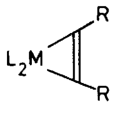
Bridging Acetylene Complexes of Nickel and Platinum; *X*-Ray Crystal Structure of $[Pt_3(Et_3P)_4(PhC_2Ph)_2]$

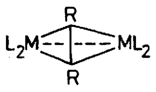
By NEIL M. BOAG, MICHAEL GREEN, JUDITH A. K. HOWARD, JOHN L. SPENCER, ROBERT F. D. STANSFIELD, F. GORDON, A. STONE, MARTYN D. O. THOMAS, JOSE VICENTE, and PETER WOODWARD
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary Di- and tri-platinum, and di-nickel acetylene complexes have been prepared, *e.g.* $[Pt_2\{\mu_2(\eta^2\text{-}PhC_2Ph)\}(\eta^2\text{-}PhC_2Ph)(Ph_3P)_2]$, $[Ni_2\{\mu_2(\eta^2\text{-}Me_3SiC_2SiMe_3)\}(cod)_2]$, and $[Pt_3\{\mu_2(\eta^2\text{-}PhC_2Ph)\}_2(Et_3P)_4]$; a single crystal *X*-ray diffraction study of the latter revealed a Pt·Pt·Pt sequence bridged transversely by two diphenylacetylene ligands.

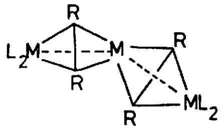
WE describe the step-wise formation of di- and tri-platinum complexes containing μ_2-PhC_2Ph ligands from the recently reported[1] bis(acetylene)platinum complex $[Pt(PhC_2Ph)_2]$ (**1**). Whereas mono-nuclear acetylene complexes of nickel, palladium, or platinum of type (A) have long been known, *e.g.* $[M(ac)L_2]$ (ac = PhC_2Ph or $CF_3C_2CF_3$; L = Ph_3P; M = Ni,[2–4] Pd,[2] or Pt[2,5]), examples of complexes of type (B) have hitherto been confined to cyclopentadienyl-nickel and -palladium[6] derivatives and the two recently reported species $[Ni_2\{\mu_2(\eta^2\text{-}PhC_2Ph)\}(cod)_2]$[7] (cod = cyclo-octa-1,5-diene) and $[Pt_2\{\mu_2(\eta^2\text{-}PhC_2Ph)\}(\eta^2\text{-}PhC_2Ph)(Me_3P)_2]$ (**2**).[1] The results described herein presage development of the chemistry of bridged-acetylene complexes of these metals, including structures of type (C).



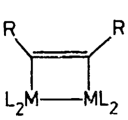
(A)



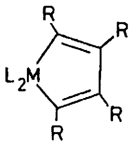
(B)



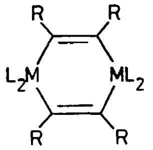
(C)



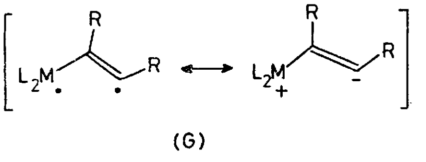
(D)



(E)



(F)



(G)

Treatment (diethyl ether solvent, room temp., 4 h) of (**1**) with 1 equiv. of $[Pt(Ph_3P)_2(C_2H_4)]$ affords yellow crystals of $[Pt_2\{\mu_2(\eta^2\text{-}PhC_2Ph)\}(\eta^2\text{-}PhC_2Ph)(Ph_3P)_2]$ (**3**) [ν_{max} (C≡C), 1 842 cm^{-1}; ^{31}P n.m.r. (^1H decoupled, in $CDCl_3$): δ, −26·6 p.p.m. (relative to H_3PO_4 external) {^1J(PtP), 3 778; ^2J(PtP), 41 Hz}], a complex analogous to (**2**). Reaction of (**1**) with 2 equiv. of $[Pt(Ph_3P)_2(C_2H_4)]$, or reaction of (**3**) with 1 equiv. of the ethylene complex, gives red–purple crystals of $[Pt_3(PhC_2Ph)_2(Ph_3P)_4]$ (**4**), the i.r. spectrum of which showed no band near 1 800 cm^{-1} corresponding to the structural mode (A). An orange compound $[Pt_3(PhC_2Ph)_2(Et_3P)_4]$ (**5**) was similarly obtained from (**1**) and $[Pt(Et_3P)_2]$,† and a single crystal *X*-ray diffraction study was carried out.

