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Additions to Metal Atom and to Coordinated Ligand in Complexes of Rhodium(I) and Iridium(I) formed by a Tridentate Olefinic Ditertiary Phosphine: Chelate Olefin Complexes and σ-Alkyls of Rhodium(III) and Iridium(III)

M. A. BENNETT,* R. N. JOHNSON and I. B. TOMKINS
Research School of Chemistry, Australian National University,
P.O. Box 4, Canberra, A.C.T. 2600 (Australia)

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Summary

The planar rhodium(I) and iridium(I) complexes MCl(bdpps) (M = Rh,Ir) formed by the tridentate chelate ligand 2,2′-bis(diphenylphosphino)-*trans*-stilbene, o-$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$-$o$ (bdpps) react with carbon monoxide or ethylene forming five-coordinate, probably trigonal bipyramidal adducts MClL(bdpps) (L = CO, C_2H_4). The order of stability with respect to M and L is Ir > Rh and CO > C_2H_4. The salts $[ML_2(bdpps)]BF_4$, which contain a five-coordinate cation, can be isolated and there is spectroscopic evidence for four-coordinate cations $[ML(bdpps)]^+$. The coordinated ethylene in $IrCl(C_2H_4)(bdpps)$ undergoes intermolecular exchange and intramolecular rotation as shown by variable temperature ^1H NMR studies. IrCl(bdpps) oxidatively adds chlorine, hydrogen chloride and hydrogen to give unusual octahedral chelate olefin complexes of iridium(III), $IrCl_3(bdpps)$, $IrHCl_2(bdpps)$ and $IrH_2Cl(bdpps)$ respectively; the addition of hydrogen is reversible. RhCl(bdpps) reacts with either chlorine or hydrogen chloride to give a chelate olefin complex of rhodium(III), $RhCl_3(bdpps)$, but does not add hydrogen. In contrast, the five-coordinate complexes MCl(CO)(bdpps) are protonated by hydrogen chloride at the coordinated double bond, the products being chelate σ-alkyls of rhodium(III) or iridium(III), $\overline{\mathrm{MCl_2(CO)}(o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2}\text{-}o)$. Likewise, hydrogen chloride reacts with RhCl(bdpps) in the presence of triphenylphosphine to give a dimer $[\overline{\mathrm{RhCl_2}(o\text{-}\mathrm{Ph_2PC_6H_4C}}\mathrm{HCH_2C_6H_4PPh_2}\text{-}o)]_2$, probably formed by protonation of a five-coordinate intermediate. In the case of rhodium, the chelate σ-alkyl unit is deprotonated by boiling ethanol, RhCl(bdpps) being re-formed. Structural assignments for the new complexes are based on IR, ^{1}H and ^{31}P NMR spectra.

Introduction

Tri-*o*-tolylphosphine, $(o\text{-}\mathrm{CH_3C_6H_4})_3\mathrm{P}$, undergoes dehydrogenation and coupling in the presence of rhodium(III)chloride in refluxing 2-methoxyethanol to give a planar, chelate rhodium(I) complex $\mathrm{RhCl}\{o\text{-}(o\text{-}\mathrm{tol})_2\mathrm{PC_6H_4CH}\overset{t}{=}\mathrm{CHC_6H_4P}(o\text{-}\mathrm{tol})_2\text{-}o\}$ which contains a tridentate ligand 2,2′-bis(di-*o*-tolylphosphino)-*trans*-stilbene [1]*. The analogous complex of 2,2′-bis(diphenylphosphino)-*trans*-stilbene, $o\text{-}\mathrm{Ph_2PC_6H_4CH}\overset{t}{=}\mathrm{CHC_6H_4PPh_2}\text{-}o$ (bdpps) is obtained in about 1% yield from the corresponding reaction between rhodium(III) chloride and diphenyl-*o*-tolylphosphine, but is formed almost quantitatively by dehydrogenation of 2,2′-bis(diphenylphosphino)bibenzyl, $o\text{-}\mathrm{Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2}\text{-}o$, promoted by the 1,5-cyclooctadiene complex $[\mathrm{RhCl(1,5\text{-}COD)}]_2$ [2,3]. The ligand bdpps can be isolated by displacement from the rhodium(I) complex (Ia) with sodium cyanide (Scheme 1). A single crystal X-ray study of Ia [2] has confirmed

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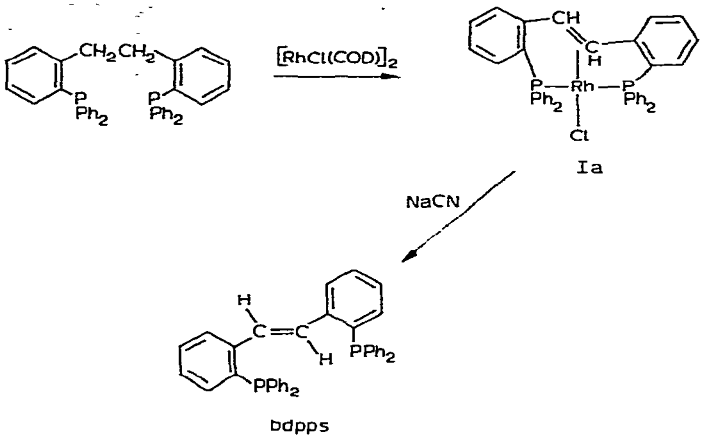
* Abbreviations: Ph = $\mathrm{C_6H_5}$; *o*-tol = $o\text{-}\mathrm{CH_3C_6H_4}$; COD = 1,5-cyclooctadiene; NBD = norbornadiene.



