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FORMATION OF TUNGSTEN CARBYNE COMPLEXES FROM VINYL- AND ALLYLSILANES AND -STANNANES*

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Abstract—$WX_2(PMe_3)_4$ [X = Cl (**1a**), Br (**1b**)] react with the vinyl reagents $CH_2{=}CHR$ [R = $SiMe_3$, $Si(OEt)Me_2$, $Si(OMe)_3$ and Sn^nBu_3] to give the tungsten methylcarbyne complexes $W({\equiv}CCH_3)X(PMe_3)_4$ [X = Cl (**2a**), Br (**2b**)] and $XSiR_3$ and $XSnR_3$. The connectivity of **2a** has been confirmed by NMR and an X-ray crystal structure. Similarly, the allyl reagents $CH_2{=}CHCH_2R$ [R = $SiMe_3$, $SiClMe_2$, $Si(OMe)_3$ and $SnMe_3$] react with **1a** and **1b** to give the ethyl carbynes $W({\equiv}CCH_2CH_3)X(PMe_3)_4$ [X = Cl (**6a**), Br (**6b**)]. Reactions of $^{13}CH_2{=}CHSiMe_3$ and $CH_2{=}CDSiMe_3$ show that the methylcarbyne ligand is formed by net migration of the methyne hydrogen to the methylene carbon, but a crossover experiment with both of these substrates shows that the rearrangement is not intramolecular. In some of the reactions, pre-equilibrium formation of a tungsten(II) vinylsilane complex is observed. The proposed mechanism for carbyne formation, based on kinetic and labeling studies, involves loss of $XSiR_3$ from the vinylsilane intermediate to give a tungsten vinyl species. The vinyl complex is deprotonated to a vinylidene which is reprotonated to the carbyne. The relative rates of carbyne formation span more than three orders of magnitude, with reactions of **1a** faster than **1b** and $CH_2{=}CHSn^nBu_3$ > $CH_2{=}CH CH_2SnMe_3$ > $CH_2{=}CHSi(OMe)_3$ > $CH_2{=}CHSiMe_3$ > $CH_2{=}CHCH_2Si(OMe)_3$ > $CH_2{=}CHCH_2SiMe_3$. A primary determinant of relative reactivity is the initial binding of the olefinic substrate to tungsten(II).

Carbyne or alkylidyne complexes have been utilized in a variety of processes including alkyne metathesis, polymerizations and coupling reactions.[1] Fischer-type carbyne complexes are most commonly synthesized via oxide or alkoxide removal from acylate or alkoxycarbene complexes such as $[(CO)_5MC(O)R]^-$ and $(CO)_5M{=}C(OR')R$.[1c] We report here the syntheses of tungsten methylcarbyne and ethylcarbyne complexes $W({\equiv}CR)X(PMe_3)_4$ from reactions of readily accessible $WX_2(PMe_3)_4$ (X = Cl, **1a**; Br, **1b**) with vinyl- and allyl-silicon and -tin reagents.[2] These compounds are isoelectronic with the classic Fischer carbyne complexes $M({\equiv}CR)X(CO)_4$ but are unusual in that they contain no strong π-acid coligands. A few closely related compounds have been prepared by reduction of d^0 alkylidynes—$W({\equiv}CCMe_3)Cl(PMe_3)_4$ and $W({\equiv}CPh)Br(PMe_3)_4$ from $W({\equiv}CR)X_3(PMe_3)_3$[3]—or by more mechanistically complex routes, $W({\equiv}CH)Cl(PMe_3)_4$ from **1a** and $AlMe_3$[3a] and $W({\equiv}CCH_3)CH_3(PMe_3)_4$ from photolysis of WMe_6 in neat PMe_3.[4] $W({\equiv}CPh)Cl[P(OMe)_3]_4$ and $W({\equiv}CPh)Cl(dppe)_2$ have also been prepared by ligand substitution under forcing conditions.[5]

The reactions reported here involve transfer of a vinyl or allyl group to tungsten from silyl or tin reagents, and subsequent rearrangement of the unsaturated fragment to a carbyne ligand. Conversion of bound vinyl groups to carbyne ligands has been observed previously,[6] but to our knowledge the allyl-to-carbyne rearrangement is without precedent. We and others have demonstrated the

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* Dedicated to Professor John E. Bercaw on the occasion of his 50th birthday.

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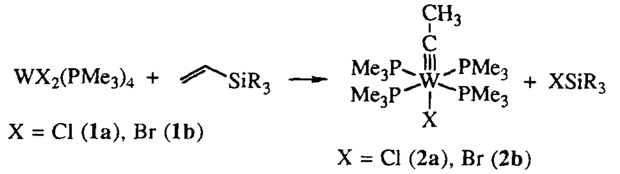
extremely high propensity of WCl_2L_4 [L = $PMePh_2$, PMe_3 (**1a**)] and related species to form metal–ligand multiple bonds, including oxo, imido, alkylidene, phosphinocarbyne, sulphido, selenido, tellurido and phosphinidine complexes.[7] The scope and mechanisms of the vinyl- and allyl-to-carbyne reactions, and their relationship to other multiple bond forming reactions of **1**, are the subject of this report. The unusual reactivity of these carbyne complexes with CO, olefins and acetylenes is discussed elsewhere.[8]

RESULTS

Reaction of vinyl compounds with $WX_2(PMe_3)_4$

Benzene solutions of $WX_2(PMe_3)_4$ [X = Cl (**1a**), Br (**1b**)] react with vinyl silanes to give the tungsten methylcarbyne complexes $W(\equiv CCH_3)X(PMe_3)_4$ [X = Cl (**2a**), Br (**2b**)] and 1 equivalent of halosilane $XSiR_3$ (equation 1).



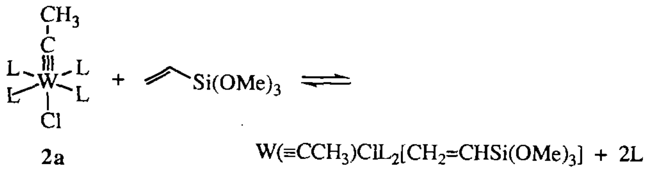
$$WX_2(PMe_3)_4 + CH_2{=}CHSiR_3 \longrightarrow W(\equiv CCH_3)X(PMe_3)_4 + XSiR_3 \qquad (1)$$

X = Cl (**1a**), Br (**1b**)

X = Cl (**2a**), Br (**2b**)

The reactions are slow at 24°C and must be heated to 69°C to proceed to completion. The presence of even small amounts of free PMe_3, which is always observed, strongly inhibits the reactions. The alkyl and alkoxy silanes $CH_2{=}CHSiMe_3$, $CH_2{=}CHSi(OEt)Me_2$ and $CH_2{=}CHSi(OMe)_3$ all give **2**, while the acetate derivative $CH_2{=}CHSi(OAc)_3$ gives different products. The silyl products were identified by NMR, and by GC-MS for $ClSi(OMe)_3$, $ClSiMe_3$ and $BrSiMe_3$. In contrast, the methyldiphenylphosphine derivative $WCl_2(PMePh_2)_4$ reacts with vinyl silanes to give paramagnetic products, with no formation of carbyne complexes under similar conditions.

Synthesis of the carbyne complex **2a** is best accomplished by refluxing a THF solution of **1a** with 5 equivalents of $CH_2{=}CHSi(OMe)_3$ for 8 h at 69°C. Under these conditions, the reaction continues to give an equilibrium mixture of **2a** and the vinylsilane adduct $W(\equiv CCH_3)Cl(PMe_3)_2[CH_2{=}CHSi(OMe)_3]$[8] (equation 2; L = PMe_3). Removal of the volatiles (including the silane), dissolution of the mixture in THF and addition of 1 equivalent of PMe_3 shifts the equilibrium back towards **2a**, which can then be isolated in >90% yield. Other methods and other vinylsilane reagents give slower reactions and lower yields.



$$W(\equiv CCH_3)ClL_4 + CH_2{=}CHSi(OMe)_3 \rightleftharpoons W(\equiv CCH_3)ClL_2[CH_2{=}CHSi(OMe)_3] + 2L \qquad (2)$$

2a

NMR spectra (Table 1) are not immediately informative as to the nature of compounds **2**, as the methyl peak of the carbyne in the ^1H NMR is partially obscured by the broad singlet for the 4 equivalent trimethylphosphine ligands, which appear as a single resonance in the ^{31}P NMR spectrum. A large number of transients are needed to observe the carbyne carbon in the ^{13}C NMR, particularly since it is a pentet due to coupling with the four phosphine ligands (δ 253.3, $^2J_{PC} = 13$ Hz in **2a**).

