# Tungsten Methylidyne Complexes[1]

Paul R. Sharp, Steven J. Holmes, and Richard R. Schrock*

*Department of Chemistry*
*Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

Melvyn Rowen Churchill* and Harvey J. Wasserman

*Department of Chemistry*
*State University of New York at Buffalo*
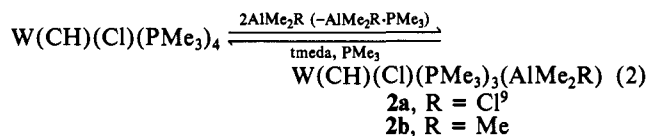*Buffalo, New York 14214*

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Intramolecular α-hydrogen abstraction reactions have been used to make early transition-metal neopentylidene and benzylidene complexes, but they do not work well for making methylene complexes, possibly in part because of the high reactivity of a methylene complex under conditions where it forms.[2] On the other hand, "Lewis acid protected" methylene ligands bound to titanium[3] or tantalum[4] have been prepared under mild conditions by adding $AlMe_3$ to chloride or methyl complexes. We have been looking for examples of this type of reaction in tungsten chemistry. This communication reports our first success in this area.

The reaction between $WCl_2(PMe_3)_4$[5] and 2 equiv of $AlMe_3$ in toluene gives an oil which redissolves over the period of 1 h to give a red-brown solution from which (after addition of tmeda[6a]) orange-yellow $W(CH)(Cl)(PMe_3)_4$ (1)[6b] can be isolated in ~60% yield (eq 1). X-ray structural data[7] suggest that the methylidyne

$$WCl_2(PMe_3)_4 \xrightarrow[\text{2. 2tmeda}]{\text{1. 2AlMe}_3\text{, toluene}} \underset{\textbf{1}}{W(CH)(Cl)(PMe_3)_4} \quad (1)$$
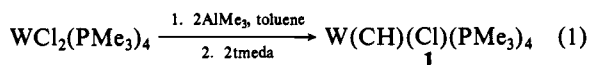
and chloride ligands are trans to one another, but they are disordered. The four $PMe_3$ ligands form a flat tetrahedron like that found in $WMe_2(PMe_3)_4$.[8a] Therefore this compound is related to the Fischer carbyne complexes of the type *trans*-$W(CO)_4$-$(CR)(Cl)$.[8b] To our knowledge this is the only example of a complex which contains a terminal methylidyne ligand. The reaction of $WCl_2(PMe_3)_4$ with 1 equiv of $AlMe_3$ followed by tmeda gave **1** in only low yield.

Before tmeda is added to the reaction mixture we can see several species by ³¹P and ¹³C NMR, among them **1** and two complexes which can be prepared in high yield from **1** by adding $AlMe_3$ or $AlMe_2Cl$ to it (eq 2). Complexes **2a** and **2b** form air- and

$$W(CH)(Cl)(PMe_3)_4 \xrightarrow[\text{tmeda, PMe}_3]{2AlMe_2R\ (-AlMe_2R\cdot PMe_3)} $$
$$W(CH)(Cl)(PMe_3)_3(AlMe_2R) \quad (2)$$
$$\textbf{2a, R = Cl}[9]$$
$$\textbf{2b, R = Me}$$

moisture-sensitive red prisms which react with tmeda in the presence of $PMe_3$ to give tmeda·$AlMe_2R$ and **1** in high yield. Unfortunately, we have not obtained either **2a** or **2b** absolutely pure. A small and variable amount of a similar methylidyne
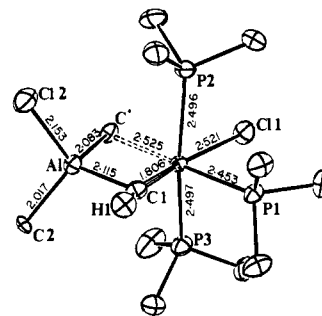
complex is always present in each case, according to ¹³C NMR studies.