SCHEME 1. Formation of bdpps from o-$Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$-$o$.

that bdpps acts as a tridentate ligand, the double bond being oriented at about 79° to the plane containing the rhodium and the two phosphorus atoms; the geometry thus approaches the 90° observed in Zeise's Salt, $K[PtCl_3(C_2H_4)].H_2O$ [4,5] and many other olefin complexes of the d^8 metals [6], including the closely related iridium(I)-ethylene complex $IrCl(C_2H_4)(PPh_3)_2$ [7]. Whereas the rhodium(I) complex $RhCl(C_2H_4)(PPh_3)_2$ is stable in solution only in the presence of ethylene [8], the chelate effect of bdpps will clearly repress dissociation of the olefinic fragment, and we were therefore interested to see if the planar complexes MCl(bdpps) (M = Rh, Ir) would resemble $MCl(CO)(PPh_3)_2$ in undergoing oxidative additions without ligand dissociation, and in forming five-coordinate adducts with other ligands [9,10]. We also wanted to know if molecules

TABLE 1. ANALYTICAL, MOLECULAR WEIGHT AND SELECTED IR DATA FOR RHODIUM AND IRIDIUM COMPLEXES OF 2,2′-BIS(DIPHENYLPHOSPHINO)-*trans*-STILBENE(BDPPS), o-$Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2$[a]

	Analysis found(calcd.) (%)				Mol Wt.	Selected IR bands (cm^{-1})	
	C	H	P	Cl		ν(CO)	Others
RhCl(CO)(bdpps). 0.5 CH_2Cl_2 (IIa)[b]	63.0 (60.5)	4.9 (4.0)	7.6 (7.9)	9.1 (9.05)	817 (717)	2020s (CH_2Cl_2)	941 m (=CH o.o.p. def.), 275 w[ν(RhCl)](Nujol)
IrCl(CO)(bdpps) (IIb)	57.7 (58.2)	4.4 (3.8)	6.9 (7.7)	4.6 (4.4)	804 (854)	1990s (Nujol)	958 m (=CH o.o.p.def.), 290 w[ν(IrCl)](Nujol)
IrCl(C_2H_4)(bdpps) (IIIb)	57.1 (59.7)	4.0 (4.3)	7.6 (7.7)	4.3 (4.4)		-	
[Rh(CO)$_2$(bdpps)]BF_4 (Va)	56.9 (58.1)	4.1 (3.7)	7.3 (7.4)			2100s, 2068s (CH_2Cl_2)	
[Ir(CO)$_2$(bdpps)]BF_4 (Vb)	52.1 (54.4)	4.0 (3.4)	6.9 (7.0)			2094s, 2054s (CH_2Cl_2)	
$IrHCl_2$(bdpps).0.05 CH_2Cl_2 (VII)	55.3 (55.9)	4.4 (3.8)	6.7 (7.6)	9.0 (9.1)	939 (813)	-	2220s[ν(IrH)](CH_2Cl_2), 948m (=CH o.o.p.def.), 305s,250s[ν(IrCl)] (Nujol)
$RhCl_3$(bdpps) (VIIIa)	59.6 (60.2)	4.3 (4.0)	7.4 (8.2)	15.3 (14.0)		-	351 vs, 330 m [ν(RhCl)] (Nujol)
$RhCl_2$(CO)(bdppsH).CH_2Cl_2 (Xa)	57.7 (57.4)	4.4 (4.0)	7.1 (7.4)	16.8 (17.0)	861 (752)	2054s (Nujol)	315s,250s [ν(RhCl)] (Nujol)
$IrCl_2$(CO)(bdppsH). 0.1 CH_2Cl_2 (Xb)	54.2 (55.3)	3.8 (3.7)	6.5 (7.3)	9.2 (9.2)	960 (841)	2040s (Nujol)	310s,270s [ν(IrCl)] (Nujol)
[$RhCl_2$(bdppsH)] .0.2 CH_2Cl_2 (XI)	62.2 (62.5)	4.5 (4.3)	7.8 (8.5)	10.4 (10.6)	1402 (1464)	-	283m [ν(RhCl)] (Nujol)

[a] Abbreviations: vs, very strong; s, strong; m, medium, w, weak; =CH o.o.p.def., olefinic C-H out-of-plane deformation; bdppsH, o-$Ph_2PC_6H_4CHCH_2C_6H_4PPh_2$-$o$

[b] High C and H values probably due to residual *n*-pentane which could not be completely removed by drying in nitrogen stream.

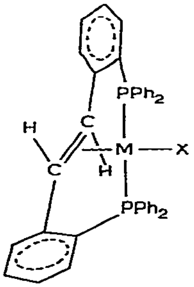
such as hydrogen, hydrogen halides or halogens which often oxidatively add to the metal in planar d^8 complexes might in this instance preferentially react with the coordinated double bond.

Results and Discussion

Analytical and IR data for the new complexes are in Table 1, ^{1}H and ^{31}P NMR data are summarised in Tables 2 and 3.

Neutral Five-Coordinate Complexes

The complexes MCl(bdpps) (M = Rh, Ia; M = Ir, Ib), dissolved in dichloromethane, react with carbon monoxide (25°, 1 atm) to give pale yellow, five-coordinate, presumably trigonal bipyramidal adducts MCl(CO)(bdpps) (M = Rh, IIa; M = Ir, IIb). Both complexes are stable in the solid state at 25°, but IIa readily loses CO in solution. In contrast, IIb does not lose CO even in refluxing



X = Cl, M = Rh ; Ia
X = Cl, M = Ir ; Ib
X = CO, M = Rh$^+$; IVa
X = CO, M = Ir$^+$; IVb

TABLE 2. ^{1}H AND ^{31}P NMR DATA FOR RHODIUM AND IRIDIUM COMPLEXES OF 2,2′-BIS(DIPHENYLPHOSPHINO)-*trans*-STILBENE(BDPPS), o-$Ph_2PC_6H_4CH{=}CHC_6H_4PPh_2$-$o$[a-d]

	δ(H)[e]	Solvent	δ(P)	J(H-H)	J(P-H)	J(P-P)	J(Rh-P)
Ia	3.66q[f]	$CDCl_3$	40.3d[g]	*h*	2.5	*h*	124
Ib	2.83t[i]	CD_2Cl_2	36.9s	*h*	3.0	*h*	–
IIa	3.97m[k] 4.18m[l]	CD_2Cl_2	42.1dd, 53.7dd	7.5	3.5, 3.5; 6.3 (sum)	380	101, 94
IIb	3.32m 3.66m	CD_2Cl_2	16.1d, 28.9d	5.8	4.9, 4.9; 3.8, 3.8	347	–
IVa	5.50dt[m]	$CDCl_3$	42.0d	*h*	2.0	*h*	107
IVb	4.23t	CD_2Cl_2	26.8s[n]	*h*	4.0	*h*	–
Va	4.67dt[o]	CD_2Cl_2	46.2d	*h*	1.5	*h*	85
Vb	4.03t	CD_2Cl_2	16.3s	*h*	4.2	*h*	–
VII	−13.30t (IrH) 4.53t	CD_2Cl_2	10.9s, 20.5s	*p*	10.5, 10.5; 1.3, 1.3	431	–
VIIIa	6.75d[q]	CD_2Cl_2	40.5d	*h*	0	*h*	77
VIIIb	6.56s	CD_2Cl_2	9.5s	*h*	0	*h*	–
IX	−5.15br, −16.95br } (IrH) 4.99m 4.58m	CD_2Cl_2	17.2d, 24.9d	*r* 10.5	*r* 1.5, 1.5 1.5, 1.5	385	–
Xa[s,t]	3.85m (H_A) 3.41m (H_B) 4.36m (H_C)	CD_2Cl_2	19.0d, 37.8d	AB −16.0 AC 10.0 BC 2.0	A,P sum ∼2 B,P 6.5, 0 C,P 0	446	85, 92
Xb[r]	3.92m (H_A) 3.66m (H_B) 4.12m (H_C)	CD_2Cl_2	−5.0d, 10.9d	AB −15.5 AC 10.5 BC 1.5	A,P sum ∼0 B,P 4.5, 0 C,P ∼0	378	–
XI[s,u]	3.83m (H_A) 3.02m (H_B) 5.67m (H_C)	$CDCl_3$	*v*	AB 16 AC 4 BC 3	A,P ∼1 B,P ∼4 C,P ∼1	*v*	*v*

