Complexes of Iridium(III) and Rhodium(III) with Metallated and Unmetallated Dimethyl(1-naphthyl)- and Methylphenyl(1-naphthyl)-phosphine †

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Dimethyl(1-naphthyl)phosphine (L) is readily metallated in the 8-(*peri*-)position by iridium(III), ($C_{10}H_6PMe_2 \equiv$ P–C). Thus iridium trichloride with L in 2-methoxyethanol gives [$IrCl_2(P\text{–}C)L_2$]. In the presence of a base and alcohol further metallation occurs to give [$IrCl(P\text{–}C)_2L$] and then [$IrH(P\text{–}C)_2L$], which on pyrolysis gives the trimetallated complex *fac*-[$Ir(P\text{–}C)_3$]. [$IrHCl_2$(cyclo-octa-1,5-diene)]$_2$ reacts with L to give [$IrHCl_2L_3$], which with chlorine gives *mer*-[$IrCl_3L_3$]. *mer*-[$IrCl_3L_3$] is converted by boiling 2-methoxyethanol into [$IrCl_2(P\text{–}C)L_2$] very rapidly. [IrCl(cyclo-octa-1,5-diene)]$_2$ reacts with L to give [$IrHCl(P\text{–}C)L_2$], which, in boiling 2-methoxyethanol, is converted to [$IrCl(P\text{–}C)_2L$]. The base-promoted metallations are readily reversed by HCl, *e.g.* [$IrCl(P\text{–}C)_2L$] gives [$IrCl_2(P\text{–}C)L_2$] and [$IrHCl(P\text{–}C)L_2$] gives [$IrHCl_2L_3$], *etc.* A few rhodium complexes were also prepared such as [$RhCl_2(P\text{–}C)L_2$] and [$RhClL_3$]. The configurations of these complexes were determined by ^1H and/or ^{31}P n.m.r. spectroscopy. I.r. data are also recorded.

REACTIONS in which a metal–carbon bond is formed by internal metallation of the alkyl or aryl groups of a co-ordinated ligand have received wide-spread attention in recent years.[1-13] A variety of metals and ligands including amines, Schiff bases, azo-compounds, phosphites, and tertiary phosphines undergo this reaction. Whilst it has been established that internal metallations giving five-membered chelates occur the most readily[1] and that metallation can be promoted by steric effects to a remarkable degree[13] there is need for further work, particularly in the case of phosphorus ligands where the results available to date indicate that different mechanisms may be involved, *i.e.* sometimes the metal appears to be acting as a nucleophile and sometimes as an electrophile.[1,6,9]

We present here the results of some studies on internal metallation reactions of dimethyl(1-naphthyl)phosphine co-ordinated to iridium(III) or rhodium(III) and of methylphenyl(1-naphthyl)phosphine co-ordinated to iridium(III). The range of iridium(III) complexes with unmetallated dimethyl(1-naphthyl)phosphine (L), and with *peri*-(or eight-)metallated dimethyl(1-naphthyl)-phosphine (represented by P–C) is extensive. For convenience the various interconversion reactions have been outlined in Scheme 1. An extensive series of *ortho*-metallated triaryl phosphite derivatives of iridium(III) has been described by Robinson and co-workers.[6] The stereochemistry of several of their complexes was unknown or not known with certainty and some of them could not be obtained as crystals. We have been able to determine the stereochemistry of almost all our complexes unambiguously.

Complexes of Dimethyl(1-*naphthyl*)*phosphine* (L).—When iridium trichloride was treated with 3·3 mole equivalents of dimethyl(1-naphthyl)phosphine in refluxing 2-methoxyethanol for several hours, conditions under which ligands such as PMe_2Ph or PBu^n_3 give good yields of the yellow *mer*-[$IrCl_3L_3$], a cream-coloured solid was obtained. This was shown to be the internally metallated complex, [$IrCl_2(P\text{–}C)L_2$] (I) on the basis of analytical data (Table 1) and the ^1H n.m.r. spectrum (Table 2) which shows two well separated 1 : 2 : 1 triplets for the non-equivalent methyls on the *trans*-phosphines and a doublet of equal intensity (to either

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† No reprints available.

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[3] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

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[11] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.

