Transition Metal–Carbon Bonds. Part XXXVI.[1] Internal Metallations of Platinum–Dimethyl(1-naphthyl)phosphine and –Dimethyl(1-naphthyl)-arsine Complexes and Attempts to effect Similar Reactions with Palladium †

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A number of complexes of the types $[MX_2\{EMe_2(1\text{-naphthyl})\}_2]$ (M = Pt or Pd; X = Cl, I, or Me; E = P or As, are described). The platinum halide complexes showed no tendency to undergo internal metallation reactions even on prolonged heating but the methyl analogues (X = Me) readily evolved methane on pyrolysis to give complexes in which the naphthyl group had been metallated in the 8- (*peri*-) position. In the presence of sodium acetate, however, the platinum halide complexes readily give metallated derivatives, *e.g. cis*- or *trans*-$[PtCl_2L_2]$ ($L = PMe_2C_{10}H_7$) gives [PtCl(P–C)L] where (P–C) ≡ the *peri*-metallated phosphine (L). We were unable to metallate the palladium complexes, either decomposition occurred or starting material was recovered. ^1H N.m.r. data are given. The resonances of protons at positions 2 and 3 for complexes of types *cis*-$[MX_2(EMe_2C_{10}H_7)_2]$ absorb at abnormally high τ-values (3—4); an explanation for which is given.

We have shown that bulky substituents on a tertiary phosphine ligand promote internal metallation by platinum(II) or palladium(II) [2-5] to give chelate systems. Ligands readily metallated in this way include PBu^t_2(*o*-tolyl), PBu^t_2(*o*-ethylphenyl), PBu^t_2(*o*-isopropylphenyl), PPh_2(*o*-tolyl), PBu^t_2Ph, and $PBu^t_2Pr^n$. We have also shown that the *peri*-position of PMe_2(1-naphthyl) is readily metallated by iridium(III) in octahedral systems. PMe_2(1-naphthyl) is not particularly bulky but six-co-ordinate octahedral iridium(II) complexes are crowded and this might promote the metallation. It was of interest therefore to see if dimethyl(1-naphthyl)phosphine or dimethyl(1-naphthyl)arsine ligands could be metallated by platinum(II) or palladium(II) in the less sterically demanding four-co-ordinate complexes.

RESULTS AND DISCUSSION

For convenience the various reactions of the dimethyl-(1-naphthyl)phosphine (L)–platinum system have been outlined in Scheme 1. Scheme 2 similarly outlines the dimethyl(1-naphthyl)arsine (Q)–platinum conversions.

$[PtCl_2(PhCN)_2]$ reacts with L to give a mixture of *cis*- and *trans*-$[PtCl_2L_2]$. The structures of these two compounds follow from the analytical and ^1H n.m.r. data, Tables 1 and 2. The unusual shielding effects with some of the naphthyl protons in the *cis*-complex are discussed below. Metathesis of *cis*-$[PtCl_2L_2]$ with sodium iodide gives *trans*-$[PtI_2L_2]$. Although *mer*-$[IrCl_3L_3]$ gives $[IrCl_2(P\text{–}C)L_2]$ very readily {P–C ≡ L metalled in the 8- or *peri*-position}, the complexes *cis*- or *trans*-$[PtCl_2L_2]$ evolved no gas on melting and were recovered unchanged after several days' reflux in 2-methoxyethanol. With iridium(III) halide–PMe_2(1-naphthyl) complexes metallation is promoted by sodium acetate [5] and we now find that sodium acetate similarly promotes metallation in *cis*- or *trans*-$[PtCl_2L_2]$ for after 1 hour's reflux in 2-methoxyethanol containing sodium acetate the metallated complex *cis*-[PtCl(P–C)L] is formed in *ca.* 85% yield. This *cis*-stereochemistry follows from the ^{31}P n.m.r. spectrum in CH_2Cl_2 with J(PP) only 14 Hz, and δ-values of $-11{\cdot}0$ and $+12{\cdot}5$ relative to 85% H_3PO_4. The high value of ν(PtCl) (305 cm^{-1}) is in agreement with Cl being trans to P. Metathesis gives the corresponding iodide as a *cis-/trans*-mixture (n.m.r. evidence). [PtCl(P–C)L] was formed from $[PtCl_2L_2]$ in a variety of ways: by heating *cis*-$[PtCl_2L_2]$ under reflux in 2-methoxyethanol containing sodium hydroxide (1 equivalent) for 1 h. This gave a complex mixture with [PtCl(P–C)L] as the major component (from ^1H n.m.r. evidence). When the *cis*-dichloride was heated under reflux in 2-methoxyethanol containing an excess of hydrazine hydrate for 1 h it gave inseparable mixtures which probably contained hydrides {ν(PtH) 2065 and 2190 cm^{-1}} along with some of the metallated complex [PtCl(P–C)L] (n.m.r. evidence). After 4 h at reflux only a trace of the hydrides remained and the major product was [PtCl(P–C)L]: several other minor products were present, however, and we were unable to isolate the metallated complex. We found no evidence of a hydride intermediate in the sodium acetate promoted metallation of $[PtCl_2L_2]$. Possibly metallation goes *via* $[PtCl(OAc)L_2]$ with electrophilic attack by the platinum on the *peri*-position. There is an analogy here with mercuric acetate which readily mercurates aromatics whereas mercuric chloride does not.[6]

Methylplatinum–tertiary phosphine complexes undergo internal metallation, more readily than chlorides, with elimination of methane.[3] We now find that PMe_2(1-naphthyl)–methylplatinum complexes also readily eliminate methane to give metallated derivatives. The dimethyl-complex *cis*-$[PtMe_2L_2]$ was prepared by treating the di-iodide with methyl-lithium: the *cis*-stereochemistry follows from the ^1H n.m.r. pattern. When heated to 200° this dimethyl-complex evolved

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† No reprints available.