[a] ^{1}H spectra measured at 100 MHz in solvent indicated with internal TMS as reference, $^{31}P\{^{1}H\}$ spectra measured at 24.3 MHz in CH_2Cl_2 with external 85% H_3PO_4 as reference, both at 32°. Chemical shifts (δ) are in ppm, downfield from reference being taken as positive, ±0.01 ppm for δ(H), ±0.3 ppm for δ(P). Coupling constants are in Hz, ±0.5 for J(H-X) and ±5 for J(P-P) and J(Rh-P).

(table conti

[b] ^{1}H NMR spectra for ethylene complexes VIa and VIb are given in Table 3.

[c] Aromatic resonances all lie in range δ 6.8 - 8.2 ppm.

[d] Multiplicities of ^{1}H and ^{31}P{^{1}H} spectra abbreviated as follows: s, singlet; d, doublet; q, 1:3:3:1 quartet; t, triplet; dt, doublet of triplets; m, multiplet; br, broad.

[e] Refers to olefinic protons except where indicated.

[f] Actually a doublet of overlapping 1:2:1 triplets, *J*(Rh-H) 2.0 Hz. Spectrum invariant down to -85°C in CD_2Cl_2, showing that one of the two possible orientations of the double bond is preferred, presumably that found in the solid state (ref.2).

[g] δ(P) for bdpps in CH_2Cl_2 = -14.1 ppm by direct measurement, *cf*. -13.7 ppm by INDOR on olefinic ^{1}H resonance (ref.3).

[h] Equivalence of nuclei prevents determination of coupling between them.

[i] Appears as singlet in ^{1}H{^{31}P} spectrum.

[j] Measured at -20°C. ^{1}H NMR (32°C) δ 4.07br s ppm.

[k] *J*(Rh-H) 1.3 Hz.

[l] *J*(Rh-H) 2.0 Hz.

[m] *J*(Rh-H) 2.0 Hz.

[n] Obtained by INDOR on olefinic ^{1}H resonance. Accuracy ±0.5 ppm estimated by comparison with direct and INDOR determination of δ(P) for $[Ir(CO)_2(bdpps)]BF_4$ (Vb)

[o] *J*(Rh-H) 2.0 Hz; spectrum unchanged down to -68°C.

[p] Fortuitous equivalence of olefinic protons prevents determination of *J*(H-H).

[q] *J*(Rh-H) 1.5 Hz.

[r] Signal broadness prevents determination of coupling.

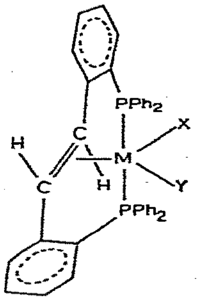
[s] Proton labelling: $-CH_AH_B-CH_C(M)-$.

[t] ^{3}*J*(Rh-H_A) 1.5 Hz; ^{2}*J*(Rh-H_C) 2 Hz.

[u] ^{2}*J*(Rh-H_C) ∿2 Hz.

[v] Could not be determined owing to decomposition.

chloroform. The complexes show IR absorptions at *ca.* 2000 cm^{-1} due to ν(CO), at *ca.* 950 cm^{-1} due to the out-of-plane C-H deformation mode of a *trans*-CH=CH group modified by coordination, and at *ca.* 300 cm^{-1} due to ν(MCl). The olefinic proton resonances in the NMR spectrum are well upfield of those of free bdpps, while the ^{31}P resonances are well downfield of that of free bdpps (Table 2) indicating tridentate coordination for the ligand. In contrast with Ia and Ib, the olefinic protons and the phosphorus atoms of IIb are inequivalent, and the magnitude of $^{2}\underline{J}$(P-P) (347 Hz) shows that the phosphorus atoms are mutually trans, as expected for the trigonal bipyramidal structure. The trans H-H coupling for the olefinic protons in IIb (5.8 Hz) is much less than is usual for trans-



X = CO, Y = Cl, M = Rh ; IIa
X = CO, Y = Cl, M = Ir ; IIb
X = C_2H_4, Y = Cl, M = Rh ; IIIa
X = C_2H_4, Y = Cl, M = Ir ; IIIb
X = Y = CO, M = Rh$^+$; Va
X = Y = CO, M = Ir$^+$; Vb
X = Y = C_2H_4, M = Rh$^+$; VIa
X = Y = C_2H_4, M = Ir$^+$; VIb

TABLE 3. VARIABLE TEMPERATURE NMR DATA FOR ETHYLENE ADDUCTS OF RHODIUM AND IRIDIUM COMPLEXES OF BDPPS[a]

Complex	Temp. (°C)	δ(=CH) (bdpps)	δ(=CH_2) (C_2H_4)
IIIa	+32	3.66s	5.36s
	−55	3.78br s	4.47br s[b]
	−70	3.90v br	3.40v br[b]
IIIb	+32	3.98br	2.3v br (coord.)
			5.2v br (free)
	−33	4.16dt, 4.00dt[c]	2.0–2.6br m (coord.)
			5.38s (free)
	−67	4.22dt, 4.03dt(2)[c]	2.7br m (2) 2.0br m (1) 1.64br m (1) (coord.)
			5.39s (free)
VIa	+28	5.08dt[d]	4.54s[b]
	−60	5.08dt(2)[d]	3.33s(8) (coord.)
			5.61s (free)
VIb	+28	4.72t(2)[e]	2.90t(8) (coord.)[f]
			5.66s (free)

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[a] Spectra run in $CDCl_3$ containing small amount of CH_2Cl_2; abbreviations as in Table 2.

