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# Synthesis, Dynamic Behavior, and X-ray Crystal Structure of $[Li(tmed)]_3[WH(C_2H_4)_4]$

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*Summary: Alkylation of $W(OMe)_3Cl_3$ with ethyllithium and N,N,N′,N′-tetramethylethylenediamine (tmed) affords the tungsten ethene/hydride complex $[Li(tmed)]_3[WH(C_2H_4)_4]$. The anion possesses an approximate trigonal bipyramidal geometry with the hydride in an equatorial site. The ethene ligands exchange with one another, presumably by means of a Berry pseudorotation process, but exchange of ethene and hydride hydrogen atoms is slow on the NMR time scale.*

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Relatively few two-electron donors are capable of forming binary complexes of transition metals in negative oxidation states; among these ligands are carbon monoxide,[1] trifluorophosphine,[2] and certain triorganophosphines and triorganophosphites.[3] Ethene is a reasonably strong $\pi$-acceptor, but despite this fact only three examples of binary ethene complexes in negative oxidation states are known: $Ni(C_2H_4)_3^{2-}$, $Co(C_2H_4)_4^{-}$, and $Fe(C_2H_4)_4^{2-}$, and only the last has been crystallographically characterized.[4] We now report the synthesis and characterization of an unusual ethene/hydride complex of tungsten(−II).

Alkylation of $W(OMe)_3Cl_3$[5] with 9 or 10 equiv of LiEt in diethyl ether at −78 °C, followed by warming to room temperature and addition of excess *N,N,N′,N′*-tetramethylethylenediamine (tmed), gives yellow-orange crystals of stoichiometry $[Li(tmed)]_3[WH(C_2H_4)_4]$, **1**.[6]

$$WCl_3(OMe)_3 \xrightarrow[\text{xs tmed}]{\text{9 LiEt}} [Li(tmed)]_3[WH(C_2H_4)_4]$$

The X-ray crystal structure of **1**[7] (Figure 1) shows that the geometry about the tungsten center is a distorted trigonal bipyramid (if each ethene ligand is regarded as occupying one site). Two ethene ligands are mutually trans and define the axial positions of the trigonal bipyramid, and the remaining two ethene units and the hydride ligand constitute the equatorial plane. The three $[Li(tmed)]^+$ cations are also located in the equatorial plane: one $[Li(tmed)]^+$ group bridges between the two equatorial ethene ligands, and the other two $[Li(tmed)]^+$ ligands bridge between an equatorial ethene group and the hydride ligand.

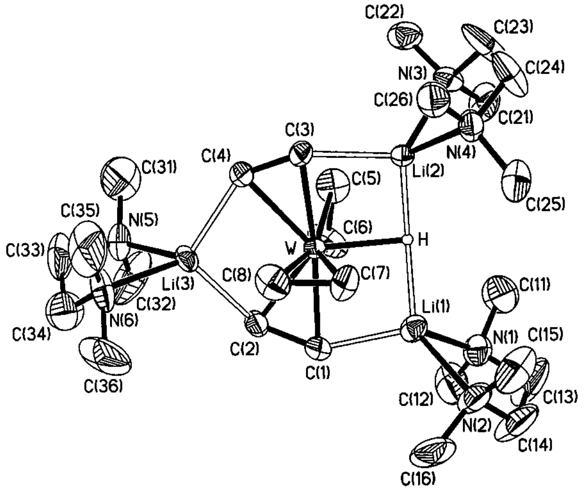

**Figure 1.** Molecular structure of $[Li(tmed)]_3[WH(C_2H_4)_4]$, **1**. Thermal ellipsoids are represented by the 30% probability surfaces except for the hydride atom, which is represented by an arbitrarily sized sphere. Selected bond distances (Å) and angles (deg): W−C(1) 2.244(8), W−C(2) 2.208(7), W−C(3) 2.229(7), W−C(4) 2.233(7), W−C(5) 2.221(9), W−C(6) 2.233(8), W−C(7) 2.197(8), W−C(8) 2.182(8), W−Cn(12) 2.103(7), W−Cn(34) 2.107(7), W−Cn(56) 2.121(8), W−Cn(78) 2.067(8), W−H 2.04(5), C(1)−C(2) 1.463(10), C(3)−C(4) 1.466(10), C(5)−C(6) 1.357(11), C(7)−C(8) 1.447(11), Li(1)···H 1.945(55), Li(2)···H 1.991(54), Cn(12)−W−Cn(34) 137.6°, Cn(12)−W−Cn(56) 96.0°, Cn(12)−W−Cn(78) 87.8°, Cn(34)−W−Cn(56) 93.9°, Cn(34)−W−Cn(78) 87.0°, Cn(56)−W−Cn(78) 173.2°, Cn(12)−W−H 108.1°, Cn(34)−W−H 114.0°, Cn(56)−W−H 69.5°, Cn(78)−W−H 104.0°, where Cn represents the centroid of an ethene ligand.

