# Synthesis of *triangulo*-Trimetal Compounds from Metal Carbene Complexes; *X*-Ray Crystal Structure of $[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PBu^t_2Me)_2]$

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*Summary* The compounds $[Pt(C_2H_4)_2(PR_3)]$ $[PR_3 = PBu^t_2Me$ or $P(cyclo\text{-}C_6H_{11})_3]$ react with carbene complexes $[M\{C(OMe)Ph\}(CO)_5]$ (M = Cr or W) to give trimetallic molecules $[MPt_2\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2]$, the structure of the tungsten compound being established by *X*-ray crystallography; in related reactions *triangulo*-triplatinum compounds with bridging $[\mu\text{-}C(OMe)Ph]$ groups are formed.

THE dipolar $M{=}CR^1R^2$ and $M{\equiv}CR$ (M = Cr, Mo, W, or Mn) bonds of metal–carbene and –carbyne compounds add $d^{10}$ species $[M'L_2]$ (M′ = Ni, Pd, or Pt; L = $PR_3$, $L_2$ = cycloocta-1,5-diene) to give heteronuclear di-metal complexes in which the metal–metal bonds are bridged by CR and $CR^1R^2$ ligands.[1] Herein we report that these syntheses can be adapted to produce trimetallic clusters by using the compounds $[Pt(C_2H_4)_2(PR_3)]$.[2]

The complexes $[Pt(C_2H_4)_2(PR_3)]$ $[PR_3 = PBu^t_2Me$ or $P(cyclo\text{-}C_6H_{11})_3]$ react with $[W\{C(OMe)Ph\}(CO)_5]$[3] in toluene at −20 °C to give (50% yield) red microcrystals (from hexane) of the compounds $[Pt_2W\{C(OMe)Ph\}(CO)_6(PR_3)_2]$, (**1**; $PR_3 = PBu^t_2Me$), m.p. 175—180 °C (decomp.) [$\nu_{CO}$(cyclohexane) 2 032s, 1 940m, 1 922s, and 1 914sh cm$^{-1}$; $^1$H n.m.r. ($CDCl_3$), $\tau$ 2·2—3·3 (m, 5H, Ph), 6·36 (s, 3H, OMe), 8·52 {d, 6H, Me, *J*(P–H) 8 and *J*(Pt–H) 38 Hz} 8·67 {d, 18H, $Bu^t$, *J*(P–H) 14 Hz}, and 9·13 {d, 18H, $Bu^t$, *J*(P–H) 14 Hz}] and [**2**; $PR_3 = P(cyclo\text{-}C_6H_{11})_3$], m.p. 192—194 °C (decomp.) ($\nu_{CO}$ 2 028s, 1 940m, 1 924sh, and 1 916s cm$^{-1}$). The $^{31}$P ($^1$H decoupled, $CDCl_3$) n.m.r. spectra of (**1**) and (**2**) revealed that they contained two platinum atoms having the arrangement $R_3P{\cdot}Pt{\cdot}Pt{\cdot}PR_3$, *e.g.* (**1**), $\delta$(rel. to external $H_3PO_4$) −53·7 p.p.m. [s, $^3J$(P–P) 68, $^1J$(Pt–P) 3758, $^2J$(Pt–P) 291, *J*(Pt–Pt) 2241, and $^2J$(W–P) 34 Hz]. The $^{13}$C n.m.r. spectrum of (**1**) ($^1$H decoupled, $CDCl_3$) showed the carbene carbon resonance at 237 p.p.m. [*J*(Pt–C) 771 Hz]. This coupling constant, and the equivalent environment of the $PR_3$ ligands, suggested that the carbene group had migrated from tungsten to a bridging position between two platinum atoms. An *X*-ray diffraction study was carried out on (**1**) to establish the structure of the molecule.†

