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Some Reactions of Tungsten Methylidyne Complexes and the Crystal Structure of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$[1]

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$W(CH)(PMe_3)_4Cl$ reacts with Me_3SiX (X = I or CF_3SO_3) to give $W(CH)(PMe_3)_4X$. $W(CH)(PMe_3)_4(BH_4)$ can then be prepared from $W(CH)(PMe_3)_4(CF_3SO_3)$ and $NaBH_4$. Both $W(CH)(PMe_3)_4I$ and $W(CH)(PMe_3)_4(CF_3SO_3)$ can be protonated by triflic acid to give "methylene" or, more accurately, face-protonated methylidyne complexes. $W(CH)(PMe_3)_4Cl$ reacts with $AlMe_2R$ (R = Cl or Me) to give $W(CH)(PMe_3)_3(Cl)(AlMe_2R)$ complexes. In the presence of ethylene the methylidyne proton is lost and a "dialuminated" methylidyne complex, $W(CAl_2Me_4Cl)(PMe_3)_2(CH_3)(C_2H_4)$, is formed. In the presence of CO the reaction between $W(CH)(PMe_3)_4Cl$ and $AlCl_3$ yields a complex in which the methylidyne ligand has been coupled to CO, $W(HCCOAlCl_3)(CO)(PMe_3)_3Cl$. In contrast, $W(CH)(H)(PMe_3)_3Cl_2$ reacts with CO to yield $W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$. A similar species can be prepared by reacting $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$ with CO. Attempts to oxidize $W(CH)(PMe_3)_4Cl$ to $W(CH)(PMe_3)_3Cl_3$ yielded a "phosphinomethylidyne" complex, $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. This complex forms monoclinic crystals ($P2_1/c$ [No. 14]) in which a = 9.773 (4) Å, b = 24.797 (14) Å, c = 12.633 (7) Å, β = 92.85 (4)°, and Z = 2. The molecule contains a planar $P_2W(\mu\text{-}Cl)_2WP_2$ framework with mutually transoid $CPMe_3$ ligands. The tungsten–carbon bond distance of 1.83 (3) Å is comparable to other tungsten–carbon "triple" bonds, and the W–C–P bond angle is large (174.0 (19)°).

Introduction

Two years ago we discovered that $W(PMe_3)_4Cl_2$ reacts with $AlMe_3$ to produce *trans*-$W(CH)(PMe_3)_4Cl$, the only example of a complex containing a terminally bound methylidyne ligand.[3] So far we have shown that $W(CH)(PMe_3)_4Cl$ reacts with $AlMe_xCl_{3-x}$ reagents to form adducts of the type $W(CH)(AlMe_xCl_{3-x})(PMe_3)_3Cl$,[3] that it can be protonated readily to give highly distorted or T-shaped "methylene" complexes,[4] and that the methylidyne ligand couples with carbon monoxide in the presence of $AlCl_3$.[5] In this paper we provide previously unreported details of some of these, and related, reactions, along with several new and unexpected reactions in which the methylidyne proton is replaced by an aluminum or a phosphorus substituent.

Results and Discussion

Simple Derivatives of $W(CH)(PMe_3)_4Cl$. We were surprised to find that $W(CH)(PMe_3)_4Cl$ is relatively inert toward nucleophilic substitution of the chloride ligand. For example, it does not react at 25 °C in 1 day with LiMe in ether, $LiCH_2CMe_3$ in toluene, $LiBEt_3H$ in THF, or $LiOCMe_3$ in toluene. Starting material is recovered in high yield in each case. We also know that PMe_3 is displaced only relatively slowly by dmpe.[4b] Therefore, although $W(CH)(PMe_3)_4Cl$ is a crowded molecule,[6] it must not readily lose PMe_3 to form a five-coordinate 16-electron intermediate; formation of a seven-coordinate intermediate in an associative reaction is relatively unlikely for electronic (20 e) as well as steric reasons.

Table I. ^1H and ^{13}C NMR Data for the Methylidyne Ligand in Complexes of Tungsten

compound	^1H NMR chem shift, ppm	^1H NMR $^2J_{HW}$, Hz	^{13}C NMR[a] chem shift, ppm	^{13}C NMR[a] J_{CH}, Hz
$W(CH)(PMe_3)_4Cl$	6.75	80.1	250	134
$W(CH)(PMe_3)_4I$	6.45	83.5	248.7	136
$W(CH)(PMe_3)_4(CF_3SO_3)$	6.54	84.2	264.9	150
$W(CH)(PMe_3)_4(BH_4)$	7.39	79.6	259.5	138.7
$W(CHAlMe_3)(PMe_3)_3Cl$	6.55	83.5	229.6	129.4
$W(CHAlMe_2Cl)(PMe_3)_3Cl$	6.64	81.6	229.9	144.0

[a] Compare these data with the characteristic chemical shift for the methylene carbon atom (219 ppm) and J_{CH} (121 Hz) in $[W(CH_2)(PMe_3)_4I][CF_3SO_3]$.

In contrast, the chloride ligand in $W(CH)(PMe_3)_4Cl$ can be replaced smoothly by using Me_3SiX (X = I or OTf). A third, more unusual derivative can then be prepared from the triflate complex (eq 1). The ^1H and ^{13}C NMR spectra

$$W(CH)(PMe_3)_4(OTf) + NaBH_4 \rightarrow NaOTf + W(CH)(PMe_3)_4(BH_4) \quad (1)$$

of the three (Table I and Experimental Section) suggest that they are all analogous to $W(CH)(PMe_3)_4Cl$. The IR spectrum of $W(CH)(PMe_3)_4(BH_4)$ shows two B–H modes at 2320 and 2050 cm^{-1}, and the ^1H NMR spectrum shows a 1:1:1:1 quartet, consistent with a bidentate mode of coordination and rapid exchange of the terminal and bridging BH protons.[7] We see no evidence that the BH_4 protons exchange with the methylidyne proton at a rate rapid enough to be observable by NMR. We note that a BD_3CN derivative has also been prepared in which no exchange of deuterium with the methylidyne proton was observed on the chemical time scale.[4b] We suspect that the structure of $W(CH)(PMe_3)_4(BH_4)$ is similar to that of *trans*-$Mo(H)(BH_4)(PMe_3)_4$[8] in which the BH_4^- ligand adopts a bi-

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[1] Multiple Metal–Carbon Bonds 33. For part 32 see: Edwards, D. S.; Biondi, L. V.; Ziller, Z. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

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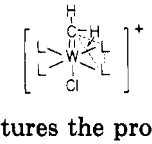
dentate mode of coordination to Mo.

Protonation of $W(CH)(PMe_3)_4I$ and $W(CH)(PMe_3)_4(OTf)$. We have discussed the protonation of $W(CH)(PMe_3)_4Cl$ by triflic acid elsewhere.[4b] On the basis of extensive ^1H and ^{13}C NMR studies we concluded that the "methylene" complex $[W(CH_2)(PMe_3)_4Cl][OTf]$ was actually best described as a face-protonated methylidyne complex, viz.



At ambient temperatures the proton on the WCP_2 face exchanges rapidly with the methylidyne-like proton, a process that results in an average signal of area two at ~-0.16 ppm with $J_{HW} \approx 50$ Hz in the ^1H NMR spectrum and a triplet at ~220 ppm with $J_{CH} \approx 120$ Hz in the ^{13}C NMR spectrum. Addition of triflic acid to $W(CH)(PMe_3)_4I$ appears to yield an analogous species. In "$[W(CH_2)(PMe_3)_4I][OTf]$" the "methylene" protons can be observed at -0.80 ppm as a quintet ($^3J_{HP} = 0.9$ Hz can be resolved) with $^2J_{HW} = 53$ Hz. In the ^{13}C NMR spectrum a triplet signal for the carbon atom is observed at 219 ppm with $J_{CH} = 121$ Hz. When a sample of $[W(CH_2)(PMe_3)_4I][OTf]$ is cooled, the signal at -0.80 ppm in the ^1H NMR spectrum broadens and disappears into the base line at 180 K. At 153 K a broad peak observed at -9.0 ppm can be assigned to the proton on the WCP_2 face. The signal for the methylidyne-like proton is probably obscured by the solvent, as in the case of $[W(CH_2)(PMe_3)_4Cl][OTf]$.[4b]

One of the reasons for preparing other derivatives of $[W(CH_2)(PMe_3)_4Cl][OTf]$ was to obtain ordered crystals (cf. $W(CH)(PMe_3)_4Cl$[6]) large enough for neutron diffraction studies. $[W(CH_2)(PMe_3)_4I][OTf]$ does form large cubic crystals, but only satisfactory X-ray data could be obtained.[9] The molecule has a trans octahedral structure. The tungsten-carbon bond length is 1.83 (2) Å, similar to that (1.86 Å) in $W(CHCMe_3)(PMe_3)_2(CO)Cl_2$,[10,11] another d^2 complex containing a high distorted neopentylidene ligand in which the W=C—H angle is 72° and the $W{=}C_\alpha C_\beta$ angle is 169°. In fact, 1.83 Å is (within experimental error) a typical value for a tungsten-carbon *triple* bond, e.g., 1.81 Å in $W(CHAlMe_2Cl)(PMe_3)_3Cl$[6] (see later). Therefore, we feel confident that our original proposal[4b] concerning the structure of the distorted methylene complex $[W(CH_2)(PMe_3)_4Cl][OTf]$ is correct. It should be noted that the reason why the molecule is not an authentic alkylidyne hydride complex analogous to $[W(CH)(H)(dmpe)_2Cl]^+$[4b] or $Ta(CCMe_3)(H)(dmpe)_2(ClAlMe_3)$[12] is primarily steric; the four PMe_3 ligands cannot lie in a pentagonal plane (along with the hydride ligand) in hypothetical pentagonal-bipyramidal $[W(CH)(H)(PMe_3)_4Cl][OTf]$. Even *four* PMe_3 ligands in $W(CH)(PMe_3)_4Cl$,[6] $[W(CH_2)(PMe_3)_4I][OTf]$,[9] and $W(CMe)(PMe_3)_4(Me)$[13] must pucker in and out of the WP_4 plane in order to avoid adverse steric interactions.

