Large-ring Complexes of Platinum and Palladium of the Type *trans*-[{$MCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x$] †

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Large-ring (12- to 45-membered) complexes of the type *trans*-[{$MCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x$] (M = Pt or Pd; n = 8, 9, 10, or 12; x = 1—3) are formed by treating [$MCl_2(NCPh)_2$] with the flexible long-chain diphosphines. The mononuclear (x = 1) complexes of platinum are volatile and have also been studied by mass spectrometry. ^1H and ^{31}P N.m.r. data are given as are values of $\bar{\nu}$(M–Cl). Bond length and bond angle data for the binuclear complex [{$PdCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_2$], with a 26-membered ring, are also given.

UNTIL recently it was thought that large chelate rings from long-chain flexible bidentate ligands would not be stable with respect to open-chain polynuclear species.[1, ‡] However, we have reported briefly [3] that diphosphines of the types $Bu^t{}_2P(CH_2)_nPBu^t{}_2$ (n = 9, 10, or 12) with the very bulky $Bu^t{}_2P$ end groups form large-ring complexes of types *trans*-[{$PtCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_x$] ($x$ = 1—3) and *trans*-[{$IrCl(CO)[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x$]. We now describe more fully our studies on these large-ring complexes of platinum and also on analogous palladium complexes.

RESULTS AND DISCUSSION

On heating a suspension of [$PtCl_2(NCPh)_2$] under reflux with the diphosphines of type $Bu^t{}_2P(CH_2)_nPBu^t{}_2$ (n = 8, 9, 10, or 12) in 2-methoxyethanol or toluene for 24 h yellow crystalline complexes *trans*-[{$PtCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x$] ($x$ = 3, n = 8; x = 1, 2, and possibly 3, n = 9 or 10; and x = 1—3, n = 12) were formed. The product mixtures were usually separated by selective solvent extraction followed by chromatography on neutral alumina. The mononuclear complexes are volatile, subliming slowly at 180—195 °C and 1 atm without decomposition, or more rapidly *in vacuo*.§ Details of the separation procedures are given in the Experimental section; the complexes were characterised by microanalytical, molecular-weight, and spectroscopic data (Tables 1 and 2).

Thus the mononuclear complex *trans*-[$PtCl_2\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}$] is readily soluble in light petroleum, volatile (180 °C, 1 atm), and has a molecular weight of 703,678 (calc., 697) (Table 1). The *trans* configuration follows from (*i*) the far-i.r. spectrum which showed one strong band at 326 cm^{-1} due to ν(Pt–Cl) and characteristic of chlorine *trans* to chlorine,[4,5] (*ii*) the 60 MHz n.m.r. spectrum which showed one well defined 1 : 2 : 1 triplet t-butyl resonance at δ 1.49 p.p.m. with [^3J(PH) + ^5J(PH)] 13.0 Hz, characteristic of equivalent *trans*-phosphorus nuclei [6] (the resonances due to the methylenic protons being very broad), and (*iii*) the ^{31}P n.m.r. spectrum consisted of a sharp singlet at δ 31.8 p.p.m. (to low field of 85% H_3PO_4) with ^{195}Pt satellites, ^1J(PtP) 2 476 Hz. Complexes of the type *cis*-[$PtCl_2(PR_3)_2$] normally have ^1J(PtP) *ca.* 3 500 Hz, whereas those of the type *trans*-[$PtCl_2(PR_3)_2$] have ^1J(PtP) *ca.* 2 500 Hz.[7,8]

The nature of the binuclear complex *trans*-[{$PtCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_2$] follows from (*i*) the molecular weight and analytical data (Table 2), (*ii*) the occurrence of only one band (at 334 cm^{-1}) due to ν(Pt–Cl) in the far-i.r. spectrum and typical of *trans* chlorines, (*iii*) the well defined 1 : 2 : 1 triplet t-butyl n.m.r. pattern at δ 1.51 p.p.m. with [^3J(PH) + ^5J(PH)] 12.8 Hz, and (*iv*) the ^{31}P n.m.r. pattern which consisted of a single sharp resonance at 29.5 p.p.m. with platinum satellites, ^1J(Pt–P) 2 451. A third and very insoluble product was also isolated from the reaction mixture. This material was always contaminated with metallic platinum and could not be obtained analytically pure. It was probably of the type *trans*-[{$PtCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_x$] ($x \geqslant 3$) since its i.r. spectrum (400—5 000 cm^{-1}) was very similar to those of *trans*-[{$PtCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]\}_x$] ($x$ = 1 or 2) and there was only one band due to ν(Pt–Cl) at 334s cm^{-1} in the far-i.r. spectrum (200—400 cm^{-1}).

