First Examples of η^1-Ligated 1,2,4-Triphosphacyclopentadienyl Ring Systems. Synthesis and Fluxional Behaviour of *trans*-[$MCl(C_2R_2P_3)(PEt_3)_2$], (R = Bu^t, Adamantyl), (M = Pd, Pt); Crystal and Molecular Structures of *trans*-[$PtX(C_2Bu^t{}_2P_3)(PR_3)_2$], (X = Cl, R = Et; X = I, R = Ph)

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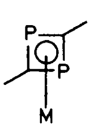
First examples of η^1-ligated 1,2,4-triphosphacyclopentadienyl ring systems are described and structural features and solution fluxional behaviour are discussed.

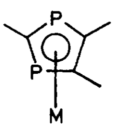
The ligating properties of unsaturated organophosphorus compounds are of considerable current interest.[1] Typical η^4- and η^5-ligated ring systems containing 2 or 3 phosphorus atoms which have been recently reported[2—6] are shown in structures (**A**)—(**D**).

We now describe the first examples of η^1-ligated 1,2,4-triphosphacyclopentadienyl ring systems which exhibit interesting structural features and fluxional behaviour.

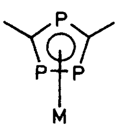
Treatment of *cis*-[$MCl_2(PEt_3)_2$], (M = Pd, Pt) with [Li(dme)$_3$][$C_2R_2P_3$],[7] (R = Bu^t, adamantyl), gives the yellow, (M = Pt), and red, (M = Pd), air-stable crystalline complexes *trans*-[$MCl(C_2R_2P_3)(PEt_3)_2$], (**1**)—(**3**). Similarly *cis*-



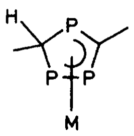
(A)



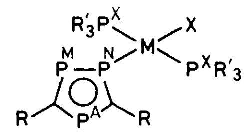
(B)



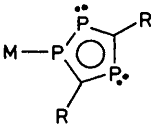
(C)



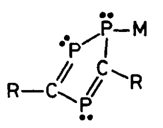
(D)



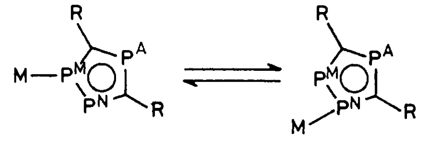
(**1**) X = Cl, M = Pd, R = Bu^t, R′ = Et
(**2**) X = Cl, M = Pt, R = Bu^t, R′ = Et
(**3**) X = Cl, M = Pt, R = ad, R′ = Et
(**4**) X = I, M = Pt, R = Bu, R′ = Ph



(X)

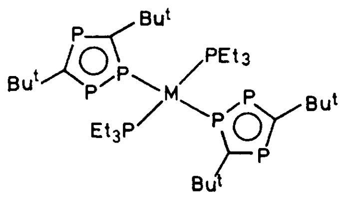


(Y)



[PtI$_2$(PPh$_3$)$_2$] affords *trans*-[PtI(C$_2$R$_2$P$_3$)(PPh$_3$)$_2$], (R = Bu^t), (**4**).†

The molecular stuctures of (**2**) and (**4**) were confirmed by single crystal *X*-ray diffraction studies and are shown in Figures 1 and 2.‡ In each case the (C$_2$Bu$^t{}_2$P$_3$) ring is bound to the metal by one of the two adjacent phosphorus atoms and is



(**5**) M = Pd
(**6**) M = Pt

Scheme 1

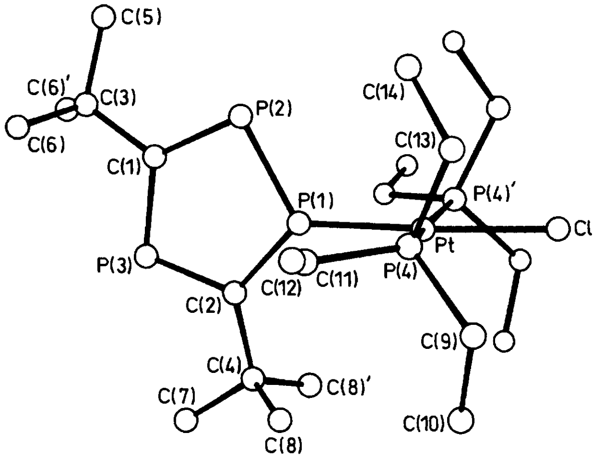


Figure 1. Molecular structure of (**2**). Selected bond lengths (Å): Pt–Cl 2.345(2); Pt–P(1) 2.243(2); Pt–P(4) 2.311(2); P(1)–P(2) 2.068(3); P(1)–C(2) 1.711(7); P(2)–C(1) 1.745(7); P(3)–C(1) 1.726(7); P(3)–C(2) 1.740(8).