The connectivity of **2a** was confirmed by an X-ray crystal structure (Fig. 1; Table 2). Structure solution was performed in the tetragonal space group ($I\bar{4}2m$) rather than other space groups with the same systematic extinctions because it gave the best behaved refinement and the lowest R_w value (5.1%). The complex has crystallographically imposed S_4 site symmetry and a distorted octahedral coordination. The S_4 axis requires that the carbyne and chloride ligands are disordered along the carbyne axis, as observed in the closely related compounds $W(\equiv CCH_3)CH_3(PMe_3)_4$ and $W(\equiv CH)Cl(PMe_3)_4$.[3,4] The symmetry also means

Table 1. NMR spectra[a]

Compound	^{1}H NMR	^{31}P NMR	^{13}C NMR
$W(\equiv CMe)Cl(PMe_3)_4$ (**2a**)	1.50 (br s, 36H, $P\underline{Me}_3$) 1.58 (p, 5, 3H, $\equiv C\underline{CH}_3$)	-20.8 (s, $J_{WP} = 285$)	23.2 (q, $J_{CH} = 128$, $P\underline{Me}_3$) 35.6 (q, $J_{CH} = 124$, $\equiv C\underline{C}H_3$) 253.3 (p, $J_{PC} = 13$, $\equiv \underline{C}CH_3$)
$W(\equiv CMe)Br(PMe_3)_4$ (**2b**)	1.53 (br s, 36H, $P\underline{Me}_3$) 1.44 (p, 5, 3H, $\equiv C\underline{CH}_3$)	-22.1 (s, $J_{WP} = 285$)	[c]
$WCl_2(PMe_3)_3[CH_2{=}CHSi(OMe)_3]$ (**3a**)[d]	6.38 (s, 9H, $CH_2{=}CHSi(O\underline{Me})_3$) 2.71, 1.35, -15.18 (each: s, 9H, $P\underline{Me}_3$)	[d]	[d]
$WBr_2(PMe_3)_3[CH_2{=}CHSi(OMe)_3]$ (**3b**)[d]	6.75 (s, 9H, $CH_2{=}CHSi(O\underline{Me})_3$) 3.66, 1.83, -17.90 (each: s, 9H, $P\underline{Me}_3$)	[d]	[d]
$WCl_2(PMe_3)_3(CH_2{=}CHSiMe_3)$ (**4a**)[d,e]	1.92, 1.49, -14.23 (each: s, 9H, $P\underline{Me}_3$)	[d]	[d]
$WCl_2(PMe_3)_3[CH_2{=}CHSi(OSiMe_3)_3]$ (**5a**)[b,d]	1.13 (s, 27H, $Si(OSi\underline{Me}_3)_3$) 2.41, 1.35, -14.10 (each: s, 9H, $P\underline{Me}_3$)	[d]	[d]
$W(\equiv CCH_2CH_3)Cl(PMe_3)_4$ (**6a**)[b]	1.51 (br s, 36H, $P\underline{Me}_3$) 1.46 (m, 2H, $C\underline{H}_2CH_3$) 0.87 (t, 7.5, 3H, $CH_2C\underline{H}_3$)	-22.1 (s, $J_{WP} = 285$)	14.4 (q, $J_{CH} = 126$, $CH_2\underline{C}H_3$) 23.6 (m, $J_{CH} = 127$, $P\underline{Me}_3$) 43.0 (t, $J_{CH} = 134$, $\underline{C}H_2CH_3$) 262.5 (m, $\equiv \underline{C}CH_2CH_3$)
$W(\equiv CCH_2CH_3)Br(PMe_3)_4$ (**6b**)[b]	1.53 (br t, 5, 36H, $P\underline{Me}_3$) 1.56 (m, 2H, $C\underline{H}_2CH_3$) 0.96 (t, 7.5, 3H, $CH_2C\underline{H}_3$)	-26.9 (s, $J_{WP} = 284$)	[c]

[a] Spectra were taken in C_6D_6 solvent *except for* **5a** *and* **6a** *(in THF-d_8*, as noted). Spectra are reported as δ (multiplicity, *J*, number of hydrogens, assignment); coupling constants are reported in Hz. Abbreviations: q = quartet, p = pentet, br = broad.

[b] Spectrum taken in THF-d_8.

[c] ^{13}C NMR spectrum not obtained.

[d] Since the ^{1}H NMR spectrum is paramagnetically shifted, no ^{31}P or ^{13}C NMR is anticipated for this compound. The vinyl resonances were not observed, presumably due to their proximity to the paramagnetic centre.

[e] The $Si\underline{Me}_3$ signal in **4a** was not observed; it was likely obscured by the large excess of $CH_2{=}CHSiMe_3$ present.

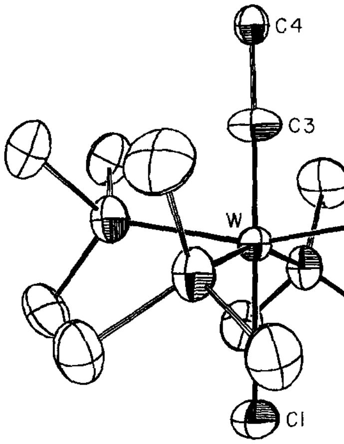


Fig. 1. ORTEP of $W(\equiv CCH_3)Cl(PMe_3)_4$ (**2a**) with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond distances and angles for $W(\equiv CCH_3)Cl(PMe_3)_4$ (**2a**)

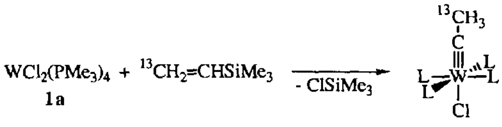
Bond distances (Å)		Bond angles (°)	
W—P	2.464(2)	P—W—P′	161.5(2)
W—Cl	2.589(15)	P—W—P″	91.48(9)
W—C(3)	1.756(36)	P—W—Cl	80.75(9)
C(3)—C(4)	1.49(9)	P″—W—Cl	99.25(9)
		Cl—W—C(3)	180.0
		W—C(3)—C(4)	176(3)

′Denotes the related atom from the symmetry operation $-x, -y, z$.

″Denotes the related atom from the symmetry operation $-x, y, -z$.

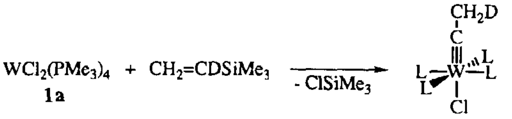
that there is only one crystallographically unique PMe_3 group. The PMe_3 ligands are staggered above and below the equatorial plane, with a significant distortion away from octahedral angles [P—W—C(3) = 80.75(9)°, 99.25(9)°], presumably as a result of steric interactions. Such steric interactions probably discourage formation of carbynes with larger phosphine ligands, for instance from $WCl_2(PMePh_2)_4$. The disorder prevents accurate determination of bond lengths involving the carbyne and chloride ligands, although the short tungsten–carbon triple bond [1.76(4) Å] is typical for tungsten carbynes.[1c]

Reaction of **1a** with $^{13}CH_2{=}CHSiMe_3$ gives $W(\equiv C^{13}CH_3)Cl(PMe_3)_4$ by ^{13}C NMR (equation 3).

