Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 37.[1] Methylene Group Transfer to Carbon–Metal Multiple Bonds; Crystal Structures of [TiW{μ-C(C_6H_4Me-4)=CH_2}(μ-CO)(CO)(η-C_5H_5)$_3$] and [PtW{μ-C(C_6H_4Me-4)=CH_2}$(CO)_2(PMe_3)_2$(η-C_5H_5)] *

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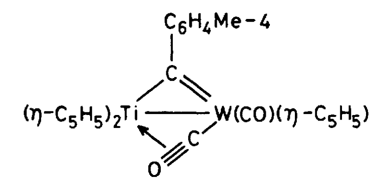
The compounds [W(≡CR)$(CO)_2$(η-C_5H_5)] (R = C_6H_4Me-4 or Me) and [Ti{Cl($AlMe_2$)CH_2}(η-C_5H_5)$_2$] react in toluene, in the presence of tetrahydrofuran, to afford the bridged vinyl complexes [TiW{μ-C(R)=CH_2}(μ-CO)(CO)(η-C_5H_5)$_3$]. The compound with R = C_6H_4Me-4 may also be prepared by treating [TiW(μ-CC_6H_4Me-4)(μ-CO)(CO)(η-C_5H_5)$_3$] with the titanium reagent. It has been structurally characterised by *X*-ray diffraction. The Ti–W bond [3.082(2) Å] is spanned by a σ:η^2-CO ligand [W–C–O 173.4(3)°, Ti–C 2.222(4), Ti–O 2.285(3) Å] and by a σ:η^2-C(C_6H_4Me)=CH_2 group, σ bonded to titanium and η^2 co-ordinated to tungsten [Ti–C 2.290(4), C=C 1.441(6), W–C 2.199(5) and 2.268(6) Å]. The tungsten atom carries a terminally bound CO ligand and a C_5H_5 group, and the titanium atom is ligated by two C_5H_5 groups. Reactions between the dimetal compounds [PtW(μ-CR)$(CO)_2(PMe_3)_2$(η-C_5H_5)] and [Ti{Cl($AlMe_2$)CH_2}(η-C_5H_5)$_2$] afford the complexes [PtW{μ-C(R)=CH_2}$(CO)_2(PMe_3)_2$(η-C_5H_5)]. An *X*-ray diffraction study on the platinum–tungsten species with R = C_6H_4Me-4 established the structure as one in which the Pt–W bond [2.820(1) Å] is bridged by a C(C_6H_4Me-4)=CH_2 group, as in the titanium–tungsten compound, being σ bonded to the platinum and η^2 co-ordinated to the tungsten. The metal–metal bond is semi-bridged by one CO ligand [W–C–O 166(1)°], while the remaining CO is terminally bound to tungsten, which also carries the C_5H_5 group. The platinum is ligated by two PMe_3 ligands, and is in a distorted square-planar environment defined by the two phosphorus atoms, and the μ-C atoms of the semi-bridging carbonyl and the vinyl group. Spectroscopic properties of the new dimetal compounds are reported, and their mechanisms of formation discussed in the light of ^{1}H and ^{13}C-{^{1}H} n.m.r. studies on reaction mixtures.

Reactions between the complexes [W(≡CR)$(CO)_2$(η-C_5H_5)] (R = C_6H_4Me-4 or Me) and low-valent metal species afford many dimetal compounds with tungsten bonded to another metallic element, and with the metal–metal bonds bridged by an alkylidyne ligand.[2,3] Compound (1) is representative of a species of this type, and its discovery[4] was in part a stimulus for the work described herein. There is currently considerable interest in polynuclear metal complexes having alkylidene or alkylidyne groups bridging the metal–metal bonds in the context of their possible role as models for C–C bond formation, and the reduction of CO at a metal surface.[5–7] In our studies on heteronuclear dimetal compounds we have observed C–C bond forming reactions between bridging alkylidyne ligands and alkynes,[8] and also between these groups and alkylating reagents.[9] We became interested in establishing for the first time a coupling reaction between an alkylidyne ligand attached either to one or to two metal centres and a carbene group derived from an alkylidene–metal complex. With this objective we have studied reactions between the titanium compound [Ti{Cl($AlMe_2$)CH_2}(η-C_5H_5)$_2$] (2)[10] and the mononuclear



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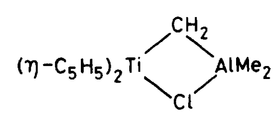

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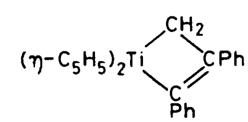


(3)

tungsten–alkylidyne complexes [W(≡CR)$(CO)_2$(η-C_5H_5)] (R = C_6H_4Me-4 or Me), and between (2) and several complexes containing the dimetallacyclopropene ring system M(μ-CR)M′ (M and M′ = transition element, R = C_6H_4Me-4 or Me).

Compound (2) is the precursor to a family of titanacyclobutanes [Ti{CH_2CR(R′)CH_2}(η-C_5H_5)$_2$] (R = R′ = alkyl; R = H, R′ = alkyl or aryl),[11] and is also a dismutation catalyst,[10] properties which demonstrate its ability to function as a methylene group transfer reagent. The expectation that (2) would react with the carbyne complexes [W(≡CR)$(CO)_2$(η-C_5H_5)] was sustained by the knowledge that compound (3) is formed in reactions between diphenylacetylene and either (2)[12]

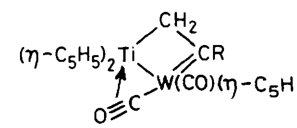
* [σ:η^2-Carbonyl-*C*(W)*CO*(Ti)]-1-carbonyl-1,2,2-tris(η^5-cyclopentadienyl)-μ-[σ:η^2-1-*p*-tolylethenyl-C^1(Ti)$C^{1,2}$(W)]-tungstentitanium(Ti–W) and 2,2-dicarbonyl-2-(η^5-cyclopentadienyl)-μ-[σ:η^2-1-*p*-tolylethenyl-C^1(Pt)$C^{1,2}$(W)]-1,1-bis(triphenylphosphine)-tungstenplatinum(W–Pt) respectively.