Three isomers of the type [{$PtCl_2[Bu^t{}_2P(CH_2)_{12}PBu^t{}_2]\}_x$] ($x$ = 1—3) were similarly prepared containing respectively 15-, 30-, and 45-atom rings. When *trans*-[$PtCl_2(NCPh)_2$] was treated with 1,12-bis(di-t-butylphosphino)dodecane in boiling 2-methoxyethanol the trinuclear species gradually precipitated as yellow plates of limited solubility in dichloromethane. The mononuclear (x = 1) and binuclear (x = 2) species were isolated from the 2-methoxyethanol mother liquors and separated by chromatography on alumina. All three complexes were fully characterized by microanalytical, molecular-weight, near- and far-i.r., and ^1H and ^{31}P n.m.r. data (see Tables). A single-crystal *X*-ray diffraction study of the mononuclear complex *trans*-[$PtCl_2\{Bu^t{}_2P(CH_2)_{12}PBu^t{}_2\}$] has confirmed the structure and determined the conformation of the 15-atom ring. One chlorine ligand is *gauche* with respect to the t-butyl groups, but closer to one set than the other in order that

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† No reprints available.

‡ Venanzi and his co-workers [2] reported a rigid bidentate ligand (dpbp) which spans *trans* positions in some square-planar complexes.

§ 1 atm = 101 325 Pa, 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] See for example, F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, p. 652.

[2] N. J. De Stefano, D. J. Johnson, and L. M. Venanzi, *Angew. Chem.*, 1974, **86**, 133.

[3] A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, 1973, 947.

[4] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

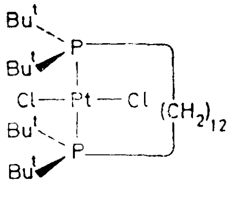
[5] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545 and refs. therein.

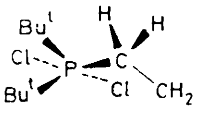
[6] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976 and refs. therein.

[7] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1922.

[8] S. O. Grim, R. L. Keiter, and W. McFarlane *Inorg. Chem.*, 1967, **6**, 1133 and refs. therein.

the other chlorine is not eclipsed by the methylene groups. The arrangement is shown diagrammatically in (I) and (II) (looking along a phosphorus–platinum bond). The detailed conformation of the polymethylene chain including torsion angles is reported elsewhere.[9] The complex $[PtCl_2\{Bu^t{}_2P(CH_2)_{12}PBu^t{}_2\}]$ is volatile and was further characterised by its mass spectrum (see below). We obtained no evidence for the formation of higher polymers ($x \geqslant 4$) and only the mono- and bi-nuclear complexes could be detected when $[PtCl_2(NCPh)_2]$ was treated with $Bu^t{}_2P(CH_2)_{12}PBu^t{}_2$ in boiling toluene (in which solvent the products remain in solution during the preparation).


(I)


(II)

Mono- and bi-nuclear complexes were similarly prepared and characterised from $Bu^t{}_2P(CH_2)_9PBu^t{}_2$, *viz.* *trans*-$[\{PtCl_2[Bu^t{}_2P(CH_2)_9PBu^t{}_2]\}_x]$ (see Experimental section and Tables). The ^{31}P n.m.r. spectrum of the mononuclear complex *trans*-$[PtCl_2\{Bu^t{}_2P(CH_2)_9PBu^t{}_2\}]$ in deuteriochloroform or benzene showed one sharp singlet with ^{195}Pt satellites, but two t-butyl triplets in the 60 MHz ^1H n.m.r. pattern. This is in contrast to the analogous mononuclear complexes *trans*-$[PtCl_2\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}]$ and *trans*-$[PtCl_2\{Bu^t{}_2P(CH_2)_{12}PBu^t{}_2\}]$ for each of which only one t-butyl triplet pattern was observed.