The addition of triflic acid to $W(CH)(PMe_3)_4(OTf)$ produces orange, crystalline $[W(CH_2)(PMe_3)_4(OTf)][OTf]$ in high yield. In dichloromethane at 280 K (where it decomposes only slowly; see below) a quintet is observed in the ^1H NMR spectrum at 0.06 ppm with $^3J_{HP} = 2$ Hz and $^2J_{HW} = 57$ Hz. At 160 K a peak at -8.47 ppm can be ascribed to the proton capping the WCP_2 face in a distorted methylene complex. These data, along with the absence of any peak attributable to a metal-hydride mode in the IR spectrum, suggest that this molecule is analogous to the better characterized $[W(CH_2)(PMe_3)_4X]^+$ species (X = Cl, I). However, it is worth noting that $[W(CH_2)(PMe_3)_4(OTf)]^+$ appears to be more easily deprotonated. For example, it rapidly decomposes in dichloromethane at 25 °C to give a 1:1 mixture of $[Me_3PH]^+$ and an unidentified phosphorus-containing species (by ^{31}P NMR); the $[W(CH_2)(PMe_3)_4X]^+$ species (X = Cl, I) do not. It also reacts with $NaBH_4$ to give $W(CH)(PMe_3)_4(OTf)$ while $[W(CH_2)(PMe_3)_4Cl]^+$ reacts with $NaBH_4$ (4 equiv) in THF to give $WH_4(PMe_3)_4$ (identified by IR and NMR[13]) in ca. 40% yield. Finally, it alone reacts with ethylene to give $[Me_3PH][OTf]$ and, in low yield (~15%), a complex that we propose is $W(CH)(C_2H_4)(PMe_3)_3(OTf)$ on the basis of a comparison of its NMR spectra with those of $W(CAl_2Me_4Cl)(C_2H_4)(PMe_3)_2(CH_3)$ (see next section). Unfortunately, $W(CH)(C_2H_4)(PMe_3)_3(OTf)$ could not be obtained free of minor impurities and so could not be fully characterized. We suspect that the triflate ion is only loosely, if at all, associated with the cation, on the basis of the complex's low solubility in hydrocarbons.

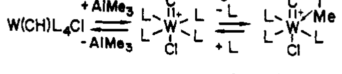
Complexes Formed in the Presence of Aluminum Reagents. We have already noted in preliminary communication[3] that aluminum reagents (2 equiv of $AlMe_3$ or $AlMe_2Cl$) react with $W(CH)(PMe_3)_4Cl$ to yield adducts (eq 2). $W(CH)(PMe_3)_4Cl$ is formed again upon adding excess

$$W(CH)(PMe_3)_4Cl \xrightarrow[-AlMe_2R\cdot PMe_3]{+2AlMe_2R} W(CH)(PMe_3)_3(Cl)(AlMe_2R) \quad (2)$$

$$R = Cl \text{ or } Me$$

PMe_3 (or one PMe_3 plus TMEDA) to $W(CH)(PMe_3)_3(Cl)(AlMe_2R)$. The surprising features of the structure[6] of $W(CH)(PMe_3)_3(Cl)(AlMe_2Cl)$ are, first, that $AlMe_2Cl$ is coordinated to the methylidyne ligand rather than the chloride ligand and, second, that the methylidyne ligand appears to be affected so little as a result; i.e., the W≡C bond length is still relatively short (1.81 Å) and the W≡C—H angle large (164 (4)°). ^1H and ^{13}C NMR data (Table I) suggest also that the methylidyne ligand has changed little. Only the chemical shift of the methylidyne carbon atom (~230 ppm) is significantly different from that of related complexes (~250–260 ppm). A full discussion of the structure can be found elsewhere.[6]

As far as the mechanism of forming $W(CH)(PMe_3)_3(Cl)(AlMe_2R)$ is concerned, it is reasonable to expect the aluminum reagent to attack the methylidyne ligand directly (e.g., eq 3). Only when L (PMe_3) is removed by a second equivalent of $AlMe_3$ is the reaction displaced all the way to the right.



(3)

In the presence of ethylene $W(CH)(PMe_3)_4Cl$ reacts with $AlMe_3$ (3 equiv) to give a radically different product; the methylidyne proton is lost (presumably to form methane) and a "dialuminated" methylidyne complex is formed (eq 4). We knew from the ^{13}C NMR spectrum that the methylidyne ligand had been deprotonated (a singlet for C_α at 308 ppm), but there were obviously many possible configurations of the remaining ligands, none of them with

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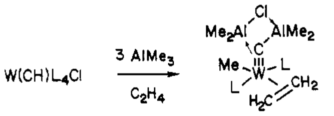


(4)

much, if any, precedent. An X-ray structural study[14] elucidated the structure shown in eq 4. A detailed discussion of the structure will not be repeated here. We note only that the "W≡C" bond length (1.813 (5) Å) is within the range of known tungsten–carbon triple bonds and the molecule therefore may be regarded as an $AlMe_2Cl$ adduct of the hypothetical "aluminomethylidyne" complex $W(CAlMe_2)(PMe_3)_2(CH_3)(C_2H_4)$.

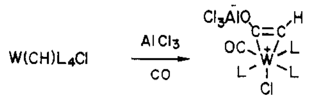
We can be fairly certain that coordination of ethylene to tungsten is not the last in the series of steps leading to $W(CAl_2Me_4Cl)(PMe_3)_2(CH_3)(C_2H_4)$. We speculate that $W(CH)(PMe_3)_3(Cl)(AlMe_3)$ (eq 3) is formed first and that ethylene then replaces one of the three PMe_3 ligands, possibly with the aid of the additional equivalent of $AlMe_3$ to remove it as $Me_3Al{\cdot}PMe_3$ (eq 5). One can believe that

$$\mathrm{W(CH)L_3(Cl)(AlMe_3)} \xrightarrow[-\mathrm{Me_3PAlMe_3}]{\mathrm{AlMe_3 + C_2H_4}} \mathrm{W(CH)L_2(C_2H_4)(Cl)(AlMe_3)} \quad (5)$$

substituting PMe_3, a good base, with ethylene, a better π acid, would enhance the acidity of the original methylidyne proton enough for it to react with a methyl group to yield methane. Where this methyl group comes from at that point (W or Al) is unclear. It is perhaps relevant that ethylene (or carbon monoxide) will react with $W(CHCMe_3)(H)(PMe_3)_2Cl_3$ to give $W(CHCMe_3)(PMe_3)_2Cl_2L$ ($L = C_2H_4$ or CO) and HCl.[10] Formation of multiple metal–carbon bonds by deprotonation or dehydrohalogenation of alkyl or alkylidene complexes is now a common feature of the chemistry of high oxidation state alkylidene or alkylidyne complexes.[15] Therefore, invoking deprotonation here is reasonable, even though details are lacking.

One aspect of coordination of ethylene to a d^2 tungsten center that may be relatively important, in light of the above discussion, is the extent to which ethylene is reduced, as evidenced by the fairly long bond length (1.409 (11) Å) (cf. a C–C bond of 1.477 (4) Å in $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$[16]). Tungsten is in effect oxidized from IV to VI upon displacement of PMe_3 by C_2H_4. The fact that the ethylene ligand does not lie in the same plane as the W≡C bond is expected, as in this manner the two ligands employ orthogonal π orbitals on the metal for forming metal–ligand π bonds. Similar orthogonal bonding patterns have been noted in many other systems.[17–20]

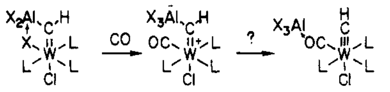
In the presence of CO the reaction between $W(CH)(PMe_3)_4Cl$ and $AlCl_3$ takes a significantly different course (eq 6). In this case CO couples with the methylidyne



(6)

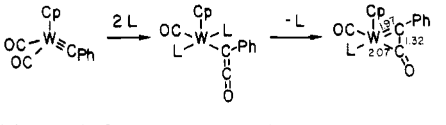
ligand to produce what one could call an alkyne or metallacyclopropene complex, as revealed by an X-ray structural study (C–C bond length = 1.316 Å).[21] The ^{13}C NMR spectrum shows a peak at 194 ppm with $J_{CH} = 202$ Hz and $J_{CP} = 22$ Hz which we ascribe to what was previously the methylidyne carbon atom. Signals for the carbon atoms belonging to the 2 equiv of added CO are found at 226 and 215 ppm. Only one of them (at 215 ppm) is coupled significantly to phosphorus ($J_{CP} \approx 35$ Hz); we ascribe this signal to the carbon atom in the CO trans to one of the three phosphine ligands. In the absence of $AlCl_3$, CO reacts with $W(CH)(PMe_3)_4Cl$ slowly, and only mixtures of unidentifiable products are formed.

In considering a mechanism of forming $W(HCCOAlCl_3)(CO)(PMe_3)_3Cl$ we must consider the possibility that the $AlCl_3$ activates either the methylidyne ligand or the CO ligand toward the coupling reaction (eq 7). However, there is precedent in the literature for



(7)

coupling of a carbyne ligand with CO in the absence of aluminum reagents (eq 8; $L = PMe_3$).[22] Therefore, $AlCl_3$ need not be involved directly in the coupling reaction. Its primary role may simply be to labilize one of the PMe_3 ligands in $W(CH)(PMe_3)_4Cl$ or to stabilize the product of the coupling reaction.



