Carbon-13 Nuclear Magnetic Resonance Study of Rhodium(I) and -(III) and Iridium(I) and -(III) Complexes Containing Chelating Unsaturated Tertiary Phosphines and Arsines

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A ^{13}C NMR spectral analysis of Rh and Ir olefin complexes containing tertiary unsaturated phosphines has been carried out. The analysis included the square-planar complexes RhX(BDPH), X = Cl or Br, RhCl(BDAH), and IrCl(BDPH); the trigonal-bipyramidal complexes [RhX(DBP)]$_2$, X = Cl or Br, Rh(CO)X(DBP), X = Cl, Br or I, Ir(CO)X(DBP), X = Cl, Br, or I, RhX(TBP), X = Cl, Br, or I, IrCl(TBP), RhX(TPP), X = Cl or Br, and IrCl(TPP); and the octahedral complexes Rh(XY)Cl(BDPH), XY = Cl$_2$ or Br$_2$, and Ir(XY)Cl(BDPH), XY = Cl$_2$, H$_2$, or HCl, where BDH = *trans*-1,6-bis(diphenylphosphino)hex-3-ene, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$CH=CHCH$_2$CH$_2$P(C$_6$H$_5$)$_2$, DBP = dibut-3-enylphenyl-phosphine, (C$_6$H$_5$)P(CH$_2$CH$_2$CH=CH$_2$)$_2$, TBP = tribut-3-enylphosphine, P(CH$_2$CH$_2$CH=CH$_2$)$_3$ and TPP = tripent-4-enyl)phosphine, P(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_3$. The coordination-induced shift of the olefin $\Delta\delta$(C) has been shown to be dependent on the stereochemistry of the metal complex and the oxidation state of the metal and reflects the relative amount of electron density at the metal center available for back-bonding to the olefin, as predicted by the Dewar–Chatt–Duncanson model of metal–olefin bonding. The [103]Rh–[13]C coupling constants to the olefinic carbons support the above trends. Variable-temperature ^{13}C NMR spectra have shown that the olefin in the complexes RhCl(TBP) and RhBr(TBP) undergoes a rotation (albeit small) about the rhodium–olefin bond, whereas in RhI(TBP) variable-temperature spectra have shown an equilibrium between coordinated and uncoordinated olefin.

Introduction

For the last 25 years, the theory of metal–olefin bonding has relied heavily on the description forwarded by Chatt and Duncanson[1] and Dewar.[2] Discussion has centered around the relative importance of olefin $\pi \rightarrow$ metal "hybrid dsp" orbital donation and metal d orbital $\rightarrow$ olefin π^* back-bonding. Following this model, attempts to assess the relative strengths of the metal–olefin bond have been made by using (a) C=C and metal–olefin symmetric and asymmetric stretching frequencies observed in infrared spectra, (b) X-ray determined C=C bond distances, (c) ^{1}H chemical shift and [1]H–[1]H coupling constants, (d) ^{13}C chemical shift and [13]C–[1]H coupling constants, and more recently (e) metal–[13]C coupling constants. The use of the C=C stretching frequency has its limitations since the C=C stretching frequency is coupled with the in-plane CH$_2$ scissor vibration in terminal olefins[3] and in symmetrically substituted olefins is very weak and often not observable.[4] Bond distances (C=C) vary little from unco-ordinated (ca. 1.34 Å) to coordinated ligands (generally <1.40 Å) and thus are also of limited value.[5] The upfield shift of the [1]H–olefin resonance (coupled with the decrease in the cis and trans [1]H–[1]H coupling constants of unsymmetrical olefins) in coordinated compared to uncoordinated ligands has been used as a diagnostic test for coordination of the olefin.[6] One study has used the ^{1}H chemical shift and [1]H–[1]H coupling constant data as an index of the relative strength of metal–olefin bonds.[7] A larger number of recent publications report ^{13}C NMR data on metal–olefin complexes.[8-28] Unfortunately, the [13]C–[1]H coupling constants of coordinated olefins vary little from those in the uncoordinated systems.[21] Further, the ^{13}C shift (upfield) of the olefinic carbons upon coordination has been shown to vary quite significantly (<1 ppm in some silver–olefin complexes[14] to 125 ppm in a rhodium(I) di-carbomethoxynorbornadiene complex[28]). These large differences in coordination-induced ^{13}C shifts have been related to the relative strength of the metal–olefin bond although the theoretical basis for their origin is not clearly understood.[12,28] The most valuable information concerning the nature of the metal–olefin bonds has been obtained from metal–[13]C coupling constants,[8,11,13,15,16,19,22-28] but this is restricted to metals with a nuclear spin of $^1/_2$.

We have recently been investigating the preparation and properties of complexes of rhodium and iridium containing

unsaturated tertiary phosphines and arsines[4,7,25,29-36] in the hope of obtaining structural and physical data relating to the nature of the metal–olefin bond. In addition, these compounds provide ideal models for the proposed intermediates in homogeneous catalytic reactions such as hydrogenation, hydroformylation, and isomerization. Our preliminary report of the ^{13}C NMR spectra of the two series of trigonal-bipyramidal rhodium complexes RhX[P(CH$_2$CH$_2$CH=CH$_2$)$_3$] and RhX[P-(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_3$], X = Cl or Br, showed that the [103]Rh–[13]C(olefin) coupling constant was only one-third to one-half that found in square-planar complexes and that the fluxional character of the olefin in RhX[P(CH$_2$CH$_2$CH=CH$_2$)$_3$] could be related to the partial rotation of the olefin about the rhodium–olefin bond.[25]

We now wish to report a comprehensive study of the ^{13}C NMR spectra of a series of rhodium and iridium olefin complexes containing chelating unsaturated tertiary phosphines and arsines, viz., *trans*-1,6-bis(diphenylphosphino)hex-3-ene (BDPH), *trans*-1,6-bis(diphenylarsino)hex-3-ene (BDAH), tribut-3-enylphosphine (TBP), tripent-4-enylphosphine (TPP), and dibut-3-enylphenylphosphine (DBP). The utility of studying the metal–olefin bond with these ligands in rhodium and iridium complexes lies in the following factors: (a) the ligands are closely related, and, therefore, factors relating to electronic differences or electronegativity are minimized; (b) the ligands form stable metal–olefin bonds due to the strong chelating effect; (c) four-coordinate (square-planar) rhodium(I) and iridium(I) complexes, five-coordinate (trigonal-bipyramidal) rhodium(I) and iridium(I) complexes, and six-coordinate (octahedral) rhodium(III) and iridium(III) complexes can be formed, and, therefore, relationships not only between stereochemistry and metal but also between oxidation states are possible; (d) rhodium isotope 103 occurs in 100% abundance with nuclear spin $I = ^1/_2$; (e) X-ray structures of RhCl(TBP),[37] IrCl(BDPH),[38] and IrH$_2$Cl(BDPH)[38] have been solved. We also report the ^{13}C NMR spectra of the simple rhodium and iridium olefin complexes [RhCl(C$_8$H$_{12}$)]$_2$, [IrCl(C$_8$H$_{12}$)]$_2$ (C$_8$H$_{12}$ = *cis,cis*-1,5-cyclooctadiene), and IrCl(C$_2$H$_4$)(PPh$_3$)$_2$ for comparison.