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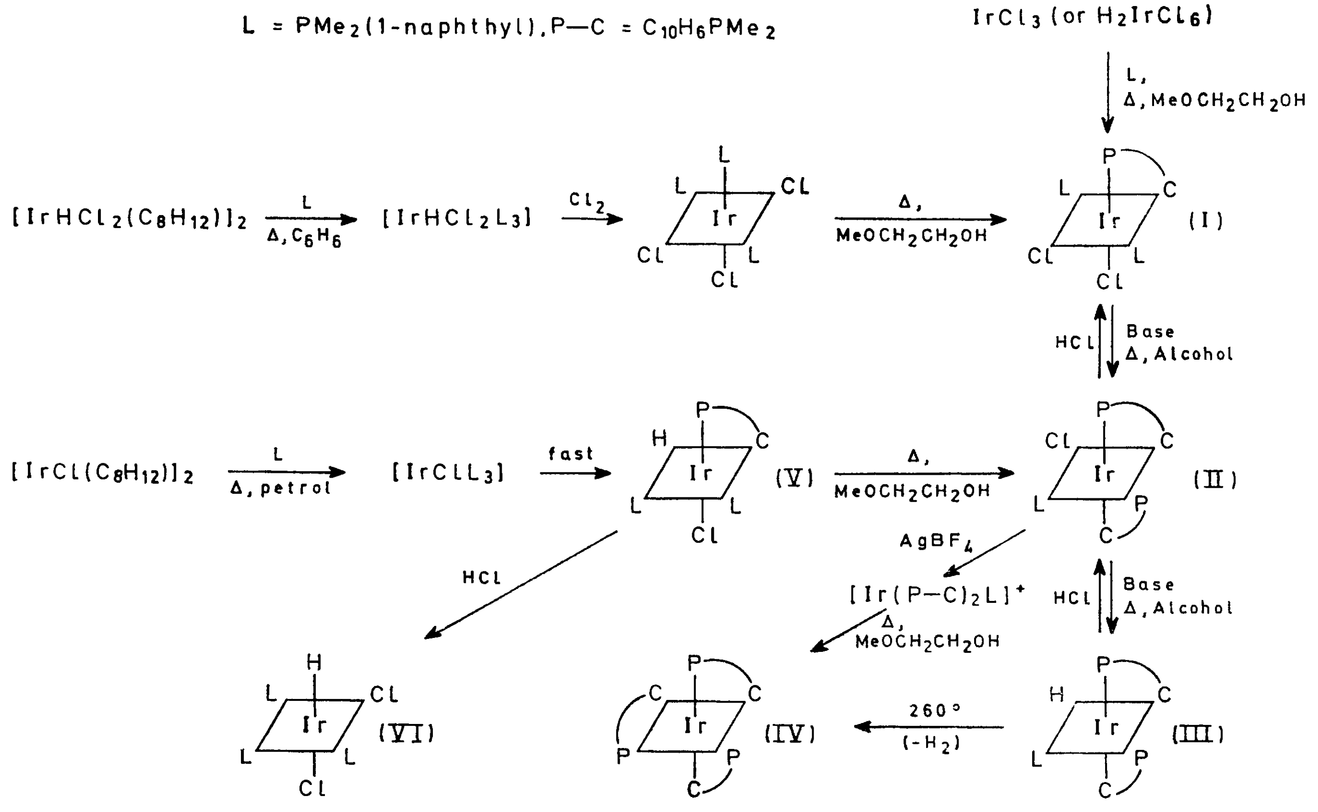
[13] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

of the 1 : 2 : 1 triplets) due to the methyls on the metallated phosphine. The same complex was obtained by treating $[IrCl_6]^{3-}$ with the phosphine for 10 min in refluxing 2-methoxyethanol. It seems likely that *mer*-$[IrCl_3L_3]$ was formed as an intermediate but we could not detect it. However, we have prepared this complex, *mer*-$[IrCl_3L_3]$, as follows; $[IrHCl_2(1,5\text{-cyclooctadiene})]_2$[14] was treated with L to give $[IrHCl_2L_3]$, which with chlorine gave *mer*-$[IrCl_3L_3]$ (see Tables 1 and 2 for analytical and n.m.r. data). On heating *mer*-$[IrCl_3L_3]$ in 2-methoxyethanol metallation occurred to give $[IrCl_2(P\text{–}C)L_2]$, of configuration (I), very rapidly (<2 min) and could therefore be an intermediate in the preparation of this metallated compound from iridium trichloride (see above). Although the mono-metallated complex (I) was thermally stable, melting without apparent decomposition above 300°, it could be readily converted into the dimetallated complex $(IrCl(P\text{–}C)_2L]$, configuration (II), in a variety of ways. Thus treatment with methyl-lithium (1 mole per g-atom iridium) gave a complex mixture from which the dimetallated complex (II) was isolated in 37% yield or treatment with a variety of bases gave the required complex in high (82—98%) yield. The assigned configuration (II) for this complex follows from the ^1H- and ^{31}P-n.m.r.



SCHEME 1 Iridium complexes of (1-naphthyl)dimethylphosphine; L = PMe_2(1-naphthyl); P–C = $C_{10}H_6PMe_2$

TABLE 1

Complex [a]	Configuration	% Yield	Colour	M.p./°C	Analytical data [b]		
					C	H	Cl
$[IrCl_3L_3],C_6H_6$	*mer*	60	Yellow	200—210 [d]	53·7 (53·5)	4·8 (4·8)	11·05 (11·3)
$[IrHCl_2L_3]$	(VI)	85	Cream	195—215 [d]	52·5 (52·2)	5·0 (4·85)	8·5 (8·55)
$[IrCl_2(P\text{–}C)L_2]$	(I)	80	Cream	303—307	52·15 (52·3)	4·65 (4·65)	8·5 (8·55)
$[IrHCl(P\text{–}C)L_2]$	(V)	86	White	188—190 [d]	54·8 (54·6)	4·7 (4·95)	4·25 (4·5)
$[IrCl(P\text{–}C)_2L]$	(II)	95	White	305—310	54·6 (54·7)	4·95 (4·7)	4·25 (4·5)
$[IrH(P\text{–}C)_2L]$	(III)	98	White	260—265 [d]	56·9 (57·2)	5·1 (5·05)	
$[Ir(P\text{–}C)_3]$	(IV)	78	Cream	340 [d]	57·1 (57·45)	4·65 (4·8)	
$[RhCl_3L_3]$	*mer*	86	Orange	190—195	55·3 (55·9)	4·9 (5·1)	13·3 (13·6)
$[RhCl_2(P\text{–}C)L_2]$	I	84	Yellow	200—205	58·65 (58·5)	5·2 (5·25)	9·6 (9·85)
$[RhClL_3]$		89	Orange	185—195	60·6 (61·6)	5·65 (5·6)	5·1 (5·05)
$[IrCl(P'\text{–}C)_2L']$		73	White	Glass	62·8 (62·7)	4·5 (4·45)	3·35 (3·6)
$[Ir(P'\text{–}C)_3]$		27	Cream	340 [d]	65·1 (64·5)	4·5 (4·65)	0·3 (0)
$[RhCl(CO)L'_2]$	*trans*	80	Yellow	197—205	62·55 (62·5)	4·7 (4·6)	

[a] L = PMe_2(1-naphthyl); P–C = $C_{10}H_6PMe_2$; L′ = PMePh(1-naphthyl); (P′–C) = $C_{10}H_6PMePh$. [b] Calculated values in parentheses. [c] *M* in benzene = 875 (863 required). [d] With decomposition.

