Formation of Large Chelate Rings and Cyclometallated Products from Diphosphines of Type $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5—8) and $Ph_2P(CH_2)_5PPh_2$ with Palladium and Platinum Chlorides: Factors affecting the Stability and Conformation of Large Chelate Rings

By **Najeeb A. Al-Salem, H. David Empsall, Richard Markham, Bernard L. Shaw,*** and **Brian Weeks**,
School of Chemistry, University of Leeds, Leeds LS2 9JT

The new diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5—7) are described and the previously known $Ph_2P(CH_2)_5PPh_2$ characterized more fully. The compounds, $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5—8) react with $[PdCl_2(NCPh)_2]$ to give crystalline complexes of the type $[\{PdCl_2[Bu^t_2P(CH_2)_nPBu^t_2]\}_x]$, where x = 2 for n = 5, 7, or 8 but unknown for n = 6. Also for n = 5 a volatile cyclometallated complex $[PdCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ is formed. With $[PtCl_2(NCPh)_2]$ or $[PtCl_2(NCBu^t)_2]$, $Bu^t_2P(CH_2)_5PBu^t_2$ gives *trans*-$[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$ (x is unknown) and a cyclometallated product $[PtX(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ (X = Cl) contaminated by a very similar species, possibly $[PtX(Bu^t_2PCH_2CH{\cdots}CH{\cdots}CHCH_2PBu^t_2)]$ from which it could not be separated. The complex $[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$ with CF_3CO_2H, however, gives pure $[PtX(Bu^t_2PCH_2CH_2CH_2CHCH_2CH_2PBu^t_2)]$ (X = O_2CCF_3) in almost quantitative yield and other pure complexes of this type with X = Cl, Br, I, or H are readily prepared by metathesis. The compound $Bu^t_2P(CH_2)_6PBu^t_2$ with $[PtCl_2(NCPh)_2]$ gives *trans*-$[\{PtCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x]$ (x is unknown) and the cyclometallated $[PtCl(Bu^t_2PCH_2CH_2CH_2CHCH_2CH_2PBu^t_2)]$. A remarkable difference in extent of deuteriation is observed on treating $[PtX(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ (X = Cl or Br) with CF_3CO_2D. The chloro-complex is not deuteriated but the bromo-complex is deuteriated in both t-butyl and methylene groups. Using ^{31}P n.m.r. spectroscopy the large-chelate mixed compounds described in this and previous papers, containing PBu^t_2 groups in 'corner' positions, are shown to be stable in solution relative to open-chain structures. The complexes *trans*-$[Pd_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$ and *cis*-$[Pt_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$ are described. The literature on large-chelate-ring compounds is surveyed. Factors affecting the stability and conformational homogeneity of carbocyclic and hetero-substituted rings, cyclic peptides, and depsipeptides, and cyclic monomer–polymer equilibria are discussed. Since the effects of sterically demanding substituents on the stability of purely organic rings (large and otherwise) has been explained purely in terms of bond lengths, angles, torsion angles, *etc.*, sterically demanding substituents must have similar effects on chelate rings. Enthalpy and entropy factors affecting the stability of large chelate rings and their conformational homogeneity in solution are discussed from this point of view. Infrared, ^1H, ^{13}C, and ^{31}P n.m.r., and mass spectral data are given and discussed.

WE have shown that diphosphines of the type $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 9, 10, or 12) give mono-, bi-, and trinuclear complexes $[\{MCl_2[Bu^t_2P(CH_2)_nPBu^t_2]\}_x]$ (M = Pd or Pt) with 12- to 45-membered rings.[1] A trinuclear complex, *trans*-$[Pt_3Cl_6\{Bu^t_2P(CH_2)_8PBu^t_2\}_3]$, with a 33-atom ring was also characterized: the octamethylene ligand, $Bu^t_2P(CH_2)_8PBu^t_2$, appears to be insufficiently long to span *trans* positions and no mononuclear complex could be isolated. We now describe the products formed from ligands of this type with shorter chain lengths, *viz.* $Bu^t_2P(CH_2)_nPBu^t_2$, n = 5—7, and palladium or platinum chlorides. We expected that these diphosphines would also give polynuclear large-ring compounds and because of the relatively short polymethylene chains they might have a strongly preferred conformation in solution. We also expected that, because the factors which promote cyclometallation of tertiary phosphines are similar to those which stabilize large chelate rings,[2] *C*-metallation might also occur, probably more readily for platinum than for palladium.

DISCUSSION

Preparation and Characterization of the Diphosphines.—The diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$, n = 5—7, were prepared in an analogous manner to their higher homologues, *viz.* by treating PBu^t_2H with $Br(CH_2)_nBr$ and treating the resulting diphosphonium salt with base. The compound $Bu^t_2P(CH_2)_5PBu^t_2$ was also prepared by treating 1,5-dilithiopentane with PBu^t_2Cl. The yield of purified pentamethylene diphosphine was only 35—40% but the latter is a more convenient method than the alternative involving the phosphonium salt, which requires PBu^t_2H. Characterizing microanalytical, i.r., and n.m.r. data for these new diphosphonium salts and diphosphines are given in Tables 1 and 2. The compound $Ph_2P(CH_2)_5PPh_2$ was prepared by the action of $Li[PPh_2]$ on $Br(CH_2)_5Br$ and also by treating 1,5-dilithiopentane with PPh_2Cl. It has previously been prepared by the action of $K[PPh_2]$·dioxan on 1,5-dihalogenopentane in tetrahydrofuran (thf)[3] but was not distilled or characterized further except through its complexes. The ^{13}C n.m.r. data for this diphosphine are given in Table 2. It showed a singlet ^{31}P resonance at $\delta = -16.9$ (in $CDCl_3$) and in the mass spectrum the molecular ion had the strongest peak at m/e = 440, as expected.

Palladium Complexes.—When a suspension of $[PdCl_2(NCPh)_2]$ in ethanol was heated with $Bu^t_2P(CH_2)_5PBu^t_2$ for 18 h the 16-atom ring complex *trans*-$[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ (1; n = 5) and the cyclometallated and more

TABLE 1

Percentage yields, melting points, microanalytical,[a] i.r. (cm^{-1}),[b] and ^1H n.m.r.[c] data for some diphosphonium salts $[HPBu^t_2(CH_2)_nHPBu^t_2]X_2$

				Microanalysis (%)				N.m.r.[d]		
n	X	Yield (%)	M.p. (θ_c/°C)	C	H	Br	ν(P–H)	$\delta(Bu^t)[^3J(PH)]$	$\delta(PH)[^2J(PH)]$	$^3J(H–CH_2)$
5	Br	65						1.57 (d) [1.48]	7.4 (dt) [473]	*e*
5	PF_6	85	254—257	38.6 (38.65)	7.35 (7.4)		2 280			
6	Br	84	272—281[f]	49.4 (49.25)	9.1 (9.4)	29.55 (29.8)	2 291	1.59 (d) [15.8]	8.12 (dt) [486]	*e*
7	Br	72	280—285[f]	50.15 (50.2)	9.45 (9.5)	29.4 (29.05)	2 278	1.60 (d) [15.7]	8.15 (dt) [478]	3.7

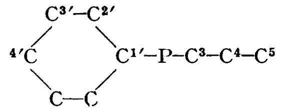
[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] In $CDCl_3$ at 34 °C and 60 MHz; d = doublet, dt = doublet of 1 : 2 : 1 triplets. δ values ± 0.02, J values ± 0.2 Hz. [d] Methylene protons appear as broad unresolved signals at δ 0.6—2.8. [e] *ca.* 3 Hz but not well resolved. [f] With sublimation.

