Methylene Group Transfer to Carbon–Metal Multiple Bonds: Crystal Structures of $[TiW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ and $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$

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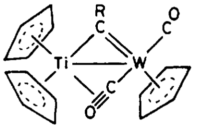
In toluene–tetrahydrofuran, the reagent $[(\eta\text{-}C_5H_5)_2\overline{Ti\cdot Cl\cdot AlMe_2\cdot CH_2}]$ reacts with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ or $[TiW(\mu\text{-}CR)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ ($R = C_6H_4Me\text{-}4$) to give $[TiW(\mu\text{-}CR{=}CH_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$, and with $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ to yield $[PtW(\mu\text{-}CR{=}CH_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$; the latter and $[TiW(\mu\text{-}CR{=}CH_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ have been structurally characterised by *X*-ray diffraction.

There is considerable interest in polynuclear metal complexes with 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 metal surfaces.[1] We have used the isolobal relationship between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) and alkynes to prepare systematically di- and tri-metal compounds with bridging CR ligands.[2] For example, the tolylmethylidyne–tungsten compound reacts with $[Ti(CO)_2(\eta\text{-}C_5H_5)_2]$ to afford complex (**1**).[3] The titanium reagent (**2**)[4] is known to react with alkynes,



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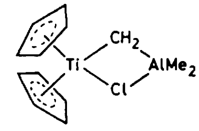

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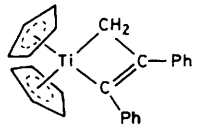

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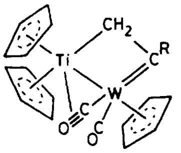

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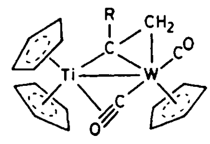

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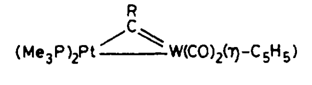

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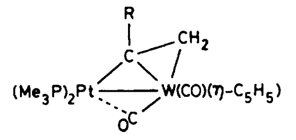

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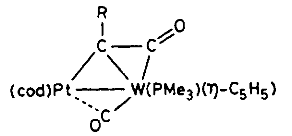
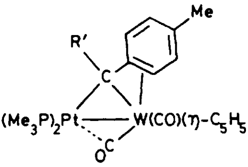


(8)

R = C6H4Me-4



(9) R′ = Me

(10) R′ = H

R = C_6H_4Me-4 in **(1)**—**(8)**

yielding titanacyclobutene complexes such as **(3)**.[5] We, therefore, studied the reaction of **(2)** with [$W(\equiv CR)(CO)_2(\eta-C_5H_5)$] in the expectation that the heterobimetallic-cyclobutene compound **(4)** would be formed. The reaction, however, followed a different pathway involving methylene group transfer from titanium to tungsten.

Treatment of [$W(\equiv CR)(CO)_2(\eta-C_5H_5)$][6] in toluene with **(2)** between −25 and 25 °C in the presence of tetrahydrofuran (*ca.* 2 to 3 equiv.) afforded compound **(5)**† in *ca.* 50% yield (i.r.); half an equivalent of the tolylidyne–tungsten species remained unreacted. Compound **(5)** was structurally identified by *X*-ray diffraction.‡

