Together with the almost planar arrangement of the $SnFe_3$ (1) or $SnFe_2Cr$ (2) core, we conclude that the zwitterionic resonance contributor $(OC)_n(\mu\text{-CO})M''^{-}\text{–}^{+}SnFp_2$ predominates, which (i) accounts for the Lewis acidity of the Sn(II) center and (ii) identifies M″–CO rather than Fe(Cp)(CO)–CO as the more basic carbonyl.

Acknowledgment. M.J.M. thanks the U.S. National Science Foundation for a grant.

Supplementary Material Available: Details of the data collection for 1, tables of isotropic and anisotropic thermal parameters, fractional atomic coordinates, and bond distances and angles for 1 and 2, an ORTEP drawing of 1, and a diagram of the disordered toluene molecule in 2 (14 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(12) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

Reaction of $[(\eta^5\text{-}C_5H_4R)Cl_2W{\equiv}WCl_2(\eta^5\text{-}C_5H_4R)]$ (R = Me, $\mathrm{Pr^i}$) with Alkynes: X-ray Crystal Structures of $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_4(\mu\text{-}C_4Me_4)]$ and $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_2(O)(\mu\text{-}C_4Me_4)]$

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Summary: The dimers $[(\eta^5\text{-}C_5H_4R)_2W_2Cl_4]$ (**1a**, R = $\mathrm{Pr^i}$; **1b**, R = Me) react with an excess of but-2-yne (C_2Me_2) to give the flyover bridge compounds *cis*-$[(\eta^5\text{-}C_5H_4R)_2W_2Cl_4(\mu\text{-}C_4Me_4)]$ (**2a,b**), which undergo thermal rearrangement in solution or in the solid state to the isomeric trans species (**3a,b**). The X-ray crystal structure of **3b** reveals a planar bridging $\mu\text{-}C_4Me_4$ group that lies symmetrically perpendicular to the W–W (2.9295 (7) Å) bond. Hydrolysis of **2** or **3** gives the monooxoditungsten derivatives *trans*-$[(\eta^5\text{-}C_5H_4R)_2W_2Cl_2(O)(\mu\text{-}C_4Me_4)]$ (**4a,b**).

Examples of "flyover bridge" compounds, in which a coupled dialkyne fragment (C_4R_4) bridges a dimetal center, are plentiful in the chemical literature.[1] A common feature of even the symmetrically substituted derivatives of this class (e.g., $[Fe_2(CO)_6(\mu\text{-}C_4Ph_4)]$[1h,2]) is that the $\mu\text{-}C_4R_4$ fragment exhibits a pronounced "lean" toward one metal atom. These structures may be formally described as a metallacyclopentadiene fragment that is η^4-bound to the second metal atom.[3] We recently described the synthesis and crystal structure of $[(\eta^5\text{-}C_5H_4R)_2W_2Cl_4]$ (**1a**, R = $\mathrm{Pr^i}$), in which the unsupported W≡W triple bond undergoes reversible addition of dihydrogen.[4] Here we report reactions of **1a** (R = $\mathrm{Pr^i}$) and **1b** (R = Me) with alkynes.