Experimental Section

Ligands and Complexes. The following ligands and complexes were prepared according to the previously published procedures: *trans*-1,6-bis(diphenylphosphino)hex-3-ene, BDPH;[35] *trans*-1,6-bis(di-phenylarsino)hex-3-ene, BDAH;[35] RhCl(BDPH);[35] RhBr(BDPH);[35] RhCl(BDAH);[35] IrCl(BDPH);[35] IrH$_2$Cl(BDPH);[38] dibut-3-enyl-

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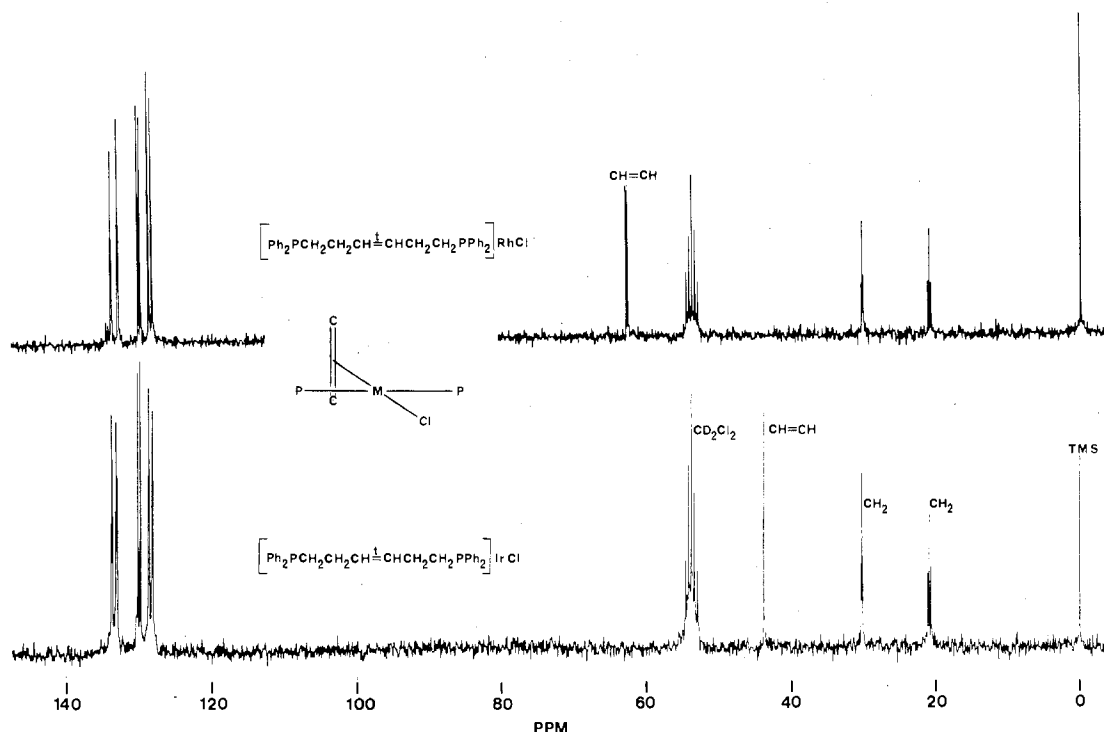
Figure 1. ^{13}C NMR spectra of RhCl(BDPH) and IrCl(BDPH).

phenylphosphine, DBP;[32] [RhCl(DBP)]$_2$;[32] [RhBr(DBP)]$_2$;[32] Rh(CO)Cl(DBP);[32] Rh(CO)Br(DBP);[32] Rh(CO)I(DBP);[32] tribut-3-enylphosphine, TBP;[7] RhCl(TBP);[7] RhBr(TBP);[7] RhI(TBP);[7] IrCl(TBP);[7] tripent-4-enylphosphine, TPP;[7] RhCl(TPP);[7] RhBr(TPP);[7] RhI(TPP);[7] IrCl(TPP);[7] [RhCl(1,5-cyclooctadiene)]$_2$;[39] [IrCl(1,5-cyclooctadiene)]$_2$;[40] IrCl(C$_2$H$_4$)(PPh$_3$)$_2$.[41] The preparation and other properties of the following complexes will be discussed in future publications:[42] RhCl$_3$(BDPH), RhBr$_2$Cl(BDPH), IrCl$_3$(BDPH), IrHCl$_2$(BDPH), Ir(CO)Cl(DBP), Ir(CO)Br(DBP), and Ir(CO)I(DBP).

^{13}C NMR spectra of the ligands and complexes were determined with a Bruker HFX-270 instrument operating at 67.89 MHZ.[43] The ^{13}C chemical shifts are relative to internal Me$_4$Si (δ = 0 ppm) and are accurate to ±0.1 ppm, and the coupling constants, measured in Hz, are accurate to ±0.5 Hz. All compounds were dissolved in CDCl$_3$ or CD$_2$Cl$_2$, and the NMR tubes were flushed with nitrogen before recording the spectra. Our experience indicates a solvent-induced shift of up to 2 ppm occurs in comparing the two solvent systems CDCl$_3$ vs. CD$_2$Cl$_2$. Small shifts have also been observed due to concentration effects. The molecular weight determination of RhI(TBP) was carried out by the Australian Microanalytical Service, CSIRO, Melbourne, by using vapor pressure osmometry on a chloroform solution of the compound. Anal. Calcd for C$_{12}$H$_{21}$IPRh: mol wt 431. Found: mol wt 440.

Results

Square-Planar Complexes. The ligands *trans*-1,6-bis(diphenylphosphino)hex-3-ene (BDPH) and *trans*-1,6-bis(diphenylarsino)hex-3-ene (BDAH) form square-planar complexes (see structure A) of rhodium(I) and iridium(I) of the
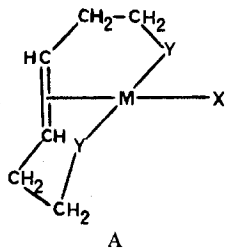
M = Rh, Y = PPh$_2$, X = Cl or Br; M = Rh, Y = AsPh$_2$, X = Cl;
M = Ir, Y = PPh$_2$, X = Cl

general formula MX(ligand) where M = Rh or Ir and X = halide.[35] An X-ray structure of IrCl(BDPH) has confirmed the information obtained from physical data; viz., the ligand acts as a tridentate ligand with the olefin firmly bound to the metal,[38] and the structure is similar to that found for IrCl-(C$_2$H$_4$)(PPh$_3$)$_2$.[44]

The ^{13}C chemical shifts and coupling constants of the ligand BDPH and of its complexes are summarized in Table I. The spectrum of the ligand exhibits the following: a phenyl region, C$_\alpha$ 139.4 ppm (J(CP) = 13.9 Hz), C$_\beta$ 133.0 ppm (J(CP) = 18.5 Hz), C$_\gamma$ 128.7 ppm (J(CP) = 9.3 Hz), C$_\delta$, 128.8 ppm (J(CP) $\approx$ 0 Hz); a methylene region, C$_1$ 28.2 ppm (J(CP) = 12.9 Hz), C$_2$ 29.3 ppm (J(CP) = 16.6 Hz); and olefinic resonance at 130.9 ppm (J(CP) = 12.9 Hz). The phenyl and methylene carbon resonances of the ligand are assigned on the basis of the observed shifts and coupling constants and by comparisons with the literature.[45-47] The ^{13}C NMR spectrum of the diarsine analogue BDAH is almost identical to that of BDPH.