[1] Part XXXV, B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1973, 2394.

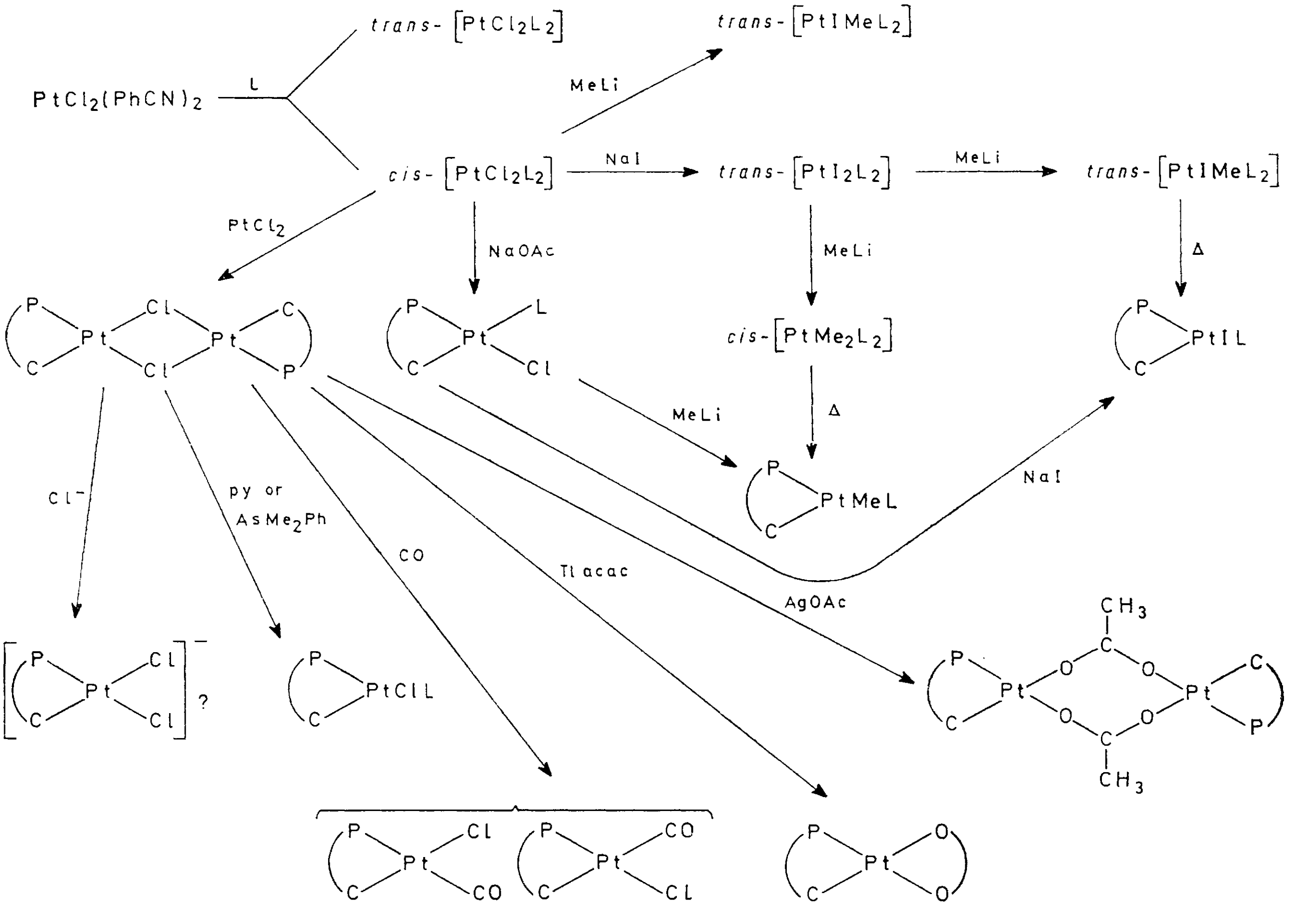
[2] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

[3] A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 754.

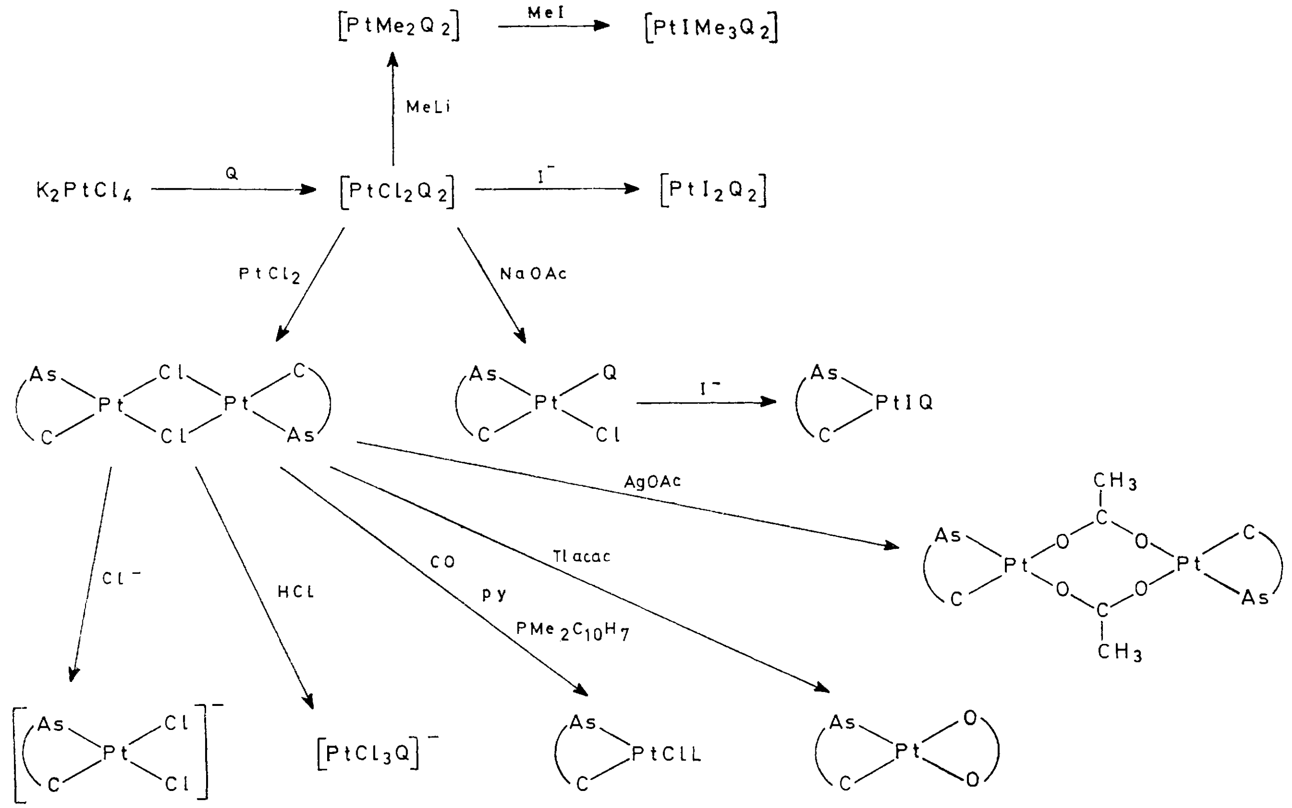
[4] D. F. Gill and B. L. Shaw, *J.C.S. Dalton*, 1972, 65.