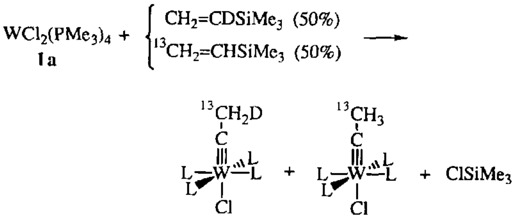


(3)

Since no enhancement of the carbyne carbon signal is observed, there is ≤5% ^{13}C at the carbyne carbon. The reaction of α-deutero-vinyltrimethylsilane, $CH_2{=}CDSiMe_3$, gives $W(\equiv CCH_2D)Cl(PMe_3)_4$, with ≤5% CHD_2 product (by ^{13}C NMR; equation 4). A crossover experiment using a 50:50 mixture of $^{13}CH_2{=}CHSiMe_3$ and $CH_2{=}CDSiMe_3$ gave significant scrambling as both $W{\equiv}C^{13}CH_3$ and $W{\equiv}C^{13}CH_2D$ (60:40) are observed by ^{13}C NMR (equation 5). The scrambling is not due to exchange between carbyne complexes, since mixtures of $W{\equiv}C^{13}CH_3$ and $W{\equiv}CCH_2D$ complexes, with and without added PMe_3, show no exchange of label after heating for 1 day at 70°C. Thus migration of the proton (or deuterium) from the α-carbon to the β-carbon to form the carbyne is not intramolecular. Reaction of 3 equivalents each of $CH_2{=}CHSiMe_3$ and $CH_2{=}CDSiMe_3$ with **1a** gave a 50:50 (±5%) mixture of $W{\equiv}CCH_3$ and $W{\equiv}CCH_2D$ by ^{13}C NMR, demonstrating no observable isotope effect.

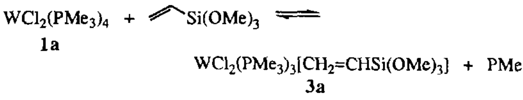


(4)



(5)

An intermediate is observed in reactions of **1a** with $CH_2{=}CHSi(OMe)_3$, at both 25 and 69°C. This species exhibits a paramagnetic NMR spectrum (Table 1) which indicates its assignment as the tungsten(II) vinylsilane complex $WCl_2(PMe_3)_3[CH_2{=}CHSi(OMe)_3]$ (**3a**) (equation 6). Four peaks of equal area are observed in the ^1H NMR of **3a**, three of which were identified as trimethylphosphine peaks by comparison to the three observed peaks in the ^2H NMR spectrum of the reaction of $WCl_2[P(CD_3)_3]_4$ with $CH_2{=}CH\,Si(OMe)_3$ to give $WCl_2[P(CD_3)_3]_3[CH_2{=}CHSi(OMe)_3]$. The final peak is due to the trimethoxysilane protons. The vinyl protons were not observed presumably because their resonances are broadened by the paramagnetic tungsten metal centre. The reaction of **1a** with ethylene is reported to give the analogous complex $WCl_2(PMe_3)_3(C_2H_4)$, which exhibits a similar NMR spectrum.[9]



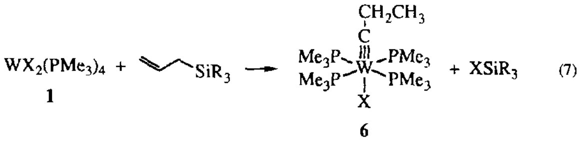
(6)

The intermediate **3a** grows in during the first 30 min of reaction, and thereafter appears to be in equilibrium with **1a** according to equation 6, with K_{eq} (69°C) ≈ 0.5 in C_6D_6. A similar intermediate, $WCl_2(PMe_3)_3(CH_2{=}CHSiMe_3)$ (**4a**), is observed on reaction of **1a** with $CH_2{=}CHSiMe_3$ but its formation is much less favourable [K_{eq} (69°C) $\approx 1 \times 10^{-3}$]. The bulky $CH_2{=}CH Si(OSiMe_3)_3$ also gives a paramagnetic adduct, $WCl_2(PMe_3)_3[CH_2{=}CHSi(OSiMe_3)_3]$ (**5a**), but this does not go on to make a carbyne complex [K_{eq} (**5a**, 69°C) ≈ 0.1 in THF-d_8; all other equilibrium constants were determined in C_6D_6]. The bromotungsten complex **1b** forms a weaker adduct with vinyltrimethoxysilane, $WBr_2(PMe_3)_3[CH_2{=}CH Si(OMe)_3]$ (**3b**), with K_{eq} (**1b**) $\approx 1 \times 10^{-2}$ vs K_{eq} (**1a**) ≈ 0.5 at 69°C. No intermediates are observed during the reaction of **1b** with vinyltrimethylsilane, even when 40 equivalents of silane are present.

Vinyltri(n-butyl)tin, $CH_2{=}CHSn^nBu_3$, also converts **1a** to the carbyne complex **2a**, as determined by ^{1}H and ^{31}P NMR. An intermediate is not observed but, as in the silyl case, free PMe_3 inhibits the reaction. If excess tin reagent is present, a second, uncharacterized product is observed to grow in with the carbyne. No reaction is observed between **1a** and either the saturated tin reagent ethoxytributyltin ($EtOSn^nBu_3$), or the sterically hindered (α-ethoxyvinyl)tributyltin, $CH_2{=}C(OEt) Sn^nBu_3$.

Reaction of allylsilanes with $WX_2(PMe_3)_4$

The tungsten(II) complexes **1a** and **1b** also react with the allyl silanes $CH_2{=}CHCH_2Si(OMe)_3$, $CH_2{=}CHCH_2SiClMe_2$ and $CH_2{=}CHCH_2SiMe_3$ to give ethyl carbynes $W({\equiv}CCH_2CH_3)X(PMe_3)_4$ [X = Cl (**6a**), Br (**6b**)] (equation 7). A remarkable amount of hydrogen migration has to occur to complete this allyl to ethylcarbyne transformation. The ^{1}H, ^{31}P and ^{13}C NMR spectra of **6a** and **6b** (Table 1) are very similar to those of **2a** and **2b**, indicating that they have the same basic structure. The 4 equivalent trimethylphosphine ligands give only one resonance in the ^{1}H and ^{31}P NMR spectra. The ^{13}C resonance of the carbyne carbon of **6a** appears at 262.5 ppm, and the presence of a triplet and quartet in the ^{1}H NMR and the proton coupled ^{13}C NMR confirms the presence of an ethyl group.



Reactions of **1a** with allylsilanes require longer reaction times than the analogous reactions of vinylsilanes (1 week at 69°C for **1a** and 5 equivalents of $CH_2{=}CHCH_2Si(OMe)_3$ to form **6a**). The reactions are inhibited by the presence of free PMe_3. The ethylcarbyne complex **6a** does not appear to bind allylsilanes, even at high concentrations (1.3 M in silane). No intermediates were observed during the reactions of allylsilanes with **1a** or **1b**, although small amounts of free PMe_3 are observed during the reaction. Allyltrimethyltin also gives **6a** on reaction with **1a**, along with small amounts of a tin containing impurity; tetraallyltin forms small amounts of **6a** but reacts further to give a gray precipitate and complex ^{1}H and ^{31}P NMR spectra. The carbyne complex **2a** is unreactive with unsaturated tin reagents, suggesting that further reaction of the carbyne is not responsible for the formation of the secondary products, the nature of which are not known.

Kinetic studies

To understand the inhibition by phosphine, the rate of phosphine loss in **1a** and **1b** has been examined by monitoring the exchange with $P(CD_3)_3$ (equation 8). The appearance of free $P(CH_3)_3$ with time was fit with a first-order approach to equilibrium model (equation 9), in which P_{eq} is the concentration of free PMe_3 at equilibrium, P_o is the initial amount of PMe_3 bound to the metal centre and P_t is the amount of free PMe_3 at time t. A similar approach has shown that $MoCl_2(PMe_3)_4$ undergoes phosphine exchange by a dissociative mechanism.[7c]

$$WX_2(PMe_3)_4 + n\,P(CD_3)_3 \rightleftharpoons WX_2(PMe_3)_{4-n}[P(CD_3)_3]_n + n\,PMe_3 \qquad (8)$$

$$4\frac{P_{eq}}{P_o}\ln\left(\frac{P_{eq}}{(P_{eq}-P_t)}\right) = k_1 t \qquad (9)$$

The rate constants, k_1, for loss of one phosphine ligand at 69°C in C_6D_6 are 2.5×10^{-3} s^{-1} for **1a** and 5.0×10^{-3} s^{-1} for **1b**. Phosphine loss from **1a** is a thousand times slower at 24°C ($k_1 = 3.2 \times 10^{-6}$ s^{-1}), which gives crude estimates of $\Delta H\ddagger \approx 30$ kcal mol^{-1} and $\Delta S\ddagger \approx +80$ e.u.

