80697-94-5; **3** (R = Me; E = $CH_2—C(Me)═CH_2$), 80719-70-6; **3** (R = Me; E = $CH_2—CH═CH_2$), 80697-95-6; **3** (R = Me; E = $CH_2—O—CH_2—Ph$), 80697-96-7; **3** (R = Me; E = $CH_2—O—O—Et$), 80697-97-8; **3** (R = Me; E = Et), 79563-30-7; **3** (R = Et; E = Me), 79563-31-8; **3** (R = n-C_8H_{17}; E = Me), 80697-98-9; **4** (R = Me; E = $CH_2—Ph$), 79563-27-2; **4** (R = Me; E = $CH_2—C(Me)═CH_2$), 79563-28-3; **4** (R = Me; E = $CH_2—CH═CH_2$), 79563-29-4; **4** (R = Me; E = $CH_2—O—CH_2—Ph$), 80697-99-0; **4** (R = Me; E = $CH_2—O—O—Et$), 80719-71-7; **4** (R = Me; E = Et), 80735-97-3; **4** (R = Et; E = Me), 80735-98-4; **4** (R = n-C_8H_{17}; E = Me), 80698-00-6; **5a** (R = Me), 80698-01-7; **5a** (R = Et), 80698-02-8; **5a** (R = n-C_8H_{17}), 80698-03-9; **5b** (R = Me), 80698-04-0; **5b** (R = Et), 80698-05-1; **5b** (R = n-C_8H_{17}), 80698-06-2; **6a**, 79563-27-2; **6c**, 80698-11-9; (*R*)-**7a**, 80698-12-0; (*R*)-**7b**, 14367-67-0; (*R*)-**7c**, 80698-13-1; (*R*)-**8a**, 77943-96-5; (*S*)-**8b**, 63930-46-1; (*R*)-**8c**, 80698-14-2; **9**, 80764-26-7; (*S*)-**10**, 80698-15-3; **11**, 79563-29-4; (*R*)-12, 55254-35-8; $PhCH_2Br$, 100-39-0; $CH_2═C(Me)CH_2I$, 3756-30-7; $CH_2═C(Me)CH_2Br$, 1458-98-6; $CH_2═CHCH_2Br$, 106-95-6; $PhCH_2OCH_2Br$, 17690-16-3; EtO_2CH_2Br, 80698-16-4; EtO_2CH_2I, 80698-17-5; EtI, 75-03-6; MeI, 74-88-4; (4*S*)-(2-propyl)oxazolidone, 17016-83-0.

Preparation and Structure of Tungsten Neopentylidene Hydride, Neopentylidene Carbonyl, and Neopentylidene Ethylene Complexes[1]

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We have found that tungsten alkylidene complexes are especially stable when a strong π donor such as an oxo[2] or imido[3] ligand is present and that a neopentylidene ligand in two such species[4] is less distorted than any we have encountered in tantalum or niobium chemistry.[5] We also know that oxo and imido alkylidene complexes are olefin metathesis catalysts.[3,4a,6] An important question is what the structure and reactivity of tungsten alkylidene complexes will be when no strong π-donor ligand is present. We report three examples of such species here. These results along with recent results concerning the structure of analogous methylene complexes[7] and the formation of W(VI) neopentylidyne complexes[8] reinforce the notion that tungsten alkylidene ligands are likely to be highly distorted in the absence of a strong π-donor ligand and, when the electron count is less than 18, may form an alkylidyne ligand by loss of an α proton.

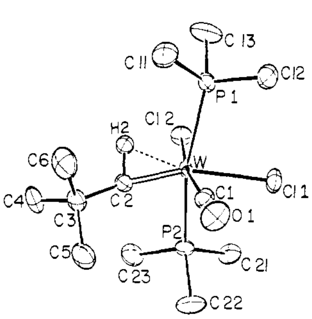


Figure 1. Overall geometry of the $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ molecule. Hydrogen atoms of the methyl groups are omitted for clarity.