[5] J. M. Duff and B. L. Shaw, *J.C.S. Dalton*, 1972, 2219.

[6] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Methuen, London, 1967, vol. 1, pp. 152—153.



Scheme 1 Some chemistry of platinum–dimethyl(1-naphthyl)phosphine complexes and their derivatives



Scheme 2 Some chemistry of platinum–dimethyl(1-naphthyl)arsine complexes and their derivatives

methane (shown by i.r. spectroscopy) and gave a residual glass which we could not crystallise but was shown by ^{1}H n.m.r. spectroscopy to be almost entirely [PtMe(P–C)L]. A pure sample of this complex was prepared by treating [PtCl(P–C)L] with MeLi. When treated with one mole MeLi per platinum *trans*-$[PtI_2L_2]$ gave *trans*-$[PtIMeL_2]$, which when pyrolysed at 195° produced a similar mixture of *cis*- and *trans*-[PtI(P–C)L] to that described above. The dimethyl compound *cis*-$[PtMe_2L_2]$ added methyl iodide to give the trimethylplatinum(IV) species $[PtIMe_3L_2]$ (analytical and n.m.r. data in the Tables).

TABLE 1

% Yields, colours, analytical, and melting point data

Compound	Yield %	Colour	C	H	Halogen	M.p.°
PMe$_2$(1-*naphthyl*)						
cis-$[PtCl_2L_2]$	32	White	45·0 (44·9)	4·05 (4·1)		215—255
trans-$[PtCl_2L_2]$	41	Yellow	44·9 (44·9)	3·9 (4·1)		217—220
cis-$[PtI_2L_2]$	91	Yellow	35·2 (35·0)	3·25 (3·15)		227—233
[PtCl(P–C)L]	77	White	47·2 (47·6)	4·1 (4·15)		220—223
[PtI(P–C)L]	60	Cream	41·5 (41·3)	3·7 (3·6)		186—193
trans-$[PtIMeL_2]$	70	White	41·8 (42·1)	4·0 (4·1)		185—190 *
cis-$[PtMe_2L_2]$	76	White	52·6 (52·0)	5·25 (5·35)		189—194 *
[PtMe(P–C)L]	88	White	51·55 (51·3)	5·1 (4·8)		Glass
cis-$[PtCl_4L_2]$	79	Yellow	40·25 (40·45)	3·7 (3·7)	20·25 (19·9)	203—210
cis-$[PtIMe_3L_2]$	22	White	43·2 (43·6)	4·7 (4·75)		150—164
$[Pt_2Cl_2(P–C)_2]$,Xylene	75	Cream	40·85 (40·85)	3·55 (3·65)	7·7 (7·5)	>310
[PtCl(P–C)py]	72	Cream	41·1 (41·15)	3·5 (3·45)		201—203
$[Pt_2(OAc)_2(P–C)_2]$,C_6H_{12}	55	Cream	42·2 (42·2)	4·45 (4·40)		120 †
[Pt(acac)(P–C)]	50	Cream	42·25 (42·4)	3·95 (3·95)		169—175
[PtCl(P–C)CO]	58	Cream	35·55 (35·05)	3·0 (2·7)	8·2 (7·95)	300 †
[PtCl(P–C)Q]	92	Cream	44·5 (44·4)	3·85 (3·9)	5·5 (5·45)	222—225
AsMe$_2$(1-*naphthyl*)						
$[PtCl_2Q_2]$	95	Yellow	39·45 (39·5)	3·75 (3·6)	9·95 (9·7)	248—250
$[PtI_2Q_2]$	96	Orange	32·0 (31·6)	3·15 (2·9)		157—158
[PtCl(As–C)Q]	52	Buff	41·7 (41·6)	3·7 (3·65)	5·4 (5·1)	215—223
[PtI(As–C)Q]	89	Cream	36·85 (36·7)	3·1 (3·2)		169—170
$[PtIMeQ_2]$	78	Cream	37·35 (37·5)	3·45 (3·65)		164—167 *
$[PtMe_2Q_2]$	78	White	45·0 (45·3)	4·75 (4·65)		145—147 *
$[PtIMe_3Q_2]$	84	Cream	39·0 (39·0)	4·15 (4·25)		155—180
$[Pt_2Cl_2(As–C)_2]$,Xylene	71	Cream	31·4 (31·2)	2·5 (2·6)	7·85 (7·7)	290 †
[PtCl(As–C)Q]	93	Cream				229—239
[PtCl(As–C)L]	46	Cream	44·5 (44·35)	3·75 (3·9)	5·5 (5·45)	218—228
[PtCl(As–C)py]	100	Cream	38·1 (37·75)	3·25 (3·15)	6·8 (6·55)	160 †
$[Pt_2(OAc)_2(As–C)_2]$,$\frac{1}{2}C_6H_{12}$	66	Yellow	37·3 (36·8)	3·6 (3·6)		170—180 *
[Pt(acac)(As–C)]	71	Yellow	38·8 (38·9)	3·65 (3·65)		95—140
$[PtCl_2(As–C)][AsPh_4]$	90	Cream	49·3 (49·1)	3·7 (3·65)	8·0 (8·05)	225—228
$[PtCl_3Q][AsPh_4]$	72	Yellow	47·3 (47·15)	3·55 (3·65)	11·4 (11·6)	215—218
[PtCl(As–C)CO]	98	Cream	32·4 (31·9)	2·5 (2·45)	7·35 (7·25)	290—305
PMe$_2$(1-*naphthyl*)						
cis-$[PdCl_2L_2]$	86	Yellow	51·9 (52·15)	4·8 (4·75)	12·7 (12·8)	225—240
trans-$[PdI_2L_2]$	100	Orange	39·0 (39·1)	3·6 (3·55)		235—242
cis-$[PdMe_2L_2]$	74	White	59·3 (59·7)	6·4 (6·15)		110—130 *
trans-$[PdClMeL_2]$	83	White	55·4 (56·3)	5·25 (5·5)		180—185 *
AsMe$_2$(1-*naphthyl*)						
cis-$[PdCl_2Q_2]\cdot 3/2C_6H_6$	79	Yellow	52·1 (52·2)	4·65 (4·6)	9·2 (9·35)	120—125 222—224
trans-$[PdI_2Q_2]$	96	Orange	35·25 (35·0)	3·25 (3·2)		191—192

