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Preliminary communication

Insertion reactions of $[Pt(PPh_3)_2]$ fragments into the four-membered ring complex $[W(CO)_5PPhC(OEt){=}CPhCHPh]$. Crystal and molecular structures of $[Pt(dppe)PPh(W(CO)_5)C(OEt){=}CPhCHPh]$ and $[Pt(PPh_3)_2((W(CO)_5)PhP{=}C(OEt)CPh{=}CHPh)(\eta^2\text{-}(P{=}C))]$

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Abstract

Insertions of platinum bis(phosphane) fragments into a 1,2-dihydrophosphete ring lead to complexes derived from a 1-phosphabuta-1,3-diene species.

In a series of recent publications, we have established a number of insertions of platinum, palladium and nickel-containing fragments into phosphirene (**1**, **2**) and phosphirane (**3**, **4**) coordination complexes [1–3]. These reactions proceed through a concerted oxidative addition of an η^2-coordinated P–C bond to the metal centre [3] and mimic the processes normally associated with industrial catalyst decomposition [4], but are clearly driven by unrepresentatively small $\sigma_{(PC)} \rightarrow \sigma^{\star}_{(PC)}$ promotion potentials induced by the strain of the three-membered rings [5,6]. To assess the significance of this strain, our studies are here extended to the interaction of the larger ring 1,2-dihydrophosphete complex (**5**) [7] with $[Pt(PR_3)_2]$ fragments.

$^{31}P\{^{1}H\}$ NMR monitoring * of a room-temperature toluene solution containing

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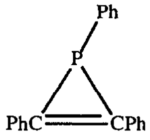
* *Spectroscopic data.* $^{31}P\{^{1}H\}$ NMR (chemical shifts in ppm relative to trimethylphosphite; positive to high frequency of the reference, J in Hz, room temperature where not stated otherwise):
For **6a**: δP(A) -117.5, δP(M) -116.0, δP(X) -75.0, ^{2}J(P(A)P(M)) 18, ^{2}J(P(A)P(X)) 246, ^{2}J(P(M)P(X)) 12, ^{1}J(PtP(A)) 2150, ^{1}J(PtP(M)) 2034, ^{1}J(PtP(X)) 1759, ^{1}J(WP(X)) 219. **6a** -60 ° C: *conformer A* δP(A) -118.9, δP(M) -121.7, δP(X) -74.7, ^{2}J(P(A)P(M)) 17, ^{2}J(P(A)P(X)) 246, ^{2}J(P(M)P(X)) 7, ^{1}J(PtP(A)) 2143, ^{1}J(PtP(M)) 2018, ^{1}J(PtP(X)) 1866. **6a** -60 ° C: *conformer B* δP(A) -118.1, δP(M) -121.2, δP(X) -85.9. ^{2}J(P(A)P(M)) 17, ^{2}J(P(A)P(X)) 248, ^{2}J(P(M)P(X)) 7, ^{1}J(PtP(A)) 2157, ^{1}J(PtP(M)) 2011, ^{1}J(PtP(X)) 1924. For **6b**: δP(A) -99.9, δP(M) -94.0, δP(X) -130.0, ^{2}J(P(A)P(M)) 0, ^{2}J(P(A)P(X)) 246, ^{2}J(P(M)P(X)) 6, ^{1}J(PtP(A)) 2194, ^{1}J(PtP(M)) 2077, ^{1}J(PtP(X)) 1978, ^{1}J(WP(X)) 186. For **7**: δP(A) -117.4, δP(M) -114.4, δP(X) -197.1, ^{2}J(P(A)P(M)) 16, ^{2}J(P(A)P(X)) 159, ^{2}J(P(M)P(X)) 28, ^{1}J(PtP(A)) 3352, ^{1}J(PtP(M)) 3150, ^{1}J(PtP(X)) 1120.