It is known from n.m.r. studies that *cis*-ligands such as chlorines lie in an approximately *gauche* position with

TABLE 1

Percentage yields, melting points, and analytical and molecular-weight data for some platinum(II) and palladium(II) complexes [a] of the type *trans*-$[\{MCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x]$

(M = Pt or Pd; n = 8, 9, 10 or 12; x = 1—3). Calculated values are given in parentheses

					Analysis(%)			
M	n	x	Yield/%	M.p.[b] (θ_c/°C)	C	H	Cl	M[c]
Pt	12	3	33,[d] 0[e]	215—245	46.2 (46.4)	8.1 (8.35)	10.0 (9.8)	2 175 (2 166)
	12	2	15,[d] 45[e]	260—265	46.35	8.5	9.6	1 459 (1 449)
	12	1	18,[d] 21[e]	225—230s	46.35	8.5	9.9	737 (725)
	10	2	54	273—277	45.05 (44.85)	8.1 (8.1)	9.85 (10.2)	1 450 (1 393)
	10	1	28	220—223s	44.8	8.2	9.95	678, 703 (697)
	9	2	62	239—251	44.15 (44.0)	8.0 (7.95)	10.6 (10.4)	1 376 (1 365)
	9	1	15	215—220s	44.1	7.9	9.9	684 (683)
	8	3	50	192—198	43.3 (43.1)	7.6 (7.85)	10.9 (10.6)	2 070, 2 120 (2 006)
Pd	12	2	48	228—248	52.8 (52.9)	9.6 (9.5)	10.95 (11.15)	1 406 (1 272)
	12	1	19	178—195	52.58	9.35	10.7	703 (636)
	10	2	62	247—274	51.6 (51.4)	9.35 (9.28)	11.8 (11.65)	1 228 (1 216)
	10	1	20	156—169	52.2 (51.4)	9.05 (9.28)	11.45 (11.65)	639 (608)

[a] All the complexes are yellow. [b] With decomposition; s = sublimes prior to melting. [c] In $CHCl_3$. [d] In 2-methoxyethanol. [e] In toluene.

TABLE 2

^1H[a] and ^{31}P n.m.r. data[b] and values of $\bar{\nu}$(M–Cl) (cm^{-1}) for the complexes *trans*-$[\{MCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x]$

(M = Pt or Pd; n = 8, 9, 10, or 12; x = 1—3)

			Proton[c]		Phosphorus		
M	n	x	$\delta(Bu^t)$	$\delta(CH_2)$	$\delta(H_3PO_4)$	^1J(Pt–P)	$\bar{\nu}$(M–Cl)[d]
Pt	12	3	1.5 (t) (12.9)	1.29 (s)	27.2	2 449	333
	12	2	1.49 (t) (13.2)	1.28 (s)	27.2	2 450	334
	12	1	1.51 (t) (13.0)	1.36 (s)	28.2	2 444	332
	10	2	1.51 (t) (12.8)	1.32 (s)	29.5	2 451	334
	10	1	1.49 (t) (13.0)	*e*	31.8	2 476	326
	9	2	1.50 (t) (12.8)	1.37 (s)	28.8	2 451	333
	9	1	1.53 (t) (12.9) 1.43 (t) (12.9)	*e*	31.0[f]	2 454	328
	8	3	1.49 (t) (12.2)	*e*	{29.3 {29.8	2 456 2 456	332
Pd	12	2	1.5 (t) (13.1)	1.29 (s)			346
	12	1	1.52 (t) (13.1)	1.24 (s)			345
	10	2	1.51 (t) (13.4)	1.32 (s)	{42.6 {41.2		347
	10	1	1.52 (13.0)	1.29 (s)	43.3		341

[a] Recorded at *ca.* 35 °C and 60 MHz in $CDCl_3$ solution. $\tau \pm 0.02$, $J \pm 0.2$ Hz; t = triplet and s = singlet. [b] Recorded at ambient temperatures at 36.43 MHz in CH_2Cl_2–CD_3COCD_3 with all ^1H decoupled. Chemical shifts (δ) are given with respect to 85% H_3PO_4 (±0.1 p.p.m.), $J \pm 2$ Hz. [c] $J = |{}^3J(PH) + {}^5J(PH)|$; J values are given in parentheses. [d] In Nujol; all the peaks were strong. [e] Obscured by t-butyl triplet. [f] No change at −42 °C.

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[9] F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 584.

respect to the two t-butyl groups of a di-t-butyl tertiary phosphine and that rotation around the phosphorus–metal bond is restricted.[10] The *X*-ray structure of *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}]$ also shows this as discussed above. Thus in the solid state the t-butyl groups will be non-equivalent. In the 12-membered ring complex ($n = 9$), *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_9PBu^t_2\}]$, rotation of the $PtCl_2$ moiety within the ring is prevented causing non-equivalence of the t-butyl groups. For the larger ring compounds ($n = 10$ or 12), *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]$ and *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}]$, either this rotation is possible or the non-equivalent t-butyl groups have the same chemical shifts.

