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SOME DIOLEFIN COMPLEXES OF IRIDIUM(I) AND A *trans*-INFLUENCE SERIES FOR THE COMPLEXES [IrCl(cod)L]

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Summary

A high-yield synthesis of $[IrCl(cod)]_2$ (cod = 1,5-cyclooctadiene) is described. The ^1H and ^{13}C NMR spectra of a number of complexes [IrCl(cod)L] are interpreted in terms of a *trans*-effect series $Cl^- <$ *sym*-collidine < 2-picoline < PCy_3 < P-i-Pr_3 < $PEt_3 \sim AsPh_3 < PMe_2Ph < PMePh_2 < PPh_3 < P(MeO)Ph_2 < PClPh_2 < P(OPh)_3 < PCl_2Ph$. Some ligand exchange reactions of [IrCl(cod)L] are discussed. A number of complexes of the type $[Ir(cod)L_n]PF_6$ (L = a variety of amines (n = 2) and phosphines (n = 2 or 3)) are described. Exchange reactions of the sort:

$$[Ir(cod)(PR_3)_2]PF_6 + [Ir(cod)(py)_2]PF_6 \rightleftharpoons [Ir(cod)(PR_3)Py]PF_6$$

are reported in which, surprisingly, the isolable mixed ligand complexes are the only detectable species at equilibrium (py = pyridine).

Introduction

The dimeric complex $[IrCl(cod)]_2$ (cod = 1,5-cyclooctadiene) is an important starting material in iridium(I) chemistry and we describe a preparation giving over 90% yield. Many related complexes of the type [IrCl(cod)L] [1—3] and $[Ir(cod)L_2]^+$ [4,5] have been isolated. Our interest in homogeneous hydrogenation has led us to prepare further complexes of these types, and their preparations and physical properties are reported here. Their reactions with hydrogen and their catalytic properties have been briefly described [6] and will be reported fully in a further paper.

Results and discussion

The synthesis of [IrCl(cod)]$_2$

$[IrCl(cod)]_2$ (I), the key starting material for the present work and for a good

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deal of iridium(I) chemistry, has been prepared by several methods in 45—85% yield [7—9]. The best yields were obtained from H_2IrCl_6 or $IrCl_3$ and (cod) in refluxing isopropanol/water [9]. We have preferred a two-step synthesis from H_2IrCl_6 and (cod) in refluxing isopropanol to give $[IrHCl_2(cod)]_2$ [10]. This colourless adduct is more readily isolated than complex I as it is less soluble and is air-stable even in solution. Removal of the coordinated HCl with aqueous sodium acetate and recrystallisation from CH_2Cl_2/EtOH gives the deep red $[IrCl(cod)]_2$ with an overall yield of 90—95%.

Synthesis and NMR spectra of the complexes [IrCl(cod)L]

In non-polar solvents, a wide variety of ligands L split the chloro bridge of I to give the neutral yellow complexes [IrCl(cod)L] (II) [1—3]. We have prepared further examples and Table 1 lists these together with the ^1H or ^{13}C chemical shifts of their (cod) vinylic protons and olefinic carbons, respectively; compared with the free ligand there is a marked upfield shift for all these complexes. Similar effects have been observed with rhodium [11], platinum [12] and nickel [13]. Clark et al. [12] suggested a relationship between π-back-bonding and ^{13}C-coordination shifts in platinum—olefin complexes. Tolman [13] showed that electron-attracting substituents on olefins bound to nickel also caused an upfield ^{13}C shift.

For complexes II two resonances are usually observed [2] for the (cod)-vinyl protons and olefinic carbons (see Table 1 and Scheme 1) and we find that $\delta(H_A)$, as well as those values of $\delta(C_A)$ that are available, correlate very well with Tolman's [14] classification of the electronic effects of the *trans*-ligands L (see Fig. 1). In those cases where L contains a phosphorus atom, only one of the two carbon resonances, $\delta(C_A)$, appears as a doublet with a $^2J(^{31}P—^{13}C)$ value appropriate [15,16] for a *trans* arrangement of phosphorus and carbon. Therefore $\delta(C_A)$ and by the analogy $\delta(H_A)$ can be assigned to the olefinic group *trans* to L.