TABLE 2

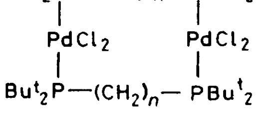
Carbon-13 n.m.r. data [a] for $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5 or 7) and $Ph_2P(CH_2)_5PPh_2$

	$C^3[^1J(PC)]$	$C^4[^2J(PC)]$	$C^5[^3J(PC)]$	C^6	$C^1[^1J(PC)]$	$C^2[^2J(PC)]$	
$Bu^t_2P(CH_2)_5PBu^t_2$ [b]	21.7 (d) [23]	30.7 (d) [26]	33.5 (t) [13]		31.2 (d) [23]	30.0 (d) [13]	
$Bu^t_2P(CH_2)_7PBu^t_2$ [b]	21.7 (d) [23]	30.9 (d) [24]	31.7 (d) [15]	26.7 (s)	31.1 (d) [23]	30.1 (d) [14]	
				$C^{1'}[^1J(PC)]$	$C^{2'}[^2J(PC)]$	$C^{3'}[^3J(PC)]$	$C^{4'}$
$Ph_2P(CH_2)_5PPh_2$ [c]	28.3 (d) [12] 25.9 (d) [17]		31.7 (t) [12]	139.9 (d) [19]	133.1 (d) [19]	128.6 (d) [5]	128.9 (s)

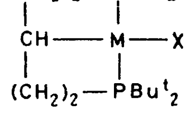
[a] Recorded at *ca.* 25 °C and 22.62 Hz in C_6D_6. Shifts relative to $SiMe_4$ as internal standard. δ values ± 0.1, J values ± 1.5 Hz. s = Singlet, d = doublet, t = 1 : 2 : 1 triplet. [b] Numbering of carbon nuclei: $H_3C^2–C^1–P–C^3–C^4–C^5–C^6$. [c] Numbering of carbon nuclei:



soluble complex $[PdCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$ (2; M = Pd, X = Cl) were isolated in yields of 62 and 12%, respectively. These complexes were characterized by elemental analysis, molecular weight (Table 3), and by i.r. and n.m.r. data (Table 3). The *trans* configuration follows in both cases from the occurrence of t-butyl triplet patterns showing ^2J(PP) is very large, *i.e.* a *trans* coupling: also for the binuclear complex only one peak due to ν(Pd–Cl) is observed and this is at a large value (346 cm^{-1}) characteristic of a *trans* Cl–Pd–Cl moiety. The value of ν(Pd–Cl) for the mononuclear cyclometallated complex is, as expected, small (256 cm^{-1}) (Cl *trans* to σ-bonded carbon). This mononuclear complex is stable and volatile, subliming slowly at 190 °C (1 atm) * on a Kofler microscope hot-stage, without apparent decomposition. The structure of the 16-atom ring binuclear complex (1; n = 5) has been determined by *X*-ray diffraction by Drs. W. S. McDonald and M. C. Norton of this Department and is discussed briefly below. It decomposes on heating above 260 °C, without melting, to the cyclometallated complex (2).



(1)



(2)

Treatment of $[PdCl_2(NCPh)_2]$ with $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 6—8) over a prolonged period, *e.g.* 20 h reflux in benzene or ethanol solution, gave complexes of the type $[\{PdCl_2[Bu^t_2P(CH_2)_nPBu^t_2]\}_x]$ where x = 2 when n = 7 or 8. With the hexamethylene diphosphine the product $[\{PdCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x]$ was crystalline but too insoluble for n.m.r. or molecular-weight determinations, but on the basis of microanalytical data (Table 3) and the occurrence of only one band due to ν(Pd–Cl) (at 337 cm^{-1}) this formulation, with mutually *trans* chlorines, is almost certainly correct. This chloro-complex was recovered unchanged after being boiled in 2-methoxyethanol with lithium iodide for 12 h. It is possible that the very bulky PBu^t_2 groups cause the iodide ion to have less affinity for the palladiums than the less bulky chloride ion.

The heptamethylene complex with a 20-atom ring (1; n = 7) (see Table 3 for characterizing data) gave well formed prisms from chloroform–light petroleum: its structure has been determined by *X*-ray diffraction [4] and is discussed below. The binuclear complex $[Pd_2Cl_4\{Bu^t_2P(CH_2)_8PBu^t_2\}_2]$ was isolated as yellow microcrystals. This compound is formulated with a 22-atom ring (1; n = 8) on the basis of (*i*) the microanalytical and molecular-weight data (Table 3), (*ii*) the occurrence of one strong band due to ν(Pd–Cl) at 348 cm^{-1} (Table 3), (*iii*) a singlet ^{31}P n.m.r. resonance at 41.3 p.p.m., and (*iv*) a t-butyl triplet ^1H n.m.r. pattern, indicating mutually and equivalent phosphorus donor atoms.

We have also studied the action of $Ph_2P(CH_2)_5PPh_2$ [3] on $[PdCl_2(NCPh)_2]$ in refluxing ethanol. This gave much palladium metal but also the yellow complex *trans*-$[Pd_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$. The formulation follows from the microanalytical, molecular-weight, and i.r. data (Tables). The ^{31}P n.m.r. spectrum, however, showed

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* Throughout this paper: 1 atm ≈ 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

two peaks at 26.6 and 16.5 p.p.m. with relative intensity *ca.* 1 : 3 indicating that two species are present in solution. The spectrum did not change appreciably over the temperature range 220—330 K (in $CDCl_3$) and was possibly due to the presence of *cis* and *trans* isomers rather than conformers.

Platinum Complexes.—For convenience these reactions are summarized in the Scheme. Treatment of $[PtCl_2(NCPh)_2]$ or $[PtCl_2(NCBu^t)_2]$ with $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ in 1 : 1 mol proportion in refluxing 2-methoxyethanol or toluene for 10—20 h gave a mixture of products. A yellow crystalline but rather insoluble complex *trans*-$[\{PtCl_2[Bu^t{}_2P(CH_2)_5PBu^t{}_2]\}_x]$ was readily isolated but was too insoluble for a molecular-weight determination. It could be binuclear ($x = 2$) like the palladium complex described above: the i.r. spectra 250—4 000 cm^{-1} were very similar. The formulation follows from the microanalytical, i.r., and ^1H and ^{31}P n.m.r. data (Table 3). The unpurified complex was accompanied by a small amount of a cream colourless glassy material, soluble in light petroleum (see Experimental, material A). We were unable to crystallize this material. It analyzed for $[\{PtCl_2[Bu^t{}_2P(CH_2)_5PBu^t{}_2]\}_y]$ (Found: C, 40.9; H, 7.7; Cl, 11.0. Calc. for $C_{21}H_{46}Cl_2P_2Pt$: C, 40.3; H, 7.4; Cl, 11.3%). It showed one very strong band at 330 cm^{-1} characteristic of a *trans* Cl–Pt–Cl moiety and a t-butyl triplet pattern in the ^1H n.m.r. pattern. The ^{31}P n.m.r. pattern at 296 K showed a central peak at $\delta = 30$, $w_{\frac{1}{2}} = ca.$ 40 Hz, with broad satellites $^1J(PtP)$ *ca.* 2 450 Hz, *i.e.* very similar to the yellow crystalline [{PtCl$_2$-

