less reactive.[20] Also, Berke[8] has shown than $Fe(CO)_2(P(OMe)_3)_2Cl(CH_2OH)$ readily inserts CO under mild conditions.

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Registry No. **1**, 86748-03-0; **2**, 86748-04-1; **3**, 86748-05-2; **4**, 86748-06-3; **5**, 80492-22-4; $CpRu(CO)_2CH_2OMe$, 80492-23-5; $[CpRu(CO)_3][PF_6]$, 31741-71-6; $[CpFe(CO)_3][BF_4]$, 12244-69-8; $[CpFe(CO)_2]_2$, 12154-95-9; $[Ir(H)(CHO)(PMe_3)_4][PF_6]$, 75592-93-7; $CpRu(CO)_2H$, 57349-59-4; $Na[CpRu(CO)_2]$, 42802-20-0; $NaBH_3CN$, 25895-60-7; MeOH, 67-56-1; Me_3SiCl, 75-77-4; formaldehyde, 50-00-0; acetyl chloride, 75-36-5; acetic anhydride, 108-24-7.

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Preparation of Tungsten(V) Alkyl Complexes and Hydride Complexes of the Type $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_x]_y$

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Summary: Alkylation of $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ with dimethylzinc yields paramagnetic $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Me_2Cl_2$ (**1**). In contrast, diamagnetic, purple $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CCMe_3)Cl_2$ (**2**) is formed from $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ and dineopentylzinc. Hydrogenation of $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Me_4$ (prepared from **1** and LiMe) at 1000 psi yielded brown $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ (~20%) and blue $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$ (~50%) in which all hydride ligands are equivalent on the ^1H NMR time scale at 25 °C. Hydrogenation of $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CCMe_3)Me_2$ (prepared from **2** and LiMe) yields a similar mixture in a lower (~30%) overall yield. Hydrogenation of all complexes containing halides, however, so far has not yielded any pure product of the type $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_xH_y]_z$.

Tantalum hydride complexes of the type $[Ta(\eta^5\text{-}C_5Me_4R)Cl_2H]_2$ (R = Me or Et) have been prepared by treating $Ta(\eta^5\text{-}C_5Me_4R)(propylene)Cl_2$ or $Ta(\eta^5\text{-}C_5Me_4R)(CH_2CMe_3)_2Cl_2$ with molecular hydrogen.[1] Interest in this type of dimeric hydrido complex arose from the fact that it reacts readily with carbon monoxide to give a compound containing a side-on bonded formyl fragment. $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4(\mu\text{-}H)(\mu\text{-}CHO)$,[2,3] one of the very few examples of formation of a formyl complex from a transition-metal[4] (or actinide[5]) hydrido complex and carbon monoxide. Extending monocyclopentadienyl chemistry to presumably less oxophilic tungsten has been problematic due to the fact that high oxidation state tungsten monocyclopentadienyl complexes are unknown. The recently discovered synthesis of $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$[6] now allows us to examine for tungsten some of the approaches and chemistry that were successful for tantalum.

$[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ can be alkylated by dimethylzinc to give yellow, paramagnetic $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Me_2Cl_2$[7] (**1**). However, if $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ is treated with with 1 equiv of $Zn(CH_2CMe_3)_2/W$ in toluene at 0 °C, the product is diamagnetic, purple $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CCMe_3)Cl_2$[8] (**2**). Addition of methyllithium in ether to **1** at −78 °C yields yellow-orange, paramagnetic $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Me_4$ (**3**)[12] while **2** reacts with methyllithium to give $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CCMe_3)Me_2$ (**4**), a distillable red oil. ^1H NMR spectra for $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$, **1**, and **3** can be observed but the signals are extremely broad. Odd-electron alkyl complexes are unusual since the metal–carbon bond is generally thought to be much more susceptible to homolytic cleavage than in an even-electron complex.[13]