Reactions of **1a** and **1b** with different allyl and vinyl silanes and stannanes in C_6D_6 solutions have been monitored by ^{1}H NMR at 69°C in sealed tubes. Pseudo-first-order conditions of excess silane or stannane have been used. The reaction rates are not always reproducible, particularly at lower silane or stannane concentrations, and do not consistently follow first order kinetics for the bulk of the reaction. These irregularities result from the presence of small and variable amounts of PMe_3, which dramatically affect the rate. The PMe_3 is formed primarily by binding of silane to **1** or **2** (equations 6 and 2, respectively), together with small amounts of decomposition and/or side reactions that may not occur to exactly the same extent in each reaction. Typically, first order kinetics are roughly followed when the concentration of PMe_3 varies by no more than ±10%, as illustrated in Fig. 2. The pseudo-first order rate constants obtained (k_{obs}) vary with the ratio of [silane]/[PMe_3] (determined from the ^1H NMR spectra), over a factor of 4 in this ratio, as shown in Fig. 3. The relative rates can be compared using a rate constant k', which incorporates the dependence of k_{obs} on the [silane]/[PMe_3] ratio (equation 10).

$$k_{obs} = k'\frac{[\text{silane}]}{[\text{PMe}_3]} \qquad (10)$$

Thus the rate law is as shown in equation 11. It should be noted, however, that the errors in the k_{obs} and [silane]/[PMe_3] ratios are ±20%, especially at high concentrations of silane, where the [silane]/[PMe_3] ratio is difficult to determine by integration of ^1H NMR spectra.

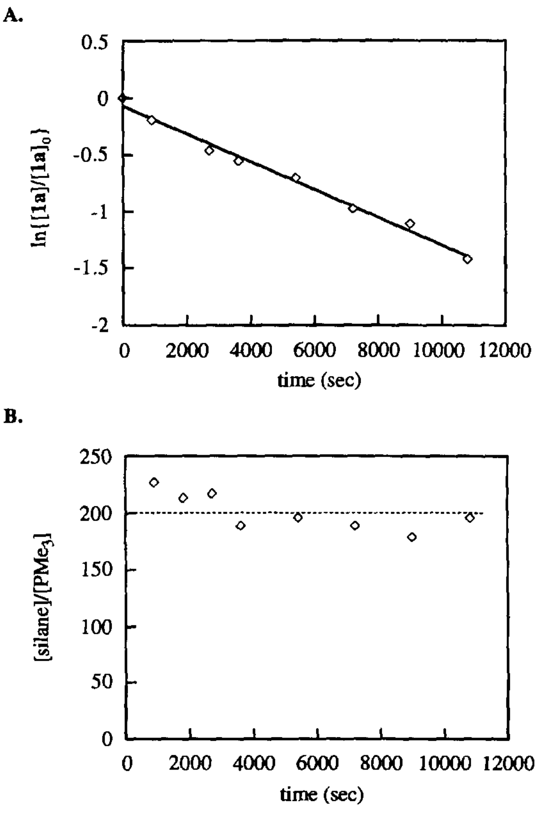


Fig. 2. Plots for the reaction of 35 equivalents of $CH_2{=}CHCH_2Si(OMe)_3$ with $WCl_2(PMe_3)_4$ (**1a**) at 69°C. (A) First-order plot of ln{[**1a**]/[**1a**]$_o$} vs time; $k_{obs} = 1.2 \times 10^{-4}\ s^{-1}$. (B) Plot of the [silane]/[PMe_3] ratio vs time. The average ratio, indicated by the dotted line, is 200±20.

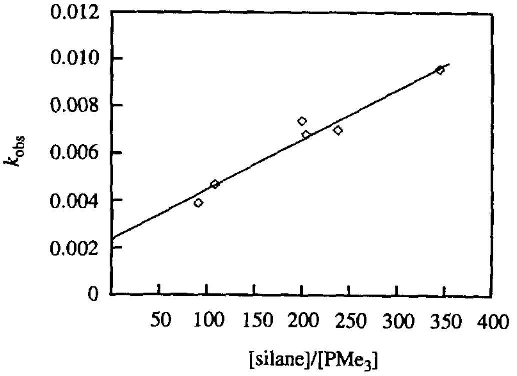


Fig. 3. Plot of k_{obs} vs [silane]/[PMe_3] for the reaction of $CH_2{=}CHCH_2Si(OMe)_3$ with $WCl_2(PMe_3)_4$ (**1a**) at 69°C.

$$\frac{d[WX_2(PMe_3)_4]}{dt} = -k'[WX_2(PMe_3)_4]\frac{[\text{silane}]}{[\text{PMe}_3]} \qquad (11)$$

Rate constants k' have been determined for reactions of **1a** with four unsaturated silanes and for allyltrimethyltin (Table 3). The fastest reactions occur with vinyltri(*n*-butyl)tin, which in the presence of >5 equivalents of stannane show k_{obs} for disappearance of **1a** equal to the rate of phosphine loss (k_1 see above): at 69°C, $k_{obs} = 2.3(3) \times 10^{-3}$ s^{-1} for **1a**+5 $CH_2{=}CHSn^nBu_3$ compared to $k_1 = 2.5(3) \times 10^{-3}$ s^{-1} for phosphine loss determined simultaneously in a constant temperature bath. In this case, calculation of k' is not appropriate (and is not possible because the ^nBu protons mask the PMe_3 resonances in the ^1H NMR).

As shown in Table 3, the relative rates are $CH_2{=}CHSn^nBu_3$ > $CH_2{=}CHCH_2SnMe_3$ > $CH_2{=}CHSi(OMe)_3$ > $CH_2{=}CHSiMe_3$ > $CH_2{=}CHCH_2Si(OMe)_3$ > $CH_2{=}CHCH_2SiMe_3$, spanning more than three orders of magnitude. The bromotungsten complex **1b** reacts more slowly than **1a** (Table 3), with $k'_{1a}/k'_{1b} = 90$ for reactions with $CH_2{=}CHSiMe_3$ and 15 for reactions of $CH_2{=}CHCH_2SiMe_3$. Quantitative data could not be obtained for the reaction of **1b** with trimethoxysilanes because the methoxy resonances overlap with the broad PMe_3 peak for **1b** in the ^1H NMR.

DISCUSSION

The one-step synthesis of $W(\equiv CR)X(PMe_3)_4$ (**2** and **6**) from $WX_2(PMe_3)_4$ (**1**) and vinyl or allyl reagents is a new and facile entry into carbyne complexes. Green and co-workers have observed rearrangements of metal-bound vinyl groups to car-

Table 3. Kinetic data for reactions of $WX_2(PMe_3)_4$ (X=Cl, **1a**; Br, **1b**) with silanes and stannanes[a]

Reaction	$k' = \frac{k_{obs}}{[Si]/[PMe_3]}$	Relative k'	K_{eq} for formation of $W(CH_2{=}CHR)X_2L_3$[b]	$k_3 \left(= \frac{k'}{K_{eq}}\right)$
1a + $CH_2{=}CHCH_2SiMe_3$	$9.7 \times 10^{-8}\ s^{-1}$	1	[c]	
1b + $CH_2{=}CHCH_2SiMe_3$	$6.5 \times 10^{-9}\ s^{-1}$	0.07	[c]	
1a + $CH_2{=}CHCH_2Si(OMe)_3$	$3.9 \times 10^{-7}\ s^{-1}$	4	[c]	
1a + $CH_2{=}CHSiMe_3$	$1.6 \times 10^{-6}\ s^{-1}$	16	1×10^{-3}	$1.6 \times 10^{-3}\ s^{-1}$
1b + $CH_2{=}CHSiMe_3$	$1.8 \times 10^{-8}\ s^{-1}$	0.2	[c]	
1a + $CH_2{=}CHSi(OMe)_3$	$6.3 \times 10^{-5}\ s^{-1}$	650	5×10^{-1}	$1.3 \times 10^{-4}\ s^{-1}$
1b + $CH_2{=}CHSi(OMe)_3$	[d]		1×10^{-2}	
1a + $CH_2{=}CHCH_2SnMe_3$	$2.0 \times 10^{-4}\ s^{-1}$	2100	[c]	
1a + $CH_2{=}CHSn^nBu_3$	$k_{obs} = k_1$ $(= 2.5 \times 10^{-3}\ s^{-1})$	not applicable	[c]	

[a] At 69°C in C_6D_6 solvent. Error bars on k', *ca* ±20%; on K_{eq}, *ca* ±50%.