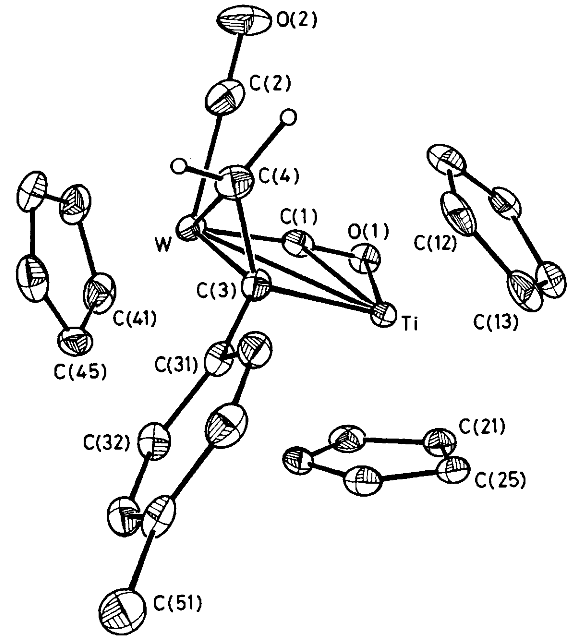


Figure 1. Molecular structure of [TiW{μ-C(C_6H_4Me-4):CH_2}(μ-CO)(CO)(η-C_5H_5)$_3$] **(5)**. Dimensions: Ti–W 3.082(2), Ti–C(1) 2.222(4), Ti–O(1) 2.285(3), Ti–C(3) 2.290(4), W–C(3) 2.199(5), W–C(4) 2.268(6), C(3)–C(4) 1.441(6), C(1)–O(1) 1.213(5), W–C(1) 1.906(5) Å. W–C(1)–O(1) 173.4(3), W–C(2)–O(2) 179.6(6), W–C(3)–Ti 86.7(2), Ti–W–C(3) 47.9(1), W–Ti–C(3) 45.4(1), W–C(3)–C(4) 73.8(3), W–C(4)–C(3) 68.6(3), C(3)–W–C(4) 37.6(2), Ti–C(3)–C(4) 117.4(3)°.

The molecular structure (Figure 1) reveals a Ti–W bond spanned by an η^2-CO ligand, and by a C(R)CH_2 fragment. Of considerable interest is the presence of the W·C(3)·C(4) ring system. Essentially, the structure of **(5)** is similar to that of **(1)**, with the C=W bond in the latter bridged by a CH_2 group in **(5)**. Thus the central core of **(5)** may be viewed either as the metallacyclopropene [$W(=CRCH_2)(CO)_2(\eta-C_5H_5)$] co-ordinated onto a $Ti(\eta-C_5H_5)_2$ moiety, or as a Ti–W system bridged by a vinyl group C(R)=CH_2 σ-bonded to the titanium.

From the apparent stoicheiometry in this synthesis of **(5)**, it seemed possible that the reaction proceeded in two discrete steps: initial formation of **(1)** with the first equivalent of **(2)** acting as a source of $Ti(\eta-C_5H_5)_2$, while the second equivalent

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† Selected spectroscopic properties, with coupling constants in Hz. Compound **(5)**: ν_{CO} at 1 912s and 1 649m cm^{-1} (toluene); n.m.r.: ^{1}H (C_6D_6), δ 2.33 (s, 3 H, Me-4), 2.42 [(AB) pattern, 2 H, CH_2, *J*(AB) 2.4], 5.02 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5), and 7.20 (m, 4 H, C_6H_4); ^{13}C-{^{1}H} (C_6D_6), δ 227.0 (CO), 220.3 (CO), 170.7 (μ-C), 157.7, 132.7, 130.9, 129.7 (C_6H_4), 110.3, 107.4, 92.5 (C_5H_5), 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) 146 and 166]. Compound **(7)**: ν_{CO} at 1 866s and 1 727m cm^{-1} (CH_2Cl_2); n.m.r.: ^{1}H ($CDCl_3$), δ 1.29 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 33], 1.55 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 22], 2.30 (s, 3 H, Me-4), 2.83 [d, 1 H, CH_2, *J*(PH) 8, *J*(PtH) 16], 3.32 [d, 1 H, CH_2, *J*(PH) 12, *J*(PtH) 110], 4.76 (s, 5 H, C_5H_5), and 6.9—7.4 (m, 4 H, C_6H_4); ^{13}C-{^{1}H} (CD_2Cl_2–CH_2Cl_2), δ 236.7 [d, CO, *J*(PC) 11, *J*(PtC) 50], 226.7 [d, CO, *J*(PC) 3, *J*(WC) 174], 153.3 [C-1 of C_6H_4, *J*(PtC) 24], 142.4 [d, μ-C, *J*(PC) 78, *J*(PtC) 608], 129.1, 128.3 (C_6H_4), 90.5 (C_5H_5), 26.7 (CH_2), 21.0 (Me-4), 19.0 [d, MeP, *J*(PC) 30, *J*(PtC) 42] and 17.8 p.p.m. [d, MeP, *J*(PC) 27, *J*(PtC) 36]; ^{31}P-{^{1}H} ($CDCl_3$), δ −17.0 [d, *J*(PP) 10, *J*(PtP) 2 678] and −23.4 p.p.m. [d, *J*(PP) 10, *J*(PtP) 3 570, *J*(WP) 24]; ^{195}Pt-{^{1}H}, δ −238.1 p.p.m. [d of d, *J*(PPt) 2 678 and 3 570]. Compound **(9)**: ν_{CO} at 1 953s and 1 812m(br.) cm^{-1} (CH_2Cl_2); n.m.r.: ^{1}H ($CDCl_3$), δ 1.58 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 37], 1.64 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 23], 2.37 (s, 3 H, Me-4), 3.03 [d of d, 3 H, μ-CMe, *J*(PH) 6 and 3, *J*(PtH) 17], 4.63 [d, 5 H, C_5H_5, *J*(PH) 1, *J*(PtH) 5], 5.90 [d br., 1 H, C_6H_4, *J*(HH) 6], 7.12 [d of d of d, 1 H, C_6H_4, *J*(HH) 6, 2, and 1], and 7.31 (m, 2 H, C_6H_4).

