lippard, S. J. *Isr. J. Chem.* **1990**, *30*, 331–341. (c) Vrtis, R. N.; Bott, S. G.; Rardin, R. L.; Lippard, S. J. *Organometallics* **1991**, *10*, 1364–1373.

Scheme I



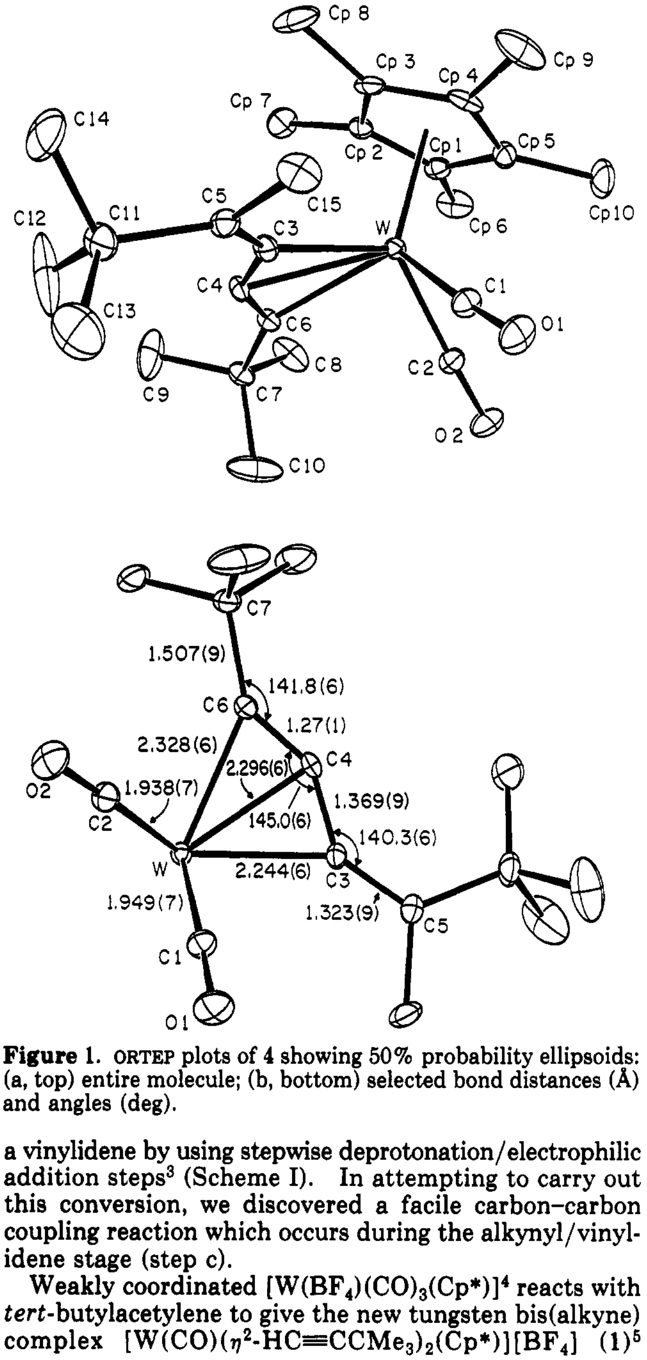
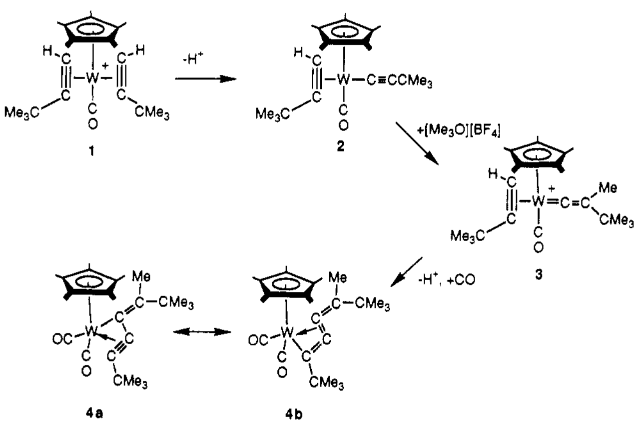