* Evolves gas on melting. † With decomposition.

Although the compound $[PtCl_2L_2]$ did not undergo metallation even on prolonged heating (7 days in refluxing 2-methoxyethanol) one might expect metallation in which the metal acts as an electrophile to be more likely to occur with bridged species $[Pt_2Cl_4L_2]$ and indeed we find that attempts to make this tetrachloro-bridged species give $[Pt_2Cl_2(P–C)_2]$ and hydrogen chloride directly. Thus a mixture of $[PtCl_2L_2]$ and $PtCl_2$ when heated in boiling xylene gives $[Pt_2Cl_2(P–C)_2]$: this is very insoluble but undergoes bridge-splitting reactions to give more soluble products.

With pyridine it gives [PtCl(P–C)(py)] or with $AsMe_2Ph$, $[PtCl(P–C)(AsMe_2Ph)]$ (both of unknown stereochemistry). $[Pt_2Cl_2(P–C)_2]$ with carbon monoxide gives a mixture of *cis*- and *trans*-[PtCl(P–C)CO]. Bridging chloride is replaced by bridging acetate on treatment with silver acetate, to give $[Pt_2(OAc)_2(P–C)_2]$ (see Scheme 1 and Tables for data).

The structure is probably very similar to that of the complex $[Pt_2(OAc)_2(P–C)_2]$ [7] where P–C $\equiv CH_2C_6H_4PBu^t(o\text{-tolyl})$ and is shown diagramatically in (I). Such structures frequently have solvents of crystallisation filling cavities in the lattice (cyclohexane, xylenes, *etc.*). ^{1}H N.m.r. spectroscopy (Table 2) shows the two methyls on $PMe_2C_{10}H_6$ are nonequivalent (they differ in τ-value by more than 1), in agreement with the proposed structure. The ^{31}P n.m.r. spectrum (in CH_2Cl_2)

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[7] G. G. Gainsford and R. Mason, unpublished results.

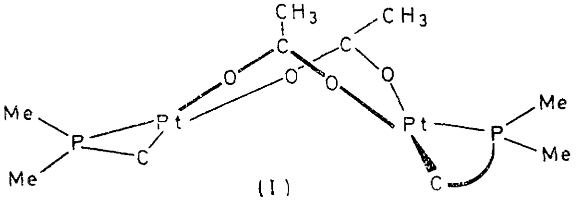
TABLE 2

N.m.r. data for platinum and palladium complexes prepared from dimethyl(1-naphthyl)phosphine (L) or dimethyl-(1-naphthyl)arsine (Q) [a]