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[14] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.

spectra. The ^{31}P spectrum shows that the three P-nuclei are non-equivalent (see Table 3 for data). The *J*-values are in the range expected for *cis*-couplings.[15-17] We find that complexed dimethyl(1-naphthyl)phosphine has a ^{31}P-shift at much higher field (42·5—45·6 p.p.m.) than a metallated ligand (4·1—19·8 p.p.m.) (Table 3). The six methyl groups in configuration (II) are non-equivalent and each gives a doublet resonance in the ^1H n.m.r. spectrum (Table 2). Far-i.r. data are frequently useful in determining the stereochemistry of chloroiridium(III)–tertiary phosphine complexes since a value of ν(Ir–Cl) is indicative of the *trans*-ligand.[18] However, dimethylnaphthylphosphine ligands show strong bands in the same region as ν(Ir–Cl) and we have generally found far-i.r. data to be of little use in assigning the stereochemistries of these complexes. It may be possible to make assignments to ν(Ir–Cl) by comparing the far-i.r. spectra with those of bromides or iodides (at present unknown). The far-i.r. (200—450 cm^{-1}) bands for our chloro-complexes are therefore recorded in Table 2.

TABLE 2

Infrared and ^1H n.m.r. data

	Infrared data [a]		^1H N.m.r. data [b]	
Complex [c]	Far-i.r.	ν(C=C)	Solvent	Assignment: τ (p.p.m.) multiplicity (coupling constant)
$[IrCl_3L_3],C_6H_6$	235w, 249w, 269s, 302w, 317w 330m		$CDCl_3$	P–Me: 7·80t(8·5); [d] 8·75d(10·5)
$[IrHCl_2L_3]$ [e]	228s, 273s, 333m		CH_2Cl_2	P–Me: 7·80t(7), 8·10t(8·5), 8·64d(10) Ir–H: 30·9dt(21, 12)
$[IrCl_2(P–C)L_2]$	247, 266, 285, 298, 330	1549	CH_2Cl_2	P–Me: 7·57t(9), 8·28t(9), 9·50d(12)
$[IrHCl(P–C)L_2]$ [f]	245s, 275m, 296s, 330m, 357w	1547	CH_2Cl_2	P–Me: 8·07d(9), 8·11d(8), 8·58d(7), 9·01d(8), 9·03d(10), 9·42d(11). Ir–H: 22·2dt(168, 21)
$[IrCl(P–C)_2L]$	252, 298	1547	CH_2Cl_2	P–Me: 7·89d(8), 8·35d(8), 8·44d(7), 8·67d(8), 9·06d(9·5), 9·95d(10·5)
$[IrH(P–C)_2L]$ [g]	291	1544	CH_2Cl_2	P–Me: 8·20d(8), 8·39d(7·5),[d] 8·45d(7·5), 8·82d(9), 9·79d(8). Ir–H: 19·2dt(144, 21)
$[Ir(P–C)_3]$	242m, 294s, 345s	1544	CH_2Cl_2	P–Me: 8·10d(7), 9·33d(8)
$[RhCl_3L_3]$	247s, 272s, 291m, 343s		$CDCl_3$	P–Me: 7·75t(7),[d] 8·81d(11)
$[RhCl_2(P–C)L_2]$	235s, 268w, 293m, 305w, 330w	1545	$CDCl_3$	P–Me: 7·52t(8), 8·23t(8), 9·51d(12)
$[RhClL_3]$	227m, 243m, 277s		$CDCl_3$	P–Me: 7·73t(9),[d] 8·79d(11)
$[IrCl(P'–C)_2L']$	247, 290, 335	1540		Unresolved
$[Ir(P'–C)_3]$	245w, 330s	1540		Insoluble
$[RhCl(CO)L'_2]$ [h]	270w, 308s, 335m		CH_2Cl_2	P–Me: 7·78 broad

[a] Data in cm^{-1}, Nujol mulls. *J*-values ±0·5 Hz; the phosphorus–methyl coupling constants for triplets are given as $|^2J(P–H) + ^4J(P–H)|$; for doublets of triplets the first figure given refers to the doublet coupling constant. [c] L = PMe_2(1-naphthyl; (P–C) = $C_{10}H_6PMe_2$; L′ = PMePhNp; (P′–C) = $C_{10}H_6PMePh$. [d] Signal has double the intensity of the other peaks in the series. [e] ν(Ir–H) 2270 broad. [f] ν(Ir–H) 2088 broad. [g] ν(Ir–H) 2010 broad. [h] ν(C=O) 1957, 1968 broad.

TABLE 3

^{31}P N.m.r. data [a]

Complex	Configuration	P_1	P_2	P_3	$J(P_1–P_2)$	$J(P_1–P_3)$	$J(P_2–P_3)$
$[IrCl(P–C)_2L]$	(II)	45·6	15·1	14·5	11·8	10·3	11·4
$[IrH(P–C)_2L]$	(III)	45·4	17·7 [b]	19·8	14·9	12·1	12·7
$[IrHCl(P–C)L_2]$	(V)	44·7 [b]	42·5	4·1	16·0	7·5	9·1

[a] Chemical shifts in p.p.m. (±0·2) upfield from 85% phosphoric acid; *J* values ±0·2 Hz. [b] *trans*- to H.