If we can take the chemical shifts of vinyl protons and olefinic carbons in a coordinated olefin as a measure of the metal—olefin bond order, or in valence

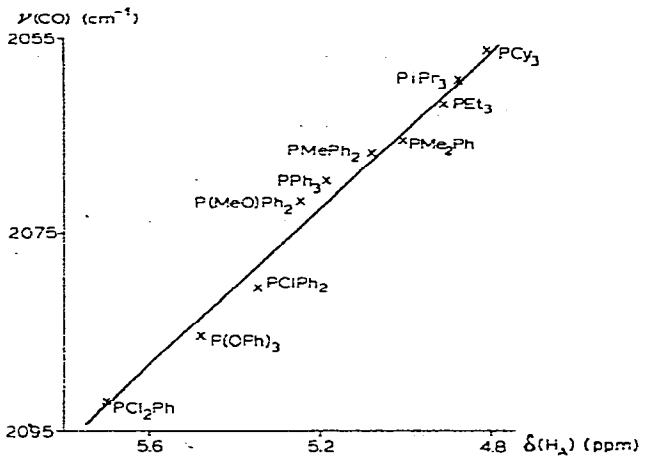


Fig. 1. Variation of $\delta(H_A)$ (ppm) of the (cod)-vinyl protons *trans* to L in [IrCl(cod)L] (II) with the A_1 ν(CO) vibration of $[LNi(CO)_3]$ after Tolman [14].

TABLE I

LIGAND EXCHANGE BEHAVIOUR AND SOME ^1H AND ^{13}C NMR CHEMICAL SHIFTS FOR THE (cod) OLEFINIC GROUPS OF THE COMPLEXES [IrCl(cod)L] (II)

L	Exchange behaviour [a]	Chemical shifts [b] (ppm)				Ref.
		δH_A	δH_B	δC_A	δC_B	
PCl_2Ph	i	5.70	3.38			1
$P(OPh)_3$ [c]	i	5.49	3.30	105.9 [d]	54.5	This work
$PClPh_2$	i	5.35	3.35	—	—	1
$P(OMe)Ph_2$ [c]	i	5.26	3.10	—	—	This work
PPh_3	ii	5.20	2.76	94.0 [e]	53.6	This work, 2
$PMePh_2$	ii	5.09	2.62	—	—	This work
PMe_2Ph	ii	5.02	2.85	—	—	This work
PEt_3 [c]	ii	4.92	3.30	—	—	This work
$AsPh_3$	iv	4.92 [f]	3.12 [f]			2
P-i-Pr_3	iii	4.89	3.20	90.0 [e]	51.5	This work
PCy_3 [g]	iii	4.81	3.17	—	—	This work
Pyridine	iv	3.87 [h]				3
2-Picoline	iii	4.47	3.08	69.8 68.6	60.0 56.6 [i]	This work
sym-Collidine	iii	4.37	2.97	—	—	This work
free (cod)		5.58		128.5		This work

[a] See Scheme 1 and text. [b] In $CDCl_3$ at 35°C (except where otherwise stated) relative to TMS. The ^{13}C NMR spectra were broad band proton decoupled. The assignments of H_A, H_B, C_A and C_B are shown in Scheme 1. [c] Not isolated (see text). [d] Doublet with $^2J(^{31}P—^{13}C)$*trans* 20.5 Hz. [e] Doublet with $^2J(^{31}P—^{13}C)$-*trans* 13 Hz. [f] At —60°C (see text). [g] Cy = cyclohexyl. [h] An exchange reaction removes the distinction between H_A and H_B (see text). [i] The aromatic ligand lies out of the square plane of the complex as four separate olefinic carbon resonances can be distinguished.

bond terms the metallacyclopropane [17] character of the system, then from the $\delta(H_A)$ values of Table 1 we can derive the following *trans*-influence series: Cl^- < *sym*-collidine < 2-picoline < PCy_3 < P-i-Pr_3 < PEt_3 ~ $AsPh_3$ < PMe_2Ph < $PMePh_2$ < PPh_3 < $P(OMe)Ph_2$ < $PClPh_2$ < $P(OPh)_3$ < PCl_2Ph.

The values of $\delta(H_B)$ vary irregularly, an effect we ascribe to through-space interactions between H_B and the aromatic substituents of the *cis*-L groups, but the values of $\delta(C_B)$ are substantially the same throughout the series.