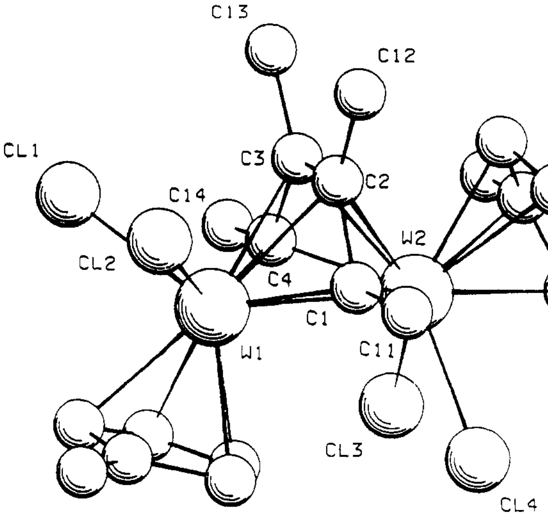

Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_4(\mu\text{-}C_4Me_4)]$ (**3b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: W(1)–W(2) = 2.9295 (7), W(1)–Cl(1) = 2.486 (3), W(1)–Cl(2) = 2.474 (4), W(2)–Cl(3) = 2.481 (1), W(2)–Cl(4) = 2.471 (4), W(1)–C(1) = 2.11 (1), W(2)–C(1) = 2.11 (1), W(1)–C(2) = 2.39 (1), W(2)–C(2) = 2.38 (2), W(1)–C(3) = 2.36 (2), W(2)–C(3) = 2.38 (1), W(1)–C(4) = 2.10 (2), W(2)–C(4) = 2.10 (1), C(1)–C(2) = 1.46 (2), C(2)–C(3) = 1.44 (2), C(3)–C(4) = 1.43 (2), C(1)–C(11) = 1.52 (2), C(2)–C(12) = 1.50 (2), C(3)–C(13) = 1.51 (2), C(4)–C(14) = 1.53 (2), W(1)–$Cp_{cent(1)}$ = 1.99, W(2)–$Cp_{cent(2)}$ = 2.06; Cl(1)–W(1)–Cl(2) = 77.7 (2), Cl(3)–W(2)–Cl(4) = 78.6 (1), Cl(1)–W(1)–W(2) = 125.7 (1), Cl(2)–W(1)–W(2) = 125.4 (1), C(2)–C(1)–C(11) = 121.3 (13), C(3)–C(4)–C(14) = 121.6 (16), C(1)–C(2)–C(12) = 121.9 (15), C(4)–C(3)–C(13) = 122.2 (16), C(2)–C(3)–C(13) = 117.2 (13), C(3)–C(2)–C(12) = 119.4 (15), W(1)–C(1)–W(2) = 88.0 (5), W(1)–C(4)–W(2) = 88.4 (6); ∠[(least-squares plane C(1)–C(4))–(plane containing W(1) and W(2))] = 89.8. $Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the calculated $\eta^5\text{-}C_5H_4Me$ ring centroids for W(1) and W(2), respectively.

When a toluene solution of $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4]$ (**1a**) was treated with an excess of but-2-yne at room temperature over 12 h, the purple microcrystalline product **2a**, analyzed as $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4(C_2Me_2)_2]$, was obtained in ca. 60% yield.[5] The ^1H NMR spectrum of **2a** showed signals assignable to a $\eta^5\text{-}C_5H_4Pr^i$ moiety and two further singlets at δ 3.53 and 1.75. The ^{13}C NMR spectrum showed, in addition to signals characteristic of an $\eta^5\text{-}C_5H_4Pr^i$ ring, two quartets at δ 33.3 and 15.8 assignable to methyl group carbon atoms and two additional singlets assignable to quaternary carbon atoms at δ 188.3 and 101.3. The compound **2a** isomerizes in THF solution at room temperature over 2 days to give the orange compound **3a** of identical empirical formula in quantitative yield. The NMR spectra of **3a** were very similar to those for **2a** but now showed two spectroscopically inequivalent $\eta^5\text{-}C_5H_4Pr^i$ ligands. Single

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(1) For examples and leading references see: (a) Curtis, D. M. *Polyhedron* **1987**, *6*, 759. (b) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101. (c) Burho, W. A.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311. (d) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 545–555. (e) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 5, pp 192–209. (f) Veldman, M. E. E.; Van der Waal, H. R.; Veenstra, S. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1980**, *197*, 59. (g) Bateman, L. R.; Maitlis, P. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 7292. (h) Riley, P. E.; Davis, R. E. *Acta Crystallogr.* **1975**, *B31*, 2928.