The spectra of the square-planar complexes (Figure 1) are quite similar. In only one case, RhCl(BDAH), was the C$_\alpha$ resonance intense enough to be clearly observed under the average experimental conditions chosen. Two sets of resonances were observed for the C$_\beta$, C$_\gamma$, and C$_\delta$ atoms. Clearly, the phenyl rings are nonequivalent on each phosphorus atom but equivalent to the corresponding phenyl ring on the other phosphorus atom. In RhCl(BDPH), RhBr(BDPH), and IrCl(BDPH), the C$_\beta$ and C$_\gamma$ resonances are triplets due to virtual coupling between the carbon and the two phosphorus atoms.[48] Although J(^{31}P–^{13}C$_\beta$) is larger than J(^{31}P–^{13}C$_\gamma$) for the uncomplexed ligand, it may be reversed for the complexed form, e.g., in Mo(CO)$_4$(Ph$_2$CH$_2$CH$_2$PPh$_2$), J(^{31}P–^{13}C$_\beta$) = 9.6 Hz and J(^{31}P–^{13}C$_\gamma$) = 12.2 Hz.[47] Thus J(CP) values cannot be used reliably as a criterion for assignment of C$_\beta$ and C$_\gamma$ carbons. No phosphorus coupling was observed on the δ carbons. Two resonances are observed in the methylene region corresponding to C$_1$ and C$_2$. In RhCl(BDPH), RhBr(BDPH), and IrCl(BDPH), these resonances were triplets, again arising from the virtual coupling with the phosphorus atoms, and were assigned on the basis of the coupling magnitudes J(^{31}P–^{13}C$_1$)

Table I. ¹³C NMR Data of Rhodium and Iridium Complexes Containing the Ligands *trans*-1,6-Bis(diphenylphosphino)hex-3-ene,[a] BDPH, and *trans*-1,6-Bis(diphenylarsino)hex-3-ene,[a] BDAH

Chemical Shifts[b] (ppm)

compd	C_1	C_2	C_3	C_α	C_β	C_γ	C_δ
BDPH	28.2 d	29.3 d	130.9 d	139.4 d	133.0 d	128.7 d	128.8 s
BDAH	27.9 s	29.8 s	131.3 s	141.3 s	133.3 s	128.7 s	128.8 s
RhCl(BDPH)	21.1 t	30.3 t	62.8 d		134.2 t	129.0 t	130.4 s
					133.2 t	128.5 t	130.1 s
RhBr(BDPH)	21.7 t	30.5 t	63.9 d		134.3 t	128.9 t	130.4 s
					133.5 t	128.3 t	130.1 s
RhCl(BDPH)	18.5 s	30.1 s	61.2 d	135.9 s	133.7 s	129.4 s	130.2 s
				135.6 s	133.0 s	129.0 s	130.0 s
RhCl₃(BDPH)	37.7 t	32.7 t	114.2 d		134.7 t	128.3 t	131.1 s
					134.3 t	127.6 t	130.4 s
cis-RhBr₂Cl(BDPH)	c	c	112.8[d] d		c	c	c
			116.9 d				
trans-RhBr₂Cl(BDPH)	39.2 t	32.8 t	115.3[d] d		135.0[e]	128.1 t	130.9 s
					134.3[e]	127.3 t	130.4 s
IrCl(BDPH)	20.9 t	30.3 t	43.8 s		134.1 t	129.0 t	130.5 s
					133.5 t	128.5 t	130.1 s
IrCl₃(BDPH)	38.1 t	32.3 t	98.7 s		134.4 t	128.2 t	131.1 s
					134.2 t	127.5 t	130.4 s
IrH₂Cl(BDPH)	42.2 dd	32.7 d	105.1 s		f	f	f
	41.0 dd	31.8 dd	92.5 s				
IrHCl₂(BDPH)	26.0 d	29.9 dd	74.4 d		136.3 d	130.7 d	132.8 s
					135.3 d	130.5 d	132.7 s
	25.4 d	29.7 dd	65.5 d		135.2 d	129.9 d	132.5 s
					134.7 d	129.7 d	132.3 s

Coupling Constants (Hz)

compd	$J(^{103}\text{Rh}-^{13}\text{C}_3)$	$J(^{31}\text{P}-^{13}\text{C}_\beta)$	$J(^{31}\text{P}-^{13}\text{C}_\gamma)$	$J(^{31}\text{P}-^{13}\text{C}_1)$	$J(^{31}\text{P}-^{13}\text{C}_2)$	$J(^{31}\text{P}-^{13}\text{C}_3)$
BDPH		18.5	9.3	12.9	16.6	12.9
RhCl(BDPH)	14.8	6.5	4.7	11.1	7.4	<1.0
		6.4	4.6			
RhBr(BDPH)	14.8	7.4	<1.0	11.1	7.4	<1.0
		5.6	3.7			
RhCl(BDPH)	13.0					
RhCl₃(BDPH)	5.6	4.6	5.5	15.7	4.6	<1.0
		4.6	4.6			
cis-RhBr₂Cl(BDPH)	d	c	c	c	c	c
trans-RhBr₂Cl(BDPH)	d	e	3.7	16.7	5.5	<1.0
			3.7			
IrCl(BDPH)		7.4	5.6	16.2	7.4	<1.0
		7.4	5.6			
IrCl₃(BDPH)		5.5	4.6	17.5	6.0	<1.0
		4.7	4.6			
IrH₂Cl(BDPH)		f	f	25.9 }	11.1 }	
				7.4	1.0	<1.0
				27.8 }	16.6 }	
				7.4	3.7	
IrHCl₂(BDPH)		9.2	11.1	29.6 }	7.3 }	
		9.2	9.2	<1.0	3.4	3.7
		7.4	3.7	29.6	5.4 }	
		9.2	3.7	<1.0	3.7	3.7

[a] Numbering system for *trans*-1,6-bis(diphenylphosphino)hex-3-ene and *trans*-1,6-bis(diphenylarsino)hex-3-ene is

Y = P or As
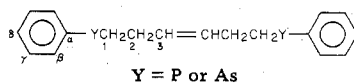
[b] s = singlet, d = doublet, t = triplet, dd = doublet of doublets. The solvent in every case was CD₂Cl₂. [c] Resonance overalpping with trans isomer. [d] Not well resolved. [e] Resonances overlapping with the cis isomer. [f] Resonances overlapping.

$> J(^{31}\text{P}-^{13}\text{C}_2)$, as previously.[47] Earlier ¹³C NMR results on similar phosphorus-containing compounds have indicated that the dominant factor determining phosphorus–carbon couplings is the C–P–C bond angle.[45] Since this angle could change dramatically in a complexed ligand, the above methylene assignments should also only be considered tentative. The olefinic carbons are observed at high field: 62.8 ppm for RhCl(BDPH), 63.9 ppm for RhBr(BDPH), 61.2 ppm for RhCl(BDAH), and 43.8 ppm for IrCl(BDPH). For the rhodium complexes, the olefinic resonances occur as doublets due to ¹⁰³Rh coupling, and for the iridium complex, they occur as a singlet. No phosphorus coupling to the olefinic carbons

was observed for any of the square-planar metal complexes. The upfield shift of the olefinic carbons is consistent with the olefin being firmly bound to the metal.[25] This upfield shift can be compared with that occurring in the trans square-planar ethylene complexes RhCl(C₂H₄)[P(*p*-tol)₃]₂, δ(C) = 44.6 ppm,[20] and IrCl(C₂H₄)(PPh₃)₂, δ(C) = 25.0 ppm (see Table IV).