‡ *Crystal data for* **(5)**: $C_{26}H_{24}O_2TiW$, *M* = 600.2, monoclinic, *a* = 13.889(7), *b* = 8.729(5), *c* = 18.270(11) Å, β = 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}. Intensities [3 061 with $I \geqslant 2.5\sigma(I)$] were measured on a Nicolet *P3m* four-circle diffractometer at 200 K and corrected for Lorentz, polarisation and *X*-ray absorption effects. Structure refined to *R* 0.023 (*R′* 0.025) by blocked cascade least squares.

Crystal data for **(7)**: $C_{22}H_{32}O_2P_2PtW$, *M* = 769.4, monoclinic, *a* = 13.181(3), *b* = 12.608(3), *c* = 14.936(4) Å, β = 96.95(2)°, *U* = 2 464(2) Å^3, *Z* = 4, D_c = 2.07 g cm^{-3}, *F*(000) = 1 447. Space group $P2_1/n$ (No. 14), μ(Mo-K_α) = 106.4 cm^{-1}. Intensities [3 107 with $I \geqslant 2\sigma(I)$] measured at 292 K as for **(5)**, refining to *R* 0.048 (*R′* 0.043).

The atomic co-ordinates for both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

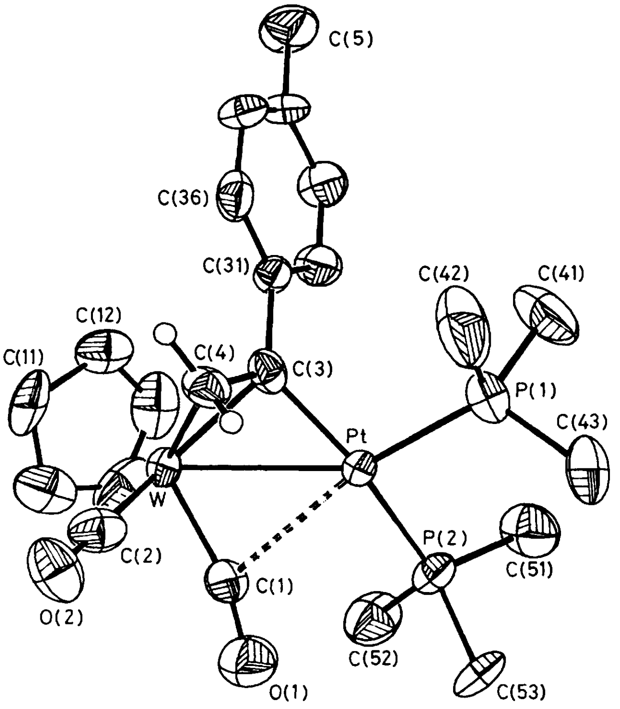

Figure 2. Molecular structure of $[\mathrm{PtW}\{\mu\text{-}\mathrm{C(C_6H_4Me\text{-}4):CH_2}\}\mathrm{(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)}]$ (7). Dimensions: Pt–W 2.820(1), Pt–P(1) 2.257(4), Pt–P(2) 2.301(4), Pt–C(3) 2.02(1), W–C(3) 2.20(1), W–C(4) 2.32(1), C(3)–C(4) 1.43(2), W–C(1) 1.92(2), C(1)–O(1) 1.20(2), Pt · · · · C(1) 2.54(1) Å. W–C(1)–O(1) 166(1), W–C(2)–O(2) 179(1), W–Pt–C(3) 50.8(3), Pt–C(3)–W 83.8(4), Pt–W–C(3) 45.4(3), W–C(3)–C(4) 76.1(7), C(3)–C(4)–W 67.0(7), C(3)–W–C(4) 36.9(4), Pt–C(3)–C(4) 119.4(9), P(1)–Pt–P(2) 98.8(2)°.

transfers a methylene group to (**1**) to yield (**5**). In accord with this proposal, (**1**) reacts with (**2**) to give (**5**).§ The CH_2 transfer reaction to a C=W bond in a C(R)=MM′ system promises to be a general reaction. Treatment of (**6**)[7] with excess of (**2**) gives the yellow crystalline compound (**7**) (80%),† the structure of which was established by *X*-ray diffraction.‡

The molecule (Figure 2) has a $W{\cdot}CH_2{\cdot}C(3)$ ring system similar to that found for (**5**). In (**7**) a carbonyl ligand semi-bridges the metal–metal bond [W–C(1)–O(1) 166°]. The structure is closely related to that recently described for (**8**)[8] in which a CO group bridges the W–C(R) bond of a C(R)=WPt system.

An interesting alternative synthesis of (**7**) involves deprotonation of (**9**) with sodium hydride in tetrahydrofuran, a reaction which may be reversed with $HBF_4{\cdot}OEt_2$. Compound (**9**) was prepared by treating (**6**) with $[OMe_3][BF_4]$ in CH_2Cl_2. The μ-η^1,η^3-bonding mode of the bridge system is similar to that established by *X*-ray crystallography for (**10**).[9]

