having the free coordination site and low steric hindrance that are presumably necessary for methyl exchange, leads to fast scrambling of the methyl labels.[13] *We suggest that this same intermediate is responsible for methyl exchange in the thermal decomposition of 2.* Thus, **9** (and **3**) may reasonably form in (or following) the rate-determining step in the thermal decomposition of **2**, after which **9** can be trapped by triphenylphosphine to give **6**. However, **9** might also react with **8** (resulting in methyl exchange) *prior* to trapping by triphenylphosphine. If this hypothesis is correct, then reaction of **2** and **8**-d_3 (Scheme II) ought to result in a high degree of methyl exchange between the carbyne decomposition product **6** and **8**-d_3. In fact, nearly a 1:1 mixture of **6** and **8** was observed after 3 h at 65 °C. Thus while it will be impossible (at least in this particular system) to determine if methyl scrambling occurs during the migration from oxygen to iron, it clearly occurs among the products under the reaction conditions.

Work is continuing in our laboratory to elucidate the details of the cis–trans isomerizations and the methyl exchange and carbyne decomposition reactions described above, as well as to introduce the additional μ-methylene moiety in place of the μ-carbonyl ligand.

Acknowledgment. Financial support for this work from Research Corp., the UCLA Committee on Research, and the Universitywide Energy Research Group is gratefully acknowledged.

Registry No. 1a, 97011-38-6; **1b**, 97011-40-0; *cis*-**1b**, 97100-76-0; *trans*-**1b**, 97100-78-2; *cis*-**2**, 97011-41-1; *trans*-**2**, 97100-79-3; **3**, 12108-13-3; **4**, 12080-06-7; **5**, 12154-95-9; **6**, 12100-51-5; **7**, 97011-42-2; **8**, 97011-43-3; **8**-d_3, 97011-44-4; $(MeCp)Mn(CO)_2(CH_3CN)$, 82648-13-3; $CpFe(CO)_2^-Na^+$, 12152-20-4.

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New Types of Organometallic Oxo Complexes Containing Tungsten

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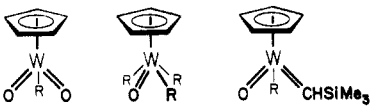
Summary: The preparation and isolation of the first examples of three new types of cyclopentadienyl oxo alkyl complexes are described. The complexes $(\eta^5\text{-}C_5H_5)W(O)_2(CH_2SiMe_3)$, **1**, $(\eta^5\text{-}C_5H_5)W(O)(CH_2SiMe_3)_3$, **2**, and $(\eta^5\text{-}C_5H_5)W(O)(CHSiMe_3)(CH_2SiMe_3)$, **3**, have been characterized by conventional spectroscopic methods, and the molecular structures of **1** and **2** in the solid state have been determined by single-crystal X-ray crystallography.

Interest in molecules which contain both organic and oxo groups attached to a metal atom derives from the expectation that their characteristic chemistry will provide some insight into how metal oxides heterogeneously catalyze various organic transformations.[1] Recent reports concerning the preparation and characterization of diverse organometallic oxo complexes such as $(\eta^5\text{-}C_5R'_5)ReO_3$ (R' = H[2] or Me[3]), $(\eta^5\text{-}C_5H_5)Re(O)Me_2$,[2b] $Re(O)I(MeC{\equiv}CMe)_2$,[4] and $W_2O_3(CH_2CMe_3)_6$[5] suggest that these types of compounds may be more accessible than was previously believed.[6] Indeed, during our investigations of the chemical properties of $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$,[7] we have encountered the first examples of three new types of cyclopentadienyl oxo alkyl complexes. Consequently, we now wish to report the isolation and characterization of these compounds **1**–**3** depicted below (R = CH_2SiMe_3).



