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RHODIUM TRICHLORIDE - PROMOTED DIMERIZATION OF A BIDENTATE OLEFINIC TERTIARY PHOSPHINE TO A TRIDENTATE OLEFINIC DITERTIARY PHOSPHINE: ADDITIONS TO METAL ATOM AND TO LIGAND AND HYDROGEN ABSTRACTIONS FROM THE LIGAND IN DERIVED COMPLEXES OF RHODIUM AND IRIDIUM.

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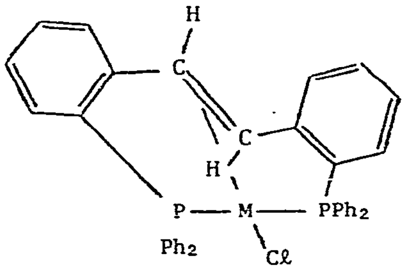
Summary

o-Styryldiphenylphosphine[(*o*-vinylphenyl)diphenylphosphine], $o\text{-}CH_2{=}CHC_6H_4PPh_2$ (sp) is dimerized by rhodium(III) chloride in refluxing 2-methoxyethanol to give a rhodium(I) complex RhCl(1-bdpb) (IV) containing the tridentate chelate olefinic ligand 1,3-bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene, $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o$ (1-bdpb) (VI). VI is liberated from IV by reaction with sodium cyanide. IV and its iridium(I) analogue VII exist as mixtures of isomers which have different conformations of the chelate ligand. The isomers of IV interconvert rapidly on the NMR time scale in solution above 122°C with an estimated free energy of activation $\Delta G^{\neq}$ (122°) of 20.5 kcal/mol; in the case of VII, the process is slow on the NMR time scale even at 122° ($\Delta G^{\neq} > 20.5$ kcal/mol). The five-coordinate carbonyl complexes MCl(CO)(1-bdpb) (M=Rh, VIII: M=Ir, IX) react with hydrogen chloride to give chelate 2-butyls $\overline{MCl_2(CO)\{o\text{-}Ph_2PC_6H_4CH_2CH}CH(CH_3)\text{-}C_6H_4PPh_2\text{-}o\}$ (M=Rh, XIV; M=Ir, XV), the addition being reversible in the case of rhodium. In the presence of triphenylphosphine, IV adds hydrogen chloride to give a chlorine-bridged dimer containing a chelate 1-butyl unit i.e. $[\overline{RhCl_2\{o\text{-}Ph_2PC_6H_4C}HCH_2CH(CH_3)C_6H_4PPh_2\text{-}o\}]$ (XVI). In the absence of auxiliary ligands, VII undergoes irreversible oxidative addition at the metal atom with chlorine and hydrogen chloride, and reversible oxidative addition with hydrogen, to give octahedral, chelate olefin complexes of iridium(III), $IrCl_3$(1-bdpb) (XII), $IrHCl_2$(1-bdpb) (XVII) and IrH_2Cl(1-bdpb) (XVIII) respectively; each isomer of VII gives rise to one corresponding isomer in the case of XII and to two corresponding isomers in the cases of XVII and XVIII. IV reacts with chlorine to give $RhCl_3$(1-bdpb) (XI) and with hydrogen chloride to give a mixture of XI and XVI. XI loses hydrogen chloride irreversibly in solution to form a pseudo-octahedral, chelate η^3-allyl $RhCl_2\{o\text{-}Ph_2PC_6H_4CH\overset{\cdots}{-}CH\overset{\cdots}{-}C(CH_3)C_6H_4PPh_2\text{-}o\}$ (XIII) in which the phosphorus atoms are mutually *trans*. Although five-coordinate cations $[M(CO)_2(1\text{-bdpb})]^+$ (M=Rh, XX; M=Ir, XXI), can be isolated as fluoroborate salts, analogous ethylene complexes cannot be obtained; in the case of iridium, the tertiary C-H bond of coordinated 1-bdpb oxidatively adds to the metal atom to give a cationic, pseudo-octahedral η^3-allyl hydrido-ethylene iridium(III) complex, $[IrH(C_2H_4)\{o\text{-}Ph_2PC_6H_4CH\overset{\cdots}{-}CH\overset{\cdots}{-}C(CH_3)\text{-}C_6H_4PPh_2\text{-}o\}]BF_4$ (XXII). There is also ^{1}H NMR spectroscopic evidence for a minor by-product formed by loss of two hydrogen atoms from 1-bdpb *viz.* $[Ir(C_2H_4)\{o\text{-}Ph_2PC_6H_4CH{=}CHC({=}CH_2)C_6H_4PPh_2\text{-}o\}]\ BF_4$ (XXIII). The reactions of IV and VII are compared with those of similar complexes containing $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o$ (bdpps), and the mechanism of dimerization of sp is shown to be analogous to that of the rhodium(III) chloride-catalyzed dimerization of ethylene to 1-butene.

Introduction

In previous papers [1-4] we have shown that complexes of rhodium and ruthenium promote coupling and dehydrogenation reactions of various *ortho*-substituted aromatic tertiary phosphines. On heating with rhodium trichloride in high-boiling alcohols such as 2-methoxyethanol, the *o*-tolylphosphines

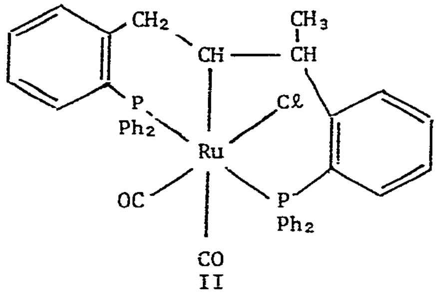
$(o\text{-}CH_3C_6H_4)_nPh_{3-n}P$ (n=1-3) undergo coupling and dehydrogenation to give chelate *trans*-stilbene complexes of rhodium(I) e.g. Ia (R=*o*-tol)[*] from tri-*o*-tolylphosphine; the yields of the coupled products decrease as the number of *o*-tolyl groups is reduced. The corresponding complex Ib (R = Ph) containing 2,2'-(diphenylphosphino)-*trans*-stilbene, $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o$ (bdpps) can be obtained almost quantitatively by dehydrogenation of the bibenzyl ligand $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o$ promoted by the 1,5-cyclooctadiene complex $[RhCl(COD)]_2$ [2]. The vinyl group of *o*-styryldiphenylphosphine, [(*o*-vinylphenyl)diphenylphosphine], $o\text{-}CH_2{=}CHC_6H_4PPh_2$, (sp) can be coupled with the vinyl group of a second molecule of sp, but the mode of coupling depends markedly on the metal complex present. The $Ru_3(CO)_{12}$-promoted coupling occurs without any apparent hydrogen atom shift to give an octahedral dicarbonyl ruthenium(II) complex containing two metal-carbon σ-bonds i.e.



Ia; M = Rh, R = *o*-tolyl.

Ib; M = Rh, R = Ph

Ic; M = Ir, R = Ph



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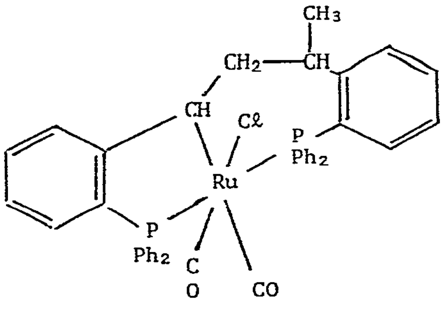

III

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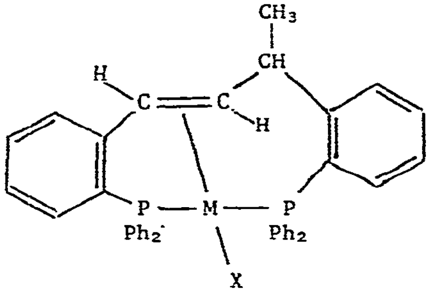
[*] Abbreviations: Me = methyl, Et = ethyl, Ph = phenyl, *o*-tol = *o*-tolyl ($o\text{-}CH_3C_6H_4$), COD = 1,5-cyclooctadiene, bdpps = 2,2'-bis(diphenylphosphino)-*trans*-stilbene, dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$

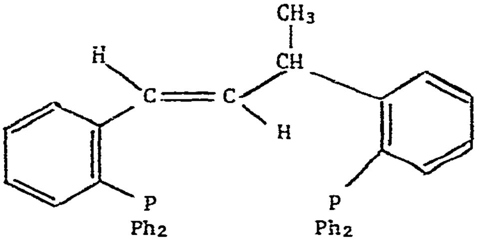
$Ru(CO)_2\{o\text{-}Ph_2PC_6H_4CHCH_2CH_2CHC_6H_4PPh_2\text{-}o\}$, which is subsequently dehydrogenated to a chelate butadiene-ruthenium(o) complex $Ru(CO)\{o\text{-}Ph_2PC_6H_4CH\overset{c}{=}CHCH\overset{t}{=}CHC_6H_4\text{-}PPh_2\text{-}o\}$ [3]. In contrast, a carbonylated solution of ruthenium chloride in 2-methoxyethanol affords a mixture of octahedral, ruthenium(II)-carbon σ-bonded chelate complexes II and III in which the coupling of vinyl groups has evidently been accompanied by hydrogen migrations [4].

We report here on the rhodium(III) chloride-promoted dimerization of sp, which is similar in some respects to the corresponding ruthenium(II) reaction, and also on some oxidative addition and hydrogen abstraction reactions of the resulting rhodium(I) and iridium(I) complexes. Some aspects of this work have appeared in preliminary communications [5,6].

Results

Reaction of an excess of sp with hydrated rhodium(III) chloride in refluxing 2-methoxyethanol gives a deep yellow crystalline complex of empirical formula $RhCl(sp)_2$ in about 70% yield based on Rh. Spectroscopic data discussed below show that this complex is a planar chlororhodium(I) complex containing the tridentate ligand 1,3-bis[(o-diphenylphosphino)-phenyl]-*trans*-1-butene, $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o$ (1-bdpb) coordinated





VI

IV M = Rh, X = Cl

V M = Rh, X = Br

VII M = Ir, X = Cl

XIX M = Rh^+, X = CO

via two phosphorus atoms and the double bond (IV). The corresponding bromo-complex, V, is prepared similarly starting from rhodium(III)bromide. The ligand 1-bdpb, VI, which is derived by coupling the vinyl groups of two sp moieties, is liberated from IV by treatment with sodium cyanide in aqueous 2-methoxyethanol, and is a colourless, crystalline, air-stable solid. In the IR spectrum of VI (Table 1) there is a strong band at *ca* 970 cm^{-1} assignable to the olefinic C-H deformation mode of a *trans*-disubstituted olefin; this stereochemistry is confirmed by the magnitude of the ^1H-^1H coupling constant between the olefinic protons (J_{12} = 17.5 Hz) (Table 2).

Reaction of 1-bdpb with $[IrCl(COD)]_2$ gives the orange air-sensitive complex IrCl(1-bdpb), VII, the iridium(I) analogue of IV. In the IR spectra of both complexes the band due to the olefinic C-H deformation mode is shifted to lower frequency from its position in the spectrum of the free ligand, hence the double bond is coordinated [1,2]. The far IR spectra of IV and VII show bands at *ca* 305 cm^{-1} assignable to ν(MCl) for Cl trans to olefin; the values are similar to those observed in the corresponding chelate *trans*-stilbene complexes of rhodium(I), Ia, and of iridium(I), Ic [1,2], and are also in the same general range as found for Cl *trans* to CO in the planar complexes $MCl(CO)(PPh_3)_2$ (M=Rh, Ir) [7].

