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INTRAMOLECULAR ISOMERIC INTERCONVERSIONS IN FOUR- AND FIVE-COORDINATE CHELATE OLEFIN COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) FORMED BY (*o*-VINYLPHENYL)DIPHENYLPHOSPHINE AND ITS ARSENIC ANALOGUE

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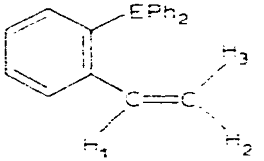
Summary

(*o*-Vinylphenyl)diphenylphosphine(*o*-styryldiphenylphosphine), *o*-CH_2=CH-$C_6H_4PPh_2$ (spp) and its arsenic analogue, *o*-CH_2=$CHC_6H_4AsPh_2$ (spas) form five-coordinate complexes of rhodium(I) and iridium(I) of general formula $MClL_2$ (M = Rh, Ir; L = spp, spas). Cationic derivatives $[MQL_2]^+$ are formed from $MClL_2$ and $AgBF_4$, NH_4PF_6 or $NaBPh_4$ in the presence of a ligand Q (M = Rh, Q = CO, PF_3, C_2H_4, PPh_3, $PMePh_2$; M = Ir, Q = CO, PF_3, $PMePh_2$, pyridine). All these complexes are believed to be trigonal bipyramidal with the Group V atoms of spp or spas in axial sites. The vinyl groups are in equatorial sites and probably lie in the equatorial plane. ^{1}H and ^{31}P NMR spectra show that many of the complexes contain two isomers, a "symmetric" isomer having equivalent vinyl groups, and an "unsymmetrical" isomer having inequivalent vinyl groups; the isomerism arises from the different possible orientations of the vinyl groups with respect to each other. The rhodium(I) isomers interconvert rapidly on the NMR time scale at or just above room temperature, whereas the iridium(I) isomers are frozen under these conditions. The complexes $[Rh(C_2H_4)L_2]^+$ undergo rapid intermolecular exchange with free ethylene at room temperature. Intramolecular isomeric interconversion is suggested to occur by dissociation of one of the vinyl groups, giving a four-coordinate intermediate. Treatment of $RhCl(spp)_2$ with $AgBF_4$ or $NaBPh_4$ generates a planar cation $[Rh(spp)_2]^+$, which contains varying proportions of *cis*- and *trans*-isomers, depending on the solvent. In contrast, the analogous reactions with $IrCl(spp)_2$ form a five-coordinate, presumably trigonal bipyramidal aquo-cation $[Ir(H_2O)(spp)_2]^+$ which also contains two isomers. One of these is "symmetric", with equivalent vinyl groups and equivalent, axial phosphorus atoms; the other is "unsymmetrical", with inequivalent vinyl groups and inequivalent, mutually *cis*-phosphorus atoms which occupy an equatorial and an axial site.

Introduction

Complexes formed by potentially chelating olefinic tertiary phosphines and arsines with rhodium(I) and iridium(I) have attracted recent attention as model systems for metal-catalysed or metal-promoted reactions of olefins, such as hydrogenation and isomerisation. Other features of interest are the relative binding tendencies of olefins to these two d^8 elements, and the tendency of the resulting complexes to adopt five- rather than four-coordinate structures. Much published work, due largely to Hartwell and co-workers [1—8], is concerned with complexes of rhodium(I) and iridium(I) with flexible bidentate or multidentate ligands containing one, two or three 3-butenyl or 4-pentenyl chains, $(CH_2)_nCH=CH_2$ (n = 2, 3), attached to phosphorus or arsenic. There are also reports of chelate olefin complexes of rhodium(I) formed by more rigid ligands e.g. those containing the o-vinylphenyl group, $(o\text{-}CH_2=CHC_6H_4)_nPPh_{3-n}$ (n = 1—3) [9—13], and tridentate ligands such as $o\text{-}R_2PC_6H_4CH\overset{t}{=}CHC_6H_4PR_2\text{-}o$ (R = Ph or $o\text{-}CH_3C_6H_4$) [14—16] and $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o$ [17]. Following our preliminary communication [9], we report here on four- and five-coordinate, uncharged and cationic complexes of rhodium(I) and iridium(I) with the bidentate ligands (o-vinylphenyl)diphenylphosphine(o-styryldiphenylphosphine, $o\text{-}CH_2=CHC_6H_4PPh_2$ (I) (abbreviated spp), and its arsenic analogue II (abbreviated spas). Our results on the rhodium(I) chemistry of spp are compared, where appropriate, with those of Brookes [12,13], which appeared after our preliminary communication had been published.



(I) spp, E = P

(II) spas, E = As

Results and discussion

Preparation and structure of $MClL_2$ and $[M(CO)L_2]^+$ (M = Rh or Ir; L = spp or spas)

The ligands spp and spas (L) react with the cyclooctene complexes $[MCl(C_8H_{14})_2]_2$ (M = Rh or Ir) to give microcrystalline complexes of empirical formula $MClL_2$ which are yellow in the case of rhodium and white in the case of iridium. The rhodium complexes are also conveniently obtained by reducing ethanolic rhodium trichloride (1 mol) with formaldehyde in the presence of more than 2 mol of L, a method which, when used with triphenylphosphine (L = PPh_3), provides a useful synthesis of $RhCl(CO)(PPh_3)_2$ [18]. The bromorhodium(I) complex $RhBr(spp)_2$ can be obtained either by metathesis from the chloride, or from rhodium tribromide, formaldehyde and an excess of spp. The 1,5-cyclooctadiene complex $[RhCl(1,5\text{-}COD)]_2$ can also be used as a pre-

TABLE 1

ANALYTICAL, MOLECULAR WEIGHT, AND CONDUCTIVITY DATA FOR RHODIUM(I) AND IRIDIUM(I) COMPLEXES OF spp AND spas [a]

Complex	Analysis found (calcd.) (%)			Λ (conc. 10^4 M) [b]
	C	H	P(As)	
RhCl(spp)$_2$ [c]	67.3	4.8	8.5	17.9 (2.25)
	(67.2)	(4.8)	(8.7)	
RhBr(spp)$_2$ [d]	63.3	4.6	8.0	n.m.
	(63.2)	(4.5)	(8.2)	
RhCl(spas)$_2$ [e]	59.7	4.5		8.2 (3.19)
	(59.8)	(4.2)		
IrCl(spp)$_2$ [f]	59.9	4.3	7.5	11.1 (2.89)
	(59.7)	(4.2)	(7.7)	
IrCl(spas)$_2$ [g]	53.95	3.9		7.7 (2.21)
	(53.8)	(3.8)		
[Rh(CO)(spp)$_2$]Cl [h]	65.9	4.9	8.1	n.m.
	(66.3)	(4.6)	(8.35)	
[Rh(CO)(spas)$_2$]Cl [i]	59.0	4.2		n.m.
	(59.2)	(4.1)		
[Rh(CO)(spp)$_2$][RhCl$_2$(CO)$_2$] [j]	54.9	3.6	6.4	58.9 (2.50)
	(55.1)	(3.6)	(6.7)	
[Rh(spp)$_2$]BF$_4$ [k]	62.5	4.1	8.3	19.6 [l]
	(62.7)	(4.4)	(8.1)	
[Rh(spas)$_2$]BF$_4$ [k]	56.9	4.65		53.6 (2.39)
	(57.1)	(4.3)		
[Rh(spp)$_2$]BPh$_4$ [k]	76.6	5.2	6.3	18.3 [l]
	(76.9)	(5.45)	(6.2)	
[Rh(spas)$_2$]BPh$_4$ [k]	70.7	4.95		51.0 (1.93)
	(70.7)	(5.0)		
[Ir(H$_2$O)(spp)$_2$]BF$_4$ [k]	56.1	3.8		63.9 (1.76)
	(55.0)	(4.2)		
[Ir(H$_2$O)(spas)$_2$]BF$_4$ [k]	50.6	3.5		68.5 (2.76)
	(50.0)	(3.8)		
[Ir(H$_2$O)(spp)$_2$]BPh$_4$ [k]	70.4	4.8		56.8 (2.60)
	(69.5)	(5.1)		
[Ir(H$_2$O)(spas)$_2$]BPh$_4$ [k]	65.5	4.7		n.m.
	(64.4)	(4.7)		
[Rh(CO)(spp)$_2$]BF$_4$	61.6	4.2	7.5	57.6 (2.50)
	(62.0)	(4.3)	(7.8)	
[Rh(CO)(spas)$_2$]BF$_4$	55.6	3.8		70.8 (2.60)
	(55.8)	(3.85)		
[Rh(CO)(spp)$_2$]PF$_6$	57.6	4.0	10.9	63.9 (2.21)
	(57.75)	(4.0)	(10.9)	
[Rh(CO)(spp)$_2$]BPh$_4$	76.25	5.4	5.55	48.1 (2.71)
	(76.0)	(5.3)	(6.0)	
[Ir(CO)(spp)$_2$]BF$_4$	55.4	4.2		75.1 (2.73)
	(55.7)	(3.85)		
[Ir(CO)(spas)$_2$]BF$_4$	50.6	3.4		75.6 (2.21)
	(50.7)	(3.5)		
[Ir(CO)(spp)$_2$]BPh$_4$	69.8	4.9		53.5 (1.89)
	(70.0)	(4.8)		
[Ir(CO)(spp)$_2$]PF$_6$	52.5	3.7		73.8 (2.30)
	(52.3)	(3.6)		
[Rh(PF$_3$)(spp)$_2$]BF$_4$	56.3	4.2	10.0	65.4 (2.28)
	(56.2)	(4.0)	(10.9)	
[Rh(PF$_3$)(spas)$_2$]BF$_4$	51.2	3.9	2.9(P)	72.5 (3.31)
	(51.0)	(3.6)	(3.3)(P)	
[Ir(PF$_3$)(spp)$_2$]BF$_4$	51.1	3.45		71.1 (2.29)
	(50.9)	(3.6)		

(to be continued)

TABLE 1 (continued)