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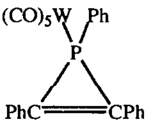

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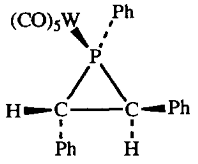

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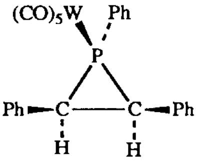

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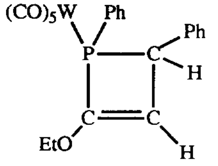
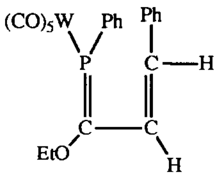
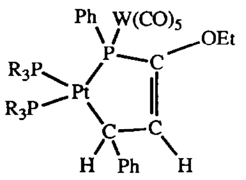


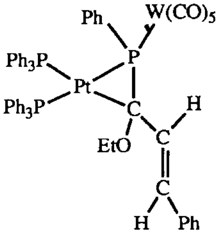
(5)



(5a)



(6)



(7)

6a : R =Ph
6b : R_3P = 1/2dppe

$[Pt(PPh_3)_2(C_2H_4)]$ and **5** over 24 hours demonstrated a clean formation of two non-interconverting complexes, **6a** and **7** (40 and 60% respectively), which were separated by fractional crystallisation in THF/EtOH. The nature of the competing insertion reactions was established unambiguously by single-crystal X-ray diffraction studies of each product type **.

** *Crystallographic data.*

For **6b** (from THF/Et_2O). $C_{48}H_{41}O_6P_3PtW$, $M = 1185.7$. Monoclinic, space group $P21/c$. a 14.924(6), b 13.889(4), c 22.735(8) Å, β 109.29(1)°, U 4448.1 Å^3, $Z = 4$, D_c 1.77 g cm^{-3}, monochromated Mo-K_α radiation, λ 0.71069 Å, μ 59.7 cm^{-1}. 6480 unique reflections were collected from an air-stable orange crystal of dimensions ca. 0.4×0.4×0.2 mm on an Enraf-Nonius CAD4 in θ–2θ mode for $2 < \theta < 23°$, of which 4176 with $|F^2| > 3\sigma(F)^2$ were refined using heavy atom methods on a Micro VAX computer. A Difabs absorption correction (max 1.28, min 0.91) was made; refinement by full-matrix least-squares with all heavy atoms anisotropic converged at $R = 0.025$, $R' = 0.033$.

For **7** (from THF/EtOH). $C_{58}H_{47}O_6P_3PtW$, $M = 1311.9$. Triclinic, space group $P\bar{1}$, a 10.222(3), b 11.800(2), c 22.308(3) Å, α 79.83(4), β 81.81(3), γ 81.84(2)°, U 2602.6 Å^3, $Z = 2$, D_c 1.67 g cm^{-3}, monochromated Mo-K_α radiation, λ 0.71069 Å, μ 51.1 cm^{-1}. The solution of the structure proceeded as above. 9121 reflections with $2 < \theta < 25°$ were collected from a 0.15×0.3×0.3 mm air stable orange crystal, and 5656 were used in a refinement which converged at $R = 0.039$, $R' = 0.045$. Tables of atomic coordinates and band lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