The NMR spectra of IV and VII show the presence of two isomers in solution. The methyl protons of the chlororhodium(I) complex IV appear as an overlapping pair of doublets, the intensity ratio being about 3:2 at room temperature; the resonances of the olefinic and methine protons overlap and complete analysis is impossible. The marked upfield shift of the olefinic protons in the two isomers relative to the free ligand provides additional evidence for double bond coordination. The $^{31}P\{^1H\}$ NMR spectrum of IV shows 16 lines corresponding to the AB quartets of the two isomers split into doublets by coupling with ^{103}Rh, and the magnitude of ^2J(P-P) (Table 3) shows that the phosphorus atoms in both isomers are mutually *trans*. Although there is only one methyl doublet in the ^1H NMR spectrum of the bromorhodium(I) complex V, the $^{31}P\{^1H\}$

TABLE 1 ANALYTICAL, MOLECULAR WEIGHT AND SELECTED IR DATA FOR RHODIUM AND IRIDIUM COMPLEXES OF 1,3-BIS (*o*-DIPHENYLPHOSPHINO)PHENYL -*TRANS*-1-BUTENE, $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o$, 1-bdpb.[a,b]

	Analysis found (calcd.)(%)					Selected IR bands (cm^{-1})	
	C	H	P	Cℓ	Mol wt	ν(MCℓ)	Others
1-bdpb (VI)	83.3 (83.3)	5.9 (5.9)	10.3 (10.7)	- -	572 (576)	-	968s(=CH o.o.p.def)
RhCℓ(1-bdpb).0.1$CH_2Cℓ_2$[a] (IV)	66.4 (66.6)	5.2 (4.8)	8.3 (8.6)	5.9 (5.9)	694 (715)	305m	895s(=CH o.o.p.def)
RhBr(1-bdpb).0.1$CH_2Cℓ_2$[a] (V)	62.6 (62.7)	4.8 (4.5)	7.8 (8.1)		723 (759)	-	897s(=CH o.o.p.def)
IrCℓ(1-bdpb).0.2$CH_2Cℓ_2$[a] (VII)	59.3 (58.8)	4.3 (4.2)	7.4 (7.5)	5.8 (6.0)	925 (804)	304m	896m,930m(=CH o.o.p.def)
RhCℓ(CO)(1-bdpb).0.25$CH_2Cℓ_2$[c] (VIII)	64.9 (64.8)	4.6 (4.6)	8.0 (8.1)	7.0 (7.0)		280w	1985s(ν(CO)) 896m,918m(=CH o.o.p.def)
IrCℓ(CO)(1-bdpb).0.1$CH_2Cℓ_2$[a] (IX)	57.6 (58.7)	4.4 (4.1)	6.9 (7.4)	5.0 (5.1)	977 (832)	270w	1965s(ν(CO)) 880m(=CH o.o.p.def)
	C		P	Cℓ	Mol wt	ν(MCℓ)	Others
RhCℓ$_3$(1-bdpb).0.3$CH_2Cℓ_2$[c] (XI)	59.7 (59.7)	4.4 (4.3)	7.2 (7.6)	15.7 (15.7)		346vs,314s	
IrCℓ$_3$(1-bdpb) (XIIA)	54.4 (54.8)	4.1 (3.9)		12.4 (12.2)			
IrCℓ$_3$(1-bdpb).0.3$CH_2Cℓ_2$[a] (XIIB)	53.4 (53.7)	4.4 (3.9)	7.1 (6.9)	14.1 (14.2)	969 (875)	318s,303s, 292s	

spectrum resembles that of IV, hence this compound also contains two isomers in solution in a ratio of about 3:2.

In the case of VII the isomer ratio varies with reaction conditions such as solvent, temperature and time. For example, reaction of $[IrCl(COD)]_2$ with 1-bdpb in dichloromethane at 25° for 10 min gives a 3:1 ratio of isomers A and B, the predominant isomer having its methyl doublet to lower field than that of B. However, the same reaction carried out

RhCℓ_2(1-bdpb-H).CH$_3$OH[d] (XIII)	63.2 (63.0)	4.3 (4.8)	7.8 (7.9)	9.7 (9.1)	766 (750)	291s,243s	
RhCℓ_2(CO)(1-bdpbH).CH$_2$Cℓ_2[c] (XIV)	58.4 (58.4)	4.5 (4.3)	6.6 (7.2)	16.0 (16.4)	921 (779)	310s,268m	2060s[ν(CO)]
IrCℓ_2(CO)(1-bdpbH) (XV)	56.1 (56.7)	4.5 (4.1)	6.1 (7.1)	8.4 (8.2)		308m,265w	2030s[ν(CO)]
[RhCℓ_2(1-bdpbH)]$_2$ (XVI)	60.2 (62.8)	4.7 (4.6)	7.4 (8.1)	10.8 (11.1)	1680 (1503)	283w	
IrHCℓ_2(1-bdpb).0.3CH$_2$Cℓ_2[c] (XVII)	55.1 (55.9)	4.7 (4.1)	6.6 (7.1)	10.3 (10.6)		307m,257m	
[Rh(CO)(1-bdpb)]BF$_4$ (XIX)	61.2 (62.0)	4.8 (4.3)	7.4 (7.8)			-	2042s[ν(CO)][e]
[Rh(CO)$_2$(1-bdpb)]BF$_4$ (XX)	61.3 (61.3)	4.3 (4.2)	7.1 (7.5)			-	2046s,2082s[ν(CO)][e]
[Ir(CO)$_2$(1-bdpb)]BF$_4$ (XXI)	52.8 (55.3)	3.8 (3.8)	6.6 (6.8)			-	2040s,2082s[ν(CO)][e]
[IrH(C$_2$H$_4$)(1-bdpb-H)]BF$_4$.0.5CH$_2$Cℓ_2[c] (XXIV)	53.1 (55.1)	4.7 (4.2)	6.4 (6.7)	4.1 (3.8)		-	2105m[ν(IrH)]

[a] Abbreviations: 1-bdpb-H ≡ o-Ph$_2$PC$_6$H$_4$CH$\overset{...}{-}$CH$\overset{...}{-}$C(CH$_3$)C$_6$H$_4$PPh$_2$-o; 1-bdpbH ≡ o-Ph$_2$PC$_6$H$_4\dot{C}$HCH$_2$CH(CH$_3$)C$_6$H$_4$PPh$_2$-o or o-Ph$_2$PC$_6$H$_4$CH$_2\dot{C}$HCH(CH$_3$)C$_6$H$_4$PPh$_2$-o; =CH o.o.p. def. = olefinic C-H out-of-plane deformation mode.

[b] IR spectral data refer to Nujol mulls, except where stated otherwise.

[c] Presence of CH$_2$Cℓ_2 confirmed by singlet at δ 5.3 ppm in ^{1}H NMR spectrum in CDCℓ_3.

[d] Presence of CH$_3$OH confirmed by singlet at δ 3.36 ppm in CD$_2$Cℓ_2.

[e] In CH$_2$Cℓ_2.

in refluxing cyclohexane for 45 min gives A and B in a ratio of 1:5. On heating this mixture to 130° in bromobenzene the ratio changes to about 1:1 and remains at this value on cooling to room temperature. The ^{31}P{^{1}H} spectra of both isomers consist of AB quartets, and, as in the case of the rhodium(I) analogues, the magnitude of ^2J(P-P) establishes that the phosphorus atoms are mutually *trans* in both isomers. Recrystallization of VII from dichloromethane/methanol gives isomer A in >95% purity, but we have not so far succeeded in obtaining B free from A.

TABLE 2. ^1H NMR SPECTRA OF COMPLEXES OF 1,3-BIS[(o-DIPHENYLPHOSPHINO)PHENYL]-*TRANS*-1-BUTENE (1-BDPB), o-$Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2$-o.$^{a-c}$

		Solvent	Chemical Shifts (δ)				Coupling Constants (*J*)					
			H_1	H_2	H_3	H_4	12	23	34	P-H_1	P-H_2	P-H_3
1-bdpb (VI)		$CDCl_3$	*d*	5.97dd	4.30m	1.11d	16.5	5.0^c	7.0	0	0	9,0,0
$RhCl$(1-bdpb) (IV)^f	A	CD_2Cl_2	←	3.2-3.7m	→	1.28d	?	?	7.0	?	?	?
	B		←	3.2-3.7m	→	1.24d	?	?	7.0	?	?	?
$IrCl$(1-bdpb) (VII)	A^g	CD_2Cl_2	2.46m	2.33m	3.27m	1.28d	9.0	0.5	7.0	5.0,0	5.0,2.0	~1(sum)
	B		2.82m	2.52m	3.02m	1.18d	9.0	3.8	7.0	4.5,1.2	6.3,0	~2(sum)
$RhCl$(CO)(1-bdpb) (VIII)		CD_2Cl_2	4.02d	3.60brt	2.86q	1.39d	9.0	6.5	6.5	~4(sum)	?	0
$RhCl$(CO)(1-bdpb) (VIII)	A	CD_2Cl_2(-40°C)	4.02m	3.88m	2.72m	1.40d	?	?	?	?	?	?
	B		4.02m	3.25m	2.72m	1.47d	?	?	?	?	?	?
$IrCl$(CO)(1-bdpb) (IX)^h	A	$CDCl_3$	3.39m	3.30m	2.90q	1.30d	7.0	6.0	6.5	5.0,4.0	6.0,1.5	0
	B		3.62m	2.66m	3.07q	1.43d	7.0	6.5	7.0	4.5,3.0	6.5,4.0	0
$IrCl(C_2H_4)$(1-bdpb) (X)^i		$CDCl_3$(-52°C)	←	3.35,3.60, 4.15brm	→	1.52d	?	?	6.5	?	?	?
[Rh(CO)(1-bdpb)]BF_4 (XIX)	A	$CDCl_3$	← 5.60brd, 5.76d →		4.06brq	1.43d	14.5	2	6.5	~2(sum)	~2(sum)	~3(sum)
	B		*d*	*d*	3.85brq	1.40d	?	<3	6.5	?	?	~1(sum)
[Rh(CO)$_2$(1-bdpb)]BF_4 (XX)		$CDCl_3$	4.77m	4.00m	3.82m	1.37d	9.5	4.5^c	6.5	2.0,5.0	2.0,6.0	~1(sum)
[Ir(CO)$_2$(1-bdpb)]BF_4 (XXI)		$CDCl_3$	4.12m	3.29m	4.03m	1.23d	8.5	5.0	6.5	3.0,6.0	2.0,7.0	~0
$RhCl_3$(1-bdpb) (XI)		CD_2Cl_2	6.57dd	5.28m	3.91m	1.70d	13.5	8.0^c	7.0	0	2.0,2.0	~1(sum)

The isomers of IV readily interconvert on heating in d^5- bromobenzene. Although the methyl doublets remain well separated in the temperature range 32-106°C, they begin to broaden at about 110°C, coalesce at 122±3°C, and sharpen to a single doublet at 135°C; the original spectrum is recovered on cooling to 32°C. The rate (*k*) of interconversion at the coalescence

$\mathrm{IrCl_3}$(1-bdpb) (XII)	A	$\mathrm{CD_2Cl_2}$	5.22d	4.84brd	4.23m	1.45d	13.5	1.5	7.0	~1(sum)	~1(sum)	~2(sum)
	B		6.41m	5.01m	3.82m	1.82d	12.0	8.5	7.0	0	3.0,0	~2.5(sum)
$\mathrm{IrHCl_2}$(1-bdpb) (XVII)[d]	A1	$\mathrm{CD_2Cl_2}$	4.15m	← 3.4-3.8m →		1.50d	11.0	?	7.0	1.5,1.5	?	?
	A2		3.99m	← 3.4-3.8m →		1.37d	11.0	?	7.0	1.5,1.5	?	?
	B1		4.52m	3.72m	4.06m	0.76d	11.0	3.5	7.0	1.5,1.5	4.0,4.0	?
	B2		4.96m	← 3.6-4.3m →		1.45d	11.5	?	7.0	1.5,1.5	?	?
$\mathrm{RhCl_2}$(1-bdpb-H) (XIII)		$\mathrm{CD_2Cl_2}$	2.05m	4.82m	-	1.70s	8.0	-	-	4.0,2.0	8.0,2.0	-
[$\mathrm{IrH(C_2H_4)}$(1-bdpb-H)]$\mathrm{BF_4}$[k] (XXII)		$\mathrm{CD_2Cl_2}$	3.26dt	4.68t	-	2.06s	7.5	-	-	7.5,4.0	8.5,0	-

[a] Measured at 100 MHz in solvent indicated with internal TMS as reference. Temperature was 32°C, except where stated otherwise. Chemical shifts (δ) are in ppm, downfield from reference being taken as positive, accuracy ±0.01 ppm. Coupling constants (J) are in Hz, accuracy ±0.5. Aromatic resonances for all the complexes were complex multiplets in the range δ 6.8-8.2 ppm.**

[b] Proton numbering: $-\overset{1}{\mathrm{CH}}-\overset{2}{\mathrm{CH}}\ \overset{3}{\mathrm{CH}}(\overset{4}{\mathrm{CH_3}})-$; $-\overset{1}{\mathrm{CH}}\cdots\overset{2}{\mathrm{CH}}\cdots(\overset{4}{\mathrm{CH_3}})-$.

