# Ene-Yne Couplings at a Ditungsten Center To Give Alkylidyne Hydrido Complexes Supported by Siloxide Ligands

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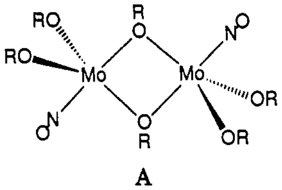
The ethyne-bridged compound $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2H_2)$ (1) and its $^{13}C$-labeled $\mu\text{-}^{13}C_2H_2$ isotopomer (1*) react in hydrocarbon solvents at *ca.* −20 °C with ethene to give $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ (2) (and 2*) and with allene to give $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3). Compounds 2 and 3 have been characterized by single-crystal X-ray crystallography, and the two are structurally related in having two five-coordinate W atoms united by a $\mu$-alkylidyne ligand and one bridging siloxide. One tungsten is coordinated to three terminal siloxide ligands while the other is bonded to two terminal siloxides and a terminal hydride. The terminal hydride was not located crystallographically, but its presence is implicated by a vacant coordination site on tungsten and by $^1H$ NMR spectroscopy. At room temperature the compounds are fluxional and the hydride ligands see two time-averaged equivalent W nuclei. The W-W distances span the range 2.56-2.65 and are consistent with a $(W\text{-}W)^{10+}$ moiety supported by bridging alkylidyne ligands. Reactions employing the $^{13}C$-labeled compound 1* and $C_2D_4$ and allene reveal some interesting aspects about the formation of the bridging hydrocarbyl ligand. These reactions are compared to the chemistry of the related *tert*-butoxy-supported compound $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$. Crystal data are the following: (i) $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ at −172 °C: $a = 14.037(2)$ Å, $b = 18.453(3)$ Å, $c = 11.681(2)$ Å, $\alpha = 91.20(1)°$, $\beta = 106.63(1)°$, $\gamma = 100.35(1)°$, $Z = 2$, $d_{calcd} = 1.412$ g cm$^{-3}$, and space group $P\bar{1}$; and (ii) $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ at −172 °C: $a = 14.211(8)$ Å, $b = 18.296(11)$ Å, $c = 11.724(6)$ Å, $\alpha = 91.24(2)°$, $\beta = 105.97(2)°$, $\gamma = 99.98(2)°$, $Z = 2$, $d_{calcd} = 1.41$ g cm$^{-1}$, and space group $P\bar{1}$.

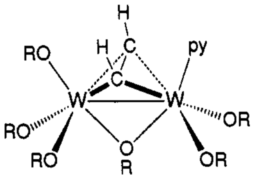
## Introduction

Alcohols and trialkylsilanols are obviously closely related and show similar properties in binding to metals much as, for example, tertiary phosphine and tertiary phosphite ligands bind to metals. The hydroxyl group of the trialkylsilanol is more acidic than its carbon counterpart,[1] and one might anticipate that the overall electron-releasing properties of a related pair of ligands $R_3EO^-$ would be E = C > Si. This is because, even though silicon is more electropositive than carbon, the negative charge on oxygen can be delocalized by back-donation to the $SiR_3$ moiety. Although it is possible to invoke Si d orbital participation and hence $Op_\pi$ to Si $d_\pi$ bonding, the best theoretical calculations indicate that the use of Si 3d orbitals is extremely small.[2] The back-bonding to the $SiR_3$ group involves $Op_\pi$ to Si-C $\sigma^*$ bonding in much the same way that a tertiary phosphine is a $\pi$-acceptor to a transition metal by metal $d_\pi$ to P-C $\sigma^*$ bonding and not by metal $d_\pi$ to P $d_\pi$ bonding.[3] Having commented on the differences in bonding between related $R_3EO^-$ ligands, Si versus C, it must be emphasized that these factors are relatively subtle and may be interpreted subjectively. For example, in the structurally related pair of compounds having the formula $Mo_2(OR)_6(NO)_2$ with structure type A the values of $\nu$(NO) for the linear nitrosyl ligand are at 1648 cm$^{-1}$ when R = $Bu^tMe_2Si$[4] versus 1625 cm$^{-1}$ for R = $Bu^t$.[5] We interpret this as a clear indication that the $Bu^tO$ ligand is overall a better $\sigma + \pi$ donor ligand relative to $Bu^tMe_2SiO$.



A

The addition of ethyne to $W_2(OR)_6$ compounds where R = $Bu^t$ and $Bu^tMe_2Si$ leads to isolable 1:1 adducts in the presence of pyridine having the structure shown in B. The metric parameters of the compounds where R = $Bu^t$[6] and $Bu^tMe_2Si$[7] are virtually identical although the reactivity of the two species in solution is remarkably different.



B

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[1] Compare, for example, the p$K_a$ of $HOBu^t$ of 19 (a) versus the p$K_a$ for $HOSiEt_3$ of 14(b): (a) McEwan, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124. (b) Arm, H.; Hochstrasser, K.; Schindler, P. W. *Chimica* **1974**, *28*, 237.

[2] For a discussion of so-called "hypervalent molecules" without the involvement of d orbitals, see: Albright, T. A.; Burdett, J. K.; Whangbo, M. H. In *Orbital Interactions in Chemistry*; J. Wiley & Sons Publishers, 1984; Chapter 14.

[3] Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

[4] Chisholm, M. H.; Cook, C. M. *Inorg. Chim. Acta* **1992**, *198*-200, 63.

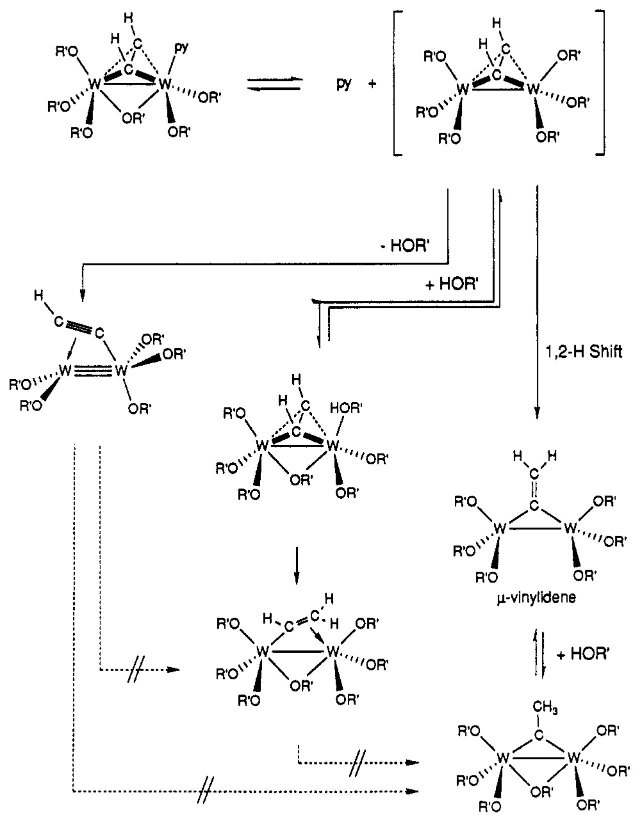
[5] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.

[6] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

[7] Chisholm, M. H.; Cook, C. M.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Dalton Trans.* **1991**, 929.

0276-7333/93/2312-2677$04.00/0

**Scheme I. Summary of the Reactions of the $\mu$-Ethyne Adduct $W_2(OR')_6(py)(\mu\text{-}C_2H_2)$, Where R′ = $SiMe_2Bu^t$ [a]**



[a] These reactions occur at 22 °C in hydrocarbon solvents as described in ref 7.

In particular, the *tert*-butoxide compound is labile to both C–C coupling with additional ethyne, eq 1, and C–C cleavage to give the methylidyne complex shown in eq 2. The latter was isolable as its quinuclidine adduct.[8]

$$W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2) + C_2H_2 \xrightarrow[\text{hexane}]{22\ °C} W_2(\mu\text{-}C_4H_4)(OBu^t)_6 + py \tag{1}$$

$$W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2) \rightleftarrows 2[(Bu^tO)_3W{\equiv}CH] + py \tag{2}$$

By contrast, the ethyne-bridged siloxide $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2H_2)$ (1) was unreactive to methylidyne formation and does not form an isolable $\mu\text{-}C_4H_4$-containing compound. It was, however quite remarkably labile to proton-transfer reactions and the formation of $W_2(\mu\text{-}CCH)$-, $W_2(\mu\text{-}CHCH_2)$-, and $W_2(\mu\text{-}CCH_3)$-containing compounds as shown in Scheme I.[7]

In this paper we describe further studies of the ethyne bridged siloxide compound 1 in its reactions with C–C double bonds.[9]

## Results and Discussion

**Syntheses. (a) General Comments.** Compound 1 reacts readily at room temperature in hydrocarbon solutions to generate $W_2(\mu\text{-}CCH)(OSiMe_2Bu^t)_5$ in *ca.* 90% yield over a period of 2 h.[7] This reaction is much slower at temperatures below 0 °C and is effectively shut down at −20 °C. Consequently, the reactions involving the addition of alkenes must occur more rapidly than the formation of the $W_2(\mu\text{-}CCH)$-containing compound which is inert to C–C coupling.

**(b) Synthesis of $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ (2).** The ethyne complex 1 and ethene (1–10 equiv) react in toluene or hexanes at −20 °C to give compound **2**, which crystallizes from toluene at −20 °C as blue-black rectangular cubes. At temperatures above −10 °C, the ene–yne coupling reaction still occurs faster than the formation of the $W_2(\mu\text{-}CCH)$-containing compound. The reactions employing **1*** $[W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}^{13}C_2H_2)]$ and ethene reveal that the formation of **2*** is essentially quantitative. Compound 2 is inert (chemically persistent) in hydrocarbon solutions and in the solid state in dry and oxygen-free $N_2$ atmosphere or under vacuum at room temperature.