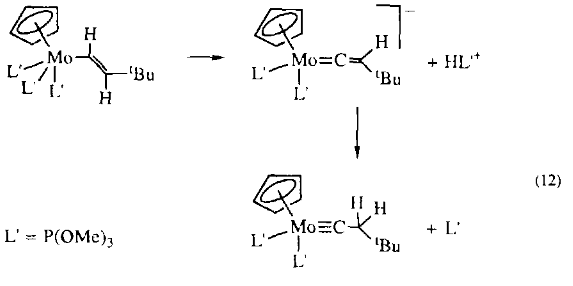
[b] $K_{eq} = [WX_2(CH_2{=}CHR)(PMe_3)_3][PMe_3]/[WX_2(PMe_3)_4][CH_2{=}CHR]$, where R is a silicon-containing substituent, as measured by NMR.

[c] $[WX_2(CH_2{=}CHR)(PMe_3)_3]$ was not observed.

[d] Overlap of O*Me* and W(P*Me*$_3$) resonances in the ^{1}H NMR prevents obtaining quantitative data, though qualitatively the reaction is faster than **1b** + $CH_2{=}CHSiMe_3$.

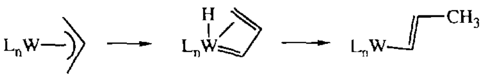
byne ligands, typically via an intermediate vinylidene complex as in equation 12 (L′ = $P(OMe)_3$) although direct 1,2 migration may also be possible.[6] Rearrangement of vinyl species to allyl complexes have also been reported.[6,10] In Green's system,[6] vinyl ligands rearrange competitively to allyl or carbyne ligands, but the allyl complexes are stable—in contrast to the allyl-to-carbyne reactions reported here (equation 7). The same mechanistic manifold leading to carbyne complexes can also be entered using alkynes, either by nucleophilic attack at a coordinated alkyne to make a vinyl ligand which rearranges, or by initial rearrangement of acetylene to vinylidene, followed by protonation to the carbyne.[1c,11]

The reactions of $WX_2(PMe_3)_4$ (**1**) with vinylsilane and vinylstannane reagents reported here involve net conversion of a vinyl group to a carbyne ligand. The labelling studies indicate that the vinyl-to-methylcarbyne rearrangement occurs by net movement of the methyne hydrogen to the methylene carbon and that the transfer is not intramolecular. A mechanism consistent with the labelling and kinetic studies is shown in Scheme 1, which draws heavily on the related pathway proposed by Green for reaction 12.[6] The vinyl reagents serve to generate a vinyltungsten complex, as discussed below. This vinyl complex, which could be either η^1 or η^2, is then deprotonated to give a vinylidene.[6] Green has suggested that this deprotonation most likely occurs from an η^1-vinyl.[6] The most plentiful base in our system is PMe_3 [$P(OMe)_3$ in Green's work], and free PMe_3 is seen in all the reactions of **1a**. The vinylidene then protonates to form the carbyne, which is a well precedented step.[1c,11] The protonation/reprotonation sequence then accounts for the intermolecular nature of the rearrangement. Although a number of carbyne complexes (including the one in equation 12) can be deprotonated to the vinylidene species,[12] this is not facile for **2a** under our conditions because no scrambling is observed between $W(\equiv C^{13}CH_3)Cl(PMe_3)_4$ and $W(\equiv CCH_2D)Cl(PMe_3)_4$.

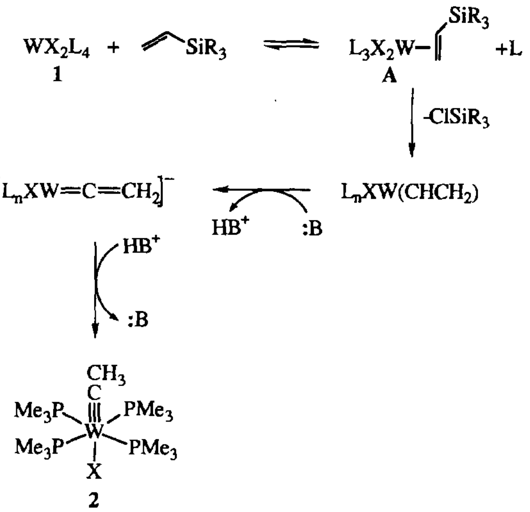


(12)

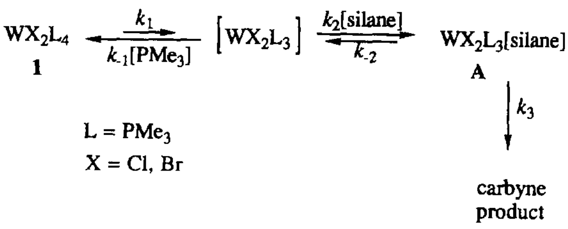
The pathway for rearrangement of allylsilanes has not been determined, but a reasonable hypothesis is initial isomerization of an allyl complex to a vinyl species (equation 13), which can then isomerize as in Scheme 1 to give the ethylcarbyne product. Green and others have observed the opposite isomerization, vinyl → allyl, in CpMo complexes.[13] The formation of a strong tungsten–carbon triple bond in the compounds reported here is presumably the driving force for rearranging the relatively stable allyl fragment to an ethylcarbyne ligand.



(13)

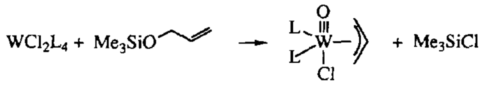


Scheme 1. Proposed mechanism for the reaction of WX_2L_4 (**1**) with vinylsilanes.



Scheme 2. Kinetic scheme for the reactions of WX_2L_4 (**1**) with unsaturated silanes.

The initial formation of the tunsten vinyl or tungsten allyl complex occurs by exchange of a tungsten halide ligand for the unsaturated organic fragment bound to silicon or tin. A similar process is observed on reactions of vinyl- and allylsilanes with $Pt_2Cl_4(C_2H_4)_2$ to give platinum vinyl and allyl complexes plus Me_3SiCl.[14] The rate limiting step in the conversion of **1** to carbynes likely occurs in this vinyl transfer stage of the reaction, prior to the vinyl rearrangement, since no deuterium isotope effect is observed in reactions of mixed $CH_2{=}CH\,SiMe_3$ and $CH_2{=}CDSiMe_3$ (equation 5). Complexes **1** do not react with saturated reagents such as $SiMe_4$, suggesting that the vinyl or allyl group provides the initial binding of the reagent to tungsten. This is consistent with the observation of vinylsilane complexes **3**–**5**. Initial substrate binding has been shown to be a key determinant of the reactivity of **1** and related compounds, in reactions of alcohols, ethers, ketones, phosphine oxides, etc.[2,7a–g] For instance saturated silyl ethers such as $MeOSiMe_3$ are unreactive with **1**, but $CH_2{=}CH\,CH_2OSiMe_3$ reacts to form a tungsten-oxo-allyl complex, with silicon again removing a halide (equation 14; L = PMe_3).[2] The unsaturated fragment acts as a "tether" to bring the substrate close to the metal centre so that rearrangement to a strong multiple bond may occur.