(8)

$W(CH)(PMe_3)_4Cl$ reacts with $AlMe_3$ in the presence of carbon monoxide to give a product analogous to that described above, i.e., $W(CHCOAlMe_3)(PMe_3)_3(CO)Cl$, according to elemental analysis and NMR studies. There is no NMR evidence that a methyl group has replaced the chloride on tungsten. A product labeled with ^{13}CO was prepared also. Its ^{13}C NMR spectrum was entirely consistent with the proposed structure.

Formation of Methylenephosphorane Complexes. An interesting question one can ask about alkylidyne hydride complexes[4b] is under what circumstances will the outcome of a reaction be more easily rationalized as arising from the tautomeric alkylidene form of the complex? For example, we discovered that $W(CCMe_3)(H)(PMe_3)_3Cl_2$ reacts with CO to give $W(CHCMe_3)(PMe_3)_2(CO)Cl_2$.[10] Therefore, we were interested in whether the analogous methylidyne hydride complex $W(CH)(H)(PMe_3)_3Cl_2$[4b] would react similarly or whether the methylidyne ligand couples with CO as above. The answer is neither (eq 9).

$$\mathrm{W(CH)(H)(PMe_3)_3Cl_2} + 30\ \mathrm{psi\ CO} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{PhCl}} \underset{\sim 50\%}{\mathrm{W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2}} \quad (9)$$

Unfortunately, this methylenephosphorane complex is unstable in the solid state; it could be characterized only by NMR comparison with its relative below. In the ^{13}C NMR spectrum two CO signals are found at 273.5 and 237.5 ppm and the signal for the ylide carbon atom (a triplet of triplets) is found at 3.5 ppm ($J_{CP} = 29$ Hz, $J_{CH} \approx 125$ Hz). Since this complex does not conduct in dichloromethane to any significant extent, we assume it is a seven-coordinate molecule with a structure related to that

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of [W(CH_2PMe_3)(PMe_3)$_3$(CO)$_2$Cl][OTf] below. We propose that CO first attacks the methylene complex that is in equilibrium[4b] with W(CH)(H)(PMe_3)$_3$$Cl_2$ to give W(CH_2)(PMe_3)$_3$(CO)Cl_2. The Me_3PCH_2 ligand could be formed intramolecularly at this stage or possibly intermolecularly after displacement of another PMe_3 ligand by CO.

A relatively straightforward example of formation of a Me_3PCH_2 complex is shown in eq 10. This product is

$$[\mathrm{W(CH_2)(PMe_3)_4Cl}][\mathrm{OTf}] + 30\ \mathrm{psi\ CO} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl}][\mathrm{OTf}] \quad (10)$$

similar to W(CH_2PMe_3)(PMe_3)$_2$(CO)$_2$$Cl_2$ spectroscopically (see Experimental Section). An X-ray structural study[23] showed [W(CH_2PMe_3)(PMe_3)$_3$(CO)$_2$Cl][OTf] to be approximately a capped trigonal prism with the methylene of the terminally bound Me_3PCH_2 ligand capping a P_2(CO)Cl face. The bond length of 2.305 Å for the ylide tungsten–carbon bond and the WCP bond angle of 126.4° for the WCH_2P functionality are indicative of a W–C single bond (or a dative interaction). Therefore, in the reaction shown in eq 10 W(IV) is reduced to W(II). It is interesting to note that [W(CH_2)(PMe_3)$_4$Cl][OTf] is stable in the presence of PMe_3. We believe steric factors must play an important role in determining whether a Me_3PCH_2 ligand can form in a given situation. Electronic considerations are perhaps *not* as important as commonly assumed. For example, W(O)(CH_2)(PEt_3)$_2$$Cl_2$, in which the methylene ligand would be thought to be more nucleophilic than electrophilic, reacts with ethylene to form (CH_2PEt_3)(C_2H_4)(PEt_3)Cl_2.[24]

Preparation of Phosphinomethylidyne Complexes. Since we had been able to prepare neopentylidyne complexes of the type W($CCMe_3$)Cl_3(PMe_3)$_x$ (x = 1–3),[25] we became interested in knowing whether one or more of the analogous methylidyne complexes could be prepared by oxidizing W(IV) to W(VI) (eq 11). Initial experiments

$$\mathrm{W(CH)L_4Cl} \xrightarrow[-\mathrm{L}]{\mathrm{Cl_2}} \mathrm{W(CH)L_3Cl_3} \quad (11)$$

involving chlorine did not seem promising. Therefore we turned to the relatively mild chlorinating agent, hexachloroethane. Aluminum trichloride was again employed to remove the first PMe_3 ligand. Typically the reaction is still not clean but we could at least isolate a product in ~17% yield (eq 12; L = PMe_3). It was immediately

$$\mathrm{W(CH)L_4Cl} + \mathrm{AlCl_3} + \mathrm{C_2Cl_6} \rightarrow 0.5[\mathrm{W_2(CPMe_3)_2L_4Cl_4}][\mathrm{AlCl_4}]_2 \quad (12)$$

obvious from the ^{13}C NMR spectrum that the methylidyne proton was missing. However, we assumed initially, on the basis of earlier results, that some type of aluminomethylidyne complex was formed, especially since the carbon atom giving rise to the low-field signal (242 ppm) was not obviously coupled to phosphorus. However, it was ^{27}Al NMR studies that first suggested to us that this was not the case.

Table II. ^{27}Al NMR Data for Representative Aluminum Compounds[26] and for Selected Tungsten Complexes

compound	chem shift, ppm	half-height peak width, Hz	solv
$AlCl_4^-$	102.4	15	CH_2Cl_2
$AlI_2Cl_2^-$	59.4	57	CH_2Cl_2
Al_2Cl_6	91.0	300	$PhCH_3$
Al_2Me_6	156	450	Neat
[W_2($CPMe_3$)$_2$(PMe_3)$_4$$Cl_4$][$AlCl_4$]$_2$	102.5	10	CH_3CN
W($CHAlMe_2Cl$)(PMe_3)$_3$Cl	151	2500	$PhCH_3$
W(CAl_2Me_4Cl)(PMe_3)$_2$(CH_3)(C_2H_4)	151	2500	$PhCH_3$

Although ^{27}Al is a quadrupolar nucleus (S = $^5/_2$), a relatively sharp signal can be observed when the symmetry about the metal is high (T_d or O_h).[26] For example, the signal for $Al(H_2O)_6^{3+}$, the chemical shift standard for ^{27}Al NMR, has a line width of ~3 Hz. Other aluminum compounds of high or relatively high symmetry also give rise to relatively narrow peaks (e.g., $AlCl_4^-$, ~15 Hz at 102 ppm in CH_2Cl_2; Table II). However, even the signal for Al_2Me_6 is fairly broad (~450 Hz). Very broad signals could be observed for the aluminum atom(s) in W($CHAlMe_2Cl$)(PMe_3)$_3$Cl and W(CAl_2Me_4Cl)(PMe_3)$_2$(CH_3)(C_2H_4), characteristic of environments of low symmetry. In contrast, the ^{27}Al NMR spectrum of [W_2($CPMe_3$)$_2$(PMe_3)$_4$$Cl_4$][$AlCl_4$]$_2$ in CH_3CN showed a narrow peak (~10 Hz) at a position characteristic of $AlCl_4^-$ (Table II). Therefore we were puzzled as to what type of "carbide" complex we had prepared.

After the X-ray structural results had been obtained (see next section) we designed some hydrolysis experiments that we hoped would be consistent with what had been shown to be a phosphinomethylidyne complex. [W_2($CPMe_3$)$_2$(PMe_3)$_4$$Cl_4$][$AlCl_4$]$_2$ can be hydrolyzed readily by aqueous HCl in 1 h at 25 °C. Two water-soluble phosphorus compounds are produced in a ratio of 2:1 (by ^{31}P NMR). That giving rise to the peak of area two was shown to be Me_3PHCl by addition of authentic Me_3PHCl to the sample; the other product is unknown. After the solution was heated for 1 week at 80 °C, the unknown product was quantitatively converted into what by ^{31}P NMR was shown most likely to be $Me_4P^+Cl^-$ (by addition of $Me_4P^+Cl^-$ to the sample).

Needless to say, we hesitate to write any mechanism of forming this unusual species, especially also since the yield is low, the fate of the methylidyne proton is unknown, and the metal has, in fact, been oxidized to what is most accurately called W(V).

X-ray Structure of [W_2($CPMe_3$)$_2$(PMe_3)$_4$$Cl_4$][$AlCl_4$]$_2$. The X-ray results are of limited accuracy due to severe disorder of the $AlCl_4^-$ ions (see Experimental Section). Fortunately, however, the [W_2($CPMe_3$)$_2$(PMe_3)$_4$$Cl_4$]$^{2+}$ ion is ordered and all atoms are well-behaved under anisotropic refinement. The experimental data for the X-ray study can be found in Table III, selected distances and angles in Table IV, and final positional and isotropic thermal parameters in Table V. Two views of the cation are shown in Figures 1 and 2. Note that the cation has exact C_i symmetry and (excluding methyl groups) approximate C_{2h} symmetry. The cation lies on a crystallographic inversion center. Atoms in the basic asymmetric unit are labeled normally; those in the "other half" of the cation are indicated by an asterisk and are related to the basic unit by the transformation ($-x$, $-y$, $1 - z$).