(2) (a) The deviation of sawhorse $[Fe_2(CO)_6(\mu\text{-}C_4H_4)]$ from ideal C_{2v} symmetry has been attributed to a second-order Jahn–Teller distortion: Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126. (b) Thermal racemization of the optically active species $[Fe_2(CO)_6(\mu\text{-}C_4H(OH)_2R)]$ is thought to proceed via a symmetrical C_{2v} transition state: Case, R.; Jones, E. R. H.; Schwartz, N. V.; Whiting, M. C. *Proc. Chem. Soc. (London)* **1969**, 256.

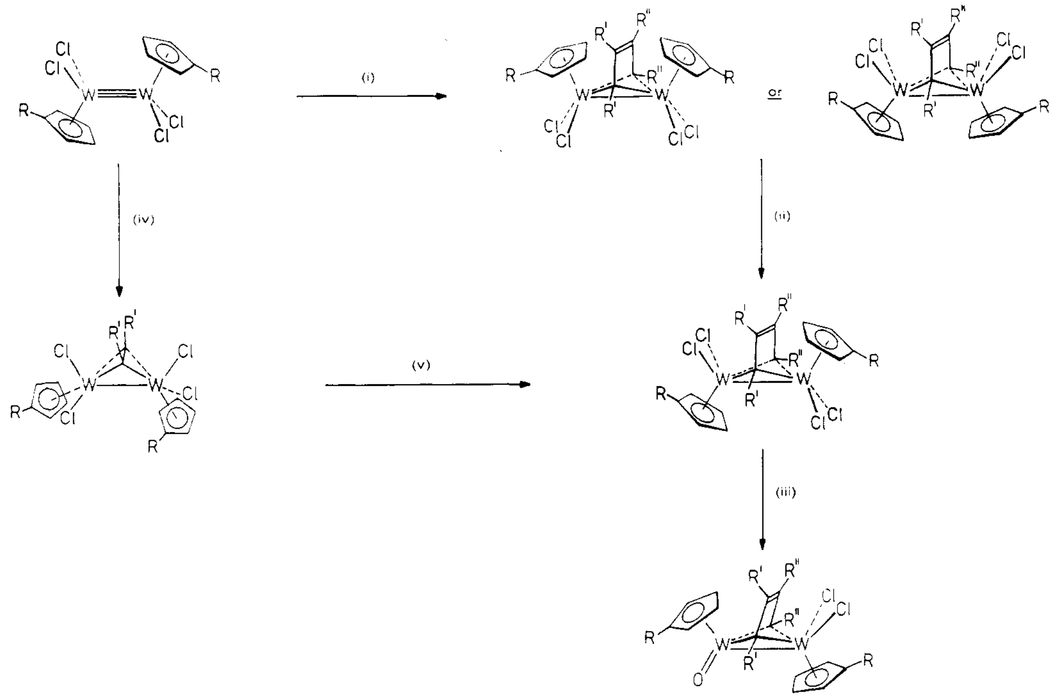
(3) The solid-state structure of $[(\eta^5\text{-}C_5H_5)_2Cr_2(CO)(\mu\text{-}C_4Ph_4)]$ differs slightly from this general description. The terminal carbon atoms of the $\mu\text{-}C_4Ph_4$ fragment were equidistant from both Cr atoms, but the internal (bridgehead) carbon atoms bond much more strongly to the Cr atom that does not bear the CO ligand: (a) Bradley, J. S. *J. Organomet. Chem.* **1978**, *150*, C1. (b) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173.

(4) Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 732.

(5) Satisfactory elemental analyses (C, H ±0.3%; Cl ±0.4%) have been obtained for all the new compounds in this work.

