computers of the Australian National University Supercomputing Facility.

Supplementary Material Available: Table of Cartesian coordinates of the 14 isomeric structures **1a**, **3a**, **1b–6b**, and **1c–6c** optimized at the 6-31G* level (7 pages). This supplementary material is provided in the archival edition of the journal, which is available in many libraries. Alternatively, ordering information is given on any current masthead page.

Formation of Tungsten–Carbyne and Tungsten–Oxo–Allyl Complexes on Reaction of WCl₂(PR₃)₄ with Unsaturated Silanes

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Reactions of the tungsten(II) complex WCl₂(PMePh₂)₄ (**1a**) show a high propensity to form metal–ligand multiple bonds, and this provides the driving force for a number of interesting transformations. Alcohols are deoxygenated to hydrocarbons,[2] epoxides to alkenes,[3] and CO₂ to CO,[4] all with the production of tungsten(IV) oxo compounds; imido, sulfido,[4] phosphinidine,[5] and alkylidene complexes[6] are formed in related reactions. This report describes reaction of **1a** and WCl₂(PMe₃)₄ (**1b**) with (allyloxy)-trimethylsilane to give rare examples of oxo-allyl complexes[7] and remarkable reactions of **1b** with vinyl- and allylsilane reagents which rearrange to give tungsten carbyne compounds.[8]

Reactions of **1** require significant initial binding of the substrate to the tungsten center. This is a primary reason why deoxygenation of simple alcohols by **1a** is slow and why deoxygenation of ethers such as Et₂O or MeOSiMe₃, while thermodynamically favorable,[9] does not occur. Addition of a potential tungsten binding site to the substrate, however, can circumvent this kinetic barrier.[10] For instance, allyl alcohol and 1-buten-4-ol are rapidly deoxygenated by **1a** to give alkenes and W(O)Cl₂(PMePh₂)₃ because the alkene function acts as a "tether" to bring the oxygen close to the metal.[2]

Use of a "tether" allows extension of this chemistry to silyl ethers. For example, 0.45 mL of (allyloxy)trimethylsilane reacts

Figure 1. ORTEP drawings of W(O)(η³-C₃H₅)Cl(PMe₃)₂ (**2b**; top) and W(≡CCH₃)(PMe₃)₄Cl (**3**; bottom) with 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) for **2b**: W–Cl1 2.639 (9), W–P1 2.483 (9), W–P2 2.491 (9), W–C1 2.29 (4), W–C2 2.25 (4), W–C3 2.31 (3), O1–W–P1 93.5 (8), O1–W–P2 90.8 (8), O1–W–Cl1 161.8 (9), O1–W–C1 114.4 (13), O1–W–C2 102.6 (14), O1–W–C3 111.0 (11), P1–W–P2 102.4 (3), C1–C2–C3 127 (4). For **3**: W–P 2.464 (2), W–Cl 2.589 (15), W–C3 1.76 (4), P–W–Cl 80.75 (9), P–W–C3 99.25 (9), W–C3–C4 176 (3), P–W–P′ 161.51 (18), P–W–P″ 91.48 (9).

with 0.50 g of **1b** in 50 mL of toluene to give an orange solution after heating of the solution at 65 °C overnight. Subsequent workup[11] gives the tungsten-oxo-allyl complex **2b** in 74% yield. **1a** also reacts with (allyloxy)trimethylsilane to give a tungsten-oxo-allyl complex W(O)(η³-C₃H₅)(PMePh₂)₂Cl (**2a**) (eq 1). The

$$\text{WCl}_2\text{L}_4 + \text{Me}_3\text{SiO}\diagup\diagup \longrightarrow \underset{\substack{\text{L} \\ \text{L}' \\ \textbf{2a,b}}}{\overset{\text{O}}{\underset{\text{Cl}}{\|}}} \text{W} -\text{>>} + \text{Me}_3\text{SiCl} \qquad (1)$$

1a,b

tungsten abstracts the oxygen atom and retains the organic fragment; the silicon removes a chloride. The formation of the strong W≡O multiple bond and the η³-allyl provide the driving force for cleavage of the Si–O bond.[12] The X-ray crystal structure of the PMe₃ derivative **2b** (Figure 1)[13] shows a pseudooctahedral complex (the η³-allyl ligand occupying two sites), with a short tungsten-oxo distance of 1.651 (17) Å.[14] The allyl ligand lies cis to the oxo, as expected for a ligand with π-acceptor orbitals,[4] and the W–C distances are typical for tungsten η³-allyl compounds.[15] NMR data for **2a** and **2b** are consistent with similar

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(7) To our knowledge, these are the first examples of oxo-(π-allyl) complexes; for related species see, for instance: Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617–623. Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391–393; Morrow, J. R.; Tonker, T. L.; Templeton, J. R.; Kenan, W. R., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5004–5005.