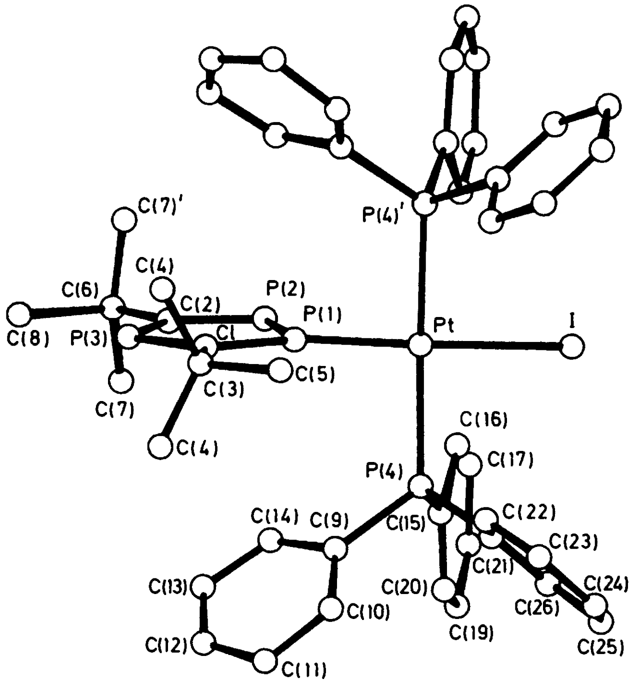


Figure 2. Molecular structure of (**4**). Selected bond lengths (Å): Pt–I 2.641(2); Pt–P(1) 2.257(7); Pt–P(4) 2.343(5); P(1)–P(2) 2.010(11); P(1)–C(1) 1.76(4); P(2)–C(2) 1.73(4); P(3)–C(1) 1.69(2); P(3)–C(2) 1.81(4).

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† ^{31}P N.m.r. spectroscopic data: (32.4 MHz; C$_6$D$_5$CD$_3$; −75 °C; δ in p.p.m. relative to P(OMe)$_3$ positive values to low field; *J* in Hz). For (**1**): δ +112.0(P^A) δ +19.1(P^M), δ −18.0(P^N) δ −122.5 (P^X); $J_{P^AP^M}$ 43, $J_{P^AP^N}$ 20, $J_{P^MP^N}$ 507, $J_{P^NP^X}$ 44.

For (**2**): δ +102.2(P^A) δ +1.8(P^M), δ −35.1(P^N), δ −127.6(P^X); $J_{P^AP^M}$ 43, $J_{P^AP^N}$ 22, J_{P^APt} 59, $J_{P^MP^N}$ 497, J_{P^MPt} 396, $J_{P^NP^X}$ 33, J_{P^NPt} 2833, J_{P^XPt} 2283.

For (**3**) δ +92.9(P^A), δ +2.7(P^M), δ −35.1(P^N), δ −127.3(P^X); $J_{P^AP^M}$ 41, $J_{P^AP^N}$ 24, J_{P^APt} 61, $J_{P^MP^N}$ 498, J_{P^MPt} 333, $J_{P^NP^X}$ 34, J_{P^NPt} 2920, J_{P^XPt} 2298.

For (**4**) δ +86.2(P^A), δ −6.8(P^M), δ −8.5(P^N), δ −126.2(P^X); $J_{P^AP^M}$ 35, $J_{P^AP^N}$ 23, J_{P^APt} 83, $J_{P^MP^N}$ 500, J_{P^MPt} 276, $J_{P^NP^X}$ 36, J_{P^NPt} 2679, J_{P^XPt} 2512.

‡ *Crystal data* for (**2**): C$_{22}$H$_{48}$ClP$_5$Pt, *M* = 698.0, orthorhombic, space group *Pnma*, *a* = 18.053(2), *b* = 13.366(3), *c* = 12.820(3) Å, *U* = 3093.4 Å^3, *Z* = 4, D_c = 1.50 g cm^{-3}, monochromated Mo-*K*α radiation, λ = 0.71069 Å, μ = 49.0 cm^{-1}. The structure was solved by routine heavy-atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic, using 2110 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. The final residuals were *R* = 0.030, *R*′ = 0.038.

For (**4**): C$_{46}$H$_{48}$IP$_5$Pt. C$_7$H$_8$, *M* = 1169.9, monoclinic, space group *Cm*, *a* = 17.516(3), *b* = 16.357(6), *c* = 10.330(4) Å, β = 122.26(3)°, *U* = 2502.8 Å^3, *Z* = 2, D_c = 1.55 g cm^{-3}, monochromated Mo-*K*α radiation, λ = 0.71069 Å, μ = 36.3 cm^{-1}. The structure was solved as for (**2**) except that *R* = 0.037, R′ = 0.045 for 1143 reflections with $I > \sigma(I)$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