(14)

The kinetic studies of the reactions of $WX_2(PMe_e)_4$ (**1**) with vinyl- and allylsilanes and -stannanes are consistent with initial phosphine loss and substrate binding (Scheme 2). The phosphine exchange study (equation 8) indicates dissociation of PMe_3 from **1a**, with $k_1 = 2.5\times10^{-3}\ s^{-1}$ at 69°C. The mechanism in Scheme 2 is consistent with the observed rate law (equation 11) in two kinetic regimes. If the rate limiting step is attack of the substrate on $[WX_2(PMe_3)_3]$, i.e. when $k_2[\text{silane}] < k_{-1}[PMe_3]$ and $k_3 > k_{-2}$, then:[15]

$$\frac{d[WX_2(PMe_3)_4]}{dt} = -\frac{k_1k_2}{k_{-1}}[WX_2(PMe_3)_4]\frac{[\text{silane}]}{[PMe_3]} \tag{15}$$

Alternatively, there could be pre-equilibrium formation of the adduct $WX_2(CH_2{=}CHR)(PMe_3)_3$ (**A**) followed by its rate limiting unimolecular decay ($k_3 < k_{-2}$). Under these conditions,

$$\frac{d[WX_2(PMe_3)_4]}{dt} = -k_3K_{eq}[WX_2(PMe_3)_4]\frac{[\text{silane}]}{[PMe_3]} \tag{16}$$

where

$$K_{eq} = \frac{k_1k_2}{k_{-1}k_{-2}}$$

The reactions of $CH_2{=}CHSi(OMe)_3$ and $CH_2{=}CHSiMe_3$ clearly fall in the latter regime ($k_3 < k_{-2}$, equation 16) because of the direct observation of equilibrium amounts of the vinylsilane adducts **A** (complexes **3a**, **3b** and **4a**). While **1b**$+CH_2 = CHSiMe_3$ does not show an intermediate, it seems likely that this is kinetically similar to the other vinyl silanes, except with a smaller K_{eq} such that the adduct is not observable. Note that **4a** is seen only at high silane concentrations and K_{eq} for **3b** is 50 times smaller than that for **3a**. For allylic substrates, however, the data do not allow determination of the kinetic regime since no intermediates are observed.

The K_{eq} values—the ability of olefins to displace a phosphine ligand in $WX_2(PMe_3)_4$ (**1**)—vary in the order $CH_2{=}CH_2 > CH_2{=}CHSi(OMe)_3 > CH_2{=}CHSi(OSiMe_3)_3 > CH_2{=}CHSiMe_3 > CH_2{=}CHCH_3$ (no binding is observed for propene[7g,9]). $SiMe_3$ and especially $Si(OR)_3$ groups enhance binding to the metal centre relative to a methyl group. The electron withdrawing OMe and $OSiMe_3$ groups may assist the binding by making the olefin a better π-acid toward the highly electron-rich tungsten centre. The effect of the silyl group likely lessens as it is moved farther away from the unsaturation, suggesting that the allylsilanes (like propene) should not bind well to the metal centre.

The relative rates of reactions of vinyl silanes with **1a** and **1b** are primarily determined by the initial substrate binding, K_{eq}. $CH_2{=}CHSi(OMe)_3$ reacts with **1a** to form a carbyne 40 times faster than the reaction of $CH_2{=}CHSiMe_3$ because its K_{eq} is 500 times larger; the k_3 step in this reaction is actually 12 times faster for the trimethylsilyl substrate (Table 3). The bromotungsten complex **1b** is slightly less reactive than **1a**, both in terms of k' and K_{eq} (Table 3). While a direct quantitative comparison of k_3 values is not available, an estimate can be made by assuming that the binding of $CH_2{=}CHSiMe_3$ to **1b** is 50 times worse than its binding to **1a** ($K_{eq,1b} \cong 2 \times 10^{-4}$), as this is the factor observed for $CH_2{=}CHSi(OMe)_3$. This would suggest a $k_3 \cong 9 \times 10^{-4}$ s^{-1} for **1b**+$CH_2{=}CHSiMe_3$, within a factor of 2 of the value for **1a**. Again, the ligating ability of the substrate appears to be the primary determinant of reactivity. $CH_2{=}CH Si(OSiMe_3)_3$ is the one exception to this binding–reactivity correlation, as it binds well but does not react further to give the carbyne complex **2**, presumably for steric reasons.

The allylic substrates are less reactive than the vinyl compounds. A detailed analysis of the k' values is not possible because of the uncertainty of their kinetic regime (equations 15 and 16 above) but it is likely that at least a portion the lower reactivity is due to poorer binding to tungsten. This poorer binding could appear in the rate constant k' through a smaller K_{eq} (equation 16) or through a slower trapping of the unsaturated intermediate, k_2 in equation 15.

The tin reagents react more rapidly than their silicon analogues: k' for $CH_2{=}CHCH_2SnMe_3$ is 2100 times larger than the k' for $CH_2{=}CH CH_2SiMe_3$ (Table 3). Vinyltri(*n*-butyl)tin is the most reactive of all the reagents, and is kinetically distinct from the other substrates: in the presence of excess $CH_2{=}CHSn^nBu_3$, reaction with **1a** occurs at the rate of phosphine exchange ($k_{obs} = k_1$). This implies that trapping of $[WX_2(PMe_3)_3]$ occurs rapidly (k_2[stannane] $> k_{-1}[PMe_3]$), suggesting that binding is again critical (although the k_2 step could conceivably be something other than binding). Note that with smaller amounts of $CH_2{=}CHSn^nBu_3$, added PMe_3 is observed to inhibit the reaction, indicating that k_2[stannane] $\approx k_{-1}[PMe_3]$ in these reactions. Tin appears to activate the unsaturated fragments, making them better traps for $[WX_2(PMe_3)_3]$, probably because tin–carbon bonds are more polarizable than those of silicon.[16] Sn—C bonds are also significantly weaker than Si—C bonds, which should facilitate delivery of the vinyl or allyl fragment to the tungsten (likely a part of the k_3 step). Easier tin–carbon bond cleavage, such that $k_3 > k_{-2}$, may be why a tungsten vinylstannane intermediate analogous to **A** (Schemes 1 and 2) is not observed.

The reactions with unsaturated silyl and stannyl reagents illustrate two important factors which influence reactivity of $WX_2(PMe_3)_4$ complexes: the affinity of the electron rich metal centre for π-acidic olefin ligands and the ability of the tungsten centre to rearrange the carbon fragments to form strong metal–carbon triple bonds. These reactions provide a new and convenient route to tungsten carbyne complexes.

EXPERIMENTAL

General considerations

Reactions were performed under nitrogen using standard vacuum line techniques. Compounds were handled and stored in a continuous nitrogen flow glovebox. Solvents were dried using standard techniques.[17] Silyl reagents (Petrarch), allyltrimethyltin (Organometallics), and vinyltri(*n*-butyl)tin (Aldrich) were dried over 4 Å sieves or sodium, degassed and distilled on the vacuum line. Tetrallyltin (Aldrich) was degassed and used without further purification. $^{13}CH_2{=}CHSiMe_3$ was prepared according to literature procedures.[18] PMe_3-d_9 was prepared from CD_3I (Cambridge) by Keith Hall following literature procedures.[19] Me_3SiCl was identified by ^{1}H NMR and spiking a reaction mixture with an authentic sample; other halosilanes were identified by GC/MS.

^{1}H NMR spectra were recorded on a Varian VXR-300, Bruker AC-200 or Bruker WM-500 using C_6D_6 as solvent unless noted otherwise. ^{13}C and ^{31}P NMR were taken at 75.4 and 121.4 MHz, respectively. Most spectra are reported in Table 1, listed as δ (multiplicity, J (Hz), number of hydrogens, assignment); coupling constants are given in Hz. ^{1}H and ^{13}C chemical shifts are reported in ppm referenced to solvent peaks or tetramethylsilane, ^{31}P spectra were referenced to external 85% H_3PO_4. Elemental analyses were performed by Canadian Microanalytical Service, Delta, B.C.