[c] Abbreviations: d, doublet; dd, double doublet; q, quartet; m, multiplet; s, singlet; br, broad; sh, sharp.

[d] Beneath aromatic resonances.

[e] J_{13} = 1.5 Hz.

[f] RhBr(1-bdpb) (V) in $\mathrm{CD_2Cl_2}$: δ 1.26 (d, $\mathrm{CH_3}$, J7.0), 3.2-3.5 (complex, H_1, H_2, H_3).

[g] Assignment of H_1 and H_2 could be reversed.

[h] $^1H\{^1H\}$ and $^1H\{^{31}P\}$ experiments required for complete assignment.

[i] $\mathrm{C_2H_4}$ resonances at -52°C (ppm): δ 1.30, 1.65, 2.00, 2.40 (br m, coordinated), 5.40 (sh s, free). At 32°C, δ($\mathrm{C_2H_4}$) 2.2-3.4 (vbrm, coordinated), 5.31 (br s, free); δ(H_1, H_2, H_3) 3.4-4.4(vbr), δ($\mathrm{CH_3}$) 1.26(br d).

[j] δ(IrH) [J(P-H)]: -14.26t(12,12)(A1); -14.74t(12,12)(A_2); -14.10t(11,11)(B1); -16.97t(11,11)(B2).

[k] δ($\mathrm{C_2H_4}$) 2.47m, 2.60m, J(P-H) ~6(sum); δ(IrH) -11.57dd, J(P-H) 15.0, 10.0.

** Data for XIV, XV and XVI are in Table 4, data for XVIII are in Table 5.

temperature is 36 sec^{-1}*, which gives the free energy of activation $\Delta G^{\neq}$ (122°) as 20.5 kcal/mol, assuming the transmission coefficient in the usual Eyring equation to be unity. As noted above, the isomer ratio of

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* Estimated from the equation $k = \pi\delta_{AB}/\sqrt{2}$, where δ_{AB} is the chemical shift difference in the slow exchange limit.

VII changes on heating, but there is no evidence of exchange broadening in the ^1H NMR spectra, so that the rate of interconversion is fast enough to establish chemical equilibrium but is slow on the NMR time scale. The free energy of activation for interconversion of the isomers of VII is therefore greater than 20 kcal/mol.

In the absence of X-ray crystallographic studies the nature of the isomers is uncertain. Single crystal X-ray structural analysis of Ib [8] has shown that the double bond is oriented at 79° to the RhP_2 coordination plane, close to the 90° which is generally favoured for planar d^8 metal-olefin complexes. In the case of Ib, the arrangement adopted is more or less required by the geometrical constraints of the ligand, but the greater flexibility of VI caused by the presence of the $CHCH_3$ group in the carbon chain gives rise to a number of possible coordination modes. Examination

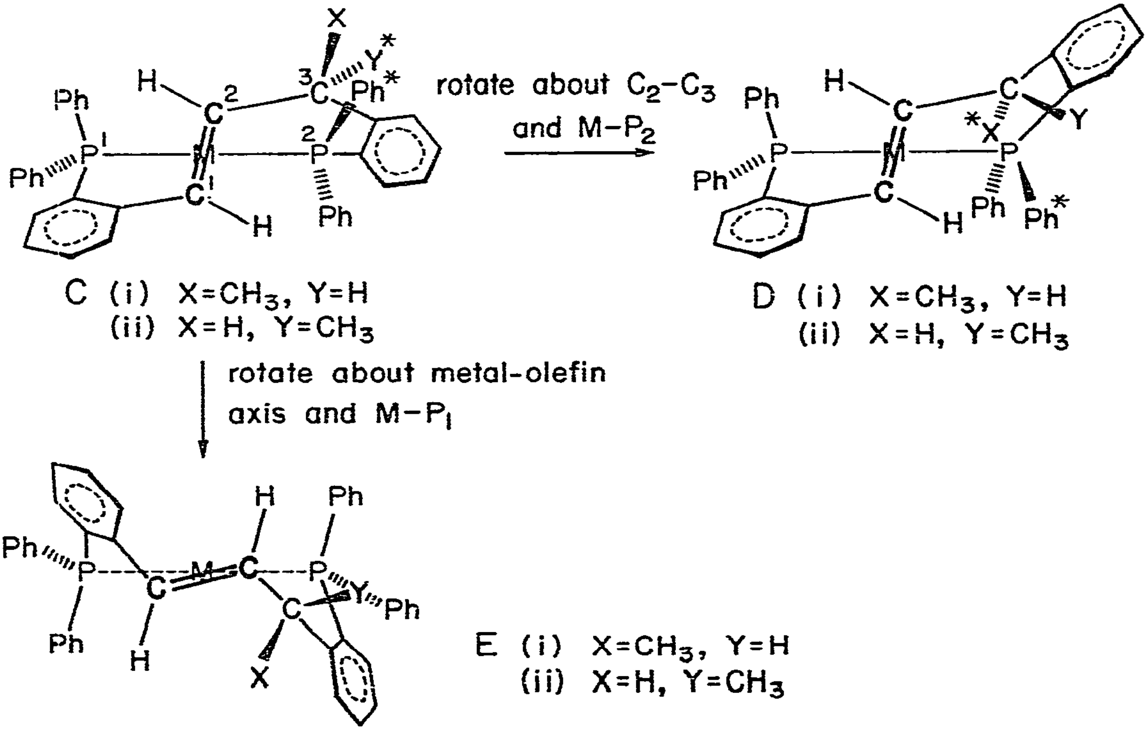


Figure 1. Possible conformational interconversions for MCl(1-bdpb). (M = Rh, IV; M = Ir, VII).

of a Dreiding model of IV or VII suggests that there is a relatively unstrained conformation C (Fig. 1) in which the double bond is approximately at right-angles to the MP_2Cl coordination plane, as in Ib. The methyl group can occupy either of two sites in which it either points away from, or is close to, the asterisked phenyl ring [C(i) and C(ii) respectively in Fig. 1]; the second possibility is sterically less favourable. Rotation about the C_2-C_3 and M-P_2 bonds while the olefin is kept fixed generates a pair of geometric isomers D(i) and D(ii), the latter being favoured because the methyl group is in the sterically less hindered site; the process is essentially an inversion of two boat-like conformations of the chelate ring formed by the metal, P_2 and the olefin, and cannot interconvert C(i) with either C(ii) or D(ii) unless some other process is involved. The model shows that in D(ii) H_2 and H_3 are mutually trans, an arrangement for which a coupling constant J_{23} of about 11 Hz might be expected [9], whereas in C(i) they are gauche. In fact *both* isomers of VII have small values of J_{23} (0.5 and 3.5 Hz) suggesting that they have a gauche arrangement of H_2 and H_3, although this argument admittedly ignores the likely bending back of the olefin protons on coordination and the possible effects of this on the magnitude of J_{23}. We therefore conclude that C(i) is the most likely structure of those considered so far.

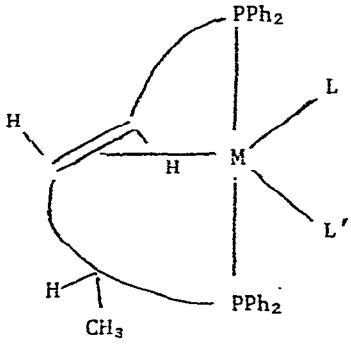
An alternative possibility is rotation about M-P, P-C and C-C single bonds leading to net rotation of the olefin into an orientation approximately parallel with the MP_2Cl coordination plane, and generating four more isomers, such as E(i) and E(ii) from C(i) and C(ii) respectively. A process of this type has been proposed to account for the existence of isomers of the octahedral complexes $M(CO)_4{}^{\frown}_{\smile}(sp)$ (M=Mo, W) and their rapid interconversion on the NMR time scale [10], and for the fluxional behaviour of the octahedral complexes $\overline{\mathrm{RuX(CO)(sp)}(o\text{-}\mathrm{CH_3C}}\mathrm{HC_6H_4PPh_2})$ (X=CO, Cl) [4]. Rotation of a coordinated olefin about the metal-olefin bond axis in planar d^8 metal complexes is well established [11-13], and it may be relevant that this process can be studied by NMR in the case of rhodium(I) but is slow on the NMR time scale in the case of iridium(I) [14], a trend also observed in this work. Since models indicate a gauche arrangement for H_2 and H_3 in E(i), we tentatively suggest that the isomers of IV and VII have conformations C(i) and E(i): undoubtedly the source of the isomerism in the various octahedral oxidative addition products of IV and VII (see below) is the same as that of IV and VII themselves. It is hoped that current work on complexes of o-$Ph_2PC_6H_4CH\overset{t}{=}CHCH_2C_6H_4PPh_2$-$o$ will help to resolve the problem.