The chloride (II) can be converted into a hydride of similar stereochemistry $[IrH(P–C)_2L]$, (III), by treatment with either sodium acetate or sodium hydroxide in refluxing 2-methoxyethanol. The ^1H n.m.r. spectrum of (III) was similar to that of (II) showing five doublets (one of double intensity) for the phosphorus methyls and a hydride resonance at τ 19·2, split into a doublet (*J* 144 Hz) of triplets (*J* 21 Hz) by respectively, the ***trans***- and *cis*-phosphorus nuclei. The ^{31}P n.m.r. spectrum was also similar (Table 3).

The hydride (III) evolved gas (presumably hydrogen) on melting (*ca.* 250°) and a tris-chelated complex $[Ir(P–C)_3]$ (IV) could be isolated from the melt by sublimation. This complex is assigned the *fac*-stereochemistry on the basis of its very simple ^1H n.m.r. spectrum, which consists of two doublets of equal intensity. Further evidence for structure (IV) was obtained from the mass spectrum which showed intense molecular ions at *m/e* 754 (relative intensity 100) and 752 (relative intensity 54) corresponding to the ^{193}Ir- and ^{191}Ir-complexes, respectively.

We have also made the tris-chelated complex (IV) by removing the chloride ligand from the bis-chelated complex $[IrCl(P–C)_2L]$ configuration (II) with silver fluoroborate in 2-methoxyethanol and heating the resultant solution for 20 min.

When the iridium(I)–cyclo-octene complex $[IrCl(C_8H_{14})_2]_2$ was treated with an excess of dimethyl-(1-naphthyl)phosphine at *ca.* 60° a white hydride $[IrHCl(P–C)L_2]$ was obtained in high yield. The ^1H

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[15] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 1734.

[16] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[17] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 48.

[18] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 920.

n.m.r. pattern of this complex (Table 2) shows six separate doublets for the phosphorus methyl signals similar to those previously observed in the bis-chelates (II) and (III). Such a pattern is only consistent with three non-equivalent facial phosphines. The hydride resonance at τ 20·47 is a doublet (*J* 173 Hz) of distorted triplets (*J ca.* 21 Hz) implying that the hydrogen is coupled approximately equally to the two P-nuclei in *cis*-position. Two configurations are consistent with these data but the ^{31}P n.m.r. pattern shows that the hydrogen is *trans* to an unmetallated phosphine showing that the configuration must be (V). A possible intermediate product in the formation of (V) is the iridium(I) species $[IrClL_3]$. This would be expected to undergo facile oxidative addition to give the observed product (V). Analogous iridium(I) complexes prepared from triphenylphosphine or triphenyl phosphite have been shown to undergo internal oxidative addition in this way.[19]

The hydrido-complex (V) melts with gas evolution (presumably dihydrogen) and resolidifies to give the bis-chelated complex $[IrCl(P{-}C)_2L]$ (II). The conversion of (V) to (II) was also readily effected in boiling 2-methoxyethanol solution.

TABLE 4

Percent yield, melting point, and ^1H n.m.r. data for phosphines

Compound	% Yield		^1H N.m.r. data: Solvent	*peri-H*	Aromatic multiplet	P–Me coupling constant
PCl_2(1-naphthyl)	55	b.p. 139—149°, 1 mmHg	CCl_4	1·54	1·8—3·0	
PMe_2(1-naphthyl)	76	b.p. 120—128°, 1 mmHg	$CDCl_3$	1·37	2·1—2·7	8·69 (3·5)
$[PMe_3$(1-naphthyl)$]I$	84	m.p. 231—240°	$CDCl_3$		1·6—2·5	7·15 (14)
PClMePh	83	b.p. 106—110°, 60 mmHg	CCl_4		2·2—3·0	8·28 (10)
PMePh(1-naphthyl)	76	b.p. 140—160°, 0·2 mmHg	CCl_4	1·46	2·2—3·0	8·45 (4·5)
$[PMe_2Ph$(1-naphthyl)$]I$	93	m.p. 197—200°	$CDCl_3$		1·2—2·5	6·97 (13)

Metallation of dimethyl(1-naphthyl)phosphine with chelate formation could occur at the 2- or at the 8-(*peri*-)position. Formation of a five-membered ring by attack on the *peri*-position seems much more likely than formation of a four-membered ring by attack on the 2-position. Our ^1H n.m.r. evidence that metallation occurs in the *peri*-position is as follows: Both the free dimethyl(1-naphthyl)phosphine and its complexes show a resonance within the range τ 1—1·5 due to a single hydrogen; all the other hydrogens absorb above τ 2·5. This isolated resonance is clearly due to the *peri*-hydrogen deshielded by some proximity effect. *peri*-Hydrogens of 1-substituted naphthalenes are known to absorb at low τ-values.[20,21] On metallation this isolated resonance at τ 1—1·5 is lost, *e.g.* for the four complexes *mer*-$[IrCl_3L_3]$, (I), (II), and (III) the area of this resonance corresponds to 3, 2, 1, and 0 hydrogens respectively. It has previously been suggested, but not proven, that 1-dimethylaminonaphthalene is metallated in the *peri*-position by palladium.[2]

Complexes containing the metallated ligand (P–C) show an i.r. absorption band at 1545—1550 cm^{-1} assigned to $\nu(C{=}C)$ (Table 2). Since this band is absent, or of very low intensity, in the unmetallated ligand complexes, it is useful in structural assignments.