Supplementary data available (No. SUP 56240, 11 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

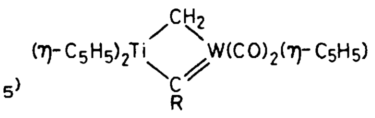
Table 1. Selected bond distances (Å) and angles (°) for the compound [TiW{μ-C(C_6H_4Me-4)=CH_2}(μ-CO)(CO)(η-C_5H_5)$_3$] (**5a**), with estimated standard deviations in parentheses

Ti–W	3.082(2)	W–C(3)	2.199(5)	W–C(1)	1.906(5)	Ti–C(1)	2.222(4)
Ti–C(3)	2.290(4)	W–C(4)	2.268(6)	W–C(2)	1.951(5)	Ti–O(1)	2.285(3)
C(3)–C(4)	1.441(6)	C(3)–C(31)	1.492(5)	C(1)–O(1)	1.213(5)	C(2)–O(2)	1.150(6)
Mean Ti–C(cp)*	2.42(1)	Mean W–C(cp)	2.38(1)	C(4)–H(4a)	0.92(5)	C(4)–H(4b)	1.14(6)
C(3)–W–Ti	47.9(1)	C(3)–Ti–W	45.4(1)	Ti–C(3)–W	86.7(2)	W–C(1)–O(1)	173.4(3)
C(3)–W–C(2)	104.7(2)	C(1)–Ti–W	37.9(1)	Ti–C(3)–C(4)	117.4(3)	W–C(2)–O(2)	179.6(6)
C(4)–W–C(2)	71.9(2)	O(1)–Ti–W	69.1(1)	C(4)–C(3)–C(31)	114.5(4)		
C(1)–W–Ti	45.8(1)	O(1)–Ti–C(3)	114.3(1)	W–C(3)–C(4)	73.8(3)		
C(1)–W–C(2)	84.3(2)	C(1)–Ti–C(3)	83.2(2)	W–C(3)–C(31)	131.8(3)		

* cp = η-C_5H_5.

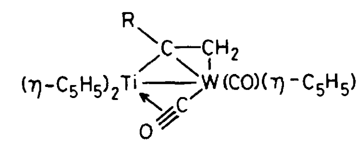


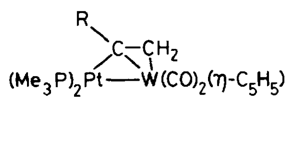
(**4a**)



(**4b**)

R = C_6H_4Me-4 or Me





	R		R
(**5a**)	C_6H_4Me-4	(**6a**)	C_6H_4Me-4
(**5b**)	Me	(**6b**)	Me

or the titanacyclobutanes.[13] Similar reactivity patterns between the alkylidyne–tungsten compounds and diphenylacetylene in organometal complex chemistry are well established.[2] Reaction with the alkylidyne–tungsten species might afford one or other of the heterobimetallic cyclobutene complexes (**4**). A preliminary account has been given of the results described herein.[14]

Results and Discussion

In initial studies, the compound [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] was treated with one equivalent of (**2**) in toluene at 0 °C, with two to three mol equivalents of tetrahydrofuran (thf) added in order to remove the aluminium-containing fragment as the adduct AlMe_2Cl·thf. A new compound (**5a**) was isolated by column chromatography (see Experimental section). However, monitoring of the reaction by i.r. showed that when the reactants were mixed in a 1:1 molar ratio only approximately half of the tungsten compound was consumed. The reaction was repeated several times at temperatures between −25 and 25 °C using two or more mol equivalents of the titanium compound. By employing excess of (**2**), compound (**5a**) was isolated in yields of 50—60%. This observation is further discussed below.

The i.r. spectrum of (**5a**) showed two CO stretching bands at 1 912 and 1 649 cm^{-1}. The low frequency of the latter absorption suggested the presence of a carbonyl group bridging a titanium–tungsten bond in a σ:η^2 mode. Indeed, the i.r. spectrum of (**5a**) was very similar to that previously reported for (**1**) [$\nu_{max.}$(CO) at 1 921 and 1 638 cm^{-1}].[4] While the i.r. data could be accommodated by the structure shown for the expected product (**4a**, R = C_6H_6Me-4), with one CO ligand bridging the Ti–W bond, the spectrum did not accord with its isomer (**4b**) where CO bridging would be unlikely. Moreover, examination of the ^{13}C-

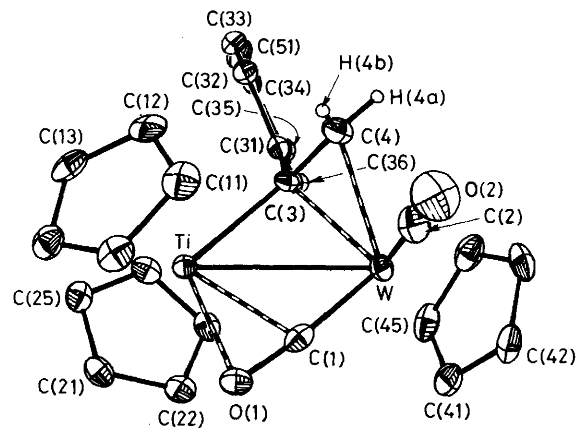


Figure 1. Molecular structure of [TiW{μ-C(C_6H_4Me-4)=CH_2}(μ-CO)(CO)(η-C_5H_5)$_3$] (**5a**) showing the atom-numbering scheme

{^{1}H} n.m.r. spectrum of (**5a**) showed that it could not be the compound (**4a**, R = C_6H_6Me-4). Apart from the expected resonances due to the CO (δ 227.0 and 220.3 p.p.m.) and C_5H_5 (110.3, 107.4, and 92.5 p.p.m.) ligands, and the C_6H_4 (157.7. 132.7, 130.9, 129.7 p.p.m.) and Me-4 (20.8 p.p.m.) groups, there were two other signals at δ 170.7 and 38.2 p.p.m. The latter was assigned to a methylene group, and this was confirmed by a ^{13}C n.m.r. spectrum when this signal appeared as a doublet of doublets, with J(HC) couplings (166 and 146 Hz) in the range found for protons bonded to an sp^2 hybridised carbon. However, the chemical shift for this methylene group was not in the region expected for a Ti–CH_2 moiety as depicted in (**4a**). Thus in the compound [Ti{C(SiMe_3)=C(SiMe_3)CH_2}(η-C_5H_5)$_2$], which has a structure similar to (**3**), the CH_2 signal in the ^{13}C-{^{1}H} n.m.r. spectrum occurs at 108.3 p.p.m.[15] Moreover, the remaining resonance at 170.7 p.p.m. in the spectrum of (**5a**) is at an abnormally high field for the ligated carbon of a C=W group,[16] thus providing further evidence against a dimetallacyclobutene species (**4a**). It was thus evident that (**5a**) had a novel structure, and an X-ray diffraction study became necessary to establish the nature of the complex. The crystallographic results are summarised in Table 1, and the structure is shown in Figure 1. The molecule contains a Ti–W bond which is spanned on one side by a σ:η^2-CO group, as predicted by the i.r. spectrum, and on the other by a C(C_6H_4Me-4)=CH_2 group, σ bonded to the titanium and η^2 co-ordinated to the tungsten atom. Alternatively, the molecule may be viewed as a 'complex' formed by co-ordination of a Ti(η-C_5H_5)$_2$ fragment with a tungstacyclopropene, [W{=C(C_6H_4Me-4)CH_2}(CO)$_2$(η-C_5H_5)]. The Ti–W separation [3.082(2) Å] is very similar to that found

Table 2. Selected bond distances (Å) and angles (°) for the compound $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ **(6a)**