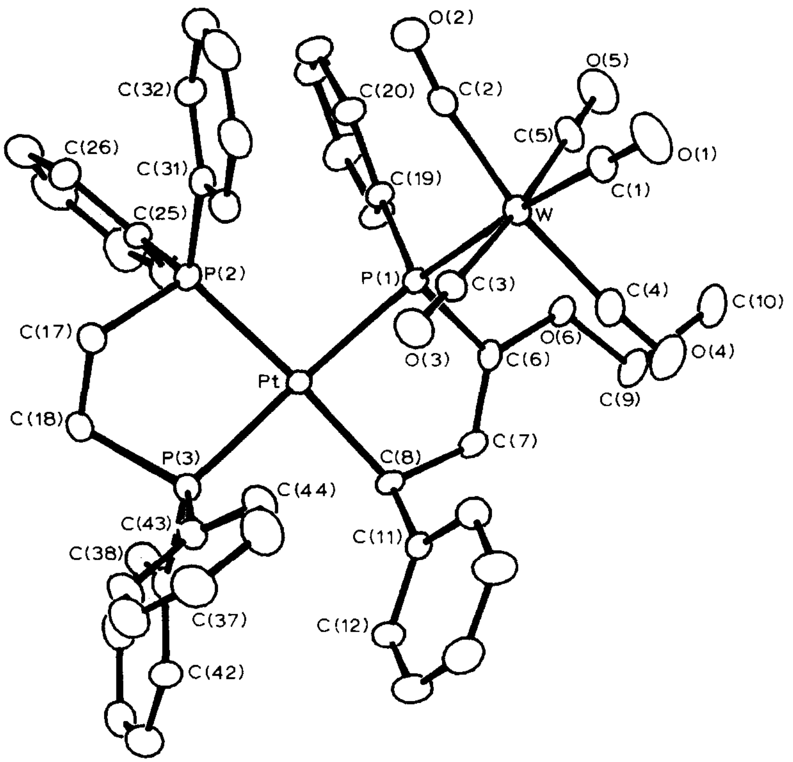


Fig. 1. Molecular structure of **6b**. Selected bond lenghts (Å) and angles (°): W–P(1), 2.588(2); Pt–P(1), 2.326(2); Pt–P(2), 2.298(2); Pt–P(3), 2.308(2); Pt–C(8), 2.116(5); P(1)–C(6), 1.832(5); P(1)–C(19), 1.835(6); C(6)–C(7), 1.329(9); C(7)–C(8), 1.522(9); W–P(1)–Pt, 124.79(6); Pt–P(1)–C(6), 99.4(2); Pt–P(1)–C(19), 108.9(2); P(1)–C(6)–C(7), 117.8(4); C(6)–C(7)–C(8), 121.1(5); P(1)–Pt–C(8), 84.5(2); P(1)–Pt–P(2), 98.47(6); P(2)–Pt–P(3), 84.02(6); P(3)–Pt–C(8), 93.3(2).

The formulation of **6a** (Fig. 1) was established indirectly by an X-ray study of the dppe analogue **6b**, prepared by insertion of [Pt(dppe)(C_2H_4)] into **5**. The molecular structure reveals a five-membered ring whose pseudo-square planar geometry at platinum, together with long P(1)–C(6) and C(7)–C(8) separations and a short C(7)–C(6) distance, require its formulation as a Pt^{II} 1-phosphabut-2-ene-1,4-diyl^{2-} complex rather than its Pt^0 1-phosphabuta-1,3-dienyl valence tautomer. This suggests extensive conjugation and a high electron affinity in 1-phosphabuta-1,3-dienes. The non-planar metallacycle undergoes inversion at room temperature on the NMR timescale, but the two contributing conformers are clearly resolved at −60 °C (146 MHz) *.

Complex 7 includes a phosphaalkene ligand which bridges the two metal centres (Fig. 2). Electronic considerations favour coordination of the [Pt(PPh_3)$_2$] fragment to the P=C bond and outweigh significant steric pressures in the product, which would be eased if the [Pt(PPh_3)$_2$] were coordinated to the C=C bond. These are reflected in a very large [9] Pt–P(1)–W angle (130.0(1)°) and a tetrahedral distortion of 12° in the platinum coordination sphere. The P(1)–C(51) distance (1.833(8) Å) is typical of a single P–C linkage and suggests very extensive electron donation