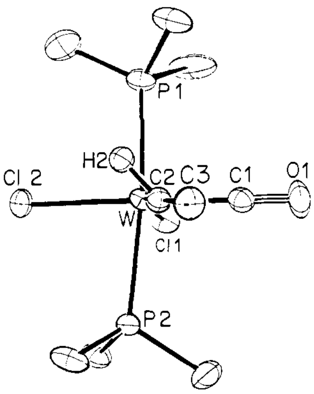
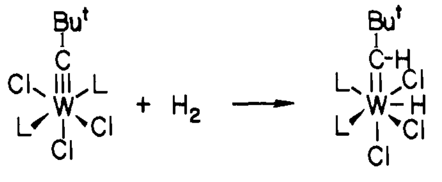


Figure 2. $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ molecule, showing the orientation of the α-hydrogen atom (H2) relative to the P1⋯Cl2⋯C2 octahedral face.

Yellow $W(CCMe_3)Cl_3L_2$[9] (L = PMe_3) reacts with molecular hydrogen (30 psi, 12 h, CH_2Cl_2) to give pale yellow $W(CHCMe_3)(H)Cl_3L_2$[10] (**1**, eq 1). The pentagonal bipyramidal



(1)

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structure is suggested by the fact that only a single type of phosphine ligand is present, by the large coupling of the hydride to phosphorus (78 Hz), and by comparison with the structure of $Ta(CCMe_3)(H)(dmpe)_2(ClAlMe_3)$ (dmpe = bis(dimethylphosphino)ethane).[5a] The neopentylidene ligand is highly distorted, as judged by a low value for J_{CH_α} (84 Hz) and ν_{CH_α} (2395 cm^{-1}) and the relatively high-field chemical shift of H_α (1.35 ppm).

Although the spectra of **1** do not change down to −60 °C, the neopentylidene ligand in **1** is likely to be rotating rapidly on the NMR time scale (i.e., H_α is not localized) as found in other complexes such as $Ta(CHCMe_3)(PMe_3)_4Cl$,[11] which contain grossly distorted neopentylidene ligands. $W(CHCMe_3)(H)Cl_3L_2$ is the first example of an alkylidene hydride complex of tungsten(VI).[12]

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(9) Prepared by treating $W(CCMe_3)Cl_3(PMe_3)_3$[8] with C_2Cl_6 in CH_2Cl_2. $[Et_3PCl]Cl$ was filtered off and the residue that remained after removing all volatiles was recrystallized from ether/pentane: yield 85%. δ C_α ($CDCl_3$) = 357 (t, $^2J_{CP}$ = 26 Hz).

(10) Anal. Calcd for $WC_{11}H_{29}Cl_3P_2$: C, 25.73; H, 5.69. Found: C, 26.13; H, 5.95. δ_{C_α} ($CDCl_3$) = 236 (dt, J_{CH} = 84 Hz, $^2J_{CP}$ = 19 Hz, J_{CW} = 87 Hz); δ_{H_α} = 1.35 (dt, $^3J_{HH}$ = 1 Hz, $^3J_{HP}$ = 2 Hz); δ_{WH} = 9.88 (dt, $^3J_{HH}$ = 1 Hz, $^2J_{HP}$ = 78 Hz, J_{HW} = 16 Hz); δ_P = −1.07 (d, $^2J_{PH}$ = 82 Hz, J_{PW} = 142 Hz); ν_{CH_α} = 2395 cm^{-1}, ν_{WH} = 1999 cm^{-1}.

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(12) Related tantalum complexes such as $Ta(CHCMe_3)(H)Cl_2(PMe_3)_3$ have been reported recently.[11]

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$W(CHCMe_3)(H)Cl_3L_2$ reacts with carbon monoxide as shown in eq 2 and with 2 equiv of PMe_3 as shown in eq 3.

$$W(CHCMe_3)(H)Cl_3L_2 + CO \rightarrow W(CHCMe_3)(CO)Cl_2L_2{}^{13} + HCl \quad (2)$$

$$W(CHCMe_3)(H)Cl_3L_2 + 2PMe_3 \rightarrow W(CCMe_3)(H)Cl_2L_3{}^{14} + Me_3PH^+Cl^- \quad (3)$$

$W(CCMe_3)(H)Cl_2L_3$ appears to be analogous with $W(CH)(H)Cl_2L_3$.[7] It reacts with CO to yield $W(CHCMe_3)(CO)Cl_2L_2$ and free PMe_3. NMR studies suggest that the PMe_3 ligands in $W(CHCMe_3)(CO)Cl_2L_2$ are mutually trans and that the neopentylidene ligand is again one of the severely distorted variety ($\delta_{C_\alpha} = 240$, $J_{CH_\alpha} = 73$ Hz). The carbonyl absorption was observed at 1935 cm^{-1} in the IR spectrum.