Some of the metallations are reversed by treatment with hydrogen chloride. Thus the di-metallated complex $[IrCl(P{-}C)_2L]$ (II) when heated with hydrochloric acid in 2-methoxyethanol for 3 min gives the mono-metallated complex (I). Similarly treatment of the bis-metallated hydride $[IrH(P{-}C)_2L]$ gives (I) with hydrogen evolution. The mono-metallated hydride $[IrHCl(P{-}C)L_2]$ readily gives the unmetallated hydride $[IrHCl_2L_3]$ when treated with hydrochloric acid at 60°.

When hydrated rhodium trichloride was treated with dimethyl(1-naphthyl)phosphine at 20° internal metallation did not occur and *mer*-$[RhCl_3L_3]$ was readily isolated. On heating in 2-methoxyethanol, however, metallation occurred and the mono-chelated complex $[RhCl_2(P{-}C)L_2]$ of configuration (I) was formed (analytical and spectroscopic data in Tables). Attempts to effect further metallation, however, were unsuccessful and conditions which were successful for the iridium complexes gave mixtures which we could not separate. When treated with sodium acetate in ethanol *mer*-$[RhCl_3L_3]$ was converted into the orange, air-sensitive rhodium(I) complex $[RhClL_3]$, which with chlorine give *mer*-$[RhCl_3L_3]$ again.

We have also attempted to study the internal metallations of methylphenyl(1-naphthyl)phosphine (L′). This asymmetric phosphine with iridium trichloride in 2-methoxyethanol, under conditions where dimethyl-(1-naphthyl)phosphine gives $[IrCl_2(P{-}C)L_2]$ gave a glass which analysed for $[IrCl(P'{-}C)_2L']$ (where $P'{-}C$ = metallated L′). There are a large number of isomers possible for these ligands, which have asymmetric centres, and it is therefore not perhaps surprising that crystalline material was not obtained. When this phosphine and iridium trichloride were heated under reflux for 20 h in 2-methoxyethanol a high-melting, white solid was obtained which analysed correctly for the tris-chelate $[Ir(P'{-}C)_3]$ but which was too insoluble for n.m.r. studies. It would appear therefore that methylphenyl(1-naphthyl)phosphine is metallated more rapidly than the less bulky dimethyl(1-naphthyl)phos-

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[19] M. A. Bennett and R. Charles, *Austral. J. Chem.*, 1971, **24**, 427.

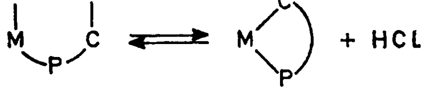
[20] G. O. Dudeck, *Spectrochim. Acta*, 1963, **19**, 691.

[21] W. R. Smith and S. Chinanjeev, *J. Phys. Chem.*, 1960, **70**, 3505.

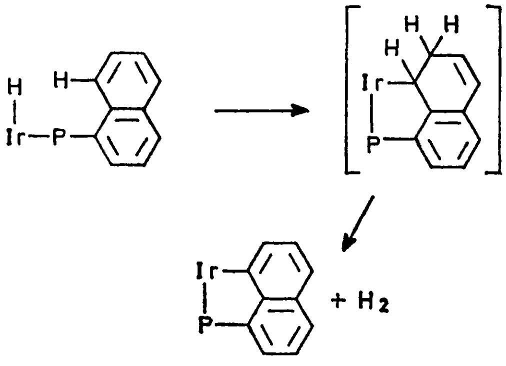
phine even though we could not characterise the products fully. Rhodium trichloride trihydrate when heated with methylphenyl(1-naphthyl)phosphine in 2-methoxyethanol gives the rhodium(I) carbonyl complex *trans*-[$RhCl(CO)L'_2$]. Triphenylphosphine reacts similarly.[22]

Dimethyl(1-naphthyl)phosphine and methylphenyl-(1-naphthyl)phosphine are new. They were prepared by adaptations of standard methods and characterized as their methiodides (See Experimental section and Table 4 for details).

Some Comments on the Internal Metallation Reactions.—Some of the internal metallation reactions required the presence of a base and these could be reversed by hydrochloric acid. Others, *e.g.* the conversion of *mer*-[$IrCl_3L_3$] to [$IrCl_2(P\text{–}C)L_2$], configuration (I), occur even in acid solution. From these observations it might be considered that the internal metallations involve an equilibrium process



and that for cases where the unmetallated phosphine is favoured the base serves merely to consume hydrogen chloride. An alternative function of the base and one that seems quite likely in some cases is to promote hydride formation, with the α-CH_2 of the alcohol solvent as the source of hydrogen. Internal metallation could then occur with elimination of dihydrogen. Thus the hydride (V) could be an intermediate in the conversion of (I) to (II) and in fact is converted into (II) much more readily in boiling 2-methoxyethanol than is (I) (in the presence of base). Similarly the hydride (III) is converted into the trimetallated complex (IV) at 260°, at which temperature the chloride (II) is stable.



SCHEME 2 A possible mechanism for the internal iridiation of 1-naphthylphosphines

In some internal metallation reactions the metal is thought to act as a nucleophile, *e.g.* the conversion of [$IrCl(PPh_3)_3$] to [$IrHCl(C_6H_4PPh_2)(PPh_3)_2$] [1,10] and in others as an electrophile *e.g.*, the palladation of dimethylbenzylamine.[1-3] Since, in the iridiation of dimethyl(1-naphthyl)phosphine, replacement of a chloride ligand by hydride enhances the rate of metallation it seems unlikely that the iridium is acting as an electrophile. The iridium could be acting as a nucleophile but six-co-ordinate iridium(III) is co-ordinatively saturated and therefore metallation probably does not go *via* ' oxidative addition '. A hydride addition–elimination mechanism, as outlined in Scheme 2 is tentatively suggested as a possible means of metallation.

