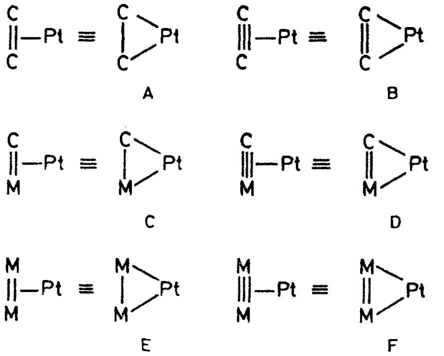
Addition of Nucleophilic Metal Complexes to Mononuclear Transition Metal Carbyne Compounds; *X*-Ray Crystal Structure of $[PtW(\mu\text{-}CC_6H_4\text{-}p\text{-}Me)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$

By Terence V. Ashworth, Judith A. K. Howard, and F. Gordon A. Stone
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Compounds containing platinum–tungsten bonds with bridging carbyne ligands are formed by reaction of the species $[Pt(C_2H_4)(PR_3)_2]$ ($PR_3 = PMe_3$ or PMe_2Ph) with carbyne complexes $[W(CR)(CO)_2(\eta\text{-}C_5H_5)]$ or $[WBr(CR)(CO)_4]$ ($R = C_6H_4\text{-}p\text{-}Me$); *X*-ray diffraction studies have established the structure of $[PtW(\mu\text{-}CC_6H_4\text{-}p\text{-}Me)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$.

Nucleophilic metal (d^8 or d^{10}) compounds, notably Pt^0, show a marked tendency to bond olefins and acetylenes having electron withdrawing substituents (*e.g.* F,[1] CF_3,[2] or CN[3]). This property has resulted in the characterization of many complexes, and the η^2-interaction between the metal and the unsaturated ligand is best represented[4] by the metallacyclo-propane and -propene formulations (A) and (B) of the Scheme. In this respect there is an analogy between electrophilic olefins and acetylenes on the one hand, and formally electron deficient di- or poly-nuclear metal complexes with metal–metal double or triple bonds on the other [(E) and (F) of the Scheme]. We have recently established that Pt^0 complexes readily add to Os=Os,[5] Re=Re, or Mo≡Mo,† affording cluster compounds. We now demonstrate that mononuclear metal carbyne complexes interact strongly with Pt^0, thus presaging a new class of transition metal compound containing heteronuclear metal–metal bonds with bridging carbyne ligands [(D) of the Scheme].



Scheme

Addition of a pentane solution of $[W(CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = p$-tolyl)[6] to suspensions of the complexes $[Pt(C_2H_4)L_2]$ ($L = PMe_3$ or PMe_2Ph) in the same solvent at 0 °C afforded (80% yield) pale red microcrystals of the compounds $[PtW(\mu\text{-}CR)(CO)_2(L_2)(\eta\text{-}C_5H_5)]$ {(**1**, $L = PMe_2Ph$), m.p. 150 °C, ν_{CO}(cyclohexane) 1 898s and 1 818s cm^{-1}; ^1H n.m.r. ($CDCl_3$): τ, 2·4—3·0 (m, 10 H, Ph), 3·3 (m, 4 H, C_6H_4), 4·60 [s, 5H, C_5H_5, *J*(PtH) 4 Hz], 7·75 (s, 3 H, $C_6H_4CH_3$), 8·17 [d, 6 H, CH_3P, *J*(PH) 8, *J*(PtH) 22 Hz], and 9·45 [d, 6 H, CH_3P, *J*(PH) 9, *J*(PtH) 38 Hz]; (**2**, $L = PMe_3$), m.p. 177—179 °C, ν_{CO} 1 898s and 1 815s cm^{-1}}. The ^{31}P (^1H-decoupled, to low frequency of H_3PO_4 external) n.m.r. spectrum of (**1**) ($CDCl_3$) indicated the presence of two non-equivalent phosphorus ligands {δ, 3·8 [d, *J*(PP) 4, *J*(PtP) 4113, *J*(WP) 14 Hz] and 10·6 p.p.m. [d, *J*(PP) 4, *J*(PtP) 2743, *J*(WP) 6 Hz]}. The *J*(PtP) value of 4113 Hz suggested a *trans* W·Pt·P configuration for the phosphorus nucleus with a shift of 3·8 p.p.m. The ^{13}C (^1H-decoupled) n.m.r. spectrum of (**1**) ($CDCl_3$) showed the carbyne carbon resonance at 336·5 p.p.m. [d, ^2J(PC) 59, *J*(PtC) 747 Hz], *ca.* 37 p.p.m. downfield from that of the parent mononuclear carbyne complex.[6] Since complexes (**1**) and (**2**) were of a new type, a single crystal *X*-ray diffraction study was carried out on (**1**).‡

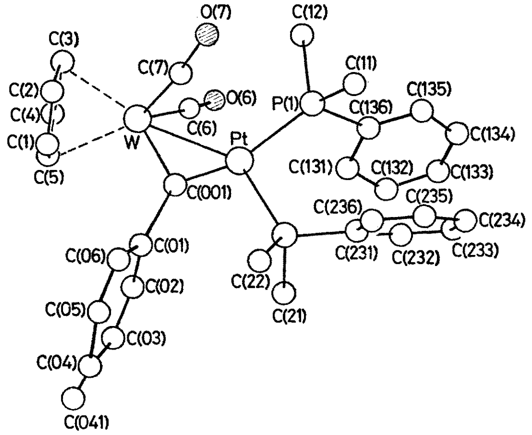


Figure. Molecular structure of $[(PhMe_2P)_2\overline{Pt(\mu\text{-}CC_6H_4\text{-}p\text{-}Me)W}(CO)_2(\eta\text{-}C_5H_5)]$.