The geometry about each tungsten atom is roughly octahedral. The *planar* bridging W(μ-Cl)$_2$W moiety has *acute* angles at the chloride ligands and *obtuse* angles at the metal atoms (W–Cl(1)–W* = W–Cl(1*)–W* = 74.1 (2)° and Cl(1)–W–Cl(1*) = Cl(1)–W*–Cl(1*) = 105.9 (2)°),

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[23] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 3913.

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[26] Hinton, J. F.; Briggs, R. W. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 9.

Table III. Experimental Data for the X-ray Diffraction Study of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$

(A) Crystal Parameters at 24 °C

cryst system: monoclinic
space group: $P2_1/c$ [No. 14]
a = 9.773 (4) Å
b = 24.797 (14) Å
c = 12.633 (7) Å
β = 92.85 (4)°
Z = 2 (dimeric units)

(B) Collection of X-ray Data

radiation: Mo Kα ($\bar{\lambda}$ = 710 730 Å)
monochromator: pyrolytic graphite
reflections measd: $+h,+k,\pm l$ for 2θ = 3.7-40.0°
scan type: coupled θ(cryst)-2θ(counter)
scan speed: 2.5 deg/min (in 2θ)
scan range: $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
standards: three (400, 060, 006) every 97 data; no decay observed.
data collected: 2844 independent reflections

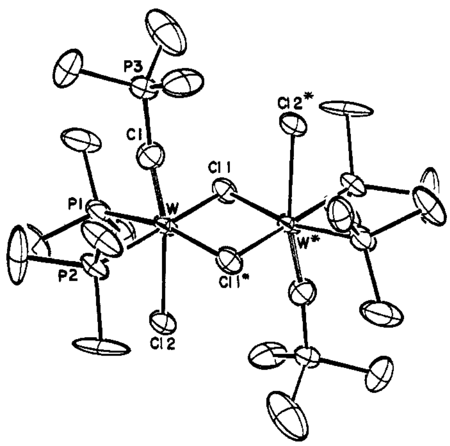

Figure 1. View of the $[W_2(CPMe_3)_2(PMe_3)_4Cl_4]^{2+}$ ion (ORTEP-II diagram, 30% ellipsoids). The dication lies on a crystallographic inversion center.

which, along with a rather short tungsten–tungsten distance of 2.970 (2) Å and the compound's diamagnetism, suggests some metal–metal interaction. The two tungsten–(bridging chloride) distances are equivalent with W–Cl(1) = 2.458 (7) Å and W–Cl(1*) = 2.470 (8) Å. An unusual feature is that the W–(μ-Cl) distances are *shorter*

Table IV. Selected Distances (Å) and Angles (deg)[a] for $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$

	(a) Distances Involving Tungsten Atom		
W-W*	2.970 (2)	W-C(1)	1.833 (30)
W-Cl(1)	2.458 (7)	W-P(1)	2.543 (9)
W-Cl(1*)	2.470 (8)	W-P(2)	2.535 (9)
W-Cl(2)	2.545 (8)		
	(b) Distances within ≡C—PMe_3 Ligand		
C(1)-P(3)	1.71 (3)	P(3)-C(32)	1.85 (4)
P(3)-C(31)	1.88 (4)	P(3)-C(33)	1.84 (5)
	(c) Distances within PMe_3 Ligands		
P(1)-C(11)	1.80 (4)	P(2)-C(21)	1.85 (5)
P(1)-C(12)	1.74 (4)	P(2)-C(22)	1.76 (4)
P(1)-C(13)	1.84 (4)	P(2)-C(23)	1.88 (4)
	(d) Aluminum-Chlorine Distances within Disordered $AlCl_4^-$ Ion		
Al(1)-Cl(4A)	2.14 (3)	Al(1)-Cl(6A)	2.15 (6)
Al(1)-Cl(4B)	2.02 (3)	Al(1)-Cl(6B)	2.13 (4)
Al(1)-Cl(5A)	2.10 (4)	Al(1)-Cl(6C)	2.12 (4)
Al(1)-Cl(5B)	2.13 (3)	Al(1)-Cl(7)	2.09 (2)
	(e) Angles around Tungsten Atom		
W*-W-Cl(1)	53.1 (2)	Cl(1*)-W-Cl(2)	89.6 (3)
W*-W-Cl(1*)	52.8 (2)	Cl(1*)-W-P(1)	168.7 (3)
W*-W-Cl(2)	91.9 (2)	Cl(1*)-W-P(2)	78.1 (3)
W*-W-P(1)	129.9 (2)	Cl(1*)-W-C(1)	97.0 (10)
W*-W-P(2)	130.8 (2)	Cl(2)-W-P(1)	79.5 (3)
W*-W-C(1)	100.3 (9)	Cl(2)-W-P(2)	84.2 (3)
Cl(1)-W-Cl(1*)	105.9 (2)	Cl(2)-W-C(1)	167.8 (10)
Cl(1)-W-Cl(2)	92.7 (3)	P(1)-W-P(2)	97.7 (3)
Cl(1)-W-P(1)	77.8 (3)	P(1)-W-C(1)	93.2 (10)
Cl(1)-W-P(2)	174.9 (3)	P(2)-W-C(1)	87.1 (10)
Cl(1)-W-C(1)	95.4 (10)		
	(f) Angles at Bridging Chloride Ligands		
W-Cl(1)-W*	74.1 (2)	W-Cl(1*)-W*	74.1 (2)
	(g) Angles within the $CPMe_3$ Ligand		
W-C(1)-P(3)	174.0 (19)	C(31)-P(3)-C(32)	108.0 (18)
C(1)-P(3)-C(31)	108.1 (16)	C(31)-P(3)-C(33)	112.1 (21)
C(1)-P(3)-C(32)	111.7 (17)	C(32)-P(3)-C(33)	101.5 (22)
C(1)-P(3)-C(33)	115.3 (20)		
	(h) Angles within the PMe_3 Ligands		
W-P(1)-C(11)	113.2 (14)	C(11)-P(1)-C(12)	101.6 (20)
W-P(1)-C(12)	121.9 (15)	C(11)-P(1)-C(13)	104.3 (17)
W-P(1)-C(13)	115.0 (11)	C(12)-P(1)-C(13)	98.5 (18)
W-P(2)-C(21)	120.3 (16)	C(21)-P(2)-C(22)	99.7 (20)
W-P(2)-C(22)	113.4 (13)	C(21)-P(2)-C(23)	104.0 (21)
W-P(3)-C(23)	114.6 (13)	C(22)-P(2)-C(23)	102.4 (18)

[a] Atoms marked with an asterisk (*) are related to the basic asymmetric unit by the transformation: $-x$, $-y$, $1 - z$.

Table V. Final Positional and Isotropic Thermal Parameters for $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$

atom	x	y	z	B, Å^2
W	0.10342 (10)	0.02542 (5)	0.43368 (18)	
Cl(1)	−0.01197 (66)	0.06726 (32)	0.58142 (60)	
Cl(2)	0.30018 (69)	−0.00909 (35)	0.55472 (67)	
P(1)	0.24029 (74)	0.11175 (36)	0.46372 (77)	
P(2)	0.24145 (75)	−0.01333 (37)	0.28701 (73)	
Al(1)	0.3809 (10)	0.15267 (52)	−0.02496 (88)	
P(3)	−0.12778 (79)	0.08256 (40)	0.24016 (74)	
Cl(4A)	0.4024 (22)	0.2211 (10)	−0.1261 (19)	6.06 (56)
Cl(4B)	0.3829 (28)	0.2035 (12)	0.8502 (23)	7.88 (80)
Cl(5A)	0.2490 (35)	0.0878 (14)	−0.0624 (27)	11.2 (10)
Cl(5B)	0.2020 (29)	0.1075 (12)	0.9319 (22)	8.52 (72)
Cl(6A)	0.3755 (51)	0.1896 (24)	0.1286 (42)	9.8 (15)
Cl(6B)	0.3065 (33)	0.1965 (16)	0.1054 (25)	5.87 (76)
Cl(6C)	0.3381 (48)	0.1757 (17)	0.1317 (32)	6.23 (91)
Cl(7)	0.5657 (15)	0.11046 (64)	−0.0131 (13)	10.24 (61)
C(1)	−0.0089 (28)	0.0555 (13)	0.3292 (24)	
C(11)	0.1531 (36)	0.1708 (16)	0.4114 (38)	
C(12)	0.4028 (32)	0.1199 (19)	0.4155 (37)	
C(13)	0.2819 (31)	0.1285 (14)	0.6034 (27)	
C(21)	0.3537 (57)	0.0310 (18)	0.2109 (41)	
C(22)	0.1394 (32)	−0.0411 (18)	0.1820 (27)	
C(23)	0.3554 (40)	−0.0715 (19)	0.3285 (30)	
C(31)	−0.2353 (37)	0.0259 (15)	0.1824 (31)	
C(32)	−0.0457 (44)	0.1170 (19)	0.1301 (32)	
C(33)	−0.2332 (40)	0.1373 (27)	0.2921 (36)	
H(11A)	0.2068	0.2024	0.4232	6.5
H(12A)	0.4415	0.1540	0.4285	6.5
H(13A)	0.3336	0.1607	0.6107	6.5
H(21A)	0.4012	0.0130	0.1572	6.5
H(22A)	0.1962	−0.0558	0.1274	6.5
H(23A)	0.4034	−0.0858	0.2721	6.5
H(31A)	−0.3015	0.0422	0.1298	6.5
H(32A)	−0.1077	0.1309	0.0789	6.5
H(33A)	−0.2974	0.1517	0.2457	6.5
H(11B)	0.1344	0.1671	0.3357	6.5
H(11C)	0.0670	0.1756	0.4431	6.5
H(12B)	0.4654	0.0923	0.4372	6.5
H(12C)	0.3967	0.1166	0.3346	6.5
H(13B)	0.2002	0.1323	0.6421	6.5
H(13C)	0.3354	0.0997	0.6378	6.5
H(21B)	0.3016	0.0605	0.1748	6.5
H(21C)	0.4227	0.0496	0.2561	6.5
H(22B)	0.0844	−0.0705	0.2055	6.5
H(22C)	0.0803	−0.0150	0.1485	6.5
H(23B)	0.4177	−0.0624	0.3860	6.5
H(23C)	0.2985	−0.1015	0.3551	6.5
H(32B)	0.0173	0.1441	0.1549	6.5
H(32C)	0.0125	0.0902	0.0923	6.5
H(33B)	−0.2817	0.1243	0.3561	6.5
H(33C)	−0.1749	0.1666	0.3230	6.5