In the context of the CH_2 transfer reactions leading to (**5**) and (**7**), it is interesting to record that neither (**1**) nor (**6**) reacts with diazomethane. Finally, the addition of CH_2 to the dimetallacyclopropene rings of (**1**) and (**6**) using (**2**) contrasts with reactions of the latter with C=C bonds where cyclopropanation does not occur to any appreciable extent.[4,10]

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References

1 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160; K. M. Motyl, J. R. Norton, C. K. Schauer, and O. P. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 7325; C. P. Casey, P. J. Fagan, and W. H. Miles, *ibid.*, p. 1134; and references 1—7 therein.
2 F. G. A. Stone, in 'Inorganic Chemistry: Towards the 21st Century,' ed. M. H. Chisholm, ACS Symp. Ser., **211**, 1983, pp. 383—395; L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101; M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *ibid.*, 1982, 2475, and references therein.
3 G. M. Dawkins, M. Green, K. A. Mead, J-Y. Salaün, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 527.
4 F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611; F. N. Tebbe, G. W. Parshall, and D. W. Ovenall, *ibid.*, 1979, **101**, 5074; P. J. Krussic and F. N. Tebbe, *Inorg. Chem.*, 1982, **21**, 2900.
5 F. N. Tebbe and R. L. Harlow, *J. Am. Chem. Soc.*, 1980, **102**, 6149.
6 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Bessenhard, *Chem. Ber.*, 1977, **110**, 3397.
7 T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609.
8 J. C. Jeffery, C. Sambale, M. F. Schmidt, and F. G. A. Stone, *Organometallics*, 1982, **1**, 1597.
9 J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1981, 1255.
10 U. Klabunde, F. N. Tebbe, G. W. Parshall, and R. W. Harlow, *J. Mol. Catal.*, 1980, **8**, 37.

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§ *Added in proof*: Subsequently, by monitoring the reaction of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with (**2**) (1:1 mol ratio) by ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy it has been established that (**5**) is formed in >50% yield. This observation eliminates a mechanism requiring a second equiv. of (**2**) and, therefore, it is suggested that compound (**4**) is an intermediate which rapidly rearranges to (**5**).