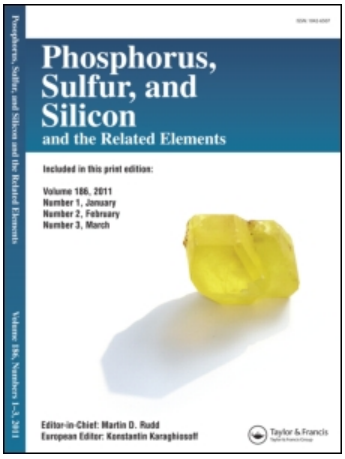

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SYNTHESIS, NMR SPECTROSCOPIC STUDIES, AND X-RAY STRUCTURES OF PLATINUM(II) COORDINATION COMPLEXES OF THE ORGANOPHOSPHORUS CAGE COMPOUNDS $P_4C_4Bu^t_4$ AND $P_5C_5Bu^t_5$

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SYNTHESIS, NMR SPECTROSCOPIC STUDIES, AND X-RAY STRUCTURES OF PLATINUM(II) COORDINATION COMPLEXES OF THE ORGANOPHOSPHORUS CAGE COMPOUNDS $P_4C_4Bu^t_4$ AND $P_5C_5Bu^t_5$†

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The first examples of platinum(II) complexes of the $P_4C_4Bu^t_4$ and $P_5C_5Bu^t_5$ "cages" are described and detailed nmr and X-ray crystallographic structural studies have been carried out on the complexes *trans*-$[PtCl_2(PR_3)(P_4C_4Bu^t_4)]$, *trans*-$[\{PtCl_2(PR_3)\}_2(P_4C_4Bu^t_4)]$, (R = Et, Bu), and *trans*-$[PtCl_2(PEt_3)(P_5C_5Bu^t_5)]$.

Key words: Organophosphorus cage compounds, $P_4C_4Bu^t_4$, $P_5C_5Bu^t_5$, platinum complexes, NMR studies, X-ray structure.

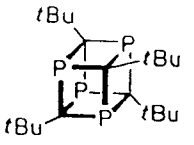
INTRODUCTION

Cyclo-oligomerisation reactions of phospha-alkynes, $RC{\equiv}P$, are of considerable current interest[1] and the relative energies of a number of HCP oligomers have been calculated.[2–5] Especially interesting are the cyclotetramers of $Bu^tC{\equiv}P$, $P_4C_4Bu^t_4$ (**1**)–(**7**), (see display). The early work of Regitz *et al.*[6] on the low yield thermal formation of the tetraphosphacubane (**1**) was superceded by the use of the precursor $[Zr(\eta^5\text{-}C_5H_5)_2(P_2C_2Bu^t_2)]$ which on treatment with C_2Cl_6 gave (**1**) in good yield.[7–9]

Syntheses of the newer tricyclotetraphospha-cyclo-octadienes (**2**) and (**3**) have also very recently been described,[5] and the 1,3,5,7-tetraphosphabarrelene (**4**) has been synthesised directly from $Bu^tC{\equiv}P$ using bis(cyclo-octatetraene)zirconium.[10] The polycyclic phospha-alkyne tetramers (**5**) and (**6**) which result from a stepwise synthetic route[10,12] can each be thermally quantitatively transformed into the more thermodynamically stable tetraphosphabishomoprismane (**7**).[12,13] The structures of all the tetramers (**1**)–(**7**) have been determined by single crystal X-ray diffraction studies and/or by multinuclear nmr spectroscopic techniques. The structure of compound (**7**) has recently been confirmed by an X-ray diffraction study on its bis-$[W(CO)_5]$ adduct.[14]

The pentamer $P_5C_5Bu^t_5$ (**8**) which is best obtained by an oxidative coupling reaction of a mixture of the $P_3C_2Bu^t_2^-$ and $P_2C_3Bu^t_3^-$ ring anions[15] has a similar structure to

† This paper is based on a part of a lecture given by JFN at a Symposium at Braunschweig, Germany, 26th August 1994, to celebrate the 60th birthday of Professor Reinhard Schmutzler, to whom it is dedicated in recognition of his many important contributions to phosphorus chemistry.



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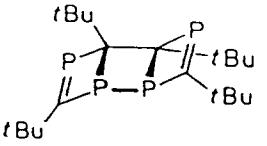

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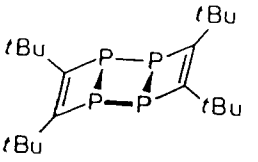

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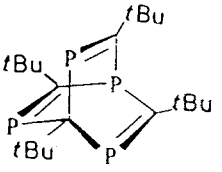

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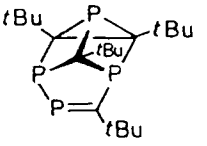

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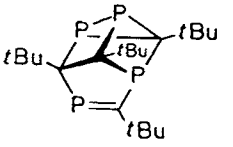

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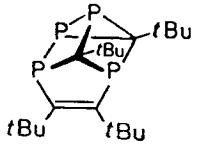

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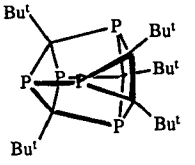

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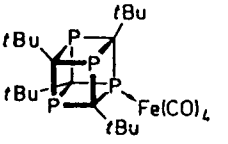


(9)

the tetraphosphacubane (**1**) in which one corner C atom may be considered to have been replaced by a C_2P triangle of atoms.

Prior to the work described in this paper the coordination chemistry of the tetraphosphacubane (**1**) was limited to a single report of the zerovalent iron compound $[Fe(CO)_4(P_4C_4Bu^t_4)]$ (**9**).[16] We now describe the coordination chemistry of both $P_4C_4Bu^t_4$ and $P_5C_5Bu^t_5$ towards divalent platinum.

RESULTS AND DISCUSSION

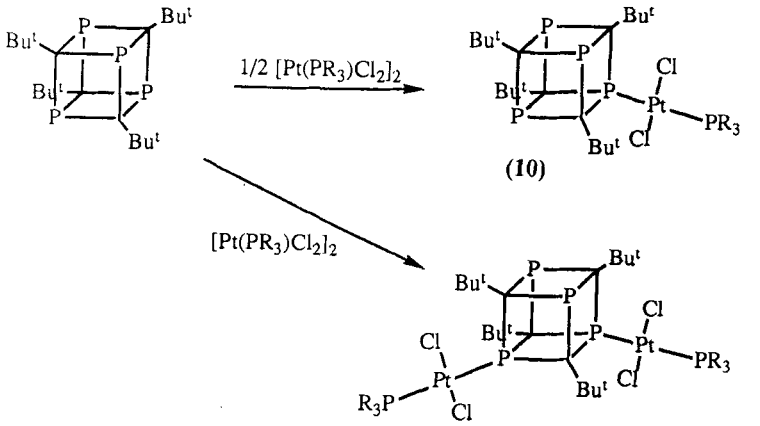
(a) Synthesis and Characterisation of trans-$[PtCl_2(PR_3)(P_4C_4Bu^t_4)]$ and trans-$[\{PtCl_2(PR_3)\}_2(P_4C_4Bu^t_4)]$, (R = Et, Bu)

An interesting feature of the tetraphosphacubane (**1**) is the very highfield ^{13}C nmr chemical shift exhibited by the skeletal C atoms of its "cage."[6] It has been established, both by He(I) photoelectron studies, and by MO calculations,[17] that the lone

pair electrons on the four phosphorus atoms in (**1**) participate significantly in the P—C σ-framework, resulting in a formal positive charge at the phosphorus centres.

This interaction greatly reduces the basicity of the P atoms in (**1**) and quarternisation is only achieved by the use of very strong electrophiles. Methyl iodide cannot quarternise (**1**) and even an excess of methyl triflate only affords the monomethylated phosphonium salt at −78°. Although monoprotonation occurs with fluorosulfuric acid in liquid SO_2 at −78°, diprotonation is only achievable with "magic acid," (FSO_3H/SbF_5).[18]

As mentioned earlier, to date only the mono tetracarbonyl iron (**0**) complex $[Fe(CO)_4(P_4C_4Bu^t_4)]$ (**9**) is known and it was synthesised under forcing conditions.[16] We anticipated that stronger Lewis acids involving metals in higher oxidation states would facilitate coordination of the tetraphosphacubane (**1**) and in accord with this proposal we find that whereas C_2H_4 cannot be easily displaced by (**1**) from the zerovalent platinum complex $[Pt(C_2H_4)(PPh_3)_2]$, a ready reaction occurs at room temperature when (**1**) is treated with the platinum(II) complexes $[PtCl_2(PR_3)]_2$ (R = Et, Bu) to afford high yields of the yellow *trans*- complexes $[PtCl_2(PR_3)(P_4C_4Bu^t_4)]$ (**10**), (R = Et) and $[\{PtCl_2(PR_3)\}_2(P_4C_4Bu^t_4)]$, (**11**), (**11a**) and (**11b**) ((a) R = Et, (b) R = Bu), depending on the molar ratio of reactants. Complexes (**11**) represent the first examples of the $P_4C_4Bu^t_4$ "cube" ligated to two metal centres.