*Crystal data:* (**1**), $C_{32}H_{50}O_7Pt_2W$, *M* 1182·7, monoclinic, space group $P2_1/a$, $a = 16{\cdot}003(5)$, $b = 15{\cdot}691(7)$, $c = 15{\cdot}261(9)$ Å, $\beta = 93{\cdot}52(4)^\circ$, $U = 3924{\cdot}9$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}98$, $D_c = 2{\cdot}01$ g cm$^{-3}$, $F(000) = 2176$, $\mu(\text{Mo-}K_\alpha) = 109{\cdot}7$ cm$^{-1}$. Current *R* is 0·070 (R′ 0·083) for 4001 absorption corrected intensities [298 K, $2\theta \leqslant 50^\circ$, $I \geqslant 2\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-$K_\alpha$ ($\lambda = 0{\cdot}71069$ Å)].

The molecular structure (Figure) shows that the tungsten and the two platinum atoms form an essentially isosceles triangle with the carbene species bridging the Pt–Pt edge. The tungsten atom carries four terminally bound carbonyl ligands while each platinum atom has a carbonyl group perturbed towards a semi-bridging interaction with the tungsten atom [mean W · · · · · C(semi-bridging) 2·50(3) Å; ∠Pt–C–O, 152(3)°]. Without this interaction the tungsten atom is formally two electrons short of an 18-electron configuration. The presence of six CO ligands in (**1**) implicates a second molecule of $[W\{C(OMe)Ph\}(CO)_5]$ or a decomposition product such as $[W(CO)_6]$ in the reaction. The $Pt(PR_3)$ group is known to abstract carbonyl groups in metal cluster formation.[4]

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† The 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.

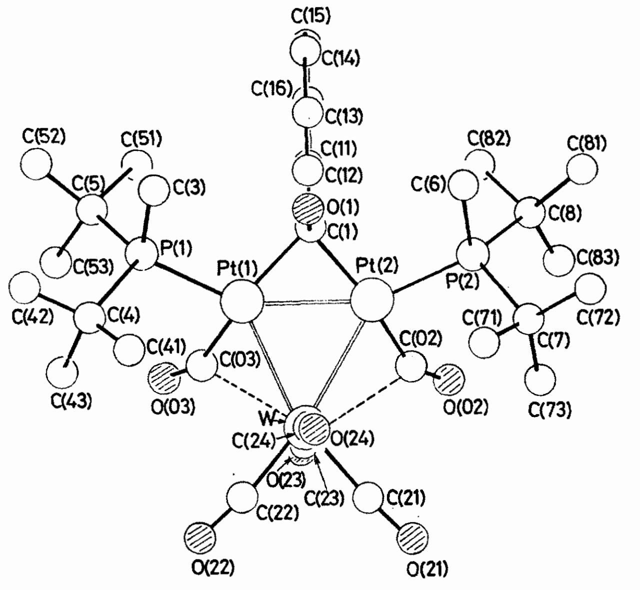
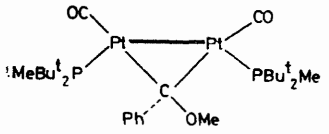


FIGURE. Molecular structure of $[Pt_2W\{C(OMe)Ph\}(CO)_6(PBu^t_2Me)_2]$ (**1**), with the C atom of the OMe group omitted for clarity. Bond lengths: Pt(1)–Pt(2), 2·628(1); W–Pt(2), 2·833(2); W–Pt(1), 2·830(2); Pt(1)–C(1), 2·09(3); and Pt(2)–C(1), 2·06(2) Å.