Hydrogenation of **1** or **2** at 30–1000 psi produced no isolable hydrido complexes, although irreproducible signals ascribable to hydrides occasionally could be observed in the ^1H NMR spectra and IR spectra of the products. However, hydrogenation of **3** at 1000 psi and 0 °C in pentane yields a pentane-soluble brown crystalline complex[14] (**5**) in ~20% yield and a relatively insoluble microcrystalline blue-black complex[15] (**6**) in ~50% yield. The ^1H NMR spectrum of **5** exhibits a hydride peak of relative area of approximately 4 at −0.8 ppm with J_{HW} = 40 Hz. The area of the satellite peaks (~25%) suggest that **5** is dimeric. This postulate was confirmed by a field-desorption mass spectrum showing a parent ion pattern that agreed with that calculated for the formulation $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$. The ^1H NMR spectrum of the blue

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[7] Solvent = CH_2Cl_2; 2 Et_4NCl/W, 2 $ZnMe_2$; −78 °C; yield 40%. Anal. Calcd for $WC_{15}H_{27}Cl_2$: C, 38.97; H, 5.85. Found: C, 38.63; H, 5.84.

[8] Yield: 60%. Anal. Calcd for $WC_{18}H_{30}Cl_2$: C, 43.11; H, 5.99. Found: C, 42.60; H, 6.23; $\delta(C_\alpha)$ 317. So far we have not been able to prepare analogous $\eta^5\text{-}C_5Me_5$ or $\eta^5\text{-}C_5Me_4Et$ complexes by treating $W(CCMe_3)(dimethoxyethane)Cl_3$[9] with Li, Na, or Tl cyclopentadienyl reagents. We suspect that a neopentyl group is significantly more prone toward loss of an α hydrogen atom in an odd-electron complex[10] than in an even-electron complex[11] and significantly more so than a methyl group. If only 0.5 equiv of $Zn(CH_2CMe_3)_2$ is employed, a yellow, paramagnetic species is obtained which we believe must be a neopentyl complex, most likely $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CH_2CMe_3)Cl_3$.

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[12] Anal. Calcd for $WC_{17}H_{33}$: C, 48.46; H, 7.84. Found: C, 48.25; H, 7.74.

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[14] ν_{MH} = 1910 (m), 1890 (m) cm^{-1}.

[15] ν_{MH} = 1910 (m), 1890 (m), 1860 (m) cm^{-1}. Anal. Calcd for $WC_{13}H_{24}$: C, 42.90; H, 6.59. Found: C, 43.17; H, 7.10.

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product **6** exhibits a peak at −1.8 ppm of relative area three with *two* sets of satellite patterns with areas approximately ~35% and ~3% of the total, corresponding to a trimeric molecule containing one and two ^{183}W centers, respectively.[16] This postulate was also confirmed by field-desorption mass spectroscopy. So far we know that $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$ (**6**) is not readily converted into $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ (**5**) under 30 psi or H_2 and **5** does not readily lose H_2 to give **6** when it is heated to 80 °C.

The reaction of $W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CCMe_3)Me_2$ with H_2 at 1000 psi also produces a mixture of **5** and **6** in a ratio of approximately 3:1 but a total yield of only ~30%.

It is unlikely that hydride ligands in **5** are all terminal or all bridging. A plausible structure would contain four bridging hydrides and two terminal hydrides on each metal (cf. $Re_2H_8(PR_3)_4$[17]). Terminal and bridging hydrides must exchange relatively rapidly since we observe only the singlet of relative area 4 in toluene-d_8 at −80 °C.

In contrast, the structure of **6** is more difficult to predict. It seems likely that the basic framework is triangular, as it is in other W(IV) clusters such as $W_3O_3Cl_4(\mu^3\text{-}Cl)(CH_3CO_2)(PBu_3)_3$[18a] or $[W_3(\mu^3\text{-}O)_2(CH_3CO_2)_6(H_2O)_3]^{2+}$.[18b,c] Upon cooling a sample of **6** the hydride peak collapses into the base line and signals for at least two different cyclopentadienyl groups appear. Unfortunately, we have not yet been able to obtain a sensible limiting spectrum in toluene-d_8 at temperatures down to −80 °C. It is clear, however, that the hydrides in **6** are equilibrating much more slowly than those in **5**.