0276-7333/90/2309-0886$02.50/0

Scheme I[a]



[a] Reagents and conditions: (i) excess C_2Me_2, toluene, 12 h, 60% (R = Pr^i, Me; R′ = R″ = Me); (ii) THF, room temperature, 2 days, ca. 100%, *or* solid state, ca. 250 °C, ca. 100% (R = Pr^i, Me; R′ = R″ = Me); (iii) H_2O/acetone, 8 h, 80% (R = Pr^i, Me; R′ = R″ = Me); (iv) $C_2R'_2$, toluene, 8 h, 40% (R = Pr^i, R′ = $SiMe_3$) or 70% (R = Pr^i, R′ = Et); (v) C_2Me_2, THF, 12 h, 70% (R = Pr^i, R′ = Et, R″ = Me).

crystals of the methylcyclopentadienyl analogue $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_4(C_2Me_2)_2]$ (**3b**) suitable for an X-ray crystal structure analysis were obtained by slow diffusion of diethyl ether into a THF solution of **3b**.[6a]

The solid-state structure of **3b** (Figure 1) consists of two mutually trans $[(\eta^5\text{-}C_5H_4Me)WCl_2]$ fragments linked by a tungsten–tungsten bond (W–W = 2.9295 (7) Å), which is bridged by a planar C_4Me_4 fragment. An unusual feature of this structure is that the C_4Me_4 fragment is symmetrically bound (within experimental error) to each tungsten atom in an η^4 fashion and is perpendicular to the tungsten–tungsten bond. There is no difference (within experimental error) between the internal carbon–carbon bond lengths of the $\mu\text{-}C_4Me_4$ fragment, indicating a high degree of delocalization of the π-electrons of this fragment. To our knowledge, this is the first example of an $[M_2(\mu\text{-}C_4R_4)]$ system in which the C_4R_4 unit symmetrically bonds to the two metal fragments.[7]

The X-ray crystal data, together with the ^{13}C NMR data, suggest a description intermediate between a buta-1,3-dienyl(2−) and a but-2-enyl(4−) representation for the C_4Me_4 moiety. The ^{13}C chemical shift (δ 185.4) for the terminal carbon atoms of the C_4Me_4 fragment in **3a** is suggestive of some degree of alkylidene character.[8] The structures of **2a** and of the methylcyclopentadienyl analogue $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_4(\mu\text{-}C_4Me_4)]$ (**2b**) may be assigned as the corresponding cis isomers of the trans compounds **3a** and **3b** (Scheme I).[9] The cis to trans isomerization of **2** to **3** also occurs quantitatively in the solid state at ca. 250 °C, a very rare example of a solid-state isomerization of an organometallic species. The energy of activation (E_a) for the isomerization of **2a** to **3a** in solution is 23.6 (2) kcal mol^{-1}.[10]

The compounds **2** and **3** undergo partial hydrolysis in wet acetone to give the red monooxo derivatives $[(\eta^5\text{-}C_5H_4R)_2W_2Cl_2(O)(\mu\text{-}C_4Me_4)]$ (**4a**, R = Pr^i; **4b**, R = Me) in >80% yield. The NMR spectra of **4** were largely similar to those of the tetrachloro precursors **2** and **3** but showed some interesting differences. The ^{13}C chemical shift of the terminal carbon atoms of the $\mu\text{-}C_4Me_4$ fragment in **4a** moves to higher field (δ 158.1 compared to 188.3 and 185.4 in **2a** and **3a**, respectively), suggestive of a lesser degree of alkylidene character. Moreover, the $^1J(^{13}C\text{-}^{183}W)$ (^{183}W, 14.5% natural abundance, $I = {}^1/_2$) coupling constant for the terminal carbon atoms of **4a** is 114 Hz, and the measured satellite area (14% of the total signal by area) is consistent with bonding predominantly to one W atom. In **3a**, a smaller coupling constant is observed ($^1J(^{13}C\text{-}^{183}W)$ = 49 Hz), and the intensity of the satellites (24.5% of the total signal) suggests equal bonding to the two tungsten atoms.[11]