**(c) Synthesis of $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3).** Compound 1 and allene (10 equiv) react in toluene at −20 °C to form **3**, which crystallizes at −20 °C as thin red needles. The reaction takes *ca.* 12 h at −20 °C. At temperatures of −10 °C and above, the formation of the $W_2(\mu\text{-}CCH)$-containing compound becomes competitive with the formation of **3**. Red solutions of **3** in hydrocarbon solvents are thermally sensitive at 22 °C and yield green solutions of as yet unknown decomposition products in *ca.* 1 h (22 °C). Compound 3 is less thermally sensitive in the solid state and can be stored *in vacuo* or under a dry and oxygen-free $N_2$ or Ar atmosphere for periods of up to 3 weeks at 22 °C.

**(d) Attempted Reactions with Propene and 1,3-Butadiene.** No reaction between 1 and propene was observed at −20 °C, and at higher temperatures only the formation of $W_2(\mu\text{-}CCH)(OSiMe_2Bu^t)_5$ was observed. With 1,3-butadiene and **1*** there was a C–C coupling reaction (as determined by $^{13}C$ NMR spectroscopy), but the rate of this coupling reaction was always unfavorable with respect to the reaction leading to $W_2(\mu\text{-}CCH)(OSiMe_2Bu^t)_5$. No pure compound derived from the coupling of the $\mu\text{-}C_2H_2$ ligand and 1,3-butadiene was obtained, but it is believed that the nature of the coupling is in some way related to that observed with allene. (See Experimental Section.)

**Molecular Structure of $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ (2).** Atomic coordinates are given in Table I, and a view of the molecular structure found in the solid state is given in Figure 1. Selected bond distances and bond angles are given in Table II.

The hydride was not located crystallographically, but from the NMR data (presented later) and the observed geometry it may reasonably be inferred to occupy a terminal site on W(2) which would otherwise be only four coordinate. The geometry about each tungsten may be viewed as a distorted trigonal bipyramid in which one terminal siloxide ligand O(31) on W(1) and O(39) on W(2) and the bridging siloxide O(7) occupy axial sites. The bridging alkylidyne ligand is then in an equatorial site with respect to both W atoms. The W–W distance of 2.66 Å is typical for a $(W\text{–}W)^{10+}$ moiety, and the W–C distance of *ca.* 1.96 Å is typical of $\mu_2$-alkylidyne-bridged W–C distances.

The bridging ligand is a 2-butenylidyne ligand, and the C(3)–C(4) distance of 1.47 Å compares favorably to the C

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[8] The structures of the $W_2(OBu^t)_6(\mu\text{-}C_4H_4)(CO)$ and $W(OBu^t)_3(CH)(quinuclidine)$ complexes have been structurally characterized: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. Results to be published.

[9] A preliminary account of the reaction involving ethylene has appeared: Chacon, S. T.; Chisholm, M. H.; Cook, C. M.; Hampden-Smith, M. J.; Streib, W. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 462.

**Table I. Fractional Coordinates and Isotropic Thermal Parameters of Compound 2**

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| W(1) | 2631.2(3) | 2723.4(2) | 1945.0(3) | 12 |
| W(2) | 4352.2(3) | 2318.8(2) | 1930.8(4) | 13 |
| C(3) | 4067(8) | 3241(6) | 2451(9) | 19 |
| C(4) | 4720(9) | 3954(6) | 2915(10) | 23 |
| C(5) | 4836(9) | 4542(6) | 2260(12) | 28 |
| C(6) | 4252(10) | 4553(7) | 996(11) | 31 |
| O(7) | 2899(5) | 1854(4) | 962(6) | 14 |
| Si(8) | 2324(2) | 1127(2) | −16(3) | 16 |
| C(9) | 2387(9) | 1401(7) | −1514(10) | 28 |
| C(10) | 997(9) | 901(7) | 58(10) | 26 |
| C(11) | 2959(9) | 304(6) | 270(10) | 23 |
| C(12) | 4083(11) | 474(7) | 537(15) | 41 |
| C(13) | 2436(13) | −305(9) | −635(15) | 51 |
| C(14) | 2818(11) | 0(8) | 1547(14) | 41 |
| O(15) | 1997(5) | 3028(4) | 428(6) | 17 |
| Si(16) | 1382(2) | 3521(2) | −600(3) | 20 |
| C(17) | 1306(10) | 4421(8) | 72(11) | 34 |
| C(18) | 2062(9) | 3706(8) | −1757(10) | 29 |
| C(19) | 62(9) | 2968(8) | −1273(10) | 29 |
| C(20) | 62(10) | 2310(8) | −2090(11) | 35 |
| C(21) | −388(10) | 2680(7) | −271(12) | 33 |
| C(22) | −620(9) | 3458(8) | −2037(12) | 36 |
| O(23) | 2161(5) | 2046(4) | 2903(6) | 17 |
| Si(24) | 1974(2) | 1603(2) | 4–78(3) | 17 |
| C(25) | 2669(11) | 826(8) | 4371(14) | 41 |
| C(26) | 2530(11) | 2249(8) | 5444(11) | 36 |
| C(27) | 559(8) | 1253(7) | 3751(10) | 25 |
| C(28) | 263(11) | 432(8) | 3319(14) | 46 |
| C(29) | 254(10) | 1368(10) | 4907(12) | 45 |
| C(30) | −66(9) | 1681(7) | 2767(10) | 28 |
| O(31) | 2219(5) | 3502(4) | 2723(6) | 21 |
| Si(32) | 2429(3) | 4218(2) | 3660(3) | 28 |
| C(33) | 3473(13) | 4155(8) | 5056(11) | 49 |
| C(34) | 2811(12) | 5100(8) | 3025(13) | 41 |
| C(35) | 1219(13) | 4299(8) | 4039(13) | 44 |
| C(36) | 892(13) | 3660(8) | 4748(14) | 46 |
| C(37) | 340(13) | 4297(9) | 2905(14) | 50 |
| C(38) | 1420(19) | 5013(10) | 4824(19) | 78 |
| O(39) | 5624(5) | 2348(4) | 3025(6) | 18 |
| Si(40) | 6428(2) | 2349(2) | 4374(3) | 24 |
| C(41) | 5866(13) | 2673(8) | 5495(12) | 46 |
| C(42) | 7617(11) | 2992(9) | 4393(13) | 53 |
| C(43) | 6651(8) | 1369(6) | 4609(10) | 23 |
| C(44) | 7532(10) | 1387(8) | 5754(12) | 38 |
| C(45) | 6960(10) | 1086(8) | 3570(12) | 37 |
| C(46) | 5703(9) | 861(7) | 4709(13) | 34 |
| O(47) | 4724(5) | 2347(4) | 468(6) | 22 |
| Si(48) | 5328(2) | 2599(2) | −512(3) | 20 |
| C(49) | 5385(10) | 1765(7) | −1387(12) | 34 |
| C(50) | 4650(8) | 3210(7) | −1545(10) | 24 |
| C(51) | 6661(8) | 3101(7) | 304(11) | 26 |
| C(52) | 6677(9) | 3729(7) | 1166(12) | 32 |
| C(53) | 7291(9) | 2538(8) | 1025(14) | 39 |
| C(54) | 7187(9) | 3411(7) | −631(12) | 33 |

sp to C sp$^2$ bond length in vinylacetylene, 1.48 Å.[10] The olefinic distance between C(4) and C(5) is 1.36 Å, which is close to that in ethene, 1.34 Å.[10] The C(5)–C(6) distance of 1.47 Å may be compared to the C sp$^2$–C sp$^3$ single bond distance of 1.50 Å in propene.[10]

The W–O distances reveal the expected trend that the W-$\mu$-O distance is longer by 0.1 Å than the terminal W–O distances,[11] but the W–O distances are remarkably similar to those associated with alkoxide ligands. The terminal W–O–Si angles span a relatively small range, 155–163°.

**Molecular Structure of $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3).** An apparent crystal fragmentation prevented a meaningful absorption correction of the crystallographic data, and the rather poor quality of the data results in large esd's. There is also a disorder involving the groups bonded to W(2). Consequently, we offer this structural determination as support for the gross structural features of the molecule and the nature of the bridging ligand that has been formed by the coupling of the $\mu$-ethyne and allene moieties. The X-ray formulation of this ligand is supported by NMR data presented subsequently.

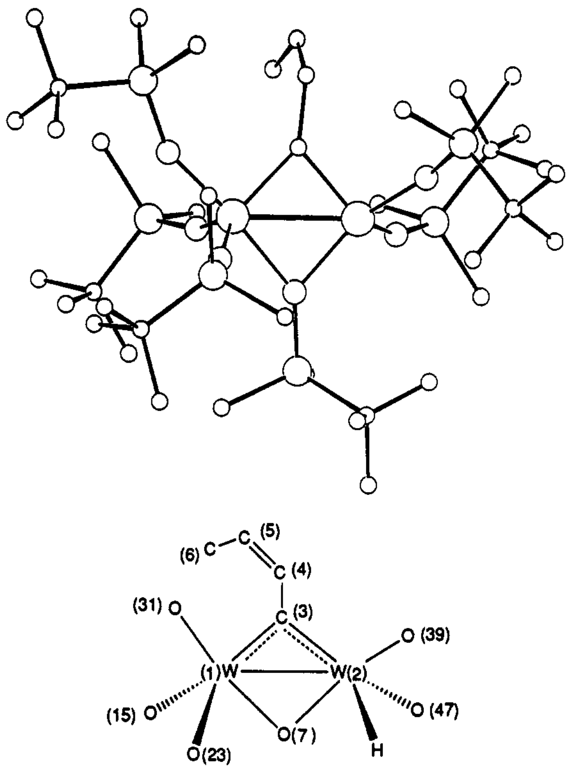

**Figure 1.** Top: Ball-and-stick representation for the molecular structure of $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ (2). Hydrogen atoms have been omitted for clarity. Bottom: Stick figure of the $HW_2(\mu\text{-}C_4)(O)_6$ core showing the atom label scheme and the proposed position of the hydride ligand.