The structure of **2a**[10] is a slightly distorted octahedron with *mer*-phosphine ligands and a terminal chloride ligand trans to the methylidyne ligand (Figure 1). The bond between the methylidyne ligand and tungsten must be close to a triple bond [W–C(1) = 1.806 (6) Å] by comparison with the W≡C bond length [1.785 (8) Å] in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$.[12] The methylidyne proton was located. The C(1)–H(1) bond length [0.90 (7) Å] is consistent with the 0.95 Å expected from an X-ray diffraction study.[13] The W–C(1)–H(1) bond angle [164.4 (43)°] is smaller than one would expect [W≡$C_\alpha$–$C_\beta$ = 175.23 (69)° in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$[12]] since aluminum is also bound to C(1) [Al–C(1) = 2.115 (6) Å, W–C(1)–Al = 84.63 (24)°, H(1)–C(1)–Al = 110.9 (43)°[14]]. This interaction must not be a strong one since the Al–C(1) bond is 0.1 Å longer than the Al–C(2) bond. The fact that $\delta C_\alpha$ and $J_{CH_\alpha}$ are similar in **1** and **2a** ($\delta C_\alpha$ = 250 ppm and $J_{CH_\alpha}$ = 134 Hz in **1**; $\delta C_\alpha$ = 230 ppm and $J_{CH_\alpha}$ = 140 Hz in **2a**) and that $AlMe_2R$ can be removed by tmeda to give **1** in the presence of $PMe_3$ are consistent with this postulate.

It is interesting to compare these results with the bonding of lithium to a "neopentylidyne" α-carbon atom in [Ta-$(CH_2CMe_3)_3(CCMe_3)]^-$;[15] Ta≡C = 1.74 Å, Ta≡$C_\alpha$–$C_\beta$ = 165°, and Ta–$C_\alpha$–Li ~ 90°. Each compound could be regarded as a Lewis acid adduct of a metal–carbon triple bond.

A complicating feature of this structure is the identity of the atom labeled C* in Figure 1. The results of occupancy refinement indicate that C* is the composite image of ca. 82% carbon and 18% chlorine. (With this atom input as carbon its refined occupancy was 1.33).[16] We infer from this result that the crystal consists of an isomorphous mixture of 82% $W(CH)(Cl)$-$(PMe_3)_3(AlMe_2Cl)$ and 18% $W(CH)(Cl)(PMe_3)_3(AlMeCl_2)$; i.e., the two constituent molecules are those shown below. **3** is almost certainly the "impurity" in **2a** noted above.

It is most unusual that a methyl group bridges Al and W in **2a** instead of a chloride. The fact that the W–C* bond is so long



**Figure 1.** ORTEP-II drawing (30% ellipsoids) of $W(CH)(Cl)(PMe_3)_3$-$(AlMeClC*)$ where C* = 82% Me and 18% Cl.

(1) Multiple Metal–Carbon Bonds. 20. For part 19, see: Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, in press.

(2) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(3) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

(4) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389–2399.

(5) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430–1431.

(6) (a) tmeda = *N,N,N',N'*-tetramethylethylenediamine. (b) Anal. Calcd for $WC_{13}H_{37}P_4Cl$: C, 29.09; H, 6.94. Found: C, 29.17; H, 7.09. $C_\alpha$ quintet at 250 ppm ($J_{CH}$ = 134 Hz, $^2J_{CP}$ = 10.6 Hz, $J_{CW}$ = 200 Hz); $H_\alpha$ quintet at 6.75 ppm ($^3J_{HP}$ = 4 Hz, $^2J_{HW}$ = 80 Hz).

(7) To be reported in detail separately by M.R.C. and H.J.W.

(8) (a) Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 926–927. (b) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59–81.

(9) $C_\alpha$ at 230 ppm (ddt, $J_{CH}$ = 140 Hz, $^2J_{CP}$ = 21 and 7 Hz); $H_\alpha$ at 6.5 ppm ($^3J_{HP}$ = 10 and 2 Hz, $J_{HW}$ = 80 Hz). Anal. Calcd for $WC_{12}H_{34}Cl_2P_3Al$: C, 26.05; H, 6.15. Found: C, 26.39; H, 6.20.

(10) The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a$ = 9.669 (2), $b$ = 11.987 (3), $c$ = 19.971 (5) Å; $\beta$ = 103.06 (2)°; $V$ = 2255 Å³; $Z$ = 4. Single-crystal X-ray diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer by using a coupled $\theta$(counter)–$2\theta$(crystal) scan technique[11] and Mo $K\alpha$ radiation. The structure was solved by a combination of Patterson and difference-Fourier techniques and the structure was refined to $R_F$ = 3.1% and $R_{wF}$ = 3.7% for those 3719 independent data with $|F_o| > \sigma(|F_o|)$ and $4.0 < 2\theta < 50.0°$. All nonhydrogen atoms were accurately located and the methylidyne hydrogen was also located directly. Anisotropic thermal parameters were used for all nonhydrogen atoms.