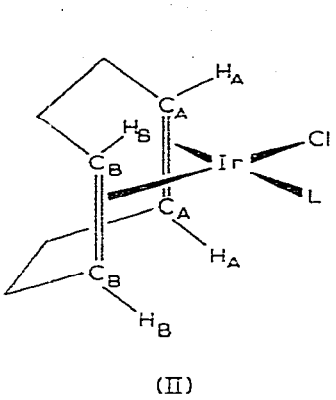
All the new complexes listed in Table 1 were isolated as yellow crystalline solids except where L = $P(OPh)_3$ and $P(OMe)Ph_2$ when only yellow oils were obtained. In these latter cases solutions for study were prepared by the addition of an equivalent of L to a solution of I in $CDCl_3$ at 35°C and their characterisation rests on their colour and on the close analogy between their ^1H and, in the case of L = $P(OPh)_3$, ^{13}C NMR spectra and those of the isolated complexes.

In two cases (L = $AsPh_3$, pyridine), exchange reactions remove the distinction between H_A and H_B but in one of these [2] (L = $AsPh_3$) measurements at —60°C give the values of $\delta(H_A)$ and $\delta(H_B)$.

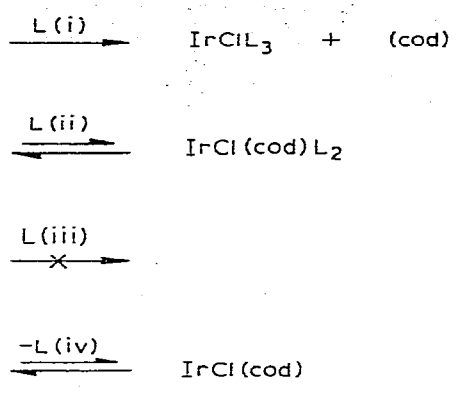
Exchange reactions of [IrCl(cod)L]

[IrCl(cod)$AsPh_3$] is known [2] to dissociate $AsPh_3$ rapidly and reversibly on the PMR timescale at 20°C and consequently only one (cod)-vinyl resonance is observed at this temperature; at —60°C two resonances are seen. The two (cod)-vinyl resonances of [IrCl(cod)PPh_3] coalesce [2] on addition of an excess of PPh_3 probably due to the intermediate formation of [IrCl(cod)$(PPh_3)_2$].

SCHEME 1. Exchange reactions of [IrCl(cod)L)] (II) and NMR assignments for the (cod) ligands.



(II)



We have therefore examined the complexes [IrCl(cod)L] both alone and in the presence of an excess of L at 35°C in $CDCl_3$ and distinguish four cases (see Scheme 1): (i) [IrCl(cod)L] (II) itself shows two (cod)-vinyl resonances but excess L displaces the (cod); (ii) II shows two resonances but these coalesce on addition of excess L; (iii) II shows two resonances which are unaffected by an excess of L; (iv) II shows only a single (cod)-vinyl resonance due to dissociation. The results of this study are indicated in Table 1.

Type i ligands are powerful π-acceptors which would be expected to weaken the metal—olefin interaction and, when present in excess, to liberate (cod) from complex II. Type iii ligands which do not exchange are particularly bulky and probably cannot give an intermediate of the type [IrCl(cod)L_2]. Type iv ligands are apparently labile and only weakly bound in complex II.

A 3-coordinate intermediate [IrCl(cod)] has been proposed [2] for this exchange process (L = $AsPh_3$); it must also be involved where L = pyridine. We have proposed a similar 3-coordinate intermediate in some exchange reactions of the cationic derivatives (see below).

Synthesis of the cationic complexes [Ir(cod)L_n]PF_6

A number of cationic complexes of the type [Ir(cod)L_n]PF_6 [4,5] (n = 2: L = $PMePh_2$, $PEtPh_2$, $P(OMe)Ph_2$, PPh_3; n = 3: L = $P(OMe)_3$, $P(OEt)_3$, PMe_2Ph) have been isolated by addition of L to complex I in acetone or ethanol and we have prepared a number of analogous complexes listed in Table 2 together with their colour, yield and characteristic PMR resonances.

It appears that phosphorus ligands having a cone angle [14] below 130° give a colourless [Ir(cod)L_3]$^+$ cation (e.g.: $P(OMe)_3$, 118°; $P(OEt)_3$, 109°; PMe_2Ph, 127°) and above 130° a red [Ir(cod)L_2]$^+$ cation (e.g.: P-n-Bu_3, 130°; $PMePh_2$, 136°; PPh_3, 145°).