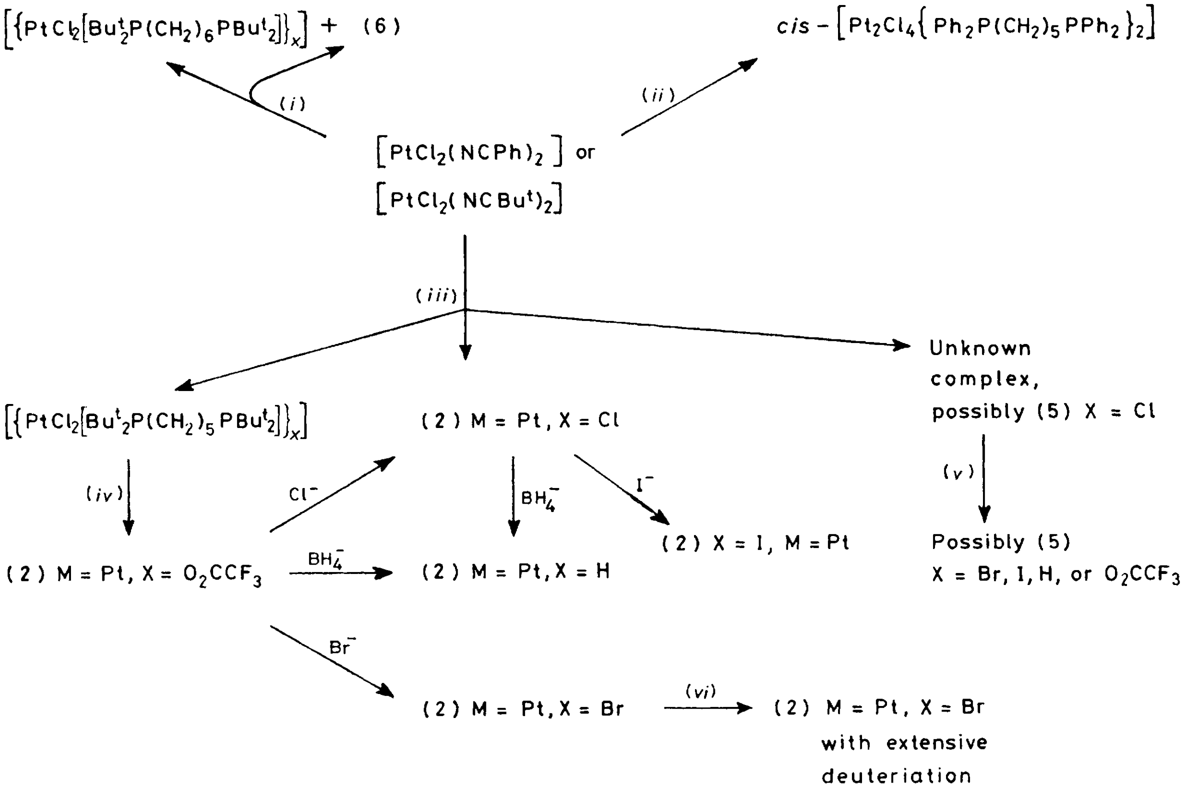
TABLE 3

Melting points,[a] microanalytical,[b] molecular-weight,[b,c] and spectroscopic data for the palladium and platinum complexes

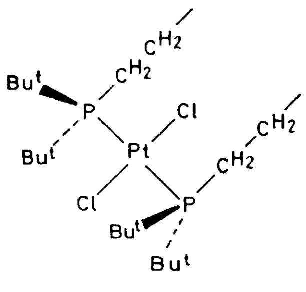
	M.p.	Microanalysis (%)				I.r.	N.m.r.		
	(θ_c/°C)	C	H	Halogen	M	(cm^{-1})[d] ν(Pd–Cl)	^1H[e] $\delta(Bu^t)$ (J)[g]	^{31}P[f] δ_P	
$[Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2]$									
n = 5	274—279s	47.1 (46.9)	8.75 (8.6)	12.75 (13.15)	1 089 (1 076)	346s	1.52 (t) (12.6)		
6	>270d	47.3 (47.6)	8.7 (8.7)	12.2 (12.9)	*h*	337s			
7	>250d	48.3 (48.8)	8.6 (8.85)	12.6 (12.5)	1 179 (1 130)	343s	1.50 (t) (13.6)	39.75	
8	278—280	48.8 (49.7)	8.9 (9.0)	12.6 (12.3)	1 202 (1 160)	348s	1.50 (t) (13.0)	41.3	
$[Pd_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$	245—248d	56.15 (56.4)	4.95 (4.9)	11.65 (11.5)	1 210 (1 234)	345s		16.5 26.6	
$[PdCl\{Bu^t{}_2P(CH_2)_2CH(CH_2)_2PBu^t{}_2\}]$	270—273s	50.55 (50.3)	9.0 (9.05)	7.2 (7.05)	505 (501)	256s	1.42 (t) (12.9)[i]	83.2	
						ν(Pt–Cl)	^1H $\delta(Bu^t)$ (J)[g]	^{31}P δ_P	$^1J(PtP)$
$[\{PtCl_2[Bu^t{}_2P(CH_2)_nPBu^t{}_2]\}_x]$									
n = 5	270—310d	40.35 (40.25)	7.25 (7.4)	11.1 (11.3)		332s	1.51 (t) (12.6)		
6	246—252	40.9 (41.25)	7.35 (7.55)	10.95 (11.05)		330s	1.53 (t) (12.7)		
cis-$[Pt_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$	245—250d	48.85 (49.35)	4.15 (4.3)	9.4 (10.0)	1 319 (1 412)	288s 310s		−1.9 7.3	3 547 3 540
$[PtX\{Bu^t{}_2P(CH_2)_2CH(CH_2)_2PBu^t{}_2\}]$									
X = Cl	253—262s	42.45 (42.75)	7.5 (7.7)	5.9 (6.0)	607 (590)	266s	1.42 (t) (12.9)	76.6	3 164
Br	288—291s	39.9 (39.8)	7.15 (7.15)	12.7 (12.6)	644 (634)		1.42 (t) (11)	75.1	3 156
I	315—325s	37.7 (37.1)	6.55 (6.65)	18.55 (18.6)	696 (682)		1.46 (t) (13.3)	73.3	3 128
O_2CCF_3	253—260d	42.8 (42.3)	7.2 (7.0)		699 (682)		1.32 (t) (14) 1.35 (t) (12)	80.4	3 239
H[j]	170—175	46.65 (45.4)	8.4 (8.3)		536 (555)[k]	ν(Pt–H) 1 875s	1.43 (t) (12) 1.38 (t) (12)	101.2	3 075
$[PtCl\{Bu^t{}_2P(CH_2)_2CH(CH_2)_3PBu^t{}_2\}]$[l]	198—235s (d)	44.05 (43.75)	7.6 (7.85)	5.95 (5.85)	618 (604)	256s	1.51 (d) (12.4) 1.39 (d) (12.4)	75.4 25.0	3 214 2 915
						Minor component, possibly (5) see Discussion			
						X = Cl		79.8	2 986
						Br		78.5	2 978
						I		76.8	2 846
						H[m]		103.2	2 997
						O_2CCF_3		84.1	3 061

[a] s = Sublimes, d = with decomposition. [b] Calculated values are given in parentheses. [c] Osmometrically in chloroform solution unless stated otherwise. [d] Nujol mulls. [e] At 60 MHz and 34 °C in $CDCl_3$; br = broad, t = 1 : 2 : 1 triplet. δ values ± 0.002, $J \pm 1$ Hz. [f] In $CDCl_3$ at *ca.* 25 °C. δ values ± 0.05, $J \pm 2$ Hz; shifts to high frequency are positive. [g] $^3J(PH) + {}^5J(PH)$. [h] Insufficiently soluble. [i] In C_6D_6 two triplets were observed: δ 1.33 (J 13) and 1.34 (J 13 Hz). [j] Proton spectrum at 220 MHz: δ_H (hydride) = −2.4, $^2J(PH)$ = 18 Hz, $^1J(PtH)$ = 762 Hz in C_6D_6 solution. [k] In benzene. [l] $^2J(PP)$ = 383 Hz. [m] δ_H (hydride) = −1.95 p.p.m., $^2J(PH)$ = 18 Hz, $^1J(PtH)$ = 762 Hz at 220 MHz.