Pt–W	2.820(1)	C(3)–Pt	2.02(1)	W–C(1)	1.92(2)	C(1)–O(1)	1.20(2)
Pt–P(1)	2.257(4)	C(3)–W	2.20(1)	W–C(2)	1.96(2)	C(2)–O(2)	1.16(2)
Pt–P(2)	2.301(4)	C(3)–C(4)	1.43(2)	W–C(4)	2.32(1)		
Pt $\cdots$ C(1)	2.54(1)	C(3)–C(31)	1.52(2)	Mean W–C(cp)*	2.35(2)		
Pt–W–C(3)	45.4(3)	W–Pt–C(3)	50.8(3)	Pt–C(3)–W	83.8(4)	W–C(1)–O(1)	166(1)
Pt–W–C(1)	61.2(4)	P(1)–Pt–P(2)	98.8(2)	C(4)–C(3)–Pt	119(1)	W–C(2)–O(2)	179(1)
C(4)–W–Pt	70.5(3)	P(1)–Pt–C(3)	92.9(4)	C(4)–C(3)–C(31)	118(1)	W–Pt–P(1)	142.7(1)
C(4)–W–C(1)	106.1(5)	P(2)–Pt–C(3)	165.8(4)	Pt–C(3)–C(31)	121(1)	W–Pt–P(2)	118.4(1)
C(4)–W–C(2)	71.7(5)			W–C(3)–C(31)	120(1)		

* cp = $\eta\text{-}C_5H_5$.

[2.997(4) Å] in **(1)**.[4] Indeed, the structures of **(1)** and **(5a)** are closely related, differing in the presence of the methylene group bridging the W–C(3) bond in the latter compound. Although both **(1)** and **(5a)** have a $\sigma{:}\eta^2$-CO ligand, the W–C(1)–O(1) angle in **(5a)** [173.4(3) Å] is more nearly linear than the corresponding angle in **(1)** [165(2)°]. However, the Ti–C(O) distances are similar [2.222(4) Å for **(5a)** and 2.20(3) Å for **(1)**]. The TiC(3)W ring in **(5a)** has somewhat different parameters [W–C(3) 2.199(5), Ti–C(3) 2.290(4) Å, Ti–C(3)–W 86.7(2)°] compared with those of the three-membered ring in **(1)** [W–μ-C 1.91(2), Ti–μ-C 2.19(3) Å, Ti–μ-C–W 92.7(8)°]. This is not surprising since what was formally a C=W bond in **(1)** has been reduced in bond order to a C–W linkage in **(5a)**.

The C(3)–C(4) separation [1.441(6) Å] is consistent with a C=C bond which has been lengthened by co-ordination to a metal. In several dimetal complexes containing $\mu\text{-}\sigma{:}\eta^2$-vinyl ligands, C=C distances have been found in the range 1.40(2)—1.36(2) Å,[17] somewhat shorter than that in **(5a)**. The W–C(3) [2.199(5) Å] and W–C(4) [2.268(6) Å] separations are as expected for an alkene group η^2 co-ordinated to tungsten. In the compound $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ the mean W–C(C_2H_4) distance is 2.27(1) Å.[18]

The two C_5H_5 groups on the titanium atom are staggered, and the angle between the C(1)TiW plane and the mean planes of the two cyclopentadienyl rings are 28.3 [C(11)—C(15)] and 23.3° [C(21)—C(25)]. In compound **(1)** these interplanar angles are 27.8 and 28.4°.

Having established the structure of **(5a)**, the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data are readily interpretable. The three $\eta\text{-}C_5H_5$ ligands are in different environments and hence give rise to three distinct signals in both spectra (see above and Experimental section). The $^{13}C\text{-}\{^1H\}$ n.m.r. resonances at 38.2 (CH_2) and 170.7 p.p.m. [$\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2$] have typical shifts for carbon nuclei of a vinyl group bridging two metal centres. Moreover, as mentioned above, in the undecoupled spectrum the signal at δ 38.2 appeared as a doublet of doublets, as expected for a C=CH_2 group.[16]

Reaction between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and **(2)** gave a red-brown crystalline compound **(5b)**, with spectroscopic properties similar to those of **(5a)**. In the i.r., a band was observed at 1 642 cm^{-1}, characteristic of a $\mu\text{-}\sigma{:}\eta^2$-CO ligand. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(5b)** showed resonances for the $\mu\text{-}C(Me){=}CH_2$ and CH_2 groups at δ 168.6 and 41.7 p.p.m., respectively. Thus **(5b)** and **(5a)** have similar structures. Formation of **(5b)** from $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and **(2)** required at least two mol equivalents of the latter to consume all of the methylmethylidyne–tungsten compound.

Although **(5a)** proved inert to PMe_2Ph in refluxing toluene, it was decomposed by CO affording an intractable brown oil, which, however, showed bands attributable to the complex $[Ti(CO)_2(\eta\text{-}C_5H_5)_2]$. Protonation of **(5a)** also resulted in decomposition. Several unsuccessful attempts were made to cleave the $Ti(\eta\text{-}C_5H_5)_2$ fragment in order to obtain the tungstacyclopropene complex $[W\{{=}C(C_6H_4Me\text{-}4)CH_2\}(CO)_2(\eta\text{-}C_5H_5)]$. These included treatment of **(5a)** with silver acetate to remove the titanium fragment as $[Ti(O_2CMe)(\eta\text{-}C_5H_5)_2]$. In contrast, treatment of **(1)** with silver acetate afforded $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ quantitatively, suggesting that the tungstacyclopropene complex, if formed in the corresponding reaction of **(5a)**, is unstable. The relationship between the molecular structures of compounds **(1)** and **(5a)**, coupled with the observation that in the synthesis of the latter from $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ an excess of the reagent **(2)** was required to bring the reaction to completion, suggested that **(1)** might be an intermediate in the formation of **(5a)**. Seemingly in accord with this idea, treatment of **(1)** in toluene with **(2)** afforded **(5a)** in *ca.* 75% yield. This observation prompted a study of reactions between **(2)** and other complexes containing dimetallacyclopropene ring systems to determine whether methylene group transfer to a bridging alkylidyne ligand was general.

Reactions between **(2)** and the compounds $[CrW(\mu\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$, $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$, and $[PtW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (R = C_6H_4Me-4) resulted in decomposition or the observation by i.r. of thermally unstable products which could not be characterised. However, addition of **(2)** to toluene–thf solutions of the compounds $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4-Me-4 or Me)[18,19] afforded yellow crystalline complexes **(6)**. These products were characterised by microanalysis and by i.r. and n.m.r. spectroscopy, but to establish the precise nature of these species an *X*-ray diffraction study was carried out on **(6a)**.

