First η^1-ligated 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene complexes and the remarkable trihydration reaction of *trans*-[$PtCl_2(PMe_3)(P_3C_3Bu^t{}_3)$] to *cis*-[$PtCl(PMe_3)(P_3O_3C_3H_5Bu^t{}_3)$], containing the novel $CH(Bu^t)PH(O)C(Bu^t)PH(O)CH(Bu^t)P(O)$ ring system

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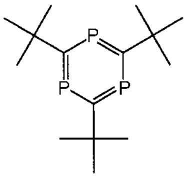
The first examples of η^1-complexes of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene are described, namely *trans*-[$PtCl_2(PR_3)(P_3C_3Bu^t{}_3)$] ($PR_3$ = PMe_3, PEt_3, PMe_2Ph or $PMePh_2$) and their structures established by ^{31}P and ^{195}Pt NMR spectroscopy. The unusual molecular structure of *cis*-[$PtCl(PMe_3)(P_3O_3C_3H_5Bu^t{}_3)$], containing the novel $CH(Bu^t)PH(O)C(Bu^t)PH(O)CH(Bu^t)P(O)$ ring system, which is formed by the trihydration of *trans*-[$PtCl_2(PMe_3)(P_3C_3Bu^t{}_3)$] is also reported.

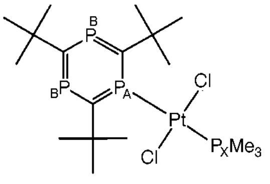
There is considerable current interest in the synthesis and ligating properties of compounds containing P–C multiple bonds.[1–4] Very recently[5,6] synthetic routes have been developed to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene **1** and its structure and PE spectrum have just been reported.[7]



1

Although η^6-arene transition metal complexes occupy a key position in the development of contemporary organometallic chemistry, heteroarenes of the type EC_5R_5 (E = N, P, As, Sb or Bi) can also form η^1-ligated metal complexes unless bulky substituents such as *tert*-butyl groups in the 2,6-positions disfavour such interactions.[8] To date, no examples of η^1-bonded 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene complexes have been reported and only a handful of η^6-complexes of **1** are known such as the triple decker Sc(I) complex [$Sc_2(\eta^5\text{-}P_3C_2Bu^t{}_2)_2$ ($\eta^6\text{-}P_3C_3Bu^t{}_3$)] the structure of which has been established by X-ray crystallography[9] and [$ML_n(\eta^6\text{-}P_3C_3Bu^t{}_3)$], [$ML_n$ = $Mo(CO)_3$, $W(CO)_3$, $Mn(\eta^5\text{-}C_5H_5)$ or Ru(cod)],[10] whose stuctures have been proposed on the basis of NMR spectroscopic studies.

We now describe the first examples of η^1-bonded 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene platinum(II) complexes of the type *trans*-[$PtCl_2(PR_3)(S_3C_3Bu^t{}_3)$] ($PR_3$ = PMe_3 **2**, PEt_3 **3**, PMe_2Ph **4** or $PMePh_2$ **5**) which are formed by treatment of **1** with the appropriate [$PtCl_2(PR_3)]_2$ complex in CH_2Cl_2 or $CHCl_3$ at room temperature. Attempts to make complexes of **1** by direct reaction with a variety of other metal halides such as MCl_4, (M = Ti or Zr), MCl_5 (M = Nb or Ta), CuX (X = Cl or I) were all unsuccessful as were ligand displacement reactions involving [$MCl_2(NCPh)_2$] (M = Pd or Pt) and [$RhClL_n$] (L = cyclooctene, n = 2; L = PPh_3, n = 3).



2

The $^{31}P\{^1H\}$ NMR spectrum of *trans*-[$PtCl_2(PMe_3)(P_3C_3Bu^t{}_3)$] **2**, which is typical for all the complexes **2–5**, is shown in Fig. 1, and exhibits the characteristic coupling constant data expected for the *trans*-isomer. The ^{195}Pt NMR spectrum exhibits the expected doublet of doublets pattern.† Solution NMR data for the platinum complexes **3–5** containing the bulkier phosphines showed that, unlike complex **2**, there was always a significant concentration of the starting [$PtCl_2(PR_3)]_2$ complex present as well as unreacted **1** and several attempts to obtain crystalline complexes invariably led to further disproportionation. Not surprisingly it proved impossible to attach more than one [$PtCl_2(PR_3)$] fragment to **1**.