$[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$. On heating the solution the peaks sharpened, *e.g.* at 330 K both the central (δ = 30.4 p.p.m.) and satellite peaks were sharp and narrow, whilst on cooling the broad central peak separated into three closely spaced sharp peaks (at 233 K) although the satellite peaks were not completely resolved [^1J(PtP) was *ca.* 2 450 Hz in each case]. We suggest that this glassy material was a mixture of open-chain species *trans*-$[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_y]$ and the behaviour at different temperatures is due to restricted rotation around the P–Pt bonds and the separation of rotamers containing the groupings (3) and (4) at low temperatures. Rotamer formation due to the high energy barrier to rotation in tertiary di-t-butylphosphine complexes is commonly observed.[5] The apparent molecular weight of the glassy material (in chloroform) was 1 104. We found that on adding 1 mol proportion of $Bu^t_2P(CH_2)_5PBu^t_2$ to a solution of $[PtCl_2(NCBu^t)_2]$ in C_6H_6–C_6D_6 at 296 K the ^{31}P resonance of the free phosphine disappeared after a few minutes. During this period two central resonances at δ = 30.1 and 28.8 with satellites ^1J(PtP) = 2 452 and 2 434 Hz respectively appeared. Evaporation of the solution gave glassy material similar to that described above. We suggest that the C_6H_6–C_6D_6 solution contained open-chain species with *trans*-phosphines similar to the material obtained but isolated in small amount from the 2-methoxyethanol or toluene solutions.



SCHEME Preparation and reactions of the platinum complexes. (*i*) $Bu^t_2P(CH_2)_6PBu^t_2$; (*ii*) $Ph_2P(CH_2)_5PPh_2$; (*iii*) $Bu^t_2P(CH_2)_5PBu^t_2$; (*iv*) CF_3CO_2H; (*v*) Br^-, I^-, $[BH_4]^-$ or, CF_3CO_2H; (*vi*) CF_3CO_2D, Br^-



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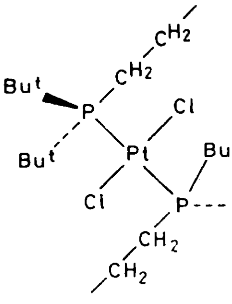


(4)

In addition to the yellow crystalline material, $[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$, and the glassy material obtained by prolonged heating of $Bu^t_2P(CH_2)_5PBu^t_2$ with $[PtCl_2(NCPh)_2]$, a colourless, highly crystalline, and readily soluble material was obtained. In one preparation this proved to be a pure compound which we established to be $[PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ (2; M = Pt, X = Cl) (see Experimental section and below). In all other preparations, however, the material was contaminated by a second component (10—20% of the whole) with very similar physical properties. Attempts at fractional crystallization, fractional sublimation under vacuum, or chromatography on silica gel failed to effect any separation. The second component was characterized by its ^{31}P n.m.r. pattern [δ_P = 79.8 p.p.m., ^1J(PtP) = 2 986 Hz] whilst (2; M = Pt, X = Cl) had

$\delta_P = 76.6$ [^1J(PtP) = 3 164 Hz]. The second component is discussed later in this paper. Fortunately, we discovered a reliable method of synthesizing pure cyclometallated complexes of the type $[\mathrm{PtX(Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2)}]$ (2; M = Pt, X = anion). Since mercury(II) carboxylates are much better at metallating a carbon atom than mercury(II) chloride, especially in the presence of a strong acid,[6] we reasoned that platinum(II) trifluoroacetates in trifluoroacetic acid solution might undergo metallation much better than platinum(II) chlorides. We therefore treated yellow crystalline $[\{\mathrm{PtCl_2[Bu^t{}_2P(CH_2)_5PBu^t{}_2]}\}_x]$ (above) with refluxing trifluoroacetic acid or a trifluoroacetic acid–chloroform (ethanol-free) mixture. This gave the trifluoroacetate complex (2; M = Pt, X = $\mathrm{O_2CCF_3}$) as white needles in excellent yield. The ^{31}P n.m.r. spectrum (data in Table 3) showed that the material was pure: the i.r. spectrum showed strong bands at 1 805 and 1 690 cm^{-1} [ν(C=O)] and a band at 1 200 cm^{-1} due to ν(C–F). Microanalytical, molecular-weight, and ^{1}H n.m.r. data (Table 3) are in agreement with the assigned structure. This trifluoroacetate complex when treated with either lithium chloride or lithium bromide in acetone gave the corresponding chloro- or bromo-complexes of configuration (2; X = Cl or Br). Moreover, the chloro-species was pure, identical to the product from one of the $\mathrm{Bu^t{}_2P(CH_2)_5PBu^t{}_2}$–$[\mathrm{PtCl_2(NCPh)_2}]$ reactions, and not contaminated with the minor component mentioned above. We therefore treated the mixture of chloro-species (2; M = Pt, X = Cl) containing *ca.* 20% of the unknown component {from the $[\mathrm{PtCl_2(NCPh)_2}]$–$\mathrm{Bu^t{}_2P(CH_2)_5PBu^t{}_2}$ reaction} with $\mathrm{CF_3CO_2H}$–$\mathrm{CHCl_3}$ (1 : 2 v/v) and found the trifluoroacetate product was mainly (*ca.* 80%) (2; M = Pt, X = $\mathrm{O_2CCF_3}$), $\delta_P = 80.4$ [^1J(PtP) = 3 238 Hz], but it was contaminated by *ca.* 20% of a component with $\delta_P = 84.1$ [^1J(PtP) = 3 061 Hz], which we could not remove by fractional crystallization. The pure chloro-complex (2; X = Cl) when heated under reflux for 2 d with sodium iodide in propan-2-ol gave the corresponding iodide (2; M = Pt, X = I). This was characterized by microanalytical, molecular-weight, and spectroscopic data (Table 3). Carbon-13 n.m.r. data and assignments for the chloro- and iodo-complexes (2; M = Pt, X = Cl or I) are given in Table 4. The contaminated chloro-complex (2; M = Pt, X = Cl) containing *ca.* 20% of the minor component when similarly treated with sodium iodide in propan-2-ol gave mainly the corresponding iodo-complex contaminated by *ca.* 20% of another (iodo-) complex $\delta_P = 76.8$ [^1J(PtP) = 2 846 Hz]. As before we could not separate this mixture by fractional crystallization, *etc.*

We also found that the pure chloro-complex (2; M = Pt, X = Cl) when treated with sodium tetrahydroborate in refluxing ethanol for 30 min gave an excellent (95%) yield of the hydrido-complex (2; X = H). The conversion was much faster when the more labile trifluoroacetate complex (2; M = Pt, X = $\mathrm{O_2CCF_3}$) was treated with $\mathrm{Na[BH_4]}$. The trifluoroacetate was also reduced to the hydride by treatment with a solution of sodium ethoxide in refluxing ethanol. The hydride complex, for which microanalytical and molecular-weight data are given in Table 3, showed a very low value for ν(Pt–H), *viz.* 1 865 cm^{-1}, due to the *trans*-bond-weakening effect of the σ-bonded carbon. The hydride resonance in the ^{1}H n.m.r. pattern was at relatively low field, δ = –2.4 with ^1J(PtH) only 762 Hz, again a consequence of the high *trans* influence of the σ-bonded carbon. We also found that the impure chloro-complex (2; X = Cl) containing *ca.* 20% of the minor component, when reduced by $\mathrm{Na[BH_4]}$ gave predominantly the hydrido-complex (2; X = H) containing *ca.* 20% of another hydride species. As before we could not separate this mixture by fractional crystallization. This minor component showed a hydride resonance at

TABLE 4

Carbon-13 n.m.r. data [a] for some internally metallated complexes of the type $[\mathrm{PtX\{Bu^t{}_2P(CH_2)_2CH(CH_2)_2PBu^t{}_2\}}]$, configuration (2)