[b] Time-averaged signal of free and coordinated ethylene.

[c] H_A, H_B: *J*(AB) 6.0, *J*(A,P) 3.0, 3.0; *J*(B,P) 3.0, 3.0.

[d] J(P-H) 2.0.

[e] J(P-H) 2.5, δ(P) 9.2s (by INDOR)

[f] J(P-H) 2.0.

disubstituted olefins (∿17 Hz), and this, together with the upfield shift, probably reflect the loss of double bond character consequent on coordination.

Both the ^{1}H and ^{31}P{^{1}H} NMR spectra of IIa are broad at 32°, the latter consisting of four equally intense peaks. On cooling the olefinic proton resonance first broadens, then splits into two peaks which sharpen. These changes are reversible and at -20° a well-resolved spectrum corresponding to the expected two inequivalent olefinic protons is obtained. At the same temperature, the ^{31}P{^{1}H} spectrum shows an eight-line spectrum consisting of an AB quartet due to the inequivalent phosphorus atoms doubled by coupling with ^{103}Rh(spin $\frac{1}{2}$, 100% abundance). Clearly IIa is structurally similar to IIb, and the NMR spectral behaviour is due to intermolecular CO exchange, which gives rise to time-averaged spectra *i.e.* equivalent environments for the olefinic protons and for the ^{31}P nuclei at room temperature.

There is no apparent reaction between Ia and ethylene at room temperature in dichloromethane or chloroform, and the ^{1}H NMR spectrum at 32° is indistinguishable from that of the components. On cooling to -55° the resonances due to the olefinic protons of bdpps and of ethylene broaden and begin to shift, the former moving slightly downfield, the latter about 2 ppm upfield (Table 3), clearly indicating formation of an ethylene complex, presumably IIIa. However, even at -86° in CD_2Cl_2, separate signals for free and coordinated ethylene are not observed, so that intermolecular exchange is still fast on the NMR time scale at this temperature.

In contrast, when ethylene is passed into a solution of the iridium(I) complex IIb there is an immediate colour change from orange to pale yellow, and the adduct IIIb can be isolated as a pale yellow microcrystalline solid. It readily loses ethylene in the solid state, and even when stored under ethylene undergoes slow decomposition. The ^{1}H NMR spectrum of IIIb in $CDCl_3$ containing excess ethylene shows a single broad resonance for the olefinic protons of bdpps, which sharpen somewhat on ^{31}P-decoupling, together with very broad signals for free and coordinated ethylene. The latter is approximately twice as intense as the olefinic resonance of bdpps, which confirms that the species in solution is $IrCl(C_2H_4)$(bdpps). On cooling to -33°C the bdpps olefinic proton resonance separates out and appears as an AB quartet split by coupling with two phosphorus atoms. The free ethylene resonance becomes a sharp singlet and the coordinated ethylene resonance, although still broad, shows evidence of two overlapping signals. Further cooling causes the coordinated ethylene resonance to broaden, then sharpen, until at -67° a "frozen" spectrum is obtained, consisting of three sets of signals corresponding to four non-equivalent protons, of which two have similar chemical shifts (Table 3). Separate transitions remain almost unresolved even with ^{31}P-decoupling. The observations are consistent with a trigonal bipyramidal structure for IIIb with ethylene in the equatorial plane; all four protons are inequivalent, and should give rise to an ABCD spectrum. On warming from -69°C to -33°C, the ethylene rotates about the metal-ethylene bond-axis [11]; this gives rise to an AA'BB' spectrum owing to time-averaged equivalence for mutually trans-protons of the olefin. Above −20°C intermolecular ethylene exchange sets in and at 32°C this is occurring at an intermediate rate on the NMR time scale.

Cationic Complexes

Treatment of IIa or IIb in dichloromethane solution with silver tetrafluoroborate gives an immediate precipitate of silver chloride and orange or red solutions which are believed to contain the planar monocarbonyl cations $[M(CO)(bdpps)]^+$ (IVa, M = Rh; IVb, M = Ir), the IR spectra of which show one $\nu(CO)$ absorption above 2000 cm^{-1}. The magnitude of $\underline{J}(Rh\text{-}P)$, 107 Hz, obtained from the $^{31}P\{^1H\}$ NMR spectrum of IVa is of the same order as those of cationic planar rhodium(I) complexes such as $[Rh(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (119 Hz) [12], in which the phosphorus atoms are mutually trans. The complexes are unstable in solution and readily deposit a metal mirror on attempted isolation or on standing at room temperature. Treatment of IIa or IIb with silver tetrafluoroborate in the presence of carbon monoxide gives stable, colourless, five-coordinate dicarbonyl cations $[M(CO)_2(bdpps)]^+$ (Va, M = Rh; Vb, M = Ir), which can be isolated as their fluoroborate salts. These cations are also formed from IVa or IVB by treatment with carbon monoxide (25°, 1 atm), but in the case of rhodium the reaction is reversed by heating or by passing nitrogen through the solution. Their IR spectra show two $\nu(CO)$ bands above 2000 cm^{-1} indicating that the carbonyl groups are mutually cis, while NMR spectra show the olefinic protons and the phosphorus atoms to be equivalent, as expected for the trigonal bipyramidal structure. The magnitude of $\underline{J}(Rh\text{-}P)$ for Va, 85 Hz, is smaller than that for IVa, this being the expected trend in going from a four-coordinate to a five-coordinate species.