1 2 3

Compound **1** may be conveniently synthesized by exposing a hexanes solution of $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$ to an atmosphere of O_2 overnight, i.e., eq 1, and it is

$$(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2 \xrightarrow[\text{hexanes, 20 °C}]{O_2\ (1\text{atm})} (\eta^5\text{-}C_5H_5)W(O)_2(CH_2SiMe_3) \quad (1)$$

isolable from the final reaction mixture as analytically pure, white crystals in 65% yield by fractional crystallization. Compound **2** is formed as a byproduct during the preparation of $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$ from $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$[7] if an excess of Grignard reagent is employed. It is separable by chromatography of the dried reaction residue on Florisil with hexanes as eluant and is obtainable from the eluate as lemon yellow crystals in 3% yield (based on W) by subsequent crystallization. Compound **3** results from the thermal decomposition of solid $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$, i.e., eq 2, and is isolable as

$$(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2 \xrightarrow[\text{20 °C, 30 days}]{N_2\ (1\text{atm})} (\eta^5\text{-}C_5H_5)W(O)(CHSiMe_3)(CH_2SiMe_3) + \text{other products} \quad (2)$$

a crystalline, pale yellow solid in 40% yield by fractional crystallization of the final mixture from hexanes. Interestingly, the alkylidene compound **3** is also obtainable in virtually quantitative yields by the thermal decomposition of **2**, i.e., eq 3. This is the first instance of an oxo alkyl

$$(\eta^5\text{-}C_5H_5)W(O)(CH_2SiMe_3)_3 \xrightarrow[\text{50 °C, 2 days}]{\text{benzene}} (\eta^5\text{-}C_5H_5)W(O)(CHSiMe_3)(CH_2SiMe_3) + Me_4Si \quad (3)$$

complex converting to an isolable oxoalkylidene complex, a possibility previously envisaged by Pedersen and Schrock.[8]

Single-crystal X-ray crystallographic analyses of **1**[9] and **2**[10] have confirmed their monomeric natures and have

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(9) Crystals of **1** are monoclinic of space group $P2_1/n$ with a = 6.3178 (7) Å, b = 19.9826 (9) Å, c = 9.6923 (11) Å, β = 93.320 (5)°, and Z = 4. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to R = 0.029 and R_w = 0.032 for 2220 absorption-corrected reflections with $I > 3\sigma(I)$ collected at 22 °C with Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer. Hydrogen atoms were fixed in idealized positions.

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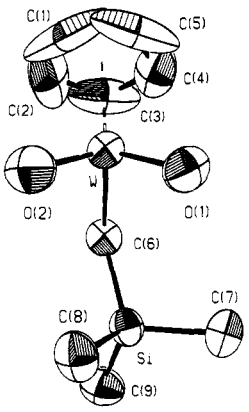

Figure 1. Molecular structure of **1**, hydrogen atoms having been omitted for clarity. Selected bond lengths (Å) and angles (deg) are W–O(1) = 1.716 (5), W–O(2) = 1.723 (5), W–C(6) = 2.134 (6), W–C_5H_5(centroid) = 2.107 (6), Si–C(6) = 1.880 (7), Si–C(CH_3, av) = 1.858 (6), O(2)–W–O(1) = 107.8 (3), O(2)–W–C(6) = 99.5 (3), C(6)–W–O(1) = 99.1 (3), W–C(6)–Si = 115.8 (3), and C(6)–Si–C(7) = 109.3 (4).

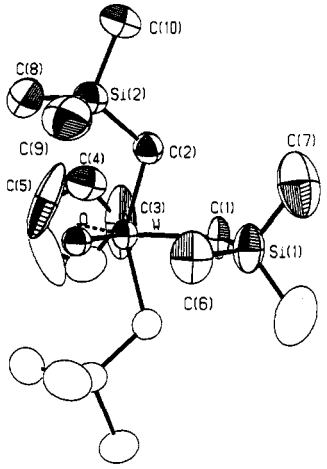

Figure 2. Molecular structure of **2**, hydrogen atoms having been omitted for clarity. Selected bond lengths (Å) and angles (deg) are W–O = 1.664 (8), W–C(1) = 2.311 (11), W–C(2) = 2.238 (7), W–C_5H_5(centroid) = 2.131 (6), Si–CH_2(av) = 1.862 (3), Si–CH_3(av) = 1.86 (1), O–W–C(1) = 120.8 (3), O–W–C(2) = 90.2 (2), O–W–C_5H_5(centroid) = 103.0 (4), W–C(1)–Si(1) = 119.0 (6), W–C(2)–Si(2) = 118.9 (3), C(1)–Si(1)–C(7) = 108.5 (5), and C(2)–Si(2)–C(10) = 108.0 (4).