	Phosphine(arsine) methyls [b]			Metal methyls			Other resonances
	τ	J(PH) [c]	^{3}J(PtH)	τ	^{3}J(PH)	^{2}J(PtH)	
cis-[PtCl$_2$L$_2$]	8·31(d)	11	32				
trans-[PtCl$_2$L$_2$] [d]	8·21(t)	7·5	22·5				
cis-[PtI$_2$L$_2$] [d]	8·23(d)	10·5	35				
trans-[PtIMeL$_2$]	7·98(t)	6	30	10·1	7	80	
cis-[PtMe$_2$L$_2$]	8·61(d)	7·5	21	9·25(c)		66	
[PtCl(P–C)L] [d]	8·01(d)	9·5	16				
	9·00(d)	12	46				
[PtMe(P–C)L] [d]	8·12(d)	8	22·5	9·2(dd)	7	65	
	9·08	9	19		8		
[PtCl$_2$Q$_2$]	8·39(s)		21				
[PtI$_2$Q$_2$] [d]	8·02(s)		19				
[PtCl(As–C)Q]	8·16(s)		9·5				
	9·12(s)		30				
[PtI(As–C)Q]	7·99(b)		*e*				
	8·09		*e*				
cis-[PdCl$_2$L$_2$]	8·3(c)						
trans-[PdI$_2$L$_2$]	7·8(t)	13					
cis-[PdCl$_2$Q$_2$]	8·3(d)	11					
trans-[PdI$_2$Q$_2$]	7·8(t)	7					
trans-[PdClMeL$_2$]	8·16(t)	6					τ (Pd*Me*) 10·35 J(PH) 6·5
cis-[PdMe$_2$L$_2$]	8·79(d)	6					τ (Pd*Me*) 9·84(c)
[Pt$_2$Cl$_2$(P–C)$_2$] [d]	8·06(d)	12	*f*				
[PtCl(P–C)py] [d]	8·14(d)	12	41·5				
[PtCl(P–C)CO] [d] (mixed isomers)	8·05(d)	12	53				
	8·08(d)	12	53				
[Pt(P–C)acac] [d]	8·19(d)	11·5	35				τ 8·09 acac methyls
							τ 7·94 acac C*H* ^{4}J(PH) 3·3 Hz
[Pt$_2$(acetate)$_2$(P–C)$_2$] [d]	8·33(d)	12·5	48				τ 7·76 acetate methyls
	9·36(d)	12·5	48				
[PtCl(P–C)Q]	8·82(d)	11·5	46				τ 8·04 As*Me* ^{3}J(PtH) 10 Hz
[Pt$_2$Cl$_2$(As–C)$_2$] [d]	8·15(s)		*f*				
	8·19(s)		*f*				
[PtCl(As–C)py] [d]	8·25(s)		28				
[PtCl(As–C)CO] [d] (mixed isomers)	7·97(s)		33				
	8·20(s)		23·5				
[Pt$_2$(acetate)$_2$(As–C)$_2$] [d]	8·46(b)						τ 7·79 acetate methyls
	9·65(b)						
[Pt(acac)(As–C)]	8·19(s)		30				τ 7·85, 8·04 acac methyls
							τ 7·63 acac *CH*
[PtCl$_2$(P–C)][AsPh$_4$] [d] (impure)	8·23(d)	12	45				
[PtCl$_2$(As–C)][AsPh$_4$] [d]	8·35(s)		30				
[PtCl$_3$Q][AsPh$_4$]	8·25(s)		20				
[PtIMe$_3$Q$_2$] [d]	8·45(c)						τ (Pt–Me) 8·75(s) ^{2}J(PtH) 66
							9·22(s) ^{2}J(PtH) 72
[PtIMe$_3$L$_2$] [d]	8·25(c)						τ (Pt–Me) 8·97(c) ^{2}J(PtH) 57
							9·39(t) ^{3}J(PH) 8 ^{2}J(PtH) 69

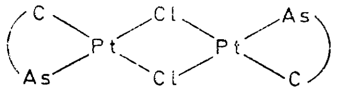
[a] τ-Values ±0·02, J-values ±0·5 Hz, in CDCl$_3$ unless stated otherwise. [b] Satellites due to coupling with platinum not included in multiplicity m = multiplet, dt = doublet of triplets, s = singlet, d = doublet, t = triplet, c = complex, b = broad. [c] If *cis* ^{3}J(PH), if *trans* ^{2}J(PH) + ^{4}J(PH). [d] In CH$_2$Cl$_2$. [e] Coupling to platinum not measured because of exchange of arsine. [f] Too insoluble to observe.

shows only one type of phosphorus $\delta = -6{\cdot}0\ ^{2}J(\mathrm{PtP}) \pm 4782$ Hz and $^{5}J(\mathrm{PtP}) \pm 25$ Hz (*i.e.* these couplings have the same sign). [Pt$_2$Cl$_2$(P–C)$_2$] is readily converted into the mononuclear acetylacetonate [Pt(acac)(P–C)] when treated with thallous acetylacetonate.

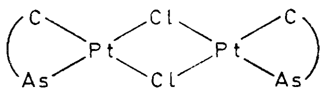


(I)

We also find that dimethyl-1-naphthylarsine (Q) is metallated by platinum in a similar manner to the phosphine (L). These reactions are outlined in Scheme 2 with analytical and n.m.r. data in the Tables and further details in the Experimental section. Reactions in which L and Q behave similarly will not be discussed further but in one or two instances [Pt$_2$Cl$_2$(As–C)$_2$] differs from [Pt$_2$Cl$_2$(P–C)$_2$] in its behaviour. Thus when treated with lithium chloride it readily gives the anion [PtCl$_2$(As–C)]$^-$, isolated as the AsPh$_4$$^+$ salt and with HCl the carbon–platinum bond is split to give [PtCl$_3$Q]$^-$, again isolated as the AsPh$_4$$^+$ salt. [Pt$_2$Cl$_2$(P–C)$_2$] did not react with lithium chloride and although it appeared to react with hydrogen chloride in ethanol we could not isolate pure products from the reaction mixture. [Pt$_2$Cl$_2$(As–C)$_2$] showed two arsenic methyl signals in the ^{1}H n.m.r. spectrum (Table 2). This may be due to a bent structure analogous to (I) or to a mixture of *trans*- and *cis*-forms, (II) and (III) respectively.



(II)



(III)

We have also prepared some palladium complexes of L and Q (see Tables and Experimental section for details). Thus *cis*-[$PdCl_2L_2$], [PdI_2L_2], and their arsine analogues were readily prepared. However, attempts to effect internal metallation by pyrolysis or by boiling in solvents either alone or with sodium acetate led either to decomposition or gave back the starting halide unchanged. We also prepared *cis*-[$PdMe_2Q_2$] and [$PdClMeQ_2$] but these both went black on thermolysis and no internally metallated species was isolated.