(11) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(12) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454–2458.

(13) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

(14) Other angles are normal; C(1)–Al–C(2) = 111.3 (2)°, C(1)–Al–Cl(2) = 110.8 (2)°, C(1)–Al–C* = 105.9 (2)°, C(2)–Al–Cl(2) = 108.6 (2)°, C(2)–Al–C* = 113.1 (2)°, and Cl(2)–Al–C* = 107.1 (2)°.

(15) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935.

(16) Our method of computing these occupancies is as follows: let the occupancy of chlorine be $x$; then that of carbon is $1 - x$, and $(1.33)(Z_C) = x(Z_{Cl}) + (1 - x)(Z_C)$. With $Z_C$ = 6 and $Z_{Cl}$ = 17, $x$ = 0.18.
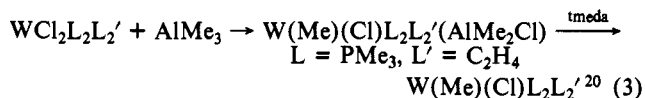
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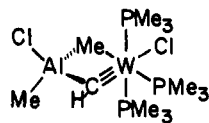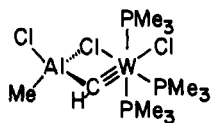
**2a**                    **3**

[2.525 (5) Å] is consistent with the AlMe₂Cl being removed readily by tmeda. Although more data are required, it is possible that the W–C* bond is long because of a complex interaction of the bridging methyl group with tungsten, e.g., AlCH₂···H···W [cf. Os₃(CO)₁₀(CH₃)(H)].[17]

We believe the first step in formation of **1** is alkylation to give W(Me)(Cl)(PMe₃)₄(AlMe₂Cl), since the analogous reaction of WCl₂(PMe₃)₂(C₂H₄)₂[18] with AlMe₃ proceeds as shown in eq 3.

$$WCl_2L_2L_2' + AlMe_3 \rightarrow W(Me)(Cl)L_2L_2'(AlMe_2Cl) \xrightarrow{tmeda}$$
$$L = PMe_3, L' = C_2H_4$$
$$W(Me)(Cl)L_2L_2'^{20} \quad (3)$$

One of the major puzzles, however, is how the metal is "oxidized". We do know that 0.9–1.2 equiv of a gas forms which preliminary results suggest is about an 8:2 mixture of methane and hydrogen. The amount of hydrogen formed is too little to account for the oxidation of a W—CH₃ complex to a W≡CH complex by loss of H₂, an unprecedented and otherwise attractive explanation.

(17) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726–7727.

(18) Green WCl₂(PMe₃)₂(C₂H₄)₂ was prepared from WCl₂(PMe₃)₄ and C₂H₄ (30 psi) at 70 °C in toluene.[19] Anal. Calcd for WC₁₀H₂₆Cl₂P₂: C, 25.94; H, 5.66. Found: C, 25.71; H, 5.58. This complex will be discussed fully elsewhere.

(19) Sharp, P. R., Ph.D. Thesis, MIT, 1980.

(20) Anal. Calcd for WC₁₁H₂₉ClP₂: C, 29.85; H, 6.60. Found: C, 29.73; H, 6.43.[19] Black W(Me)(Cl)(PMe₃)₂(C₂H₄) will be described fully elsewhere.

## Preparation of Fe₃(μ₂-H)₃(CO)₉(μ₃-CCH₃) from Fe(CO)₅
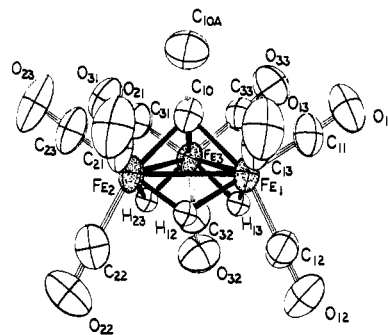
Kwai Sam Wong and Thomas P. Fehlner*

*Department of Chemistry, University of Notre Dame*
*Notre Dame, Indiana 46556*

We have previously reported the preparation of B₃H₇Fe₂(CO)₆ and B₂H₆Fe₂(CO)₆ from B₅H₉, Fe(CO)₅, and LiAlH₄.[1] Recently we discovered that if the above synthesis is carried out with Vitride (sodium dihydrobis(2-methoxyethoxy)aluminate: 70% solution in toluene) instead of LiAlH₄, the reaction produces not only ferraboranes but also novel alkylidynetriiron nonacarbonyl trihydride complexes. The methyl derivative, Fe₃(μ₂-H)₃(CO)₉-(μ₃-CCH₃) (**I**), has been isolated and structurally characterized.