The structure is shown in Figure 2, and important interatomic distances and angles are summarised in Table 2. As in compound **(5a)**, the heteronuclear metal–metal bond is bridged by the $C(C_6H_4Me\text{-}4){=}CH_2$ unit in the $\sigma{:}\eta^2$ bonding mode. The C(3)–C(4) separation [1.43(2) Å] is similar to that in **(5a)** [1.441(6) Å], and the W–C(3) and W–C(4) distances are also similar in the two molecules (Tables 1 and 2). The Pt–W distance [2.820(1) Å] in **(6a)** is somewhat longer than the metal–metal bonds in the tolylmethylidyne-bridged dimetal complex $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [2.751(1) Å],[19] and in the compound $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{12})]$ [2.728(1) Å].[20] The bridging unit in the latter species is similar to that in **(6a)** with a CO group replacing the methylene group.

In **(6a)** one of the two carbonyl ligands on the tungsten semi-bridges the Pt–W bond [W–C(1)–O(1) 166(1)°, Pt $\cdots$ C(1) 2.54(1) Å]. Similar semi-bridging of a CO group occurs in $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{12})]$ [W–C–O 159(1)°].[20] If the metal–metal bond in **(6a)** is ignored, the platinum atom is in a distorted square-planar environment with

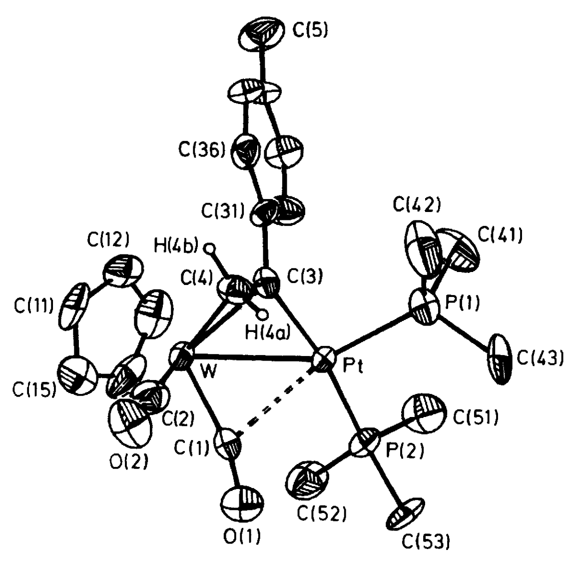
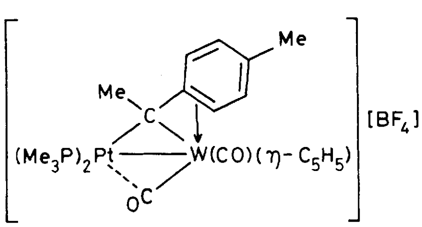


Figure 2. Molecular structure of [PtW{μ-C(C_6H_4Me-4)=CH_2}$(CO)_2$-$(PMe_3)_2$(η-C_5H_5)] (**6a**) showing the atom-numbering scheme. The hydrogen atoms on C(4) are shown at calculated positions



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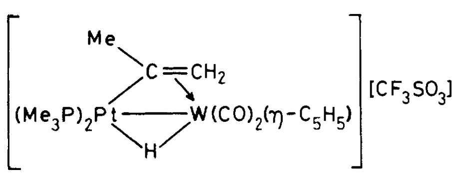
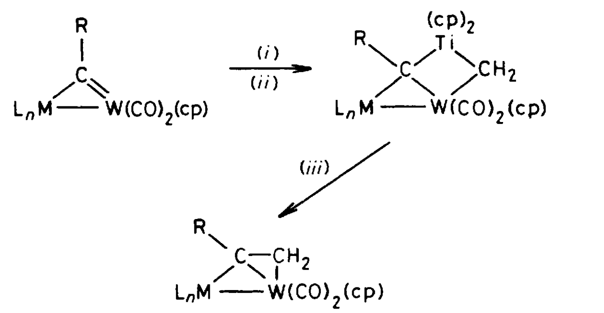


(**8**)

respect to P(1), P(2), C(1), and C(3) [C(1)–Pt–C(3) 89.6(5), P(1)–Pt–P(2) 98.8(2), C(1)–Pt–P(2) 83.5(4), and C(3)–Pt–P(1) 92.9(4)°], although these four ligating atoms are not co-planar. The dihedral angle between the planes defined by the atoms C(3)PtW and P(1)PtP(2) is 12.7°. The semi-bridging carbonyl carbon C(1) is significantly displaced (0.73 Å) from the C(3)PtW plane, in contrast with the virtual co-planarity of C(1) with the C(3)TiW plane in (**5a**), where this atom deviates only by 0.07 Å. The Pt–P(2) bond [2.301(4) Å] is somewhat longer than Pt–P(1) [2.257(4) Å], due to the *trans* influence of the bridging carbon atom C(3), a feature we have discussed previously.[21]

During related work in our laboratory, alternative syntheses of the compounds (**6**) were discovered. Deprotonation of the salt (**7**) with NaH affords (**6a**),[22] while deprotonation of (**8**) with K[BH(CHMeEt)$_3$] yields (**6b**).[18] The n.m.r. data for (**6a**)[22] and (**6b**)[23] are in accord with the presence of bridging vinyl groups in these molecules as established for the former complex by the *X*-ray diffraction study. In their ^{13}C-{^{1}H} n.m.r. spectra both compounds show characteristic resonances for the ligating carbon atoms of the bridging vinyl groups {(**6a**), μ-C [142 p.p.m., d, *J*(PC) 78, *J*(PtC) 608 Hz] and CH_2 (26.7 p.p.m.); (**6b**),



Scheme 1. cp = η-C_5H_5, ML_n = Ti(cp)$_2$, R = C_6H_4Me-4; ML_n = Pt$(PMe_3)_2$, R = C_6H_4Me-4 or Me; (*i*) +[Ti{Cl(AlMe$_2$)CH_2}(cp)$_2$], + thf; (*ii*) −AlMe$_2$Cl·thf; (*iii*) −Ti(cp)$_2$

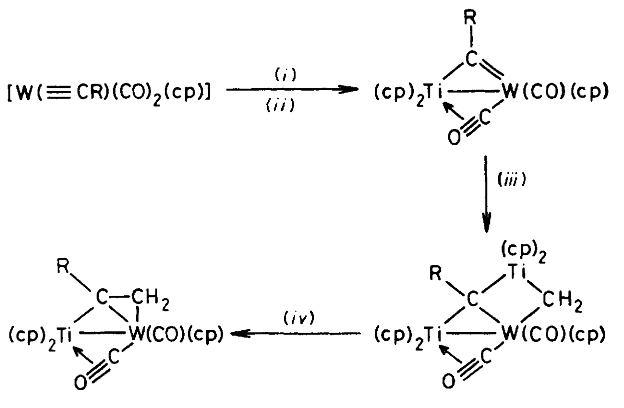
μ-C [147.8 p.p.m., d, *J*(PC) 83, *J*(PtC) 635, *J*(WC) 43 Hz] and CH_2 (42.2 p.p.m.)}. In the ^{1}H n.m.r. spectra of both compounds the CH_2 group gives rise to two signals as expected because the protons are in different environments: (**6a**), δ 2.83 [d, 1 H, *J*(PH) 8, *J*(PtH) 16] and 3.32 [d, 1 H, *J*(PH) 12, *J*(PtH) 110 Hz]; (**6b**), δ 2.41 [d, 1 H, *J*(PH) 8, *J*(PtH) 12] and 3.23 [d, 1 H, *J*(PH) 11, *J*(PtH) 60 Hz]. The protons of the methylene groups only couple with the phosphorus of the PMe_3 group in the *transoid* position; ^{31}P–^{1}H coupling with the *cisoid* PMe_3 ligand is customarily too small to be observed.