The axial $\eta^2$-$C_2H_4$ ligands are staggered with respect to one another to minimize the competition for back-donation from the filled metal $d_{xz}$ and $d_{yz}$ orbitals on

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(6) To a solution of $W(OMe)_3Cl_3$ (0.25 g, 0.65 mmol) in $Et_2O$ (10 mL) at −78 °C was added a solution of LiEt (0.235 g, 6.50 mmol) in $Et_2O$ (20 mL) at −78 °C. The solution color changed from pale yellow to pale blue to pale green to brown-yellow within 1 min. The solution was stirred for 1 h at −78 °C and then was warmed to room temperature and stirred for another 2 h. The solution was filtered, concentrated to 20 mL, and then treated with freshly distilled *N,N,N′,N′*-tetramethylethylenediamine (1.00 mL). The solution was recooled to −78 °C, filtered, and kept at −20 °C for 6 h to afford yellow-orange crystals of **1**. Yield: 0.0215 g; 5%. Anal. Calcd for $C_{26}H_{65}N_6WLi_3$: C, 46.8; H, 9.83; N, 12.6; W, 27.6; Li, 3.1. Found: C, 44.0; H, 9.11; N, 11.1; W, 26.7; Li, 3.1. $^1H$ NMR (thf-$d_8$, −90 °C): $\delta$ 2.18 (br s, $NCH_2$, $NMe_2$, 48H) −0.40 (br s, ax-$C_2H_4$, 8H), −0.80 (br s, eq-$C_2H_4$, 4H), −1.30 (br s, eq-$C_2H_4$, 4H), −8.22 (br s, W*H*, 1H). $^1H$ NMR (thf-$d_8$, 20 °C): $\delta$ 2.33 (s, $NCH_2$, 12 H), 2.19 (s, N $Me_2$, 36 H), −0.66 (s, $C_2H_4$, 16H), −8.14 (br s, W*H*, 1H). $^{13}C$ NMR (thf-$d_8$, −90 °C): $\delta$ 57.7 (br s, $NCH_2$), 46.3 (br s, N $Me_2$), 35.1 (t, $^1J_{CH}$ = 140 Hz, ax-$C_2H_4$), 19.7 (t, $^1J_{CH}$ = 136 Hz, eq-$C_2H_4$), 18.3 (t, $^1J_{CH}$ = 131 Hz, eq-$C_2H_4$). $^{13}C$ NMR (thf-$d_8$, 20 °C): $\delta$ 58.4 (t, $^1J_{CH}$ = 132 Hz, $NCH_2$), 46.4 (t, $^1J_{CH}$ = 133 Hz, $NCH_3$), 26.9 (t, $^1J_{CH}$ = 137 Hz, $C_2H_4$).

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tungsten. The two equatorial $\eta^2$-$C_2H_4$ ligands are coplanar. The W−C distances range from 2.182 to 2.244 Å and are within the 2.15−2.44 Å range obtained for other structurally characterized tungsten ethene complexes.[8] The W−C distances are also comparable to those found in tungsten−ethyl complexes.[9] The C(5)−C(6) bond distance in **1**, 1.357(11) Å, is the shortest in the molecule and is only 0.020 Å longer than the C−C distance reported for free ethene.[10,11] The C−C bond distances in the remaining three ethene groups, 1.463(10), 1.466(10), and 1.447(11) Å, are significantly longer, probably because these ethene groups are involved in Li···C contacts with the lithium cations. The Li···C(equatorial) distances range from ca. 2.16 to 2.20 Å. Carbon atoms C(7) and C(8) are involved in longer-ranged Li···C contacts of ~2.6 Å. There are no significant Li···C contacts to carbon atom C(5) or C(6).