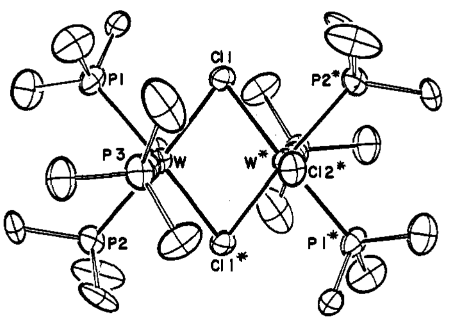

Figure 2. View of the cation, showing the geometry of the $W_2(\mu\text{-}Cl)_2$ core. Note the approximate C_{2h} symmetry of the $W_2(CPMe_3)_2(P)_4Cl_4$ moiety.

than the terminal tungsten–chloride distance, W–Cl(2) = 2.545 (8) Å. This can be attributed to the trans-lengthening influence of the $CPMe_3$ ligand, rather than to any feature of the molecule that would result in especially short W–(μ-Cl) bond lengths. The metal–metal-bonding interaction results in some overall distortions of the octahedral geometry; for example Cl(2)–W–C(1) = 167.8 (10)°, Cl(1*)–W–P(1) = 168.7 (3)°, Cl(1)–W–P(2) = 174.9 (3)°, and P(1)–W–P(2) = 97.7 (3)°.

The two PMe_3 groups are equivalent (W–P(1) = 2.543 (9) Å and W–P(2) = 2.535 (9) Å), and within these ligands the P–C distances range from 1.74 (4) Å through 1.88 (4) Å, averaging 1.81 (5) Å.[27]

The most interesting feature of this molecule to us is the trimethylphosphonium methylidyne ($CPMe_3$) ligand. The W–C(1) distance of 1.83 (3) Å is comparable to other tungsten–alkylidyne distances (cf. W≡C = 1.785 (8) Å in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$,[28] 1.807 (6) Å in $W(CH{\cdot}AlMe_{2-x}Cl_{1+x})(PMe_3)_3(Cl)$,[11] 1.813 (5) Å in $W(CAl_2Me_4Cl)(PMe_3)_2(CH_3)(\eta^2\text{-}C_2H_4)$,[14] 1.82 (2) Å in $W(C(p\text{-tol}))(\eta^5\text{-}C_5H_5)(CO)_2$,[29] and 1.89 (2) Å in W(CMe)-

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[27] Estimated standard deviations of average values are calculated as

$$[\sigma] = [\sum_{i=0}^{i=N}(d_i - \bar{d})^2/(N-1)]^{1/2}$$

[28] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

[29] Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976–1977**, *15*, 133.

$(PMe_3)_4(CH_3)$[13]). It is also interesting to note that the C(1)–P(3) distance of 1.71 (3) Å is substantially shorter than the three P(3)–C(methyl) distances (1.88 (4), 1.85 (4), 1.84 (5) Å). While some of the shortening can be ascribed to the greater s character of the C(1) orbital used to form the bond to P(3) (approximately sp), one could entertain the possibility that there is some multiple-bond character to the C(1)–P(3) linkage. In fact, an ylide-like valence bond description ($Me_3P{=}C{=}W^+$) is not out of the question. However, the question as to whether this or the alternative description ($Me_3P^+{-}C{\equiv}W$) is more valid is moot when it comes to rationalizing the relatively large W–C(1)–P(3) angle of 174.0 (19)°. We believe this angle is not 180° solely as a result of steric interaction between the PMe_3 group bound to the methylidyne carbon atom and the two bound to the metal in positions cis to the phosphinomethylidyne ligand.

Conclusion

It is now fairly certain that the terminal methylidyne ligand in $W(CH)(PMe_3)_4Cl$ is quite reactive, once a PMe_3 ligand is removed. The methylidyne ligand appears to be nucleophilic; it binds both Lewis and Brønsted acids. The methylidyne proton can be removed under a variety of conditions to yield main-group-substituted methylidyne complexes. There should be many strange reactions of this type, the mechanisms of which may remain relatively obscure for some time. What is most needed at this point are other types of terminal methylidyne complexes to compare with $W(CH)(PMe_3)_4Cl$.

It is interesting to speculate that coupling reactions involving methylidyne (and methylene) ligands with carbon monoxide might be faster for steric reasons than analogous reactions involving substituted methylidyne and methylene complexes. Conceivably this rate difference could be large enough to allow CO to be reduced selectivity to a C_2 product via a process involving formation of methylidyne and/or methylene ligands and coupling them with CO.

Experimental Section

General Procedures. All experiments were performed under N_2 in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Solvents were dried and purified under nitrogen by standard techniques. NMR chemical shifts are reported in parts per million and are referenced to Me_4Si for ^1H and ^{13}C NMR, 85% H_3PO_4 for ^{31}P NMR, $Al(H_2O)_6^{3+}$ for ^{27}Al NMR, and CCl_3F for ^{19}F NMR. PMe_3,[30] dmpe,[31] and $W(CH)(PMe_3)_4Cl$[4b] were prepared by published methods. $AlCl_3$ was sublimed prior to use.

X-ray Structural Procedures. A small, approximately equidimensional crystal was mounted on the Syntex $P2_1$ automated four-circle diffractometer and diffraction data were collected as described previously.[32] Details are given in Table III. All data were corrected for the effects of absorption and for Lorentz and polarization effects. It should be noted that the crystals gave a rather weak diffraction pattern (consistent with the later observed disordered structure) with virtually no data observable beyond $2\theta = 40°$.

The positions of the symmetry-related tungsten atoms were determined from a Patterson map; all remaining non-hydrogen atoms were located from difference Fourier maps. The $AlCl_4^-$ anion is severely disordered but the eight independent aluminum···(partial)chlorine distances are self-consistent and range from Al(1)–Cl(4B) = 2.02 (3) through Al(1)–Cl(6A) = 2.15 (6) Å. (Attempts to refine this system anisotropically were unsuccessful.) Fortunately, the $[W_2(CPMe_3)_2(PMe_3)_4Cl_4]^{2+}$ ion is ordered, and all atoms were well-behaved under anisotropic refinement.

Convergence was reached with $R_F = 8.7\%$ by using those 2408 reflections with $|F_0| > 3\sigma(F_0)$. A final difference Fourier map was devoid of significant detail except in the vicinity of the $AlCl_4^-$ ion.

All hydrogen atoms were included in calculated positions (staggered tetrahedral geometry with $d(C–H) = 0.95$ Å[33]).

Final positional parameters are presented in Table V.

Preparation of Compounds. $W(CH)(PMe_3)_4I$. $W(CH)(PMe_3)_4Cl$ (3.0 g, 5.6 mmol) was suspended in 50 mL of ether and Me_3SiI (1.25 g, 6.3 mmol) was added at 25 °C. After 12 h the volatiles were removed in vacuo. The crude product contained a small amount of starting material (by ^{31}P NMR). The crude product was dissolved in 40 mL of toluene, and an additional 0.1 g of Me_3SiI was added. After 12 h the solution was stripped to dryness, and the residue was dissolved in THF. Concentration of the solution yielded 3.31 g of pure $W(CH)(PMe_3)_4I$ (94%): ^1H NMR (C_6D_6) δ 6.45 (quin, 1, $^3J_{HP} = 3.7$ Hz, $^2J_{HW} = 84$ Hz, WCH), 1.61 (virtual t, 36, $^2J_{HP} = 3.0$ Hz, PMe_3); ^{13}C NMR (C_6D_6) δ 248.7 (d of quin, $^2J_{CP} = 13.9$ Hz (q), $J_{CH} = 136$ Hz (d), WCH), 26.6 (q, $J_{CH} = 128$ Hz, PMe_3); ^{31}P NMR (C_6D_6) δ −34.6 (s, $J_{PW} = 281$ Hz, PMe_3). The analogous chloride complex $W(CH)(PMe_3)_4Cl$ has been analyzed[4b] and its X-ray structure determined.[6]

$W(CH)(PMe_3)_4(CF_3SO_3)$. $W(CH)(PMe_3)_4Cl$ (3.0 g, 5.6 mmol) and 1.1 equiv of $Me_3Si(OTf)$ (1.35 g, 6.1 mmol) were combined in 30 mL of toluene at 25 °C. After 16 h, the yellow solution was filtered and concentrated to 5 mL to give 3.5 g of pure $W(CH)(PMe_3)_4(CF_3SO_3)$ (96%): ^1H NMR (C_6D_6) δ 6.54 (quin, 1, $^3J_{HP} = 2.6$ Hz, $^2J_{HW} = 84$ Hz, WCH), 1.47 (virtual t, 36, $^2J_{HP} = 2.8$ Hz, PMe_3); ^{13}C NMR (C_6D_6) δ 264.9 (d, $J_{CH} = 150$ Hz, WCH), 120.5 (q, $J_{CF} = 319$ Hz, CF_3SO_3), 24.6 (q, $J_{CH} = 125$ Hz, PMe_3); ^{31}P NMR (toluene) δ −16.2 (s, $J_{PW} = 288$ Hz, PMe_3). Anal. Calcd for $WC_{14}H_{37}F_3O_3P_4S$: C, 25.85; H, 5.69. Found: C, 26.04; H, 5.81.