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† The unsaturated dirhenium complex $[Re_2(\mu\text{-}H)_2(CO)_8]$ (M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Amer. Chem. Soc.*, 1972, **94**, 6232; M. A. Andrews, S. W. Kirtley, and H. D. Kaesz, *Inorg. Chem.*, 1977, **16**, 1556) reacts with $[Pt(C_2H_4)_2(PPh_3)]$ to give trinuclear $[Re_2Pt(\mu\text{-}H)_2(CO)_9(PPh_3)]$ (L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone, and P. Woodward, to be published), and the compound $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85; K. J. Klingler, W. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 3535) also adds nucleophilic platinum complexes (unpublished observations).

‡ Atomic co-ordinates for this work 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.

Crystal data: $C_{31}H_{34}O_2P_2PtW$, M 879·5, monoclinic, space group $P2_1/c$, $a = 12{\cdot}211(11)$, $b = 9{\cdot}339(6)$, $c = 26{\cdot}125(23)$ Å, $\beta = 92{\cdot}77(7)°$, $U = 2975{\cdot}3$ Å^3, $Z = 4$, $D_m = 1{\cdot}95$, $D_c = 1{\cdot}97$ g cm^3, $F(000) = 1676$, $\mu(\text{Mo-}K_\alpha) = 91{\cdot}6$ cm^{-1}. Current R 0·065 (R' 0·086) for 4638 intensities [200 K, $2\theta \leqslant 55°$, $I \geqslant 2\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-K_α ($\lambda = 0{\cdot}71069$ Å)].

The molecular structure (Figure) shows that the $[W(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(PMe_2Ph)_2]$ units are linked by a metal–metal bond [2·753(1) Å] (sum of covalent radii 2·85 Å) supported by the bridging $C{\cdot}C_6H_4\text{-}p\text{-}Me$ group. The carbyne carbon atom is 1·96(2) Å from the tungsten and 2·05(2) Å from the platinum. The former distance is 0·14 Å longer than in $[W(CC_6H_4\text{-}p\text{-}Me)(CO)_2(\eta\text{-}C_5H_5)]$;[7] the latter is within the range [1·99(3)—2·15(2) Å] previously observed for Pt–C separations.[8] In (**1**) the plane of the *p*-tolyl ring is inclined at 70° to the plane $\overline{\mathrm{W{\cdot}Pt{\cdot}C}}$.

At −50 °C in pentane, $[Pt(C_2H_4)(PMe_3)_2]$ and $[WBr(CC_6H_4\text{-}p\text{-}Me)(CO)_4]$[9] react quantitatively to give red crystalline $[(Me_3P)_2\overline{\mathrm{Pt}(\mu\text{-}\mathrm{CC_6H_4Me})\mathrm{W}}\mathrm{Br}(CO)_4]$ (**3**) {m.p. 132—134 °C; ν_{CO}(Nujol), 2 080s, 2 020s, 1 978s br, and 1 870s br cm^{-1}. N.m.r. (in $CDCl_3$): ^1H (−20 °C), τ, 2·98 (m, 4 H, C_6H_4Me), 7·59 (s, 3 H, $p\text{-}C_6H_4CH_3$), 8·26 [d, 9 H, CH_3P, J(PH) 8, J(PtH) 23 Hz], and 8·73 [d, 9 H, CH_3P, J(PH) 10, J(PtH) 38 Hz]; ^{31}P (−30 °C), δ 8·7 [d, J(PP) 13, J(PtP) 4015 Hz], and 21·8 p.p.m. [d, J(PP) 3, J(PtP) 2 670 Hz]; ^{13}C (−50 °C), 349 ($\mu\text{-}CC_6H_4Me$) and 200 (CO) p.p.m.}.

Although the concept of a relationship between the interaction of C≡C or W≡C groups with d^{10} metal ions (Scheme) is over simplistic, nevertheless it may be used to develop new chemistry. We have recently characterised bis(acetylene) complexes $[Pt(RC_2R)_2]$ (R = Ph, $p\text{-}C_6H_4Me$, $SiMe_3$, Bu^t, Me)[10] by ligand displacement from $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) or $[Pt(C_2H_4)_3]$. Analogously, from $[Ni(cod)_2]$, $[Pd(dba)_2]$ (dba = dibenzylideneacetone), or $[Pt(C_2H_4)_3]$ and metal carbynes we have been able to prepare trimetallic compounds, *e.g.* purple $[M\{W(CC_6H_4Me)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Ni, Pd, or Pt). This route to metal cluster compounds with bridging carbynes is being developed.

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