(**10**)

(**11**)

As expected, coordination of the tetraphosphacubane (**1**) to one or two Pt(II) centres in complexes (**10**) and (**11**), respectively, has a pronounced effect on its $^{31}P\{^1H\}$ nmr spectrum. In (**10**), the $^{31}P\{^1H\}$ nmr spectra consist of an $[AB_3X]$ spin system (A = B = X = ^{31}P) with the A and X parts of the spectrum exhibiting ^{195}Pt satellites (Figure 1). Chemical shift and coupling constant data are listed in Table I. The resonance of the P^A phosphorus of the tetraphosphacubane, which is attached to the metal, is moved significantly upfield from that of the uncoordinated (**1**), while the three P^B phosphorus resonances are changed only slightly. As expected, the PR_3 ligands (P^X) attached to platinum are in *trans*-positions to the "cube" in view of the steric bulk of the tetraphosphacubane ligand as evidenced by the large value of $^2J_PA_PX$ (433 Hz). This stereochemical assignment was subsequently confirmed by a single crystal X-ray diffraction study on (**10**) and (**11b**) (*vide infra*). Interestingly the $^1J_{PtP}A$ value (1957 Hz) in (**10**) is smaller than the $^1J_{PtP}X$ (2474 Hz) (cf. *trans*-

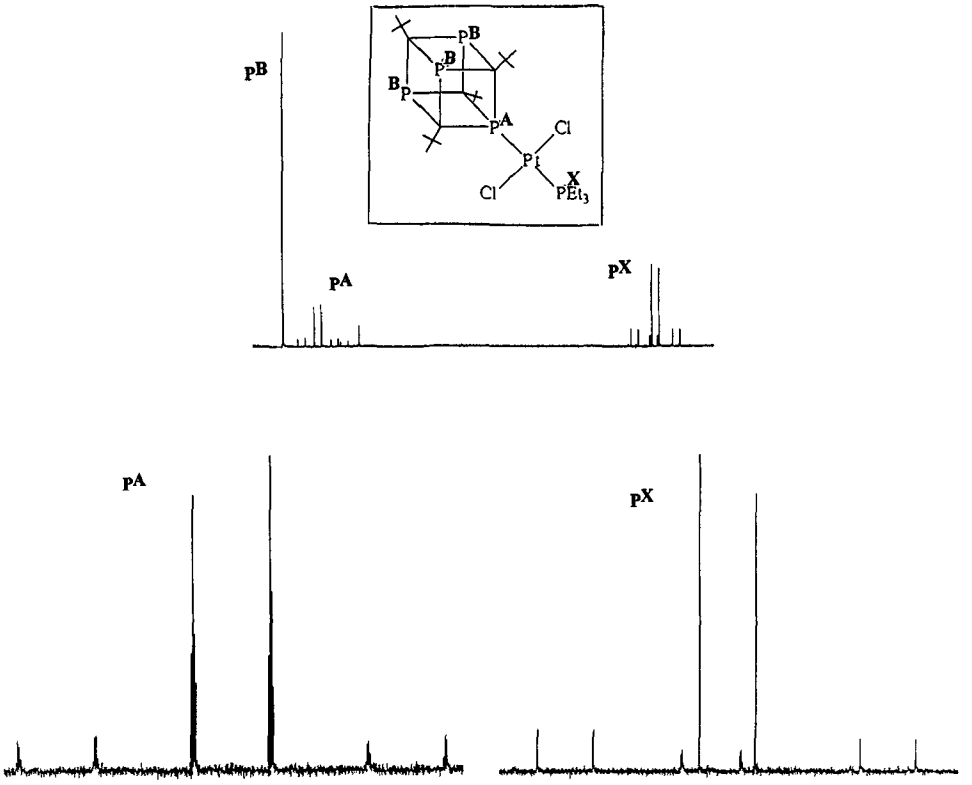


FIGURE 1 $^{31}P\{^1H\}$ n.m.r. spectrum of compound (**10**).

TABLE I

^{31}P nmr chemical shift and coupling constant data for *trans*-$[PtCl_2(PR_3)(P_4C_4Bu^t_4)]$ (**10**) and *trans*-$[\{PtCl_2(PR_3)\}_2(P_4C_4Bu^t_4)]$ (**11**)

Complex	$\delta_P A$	$\delta_P B$	$\delta_P X$	$^1J_{PtP}A$	$^1J_{PtP}X$	$^2J_PA_PX$	$^2J_PA_PB$	$^2J_PB_PX$
(10) **R = Et**[c]	212.3	231.6	14.1	1957	2474	433	9.1	2.3
(11) **(a) R = Et**	196.5	187.3	15.3	2011	2562	453	6	3
(b) R = Bu	196.1	187.2	7.8	1980	2564	454	6	3

(a) δ_P in ppm rel. H_3PO_4

(b) Coupling constants J in Hz

(c) $^3J_{PtP}B$ = 5.2 Hz

$[PtCl_2(PR_3)_2]$ $^1J_{PtP}$ = 2394 Hz) and this is reflected in the much longer Pt—P^A distance (2.338(3) Å) compared with the Pt—P^X distance (2.284(5) Å) (*vide infra*).

Close inspection of the $^{31}P\{^1H\}$ nmr spectrum of the reaction products for the 2:1 reaction of (**1**) with $[PtCl_2(PR_3)]_2$, (R = Et, Bu) revealed further weak lines which were consistent with the formation of small amounts of the bis-adduct [{$PtCl_2$-

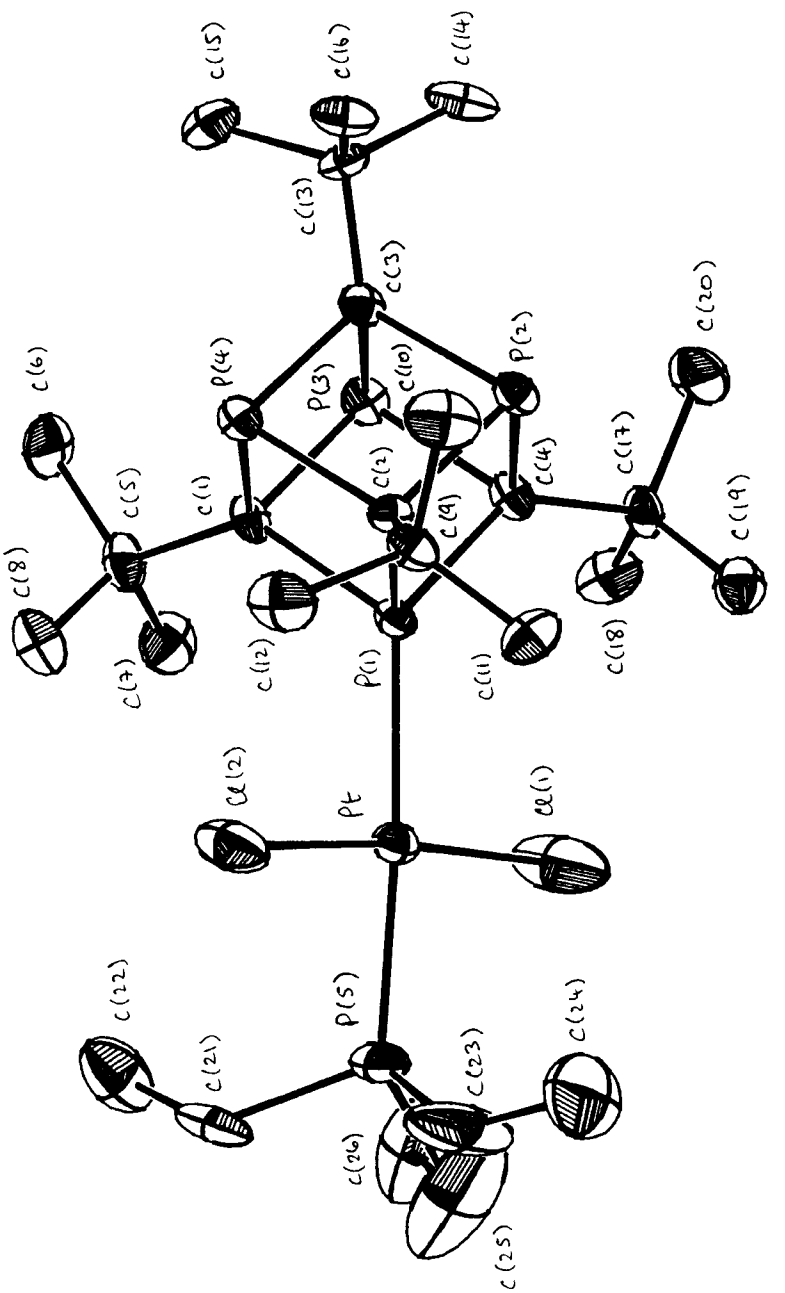


FIGURE 2 Molecular structure of compound (10).