The ^{13}C-{^{1}H} n.m.r. spectra of (**6**) show two resonances for the CO ligands: (**6a**), 236.7 [d, *J*(PC) 11, *J*(PtC) 50] and 226.7 p.p.m. [d, *J*(PC) 3, *J*(WC) 174 Hz]; (**6b**), 233.3 [*J*(WC) 144] and 230.4 p.p.m. [*J*(WC) 144 Hz]. The most deshielded signal may be assigned to the semi-bridging carbonyl ligands which reveal themselves in the i.r. spectra with bands of 1 727 (**6a**) and 1 735 cm^{-1} (**6b**). The terminally bound CO groups show absorptions at 1 866 (**6a**) and 1 886 cm^{-1} (**6b**).

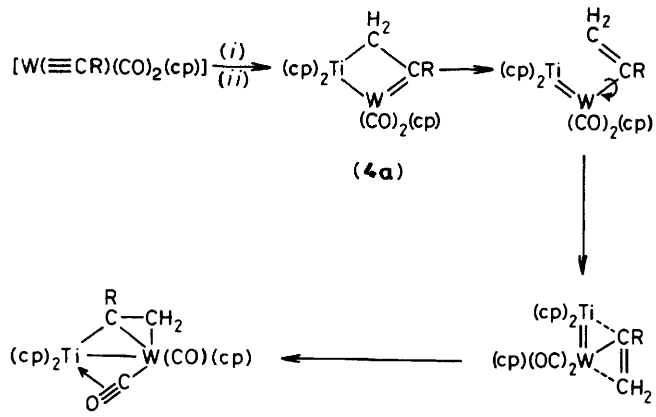
Synthesis of the compounds (**5**) and (**6**), by employing the titanium reagent (**2**), raises interesting questions as to the mechanisms of the various reactions. Formation of the species (**6**), and the synthesis of (**5a**) from compound (**1**), are akin to cyclopropanation of an alkene by (**2**), yet the titanium reagent does not undergo such reactions readily.[10] For example, the cyclopropanation of cyclohexene with (**2**) affords bicyclo-[4.1.0]heptane in only 4% yield.[24] However, the well established[10,11] involvement of four-membered ring intermediates in the chemistry of [Ti(=CH_2)(η-C_5H_5)$_2$] suggests that both the synthesis of (**5a**) from (**1**), and the preparation of (**6a**) and (**6b**) from the complexes [PtW(μ-CR)$(CO)_2(PMe_3)_2$-(η-C_5H_5)] (R = C_6H_4Me-4 or Me), proceed *via* intermediates possessing a similar ring system (Scheme 1), for which there is precedent. Thus an intermediate analogous to that shown in Scheme 1 has been proposed to account for the formation of [TaMe(η-C_2H_4)(η-C_5H_5)$_2$] in the decomposition of [Ta(=CH_2)Me(η-C_5H_5)$_2$].[25] A similar methylene group transfer from one metal centre to another evidently occurs in the decomposition of the complex [Re(=CH_2)(NO)(PPh$_3$)(η-C_5H_5)]$^+$ which yields [Re(NO)(PPh$_3$)(η-C_2H_4)(η-C_5H_5)],$^+$ and a dimetallacyclobutane intermediate has again been suggested.[26]

Reference was made earlier to the observation that in the syntheses of the complexes (**5**) from [W(≡CR)$(CO)_2$(η-C_5H_5)] it was apparently necessary to employ somewhat more than a two-fold excess of (**2**) to drive the reactions to completion. This suggested a two-stage mechanism, such as that shown in Scheme 2, involving an intermediate which was then attacked by a second molecule of [Ti(=CH_2)(η-C_5H_5)$_2$]; an idea seemingly supported by the alternative preparation of (**5a**) by treating (**1**) with (**2**).

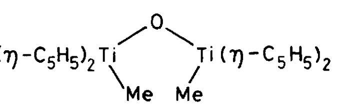
In order to verify the molar quantities of (**2**) required to convert [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] into (**5a**), the reac-



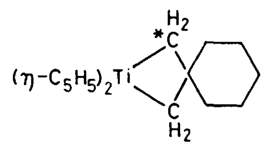
Scheme 2. cp = η-C_5H_5, R = C_6H_4Me-4 or Me; (*i*) [$\overline{Ti\{Cl(AlMe_2)CH_2\}}(cp)_2$] and thf; (*ii*) $-AlMe_2Cl$·thf and $(CH_2)_n$; (*iii*) [$Ti(=CH_2)(cp)_2$]; (*iv*) $-Ti(cp)_2$



Scheme 3. cp = η-C_5H_5, R = C_6H_4Me-4 or Me; (*i*) thf and [$\overline{Ti\{Cl(AlMe_2)CH_2\}}(cp)_2$]; (*ii*) $-AlMe_2Cl$·thf



(9)



(10)

tion was monitored by both ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectroscopy with all manipulations carried out in a Vacuum Atmosphere Corporation dry-box to minimise hydrolytic decomposition of **(2)**. Equimolar amounts of the reactants were mixed in [$^2H_6$]benzene in the presence of two mol equivalents of [$^2H_8$]thf. After *ca.* 1 h, aliquots of the solution were removed for n.m.r. measurements. Integration of peaks in the ^1H n.m.r. spectrum, and inspection of the relative intensities of the resonances in the ^{13}C-$\{^1H\}$ n.m.r. spectrum, showed that **(5a)** had been formed in >50% yield based on **(2)**. These observations eliminate a mechanism which requires a second equivalent of **(2)**. However, the reaction was not quantitative. Close inspection of the spectra showed peaks attributable to the μ-oxo-complex **(9)**,[27] discussed further below, which must form from traces of moisture in spite of rigorous attempts to eliminate this possibility.

The results of the *in situ* experiments, which were n.m.r. monitored, thus showed that a second equivalent of **(2)** was not necessary in the synthesis of **(5a)** from [$W(\equiv CC_6H_4Me$-4)$(CO)_2(\eta$-$C_5H_5)$] (Scheme 2), and support a mechanism whereby the reagents combine to give a 1:1 adduct, perhaps **(4a)**, which rapidly rearranges to yield the product. A possible mechanism is shown in Scheme 3, and a similar pathway could be involved if **(4b)** were an intermediate rather than **(4a)**. Since the groups CR and $W(CO)_2(\eta$-$C_5H_5)$ are isolobal, the dimetallabutadiene intermediate shown in Scheme 3 is very similar to metallabutadiene species postulated to account for the end products in reactions of alkynes with metal–carbene complexes, *via* analogous ring opening reactions.[28,29] Thus the scheme presented by Katz and Lee[28] for the metal–carbene propagation of the polymerisation of alkynes is especially relevant to the pathway depicted in Scheme 3.