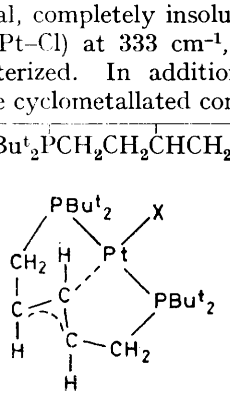
X	δ	Assignment	J(PC)	J(PtC)
Cl	40.96 (s)	$\mathrm{P{-}CH_2{-}CH_2{-}}\underset{\underset{\mathrm{Pt}}{\mid}}{C}\mathrm{H}$	0	^1J(PtC) = 732
	39.92 (t)	P–CH$_2$–*C*H$_2$–CH	|^2J(PC) + ^4J(PC)| = 13	^2J(PtC) = 25.5
	36.48 (t)	P–*C*–(CH$_3$)$_3$	|^1J(PC) + ^3J(PC)| = 25.5	*b*
	35.37 (t)	P–*C*–(CH$_3$)$_3$	|^1J(PC) + ^3J(PC)| = 23	*b*
	29.65 (s)	P–C–(*C*H$_3$)$_3$	0	0
	29.32 (s)	P–C–(*C*H$_3$)$_3$	0	0
	24.77 (t)	P–*C*H$_2$	|^1J(PC) + ^3J(PC)| = 25.5	^2J(PtC) = 77.5
I	51.23 (s)	$\mathrm{P{-}CH_2{-}CH_2{-}}\underset{\underset{\mathrm{Pt}}{\mid}}{C}\mathrm{H}$	0	^1J(PtC) = 731
	39.79 (t)	P–CH$_2$–*C*H$_2$–CH	|^2J(PC) + ^4J(PC)| = 10.5	^2J(PtC) = 31.0
	36.93 (t)	P–*C*–(CH$_3$)$_3$	|^1J(PC) + ^3J(PC)| = 20.5	^2J(PtC) = 10.5
	36.15 (t)	P–*C*–(CH$_3$)$_3$	|^1J(PC) + ^3J(PC)| = 24.5	^2J(PtC) = 10.5
	30.62 (s)	P–C–(*C*H$_3$)$_3$	0	0
	29.75 (s)	P–C–(*C*H$_3$)$_3$	0	0
	25.62 (t)	P–*C*H$_2$	|^1J(PC) + ^3J(PC)| = 25.0	^2J(PtC) = 75.5

[a] Spectra recorded at ambient temperature and 22.62 MHz in CDCl$_3$ solution. Shifts are relative to SiMe$_4$ as internal standard (with decreasing field taken as being positive). δ values ±0.1, J values ±1.5 Hz. s = Singlet, t = triplet. [b] Satellites due to ^{195}Pt were obscured and ^2J(PtC) not measurable.

δ = 1.95 with ^2J(PH) = 18 Hz and ^1J(PtP) = 762 Hz, *i.e.* exactly the same coupling constants as the major component.

Thus we prepared pure samples of complexes of the type [$PtX(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$] (2) with X = Cl, Br, I, O_2CCF_3, or H and contaminated samples for which the minor component (10—20%) always showed a phosphorus resonance at lower field than the corresponding (2) with a smaller value for ^1J(PtP), see data in Table 3. In no case, *i.e.* with X = Cl, Br, I, O_2CCF_3, or H, could we separate or even alter the relative proportions of the mixtures by fractional crystallization, sublimation, chromatography, *etc.* Also the pure complex [$PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$] was recovered unchanged after being refluxed for several days in ethanol, *i.e.* none of the minor component was produced. The yellow poly-(bi-?) nuclear complex [$\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x$] gave no metallated complexes and was recovered unchanged after being refluxed for several days in 2-methoxyethanol. Thus the minor components were not identified but are clearly isomorphous and closely similar to the complexes of type [$PtX(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$]. We tentatively suggest that they are π-allylic complexes of type [$PtX(Bu^t_2PCH_2CH{\cdots}CH{\cdots}CHCH_2PBu^t_2)$] (5). If this is correct then the chloro-complex, tentatively formulated as [$PtCl(Bu^t_2PCH_2CH{\cdots}CH{\cdots}CHCH_2PBu^t_2)$], is produced in small amount by a cyclometallation and dehydrogenation reaction when [$PtCl_2(NCPh)_2$] is heated with $Bu^t_2P(CH_2)_5PBu^t_2$ in 2-methoxyethanol or toluene for prolonged periods.

We also treated [$PtCl_2(NCPh)_2$] with the hexamethylene diphosphine, $Bu^t_2P(CH_2)_6PBu^t_2$, for a prolonged period in refluxing 2-methoxyethanol. This gave a yellow crystalline material *trans*-[$\{PtCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x$] slightly soluble in chloroform but insufficiently so for a molecular-weight measurement. Another yellow material, completely insoluble in chloroform and which had υ(Pt–Cl) at 333 cm^{-1}, was also produced but not characterized. In addition a colourless, soluble, and volatile cyclometallated complex [$PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2CH_2PBu^t_2)$] (6) was formed in which the tridentate ligand has fused five- and six-membered rings. The microanalytical and molecular-weight data are given in Table 3. The ^{31}P n.m.r. spectrum (data in Table 3) showed an *AB* pattern with ^2J(PP) = 383 Hz typical of *trans*-phosphorus donor atoms together with satellites due to platinum-195 coupling. The ^{1}H n.m.r. pattern showed two t-butyl doublets. ν(Pt–Cl) occurred at 256s cm^{-1}, typical of a *trans* σ-bonded carbon. In the corresponding treatment of $Bu^t_2P(CH_2)_6PBu^t_2$ with [$PdCl_2(NCPh)_2$] no cyclometallated complex could be detected. These results illustrate the greater tendency for platinum to metallate tertiary phosphines.



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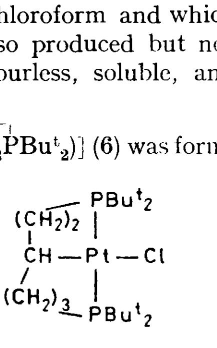


(6)

By heating a mixture of *trans*-[$PtCl_2(NCBu^t)_2$] and $Ph_2P(CH_2)_5PPh_2$ in refluxing 2-methoxyethanol for 16 h a cream microcrystalline solid was isolated which was deduced to be *cis*-[$Pt_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2$] on the basis of the evidence presented in Table 3.

Deuteriation and Mass-spectral Studies.—As discussed above, cycloplatination of $Bu^t_2P(CH_2)_5PBu^t_2$ occurred readily in CF_3CO_2H or CF_3CO_2H–$CHCl_3$. We thought it possible that under these highly acidic conditions some reversible fission of the platinum–carbon bond by protonation might be occurring. We therefore heated [$PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$] with CF_3CO_2D in $CDCl_3$ (ethanol free) for 2 d but found no incorporation of deuterium (i.r. evidence) in the complex. However, we found that the corresponding bromo-complex [$PtBr(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$] (2) when refluxed in CF_3CO_2D–$CDCl_3$ (1 : 2 v/v) for 2 d followed by metathesis with LiBr in acetone gave the partially deuteriated bromo-complex with several i.r. absorptions of medium intensity due to ν(C–D) in the region 2 100—2 200 cm^{-1}. The mass spectra of the undeuteriated and deuteriated complexes [$PtBr(C_{21}H_{45-x}D_xP_2)$] shows that (*i*) deuteriation has occurred both in the t-butyl groups and in the methylene chain and (*ii*) several deuteriums per molecule are incorporated in a typical product. The undeuteriated bromo-complex [$PtBr(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)$] showed a parent molecular ion at *m/e* 632—637 with the most intense peak at *m/e* = 634, as expected. Another group of peaks at *m/e* 552—555 [M − Br]$^+$, and also groups due to successive loss of one, two, three, and finally four C_4H_8 groups, could readily be seen *e.g.* a group of peaks at *m/e* 323—327 due to [$M - Br - 4(C_4H_8)$]$^+$ with the most intense at 325. In the partially deuteriated complex [$PtBr(C_{21}H_{45-x}D_xP_2)$] the parent ion occurred at *m/e* = 632—654, [M − Br]$^+$ at *m/e* = 554—576, and strong groups of peaks due to successive loss of four partially deuteriated $C_4H_{8-n}D_n$ fragments could also be observed, *e.g.* the group of peaks due to [$M - Br - 4(C_4H_{8-n}D_n)$] occurred at *m/e* = 322—333 with the most intense at 329. This suggests that deuteriation of the methylene chain had also occurred.