^1H and ^{31}P NMR spectra indicate that by-products (∿10%) in the preparation of the monocarbonyl cation IVa are the dicarbonyl cation Va and Ia, which are probably formed by a CO-transfer reaction:

$$RhCl(CO)(bdpps) + [Rh(CO)(bdpps)]^+ \rightarrow RhCl(bdpps) + [Rh(CO)_2(bdpps)]^+$$

Colourless ethylene-containing cations $[M(C_2H_4)_2(bdpps)]^+$ (VIa, M = Rh; VIb, M = Ir) analogous to Va and Vb are formed from Ia or Ib by treatment with silver tetrafluoroborate in the presence of ethylene. In the absence of ethylene, the solutions decompose to form orange-red solutions which probably contain the mono-ethylene species. These too are unstable and readily disporportionate to form a metal mirror and the bis(ethylene) cation. The ^1H NMR spectrum of VIa at 25°C in $CDCl_3$ saturated with ethylene shows a doublet of triplets arising from equivalent olefinic protons of bdpps split by two equivalent ^{31}P nuclei and one ^{103}Rh nucleus, together with a slightly broad singlet due to ethylene undergoing intermolecular exchange at a rate which is fast on the NMR time scale. On cooling, the ethylene singlet broadens and separates into a sharp singlet for free ethylene and a broad, unresolved singlet assignable to two coordinated ethylene molecules. The latter signal continues to broaden on further cooling,but even at -60° does not give the separate signals expected for slow intramolecular ethylene rotation.

The ^1H NMR spectrum of the corresponding iridium(I) complex VIb, run under the same conditions as that of VIa, shows separate signals for free and coordinated ethylene at 28°, hence intermolecular exchange is slow on the NMR time scale. The resonances due to the olefinic protons of bdpps and of ethylene appear as triplets because of coupling with two equivalent ^{31}P nuclei. On cooling to -68° the coordinated ethylene resonance broadens considerably, probably owing to the slowing down of intramolecular ethylene rotation, but separate resonances are not observed.

Complex Ib and $IrCl(CO)(PPh_3)_2$ are clearly similar in their ability to reversibly add a fifth ligand. Thus, carbon monoxide reacts reversibly with $IrCl(CO)(PPh_3)_2$ to give a trigonal bipyramidal dicarbonyl complex in which the triphenylphosphine ligands occupy axial positions [13, 14]. Ethylene is also reported to form a 1:1 adduct with $IrCl(CO)(PPh_3)_2$, though it is much less stable than the analogous carbon monoxide adduct and has not been isolated [15, 16]; the iodo-complex $IrI(CO)(C_2H_4)(PPh_3)_2$ forms colourless crystals which are stable only in the presence of ethylene [15]. The adducts formed by Ia are much less stable than those of Ib, exemplifying the preference of iridium(I) relative to rhodium(I) for five-coordination. Qualitatively, it appears from the results with iridium(I) that five-coordinate adducts are formed more readily with bdpps than with the equivalent ligand set $(CO)(PPh_3)_2$. This is also evident from the rhodium(I) chemistry, since the adduct RhCl(CO)(bdpps) can be isolated, whereas the existence of $RhCl(CO)_2(PPh_3)_2$ as an intermediate can only be inferred from the rapid intermolecular ^{14}CO exchange observed with $RhCl(CO)(PPh_3)_2$ [17].

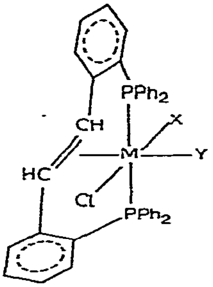
The cationic complexes IVb and Vb are very similar to cationic four- and five-coordinate iridium(I) carbonyl complexes $[Ir(CO)_n(PR_3)_2]^+$ (n = 2 or 3; PR_3 = various tertiary phosphines) which have been made by reaction of $IrCl(CO)(PR_3)_2$ with $AgBF_4$, $NaBF_4$, or $NaBPh_4$, with or without CO, as well as by other methods [18-22]; the cation in $[Ir(CO)_3(PMe_2Ph)_2]ClO_4$ has the expected trigonal bipyramidal structure with the phsophine ligands in axial positions [23], thus emphasizing the resemblance with Vb. VIb is analogous to the bis(ethylene) cation $[Ir(CO)(C_2H_4)_2(PMe_2Ph)_2]^+$ [24]. Although less work has been reported on analogous rhodium(I) systems, the silver ion-promoted removal of chloride from $RhCl(CO)(PPh_3)_2$ to give a labile cation $[Rh(CO)(acetone)(PPh_3)_2]^+$ has been described [25].

Oxidative Addition Reactions. Ib reacts quantitatively with hydrogen chloride to give a colourless hydrido-iridium(III) complex $IrHCl_2$(bdpps).

The IR spectrum shows a band at 2220 cm^{-1} (nujol mull) assignable to ν(IrH), the value being in the range quoted for H trans to Cl in octahedral hydrido-iridium(III) complexes [26]. There are also two ν(IrCl) bands due to mutually cis-chlorines at 305 and 250 cm^{-1}, the latter being typical of Cl trans to H; the former is presumably due to Cl trans to the coordinated olefin, the value being very close to that observed for Cl trans to CO in $IrHCl_2(CO)(PPh_3)_2$ and similar complexes with other tertiary phosphines [27-29]. The $^{31}P\{^1H\}$ spectrum of $IrHCl_2$(bdpps) consists of an AB quartet with a large value of $^2\underline{J}$(P-P) (Table 2), hence the phosphorus atoms are inequivalent and mutually trans. In the ^1H NMR spectrum the hydride resonance appears as a triplet owing to almost equal couplings with the two ^{31}P nuclei [$\underline{J}$(P-H) 10.5 Hz]. The magnitude of this coupling shows that the hydride is cis to both phosphorus atoms, and the chemical shift (δ-13.30 ppm, τ 23.30) is close to the values found for H trans to Cl in complexes of the type $IrHCl_2(CO)(PR_3)_2$ [29]. The olefinic protons of bdpps are shifted upfield relative to those of the free ligand, and are coupled equally to the two ^{31}P nuclei, so that the double bond is coordinated. Thus all the spectroscopic data are in accord with the octahedral structure VII. It should be noted that the olefinic protons of coordinated bdpps in VII, though inequivalent, fortuitously have identical chemical shifts, which could have led to an incorrect assignment for the stereochemistry of the complex.

Although VII has a metal-hydrogen bond cis to a coordinated olefin, it shows no tendency to undergo the expected rearrangement to a chelate iridium(III) alkyl. This may be a consequence both of the rigidity of the chelate olefin group and of the reluctance of iridium(III) to depart from its favoured six-coordinate geometry, *cf.*, the stability of the 1,5-cyclooctadiene complex $[IrHCl_2(1,5\text{-cod})]_2$ [30].