It is interesting to compare the results observed here with those obtained upon hydrogenation of $Ta(\eta^5\text{-}C_5Me_5)Me_4$.[19,20] In the absence of coordinating ligands such as phosphines only unidentifiable brown to black solids or oils were obtained upon hydrogenation of $Ta(\eta^5\text{-}C_5Me_5)Me_4$ at 30–1500 psi. In the presence of PMe_3 $Ta(\eta^5\text{-}C_5Me_5)(PMe_3)_2H_4$ can be isolated.[20] Therefore it appears at this point that ligand-free complexes of the type $[Ta(\eta^5\text{-}C_5Me_5)H_x]_y$ either are not formed selectively or are not stable.

We are now in the process of preparing simpler $\eta^5\text{-}C_5R_5$ analogues of **5** and **6** more directly, elucidating their structures, and studying their reactions with carbon monoxide.

Acknowledgment. This work has been supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A002. We are indebted to Dr. Catherine Costello for obtaining FD mass spectra at a facility supported by the National Institutes of Health, Grant RR00317.

Registry No. 1, 86823-25-8; 2, 86823-26-9; 3, 86823-27-0; 4, 86823-28-1; 5, 86834-30-2; 6, 86834-31-3; $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$, 83511-04-0; $ZnMe_2$, 544-97-8; $Zn(CH_2CMe_3)_2$, 54773-23-8.

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[16] The theoretical distribution is $(^{184}W)^3$ = 63.6%, $(^{184}W)^2(^{183}W)$ = 31.0%, $(^{184}W)(^{183}W)^2$ = 5.1%, and $(^{183}W)^3$ = 0.3%. Half of the triplet pattern for $(^{184}W)(^{183}W)^2$ is found under the main peak due to the hydride in $(^{184}W)^3$.

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Disilene System ($R_2Si{=}SiR_2$). The Tetra-*tert*-butyl Derivative

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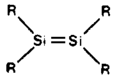
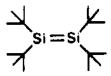
Summary: Low-temperature photolysis of 2,3-benzo-7,7,8,8-tetra-*tert*-butyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene provides, in addition to naphthalene, tetra-*tert*-butyldisilene, which exhibits UV absorption maxima at 305 (ϵ 5200) and 433 nm (2800). This disilene is thermally unstable and has a half-life of only several hours at room temerature (ca. 10^{-2} M in methylcyclohexane).

Stable, crystalline tetramesityl-[1] and tetrakis(2,6-dimethylphenyl)disilene[2] (**1** and **1a**) that have been synthesized recently provide valuable chemical information on the silicon–silicon double bond. The aryl substituents of these compounds, however, significantly perturb the intrinsic electronic structure of this double-bond system and thus create extra complications in the interpretation of physical data such as ultraviolet[3] and photoelectron spectra.[4] Obviously, the majority of these complications can be eliminated by the synthesis of alkyl (rather than aryl) substituted disilenes; therefore tetra-*tert*-butyldisilene (**2**)[5] has been selected as our synthetic target. We record herein that low-temperature photolysis of 2,3-benzo-7,7,8,8-tetra-*tert*-butyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**3**) leads to the formation of **2**. This compound is found to be rather unstable thermally, (the half-life being approximately several hours at room temperature) and also to be extraordinarily sensitive toward air and moisture. Despite these undesirable properties, however, this disilene



1 : R = mesityl
1a : R = 2,6-dimethylphenyl
1b : R = 1-ethylpropyl



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[4] A photoelectron spectrum of **1a** has been measured (private communication from Dr. T. Bally, Institut de Chimie Physique, Universite de Fribourg Suisse). The first VIP is 8.4 eV.

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