Complex	Analysis found (calcd.) (%)			Λ (conc. 10^4 M) [b]
	C	H	P(As)	
$[Ir(PF_3)(spas)_2]BF_4$	46.0	3.1		75.8 (1.77)
	(46.6)	(3.3)		
$[Rh(PMePh_2)(spp)_2]BF_4$	65.9	5.1	9.1	65.9 (1.95)
	(65.8)	(4.9)	(9.4)	
$[Rh(PMePh_2)(spas)_2]BF_4$	60.0	4.7	3.1(P)	71.7 (2.37)
	(60.3)	(4.5)	(2.9)(P)	
$[Ir(PMePh_2)(spp)_2]BF_4$	60.5	4.9		77.0 (2.39)
	(60.3)	(4.45)		
$[Ir(PMePh_2)(spas)_2]BF_4$	55.4	4.0		76.7 (2.17)
	(55.6)	(4.1)		
$[Rh(PPh_3)(spp)_2]BF_4$	67.6	5.1	8.8	69.7 (2.01)
	(67.7)	(4.8)	(9.05)	
$[Ir(py)(spp)_2]BF_4$	56.8	4.5	1.4(N)	n.m.
	(57.8)	(4.2)	1.5(N)	

[a] Abbreviation: n.m., not measured. Molecular weights measured by osmometry in $CHCl_3$ at 25°C. [b] In nitromethane at 23°C; Λ_M for a 1 : 1 electrolyte in this solvent is generally in the range 60—115 ohm^{-1} cm^2 mol^{-1}. [c] % Cl found, 5.3; calcd., 5.0. Mol. wt. found, 714; calcd., 714. [d] % Br found, 10.65; calcd., 10.5. [e] % Cl found, 4.2; calcd., 4.4. Mol. wt. found, 735; calcd., 802. [f] % Cl found, 4.1; calcd., 4.4. Mol. wt. found, 809; calcd., 804. [g] % Cl found, 3.7; calcd., 4.0. Mol. wt. found, 880; calcd., 891. [h] % Cl found, 5.2; calcd., 4.8. Mol. wt. found, 386, calcd., 401 (for completely dissociated 1 : 1 electrolyte). [i] % Cl found, 4.4; calcd., 4.3. Mol. wt. found, 400; calcd., 415 (for completely dissociated 1 : 1 electrolyte). [j] % Cl found, 7.7; calcd., 7.6. Mol. wt. found, 505; calcd., 464 (for completely dissociated 1 : 1 electrolyte). [k] % Cl found, 0.0; calcd., 0.0. [l] Complex insoluble in nitromethane.

cursor instead of the cyclooctene complex [12], and $IrCl(spas)_2$ is formed from $[IrCl(1,5\text{-}COD)]_2$ and spas on heating in benzene. All the complexes are monomeric in chloroform and non-conducting in nitromethane (Table 1). The characteristic bands due to the vinyl group frequencies of spp and spas at ca. 1620 cm^{-1} (C=C stretch) and 990 and 920 cm^{-1} (vinyl CH deformations) are absent from the IR spectra of the complexes, but bands at ca. 1260 cm^{-1} are present. Absorption in this region has been observed in the rhodium(I) complexes of tri(*o*-styryl)phosphine, $(o\text{-}CH_2{=}CHC_6H_4)_3P$, and related ligands, and can be assigned to a coupled mode '$\nu(C{=}C) + \delta(CH_2)$' [10]. The solid state Raman spectra of $RhX(spp)_2$ (X = Cl or Br) show two bands at 1480 and 1490 cm^{-1}, which are characteristic of a double bond modified by coordination in mono-olefin complexes of platinum(II) and rhodium(I) [19,20], and can also be assigned to a coupled mode '$\nu(C{=}C) + \delta(CH_2)$'. A band at 236 cm^{-1} in the far IR spectrum of $RhCl(spp)_2$ is assigned to $\nu(RhCl)$; the corresponding $\nu(RhBr)$ band in $RhBr(spp)_2$ is at 143 cm^{-1}. Brookes [12] reports two bands at 253 and 239 cm^{-1} for $\nu(RhCl)$ in $RhCl(spp)_2$, but we find that the higher frequency absorption occurs in both $RhCl(spp)_2$ and $RhBr(spp)_2$.

The vinyl resonances in the ^1H NMR spectra of $MClL_2$ are shifted well upfield of those of the free ligands (see below) and this evidence, taken in conjunction with the evidence discussed above, suggests that the complexes are five-coordinate with both double bonds coordinated.

The complexes undergo chloride abstraction reactions on treatment with silver tetrafluoroborate to give cationic species in solution which we shall provisionally regard as $[ML_2]^+$ (M = Rh or Ir; L = spp or spas); their exact nature is discussed below. Solutions of these cations react rapidly under ambient conditions with carbon monoxide to give stable cationic carbonyls $[M(CO)L_2]^+$, which can be isolated as their BF_4, PF_6 or BPh_4 salts. The reaction is marked by colour changes in the solutions from dark orange to pale yellow in the case of rhodium, and from red to colourless in the case of iridium. The complexes behave as 1 : 1 electrolytes in nitromethane, and their IR spectra show one $\nu(CO)$ band at ca. 2040 cm^{-1}, both in the solid state and in solution. ^1H NMR spectra (see below) show that both vinyl groups are coordinated, so that the cations are five-coordinate.

The $[Rh(CO)L_2]^+$ cations can also be isolated as their pale yellow chloride salts by reaction of carbon monoxide with $RhClL_2$, but these readily lose CO in solution and revert to the starting materials. Reaction of 2 mol of spp with $[RhCl(CO)_2]_2$ gives the salt $[Rh(CO)(spp)_2][RhCl_2(CO)_2]$, which is a 1 : 1 electrolyte in nitromethane (Table 1). The IR spectrum shows $\nu(CO)$ bands at 2060 and 1980 cm^{-1} characteristic of the anion and at 2039 cm^{-1} due to the cation, and the ^1H NMR spectrum is identical with that of other salts of $[Rh(CO)(spp)_2]^+$, which can be isolated from $[Rh(CO)(spp)_2][RhCl_2(CO)_2]$ by metathesis, e.g. with $NaBF_4$ or $NaBPh_4$. There is no evidence for the formation of monomeric complexes such as RhCl(CO)(spp) or $RhCl(CO)_2(spp)$, although these may be intermediate in the formation of the chelate σ-alkyl $[RhCl_2(CO)(o\text{-}CH_3CHC_6H_4PPh_2)]_2$ in the reaction of $[RhCl_2(CO)_2]^-$, spp and HCl [21]. In contrast with the rhodium complexes, neither $IrCl(spp)_2$ nor $IrCl(spas)_2$ react with carbon monoxide. Likewise, whereas the iridium(I) complexes do not react with t-butyl isocyanide, the rhodium(I) complexes form an inseparable mixture of thermally unstable complexes [probably $[Rh(spp)_2(t\text{-}BuNC)]Cl$ and $[Rh(spp)(t\text{-}BuNC)_2]Cl$], both of which show a $\nu(CN)$ band at 2170 cm^{-1}.

In discussing the structures of the five-coordinate complexes of spp and spas, it is convenient to consider first the cationic carbonyls, because they are more soluble in the usual organic solvents, e.g. chloroform, dichloromethane and acetone than are the parent chlorides, and generally give better resolved NMR spectra. The ^1H NMR spectrum of $[Rh(CO)(spas)_2]BF_4$ in CD_2Cl_2 at 32°C shows coordinated vinyl resonances at δ 4.88 ppm (broad triplet) and δ 3.30 ppm (doublet) in the ratio 1 : 2, in addition to aromatic resonances (Table 2). On cooling, these resonances broaden and finally sharpen at −58°C into a multiplet pattern; the process is reversible and the coalescence temperature is about −20°C. Similarly the ^1H NMR spectrum of $[Rh(CO)(spp)_2]BF_4$ which, at 32°C, consists of three broad and ill-resolved resonances due to coordinated vinyl protons at δ 3.0, 3.4 and 4.55 ppm, changes on cooling to −43°C into a number of multiplets (Table 2). In the $^1H\{^{31}P\}$ spectrum at this temperature nine vinyl proton resonances can be discerned. The ^1H NMR spectra of the $[Rh(CO)L_2]^+$ species clearly show the presence of isomers which are interconverting sufficiently rapidly at room temperature that the vinyl proton resonances are time-averaged, but in which both vinyl groups are coordinated to rhodium. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh(CO)(spp)_2]BF_4$ at room temperature is broad and featureless, but in the temperature range −15 to −68°C it consists of a doublet and an *AB* quartet of doublets, the intensity ratio being approximately 1 : 1 (Table 3).

(continued on p. 196)

TABLE 2

^1H NMR DATA FOR RHODIUM(I) AND IRIDIUM(I) COMPLEXES OF spp AND spas [a, b]

Complex		Solvent (T °C)	$\delta(H_1)$	$\delta(H_2)$	$\delta(H_3)$	J_{12}	J_{13}	J_{23}
$RhCl(spp)_2\{^{31}P\}$ [c] (prob. one predominant isomer)		CD_2Cl_2	4.17dt	3.28(br)d	3.01dt	8.0	11.0	2.0
		CD_2Cl_2 (−65)	← 3.0(br)d, 3.74cd, 4.04ct →			?	?	?
$RhCl(spas)_2$ (prob. one predominant isomer)		CD_2Cl_2	4.88t	3.65d	3.07d	7.8	11.7	1.0
$IrCl(spp)_2\{^{31}P\}$ major isomer [d,e]		CD_2Cl_2	3.91t	3.41dd	2.51dd	8.0	8.0	2.5
			3.21t	2.43d	2.43d	8.5	8.5	?
$IrCl(spas)_2$ (isomeric mixture)		$CDCl_3$	4.68t	3.82d(om)	2.64d(om)	8.5	8.5	<2
			4.85t	3.8–3.9om	2.5–2.8om	9.0	9.0	?
			4.64t	3.8–3.9om	2.5–2.8om	8.0	8.0	?
$[Ir(CO)(spp)_2]BF_4\{^{31}P\}$	Sym. isomer	1 : 1 $CDCl_3/CD_2Cl_2$	3.98t	2.38dd	2.68dd	8.0	10.0	1.5
	unsym. isomer		3.99t	3.61dd	2.96dd	8.5	9.0	2.5
			4.04t	2.65dd	2.99dd	8.0	11.0	2.0
$[Ir(CO)(spas)_2]BF_4$	sym. isomer	$CDCl_3$	4.10dd	2.84dd	2.66dd	8.0	10.5	2.0
	unsym. isomer		4.56dd	3.93dd	2.6–2.9om	8.5	9.5	?
			4.35dd	3.6–2.9om	2.6–2.9om	8.5	11.0	?
$[Rh(CO)(spp)_2]BF_4$ (isomeric mixture)		CD_2Cl_2 (−43)	← 2.60m, 3.00m, 3.12m, 3.34m, 3.73m, 3.81m, 4.42m, 4.45m, 4.55m →			?	?	?
		CD_2Cl_2	← 3.0m, 3.4m, 4.55m, →					
$[Rh(CO)(spas)_2]BF_4$ (prob. isomeric mixture)		CD_2Cl_2	4.88(br)t	← 6.70d →		?	12.0	?
$[Rh(spp)_2]BF_4\{^{31}P\}$ [f, g, h]	sym. isomer	$CDCl_3$ (−43)	6.18dd	5.09d	4.48d	8.5	14.5	<2
	unsym. isomer	3 : 1 $CDCl_3$/acetone-d_6 (−43)	4.68(br)m, 4.78(br)m	← 3.36, 3.84, 4.1, 4.2(br)m →		?	?	?
$[Ir(H_2O)(spp)_2]BF_4\{^{31}P\}$ [i] (isomeric mixture)		$CDCl_3$ (−15)	4.86(br)t	← 3.80, 3.84om →		← sum 16.0 →		<2
			3.99om	3.32d	3.15d	8.5	11.5	~2
$[Ir(NH_3)(spp)_2]BF_4\{^{31}P\}$ [j] (isomeric mixture)		$CDCl_3$	← −2.5m, 2.88m, 3.16m, 3.51m, 3.95m, 4.50m →			?	?	?