Crystal data: monoclinic, *C*2/*c*, $a = 17\cdot047(2)$, $b = 13\cdot677(2)$, $c = 25\cdot073(3)$ Å, $\beta = 105\cdot79(1)°$, $U = 5625(1)$ Å^3, $Z = 4$, $F(000) = 2744$, $\mu(\text{Mo-}K_\alpha) = 72\cdot8$ cm^{-1}. *R* is currently 0·050 for 3226 independent reflections with $I \geqslant 3\cdot0\,\sigma(I)$ collected on a Syntex P2$_1$ four-circle diffractometer, measured to $2\theta_{max} = 50\cdot0°$.‡

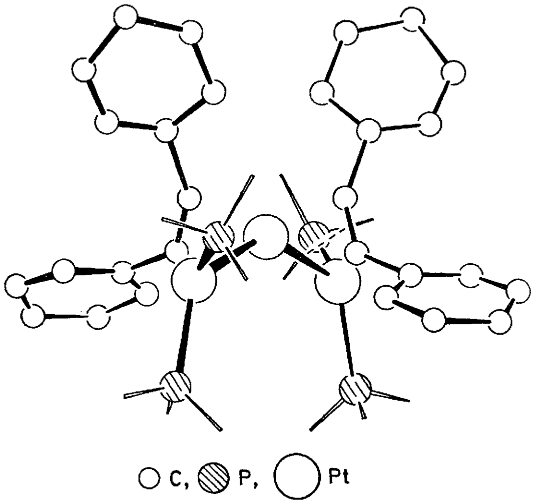


FIGURE. Molecular structure of $[Pt_3\{\mu_2(\eta^2\text{-}PhC_2Ph)\}_2(Et_3P)_4]$.

The molecular structure (Figure) shows that the platinum atoms adopt a *V*-shaped arrangement, with Pt–Pt = 2·905(1) Å and ∠Pt·Pt·Pt = 144°; the whole molecule is constrained crystallographically to C_2 symmetry. The acetylenic units form transverse bridges across each pair of platinum atoms with the C-C bonds turned towards the under side of the V-arrangement and making an angle of 34° with the two-fold axis. The C–C distance is 1·34(3) Å, the mean Pt–C distance is 2·07(2) Å, and the phenyl rings are bent away from the metal atoms (∠C·C·Ph = 141°). The phosphine geometries are normal [Pt–P = 2·267(9) Å], but the ethyl groups are probably disordered. For the two 'outer' platinum atoms, if the acetylene ligand is assumed to occupy one co-ordination site and the existence of a Pt–Pt

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† Prepared by Dr. G. K. Barker of this Laboratory.

‡ 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.

bond is ignored,§ the stereochemistry is plane-triangular, but with a P·Pt·P angle of 107°. The P·Pt·C angles, however, are also *ca.* 107° as the C·Pt·C angle is 36°. With respect to the central metal atom, the two co-ordination sites of the acetylenes form another *V*-shape inverted relative to Pt·Pt·Pt; the two V-planes being at an angle of 37°.