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(6) (a) X-ray diffraction data for **3b**: orthorhombic; space group *Pbca*; a = 11.847 (2), b = 14.001 (2), c = 25.148 (4) Å; V = 4171.8 Å^3; Z = 8; absorption coefficient 117.8 cm^{-1}; Enraf-Nonius CAD4F diffractometer; graphite-monochromated Mo Kα radiation (λ = 0.71069 Å); temperature 293 K; scan range 3° ≤ 2θ ≤ 50°; 2118 reflections ($I > 3\sigma(I)$); 236 variables; R = 0.029, R_w = 0.031 (unit weights). (b) X-ray diffraction data for **4b**: monoclinic; space group $P2_1/n$; a = 9.006 (3), b = 24.271 (5), c = 9.005 (3) Å; β = 94.51 (3)°; V = 1978.3 Å^3; Z = 4; absorption coefficient 121.6 cm^{-1}; Enraf-Nonius CAD4F diffractometer; graphite-monochromated Mo Kα radiation (λ = 0.71069 Å); temperature 293 K; scan range 3° ≤ 2θ ≤ 50°; 3106 reflections ($I > 3\sigma(I)$); 216 variables; R = 0.068, R_w = 0.071. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (C–H = 0.96 Å) and refined riding on attached carbons. An apparent unit cell transformation for **4b** to higher symmetry was investigated but found not to possess full orthorhombic symmetry.

(7) Examples of trinuclear cluster compounds are known where a $[MC_4R_4]$ metallacyclopentadiene fragment bonds symmetrically to two further metal fragments: (a) Didier, N.; Dahan, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658. (b) Hessen, B.; Spek, A. L.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1058.

(8) ^{13}C chemical shifts for authentic bridging alkylidene carbons [M-(μ-CRR′)M] generally fall in the range δ 100–210: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 160.

(9) We cannot distinguish, from spectroscopic data alone, between the two possible isomeric C_{2v} structures that may have the $\eta^5\text{-}C_5H_4R$ rings either cis or trans to the $\mu\text{-}C_4Me_4$ fragment.

(10) By ^1H NMR spectroscopy in C_3D_6O and with the assumption of a first-order rate equation for the process **2a** → **3b**. E_a was determined from an Arrhenius plot for k_1 at four temperatures.