In all reactions of compound **(2)** it was assumed that the CH_2 group was derived from [$Ti(=CH_2)(\eta$-$C_5H_5)_2$] and not from the $AlClMe_2$ moiety. In order to confirm this assumption, the ^{13}C-enriched (45%) complex **(10)**[11] was prepared *in situ* from **(2)** and labelled (90%) $H_2{}^*C{=}\overline{C(CH_2)_4CH_2}$, using toluene as solvent, and with thf added to complex with the aluminium halide. This equilibrating mixture of **(2)** and **(10)** was then treated with [$W(\equiv CC_6H_4Me$-4)$(CO)_2(\eta$-$C_5H_5)$] in toluene at 0 °C (2 h), and the ^{13}C-$\{^1H\}$ n.m.r. spectrum of the resulting solution examined. Apart from the peaks due to the solvent, the two most intense signals in the spectrum could be assigned to the methylene carbon of the free alkene $H_2C^*{=}\overline{C(CH_2)_4CH_2}$ and the CH_2 carbon of the vinyl group of **(5a)**. The relatively high intensity of the signal for the labelled $^*CH_2$ group of the alkene indicated that formation of **(10)** was not complete before addition of the tolylmethylidyne–tungsten compound. Apart from the CH_2 group present in **(5a)**, no other resonances were enriched with ^{13}C. Moreover, the three C_5H_5 signals for **(5a)** in the mixture were greater in intensity by a factor of *ca.* 4 compared with the C_5H_5 resonance for the remaining [$W(\equiv CC_6H_4Me$-4)$(CO)_2(\eta$-$C_5H_5)$], indicating a yield of *ca.* 80% of **(5a)**. These results confirm that in compound **(5a)** the methylene and titanocene groups are derived from **(2)**, with the reaction proceeding *via* [$Ti(=CH_2)(\eta$-$C_5H_5)_2$].

In the ^{13}C-$\{^1H\}$ spectrum of the mixture obtained from **(10)** $\rightleftharpoons$ **(2)**, and [$W(\equiv CC_6H_4Me$-4)$(CO)_2(\eta$-$C_5H_5)$], resonances were observed at δ 115.6 (C_5H_5) and 49.2 p.p.m. (Me) attributable to the aforementioned oxo-complex **(9)**. The resonance due to the latter at 49.2 p.p.m. showed no ^{13}C enhancement, indicating that formation of the oxo-species had occurred earlier before addition of $H_2C^*{=}\overline{C(CH_2)_4CH_2}$. Thus it was probably present in the 0.25 mol dm^{-3} solution of **(2)** employed (see Experimental section). The peak assignments for **(9)** were made on the basis of an independent synthesis of the complex *via* hydrolysis of **(2)**, a reaction which also afforded traces of [$Ti_2(\mu$-$O)Cl_2(\eta$-$C_5H_5)_4$].[30] In the undecoupled ^{13}C n.m.r. spectrum of **(9)** the signal at 115.6 became a doublet [*J*(HC) 174 Hz], and that at 49.2 p.p.m. a quartet [*J*(HC) 128 Hz], thereby confirming the assignments. The signals observed in the ^1H n.m.r. spectrum (C_6D_6) [δ 5.8 (s, 10 H, C_5H_5) and 0.9 (s, 3 H, Me)] were somewhat shifted from those reported previously (δ 5.78 and 0.48). However, in the earlier report[27] the solvent and reference standard employed were not specified.

Experimental

Except for the synthesis of the reagent [$\overline{Ti\{Cl(AlMe_2)CH_2\}}(\eta$-$C_5H_5)_2$] described below, all reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen or argon. Reaction vessels were flame-dried *in vacuo*, and refilled with argon or nitrogen prior to use. Solvents were freshly distilled and rigorously dried. Light petroleum refers to that fraction of b.p. 30—40 °C. Florisil (100—200 mesh) or alumina

(Brockman activity II) were used for the chromatography columns. Infared spectra were measured with a Nicolet MX-10 FT spectrometer, n.m.r. spectra were recorded with JEOL FX 90Q and FX 200 spectrometers. Data given are for room temperature measurements. The compounds [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4 or Me),[31] [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$],[4] and [PtW(μ-CR)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4 or Me)[18,19] were prepared as described previously.

The procedure for preparing [Ti{Cl(AlMe$_2$)CH$_2$}(η-C$_5$H$_5$)$_2$] was a modification[24] of those described earlier.[10,11] A suspension of [TiCl$_2$(η-C$_5$H$_5$)$_2$] (62 g, 0.25 mol) in toluene (250 cm^3) contained in a 500-cm^3 two-necked flask was treated with AlMe$_3$ (48 cm^3) using a syringe for transfer (**CAUTION**: this reagent and the reaction product are pyrophoric). The flask was rotated briefly to dissolve [TiCl$_2$(η-C$_5$H$_5$)$_2$], and the mixture allowed to stand for 60 h. Throughout this period the flask was vented *via* a bubbler, since large amounts of methane are evolved. The reaction vessel was connected to a solvent trap (three-necked flask cooled with liquid nitrogen) and solvent was removed *in vacuo*. Nitrogen gas was then re-introduced into the trap and the reaction flask, and the vessel containing the solvent was disconnected and removed. The recovered solvent, containing AlClMe$_2$, was carefully treated with an n-butanol–toluene mixture (300 cm^3). This mixture was added in very small portions as the contents of the solvent trap melted, large amounts of methane being evolved (**CAUTION**). The crude product remaining in the reaction flask was dissolved in toluene–hexane (300 cm^3, 2:1), and cooled to *ca.* −25 °C in a freezer. Crystals appeared over a 2-d period. The supernatant liquid was removed *via* a cannula, and the product washed with pentane (2 × 50 cm^3). The solid was dried *in vacuo* affording (42.2 g) a mixture of [Ti{Cl(AlMe$_2$)CH$_2$}(η-C$_5$H$_5$)$_2$] and [Ti{Cl[Al(Me)Cl]CH$_2$}(η-C$_5$H$_5$)$_2$] (*ca.* 85:15, as deduced from ^{1}H n.m.r. spectroscopy). Further product (19.0 g, total yield 86%) of the same composition was obtained from the combined supernatant liquid and pentane washings by evaporation and cooling to −25 °C. Both titanium–aluminium species act as sources of [Ti(=CH$_2$)(η-C$_5$H$_5$)$_2$],[24] and the material obtained was of adequate purity for the work described below. It was conveniently stored as a 0.25 mol dm^{-3} solution in toluene, contained in a 200-cm^3 Schlenk tube, fitted with a Teflon high-pressure stopcock.