Triethylphosphine, having a cone angle of 130°, appears to be an intermediate case. No analytically pure solid was isolated from solutions of $[Ir(cod)Cl]_2$ and PEt_3 in ethanol in the presence of NH_4PF_6 but faintly pink solids that we suppose to be the nearly pure [Ir(cod)L_3]$^+$ derivative can be obtained. These become red oils on standing in air, or heating to 60°C in vacuo, apparently due to loss of phosphine, and while we have not been able to crystallise these materials,

TABLE 2

COLOUR, YIELD, ANALYSIS AND PMR DATA FOR THE NEW COMPLEXES OF THE TYPE [Ir(cod)LL']PF_6

[Ir(cod)LL']PF_6 [a]			Colour	Yield (%)	Analysis (found (calcd.) (%))			PMR data [b] (δ(ppm))	
L	LL'	L'			C	H	N	cod-vinyl [c]	L
	$(P\text{-}n\text{-}Bu_3)_2$		red	30	45.1 (45.2)	7.8 (7.8)	—	4.51	0.8—2.1, c, n-Bu
	(diop)		red	85	50.0 (49.6)	4.8 (4.7)	—	4.15	1.1, s, CH_3; 1.8—2.4, c, CH and CH_2
	$(py)_2$		yellow	80	36.0 (35.8)	3.5 (3.7)	4.6 (4.9)	3.84	7.1—7.7 and 8.6—8.8, c, Ar
	$(2\text{-}pc)_2$		yellow	75	38.5 (38.0)	4.0 (4.1)	4.8 (4.4)	3.81	3.15, s, Me; 7.2—7.9 and 8.7—8.9, c, Ar
	$(4\text{-}pc)_2$		yellow	65	37.8 (38.0)	4.0 (4.1)	4.5 (4.4)	3.81	2.55, s, Me; 7.3 and 8.5, d, 7, Ar
PPh_3		py	orange	80	46.9 (47.3)	3.7 (4.1)	2.1 (1.8)	4.44 3.60	7.0—7.6 and 8.2—8.4, c, Ar
$AsPh_3$		py	orange	35	44.5 (44.8)	3.8 (3.9)	1.7 (1.7)	4.15	7.1—7.5 and 8.4—8.6, c, Ar
$P\text{-}i\text{-}Pr_3$		py	orange	70	38.7 (38.7)	5.3 (5.3)	2.2 (2.1)	4.18 4.02	1.3, d x d, 6 and 12, Me; 2.0, c, CH; 7.5—7.8 and 8.8—8.9, c, Ar
$P\text{-}i\text{-}Pr_3$		imid	orange	80	36.2 (36.7)	5.3 (5.5)	4.1 (4.2)	4.02	1.3, d x d, 6 and 12, Me; 2.0, c, Me_2—CH; 7.1, 7.3 and 8.0, s, Ar
PCy_3		py	orange	80	47.1 (46.3)	6.1 (6.3)	1.8 (1.7)	4.00	0.8—2.5, c, Cy; 7.6—7.8 and 8.6—8.9, c, Ar
PMe_2Ph		2-pc	orange	*d*	—	—	—	4.55 3.75	1.8, d, 9, MeP; 2.7, s, MeAr; 8.4 and 8.8, d, 7, Ar
$PMePh_2$		4-pc	orange	*d*	—	—	—	4.40 3.75	1.8, d, 9, MeP; 2.3, s, MeAr; 8.15, d, 7, Ar

[a] diop = L-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; py = pyridine; Cy = cyclohexyl; *n*-pc = *n*-methylpyridine; imid = imidazole. [b] In $CDCl_3$ at 35°C. Resonances reported as follows: position (δ, ppm) multiplicity, coupling constant (Hz), assignment. s = singlet, d = doublet, c = complex resonance, Ar = aromatic group. In all cases satisfactory integrals were obtained. All complexes have a complex resonance at δ 1.8—2.6 ppm assigned to (cod)—CH_2 protons and those complexes containing PPh groups showed a complex resonance at δ 7.0—7.9 ppm assigned to the aromatic protons. [c] Broad unresolved resonances: $\omega(1/2) \sim 10$ Hz. [d] Not isolated (see text.)

their NMR spectra are consistent with the formula $[Ir(cod)(PEt_3)_2]PF_6$.