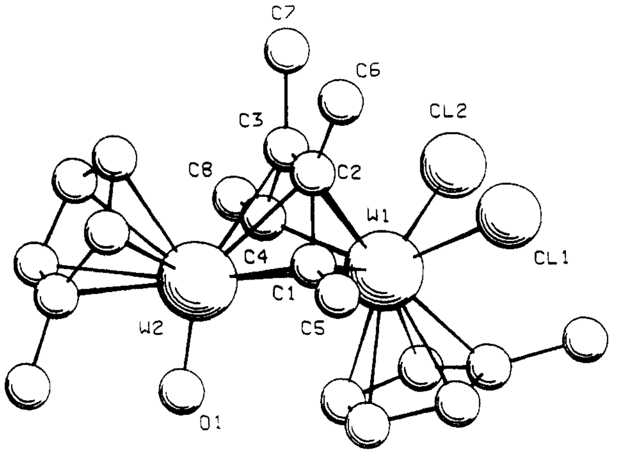

Figure 2. Molecular structure of $[(\eta^5\text{-}C_5H_4Me)_2W_2Cl_2(O)(\mu\text{-}C_4Me_4)]$ (**4b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: W(1)–W(2) = 2.9097 (6), W(1)–Cl(1) = 2.472 (3), W(1)–Cl(2) = 2.475 (3), W(2)–O(1) = 1.71 (1), W(1)–C(1) = 2.14 (1), W(2)–C(1) = 2.10 (1), W(1)–C(2) = 2.35 (1), W(2)–C(2) = 2.49 (1), W(1)–C(3) = 2.36 (1), W(2)–C(3) = 2.49 (1), W(1)–C(4) = 2.16 (1), W(2)–C(4) = 2.09 (1), C(1)–C(2) = 1.46 (1), C(2)–C(3) = 1.45 (1), C(3)–C(4) = 1.44 (1), C(1)–C(5) = 1.51 (1), C(2)–C(6) = 1.52 (1), C(3)–C(7) = 1.52 (1), C(4)–C(8) = 1.50 (1), W(1)–$Cp_{cent(1)}$ = 1.99, W(2)–$Cp_{cent(2)}$ = 2.10; Cl(1)–W(1)–Cl(2) = 79.3 (1), Cl(1)–W(1)–W(2) = 127.51 (8), Cl(2)–W(1)–W(2) = 127.18 (8), O(1)–W(2)–W(1) = 97.5 (3), $Cp_{cent(1)}$–W(1)–W(2) = 105.4, $Cp_{cent(2)}$–W(2)–W(1) = 153.0, C(2)–C(1)–C(5) = 123.6 (11), C(3)–C(4)–C(8) = 122.8 (11), C(1)–C(2)–C(6) = 119.4 (10), C(4)–C(3)–C(7) = 120.9 (11), C(2)–C(3)–C(7) = 119.6 (10), C(3)–C(2)–C(6) = 120.3 (10), W(1)–C(1)–W(2) = 86.6 (4), W(1)–C(4)–W(2) = 86.4 (4); ∠[(least-squares plane C(1)–C(4))–(plane containing W(1) and W(2))] = 83.3. $Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the calculated $\eta^5\text{-}C_5H_4Me$ ring centroids for W(1) and W(2), respectively.

A single-crystal X-ray structure analysis of **4b** was carried out, and the molecular structure is shown in Figure 2, along with selected bond lengths and angles.[6b] The overall structure of **4b** is similar to that of **3b** and shows a trans disposition of the $\eta^5\text{-}C_5H_4Me$ rings with a terminal tungsten–oxygen double bond (W=O = 1.71 (1) Å) trans to a bridging $\mu\text{-}C_4Me_4$ moiety.[12] The C_4Me_4 ligand is no longer symmetrically bound to each W atom; the terminal carbons bond more strongly to W(2), while the internal bridgehead carbon atoms (C(2) and C(3)) bond more strongly to W(1). This is consistent with the ^{13}C NMR data described above for the more soluble isopropylcyclopentadienyl analogue (**4a**). The overall deviation of the $\mu\text{-}C_4Me_4$ fragment from the idealized perpendicular geometry found in the case of **3b** is ca. 7°.[13] This suggests competition between the terminal oxo and the $\mu\text{-}C_4Me_4$ fragment π-electron systems for a vacant orbital(s) on the metal atom.[14] Compounds 4 are rare examples of hydrocarbyloxotungsten species.[15,16]

Monoadducts of alkynes with $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4]$ (**1a**) have also been prepared (Scheme I).[17] Thus, treatment of **1a** with 1 equiv of bis(trimethylsilyl)acetylene ($C_2(SiMe_3)_2$) or hex-2-yne (C_2Et_2) gives the monoadducts $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_2(\mu\text{-}Cl)_2(\mu\text{-}C_2R_2)]$ (**5**, R = $SiMe_3$; **6**, R = Et) in 40 and 70% yields, respectively. The ^1H NMR spectra of **5** and **6** reveal the presence of prochiral $\eta^5\text{-}C_5H_4Pr^i$ ligands (i.e., an ABCD spin system for the ring protons and nonequivalent Me's for the isopropyl group), and for **6** the methylene groups of the $\mu\text{-}C_2Et_2$ fragment are prochiral and appear as doublets of quartets. The ^{13}C NMR spectrum of **5** shows a singlet at δ 237.3, assignable to the internal carbon atoms of the $\mu\text{-}C_2(SiMe_3)_2$ ligand.[18] To account for these data, we propose the structure shown in Scheme I.