Figure 1. ORTEP plots of 4 showing 50% probability ellipsoids: (a, top) entire molecule; (b, bottom) selected bond distances (Å) and angles (deg).

a vinylidene by using stepwise deprotonation/electrophilic addition steps[3] (Scheme I). In attempting to carry out this conversion, we discovered a facile carbon–carbon coupling reaction which occurs during the alkynyl/vinylidene stage (step c).

Weakly coordinated $[W(BF_4)(CO)_3(Cp^*)]$[4] reacts with *tert*-butylacetylene to give the new tungsten bis(alkyne) complex $[W(CO)(\eta^2\text{-HC}{\equiv}\text{CCMe}_3)_2(Cp^*)][BF_4]$ (1)[5]

Scheme II



(Scheme II). Deprotonation of 1 with KH gives the alkynyl–alkyne complex 2.[6] Methylation of 2 with $[Me_3O][BF_4]$ gives the alkyne/vinylidene cation 3 in 76% yield.[7] Two isomers of 3, which may differ by the orientation of the alkyne or the vinylidene ligand, are detected

---

[3] Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197–257.

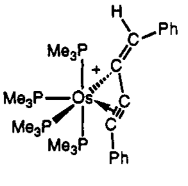
[4] Prepared analogously to $[W(BF_4)(CO)_3(Cp)]$ and $[Mo(BF_4)(CO)_3(Cp^*)]$: (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405–1421. (b) Beck, W.; Schloter, K.; Sünkel, K.; Urban, G. *Inorg. Synth.* **1990**, *28*, 5–15. (c) Leoni, P.; Aquilini, E.; Pasquali, M.; Marchetti, F.; Sabat, M. *J. Chem. Soc., Dalton Trans.* **1988**, 329–333.

[5] $[W(CO)(\eta^2\text{-HC}{\equiv}\text{CBu}^t)_2(Cp^*)]BF_4$ (1): Solid $[WH(CO)_3(Cp^*)]$ (3.629 g, 8.98 mmol) was added to Ph_3CBF_4 (2.745 g, 8.31 mmol) in CH_2Cl_2 (20 mL) at −50 °C. The resulting deep purple solution was chilled to −78 °C after 10 min. Pentane (120 mL, chilled to −78 °C) was added to precipitate $[W(BF_4)(CO)_3(Cp^*)]$. After decanting and washing with pentane (3 × 20 mL at −78 °C), $[W(BF_4)(CO)_2(Cp^*)]$ was dissolved in $ClCH_2CH_2Cl$ (20 mL, room temperature) and the solution transferred to a thick-walled glass pressure tube. *tert*-Butylacetylene (4.1 mL, 33.3 mmol) was added by syringe. The tube was sealed and heated in an oil bath at 60–80 °C with occasional shaking. After 1 h, the tube was cooled to room temperature and degassed. This heating and degassing procedure was repeated twice. The deep amber solution was filtered through Celite and evaporated to dryness. The residue was twice recrystallized from CH_2Cl_2/Et_2O to give $[W(CO)(\eta^2\text{-HC}{\equiv}\text{CBu}^t)_2(Cp^*)]BF_4$ (4.039 g, 81.2%) as a pale gold solid, mp 156–158 °C dec. IR (Nujol, cm^{-1}): 2111 (s, ν_{CO}); 2039 (vs, ν_{CO}); 1984 (s, ν_{CO}); 1700 (w, br, $\nu_{C\equiv C}$); 1078, 1061, 1039 (vs, br, BF_4). ^1H NMR (200 MHz, $CDCl_3$, δ_H): 10.38 (s, 2 H, $H\text{C}{\equiv}\text{CBu}^t$); 2.02 (s, 15 H, $\eta^5\text{-C}_5Me_5$); 1.30 (s, 18 H, $\text{HCC}Bu^t$). ^{13}C NMR (50 MHz, $CDCl_3$, δ_C): 216.7 (CO, $^1J_{CW}$ = 120 Hz), 164.4 ($\text{HC}{\equiv}C\text{CMe}_3$, $^1J_{CW}$ = 23 Hz), 157.8 ($\text{H}C{\equiv}\text{CCMe}_3$, $^1J_{CW}$ = 39 Hz), 110.4 (C_5Me_5), 37.4 (CMe_3), 30.3 (CMe_3), 10.0 (C_5Me_5); minor peaks (attributed to a trace of $[W(CO)_4(Cp^*)]BF_4$) 207.3 (CO, $^1J_{CW}$ = 127 Hz), 109.1 (C_5Me_5), 10.2 (C_5Me_5). Anal. Calcd for $C_{23}H_{35}BF_4OW$: C, 46.18; H, 5.90. Found: C, 45.23; H, 5.62. $[W(CO)(\eta^2\text{-HC}{\equiv}\text{CBu}^t)_2(Cp^*)]PF_6$ was made in an identical manner by using Ph_3CPF_6. Anal. Calcd for $C_{23}H_{35}PF_6OW$: C, 42.09; H, 5.38. Found: C, 41.65; H, 5.33.