**Table II. Selected Bond Distances (Å) and Angles (deg) for $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$ (2)**

| | | | |
|---|---|---|---|
| W(1)–W(2) | 2.658(1) | W(2)–O(47) | 1.92(1) |
| W(1)–O(7) | 2.10(1) | W(1)–C(3) | 1.98(1) |
| W(1)–O(15) | 1.89(1) | W(2)–C(3) | 1.93(1) |
| W(1)–O(23) | 1.94(1) | C(3)–C(4) | 1.47(2) |
| W(1)–O(31) | 1.94(1) | C(4)–C(5) | 1.36(2) |
| W(2)–O(7) | 2.05(1) | C(5)–C(6) | 1.47(2) |
| W(2)–O(39) | 1.87(1) | | |

| | | | |
|---|---|---|---|
| W(2)–W(1)–O(7) | 49.2(2) | O(7)–W(2)–O(39) | 156.1(3) |
| W(2)–W(1)–O(15) | 109.9(2) | O(7)–W(2)–O(47) | 89.0(3) |
| W(2)–W(1)–O(23) | 101.2(2) | O(7)–W(2)–C(3) | 97.1(4) |
| W(2)–W(1)–O(31) | 137.5(2) | O(39)–W(2)–O(47) | 99.4(3) |
| W(2)–W(1)–C(3) | 46.2(3) | O(39)–W(2)–C(3) | 99.5(4) |
| O(7)–W(1)–O(15) | 84.8(3) | O(47)–W(2)–C(3) | 114.6(4) |
| O(7)–W(1)–O(23) | 89.0(3) | W(1)–O(7)–W(2) | 79.7(3) |
| O(7)–W(1)–O(31) | 173.1(3) | W(1)–O(7)–Si(8) | 143.3(4) |
| O(7)–W(1)–C(3) | 93.7(4) | W(2)–O(7)–Si(8) | 137.0(4) |
| O(15)–W(1)–O(23) | 131.9(3) | W(1)–O(15)–Si(16) | 160.1(5) |
| O(15)–W(1)–C(3) | 108.2(4) | W(1)–O(23)–Si(24) | 162.9(5) |
| O(23)–W(1)–O(31) | 90.6(3) | W(1)–O(31)–Si(32) | 153.7(5) |
| O(23)–W(1)–C(3) | 119.7(4) | W(2)–O(39)–Si(40) | 155.0(5) |
| O(31)–W(1)–C(3) | 92.5(4) | W(2)–O(47)–Si(48) | 160.8(5) |
| W(1)–W(2)–O(7) | 51.1(2) | W(1)–C(3)–W(2) | 85.9(5) |
| W(1)–W(2)–O(39) | 136.8(2) | W(1)–C(3)–C(4) | 142.0(8) |
| W(1)–W(2)–O(47) | 118.7(2) | W(2)–C(3)–C(4) | 132.0(8) |
| W(1)–W(2)–C(3) | 47.9(3) | | |

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[10] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; J. Wiley & Sons Publishers, 1981 and references therein.

[11] Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

**Table III. Fractional Coordinates and Isotropic Thermal Parameters for Compound 3**

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| W(1) | 7548(1) | 2336.4(5) | 8212(1) | 13 |
| W(2) | 5788(1) | 2629(1) | 8216(1) | 23 |
| O(3) | 7895(11) | 3060(8) | 7189(12) | 23 |
| Si(4) | 8080(5) | 3417(4) | 5987(5) | 22 |
| C(5) | 7668(19) | 2677(15) | 4745(22) | 37 |
| C(6) | 7326(21) | 4123(16) | 5532(23) | 41 |
| C(7) | 9476(16) | 3824(14) | 6325(20) | 29 |
| C(8) | 9670(19) | 4647(15) | 6744(23) | 41 |
| C(9) | 10090(18) | 3402(16) | 7281(22) | 38 |
| C(10) | 9791(22) | 3723(20) | 5185(27) | 62 |
| O(11) | 8251(10) | 2129(8) | 9755(11) | 22 |
| Si(12) | 8891(5) | 1754(4) | 10900(5) | 27 |
| C(13) | 8939(18) | 807(13) | 10462(20) | 38 |
| C(14) | 8267(22) | 1711(18) | 12140(21) | 50 |
| C(15) | 10169(16) | 2337(16) | 11395(19) | 36 |
| C(16) | 10186(18) | 3038(16) | 12188(21) | 38 |
| C(17) | 10848(18) | 1862(16) | 12278(22) | 38 |
| C(18) | 10622(16) | 2545(15) | 10446(20) | 31 |
| O(19) | 8050(10) | 1603(9) | 7507(12) | 27 |
| Si(20) | 8053(5) | 832(4) | 6739(6) | 25 |
| C(21) | 7669(19) | −1(14) | 7510(24) | 35 |
| C(22) | 7164(17) | 731(13) | 5230(21) | 32 |
| C(23) | 9319(16) | 804(13) | 6551(16) | 23 |
| C(24) | 10136(18) | 1062(18) | 7754(22) | 42 |
| C(25) | 9395(19) | 33(15) | 6200(23) | 37 |
| C(26) | 9528(19) | 1307(15) | 5622(24) | 39 |
| O(27) | 7147(9) | 3181(8) | 9126(11) | 17 |
| Si(28) | 7680(4) | 3956(4) | 10025(5) | 22 |
| C(29) | 7652(17) | 3737(14) | 11576(18) | 28 |
| C(30) | 8960(16) | 4197(14) | 9880(21) | 31 |
| C(31) | 7031(17) | 4720(15) | 9586(23) | 36 |
| C(32) | 5945(23) | 4535(17) | 9499(28) | 52 |
| C(33) | 7525(27) | 5409(17) | 10438(28) | 59 |
| C(34) | 7071(20) | 4963(15) | 8299(25) | 40 |
| O(35) | 5397(10) | 2678(9) | 9672(13) | 29 |
| Si(36) | 4808(5) | 2449(4) | 10666(6) | 26 |
| C(37) | 5489(18) | 1842(15) | 11782(22) | 34 |
| C(38) | 4710(18) | 3296(16) | 11455(22) | 37 |
| C(39) | 3501(7) | 1897(14) | 9880(22) | 32 |
| C(40) | 2900(17) | 2440(16) | 9125(24) | 39 |
| C(41) | 2971(19) | 1611(19) | 10815(25) | 50 |
| C(42) | 3581(19) | 1273(15) | 9104(25) | 43 |
| O(43) | 4564(10) | 2536(9) | 7113(12) | 28 |
| Si(44) | 3788(5) | 2574(4) | 5775(6) | 32 |
| C(45) | 2675(19) | 1857(18) | 5663(28) | 55 |
| C(46) | 4370(26) | 2343(19) | 4596(26) | 58 |
| C(47) | 3513(20) | 3504(18) | 5673(23) | 46 |
| C(48) | 4413(19) | 4105(17) | 5594(29) | 55 |
| C(49) | 3186(19) | 3757(16) | 6682(26) | 47 |
| C(50) | 2642(22) | 3551(19) | 4530(24) | 56 |
| C(51) | 6129(19) | 1804(19) | 7919(23) | 74 |
| C(52) | 5692(19) | 980(13) | 7647(23) | 32 |
| C(53) | 5078(22) | 669(17) | 6608(34) | 66 |
| C(54) | 5733(23) | 475(18) | 8639(34) | 54 |
| C(55) | 6195(28) | 720(20) | 9746(36) | 67 |

Atomic coordinates are given in Table III, and selected bond distances and angles are given in Table IV. A ball-and-stick drawing of the molecule is given in Figure 2.

The hydride ligand was not located crystallographically, but it is proposed to occupy a site on W(2) so that each metal is again (as in compound 2) in a pseudo trigonal bipyramidal environment. A comparison of the angles at W(2) in compound 2 and 3 with those for an idealized trigonal bipyramid is given in Table V. Again the two tungsten atoms are joined through the agency of a common equatorial and axial edge formed by the $\mu$-alkylidyne and $\mu$-siloxide ligands, respectively. The bridging hydrocarbyl ligand in 3 may be termed a 2-vinylpropenylidyne ligand, and the C–C distances associated with the vinylidene ($C{=}CH_2$) and vinyl ($CH{=}CH_2$) moieties are notably shorter, *ca.* 1.3 Å, relative to the C–C single bonds, *ca.* 1.5 Å.