revealed their normal "piano stool" molecular structures with mirror symmetry at the central tungsten atoms (Figures 1 and 2). The most chemically interesting features of both structures involve the tungsten–oxygen linkages whose bond lengths (1.720 (4) Å (av) in **1** and 1.664 (8) Å in **2**) are consistent with the existence of W=O double bonds.[5]

Under ambient conditions, complexes **1–3** are diamagnetic solids which are freely soluble in common organic solvents, the solutions of **2** and **3** being moderately air-sensitive. Their spectroscopic properties[11] indicate that their molecular structures in solution are as depicted above. All three compounds are thus best viewed as being 16-electron species, formally containing tungsten in its highest oxidation state of VI. Consistent with this view is the fact that compounds **1–3** appear to be reactive toward both electrophiles and nucleophiles. This reactivity and the mechanisms of reactions 1–3 are currently being investigated.

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Registry No. **1**, 96760-75-7; **2**, 96760-76-8; **3**, 96791-10-5; $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$, 94620-67-4; $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, 71341-43-0.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^1H and $^{13}C\{^1H\}$ NMR, mass spectral) data for **1**, **2**, and **3** and tables of fractional coordinates, isotropic and anisotropic thermal parameters, and structure factors for **1** and **2** (35 pages). Ordering information is given on any current masthead page.

(10) Crystals of **2** are orthorhombic of space group *Cmcm* with a = 18.6342 (11) Å, b = 9.8767 (6) Å, c = 13.1985 (8) Å, and Z = 4. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to R = 0.028 and R_w = 0.032 for 1562 absorption-corrected reflections with $I \geq 3\sigma(I)$ collected at 22 °C with Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer. The molecule (which possesses exact C_s symmetry) was found to be twofold disordered about a site having crystallographic C_{2v} (*mm*2) symmetry. No satisfactory refinement could be achieved in the noncentrosymmetric space group $Cmc2_1$ as the disorder persisted. Hydrogen atoms were fixed in calculated positions.

(11) Supplementary material.

Extrusion of Dimethylsilylene from 1,1-Dimethyl-1-silacyclopent-3-enes

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Summary: Dimethylsilylene Me_2Si: has been trapped by addition to 1,3-dienes in the vacuum flow pyrolysis of 1,1-dimethyl-1-silacyclopent-3-ene, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene, and 1,1,2-trimethyl-1-silacyclopent-3-ene. Intramolecular rearrangement products obtained in the pyrolysis of the last compound point to a stepwise extrusion mechanism via alkenylsilirane intermediates.

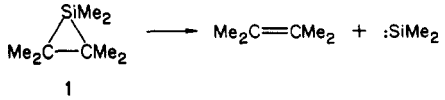
Silylenes differ markedly from carbenes in the ease with which their carbene-like reactions can be reversed. α-Elimination, the inverse of insertion, is a standard route for the generation of silylenes, pioneered by Atwell and Weyenberg.[1,2]

$$XYZSi\text{–}SiXYZ \xrightarrow{\Delta} X_2YZSi + :SiYZ$$

X = H, halogen alkoxy, alkyl, etc.

Y, Z = H, halogen, alkoxy, alkyl, aryl, etc.

Extrusion of dimethylsilylene from hexamethylsilirane, **1**, another α-elimination that is the inverse of π-addition to an olefin, has been developed by Seyferth as a convenient and mild source of Me_2Si:.[3]



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