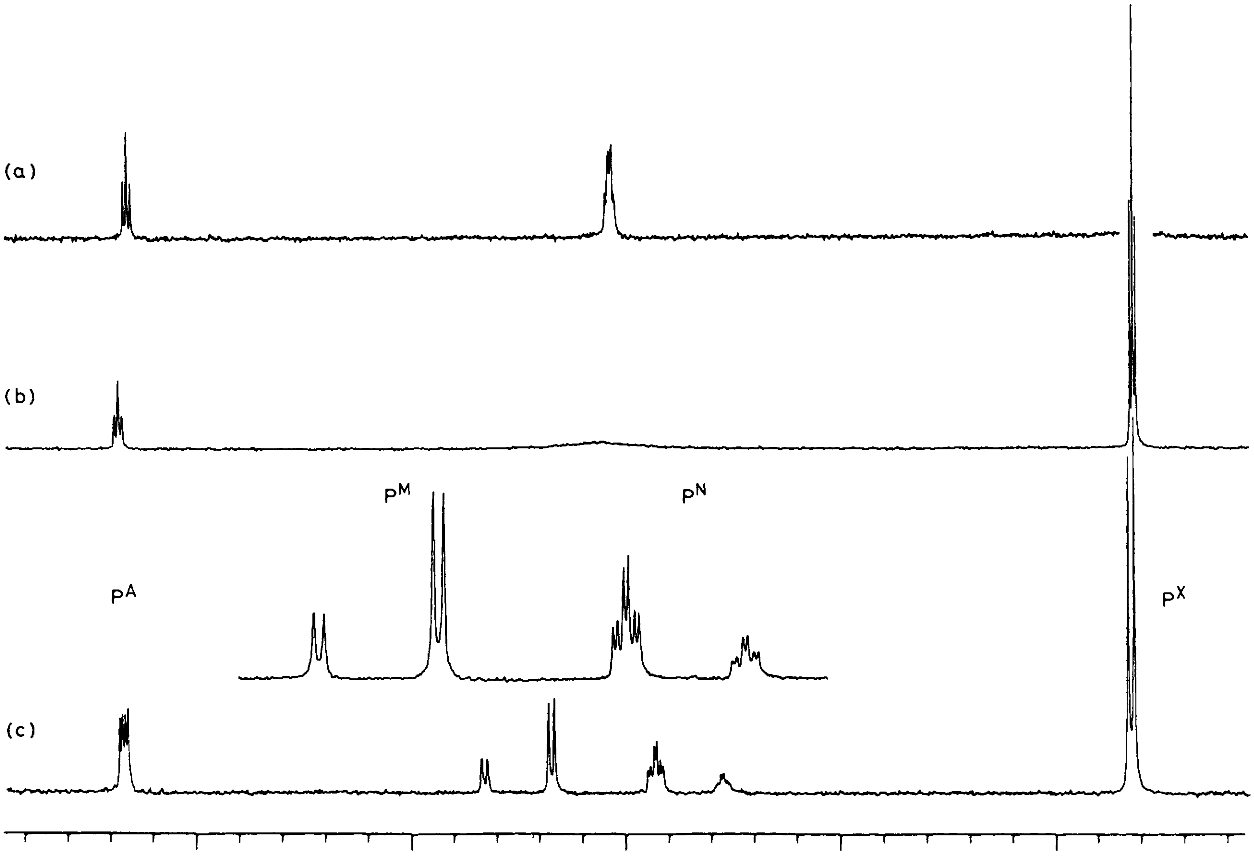

Figure 3. 32.4 MHz ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**1**) recorded at (a) +50 °C, (b) −30 °C, and (c) −75 °C ([$^2H_8$] toluene).

perfectly flat, lying on a crystallographic mirror plane together with the Pt and halogen atom. This indicates that the bonding mode is best represented by (**X**) rather than (**Y**).

Accordingly the ^{31}P-$\{^1H\}$ n.m.r. spectra of the platinum complexes (**2**) and (**3**) exhibit values for $^1J_{PtP^N}$ of *ca.* 2900 Hz which are indicative of a phosphane ligand *trans* to Cl in a square planar Pt^{II} complex.[8] The phosphido structure (**Y**) would be expected[9] to show a much smaller value of $^1J_{PtP^N}$.

Variable temperature ^{31}P-$\{^1H\}$ n.m.r. studies reveal that all the complexes are fluxional in solution. At −75 °C the spectrum of (**1**) shown in Figure 3 exhibits the characteristic [$AMNX_2$] pattern expected for the known rigid structure ($X = PR_3$ resonance). As the temperature is raised resonances P^M and P^N broaden and coalesce while those of P^A and P^X also simplify as the averaged [AM_2X_2] spectrum results at + 50 °C.

In the platinum complexes (**2**)—(**4**) the retention of $^3J_{PtP^A}$ throughout the temperature range rules out a dissociative mechanism for the fluxional process, which is best visualised as an *intra*molecular 1,2-shift of the metal between P^M and P^N as shown in Scheme 1. This type of mechanism has been postulated in related systems involving N, S, and Se heterocycles.[10,11]

Further treatment of (**1**) and (**2**) with [$Li(dme)_3$][$C_2R_2P_3$], ($R = Bu^t$), gives rise to the expected bis(η^1-1,2,4-triphosphacyclopentadienyl) complexes *trans*-[$M(C_2Bu^t{}_2P_3)_2(PEt_3)_2$], [(**5**), M = Pd; (**6**), M = Pt], which exhibit similar fluxional behaviour in solution to (**1**)—(**4**).

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