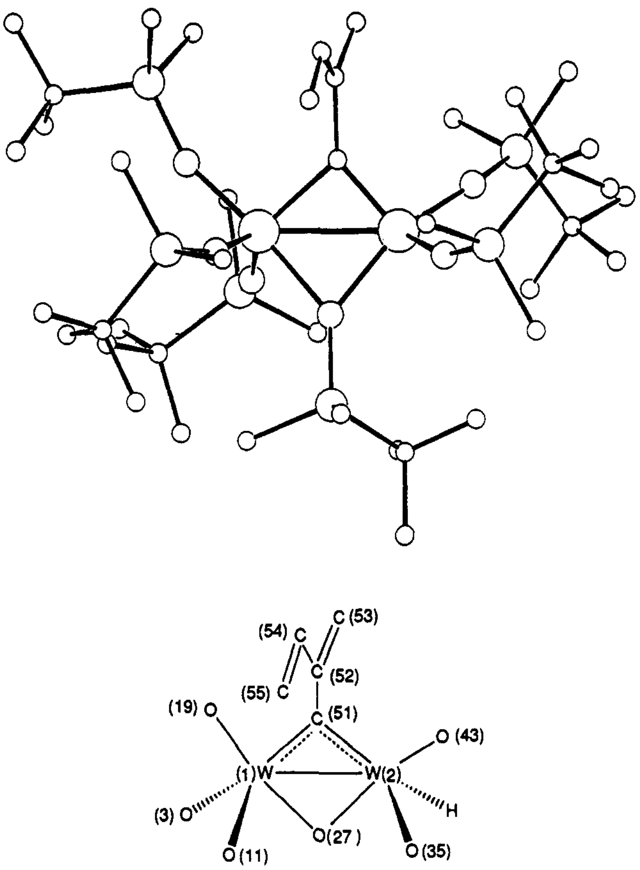


**Figure 2.** Top: Ball-and-stick representation for the molecular structure of $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3). Hydrogen atoms have been omitted for clarity. Bottom: Stick figure for the $HW_2(\mu\text{-}C_5)(O)_6$ core showing the atom label scheme and the proposed position of the hydride ligand.

**Table IV. Selected Bond Distances (Å) and Angles (deg) for $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3)**

| | | | |
|---|---|---|---|
| W(1)–W(2) | 2.561 | W(2)–O(43) | 1.84(1) |
| W(1)–O(11) | 1.89(1) | W(2)–C(51) | 1.72(4) |
| W(1)–O(19) | 1.90(2) | W(2)–C(52) | 1.52(4) |
| W(1)–O(27) | 2.11(1) | C(52)–C(53) | 1.33(4) |
| W(1)–C(51) | 2.01(2) | C(53)–C(54) | 1.50(4) |
| W(2)–O(27) | 2.01(1) | C(54)–C(55) | 1.31(5) |
| W(2)–O(35) | 1.94(1) | | |
| | | | |
| O(3)–W(1)–O(11) | 130.9(6) | O(35)–W(2)–C(51) | 114.3(9) |
| O(3)–W(1)–O(19) | 92.3(6) | O(43)–W(2)–C(51) | 101.2(10) |
| O(3)–W(1)–O(27) | 87.8(6) | W(1)–O(3)–Si(4) | 159.6(9) |
| O(3)–W(1)–C(51) | 120.9(9) | W(1)–O(11)–Si(12) | 164.9(10) |
| O(11)–W(1)–O(19) | 91.2(6) | W(1)–O(19)–Si(20) | 159.2(9) |
| O(11)–W(1)–O(27) | 84.1(6) | W(1)–O(27)–W(2) | 80.2(5) |
| O(11)–W(1)–C(51) | 106.7(8) | W(1)–O(27)–Si(28) | 139.8(8) |
| O(19)–W(1)–O(27) | 173.8(5) | W(2)–O(27)–Si(28) | 139.8(8) |
| O(19)–W(1)–C(51) | 99.2(2) | W(2)–O(35)–Si(36) | 159.7(10) |
| O(27)–W(1)–C(51) | 86.0(2) | W(2)–O(43)–Si(44) | 155.5(9) |
| O(27)–W(2)–O(35) | 88.2(5) | W(1)–C(51)–W(2) | 90.0(12) |
| O(27)–W(2)–O(43) | 154.1(7) | W(1)–C(51)–C(52) | 129.6(25) |
| O(27)–W(2)–C(51) | 97.5(9) | W(2)–C(51)–C(52) | 140.3(21) |
| O(35)–W(2)–O(43) | 100.0(6) | | |

**NMR Characterization of the Alkylidyne–Hydride Complexes. (a) Compound 2.** The $^{13}C$ NMR data for compound 2* [derived from $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ and labeled ethylene, $^{13}C_2H_4$] provide a complete characterization of the $\mu$-butenylidyne ligand, and a summary of the NMR data is given in Figure 3. In the unlabeled compound 2, three $^1H$ NMR signals are seen at $\delta$ 8.22, 5.64, and 1.88 in the integral ratio 1:1:3, respectively. The vinylic protons, $\delta$ 8.22 and 5.64, show a $J_{HH}$ coupling

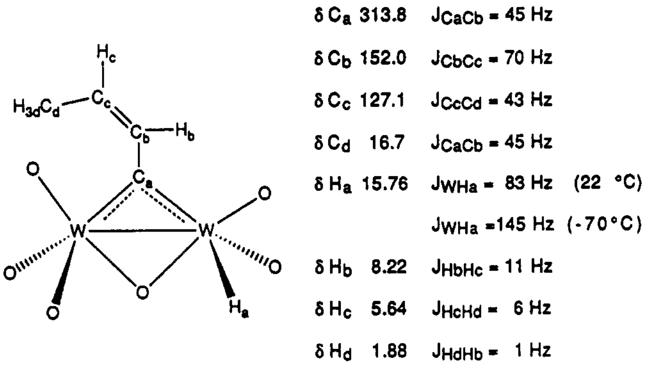


**Figure 3.** Atom label scheme for the 2-butenylidyne and hydride ligands in 2 with accompanying NMR data.

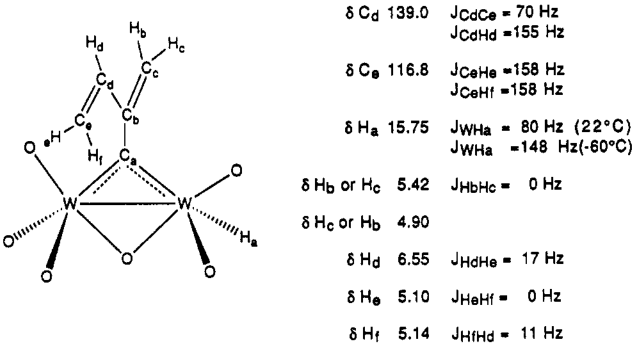


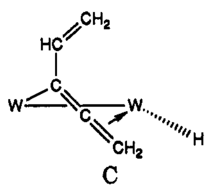
**Figure 4.** Atom label scheme for the 2-vinylpropenylidyne and hydride ligands in 3 with accompanying NMR data.

**Table V. Comparison Data for the Angles (deg) about W(2) in 2 and 3 and Angles Observed in an Ideal Trigonal Bipyramid (tbp)**

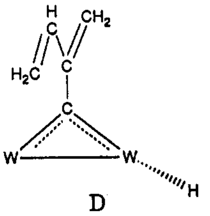
| data for 2 | | | data for 3 | |
|---|---|---|---|---|
| | angle obsd | angle for top | angle obsd | |
| C(3)-W(2)-O(47) | 115 | 120 | 114 | C(51)-W(2)-O(35) |
| C(3)-W(2)-O(39) | 100 | 90 | 101 | C(51)-W(2)-O(43) |
| C(3)-W(2)-O(7) | 97 | 90 | 96 | C(51)-W(2)-O(27) |
| O(39)-W(2)-O(47) | 99 | 90 | 100 | O(35)-W(2)-O(43) |
| O(39)-W(2)-O(7) | 156 | 180 | 154 | O(27)-W(2)-O(43) |

of 11 Hz suggestive of a *cis* placement about the double bond. Each of these protons is coupled to the $CH_3$ group, and from the magnitude of this coupling we can assign $H_b$ to δ 8.22 and $H_c$ to δ 5.64. The $C_b$–$C_c$ coupling constant of 70 Hz confirms the presence of a C–C double bond.[12] The alkylidyne carbon displays the characteristic downfield shift, δ 313.8, and shows a large coupling to $^{183}W$, $I = {}^1/_2$, 14.5% natural abundance, $J_{^{183}W-^{13}C} = 142$ Hz, with an integral satellite intensity of 22% suggestive of a bridging alkylidyne.[13]

**(b) Compound 3.** The NMR identification of the organometallic ligand in 3 was not as easily performed as that just described for 2 due to the inaccessibility of $^{13}C$-enriched allene from commercial sources. The $^{13}C$ data for 3 are limited to that of the original $^{13}C$ atoms in 2*. An atom label scheme for the 2-vinylpropenylidyne ligand and a summary of the NMR data are shown in Figure 4. The $^1H$ NMR spectrum of the organometallic ligand in 3 displays five $^1H$ signals of equal intensity in the vinyl region of the $^1H$ NMR spectrum, as shown in Figure 5. Homonuclear decoupling techniques established the assignment of a vinyl group displaying $^1H$ NMR signals at δ 6.55, 5.14, and 5.10. The signal at δ 6.55 can be assigned to $H_d$ of the vinyl ligand because it shows coupling to two protons. Furthermore, the signals at δ 5.14 and 5.10 can be assigned as $H_e$ and $H_f$, as the observed coupling to $H_d$ reflects the coupling constant values typically observed for *trans* H–H olefinic protons and *cis* H–H olefinic protons, respectively. The signal for the geminal protons of this vinyl group (δ 5.14 and 5.10) are broad (relative to the signal at δ 6.55), and no geminal H–H coupling is resolved. From the reaction of 1* with allene, the signals assigned to the vinyl protons in 3 were observed to be connected to the carbons originating from the alkyne ligand in 1*. These carbon signals did not show coupling to tungsten. The $^1H$ NMR signals at δ 5.41 and 4.90 are also broad singlets (relative to the signal at δ 6.55). Upon selective decoupling at δ 5.42 the signal at δ 4.90 sharpens. This observation and the chemical shift values indicate that these two signals arise from a methylidene group ($=CH_2$), where no geminal H–H coupling is resolved. These two signals were unaffected in reactions employing 1* and allene. It then follows that the protons responsible for these signals, assigned to be $H_b$ and $H_c$, are attached to a carbon atom in 3 derived from the added allene. Two organometallic moieties C and D, shown below, are reconcilable with the NMR data. The X-ray structure confirmed the 2-vinylpropenylidyne formulation for the ligand shown in D.