The structure[15,16] of $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ is shown in Figures 1 and 2. The geometry about the central tungsten(IV) atom may be regarded as intermediate between distorted octahedral and capped octahedral. Within the distorted octahedral description, the trans angles are Cl1–W–C2 = 156.37 (11)°, Cl2–W–C1 = 169.02 (11)°, and P1–W–P2 = 165.46 (3)°, while cis angles range from Cl1–W–C1 = 78.36 (11)° through Cl2–W–C2 = 110.67 (11)°. The α-hydrogen atom of the neopentylidene ligand, H2, lies over the P1···Cl2···C2 face in a capping position (see figure 2). The tungsten–alkylidene distance, W–C2, is 1.859 (4) Å, the C2–H2 distance is 1.053 (36) Å, and the W···H2 distance is only 1.835 (36) Å, indicative of a substantial metal–hydrogen interaction. The W=C2–C3 angle is 168.7 (3)°, while W=C2–H2 = 72.2 (20)° and H2···W–C2 = 33.1 (11)°. The neopentylidene ligand is one of the most distorted observed to date by structural studies (cf. $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(PMe_3)(C_2H_4)$,[5e] where $Ta{=}C_\alpha{-}H_\alpha = 78.1$ (3)°, $Ta{\cdots}H_\alpha = 2.042$ (5) Å, $J_{CH_\alpha} = 74$ Hz). Note that the tungsten(VI) species $W(O)(CHCMe_3)Cl_2(PEt_3)$ has $W{=}C_\alpha = 1.882$ (14) Å and $W{=}C_\alpha{-}C_\beta = 140.6$ (11)°, with no evidence for any substantial $W{\cdots}H_\alpha$ interaction.[4b]

The capped octahedral face is the largest of the eight possible octahedral faces and is defined by the angles Cl2–W–C2 = 110.67 (11)°, P1–W–C2 = 103.69 (11)°, and Cl2–W–P1 = 89.38 (3)°. The octahedral face opposite the capped face is associated with the same essential ligand atoms (Cl, P, C) but smaller interligand angles, viz., Cl1–W–C1 = 78.36 (11)°, Cl1–W–P2 = 82.25 (3)°, and P2–W–C1 = 97.25 (11)°.

$W(CHCMe_3)(H)Cl_3L_2$ and $W(CCMe_3)(H)Cl_2L_3$ also react with ethylene (slowly) to give $W(CHCMe_3)(C_2H_4)Cl_2(PMe_3)_2$.[17] Its ^{13}C NMR spectrum shows that the neopentylidene ligand is similar to that in $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ ($\delta_{C_\alpha} = 237$, $J_{CH_\alpha} = 70$ Hz) and that only one type of ethylene carbon atom is present ($\delta_C = 36$, $J_{CH} = 154$ Hz). Since two sets of ethylene protons are found at 1.85 and 1.74 ppm, the ethylene probably lies along the P–W–P axis in a structure analogous with that found for $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$.