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(9) **1a** will remove an oxygen atom from CO₂, which requires 127 kcal/mol.[6] ΔH° values for Et₂O → C₄H₁₀ + O and for EtOSiMe₃ → EtSiMe₃ + O are 90 and 120 kcal/mol, respectively. Based on data from the following: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 371–391.

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(11) The solution was reduced to 7 mL, cooled at −76 °C, filtered, and dried in vacuo to give 0.15 g of orange **2b**; a second crop from toluene/pentane gave an overall yield of 74%. Anal. Calcd for WClP₂OC₉H₂₃: O, 3.73; C, 25.23; H, 5.41; Found: O, 3.58; C, 25.68; H, 5.43.

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(13) Crystal data (CAD4) for **2b**: *P*2₁2₁2₁ (orthorhombic setting), *a* = 8.661 (1) Å, *b* = 10.834 (1) Å, *c* = 16.890 (2) Å, *Z* = 4, *V* = 1584.9 (6) Å³, μ = 77.93 cm⁻¹; 77 parameters were refined using 992 unique data (*I* > 2σ_I) to *R* = 6.6%, *R*_w = 7.8%, GOF = 1.420. For **3**: *I*42*m* (tetragonal setting), *a* = 9.6854 (13) Å, *c* = 12.5307 (14) Å, *Z* = 2, *V* = 1175.5 (4) Å³, μ = 53.97 cm⁻¹; 38 parameters were refined using 427 unique data (*I* > 3σ_I) to *R* = 3.8%, *R*_w = 5.1%, GOF = 1.288; the CCH₃ and Cl are disordered because of the *S*₄ site symmetry.
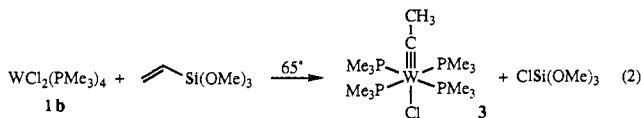
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structures in solution.[16] The analogous 2-methylallyl complex is formed slowly from **1a** and $CH_2{=}CMeCH_2OSiMe_3$.
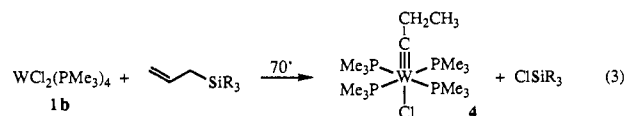
Since $CH_2{=}CRCH_2OSiMe_3$ delivers an allyoxy fragment to tungsten, we investigated whether $CH_2{=}CHSi(OMe)_3$ would transfer a methoxy group, with the vinyl acting as the tether. A clean reaction is observed with **1b**, but the product is the carbyne complex $W({\equiv}CCH_3)(PMe_3)_4Cl$ (**3**) (eq 2).[17] Thus vinyl is transferred instead of methoxy, with rearrangement of $CH_2{=}CH-$ to $CH_3C{\equiv}$. The carbyne complex **3** has been characterized by NMR[16] and an X-ray crystal structure,[13] which is quite

$$WCl_2(PMe_3)_4 + \underset{\textbf{1b}}{\diagup\!\!\!\diagdown Si(OMe)_3} \xrightarrow{65^\circ} \underset{\textbf{3}}{Me_3P\!\!-\!\!\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{\underset{|}{\overset{C}{\|\|}}}}{W}}\!\!\overset{PMe_3}{\underset{PMe_3}{\diagdown}}} + ClSi(OMe)_3 \quad (2)$$

similar to the structures of $W({\equiv}CCH_3)(PMe_3)_4Me$ and $W({\equiv}CH)(PMe_3)_4Cl$.[18] An intermediate is observed in the formation of **3**, believed to be the vinylsilane complex $WCl_2[CH_2{=}CHSi(OMe)_3](PMe_3)_3$ on the basis of its paramagnetic NMR spectrum,[19] consistent with the vinyl acting as a tether. Vinylsilanes $CH_2{=}CHSiMe_3$ and $CH_2{=}CHSi(OEt)Me_2$ also react with **1b** to give **3**, but carbyne products have not been observed starting from **1a**.

Kinetic and mechanistic studies are in progress to map out this transformation in detail. Labeling studies indicate that the formal vinyl to methylcarbyne rearrangement (eq 2) involves net movement of the methine hydrogen to the methylene group. Reaction of $^{13}CH_2{=}CHSiMe_3$ gives $W({\equiv}C^{13}CH_3)(PMe_3)_4Cl$ with <1% label at the carbyne carbon, and $CH_2{=}CDSiMe_3$ gives $W({\equiv}CCH_2D)(PMe_3)_4Cl$, with ≤5% CHD_2 product (by ^{13}C NMR). A crossover experiment using a 50:50 mixture of $^{13}CH_2{=}CHSiMe_3$ and $CH_2{=}CDSiMe_3$ shows that the reaction is not intramolecular: both $W{\equiv}C^{13}CH_3$ and $W{\equiv}C^{13}CH_2D$ (60:40) are observed by ^{13}C NMR. These data are consistent with the mechanism proposed by Green for the other reported vinyl to carbyne rearrangement:[20] deprotonation of the vinyl complex gives a vinylidene, which protonates to form the carbyne.