$[W(CH_2)(PMe_3)_4I][CF_3SO_3]$. To $W(CH)(PMe_3)_4I$ (1.0 g, 1.6 mmol) dissolved in 40 mL of ether was added 1.0 equiv of CF_3SO_3H (0.24 g) in several milliliters of ether. A precipitate formed immediately. After 1 h, the precipitate was filtered off and washed with 2 × 15 mL of toluene. It was dissolved in dichloromethane, and the solution was filtered and concentrated to 3 mL. Chlorobenzene (15 mL) was added, and the solution was cooled to −30 °C. After 1 day, 0.92 g of red-brown crystals was collected (74%): ^1H NMR (CD_2Cl_2) δ −0.80 (quin, 2, $J_{HP} = 0.9$ Hz, $J_{HW} = 53$ Hz, WCH_2), 1.88 (virtual t, 36, $J_{HP} = 3.4$ Hz, PMe_3); ^1H NMR (CD_2Cl_2, 190 K) δ −1.0 (br s, WCH_2), 1.85 (br s, PMe_3); ^1H NMR (CD_2Cl_2, 153 K) δ −9.0 (br s, WCH^TH^B), 1.85 (br s, PMe_3); ^{13}C NMR (CD_2Cl_2) δ 218.9 (t of quin, $J_{CH} = 121$ Hz (t), $J_{CP} = 14.5$ Hz, WCH_2), 121.3 (q, $J_{CF} = 322$ Hz, CF_3SO_3), 24.6 (virtual t of q, $J_{CH} = 13$ Hz (q), $J_{CP} = 14.6$ Hz, PMe_3); ^{31}P NMR (CH_2Cl_2) δ −46.9 (s, $J_{PW} = 246$ Hz, PMe_3). The analogous chloride complex has been analyzed[4b] and the X-ray structure of $[W(CH_2)(PMe_3)_4I][CF_3SO_3]$ determined.[9]

$[W(CH_2)(PMe_3)_4(CF_3SO_3)][CF_3SO_3]$. $W(CH)(PMe_3)_4(CF_3SO_3)$ (3.0 g, 4.6 mmol) was suspended in 50 mL of ether at 25 °C, and 1.0 equiv of CF_3SO_3H (0.69 g) in 5 mL of ether was added over a period of several minutes. A precipitate formed immediately. After 20 min the precipitate was filtered off washed with 2 × 10 mL of toluene. The product was dissolved in cold dichloromethane (−30 °C). The solution was filtered and concentrated to 3 mL, and 20 mL of cold chlorobenzene was added. After the solution was left standing for 1 day at −30 °C, 3.65 g of orange, crystalline $[W(CH_2)(PMe_3)_4(CF_3SO_3)][CF_3SO_3]$ was collected (98%): ^1H NMR (CD_2Cl_2, 280 K) δ 0.06 (quin, 2, $^3J_{HP} = 2$ Hz, $^2J_{HW} = 57$ Hz, WCH_2), 1.85 (br s, 36, PMe_3); ^{13}C NMR (CD_2Cl_2, 265 K) δ 245.3 (br s, WCH_2), 120.9 (q, $J_{CF} = 320$ Hz, CF_3SO_3), 22.3 (br s, PMe_3); ^{31}P NMR (CH_2Cl_2, 300 K) δ −25.7 (s, $J_{PW} = 247$ Hz, PMe_3). This methylene complex decomposes rapidly in dichloromethane at 25 °C to produce a white solid and a colorless solution. The molecular was characterized by NMR methods only, in view of its relationship to similar compounds.

$W(CH)(PMe_3)_4(BH_4)$. $W(CH)(PMe_3)_4(CF_3SO_3)$ (1.0 g, 1.5 mmol) was dissolved in 20 mL of THF at 25 °C, and $NaBH_4$ (0.23 g, 6.2 mmol) was added rapidly as a solid. After the mixture was

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stirred for 16 h, the volatiles were removed in vacuo and the residue was extracted with chlorobenzene. The solution was concentrated to 2 mL, 4 mL of pentane was added, and the solution was cooled to −30 °C. After 1 day 0.44 g of red-orange crystals was collected (56%): ^{1}H NMR (C_6D_6) δ 7.39 (br s, 1, $^2J_{HW}$ = 80 Hz, WCH), 1.53 (br s, 36, PMe_3), −1.70 (br q, J_{HB} = 82 Hz, BH_4); ^{13}C NMR (C_6D_6) δ 259.5 (d, J_{CH} = 139 Hz, WCH), 23.4 (q, J_{CH} = 128 Hz, PMe_3); ^{31}P NMR (PhCl) δ −23.2 (s, J_{PW} = 282 Hz, PMe_3); IR (Nujol) 2320 (br, m, ν_{BH^t}), 2050 cm^{-1} (br, w, ν_{BH^b}). Anal. Calcd for $WC_{13}H_{41}BP_4$: C, 30.26; H, 7.95. Found: C, 29.75; H, 7.83.

Observation of $W(CH)(C_2H_4)(PMe_3)_3(CF_3SO_3)$. $[W(CH_2)(PMe_3)_4(CF_3SO_3)][CF_3SO_3]$ (3.0 g, 3.8 mmol) was suspended in 40 mL of THF at 25 °C, and the solution was placed under 30 psi of ethylene. After 1 day, the yellow-brown solution was concentrated to dryness and the residue was extracted with 50 mL of chlorobenzene. Upon filtration of the extracts, 0.55 g of $[PMe_3H][CF_3SO_3]$ (2.3 mmol, 63%) was collected. The filtrate was concentrated to 5 mL, and the mother liquor was decanted from 0.5 g of solid. The solid was crystallized from a 1:2 mixture of dichloromethane and THF at −30 °C to give 0.33 g (0.55 mmol, 14%) of $W(CH)(C_2H_4)(PMe_3)_3(CF_3SO_3)$: ^{1}H NMR ($CDCl_3$) δ 5.89 (d of t, 1, $^3J_{HP}$ = 2.0 Hz (d), $^3J_{HP}$ = 3.9 Hz (t), $^2J_{HW}$ = 83 Hz, WCH), 1.77 (virtual t, 18, $^2J_{HP}$ = 3.5 Hz, PMe_3), 1.69 (d, 9, $^2J_{HP}$ = 7.8 Hz, PMe_3), 2.1 (m, 2, $CH\mathit{H}'CH\mathit{H}'$), 1.3 (m, 2, $C\mathit{H}H'C\mathit{H}H'$); ^{13}C NMR ($CD_2Cl_2$) δ 268.3 (d of t of d, $^2J_{CP}$ = 8.3 Hz (d), $^2J_{CP}$ = 16.6 Hz (t), J_{CH} = 142 Hz (d), WCH), 119.6 (q, J_{CF} = 319.6 Hz, CF_3SO_3), 36.2 (t, J_{CH} = 154 Hz, C_2H_4), 22.2 (virtual t of q, J_{CP} = 13.9 Hz (t), J_{CH} = 127.9 Hz (q), PMe_3), 20.3 (d of q, J_{PC} = 25 Hz (d), J_{CH} = 131 Hz (q), PMe_3); ^{31}P NMR (CH_2Cl_2) δ −11.0 (d, $^2J_{PP}$ = 34.2 Hz, J_{PW} = 215 Hz, PMe_3), −17.5 (t, $^2J_{PP}$ = 34.2 Hz, J_{PW} = 230 Hz, PMe_3). The presence of small amounts of impurities prevented reproducible elemental analyses.

The chlorobenzene mother liquor was concentrated to dryness, and the residue was extracted with ether to yield a yellow solution and a brown oily solid. The ether solution was filtered and concentrated to dryness to yield 0.7 g of $W(CH)(PMe_3)_4(CF_3SO_3)$ (1.3 mmol, 34%).

$W(CHAlMe_3)(PMe_3)_3Cl$. $W(CH)(PMe_3)_4Cl$ (1.0 g, 1.9 mmol) was suspended in 10 mL of pentane, and $AlMe_3$ (0.27 g, 3.8 mmol) was added at 25 °C. The pale yellow solution became red and after 8 h was filtered and concentrated to dryness. The $AlMe_3{\cdot}PMe_3$ byproduct was removed by sublimation at 40 °C. The residue was washed with 30 mL of pentane at −30 °C to yield 0.85 g of crude $W(CHAlMe_3)(PMe_3)_3Cl$ (85%). The product could be recrystallized from a mixture of toluene and pentane: ^{1}H NMR (C_6D_6) δ 6.55 (d of t, 1, $^3J_{HP}$ = 8.8 Hz (d), $^3J_{HP}$ = 1.8 Hz (t), $^2J_{HW}$ = 84 Hz, $C\mathit{H}AlMe_3$), 1.2 (m, 27, PMe_3), −0.20 (s, 6, $Al\mathit{Me}_2Me'$), −0.28 (s, 3, $AlMe_2\mathit{Me}'$); ^{13}C NMR (C_6D_6) δ 229.6 (m, of d, J_{CH} = 139 Hz, $\mathit{C}HAlMe_3$), 27.1 (d of q, J_{CH} = 128 Hz, J_{CP} = 28 Hz, PMe_3), −2.9 (br q, J_{CH} = 102 Hz, $AlMe_2\mathit{Me}'$), −15.2 (q, J_{CH} = 112 Hz, $Al\mathit{Me}_2Me'$); ^{31}P NMR (C_6D_6) δ −23.0 (s, 2, J_{PW} = 298 Hz, PMe_3), −22.8 (s, 1, J_{PW} = 300 Hz, PMe_3). The molecule was characterized by NMR methods only in view of its great sensitivity to air and its similarity to the $AlMe_2Cl$ analogue below.