EXPERIMENTAL

Reactions were carried out in an atmosphere of nitrogen or argon. M.p., yields, analytical, n.m.r., and i.r. data, *etc.* are given in the Tables. M.p.'s were determined on a Kofler hot-stage and are corrected.

Dichloro-[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*-(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (I).—A suspension of iridium trichloride (1·90 g, 4·8 mg-atom of iridium) in 2-methoxyethanol (30 ml) containing conc. hydrochloric acid (1·4 ml) was refluxed for 5 min. Dimethyl(1-naphthyl)phosphine (3·17 g, 16·9 mmol) was then added and the light brown suspension refluxed for 25 h. The resultant beige solid was extracted with dichloromethane (300 ml) and the extract evaporated to *ca.* 100 ml and diluted with methanol (*ca.* 400 ml). This gave the required product as *prisms* (3·19 g).

Hydridodichlorotris[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), (*Mixed Isomers*).—A suspension of dihydridotetrachlorobis(1,5-cyclo-octadiene)di-iridium(III) (0·19 g, 0·50 mmol) in benzene (10 ml) was treated with dimethyl-(1-naphthyl)phosphine (0·376 g, 2·0 mmol) and the resultant yellow solution was refluxed for 45 min. The hot solution was filtered to remove a small amount of sediment and the solvent and cyclo-octadiene were removed at reduced pressure. Spectroscopic examination (^1H n.m.r. and i.r.) of the resulting oil indicated it to be a mixture of two isomeric hydrides, [$IrHCl_2L_3$] (H *trans* to Cl and H *trans* to P).

Attempts to crystallize this oil were unsuccessful and irradiation of a benzene solution of the oil with light from a fluorescent lamp for several days failed to significantly alter the relative proportions of the two isomers.

mer-*Trichlorotris*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*-(III).—A dichloromethane (25 ml) solution of the crude isomeric hydrides, obtained from the treatment of dihydridotetrachlorobis(1,5-cyclo-octadiene)di-iridium(III), [$IrHCl_2(C_8H_{12})]_2$ (0·370 g, 1·0 mmol) with dimethyl(1-naphthyl)phosphine as described above, was treated with a solution of chlorine in carbon tetrachloride (1·9 ml, 1·1 mmol). The resultant clear yellow solution was evaporated to dryness immediately and the residue, a thick yellow oil, was crystallized from dichloromethane–methanol giving the desired product as bright yellow *prisms* (0·516 g). Recrystallization from benzene gave crystals containing one mole of benzene per g-atom iridium.

Thermal Conversion of mer-*Trichlorotris*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III) *to Dichloro*[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*-(III), *Configuration* (I).—A suspension of the trichloride (0·025 g) in 2-methoxyethanol (0·5 ml) was heated to reflux. The complex dissolved to give a clear yellow solution which

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[22] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1961, 290.

soon turned nearly colourless. After 2·5 min cream crystals were formed. The suspension was cooled and filtered, giving dichloro[1-(8-dimethylphosphino)naphthyl]-bis[dimethyl(1-naphthyl)phosphine]iridium(III) (0·018 g, 75%), identified by its m.p. and ^{1}H n.m.r. spectrum.

Chlorobis[1-(8-*dimethylphosphino*)*naphthyl*][*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (II).—A suspension of dichloro-[1-(8-dimethylphosphino)naphthyl]bis-[dimethyl(1-naphthyl)phosphine]iridium(III) (1·66 g, 2·0 mmol) in 2-methoxyethanol (20 ml), containing sodium acetate trihydrate (0·272 g, 2·0 mmol) was heated under reflux for 1·75 h. The mixture was cooled giving the required product as *needles* (1·48 g) from dichloromethane–methanol.

This product was also prepared from the same starting material in high yield by using the following conditions: (a) Potassium hydroxide (2 mmol) in place of sodium acetate in the above procedure. (b) A five-fold excess of hydrated sodium acetate and a reflux time of *ca.* 20 h in ethanol. (c) By refluxing a solution of the dichloride in 2-diethylaminoethanol for 1 h.

It was also obtained, in 37% yield, by treating the dichloride in benzene with an equimolar amount of methyllithium. However, unidentified products were also formed in this reaction.

Hydrobis[1-(8-*dimethylphosphino*)*naphthyl*][*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (III).—Aqueous potassium hydroxide (2·0 ml, 2 mmol) was added to a refluxing solution of chlorobis[1-(8-dimethylphosphino)-naphthyl][dimethyl(1-naphthyl)phosphine]iridium(III) (0·790 g, 1·0 mmol) in 2-methoxyethanol (15 ml). After 30 min the solvent was removed at reduced pressure and the residue recrystallized from dichloromethane–methanol giving the required product as *needles* (0·74 g). The same product was obtained in 78% yield by treating the dichloride with a five-fold excess of sodium acetate in 2-methoxyethanol for 9 h.

Tris[1-(8-*dimethylphosphino*)*naphthyl*]*iridium*(III), *Configuration* (IV).—*Method* 1. Hydridobis[1-(8-dimethylphosphino)naphthyl][dimethyl(1-naphthyl)phosphine]iridium(III) (100 mg) was heated in a glass tube at 270° for 10 min. The complex melted, evolving gas, then resolidified as a glass. The glass was sublimed (270°, 0·1 mmHg) to give light yellow *needles* (30 mg).