Many reactions were performed in sealed NMR tubes. In a typical procedure, $WCl_2(PMe_3)_4$ (0.012 g, 2.1×10^{-5} mol) in C_6D_6 (0.5 cm^3 by automatic pipette) were loaded along with other reagents (by microlitre syringe) in an NMR tube sealed to a ground glass joint in the drybox, then capped with a teflon valve. The tube was frozen at -196°C and evacuated on the vacuum line, tetramethylsilane (if needed) was transferred in and the tube was sealed with a torch.

Syntheses and reactions

$WCl_2(PMe_3)_4$ (**1a**) was prepared by a modification of the published procedure[20] using Mg as the reductant instead of Na/Hg amalgam, which gives an easier workup and has no mercury waste. $WCl_4(PMe_3)_3$ (4.0 g, 7.2×10^{-3} mol), Mg (0.24 g, 9.9×10^{-3} mol), THF (80 cm^3) and PMe_3 (0.9 cm^3) were loaded in a 200 cm^3 flask along with a stir bar. The red solids and Mg were suspended in a pale red solution and stirred at room temperature until the Mg was activated (from 1 h to overnight), and until the solution turned olive green. The volatiles were removed from the solution and the orange residue was redissolved in 50 cm^3 toluene and filtered to remove the $MgCl_2$. The volatiles were removed from the filtrate and the residue was dissolved in *ca* 40 cm^3 THF with slight warming. The volume was reduced to 20 cm^3, and the solution was cooled slowly to 0°C to give 1.5 g orange crystals which were rinsed with 1×15 cm^3 diethylether and dried *in vacuo*. Second (0.9 g) and third (0.7 g) crops were obtained following the above procedure to give a total yield of 3.0 g (76%). ^{1}H NMR (C_6D_6): 3.8 (br s, $\Delta\nu_{1/2} \approx 4$ Hz).

$WBr_2(PMe_3)_4$ (**1b**). $WCl_2(PMe_3)_4$ (**1a**) (0.50 g, 8.9×10^{-4} mol) and LiBr (0.50 g, 5.6×10^{-3} mol) were refluxed at 65°C in 25 cm^3 of THF in a 50 cm^3 glass bomb sealed with a teflon stopcock. After 20 h, the solution was cooled to room temperature, the volatiles were removed *in vacuo* and toluene (30 cm^3) was added. White solids were filtered away from the yellow solution and the volatiles were removed. ^{1}H NMR of the residue showed a mixture of $WClBr(PMe_3)_4$ and $WBr_2(PMe_3)_4$. The residue was dissolved in 25 cm^3 THF, more LiBr (0.40 g, 4.6×10^{-3} mol) was added, and the solution refluxed overnight. The volatiles were removed, toluene (50 cm^3) was added, and the solution was filtered. Removal of the volatiles and recrystallization from 15 cm^3 THF at 0°C gave **1b** as a red–orange powder (0.23 g, 39% yield). ^{1}H NMR: 3.38 (broad s, $\Delta\nu_{1/2} \approx 40$ Hz, $WBr_2(P\underline{Me_3})_4$); $WClBr(P\underline{Me_3})_4$, 3.65 (broad s, $\Delta\nu_{1/2} \approx 40$ Hz).

$WCl_2[P(CD_3)_3]_4$. $WCl_2(PMe_3)_4$ (**1a**) (20 mg, 3.6×10^{-5} mol) and 10 equivalents of $P(CD_3)_3$ were refluxed in benzene (0.6 cm^3) at 70°C in a sealed NMR tube overnight. The tube was broken open and the volatiles removed, then benzene (0.6 cm^3) and 10 equivalents of $P(CD_3)_3$ were added to the residue, sealed in a new tube and refluxed for another day. The volatiles were removed to give yellow solids which contained *ca* 10% $P(CH_3)_3$. ^{2}H NMR: 3.57 (broad s, $\Delta\nu_{1/2} \approx 40$ Hz, $WCl_2[P(C\underline{D_3})]_4$).

Reaction of $WCl_2[P(CD_3)_3]_4$ *with* $CH_2{=}CHSi(OMe)_3$. $WCl_2[P(CD_3)_3]_4$ plus 5 equivalents of $CH_2{=}CHSi(OMe)_3$ (0.025 cm^3) in C_6H_6 (0.5 cm^3) in an NMR tube was heated at 70°C for 15 min. The yellow solution turned pale green to give ~35% $WCl_2[P(CD_3)_3]_3[CH_2{=}CHSi(OMe)_3]$ (**3a**) and ~8% $W(\equiv CCH_3)Cl[P(CD_3)_3]_4$ (**2a**-d_{36}). Further heating resulted in full conversion to the carbyne product. ^{2}H NMR: 2.71, 1.35, -15.2 (3 s, 9H each, $P(C\underline{D_3})_3$). Repeating the above reaction in C_6D_6 gave one new peak in the ^{1}H NMR: 6.38 (s, $CH_2{=}CHSi(\underline{OMe})_3$).

$W(\equiv CCH_3)Cl(PMe_3)_4$ (**2a**). $WCl_2(PMe_3)_4$ (**1a**) (1.00 g, 1.8×10^{-3} mol) and $CH_2{=}CHSi(OMe)_3$ (0.55 cm^3, 3.6×10^{-3} mol) were loaded into a 100 cm^3 bomb in the dry box. THF (60 cm^3) was vacuum transferred into the bomb, and the yellow solution was stirred at 65°C. The solution turned a pale green colour, and aliquots of the reaction mixture indicated formation of intermediate $WCl_2(PMe_3)_3[CH_2{=}CHSi(OMe)_3]$ (**3a**) by ^{1}H NMR, as well as product **2a**. The reaction was complete after 2 days at 65°C. All volatiles were removed from the pale yellow–green solution *in vacuo*, then THF (50 cm^3) and PMe_3 (0.18 cm^3) were added and the solution stirred overnight. The volatiles were removed *in vacuo*, 20 cm^3 pentane was added and the solution was cooled to 0°C to give 0.750 g bright yellow solids. Second (0.10 g) and third (0.07 g) crops of **2a** were obtained from the filtrate, to give a 93% total yield. Found for $WClP_4C_{14}H_{39}$: C, 30.54; H, 7.15%. Calc.: C, 30.53; H, 7.07%.

Reaction of $WBr_2(PMe_3)_4$ (**1b**) *with* $CH_2{=}CHSi(OMe)_3$. $CH_2{=}CHSi(OMe)_3$ (0.050 cm^3, 3.3×10^{-4} mol) and $WBr_2(PMe_3)_4$ (**1b**) (0.014 g, 2.2×10^{-5} mol) were heated in C_6D_6 (0.5 cm^3) in a sealed NMR tube. An intermediate $WBr_2(PMe_3)_3[CH_2{=}CHSi(OMe)_3]$ (**3b**) was observed during the reaction, which went on to form product $W(\equiv CCH_3)Br(PMe_3)_4$ (**2b**). $W(\equiv CCH_3)Br(PMe_3)_2[CH_2{=}CHSi(OMe)_3]$ was also observed, due to excess $CH_2{=}CHSi(OMe)_3$ in solution.[8]

Reaction of $WCl_2(PMe_3)_4$ (**1a**) *with* $CH_2{=}CHSi(OSiMe_3)_3$. $WCl_2(PMe_3)_4$ (**1a**) (0.012 g, 2.1×10^{-5} mol) and $CH_2{=}CHSi(OSiMe_3)_3$ (0.007 cm^3, 4.2×10^{-5} mol) were refluxed with THF-d_8 in an NMR tube at 65°C overnight. The yellow solution turned pale green and 20% of **1a** reacted to form an intermediate $WCl_2(PMe_3)_3[CH_2{=}CHSi(OSiMe_3)_3]$ (**5a**) by ^{1}H NMR. Further heating gave no evidence for formation of the carbyne **2a** or $ClSi(OSiMe_3)_3$. After heating for a week at 65°C, the reaction mixture contained 70% unreacted **1a**, 20% **5a** and paramagnetic materials.