The results demonstrate the step-wise formation of complexes of type (A), (B), and (C). Moreover, for platinum, complexes (B) form very readily. For example, treatment of $[Pt(cod)_2]$,[8] in pentane saturated with ethylene, with stoicheiometric amounts of Me_3P and PhC_2Ph affords yellow crystalline $[Pt_2\{\mu_2(\eta^2\text{-}PhC_2Ph)\}(Me_3P)_4]$ (**6**), m.p. 128—130 °C (decomp.) [n.m.r.: ^{31}P, δ 31·3 p.p.m., $^1J(PtP)$ 3 340, $^2J(PtP)$ −83, $J(PtPt)$ 470, and $^3J(PP)$ 15 Hz; ^{13}C (^1H decoupled, in CH_2Cl_2–CD_2Cl_2 at −70 °C, enriched $Ph^{13}C_2Ph$): acetylenic carbon resonance at 80·9 p.p.m., $J(PtC)$ 278 Hz]. It has been mentioned[7] that alkyl-substituted acetylenes do not yield isolable nickel complexes of type (B) with $L_2 =$ cod, on account of steric factors. However, sterically demanding $Me_3SiC_2SiMe_3$ reacts with $[Ni(cod)_2]$ to give red $[Ni_2\{\mu_2(\eta^2\text{-}Me_3SiC_2SiMe_3)\}(cod)_2]$ (**7**) (i.r.: $\nu_{C\equiv C}$ 1 526 cm^{-1}, ^{13}C n.m.r.: acetylenic carbon resonance at 115·9 p.p.m.). Furthermore, the electronegatively substituted acetylene $CF_3C_2CF_3$ with $[Ni(Bu^tNC)_4]$ affords $[Ni_2\{\mu_2(\eta^2\text{-}CF_3C_2CF_3)\}(Bu^tNC)_4]$ (**8**), m.p. 170 °C (decomp.) [i.r.: $\nu_{C\equiv C}$ 1 562 cm^{-1}; n.m.r.: ^1H (−80 °C, $C_6D_5CD_3$) τ 9·2 (s, Me), ^{19}F (30 °C, toluene) 48·0 (s, CF_3) p.p.m. (relative to CCl_3F)], a complex which also forms readily from the reaction of $[Ni_4(Bu^tNC)_7]$[9] with the acetylene.

In contrast to the reaction of PhC_2Ph with $[Ni(cod)_2]$, which affords a complex of type (B),[7] treatment of $[Pt(cod)_2]$ with a deficiency of PhC_2Ph yields a compound $[Pt_2(PhC_2Ph)(cod)_2]$ (**9**) of similar stoicheiometry but with a ^{13}C n.m.r. spectrum [−60 °C, ^{13}C enriched sample, acetylenic carbon 139·8 p.p.m., $^1J(PtC)$ 671, $^2J(PtC)$ 242 Hz] in accord with a diplatinacyclobutene structure (D). This ring system exists in $[Pt_3(CF_3C_2CF_3)_4(cod)_2]$,[10] and in the rhodium complex $[Rh_2\{\mu_2(\eta^1\text{-}CF_3C_2CF_3)\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$.[11] Moreover, although the dicobalt complexes $[Co_2(ac)(CO)_6]$ have the bridging acetylene normal to the metal–metal axis as in (B), insertion reactions with CO may involve the intermediacy of a structural isomer (D).[12] Interconversion (B) $\rightleftharpoons$ (D) in catalysis and cluster chemistry should, therefore, be considered.

For the nickel group metals, metallacyclopentadiene-type structures (E) are less common, although established for palladium,[13] and found in $[Pt\{C_4(CF_3)_4\}(cod)]$.[10,14] The dimetallacyclohexadiene structure (F) occurs in $[Pt_2(CF_3C_2CF_3)_2(cod)_2]$ and related molecules.[10] We propose that (A)–(F) form *via* initial attack of an electron-rich metal species to give (G). The latter could ring-close to give (A), yield (B) or (D) on reaction with $[ML_2]$, dimerise to give (F), and react with an acetylene molecule to yield (E). If L_2 in (B) is an acetylene unit, clearly addition of an $[ML_2]$ fragment is possible. The nature of the structural-types produced in the various reactions will depend on a variety of factors. Moreover, any loss of the ligands L can lead to metal clusters as, for example, in the release of CO from $[Ni(CF_3C_2CF_3)(CO)_2]$ to give $[Ni_4\{\mu_3(\eta^2\text{-}CF_3C_2CF_3)\}_3(CO)_4]$.[15]

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§ In complexes of structural type (B) or (C) the metal can have a 16-electron configuration (no M–M bond) or an 18-electron configuration (M=M double bond) (see ref. 7). The Pt–Pt distances in complexes (**5**) (2·905 Å) and (**2**) (2·890 Å) are longer than in most bridged diplatinum complexes, perhaps implying little if any direct metal–metal bonding. Moreover, in acetylene-diplatinum complexes of type (B), values of $J(^{195}Pt\text{–}^{195}Pt)$ are *ca.* 500 Hz: at the low end of the range (100—9000 Hz) found in diplatinum species (Dr. M. Murray, personal communication). We take these relatively low coupling constants also to reflect negligible Pt–Pt bonding.

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