$[\mathrm{Ir(py)(spp)_2}]\mathrm{BF_4}\{^{31}\mathrm{P}\}$ [h]	sym. isomer	$\mathrm{CDCl_3}$	3.96t	2.24dd	2.16dd	8.0	8.0	1.5
	unsym. isomer		5.08t 3.40t	3.32dd 2.94dd	2.09dd 2.83dd	8.0 8.0	8.0 8.0	1.5 3.0
$[\mathrm{Ir(PMePh_2)(spp)_2}]\mathrm{BF_4}\{^{31}\mathrm{P}\}$ [l]	sym. isomer	$\mathrm{CDCl_3}$	3.43t	2.59d	2.29d	9.0	8.0	1.5
	unsym. isomer		4.06t 3.23t	3.72d 2.73d	3.27d 2.27d	8.0 9.0	8.0 8.0	1.5 3.0
$[\mathrm{Ir(PMePh_2)(spas)_2}]\mathrm{BF_4}$ [m] (isomeric mixture)		$\mathrm{CDCl_3}$	← 2.33m, 2.80d, 3.4m, 3.79t, 5.0m →			?	?	?
$[\mathrm{Rh(PMePh_2)(spp)_2}]\mathrm{BF_4}$ [n] (isomeric mixture)		$\mathrm{CDCl_3}$	← 2.2m, 2.7m, 3.1m, 3.4m, 3.7m, 4.1m →			?	?	?
$[\mathrm{Rh(PMePh_2)(spas)_2}]\mathrm{BF_4}$ [o]		$\mathrm{CDCl_3}$	← 2.3m, 2.59d, 2.88d, 3.10d, 3.5m, 3.79t, 4.2m →			?	?	?
$[\mathrm{Rh(PPh_3)(spp)_2}]\mathrm{BF_4}$ (isomeric mixture)		$\mathrm{CDCl_3}$	← 2.2m, 2.8m, 3.1m, 3.4m, 3.7m, 4.1m →			?	?	?
$[\mathrm{Rh(PF_3)(spp)_2}]\mathrm{BF_4}$ [p] (prob. isomeric mixture)		$\mathrm{CD_2Cl_2}$	← 2.6(br)m, 3.2(br)m, 3.6(br)m →			?	?	?
$[\mathrm{Rh(C_2H_4)(spp)_2}]\mathrm{BF_4}$ [q] (prob. isomeric mixture)		$\mathrm{CD_2Cl_2}$	← 3.5(br)m, 4.5(br)m, 4.9(br)m →			?	?	?

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[a] Chemical shifts (δ) in ppm downfield of internal TMS, coupling constants (J) in Hz (±0.5). Aromatic resonances are complex multiplets in the range δ 6.8–8.2 ppm. Spectra measured at 32°C, except where stated. Protons are numbered as in I and II. [b] Abbreviations: s, singlet; d, doublet, t, triplet; dd, doublet of doublets; dt, doublet of triplets; c, complex; m, multiplet; (br), broad; om, overlapping multiplets. [c] $J(\mathrm{Rh{-}H_1})$ 2, $J(\mathrm{Rh{-}H_2})$ 1.5, $J(\mathrm{Rh{-}H_3})$ 1.5, $J(\mathrm{P{-}H_3})$ 4.8 Hz. [d] Signals in normal ^{1}H spectrum were broad multiplets. [e] $^1\mathrm{H}\{^{31}\mathrm{P}\}$ spectrum of minor isomer not clearly resolved. [f] In $\mathrm{CD_2Cl_2}$, there are nine vinyl proton resonances corresponding to an approximately 1 : 1 mixture of the "symmetrical" and "unsymmetrical" isomers. [g] Signals of "symmetrical" isomer were only slightly sharper in $^1\mathrm{H}\{^{31}\mathrm{P}\}$ spectrum than in normal spectrum. [h] In $^1\mathrm{H}\{^{31}\mathrm{P}\}$ spectrum a doublet due to aromatic protons appears at δ 6.54, 6.62 ppm. [i] $\mathrm{H_2O}$ resonance at δ 2.63 ppm((br)s); this does not disappear on addition of $\mathrm{D_2O}$. [j] $\mathrm{NH_3}$ resonance at δ 1.72 ppm ((br)s). [k] Pyridine α-proton resonances at δ (ppm) 8.36 (d, J 4.5 Hz), 9.06 (d, J 4.5 Hz). Unassigned resonances also appear at δ 3.63, 3.68 ppm (unsym. d) and 4.24(s). [l] δ (ppm) 1.45d ($\mathrm{P{-}CH_3}$, J 8), 1.07d ($\mathrm{P{-}CH_3}$, J 7.5 Hz), in normal ^{1}H spectrum. Aromatic resonances appear at δ (ppm) 5.8s [d in normal spectrum, $J(\mathrm{P{-}H})$ 7 Hz] 6.54 (d, J 8 Hz) and 6.66 (d, J 8 Hz). [m] δ (ppm) 1.40d ($\mathrm{P{-}CH_3}$, J 7 Hz), 1.05d ($\mathrm{P{-}CH_3}$, J 7 Hz). [n] δ (ppm) 1.33(br)d ($\mathrm{P{-}CH_3}$, J 6 Hz). [o] δ (ppm) 1.3(br)s ($\mathrm{P{-}CH_3}$). [p] Coordinated vinyl resonances of other $[\mathrm{M(PF_3)L_2}]\mathrm{BF_4}$ complexes are similar to those of $[\mathrm{Rh(PF_3)(spp)_2}]\mathrm{BF_4}$. [q] δ (ppm) 3.95(br)s ($\mathrm{C_2H_4}$). Also unassigned resonance at δ 1.5 ppm.

TABLE 3

^{31}P NMR DATA [a]

Complex	Solvent	T (°C)	δ(P) (intensity)	^2J(P—P)	J(Rh—P)
RhCl(spp)$_2$	CDCl$_3$ or CH$_2$Cl$_2$	+38	37.9d	[b]	103
		−30	38.2d, 24.5d	[c]	101
RhBr(spp)$_2$	CH$_2$Cl$_2$	+38	37.0(br)d	[b]	[d]
IrCl(spp)$_2$	CH$_2$Cl$_2$	+38	15.6, 4.8q (4) 12.2s (1)	433 [b]	
[Rh(CO)(spp)$_2$]BF$_4$	CH$_2$Cl$_2$	−15 or −68	48.9, 35.3qd (1) 47.0d (1)	354 [b]	86, 85 86
[Ir(CO)(spp)$_2$]BF$_4$	CH$_2$Cl$_2$	+32 or −68	18.3, 4.6q (1) 16.8s (1)	321 [b]	
[Rh(spp)$_2$]BF$_4$	CHCl$_3$	−15	42.8, 38.4t (1) 34.2d (9)	$\leq$3 [b]	106 151
	CH$_2$Cl$_2$	−15	42.3, 38.1t (1) 34.6d (1)	$\leq$3 [b]	103 147
	CHCl$_3$/Me$_2$CO (3 : 1)	−15	41.1, 36.9t (9) 33.6d (1)	$\leq$3 [b]	102 148
[Ir(H$_2$O)(spp)$_2$]BF$_4$	CHCl$_3$	−12	12.2d, 7.7d ($>$9) 19.7s ($<$1)	13 [b]	
	CH$_2$Cl$_2$	−12	12.8d, 8.6d (4) 20.1s (1)	13 [b]	
	CHCl$_3$/Me$_2$CO (98 : 2)	−12	12.2d, 8.0d (9) 19.9s (1)	13 [b]	
	CHCl$_3$/Me$_2$CO (9 : 1)	−12	12.2d, 8.1d (4) 19.8s (1)	13 [b]	
	CHCl$_3$/Me$_2$CO (1 : 1)	−12	11.7d, 8.2d (7) 19.3s (3)	13 [b]	
	Me$_2$CO	−12	11.7d, 8.1d (1) 19.3s (1)	13 [b]	
[Ir(NH$_3$)(spp)$_2$]BF$_4$	CDCl$_3$	+32	15.9d, 3.2d (8) 16.7s (1)	14 [b]	
[Ir(py)(spp)$_2$]BF$_4$	CDCl$_3$	+32	15.2s(2), 11.3s(1), 10.0s(1), 8.7s(1)	[c]	
	CD$_2$Cl$_2$	+32	15.5s (4), 11.7s (3), 10.0s (3), 8.8s (3)		
[Rh(PMePh$_2$)(spas)$_2$]BF$_4$	CH$_2$Cl$_2$	+38	−1.42d		112
[Ir(PMePh$_2$)(spp)$_2$]BF$_4$	CDCl$_3$	+32	8.0d(spp), −37.5t (PMePh$_2$) (5) 6.8d(spp), −41.3t (PMePh$_2$) (1)	22 [e] 21 [e]	

[a] Chemical shifts in ppm relative to external 85% H$_3$PO$_4$, downfield being taken as positive. Coupling constants accurate to within $\pm$5 Hz. Abbreviations as in Table 2. [b] Could not be determined owing to equivalence of phosphorus atoms. [c] Could not be determined because outer lines of *AB* quartet(s) were not observed. [d] Could not be determined owing to broadness of spectrum. [e] Refers to coupling between ^{31}P nuclei of spp and PMePh$_2$, coupling between inequivalent ^{31}P nuclei of spp in major isomer could not be determined from observed spectrum.