C



D

Although the hydride ligands of 2 and 3 were not located in the X-ray structure, the $^1H$ NMR data support the position shown in Figures 1 and 2. At −70 °C, the hydride signal for each compound shows a large W–H coupling constant of *ca.* 145 Hz that is typical of terminally bound hydride ligands.[14] At low temperature, six types of siloxide ligands containing diastereotopic methyl groups are observed. Thus, no siloxide ligand lies on a mirror plane of symmetry within the molecule in solution. These data are consistent with the observed solid-state structures of 2 and 3. The $^1H$ NMR spectra of 2 and 3 are temperature dependent. At 25 °C, only one type of siloxide ligand is observed and the hydride signal shows a greater integral intensity of tungsten satellites and a smaller W–H coupling constant (*ca.* 80 Hz) than was previously observed in the low-temperature spectrum. The smaller W–H coupling constant value suggests the hydride ligand is passed between the two W atoms and thus may be considered to take on a time-averaged bridge position. The fluxional process involves rapid bridging-to-terminal site exchange of both the hydride and siloxide ligands.

**Labeling Studies and Interpretations.** Insight into the reaction pathways leading to the formation of 2 and 3 may be gleaned from the following observations involving the use of isotopically-labeled compounds.

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(12) For C–C coupling constants in single-, double-, and triple-bonded compounds, see: Stothers, J. B. In *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; Table 9.3, p 327.

(13) Chisholm, M. H.; Heppert, J. A. *Adv. Organomet. Chem.* **1986**, *26*, 97.

(14) Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics* **1989**, *8*, 67.

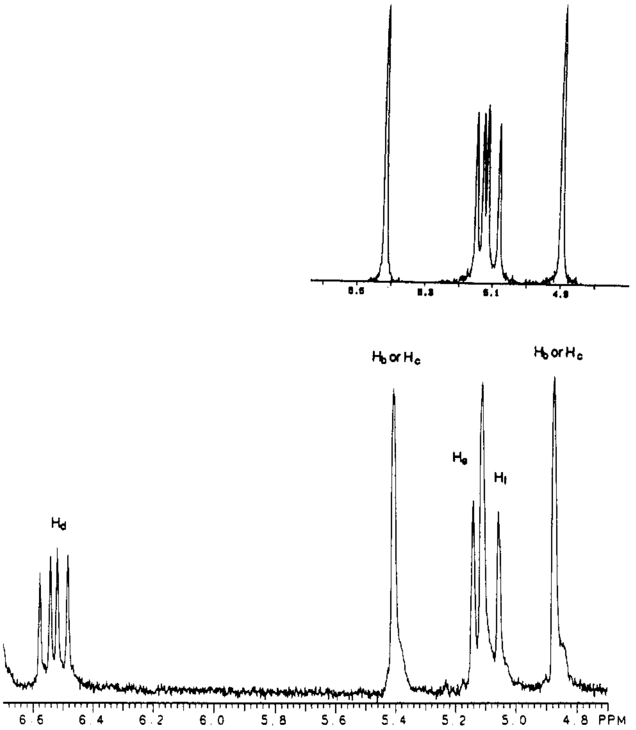
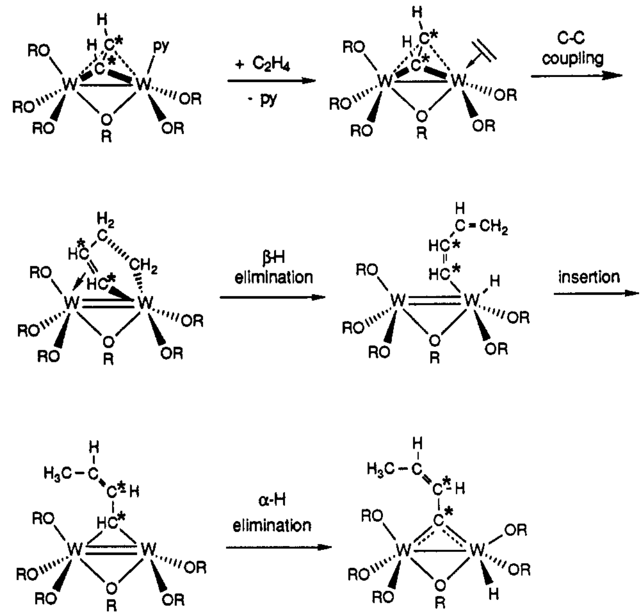


**Figure 5.** Bottom: 300-MHz $^1H$ NMR spectrum of the 2-vinylpropenylidyne ligand in 3 showing the signal assignment. Top: 500-MHz $^1H$ NMR spectrum that separates the signals corresponding to $H_e$ and $H_f$ that overlap in the 300-MHz spectrum.

**Scheme II. A Possible Reaction Pathway for 1 and Ethene That Could Lead to the Alkylidyne and Hydride Ligands in 2**[a]

$$W_2(OR)_6(py)(\mu\text{-}{}^{13}C_2H_2) + C_2H_4 \xrightarrow{-\ py} HW_2(OR)_6(\mu\text{-}{}^{13}C^{13}CH{=}CHCH_3)$$

$$W_2(OR)_6(py)(\mu\text{-}C_2D_2) + C_2H_4 \xrightarrow{-\ py} DW_2(OR)_6(\mu\text{-}CCD{=}CHCH_3)$$



[a] R′ = $SiMe_2Bu^t$.

(1) The reaction between $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}{}^{13}C_2H_2)$ and $C_2H_4$ yields the isotopomer of 2 $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}{}^{13}C^{13}CH{=}CHCH_3)$ while the reaction between $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2D_2)$ and $C_2H_4$ gives $DW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCD{=}CHCH_3)$. The stereospecific transfer of H/D atoms and the stereochemistry about the C–C double bond in 2 suggest the following process. Once coordinated to the metal, the ethene and the ethyne ligands couple to generate a metallacyclopentenyl ligand. This would parallel the chemistry of $W_2(OR)_6$ complexes in which the coupling of two alkyne ligands to give a $W_2(\mu\text{-}C_4R_4)$ center occurs.[15] From the metallacyclopentenyl complex, β-H elimination and reinsertion could generate an alkenyl ligand. Subsequent α-C–H bond activation would form the hydrido and alkylidyne ligands (see Scheme II). The reaction between $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}{}^{13}C_2H_2)$ and $^{13}C_2H_4$ was monitored by low-temperature $^{13}C$ NMR spectroscopy in hope of observing reaction intermediates. However, none were detected.

(2) The reaction between $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}{}^{13}C_2H_2)$ and $C_3H_4$ yields the isotopomer of 3, $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)({}^{13}CH{=}{}^{13}CH_2)]$, while the reaction between $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2D_2)$ and $C_3H_4$ forms $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CD{=}CDH)]$. The stereochemistry of the two deuterium atoms is exclusively *trans*. In the reaction to form 2 the $C_a$ carbon and the $C_b$ carbon atoms of the alkylidyne ligand originate from the alkyne carbon atoms in 1 whereas in the reaction to form 3 the alkylidyne $C_a$ and $C_b$ carbons originate from the added allene. Perhaps this difference arises from a favorable interaction of the exo π-system (originating from allene) on the metallacycle that would be formed by allene–alkyne coupling with the ditungsten center. Such an interaction could tether the original allene carbon atoms to the $W_2$ center prior to H atom transfer reactions. On the basis of the H/D transfer results, α-C–H elimination from a carbon atom originating from allene and reinsertion to a carbon atom originating from the ethyne ligand form the vinyl fragment and generate a μ-alkenyl ligand. Subsequent α-C–H bond activation would then lead to the alkylidene and hydride ligands of 3 (see Scheme III).

The observation of the *trans* stereochemistry of the vinyl group in the isotopomer of 3, $HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CD{=}CDH)]$, was unexpected. Vinyl and olefin ligands derived from an alkyne generally have *cis* stereochemistry. The first example of *trans* stereochemistry at a vinyl ligand was reported by Meutterties[16] in 1981 for a diiron complex. More recently, Adams[17] has reported that the addition of $H_2$ to $Re_2(CO)_8(\mu\text{-}MeC{=}CNMe_2)$ gives the product $Re_2(CO)_8(\textit{trans}\text{-}\mu\text{-}Me(H)CC(H)NMe_2)$ via the *trans* vinyl complex $(\mu\text{-}H)Re_2(CO)_8[\mu\text{-}Me(H)C{=}C(NMe_2)]$. The mechanism responsible for giving products of *trans* stereochemistry is not known. However, Adams has speculated[17] that an interaction involving the dinuclear center is involved.