Trigonal-Bipyramidal Complexes. The ligands dibut-3-enylphenylphosphine (DBP), tribut-3-enylphosphine (TBP), and tripent-4-enylphosphine (TPP) form trigonal-bipyramidal complexes of rhodium(I) and iridium(I) which have the following formulas: [MX(DBP)]₂ (structure B), M(CO)-

Table II. ^{13}C NMR Data of Rhodium and Iridium Complexes Containing the Ligand Dibut-3-enylphenylphosphine,^{a} DBP

Chemical Shifts^b (ppm)

compd	C_1	C_2	C_3	C_4	C_β	C_γ	C_δ	CO
DBP	114.4 s	139.5 d	30.5 d	27.8 d	132.8 d	128.7 d	129.1 s	
[RhCl(DBP)]$_2$·CH$_2$Cl$_2$	~54^c	83.5 s	30.2 s	27.8 d	128.8 d	131.5 d	130.9 s	
[RhBr(DBP)]$_2$·CH$_2$Cl$_2$	51.6 s	81.7 s	30.1 s	27.3 d	128.6 d	131.9 d	130.9 s	
Rh(CO)Cl(DBP)	50.2 d	79.2^d	26.9 s	28.3 d	129.1 d	130.0 d	131.9 s	195.7 d
Rh(CO)Br(DBP)	50.5 d	79.5^d	27.5 s	28.0 d	129.4 d	130.4 d	131.9 s	194.8 d
Rh(CO)I(DBP)	46.2^d	76.0^d	27.4 s	26.6 d	129.3 d	130.4 d	132.0 s	194.8 d
Ir(CO)Cl(DBP)	33.9 s	61.4 d	27.3 d	28.1 d	129.4 d	130.6 d	132.0 d	177.8 s
Ir(CO)Br(DBP)	32.4 s	60.8 d	27.5 d	27.4 d	129.4 d	130.6 d	132.0 d	177.0 s
Ir(CO)I(DBP)	29.7 s	57.8 d	28.0 s	26.0 d	129.5 d	130.6 d	132.1 s	e

Coupling Constants (Hz)

compd	$J(^{103}Rh-^{13}C_1)$	$J(^{103}Rh-^{13}C_2)$	$J(^{103}Rh-^{13}CO)$	$J(^{31}P-^{13}C_2)$	$J(^{31}P-^{13}C_3)$	$J(^{31}P-^{13}C_4)$	$J(^{31}P-^{13}C_\beta)$	$J(^{31}P-^{13}C_\gamma)$	$J(^{31}P-^{13}C_\delta)$
DBP				12.0	14.8	13.0	19.4	6.5	<1.0
[RhCl(DBP)]$_2$·CH$_2$Cl$_2$	<1.0	<1.0		<1.0	<1.0	29.6	9.2	9.2	<1.0
[RhBr(DBP)]$_2$·CH$_2$Cl$_2$	<1.0	<1.0		<1.0	<1.0	29.6	11.1	7.4	<1.0
Rh(CO)Cl(DBP)	7.4	f	59.2	f	<1.0	27.2	9.3	9.2	<1.0
Rh(CO)Br(DBP)	5.5	f	60.7	f	<1.0	27.8	9.2	7.4	<1.0
Rh(CO)I(DBP)	5.6	f	59.2	f	<1.0	27.8	9.2	9.2	<1.0
Ir(CO)Cl(DBP)				5.6	3.7	35.2	11.1	9.3	3.7
Ir(CO)Br(DBP)				3.7	3.7	35.1	9.2	9.2	3.7
Ir(CO)I(DBP)				3.7	f	33.3	11.1	9.2	f

^{a} Numbering system for dibut-3-enylphenylphosphine is
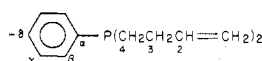
^{b} s = singlet, d = doublet, t = triplet. The solvent in every case was CD$_2$Cl$_2$. ^{c} Obscured by the CD$_2$Cl$_2$ resonances. ^{d} Broadened singlets. ^{e} Not observed. ^{f} Not resolved.

X(DBP) (structure C), MX(TBP), and MX(TPP) (structure D) where M= Rh or Ir and X = halide.[7,32,42] An X-ray structure on the complex RhCl(TBP) has shown that tri-

B

X = Cl or Br

C

M = Rh or Ir;
X = Cl,
Br, or I

D
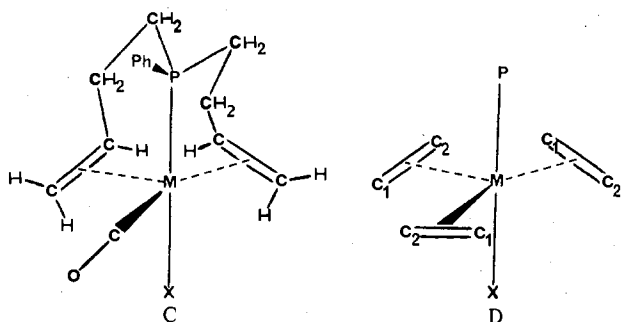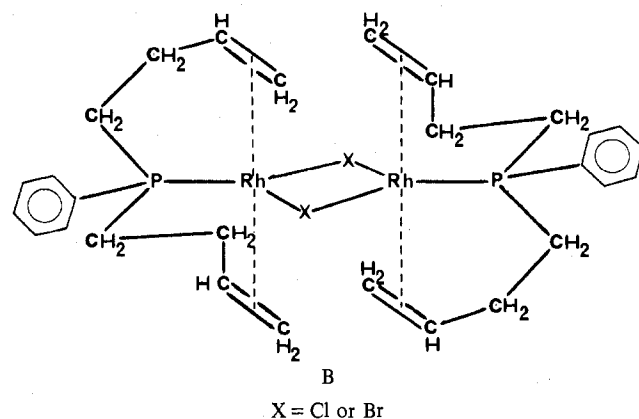
essential features of
the compounds
MX[P(CH$_2$CH$_2$CH=CH$_2$)$_3$],
for M = Rh, X = Cl, Br, or I
and for M = Ir, X = Cl, and
MX[P(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_3$],
for M = Rh, X = Cl or Br
and for M = Ir, X = Cl

but-3-enylphosphine acts as a tetradentate ligand with the phosphorus and chlorine atoms occupying the apical positions and the olefins occupying the equatorial positions of a trigonal-bipyramidal structure.[37]