These resonances clearly arise from a pair of isomers, of which one has equivalent phosphorus atoms [J(Rh—P) 86 Hz], the other inequivalent phosphorus atoms [^2J(P—P) 354 Hz, J(Rh—P) 86, 85 Hz]; the magnitude of ^2J(PP) indicates that the inequivalent phosphorus atoms are mutually *trans*.

The ^{1}H NMR spectra of [Ir(CO)(spp)$_2$]BF$_4$ and [Ir(CO)(spas)$_2$]BF$_4$ show complex vinyl resonance patterns in the range δ 2.6—5.0 at room temperature. In the ^{1}H{^{31}P} NMR spectrum of the former three sets of mutually coupled

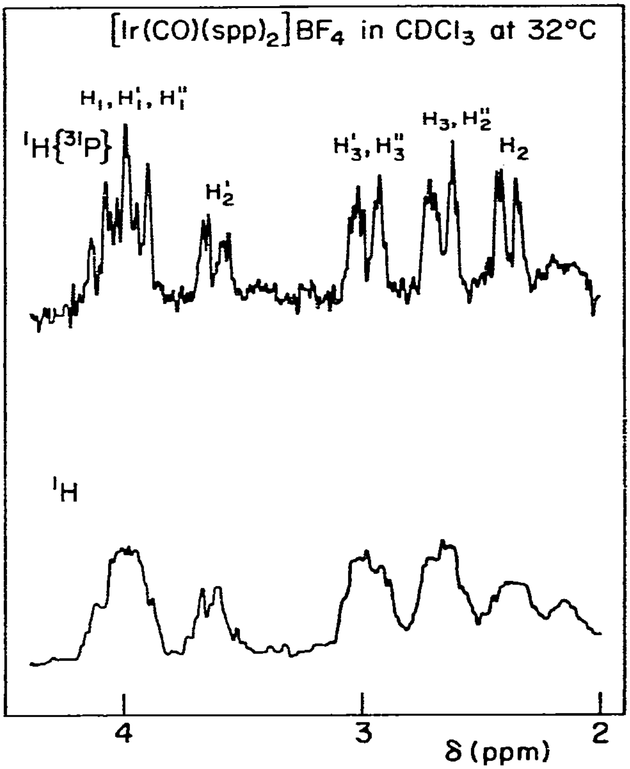


Fig. 1. ^{1}H NMR spectrum of [Ir(CO)(spp)$_2$]BF$_4$ in CDCl$_3$ at 32 C, with and without ^{31}P-decoupling. H$_1$, H$_2$, H$_3$ are the α-, *cis* β and *trans*-β vinyl protons respectively of the isomer with equivalent vinyl groups, H$_1$', H$_2$', H$_3$' and H$_1$'', H$_2$'', H$_3$'' are the corresponding vinyl protons of the isomer with inequivalent vinyl groups.

vinyl resonances can be picked out (Fig. 1) and the chemical shifts of the α- and β-protons and the *cis*- and *trans*-coupling constants can be obtained (Table 2). The ^{31}P{^{1}H} spectrum, which does not change between 30°C and —68°C in CD$_2$Cl$_2$, consists of a singlet and an *AB* quartet [^2J(P—P) 321 Hz] in approximately 4 : 5 ratio (Table 3). Thus [Ir(CO)(spp)$_2$]$^+$, like [Rh(CO)(spp)$_2$]$^+$, consists of two isomers, one having equivalent phosphorus atoms, the other having inequivalent, *trans*-phosphorus atoms; in contrast with the rhodium compound, the isomers do not interconvert rapidly on the NMR time scale at room temperature and the isomer with inequivalent phosphorus atoms is slightly favoured (ca. 5 : 4). The fact that three sets of vinyl resonances are observed for each complex [M(CO)(spp)$_2$]$^+$ (M = Rh, Ir) suggests that one of the isomers (presumably that with equivalent phosphorus atoms) has equivalent vinyl groups, while in the other isomer the vinyl groups are inequivalent. The ^{1}H NMR spectrum of [Ir(CO)(spas)$_2$]BF$_4$ in CDCl$_3$ at 32°C (Fig. 2 and Table 2) also shows the presence of two such isomers; in this case the isomer with equivalent vinyl groups is slightly favoured (ca. 5 : 4).

The NMR spectra of MClL$_2$ are generally similar to those of [M(CO)L$_2$]$^+$.

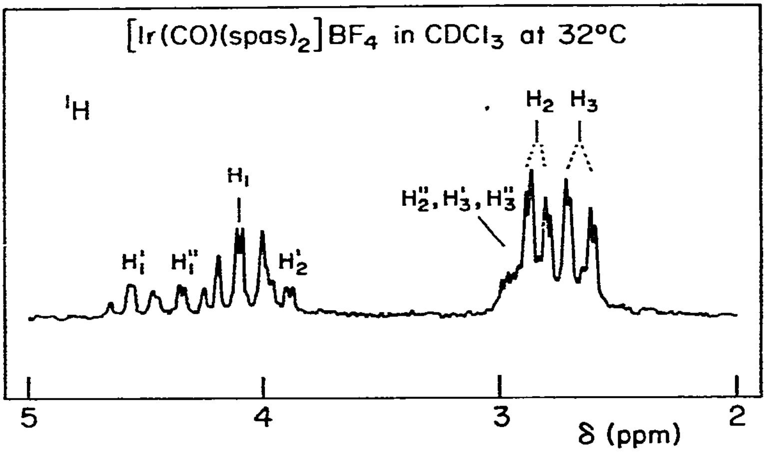


Fig. 2. ¹H NMR spectrum of [Ir(CO)(spas)$_2$]BF$_4$ in CDCl$_3$ at 32°C. Protons are numbered as in Fig. 1.

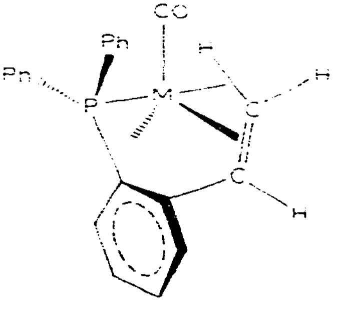
The three broad multiplets due to the coordinated vinyl protons in IrCl(spp)$_2$ simplify on ^{31}P-decoupling to a multiplet pattern, and the presence of two isomers is evident. The chemical shifts of the α- and β-protons and the ^{1}H—^{1}H coupling constants of the major isomer can be extracted (Table 2). The isomers appear in the ^{31}P{^{1}H} NMR spectrum at room temperature as an *AB* quartet [^2J(P—P) 433 Hz] and a singlet, the isomer with *trans*, inequivalent phosphorus atoms and inequivalent vinyl groups being about four times more abundant than the more symmetrical isomer. The ^{1}H spectrum of IrCl(spas)$_2$ is similar to, but more complex than, the ^{1}H{^{31}P} spectrum of IrCl(spp)$_2$, and there appear to be at least two isomers present. On warming from 32°C the resonances coalesce and at 135°C the spectrum shows three broad resonances, similar in general outline to the spectra of RhCl(spp)$_2$ and RhCl(spas)$_2$ at room temperature (see below).

The ^{1}H NMR spectrum of RhCl(spp)$_2$ at 32°C consists of two broad multiplets at δ 3.0 and δ 3.3 ppm due to the β-vinyl protons and an approximate triplet with further small splittings at δ 4.2 ppm due to the α-proton; the β-proton resonances simplify on ^{31}P-decoupling to two doublets with additional small splittings. The derived ^{1}H—^{1}H and ^{1}H—^{103}Rh coupling constants are in Table 2. On cooling, these resonances broaden and finally, at —65°C, a spectrum corresponding to two inequivalent vinyl groups is obtained. The ^{31}P{^{1}H} spectrum in dichloromethane or *cis*-dichloroethylene at 38°C consists of a doublet [J(Rh—P) 103 Hz] which collapses on cooling and sharpens at —30°C to give a pair of overlapping doublets [average J(Rh—P) 101 Hz] arising from inequivalent phosphorus atoms. There is no sign in our spectra of small coupling between the phosphorus atoms, or of the lower intensity outer lines of an *AB* quartet, but if ^2J(P—P) were about 400 Hz the latter would have only 5—10% of the intensity of the central lines and could well have escaped detection. By analogy with [M(CO)L$_2$]$^+$ (M = Rh, Ir; L = spp, spas), we suggest that the phosphorus atoms are mutually *trans*, i.e. that RhCl(spp)$_2$ consists predominantly of an isomer with *trans*, inequivalent phosphorus atoms and inequivalent vinyl groups. An isomer or isomers with equivalent vinyl groups and equivalent phosphorus atoms may be present in low concentration but could not be detected by ^1H or ^{31}P NMR.

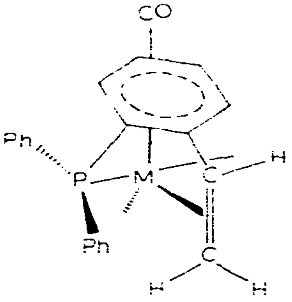
It is worth noting that to obtain reproducible $^{31}P\{^1H\}$ NMR spectra for $RhCl(spp)_2$ we had to use freshly prepared samples. Aged samples, or samples which were allowed to remain in the NMR solvent for >6 h developed spurious peaks, presumably arising from decomposition and/or reaction with the solvent. The appearance of a doublet [J(Rh—P)(?) 124 Hz] was characteristic of this behaviour, but the nature of the species responsible could not be determined.

We assume that the coordination geometry about rhodium(I) or iridium(I) in $MClL_2$ and $[M(CO)L_2]^+$ is essentially trigonal bipyramidal with two phosphorus atoms in axial positions and the double bonds in equatorial positions parallel with the equatorial plane. This has been established for coordinated spp by an X-ray study of $Fe(CO)_2(spp)_2$ [22], and in the related chelate complexes $RhCl[P(CH_2CH_2CH=CH_2)_3]$ [7] and $RhBr[P(o\text{-}CH_2=CHC_6H_4)_3]$ [11] the phosphorus atom is in an axial position and all three coordinated double bonds are almost parallel to the equatorial plane. However, in $RhCl[Ph_2PCH_2CH_2CH=CH_2]_2$, although both double bonds lie approximately in the equatorial plane, one of the phosphorus atoms is axial and the other equatorial [8].