^{1}H N.M.R. Spectra.—An interesting feature of the *cis*-complexes of types [PtX_2L_2] or [PtX_2Q_2] is the large spread in τ-value for the naphthyl hydrogens (τ 2—3·9). In the complexes with *trans*-P or -As ligands the *peri*-hydrogen resonance is at a low τ-value (*ca.* 1·0) but the rest of the naphthyl hydrogens form a complex pattern spread over quite a small τ range (1·9—2·8) which is similar to the spread in the free ligands. However, with the *cis*-isomers [MX_2L_2] or [MX_2Q_2] (M = Pt or Pd, X = halogen) the *peri*-hydrogen again absorbs at τ *ca.* 1·0 but two of the remaining six hydrogens absorb above τ 3 as well defined patterns capable of first-order analysis at 90 MHz. Thus for *cis*-[$PtCl_2Q_2$] there is a doublet of doublets at τ 3·15 $J(2,3)$ 7 Hz and $J(3,4)$ 8·0 Hz and a doublet of doublets at τ 3·88 $J(2,3)$ and 6·9 $J(2,4)$ 1·0 Hz. In the corresponding phosphine complex *cis*-[$PtCl_2L_2$] these resonances are split by coupling to phosphorus giving a doublet of triplets at τ 3·8, $J(2,3) = J(3,4) =$ 7·5 Hz (J(PH) 1·5 Hz and a broad doublet of doublets at τ 3·78 with J(PH) 11·6 Hz, $J(2,3)$ 7 Hz, and $J(2,4)$ too small to observe but possibly responsible for the broadening. Clearly therefore the resonances at *ca.* 3·8 are due to proton (2) *ortho* to the arsenic or phosphorus and the resonances at *ca.* 3—3·1 to proton (3) in the *meta*-position.

We suggest that the unusually large shielding of protons 2 and 3 is caused by a ring current effect of the neighbouring naphthyl ring. It has been shown by *X*-ray crystallography that in *cis*-[$PdCl_2(PMe_2Ph)_2$] the phenyls are parallel and quite close (3·2 Å) implying some attractive force between the rings.[8] Similarly in 5-alkyl-5*H*-dibenzophosphole–palladium(II) or -platinum(II) complexes the aromatic rings of adjacent ligands are parallel and quite close.[9] We suggest therefore that in our compounds of types *cis*-[$MX_2(EMe_2C_{10}H_7)_2$] (M = Pt or Pd, E = P or As) the rings are eclipsed, hence the shifts of protons of types 2 and 3 are abnormal.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Spectra were obtained as follows: i.r. 4000—400 cm^{-1}, Perkin-Elmer 457 spectrometer; i.r. 500—200 cm^{-1}, Grubb-Parsons DM4 spectrometer; ^{1}H n.m.r., Bruker Spectrospin HFX 90 MHz and Perkin-Elmer R12 60 MHz spectrometers; ^{31}P n.m.r., Bruker Spectrospin HFX spectrometer.

cis- *and* trans-*Dichlorobis{dimethyl(1-naphthyl)phosphine}platinum*(II).—A solution of dichlorobis(benzonitrile)-platinum(II) (1·53 g, 3·25 mmol) in dichloromethane (20 ml) was treated with dimethyl(1-naphthyl)phosphine (1·28 g, 6·8 mmol). The resultant yellow solution was stirred at room temperature for 10 min then diluted with methanol (60 ml). This gave a yellow solid which when extracted with hot benzene (20 ml) gave a residue of the pure *cis*-isomer as *needles* (0·542 g). The filtrate on being exposed to the air slowly deposited the *trans*-isomer as large clear yellow *prisms* (0·981 g). The methanolic mother-liquors slowly deposited a further crop of the *cis*-isomer (0·218 g).

cis-*Di-iodobis{dimethyl(1-naphthyl)phosphine}platinum*(II).—A suspension of the *cis*-dichloride (0·640 g, 1·0 mmol) in acetone (10 ml) containing sodium iodide (1·5 g, 10 mmol) was heated under reflux for 15 min and then diluted with methanol (50 ml). This gave the required compound as yellow *prisms* (0·748 g). The other di-iodides shown in Table 1 were prepared similarly.

Chloro{1-(8-dimethylphosphino)naphthyl}dimethyl(1-naphthyl)phosphineplatinum(II).—A suspension of *cis*-dichlorobis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·256 g, 0·40 mmol) in 2-methoxyethanol (10 ml) containing sodium acetate trihydrate (0·272 g, 20 mmol) was heated. The complex dissolved giving a light solution which gradually darkened. After 1 h the mixture was evaporated to dryness under reduced pressure, water was added and the product isolated with benzene. It formed light yellow *prisms* from dichloromethane–methanol. Similar treatment of *trans*-dichlorobis{dimethyl(1-naphthyl)phosphine}platinum(II) gave the same product in similar yield.

Chloro{1-(8-dimethylarsino)naphthyl}dimetnyl(1-naphthyl)-arsineplatinum(II) was prepared similarly (35 min reflux).

Iodo{1-(8-dimethylphosphino)naphthyl)}dimethyl(1-naphthyl)phosphineplatinum(II).—A solution of the corresponding chloride (0·095 g, 0·157 mmol) in acetone (1 ml) was stirred with sodium iodide (0·12 g, 0·8 mmol) at 20° for 20 min. The mixture was evaporated to dryness and the product isolated with dichloromethane and recrystallised from dichloromethane–methanol to give a mixture of *needles* and *microprisms* adjudged to be a mixture of *cis*- and *trans*-isomers (*ca.* 3 : 1) by microanalysis and ^{1}H n.m.r. spectroscopy (see Tables).