We also investigated the action of $Bu^t_2P(CH_2)_8PBu^t_2$ on $[PtCl_2(NCPh)_2]$ but could only isolate the trinuclear species, *trans*-$[\{PtCl_2[Bu^t_2P(CH_2)_8PBu^t_2]\}_3]$, from the reaction mixture. This material was of interest because its ^{31}P n.m.r. spectrum showed two equally intense singlets with ^{195}Pt satellites (Table 2). Presumably it exists in solution as two conformers in each of which the phosphorus nuclei are equivalent, otherwise the t-butyl groups would not give a triplet pattern in the ^1H n.m.r. spectrum.

The mononuclear complexes *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_nPBu^t_2\}]$ ($n = 9$, 10, or 12) are sufficiently volatile and stable for study by mass spectrometry. Four isotopes of platinum account for 99% of the total natural abundance, *viz.* ^{194}Pt(32.9), ^{195}Pt(33.8), ^{196}Pt(25.3), and ^{198}Pt (7.2%). The parent molecular ion is therefore expected to exhibit seven major peaks. For the three platinum complexes we observed seven major peaks for the molecular ion of the correct relative intensities (allowing for ^{13}C), *e.g.* for $n = 10$ the most intense was at m/e 696 corresponding mainly to ($^{196}Pt + 2\ ^{35}Cl$) and ($^{194}Pt + {}^{37}Cl + {}^{35}Cl$). The accurate mass of the peak at m/e 696 was 696.2817, (Calc. for $C_{26}H_{56}{}^{35}Cl_2{}^{31}P_2{}^{196}Pt$: m/e 696.2844. Calc. for $C_{26}H_{56}{}^{37}Cl^{35}Cl^{31}P_2{}^{194}Pt$: m/e 696.2820). The degradation path of the molecular ion is difficult to elucidate due to the large number of isotopes, but a strong multiplet at $M - 56$ corresponds to the elimination of C_4H_8 (isobutene), and peaks due to the loss of one or two chlorines were also easily identified. The dodecane complex showed the most intense parent-ion peak at m/e 724 and the nonane complex at m/e 682, both as expected. Interestingly for *trans*-$[PtCl_2\{Bu^t_2P(CH_2)_9PBu^t_2\}]$, although the peak at m/e 682 was strong, it was not the base peak: this occurred at m/e 495 and is assigned to loss of $PBu^t_2CH_2CH:CH_2$ from the molecular ion.

Large-ring Complexes of Palladium.—When either $[PdCl_2(NCPh)_2]$ or sodium tetrachloropalladate(II) in ethanol or 2-methoxyethanol was heated under reflux with the diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$ ($n = 10$ or 12) a mixture of two yellow crystalline isomers *trans*-$[\{PdCl_2[Bu^t_2P(CH_2)_nPBu^t_2]\}_x]$ ($x = 1$ or 2) was produced after *ca.* 2—4 h. These mixtures were readily separated either by column chromatography on neutral alumina, in a similar manner to the platinum complexes, or by extraction of the solid mixtures with light petroleum (see Experimental section). The complexes were characterized by ^1H n.m.r., ^{31}P n.m.r., and i.r. spectroscopy, and analytical and molecular-weight data (Tables). In the ^1H n.m.r. spectra the complexes showed 1 : 2 : 1 triplet patterns for the t-butyl resonances superimposed on broad resonances due to the methylene protons. The mononuclear species $[PdCl_2\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]$ showed a singlet ^{31}P n.m.r. resonance at 43.3 p.p.m. in dichloromethane–deuterioacetone solution, whereas the corresponding binuclear species showed two equally intense singlets at 41.2 and 42.6 p.p.m. We ascribe this behaviour to the existence of two conformational isomers in solution.

The binuclear complex forms monoclinic needles from dichloromethane–methanol, space group $P2_1/c$, with four molecules in the unit cell. The structure has been investigated by Dr. W. S. McDonald and M. C. Norton of this Department, using photographic methods. Unfortunately, it was only possible to collect four layers of data because the complex slowly decomposes in the *X*-ray beam. Although the *R* is 16%, the data are sufficient to show the overall shape and geometry of the molecule. The structure is shown in Figures 1 and 2. The molecule is centrosymmetric and the torsion angles (±6°) for the groups Pd–P(1)–C(1)–C(2) and P(1)–C(1)–C(2)–C(3) · · · C(9)–C(10)–P(2)–Pd are −56, 170, 179, 67, 179, 176, 179, −106, 172, −160, and 63°. These torsion angles are similar to those found for the 26-atom ring complex *trans*-$[\{RhCl(CO)[Bu^t_2P(CH_2)_{10}PBu^t_2]\}_2]$ the structure of which has been determined more accurately (*R* 7.9%). The two complexes are isomorphous. Some distances are: Pd–Cl(1) 225.6(12); Pd–Cl(2) 229.5(12); Pd–P(1) 237.2(10); and Pd–P(2) 237.3(10) pm. One chloride ligand is *gauche* with respect to the set of four t-butyl groups, but closer to two of them in order that the *trans*-chlorine is not eclipsed by the methylene groups at C(1) and C(10′). The central portions of the polymethylene chains on opposite sides of the ring, *i.e.* C(3)–C(8) and C(3′)–C(8′), are arranged in a similar fashion to methylene chains in linear alkanes and long-chain fatty acids.