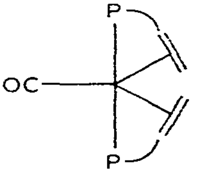
In the case of spp or spas, each chelate group has two possible orientations III and IV with respect to the monodentate ligand in the equatorial position of the trigonal bipyramids. The presence of the Cl or CO and the second chelate ring thus give rise to three conceivable geometric isomers for $MClL_2$ and $[M(CO)L_2]^+$, owing to the different possible mutual orientations of the vinyl groups, i.e. head-to-head (V), tail-to-tail (VI) and head-to-tail (VII). The situation is



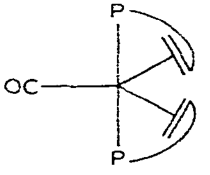
(III)



(IV)



(V)



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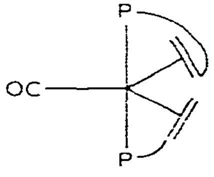


(VII)

precisely that described previously for $Ru(CO)(spp)_2$ [23], which is isoelectronic with $[Rh(CO)(spp)_2]^+$; the ruthenium compound has two isomers in a 2 : 1 ratio, the isomer having inequivalent vinyl groups and inequivalent phosphorus atoms predominating. This isomer is readily assigned structure VII, while the isomer with equivalent vinyl groups and equivalent phosphorus atoms (assumed to be *trans*) could have either structure V or VI. VII is the predominant isomer in the case of $IrCl(spp)_2$, and the same is probably true of $IrCl(spas)_2$, $RhCl(spp)_2$ and $RhCl(spas)_2$, but in the other cases the ratio, where it can be determined, is about 1 : 1. The isomers can only interconvert if one of the double bonds dissociates from the coordination sphere, and the fact that this occurs more readily for the rhodium(I) complexes than for either the iridium(I) complexes or for $Ru(CO)(spp)_2$ is in line with the general tendency of these d^8 metals to increase their coordination number from four to five viz. Ru(0) > Ir(I) >> Rh(I) [24].

There is evidence that spas is more labile than spp in its rhodium(I) complexes. The IR spectrum of a solution of $[Rh(CO)(spas)_2]BF_4$ which has been treated with carbon monoxide shows a medium intensity band at 2092 cm^{-1} in addition to the band at 2040 cm^{-1}; the former, but not the latter, disappears when nitrogen is passed through the solution. The ^1H NMR spectrum of $[Rh(CO)(spas)_2]BF_4$ is unaffected by the presence of CO at room temperature but, at −58°C, the vinyl resonances broaden and shift 6—7 Hz downfield. The observations are consistent with the presence in solution of a small amount of a dicarbonyl cation $[Rh(CO)_2(spas)_2]^+$ in which either one of the vinyl groups or one of the arsenic atoms has been displaced from the coordination sphere. In contrast, $[Rh(CO)(spp)_2]BF_4$ does not react with CO even at −58°C. The iridium(I) complexes $[Ir(CO)L_2]BF_4$ (L = spp or spas) are also inert to CO.

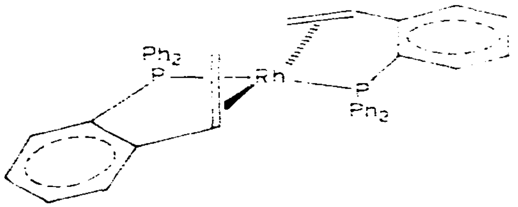
Preparation and structure of cationic complexes $[RhL_2]^+$ from $RhClL_2$ (L = spp or spas)

Treatment of $RhCl(spp)_2$ or $RhCl(spas)_2$ with sodium tetrafluoroborate, sodium tetraphenylborate or, more conveniently, silver tetrafluoroborate gives orange-red solutions from which orange crystalline salts $[RhL_2]Y$ (Y = BF_4 or BPh_4) can be isolated. Brookes [13] generated the $[Rh(spp)_2]^+$ cation in situ but did not isolate any of its salts. Samples of $[RhL_2]^+$ salts which are exposed to moisture gradually lighten in colour and show bands at ~ 3300 cm^{-1} and 1600 cm^{-1} due to water. If $[Rh(spp)_2]^+$ is prepared with rigorous exclusion of moisture using carefully dried $AgBF_4$ a bright red solution results but, on addition of water, the colour lightens. However, the ^1H and ^{31}P NMR spectra of the $[Rh(spp)_2]BF_4$ solutions are not altered by addition of water. The IR spectra and the ^1H NMR spectra (see below) show that both vinyl groups are coordinated, and the conductivities of $[Rh(spas)_2]Y$ (Y = BF_4 or BPh_4) in nitromethane are as expected for a 1 : 1 electrolyte. The values for $[Rh(spp)_2]Y$ are considerably lower than this, and are about equal to the value for $RhCl(spp)_2$. This may be a consequence of extensive ion-pairing, but the values may not be very reliable because the salts are virtually insoluble in nitromethane.

The ^1H NMR spectra of isolated salts of $[Rh(spp)_2]^+$ and $[Rh(spas)_2]^+$ show broad, ill-resolved multiplets in the range δ 3.0—6.2 which must be due to coordinated vinyl protons of different isomers, but as the spectra vary with method of preparation we have studied the spectra of $[Rh(spp)_2]^+$ generated in situ in the NMR solvent. Under these conditions the room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra are still broad and poorly resolved, but at −15°C two isomers are clearly evident in the $^{31}P\{^1H\}$ NMR spectrum, the relative amounts of which are remarkably solvent-dependent (Table 3). In chloroform, 90% of one isomer (A) is present, whereas in 3 : 1 chloroform/acetone 95% of the other isomer (B) is formed, and in dichloromethane the proportions are approximately equal. The $^{31}P\{^1H\}$ NMR spectrum of A at −15°C consists of a simple doublet [J(Rh—P) ~150 Hz], showing that A has equivalent phosphorus atoms, while the spectrum of B consists of a 1 : 2 : 1 triplet arising from overlap of the two inner lines of a pair of doublets [J(Rh—P) ~ 105 Hz], indicating that B has inequivalent phosphorus atoms. These conclusions are supported by the $^1H\{^{31}P\}$ NMR spectrum of $[Rh(spp)_2]^+$ in $CDCl_3$ at −43°C which shows only three vinyl resonances assignable to the α- and β-protons of the equivalent vinyl groups of isomer A (Table 2 and Fig. 3). In $CDCl_3$/acetone-d_6 at −43°C the $^1H\{^{31}P\}$ spectrum can be interpreted on the basis of six vinyl protons arising from two inequivalent vinyl groups of isomer B (Table 2 and Fig. 3), while in CD_2Cl_2 at −43°C there are nine vinyl resonances which can be satisfactorily assigned to an approximately 1 : 1 mixture of A and B, in agreement with the $^{31}P\{^1H\}$ spectrum.

The magnitude of J(Rh—P) for B is near the range observed for planar rhodium(I) complexes such as $RhCl(CO)(PR_3)_2$ (120—130 Hz) [25—27] and is very close to the values found for the cationic chelate olefin complexes of rhodium(I) $[Rh(CO)(o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)]^+$ (107 Hz) [28] and $[Rh(CO)\{o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o\}]^+$ (109, 110 Hz; 100, 102 Hz for the inequivalent *trans*-phosphorus atoms in two isomers) [17,28]. Thus the phosphorus atoms in B are mutually *trans*, and B probably contains planar coordinated rhodium(I). Since ^2J(P—P) in such complexes is generally 300-400 Hz, the outer lines of the AB quartet in the $^{31}P\{^1H\}$ NMR spectrum are too weak to be detected, as discussed for $RhCl(spp)_2$.

B may have the *trans*-planar structure VIII, in which one vinyl group is



(VIII)

oriented at right-angles to the RhP_2 plane and the other vinyl group is in the plane. IR evidence has been adduced for rotational isomerism of this type in solutions of $M(CO)_4(spp)$ (M = Mo or W), although in this case interconversion between the rotamers is fast on the NMR time scale down to −90°C [29]. The complex $RuCl(CO)(spp)(o\text{-}CH_3CHC_6H_4PPh_2)$ shows temperature-dependent ^1H and ^{31}P NMR behaviour which may be due to the presence of interconverting rotamers, though the possibility of geometric isomers of the type discussed

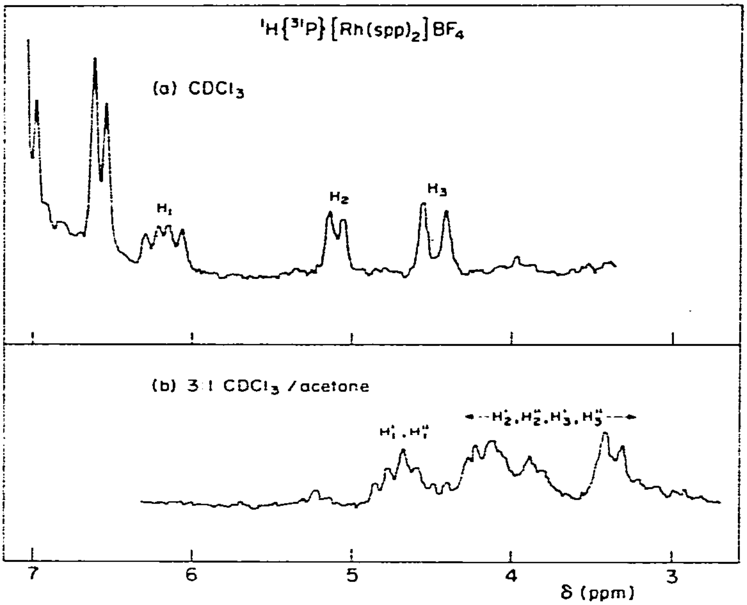


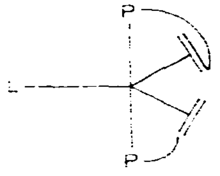
Fig. 3. $^1H\{^{31}P\}$ NMR spectrum of [Rh(spp)$_2$]BF$_4$ at −43°C in (a) CDCl$_3$ in which 97% of the isomer with equivalent vinyl groups is present, and (b) 3 : 1 CDCl$_3$/acetone-d_6, in which about 90% of the isomer with inequivalent vinyl groups is present.

above for [M(CO)L$_2$]$^+$, which can interconvert only by initial dissociation of the double bond, could not be ruled out [30]. Both possible conformations for chelated olefinic tertiary phosphines have been found in different complexes by X-ray studies, e.g. in planar Pt(CH$_3$)$_2$(spp) [31] and trigonal bipyramidal Fe(CO)$_2$(spp)$_2$ [22] the coordinated double bond is at right-angles to the plane of the chelate ring, whereas in octahedral Mo(CO)$_4$(o-CH$_3$CH=CHC$_6$H$_4$PPh$_2$) [32] and RuCl(CO)(spp)(o-OHCCHC$_6$H$_4$PPh$_2$) [33] it is in the plane of the chelate ring. In planar mono-olefin complexes of platinum(II) and rhodium(I) the preferred orientation of the double bond in the solid state is at right-angles to the coordination plane, and if structure VIII is correct, one must explain why the vinyl groups should adopt different orientations. Possibly this arrangement allows the double bonds to accept electron density from different filled *d* orbitals on the metal.