Method 2. To a suspension of chlorobis[1-(8-dimethylphosphino)naphthyl][dimethyl(1-naphthyl)phosphine]iridium(III) (0·237 g, 0·30 mmol) in 2-methoxyethanol (10 ml) was added silver fluoroborate (0·076 g, 0·40 mmol). The complex dissolved and a fine precipitate of silver chloride formed. After 5 min the suspension was filtered with charcoal and the resultant clear solution was refluxed for 20 min. A grey precipitate formed. The suspension was cooled and concentrated aqueous ammonia (0·2 ml) was added to remove the grey colouration. This gave the required *product* (0·172 g).

Hydridochloro[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (V).—To a suspension of dichlorobis(1,5-cyclo-octadiene)diiridium(I) (0·134 g, 0·20 mmol) in refluxing light petroleum (20 ml; b.p. 60—80°) was added dimethyl(1-naphthyl)phosphine (0·376 g, 2·0 mmol). The resultant yellow suspension was refluxed for 30 min until it became white. The suspension was allowed to cool and the product was obtained as white *microcrystals* (0·274 g).

This complex evolved gas above its melting point (*ca.* 210—230°) and resolidified as *needles*; remelting occurred at 280—300° [this product was presumably impure (II)].

Conversion of Hydridochloro[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (V), *to Chlorobis*[1-(8-*dimethylphosphino*)*naphthyl*]*dimethyl*(1-*naphthyl*)*phosphineiridium*(III), *Configuration* (II), *in Refluxing* 2-*Methoxyethanol*.—A sample of hydridochloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]iridium(III) (0·100 g) in 2-methoxyethanol (1 ml) was heated to reflux. The complex dissolved to give a clear, light yellow solution from which a white solid crystallized after about 4 min. The suspension was cooled and filtered to give white *needles* (0·062 g) which were identified as chlorobis[1-(8-dimethylphosphino)-naphthyl]dimethyl(1-naphthyl)phosphineiridium(III), configuration (II), by melting point (304—311°) and ^{1}H n.m.r. spectroscopy.

Action of Hydrochloric Acid on the Chelate Complexes

Chlorobis[1-(8-*dimethylphosphino*)*naphthyl*]*dimethyl*(1-*naphthyl*)*phosphineiridium*(III), *Configuration* (II).—A suspension of the complex (0·100 g) in 2-methoxyethanol (1 ml) containing concentrated hydrochloric acid (0·1 ml) was refluxed for 3 min. The complex partly dissolved and a cream solid precipitated from the solution. Cooling the solution gave pure dichloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]iridium(III), configuration (I) (0·091 g, 87%), identified by its ^{1}H n.m.r. spectrum.

Hydridobis[1-(8-*dimethylphosphino*)*naphthyl*][*dimethyl*-(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration* (III).—A sample of the hydride (0·050 g) was warmed gently in 2-methoxyethanol (1 ml) containing concentrated hydrochloric acid (0·1 ml). The complex dissolved with gas evolution. When the solution was heated to reflux a cream precipitate formed. After 3 min the suspension was cooled and filtered to give dichloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]-iridium(III), configuration (II) (0·047 g, 86%), identified by its ^{1}H n.m.r. spectrum.

Hydridochloro[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*(1-*naphthyl*)*phosphine*]*iridium*(III), *Configuration*, (V).—*Preparation of hydridodichlorotris*[*dimethyl*(1-*naphthyl*)-*phosphine*]*iridium*(III), *configuration* (VI). A suspension of hydridochloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]iridium(III) (0·100 g) in 2-methoxyethanol (1 ml) containing concentrated hydrochloric acid (0·1 ml) was warmed gently to *ca.* 60°; a clear light yellow solution was obtained. The solvent was removed at reduced pressure and the residue, an oil, was crystallized from dichloromethane–methanol giving hydridodichlorotris[dimethyl(1-naphthyl)phosphine]iridium(III), as large clear *prisms* (0·089 g).

mer-*Trichlorotris*[*dimethyl*(1-*naphthyl*)*phosphine*]*rhodium*(III). Rhodium trichloride (0·75 g, 3·0 mg-atom rhodium) was hydrated and dissolved in ethanol (50 ml). Dimethyl(1-naphthyl)phosphine (1·8 g, 9·9 mmol) was added and the orange suspension was well stirred for 1 h at room temperature then was filtered, giving orange *microcrystals* (2·00 g).

Dichloro[1-(8-*dimethylphosphino*)*naphthyl*]*bis*[*dimethyl*(1-*naphthyl*)*phosphine*]*rhodium*(III), *configuration* (I). A suspension of trichlorotris[dimethyl(1-naphthyl)phosphine]-rhodium(III) (1·20 g) in 2-methoxyethanol (20 ml) was warmed on a steam bath with periodic agitation for 3 h, when the suspension had changed from orange to yellow. The mixture was cooled giving the required product as yellow *prisms* (0·963 g).

Chlorotris[dimethyl(1-naphthyl)phosphine]rhodium(I).— A suspension of trichlorotris[dimethyl(1-naphthyl)phosphine]-rhodium(III) (0·185 g, 0·25 mmol) in ethanol (5 ml) containing sodium acetate trihydrate (0·167 g, 1·25 mmol) was refluxed under nitrogen for 20 min. The mixture was cooled to 0° giving the required product as orange *needles* (0·149 g). This complex is air sensitive, turning dark green after about 1 day.