The analogous arsine complex was similarly prepared.

cis-*Dichlorobis{dimethyl(1-naphthyl)arsine}platinum*(II).—A solution of potassium tetrachloroplatinite(II) (2·730 g, 6·55 mmol) in water (50 ml) was treated with dimethyl-(1-naphthyl)arsine (3·192 g, 13·7 mmol) and then the mixture was shaken for 2¼ h. The resultant pink precipitate was filtered off, dried and boiled in ethanol (50 ml)

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[8] L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, 1971, **10**, 1795.

[9] H. M. Powell and K. M. Chui, *Chem. Comm.*, 1971, 1037.

for 15 min. The product was then filtered off as pale yellow *plates* (4·6 g).

cis-*Dichlorobis{dimethyl(1-naphthyl)phosphine}palladium*(II).—A solution of dichlorobis(benzonitrile)palladium(II) (0·98 g, 2·5 mmol) in dichloromethane (15 ml) was treated with dimethyl(1-naphthyl)phosphine (0·96 g, 5·13 mmol). After 5 min the resultant clear solution was diluted with methanol and most of the dichloromethane removed by evaporation. The product separated as light yellow *microcrystals* (1·21 g).

cis-*Dichlorobis{dimethyl(1-naphthyl)arsine}palladium*(II).—A solution of sodium chloropalladite(II) (0·821 g, 2·762 mmol) in methanol (50 ml) was treated with dimethyl(1-naphthyl)arsine (1·345 g, 5·80 mmol) and the resultant yellow solution was stirred at room temperature for 10 min. The yellow solid obtained was filtered off, washed with methanol and water then recrystallised from benzene to give the product as yellow *needles* (1·409 g).

trans-*Iodo(methyl)bis{dimethyl(1-naphthyl)phosphine}platinum*(II).—A suspension of *cis*-di-iodobis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·413 g, 0·50 mmol) in benzene (5 ml) was treated with methyl-lithium (0·55 mmol) in diethyl ether (0·8 ml). The resultant suspension was stirred at 20° for 16 h then hydrolysed (water) and the required product isolated with benzene. It formed white *needles* (0·251 g) from dichloromethane–methanol.

The analogous palladium complex was similarly prepared.

cis-*Dimethylbis{dimethyl(1-naphthyl)phosphine}platinum*(II).—A suspension of *cis*-di-iodobis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·207 g, 0·25 mmol) in benzene (5 ml) was treated with methyl-lithium (0·55 mmol) in ether (0·8 ml). A nearly colourless solution formed in minutes. The solution was stirred for 16 h at 20° and the product isolated with benzene. It formed white *prisms* (0·115 g) from dichloromethane–methanol.

The analogous palladium complex was similarly prepared.

Iodo{1-(8-dimethylphosphino)naphthyl}dimethyl(1-naphthyl)phosphineplatinum(II) *by Pyrolysis*.—*trans*-Iodo(methyl)bis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·035 g) was heated at 195° for 5 min by which time gas evolution had ceased. An ^{1}H n.m.r. spectrum of the pyrolysate indicated it to be a mixture of *cis*- and *trans*-isomers of the product and which we have already described above.

Methyl{1-(8-dimethylphosphino)naphthyl}dimethyl(1-naphthyl)phosphineplatinum(II).—*cis*-Dimethylbis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·136 g) was heated at 200° for 10 min. The resultant glass was dissolved in dichloromethane and a small amount of insoluble residue filtered off. The ^{1}H n.m.r. spectrum indicated the product to be almost pure, but attempts to purify by a variety of methods were unsuccessful. An analytically pure sample was prepared as follows. A solution of chloro{1-(8-dimethylphosphino)naphthyl}dimethyl(1-naphthyl)phosphineplatinum(II) (0·152 g, 0·25 mmol) in benzene (5 ml) was treated with methyl-lithium (1·2 mmol) in ether (1·0 ml). After 2½ h the product was isolated by hydrolysis and evaporation. Treatment of the residue with light petroleum gave the product as a cream powder (0·128 g) characterised by microanalysis and ^{1}H n.m.r. spectroscopy (see Tables). The ^{1}H n.m.r. spectrum was virtually identical with that of a sample prepared by pyrolysis of the dimethyl-complex (see above).

trans-*Chloro(methyl)bis{dimethyl(1-naphthyl)phosphine}palladium*(II).—A suspension of *cis*-dichlorobis{dimethyl(1-naphthyl)phosphine}palladium(II) (0·277 g, 0·50 mmol) in benzene (5 ml) was treated with methyl-lithium (0·55 mmol) in diethyl ether (0·8 ml). After 16 h, aqueous work-up, and isolation with benzene gave the product as needles (0·221 g) from dichloromethane–methanol.

Di-μ-chloro-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) *Xylene Solvate*.—A suspension of platinous(II) chloride (0·147 g, 0·55 mmol) and *cis*-dichlorobis{dimethyl(1-naphthyl)phosphine}platinum(II) (0·320 g, 0·50 mmol) in xylene (15 ml) was heated under reflux for 17 h. The resultant dark solution was filtered hot with animal charcoal. On cooling the product was obtained as pale yellow *needles* (0·316 g).

The analogous arsine complex was prepared similarly (5 h reflux).

Chloro{1-(8-dimethylphosphino)naphthyl}pyridineplatinum(II).—Pyridine was added dropwise to a stirred suspension of di-μ-chloro-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) (xylene solvate; 0·100 g, 0·106 mmol) in dichloromethane (5 ml) until dissolution was complete. Addition of light petroleum to the solution gave the required product as cream *needles* (0·076 g).

The analogous arsine complex was prepared similarly.