**Steric Limitations of the Coupling Reaction.** The ene–yne coupling reaction involving 1 and olefins is limited to sterically unencumbered olefins. The coupling reaction is quite facile between 1 and ethene. However, propene does not react with 1 even when propene is added in a large excess. The increase in the steric bulk of propene compared to that of ethene presumably prevents coordination of propene to the dimetal center. The allene–

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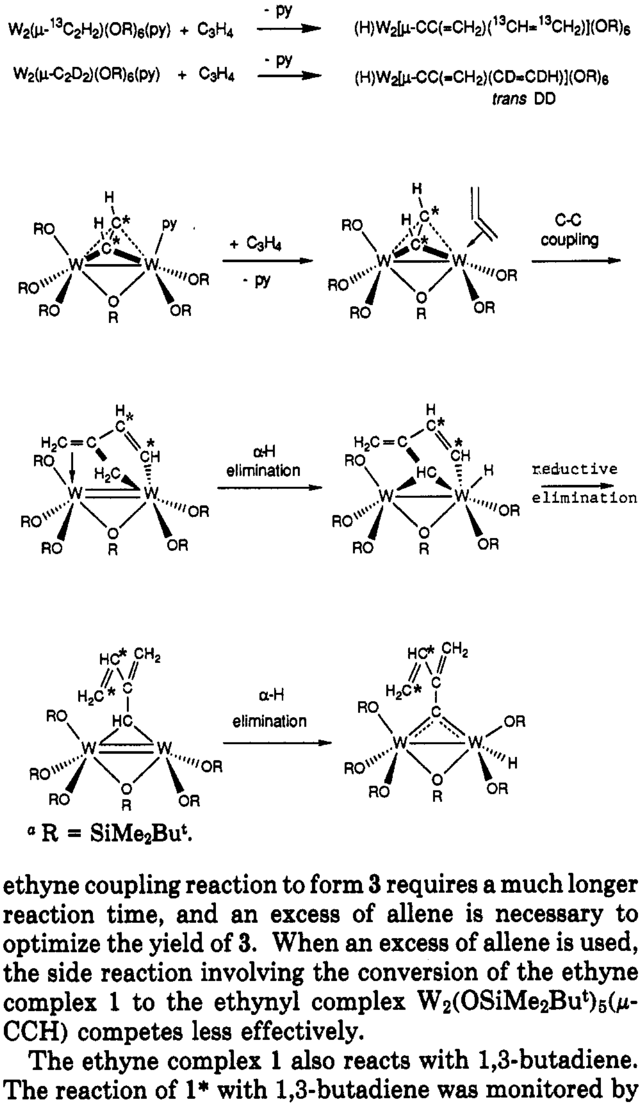
[15] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

[16] Burch, R. R.; Muetterties, E. L.; Teller, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 4257.

[17] Adams, R. D.; Chen, G.; Yin, J. *Organometallics* **1991**, *10*, 2087.

**Scheme III. A Possible Reaction Pathway for 1 and Allene That Could Lead to the Alkylidyne and Hydride Ligands in 3**[a]



[a] R = SiMe$_2$Bu$^t$.

ethyne coupling reaction to form 3 requires a much longer reaction time, and an excess of allene is necessary to optimize the yield of 3. When an excess of allene is used, the side reaction involving the conversion of the ethyne complex 1 to the ethynyl complex W$_2$(OSiMe$_2$Bu$^t$)$_5$($\mu$-CCH) competes less effectively.

The ethyne complex 1 also reacts with 1,3-butadiene. The reaction of 1* with 1,3-butadiene was monitored by $^{13}$C NMR spectroscopy. The data for the original ethyne carbon atoms indicate ene–yne coupling has occurred to give a vinyl group attached to a W$_2$ center (see the Experimental Section). The competing reaction of 1 to form W$_2$(OSiMe$_2$Bu$^t$)$_5$($\mu$-CCH) occurs significantly even when a large excess of butadiene is used in the reaction. Roughly 60% of the ethyne carbons account for the vinyl carbons of the ene–yne coupled product. The new compound could not be isolated in a pure form [free of W$_2$(OSiMe$_2$Bu$^t$)$_5$($\mu$-CCH)] and was not characterized further.

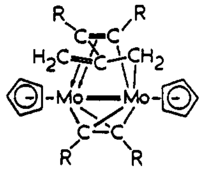
**Reaction of W$_2$(OSiMe$_2$Bu$^t$)$_6$(py)($\mu$-C$_2$H$_2$) with Ethyne.** The reaction between W$_2$(OSiMe$_2$Bu$^t$)$_6$(py)($\mu$-$^{13}$C$_2$H$_2$) (1*) and $^{13}$C-labeled ethyne was followed by low-temperature $^{13}$C NMR spectroscopy, and there was evidence for the formation of a W$_2$($\mu$-$^{13}$C$_4$H$_4$) metallacycle at low temperature (see Experimental Section). However, this compound was short-lived, and no metallacycle complex was isolated in preparative-scale reactions. With respect to the $\alpha$-C–H bond activation reactions occurring in the reactions of 1 with olefins, it is likely that the W$_2$($\mu$-C$_4$H$_4$) metallacycle forms a kinetically labile product through a similar route.

**Reactions of W$_2$(OBu$^t$)$_6$(py)($\mu$-C$_2$H$_2$) with Olefins.** It is of continuing interest to compare the reactivity of siloxide- vs alkoxide-supported tungsten complexes. Reactions of W$_2$(OBu$^t$)$_6$(py)($\mu$-$^{13}$C$_2$H$_2$) with ethene, allene, and butadiene were carried out in sealed NMR tubes in toluene-$d_8$ and monitored by variable-temperature $^{13}$C NMR spectroscopy. In all cases, no reaction of the ethyne ligand with the olefin occurred. Only the $^{13}$C signals corresponding to the compounds in the equilibrium involving the methylidyne and the bridging ethyne complex were observed.[6]

**Concluding Remarks.** Adams[18] has reported an example of carbon–carbon bond formation between an alkyne ligand and allene in the synthesis of a 1-carbomethoxy-2-allylvinyl ligand from the reaction shown in eq 3. Knox[19] has reported an example of the coupling of allene with an alkyne in the reaction shown in eq 4. The structure of the product of eq 4 is represented by E, where R = CO$_2$Me. In these reactions and in the W$_2$($\mu$-C$_4$H$_4$) metallacycle complexes supported by alkoxide ligands discussed previously,[15] the coupled product has not undergone further reactivity via carbon–hydrogen bond activation.

$$\begin{aligned}&Os_4(CO)_{11}(\mu_4\text{-}HC{\equiv}CCO_2Me)(\mu_4\text{-}S) + \\ &\quad 2\,CH_2{=}C{=}CH_2 \rightarrow Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-} \\ &\qquad (CH_2)_2CC(H)C(CO_2Me)](\mu_3S) \quad (3)\end{aligned}$$

$$\begin{aligned}&Mo_2(\mu\text{-}\eta^3\text{-}CH_2CCH_2)(CO)_4Cp_2 + \\ &\quad MeO_2CC{\equiv}CCO_2Me\ (xs) \rightarrow Mo_2[\mu\text{-}C_2(CO_2Me)_2][\mu\text{-} \\ &\qquad C(CH_2)_2C(CO_2Me)C(CO_2Me)]Cp_2 + 4CO \quad (4)\end{aligned}$$



E

The facile formation of the alkylidene ligands in 2 and 3 by ene–yne coupling followed by C–H bond activation represents a new route to alkylidyne complexes. The most common synthetic routes to alkylidyne complexes involve (i) reactions of carbonyl ligands, (ii) $\alpha$-hydrogen atom transfer from alkyl and/or alkylidene ligands, and (iii) C–C scission of coordinated alkynes.[20]

## Experimental Section

**General Methods and Spectroscopic Methods.** Ethene (Matheson), butadiene (Matheson), allene (Air Products), and isotopically-enriched ethene ($^{13}$C$_2$H$_4$:$^{13}$C, 99%; Cambridge Isotope Laboratories) were used without further purification. A published method was used in the preparation of W$_2$(OSiMe$_2$Bu$^t$)$_6$(py)($\mu$-C$_2$H$_2$)[7] and W$_2$(OBu$^t$)$_6$(py)($\mu$-$^{13}$C$_2$H$_2$).[6]

**Preparation of H$_a$W$_2$(OSiMe$_2$Bu$^t$)$_6$($\mu$-C$_a$C$_b$H$_b$=C$_c$H$_c$C$_d$H$_{3d}$) (2).** A 30-mL Schlenk flask charged with the brown-black crystalline solid W$_2$(OSiMe$_2$Bu$^t$)$_6$(py)($\mu$-C$_2$H$_2$) [1 (330 mg, 0.26 mmol)] and a stir bar was placed in a −72 °C CO$_2$(s)/ethanol cold bath. Toluene (10 mL) was then added via cannula. The resulting heterogeneous mixture was frozen at −196 °C, the flask evacuated, and C$_2$H$_4$ (1.31 mmol) added via a calibrated vacuum manifold.

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(18) Adams, R. D.; Wang, S. *Organometallics* **1987**, *6*, 45.