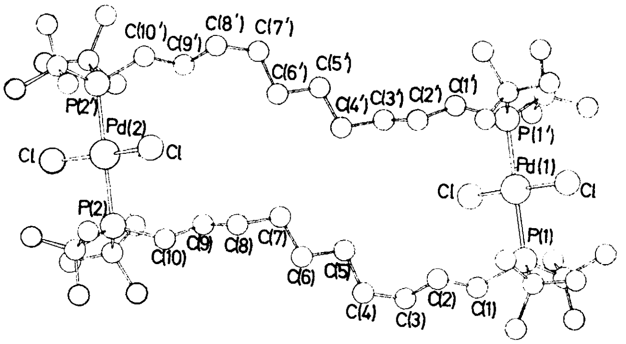

FIGURE 1 Structure of *trans*-$[\{PdCl_2[Bu^t_2P(CH_2)_{10}PBu^t_2]\}_2]$ showing the 26-atom ring

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[10] B. E. Mann, C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 1103.

There can be no doubt that the complexes described above are correctly formulated as large-ring complexes of the type *trans*-[{$MCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]$}$_x$]. They analysed correctly and gave measured molecular weights close to the calculated values. All showed one (or, for M = Pt, n = 9, two) t-butyl triplet ^1H n.m.r. pattern within the ranges δ 1.49—1.53 p.p.m. and $|^3J(P\text{-}H) + {}^5J(P\text{-}H)|$ 12.2—13.4 Hz; apart from the complex discussed above, singlet ^{31}P resonances (with satellites due to ^{195}Pt) δ 27.2—31.8 p.p.m. (platinum) and $^1J(Pt\text{-}P)$ 2 449—2 476 Hz or δ 41—43.3 p.p.m. (palladium) and values of ν(Pt–Cl) within the range 326—333s cm^{-1} or ν(Pd–Cl) 341—347 cm^{-1} were obtained.

It has been suggested that favourable conformational and internal-entropy effects are responsible for the formation of large-ring chelates with these long-chain flexible diphosphines carrying bulky end groups.[11] We have found for example that $Ph_2P(CH_2)_{10}PPh_2$ when treated with either $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCPh)_2]$ rapidly gives intractable sticky mixtures, similar results being obtained with $Me_2As(CH_2)_{12}AsMe_2$.

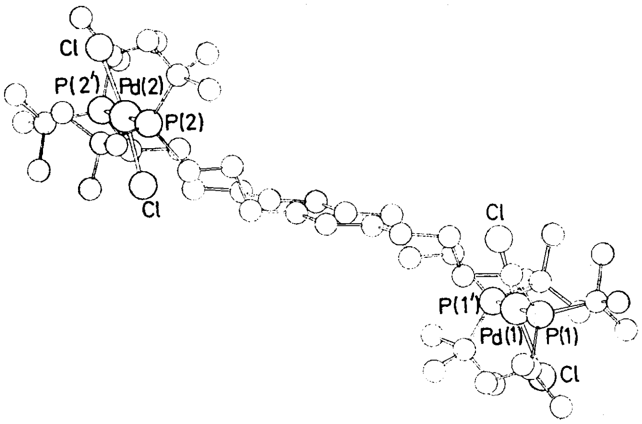

FIGURE 2 Structure of *trans*-[{$PdCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]$}$_2$] viewed along the phosphorus–palladium vector showing the arrangement of the chlorines with respect to the t-butyl and methylene groups

TABLE 3

Percentage yields, melting points, boiling points, and analytical,[a] i.r. (cm^{-1}), and n.m.r. data for the phosphonium salts, $[Bu^t{}_2HP(CH_2)_nPHBu^t{}_2]X_2$, and diphosphines, $Bu^t{}_2P(CH_2)_nPBu^t{}_2$