Synthesis of the Compound [TiW{μ-C(C$_6$H$_4$Me-4)=CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_3$].—(*a*) *From* [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. A toluene (20 cm^3) solution of [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.20 g, 0.50 mmol) at 0 °C was treated with the titanium reagent (**2**) (1.00 mmol, 4 cm^3 of a 0.25 mol dm^{-3} toluene solution) followed by thf (0.2 cm^3, 2 mmol). After stirring for 8 h, the solution was warmed to room temperature, and solvent removed *in vacuo* affording a dark brown residue. A toluene–hexane mixture (1:4, 20 cm^3) was added to the Schlenk tube, followed by *ca.* 3 g of oven-dried Florisil. After stirring for 2 h, the solution was decanted and the Florisil washed with more of the toluene–hexane mixture (6 × 50 cm^3). This procedure was necessary prior to chromatography to remove selectively aluminium and titanium containing residues in the reaction solution. Failure to do this leads to difficulties on chromatography. The decanted solution and the toluene–hexane washings were combined and chromatographed on a water-cooled Florisil column. Elution with toluene–hexane (1:1) gave a brown eluate which on removal of solvent *in vacuo* afforded red-brown *microcrystals* of [TiW{μ-C(C$_6$H$_4$Me-4)=CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (**5a**) (0.15 g, 52%) (Found: C, 51.9; H, 4.1. C$_{26}$H$_{24}$O$_2$TiW requires C, 52.0; H, 4.0%); m.p. 210 °C (with decomp.); $\nu_{max.}$(CO) at 1 912m and 1 649m cm^{-1} (toluene); n.m.r. (C$_6$D$_6$): ^{1}H, δ 2.33 (s, 3 H, Me-4), 2.42 [(AB), 2 H, CH$_2$, *J*(AB) 2], 5.02 (s, 5 H, C$_5$H$_5$W), 5.18 (s, 5 H, C$_5$H$_5$Ti), 5.30 (s, 5 H, C$_5$H$_5$Ti), and 7.20 (m, 4 H, C$_6$H$_4$); ^{13}C-{^{1}H} (CD$_2$Cl$_2$–CH$_2$Cl$_2$), δ 227.0 (μ-CO), 220.3 (CO), 170.7 (μ-C), 157.7 [C^1(C$_6$H$_4$)], 132.7, 130.9, 129.7 (C$_6$H$_4$), 110.3 (C$_5$H$_5$Ti), 107.4 (C$_5$H$_5$Ti), 92.5 (C$_5$H$_5$W), 38.2 (CH$_2$), and 20.8 p.p.m. (Me-4); ^{13}C, δ 38.2 p.p.m. [d of d, *J*(HC) 166 and 146 Hz].

(*b*) *From* [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$]. A toluene (20 cm^3) solution of (**1**) (0.10 g, 0.17 mmol) at 0 °C was treated with the titanium reagent (**2**) (0.62 mmol, 2.5 cm^3 of a 0.25 mol dm^{-3} solution), followed by thf (0.12 cm^3, 1.5 mmol). The mixture was warmed to room temperature and stirred for 12 h. Removal of solvent *in vacuo* gave a brown residue. The latter was treated with toluene–hexane (1:4, 20 cm^3) and Florisil, as described above, and the solution and extracts were chromatographed leading to the isolation of red-brown *microcrystals* of (**5a**) (0.078 g, 76%).

Synthesis of the Compound [TiW{μ-C(Me)=CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_3$].—The compound [W(≡CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.33 g, 1.00 mmol) in toluene (20 cm^3) at −25 °C was treated with 8 cm^3 of the solution of the titanium reagent (**2**) (2 mmol), followed by thf (0.32 cm^3, 4 mmol). An i.r. spectrum revealed that the reaction had gone to completion immediately. Solvent was removed *in vacuo* and the residue treated as described above. Chromatography on an alumina column, maintained at *ca.* 10 °C, and eluting with toluene afforded a red-brown oil. The latter was dissolved in diethyl ether (10 cm^3) which was slowly evaporated to give red-brown *microcrystals* of [TiW{μ-C(Me)=CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (**5b**) (0.10 g, 20%) (Found: C, 45.6; H, 4.1. C$_{20}$H$_{20}$TiW requires C, 45.8; H, 3.8%); m.p. 177 °C (with decomp.); $\nu_{max.}$(CO) at 1 903vs and 1 642w cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^{1}H, δ 1.84 (s, 1 H, CH$_2$), 2.21 (s, 1 H, CH$_2$), 2.81 (s, 3 H, Me), 5.29 (s, 5 H, C$_5$H$_5$W), 5.35 (s, 5 H, C$_5$H$_5$Ti), and 5.53 (s, 5 H, C$_5$H$_5$Ti); ^{13}C-{^{1}H} (CD$_2$Cl$_2$–CH$_2$Cl$_2$), δ 226.4 (μ-CO), 221.7 (CO), 168.6 (μ-C), 109.3 (C$_5$H$_5$Ti), 106.9 (C$_5$H$_5$Ti), 93.2 (C$_5$H$_5$W), 42.4 (Me), and 41.7 p.p.m. (CH$_2$).

Preparation of the Compounds [PtW{μ-C(R)=CH$_2$}(μ-CO)(CO)(PMe$_3$)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4 *or* Me).—(*a*) A toluene (20 cm^3) solution of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (0.078 g, 0.10 mmol) at 0 °C was treated with (**2**) (2.5 cm^3 of the 0.25 mol dm^{-3} solution), followed by thf (0.1 cm^3). The mixture was stirred for 8 h before removing solvent *in vacuo*. The residue was dissolved in dichloromethane and chromatographed on alumina, the yellow eluate affording, after removal of solvent, yellow-orange *microcrystals* of [PtW{μ-C(C$_6$H$_4$Me-4)=CH$_2$}(μ-CO)(CO)(PMe$_3$)$_2$(η-C$_5$H$_5$)] (**6a**) (0.062 g, 80%). Analytical and spectroscopic (i.r., and ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H}, and ^{195}Pt-{^{1}H} n.m.r.) data for this compound have been previously reported.[22]

(*b*) In a similar experiment, a mixture of [PtW(μ-CMe)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (0.76 g, 1.0 mmol) and (**2**) (2.25 mmol, 9.0 cm^3 of a 0.25 mol dm^{-3} solution) in toluene (30 cm^3), with thf (0.32 cm^3, 4 mmol), was stirred for 3 h. The volume of solution was reduced *in vacuo* to *ca.* 5 cm^3. Chromatography on alumina, eluting first with toluene and subsequently with diethyl ether–toluene (1:9), gave a yellow solution. Removal of solvent afforded yellow *microcrystals* of [PtW{μ-C(Me)=CH$_2$}(μ-CO)(CO)(PMe$_3$)$_2$(η-C$_5$H$_5$)] (**6b**) (0.22 g, 31%), characterised as reported elsewhere.[21,23]