The ^{13}C NMR spectrum of the ligand dibut-3-enylphenylphosphine (DBP) (Figure 2 and Table II) exhibits three distinct regions: (a) phenyl, C_α 139.0 ppm (J(CP) = 18.5 Hz), C_β 132.8 ppm (J(CP) = 19.4 Hz), C_γ 128.7 ppm (J(CP) = 6.5 Hz), C_δ 129.1 ppm (J(CP) ≈ 0 Hz); (b) methylene, C_3 30.5 ppm (J(CP) = 14.8 Hz), C_4 27.8 ppm (J(CP) = 13.0 Hz); (c) olefinic, C_2 139.5 ppm (J(CP) = 12.0 Hz), C_1 114.4 ppm (J(CP) ≈ 0 Hz). Assignments were made as above for BDPH. The ^{13}C NMR chemical shifts in the complexes (Figure 2) containing the ligand dibut-3-enylphenylphosphine (DBP) are quite similar (see Table II). The resonance for the C_α carbon in the complexes was too low in intensity to be observed. The $J(^{31}P-^{13}C_\beta)$ and $J(^{31}P-^{13}C_\gamma)$ are equivalent or nearly equivalent, but the C_β and C_γ carbons were tentatively assigned as described earlier. No phosphorus coupling to C_δ was observed in the rhodium complexes, but it is 3.7 Hz in Ir(CO)Cl(DBP) and Ir(CO)Br(DBP). This coupling was not resolved in the corresponding iodide complex Ir(CO)I(DBP). The methylene carbon resonance possessing the larger phosphorus coupling was assigned to C_4 (average J(CP) ≃ 30 Hz) and the other to C_3. The changes in the ^{31}P coupling constants to C_4 on complex formation are quite characteristic and similar changes have been observed in uncomplexed and complexed tri-n-butylphosphine [13.4 Hz in the ligand to 25.0 Hz in the complex W(CO)$_5$(P-n-Bu$_3$)] and in uncomplexed and complexed 1,2-bis(diphenylphosphino)ethane [<1.2 Hz in the ligand to 31.8 and 41.5 Hz in the complexes Mo-(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) and W(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$), respectively[47]]. The corresponding decrease in the aliphatic ^2J(CP) has also been observed.[47] The olefinic resonances in all the DBP rhodium complexes were broadened and show no visible coupling at ambient temperatures (~35 °C). Such broadening in the olefinic resonances has been observed previously in rhodium compounds containing tribut-3-enyl-
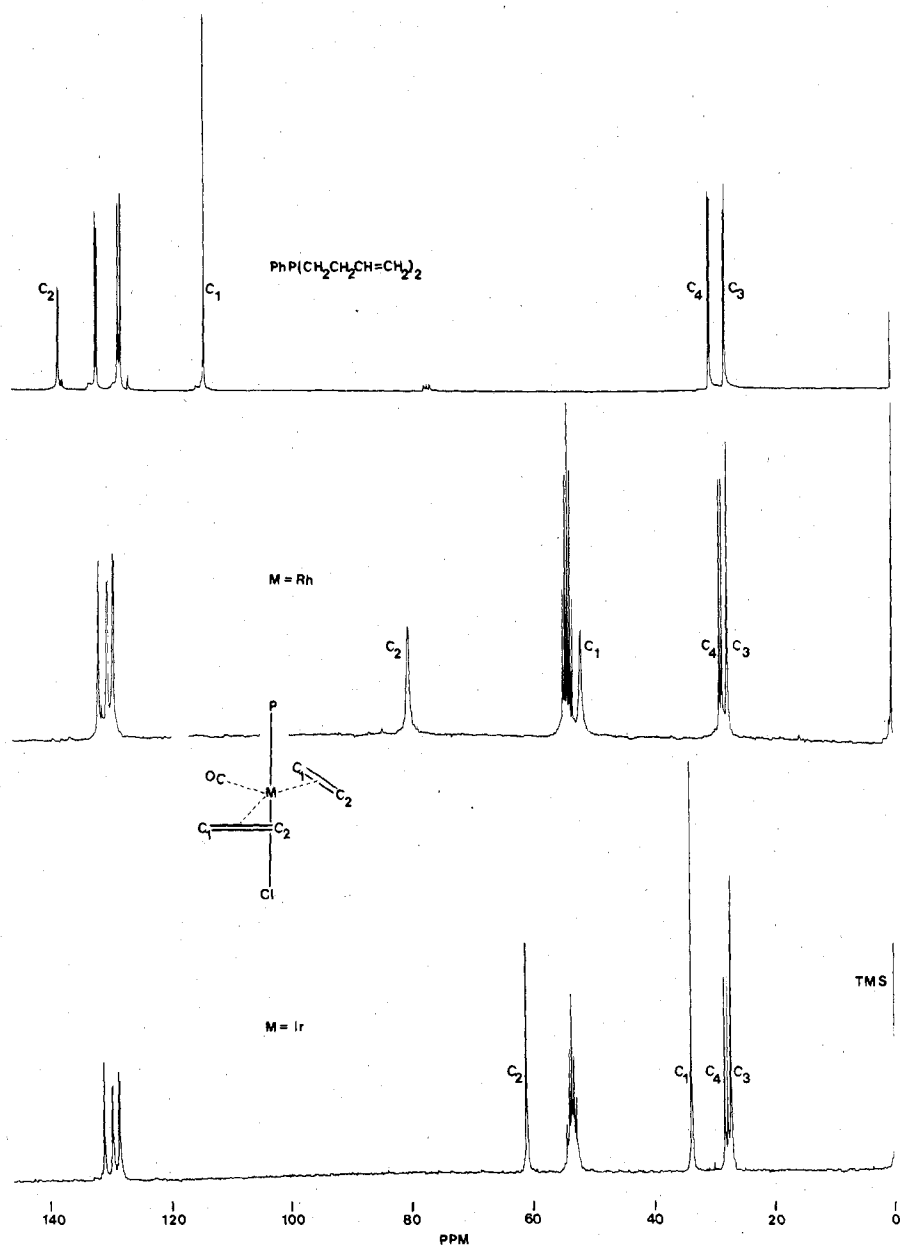
Figure 2. 13C NMR spectra of dibut-3-enylphenylphosphine (DBP), Rh(CO)Cl(DBP), and Ir(CO)Cl(DBP).

phosphine.[25] Low-temperature studies to –60 °C did little to resolve the olefinic part of the spectra, but small rhodium couplings, $J(^{103}Rh-^{13}C) \approx 6$ Hz, were observed in some cases. The olefinic resonances of Rh(CO)I(DBP) occur as triplets due to approximately equal phosphorus and rhodium coupling. The olefinic resonances for the iridium complexes, Ir(CO)-X(DBP), X = halide, are sharp singlets (C_1) and resolved doublets (C_2), the latter arising from 31P coupling. This coupling, $^3J(CP)$, is presumably transmitted via the alkyl chain and not the metal since no 31P coupling was observed at C_1. However, J value angular dependencies (P-Ir-C_2 vs. P-Ir-C_1) cannot be ruled out. The carbonyl resonances were observed by using long pulse delays ($\sim$10 s) or by the addition of tris(acetylacetonato)chromium(III) (0.3 M solution). These resonances are observed at 195 ppm, $J(^{103}Rh-^{13}C) \approx 60$ Hz, and at 177 ppm in the rhodium and iridium complexes, respectively. The chemical shifts and $^{103}Rh-^{13}C$ coupling constants in the Rh cases fall midway between those reported for terminal and bridging carbonyls in rhodium(I) complexes.[49] The 13C NMR spectra of the DBP complexes support the structures originally proposed.[32]

The 13C NMR spectrum of the ligand tribut-3-enyl-phosphine (TBP) (Figure 3) exhibits two regions: (a) methylene, C_4 29.8 ppm ($J(CP)$ = 12.8 Hz), C_3 26.1 ppm ($J(CP)$ = 14.7 Hz); (b) olefinic, C_2 137.7 ppm ($J(CP)$ = 11.0 Hz), C_1 113.2 ppm ($J(CP) \approx 0$ Hz). All three rhodium complexes of this ligand exhibit fluxional behavior. In the complexes RhCl(TBP) and RhBr(TBP), the methylene peaks are quite sharp, but the olefinic resonances are broadened. The latter sharpen at lower temperatures ($\sim$–40 to –60 °C). The fluxional behavior has been related to a partial rotation of the olefin about the rhodium–olefin bond.[25] However, the fluxional behavior occurring in RhI(TBP) is quite different as evidenced by its infrared spectrum in methylene chloride,[7] which shows there is uncoordinated olefin in solution at room temperature. In the solid state, the IR and Raman spectra are similar to those of the closely related dimeric compounds [RhX-(DBP)]$_2$.[32] The molecular weight determination in chloroform (under an atmosphere of nitrogen) shows that RhI(TBP) is monomeric in solution (cf. 7). At lower temperatures (Figure 3) the 13C NMR spectrum of RhI(TBP) is quite similar to those of the chloride and bromide complexes. The IR spectrum
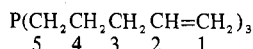
Table III. ^{13}NMR Data of Rhodium and Iridium Complexes Containing the Ligands Tribut-3-enylphosphine,[a] TBP, and Tripent-4-enylphosphine,[a] TPP