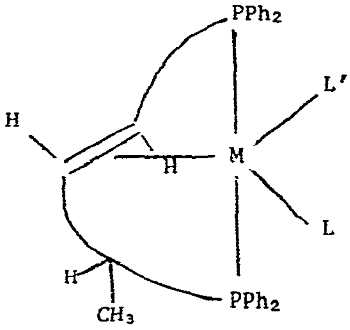
Five-Coordinate Complexes. Both IV and VII react with carbon monoxide at 25°/1atm to give five-coordinate adducts MCl(CO)(1-bdpb) (M=Rh, VIII; M=Ir, IX), the reaction being reversible in the case of rhodium. These complexes show a single intense ν(CO) band in the 2000 cm^{-1} region of the IR spectrum and a weak band below 300 cm^{-1} in the far IR spectrum assignable to ν(MCl). Coordination of the olefin is indicated by the absence of the characteristic ligand band at 970 cm^{-1} and the appearance of bands due to modified olefin C-H deformation modes in the 900 cm^{-1} region (Table 1). Thus VIII and IX are five-coordinate and probably trigonal bipyramidal. The ^1H NMR spectrum of VIII is slightly broadened at 32°C and apparently indicates the presence of only one isomer, while the $^{31}P\{^1H\}$ NMR spectrum, which is also broad at 32°C, consists of an AB quartet of doublets arising from inequivalent, mutually *trans*-phosphorus atoms coupled to ^{103}Rh (Table 3). At -24°C the $^{31}P\{^1H\}$ NMR spectrum becomes more complex and can be resolved into two AB quartets of doublets in a ratio of about 2:1, although the outer lines of the less intense pattern could not be discerned owing to the small chemical shift difference between the inequivalent phosphorus atoms. The presence of two isomers is also evident from the ^1H NMR spectrum at -40°C which, although too complex for detailed analysis, clearly shows *two* methyl doublets. The magnitude of ^2J(P-P) in the major isomer and the similarity of the values of J(Rh-P) suggest that both isomers have mutually *trans*-phosphorus atoms occupying axial positions of a trigonal bipyramid. In the case of IX, the presence of two isomers having mutually *trans*-phosphorus atoms is evident from the room temperature ^1H and $^{31}P\{^1H\}$ NMR spectra, exchange between the two being slow on the NMR time scale. The isomeric composition of IX is independent of that of the sample of VII used to prepare it, an observation which suggests that the isomers of VIII and IX differ according to which of the two possible equatorial sites of the trigonal bipyramid is occupied by CO (structures a and b), and that the temperature-dependence of the NMR spectra of VIII is caused by intermolecular CO exchange. A similar process accounts for the observation that the olefinic hydrogen atoms and phosphorus atoms of the complex RhCl(CO)(bdpps) are each equivalent at 32°C and inequivalent at -40°C [15]. The possibilities for isomerism discussed for IV and VII apply equally to VIII and IX, although there is no evidence that such isomers exist for these two compounds. It seems likely that the double bond lies in the equatorial plane, since this orientation is found in almost all trigonal bipyramidal olefin complexes [16] and appears to be preferred on electronic grounds [17].

VII reacts with ethylene at 25°/1atm to give a pale yellow solution from which the adduct IrCl(C_2H_4)(1-bdpb) (X) can be isolated at 0°C. This is stable in solution only in the presence of ethylene, and in the solid state is unstable over long periods even when ethylene is present. The resonances due to free and to coordinated ethylene in X are broad at room temperature, as are those of the ligand protons. The intermolecular exchange of ethylene which is responsible for this behaviour is slowed at -33°C, at which temperature the free ethylene resonance appears as a sharp singlet and a doublet methyl resonance of coordinated 1-bdpb can be distinguished; the remaining ligand protons and the coordinated ethylene protons appear as broad, complex multiplets. The $^{31}P\{^1H\}$ NMR spectrum of X at -22°C is complex and suggests the presence of at least two isomers, presumably Xa and Xb. The complex is otherwise analogous to IrCl(C_2H_4)(bdpps) [15], in which the ethylene is assumed to lie in the equatorial plane but undergoes rotation about the metal-olefin bond axis; however, there was no NMR evidence for the latter process in the present work. ^1H NMR spectra show that the rhodium(I) complex IV does not react with ethylene, even at -68°C, in contrast with RhCl(bdpps) (Ib), which forms an unstable adduct under the same conditions [15].

Oxidative Additions and Addition to the Coordinated Ligand.

1. Chlorine. Oxidative addition of chlorine to IV or VII affords octahedral chelate olefin complexes of the trivalent metals, MCl_3(1-bdpb) M=Rh, XI; M=Ir, XII), which are orange in the case of rhodium, yellow in the case of iridium. The ^{1}H NMR spectra (Table 2) show the presence of the intact 1-bdpb ligand, the upfield shift of the olefin resonances on coordination being less than in the starting planar complexes; this may be a reflection of weaker olefin bonding to the octahedral trivalent metals than to the planar univalent metals. The ν(MCl) bands in the far IR spectra (Table 1) are very similar in frequency to those of the analogous bdpps complexes and of the trivalent metal carbonyl complexes $MCl_3(CO)(PPh_3)_2$, and the magnitude of ^2J(P-P) derived from the $^{31}P\{^1H\}$ NMR spectra (Table 3) confirms the mutually *trans*-arrangement of the phosphorus atoms. Whereas the ^{1}H NMR spectrum of XI shows the presence of only one isomer, XII contains two isomers XIIA and XIIB which are formed stereospecifically from the isomeric precursors VIIA and VIIB respectively; XIIB can be obtained free





VIIIa

IXa

Xa

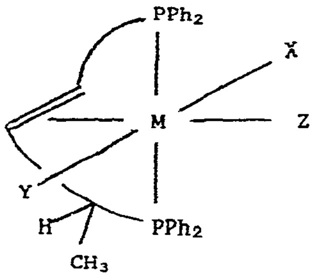
VIIIb M = Rh, L = CO, L' = Cℓ

IXb M = Ir, L = CO, L' = Cℓ

Xb M = Ir, L = C_2H_4, L' = Cℓ

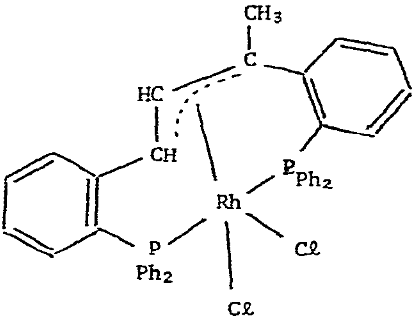
from XIIA by direct reaction between hydrated iridium(III) chloride and 1-bdpb in refluxing 2-methoxyethanol. In contrast, the corresponding reaction using rhodium(III) chloride gives a chelate 1-3η-allylic complex $\text{RhCl}_2\{o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}\cdots\text{CH}\cdots\text{C(CH}_3)\text{C}_6\text{H}_4\text{PPh}_2\text{-}o\}$ (XIII), the structure of which has been established by X-ray analysis [6]. Complex XI is probably an intermediate in this reaction, since it forms XIII with loss of hydrogen chloride in hot 2-methoxyethanol or, more slowly, in dichloromethane at room temperature. This reaction is irreversible; XIII does not react with excess hydrogen chloride to give XI. The far IR spectrum of XIII shows two ν(MCl) bands, which confirms the *cis*-arrangement of the chlorine atoms, and the magnitude of ^2J(P-P) derived from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Table 3) establishes that the mutually *trans*-arrangement of phosphorus atoms found in the solid state is preserved in solution. The coupling constant of 8.0 Hz between the mutually *trans*-allylic protons is unexpectedly small [18], and would have suggested these protons to be mutually *cis*, in contradiction with the X-ray result [6]. XIII is formally analogous to known η^3-allylrhodium(III) complexes such as $\text{RhCl}_2(\eta^3\text{-C}_3\text{H}_5)(\text{EPh}_3)_2$ (E=P, As) [19,20], though the triphenylarsine complex has *trans*-chlorine atoms and *cis*-triphenylarsine ligands [21]. Deprotonation of 1-bdpb at the methine carbon atom to form a chelate η^3-allyl complex also occurs in the presence of nickel(II) chloride [22]. The magnitudes of ^2J(P-P) in both isomers of the five-coordinate product $\text{NiCl}\{o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}\cdots\text{CH}\cdots\text{C(CH}_3)\text{C}_6\text{H}_4\text{PPh}_2\text{-}o\}$ suggest that the P-M-P angle is in the range 90-120° for both compounds; a planar chelate η^3-allylpalladium(II) cation $[\text{Pd}\{o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}\cdots\text{CH}\cdots\text{C(CH}_3)\text{C}_6\text{H}_4\text{PPh}_2\text{-}o\}]^+$ containing *cis*-phosphorus atoms is also known [22]. Possibly relief of crowding in the coordination sphere of the octahedral rhodium(III) complex XIII favours the arrangement with *trans*-phosphorus atoms.

2. *Hydrogen Chloride.* We have noted elsewhere [15] that addition of hydrogen chloride to the bdpps complexes Ib or Ic can occur in two ways. In the presence of an auxiliary ligand such as CO or triphenylphosphine, the double bond is protonated and the chlorine atom adds to the metal to give a chelate σ-alkyl e.g. $\overline{\text{RhCl}_2(\text{CO})(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}}\text{HCH}_2\text{C}_6\text{H}_4\text{PPh}_2\text{-}o)$ is obtained



(Olefinic hydrogen atoms omitted for clarity.)

M = Rh; X = Y = Z = Cℓ	XI (2 isomers possible, only one observed)
M = Ir; X = Y = Z = Cℓ	XII (2 isomers possible, both observed)
M = Ir; X = H; Y = Z = Cℓ Y = H; X = Z = Cℓ	XVII (4 isomers possible, all observed)
M = Ir; X = Cℓ; Y = Z = H Y = Cℓ; X = Z = H	XVIII (4 isomers possible, all observed)



XIII

from RhCl(CO)(bdpps) and HCl. In the absence of such a ligand, addition takes place exclusively at the metal atom e.g. $IrHCl_2$(bdpps) is obtained from Ic and HCl and $RhCl_3$(bdpps) is obtained from Ib and HCl, presumably via $RhHCl_2$(bdpps) as an intermediate. In the analogous 1-bdpb systems, there is a similar, though less clear-cut dependence of the course of addition on the presence or absence of auxiliary ligand.

The five-coordinate complex RhCl(CO)(1-bdpb) (VIII), formed in situ from IV and carbon monoxide, reacts with hydrogen chloride to give as the main product a colourless chelate σ-alkyl $\overline{\mathrm{RhCl_2(CO)\{\mathit{o}\text{-}Ph_2PC_6H_4CH_2C}}\mathrm{HCH(CH_3)\text{-}PPh_2\text{-}\mathit{o}\}}$ (XIV), which on heating in ethanol or 2-methoxyethanol reverts to IV. The far IR spectrum shows two ν(MCl) bands arising from *cis*-chlorine atoms which are *trans* to CO and to σ-alkyl respectively (Table 1), and the $^{31}P\{^1H\}$ NMR spectrum shows the phosphorus atoms to be mutually *trans*. The NMR spectrum of the crude reaction product shows three methyl doublets in an approximate ratio of 5:1:1; the minor products are removed by one recrystallization, and have not been further investigated. In addition to the aromatic resonances and the characteristic $CHCH_3$ methyl doublet, the ^1H NMR spectrum of the major product shows the resonances of four protons. The methine proton is strongly coupled to the methyl group and to only one other proton, which suggests the presence of the chelate 2-butyl grouping, $-CH_2CH(Rh)CH(CH_3)-$, rather than the isomeric 1-butyl $-CH(Rh)CH_2CH(CH_3)-$. The large geminal methylene coupling, 18.0 Hz, between the other two protons is typical of a CH_2 group attached to a sp^2-hybridized carbon atom [22], while the two vicinal couplings of the CH_2CH moiety are normal (Table 4). The ^1H-^1H coupling constants of XIV are very similar to those of the chelate 2-butylruthenium(II) complex (II) obtained by addition of hydrogen chloride to the five-coordinate complex $Ru(CO)_2$(1-bdpb) [4], which provides support for the present structural assignment.

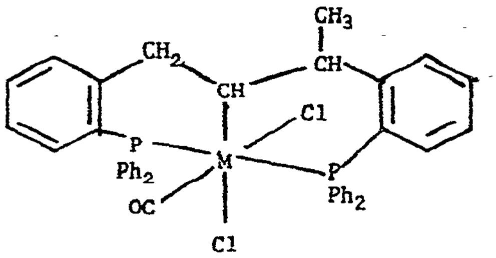
Reaction of IrCl(CO)(1-bdpb) (IX) with hydrogen chloride gives an approximately 3:1 mixture of isomeric chelate σ-alkyls (XV) which are analogous to XIV; they could not be separated by fractional crystallization. The major isomer appears to be similar to XIV in respect of its IR spectrum (Table 1) and ^1H NMR spectrum (Table 4), but overlap of resonances in the latter has prevented complete analysis. Unfortunately the major isomer exhibits only a singlet in its $^{31}P\{^1H\}$ NMR spectrum (Table 3), presumably owing to fortuitously equal chemical shifts, while the minor isomer gives a doublet; these are assumed to be the central lines of an AB quartet arising from strongly coupled, mutually *trans*-phosphorus atoms, the outer lines being undetectably weak. The source of the isomerism of XV is therefore unknown.