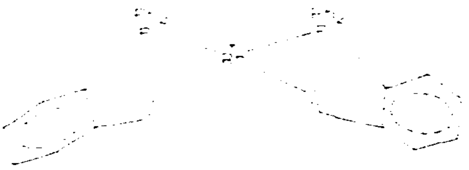
An alternative possibility is that B is actually five-coordinate (structure IX), with water or acetone occupying an equatorial site, and the vinyl groups being in the equatorial plane in a head-to-tail arrangement as in VII. We were unable to detect the presence of water in the $^1H\{^{31}P\}$ NMR spectra of solutions of [Rh(spp)$_2$]$^+$ in dichloromethane or CDCl$_3$/acetone-d_6 (cf. the analogous iridium complex below), and the IR spectra of freshly prepared solutions of [Rh(spp)$_2$]$^+$ did not show characteristic absorptions due to water. We therefore favour the planar structure.

Since the phosphorus atoms in A are equivalent, we cannot use P—P coupling constants to say whether they are *cis* or *trans*. However, the magnitude of

J(Rh—P) (~150 Hz) is very similar to that observed in both neutral and cationic rhodium(I)—diolefin complexes such as RhCl(diene)(PR_3) [26] and [Rh(diene)(PR_3)$_2$]$^+$ (140—160 Hz) [34], in which the double bond is *trans* to PR_3. On this basis we assign isomer A a *cis*-planar structure in which both double bonds are probably at right-angles to the RhP_2 plane; as noted above, this is the favoured orientation for d^8 metal—olefin complexes. In this case, there are two possible isomers in which the double bonds are respectively head-to-head (X) or head-to-tail (XI), but we cannot say which of these is favoured.



(IX) L = H_2O or $(CH_3)_2CO$



(X)

(XI)

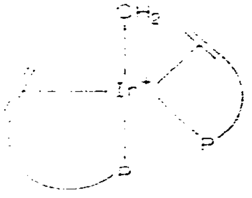
It is surprising at first sight that the *trans*-structure VIII should be favoured over the *cis*-structures X or XI in more polar media, since the equilibrium between *cis*- and *trans*-planar palladium(II) complexes $PdCl_2(PR_3)_2$ (PR_3 = $PMePh_2$ or PMe_2Ph) shifts towards the more polar *cis*-isomer with increasing solvent polarity [35,36]. However, in the case of [Rh(spp)$_2$]$^+$, the important factor may be the donor ability of the solvent, i.e. the ease with which it can occupy a fifth coordination site, rather than its polarity. An adduct such as IX may be more readily formed from the *trans*-isomer than from the *cis*-isomer as a consequence of steric crowding of the axial sites in the latter.

Brookes [13] has suggested that [Rh(spp)$_2$]$^+$ is only stable in solution in the presence of tetraphenylborate ion as a consequence of a π-interaction with an arene ring of the latter. Our results show that [Rh(spp)$_2$]$^+$ is formed in solution in the absence of $NaBPh_4$, and we suspect that some of the various weak complex resonances in the region δ 5.2—6.5 assigned by Brookes to the coordinated arene rings are in fact coordinated vinyl resonances (Table 2). As discussed elsewhere [37], a π-interaction between [Rh(spp)$_2$]$^+$ and $NaBPh_4$ certainly occurs in the presence of hydrogen. It is of interest that the ^{1}H NMR spectra of both isomers of [Rh(spp)$_2$]$^+$, and of [Rh(spas)$_2$]$^+$ (probably an isomeric mixture) show highly shielded aromatic resonances at about δ 6.5 ppm, perhaps because aromatic rings are forced into proximity in the crowded coordination spheres.

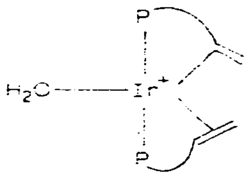
Preparation and structure of cationic complexes $[IrL_2(H_2O)]^+$ from $IrClL_2$ (L = spp or spas)

Treatment of $IrClL_2$ with $AgBF_4$, $NaBF_4$ or $NaBPh_4$ gives a brown red solution from which red salts of apparent composition $[IrL_2]Y$ (Y = BF_4 or BPh_4) can be isolated; their conductivities in nitromethane are as expected for 1 : 1 electrolytes (Table 1). The red solution prepared in situ from $IrCl(spp)_2$ and $AgBF_4$ in $CDCl_3$ without particular precautions to exclude moisture gives a broad and poorly resolved ^1H NMR spectrum at room temperature. At +15°C with ^{31}P-decoupling the spectrum sharpens and six multiplet resonances arising from two inequivalent vinyl groups can be discerned; the derived chemical shifts and coupling constants are in Table 2. In addition, there is a broad singlet at δ 2.63 ppm which is assigned to coordinated water. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at −12°C demonstrates the presence of a pair of isomers C and D, characterised by a pair of doublets [^2J(P—P) 13 Hz] and a sharp singlet respectively, the ratio of C to D being about 97 : 3. On warming to 32°C this spectrum remains essentially unchanged except for slight broadening, but another singlet (broad) appears between the resonances of C and D. This singlet presumably arises from a third isomer E in temperature-dependent equilibrium with C and D. Its intensity decreases as the temperature is lowered, and is almost zero at −12°C. The behaviour in dichloromethane, acetone and chloroform containing varying amounts of acetone is similar, except that the proportion of isomer D is higher in these solvents (Table 3). The $^1H\{^{31}P\}$ NMR spectra in CD_2Cl_2 and acetone-d_6 are too broad and complex to be readily interpreted. The amount of E is very small (<5%) in the temperature range studied.

Clearly C has inequivalent *cis*-phosphorus atoms and inequivalent vinyl groups, and we accordingly propose structure XII, in which water occupies the axial position of a trigonal bipyramid and the vinyl groups are in the equatorial plane. Little can be said about D except that it has equivalent, presumably *trans*-phosphorus atoms. If trigonal bipyramidal geometry is maintained, the most likely structure is XIII, with water in an equatorial site.



(XII)



(XIII)

Attempts to generate the planar cation $[Ir(spp)_2]^+$ have met with only limited success. The $^1H\{^{31}P\}$ NMR spectrum of the deep red solution obtained from $IrCl(spp)_2$ and $AgBF_4$ in $CDCl_3$ with rigorous exclusion of moisture (see Experimental) shows broad vinyl resonances in the range δ 2.2—5.2 ppm, even at −40°C. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows three broad resonances ($\Delta\nu_{1/2}$ ~20 Hz), suggestive of at least three species; at −10°C the signals are sharper, but only two compounds or isomers seem to be present. The minor component (ca. 20%) has a singlet resonance at δ(P) 29.4 ppm, while the major component has a doublet of doublets, the chemical shifts and coupling constant being identical with those of the aquo-complex (isomer C), which is presumably formed in the presence of traces of water. On addition of a drop of water to the solution, the singlet at δ(P) 29.4 ppm disappears, and the spectrum is now identical with that of a solution prepared without rigorous exclusion of moisture. Thus, the minor component responsible for the singlet at δ(P) 29.4 ppm is probably $[Ir(spp)_2]^+$, which clearly has a very high affinity for water (and other ligands, see below).

Other cationic complexes $[MQL_2]^+$ (M = Rh; Ir; L = spp, spas; Q = various neutral ligands)

Many ligands in addition to carbon monoxide react with the cations $[RhL_2]^+$ and $[IrL_2(H_2O)]^+$ to give five-coordinate cationic complexes which have generally been isolated as their tetrafluoroborate salts. The reactions are marked by characteristic colour changes from orange-red to pale yellow in the case of rhodium, and from red to almost colourless in the case of iridium. The trifluorophosphine complexes $[M(PF_3)L_2]BF_4$ (M = Rh, Ir; L = spp, spas), which are 1 : 1 electrolytes in nitromethane, are rare examples of cationic derivatives of this strong π-acceptor ligand. Their IR spectra show broad ν(P—F) bands in the 850 cm^{-1} region, and their ^{1}H NMR spectra exhibit broad and complex resonances in the range δ 2.6—4.0, indicative of coordinated vinyl groups. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh(PF_3)(spp)_2]^+$ shows very broad signals at room temperature, and has not been further investigated. By analogy with the corresponding carbonyl complexes, the presence of interconverting isomers is likely.

Ethylene reacts reversibly with $[Rh(spp)_2]^+$ or $[Rh(spas)_2]^+$ to give yellow solutions from which unstable, pale orange salts, $[Rh(C_2H_4)L_2]BF_4$, can be isolated. Under the same conditions, ethylene reacts with $[Ir(H_2O)L_2]^+$ to give white, insoluble solids of indefinite composition which have not been characterised. The ^{1}H NMR spectra of the rhodium complexes show a broad singlet at ca. δ 4.0 ppm due to coordinated ethylene (1 mole per mole of complex), in addition to the usual broad complex vinyl resonances of spp or spas. In the presence of excess ethylene, the singlet at δ 4.0 ppm shifts to lower field (ca. δ 5.2 ppm), showing that intermolecular ethylene exchange is rapid on the NMR time scale at room temperature. This exchange also probably induces equilibration of isomers of $[Rh(C_2H_4)(spp)_2]BF_4$, since the vinyl resonances sharpen in the presence of ethylene. Brookes [13], who has independently isolated $[Rh(C_2H_4)(spp)_2]BPh_4$, states that intermolecular exchange with ethylene is slow on the NMR time scale, on the basis of his observation of two peaks, a doublet at δ 1.49 ppm (J 1.5 Hz) assigned to coordinated ethylene, and a singlet at δ 4.59 ppm assigned to free ethylene. However, we find the signal for ethylene in $CDCl_3$ at 32°C to be at δ 5.33 ppm [cf. lit. value [38]; δ 5.33 ppm (CCl_4)], and we suspect that the peak at δ 4.59 ppm is a time-averaged ethylene resonance, the exact position of which will depend on the relative concentrations of free and coordinated ethylene. The origin of the reported doublet at δ 1.49 ppm remains obscure (we find a singlet at this position), but the chemical shift would imply that the ethylene protons are highly shielded which seems most unlikely for a cationic rhodium(I) complex.