Phosphonium salts

				Microanalysis(%)				N.m.r.[c]		
n	X	Yield (%)	M.p. (θ_c/°C)	C	H	Br	$\tilde{\nu}$(P–H)[b]	δ(Bu^t)[d]	δ(P–H)	^3J(H–CH_2)
8	Br	69	250—265	51.0 (51.05)	9.6 (9.65)	28.0 (28.3)	2 224	1.6 (d) (16.0)	8.14 (dt) (478)	3.8
9	PF_6	85[e]	196—205	42.3 (42.4)	7.85 (7.95)		2 263	1.6 (d) (16.0)	7.98 (dt) (476)	3.5
10	Br	74	228—240	52.85 (52.7)	9.85 (9.85)	26.6 (26.95)	2 228	1.59 (d) (16.0)	8.2 (dt) (480)	
12	PF_6	85[e]	148—155	45.2 (44.8)	8.05 (8.3)		2 241	1.63 (d) (15.8)	8.97 (dt) (477)	3.9

Diphosphines

			N.m.r.	
n	Yield/ %	B.p. (θ_c/°C), P/mmHg	δ(Bu^t)[c,f]	δ(H_3PO_4)[g]
8	72	173—176, 0.02	1.14 (d) (10.3)	
9	78	180—185, 0.01	1.09 (d) (10.0)	27.7
10	79	190—193, 0.04	1.12 (d) (10.0)	27.8
12	77	192—195, 0.02	1.13 (d) (10.5)	27.1

[a] Calculated values are given in parentheses. [b] As Nujol mulls. [c] At 60 MHz in $CDCl_3$ solution; δ ±0.02 p.p.m., J ±0.2 Hz. d = Doublet and dt = doublet of triplets. Phosphorus–hydrogen coupling constants are given in parentheses. [d] Methylene signals appeared as broad unresolved resonances at δ *ca.* 0.6—2.8 p.p.m. [e] Yield of dibromide, 75%. [f] Methylene signals appeared as broad unresolved resonances at δ *ca.* 1.4 p.p.m. [g] In CH_2Cl_2–CD_3COCD_3; δ ±0.1 p.p.m.

Preparation of the Diphosphines $Bu^t{}_2P(CH_2)_nPBu^t{}_2$ *and their Salts.*—We did not attempt to prepare these diphosphines by treating $X(CH_2)_nX$ (X = Cl or Br) with say $Li(PBu^t{}_2)$ since one would expect halogen–metal exchange to occur giving much $Bu^t{}_2PPBu^t{}_2$.[12,13] We have found a satisfactory method of preparation which involves treating the polymethylene α, ω-dibromide with di-t-butylphosphine in isobutyl methyl ketone. In this way the crystalline salts $[Bu^t{}_2HP(CH_2)_nPHBu^t{}_2]Br_2$ (n = 8 or 10) were obtained and characterized, but the corresponding salts with n = 9 or 12 were more difficult to crystallise and were characterized as their less soluble hexafluorophosphate salts. Due to the very strong coupling $^1J(P\text{-}H)$ *ca.* 470 Hz, complete proton decoupling of the ^{31}P spectrum could not be achieved and the resonance formed a symmetrical multiplet. Addition of D_2O to a deuteriochloroform solution of the dibromide (n = 10)

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[11] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856.

[12] K. Issleib, A. Tzschach, and H. U. Block, *Chem. Ber.*, 1968, **101**, 2931.

[13] P. G. Douglas and B. L. Shaw, unpublished work.

effected deuterium exchange of the P–H proton and a sharp 1 : 1 : 1 triplet, ^{1}J(P–D) 70 Hz, formed in the ^{31}P n.m.r. spectrum.

All the dibromides $[\mathrm{Bu^t{}_2HP(CH_2)_{\mathit{n}}PHBu^t{}_2}]\mathrm{Br_2}$ are water soluble and were readily converted into the diphosphines, $\mathrm{Bu^t{}_2P(CH_2)_{\mathit{n}}PBu^t{}_2}$, by treatment with an aqueous solution of sodium hydroxide (10-fold excess). The diphosphines were extracted into diethyl ether and isolated by distillation over short path lengths as viscous air-sensitive liquids. It is important that a good vacuum ($<10^{-2}$ mmHg) and a short path length is used for the distillation otherwise extensive decomposition occurs (possibly isobutene is evolved). At 250 °C and an initial pressure of 0.5 mmHg in a closed system, a sample of $\mathrm{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2}$ evolved isobutene (identified by i.r. spectroscopy).