TABLE II

Intramolecular distances (Å) and angles (°) for (**10**) with estimated standard deviations in parentheses

a) Bonds			
Pt-Cl(1)	2.214(6)	Pt-Cl(2)	2.294(5)
Pt-P(1)	2.338(3)	Pt-P(5)	2.284(5)
P(1)-C(1)	1.886(12)	P(1)-C(2)	1.868(12)
P(1)-C(4)	1.891(12)	P(2)-C(2)	1.919(11)
P(2)-C(3)	1.910(13)	P(2)-C(4)	1.877(14)
P(3)-C(1)	1.905(11)	P(3)-C(3)	1.912(13)
P(3)-C(4)	1.910(13)	P(4)-C(1)	1.888(12)
P(4)-C(2)	1.882(12)	P(4)-C(3)	1.900(12)
P(5)-C(21)	1.79(2)	P(5)-C(23)	1.86(3)
P(5)-C(25)	1.97(4)	C(1)-C(5)	1.54(2)
C(2)-C(9)	1.56(2)	C(3)-C(13)	1.51(2)
C(4)-C(17)	1.56(2)	C(5)-C(6)	1.49(2)
C(5)-C(7)	1.53(2)	C(5)-C(8)	1.50(2)
C(9)-C(10)	1.57(2)	C(9)-C(11)	1.50(2)
C(9)-C(12)	1.54(2)	C(13)-C(14)	1.56(2)
C(13)-C(15)	1.51(2)	C(13)-C(16)	1.50(2)
C(17)-C(18)	1.55(2)	C(17)-C(19)	1.47(2)
C(17)-C(20)	1.54(2)	C(21)-C(22)	1.54(3)
C(23)-C(24)	1.34(4)	C(25)-C(26)	1.16(5)
b) Angles			
Cl(1)-Pt-Cl(2)	173.0(2)	Cl(1)-Pt-P(1)	95.4(2)
Cl(1)-Pt-P(5)	88.1(2)	Cl(2)-Pt-P(1)	90.9(1)
Cl(2)-Pt-P(5)	85.7(2)	P(1)-Pt-P(5)	175.9(1)
Pt-P(1)-C(1)	123.2(4)	Pt-P(1)-C(2)	125.7(4)
Pt-P(1)-C(4)	132.5(5)	C(1)-P(1)-C(2)	86.6(5)
C(1)-P(1)-C(4)	87.6(5)	C(2)-P(1)-C(4)	87.4(5)
C(2)-P(2)-C(3)	86.2(5)	C(2)-P(2)-C(4)	86.4(5)
C(3)-P(2)-C(4)	87.9(6)	C(1)-P(3)-C(3)	85.9(5)
C(1)-P(3)-C(4)	86.5(5)	C(3)-P(3)-C(4)	86.9(6)
C(1)-P(4)-C(2)	86.2(5)	C(1)-P(4)-C(3)	86.8(5)
C(2)-P(4)-C(3)	87.6(5)	Pt-P(5)-C(21)	115.8(6)
Pt-P(5)-C(23)	110.7(9)	Pt-P(5)-C(25)	132.2(7)
C(21)-P(5)-C(23)	99(1)	C(21)-P(5)-C(25)	99(1)
C(23)-P(5)-C(25)	94(1)	P(1)-C(1)-P(3)	93.0(5)
P(1)-C(1)-P(4)	93.2(5)	P(1)-C(1)-C(5)	129(1)
P(3)-C(1)-P(4)	93.9(5)	P(3)-C(1)-C(5)	117.3(8)

TABLE II (*Continued*)

b) Angles			
P(4)-C(1)-C(5)	122(1)	P(1)-C(2)-P(2)	92.7(5)
P(1)-C(2)-P(4)	93.9(5)	P(1)-C(2)-C(9)	130.4(9)
P(2)-C(2)-P(4)	93.1(5)	P(2)-C(2)-C(9)	115.4(7)
P(4)-C(2)-C(9)	122.2(9)	P(2)-C(3)-P(3)	92.0(6)
P(2)-C(3)-P(4)	92.9(6)	P(2)-C(3)-C(13)	124.8(8)
P(3)-C(3)-P(4)	93.3(6)	P(3)-C(3)-C(13)	122.2(8)
P(4)-C(3)-C(13)	123.0(9)	P(1)-C(4)-P(2)	93.3(6)
P(1)-C(4)-P(3)	92.7(6)	P(1)-C(4)-C(17)	132(1)
P(2)-C(4)-P(3)	93.1(6)	P(2)-C(4)-C(17)	118.8(9)
P(3)-C(4)-C(17)	118.3(8)	C(1)-C(5)-C(6)	109(1)
C(1)-C(5)-C(7)	108(1)	C(1)-C(5)-C(8)	110(1)
C(6)-C(5)-C(7)	112(1)	C(6)-C(5)-C(8)	109(1)
C(7)-C(5)-C(8)	109(1)	C(2)-C(9)-C(10)	108(1)
C(2)-C(9)-C(11)	110(1)	C(2)-C(9)-C(12)	110(1)
C(10)-C(9)-C(11)	109(1)	C(10)-C(9)-C(12)	106(1)
C(11)-C(9)-C(12)	113(1)	C(3)-C(13)-C(14)	108(1)
C(3)-C(13)-C(15)	110(1)	C(3)-C(13)-C(16)	109(1)
C(14)-C(13)-C(15)	111(1)	C(14)-C(13)-C(16)	110(1)
C(15)-C(13)-C(16)	109(1)	C(4)-C(17)-C(18)	109(1)
C(4)-C(17)-C(19)	107(1)	C(4)-C(17)-C(20)	107(1)
C(18)-C(17)-C(19)	114(1)	C(18)-C(17)-C(20)	110(1)
C(19)-C(17)-C(20)	109(1)	P(5)-C(21)-C(22)	112(1)
P(5)-C(23)-C(24)	123(2)	P(5)-C(25)-C(26)	93(3)

$(PR_3)\}_2P_4C_4Bu^t_4]$ ((**11a**) and (**11b**)). This was confirmed by increasing the ratio of $[PtCl_2(PR_3)]_2$ to $P_4C_4Bu^t_4$ when the resonances due to (**10**), (R = Et) were replaced by those due to (**11a**). So far it has not been possible to attach a third $[PtCl_2(PR_3)]$ fragment to (**1**). The $^{31}P\{^1H\}$ nmr spectrum of (**11a** and **b**) each exhibits a pattern of lines typical of an $[A_2B_2X_2]$ spin system with ^{195}Pt satellites (see Table I). The positive ion FAB mass spectrum of (**10**) exhibited a parent ion at m/e 784 (M^+ 6%) together with the expected fragmentation ions. Likewise the positive ion FAB mass spectrum of (**11a**) exhibited ions at m/e 1133 (M^+-HCl 4%) and 784 (M^+-$PtCl_2(PEt_3)$). In both cases the strongest peak was that for the $(P_4C_4Bu^t_4)^+$ ion.

Further detailed nmr studies on the $P_4C_4Bu^t_4$-$[PtCl_2(PR_3)]_2$ mixtures showed clearly that the 1:1 and 1:2 adducts are in equilibrium with unreacted $[PtCl_2(PR_3)]_2$ dimer. Confirmation of the proposed structures of (**10**) and (**11**) comes from single crystal X-ray diffraction studies on (**10**) and (**11b**). Attempts to extend the coordination chemistry of the tetraphosphacubane to a variety of other metal centres, for example via reactions with $[RhCl(COD)]_2$, $[Ir(COD)(py)_2][PF_6]$, $[PtCl_2(COD)]$, K_2PtCl_4 and $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]$ were all unsuccessful.

TABLE III

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å \times 10^3$) for **(10)**

	x	y	z	Ueq
Pt	1789.4(2)	798.7(3)	2500	53(1)
Cl(1)	2634(3)	804(6)	3867(6)	191(6)
Cl(2)	824(2)	842(4)	1268(5)	118(4)
P(1)	2540(2)	1005(2)	866(3)	45(2)
P(2)	3372(2)	2056(2)	-436(4)	49(2)
P(3)	3674(2)	396(2)	-384(4)	53(2)
P(4)	2492(2)	957(2)	-1589(3)	49(2)
P(5)	1006(3)	546(3)	4008(4)	86(3)
C(1)	2685(6)	205(6)	-339(12)	45(6)
C(2)	2396(6)	1759(6)	-378(11)	41(6)
C(3)	3470(6)	1196(7)	-1596(12)	47(7)
C(4)	3509(6)	1254(7)	757(13)	49(7)
C(5)	2434(8)	-701(7)	-388(15)	69(9)
C(6)	2746(9)	-1101(9)	-1465(18)	90(11)
C(7)	2664(10)	-1131(9)	771(18)	90(12)
C(8)	1646(8)	-735(10)	-480(22)	91(12)
C(9)	1868(6)	2493(8)	-484(14)	56(7)
C(10)	2128(9)	3083(10)	-1510(18)	96(12)
C(11)	1842(8)	2962(10)	671(16)	81(10)
C(12)	1138(8)	2176(12)	-885(17)	98(12)
C(13)	3896(6)	1261(7)	-2729(9)	50(7)
C(14)	4671(7)	1459(9)	-2376(18)	83(8)
C(15)	3859(8)	462(10)	-3427(14)	74(9)
C(16)	3597(7)	1942(9)	-3487(14)	69(9)
C(17)	4078(6)	1411(8)	1740(14)	57(8)
C(18)	4200(7)	604(9)	2460(20)	84(9)
C(19)	3832(7)	2109(8)	2475(19)	74(8)
C(20)	4764(7)	1658(14)	1088(17)	103(13)
C(21)	284(7)	-114(11)	3633(16)	100(11)
C(22)	527(11)	-957(12)	3136(26)	144(20)
C(23)	506(14)	1499(15)	4394(26)	263(20)
C(24)	813(16)	2233(16)	4602(33)	214(26)
C(25)	1133(12)	223(28)	5694(34)	377(31)
C(26)	1468(11)	-348(18)	5451(27)	193(20)

Ueq is defined as one third of the trace of the orthogonalised Uij tensor.