The very bulky ligands do not appear to form $[Ir(cod)L_2]^+$ cations and only [IrCl(cod)L] are isolated (e.g.: P-i-Pr_3, 160°; PCy_3, 179°).

Amines, such as pyridine, only give $[Ir(cod)L_2]^+$ derivatives, so that either the metal centre is too electron-rich to coordinate a further relatively basic amine, or these ligands have effective cone angles greater than 130°.

The very bulky *sym*-collidine only gives an [IrCl(cod)L] derivative.

Synthesis of the mixed ligand complexes [Ir(cod)LL']PF_6

We were surprised to find that an equimolar mixture of $[Ir(cod)(PPh_3)_2]PF_6$ and $[Ir(cod)(py)_2]PF_6$ in CH_2Cl_2 at room temperature rapidly rearranges to give a new complex $[Ir(cod)(PPh_3)py]PF_6$ which can be crystallised in high yield by addition of ether. The same cation was also formed from II (L = PPh_3) by treatment with pyridine in ethanol. A number of similar complexes were also obtained and these are listed in Table 2.

The exchange reaction between $[Ir(cod)(PMePh_2)_2]PF_6$ (III) and an equivalent of $[Ir(cod)(4\text{-picoline})_2]PF_6$ in CD_2Cl_2 at 35°C as monitored by PMR spectroscopy was complete in 20 minutes. The reaction between III and the more hindered 2-picoline analogue took several days.

The complexes $[Ir(cod)L'_2]PF_6$ (where L' is a pyridine derivative) rapidly underwent a stepwise substitution in the presence of $PMePh_2$, giving the mixed ligand derivative with one equivalent, and complex III with two equivalents. In contrast complex III is unaffected even by neat pyridine. This leads us to believe that the first step of the exchange reaction is dissociation of PMe_2Ph from III presumably to give a 3-coordinate 14-electron intermediate; the free PMe_2Ph then attacks the bis-pyridine complex to give the mixed ligand derivative. A 3-coordinate intermediate has been proposed [2] for the exchange reactions of some of the complexes II.

We were not able to isolate the picoline-containing mixed-ligand complexes other than as oils but we list their PMR resonances and colours in Table 2.

Experimental

The complexes were isolated by standard Schlenk-tube techniques; even solutions were not air-sensitive except in the cases of $[IrCl(cod)]_2$ and $[Ir(cod)(PR_3)py]PF_5$.

NMR spectra were measured on Perkin—Elmer R12A (^1H) and Bruker H-90 (^{13}C) instruments. H_2IrCl_6 was a generous loan of the Compagnie des Métaux Précieux. The other reagents were obtained from Fluka A.G. and used as received except PCy_3, which was prepared from CyMgBr and PCl_3 [18] by M. Claude Frajerman. Microanalyses were performed by the Service de Microanalyse, C.N.R.S., Gif-sur-Yvette.

Di-μ-chlorodi-η^4-1,5-cyclooctadienediiridium(I)

A solution of H_2IrCl_6 (12 g, containing 3 g Ir) was treated with 20 ml of (cod) in refluxing i-PrOH (30 ml) for 6 h. The volatile solvents were removed in vacuo (60°C, 1 h) and the residue washed with hexane (2 × 10 ml) and dried in vacuo (20°C, 5 min). The white solid was shaken for 24 h with a solution of

sodium acetate (4.2 g) in water (30 ml) during which time it became deep red; it was filtered, washed (2 × 10 ml H_2O) and dried (60°C, 30 min). The solid was dissolved in CH_2Cl_2, filtered and recrystallised as deep red prisms by addition of an equal volume of ethanol and reducing the volume of the solution under reduced pressure. Yield 4.75 g (91%). (Found: C, 28.6; H, 3.6; Cl, 10.6. $C_8H_{12}ClIr$ calcd.: C, 28.6; H, 3.6; Cl, 10.6%).