The W−H distance of 2.04(5) Å is one of the longest reported.[12] The long distance is probably a consequence of the low formal oxidation state of the tungsten atom and the presence of two close contacts of 1.97 Å between the hydride ligand and the lithium cations. The Li···H contact distances in compound **1** are within the 1.73(5)−2.02(5) range seen for $\{Li[WH_5(PMe_3)_3]\}_4$.[12] Interestingly, the hydride ligand is displaced by 0.24 Å out of the plane described by the tungsten atom and the two equatorial ethene ligands: it is tilted toward the C(5)−C(6) ethene group by 20.5°. The displacement of the hydride ligand out of the equatorial plane minimizes the steric repulsion with atom C(7).

The $^1H$ NMR spectrum of **1** in tetrahydrofuran-$d_8$ at −80 °C contains three broad ethene resonances at $\delta$ −0.38, −0.79, and −1.27 with intensities 8:4:4, respectively, and a high-field resonance at $\delta$ −8.22 of intensity 1 due to the hydride ligand. We assign the resonance of intensity 8 to the two axial ethene ligands, which evidently are rotating rapidly about the W−$C_2H_4$ bonds even at low temperatures. Low rotation barriers for the two axial $C_2H_4$ groups are expected because both the $d_{xz}$ and $d_{yz}$ orbitals on the tungsten center are filled. We assign the two resonances of intensity 4 to the equatorial ethene ligands: specifically, to hydrogen atoms that are proximal to, and distal from, the W−H ligand. The W−H resonance at $\delta$ −8.22 exhibits tungsten satellites, which are seen most clearly at −30 °C. The observed tungsten-to-hydride coupling constant, $J_{WH}$ = 69.1 Hz, is within the 28−80 Hz range seen for other tungsten hydride complexes.[13]

As the sample is warmed, the three signals due to the ethene ligands broaden and coalesce. At room temperature, the spectrum consists of one sharp singlet at $\delta$ −0.66 for the protons of the four ethene groups and one signal for the hydride ligand at $\delta$ −8.14. Corresponding changes are seen in the $^{13}C$ NMR spectrum of **1**. At low temperature, there are three ethene resonances at $\delta$ 35.1, 19.7, and 18.3 of relative intensity 4:2:2 (the first resonance is assigned to the axial ethene groups and the latter two to the proximal/distal sites of the equatorial ethene groups), whereas the room-temperature spectrum shows one singlet at $\delta$ 26.9 for all eight carbons of the four ethene groups.

We attribute the changes in the NMR spectra to an exchange process involving only the ethene ligands. The line shapes of the ethene proton resonances were compared with computer-generated spectra to determine the exchange rate. The activation parameters $\Delta H^\ddagger$ = 9.5(10) kcal mol$^{-1}$ and $\Delta S^\ddagger$ = −5(4) cal mol$^{-1}$ K$^{-1}$ for this exchange process were calculated from an Eyring plot. Presumably, the ethene ligands interconvert via a Berry pseudorotation process in which the hydride ligand is the pivot atom. The ethene exchange barrier increases if excess tmed is added, suggesting that the fluxional barrier is raised when the Li···H interactions are absent.

Interestingly, variable-temperature NMR spectroscopy shows that the hydride resonance is broad at −90 °C (59 Hz), is narrowest near −10 °C (15 Hz), and is broad again at room temperature (53 Hz). The changes in the line width of the W−H resonances as a function of temperature probably reflect temperature-dependent ion-pairing equilibria between the [Li(tmed)$^+$] cations and the $[WH(C_2H_4)_4{}^{3-}]$ ions. A spin saturation transfer experiment carried out at 35 °C showed that the hydride and ethene protons do not exchange.

In the synthesis of $[WH(C_2H_4)_4{}^{3-}]$, it is possible that ethyltungstate species such as "$WEt_8{}^{2-}$" are produced initially; its methyl analogue, $WMe_8{}^{2-}$, has been reported.[14] It is clear, however, that the ethyltungsten complex formed initially is unstable and undergoes rapid and successive $\beta$-hydrogen elimination processes

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[7] Crystal data for $C_{26}H_{65}Li_3N_6W$ ($T$ = 198(2) K): orthorhombic, space group *Pbca*, $a$ = 15.3935(4) Å, $b$ = 13.3225(4) Å, $c$ = 34.6471(6) Å, $V$ = 7105.4(3) Å$^3$, $Z$ = 8, $R_1$ = 0.0531, $wR_2$ = 0.1203 for 341 variables and 8691 unique data.

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to afford the trianionic tetrakis(ethene)hydridotungsten(−II) complex reported here. Studies of the reactivity of this ionic species are under way.

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**Supporting Information Available:** X-ray crystal structure of **1** with view down the C(3)−W−C(1) vector; tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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