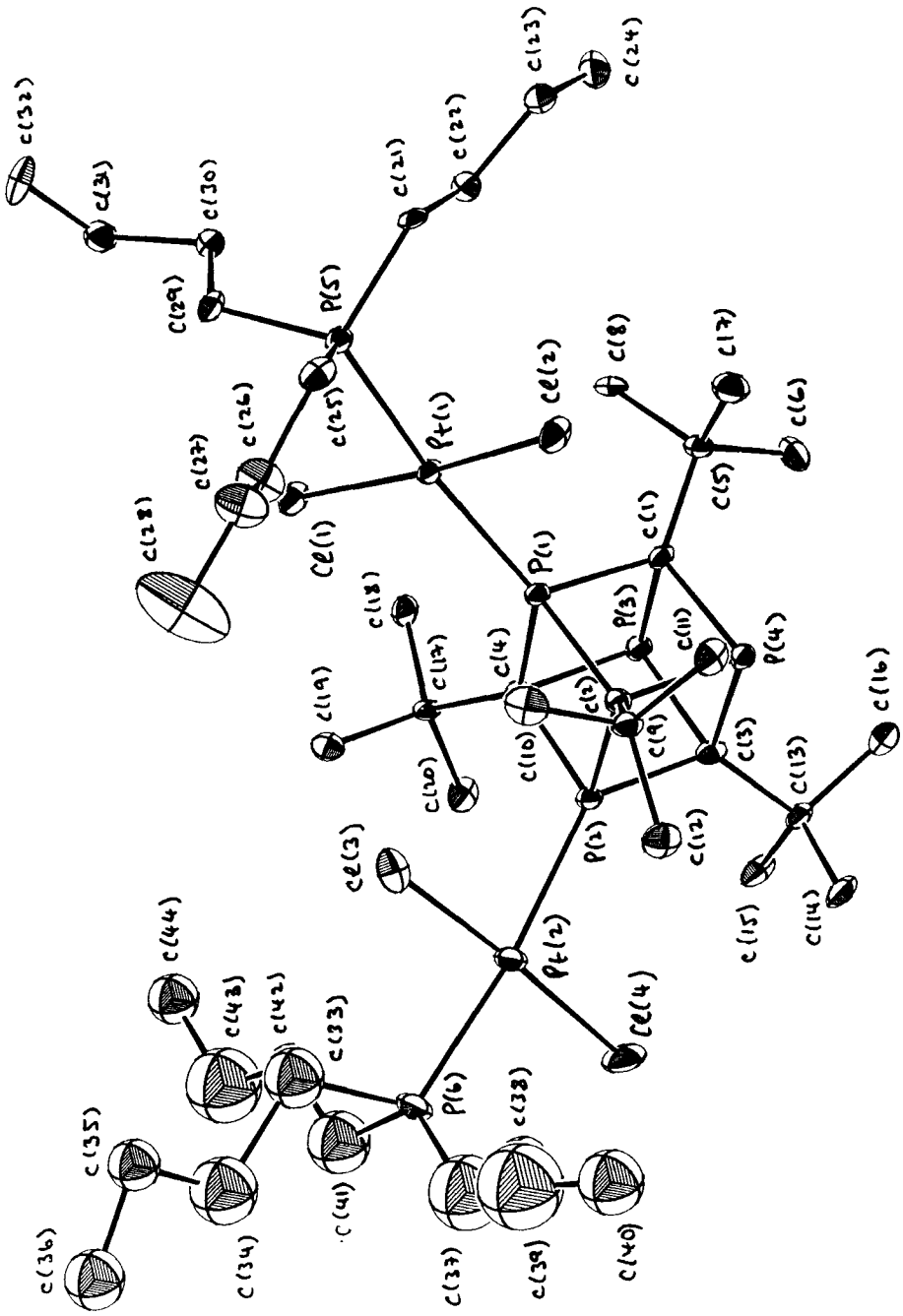


FIGURE 3 Molecular structure of compound 11(b).

TABLE IV

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for compound **11b**

a) Bonds			
Pt(1)-Cl(1)	2.277(3)	Pt(1)-Cl(2)	2.301(3)
Pt(1)-P(1)	2.323(4)	Pt(1)-P(5)	2.302(4)
Pt(2)-Cl(3)	2.290(5)	Pt(2)-Cl(4)	2.291(5)
Pt(2)-P(2)	2.321(3)	Pt(2)-P(6)	2.296(4)
P(1)-C(1)	1.88(2)	P(1)-C(2)	1.914(13)
P(1)-C(4)	1.914(11)	P(2)-C(2)	1.865(11)
P(2)-C(3)	1.87(2)	P(2)-C(4)	1.889(13)
P(3)-C(1)	1.881(11)	P(3)-C(3)	1.907(13)
P(3)-C(4)	1.872(15)	P(4)-C(1)	1.883(13)
P(4)-C(2)	1.876(15)	P(4)-C(3)	1.887(11)
P(5)-C(21)	1.822(14)	P(5)-C(25)	1.798(15)
P(5)-C(29)	1.83(2)	P(6)-C(33)	2.05(4)
P(6)-C(37)	1.70(4)	P(6)-C(41)	1.67(3)
C(1)-C(5)	1.52(2)	C(2)-C(9)	1.59(2)
C(3)-C(13)	1.54(2)	C(4)-C(17)	1.55(2)
C(5)-C(6)	1.51(2)	C(5)-C(7)	1.52(2)
C(5)-C(8)	1.56(2)	C(9)-C(10)	1.52(3)
C(9)-C(11)	1.51(2)	C(9)-C(12)	1.53(2)
C(13)-C(14)	1.50(2)	C(13)-C(15)	1.51(2)
C(13)-C(16)	1.52(2)	C(17)-C(18)	1.50(2)
C(17)-C(19)	1.53(2)	C(17)-C(20)	1.53(2)
C(21)-C(22)	1.50(2)	C(22)-C(23)	1.49(2)
C(23)-C(24)	1.53(2)	C(25)-C(26)	1.56(2)
C(26)-C(27)	1.51(2)	C(27)-C(28)	1.52(3)
C(29)-C(30)	1.50(2)	C(30)-C(31)	1.53(2)
C(31)-C(32)	1.51(3)	C(33)-C(34)	1.77(4)
C(34)-C(35)	1.51(5)	C(35)-C(36)	1.55(3)
C(37)-C(38)	1.45(4)	C(38)-C(39)	1.38(5)
C(39)-C(40)	1.47(6)	C(41)-C(42)	1.47(4)
C(42)-C(43)	1.39(4)	C(43)-C(44)	1.50(5)

TABLE IV (*Continued*)