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The flask was immediately placed in a −72 °C cold bath for 30 min with stirring. The flask was then placed in a −20 °C cold bath and allowed to warm to 10 °C over a 2-h period. During this time, the mixture became homogeneous and the dark brown solution gained a blue tint. The solvent volume was reduced by half *in vacuo*, and the flask was placed at −20 °C. Blue-black crystals of **2** formed overnight and were isolated by removing the supernatant liquid to a separate flask. Combined crystallizations gave **2** in a 45% yield (142 mg, 0.12 mmol). Anal. Calcd for $C_{40}H_{97}O_6Si_6W_2$: C, 39.69; H, 8.07. Found: C, 39.88; H, 8.02. $^{1}$H NMR (benzene-$d_6$, 22 °C, 300 MHz): $\delta$ 15.76 (s, $H_a$, $J_{WH} = 83$ Hz with $I = 32\%$, 1H); 8.22 (dq, $H_b$, $^{3}J_{HbHc} = 11$ Hz, $^{4}J_{Hbhd} = 1$ Hz, 1H); 5.64 (dq, $H_c$, $^{3}J_{HcHb} = 11$ Hz, $^{3}J_{HcHd} = 6$ Hz, 1H); 1.88 (dd, $H_d$, $^{3}J_{HdHc} = 6$ Hz, $^{4}J_{HdHb} = 1$ Hz, 3H); 1.10 (s, br, $CMe_3$, 54H); 0.34 (s, br, $Me_2$, 36H). $^{1}$H NMR (toluene-$d_8$, −70 °C, 360 MHz): $\delta$ 15.56 (s, $H_a$, $J_{WH} = 145$ Hz with $I = 22\%$, 1H); 8.22 (dq, $H_b$, 1H); 5.64 (dq, $H_c$, 1H); 1.88 (dd, $H_d$, 3H); 1.35, 1.24, 1.14, 1.12, 1.06, 1.02 (s, $CMe_3$, 9H each); 0.70, 0.66, 0.48, 0.47, 0.32, 0.30, 0.29, 0.26, 0.21, 0.17, 0.16 (s, $Me_2$, with intensity ratio 1:1:1:1:1:1:1:2:1:1, respectively; the signal of intensity 2 is apparently due to accidental degeneracy). $^{13}$C($^{1}$H) NMR (benzene-$d_6$, 22 °C, 75 MHz): $\delta$ ($\mu$-$^{13}C_a$ $^{13}C_bH_b{=}^{13}C_cH_c{}^{13}C_dH_{3d}$) ligand only; 313.8 (d, $C_a$, $J_{CaCb} = 45$ Hz, $J_{WC} = 142$ Hz with $I = 22\%$); 152.0 (dd, $C_b$, $J_{CbCc} = 70$ Hz, $J_{Cbca} = 45$ Hz); 127.1 (dd, $C_c$, $J_{CcCb} = 70$ Hz, $J_{CcCd} = 43$ Hz); 16.7 (d, Cd, $J_{CdCe} = 43$ Hz). Chemical shifts and coupling constants are invariant with temperature (22–70 °C). $^{13}$C NMR (benzene-$d_6$, 22 °C, 75 MHz): ($\mu$-$^{13}C_a{}^{13}C_bH_b{=}^{13}C_cH_c{}^{13}C_dH_{3d}$) ligand only: $\delta$ 313.8 (dd, $C_a$, $J_{CaCb} = 45$ Hz, $^{2}J_{CaHb} = 10$ Hz); 152.0 (dddd, $C_b$, $J_{CbHb} = 154$ Hz, $J_{CbCc} = 70$ Hz, $J_{CbCa} = 45$ Hz, $^{2}J_{CbHc} = 4$ Hz); 127.1 (dddq, $C_c$, $J_{CcHc} = 157$ Hz, $J_{CcCb} = 70$ Hz, $J_{CcCd} = 43$ Hz, $^{2}J_{CcHd} = 7$ Hz); 16.7 (dq of virtual triplets, $C_d$, $J_{CdHd} = 126$ Hz, $J_{CdCc} = 43$ Hz, $^{2}J_{CdHb} \approx {}^{4}J_{CdHa}$ (*trans*) $\approx$ 11 Hz, giving rise to second-order fine coupling which appears as virtual triplets).

**Preparation of $H_aW_2(OSiMe_2Bu^t)_6[\mu\text{-}C_aC_b({=}C_cH_bH_c)(C_dH_d{=}C_eH_eH_f)]$ (3).** A 30-mL Schlenk flask charged with the brown-black crystalline solid $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2H_2)$ [**1** (298 mg, 0.24 mmol)] and a stir bar was placed in a −72 °C $CO_2$(s)/ethanol cold bath. Toluene (15 mL) was then added via cannula. The resulting heterogeneous mixture was frozen at −196 °C, the flask evacuated, and $C_3H_4$ (1.20 mmol) added via a calibrated vacuum manifold. The flask was immediately placed in a −72 °C cold bath with stirring. The cold bath was allowed to warm to −20 °C over a 4-h period, during which time the solution gained a red tint. The flask was then placed in a freezer kept at −20 °C for 12 h (without stirring), after which time the solution color had turned deep red. The solution volume was reduced *in vacuo* to 3 mL. The flask was stored at −20 °C, and after 5 days feather-like crystals of **3** had formed. The crystals were deeply colored (black) and were isolated by transferring the supernatant liquid to a separate flask (78 mg, 0.064 mmol, 27%). Anal. Calcd for $C_{41}H_{97}O_6Si_6W_2$: C, 40.28; H, 8.00. Found: C, 39.41; H, 7.90. $^{1}$H NMR (benzene-$d_6$, 23 °C, 300 MHz): $\delta$ 15.75 (s, $H_a$, $J_{WH} = 80$ Hz with $I = 24\%$, 1H); 6.55 (dd, $H_d$, $J_{HdHe} = 17$ Hz, $J_{HdHf} = 11$ Hz, 1H); 5.42 (s, br, $H_b$ or $H_c$, 1H); 5.14 (d, $H_f$, $J_{HfHd} = 11$ Hz, 1H); 5.10 (d, $H_e$, $J_{HeHd} = 17$ Hz, 1H); 4.90 (s, br, $H_b$ or $H_c$, 1H); 1.12 (s, $CMe_3$, 54H); 0.35 (s, $Me_2$, 36H). $^{1}$H NMR (toluene-$d_8$, −60 °C, 300 MHz): $\delta$ 15.46 (s, $H_a$, $J_{WH} = 148$ Hz with $I = 16\%$, 1H); 6.58 (dd, $H_d$, 1H); 5.38 (s, $H_b$ or $H_c$, 1H); 5.12 (d, $H_f$, 1H); 4.98 (s, $H_b$ or $H_c$, 1H); 4.93 (d, $H_e$, 1H); 1.32, 1.24, 1.19, 1.12, 1.06 (s, $CMe_3$ with intensity ratio 1:1:1:1:2, respectively; the signal of intensity 2 is apparently due to accidental degeneracy); 0.67, 0.56, 0.51, 0.49, 0.42, 0.32, 0.31, 0.28, 0.21, 0.19, 0.18 (s, $Me_2$, with intensity ratio 1:1:1:1:1:1:1:1:1:2:1, respectively; the signal of intensity 2 is apparently due to accidental degeneracy). $^{13}$C{$^{1}$H} NMR (benzene-$d_6$, 22 °C, 75 MHz): $\delta$ $^{13}$C atoms of the [$\mu$-$C_aC_b({=}C_cH_bH_c)(^{13}C_dH_d{=}^{13}C_eH_eH_f)$] ligand only; 139.0 (d, $C_d$, $J_{CdCe} = 70$ Hz); 116.8 (d, $C_e$, $J_{CeCd} = 70$ Hz). $^{13}$C NMR (benzene-$d_6$, 22 °C, 75 MHz): $^{13}$C atoms of the [$\mu$-$C_aC_b({=}C_cH_bH_c)(^{13}C_dH_d{=}^{13}C_eH_eH_f)$] ligand only; $\delta$ 139.0 (dd, $C_d$, $J_{CdHd} = 155$ Hz, $J_{CdCe} = 70$ Hz); 116.8 (overlapping ddd with appearance of a 1:2:1 td, $C_e$, $J_{CeHe} = J_{CeHf} = 158$ Hz, $J_{CeCd} = 70$ Hz).

**NMR Studies of the Reaction of $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ (1*) with Butadiene.** The black crystalline solid **1*** (25 mg, 0.020 mmol) was weighed into an extended 5-mm NMR tube equipped with a Kontes vacuum line adapter. The bottom third of the NMR tube was placed at −72 °C, and toluene-$d_8$ (0.5 mL) also at −72 °C was added via a 1-mL syringe. The solution was frozen at −196 °C, the NMR tube evacuated, and butadiene (0.200 mmol) added via a calibrated vacuum manifold. The NMR tube was flame sealed and placed in a −20 °C cold bath. The NMR tube was shaken periodically. After 7 h at −20 °C, a $^{13}$C NMR spectrum of the reaction was taken at −20 °C. In addition to **1*** a new product was observed having the following NMR data. $^{13}$C{$^{1}$H} NMR (toluene-$d_8$, −20 °C, 75 MHz): $\delta$ 165.9 (d, $J_{CC} = 31$ Hz, $J_{WC} = 123.8$ Hz, $J_{WC} = 16$ Hz); 103.2 (d, $J_{CC} = 31$ Hz, $J_{WC} = 33$ Hz). $^{13}$C NMR (toluene-$d_8$, −20 °C, 75 MHz): $\delta$ 165.9 (ddd, $J_{CH} = 150$ Hz, $J_{CC} = 31$ Hz, $^{2}J_{CH} = 5$H); 103.2 (dd, $J_{CH} = 144$ Hz, $J_{CC} = 31$ Hz). After 10 d at −20 °C, the ethynyl compound $W_2(OSiMe_2Bu^t)_5(\mu\text{-}CCH)$ was observed by $^{13}$C NMR spectroscopy in addition to the signals for **1*** and the new coupled product. The NMR tube was placed at −4 °C. After 2 days only the ethynyl compound and the new product were detected by $^{13}$C NMR spectroscopy. The ratio of the ethynyl compound to the new product was 2:1. The new compound could not be isolated in preparative-scale reactions (see below) and was not characterized further.