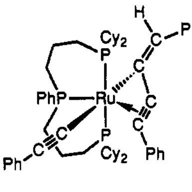
[6] $[W(C{\equiv}\text{CBu}^t)(CO)(\eta^2\text{-HC}{\equiv}\text{CBu}^t)(Cp^*)]$ (2): Tetrahydrofuran (35 mL) was added to a mixture of 1 (0.432 g, 0.722 mmol) and KH (0.341 g, 8.50 mmol). After it was stirred for 2 h at room temperature, the deep purple solution was evaporated to dryness. Extraction with pentane, filtration through Celite, and evaporation to dryness gave deep purple 2 (0.362 g, 98.3%), mp 96–98 °C. IR (Nujol, cm^{-1}): 1919 (s, ν_{CO}); 1912 (s, ν_{CO}); 1603 (w, $\nu_{HC\equiv CR}$). ^1H NMR (200 MHz, C_6D_6, δ_H): 10.31 (s, 1 H, $H\text{C}{\equiv}\text{CBu}^t$); 1.82 (s, 15 H, $\eta^5\text{-C}_5Me_5$); 1.53 (s, 9 H, $\text{C}{\equiv}\text{C}Bt^t$); 1.24 (s, 9 H, $\text{C}{\equiv}\text{C}Bu^t$). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C): 241.3 (CO, $^1J_{CW}$ = 148 Hz), 214.2 ($\text{HC}{\equiv}C\text{CMe}_3$), 181.2 ($\text{H}C{\equiv}\text{CCMe}_3$, $^1J_{CW}$ = 54 Hz), 146.2 ($\text{C}{\equiv}C\text{CMe}_3$), 104.5 ($C_5Me_5$), 102.9 ($C{\equiv}\text{CCMe}_3$, $^1J_{CW}$ = 91 Hz), 40.1 ($\text{HC}{\equiv}\text{C}C\text{Me}_3$), 33.0 ($\text{C}{\equiv}\text{CC}Me_3$), 31.3 ($\text{HC}{\equiv}\text{CC}Me_3$), 30.2 ($\text{C}{\equiv}\text{C}C\text{Me}_3$), 11.1 ($C_5Me_5$). MS ($C_{23}H_{34}O^{184}W$, *m/e*): 510 $[M]^+$; 482, $[M - CO]^+$; 425, $[M - CO - Bu^t]^+$, 400, $[CpW(CCBu^t)]^+$. Anal. Calcd for $C_{23}H_{34}OW$: C, 54, 13; H, 6.71. Found: C, 54.03; H, 6.83.