b) Angles			
Cl(1)-Pt(1)-Cl(2)	173.3(2)	Cl(1)-Pt(1)-P(1)	95.6(1)
Cl(1)-Pt(1)-P(5)	89.8(1)	Cl(2)-Pt(1)-P(1)	90.9(1)
Cl(2)-Pt(1)-P(5)	83.9(1)	P(1)-Pt(1)-P(5)	173.9(1)
Cl(3)-Pt(2)-Cl(4)	176.1(2)	Cl(3)-Pt(2)-P(2)	86.5(1)
Cl(3)-Pt(2)-P(6)	87.5(2)	Cl(4)-Pt(2)-P(2)	97.4(2)
Cl(4)-Pt(2)-P(6)	88.7(2)	P(2)-Pt(2)-P(6)	173.0(2)
Pt(1)-P(1)-C(1)	122.3(4)	Pt(1)-P(1)-C(2)	127.3(4)
Pt(1)-P(1)-C(4)	133.3(5)	C(1)-P(1)-C(2)	86.0(6)
C(1)-P(1)-C(4)	86.0(5)	C(2)-P(1)-C(4)	87.0(5)
Pt(2)-P(2)-C(2)	124.6(4)	Pt(2)-P(2)-C(3)	135.4(4)
Pt(2)-P(2)-C(4)	119.9(4)	C(2)-P(2)-C(3)	86.8(6)
C(2)-P(2)-C(4)	89.2(5)	C(3)-P(2)-C(4)	87.5(6)
C(1)-P(3)-C(3)	87.2(5)	C(1)-P(3)-C(4)	87.3(6)
C(3)-P(3)-C(4)	86.8(6)	C(1)-P(4)-C(2)	87.1(6)
C(1)-P(4)-C(3)	87.7(5)	C(2)-P(4)-C(3)	85.9(6)
Pt(1)-P(5)-C(21)	111.3(5)	Pt(1)-P(5)-C(25)	110.7(5)
Pt(1)-P(5)-C(29)	118.0(4)	C(21)-P(5)-C(25)	104.8(6)
C(21)-P(5)-C(29)	106.5(6)	C(25)-P(5)-C(29)	104.5(7)
Pt(2)-P(6)-C(33)	111.5(8)	Pt(2)-P(6)-C(37)	115(1)
Pt(2)-P(6)-C(41)	115(1)	C(33)-P(6)-C(37)	90(2)
C(33)-P(6)-C(41)	94(2)	C(37)-P(6)-C(41)	123(2)
P(1)-C(1)-P(3)	93.6(5)	P(1)-C(1)-P(4)	93.8(6)
P(1)-C(1)-C(5)	127(1)	P(3)-C(1)-P(4)	92.9(5)
P(3)-C(1)-C(5)	117.3(8)	P(4)-C(1)-C(5)	123.4(9)
P(1)-C(2)-P(2)	92.1(5)	P(1)-C(2)-P(4)	93.0(5)
P(1)-C(2)-C(9)	128(1)	P(2)-C(2)-P(4)	93.9(6)
P(2)-C(2)-C(9)	126.3(8)	P(4)-C(2)-C(9)	114.5(9)
P(2)-C(3)-P(3)	92.6(7)	P(2)-C(3)-P(4)	93.5(6)
P(2)-C(3)-C(13)	130.6(8)	P(3)-C(3)-P(4)	91.9(5)
P(3)-C(3)-C(13)	119.0(9)	P(4)-C(3)-C(13)	119.9(9)
P(1)-C(4)-P(2)	91.4(5)	P(1)-C(4)-P(3)	92.9(5)
P(1)-C(4)-C(17)	132(1)	P(2)-C(4)-P(3)	93.1(7)

TABLE IV (*Continued*)

b) Angles			
P(2)-C(4)-C(17)	125.3(8)	P(3)-C(4)-C(17)	112.2(8)
C(1)-C(5)-C(6)	109(1)	C(1)-C(5)-C(7)	111(1)
C(1)-C(5)-C(8)	109(1)	C(6)-C(5)-C(7)	107(1)
C(6)-C(5)-C(8)	110(1)	C(7)-C(5)-C(8)	111(1)
C(2)-C(9)-C(10)	113(1)	C(2)-C(9)-C(11)	110(1)
C(2)-C(9)-C(12)	106(1)	C(10)-C(9)-C(11)	108(1)
C(10)-C(9)-C(12)	111(1)	C(11)-C(9)-C(12)	109(1)
C(3)-C(13)-C(14)	108(1)	C(3)-C(13)-C(15)	110(1)
C(3)-C(13)-C(16)	108(1)	C(14)-C(13)-C(15)	112(1)
C(14)-C(13)-C(16)	110(1)	C(15)-C(13)-C(16)	109(1)
C(4)-C(17)-C(18)	109.4(9)	C(4)-C(17)-C(19)	114(1)
C(4)-C(17)-C(20)	106(1)	C(18)-C(17)-C(19)	109(1)
C(18)-C(17)-C(20)	110(1)	C(19)-C(17)-C(20)	108(1)
P(5)-C(21)-C(22)	116.5(8)	C(21)-C(22)-C(23)	115(1)
C(22)-C(23)-C(24)	114(1)	P(5)-C(25)-C(26)	112.4(9)
C(25)-C(26)-C(27)	111(1)	C(26)-C(27)-C(28)	113(2)
P(5)-C(29)-C(30)	116(1)	C(29)-C(30)-C(31)	113(1)
C(30)-C(31)-C(32)	115(1)	P(6)-C(33)-C(34)	114(2)
C(33)-C(34)-C(35)	112(2)	C(34)-C(35)-C(36)	93(2)
P(6)-C(37)-C(38)	123(3)	C(37)-C(38)-C(39)	136(3)
C(38)-C(39)-C(40)	124(5)	P(6)-C(41)-C(42)	120(2)
C(41)-C(42)-C(43)	125(2)	C(42)-C(43)-C(44)	121(3)

Structural Studies. The molecular structure of *trans*-[$PtCl_2(PEt_3)(P_4C_4Bu^t_4)$], (**10**), and the atomic labelling scheme are shown in Figure 2, while selected bond distances and angles are listed in Table II. Table III lists the Atomic Coordinates.

As expected from the $^{31}P\{^1H\}$ nmr spectroscopic data on (**10**) the tetraphosphacubane is attached to Pt(II) by one of the four phosphorus atoms and the "cage" occupies a *trans*-position to the coordinated PEt_3 ligand. The Pt—P(1) cage distance (2.338(3) Å) is significantly longer than the Pt—PEt_3 distance (2.284(5) Å). Interestingly, the two Pt—Cl bond lengths are distinctly different and the Cl—Pt—Cl bond angle is 173°. The P—C bond lengths and bond angles within the coordinated tetraphosphacubane, however, are not significantly changed from those of the uncoordinated species.

The molecular structure of *trans*-[{$PtCl_2(PR_3)$}$_2(P_4C_4Bu^t_4)$], (R = Bu) (**11b**) is shown in Figure 3 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table IV, while Table V lists the Atomic Coordinates.

TABLE V

Fractional atomic coordinates and equivalent isotropic thermal parameters for compound **11b**

	x	y	z	Ueq
Pt(1)	0.19114(5)	0.14027(3)	0.30477(3)	0.030(1)
Pt(2)	0.16868(6)	0.59145(4)	0.20170(3)	0.043(1)
Cl(1)	-0.0438(3)	0.1923(2)	0.2974(2)	0.047(3)
Cl(2)	0.4293(3)	0.0731(3)	0.3063(2)	0.051(3)
Cl(3)	0.1633(4)	0.4654(3)	0.1551(2)	0.066(4)
Cl(4)	0.1733(4)	0.7242(3)	0.2418(3)	0.072(4)
P(1)	0.2081(3)	0.2853(2)	0.3282(2)	0.028(3)
P(2)	0.2148(3)	0.4755(2)	0.2908(2)	0.031(3)
P(3)	0.1168(3)	0.4123(2)	0.4140(2)	0.031(3)
P(4)	0.3984(3)	0.3553(2)	0.3681(2)	0.032(3)
P(5)	0.1939(3)	-0.0117(2)	0.2876(2)	0.034(3)
P(6)	0.1077(4)	0.6944(3)	0.1110(2)	0.061(4)
C(1)	0.2528(12)	0.2932(8)	0.4062(6)	0.030(10)
C(2)	0.3484(12)	0.3554(8)	0.2900(6)	0.029(10)
C(3)	0.2604(12)	0.4754(8)	0.3693(6)	0.031(10)
C(4)	0.0764(12)	0.4095(8)	0.3348(6)	0.028(10)
C(5)	0.2627(13)	0.2147(9)	0.4648(7)	0.037(11)
C(6)	0.2800(15)	0.2577(11)	0.5188(7)	0.051(13)
C(7)	0.3915(15)	0.1295(10)	0.4545(8)	0.052(13)
C(8)	0.1243(14)	0.1794(9)	0.4820(7)	0.043(11)
C(9)	0.4791(13)	0.3279(9)	0.2359(7)	0.036(11)
C(10)	0.4463(17)	0.2786(12)	0.1879(7)	0.059(15)
C(11)	0.6035(13)	0.2600(10)	0.2649(7)	0.045(12)
C(12)	0.5175(15)	0.4235(11)	0.2040(8)	0.054(13)
C(13)	0.2860(12)	0.5573(8)	0.3964(6)	0.032(10)
C(14)	0.4027(13)	0.5935(9)	0.3522(8)	0.050(12)
C(15)	0.1510(13)	0.6378(9)	0.4039(7)	0.044(12)
C(16)	0.3312(14)	0.5150(10)	0.4609(7)	0.051(12)
C(17)	-0.0848(12)	0.4461(8)	0.3315(6)	0.032(10)
C(18)	-0.1627(12)	0.3844(9)	0.3817(7)	0.038(11)