We also refluxed [$\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x$] with a mixture of LiCl, CF_3CO_2D, and $CDCl_3$ for 1 d followed by metathesis with LiCl in acetone after removal of the CF_3CO_2D-$CDCl_3$ mixture. No deuterium was incorporated into the resulting cyclometallated product. In contrast, replacement of LiCl by LiBr in this experiment caused extensive deuteriation (i.r. and mass spectral evidence). We cannot explain the remarkable difference between the behaviour of bromo- and chloro-systems. Possibly halogeno-bridged intermediate complexes are necessary for the deuteriation and bromide is a better bridging ligand than chloride. It is also possible that bromine radicals are involved. Masters [7,8] has shown that chloro-bridged complexes of the type *sym-trans*-[$Pt_2Cl_4L_2$] where L = $PPr^n{}_3$, $PBu^t{}_3$, $PPr^nBu^t{}_2$, $PBu^t{}_2Bu^n$, PBu^tPh_2, *etc.* undergo hydrogen–deuterium exchange in boiling D_2O–CH_3CO_2D containing $HClO_4$. There have been several other studies [9–11] involving chloroplatinum complexes as catalysts for promoting hydrogen–deuterium exchange: generally the rates of exchange are very low. In view of our results bromo- and possibly iodo-platinum complexes would be worth investigating and might lead to considerably faster exchange.

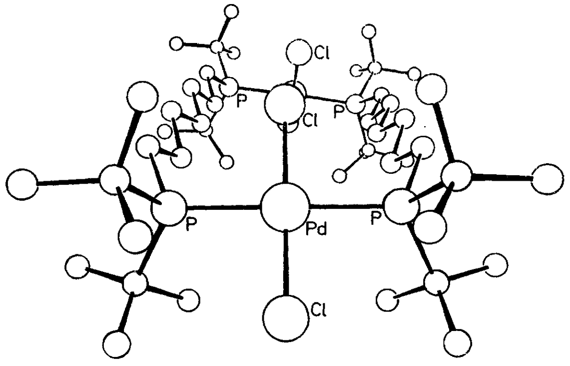
Factors affecting the Stability of Complexes of the Type trans-[$M_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2$] (M = Pd *or* Pt) *and Other Large-ring Chelates.*—In addition to our own work a variety of large-ring chelate complexes using flexible bidentate ligands has been described.[12–19] There are also many examples where long-chain flexible bidentate ligands preferentially give open-chain (polynuclear) rather than large-ring chelate complexes.[1,20–28] It would appear therefore that sometimes a large chelate ring is favoured and sometimes open-chain polymers are preferred and that the free-energy difference between the two possibilities is not large. A similar situation often occurs with large organic rings and their corresponding open-chain precursors (isomers). Interestingly the yields of large ring cobalt(III) chelates with α,ω-diamines $H_2N(CH_2)_nNH_2$ described by Ogino and Fujita [28] pass through a minimum (almost zero) for ten-membered rings but increase again and maximize for fifteen-membered rings, *i.e.* with $H_2N(CH_2)_{12}NH_2$. As they point out, these effects of ring size on yields are strikingly similar to those obtained by Ruzicka *et al.*[29] and by Ziegler and co-workers [30,31] for large-ring ketones (by the Thorpe–Ziegler reaction) and they explained them in a similar way (*i.e.* ring-strain and entropy factors).

Examples where large-chelate-ring complexes dissociate in solution include [$Rh_2Cl_2(CO)_2(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)_2$] [17] and *trans*-[$PtCl_2\{CH_2{=}CH(CH_2)_nC(O)O(CH_2)_3C_5H_2Me_2N\}$],[15] but for the most of the large-ring chelate complexes reported in the literature there is little or no information as to what is present in their solutions. Species such as *trans*-[$PdCl_2\{Me_2As(CH_2)_{12}AsMe_2\}$], *trans*-[$MX_2\{Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2\}$], and *trans*-[$MX_2\{PhS(CH_2)_{12}SPh\}$] appear to be stable (molecular weight measurements) but can take weeks or months to crystallize out,[12–14] which suggests the presence of many conformers in solution. None of these large-ring chelates has been subjected to the prolonged stability tests to which our complexes have been subjected. Thus ^{31}P n.m.r. spectroscopy shows that, in solution, complexes of the type *trans*-[$Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2$] (*n* = 5, 7, or 10) do not change over several days or weeks. We have also found that they can be recovered unchanged even after boiling in solvents such as 2-methoxyethanol (b.p. 124 °C) or toluene for 12 h. A ^{31}P n.m.r. study [32] has shown that the mononuclear platinum complex *trans*-[$PtCl_2\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}$] [1] when heated in xylene at 135 °C gradually equilibrates with the binuclear species *trans*-[$Pt_2Cl_4\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}_2$] [1] but that there is no evidence for the formation of other phosphine-containing species, such as open-chain compounds, even after 1 month at 135 °C. Similarly, the binuclear species when heated equilibrates with the mononuclear species. Thus we believe that our large-ring chelates containing several bulky $PBu^t{}_2$ groups show a special stability. The question arises as to why these bulky groups confer stability on ring systems relative to open-chain structures. Examination of the literature in different areas of organic chemistry reveals that sterically demanding substituents suitably positioned confer stability on ring systems. The effect is mainly a function of bond lengths, bond angles, torsion angles, and atomic sizes *and therefore it must apply generally*, i.e. *to both organic and inorganic* (*including chelate*) *ring systems*. This is certainly not widely known nor appreciated and because of this we give a brief survey of some areas to which it has been applied before discussing our large chelate compounds.

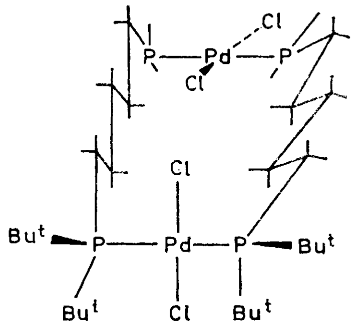
The observation of the effect of substituents on ring stability dates back to the Thorpe–Ingold or *gem*-dimethyl effect (1915).[33–36] There are innumerable examples of methyl and other substituents promoting the formation of carbocyclic and heterocyclic rings [35,36] and apparently no examples are known where one would expect it to apply and where it does not. Early examples were with small rings but more recently substituents have been shown to promote the formation of and stabilize large and medium rings. A feature is that the methyl substituent(s) occupy ' corner ' positions on the ring.[37–40] A convincing explanation for the Thorpe–Ingold effect was not forthcoming for over 40 years but in 1956 Hammond [41] explained it in terms of changes in rotational entropy which occur on cyclization. This was extended and quantified by Allinger and Zalkow [42] who showed that there was also a favourable enthalpy (conformational or torsion-angle effect). Similar entropy and enthalpy effects have been used by Dainton and co-workers [43,44] to explain the effect of methyl substituents in stabilizing cyclic compounds relative to open-chain polymers. Good illustrations of the importance of substituents in stabilizing large rings including dramatic increases in conformational stability (homogeneity) are also to be found in the area of cyclic peptides, depsipeptides, *etc.*[45] Thus the cyclic oligomers of *N*-methylglycine (sarcosine) of the type [$N(Me)CH_2CO$]$_n$ (*n* = 2—8) have remarkable conformational stability in contrast with cyclic oligomers of glycine, as shown by Dale and other workers.[46–48] Two features of naturally occurring cyclic peptides or depsipeptides are (*i*) that valyl, leucyl, and isoleucyl residues are common, these amino-acids carrying the bulky groups isopropyl, isobutyl, and sec-butyl, respectively, and (*ii*) both L and D configurations are present. Naturally occurring open-chain peptides only have L residues but the presence of both L and D configurations in the cyclic compounds allows the bulky substituents to be more suitably positioned around the rings. There are several illustrations of this: one is the crystal structure of the enniatin–potassium iodide complex which has six isopropyl groups suitably positioned around the 18-atom ring. Low-temperature n.m.r. spectroscopy has established that the conformation of the free depsipeptide is similar to that in the potassium complex.[47,49,50] There are many examples where the configurational sequence of amino-acids in oligopeptides (and of hydroxy-acids in depsipeptides) has a profound effect on cyclization yields, *i.e.* a mixture of L and D forms always gives a greater yield than L or D alone.[45]