[7] $[W(CO)(\text{C}{=}\text{CMeBu}^t)(\eta^2\text{-HC}{\equiv}\text{CBu}^t)(Cp^*)]BF_4$ (3): Compound 2, freshly generated from 1 (2.095 g, 3.50 mmol) and KH (1.8898 g, 47.1 mmol), was dissolved in CH_2Cl_2 (50 mL at −15 °C). Solid Me_3OBF_4 (0.529 g, 3.58 mmol) was added. The solution was warmed to room temperature overnight with stirring, filtered, and evaporated to about 3 mL. Et_2O (30 mL) was added to precipitate 3, which was recrystallized from CH_2Cl_2/Et_2O to give gold microcrystals (1.630 g, 76.0%). IR (Nujol, cm^{-1} 2039 (s, ν_{CO}); 1980 (w, ν_{CO}); 1729 (w, $\nu_{C\equiv C}$); 1066, 1032 (s, br, BF_4). ^1H NMR (200 MHz, $CDCl_3$, δ_H): major isomer (ca. 60%) 11.50 (s, 1 H, $H\text{C}{\equiv}\text{CCMe}_3$), 2.21 (s, 15 H, C_5Me_3), 1.57 (s, 3 H, $\text{C}{=}\text{C}Me\text{CMe}_3$), 1.38 (s, 9 H, CMe_3), 0.85 (s, 9 H, CMe_3); minor isomer (ca. 40%) 11.56 (s, 1 H, $H\text{CCCMe}_3$), 2.19 (s, 15 H, C_5Me_5), 1.39 (s, 3 H, $\text{CC}Me\text{CMe}_3$), 1.37 (s, 9 H, CMe_3), 1.04 (s, 9 H, CMe_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C): major isomer (ca. 60%) 393.9 ($C{=}\text{CMeCMe}_3$), 218.0 (CO), 212.6 ($\text{H}C{\equiv}\text{CCMe}_3$), 211.1 ($\text{HC}{\equiv}C\text{CMe}_3$), 144.3 ($\text{C}{=}C\text{MeCMe}_3$), 110.8 ($C_5Me_5$), 43.4, 37.1 ($CMe_3$), 30.1, 30.0 ($CMe_3$), 22.3 ($\text{C}{=}\text{C}Me\text{CMe}_3$), 10.2 ($C_5Me_5$); minor isomer (ca. 40%) 236.0 (CO), 220.5 ($\text{HC}{\equiv}C\text{CMe}_3$), 192.2 ($\text{H}C{\equiv}\text{CCMe}_3$), 156.2 ($\text{C}{=}C\text{MeCMe}_3$), 116.1 ($C_5Me_5$), 43.3, 36.1 ($CMe_3$), 30.6, 29.0 ($CMe_3$), 22.6 ($\text{C}{=}\text{C}Me\text{CMe}_3$), 10.5 ($C_5Me_5$).