The compound **6** reacts with but-2-yne in THF at 30 °C over 12 h to give orange *trans*-$[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4(\mu\text{-}(1,2)\text{-}C_4Me_2Et_2)]$ (**7**) in good yield. Examination of the reaction mixture by ^1H NMR spectroscopy at an intermediate stage revealed signals assignable to the corresponding cis isomer, but this compound was not isolated. Products containing a $[\mu(1,4\text{-}C_4Me_2Et_2]$ or $[\mu(1,3)\text{-}C_4Me_2Et_2]$ fragment were not observed but may be independently prepared as a mixture of isomers from **1a** and pent-2-yne.

Our results suggest that the mechanism for the coupling of alkynes by **1** proceeds via a monoadduct (such as **5** or **6**), followed by insertion of a second molecule of alkyne into the W–C bond of the monoadduct. This is consistent with the mechanisms postulated for other coupled alkyne systems.[1a,c] The coupling reactions described above give the cis isomer as the initial (kinetic) product, which then isomerizes in solution to give the trans isomer as the final (thermodynamic) product. To date we have not found any evidence for alkyne C–C bond cleavage or metathesis in these reactions.

Acknowledgment. We wish to thank the SERC and British Petroleum plc for a CASE award (to P.M.).

Supplementary Material Available: Listings of analytical, ^1H NMR, and ^{13}C NMR data for the new compounds, a summary of crystal data and data collection parameters, and tables of positional and thermal parameters and interatomic bond distances and angles for **3b** and **4b** (22 pages); listings of observed and calculated structure factors for **3b** and **4b** (42 pages). Ordering information is given on any current masthead page.

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(11) Although the differences between the inductive and π-donor effects of the $(Cl)_2$ and O ligands in 3 and 4 will clearly influence the chemical shift of the terminal carbons of the $\mu\text{-}C_4Me_4$ fragment, the observed differences in $^1J(^{13}C\text{-}^{183}W)$ are quite compelling. Coupling of the terminal carbons of the $\mu\text{-}C_4Me_4$ fragment to the second W atom in 4 could not be resolved.

(12) The W=O bond length (1.71 (1) Å) in **4b** is typical of that found for other W=O systems. For leading references and listings of W=O bond lengths see: (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(13) This is the deviation of the angle ∠ [(least-squares plane C(1)–C(4))–(horizontal plane containing W(1) and W(2))] from the ideal perpendicular angle (90°).

(14) Structural evidence for the strong trans influence of a terminal oxo ligand on an η-hydrocarbyl group has been reported. The formally η^5 C_5Me_5 ring in $[(\eta^5\text{-}C_5Me_5)W(O)_2OC_5Me_5]$ had a significant amount of η^1,η^4 character: Parkin, G.; Marsh, R. E.; Schaefer, W. P.; Bercaw, J. E. *Inorg. Chem.* **1988**, *27*, 3262.

(15) A μ_3-alkyne trinuclear cluster containing a $[(\eta^5\text{-}C_5H_5)W(O)]$ unit has been reported: Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

(16) (a) The singly bonded (W–W = 2.877 (3) Å) dimer $[(\eta^5\text{-}C_5Me_5)(CO)_3W{-}W(O)_2(\eta^5\text{-}C_5Me_5)]$ has been prepared by aerial oxidation of $[(\eta^5\text{-}C_5Me_5)_2W_2(CO)_6]$: Alt, H. G.; Hayen, H. I.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1795. (b) Other workers have found that the same reaction gives $\{[(\eta^5\text{-}C_5Me_5)W(O)]_2(\mu\text{-}O)_2\}$ and $\{[(\eta^5\text{-}C_5Me_5)W(CO)]_2(\mu\text{-}O)_2\}$, but no structural data were presented: Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111.

(17) For other examples of the direct addition of an alkyne to an unsupported M≡M bond, see: (a) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B.; Tipton, D. T.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41. (c) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (d) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1979**, *23*, 85. (e) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 152. (f) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2171.

(18) This value is similar to those found in the related ditungsten halide compounds $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2RR')(THF)_2]$: Bott, S. J.; Clark, D. L.; Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 418.