We have previously noted [4] that II isomerizes completely in hot 2-methoxyethanol to the 1-butyl isomer (III). Attempts to induce such an isomerization in the case of XIV lead only to loss of hydrogen chloride (see above), but the minor products detected in the addition of hydrogen chloride to VIII or IX may well contain the chelate 1-butyl moiety.

In the absence of other ligands, IV reacts slowly with hydrogen chloride to give an approximately 1:1 mixture of $RhCl_3$(1-bdpb) (XI) and a dimeric, chlorine-bridged chelate σ-alkyl which we believe contains the chelate 1-butyl group i.e. $[\mathrm{RhCl_2\{\mathit{o}\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}]_2}$ (XVI). XI is presumably formed by initial oxidative addition of hydrogen chloride at the metal atom to give $RhHCl_2$(1-bdpb) (*cf.* the iridium analogue below) and subsequent rapid cleavage of the Rh-H bond by hydrogen chloride. The action of hydrogen chloride on RhCl(bdpps) (Ib) gives $RhCl_3$(bdpps) as the only product [15], presumably by a similar mechanism, but we do not know why oxidative addition occurs exclusively in this case. Triphenylphosphine, like carbon monoxide, promotes protonation of the ligand in RhCl(1-bdpb), the product being exclusively XVI. The assignment as a 1-butyl complex is based primarily on ^{1}H NMR data (Table 4). The methyl protons appear as the expected doublet and the methine proton resonance at δ3.2 ppm is complex; ^{31}P- and ^{1}H-decoupling experiments show that it is coupled to two other protons which resonate at δ2.2 ppm (J=4 Hz) and at δ3.6 ppm (J=10 Hz). The former has two more couplings each of 13 Hz, one of which must be the geminal methylene coupling, while the other is assigned to the vicinal (Rh)CH-CH_2 coupling. The general similarity of chemical shifts and coupling constants between XVI and the 1-butylruthenium(II) complex III supports the present assignment. A surprising feature revealed by the small magnitude of ^2J(P-P) obtained from the $^{31}P\{^1H\}$ spectrum of XVI is that the phosphorus atoms are mutually *cis*, not *trans* as in III and XIV. The magnitudes of the two Rh-P couplings, *ca* 145 Hz, are larger than those characteristic of P *trans* either to P (∿85 Hz) or Cl (∿115 Hz) in octahedral rhodium(III) complexes of the type $RhCl_3(PR_3)_3$ [24-26], but are in good agreement with the values reported for P *trans* to Cl in octahedral σ-alkyls or σ-aryls $Rh(R)Cl_2(PMe_2Ph)_3$ (R=Me, Ph) (∿136 Hz) [27]. A band due to ν(RhCl) at 283 cm^{-1} in the far IR spectrum can be assigned to a terminal chlorine *trans* to phosphorus, but we could not locate ν(RhCl) bands due to bridging chlorine atoms above 200 cm^{-1}. These data are best accommodated by structures XVIa or XVIb.

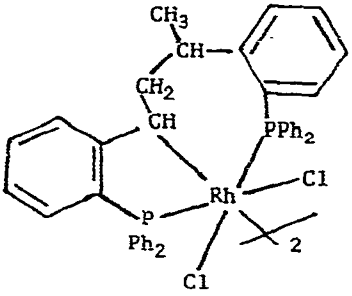
Our work shows that both carbon monoxide and triphenylphosphine promote protonation of the double bond of RhCl(1-bdpb), the reactive species probably being five-coordinate complexes RhClL(1-bdpb) (L=CO, PPh_3), but the site of protonation and the disposition of the phosphorus atoms in the resulting tridentate chelate groups differ. The greater steric bulk of triphenylphosphine probably accounts for its failure to remain in the coordination sphere after protonation has occurred, but studies with other ligands will be required to establish the factors responsible for the differences noted above.

In the absence of other ligands, VII reacts irreversibly with hydrogen chloride to give exclusively the oxidative addition product $IrHCl_2$(1-bdpb) (XVII), which shows an IR band at 2220 cm^{-1} typical of ν(IrH) (H *trans* to Cl) and two ν(IrCl) bands in the far IR spectrum which are typical of Cl *trans* to hydride and to olefin respectively (Table 1). These data are very similar to those found for $IrHCl_2$(bdpps) [15] and the same octahedral ligand arrangement can be assumed. However, the ^1H NMR spectrum of XVII in the metal-hydride region shows that four isomers are present, each isomer of VII giving two isomers of XVII. The four hydride resonances appear as triplets owing to almost equal couplings with two ^{31}P nuclei which are *cis* to the hydride [*J*(P-H) ∿ 12 Hz], and their chemical shifts are in the region δ -15 ppm (τ25) (Table 2), similar to that found for H *trans* to Cl in complexes of the type $IrHCl_2(CO)(PR_3)_2$ [28]. The $^{31}P\{^1H\}$

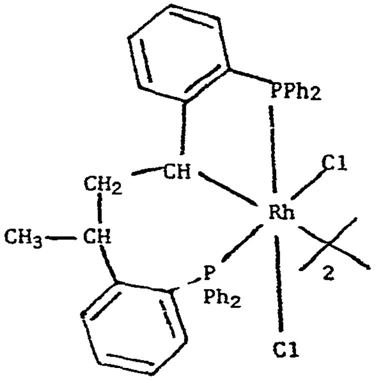


XIV M=Rh

XV M=Ir (major isomer)



XVIa



XVIb

NMR spectra show that all four isomers have inequivalent, mutually *trans*-phosphorus atoms, and the olefinic proton couplings in the ^{1}H NMR spectra show that the *trans*-configuration about the double bond is maintained. Thus the isomers must arise by interchange of the mutually *trans* hydride and chloride ligands in each of the two isomers which have different conformations of coordinated 1-bdpb (XVIIa-d).

3. *Hydrogen.* VII reacts reversibly with hydrogen under ambient conditions to give a colourless dihydride $IrH_2Cl(1\text{-bdpb})$ (XVIII), which shows two ν(IrH) bands at *ca* 2200 cm^{-1} and 2100 cm^{-1} assignable to H *trans* to Cl and to olefin respectively. In the ^{1}H NMR spectrum, there are eight hydride resonances which occur in pairs corresponding to four

isomers. Each isomer has one hydride *trans* to chlorine (δ -18 to -21 ppm) τ28-31) and one hydride *trans* to olefin (δ-7 to -8 ppm, τ17-18); these values are similar to those observed in the complex IrH_2Cl(bdpps) (one isomer only), and also to the values for H *trans* to Cl and CO respectively in complexes of the type $IrH_2Cl(CO)(PR_3)_2$ (PR_3 = PMe_2Ph, PEt_2Ph) [29]. The isomers derived from VIIA are formed in a 2:1 ratio, those from VIIB in a 4:3 ratio; when the isomers are allowed to equilibrate for 12 hr, the former pair predominates over the latter by about 3:1, as estimated from the relative areas of the methyl and of the hydride resonances. All four isomers exhibit AB quartets in their ^{31}P NMR spectra with large values of ^2J(P-P), hence the phosphorus atoms are mutually *trans*. This is also indicated by the fact that all the hydride resonances appear as approximate triplets with small P-H couplings (Table 5), showing that each hydride is *cis* to two phosphorus atoms. Thus, all four isomers of XVIII probably have the same octahedral arrangement of ligands about the metal atom, and the source of isomerism is the same as that discussed above for $IrHCl_2$(1-bdpb) (XVII).

Cationic Complexes and Hydrogen Migration between Ligand and Metal.

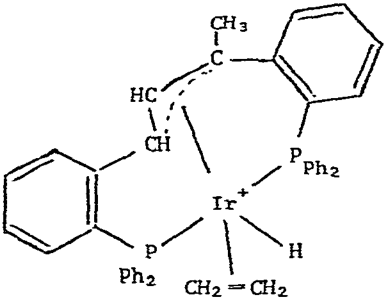
Treatment of RhCl(CO)(1-bdpb) (VIII) in dichloromethane with silver tetrafluoroborate gives an orange solution from which the planar monocarbonyl cation $[Rh(CO)(1\text{-bdpb})]^+$ can be isolated as its BF_4 salt (XIX). This species is fairly stable in solution for several days, in contrast with the analogous bdpps cation [15]. The corresponding iridium(I) cation $[Ir(CO)(1\text{-bdpb})]^+$ is probably responsible for the transient orange colour which is observed on treatment of IrCl(CO)(1-bdpb) (IX) with $AgBF_4$, but it rapidly decomposes to give a pale yellow solution (see below). Reaction of MCl(1-bdpb) or MCl(CO)(1-bdpb) (M=Rh, Ir) with $AgBF_4$ in the presence of carbon monoxide gives pale yellow (Rh) or colourless (Ir), five-coordinate dicarbonyl salts $[M(CO)_2(1\text{-bdpb})]BF_4$ (M=Rh, XX; M=Ir, XXI). Heating or passage of nitrogen through solutions of XX causes loss of carbon monoxide and formation of XIX, whereas XXI is stable under these conditions. The rhodium(I) dicarbonyl cation $[Rh(CO)_2(1\text{-bdpb})]^+$ is also formed *in situ* on passing CO into a solution of IV in nitromethane. XIX shows one ν(CO) band in its IR spectrum and its ^1H NMR spectrum (Table 2) shows methine and methyl resonances arising from two isomers in a ratio (3:2) similar to that of the precursor IV. The ^2J(P-P) and J(Rh-P) values for both isomers (Table 3) are very similar to those of $[Rh(CO)(bdpps)]^+$ [15] and of other cationic planar rhodium(I) complexes containing mutually *trans*-phosphorus atoms.

The dicarbonyl cations XX and XXI show two ν(CO) bands in their IR spectra indicative of *cis*-carbonyls, and the upfield shift of the olefinic protons in their ^1H NMR spectra relative to their positions in bdpb itself shows the olefin to be coordinated. The ^1H and $^{31}P\{^1H\}$ NMR spectra at room temperature suggest that only one isomer is present, though the possibility of two isomers interconverting rapidly on the NMR time scale cannot be ruled out. The magnitude of ^2J(P-P) obtained from the $^{31}P\{^1H\}$ NMR spectra shows that the phosphorus atoms are mutually *trans*, and we accordingly propose a trigonal bipyramidal structure, with the olefin parallel to the equatorial plane. The magnitude of J(Rh-P) for five-coordinate XX is less than that for four-coordinate XIX (Table 3) as was also noted for the corresponding bdpps complexes [15].