The effects of substituents on the synthetic yield, stability, and conformational homogeneity of many-membered rings has also been discussed in Dale's review [45] and in more recent papers.[2,51] Much is also known about the effect of heteroatoms (oxygen and nitrogen) and of functional groups on the stability and synthetic yield of large rings, and has been explained in a similar way.[38,45]

The structure of the 20-atom ring complex $[Pd_2Cl_4\{Bu^t_2P(CH_2)_7PBu^t_2\}_2]$ has been determined accurately by Dr. W. S. McDonald of this Department [4] and is shown in the Figure. The structure of the pentamethylene complex $[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ has also been determined but less accurately since the crystal decomposed somewhat in the X-ray beam and there was a disorder problem. The structure was determined sufficiently accurately to show that it is analogous to the heptamethylene complex shown in the Figure.[4] The structure is shown diagrammatically in (7). Bond angles and bond lengths are normal for both structures. The polymethylene chains are in the extended conformation and the torsion angles of all the $Pd-P-CH_2-CH_2$ groupings lie within the range 56—60° as shown in the Newman projection (8). Space-filling molecular models suggest that this is the preferred conformation, *i.e.* Bu^t is more sterically demanding that $PdCl_2$. Such models also show that in the structures in the Figure and (7) the Cl–Pd–Cl groups are in favourable arrangements with respect to the $Bu^t_2PCH_2CH_2CH_2$ moieties. One chlorine is approximately *gauche* with respect to the two sets of PBu^t_2 groups, which are eclipsed. The other chlorine lies in the gap above the two inward-pointing pseudo-equatorial hydrogens of the β-methylene groups. This arrangement also occurs in the other structures of large-ring complexes containing PBu^t_2 groups at the corners.[1,2] Thus we suggest that an open-chain precursor $Bu^t_2P(CH_2)_nPBu^t_2PdCl_2Bu^t_2P(CH_2)_nPBu^t_2PdCl_2(NCPh)$ will have a preferred conformation closely similar to those of the two large-ring chelate compounds in the Figure and (7) and that ring closure will not introduce additional torsional strain. This would not be the case with less bulky end groups, *e.g.* Me_2P. One would expect the preferred conformation of a $-Pd-PMe_2-CH_2-CH_2-$ moiety to be transoid as shown in (9) and therefore ring formation would introduce some torsional strain. It is difficult to predict the behaviour of PPh_2 end groups because of the planarity of the phenyl group but one would anticipate the steric effect to be between those of PBu^t_2 and PMe_2. Strong steric interaction between bulky t-butyl groups and the chlorines and methylenes will restrict rotation in the open-chain precursor (above) and therefore the loss of internal rotational entropy, which occurs in cyclization, will be reduced, as suggested by Hammond [41] and Allinger [42] to explain the Thorpe–Ingold effect, by Dainton and co-workers [43,44] to explain the effect of methyl substituents on cyclic monomer–polymer equilibria, and by one of us to partly explain the effect of bulky substituents on cyclometallation.[2] Translational-entropy and external rotational-entropy effects in solution generally favour cyclization since the open-chain precursor is less free to move through the solvent than the cyclic product.



ORTEP drawing of the structure of the 20-atom ring complex $[Pd_2Cl_4\{Bu^t_2P(CH_2)_7PBu^t_2\}_2]$ kindly supplied by Dr. W. S. McDonald of this department. A small packing effect causes one P–Pd–P to be inclined 9° to the other



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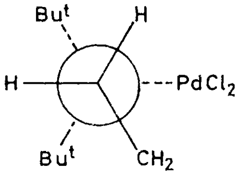

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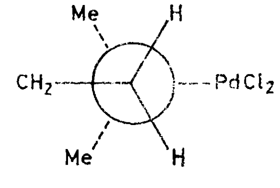

(9)

The ligands $Bu^t_2P(CH_2)_nPBu^t_2$ with an even number of methylene groups ($n = 6$, 8, or 10) cannot form strain-free large-ring binuclear complexes of the type $[Pd_2Cl_4\{Bu^t_2P(CH_2)_nPBu^t_2\}_2]$. We have published the crystal structure of the 26-atom-ring decamethylene complex ($n = 10$).[1] The two $[PdCl_2(Bu^t_2PCH_2CH_2CH_2-)_2]$ moieties at the near and far sides of the ring are virtually the same as in the heptamethylene and pentamethylene complexes except for a centre of inversion rather than a mirror plane, but the central portions of the decamethylene chains are twisted with torsion angles differing markedly from 180°.

In conclusion we make the general suggestion that factors which stabilize large organic rings such as suitably positioned sterically demanding substituents, heteroatoms (–O–, –NH–, or –S–), double and triple bonds should also stabilize large chelate rings. Moreover these factors would sometimes increase the conformational homogeneity and ease of crystallization and therefore ease of isolation of the large-ring cyclic compound. Some large chelate-ringed compounds have taken weeks or months to crystallize.[13,14] The relationships between these various effects in organic rings have been discussed by Dale [38,45,52] and should also apply to chelate rings.

EXPERIMENTAL

The general preparative and spectroscopic techniques were the same as those described in other recent papers from this laboratory.[53]

Preparation of the Diphosphines.—1,7-*Bis(di-t-butylphosphonio)heptane dibromide and other phosphonium salts.* Di-t-butylphosphine (6.18 g, 42.3 mmol) was added to a solution of 1,7-dibromoheptane (5.47 g, 21.2 mmol) in isobutyl methyl ketone (3.2 cm^3) and the mixture heated under reflux for 8 h, then cooled and the product (10.0 g, 85%) isolated as prisms.

The other phosphonium salts were made similarly. The pentamethylene complex was very hygroscopic and, for characterization purposes, a portion was treated with an excess of ammonium hexafluorophosphate in methanol. This gave a precipitate of $[HPBu^t_2(CH_2)_5HPBu^t_2][PF_6]_2$ as prisms, which were much less hygroscopic than the dibromide and analyzed correctly for carbon and hydrogen (Table 1).

1,7-*Bis(di-t-butylphosphino)heptane.* A solution of 1,7-bis(di-t-butylphosphonio)heptane dibromide (10.0 g, 18.2 mmol) in degassed water (28 cm^3) and under a layer of diethyl ether (18 cm^3) was treated with a saturated solution of sodium hydroxide (7.3 g, 182 mmol) in water. The product was isolated with ether and distilled, b.p. 160—170 °C (0.01 mmHg), yield 5.77 g (72%). N.m.r. spectra: ^1H in $CDCl_3$, $\delta(Bu^t)$ 1.14, $^3J(PH) = 10.7$ Hz; ^{31}P in CH_2Cl_2, $\delta(H_3PO_4) = 27.9$ p.p.m.

The pentamethylene and hexamethylene diphosphines were made similarly. 1,5-Bis(di-t-butylphosphino)pentane: b.p. 149—153 °C (0.01 mmHg); ^1H n.m.r. in $CDCl_3$, $\delta(Bu^t)$ 1.13 p.p.m., $^3J(PH) = 11.1$ Hz; ^{31}P n.m.r. in CH_2Cl_2, $\delta(H_3PO_4) = 27.8$ p.p.m. 1,6-Bis(di-t-butylphosphino)hexane: b.p. 155—160 °C (0.008 mmHg); ^1H n.m.r. in $CDCl_3$, $\delta(Bu^t)$ 1.13 p.p.m., $^3J(PH) = 10.8$ Hz; ^{31}P n.m.r., $\delta(H_3PO_4) = 28.2$ p.p.m.