Chemical Shifts[b] (ppm)

compd	solvent	C_1	C_2	C_3	C_4	C_5
TBP	CDCl$_3$	113.2 s	137.7 d	26.1 d	29.8 d	
RhCl(TBP)[c]	CDCl$_3$	59.4 d	81.0 t	26.5 s	19.7 d	
RhBr(TBP)[c]	CDCl$_3$	58.9 d	81.7 t	26.8 s	19.8 d	
RhI(TBP)[c]	CD$_2$Cl$_2$	56.7 d	81.6 t	27.3 s	19.4 d	
IrCl(TBP)	CDCl$_3$	45.9 s	66.6 d	28.2 s	18.8 d	
TPP	CDCl$_3$	113.7 s	136.9 s	35.0 d	25.1 d	26.4 d
RhCl(TPP)	CDCl$_3$	55.4 d	78.5 d	16.8 s	29.5 s	22.4 d
RhBr(TPP)	CDCl$_3$	54.4 d	77.6 d	16.7 s	29.4 d	22.4 d
IrCl(TPP)	CD$_2$Cl$_2$	42.0 s	62.6 s	17.8 s	29.1 s	20.3 d

Coupling Constants[b,c] (Hz)

compd	$J(^{103}\text{Rh}-^{13}C_1)$	$J(^{103}\text{Rh}-^{13}C_2)$	$J(^{31}\text{P}-^{13}C_2)$	$J(^{31}\text{P}-^{13}C_3)$	$J(^{31}\text{P}-^{13}C_4)$	$J(^{31}\text{P}-^{13}C_5)$
TBP			11.0	14.7	12.8	
RhCl(TBP)	6.4	6.0	6.0	<1.0	26.6	
RhBr(TBP)	5.5	5.5	5.5	<1.0	27.8	
RhI(TBP)	7.4	5.5	5.5	<1.0	27.8	
RiCl(TBP)			5.5	<1.0	31.4	
TPP			<1.0	11.0	14.7	12.8
RhCl(TPP)	5.5	5.5	<1.0	<1.0	<1.0	33.0
RhBr(TPP)	6.4	5.5	<1.0	<1.0	2.8	32.0
IrCl(TPP)			<1.0	<1.0	<1.0	38.8

[a] Numbering system for tribut-3-enylphosphine is

$$\underset{4\quad3\quad2\quad1}{\text{P(CH}_2\text{CH}_2\text{CH=CH}_2)_3}$$
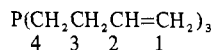
Numbering system for tripent-4-enylphosphine is

$$\underset{5\quad4\quad3\quad2\quad1}{\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2)_3}$$

[b] s = singlet, d = doublet, t = triplet. [c] RhCl(TBP) spectrum measured at −40 °C, RhBr(TBP) spectrum measured at −40 °C, RhI(TBP) spectrum measured at −60 °C.

in solution,[7] the ^{1}H NMR spectrum,[7] the molecular weight determination, and the ^{13}C NMR spectrum of RhI(TBP) are all consistent with the equilibrium (see equilibrium E) between

E
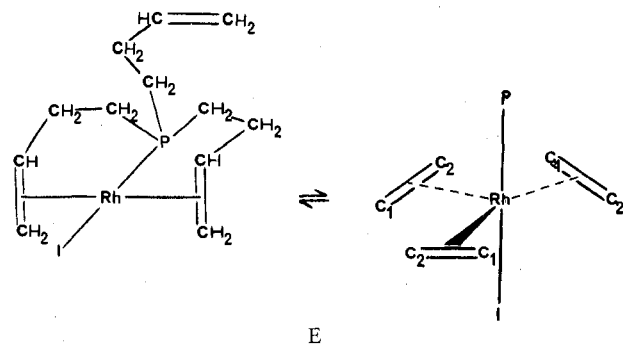
methylene carbons omitted for clarity

coordinated and uncoordinated olefin, and between square-planar and trigonal-bipyramidal stereochemistries.

The iridium complex IrCl(TBP) exhibited no fluxional behavior at ambient temperature which is consistent with the olefin being more firmly bound to iridium than to rhodium.

The ^{13}C NMR spectrum of the ligand tripent-4-enyl-phosphine (TPP) exhibits two regions: (a) methylene, C_5 26.4 ppm (J(CP) = 12.8 Hz), C_4 25.1 ppm (J(CP) = 14.7 Hz), C_3 35.0 ppm (J(CP) = 11.0 Hz); (b) olefinic, C_2 136.9 ppm (J(CP) ≈ 0 Hz), C_1 113.7 ppm (J(CP) ≈ 0 Hz). Neither the rhodium nor the iridium complexes of TPP exhibit fluxional character, which supports the view[7] that this ligand is better at chelating than TBP. That the olefinic carbons are shifted to even higher field (see Table III) in the TPP complexes compared to the TBP complexes suggests that the angle of inclination of the olefin to the equatorial plane is less in the former. The methylene carbons of the ligands TBP and TPP are assigned following earlier trends.[45–47] The C_3 carbon of the TPP complexes shows an unusually high field shift (17

ppm) compared to that in the ligand (35 ppm). It has been pointed out that coordinated TPP would be a very bulky ligand,[7] and thus we suggest that the upfield shift of C_3 in this ligand is probably due to steric factors.

Octahedral Complexes. The ligand *trans*-1,6-bis(diphenylphosphino)hex-3-ene (BDPH) forms octahedral complexes (see structure F) of rhodium(III) and iridium(III)

F
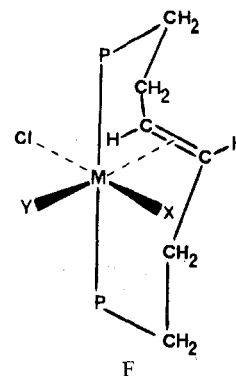
P = PPh$_2$; M = Rh, XY = Cl$_2$, Br$_2$; M = Ir, XY = Cl$_2$, H$_2$, HCl

of the general formula MCl(XY)(BDPH) where M = Rh or Ir and XY = H$_2$, Cl$_2$, HCl, Br$_2$, and MeI.[38,42] We report ^{13}C NMR data on some of the more soluble octahedral complexes in Table I. Besides those listed in Table I, there have been very few rhodium(III) or iridium(III) nonconjugated olefin complexes reported in the literature, and these mostly contain a chelated olefin.[40,50–53]

The ^{13}C NMR spectra of the rhodium(III) and iridium(III) complexes exhibit three distinct regions: (a) phenyl, (b) methylene, and (c) olefinic. For the complexes MCl$_3$(BDPH), M = Rh or Ir, the spectra are comparatively easy to interpret. They comprise two methylene resonances for C_1 and C_2 which are split into triplets by virtual ^{31}P couplings. The olefinic
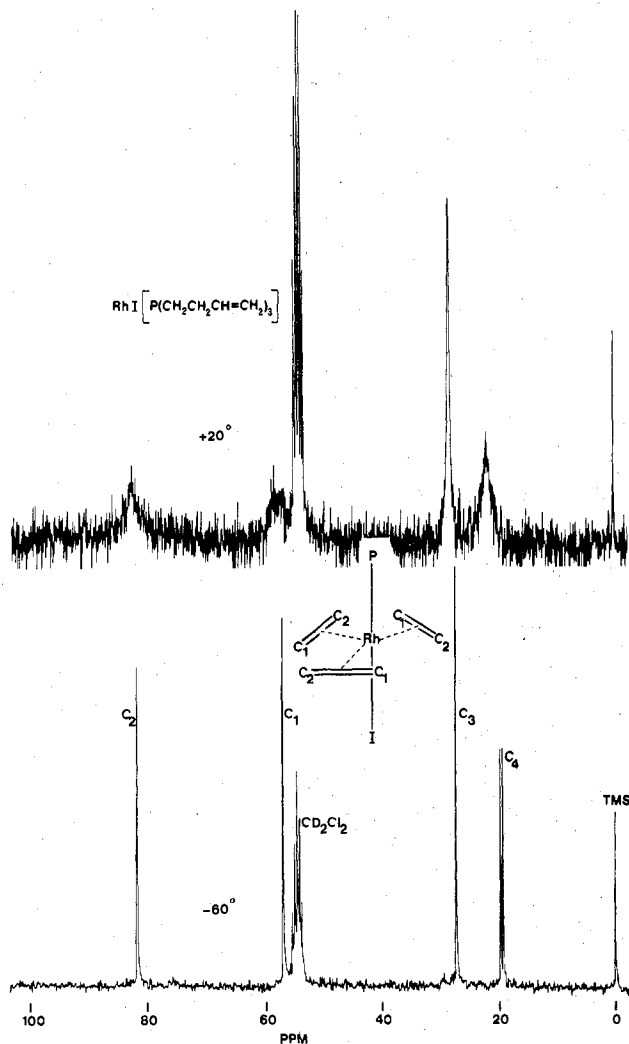
Figure 3. Variable-temperature ^{13}C NMR spectra of RhI(TBP).