**Reaction of $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}C_2H_2)$ (1) with Butadiene.** A 30-mL Schlenk flask charged with the brown-black crystalline solid **1** (160 mg, 0.127 mmol) was placed in a −72 °C $CO_2$(s)/ethanol cold bath. Toluene (5 mL) and hexane (2 mL) were added via cannula. The resulting heterogeneous mixture was frozen at −196 °C, the flask evacuated, and butadiene (0.635 mmol) added via a calibrated vacuum manifold. The flask was immediately placed at −20 °C with stirring. Over a 5-h period, the solution color changed from dark brown to green-brown. The solution was then placed at −15 °C without stirring for 18 h. The volatile components were removed *in vacuo*, and the resulting oily solid was redissolved in cold (−20 °C) pentane (3 mL). The flask was stored at −15 °C, and after 14 days a small amount (*ca.* 20 mg) of a crystalline solid had precipitated. The $^{1}$H NMR spectrum of this solid showed that the ethynyl compound $W_2(OSiMe_2Bu^t)_5(\mu\text{-}CCH)$ accounted for roughly 30% of the reaction product. Further crystallizations yielded only a small amount (*ca.* 20 mg) of $W_2(OSiMe_2Bu^t)_5(\mu\text{-}CCH)$. No further analytical characterization could be performed due to difficulties in isolating the new product free of $W_2(OSiMe_2Bu^t)_5(\mu\text{-}CCH)$.

**NMR Studies of the Reactions of $W_2(OBu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ with Ethene, Allene, and Butadiene.** The green crystalline compound $W_2(OBu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ (25 mg, 0.027 mmol) was weighed into an extended NMR tube equipped with a Kontes vacuum line adapter. The bottom third of the NMR tube was placed in a −72 °C bath, and toluene-$d_8$ (0.5 mL) also at −72 °C was added via a 1-mL syringe. The NMR sample was frozen at −196 °C, the NMR tube evacuated, and 9 equiv of the gas (0.240 mmol) added via a calibrated vacuum manifold. The NMR tube was flame sealed and placed in a −20 °C cold bath. The reactions were monitored by $^{13}$C NMR spectroscopy after 7 h and 2 d of reaction time at −20 °C. In all cases, only the $^{13}$C NMR signals for $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ and $(Bu^tO)_3W{\equiv}CH$ were observed. The samples were warmed to −4 °C for 1 d, with no reaction detected by $^{13}$C NMR spectroscopy. Above this temperature the $W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)$ compound began to decompose.

**NMR Study of the Reaction of $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ with $^{13}C_2H_2$.** The brown-black crystalline compound $W_2(OSiMe_2Bu^t)_6(py)(\mu\text{-}^{13}C_2H_2)$ (25 mg, 0.020 mmol) was weighed into an extended NMR tube equipped with a Kontes vacuum line adapter. The bottom third of the NMR tube was placed in a −72 °C bath, and toluene-$d_8$ (0.5 mL) also at −72 °C was added via a 1-mL syringe. The NMR sample was frozen at −196 °C, the NMR tube evacuated, and 1.1 equiv of $^{13}C_2H_2$ (0.21 mmol) added via a calibrated vacuum manifold. The NMR tube was flame sealed and placed in a −72 °C cold bath. The reaction was monitored by low-temperature $^{13}$C NMR spectroscopy. After 1

**Table VI. Summary of Crystal Data**[a]

| | | |
|---|---|---|
| formula | $C_{40}H_{96}O_6Si_6W_2$ | $C_{41}H_{96}O_6Si_6W_2$ |
| color of cryst | blue-green | black |
| cryst dimensions (mm) | 0.16 × 0.16 × 0.24 | 0.12 × 0.15 × 0.20 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| cell dimensions | | |
| temp (°C) | −172 | −172 |
| *a* (Å) | 14.037(2) | 14.211(8) |
| *b* (Å) | 18.453(3) | 18.296(11) |
| *c* (Å) | 11.681(2) | 11.724(6) |
| $\alpha$ (deg) | 91.20(1) | 92.24(2) |
| $\beta$ (deg) | 106.63(1) | 105.97(2) |
| $\gamma$ (deg) | 100.35(1) | 99.98(2) |
| *Z* (molecules/cell) | 2 | 2 |
| volume (Å$^3$) | 2842.75 | 2878.62 |
| calcd density (gm/cm$^3$) | 1.412 | 1.409 |
| wavelength (Å) | 0.71069 | 0.71069 |
| mol wt | 1209.41 | 1221.42 |
| linear absorption coeff (cm$^{-1}$) | 42.878 | 42.366 |
| detector to sample distance (cm) | 22.5 | 22.5 |
| sample to source distance (cm) | 23.5 | 23.5 |
| av Ω scan width at half-height | 0.25 | 0.25 |
| scan speed (deg/min) | 6.0 | 8.0 |
| scan width (deg + dispersion) | 2.0 | 2.0 |
| individual background (s) | 6 | 4 |
| aperture size (mm) | 3.0 × 4.0 | 3.0 × 4.0 |
| 2$\theta$ range (deg) | 6–45 | 6–45 |
| total no. of reflections collected | 8821 | 10 315 |
| no. of unique intensities | 7482 | 7520 |
| no. with $F_\sigma$ 0.0 | 7028 | 6961 |
| no. with $F_\sigma$ 3.0 (*F*) | 6625 | |
| no. with $F_\sigma$ 2.33 (*F*) | | 5290 |
| *R*(*F*) | 0.0535 | 0.0826 |
| $R_w(F)$ | 0.0527 | 0.0847 |
| goodness of fit for the last cycle | 1.778 | 1.890 |
| max $\Delta/\sigma$ for last cycle | 0.001 | 0.34 |

[a] **2** = $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CCH{=}CHMe)$; **3** = $HW_2(OSiMe_2Bu^t)_6(\mu\text{-}CC({=}CH_2)(CH{=}CH_2)$.

h of reaction time at −40 °C, signals corresponding to a $W_2(\mu\text{-}C_4H_4)$ metallacycle were observed. During the next 30 min of reaction time the intensity of the signals had decreased significantly. $^{13}C\{^1H\}$ NMR (toluene-$d_8$, −40 °C, 75 MHz): $\delta$ 168.9 (dd, $J_{CC}$ = 21 Hz, $J_{CC}$ = 18 Hz); 121.5 (dd, $J_{CC}$ = 25 Hz, $J_{CC}$ = 17 Hz). $^{13}C$ NMR (toluene-$d_8$, −40 °C, 75 MHz): 168.9 (ddd, $J_{CH}$ = 156 Hz, $J_{CC}$ = 21 Hz, $J_{CC}$ = 18); 121.5 (ddd, $J_{CH}$ = 158 Hz, $J_{CC}$ = 25 Hz, $J_{CC}$ = 17 Hz).

**Crystallographic Studies.** General operating procedures and listings of programs have been given previously.[21] A summary of crystal data is given in Table VI.

**$HW_2(\mu\text{-}CCH{=}CHMe)(OSiMe_2Bu^t)_6$ (2).** A crystal of suitable size although somewhat irregular in shape was obtained by cleaving a large piece of the sample in a nitrogen atmosphere glove bag. The crystal was mounted using silicone grease and was transferred to a goniostat, where it was cooled to −172 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry among the observed intensities. An initial choice of space group $P\bar{1}$ was later proven correct by the successful solution of the structure. Following complete intensity data collection and correction for absorption, data processing gave a residual of 0.027 for the averaging of 1239 unique intensities which had been observed more than once. Four standards measured every 400 data showed no significant trends.

The structure was solved by initially locating the tungsten positions from a Patterson map using the SHELXS-86 package. The remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculations. Hydrogen atoms bonded to carbon were included in fixed calculated positions, with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded. The hydride ligand could not be located, and no further attempt was made to include it in the refinement. It is included in the formula and the density calculation since its presence was established by spectroscopy and is required to satisfy the overall requirements of valency and diamagnetism of the compound.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to a final *R*(*F*) = 0.054. The largest peaks in the final difference map were tungsten residuals of 1.5–3.0 e/Å$^3$.

**$HW_2(OSiMe_2Bu^t)_6[\mu\text{-}CC({=}CH_2)(CH{=}CH_2)]$ (3).** The sample consisted of clumps of black material, most of which was not crystalline. After numerous attempts a small fragment was isolated which was deemed suitable. It was mounted on a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −172 °C for characterization and data collection. Ω scans indicated a shoulder present, and the scans were not isotropic. In spite of the difficulties, data were collected.

A search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric space group $P\bar{1}$.

Data were collected using a continuous $\theta$–2$\theta$ scan with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects, and equivalent data were averaged.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced as fixed atom contributors.

The anisotropic thermal parameters indicate that an absorption correction is needed. Unfortunately, the irregular shape of the sample and the presence of an apparent fragment did not allow a meaningful correction. The rather poor quality of the data is indicated in the large esd's.

A final difference Fourier indicated several peaks of intensity 1–7 e/Å$^3$, primarily in the vicinity of the tungsten atoms.

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**Supplementary Material Available:** Tables giving anisotropic thermal parameters and complete listings of bond distances and bond angles and figures showing VERSORT and stereodrawings for compounds 2 and 3 (21 pages). Ordering information is given on any current masthead page.

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