$W(CHAlMe_2Cl)(PMe_3)_3Cl$. $W(CH)(PMe_3)_4Cl$ (3.0 g, 5.6 mmol) was dissolved in 60 mL of toluene, and 2 equiv of $AlMe_2Cl$ (1.02 g, 11.0 mmol) was added. After 24 h the red solution was filtered and concentrated to 5 mL to yield 1.88 g of $W(CHAlMe_2Cl)(PMe_3)_3Cl$ (61%): ^{1}H NMR (C_6D_6) δ 6.64 (d of t, 1, $^3J_{HP}$ = 9.9 Hz (d), $^3J_{HP}$ = 2.2 Hz (t), $^2J_{HW}$ = 82 Hz, $C\mathit{H}AlMe_2Cl$), 1.3 (m, 27, PMe_3), 0.021 (s, $AlMe_2Cl$), −0.10 (s, $AlMe_2Cl$); ^{13}C NMR (C_6D_6) δ 229.9 (two d of t, J_{CH} = 144 Hz, $^2J_{CP}$ = 22 Hz (d), $^2J_{CP}$ = 7.3 Hz (t), $\mathit{C}HAlMe_2Cl$), 26.6 (d of q, J_{CH} = 127 Hz, J_{CP} = 29 Hz, PMe_3), 19.3 (two d of q, J_{CH} = 132 Hz, $^2J_{CP}$ = 4.9 Hz (d), J_{CP} = 20 Hz (d), PMe_3), 18.7 (two d of q, $^2J_{CP}$ = 4.9 Hz, J_{CP} = 22 Hz, J_{CH} = 122 Hz, PMe_3); ^{31}P NMR (C_6D_6) δ −25.5 (d, $^2J_{PP}$ = 5.5 Hz, J_{PW} = 292 Hz, PMe_3), −25.3 (d, $^2J_{PP}$ = 5.5 Hz, J_{PW} = 292 Hz, PMe_3), −22.5 (d of d, $^2J_{PP}$ = 5.5 Hz, $^2J_{PP}$ = 5.5 Hz, J_{PW} = 338 Hz, PMe_3); ^{27}Al NMR ($PhCH_3$, 23.3 MHz) δ ~150 (~2.5 KHz wide, $CHAlMe_2Cl$). Anal. Calcd for $WC_{12}H_{34}AlCl_2P_3$: C, 26.05; H, 6.15. Found: C, 26.39; H, 6.20.

$W(CAl_2Me_4Cl)(PMe_3)_2(CH_3)(C_2H_4)$. $W(CH)(PMe_3)_4Cl$ (2.0 g, 3.7 mmol) and 3 equiv of $AlMe_3$ (0.81 g, 11.2 mmol) were combined in 10 mL of toluene. The reaction vessel was pressurized with ethylene (30 psi), and after 1 day the red solution had become pale yellow-brown and a tan precipitate had formed. All volatile components were removed in vacuo, and the residue was dissolved in chlorobenzene. The solution was concentrated to 7 mL, 7 mL of pentane was added, and, after 1 day at −30 °C, 1.3 g of tan crystals was collected. A second crop of 0.5 g was obtained from the mother liquor in the same manner (total 1.8 g, 90%): ^{1}H NMR (C_6D_6) δ 1.91 (br m, 2, C_2H_4), 1.18 (virtual t, 18, $^2J_{HP}$ = 3.5 Hz, PMe_3), 0.19 (t, 3, $^2J_{HP}$ = 17 Hz, WMe), 0.09 (m, 2, C_2H_4), −0.21 (br s, 12, AlMe); ^{13}C NMR (C_6D_6) δ 308.3 (s, $W\mathit{C}Al_2Me_4Cl$), 30.9 (t, J_{CH} = 151 Hz, C_2H_4), 25.4 (q of t, J_{CH} = 119 Hz (q), $^2J_{CP}$ = 10.6 Hz (t), WCH_3), 15.7 (virtual t of q, J_{CH} = 127.4 Hz (q), J_{CP} = 13.3 Hz (t), PMe_3), −5 (br s, AlMe); ^{31}P NMR ($C_2H_4Cl_2$) δ 4.1 (s, J_{PW} = 200 Hz, PMe_3); ^{27}Al NMR (CH_2Cl_2, 23.3 MHz) δ ~150 (~2.5 KHz wide, $W(CAl_2Me_4Cl)$). The crystal for the X-ray study[14] was selected from a homogeneous, crystalline sample.

$W(CHCOAlCl_3)(PMe_3)_3(CO)Cl$. $W(CH)(Cl)(PMe_3)_4$ (2.0 g, 3.7 mmol) was dissolved in 10 mL of chlorobenzene, and $AlCl_3$ (1.0 g, 7.5 mmol) was added rapidly as a solid. The mixture was then stirred under 30 psi of carbon monoxide at 25 °C for 1 day. The resulting dark brown solution contained a precipitate which was filtered off and washed with 10 mL of acetonitrile at −10 °C. The orange-red precipitate was dissolved in dichloromethane, and the solution was filtered. The dichloromethane solution was concentrated to 3 mL and to give 1.2 g of orange solid (50%): ^{1}H NMR (CD_2Cl_2) δ 12.1 (d, 1, J_{HP} = 12.5 Hz, $WCHCOAlCl_3$), 1.8 (d, 9, J_{HP} = 7.5 Hz, PMe_3), 1.4 (t, 18, J_{HP} = 4.4 Hz, PMe_3); ^{13}C NMR (CD_2Cl_2) δ 230.8 (br s, WCO), 213.5 (d, J_{CP} = 39 Hz, WCO), 194.4 (d of d, J_{CH} = 203 Hz, J_{CP} = 22.2 Hz, $W(\mathit{C}HCOAlCl_3)$), 18.7 (br q, J_{CH} = 130 Hz, PMe_3), 18.4 (q of d, J_{CH} = 130 Hz, J_{CP} = 16.7 Hz, PMe_3); ^{31}P NMR (CH_2Cl_2) δ −25.7 (d, J_{PP} = 19.5 Hz, J_{PW} = 264 Hz, PMe_3), −30.5 (t, J_{PP} = 19.5 Hz, J_{PW} = 144 Hz, PMe_3); IR (Nujol) 1970, 1605 cm^{-1} Λ (1.6×10^{-3} M, CH_2Cl_2) = 1.95 Ω^{-1} cm^{-1} M^{-1}.

$W(CHCOAlMe_3)(PMe_3)_3(CO)Cl$. $W(CH)(Cl)(PMe_3)_4$ (1.0 g, 1.9 mmol) was dissolved in toluene, and $AlMe_3$ (0.13 g, 1.9 mmol) was added at 25 °C. The mixture was stirred under 30 psi of CO at 25 °C for 2 days, and the solvent was removed in vacuo. The residue was dissolved in dichloromethane, and the solution was filtered and concentrated to 4 mL. Pentane (3 mL) was added, and after the solution was left standing at −10 °C for 1 day, 0.54 g of orange-red crystals was collected. A second crop of 0.21 g was obtained from the mother liquor by the same procedure: total yield 0.75 g (83%); ^{1}H NMR (CD_2Cl_2) δ 12.75 (br d, 1, J_{HP} = 19 Hz, $C\mathit{H}COAlMe_3$), 1.70 (d, 9, J_{HP} = 6.7 Hz, PMe_3), 1.36 (t, 18, J_{HP} = 3.7 Hz, PMe_3), −1.0 (br s, 9, $AlMe_3$); ^{13}C NMR (CD_2Cl_2) 226.3 (s, WCO), 215.2 (d, J_{CP} = 35 Hz, WCO), 196.2 (br d, J_{CH} = 200 Hz, $\mathit{C}HCOAlMe_3$), 18.3 (br m, J_{CP} = 5.8 Hz, PMe_3), 18.6 (d, J_{CP} = 17.4 Hz, PMe_3), −7.8 (br q, J_{CH} = 110 Hz, $AlMe_3$); ^{31}P NMR (CH_2Cl_2) δ −25.4 (d, J_{PP} = 19.5 Hz, PMe_3), −31.3 (t, J_{PP} = 20.1 Hz, PMe_3); IR (Nujol) 1960, 1615 cm^{-1}. Anal. Calcd for $WC_{15}H_{37}AlClO_2P_3$: C, 30.58; H, 6.29. Found: C, 30.12; H, 6.18. The molecule was positively identified by X-ray structural studies.[21]

$W(CH^{13}COAlMe_3)(PMe_3)_3(^{13}CO)Cl$. $W(CH)(PMe_3)_4Cl$ (0.3 g, 0.6 mmol) and $AlMe_3$ (0.04 g, 0.6 mmol) were combined in 10 mL of toluene, and the solution was degassed by three freeze–pump–thaw cycles. Five equivalents of ^{13}CO (100 mL, 480 torr) were transferred to the reaction vessel through the use of a Toepler pump. The reaction mixture was stirred for 2 days. The solution was concentrated to dryness, and the residue was extracted with dichloromethane. The extract was filtered and concentrated to 1 mL, and 1 mL of pentane was added. After 1 day at −30 °C, 0.2 g of red-orange crystals was collected (60%): ^{1}H NMR ($CDCl_3$) δ 12.34 (d of d, 1, $^2J_{HC}$ = 3.8 Hz, $^3J_{HP}$ = 15 Hz, $C\mathit{H}^{13}COAlMe_3$); ^{13}C NMR (CD_2Cl_2) δ 226.1 (s, WCO), 215.0 (d, $^2J_{CP}$ = 35 Hz, WCO); all other ^{1}H and ^{13}C NMR signals were unaffected by ^{13}CO enrichment; IR (Nujol) 1915 (s, sh, $W^{13}CO$), 1575 cm^{-1} (s, sh, $HC^{13}COAlMe_3$).