TABLE V (*Continued*)

	x	y	z	Ueq
C(19)	-0.1222(14)	0.4463(9)	0.2670(7)	0.043(12)
C(20)	-0.1300(13)	0.5510(9)	0.3448(7)	0.042(11)
C(21)	0.2669(14)	-0.1074(9)	0.3493(7)	0.045(11)
C(22)	0.2166(14)	-0.0886(10)	0.4160(7)	0.043(12)
C(23)	0.2961(16)	-0.1591(10)	0.4640(8)	0.061(13)
C(24)	0.2433(16)	-0.1367(12)	0.5313(8)	0.070(15)
C(25)	0.3094(14)	-0.0399(9)	0.2155(7)	0.045(12)
C(26)	0.2683(17)	0.0383(14)	0.1569(9)	0.075(17)
C(27)	0.3655(21)	0.0115(15)	0.0969(9)	0.085(19)
C(28)	0.3275(31)	0.0852(26)	0.0387(13)	0.201(39)
C(29)	0.0265(13)	-0.0330(9)	0.2801(7)	0.038(11)
C(30)	-0.0733(13)	-0.0464(9)	0.3407(6)	0.034(10)
C(31)	-0.2216(14)	-0.0438(10)	0.3300(7)	0.047(12)
C(32)	-0.2278(14)	-0.1248(11)	0.2976(8)	0.064(13)
C(33)	0.0990(29)	0.6184(21)	0.0432(14)	0.149(11)
C(34)	0.0695(36)	0.6919(25)	-0.0308(17)	0.190(14)
C(35)	0.0627(24)	0.6325(17)	-0.0784(11)	0.112(8)
C(36)	0.0267(30)	0.7238(21)	-0.1292(14)	0.152(11)
C(37)	0.2409(42)	0.7379(30)	0.0631(20)	0.235(19)
C(38)	0.3867(24)	0.6807(17)	0.0537(11)	0.113(8)
C(39)	0.4895(52)	0.6590(37)	0.0023(25)	0.309(26)
C(40)	0.6428(33)	0.6366(24)	0.0033(16)	0.176(13)
C(41)	-0.0616(32)	0.7568(23)	0.1153(15)	0.165(12)
C(42)	-0.1730(17)	0.7128(12)	0.1540(8)	0.068(5)
C(43)	-0.3176(42)	0.7569(29)	0.1597(20)	0.233(19)
C(44)	-0.4241(23)	0.7041(16)	0.1984(11)	0.104(7)

Ueq is defined as one third of the trace of the orthogonalised Uij tensor.

The solid state structure of (**11b**) is fully in accord with the solution $^{31}P\{^{1}H\}$ nmr data with the tetraphosphacubane being ligated to two $[PtCl_2(PBu_3)]$ fragments. As in complex (**10**) the Pt—P (cage) distance (av. 2.323(3) Å) is longer than the *trans*-Pt—$P(PBu_3)$ distance (av. 2.299(4) Å). No significant bond length or bond angle changes are observed within the tetraphosphacubane compared with the uncomplexed

TABLE VI

^{31}P nmr chemical shift and coupling constant data for (**8**) and *trans*- $[PtCl_2(PEt_3)(P_5C_5Bu^t_5)]$ (**12**)[a,b]

Compound	$\delta_P A$	$\delta_P M$	$\delta_P N$	$\delta_P X$	$\delta_P Y$
(**8**)	179.1	58.7	82.5	218.5	-
(**12**)	163.3	72.7	89.5	236.2	14.8

Compound	$^1J_{PtP}N$	$^1J_{PtP}Y$	$^1J_{P_AP_N}$
(**8**)	-	-	262
(**12**)	1967	2933	340

Compound	$^2J_{PtP}A$	$^2J_{P_NP_Y}$	$^2J_{P_AP_X}$	$^2J_{P_NP_X}$	$^2J_{P_MP_X}$	$^2J_{P_AP_M}$
(**8**)	-	-	20.2	14.0	6.4	6.6
(**12**)	190	486	5.3	19.4	-	12.4

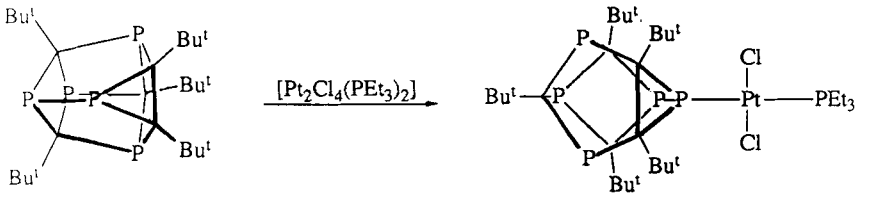
Compound	$^3J_{P_MP_N}N$	$^3J_{P_YP_A}A$
(**8**)	7.7	-
(**12**)	7.7	10.4

(a) δ_P in ppm rel. H_3PO_4

(b) Coupling constants J in Hz

compound. Interestingly, although the mass spectrum of (**11b**) exhibits a peak at M^+-(HCl), there is no apparent agostic interaction between the closest Bu^t group on platinum. Likewise, no HCl elimination reaction occurred when (**11b**) was treated with either Et_3N or DBU. It seems clear that the ligating properties of the tetraphosphacubane (**1**) are likely to be fairly restricted, both on account of the lower Lewis basicity of the P lone pair electrons referred to earlier, but also because of its high steric hindrance. We estimate the cone angle of (**1**) to be 172°.

Synthesis and Structural Characterisation of trans-[$PtCl_2(PEt_3)(P_5C_5Bu^t_5)$]. There were no reports of the coordination chemistry of the pentameric $P_5C_5Bu^t_5$ (**8**) prior to this study; however, Bartsch and Nixon[19] synthesised the monosulfur adduct $P_5C_5Bu^t_5S$ and established the structure by $^{31}P\{^1H\}$ nmr spectroscopy in which only the P atom of the 3-membered ring was sulfurised, even though an excess of sulfur was used in the synthesis.



(**8**) (**12**)

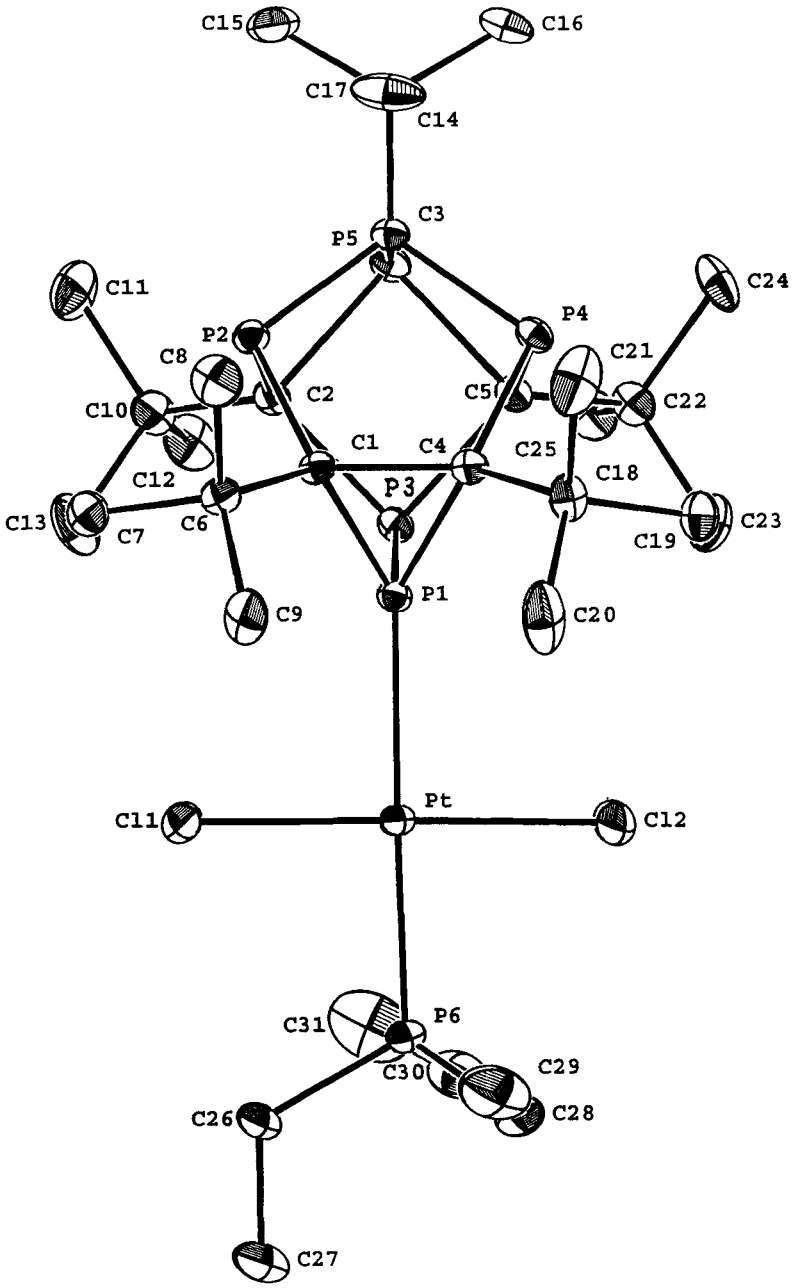


FIGURE 4 Molecular structure of compound (**12**).