The triphenylphosphine, diphenylmethylphosphine and pyridine complexes $[MQL_2]BF_4$ (M = Rh, Ir; L = spp, spas; Q = PPh_3, $PMePh_2$, C_5H_5N) do not readily lose the fifth ligand, and can be recrystallised from ethanol. Since intramolecular rearrangements in these five-coordinate complexes are expected to be slower on the NMR time scale for iridium(I) than for rhodium(I) we have concentrated on the room temperature NMR spectra of the iridium(I) complexes in an effort to obtain structural information.

The complex $[Ir(PMePh_2)(spp)_2]^+$, generated in situ in $CDCl_3$ from $IrCl(spp)_2$, $AgBF_4$ and an excess of diphenylmethylphosphine, shows two P—CH_3 doublets due to coordinated $PMePh_2$ in a ratio of 3 : 2, but on standing for 24 h, or after isolation and recrystallisation from ethanol, the ratio changes to 1 : 6. The major isomer in the equilibrium mixture contains inequivalent vinyl groups, the minor isomer has equivalent vinyl groups. The chemical shifts and coupling constants (Table 2) show the vinyl groups to be coordinated, hence both isomers are five-coordinate. The $^{31}P\{^1H\}$ spectrum of both isomers (Table 3) consists of a doublet and a triplet due respectively to the phosphorus atoms of spp and $PMePh_2$, the coupling between them being about 20 Hz, i.e. in both isomers the diphenylmethylphosphine must be *cis* to the phosphorus atoms of the spp ligands. Thus the likely structures are V and VI for the 'symmetrical' isomer, and VII for the 'unsymmetrical' isomer, with $PMePh_2$ replacing CO in an equatorial site. Two surprising features of the ^{31}P spectra are, first, that there is no indication of the expected inequivalence of the mutually *trans* ^{31}P nuclei of the major isomer, and, second, that the coordinated $PMePh_2$ triplets appear upfield both of the 85% H_3PO_4 reference and of the free ligand itself. This marked upfield shift of coordinated methyldiphenylphosphine is also observed in $[Rh(PMePh_2)(spas)_2]BF_4$ (Table 3).

The $^1H\{^{31}P\}$ NMR spectrum of the pyridine-containing salt $[Ir(py)(spp)_2]BF_4$ shows two doublets due to the α-protons of coordinated pyridine together with seven multiplets which can be satisfactorily assigned to the coordinated vinyl resonances of two isomers containing equivalent and inequivalent vinyl groups respectively. In dichloromethane, the ratio of unsymmetrical to symmetrical isomer is about 4 : 3, whereas for a sample prepared in situ in $CDCl_3$ the ratio is about 2 : 1. Unexpectedly, the $^{31}P\{^1H\}$ spectrum in dichloromethane exhibits four lines in a ratio of 2 : 1 : 1 : 1, the latter three at higher field being closely grouped. The spectrum in chloroform is almost identical (there are slight differences in the relative intensities of the three closely grouped lines), although the separation between the second and third lines decreases from 42 to 30 Hz.

The most intense line probably arises from the isomer with equivalent vinyl groups (hence equivalent ^{31}P nuclei), and two of the remaining lines presumably represent the inner lines of the expected *AB* quartet arising from the isomer with inequivalent vinyl groups (hence inequivalent ^{31}P nuclei). The origin of the remaining line is at present obscure, and at present all that can be said with certainty about the nature of the isomers present is that one of them must have either of the 'symmetrical' structures V or VI, with pyridine replacing CO in an equatorial site.

Preliminary experiments suggest that the nature of the fifth ligand (Q) determines the structure adopted by 'unsymmetrical' isomer of the $[IrQ(spp)_2]^+$

complexes. Thus, the ammine cation ($Q = NH_3$) obtained in situ by treatment of $IrCl(spp)_2$ and silver tetrafluoroborate in $CDCl_3$ with ammonia gas, shows six coordinated resonances due to two isomers. The $^{31}P\{^1H\}$ spectrum shows that these isomers must be structurally similar to those present in the original aquo-cation; the minor component is 'symmetrical' (structure XIII), while the major 'unsymmetrical' component shows a pair of doublets due to inequivalent, mutually *cis*-phosphorus atoms [$^2J(P—P) = 14$ Hz], and probably has structure XII, with ammonia replacing water in the axial position of the trigonal bipyramid.

General conclusions

This work shows that spp and spas promote five-coordination for rhodium(I) and iridium(I) far more readily than their more flexible aliphatic counterparts 3-butenyldiphenylphosphine (mbp) and 4-pentenyldiphenylphosphine (mpp) [6]. The following comparisons make this clear:

(1) Although $RhCl(mbp)_2$ is five-coordinate in the solid state [6,8], it is four-coordinate in solution, exchange between free and coordinated olefins being rapid on the NMR time scale at room temperature. Although a four-coordinate species may be involved in the fluxional behaviour of $RhCl(spp)_2$, its concentration is too small to be detected by the usual spectroscopic methods. In contrast with $RhCl(mbp)_2$, the double bonds of $RhCl(spp)_2$ do not add hydrogen, at least under ambient conditions. Both mbp and mpp form stable, dimeric, four-coordinate complexes, e.g. $Rh_2Cl_2(mbp)_2$, whereas spp and spas give only five-coordinate complexes, $RhCl(spp)_2$ and $RhCl(spas)_2$.

(2) Reaction of $RhCl(mbp)_2$ with carbon monoxide is irreversible, and the product, $RhCl(CO)(mbp)_2$, has a square planar structure in benzene solution, the double bonds being free [1]. In contrast, $[Rh(CO)(spp)_2]Cl$ contains a five-coordinate cation with two coordinated double bonds, and it readily reverts to $RhCl(spp)_2$.

(3) The salt $[Rh(mbp)_2]BPh_4$ in solution is believed to exist in equilibrium with a π-bonded tetraphenylborate complex, one of the double bonds being displaced from the coordination sphere [6]. We have no evidence to show that this process occurs to any measurable extent in the case of $[Rh(spp)_2]BPh_4$, despite an assertion to the contrary [13], although it may be an important step in the reaction of this salt with hydrogen [37].

Experimental

IR and NMR spectroscopic procedures followed those previously described [23]. The IR spectra of $RhX(spp)_2$ (X = Cl, Br) below 250 cm^{-1} were measured as Nujol mulls on a Hitachi FIS-3 grating instrument, and the Raman spectra were measured on Spex Ramalog 1401 instrument using Carson Model 101 argon and 103 krypton ion laser sources. Conductivities were measured on a Philips GM4144/01 Universal Measuring Bridge. Analytical, molecular weight and conductivity data are in Table 1, ^1H and ^{31}P NMR data are in Tables 2 and 3 respectively.

Aromatic and ether solvents were dried over sodium before use and then distilled from $LiAlH_4$. All other solvents were A.R. grade and were dried over molecular sieves. o-Styryldiphenylphosphine (spp) and o-styryldiphenylarsine (spas) were prepared as previously described [29,39]. Rhodium(I) and iridium(I) precursors were obtained by standard procedures starting from hydrated rhodium trichloride and hexachloroiridic acid respectively (Johnson—Matthey).

Preparations

Bis(o-styryldiphenylphosphine)chlororhodium(I), $RhCl(spp)_2$. (a) A slurry of bis(cyclooctene)chlororhodium(I), $[RhCl(C_8H_{14})_2]_2$ (0.5 g, 0.70 mmol) and o-styryldiphenylphosphine (spp) (1.0 g, 3.5 mmol) was stirred in 1 : 5 benzene/n-pentane (30 ml) for 3 h at room temperature. The supernatant liquid was decanted and the yellow crystalline residue was washed with benzene (2 × 15 ml) to remove cyclooctene and unreacted spp. Recrystallisation from chloroform or dichloromethane at room temperature gave yellow crystals (0.7 g, 70%) which were dried in vacuo.

(b) Hydrated rhodium trichloride (1.00 g, 3.8 mmol) dissolved in ethanol (25 ml) at 60°C was added to a boiling solution of spp (2.7 g, 9.4 mmol) in ethanol (50 ml). A 39% aqueous solution of formaldehyde (15 ml) was added and the solution was stirred under reflux for 3 h. The bright yellow, crystalline product was filtered off, washed with ether, and recrystallised from chloroform (2.3 g, 85%). M.p. 208—210°C (dec.). IR: ν(RhCl) 236 cm^{-1} (Nujol). Raman: ν(C=C) 1491w, 1480m cm^{-1} (solid).

Bis(o-styryldiphenylphosphine)bromorhodium(I), $RhBr(spp)_2$. This was obtained in 71% yield by method (b) above, starting with hydrated rhodium tribromide. IR: ν(RhBr) 143 cm^{-1}.

Bis(o-styryldiphenylarsine)chlororhodium(I), $RhCl(spas)_2$. This yellow, microcrystalline complex, m.p. 210—214°C (dec.), was obtained similarly to $RhCl(spp)_2$, using o-styryldiphenylarsine (spas) in place of spp. Yields: 73% by method (a), 83% by method (b). Raman: ν(C=C) 1492w, 1481m cm^{-1} (solid).

Bis(o-styryldiphenylphosphine)chloroiridium(I), $IrCl(spp)_2$. A slurry of bis(cyclooctene)chloroiridium(I), $[IrCl(C_8H_{14})_2]_2$ (0.27 g, 0.30 mmol) and spp (0.35 g, 1.12 mmol) was stirred in 1 : 1 benzene/n-pentane (15 ml) for 1½ h. The supernatant liquid was decanted and the white crystalline residue was washed with benzene (2 × 5 ml) to remove cyclooctene and unreacted spp. Recrystallisation from chloroform and drying in vacuo gave colourless microcrystals (0.41 g, 75%) m.p. 256—260°C (dec.) Raman: ν(C=C) 1490w, 1478m cm^{-1} (solid).

Bis(o-styryldiphenylarsine)chloroiridium(I), $IrCl(spas)_2$. This was prepared in 66% yield similarly to $IrCl(spp)_2$ using spas in place of spp.