$W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$. $W(CH)(H)(PMe_3)_3Cl_2$ (0.93 g, 1.9 mmol) was dissolved in 5 mL of chlorobenzene, the solution was cooled to 0 °C in a pressure bottle, and 40 psi of CO was added. After 1.5 h at 0 °C the red solution had become yellow and a yellow soild had precipitated. The mixture was concentrated to dryness and the residue extracted with dichloromethane. The extract was filtered through Celite and concentrated to 2 mL, and 4 mL of ether was added. After 1 day at −30 °C, 0.55 g of yellow crystalline $W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$ was collected (53%): ^{1}H NMR ($CDCl_3$) δ 1.83 (d, 9, $^2J_{HP}$ = 13.2 Hz, CH_2PMe_3), 1.46 (br virtual t, 18, PMe_3), 0.80 (m, 2, CH_2PMe_3); ^{13}C NMR ($CDCl_3$) δ 273.5 (t, $^2J_{CP}$ = 39 Hz, CO), 237.5 (s, CO), 15.3 (d of q, J_{CH} = 131 Hz (q), J_{CP} = 55 Hz (d), CH_2PMe_3), 14.5 (d, J_{CP} = 32 Hz, PMe_3), 13.2 (d, J_{CP} = 23 Hz, PMe_3), 3.5 (t of t, J_{CP} = 29 Hz, J_{CH} ≈ 125 Hz, CH_2PMe_3); ^{31}P NMR (CH_2Cl_2) δ -10.0 (d, $^2J_{PP}$ = 24 Hz, J_{PW} = 168 Hz, PMe_3), 35.2 (t, $^2J_{PP}$ = 23 Hz, CH_2PMe_3); IR (Nujol) 1895 (s, sh) 1772 cm^{-1} (s, sh); conductivity (CH_2Cl_2, 273 K) $\Lambda = 0.49\ \Omega^{-1}\ cm^{-1}\ M^{-1}$ at 1.02×10^{-3} M.

This product is unstable in the solid state; the yellow crystals become brown after 12 at 25 °C. A yellow solution of the pure compound in chloroform becomes brown after several hours at 25 °C. It could be characterized only by comparison of its NMR spectra with those of its stable relative below.

$[W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl][CF_3SO_3]$. $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$ (0.42 g, 0.61 mmol) was dissolved in 5 mL of 1,2-dichloroethane, and the solution was placed under 30 psi of CO. After 24 h the red solution had become yellow. Upon concentration of the solution to 2 mL, addition of 10 mL of toluene, and cooling to -30 °C for 1 day, 0.30 g of yellow crystals was obtained. A second crop of 0.05 g was collected from the mother liquor in a similar manner (total 0.35 g, 78%): ^{1}H NMR ($CDCl_3$) δ 1.79 (d, 9, $^2J_{HP}$ = 13.2 Hz, PMe_3), 1.38 (d, 9, $^2J_{HP}$ = 8.3 Hz, PMe_3), 1.73 (d, 9, PMe_3), 1.66 (d, 9, PMe_3), 0.95 (m, 2, CH_2PMe_3); ^{13}C NMR ($CDCl_3$) δ 250.8 (m, CO), 228 (m, CO), 120.9 (q, J_{CF} = 319 Hz, CF_3SO_3), 18.6 (d, J_{CP} = 34.5 Hz, PMe_3), 16.7, 16.0, and 13.2 (each a d, J_{CP} = 24 Hz, PMe_3), 2.3 (br t, J_{CH} = 122 Hz, CH_2PMe_3); ^{31}P NMR ($CDCl_3$) δ 33 (m, PMe_3), -5 (m, PMe_3), -11 (m, PMe_3), -33 (m, PMe_3); IR (Nujol) 1895 (s, sh), 1790 cm^{-1} (s, sh); conductivity ($C_2H_4Cl_2$) $\Lambda = 17.3\ \Omega^{-1}\ cm^{-1}\ M^{-1}$ at 0.72×10^{-3} M. Anal. Calcd for $WC_{16}H_{38}ClF_3O_5P_4S$: C, 25.90; H, 5.12. Found: C, 26.10; H, 5.28. The structure was positively identified by X-ray methods.[23]

$[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. $W(CH)(PMe_3)_4Cl$ (2.5 g, 4.7 mmol) was dissolved in 20 mL of chlorobenzene, and $AlCl_3$ (1.24 g, 9.3 mmol) was added rapidly as a solid. The mixture was stirred for 5 min at 25 °C. Hexachloroethane (2 equiv) was then added slowly, as a solid, over a period of 5 min. A white powder and a brown oily solid formed immediately. The mixture was stirred for 12 h, and the solvent was decanted away from the solid. The solid was dissolved in acetonitrile. The solution was concentrated, toluene was added, and the mixture was cooled to -30 °C. After 1 day some yellow crystals were collected. After a second crystallization by the same procedure, 0.53 g of product was collected (17%): ^{1}H NMR (CD_3CN) δ 2.03 (m, 18, PMe_3), 1.47 (d, 9, $^2J_{HP}$ = 14 Hz, $WCPMe_3$); ^{13}C NMR (CD_3CN, 270 K) δ 241.9 (br s, $WCPMe_3$), 20.8 (virtual t of q, J_{CH} = 120 Hz, J_{CP} = 16 Hz, PMe_3), 13.1 (d of q, J_{CH} = 130 Hz, J_{CP} = 61 Hz, $WCPMe_3$); ^{31}P NMR (CH_3CN) δ 6.8 (s, J_{PW} = 166 Hz, $WCPMe_3$), -18.7 (s, J_{PW} = 300 Hz, PMe_3); ^{27}Al NMR (CH_3CN) δ 102.5 (sharp s, $AlCl_4^-$). The crystal for the X-ray study was selected from a homogeneous, crystalline sample.

Hydrolysis of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. A 1-mL sample of aqueous 1 N HCl was shaken for a few minutes with approximately 0.05 g of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. After being left standing at 25 °C for 1 h, the solution was filtered. A ^{31}P NMR spectrum of the filtrate showed a 2.2:1 ratio of Me_3PHCl to another phosphorus-containing species. After the NMR sample was heated at 80 °C for 1 week, the Me_3PHCl remained, but the other compound had been quantitatively converted into Me_4PCl: ^{31}P NMR (H_2O) δ 22.8 (s, 1, Me_4PCl), -2.9 (d, 2, J_{HP} = 505 Hz, Me_3PHCl).

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Registry No. $W(CH)(PMe_3)_4Cl$, 76642-46-1; $W(CH)(PMe_3)_4I$, 87862-02-0; $W(CH)(PMe_3)_4(CF_3SO_3)$, 87862-03-1; Me_3SiI, 16029-98-4; $Me_3Si(OTf)$, 27607-77-8; $[W(CH_2)(PMe_3)_4I]CF_3SO_3]$, 87862-05-3; $[W(CH_2)(PMe_3)_4(CF_3SO_3)][CF_3SO_3]$, 87869-37-2; $W(CH)(PMe_3)_4(BH_4)$, 87862-06-4; $W(CH)(C_2H_4)(PMe_3)_3(CF_3SO_3)$, 87862-07-5; C_2H_4, 74-85-1; $W(CHAlMe_3)(PMe_3)_3Cl$, 76657-21-1; $AlMe_3$, 75-24-1; $W(CHAlMe_2Cl)(PMe_3)_3Cl$, 76642-47-2; $AlMe_2Cl$, 1184-58-3; $W(CAl_2Me_4Cl)(PMe_3)_2(CH_3)(C_2H_4)$, 79255-12-2; $W(CHCOAlCl_3)(PMe_3)_3(CO)Cl$, 81391-10-8; $AlCl_3$, 7446-70-0; $W(CHCOAlMe_3)(PMe_3)_3(CO)Cl$, 81371-73-5; CO, 630-08-0; $W(CH^{13}COAlMe_3)(PMe_3)_3(^{13}CO)Cl$, 87862-08-6; $W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$, 87869-38-3; $W(CH)(H)(PMe_3)_3Cl_2$, 79197-72-1; $[W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl][CF_3SO_3]$, 82880-78-2; $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$, 79197-71-0; $[W_2(CPMe_3)(PMe_3)_4Cl_4][AlCl_4]_2$, 87862-10-0.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated factors (18 pages). Ordering information is given on any current masthead page.

Theoretical Studies of Polyvinyl-Substituted Carbenium and Silylenium Ions

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Ab initio (STO-2G and 3-21G) calculations have been performed to analyze the ability of one, two, and three vinyl groups to stabilize the CH_3^+ and SiH_3^+ ions. Vinyl groups appear to be quite effective at stabilizing the positive charge on the silylenium ion, and successive vinylization preferentially stabilizes the silicon relative to the carbon ion.

Introduction

Carbenium ions, R_3C^+, are readily accessible species in all three phases and possess a well-developed chemistry. In contrast, the silicon analogues, silylenium ions, R_3Si^+, are far more elusive.[1] They are easily produced only as a gas, typically in the mass spectrometer, and only very recently was the first silylenium ion detected in a condensed phase.[2] The difficulty in obtaining stable R_3Si^+ species in solution is probably because silicon has energetically very favorable reaction paths involving pentavalent or hexavalent intermediates that ensure a short life-

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