Careful addition of $[PtCl_2(PEt_3)]_2$ to $P_5C_5Bu^t_5$ in $CDCl_3$ was monitored by $^{31}P\{^1H\}$ nmr spectroscopy until all the pentamer had reacted. The formation of the new complex *trans*-$[PtCl_2(PEt_3)(P_5C_5Bu^t_5)]$ (**12**) was evident by the replacement of the original characteristic, almost first order, $[AMNX_2]$ spectrum of $P_5C_5Bu^t_5$

TABLE VII

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for compound (12)

a) Bonds			
Pt-Cl1	2.290(2)	Pt-Cl2	2.294(2)
Pt-P1	2.333(1)	Pt-P6	2.279(2)
P1-P3	2.179(2)	P1-C1	1.849(5)
P1-C4	1.847(6)	P2-C1	1.886(5)
P2-C2	1.874(5)	P2-C3	1.848(5)
P3-C2	1.872(6)	P3-C5	1.864(5)
P4-C3	1.855(5)	P4-C4	1.883(5)
P4-C5	1.879(5)	P5-C2	1.916(5)
P5-C3	1.895(5)	P5-C5	1.911(5)
P6-C26	1.816(6)	P6-C28	1.823(8)
P6-C30	1.791(8)	C1-C4	1.620(7)
C1-C6	1.583(7)	C2-C10	1.529(8)
C3-C14	1.545(8)	C4-C18	1.586(8)
C5-C22	1.539(7)	C6-C7	1.520(8)
C6-C8	1.516(9)	C6-C9	1.519(9)
C10-C11	1.510(10)	C10-C12	1.513(9)
C10-C13	1.519(10)	C14-C15	1.528(9)
C14-C16	1.515(8)	C14-C17	1.508(9)
C18-C19	1.510(8)	C18-C20	1.520(10)
C18-C21	1.527(10)	C22-C23	1.513(9)
C22-C24	1.530(9)	C22-C25	1.540(9)
C26-C27	1.513(10)	C28-C29	1.503(12)
C30-C31	1.492(14)		
b) Angles			
Cl1-Pt-Cl2	177.14(9)	Cl1-Pt-P1	90.21(5)
Cl1-Pt-P6	91.59(6)	Cl2-Pt-P1	90.78(6)
Cl2-Pt-P6	87.04(6)	P1-Pt-P6	171.55(6)
Pt-P1-P3	110.08(7)	Pt-P1-C1	136.8(2)
Pt-P1-C4	136.9(2)	P3-P1-C1	104.3(2)
P3-P1-C4	103.9(2)	C1-P1-C4	52.0(2)

TABLE VII (*Continued*)

b) Angles			
C1-P2-C2	105.4(2)	C1-P2-C3	101.6(2)
C2-P2-C3	87.6(2)	P1-P3-C2	99.3(2)
P1-P3-C5	100.0(2)	C2-P3-C5	86.9(2)
C3-P4-C4	101.4(2)	C3-P4-C5	86.8(2)
C4-P4-C5	105.4(2)	C2-P5-C3	85.1(2)
C2-P5-C5	84.3(2)	C3-P5-C5	84.7(2)
Pt-P6-C26	115.8(2)	Pt-P6-C28	112.7(3)
Pt-P6-C30	111.3(3)	C26-P6-C28	105.6(3)
C26-P6-C30	105.8(3)	C28-P6-C30	104.7(4)
P1-C1-P2	112.3(3)	P1-C1-C4	64.0(3)
P1-C1-C6	122.7(4)	P2-C1-C4	111.3(3)
P2-C1-C6	109.3(3)	C4-C1-C6	130.5(4)
P2-C2-P3	113.4(3)	P2-C2-P5	91.6(2)
P2-C2-C10	118.0(4)	P3-C2-P5	91.8(2)
P3-C2-C10	116.7(4)	P5-C2-C10	120.3(4)
P2-C3-P4	108.4(3)	P2-C3-P5	93.1(2)
P2-C3-C14	119.3(3)	P4-C3-P5	93.7(2)
P4-C3-C14	118.6(4)	P5-C3-C14	118.3(4)
P1-C4-P4	112.7(3)	P1-C4-C1	64.1(3)
P1-C4-C18	121.3(4)	P4-C4-C1	111.8(3)
P4-C4-C18	109.3(4)	C1-C4-C18	130.7(4)
P3-C5-P4	113.4(3)	P3-C5-P5	92.2(2)
P3-C5-C22	116.8(4)	P4-C5-P5	92.4(2)
P4-C5-C22	118.2(4)	P5-C5-C22	118.6(4)
C1-C6-C7	108.9(4)	C1-C6-C8	108.7(5)
C1-C6-C9	115.7(4)	C7-C6-C8	108.3(5)
C7-C6-C9	105.4(5)	C8-C6-C9	109.6(5)
C2-C10-C11	110.5(5)	C2-C10-C12	110.5(5)
C2-C10-C13	109.0(5)	C11-C10-C12	108.4(6)
C11-C10-C13	110.4(6)	C12-C10-C13	107.9(6)
C3-C14-C15	109.9(5)	C3-C14-C16	109.4(5)
C3-C14-C17	110.2(5)	C15-C14-C16	109.0(5)
C15-C14-C17	108.9(5)	C16-C14-C17	109.4(5)

TABLE VII (*Continued*)

b) Angles			
C4-C18-C19	108.0(4)	C4-C18-C20	116.4(5)
C4-C18-C21	108.9(5)	C19-C18-C20	106.0(5)
C19-C18-C21	107.6(5)	C20-C18-C21	109.7(5)
C5-C22-C23	109.1(5)	C5-C22-C24	111.3(5)
C5-C22-C25	109.7(5)	C23-C22-C24	110.7(5)
C23-C22-C25	109.2(5)	C24-C22-C25	106.9(5)
P6-C26-C27	116.3(4)	P6-C28-C29	113.2(5)
P6-C30-C31	113.5(6)		

(PA and PN are the two directly bonded P atoms) by a pattern of lines corresponding to an [A'M'N'X_2'Y] spin system (Y = PEt_3 resonance). This provided clear evidence that the high symmetry of the $P_5C_5Bu^t_5$ cage is retained on coordination. The observation of large one-bond phosphorus-platinum coupling constants for P^N ($^1J_{PtP}N$ = 1967 Hz) and P^Y ($^1J_{PtP}Y$ = 2933 Hz) (see Table VI) together with the smaller value of $^2J_{PtP}A$ (190 Hz) and the large value for $^2J_PN_PY$ (486 Hz) firmly established the proposed structure. Interestingly, the magnitude of $^1J_PA_PN$ increases from 262 Hz to 340 Hz on coordination of P^N to platinum. The higher value of $^1J_PA_PN$ is more typical for a one-bond coupling between λ^3-P and λ^5-P atoms. Support for the structure comes from the $^{195}Pt\{^1H\}$ nmr spectrum which showed a doublet of doublet of doublets pattern ($^1J_{PtP}N$ = 1967 Hz, $^1J_{PtP}Y$ = 2933 Hz, $^2J_{PtP}A$ = 190 Hz).

Confirmation of the structure was by a single crystal X-ray diffraction study on yellow crystals obtained from thf, and the molecular geometry of (**12**) is shown in Figure 4, while selected bond lengths and bond angles are listed in Table VII. Table VIII lists Atomic Coordinates.

The structure reveals that, as in the case of $P_5C_5Bu^t_5S$, it is the P(1) of the 3-membered CCP ring that is the ligating atom. The overall symmetry of the $P_5C_5Bu^t_5$ is retained on complexation in accord with the solution nmr spectroscopic data on (**12**), and inspection of the bond length and bond angle data shows that there is only slight perturbation of the $P_5C_5Bu^t_5$ "cage" on coordination to the platinum(II) centre, (e.g. P(1)—P(3) 2.179(2) Å in (**12**) and 2.175(2) Å in (**8**); C(1)—C(4) 1.620(7) Å in (**12**) and 1.588(7) in (**8**); C(1)P(1)C(4) bond angle in (**12**) 52.0(2)° and 49.7(1)° in (**8**)).

The symmetry around the Pt(II) atom is close to the idealised square planar geometry but, unlike (**10**), both Pt—Cl bonds are the same within experimental error. Interestingly the Pt—PEt_3 bond distance in (**12**) (2.279(2) Å) is very similar to the Pt—PEt_3 bond distance in (**10**) (2.284(5) Å) and the Pt-"cage" distances Pt—$P_5C_5Bu^t_5$ and Pt—$P_4C_4Bu^t_4$ are also essentially identical (2.333(1) Å) (**12**) and (2.338(3) Å) (**10**).