Table IV. $\Delta\delta$(C)^a and $\Delta\Delta\delta$(C)^b Values for Rhodium and Iridium Olefin Complexes

compd	$\Delta\delta$(C$_1$)	$\Delta\delta$(C$_2$)	$\Delta\Delta\delta$(C$_1$)	$\Delta\Delta\delta$(C$_2$)
Square-Planar Complexes				
RhCl(BDPH)	68.1			
RhBr(BDPH)	67.0			
RhCl(BDAH)	70.1			
RhCl(C$_2$H$_4$)[P(p-tolyl)$_3$]$_2$ ^{c}	78.2			
[RhCl(C$_8$H$_{12}$)]$_2$ ^{d}	50.0			
IrCl(BDPH)	87.1		19.0	
IrCl(C$_2$H$_4$)(PPh$_3$)$_2$ ^{d,e}	97.8		19.6	
[IrCl(C$_8$H$_{12}$)]$_2$ ^{d}	66.5		16.5	
Trigonal-Bipyramidal Complexes				
RhCl(TBP)	53.8	56.7		
RhBr(TBP)	54.3	56.0		
RhI(TBP)	56.6	56.1		
RhCl(TPP)	58.3	58.4		
RhBr(TPP)	59.3	59.3		
[RhCl(DBP)]$_2$	~60.4	56.0		
[RhBr(DBP)]$_2$	62.8	57.8		
Rh(CO)Cl(DBP)	64.2	60.3		
Rh(CO)Br(DBP)	63.9	60.0		
Rh(CO)I(DBP)	68.2	63.5		
IrCl(TBP)	67.3	71.1	13.5	14.4
IrCl(TPP)	71.7	74.3	13.4	15.9
Ir(CO)Cl(DBP)	80.5	78.1	16.3	17.8
Ir(CO)Br(DBP)	82.0	78.7	18.1	18.7
Ir(CO)I(DBP)	84.7	81.9	16.5	18.4
Octahedral Complexes				
RhCl$_3$(BDPH)	16.7			
cis-RhBr$_2$Cl(BDPH)	14.0	18.1		
trans-RhBr$_2$Cl(BDPH)	15.6			
IrCl$_3$(BDPH)	32.2		15.5	
IrH$_2$Cl(BDPH)	25.8	38.4		
IrHCl$_2$(BDPH)	56.6	65.4		

^{a} $\Delta\delta$(C) is the difference in the chemical shift between the coordinated an uncoordinated olefin measured in ppm. ^{b} $\Delta\Delta\delta$(C) is the difference in the chemical shift between the olefin coordinated in the iridium complex and the olefin coordinated in the corresponding rhodium complex measured in ppm. ^{c} Reference 20, and misquoted as RhCl(C$_2$H$_4$)(PPh$_3$)$_2$ in ref 21. ^{d} This work: for cyclooctadiene, C$_8$H$_{12}$, δ(C)(olefin) = 128.7 ppm [cf. δ(C)-(olefin)^8 = 127.4 ppm], δ(C)(methylene) = 28.3 ppm; for [RhCl-(C$_8$H$_{12}$)]$_2$, δ(C)(olefin) = 78.7, ^{1}J(^{103}Rh-^{13}C) = 13.0 Hz, δ(C)-(methylene) = 30.9 ppm; for [IrCl(C$_8$H$_{12}$)]$_2$, δ(C)(olefin) = 62.2 ppm, δ(C)(methylene) = 31.8 ppm; for IrCl(C$_2$H$_4$)(PPh$_3$)$_2$, δ(C)-(ethylene) = 25.0 ppm. δ(C)(free ethylene) = 122.8 ppm.^{21} ^{e} $\Delta\Delta\delta$(C) value is the difference between the chemical shift of the ethylene in RhCl(C$_2$H$_4$)[P(p-tol)$_3$]$_2$ and IrCl(C$_2$H$_4$)(PPh$_3$)$_2$.

carbons occur at 114.2 ppm (d, J(RhC) = 5.6 Hz) for the rhodium complex and at 98.7 ppm for the iridium complex. The β, γ, and δ carbons of the MCl$_3$(BDPH) exhibit similar patterns to those in the rhodium(I) and iridium(I) square-planar complexes of BDPH. The ^{13}C NMR spectrum of RhBr$_2$Cl(BDPH) is far more complex, but it clearly indicates the presence of both the cis and trans isomers. The cis isomer exists in ca. 20% abundance. The olefinic resonance for the trans isomer occurs at 115.3 ppm while the olefinic resonances for the cis isomer occur at 112.8 and 116.9 ppm. Due to the low solubility of RhBr$_2$Cl(BDPH) not all the resonances were detected. In IrH$_2$Cl(BDPH) (cf. X-ray structure data) and IrHCl$_2$(BDPH), the ^{13}C NMR spectra are consistent with cis products. The four methylene carbon resonances are nonequivalent and are either doublets or doublets of doublets reflecting nonequivalent P atoms. In addition, the olefinic carbons are nonequivalent, occurring at 105.1 and 92.5 ppm in IrH$_2$Cl(BDPH); but in IrHCl$_2$(BDPH) these resonances occur at relatively high field (74.4 and 65.5 ppm) compared to all other Ir(III) complexes (see Table I). The phenyl regions of IrH$_2$Cl(BDPH) and IrHCl$_2$(BDPH) are quite complex. In IrH$_2$Cl(BDPH), the phenyl carbons overlap and are not completely resolved. In IrHCl$_2$(BDPH), the phenyl resonances are well resolved, and the β, γ, and δ carbons occur as four resonances with ^{31}P coupling to the β and γ carbons.

Discussion

In general, the ^{13}C NMR parameters of the complexes we have studied support the Dewar–Chatt–Duncanson model (see

Introduction) of metal–olefin bonding. The difference between the ^{13}C chemical shift of the complexed and uncomplexed ligand provides the coordination-induced shift values, $\Delta\delta$(C), and these are summarized in Table IV. Since similar coordination-induced shifts have previously been correlated with M–C distances in rhodium[28] and platinum complexes,[12,27] we shall focus our attention on this parameter. From the $\Delta\delta$(C) values presented in Table IV it is possible to draw a series of generalizations.

Changes in stereochemistry of the metal complex and in the oxidation state of the metal are reflected in the $\Delta\delta$(C) values, presumably the consequences of changes in electron density at the metal. Thus the following orders are established: (a) $\Delta\delta$(C) Rh(I) square planar (~70 ppm) < $\Delta\delta$(C) Ir(I) square planar (~90 ppm), $\Delta\delta$(C) Rh(I) trigonal bipyramidal (~59 ppm) < $\Delta\delta$(C) Ir(I) trigonal bipyramidal (~77 ppm), $\Delta\delta$(C) Rh(III) octahedral (~16 ppm) < $\Delta\delta$(C) Ir(III) octahedral (~32 ppm); (b) $\Delta\delta$(C) M(I) square planar > $\Delta\delta$(C) M(I) trigonal bipyramidal ≫ $\Delta\delta$(C) M(III) octahedral, where M = Rh or Ir.