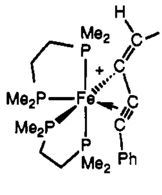
by NMR spectroscopy. Deprotonation of **3** with sodium bis(trimethylsilyl)amide under 1 atm of CO at −78 °C gives **4**.[8] The spectroscopic properties of **4**, in particular the absence of a vinylidene C_α resonance downfield of 300 ppm, were inconsistent with the anticipated alkynyl/vinylidene complex $[W(C{\equiv}CCMe_3)(C{=}CMeCMe_3)(CO)_2(Cp^*)]$. Structural characterization of **4** revealed that it is actually $[W(CO)_2(\eta^3\text{-}Me_3CC{\equiv}CC{=}CMeCMe_3)(Cp^*)]$, containing an unusual η^3-enynyl ligand (Figure 1).[9] The geometry within this ligand, as well as η^2-alkyne resonances at 148.6 and 136.2 ppm in the ^{13}C NMR spectrum, are more consistent with the η^3-enynyl description **4a** than the alternative η^3-trienyl description **4b**. In particular, the C4–C6 distance is 0.10 Å shorter than the C3–C4 distance, indicative of triple-bond character for C4–C6 and single-bond character for C3–C4. The enynyl ligand is not quite planar, folding slightly at C4. The dihedral angle between planes C3-C4-C5-C11-C15-W and C4-C6-C7 is 14.7°. The geometry of carbon atom C4, especially the W–C4–C3 angle of only 70.4 (3)°, is atypical of a coordinated alkyne carbon because of the cyclic nature of **4**. Typical Mo(II) and W(II) alkyne complexes display M–C–R angles of 140 ± 5° (cf. the W–C6–C7 angle of **4**).[10] The structure of **4** resembles those of the previously characterized iron-group η^3-enynyls **5**,[11] **6**,[12] and **7**,[13] although for **4** the C3–C4–C6 and C4–C6–C7 angles are 4–8° more acute and the C4–C3–C5 angle is 7–8° more obtuse than the corresponding angles in **5**–**7**. The structure of **4** is also similar to those of the "deprotiometallacyclobutadiene" complexes such as $[WCl\{\eta^3\text{-}C_3(CMe_3)_2\}(Cp)]$ (**8**) reported by Schrock and co-workers,[14] although the W–C bonds are 0.3–0.4 Å shorter in the higher valent compound **8**.



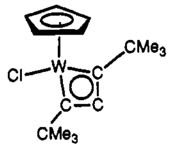
5



6



7



8

Similar alkynyl–vinylidene couplings to give enynyls have been implicated in several reactions of divalent group 8 metal complexes. Robinson and co-workers reported that reactions of $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ (M = Ru, Os) with phenylacetylene or $PhC{\equiv}CC{\equiv}CPh$ gave $[M(\eta^1\text{-}PhC_3CHPh)(\eta^2\text{-}O_2CCF_3)(CO)(PPh_3)_2]$.[15] Werner and co-workers oxidized *cis*-$[Os(C{\equiv}CPh)_2(PMe_3)_4]$ with $AgBF_4$ to give $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)][BF_4]$ (**5**).[11] Meek and co-workers found that $[RuH_4\{Cy_2P(CH_2)_3PPh(CH_2)_3PCy_2\}]$ incorporated 3 equiv of phenylacetylene to give $[Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)\{Cy_2P(CH_2)_3PPh(CH_2)_3PCy_2\}]$ (**6**).[12] Similarly, either $[FeCl_2(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) or $[FeH(H_2)(dmpe)_2]^+$ reacts with phenylacetylene to give $[Fe(\eta^3\text{-}PhC_3CHPh)(dmpe)_2]^+$ (**7**).[13] The $[\{RhCl(cod)\}_2]/AgBF_4$-catalyzed formation of 1,3,6-tri-*tert*-butylfulvene from *tert*-butylacetylene is presumed to proceed via an η^2-alkyne–vinylidene coupling.[16] A related alkenyl–vinylidene coupling was recently reported on an Ir(III) center.[17]

Despite substantial precedent on d^6 metal centers, the formation of **4** is the first alkynyl–vinylidene coupling on a d^4 metal, as well as the first with an isolated alkynyl/alkyne precursor. The evidence presented here supports the mechanistic conjectures of the previous investigators. The insertion of coordinated vinylidene into an adjacent metal–carbon bond is evidently a very facile process.

Acknowledgment. We are grateful to the U.S. Department of Energy (Contract No. DE-FG05-85ER13432) and the Kentucky EPSCoR program (NSF Grant RII-8610671) for financial support, the University of Kentucky Center for Computational Science for computing time and facilities, and the University of Kentucky Major Research Instrumentation Bond Program for equipment.