Chloro(η^4-1,5-cyclooctadiene)(tertiary phosphine)iridium(I)

$[IrCl(cod)]_2$ (335 mg) was dissolved in CH_2Cl_2 (4 ml) and a slight molar excess of tertiary phosphine added (1.2 mol-equiv.). The solution became yellow and the product was isolated by the addition of octane followed by reduction of the volume of the solvent under reduced pressure. The complexes were filtered, washed with hexane (2 × 2 ml), and recrystallised from CH_2Cl_2/Et_2O. The following new complexes were isolated as yellow prisms: L = P-i-Pr_3: yield 370 mg (75%) (Found: C, 41.7; H, 6.7; Cl, 7.1. $C_{17}H_{33}ClPIr$ calcd.: C, 41.2; H, 6.7; Cl, 7.1%). L = PCy_3: yield 460 mg (75%) (Found: C, 50.5; H, 7.3; Cl, 5.5. $C_{26}H_{45}ClPIr$ calcd.: C, 50.7; H, 7.4; Cl, 5.8%.) L = $PMePh_2$: yield 320 mg (60%) (Found: C, 47.1; H, 4.7; Cl, 7.1. $C_{21}H_{25}ClPIr$ calcd.: C, 47.0; H, 4.7; Cl, 6.6%). PMR spectra (in $CDCl_3$ at 35°C; reported as: position (δ, ppm), multiplicity, coupling constant (Hz), assignment; see also Table 2): L = P-i-Pr_3, 1.3, dd, 6 and 12; Me; 1.5—2.9, c, $Me_2\underline{CH}$ and (cod)CH_2. L = PCy_3: 0.9—2.5, c, cyclohexyl and (cod)CH_2. L = $PMePh_2$: 1.3—2.4, c, (cod)CH_2; 2.1, d, 9, Me; 7.3—7.9, c, aromatic.

Chloro(η^4-1,5-cyclooctadiene)(amine)iridium(I)

$[IrCl(cod)]_2$ (335 mg) in CH_2Cl_2 (4 ml) was treated with an excess of amine (0.3 ml) and the following yellow products isolated as above: L = 2-picoline: yield 260 mg (60%) (Found: C, 39.1; H, 4.5; Cl, 8.3; N, 3.0. $C_{14}H_{19}ClNIr$ calcd.: C, 39.2; H, 4.5; Cl, 8.3; N, 3.3%. L = 3-picoline: yield 270 mg (63%) (Found: C, 39.2; H, 4.5; Cl, 8.1; N, 3.0%; $C_{14}H_{19}ClNIr$ calcd. as above). L = 4-picoline: yield 300 mg (70%) (Found: C, 39.5; H, 4.2; Cl, 8.3; N, 3.5. $C_{14}H_{19}ClNIr$ calcd. as above). L = *sym*-collidine: yield 340 mg (75%) (Found: C, 42.2; H, 5.4; Cl, 8.0. $C_{16}H_{23}ClNIr$ calcd.: C, 42.1; H, 5.1; Cl, 7.8%). PMR spectra (reported as above; see Table 1): L = 2-picoline: 1.2—2.5, c, (cod)CH_2; 3.1, s. Me; 7.0—7.8 and 8.6—8.8, c, aromatic. L = 3-picoline: 1.4—2.6, c, (cod)CH_2; 2.35, s, Me; 3.9, broad, (cod) vinyl; 7.1—7.7 and 8.4—8.8 c, aromatic, L = 4-picoline: 1.1—2.5, c, (cod)CH_2; 2.30 s, Me; 3.82, broad, (cod) vinyl; 7.1—7.3 and 8.4—8.6, c, aromatic. L = *sym*-collidine: 1.1—2.5, c, (cod) CH_2; 2.27, s, Me; 3.14, s, *o*-Me; 6.9, s, aromatic.

Observation of the NMR spectra of [IrCl(cod)L]

$[IrCl(cod)]_2$ (35 mg (^1H); or 150 mg (^{13}C)) in $CDCl_3$ (0.5 ml, 1% TMS (^1H); or 2.0 ml, 5% TMS (^{13}C)) were treated with 1.0 molar equivalent of L (L = $P(OPh)_3$ (^1H and ^{13}C); or $P(OMe)Ph_2$ (^1H)) and the solutions transferred to the appropriate NMR tubes with flexible stainless steel tubing under a positive nitrogen pressure. Where L = $PMePh_2$ it was verified that the spectra obtained in this way were identical to those obtained from the isolated complex [IrCl(cod)$PMePh_2$].