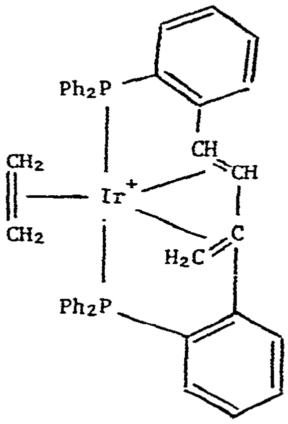
Reaction of IV with ethylene in the presence of $AgBF_4$ gives a precipitate of silver chloride and an orange-yellow solution which presumably contains $[Rh(C_2H_4)_n(1\text{-bdpb})]^+$ (n=1 or 2); the solution is too unstable for NMR study. In contrast, $[Rh(C_2H_4)_2(bdpps)]^+$ is stable in the presence of excess ethylene [15]. The corresponding reaction with VII at room temperature gives a pale yellow solution which does not contain the expected iridium(I)-ethylene cation $[Ir(C_2H_4)_2(1\text{-bdpb})]^+$. ^1H NMR spectroscopy shows the presence of two complexes in proportions which vary depending on solvent and temperature; in dichloromethane at room temperature, the ratio is about 7:1. The major product can be isolated in a pure state by addition of *n*-hexane to give colourless needles. Microanalytical data are in fair agreement with the formulation $[Ir(C_2H_4)(1\text{-bdpb})]BF_4$ (see Experimental for comments regarding low carbon analyses), but the spectroscopic data show unequivocally that the complex is a hydride $[IrH(C_2H_4)(1\text{-bdpb-H})]BF_4$ (XXII) formed by migration of the hydrogen atom from the tertiary carbon atom to the metal. The IR spectrum shows a typical ν(IrH) band at *ca* 2100 cm^{-1} (Table 1) and the ^1H NMR spectrum shows a doublet of doublets hydride resonance at δ-11.57 ppm (τ21.57), the magnitude of the splittings being characteristic of hydride *cis* to two phosphorus atoms. Signals due to a coordinated 1-methallyl group are readily identified by comparison with those of XIII (Table 2), and in particular the singlet methyl resonance shows the absence of the tertiary carbon-hydrogen bond. The four protons of coordinated ethylene appear as a symmetrical multiplet after ^{31}P-decoupling, and the $^{31}P\{^1H\}$ NMR spectrum consists of an AB quartet with a large value of $^2J(P\text{-}P)$ (Table 3), hence the phosphorus atoms are mutually *trans*. These data establish the illustrated pseudo-octahedral, chelate η^3-allylic structure for XXII. Since this structure has no plane of symmetry, the ethylene protons should all be inequivalent (ABCD). The observed AA'BB' multiplet probably arises from rapid rotation of ethylene about the metal-ethylene axis [11-13] which makes mutually *trans*-pairs of protons equivalent; however, there was no evidence for slowing down of this process at -85°C.

The ^1H NMR spectrum of the minor product from the reaction of VII with $AgBF_4$ and ethylene surprisingly shows no methyl resonance; there are four multiplets in the range δ2-6 ppm each corresponding to one proton and a doublet of doublets containing four protons due to coordinated ethylene. The only structure we can suggest which is compatible with these data is a five-coordinate, probably trigonal bipyramidal cation (XXIII), containing a chelate 1-4$\acute{\eta}$ 1,3-butadiene unit formed by abstraction of two hydrogen atoms from the $CHCH_3$ group of the presumed intermediate $[Ir(C_2H_4)(1\text{-bdpb})]^+$. The interproton coupling constants are comparable with those of typical butadiene complexes, and the ^{31}P coupling constants to the two terminal protons are close to the corresponding values for the chelate butadiene complex $Ru(CO)(o\text{-}Ph_2PC_6H_4CH\overset{c}{=}CHCH\overset{t}{=}CHC_6H_4PPh_2\text{-}o)$ {[3] (Table 7)}.

^1H NMR and IR spectroscopic studies show that the yellow solution formed by decomposition of the presumed species $[Ir(CO)(1\text{-}bdpb)]^+$ (see above) contains hydrido η^3-allyl complexes similar to XXII, in addition to $[Ir(CO)_2(1\text{-}bdpb)]^+$ and other unknown products. Attempts to isolate these compounds in a pure state are in progress.



XXII



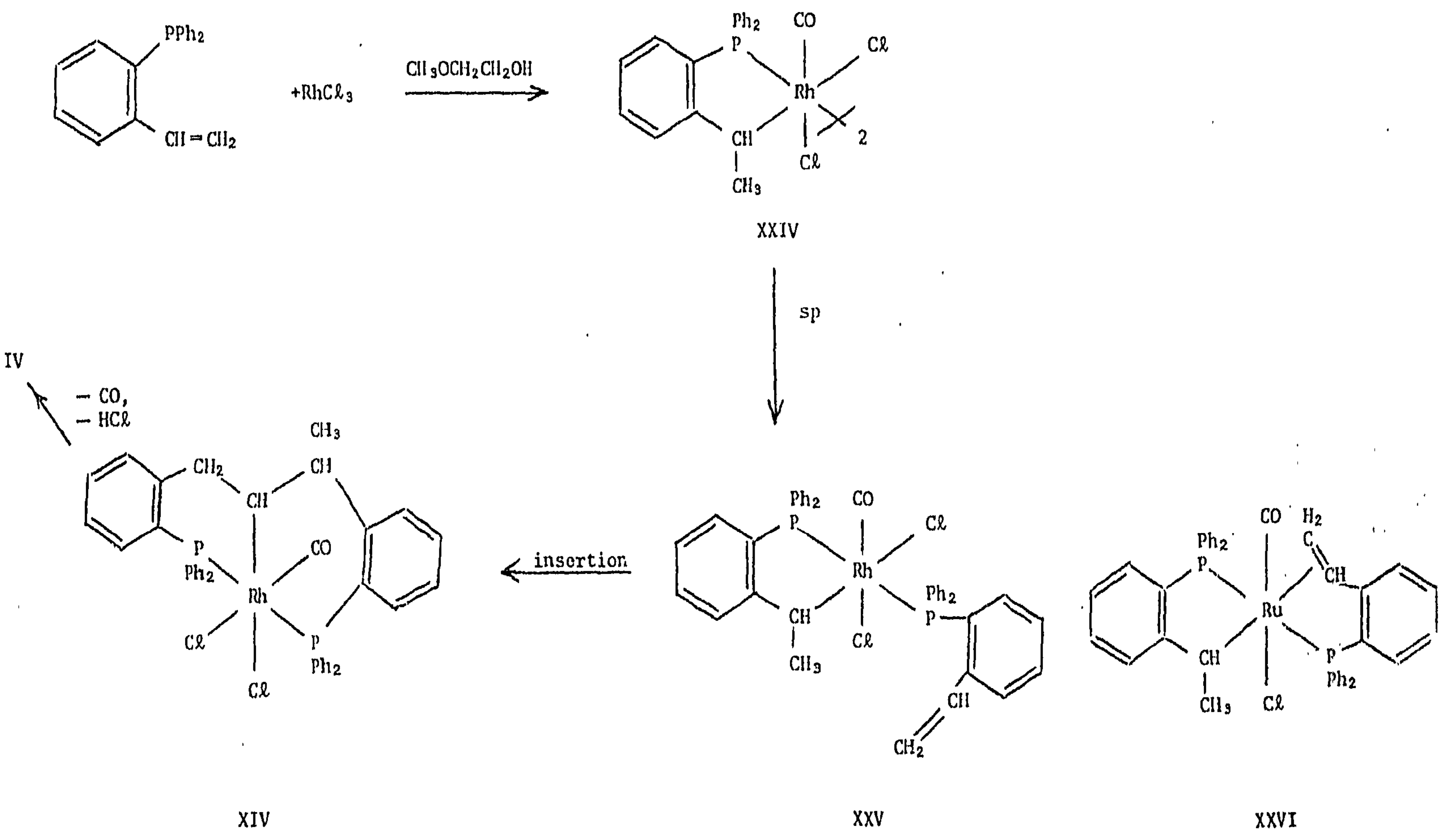
XXIII

Discussion

The reaction of rhodium trichloride with an excess of sp resembles the corresponding reaction with tri-*o*-tolylphosphine [1] in that two ligand molecules are coupled at the metal centre to give a planar rhodium(I) complex, but differs from it in that the coupling is accompanied by a hydrogen atom shift instead of by hydrogen loss. Although the five-coordinate complex $RhCl(sp)_2$ is isomeric with RhCl(1-bdpb) (IV) and is readily formed from ethanolic rhodium trichloride and sp in the presence of formaldehyde [30], it is unaffected by refluxing 2-methoxyethanol and cannot therefore be intermediate in the dimerization of sp. However, (IV) is formed in good yield by heating the chlorine-bridged, chelate σ-alkyl complex $[RhCl_2(CO)(o\text{-}CH_3CHC_6H_4PPh_2)]_2$ (XXIV) with spp in 2-methoxyethanol; XXIV has been prepared by reaction of $[RhCl_2(CO)_2]^-$ with one equivalent of sp per g atom of rhodium [31], and is known to react with monodentate tertiary phosphines (PR_3) to give monomeric chelate σ-alkyls $RhCl_2(CO)(PR_3)\{o\text{-}CH_3CHC_6H_4PPh_2\}$ [31,32]. In view of the ease with which CO is abstracted from primary alcohols by rhodium(III) chloride in the presence of tertiary phosphines [33], it seems reasonable to suggest that XXIV, or a monomeric sp derivative such as XXV, is formed in the reaction between rhodium(III) chloride and sp in 2-methoxyethanol. The pendant double bond of XXV can then insert into the Rh-C σ-bond to give the octahedral rhodium(III) chelate σ-alkyl XIV, which we have shown to be formed by reversible addition of hydrogen chloride to IV in the presence of CO; thus elimination of CO and HCl from XIV probably constitutes the last step in the formation of IV (Scheme 1).

The intermediacy of XXIV is supported by the observation that the analogous iridium compound can be isolated from the reaction of chloroiridi acid with sp in refluxing 2-methoxyethanol [31]. In both cases, hydrolysis of the hydrated metal halide in the alcoholic medium provides sufficient HCl for protonation of a presumed rhodium(I) or iridium(I) intermediate MCl(CO)(sp).

Scheme 1 is similar to that proposed for the coupling of sp promoted by ruthenium(II) species in 2-methoxyethanol [4]. Reaction of hydrated ruthenium(III) chloride with sp in refluxing 2-methoxyethanol produces ultimately the chelate σ-alkyl XXVI in about 60% yield and the chelate 1-butyl complex III in about 18% yield. Treatment of XXVI with CO in 2-methoxyethanol induces insertion of the vinyl group into the Ru-C σ-bond (perhaps by first displacing the olefin from the coordination sphere) to give the 2-butyl complex II which subsequently isomerizes to III. In the reactions promoted by both rhodium(III) and ruthenium(II), Scheme 1. Proposed mechanism for $RhC\ell_3$-promoted coupling of sp.



CO (either present as such or abstracted from 2-methoxyethanol) seems to play a key role; it stabilizes intermediate olefin complexes which can be protonated to form chelate σ-alkyls, and it promotes the coupling of vinyl residues as noted above. At present we do not know how the insertion reaction occurs.

Scheme 1 also resembles the mechanism proposed for the dimerization of ethylene catalyzed by ethanolic rhodium(III) chloride [34], in which the key steps are thought to be: (1) reduction of rhodium(III) to rhodium(I) and formation of a bis(ethylene) rhodium(I) complex (2) protonation of the Rh-C_2H_4 bond to form an ethylrhodium(III) complex (3) insertion of ethylene into the Rh-C_2H_5 bond to form a *n*-butylrhodium(III) complex and (4) β-elimination of 1-butene and reductive elimination of HCl with re-formation of the initial ethylene-rhodium(I) complex. We have not been able to make our reaction catalytic, probably because 1-bdpb is not easily displaced from IV under the reaction conditions.

Our qualitative observations indicate that IV and VII are less prone to ligand addition than their bdpps analogues Ib and Ic, perhaps as a consequence of steric hindrance by the additional $CHCH_3$ group in the chain bridging the coordinated phosphorus atoms. The same factor may also be responsible for the fact that, in the absence of added ligands, IV undergoes protonation by HCl partly at the metal atom and partly at the coordinated olefin, whereas Ib adds HCl exclusively at the metal atom [15]. In most other respects, however, the oxidative additions of corresponding complexes of bdpps and 1-bdpb are very similar.