Chloro{1-(8-dimethylphosphino)naphthyl}(carbonyl)platinum(II).—A suspension of di-μ-chloro-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) (xylene solvate; 0·832 g, 1·0 mmol) in benzene (40 ml) was heated at reflux for 22 h with carbon monoxide bubbling through. The resultant suspension was cooled and filtered to give the product as a *microcrystalline* cream solid (0·507 g). The product was judged by ^{1}H n.m.r. to be a mixture (*ca.* 1 : 1) of two products (presumably isomeric carbonyls). Fractional crystallisation from dichloromethane–methanol failed to change the proportion of the two isomers.

The analogous arsine complex was prepared similarly.

Acetylacetonato{1-(8-dimethylphosphino)naphthyl}platinum(II).—A suspension of di-μ-chloro-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) (xylene solvate; 0·235 g, 0·24 mmol) in benzene (10 ml) containing thallous acetylacetonate (0·180 g, 0·60 mmol) was shaken in darkness for 16 h. The resultant mixture was filtered and the yellow filtrate evaporated to dryness to give the product as pale yellow *microcrystals* (0·115 g) from dichloromethane–methanol.

The analogous arsine complex was prepared similarly.

Di-μ-acetato-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) *Cyclohexane Solvate*.—This was prepared using silver acetate in an analogous fashion to the acetylacetonate. It formed yellow prisms from dichloromethane–cyclohexane.

Di-μ-acetato-bis{1-(8-dimethylarsino)naphthyl}diplatinum(II) *Cyclohexane Solvate*.—This was similarly prepared and formed microcrystals from dichloromethane–cyclohexane.

Chloro{1-(8-dimethylphosphino)naphthyl}dimethyl(1-naphthyl)arsineplatinum(II).—A rapidly stirred suspension of di-μ-chloro-bis{1-(8-dimethylphosphino)naphthyl}diplatinum(II) (xylene solvate; 0·479 g, 0·5 mmol) in dichloromethane (5 ml) was treated with dimethyl(1-naphthyl)arsine (0·254 g, 1·1 mmol). The complex dissolved at once. Addition of methanol gave the required product as large *prisms* (0·600 g).

Chloro{1-(8-dimethylarsino)naphthyl}dimethyl(1-naphthyl)phosphineplatinum(II).—To a suspension of di-μ-chloro-bis{1-(8-dimethylarsino)naphthyl}diplatinum(II) (xylene solvate; 0·103 g, 0·1 mmol) in dichloromethane (1 ml) was added dimethyl(1-naphthyl)phosphine (25·5 μl, 1·1 mol per g-atom platinum). The resultant pale yellow solution was diluted with light petroleum (b.p. 60—80°) to give the product as cream *plates* (0·061 g).

Dichloro{1-(8-*dimethylphosphino*)*naphthyl*}*platinum*(II) *Tetraphenylarsonium Salt*.—A suspension of di-μ-chlorobis-{1-(8-dimethylphosphino)naphthyl}diplatinum(II) (0·208 g, 0·25 mmol) in 2-methoxyethanol (5 ml) containing lithium chloride (0·086 g, 2·0 mmol) was warmed on a steam-bath for 5 min. The complex dissolved to give a clear light yellow solution. Addition of tetraphenylarsonium chloride (0·26 g, 0·6 mmol) followed by methanol gave the product as cream *needles* (0·155 g).

Dichloro{1-(8-*dimethylarsino*)*naphthyl*}*platinum*(II), *Tetraphenylarsonium Salt*.—A suspension of di-μ-chloro-bis-{1-(8-dimethylarsino)naphthyl}diplatinum(II) (0·231 g, 0·25 mmol) in 2-methoxyethanol (3 ml) containing lithium chloride (0·082 g, 2·0 mmol) was warmed on the steam-bath. The complex dissolved in 10 min and the resultant light yellow solution was cooled and treated with tetraphenylarsonium chloride (0·24 g, 0·55 mmol). A thick solid formed. Methanol was added and the suspension was filtered to give *needles* (0·232 g). The mother liquor was evaporated to dryness and the residue recrystallised from methanol to give a second crop (0·162 g) of the same material.

Trichlorodimethyl(1-*naphthyl*)*arsineplatinum*(II), *Tetraphenylarsonium Salt*.—A suspension of di-μ-chloro-bis{1-(8-dimethylarsino)naphthyl}diplatinum(II) (0·257 g, 0·25 mmol) in refluxing 2-methoxyethanol (8 ml) was treated with conc. hydrochloric acid (0·5 ml). The resultant clear yellow solution was refluxed for 1 h then cooled; no crystals could be obtained from the solution. Addition of tetraphenylarsonium chloride (0·25 g, 0·60 mmol) and methanol gave bright yellow *prisms* (0·331 g).

Tetrachlorobis{*dimethyl*(1-*naphthyl*)*phosphine*}*platinum*-(IV).—A solution of *cis*-dichlorobis{dimethyl(1-naphthyl)-phosphine}platinum(II) (0·321 g, 0·50 mmol) in dichloromethane (5 ml) was treated at 0° with a solution of chlorine (0·58 mmol) in carbon tetrachloride (1 ml). A deep yellow solution formed at once. After 10 min methanol (15 ml) was added to give the product as fine yellow-orange *needles* (0·28 g). A similar addition to *trans*-dichlorobis{dimethyl-(1-naphthyl)phosphine}platinum(II) gave the same product (81% yield).

Iodo(*trimethyl*)*bis*{*dimethyl*(1-*naphthyl*)*arsine*}*platinum*-(IV).—A solution of *cis*-dimethylbis{dimethyl(1-naphthyl)-arsine}platinum(II) (0·320 g, 0·457 mmol) in iodomethane (5 ml) was put aside at room temperature in the dark for 7 days. The iodomethane was then allowed to evaporate giving the required product as cream *prisms* (0·326 g).

Iodo(*trimethyl*)*bis*{*dimethyl*(1-*naphthyl*)*phosphine*}*platinum*(IV) was similarly prepared.

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