Reaction of Fe(CO)₅, B₅H₉, and Vitride (about 2:1:2 molar ratio in toluene) was carried out at 0 °C for 1 h, and then at room temperature for several hours. After treatment with 1 mol of HCl (gas) per mol of Vitride added in several portions, the ferraboranes and the alkylidynetriiron clusteres were separated by trap-to-trap distillation at −15 and −5 °C, respectively. The optimum yield of **I** is about 10% and is sensitive to reaction temperature and the procedure of acidification. Boranes are required for the production of **I**. The compound is volatile enough to handle in a standard

(1) Andersen, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 4606. Andersen, E. L.; Haller, K. J.; Fehlner, T. P. *Ibid.* **1979**, *101*, 4390.



**Figure 1.** Structure of Fe₃(μ₂-H)₃(CO)₉(μ₃-CCH₃). Atoms are represented by 90% elipsoids (except hydrogens, 50%) and methyl hydrogens are omitted for clarity.

vacuum line and is readily soluble in a wide range of organic solvents. It is a brown solid at room temperature and decomposes slowly in air.

The new compound has been partially characterized spectroscopically. The parent ion in the mass spectrum fragments by the sequential loss of nine CO molecules. The mass spectrometric results also suggest the presence of other triiron analogues, namely Fe₃(μ₂-H)₃(CO)₉(μ₃-CH) (**II**) and Fe₃(μ₂-H)₃(CO)₉(μ₃CC₂H₅) (**III**) in the product mixture. The 100-MHz ¹H FT NMR spectrum of **I** in CD₃C₆D₅ exhibits two singlets at δ 4.33 and −23.55 (area ratio 1:1), showing that the molecule contains equal numbers of metal bound and carbon bound hydrogens. The 25.2-MHz ¹³C FT NMR spectrum of **I** consists of singlets at 206.4 and 46.2 ppm downfield from Me₄Si assigned to CO and methyl carbons, respectively.[2] The proton NMR also suggests the presence of **II** (δ −24.27).[3] Unambiguous identification of **I** resulted from an X-ray crystallographic structure determination.

A crystal of 0.3 × 0.4 × 0.7 mm³ was formed from the gas phase by slow cooling of a pure sample. The crystal was mounted in a capillary under nitrogen and was determined as triclinic (space group P1̄) with a = 7.979 (2), b = 9.478 (3), c = 12.714 Å (4); α = 93.45 (3), β = 106.94 (3), γ = 60.79 (3)°. If Z = 2 is assumed, ρ_calcd = 1.87 g cm⁻³. The iron atoms were located by direct methods using the MULTAN package.[4] The rest of the nonhydrogen atoms were located by Fourier techniques, and the model was refined to convergence, assuming the atoms to vibrate anisotropically. The bridging hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms. Two of the three methyl hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms, while the calculated position of the third methyl hydrogen atom was included in the model but not refined. Several cycles of full-matrix least-squares refinement (based on 2561 unique observed reflections with F₀ > 3σF₀) resulted in convergence with a current R = 0.077.

The structure of **I** with the atoms represented as 90% ellipsoids is shown in Figure 1 (hydrogens represented as 50% ellipsoids). The iron atoms form an equilateral triangular framework with an average Fe–Fe distance of 2.618 Å. The three iron atoms are equivalent, each being coordinated to three terminal carbonyl groups, two bridging hydrogens and one apical carbon. Each pair of iron atoms, the bridging hydrogen atom, and the alkylidyne carbon atom are roughly in the same plane. The Fe–H–Fe angle is about 104° while the Fe–C_apical–Fe angle is about 85°. The

(2) These are similar to the absorptions observed for the ruthenium analogue, H₃Ru₃(CO)₉CCH₃. As is the case with H₃Ru₃(CO)₉CCH₃, as well as HRu₃(CO)₉C₆H₉, a resonance for the quaternary carbon was not observed. Canty, A. J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1331.

(3) For the ruthenium analogues the high field metal bound proton resonances are δ = −17.45 (C–CH₃) and δ = −17.52 (CH). Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 477.

(4) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect A* **1971**, *27*, 368. Other programs used as well as a description of data collection and data reduction methods can be found in: Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84.