Alternatively, a mixture of $[IrCl(COD)]_2$ (0.205 g, 0.61 mmol) and spas (0.405 g, 1.22 mmol) in benzene (25 ml) was heated under reflux with stirring under nitrogen for 1 h. Dropwise addition of n-hexane (50 ml) gave a pale cream solid, which was filtered off, washed with n-hexane and dried in vacuo to give 0.42 g (77%) of product.

Bis(o-styryldiphenylphosphine)carbonylrhodium(I) chloride, $[Rh(CO)(spp)_2]Cl$. Carbon monoxide was passed through a solution of $RhCl(spp)_2$ (0.4 g, 0.56 mmol) in dichloromethane (10 ml) at room temperature for 10 min. Methanol (10 ml) was added and the mixture was evaporated in a stream of carbon monoxide. The product separated from solution as pale yellow crystals which were recrystallised from dichloromethane/methanol in an atmosphere of carbon monoxide. Yield: 0.32 g, 76%. IR: ν(CO) 2039 cm^{-1} (CH_2Cl_2).

Bis(o-styryldiphenylarsine)carbonylrhodium(I) chloride, [Rh(CO)(spas)$_2$]Cl. This was prepared in 68% yield from RhCl(spas)$_2$ and carbon monoxide as described for the analogous spp complex. IR: ν(CO) 2038 cm^{-1} (CH_2Cl_2).

Bis(o-styryldiphenylphosphine)carbonylrhodium(I) dicarbonyldichlororhodate(I), [Rh(CO)(spp)$_2$][RhCl$_2$(CO)$_2$]. A solution of spp (0.5 g, 1.74 mmol) in benzene (10 ml) was added dropwise to a stirred solution of rhodium(I) carbonyl chloride, [RhCl(CO)$_2$]$_2$ (0.34 g, 0.88 mmol) in benzene (10 ml). After stirring for 1 h at room temperature the resulting pale yellow solid was filtered off, washed with benzene (5 ml) and recrystallised from chloroform/ether. Yield: 0.73 g (90%). IR: ν(CO) 2060, 2039, 1980 cm^{-1} (Nujol).

Bis(o-styryldiphenylphosphine)rhodium(I) tetrafluoroborate, [Rh(spp)$_2$]BF$_4$ and its o-styryldiphenylarsine analogue, [Rh(spas)$_2$]BF$_4$. (a) Silver tetrafluoroborate (0.05 g, 0.28 mmol) was added to a solution of RhCl(spp)$_2$ (0.2 g, 0.28 mmol) in chloroform (20 ml) and the mixture was stirred at room temperature for 5 min. The precipitated silver chloride was filtered off and the bright red solution evaporated at room temperature under reduced pressure to give orange crystals of the product (0.19 g, 86%). Starting from RhCl(spas)$_2$, [Rh(spas)$_2$]-BF$_4$ was similarly obtained in 84% yield.

(b) A solution of RhCl(spp)$_2$ (0.4 g, 0.56 mmol) in chloroform (20 ml) was stirred under reflux with sodium tetrafluoroborate (0.2 g, excess) in isopropanol (30 ml) for 1 h. The solvent was removed under reduced pressure and the residue was extracted with ether (2 × 20 ml). Evaporation of the orange-red ether extract yielded the orange, crystalline product (0.3 g, 76%). [Rh(spas)$_2$]-BF$_4$ was also obtained by this method in 70% yield.

Bis(o-styryldiphenylphosphine)rhodium(I) tetraphenylborate, [Rh(spp)$_2$]-BPh$_4$ and its o-styryldiphenylarsine analogue [Rh(spas)$_2$]BPh$_4$. Sodium tetraphenylborate (0.5 g, 1.46 mmol) was added to a solution of RhCl(spp)$_2$ (0.5 g, 0.7 mmol) in chloroform (25 ml) and the mixture was stirred at room temperature for 5 min. Precipitated sodium chloride and unreacted NaBPh$_4$ were centrifuged off and the orange-red solution was concentrated by evaporation to yield the orange, crystalline product (0.54 g, 77%). [Rh(spas)$_2$]BPh$_4$ was similarly obtained in 65% yield.

Aquobis(o-styryldiphenylphosphine)iridium(I) tetrafluoroborate and tetraphenylborate, [Ir(H$_2$O)(spp)$_2$]Y (Y = BF$_4$, BPh$_4$). These were prepared as red solids in 92% and 65% yields respectively by the reaction of IrCl(spp)$_2$ with AgBF$_4$ or NaBPh$_4$ in chloroform as described above for [Rh(spp)$_2$]BF$_4$ and [Rh(spp)$_2$]BPh$_4$.

The following experiment was carried out in an attempt to detect the anhydrous salt [Ir(spp)$_2$]BF$_4$. IrCl(spp)$_2$ (0.05 g) and AgBF$_4$ (~0.2 g, excess) were dried at 25°C/0.001 mm Hg over P_4O_{10} for 5 d. The sealed samples were transferred to a nitrogen-filled dry-box (HE-493 Drilab) and allowed to react in chloroform or deuterochloroform (1 ml), which had previously been dried by distillation from P_4O_{10} in pre-dried glassware. After 5 min precipitated silver chloride was removed by filtration through dry glass wool and the red solution was examined by ^1H and $^{31}P\{^1H\}$ NMR. On addition of 5—10 mg of water, the colour of the solution lightened and resembled that obtained under "non-anhydrous" conditions.

Bis(o-styryldiphenylphosphine)carbonylrhodium(I) tetrafluoroborate, $[Rh(CO)(spp)_2]BF_4$ *and its o-styryldiphenylarsine analogue,* $[Rh(CO)(spas)_2]BF_4$. (a) Carbon monoxide was passed through a solution of $[Rh(spp)_2]BF_4$ (0.28 g, 0.28 mmol) in chloroform (5 ml) at room temperature. The colour changed from orange-red to yellow, and after 1 min solvent was removed under reduced pressure. The residue after recrystallisation from a small volume of ethanol gave a pale yellow solid (0.74 g, 93%). A similar result was obtained by using a solution of $[Rh(spp)_2]BF_4$ prepared in situ from $RhCl(spp)_2$ and $AgBF_4$ in chloroform as described above.

(b) Carbon monoxide was passed through a slurry of $RhCl(spp)_2$ (0.4 g, 0.56 mmol) and sodium tetrafluoroborate (0.2 g, excess) in 1 : 1 dichloromethane/methanol or chloroform/methanol (40 ml) at room temperature for 30 min. The mixture was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane (10 ml). This was again evaporated to dryness and the residue was recrystallised from ethanol. Yield: 0.35 g (80%). The corresponding PF_6 and BPh_4 salts were obtained by substituting NH_4PF_6 or $NaBPh_4$ for $NaBF_4$. IR: $\nu(CO)$ 2039 cm^{-1} (Nujol, $CHCl_3$ or CH_2Cl_2).

$[Rh(CO)(spas)_2]BF_4$ was obtained from $RhCl(spas)_2$ either by method (a) (89% yield) or method (b) (80% yield).

Bis(o-styryldiphenylphosphine)carbonyliridium(I) tetrafluoroborate, tetraphenylborate or hexafluorophosphate, $[Ir(CO)(spp)_2]Y$ *(*$Y = BF_4, BPh_4$ *or* PF_6*) and the analogous o-styryldiphenylarsine compound* $[Ir(CO)(spas)_2]BF_4$. Carbon monoxide was passed into a solution of $[Ir(H_2O)(spp)_2]BF_4$ generated in situ from $IrCl(spp)_2$ and $AgBF_4$, $NaBF_4$, $NaBPh_4$ or NH_4PF_6 as described above for the analogous rhodium system. A similar work-up gave the colourless compounds in 80—90% yield. IR: $\nu(CO)$ 2038 cm^{-1} (Nujol, $CHCl_3$ or CH_2Cl_2). Starting from $IrCl(spas)_2$, $[Ir(CO)(spas)_2]BF_4$ was obtained in 70—80% yield. IR: $\nu(CO)$ 2038 cm^{-1} (Nujol, $CHCl_3$ or CH_2Cl_2).

Bis(o-styryldiphenylphosphine)trifluorophosphine-rhodium(I) or -iridium(I) tetrafluoroborates, and their o-styryldiphenylarsine analogues $[M(PF_3)L_2]BF_4$ *(*$M = Rh, Ir$*;* L *= spp, spas).* Trifluorophosphine (PF_3) was passed through a dry-ice/acetone trap and then into a solution of $[RhL_2]BF_4$ or $[Ir(H_2O)L_2]BF_4$ (conveniently generated in situ as described above) in chloroform (5 ml). When the solution had turned yellow (ca. 1 min) the solvent was removed by evaporation and the pale yellow residue was recrystallised from a small volume of ethanol. Yields were 70—80%.

Bis(o-styryldiphenylphosphine)ethylenerhodium(I) tetrafluoroborate and its o-styryldiphenylarsine analogue, $[Rh(C_2H_4)L_2]BF_4$ *(*L *= spp, spas).* Ethylene was bubbled into a solution of $[Rh(spp)_2]BF_4$ (0.3 g, 0.39 mmol) in dichloromethane (5 ml) at room temperature until the solution turned yellow. Ethanol (5 ml) was added and solvent was removed in a stream of ethylene. The pale orange precipitate was centrifuged under ethylene and the supernatant liquid was decanted. The precipitate was washed thoroughly with ethanol and dried in a stream of ethylene. The yields of this and the similarly prepared spas compound were ca. 80%. Satisfactory analytical data could not be obtained for the complexes owing to the ready loss of ethylene, and they were characterised by their ^1H NMR spectra (text and Table 2).

Bis(o-styryldiphenylphosphine)ligand-rhodium(I) or -iridium(I) tetrafluoro-

borates, and their o-styryldiphenylarsine analogues, $[MQL_2]BF_4$ *(M = Rh, Ir; L = spp, spas; Q =* PPh_3, $PMePh_2$*; for M = Ir only, L = spp and Q =* C_5H_5N*).* The preparation of $[Rh(PMePh_2)(spp)_2]BF_4$ is representative. Methyldiphenylphosphine (0.08 g, 0.4 mmol) was added to a stirred solution of $[Rh(spp)_2]BF_4$ (0.3 g, 0.39 mmol) which had been generated in situ from $RhCl(spp)_2$ and $AgBF_4$ in chloroform (20 ml). The yellow solution was evaporated to small volume under reduced pressure and the product was precipitated with n-pentane. Pale yellow crystals of the product were obtained in 86% yield on recrystallisation from ethanol.

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