Preparation of $CH_2{=}CDSiMe_3$. $CH_2{=}CBrSiMe_3$ (2.5 cm^3, 1.6×10^{-2} mol) in 6 cm^3 THF were syringed into a stirred solution of Mg (0.5 g, 1.9×10^{-2} mol) in 25 cm^3 THF. After stirring for 2 h, 2 cm^3 of D_2O (0.1 mol) were syringed into the flask. The volatiles were transferred to another flask, and 12 cm^3 pentane was added. The solution was washed with water (to remove THF), and the organic layer was dried over $MgSO_4$, then sodium and distilled (yield: 0.3 g, 20%). ^{2}H NMR: 6.17 (m, $CH_2{=}C\underline{D}SiMe_3$); ^{1}H NMR: 5.91, 5.62 (m, 1H each, $C\underline{H_2}{=}CDSiMe_3$), 0.05 (s, 9H, $CH_2{=}CDSi\underline{Me_3}$).

Reaction of **1a** *with* $^{13}CH_2{=}CHSiMe_3$ *and* $CH_2{=}CDSiMe_3$. A 50:50 mixture of $^{13}CH_2{=}CHSiMe_3$ and $CH_2{=}CDSiMe_3$ (11 mg, 1.1×10^{-4} mol of each) were refluxed with **1a** (12 mg, 2.1×10^{-5} mol) in C_6D_6 (0.5 cm^3) at 70°C for 1 day. ^{13}C{H} NMR: 36.07 (s, $W({\equiv}C^{13}\underline{C}H_3)Cl(PMe_3)_4$ (60%)); 35.76 (t, $J_{CD} = 23.4$, $W({\equiv}C^{13}\underline{C}H_2D)Cl(PMe_3)_4$ (40%)).

$W({\equiv}CCH_2CH_3)Cl(PMe_3)_4$ (**6a**). $WCl_2(PMe_3)_4$ (**1a**) (200 mg, 3.6×10^{-4} mol), $CH_2{=}CHCH_2Si(OMe)_3$ (0.18 cm^3, 1.1×10^{-3} mol) and 30 cm^3 THF were heated for a week at 70°C in a 100 cm^3 glass bomb sealed with a teflon stopcock. The volatiles were removed and the residue redissolved in 15 cm^3 Et_2O, reduced in volume to 4 cm^3, and 5 cm^3 pentane was added. Cooling to −78°C for 1 h gave **6a** as a yellow–brown powder (0.090 g, 44% yield).

Reaction of **1b** *with* $CH_2{=}CHCH_2SiMe_3$. $WBr_2(PMe_3)_4$ (**1b**) (0.014 g, 2.2×10^{-5} mol) and ferrocene (4 mg, 2×10^{-5} mol) were sealed in an NMR tube with $CH_2{=}CHCH_2SiMe_3$ (0.13 cm^3, 8.2×10^{-4} mol) and C_6D_6 (0.5 cm^3). The tube was heated at 69°C for 3 days to give 90% yield of $W({\equiv}CCH_2CH_3)Br(PMe_3)_4$ (**6b**) by ^{1}H NMR.

Reactions of **1a** *with* $CH_2{=}CHSn^nBu_3$ *and* $CH_2{=}CHCH_2SiMe_3$. $CH_2{=}CHSn^nBu_3$ (0.10 cm^3, 3.4×10^{-4} mol) and **1a** (12 mg, 2.1×10^{-5} mol) were refluxed at 70°C to give a yellow solution containing **2a** and another product, in a *ca* 3:2 ratio by ^{31}P NMR. The higher the concentration of tin reagent, the more secondary product is formed. For the secondary product: ^{31}P{H} NMR: −21.4 (s, $J_{WP} = 285$, $J_{SnP} = 45$); FAB-MS: 847. $CH_2{=}CHCH_2SiMe_3$ (0.006 cm^3, 6.2×10^{-5} mol) and **1a** (12 mg, 2.1×10^{-5} mol) were refluxed in C_6D_6 (0.5 cm^3) at 70°C to give a darker yellow solution containing **6a** and a second product, by ^{31}P{^{1}H} NMR: −23.7 ($J_{WP} = 280$, $J_{SnP} = 40$).

Kinetics

Reactions were run in sealed NMR tubes in C_6D_6 with an internal standard, $SiMe_4$ for reactions of **1a** and ferrocene for reactions of **1b**. In a typical procedure, a solution of 36 mg **1a** in 1.5 cm^3 C_6D_6 (4.3×10^{-2} M) was prepared in the drybox and 0.5 cm^3 was pipetted into an NMR tube using an automatic pipette and a silane added with a microliter syringe. The tube was removed from the drybox, frozen at −196°C, degassed, $SiMe_4$ vacuum transferred in if required, and sealed with a torch. After an initial NMR spectrum, the tube was heated in an oil bath at 69°C, and periodically taken out of the bath, cooled to room temperature and the NMR spectra taken on the VXR-300. Relaxation delay times of 15 s were used and times were recorded as time heated in bath. The [silane]/[PMe_3] ratios were calculated from measured integrals and the average ratio was calculated by fitting the observed ratios to a third order polynomial, integrating the expression and evaluating the integral over the time period of the reaction and finding the average value by dividing by the total reaction time. For example, the reaction of **1a** with 35 equivalents of $CH_2{=}CHCH_2Si(OMe)_3$ has [silane]/[PMe_3] ratios of 200 ± 20 for more than two half lives (Fig. 2B). A reaction run at half the standard **1a** concentration (2.2×10^{-2} M) with 1.5 M $CH_2{=}CHCH_2Si(OMe)_3$ gave the same observed rate constant as another tube with twice the tungsten concentration and the same silane concentration. The K_{eq} (69°C) values for the vinylsilanes were measured at 24°C, immediately after removing the tube from the 69°C bath.

X-Ray crystallographic structure determination

Pale yellow globular crystals of $W({\equiv}CCH_3)Cl(PMe_3)_4$ (**2a**) were grown by slow diffusion of pentane into a diethylether solution. The crystals were mounted in capillary tubes in the drybox and sealed under an atmosphere of nitrogen. The crystal was tetragonal and its space group, $I\bar{4}2m$, was chosen from other possible space groups with the same systematic extinctions because it refined to give the lowest R_w value, and was the most well behaved during refinement. Data collection (24°C) was performed on a Enraf–Nonius CAD4 diffractometer operating in the θ–2θ scan mode with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), as previously described.[21] The structure was solved using the SHELX direct methods structure package and was refined with full matrix least squares, giving $a = 9.6854(13)$ Å, $c = 12.5307(14)$ Å, $Z = 2$, $V = 1175.5(4)$, $R = 3.8\%$, $R_w = 5.1\%$, GOF = 1.288. All non-hydrogen atoms were refined anisotropically. The isotropic hydrogen atoms were placed in calculated positions (C—H = 0.95 Å) confirmed by a difference map. The structure of **2a** is disordered due to the crystallographically imposed S_4 site symmetry, with half occupancy of the *trans* chloride and ethylidyne ligands in the axial positions and 4-fold disorder of the carbyne methyl group along the W≡C axis. These disorders have been observed in similar structures.[3,4] Crystallographic data have been deposited with Ref. 2.

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15. Assuming a steady state concentration of $[\mathrm{WX_2(PMe_3)_3}]$ and that $k_3 > k_{-2}$,

$$\frac{\mathrm{d}[\mathrm{WX_2L_4}]}{\mathrm{d}t} = -\frac{k_1[\mathrm{WX_2L_4}]}{1 + k_{-1}[\mathrm{PMe_3}]/k_2[\mathrm{silane}]}$$

When $k_{-1}[\mathrm{PMe_3}]/k_2[\mathrm{silane}] \gg 1$ (the observed pseudo-first order rate constants are much less than k_1, except for the reaction of $\mathrm{CH_2{=}CHSn^nBu_3}$), this expression reduces to equation 15.

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