Prolonged reaction of Ib or VII with hydrogen chloride gives the yellow trichloro-complex $IrCl_3$(bdpps) (VIIIb), identical with the product isolated from the reaction of bdpps with iridium trichloride in 2-methoxyethanol [3]. Addition of hydrogen chloride to Ia gives the corresponding trichlororhodium(III) complex $RhCl_3$(bdpps), VIIIa, as the only isolable product, presumably formed *via* an intermediate hydrogen chloride adduct analogous to VII, though this could not be detected. VIIIa shows two strong bands in its far IR spectrum at 351 and 330 cm^{-1}, assignable to ν(RhCl) vibrations of Cl trans to Cl and Cl trans to olefin respectively, *cf.* $RhCl_3(CO)(PPh_3)_2$, which has bands at 341 cm^{-1} (Cl trans to Cl) and 316 cm^{-1} (Cl trans to CO) [28]. In the case of VIIIb, only the band at 330 cm^{-1} could be located [3]. The olefinic protons and the ^{31}P nuclei are equivalent, as expected for the octahedral structure. There is only a very small upfield shift

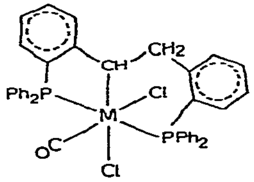


X = H, Y = Cl, M = Ir; VII
X = Y = Cl, M = Rh; VIIIa
X = Y = Cl, M = Ir; VIIIb
X = Y = H, M = Ir; IX

of the olefinic protons relative to those of the uncomplexed ligand, and no ^{31}P coupling is observed. However, olefin coordination is indicated by the observation of ^{103}Rh coupling to the olefinic protons of VIIIa (Table 2), and the small upfield proton shifts probably reflect the fact that the metal-olefin interaction in VIIIa and VIIIb is weaker than in the planar rhodium(I) and iridium(I) complexes Ia and Ib. It may be noted that relatively few olefin complexes of octahedral rhodium(III) or iridium(III) are known, and these usually either contain 1,5-cyclooctadiene *e.g.* $RhCl(1,5\text{-}cod)(SiCl_3)_2$ [31] or $IrCl_3(py)(1,5\text{-}cod)$ [32] or have the olefin incorporated into a chelate group, *e.g.* $Rh_2Cl_4\{CH_2CH(CH_2OH)CH_2CH{=}CH_2\}_2$ [33]; complexes of rhodium(III) and iridium(III) containing bridging transoid butadiene are also known [34, 35]. The ease with which the metal-hydrogen bond in VII, and in its presumed rhodium analogue, is cleaved by hydrogen chloride is surprising, and is reminiscent of the behaviour of a metal-hydrogen bond trans to a tertiary phosphine [36]. A similar conversion of $IrHCl_2(CO)(PPh_3)_2$ into $IrCl_3(CO)(PPh_3)_2$ under forcing conditions has been reported [37].

Ib reacts in solution with hydrogen gas (25°, 1 atm) to give an almost colourless, octahedral *cis*-dihydridoiridium(III) complex IrH_2Cl(bdpps), IX. Ia does not react with hydrogen under similar conditions. Attempts to isolate IX lead to loss of hydrogen and re-formation of Ib, but the structure of IX can be inferred unambiguously from spectroscopic data. The IR spectrum shows two ν(IrH) bands at *ca.* 2200 cm^{-1} and 2100 cm^{-1} due to H trans to Cl and olefin respectively, the latter being in the same region as observed for H trans to CO in the hydrogen adduct of $IrCl(CO)(PPh_3)_2$ [37]. The $^{31}P\{^1H\}$ NMR spectrum consists of an AB quartet, and the magnitude of $^2J(P\text{-}P)$ (Table 2) shows that the phosphorus atoms are mutually trans. The hydride resonances in the ^1H spectrum appear at δ −5.15 ppm (τ 15.15) (H trans to olefin) and δ −16.95 ppm (τ 26.95) (H trans to Cl), and are slightly broadened by intermolecular exchange with the excess of hydrogen present. The olefinic protons show the expected non-equivalence and surprisingly show no exchange broadening. This appears to suggest that the intermolecular exchange process which is responsible for the broadening of the hydride resonances does not proceed *via* Ib, *i.e.* it is not simply the expected reversible loss of hydrogen. Possibly an intermediate tetrahydride is involved, as has been suggested for the H_2/D_2 exchange catalyzed by $IrCl(CO)(PPh_3)_2$ [38]. The olefinic trans H-H coupling in IX, 10.5 Hz, is much larger than that observed in the five-coordinate complex IIb, 5.8 Hz, and the chemical shifts (δ 4.58, 4.99 ppm) are closer to those of the uncomplexed ligand than are those of IIb (δ 3.32, 3.66 ppm). These features imply that the metal-olefin bond in IX is weaker than in IIb, presumably as a consequence both of the different stereochemistries of the two complexes and of the trans-bond weakening influence of the hydride ligand. As with VII, there is no evidence for isomerization of IX to give a chelate σ-alkyl.

Addition to the Coordinated Ligand. As noted above, hydrogen chloride adds oxidatively to the metal atom in Ia or Ib, leaving the coordinated olefin intact. In contrast, in the presence of carbon monoxide, Ia and Ib (or pre-isolated IIa and IIb) react with hydrogen chloride in dichloromethane solution to give pale yellow, octahedral, chelate σ-alkyl complexes $\overline{MCl_2(CO)\{o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o\}$ (M = Rh, Xa; M = Ir, Xb) *i.e.* the proton of HCl has added to the coordinated double bond and chlorine has added to the metal. In the case of the rhodium