Supplementary Material Available: Listings of crystal structure data, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes for **4** (7 pages); a listing of experimental and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

---

(8) $[W(CO)_2(\eta^3\text{-}Me_3CC{\equiv}CC{=}CMeCMe_3)(Cp^*)]$ (**4**): Compound **3** (0.472 g, 0.771 mmol) was suspended in Et_2O (30 mL) at −78 °C. A solution of $NaN(SiMe_3)_2$ (0.140 g, 0.772 mmol) in Et_2O (10 mL) was added by syringe; the system was purged with CO during the addition and for 5 min longer. After several hours at −78 °C, the solution was warmed to room temperature overnight and then evaporated to dryness. The residue was dissolved in benzene and the solution then eluted through ca. 4 cm of activity III neutral alumina with 2:1 hexane/benzene. Recrystallization from pentane gave orange crystals of **4** (0.268 g, 62.9%), mp 130–150 °C dec. IR (Nujol, cm^{-1}): 1922 (s, ν_{CO}); 1836 (s, ν_{CO}); 1667 (w, $\nu_{C{=}C}$). ^1H NMR (200 MHz, C_6D_6, δ_H): 2.43 (s, 3 H, $C{=}C\mathit{Me}CMe_3$), 1.70 (s, 15 H, $C_5\mathit{Me}_5$), 1.42 and 1.22 (s, each 9 H, $C\mathit{Me}_3$). ^{13}C NMR (200 MHz, C_6D_6, δ_C): 238.1 (CO), 235.8 (CO), 148.6 ($C{=}\mathit{C}MeCMe_3$), 136.2 ($\mathit{C}{=}CMeCMe_3$), 118.2 ($C{\equiv}\mathit{C}CMe_3$), 103.7 (C_5Me_5), 45.8 ($\mathit{C}{\equiv}CCMe_3$), 37.6 and 35.2 ($\mathit{C}Me_3$), 32.9 and 29.6 ($C\mathit{Me}_3$), 21.3 ($C{=}C\mathit{Me}CMe_3$), 10.6 ($C_5\mathit{Me}_5$). MS ($C_{25}H_{36}O_2{}^{184}W$, *m/e*): 552, $[M]^+$; 524, $[M - CO]^+$; 496, $[M - 2CO]^+$; 439, $[M - 2CO - Bu^t]^+$. Anal. Calcd for $C_{25}H_{36}O_2W$: C, 54.36; H, 6.57. Found: C, 54.78; H, 6.83.

(9) Crystallographic data for **4**: Enraf-Nonius CAD4 diffractometer, MoKα radiation, 4516 reflections measured, 3807 with $(F_o)^2 \geq 3\sigma(F_o)^2$ used, space group $P2_1/n$, $Z = 4$, $a = 11.165$ (2) Å, $b = 17.325$ (1) Å, $c = 13.201$ (3) Å, $\beta = 106.758$ (8)°, $V = 2445.0$ (7) Å^3, $\rho_{calcd} = 1.503$ g cm^{-3}, $\mu = 48.49$ cm^{-1}. The tungsten atom was located by using Patterson methods and the remaining non-hydrogen atoms by using difference Fourier methods. All atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the solution. A linear decomposition correction (maximum 9%) and an empirical absorption correction (CAMEL[18]) were applied to the data. Full-matrix least-squares refinement led to $R = 3.6\%$, $R_w = 5.0\%$.

(10) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1–100.

(11) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247–254.

(12) (a) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444–1450. (b) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378–1380.

(13) (a) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565–4569. (b) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522–524.

(14) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729–6730.

(15) (a) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M. B.; New, L. *J. Organomet. Chem.* **1979**, *177*, C8–C12. (b) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M. B.; New, L. *Polyhedron* **1985**, *4*, 1119–1130.

(16) Moran, G.; Green, M.; Orpen, A. G. *J. Organomet. Chem.* **1983**, *250*, C15.

(17) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008–4009.

(18) Flack, H. D. *Acta Crystallogr.* **1977**, *A33* 890–898.