An interesting effect on the $CHCH_3$ group in the connecting chain of 1-bdpb is the activation of the tertiary C-H bond, either resulting in its elimination as HCl (XI → XIII) (see also ref. 22), or in an internal oxidative addition to the metal (XXII). A similar hydrogen migration to the metal has been observed in both neutral and cationic iridium(I) complexes of the *trans*-chelating bibenzyl ligand *o*-$Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$-*o* [35], and in the *ortho*-metallation of $IrCl(PPh_3)_3$ [36]. We plan to examine the factors which promote this behaviour in cationic complexes of 1-bdpb.

The octahedral iridium(III) complexes XVII and XVIII, like their bdpps counterparts [15], are rare examples of stable hydrido-olefin complexes in which the olefin shows no apparent tendency to react with the metal-hydrogen bond to form a σ-alkyl. While this lack of reactivity could reasonably be attributed to the incorporation of the olefin into a fairly rigid chelate ligand, such an explanation clearly cannot apply to the cationic hydrido-ethylene complex XXII, which shows no tendency to isomerize to a σ-ethyl complex. Remarkably, since the phosphorus atoms of XXII are mutually *trans*, the ethylene and hydride ligands are forced be *cis*, an arrangement which should favour migratory insertion. The fact that complexes such as $ReH(C_2H_4)(dppe)_2$ [36] and $[PtH(C_2H_4)(PEt_3)_2]^+$ [37,38] can be prepared may be due to the *trans*-disposition of hydride and ethylene ligands, and indeed isomerization of the latter to its *cis*-isomer is believed to be a rate-determining step in the insertion reaction of $[PtH(acetone)(PEt_3)_2]^+$ with ethylene to give $[Pt(C_2H_5)(acetone)(PEt_3)_2]^+$ [38]. Similarly, the cationic complex $[MoH(C_2H_4)_2(dppe)_2]^+$ appears to be in equilibrium with a σ-ethyl formed by reaction of the Mo-H bond with *one* of the ethylene ligands (presumably that *cis* to the hydride) [39]. As far as we know, the only other examples of stable *cis*-hydrido-ethylene complexes are the bis(η-cyclopentadienyl) metal complexes $(C_5H_5)_2NbH(C_2H_4)$ [40] and $[(C_5H_5)_2MH(C_2H_4)]^+$ (M = Mo, W) [41], all of which readily undergo ligand-induced insertions to form σ-ethyl derivatives. Since migratory insertion in the case of XXII would lead to a formally five-coordinate iridium(III) species, it seems likely that the stability of XXII is a reflection of the remarkable stability of the octahedral ligand arrangement for iridium(III).

Experimental

The procedures and instrumentation for microanalysis, solvent drying, IR spectra and NMR spectra are as described previously [3,4]. Molecular weights were determined in $CHCl_3$ at 37°C using a Knauer vapour pressure osmometer. Conductivity measurements were made on a Philips GM4144/01

Universal Measuring Bridge. The complexes $[MCl(COD)]_2$ (M=Rh, Ir) were prepared by literature methods [42,43]. Analytical and selected IR data are in Table 1, ^1H NMR data are in Tables 2, 4 and 5, ^{31}P NMR data are in Table 3.

Many of the complexes of 1-bdpb contained solvent of crystallization which could not be removed in vacuo (Table 1). This was most frequently dichloromethane, which could be detected by its characteristic singlet at δ5.3 ppm in $CDCl_3$, and which gave rise to low C,H and high Cl analyses. The presence of small amounts of dichloromethane (< 0.5% v/v) will cause slight errors in osmometric measurements performed in the less volatile chloroform, so that the molecular weights in Table 1 are necessarily approximate. However, they are generally sufficiently accurate to establish the molecularity of the complexes.

The carbon analyses for the fluoroborate salts XIX, XXI and XXIV were consistently about 2% lower than the calculated values (in absolute terms), although the NMR spectra were in agreement with the formulations. This analytical problem is believed to be associated with the presence of phosphorus, boron and fluorine together with the precious metal [44].

Preparations

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}chlororhodium(I), RhCl(1-bdpb), IV. A solution containing hydrated rhodium trichloride (0.3g, 1.14 mmoles) and *o*-styryldiphenylphosphine (sp) (1.0g, 3.5 mmoles) in degassed 2-methoxyethanol (40 ml) was stirred and heated under reflux in a nitrogen atmosphere for 1.5 h. The orange solution was evaporated to dryness under reduced pressure and the residue was taken up in dichloromethane (15 ml). The solution was filtered, treated with methanol (40 ml) and refrigerated overnight. The supernatant liquid was decanted and the yellow crystalline product was washed with methanol (2×5 ml). After drying in vacuo at 50°C, the yield was 0.63g (77%).

(Continued on p. 264)

TABLE 3. ^{31}P NMR DATA[a]

		δ(P)	J(P-P)	J(Rh-P)
1-bdpb (VI)		-16.5s,-13.5s	0	-
RhCℓ(1-bdpb) (IV)	A	39.1dd,17.3dd	400	129,127
	B	40.0dd,15.5dd	400	130,127
IrCℓ(1-bdpb) (VII)	A	34.3d,9.5d	392	-
	B	35.2d,6.2d	392	-
RhCℓ(CO)(1-bdpb) (VIII)[b]		46.9dd,30.3brdd	382	93,[c]102
(VIII)[d]	A	53.2dd,30.6dd	374	95,97
(VIII)[d]	B	40.9,36.7[e]	398[e]	*ca*96,96
IrCℓ(CO)(1-bdpb) (IX)	A	26.2d,-3.1d	347	-
	B	11.5,3.9[f]	?	-
RhCℓ$_3$(1-bdpb) (XI)		44.1dd, 9.3dd	548	77,74
IrCℓ$_3$(1-bdpb) (XII)	A	2.7d,-22.7d	468	-
	B[g]	10.2d,-23.8d	430	-
RhCℓ$_2$(1-bdpb-H) (XIII)[h]		55.6dd,30.0dd	493	98,75
RhCℓ$_2$(CO)(1-bdpbH) (XIV)		18.2dd,8.0dd	444	93,94
IrCℓ$_2$(CO)(1-bdpbH) (XV)	A	-8.0s	?	-
	B	*ca.* -7.7,-16.5	?	-
[RhCℓ$_2$(1-bdpbH)]$_2$ (XVI)		45.9dd,34.1dd	26	147,145
IrHCℓ$_2$(1-bdpb) (XVII)	A1	18.6d, -3.5d	419	-
	A2	9.9d,-15.7d	422	-
	B1	12.1d,-11.4d	420	-
	B2	22.2d,-3.6d	415	-
IrH$_2$Cℓ(1-bdpb) (XVIII)	A1	24.4d,7.1d	370	-
	A2	16.9d,0.5d	371	-
	B1	25.8d,4.8d	347	-
	B2	23.7d,-0.1d	329	-

TABLE 3 (Cont'd)

	δ(P)	J(P-P)	J(Rh-P)
$[Rh(CO)(1\text{-}bdpb)]BF_4$ (XIX) A	41.1dd,20.6dd	273	110,109
B	41.7dd,19.5dd	290	100,102
$[Rh(CO)_2(1\text{-}bdpb)]BF_4$ (XX)[i]	43.1dd,17.9dd	296	81,83
$[Ir(CO)_2(1\text{-}bdpb)]BF_4$ (XXI)	12.8d,-20.5d	259	-
$[IrH(C_2H_4)(1\text{-}bdpb\text{-}H)BF_4$ (XXII)	28.9d,13.2d	324	-

[a] Chemical shifts in ppm relative to external 85% H_3PO_4, downfield being taken as positive. Solvent was $CH_2C\ell_2$ and temperature was 32°C except where stated otherwise. Coupling constants accurate to within ±5 Hz except where stated otherwise.

[b] Time-averaged spectrum at 32°C.

[c] ±10 Hz owing to broadness of lowfield signal.

[d] At -24°C.

[e] Owing to small chemical shift difference, outer lines of AB quartet could not be detected, hence δ(P) and J(P-P) could not be evaluated directly. They were calculated from the equation J(P-P) (average at 32°C) = $p_A J$(P-P)(A) + $p_B J$(P-P)(B), where p_A, p_B are the populations of isomers A and B (0.7 and 0.3 respectively in this case) at -24°C. δ(P) was then calculated from J(P-P) and the observed positions of the inner lines of the AB quartet.

[f] Could not be evaluated directly (see *e*). Calculated assuming J(P-P) same as for isomer A.

[g] Determined by INDOR $^1H\{^{31}P\}$.

[h] Chemical shifts given in ref. 6 are incorrect.

[i] Measured in $CDC\ell_3$.

TABLE 4. ^{1}H NMR DATA FOR ISOMERIC CHELATE σ-ALKYLS FORMED BY PROTONATION OF 1-bdpb.[a-c]

	Chemical shifts (δ)					Coupling Constants (J)				
	H_1	H_2	H_3	H_4	H_5	12	13	23	34	45
$\mathrm{RhCl_2(CO)\{\mathit{o}\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}}$ (<u>XIV</u>)[d]	3.24dd	2.58d	2.92m	3.32qd	1.43d	18.0	11.5	1.5	6.0	6.5
$\mathrm{IrCl_2(CO)\{\mathit{o}\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}}$ (<u>XV</u>)[e]	3.76dd	← 2.4-3.1m →		3.54m	1.19d	16.5	11.0	?	?	7.0
$\mathrm{RuCl(CO)_2\{\mathit{o}\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}}$ (<u>II</u>)[f]	3.66dd	2.95dd	1.81m	3.30t	1.23d	16.0	9.5	2.5	7.0	7.0
$\mathrm{[RhCl_2\{\mathit{o}\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}]_2}$ (<u>XVI</u>)	← 3.6m →		2.2m	3.2m	1.14d	?	13.0	13.0	4.0 10.0[g]	6.0
$\mathrm{RuCl(CO)_2\{\mathit{o}\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)\text{-}C_6H_4PPh_2\text{-}\mathit{o}\}}$ (<u>III</u>)[f]	2.51d	2.00dd	1.82dd	2.97m	1.14d	3.8	13.0	13.5	10.5 4.8[g]	7.0

[a] Proton numbering for first 3 complexes: $\mathrm{-CH^1H^2CH^3(M)CH^4(CH_3^5)-}$; proton numbering for last 2 complexes: $\mathrm{-CH^1(M)CH^2H^3CH^4(CH_3^5)-}$. [b] See Table 2 for experimental conditions; solvent was $\mathrm{CD_2Cl_2}$ in all cases.

[c] Abbreviations as in Table 2, plus qd, quartet of doublets.

[d] Minor isomers (each ∿15% of total) showed $\mathrm{CH_3}$ resonances at δ 1.15 ppm (d, J=6.5) and δ 1.21 ppm (d, J=6.5).

[e] Minor isomer (∿25% of total) showed signals at δ(ppm) 2.4-3.1m (H_1, H_2, H_3), 3.50 m (H_4) and 1.42 (d, J=7.0, $\mathrm{CH_3}$).

[f] Data from ref. 4. [g] J_{24}.

TABLE 5. ^1H NMR DATA FOR $IrH_2C\ell(1\text{-bdpb})$ (XVIII)[a,b]

	← Chemical shifts (δ)					→	← Coupling constants (*J*)				→
	H_1	H_2	H_3	H_4	H_5	H_6	12	34	56	P-H_5	P-H_6
A1	← 2.7-4.8m →			1.49d	-18.27m	-7.58m	?	7.0	1.0	14.0,14.0	16.0,16.0
A2	← 2.7-4.8m →			1.61d	-18.79m	-6.79m	?	7.0	4.0	14.0,14.0	16.0,16.0
B1	5.60d	← 2.7-4.8m →		1.59d	-21.43m	-8.11m	12.0	7.0	5.0	12.0,14.0	14.0,19.0
B2	5.35d	← 2.7-4.8m →		1.71d	-20.80m	-7.62m	12.0	7.0	4.0	15.0,15.0	16.0,16.0

[a] Isomers A1, A2 of XVIII are formed in approx. 2:1 ratio from isomer A of VII, isomers B1 and B2 of XVIII are formed in approx. 4:3 ratio from isomer B of VII.