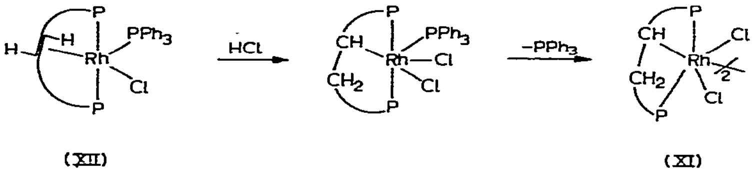
M = Rh ; Xa
M = Ir ; Xb

complex Xa, the reaction is reversed by heating in mildly basic solvents such as ethanol. Hydrogen gas does not react with IIa or IIb under similar conditions. The complexes show one ν(CO) band at *ca.* 2050 cm^{-1} and two ν(MCl) bands at *ca.* 310 cm^{-1} and 250 cm^{-1} indicative of mutually *cis*-chlorine atoms which are trans to CO and to the metal-carbon σ-bond respectively. The ^{31}P{^{1}H} NMR spectra of both complexes consist of an AB quartet which is doubletted in the case of Xa by Rh-P coupling; the magnitude of $^{2}\underline{J}$(P-P) shows the phosphorus atoms to be mutually trans. The ^{1}H spectra of Xa and Xb are very similar and show, in addition to aromatic resonances, a multiplet pattern arising from the aliphatic protons of the chelate ring, which form an ABC system. The ^{1}H-^{1}H coupling constants and their relative signs derived by iterative analysis are given in Table 2. The largest coupling (Xa, 16.0 Hz; Xb, 15.5 Hz) is of opposite sign to the other two and is clearly the geminal coupling constant; the magnitudes are close to those expected for a methylene group adjacent to sp^{2}-hybridized carbon, $|J_{gem}| \sim$16-18 Hz [39]. The other two ^{1}H-^{1}H couplings (Table 2) for both Xa and Xb are within the normal range for vicinal protons. In both compounds only one of the three protons, the geminal proton with the smaller ^{1}H-^{1}H vicinal coupling constant, is significantly coupled to ^{31}P. ^{103}Rh-coupling is observed both to the methine proton and, surprisingly, to the geminal proton having the larger vicinal ^{1}H-^{1}H coupling constant; the latter is a rare example of a three-bond ^{103}Rh coupling.

The tridentate chelate σ-alkyl group $o\text{-}Ph_2PC_6H_4\dot{C}HCH_2C_6H_4PPh_2\text{-}o$ has been identified previously in its palladium(II) and platinum(II) complexes formed by deprotonation of 2,2′-bis(diphenylphosphino)-bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ [3].

Preliminary experiments suggest that carbon monoxide is not unique in its ability to change the course of hydrogen chloride addition to Ia or Ib. Thus, in the presence of triphenylphosphine, Ia reacts with hydrogen chloride to give exclusively a yellow, chelate σ-alkylrhodium(III) complex $[\overline{Rh}Cl_2(o\text{-}Ph_2PC_6H_4\overline{C}HCH_2C_6H_4PPh_2\text{-}o)]_2$, XI, which is dimeric in chloroform and which reverts to Ia on heating in ethanol. The IR spectrum shows one strong band assignable to ν(RhCl) of a terminal Rh-Cl bond, and although no absorption due to bridging chlorine atoms could be clearly identified, the rhodium atoms probably attain octahedral configuration by the formation of such bridges. XI decomposes in solution over a period of hours to give unidentified products, so that a $^{31}P\{^{1}H\}$ NMR spectrum could not be obtained, but the ^{1}H NMR spectrum clearly shows the presence of the $CHCH_2$ group. In contrast with Xa, the methine proton is well downfield of the methylene resonances and *both* vicinal couplings are small (Table 2). This may indicate a different conformation for the six-membered chelate ring in XI compared with Xa, perhaps resulting from a cis- arrangement of the phosphorus atoms.

We suggest that hydrogen chloride reacts initially with a five-coordinate triphenylphosphine adduct XII exactly as described



SCHEME 2. Addition of HCl to RhCl(bdpps) in presence of triphenylphosphine

above for the carbonyl complex, and that the resulting octahedral rhodium(III) complex XIII loses triphenylphosphine to relieve steric hindrance forming XI (Scheme 2). A five-coordinate triphenylphosphine adduct of the iridium(I) complex Ib can be isolated though it readily dissociates in solution [40]. We are currently examining the reactions of Ia and Ib with other ligands, and the reaction of hydrogen chloride with the resulting adducts. It is not at present possible to say whether protonation of the coordinated double bond proceeds by initial protonation of the metal atom and subsequent hydrogen migration, or whether hydrogen chloride attacks the double bond directly.

Conclusion

This work shows that use of the tridentate chelating olefinic ditertiary phosphine bdpps permits isolation of olefin complexes of planar rhodium(I) and iridium(I), and of octahedral rhodium(III) and iridium(III), from which the olefin does not readily dissociate. In the absence of other ligands, the planar complexes undergo typical oxidative addition reactions and thus behave similarly to $IrCl(CO)(PPh_3)_2$. The complexes $IrHCl_2$(bdpps) and IrH_2Cl(bdpps) are rare examples of stable hydrido-olefin complexes which, unexpectedly, do not isomerise to a metal alkyl. Their stability suggests that this hydrogen transfer step could be one of the rate-determining steps in olefin hydrogenation homogeneously catalyzed by d^8 complexes such as $IrCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ [41].

Experimental

Preparative, analytical, and spectroscopic procedures have been described previously [42, 43]. The complex RhCl(bdpps), Ia, was prepared by the reaction of $[RhCl(1,5\text{-}COD)]_2$ with 2,2'-bis(diphenylphosphino)bibenzyl, $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$, and the ligand bdpps was displaced from Ia with sodium cyanide [3]. The iridium(I) complex IrCl(bdpps), Ib, was obtained from $[IrCl(1,5\text{-}COD)]_2$ and bdpps [3]. The preparations and reactions described below gave essentially quantitative yields, except where stated. Analytical data are in Table 1.

Many of the complexes contained residual dichloromethane of crystallisation, as shown by the analytical data and by ^1H NMR spectra in $CDCl_3$, which could not be removed even by prolonged pumping. Its presence in small amounts (<0.5% v/v) will lead to slightly high (∿5%) apparent molecular weights in chloroform (osmometry, 25°C). Thus the molecular weights in Table 1 must be regarded as approximate, though the values are generally close enough to those calculated to establish the molecularity of the complexes.

2,2'-Bis(diphenylphosphino)-*trans*-stilbenecarbonylchloro-rhodium(I), and -iridium(I), MCl(CO)(bdpps) IIa (M = Rh) and IIb (M = Ir).

Carbon monoxide was passed into a solution of Ia or Ib (0.2 g) in dichloromethane (10 ml) for 2 min. *n*-Pentane (20 ml) was then added to the pale yellow solution, the atmosphere of carbon monoxide being maintained. After 20 min the supernatant liquid was decanted, the colourless crystalline product was washed with two 10 ml portions of *n*-pentane and dried in a stream of carbon monoxide (IIa), or *in vacuo* at 50°C (IIb).

2,2'-Bis(diphenylphosphino)-*trans*-stilbenechloro(ethylene)rhodium(I), $RhCl(C_2H_4)(bdpps)$, IIIa. This complex was obtained by passing ethylene into a solution of IIa in $CDCl_3$ contained in an NMR tube, and was identified by its ^1H NMR spectrum (Table 3).