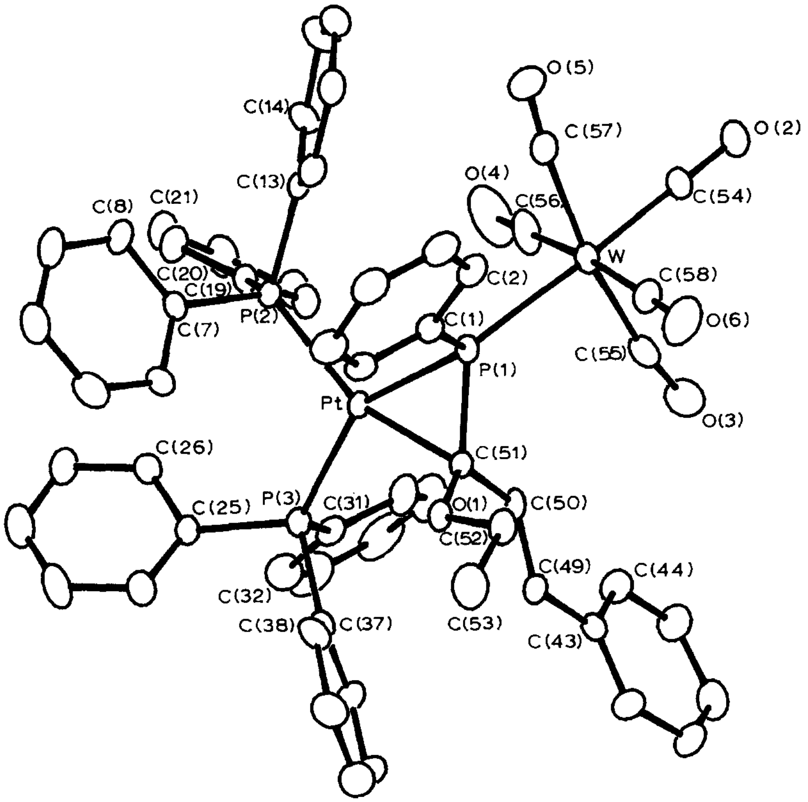


Fig. 2. Molecular structure of 7. Selected bond lengths (Å) and angles (°): W–P(1), 2.564(2); Pt–P(1), 2.308(2); Pt–P(2), 2.309(3); Pt–P(3), 2.325(2); Pd–C(51), 2.157(8); P(1)–C(51), 1.833(8); P(1)–C(1), 1.842(10); C(49)–C(50), 1.344(12); C(50–C(51), 1.463(12); C(51)–O(1), 1.392(11); W–P(1)–Pt, 130.0(3); P(1)–C(51)–Pt, 70.2(3); Pt–P(1)–C(51), 61.5(3); Pt–P(1)–C(1), 105.8(3); P(1)–Pt–C(51), 48.3(2); P(1)–Pt–P(2), 107.27(8); P(2)–Pt–P(3), 103.85(8); P(3)–Pt–C(51), 100.9(2).

from the metal to the ligand. Whilst the steric influence of the [W(CO)$_5$] group upon this separation is difficult to evaluate [8], a significant degree of oxidation of the platinum centres in both **6** and **7** is consistent with their non-equilibration at room temperature.

Consideration of the reactivity of **5** allows a comparison of the relative ease of insertion of the [Pt(PPh$_3$)$_2$] fragment into P–C$_{(sp^3)}$ and P–C$_{(sp^2)}$ bonds. Earlier studies [4] indicate that phosphorus–carbon bonds are generally cleaved by electron-rich metal species in the order P–C$_{(sp)}$ > P–C$_{(sp^2)}$ > P–C$_{(sp^3)}$ but we observe insertion exclusively at the P–C$_{(sp^3)}$ linkage of **5**. This suggests that the reaction profile may be influenced more by the phosphabutadiene resonance hybrid form **5a** [7], previously authenticated in high-temperature trapping reactions by two of us [10,11], than by simple strain inherent in the four-membered ring.

The results of this preliminary study imply that insertion reactions should be useful for the stabilisation of functionally complex phosphabutadiene species, which may be generated from phosphetes in the coordination spheres of later transition metals. This area will be explored in more detail in future studies.

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