[b] Proton numbering as in Table 2; H_5, H_6 = IrH trans to Cℓ and to olefin respectively.

IV was also prepared in 63% yield from $[\overline{\mathrm{RhCl_2(CO)(}\textit{o}\mathrm{\text{-}CH_3C}}\mathrm{HC_6H_4PPh_2)}]_2$ [31] (0.25g, 0.25 mmole) and sp (0.2g, 0.7 mmole) in refluxing 2-methoxyethanol (40 ml).

The bromo-complex RhBr(1-bdpb), V, was prepared as described above from hydrated rhodium tribromide (0.1g, 0.25 mmole) and sp (0.35g, 1.21 mmoles) in 2-methoxyethanol (15 ml). The yield of yellow product was 0.105g (55%).

2,2'-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene, 1-bdpb, VI. A mixture of IV (1g) and sodium cyanide (3.5g, excess) was heated under reflux in 90% aqueous ethanol or 2-methoxyethanol (50 ml) for 1h. Addition of water (50 ml) gave a white precipitate, which was filtered off and recrystallized from ethanol to give 0.71g (90%) of VI, m.p. 122°C.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}chloroiridium(I), IrCl(1-bdpb), VII. (i) A solution containing $[\mathrm{IrCl(COD)}]_2$ (0.19g, 0.28 mmole) and 1-bdpb (0.33g, 0.56 mmole) in dichloromethane (10 ml) was stirred under nitrogen at room temperature for 10 min. A portion of this solution was evaporated to dryness and the residue was redissolved in $\mathrm{CD_2Cl_2}$; the ^{1}H NMR spectrum showed the presence of isomers VIIA and VIIB in *ca* 3:1 ratio. The bulk of solution was filtered and treated with methanol (30 ml). After 12h, the supernatant liquid was decanted and the orange crystalline product was washed with methanol. After drying in vacuo the yield was 0.3g (66%). ^{1}H NMR spectroscopy showed it to contain >95% of isomer A.
(ii) The same reaction was carried out in refluxing cyclohexane or benzene (30 ml) under nitrogen for 45 min. Solvent was removed under reduced pressure and a small portion of the residue dissolved in $\mathrm{CD_2Cl_2}$; the ^{1}H NMR spectrum showed the ratio of VIIA to VIIB to be 1:5. The residue was recrystallized from dichloromethane/methanol to give 70% yield of an orange crystalline product which contained a 1:3 ratio of VIIA and VIIB according to its ^{1}H NMR spectrum.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}carbonylchlororhodium(I) and -iridium(I), MCl(CO)(1-bdpb), M=Rh (VIII) or Ir (IX). Carbon monoxide was bubbled into solutions of IV or VII ($\sim$0.2g) in dichloromethane (10 ml) for 10 min. *n*-Pentane or *n*-hexane (20 ml) was added in an atmosphere of CO. After 20 min, the supernatant liquid was decanted, and the colourless crystalline product was washed with *n*-pentane. It was then dried, in a stream of CO in the case of VII, in vacuo at 50°C in the case of IX; yields were almost quantitative.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}chloro(ethylene) iridium(I), IrCl(C_2H_4)(1-bdpb), X. This was prepared similarly to IX using ethylene instead of carbon monoxide. The pale yellow product, which readily reverted to VII at room temperature, was dried in a current of ethylene. Solutions of X for ^{1}H NMR work were prepared in situ by passing ethylene into a solution of VII in CD_2Cl_2.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}trichloro-rhodium(III) and -iridium(III), MCl$_3$(1-bdpb), M=Rh (XI) or Ir (XII). (i) Chlorine gas was bubbled into solutions of IV or VII ($\sim$0.2g) in dichloromethane (10 ml) for 1 min at room temperature. Solvent was removed under reduced pressure and the residue was dissolved in CD_2Cl_2 for ^{1}H and ^{31}P{^{1}H} NMR examination. Crude XI contained only a single isomer, even though the precursor IV contained two isomers in a 3:2 ratio. In contrast, crude XII contained two isomers; by starting with almost pure VIIA, or with VII containing different proportions of A and B (see above), it could be shown that the isomers XIIA and XIIB arose from VIIA and VIIB respectively. The products were recrystallized from dichloromethane/methanol and after drying at 70° in vacuo the yields were almost quantitative. XI was yellow-orange, XII was yellow.

(ii) A mixture of chloroiridic acid (0.147g, 0.29 mmole) and 1-bdpb (0.2g, 0.35 mmole) in 2-methoxyethanol (35 ml) was heated under reflux in a nitrogen atmosphere for 2h. Solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane/methanol to give a yellow crystalline solid. After drying in vacuo at 30° the yield of XIIB was 0.08g (22%).

{Bis[1-*anti*,3-*syn*-(*o*-diphenylphosphino)phenyl]-1-methallyl(1-3η)}cis-dichlororhodium(III), $RhCl_2\{o\text{-}Ph_2PC_6H_4CH{\cdots}CH{\cdots}C(CH_3)C_6H_4PPh_2\text{-}o\}$, XIII.

(i) A mixture of hydrated rhodium trichloride (0.07g, 0.27 mmole) and 1-bdpb (0.17g, 0.29 mmole) in 2-methoxyethanol (25 ml) was heated under reflux in a nitrogen atmosphere for 2h. After removal of solvent under reduced pressure, the residue was taken up in a mixture of dichloromethane (15 ml) and methanol (30 ml). After 1h a small crop of yellow crystals of IV had formed. The supernatant orange solution was decanted and deposited overnight orange crystals of XIII, which were dried in vacuo (0.122g, 60%).

(ii) XI (0.05g) was heated under reflux in 2-methoxyethanol (15 ml) for 2h. After removal of solvent under reduced pressure, the residue was recrystallized from dichloromethane/methanol to give XIII, identified by its ^1H NMR spectrum (Table 2). A solution of XI in CD_2Cl_2 lost hydrogen chloride over a 10d period at 25°C giving XIII; the reaction was not reversed by saturation of the solution with hydrogen chloride.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-2-butyl}carbonyldichloro-rhodium(III) and -iridium(III), $MCl_2(CO)\{o\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)C_6H_4PPh_2\text{-}o\}$, M=Rh (XIV) or Ir (XV). Solutions of VIII or IX generated in situ by carbonylation of IV or VII as described above were treated with dry hydrogen chloride for 5 min. The products were crystallized by dropwise addition of *n*-pentane or *n*-hexane and were dried in vacuo; yields were almost quantitative.

Reaction of RhCl(1-bdpb) with hydrogen chloride: preparation of {1,3-bis[(*o*-diphenylphosphino)phenyl]-1-butyl}dichlororhodium(III) $[RhCl_2\{o\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)C_6H_4PPh_2\text{-}o\}]_2$, XVI. A sample of IV was purified by four recrystallizations from dichloromethane/methanol to ensure complete removal of small amounts of free spp or 1-bdpb (see below). *Ca* 0.3g was then dissolved in CD_2Cl_2 and treated with dry hydrogen chloride at room temperature for 15 min. The ^1H NMR spectrum at this stage showed the presence of *ca* 10% $RhCl_3$(1-bdpb) (XI) in addition to unreacted IV. The solution was then saturated with hydrogen chloride gas and set aside at room temperature for 5d. The ^{1}H NMR spectrum now showed that IV had completely reacted to give approximately equal amounts of XI and XVI in addition to a small amount of the chelate 1-3η-allyl complex XIII. Attempts to separate XI and XVI by fractional crystallization were unsuccessful.

The same experiment was carried out in the presence of triphenylphosphi (1 mol per mol of IV). After 2h at 25°C, the ^{1}H NMR spectrum showed the presence of about 80% of XVI, 5% of XI and 15% of an unknown compound having $\delta(CH_3)$ 1.62 ppm, $J(CH_3\text{-}CH)$ 6.5 Hz (possibly the 2-butyl isomer of XVI); the same composition was obtained if only a trace of triphenylphosphine, sp or 1-bdpb were present initially. Fractional crystallization from dichloromethane/*n*-hexane removed the small amount of XI, but failed to separate XVI from the unknown compound.

Dehydrochlorination of XIV or XVI. XIV or XVI (*ca* 0.1g) were separately heated under reflux in ethanol (20 ml) for 1h. After cooling to room temperature and allowing to stand for 1h, the yellow solid product was centrifuged off, dried in vacuo, and identified by its ^{1}H NMR spectrum as RhCl(1-bdpb) (IV).

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}dichlorohydridoiridium(III), $IrHCl_2$(1-bdpb), XVII. A solution of VII (0.2g) in dichloromethane (10 ml) was treated with dry hydrogen chloride gas for 5 min. The colourless product crystallized on dropwise addition of *n*-pentane and was dried in vacuo; the yield was almost quantitative.

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}chlorodihydridoiridium(III), IrH_2Cl(1-bdpb), XVIII. Hydrogen was passed into a solution of VII (0.2g) in dichloromethane (10 ml); the colour changed immediately from orange to very pale yellow. Attempts to isolate the adduct were unsuccessful owing to its ready reversion to VII, and it was therefore characterised by its IR spectrum [ν(IrH)2210s, 2100s cm^{-1}(CH_2Cl_2)] and by NMR spectroscopy (Table 5).

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}carbonylrhodium(I) tetrafluoroborate, [Rh(CO)(1-bdpb)]BF_4, XIX. A solution of IV (~0.1g) in dichloromethane (10 ml) was treated with an excess of $AgBF_4$ under nitrogen. The orange solution was filtered and the complex was precipitated by addition of *n*-pentane. The sample for analysis was recrystallized from dichloromethane/ether; the yield was almost quantitative. Solutions for measurement of IR and NMR spectra were prepared in situ in CH_2Cl_2 and CD_2Cl_2 respectively. A solution of XIX reacted with CO to give XX (see below).

{1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene}dicarbonyl-rhodium(I), and -iridium(I) tetrafluoroborate [M(CO)$_2$(1-bdpb)]BF_4, M=Rh (XX) or Ir (XXI). These colourless salts were prepared as described above, an atmosphere of CO being employed instead of nitrogen. A suspension of IV (5.55 mg) in nitromethane (10 ml) dissolved on passage of CO giving a colourless solution having Λ = 68.1 ohm^{-1} cm^2 mol^{-1}, typical of a 1:1 electrolyte [45], suggesting the formation of [Rh(CO)$_2$(1-bdpb)]$^+$. Passage of nitrogen through the solution caused it to turn yellow and become almost non-conducting, presumably due to the re-formation of RhCl(1-bdpb).

Reaction of VII with $AgBF_4$ and ethylene. A solution of VII (0.1g) in dichloromethane (5 ml) was saturated with ethylene (1 atm) and treated with an excess of $AgBF_4$. The yellow colour of VII was immediately discharged and a white precipitate of AgCl appeared. The mixture was stirred under ethylene at 25°C for 10 min and the precipitate was removed by centrifuging. N.m.r. examination of the clear supernatant liquid showed the presence of the hydrido (ethylene) complex XXII (87%) and the butadiene complex XXIII (13%). These proportions remained unaltered when the solution in the n.m.r. tube was set aside for 2 weeks at room temperature or on addition of an equal volume of $CDCl_3$. Addition of *n*-hexane to the bulk of the solution caused XXII to crystallize as colourless needles. After washing with *n*-hexane and drying in vacuo, the yield was *ca* 50%. Attempts to isolate XXIII were not successful.

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