1,5-*Bis(di-t-butylphosphino)pentane* (*method* 2). 1,5-Dibromopentane (14.4 g, 63 mmol) in diethyl ether (50 cm^3) was added dropwise to a suspension of lithium flakes (1.75 g, 250 mmol) in diethyl ether (75 cm^3) at *ca.* −20 °C over 2 h. The resulting mixture was stirred at *ca.* 20 °C for 18 h and then a solution of PBu^t_2Cl (20.9 g, 116 mmol) in diethyl ether (10 cm^3) added dropwise with stirring over 20 min. The mixture was stirred for another hour and benzene (30 cm^3) and water (65 cm^3) added. The product was separated from the organic layer by distillation, yield 8.6 g (24 mmol, 41%).

1,5-*Bis(diphenylphosphino)pentane.* A solution of 1,5-dilithiopentane (93 mmol) in diethyl ether (210 cm^3), prepared as described above, was treated dropwise with PPh_2Cl (38.9 g, 177 mmol), with stirring at 0 °C over 0.5 h. Benzene (50 cm^3) and water (100 cm^3) were then added and the product isolated by distillation, b.p. 180—200 °C (10^{-3} mmHg), yield 17.6 g (40 mmol, 43%).

The Action of $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[PdCl_2(NCPh)_2]$.—A mixture of $[PdCl_2(NCPh)_2]$ (1.67 g, 4.36 mmol) and $Bu^t_2(CH_2)_5PBu^t_2$ (1.58 g, 4.36 mmol) in ethanol (50 cm^3) was heated under reflux for 18 h. The resulting mixture was cooled to give ***trans***-di-μ-[1,5-bis(di-t-butylphosphino)pentane]-tetrachlorodipalladium(II) (1.46 g, 1.35 mmol, 62%) as yellow plates, from chloroform–light petroleum (b.p. 60—80 °C). This was converted into the cyclometallated complex (below) when heated above 260 °C without melting. Evaporation of the ethanolic mother liquor and trituration with methanol gave [1,5-bis(di-t-butylphosphino)pentan-3-yl-*CPP′*]chloropalladium(II) as colourless plates, m.p. 270—273 °C, with sublimation, yield 0.26 g (0.52 mmol, 12%) from light petroleum (b.p. 60—80 °C).

trans-$[\{PdCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x]$.—The compound $[PdCl_2(NCPh)_2]$ (0.84 g, 2.18 mmol) was added to a solution of $Bu^t_2P(CH_2)_6$ PBu^t_2 (0.82 g, 2.18 mmol) in benzene (25 cm^3). The resulting mixture was refluxed for 20 h, cooled, and the yellow microcrystalline precipitate collected, washed with benzene, and dried. The product decomposes without melting at >270 °C; yield 0.96 g (76%).

trans-*Di-μ-[1,7-bis(di-t-butylphosphino)heptane]-tetrachlorodipalladium*(II).—A mixture of $[PdCl_2(NCPh)_2]$ (0.54 g, 1.41 mmol) and $Bu^t_2P(CH_2)_7PBu^t_2$ (0.55 g, 1.41 mmol) in ethanol (15 cm^3) was refluxed for 19 h. The resulting dark precipitate was collected, extracted with dichloromethane, and the solution filtered through Fluorosil. The extract was concentrated by evaporation and ethanol added to give the required complex as yellow prisms, which decomposed at >250 °C, yield 0.79 g (0.51 mmol, 36%). trans-*Di-μ-[1,8-bis(di-t-butylphosphino)octane]-tetrachlorodipalladium*(II) was prepared and isolated in a similar manner as yellow microprisms, m.p. 278—280 °C, yield 56%.

Di-μ-[1,5-bis(diphenylphosphino)pentane]-tetrachlorodipalladium(II).—A mixture of $[PdCl_2(NCPh)_2]$ (0.84 g, 2.2 mmol) and $Ph_2P(CH_2)_5PPh_2$ (0.96 g, 2.2 mmol) in ethanol (25 cm^3) was refluxed for 16 h. The yellow precipitate which formed was accompanied by much palladium metal. The required complex was isolated with dichloromethane and formed yellow needes, m.p. 245—248 °C with decomposition, from dichloromethane–methanol. Yield 0.32 g (0.51 mmol, 24%).

The Action of $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[PtCl_2(NCPh)_2]$.—A suspension of *trans*-bis(benzonitrile)dichloroplatinum(II) (2.64 g, 5.6 mmol) in 2-methoxyethanol (75 cm^3) was treated with the diphosphine (2.09 g, 5.6 mmol) and the mixture heated under reflux for 20 h, then cooled to room temperature. The solids were filtered off and extracted with light petroleum (b.p. 60—80 °C) which when evaporated to dryness gave a pale yellow glass (*ca.* 0.2 g), material A (see Discussion). The residue was recrystallized from chloroform–ethanol to give *trans*-$[\{PtCl_2[Bu^t_2(CH_2)_5PBu^t_2]\}_x]$ (1.57 g, 45%). The 2-methoxyethanol mother liquor was evaporated to dryness and the residue recrystallized from light petroleum (b.p. 60—80 °C) to give material B (0.96 g) as colourless needles which were mainly [1,5-bis(di-t-butylphosphino)pentan-3-yl-*CPP'*]chloroplatinum(II), see Discussion.

The compounds *trans*-$[\{PtCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x]$, as yellow prisms from chloroform–ethanol (yield 50%), and $[PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2CH_2PBu^t_2)]$ (6), as colourless plates from light petroleum (b.p. 60—80 °C) (yield 11%), were prepared in an analogous manner by the action of $Bu^t_2P(CH_2)_6PBu^t_2$ on $[PtCl_2(NCPh)_2]$ in 2-methoxyethanol. A small amount of yellow material, totally insoluble in chloroform but with an i.r. spectrum (200—4 000 cm^{-1}) very similar to that of *trans*-$[\{PdCl_2[Bu^t_2P(CH_2)_6PBu^t_2]\}_x]$, was also obtained.

Action of Trifluoroacetic Acid on trans-$[\{PtCl_2[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$.—A suspension of the platinum complex (1.0 g) in a mixture of ethanol-free chloroform (10 cm^3) and trifluoroacetic acid (5 cm^3) was heated under reflux for 2 d. The resulting solution was evaporated to dryness and the residue recrystallized from acetone. This gave [1,5-bis(di-t-butylphosphino)pentan-3-yl-*CPP'*]trifluoroacetatoplatinum(II) as white needles (0.97 g, 1.5 mmol, 86%), m.p. 269—275 °C with decomposition.

$[PtBr\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$ (2; X = Br).—A solution of the corresponding trifluoroacetate (0.80 g, 1.12 mmol) and lithium bromide (0.80 g, 11 mmol) in acetone (40 cm^3) was heated under reflux for 1 h. The solution was then evaporated, and the residue washed with water and recrystallized from light petroleum (b.p. 60—80 °C) to give the required product as colourless plates (0.64 g, 1.00 mmol, 84%), m.p. 288—291 °C with sublimation. The compound $[PtCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$ (2; X = Cl) was made similarly, by treating $[Pt(O_2CCF_3)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$ with LiCl, as colourless needles (yield 90%) from light petroleum (b.p. 60—80 °C), m.p. 253—262 °C with sublimation.

$[PtI\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$ (2; X = I).—A suspension of the corresponding chloro-complex (0.15 g, 0.25 mmol) and sodium iodide (0.38 g, 2.5 mmol) in propan-2-ol (6 cm^3) was heated under reflux for 2 d. Isolation gave the required product as colourless plates (0.15 g, 0.22 mmol, 88%) from light petroleum (b.p. 60—80 °C), m.p. 315—325 °C (with sublimation).

cis-$[Pt_2Cl_4\{Ph_2P(CH_2)_5PPh_2\}_2]$.—A mixture of the diphosphine (0.73 g, 1.7 mmol) and *trans*-$[PtCl_2(NCBu^t)_2]$ (0.79 g, 1.7 mmol) in 2-methoxyethanol (25 cm^3) was refluxed for 16 h. The mixture was evaporated to dryness and the product recrystallized from chloroform–ethanol as white prisms, yield 74%; m.p. 245—250 °C (decomp.).

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