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are corrected. ^{1}H N.m.r. spectra (60 HMz) were recorded on a Perkin-Elmer R12A spectrometer at *ca.* 35 °C; ^{1}H (90 MHz), ^{13}C(22.62 MHz), and ^{31}P(36.43 MHz) n.m.r. spectra were obtained on a Bruker HFX spectrometer at *ca.* 25 °C. Infrared spectra were recorded on Perkin-Elmer model 457 (250—4 000 cm^{-1}) and Grubb–Parsons DB3/DN2 spectrometers (200—500 cm^{-1}). Mass spectra were obtained with an A.E.I. MS902 spectrometer.

Preparation of the Ditertiary Phosphines, $\mathrm{Bu^t{}_2P(CH_2)_{\mathit{n}}PBu^t{}_2}$ (n = 8, 9, 10, *or* 12).—1,10-*Bis(di-t-butylphosphonio)decane dibromide*. Di-t-butylphosphine (5.77 g, 39.4 mmol) was added to a solution of 1,10-dibromodecane (5.93 g, 19.7 mmol) in degassed isobutyl methyl ketone (30 cm^3). The mixture was heated under reflux for 8 h, then cooled, and the product (8.6 g, 14.5 mmol, 74%) isolated as prisms. The other phosphonium salts shown in Table 1 were prepared in a similar manner.

1,12-*Bis(di-t-butylphosphonio)dodecane bishexafluorophosphate*. A solution of ammonium hexafluorophosphate (0.95 g, 5.8 mmol) in methanol (10 cm^3) was added to a solution of 1,12-bis(di-t-butylphosphonio)decane dibromide (0.36 g, 0.58 mmol) in methanol (5 cm^3). The mixture was set aside at *ca.* 10 °C for 12 h. Isolation gave the *product* (0.38 g, 5.0 mmol, 86%) as prisms. The other hexafluorophosphate salts were prepared similarly.

1,10-*Bis(di-t-butylphosphino)decane*. A solution of 1,10-bis(di-t-butylphosphonio)decane dibromide (4.3 g, 7.28 mmol) in degassed water (20 cm^3) was treated with a solution of sodium hydroxide (2.9 g, 73 mmol) in water (5 cm^3) under argon. The product was isolated with diethyl ether and distilled as a colourless liquid (2.46 g, 5.7 mmol, 79%). The other diphosphines (Table 1) were prepared similarly.

1,10-*Bis(diphenylphosphino)decane*. A solution of 1,10-dibromodecane (16.5 g, 55 mmol) in tetrahydrofuran (thf) (50 cm^3) was added slowly (over 1.5 h) to a stirred solution of lithium diphenylphosphide (112 mmol) in thf (80 cm^3), formed from lithium flakes and chlorodiphenylphosphine. The mixture was stirred for a further 1 h, and then the volume was reduced to *ca.* 30 cm^3. Addition of methanol gave the *product* (18.1 g, 36 mmol, 65%) as prisms from benzene–methanol, m.p. 95—96.5 °C (Found: C, 79.85; H, 7.95. $\mathrm{C_{34}H_{40}P_2}$ requires C, 79.95; H, 7.9%).

1,10-*Bis(methyldiphenylphosphonio)decane di-iodide*. Methyl iodide (0.6 cm^3) was added to a solution of 1,10-bis(diphenylphosphino)decane (0.21 g, 0.4 mmol) in acetone (10 cm^3) and the mixture was set aside for 48 h in the dark at room temperature. Isolation gave the *product* (0.28 g, 0.35 mmol, 86%) as prisms, m.p. 214—218 °C (Found: C, 54.15; H, 5.95; I, 32.15. $\mathrm{C_{36}H_{46}I_2P_2}$ requires C, 54.4; H, 5.85; I, 31.95%).

$[\{\mathrm{PtCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]}\}_x]$ (x = 1, 2, *and* >2).—A suspension of *trans*-bis(benzonitrile)dichloroplatinum(II) (0.73 g, 1.54 mmol) in 2-methoxyethanol (60 cm^3) was treated with $\mathrm{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2}$ (0.66 g, 1.54 mmol) and the resulting mixture was heated under reflux. A solution formed rapidly, but after reflux for 24 h a yellow precipitate had formed. This was collected and extracted with chloroform. The chloroform solution on evaporation gave the binuclear complex (x = 2) (0.40 g, 0.29 mmol, 37%) as yellow prisms. The chloroform-insoluble product had an i.r. absorption spectrum (250—4 000 cm^{-1}) almost identical to that of the binuclear complex: it was therefore probably polynuclear (x > 2), yield 0.089 g (*ca.* 8%). The 2-methoxyethanol mother liquor was evaporated to give a yellow oil which when chromatographed on neutral alumina (activity I—II on the Brockman scale) gave on elution with dichloromethane–light petroleum (b.p. 60—80 °C) (*ca.* 1 : 9 v/v) the mononuclear complex (x = 1) (0.30 g, 0.43 mmol, 28%) as yellow prisms from dichloromethane–light petroleum. Elution of the column with chloroform gave more of the binuclear complex (0.18 g, 0.13 mmol, 17%). The *complexes* $[\{\mathrm{PtCl_2[Bu^t{}_2P(CH_2)_9PBu^t{}_2]}\}_x]$ (x = 1 and 2) were prepared similarly.