2,2'-Bis(diphenylphosphino)-*trans*-stilbenechloro(ethylene)iridium(I), $IrCl(C_2H_4)(bdpps)$, IIIb. A solution of Ib (0.2 g) in dichloromethane (10 ml) was saturated with ethylene (1 atm). An ethylene atmosphere was maintained as *n*-pentane (∿20 ml) was added. The supernatant liquid was decanted, and the pale yellow product was dried in a stream of ethylene. Solutions for ^1H NMR spectra were prepared *in situ* as described for IIIa.

2,2'-Bis(diphenylphosphino)-*trans*-stilbenedicarbonyl-rhodium(I) and -iridium(I) tetrafluoroborates, $[M(CO)_2(bdpps)]BF_4$, Va (M = Rh) and Vb (M = Ir). Solutions of Ia or Ib (∿0.2 g) in dichloromethane (10 ml) were saturated with carbon monoxide (1 atm) and treated with an excess of solid silver tetrafluoroborate in a carbon monoxide atmosphere. After allowing to stand for a few minutes, the solutions were filtered to remove silver chloride and the colourless salts were precipitated by the addition of *n*-pentane (20 ml). The rhodium complex Va was dried in a stream of carbon monoxide, the iridium complex Vb was dried *in vacuo*. Samples for ^1H and ^{31}P NMR studies were usually prepared *in situ* in CD_2Cl_2.

2,2′-Bis(diphenylphosphino)-*trans*-stilbenecarbonyl-rhodium(I) and -iridium(I) tetrafluoroborates, $[M(CO)(bdpps)]BF_4$, IVa (M = Rh) and IVb (M = Ir). Solutions of the monocarbonyl complexes IIa or IIb prepared from Ia or Ib (0.2 g) in dichloromethane (10 ml) were treated with an excess of silver tetrafluoroborate in a nitrogen atmosphere. After removal of silver chloride by filtration, the orange or red solutions were characterised by their ^1H NMR spectra (Table 2) and IR spectra [ν(CO) 2064 cm^{-1} (M = Rh), 2035 cm^{-1} (M = Ir)]. Attempts to isolate the solid fluoroborate salts were unsuccessful owing to decomposition in solution, which was evident after 15 min. The rhodium(I) cation IVa was also formed when Va was heated in dichloromethane for a few minutes. Both IVa and IVb reacted immediately with carbon monoxide to give Va and Vb respectively.

2,2′-Bis(diphenylphosphino)-*trans*-stilbenebis(ethylene)-rhodium(I) and -iridium(I) tetrafluoroborates, $[M(C_2H_4)_2(bdpps)]BF_4$, VIa (M = Rh) and VIb (M = Ir). Colourless solutions of these salts were prepared similarly to their carbonyl analogs Va and Vb, using ethylene in place of CO. The solutions were filtered into NMR tubes and re-saturated with ethylene before spectra were recorded. The rapid loss of ethylene prevented isolation of the solid salts. On passing nitrogen into a dichloromethane solution of VIa or VIb an orange colour developed, and the solution immediately began to deposit a metal mirror on the wall of the flask. The orange species are probably the mono-ethylene cations $[M(C_2H_4)(bdpps)]^+$, by analogy with IVa and IVb.

2,2′-Bis(diphenylphosphino)-*trans*-stilbenedichlorohydridoiridium(III), $IrHCl_2(bdpps)$, VII. A solution of Ib (0.2 g) in dichloromethane (10 ml) was treated with dry hydrogen chloride for 5 min, giving a colourless solution. The product crystallized on addition of *n*-pentane (10 ml) and was dried at 50° *in vacuo*.

2,2′-Bis(diphenylphosphino)-*trans*-stilbenetrichloro-rhodium(III) and -iridium(III), MCl_3(bdpps), VIIIa (M = Rh) and VIIIb (M = Ir). Dry chlorine gas was passed into a solution of Ia or Ib (0.2 g) in dichloromethane (10 ml) at room temperature. After removal of chlorine by flushing with nitrogen, methanol was added dropwise to give orange crystals of VIIIa, or deep yellow crystals of VIIIb, respectively. VIIIa was also obtained by treating a dichloromethane solution of Ia with hydrogen chloride for 30 min.

[{1,2-Bis(*o*-diphenylphosphino)phenyl}ethyl]carbonyldichlororhodium(III) and -iridium(III), $\overline{MCl_2(CO)\{o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o\}$, Xa (M = Rh) and Xb (M = Ir). Solutions of Ia or Ib (0.2 g) in dichloromethane (10 ml) were treated first with carbon monoxide to generate the carbonyl complexes IIa or IIb *in situ*, and then with dry hydrogen chloride for 5 min. The products crystallized on addition of *n*-pentane and were dried *in vacuo* at 50°C.

Di[{1,2-Bis(*o*-diphenylphosphino)phenyl}ethyl]-dichloro-di-μ-chloro-dirhodium(III), $[\overline{RhCl_2\{o\text{-}Ph_2PC_6H_4C}HCH_2C_6H_4PPh_2\text{-}o\}]_2$, XI. A solution containing Ia (0.2 g) and triphenylphosphine (0.05 g) in dichloromethane (10 ml) was treated with dry hydrogen chloride for 5 min. The product precipitated on addition of *n*-pentane (15 ml) and was dried *in vacuo*.

2,2-Bis(diphenylphosphino)-*trans*-stilbenechlorodihydridoiridium(III), IrH_2Cl(bdpps), IX. Hydrogen was passed into a solution of Ib (0.2 g) in dichloromethane (10 ml) at room temperature, causing an immediate colour change from orange to very pale yellow. All attempts to isolate the adduct were frustrated by its ready reversion to starting material, and it was characterised by IR spectra [ν(IrH) 2205s, 2090 s cm^{-1}) (CH_2Cl_2)] and by NMR spectroscopy (text and Table 2). Samples for ^1H and ^{31}P NMR spectra were prepared *in situ* in CD_2Cl_2 and CH_2Cl_2 solutions contained in NMR tubes.

Elimination of HCl from the Chelate Alkyls of Rhodium(III), Xa and XI, forming Ia. Xa or XI (0.1 g) was heated under reflux in ethanol (20 ml) for 1 hr. After cooling to room temperature and setting aside for 1 hr, the yellow solid which had formed was centrifuged and dried *in vacuo*. It was identified as RhCl(bdpps), Ia, by its ^1H NMR spectrum.

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