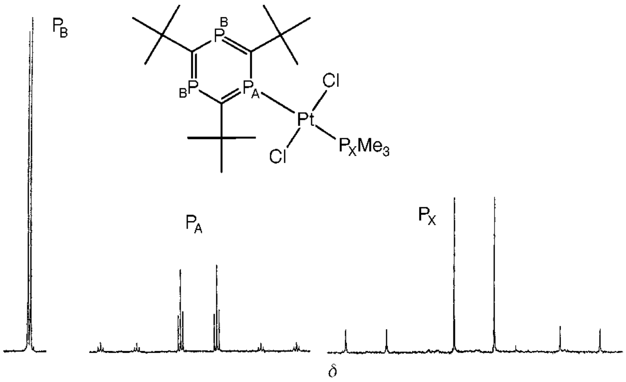
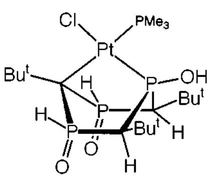


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum of **2**.

It is interesting to compare the magnitude of the $^1J(PtP)$ coupling constant to the triphosphabenzene ring in **2** (2418 Hz) with that of the *trans* ligated PMe_3 (2901 Hz) indicating the smaller s-character of the P-lone pair in the triphosphabenzene. In the analogous 2,4,6-tri-*tert*-butyl-1-phosphabenzene[11] complex *trans*-[$PtCl_2(PMe_3)(PC_5H_2Bu^t{}_3)$], synthesised in a similar manner, $^1J(PtP)$ is 2548 Hz, indicating that the presence of additional phosphorus atoms in the aromatic ring reduces the s-character of the P-lone pair electrons.

It has been previously shown that η^1-ligation of phosphaarenes can enhance their reactivity and we observe a remarkable reaction when **2** was recrystallised from CH_2Cl_2 in the air at room temperature. Addition of three water molecules to the coordinated triphosphabenzene ring occurs, together with HCl elimination, to afford the unusual complex [$PtCl(PM_3)(P_3O_3C_3H_5Bu^t{}_3)$] **6**. The molecular structure of **6**, which was established by a single crystal X-ray diffraction study‡ and is shown in Fig. 2, clearly results from addition of H_2O across each of the unsaturated P–C bonds in **2** in which the H adds to carbon and the OH to phosphorus in accord with the expected



6

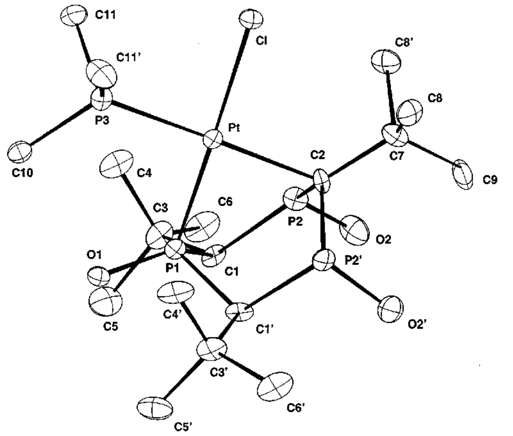


Fig. 2 Molecular structure of **6**. Selected distances (Å) and angles (°): Pt–P(1) 2.224(6), Pt–Cl 2.416(5), Pt–P(3) 2.273(6), Pt–C(2) 2.24(2), P(1)–O(1) 1.479(15), P(2)–O(2) 1.528(12), P(1)–C(1) 1.843(16), P(2)–C(2) 1.777(12), P(2)–C(1) 1.818(15); P(1)–Pt–C(2) 82.6(6), P(1)–Pt–P(3) 96.6(2), C(2)–Pt–P(3) 179.2(6), P(1)–Pt–Cl 178.84(19), C(2)–Pt–Cl 98.6(6), P(3)–Pt–Cl(1) 82.3(2), C(1)–P(1)–C(1)′ 97.3(9), C(2)–P(2)–C(1) 109.3(8), P(2)–C(2)–P(2)′ 114.6(12) P(2)–C(1)–P(1) 105.6(7)

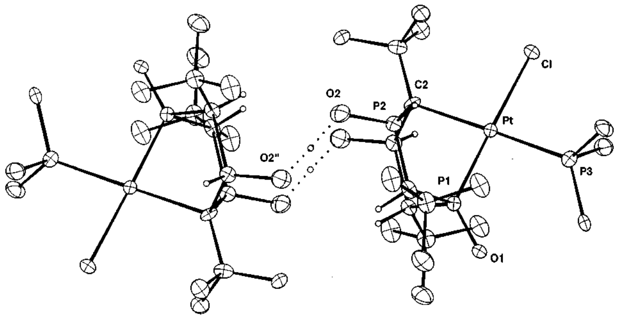
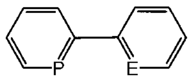


Fig. 3 Dimeric structure of **6**.

polarity of the bond. The resulting intermediate presumably then undergoes Arbusov-type rearrangement at *two* of the newly formed –P(OH)CHBu^t–centres to produce –PH(O)CHBu^t–ring fragments with the rearrangement at the third phosphorus centre unable to proceed because of ligation of the P atom to Pt. The accompanying loss of HCl and formation of a Pt–C bond leads to the observed product **6**. Mathey, Venanzi and their coworkers,[12–14] have previously noted selective addition of water and methanol to 2-pyridylphosphinines **7** and 2,2′-biphosphinines **8** coordinated to electrophilic metal centres as a result of the partial dearomatisation of the ligand.