Allylsilanes also react with **1b** to give a carbyne complex, in this case the ethylcarbyne $W({\equiv}CCH_2CH_3)(PMe_3)_4Cl$ (**4**) (eq 3). A remarkable amount of hydrogen migration has to occur to complete this allyl to ethylcarbyne transformation. The ^1H, ^{31}P, and ^{13}C NMR spectra of **4** are very similar to those of **3**,

$$WCl_2(PMe_3)_4 + \underset{\textbf{1b}}{\diagup\!\!\!\diagdown\!\!\!\diagdown SiR_3} \xrightarrow{70^\circ} \underset{\textbf{4}}{\overset{\overset{CH_2CH_3}{\underset{|}{\overset{C}{\|\|}}}}{\underset{\underset{Cl}{|}}{Me_3P\!\!-\!\!W\!\!-\!\!PMe_3}}} + ClSiR_3 \quad (3)$$

indicating the same basic structure. Reactions of **1b** with allylsilanes are slower than reactions of **1b** with vinylsilanes. Equations 2 and 3 are a new and quite convenient route to tungsten–carbon multiple bonds.

Three unusual transformations are reported here: formally allyloxy to oxo-allyl, vinyl to methylcarbyne, and allyl to ethylcarbyne. These reactions support the idea that the alkene function acts as a "tether" in the activation of silyl ethers, with the silicon acting as the organic fragment donor and as chloride acceptor. Once a substrate is bound to the tungsten, the formation of a very strong metal–ligand multiple bond, $W{\equiv}O$ or $W{\equiv}C$, provides the driving force for cleavage of the Si–O bond and for the unusual rearrangements.

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(16) Selected NMR data (C_6D_6): δ (multiplicity, *J*, number of hydrogen atoms, type). For **2b**, ^1H: 1.49 (d, 9, 9 H, PMe_3), 2.01 (dd, 6, 15, 2H, $CH_aH_bCHH_aH_b$), 3.28 (m, 1 H, CH_2CHCH_2), 4.23 (m, 2 H, $CH_aH_bCH-CH_aH_b$). For **2b**, $^{31}P\{^1H\}$: -26.8 (s, J_{WP} = 428). For **2b**, ^{13}C: 58.8 (t, 154, CH_2CHCH_2), 19.6 (quartet, 130 PMe_3), 82.5 (d, 154, CH_2CHCH_2). For **3**, ^1H: 1.50 (s, 36 H, PMe_3), 1.58 (quintet, 5, 3 H, ${\equiv}CCH_3$). For **3**, $^{31}P\{^1H\}$: -20.8 (s, J_{WP} = 285). For **3**, ^{13}C: 253.3 (t, J_{CP} = 13, ${\equiv}CCH_3$), 23.2 (quartet, 128, PMe_3), 35.6 (quartet, 124, ${\equiv}CCH_3$).

(17) A THF solution (60 mL) of 1.00 g of **1b** and 0.55 mL of vinyltrimethoxysilane was refluxed at 65 °C for 2 days. The volatiles were removed, PMe_3 (0.18 mL) and THF (50 mL) were added, and the yellow solution was stirred at 25 °C overnight. The volatiles were removed, and the residue was recrystallized from 20 mL of pentane to give 0.75 g of bright yellow solids of **3**. Second and third crops were obtained from the filtrate to give a 93% yield. Anal. Calcd for $WClP_4C_{14}H_{39}$: C, 30.54; H, 7.15. Found: C, 30.53; H, 7.07.

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(19) ^1H NMR (C_6D_6; all singlets): δ 2.71, 1.35, -15.18 (PMe_3), 6.38 $[CH_2{=}CHSi(OMe)_3]$; assignments confirmed by ^1H and ^2H NMR of $WCl_2[P(CD_3)_3]_4 + CH_2{=}CHSi(OMe)_3$.

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Synthesis and Characterization of a Branched-Chain Hexacarbene in a Tridecet Ground State. An Approach to Superparamagnetic Polycarbenes

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Design and synthesis of organic molecules in very high-spin ground states are current subjects of great importance.[1] The basic principle underlying the design is the desire to endow organic molecules with many half-filled orthogonal orbitals. Their presence is dictated by symmetry and can be achieved in two ways: orthogonality in space and topological symmetry. Carbenes in triplet ground states are examples of the former. In π-diradicals, parallel alignment of the two spins can become favored if the radical centers are placed in phase with the spin polarization of the intervening π-bonds. A Schlenk hydrocarbon in the triplet ground state is such an example.[2] Poly(m-phenylenecarbenes) **1**[3] combine these two concepts in the construction of higher spin organic molecules.[1,4] The spin alignment in **1** is, however, one-dimen-

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