Observation of exchange reactions of [IrCl(cod)L] (II) with excess L

The solutions of the complexes [IrCl(cod)L] made up for ^{1}H NMR spectroscopy were treated with an excess of the ligand L (10 mol equiv.). Four types of behaviour were observed. Type i (scheme 1 and text): Free (cod) (δ 5.58 and 2.30 ppm) was liberated. Type ii: The (cod)-vinyl resonances $\delta(H_A)$ and $\delta(H_B)$ coalesced on addition of an excess of L and were replaced by a broad resonance ($\omega_{1/2} \simeq 30$ Hz) at $1/2(\delta(H_A) + \delta(H_B))$. Type iii: The spectrum of II was unaffected and in some cases (L = 2-picoline, *sym*-collidine and PPr_3) free and complexed L could be distinguished. Type iv: II shows only one (cod)-vinyl resonance and addition of L brought about no apparent change; the L resonances shift on addition of L and free and complexed L could not be distinguished. The results are reported in Table 1.

(η^4-1,5-cyclooctadiene)bis(tertiary phosphine)iridium(I) hexafluorophosphates

The following new complexes were prepared by the method of Haines and Singleton [4]: L = P-n-Bu_3 and L_2 = L-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane. (Table 2 lists the properties of all the new cationic complexes).

(η^4-1,5-cyclooctadiene)bis(amine)iridium(I) hexafluorophosphates

The following new complexes were prepared by the method of ref. 19: L = pyridine and 4-picoline.

(η^4-1,5-cyclooctadiene)(amine)(tertiary phosphine)iridium(I) hexafluorophosphates

Method A. [IrCl(cod)L] (1 mmol, L = PR_3) in methanol (40 ml) was treated with an excess of tertiary amine (L', 0.5 ml) for 60 min and then with NH_4PF_6 (550 mg). The orange precipitate was filtered, washed with water (5 ml) then methanol (5 ml), dried in vacuo and recrystallised from CH_2Cl_2/Et_2O to give orange crystals. The following complexes were prepared in this way. L = PPh_3, L' = pyridine and L = P-i-Pr_3, L' = imidazole. A tertiary arsine analogue was prepared by the same method. L = $AsPh_3$, L' = pyridine (see Table 2).

Method B. [Ir(cod)py_2]PF_6 (1 mmol) in acetone (5 ml) was treated with PR_3 (R = i-Pr, 300 mg; R = Cy, 400 mg) and to the orange solution was added ethanol (5 ml). The mixture was reduced in volume to give orange crystals which were isolated and recrystallised from CH_2Cl_2/Et_2O. By this method were isolated [Ir(cod)LL']PF_6. L = P-i-Pr_3, L' = pyridine and L = PCy_3, L' = pyridine (see Table 2).

Method C. [Ir(cod)L_2]PF_6 (0.5 mmol, L = PR_3) and [Ir(cod)L'_2]PF_6 (0.5 mmol, L' = amine) were dissolved in CH_2Cl_2 (10 ml). After 10 min (L' = py), 60 min (L' = 4-picoline) or 2 weeks (L' = 2-picoline) the solvent was evaporated and, where L' = pyridine, the product was recrystallised from CH_2Cl_2/Et_2O. The following complex was prepared in this way. L = PPh_3, L' = pyridine: (yield 75%). The following complexes could only be isolated as orange oils. L = $PMePh_2$, L' = 2- and 4-picoline (quantitative yield).

Monitoring of exchange reactions of [Ir(cod)L_2]PF_6 derivatives by PMR spectroscopy

Equimolar quantities of [Ir(cod)L_2]PF_6 (L = PR_3) and [Ir(cod)L'_2]PF_6 (L'

= amine) were dissolved in CD_2Cl_2 (0.5 ml, 1% TMS) and monitored at 35°C by PMR spectroscopy. Where L = PPh_3 and L′ = pyridine the only resonances observable were those of $[Ir(cod)LL']PF_6$. Where L = $PMePh_2$ and L′ = 4-picoline the reaction was substantially complete in 20 minutes and where L = $PMePh_2$ and L′ = 2-picoline the reaction was ca. 50% complete after 3 days.

The reaction of $[Ir(cod)L'_2]PF_6$ (L′ = pyridine and 2-picoline) with free $PMePh_2$(L) was monitored similarly and proved to be effectively instantaneous. The phosphine was added by means of a microsyringe. The signals of $[Ir(cod)LL']PF_6$ appeared and died away with incremental amounts of L ultimately to give $[Ir(cod)L_2]PF_6$; the signals of free L′ were also detected.

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