From $[Cr\{C(OMe)Ph\}(CO)_5]$[3] the red crystalline compounds $[CrPt_2\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2]$ were similarly prepared: (**3**; $PR_3 = PBu^t_2Me$), m.p. 240—243 °C (decomp.) [$\nu_{CO}$, 2 019vs, 1 936vs, 1 908vs, br, and 1 876m cm$^{-1}$; n.m.r.: $^1H$ ($CDCl_3$), $\tau$, 2·4—3·2 (m, 5H, Ph), 6·30 (s, 3H, OMe), 8·56 {d, 6H, Me, *J*(P–H) 9 and *J*(Pt–H) 42 Hz}, 8·61 {d, 18H, Bu$^t$, *J*(P–H) 15 Hz}, and 9·20 {d, 18H, Bu$^t$, *J*(P–H) 15 Hz}; $^{31}P$ ($CDCl_3$), −45·4 p.p.m. {*J*(P–Pt) 3688 and 278, *J*(P–P) 67, and *J*(Pt–Pt) 2092 Hz}] and [**4**; $PR_3 = P(cyclo\text{-}C_6H_{11})_3$], m.p. 179—181 °C (decomp.) [$\nu_{CO}$, 2 006vs, 1 938s, and 1 895vs,br cm$^{-1}$; $^{31}P$ n.m.r. −45·8 p.p.m. {*J*(Pt–P) 3 678 and 219, *J*(P–P) 61 Hz}]. Synthesis of these chromiumdiplatinum compounds is accompanied by formation of the di- and tri-platinum complexes (**5**), (**6**), and (**7**), in low yield (5—10%).

*triangulo*-Triplatinum compounds readily form from some carbene–metal complexes. Thus $[Mn\{C(OMe)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)_2(PMe_3)]$ in pentane–toluene at room temperature afford a mixture of (**8**) (50%) and (**9**) (2%). Chromatography separated (**8**) into two isomers with distinctive i.r. [$\nu_{CO}$ (i) 1 785 and (ii) 1 793 cm$^{-1}$] and $^1H$ n.m.r. [(i) in $(CD_3)_2CO$, $\tau$, 2·10—3·02 (m, 10H, Ph), 6·07 (s, 6H, OMe), and 8·44—9·22 (m, 27H, Me); (ii) in $(CD_3)_2CO$ $\tau$ 2·15—3·00 (m, 10H, Ph), 6·24 (s, 6H, OMe), and 8·24—9·25 (m, 27H, Me)] spectra. Compounds (**8**) and (**9**) probably form *via* unstable hetero-nuclear dimetal species $[(\eta\text{-}C_5H_5)(OC)_2\overline{Mn\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)]$. Indeed, the compound[1] $[(OC)_5\overline{Cr\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ in toluene at 80 °C (1 h) gives a chromatographically separable mixture of $[Cr(CO)_5(PMe_3)]$, the two isomers of (**8**) (25%), and complex (**9**) (16%). The n.m.r. spectrum of the latter establishes that it is formed as an isomer having two environments for the MeO groups. Formation of (**9**) in this manner must be related to the synthesis of $[Ni_3\{\mu\text{-}C(OMe)Ph\}_3(CO)_3]$ from $[Mo\{C(OMe)Ph\}(CO)(NO)(\eta\text{-}C_5H_5)]$ and $[Ni(CO)_4]$.[5]



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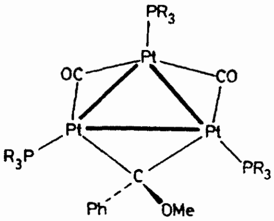
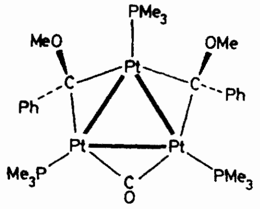


(6), $PR_3 = PBu^t_2Me$
(7), $PR_3 = P(cyclo\text{-}C_6H_{11})_3$



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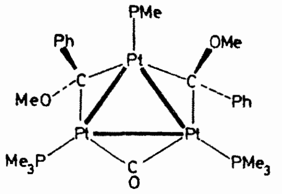

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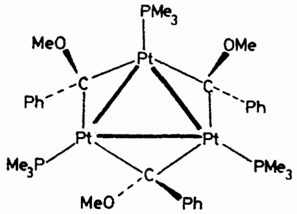

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