Crystal-structure Determinations.—(*a*) [TiW{μ-C(C$_6$H$_4$Me-4)=CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (**5a**). Data were collected at 200 K from a small crystal sealed under nitrogen in a Lindemann capillary, using a Nicolet *P*3/*m* diffractometer system. Of the total of 3 526 unique reflections (2θ ⩽ 50°), 3 061 satisfied

Table 3. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) with estimated standard deviations in parentheses for compound (**5a**)

Atom	*x*	*y*	*z*
W	2 050(1)	2 149(1)	1 015(1)
Ti	2 344(1)	4 719(1)	2 217(1)
O(1)	2 316(2)	5 693(3)	1 050(2)
C(1)	2 191(3)	4 319(5)	987(2)
C(4)	1 048(3)	1 623(5)	1 768(3)
C(3)	2 026(3)	2 144(4)	2 213(3)
C(11)	561(3)	5 178(5)	1 806(3)
C(12)	810(3)	4 610(5)	2 568(3)
C(13)	1 431(3)	5 692(5)	3 056(3)
C(14)	1 551(4)	6 951(5)	2 595(3)
C(15)	1 020(3)	6 641(5)	1 840(3)
C(21)	3 787(3)	6 341(5)	2 653(3)
C(22)	4 086(3)	5 174(5)	2 230(3)
C(23)	4 083(3)	3 784(5)	2 611(3)
C(24)	3 798(3)	4 076(5)	3 281(3)
C(25)	3 629(3)	5 659(5)	3 312(3)
C(31)	2 528(3)	1 136(4)	2 872(2)
C(32)	2 011(3)	871(4)	3 426(2)
C(33)	2 422(3)	5(5)	4 080(3)
C(34)	3 375(4)	−650(5)	4 233(2)
C(35)	3 877(3)	−427(5)	3 680(3)
C(36)	3 477(3)	430(4)	3 026(2)
C(51)	3 834(4)	−1 572(6)	4 945(3)
C(41)	3 355(4)	1 630(6)	448(3)
C(42)	2 433(4)	1 106(5)	−46(3)
C(43)	2 097(4)	−131(5)	324(3)
C(44)	2 807(4)	−342(5)	1 047(3)
C(45)	3 590(4)	738(5)	1 122(3)
O(2)	−156(3)	2 789(4)	75(2)
C(2)	661(4)	2 550(6)	426(3)

the criterion $I \geqslant 2.5\sigma(I)$, and these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the last using an empirical method based on azimuthal scan data ($\mu R = 0.84$).[32]

Crystal data. $C_{26}H_{24}O_2TiW$, $M = 600.2$, monoclinic, $a = 13.889(7)$, $b = 8.729(5)$, $c = 18.270(11)$ Å, $\beta = 106.74(4)°$, $U = 2\,121(2)$ Å^3, $Z = 4$, $D_c = 1.85$ g cm^{-3}, $F(000)$ 1 168, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 59.3 cm^{-1}.

The structure was solved by conventional heavy-atom and electron-density difference methods. Anisotropic thermal parameters were applied to all atoms except hydrogen, the latter being included at calculated positions (C–H 0.96 Å), and given fixed isotropic thermal parameters. Those hydrogen atoms attached to C(4) were located and refined isotropically. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The maximum residual density (± 1 e Å^{-3}) was close to the metal atom centres. Scattering factors and corrections for anomalous dispersion were from ref. 33. Refinement by blocked-cascade least squares converged at *R* 0.023 (*R'* 0.025). All calculations were carried out on an 'Eclipse' Data General computer with the SHELXTL system of programs.[32] The atom co-ordinates are given in Table 3.

(*b*) [PtW{μ-C(C_6H_4Me-4)=CH_2}$(CO)_2(PMe_3)_2$(η-C_5H_5)] (**6a**). Intensity data were recorded at room temperature and collected as described above for (**5a**). Of the total of 4 333 reflections ($2\theta \leqslant 50°$), 3 107 with $I \geqslant 2\sigma(I)$ were used in the structure solution and refinement, after correction for Lorentz, polarisation, and *X*-ray absorption effects ($\mu R = 0.25$).[32]

Crystal data. $C_{22}H_{32}O_2P_2PtW$, $M = 771.4$, monoclinic, $a = 13.181(3)$, $b = 12.608(3)$, $c = 14.936(4)$ Å, $\beta = 96.95(2)°$, $U = 2\,464(2)$ Å^3, $Z = 4$, $D_c = 2.09$ g cm^{-3}, $F(000)$ 1 448, space group $P2_1/n$ (no. 14, non-standard setting), μ(Mo-K_α) 106.4 cm^{-1}.

Table 4. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) with estimated standard deviations in parentheses for compound (**6a**)

Atom	*x*	*y*	*z*
Pt	4 300(1)	1 784(1)	1 948(1)
W	4 232(1)	2 816(1)	267(1)
C(1)	2 966(11)	2 432(12)	702(9)
O(1)	2 090(8)	2 297(10)	808(8)
C(2)	3 540(11)	4 188(12)	263(11)
O(2)	3 134(9)	5 001(8)	267(8)
P(1)	5 115(3)	1 787(3)	3 366(3)
C(41)	6 092(15)	779(18)	3 674(16)
C(42)	5 794(18)	3 006(14)	3 649(13)
C(43)	4 361(15)	1 689(18)	4 278(11)
P(2)	3 108(3)	488(3)	2 115(3)
C(51)	3 636(14)	−655(13)	2 764(14)
C(52)	2 480(14)	−165(14)	1 081(13)
C(53)	2 038(12)	890(16)	2 687(12)
C(11)	4 921(14)	3 156(12)	−1 088(10)
C(12)	5 556(12)	2 378(13)	−633(11)
C(13)	4 983(16)	1 453(13)	−544(12)
C(14)	3 981(16)	1 647(16)	−940(12)
C(15)	3 917(14)	2 658(18)	−1 286(11)
C(3)	5 336(10)	2 762(10)	1 493(9)
C(31)	6 431(9)	2 401(9)	1 442(9)
C(32)	6 645(11)	1 305(11)	1 438(11)
C(33)	7 641(11)	946(11)	1 397(11)
C(34)	8 460(9)	1 627(11)	1 339(10)
C(35)	8 250(11)	2 678(13)	1 383(11)
C(36)	7 240(11)	3 078(10)	1 427(10)
C(5)	9 507(12)	1 238(15)	1 277(15)
C(4)	5 104(9)	3 867(10)	1 378(10)

The structure was solved using the SHELXTL system of programs,[32] as described above for (**5a**). Individual weights were apportioned according to the scheme $w = [\sigma^2(F) + 0.000\,5|F^2|]^{-1}$, and refinement converged at *R* 0.048 (*R'* 0.043). All hydrogen atoms, including those on C(4), were placed at calculated positions. The maximum residual density (± 1 e Å^{-3}) was again close to the metal atom centres. Atom co-ordinates are given in Table 4.

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