We believe these three neopentylidene complexes are important for several reasons. First, they illustrate what appears to be a trend toward alkylidyne hydride complexes *in the absence of good π-donor ligands*. Since H_α in $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ is interacting substantially with the metal (1.835 (36) Å), the W=C2–C3 angle is large (168.7 (3)°), and the $W{=}C_\alpha$ bond length is short (1.859 (4) Å), one could argue that it is essentially a neopentylidyne hydride complex. This result is consistent with recent results in the chemistry of "reduced" tantalum[5a] and tungsten[18] neopentylidene complexes. Second, carbon monoxide is found to bind to a metal that one could argue is in a fairly high oxidation state and, further, does not react with the alkylidene ligand to form a ketene ligand, a type of reaction that appears common for certain tantalum and niobium alkylidene complexes.[19] Third, in a related vein, an olefin is found to be compatible with a "reduced alkylidene" complex, in keeping with recent results for tantalum[20] and niobium,[21] suggesting that *undistorted* alkylidene ligands, especially in tungsten(VI) oxo and imido complexes, are those characteristic of a system that will metathesize olefins. Fourth, the fact that HCl evolves when $W(CHCMe_3)(H)Cl_3(PMe_3)_2$ is treated with carbon monoxide or ethylene suggests that this may be an important, heretofore unrecognized, means of forming tungsten–carbon multiple bonds.

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Registry No. 1, 80679-42-1; $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$, 80679-43-2; $W(CHCMe_3)(C_2H_4)Cl_2(PMe_3)_2$, 80679-44-3; $W(CCMe_3)Cl_3(PMe_3)_2$, 80679-45-4; $W(CCMe_3)Cl_3(PMe_3)_3$, 80679-46-5.

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(13) Anal. Calcd for $WC_{12}H_{28}Cl_2P_2O$: C, 28.54; H, 5.59. Found: C, 28.50; H, 5.62.

(14) Anal. Calcd for $WC_{14}H_{37}Cl_2P_3$: C, 30.40; H, 6.74. Found: C, 30.81; H, 6.86. δ_{C_α} (C_6D_6) = 285 (q, $^2J_{CP} = 15$ Hz, $J_{CW} = 205$ Hz); δ_{WH} (toluene-d_8) = 3.86 (q, $^2J_{HP} = 73$ Hz, $J_{HW} = 18$ Hz); $\delta_{P_A} \approx -2.3$, $\delta_{P_B} \approx -9.7$, $\delta_{P_C} \approx -20.5$ ($J_{AB} = 46$ Hz, $J_{AC} = 137$ Hz, $J_{BC} = 54$ Hz).

(15) $W(CHCMe_3)(CO)Cl_2(PMe_3)_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 15.460$ (3) Å, $b = 9.795$ (1) Å, $c = 12.923$ (2) Å, $\beta = 90.66$ (1)°, $V = 1956.8$ (5) Å^3, $Z = 4$. Single-crystal X-ray diffraction data (*Mo* Kα radiation) were collected by using a coupled θ–2θ scan technique[16] on a Syntex $P2_1$ diffractometer. A combination of Patterson and difference-Fourier techniques allowed the location of all atoms, including all 28 hydrogen atoms in the molecule. Full-matrix least-squares refinement led to $R_F = 2.6\%$ and $R_{wF} = 2.3\%$ for all 3471 reflections with $3.5° \leq 2\theta \leq 50.0°$ (not one datum rejected).

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(17) In each case the reaction requires 3 days at 30 psi of ethylene to go to completion (solvent = toluene). The reaction cannot be heated as $W(CHCMe_3)(C_2H_4)Cl_2(PMe_3)_2$ begins to decompose above ~50 °C. A signal for H_α is observed at −3.64 ppm at −30 °C. This signal broadens and disappears into the bseline at +35 °C but no new H_α resonance(s) could be found. The signals due to the ethylene protons are not affected. We propose that H_α is still hopping rapidly from one $PClC_\alpha$ face to the other at low temperatures, but at higher temperatures it hops around all four faces in the upper half of the molecule.

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Photoelectron Spectroscopic Measurements of the Relative Charge on Carbyne Fragments Bound to Polynuclear Cobalt Carbonyl Clusters

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Definition of the changes in the internal bonding of an organic admolecule on being bound to a metal surface is the driving force behind much contemporary physical and chemical research.[1] Analogies drawn between organometallic chemistry and organic reactions on surfaces ("surface organometallic chemistry")[2] provide one fruitful avenue of approach in that metal cluster fragments are thought to usefully mimic metal surfaces.[3] This is particularly true insofar as the covalent interaction of a ligand with two or more metals is concerned, and structures of multinuclear transition-metal clusters have been suggested as models for binding sites on actual metal surfaces.[4] Further, transfor-

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