TABLE VIII

Fractional atomic coordinates and equivalent isotropic thermal parameters for compound (12)

	x	y	z	Ueq
Pt	0.17867(2)	0.45585(2)	0.20093(2)	0.035(1)
Cl1	-0.01533(17)	0.33923(14)	0.20801(14)	0.075(1)
Cl2	0.37097(19)	0.57708(16)	0.20010(21)	0.110(1)
P1	0.30115(13)	0.30516(11)	0.22189(9)	0.030(1)
P2	0.31776(14)	0.05678(12)	0.26197(9)	0.033(1)
P3	0.35135(14)	0.29769(12)	0.35436(9)	0.033(1)
P4	0.57137(13)	0.20859(12)	0.24644(9)	0.031(1)
P5	0.49316(14)	0.12623(13)	0.39307(9)	0.036(1)
P6	0.06712(16)	0.61104(12)	0.20061(11)	0.044(1)
C1	0.2988(5)	0.1580(4)	0.1783(3)	0.029(2)
C2	0.3112(5)	0.1424(4)	0.3631(3)	0.034(2)
C3	0.5005(5)	0.0704(4)	0.2807(3)	0.032(2)
C4	0.4356(5)	0.2400(4)	0.1704(3)	0.032(2)
C5	0.5290(5)	0.2713(4)	0.3504(3)	0.030(2)
C6	0.1914(6)	0.1017(5)	0.1088(3)	0.037(3)
C7	0.0680(6)	0.0542(5)	0.1506(4)	0.050(3)
C8	0.2477(7)	0.0049(6)	0.0625(4)	0.063(4)
C9	0.1427(7)	0.1805(6)	0.0469(4)	0.061(3)
C10	0.2015(6)	0.1058(5)	0.4210(4)	0.048(3)
C11	0.2001(8)	-0.0177(6)	0.4359(5)	0.073(4)
C12	0.2238(7)	0.1735(7)	0.5042(4)	0.066(4)
C13	0.0683(7)	0.1284(8)	0.3822(4)	0.078(4)
C14	0.5754(6)	-0.0334(5)	0.2626(4)	0.045(3)
C15	0.5125(7)	-0.1334(5)	0.3072(5)	0.066(4)
C16	0.7197(6)	-0.0059(5)	0.2938(4)	0.058(3)
C17	0.5684(8)	-0.0653(6)	0.1702(5)	0.078(4)
C18	0.5006(6)	0.2908(5)	0.0913(3)	0.042(3)
C19	0.6075(6)	0.3848(5)	0.1217(4)	0.049(3)
C20	0.4080(8)	0.3420(7)	0.0312(5)	0.092(4)
C21	0.5680(8)	0.1995(7)	0.0446(4)	0.081(4)
C22	0.6328(6)	0.3591(5)	0.3982(4)	0.042(3)
C23	0.6313(7)	0.4711(6)	0.3597(4)	0.062(4)

TABLE VIII (*Continued*)

	x	y	z	Ueq
C24	0.7719(6)	0.3209(6)	0.3977(4)	0.062(4)
C25	0.5981(7)	0.3733(6)	0.4901(4)	0.056(3)
C26	-0.1128(6)	0.5836(5)	0.1862(4)	0.050(3)
C27	-0.1887(7)	0.6855(6)	0.1926(6)	0.078(4)
C28	0.1189(7)	0.7042(6)	0.1201(5)	0.077(4)
C29	0.1031(9)	0.6465(8)	0.0338(6)	0.112(5)
C30	0.0997(8)	0.6969(6)	0.2963(5)	0.079(4)
C31	0.0540(11)	0.6388(10)	0.3708(6)	0.130(7)

Ueq is defined as one third of the trace of the orthogonalised Uij tensor.

TABLE IX

Crystallographic data for complexes (**10**), (**11b**), and (**12**)

Compound	(10)	(11b)	(12)
Formula	$C_{26}H_{51}Cl_2P_5Pt$	$C_{44}H_{90}Cl_4P_6Pt_2$	$C_{31}H_{60}Cl_2P_6Pt$
fw	784.6	1337.0	884.7
dimens (mm)	0.3 x 0.2 x 0.2	0.4 x 0.4 x 0.2	0.15 x 0.15 x 0.1
space group	$Pna2_1$ (No. 33)	P1 (No. 2)	P1 (No. 2)
(a) Å	19.006(7)	9.979(3)	10.126(4)
(b) Å	16.185(5)	14.486(5)	11.958(6)
(c) Å	11.157(4)	21.895(6)	16.105(4)
α deg		77.83(2)	93.74(3)
β deg		78.04(2)	92.75(3)
γ deg		73.37(3)	96.46(3)
Temperature °K	293	173	293
V, $Å^3$	3432.2	2928	1931
Z	4	2	2
D_{calc} g/cm^3	1.52	1.52	1.52
μ cm^{-1}	45.3	52.0	40.8
No. of independent reflections measured	3406	7157	6768
No. of obs. refl. I>2σ	2242	5971	5504
$R_{(F)}$	0.040	0.055	0.036
$R_{w(F)}$	0.047	0.073	0.038

EXPERIMENTAL

All manipulations were carried out using Schlenk tube techniques in inert atmospheres and/or under high vacuum. Solvents were rigorously dried and redistilled before use. $P_4C_4Bu^t_4$ and $P_5C_5Bu^t_5$ were synthesised by literature methods[6,15] and their purity confirmed prior to use by ^{31}P nmr spectroscopy. ^1H and ^{31}P nmr spectra were obtained using Bruker AMX 500 MHz or AC 250 MHz instruments using deuterated solvents as lock and reference.

X-Ray Measurements

The X-ray crystallographic studies on compounds (**10**), (**11b**), and (**12**) were carried out with an Enraf-Nonius CAD4 diffractometer using monochromated Mo(Kα) radiation λ = 0.71069 Å. The structures were solved by full matrix least squares, non-H atoms anisotropic, using Enraf-Nonius MolEN programmes. Crystallographic data are summarised in Table IX.

Preparation of trans-[$PtCl_2(PEt_3)(P_4C_4Bu^t_4)$] (**10**)

Stirring a mixture of a 2:1 ratio of $P_4C_4Bu^t_4$ and $[PtCl_2(PEt_3)]_2$ in thf room temperature afforded (**10**) in 84% yield after recrystallisation. mp 196°C. Found, C, 39.5, H, 6.44%. Calculated, C, 39.80, H, 6.55%. The ^{31}P nmr data are discussed in the text. ^{1}H nmr data (C_6D_6): δ 0.95 (br.s, 9H, Bu^t); 1.52 (br.s, 27H, 3 Bu^t); 1.03 (s, 9H, $3CH_3$); 2.05 (br.s, 6H, $3CH_2$).

+ion FABMS: m/e 784 M^+ (6%); 711 M^+-C_2H_5 + CH_3 (3%); 400 M^+-$PtCl_2$ (PEt_3) (100%); 262 $P_4C_4Bu^t_4$-2Bu^tCC (79%); 169 $P_4C_4Bu^t_4$-2Bu^tCCP-P (77%); 119 PEt_3H^+ (37%).

Preparation of trans-[{$PtCl_2(PEt_3)$}$_2$($P_4C_4Bu^t_4$)] (**11a**)

An equimolar amount of $[PtCl_2(PEt_3)]_2$ and $P_4C_4Bu^t_4$ were reacted in thf at room temperature to afford (**11**) in 87% yield after recrystallisation from ethanol. Found, C, 33.0; H, 5.56%. Calculated, C, 32.89; H, 5.69%. mp 182°C. ^{31}P nmr data are discussed in the text. ^{1}H nmr data (C_6D_6): δ 1.02 (br.s, 18H, Bu^t); 1.48 (br.s, 18H, Bu^t); 1.10 (s, 18H, $6CH_3$); 2.11 (br.s, 12H, $6CH_2$).

+ion FABMS: m/e 1132 M^+-HCl (4%); 784 M^+-$PtCl_2(PEt_3)$ 4%; 400 M^+-2$PtCl_2(PEt_3)$ (100%); 262 $P_4C_4Bu^t_4$-2Bu^tCC 76%; 169 $P_4C_4Bu^t_4$-2Bu^tCCP-P (70%); 119 PEt_3H^+ (63%).

Preparation of trans-[{$PtCl_2(PBu_3)$}$_2$($P_4C_4Bu^t_4$)] (**11b**)

This complex was synthesised in 89% yield in a similar fashion to that described for (**11a**). mp 119°C. ^{31}P nmr data are discussed in the text.

Preparation of trans-[$PtCl_2(PEt_3)(P_5C_5Bu^t_5)$] (**12**)

To $P_5C_5Bu^t_5$ dissolved in $CDCl_3$ in an nmr tube was added solid $[PtCl_2(PEt_3)]_2$ stepwise and the mixture allowed to equilibrate. When no resonances remained in the $^{31}P\{^1H\}$ nmr spectra of the solution corresponding to unreacted $P_5C_5Bu^t_5$ the solvent was removed *in vacuo* and the resulting yellow solid was washed with Et_2O and recrystallisation from thf afforded the yellow compounds used in the single crystal X-ray diffraction study. ^{31}P nmr data are discussed in the text. ^{195}Pt nmr data (53.8 MHz) 25°C $CDCl_3$. δ-3765 (ddd $^1J_{PtP}$Y 2933 Hz, $^1J_{PtP}$N 1967 Hz; $^2J_{PtP}$A 190 Hz).

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