$[\{\mathrm{PtCl_2[Bu^t{}_2P(CH_2)_{12}PBu^t{}_2]}\}_x]$ (x = 1, 2, *and* 3).—*In toluene*. A suspension of *trans*-$[\mathrm{PtCl_2(NCPh)_2}]$ (1.23 g, 2.6 mmol) in toluene (60 cm^3) was treated with 1,12-bis(di-t-butylphosphino)dodecane (1.19 g, 2.6 mmol) and the mixture was heated under reflux for 20 h. The resulting yellow solution was evaporated to dryness and triturated with methanol to give a yellow solid. Continuous Soxhlet extraction of the solid with boiling light petroleum (b.p. 60—80 °C) for 2 h gave a yellow oil, which, when chromatographed on neutral alumina with dichloromethane–light petroleum (b.p. 60—80 °C) (*ca.* 1 : 9) as eluant, gave the mononuclear complex (x = 1) (0.39 g, 0.55 mmol, 21%).

In 2-methoxyethanol. A suspension of *trans*-$[\mathrm{PtCl_2(NCPh)_2}]$ (1.28 g, 2.7 mmol) in 2-methoxyethanol (70 cm^3) was treated with 1,12-bis(di-t-butylphosphino)dodecane (1.24 g, 2.7 mmol) and the mixture was heated under reflux for 24 h. The precipitated yellow solid was extracted continuously in a Soxhlet apparatus with dichloromethane to give the trinuclear complex (x = 3) as pale yellow plates (0.64 g, 0.3 mmol, 33%) from dichloromethane–methanol. Evaporation of the 2-methoxyethanol mother liquor gave a yellow oil, which, when chromatographed on neutral alumina with dichloromethane–light petroleum (b.p. 60—80 °C) (*ca.* 1 : 9) as eluant gave the mononuclear complex (0.35 g, 0.49 mmol, 18%) as needles. Elution of the column with chloroform gave the binuclear complex (0.3 g, 0.21 mmol, 15%) as prisms.

$[\{\mathrm{PdCl_2[Bu^t{}_2P(CH_2)_{10}PBu^t{}_2]}\}_x]$ (x = 1 *and* 2).—A suspension of *trans*-$[\mathrm{PdCl_2(NCPh)_2}]$ (0.92 g, 2.4 mmol) in 2-methoxyethanol (50 cm^3) was treated with 1,10-bis(di-t-butylphosphino)decane (1.04 g, 2.4 mmol) and the mixture was heated under reflux for 3 h. The precipitated orange-yellow binuclear complex (x = 2) (0.92 g, 0.75 mmol, 62%) was collected and formed needles from dichloromethane–methanol. Evaporation of the 2-methoxyethanol mother liquor gave an oil, which, when chromatographed on neutral alumina with light petroleum (b.p. 60—80 °C) as eluant, gave the mononuclear complex (0.29 g, 0.48 mmol, 20%) as prisms from dichloromethane–light petroleum (60—80 °C). The complexes $[\{PdCl_2[Bu^t_2P(CH_2)_{12}PBu^t_2]\}_x]$ (x = 1 and 2) were prepared similarly, the mononuclear species as yellow prisms from light petroleum (b.p. 60—80 °C) and the binuclear species as yellow plates from dichloromethane–methanol.

$[\{PdCl_2[Bu^t_2P(CH_2)_9PBu^t_2]\}_2]$.—Similar treatment of *trans*-$[PdCl_2(NCPh)_2]$ (0.50 g, 1.3 mmol) with $Bu^t_2P(CH_2)_9PBu^t_2$ (0.54 g, 1.3 mmol) in boiling 2-methoxyethanol for 22 h gave a precipitate of the binuclear species (0.54 g) which formed either yellow needles or prisms from dichloromethane–methanol. The 2-methoxyethanol mother liquor yielded only a mixture of complexes.

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