Addition of Chlorine to Chlorotris[dimethyl(1-naphthyl)-phosphine]rhodium(I).—A freshly prepared solution of chlorine in benzene (0·55 ml, 0·45M) was added to chlorotris[dimethyl(1-naphthyl)phosphine]rhodium(I) (0·149 g, 0·21 mmol), suspended in benzene (2 ml). The orange needles dissolved and a fine orange precipitate formed. Methanol (2 ml) was then added giving trichlorotris[dimethyl(1-naphthyl)phosphine]rhodium(III) (0·138 g, 84%), identified by its n.m.r. spectrum.

Chlorobis[1-(8-methylphenylphosphino)naphthyl]methylphenyl(1-naphthyl)phosphineiridium(III).—A refluxing suspension of iridium trichloride (0·75 g, 2·0 mg-atom of iridium) in 2-methoxyethanol (10 ml) containing concentrated hydrochloric acid (0·60 ml) was treated with methylphenyl(1-naphthyl)phosphine (1·5 g, 6·6 mmol). The light brown suspension initially turned green and then yellow. After 2·5 h at reflux a yellow solution was obtained. This was filtered while hot to remove a trace of fine precipitate and the solvent was removed at reduced pressure to give a light yellow solid. A solution of this in dichloromethane, when diluted with methanol, gave a brittle glass which was ground up and filtered to give a white *powder* (1·378 g).

This material had no defined melting point and its n.m.r. spectrum (in deuteriochloroform) was very complex in the τ 7·5—8·5 region (phosphorus-methyl signals). It is presumed to be a mixture of isomers of the monochlorobischelated complex on the basis of its elemental analyses.

Tris[1-(8-methylphenylphosphino)naphthyl]iridium(III).—A suspension of iridium trichloride (0·507 g, 1·35 mg-atom of iridium) in refluxing 2-methoxyethanol (15 ml) containing concentrated hydrochloric acid (0·30 ml) was treated with methylphenyl(1-naphthyl)phosphine (1·11 g, 4·45 mmol). After 19 h at reflux a solid crystallized from the hot solution. This was isolated after cooling as a cream *microcrystalline solid* (0·34 g).

trans-*Chloro(carbonyl)bis[methylphenyl(1-naphthyl)phosphine]rhodium*(I).—A solution of hydrated rhodium trichloride in 2-methoxyethanol (7 ml) was treated with methylphenyl(1-naphthyl)phosphine (0·33 g, 1·32 mmol). The resultant red-brown suspension gave an orange solution when it was heated. The solution was heated at reflux for 97 h until the colour had become light yellow. Light yellow *needles* (0·020 g) were obtained on cooling the solution. The mother liquor was evaporated to dryness and the residue was recrystallized from dichloromethane–methanol to give a further amount of the same material (0·191 g).

1-*Naphthyldichlorophosphine*.—To a solution of bis(diethylamino)chlorophosphine [23] (101·5 g, 0·484 mol) in diethyl ether (1 l), cooled to −78°, was added 1-naphthylmagnesium bromide in 1 : 1 diethyl ether–benzene (570 ml, 0·532 mol). Following addition (over 2 h) the resultant beige suspension was refluxed for 30 min then was cooled to 0°. Hydrogen chloride in diethyl ether (910 ml, 2·0 mol) was then slowly added and the mixture was filtered through Celite, the solvent was removed and the residue was distilled at reduced pressure to give 1-naphthyldichlorophosphine (60·6 g).

Dimethyl(1-naphthyl)phosphine.—To a solution of 1-naphthyldichlorophosphine (24·15 g, 0·107 mol) in 2 : 1 diethyl ether–hexane, cooled to −78°, was slowly added (over 3 h) a solution of methyl-lithium in diethyl ether (300 ml, 0·26 mol). The resultant yellow suspension was heated to reflux (10 min) then was cooled to 0° and was worked up with degassed water. Separation, drying, and distillation of the organic layer gave dimethyl(1-naphthyl)-phosphine (15·31 g).

Trimethyl(1-naphthyl)phosphonium Iodide.—An excess of iodomethane (0·5 ml) was added to a solution of dimethyl-(1-naphthyl)phosphine (0·20 g) in acetone (5 ml). The product crystallized as white *needles* (0·297 g) (Found: C, 47·2; H, 5·05. $C_{13}H_{16}IP$ requires C, 47·7; H, 4·9%).

Methylphenylchlorophosphine.— Methylphenyl(dimethylamino)phosphine (25·4 g, 0·152 mol) in diethyl ether (500 ml) was treated with hydrogen chloride in diethyl ether (162 ml, 0·32 mol). Addition over 1 h gave a white suspension which was filtered through Celite. The filtrate was distilled at reduced pressure to give methylphenylchlorophosphine (19·9 g).

Methylphenyl(1-naphthyl)phosphine.—To methylphenylchlorophosphine (9·44 g, 0·0594 mol) in diethyl ether (200 ml) cooled to −78° was added (dropwise over 30 min) 1-naphthylmagnesium bromide in 1 : 1 diethyl ether–benzene (100 ml, 0·084 mol). The resultant suspension was warmed to reflux for 30 min. Work-up with saturated aqueous ammonium chloride followed by distillation of the organic layer gave methylphenyl(1-naphthyl)phosphine (11·2 g).

A small sample of the phosphine, a thick oil, was crystallized from methanol as white *prisms*, m.p. 51—55°.

Dimethylphenyl(1-naphthyl)phosphonium Iodide.—A solution of methylphenyl(1-naphthyl)phosphine (0·228 g) in acetonitrile (5 ml) was treated with iodomethane (0·2 ml) and the solution was boiled for 2 min. The product separated as large clear *needles* (0·333 g) (Found: C, 55·05; H, 4·7. $C_{18}H_{18}IP$ requires C, 55·1; H, 4·6%).

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