E = N **7** or P **8**

Complex **6** shows the following interesting features, (i) the structure consists of a H-bonded dimer; (ii) this H atom lies on a crystallographic twofold axis and was refined to a distance of 2.39 Å between O(2) and O(2)″; (iii) each individual molecule is bisected by a mirror plane through Pt and the ring C and P atoms to which it is bonded; (iv) the ring P–C bond lengths (ranging between 1.78 and 1.84 Å) are elongated compared with those in **1** and are typical for P–C single bonds; (v) the two P(2)=O double bond distances [1.528(12) Å] are similar to that of the formally single P(1)–O bond [1.479(15) Å] for the phosphorus attached to platinum. The structure suggests that the acidic H responsible for the dimeric structure of **6** may be capable of replacement by other cations, or substituted by organic groups, leading to significant structural changes (Fig. 3) and this is currently under study along with other aspects of the ligating behaviour of **1**.

We thank NSERC for a scholarship (for S. B. C.) and EPSRC for their continuing support (to J. F. N.) for phospha-organometallic chemistry.

Notes and references

† ^{31}P {^{1}H} NMR data: **2**: δP_A 203.0, δP_B 264.8, δP_X −18.3; $^1J(PtP_A)$ 2418, $^1J(PtP_X)$ 2886, $^2J(P_AP_B)$ 36.3, $^2J(P_AP_X)$ 543.3 Hz. **3**: δP_A 207.1, δP_B, 264.5, δP_X 12.1; $^1J(PtP_A)$ 2378, $^1J(PtP_X)$ 2884, $^2J(P_AP_B)$ 36.4, $^2J(P_AP_X)$ 508.5 Hz: **4**: δP_A, 202.5, δP_B, 265.4, δP_X −11.4; $^1J(PtP_A)$ 2487, $^1J(PtP_X)$ 2920, $^2J(P_AP_B)$ 36.6, $^2J(P_AP_X)$ 543.6 Hz. **5**: δP_A 200.4, δP_B 267.0, δP_X 1.3; $^1J(PtP_A)$ 2569, $^1J(PtP_X)$ 2961, $^2J(P_AP_B)$ 37.0, $^2J(P_AP_X)$ 545.5 Hz. **6**: $\delta P_{P(O)H}$ 31.4 [d, $^1J(PH)$ 552 Hz], $\delta P_{P(OH)}$ −0.6 [br, $^1J(PtP)$ 3155 Hz] $\delta P_{(PMe_3)}$, 10.1 [br, $^1J(PtP)$ 3181 Hz].

^{195}Pt NMR data (rel. K_2PtCl_6): **2**: δPt −3705; **3**: δPt −3738; **4**: δPt −3710; MS data (EI): **6**: *m*/*z* 660 (M$^+$).

‡ *Crystal data*: **6**, $C_{18}H_{41}ClO_3P_4Pt\cdot 2.5CH_2Cl_2$, M = 872.2, orthorhombic, space group *Cmca* (no. 64), a = 14.508(9), b = 15.924(9), c = 29.018(12) Å, U = 6704(6) Å^3, Z = 8, D_c = 1.73 Mg m^{-3}, crystal dimensions 0.3 × 0.2 × 0.05 mm, $F(000)$ = 3464, T = 173(2) K, Mo-Kα radiation (λ = 0.71073 Å). Data were collected on an Enraf-Nonius CAD4 diffractometer and of the total 2428 independent reflections measured, 1951 having $I > 2\sigma(I)$, were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1$ = 0.075, $wR2$ = 0.196. The complex lies on a crystallographic mirror plane and forms H-bonded dimers across a twofold rotation axis. All non-H atoms were anisotropic. H atoms were included in riding mode with U_{iso}(H) equal to 1.2eq(C) or 1.5eq(C) for methyl groups. The H-bonded H atom lies on a crystallographic twofold axis and was refined.

CCDC 182/1284. See http://www.rsc.org/suppdata/cc/1999/1377/ for crystallographic files in .cif format.

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