The above two orders of $\Delta\delta$(C) values also reflect the normal trends that would be expected in the availability of electron

density for back-bonding to the olefin. Further, the change in the relative coordination-induced shifts between rhodium and the analogous iridium complex, $\Delta\Delta\delta(C)$ (see Table IV), appears to be reasonably uniform, ~16.7 ppm.[54] A similar effect ($\Delta\Delta\delta(C) \approx 20$ ppm) can be calculated between palladium and platinum complexes.[15] It is well established that the M–C distances are comparable in rhodium and iridium complexes of the same stereochemistry and oxidation state containing similar olefinic ligands.[38,44,55] Thus we suggest that the $\Delta\delta(C)$ values reflect the relative ability of the metal to back-bond. That is, Ir > Rh in its ability to back-bond, and the $\Delta\Delta\delta(C)$ value is positive in going from rhodium to iridium. As a corollary to the above generalizations we add (c) that the value of the ^{103}Rh–^{13}C coupling constants (Tables I–III) reflect the changes in the metal–olefin bond, in particular, with changes in stereochemistry. Spin-coupling interactions are largely dependent upon Fermi contact. Hence the degree of orbital overlap in the metal–olefin bond or the hybridization of the metal is reflected in the magnitude of the M–^{13}C coupling constant. Here we note $^{1}J(RhC)$ for Rh(I) square-planar complexes {dsp^2} > $^{1}J(RhC)$ for Rh(I) trigonal-bipyramidal complexes {dsp^3} ≥ $^{1}J(RhC)$ for Rh(III) octahedral complexes {d^{2}sp^3}. Following the analogy between the rhodium and iridium complexes, one would expect that the degree of orbital overlap in the iridium–olefin bonds would follow an order similar to that defined by the $^{1}J(RhC)$ values in the corresponding rhodium complexes.

The structures of some of the complexes described in this paper have been verified by X-ray analyses. These are the complexes IrCl(BDPH),[38] IrCl(C_2H_4)(PPh$_3$)$_2$,[44] RhCl(TBP),[37] and IrH$_2$Cl(BDPH).[38] In an earlier paper[38] we have shown that the olefinic double bond in IrCl(BDPH) is oriented at an angle of 80.2° in the plane containing the two phosphorus atoms, the iridium, and the chlorine atoms. The Ir–C distance is 2.09 Å while the C=C distance is 1.42 Å. These values compare with the corresponding ones in the complex IrCl-(C_2H_4)(PPh$_3$)$_2$, 92.3°, 2.12 Å, and 1.38 Å, respectively.[44] In RhCl(TBP), the rhodium to olefinic carbon distances are Rh–C_1 = 2.23 and Rh–C_2 = 2.26 Å, and the olefin is oriented at an angle (average) of 13.7° with respect to the equatorial plane. In IrH$_2$Cl(BDPH), the Ir–C distances are also unequal, 2.28 and 2.34 Å, while the C=C distance is 1.34 Å.[38] In addition, the olefin in IrH$_2$Cl(BDPH) is inclined at an angle of 40.2° with respect to the plane containing the two phosphorus atoms and the iridium atom. In all of the above compounds, the angle of orientation of the olefinic bond is different from that in which back-bonding would be maximized (90 or 0°), presumably due to the structural constraints of the ligand. We suggest that it is this parameter which would bear closer analysis concerning the coordination-induced ^{13}C shifts, since the angle of orientation of the olefinic bond will also reflect the degree of orbital overlap between the metal and the olefinic bond.

The asymmetry in the olefinic carbon to metal bond distances, in particular, in the octahedral complex IrH$_2$Cl(BDPH), is reflected in the large chemical-shift separation of the olefinic carbon atoms (92.5 and 105.1 ppm). The fact that the $\Delta\delta(C)$ values (Table IV) for this octahedral complex (average 29.5 ppm) are much smaller than the $\Delta\delta(C)$ values for the square-planar and trigonal-bipyramidal complexes ($\Delta\delta(C) \approx 50$–90 ppm) can be attributed to the differences in stereochemistry and oxidation state. Since the metal–olefin carbon distances in IrH$_2$Cl(BDPH) are greater than those in IrCl(BDPH) and the angle of orientation of the olefin in IrH$_2$Cl(BDPH) is 40.2° with respect to the plane containing the two phosphorus atoms and the iridium atom, the back-bonding from the metal to the olefin carbons will be minimized in IrH$_2$Cl(BDPH). Clearly, these results demonstrate that

the $\Delta\delta(C)$ values are a complex function of stereochemistry, oxidation state, M–C distance, and the degree of metal–olefin orbital overlap.

At this point it seems appropriate to comment on some previous ^{13}C NMR work involving the relationship of M–C distance to $\Delta\delta(C)$ values.[12,16,28] We reiterate the view, originally expressed in 1974 by Evans and Norton,[12c] that the "current" level of understanding of the ^{13}C chemical shift data of carbon nuclei bonded to metals is lacking in direct considerations concerning the contributions made by the metal. Further, we note that the consideration of the total screening constant of the carbon nucleus in terms of atomic components, following Karplus and Pople,[56] inevitably will lead to approximate distance-dependent relationships whether the σ_p (paramagnetic) and/or the σ_d (diamagnetic) terms are considered, since both the σ_p and σ_d screening components contain the elements of electron density as related to the radius of the appropriate orbital. In the case of the metal hydrides, discussed by Buckingham et al.,[57] it may appear reasonable to assume that the radius of the hydrogen s orbital will correlate with the M–H distance, but no distance–shift correlation emerges.[12c] For the olefinic carbon bound to a metal, analogous distance approximations using Buckingham's theory involving the Dewar–Chatt–Duncanson[1,2] model of carbon pπ to metal d-orbital overlap are clearly inappropriate since we have shown above that the $\Delta\delta(C)$ value is a complex function not only of M–C distance but also of stereochemistry, oxidation state, and the orientation of the olefin.

The ^{13}C chemical shifts of coordinated olefins (the coordination-induced shifts) have little but qualitative significance in describing the bonding between the metal and the olefin as long as the theory neglects the interactive contributions made by the metal. Clearly, within a given ligand series the coordination-induced shifts can be related to the oxidation state of the metal and the stereochemistry of the metal–olefin complex and hence provide a relative picture to the degree of back-bonding as described by Dewar, Chatt, and Duncanson. The M–^{13}C coupling constants also define these features and appear to have more validity than the shifts in describing the bonding mode in the complexes.

References and Notes

(1) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).
(2) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).
(3) D. B. Powell, J. G. V. Scott, and N. Sheppard, *Spectrochim. Acta, Part A*, **28**, 327 (1972).
(4) P. W. Clark, *J. Organomet. Chem.*, **110**, C13 (1976), and references therein.
(5) M. L. H. Green, "Organometallic Chemistry", Vol. 2, Methuen and Co. Ltd., London, 1968, p 31.
(6) See, for example, M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).
(7) P. W. Clark and G. E. Hartwell, *J. Organomet. Chem.*, **97**, 117 (1975).
(8) C. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).
(9) R. G. Parker and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 743 (1970).

(10) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(11) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972).
(12) (a) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972); (b) D. G. Cooper and J. Powell, *Inorg. Chem.*, **15**, 1959 (1976); (c) J. Evans and J. R. Norton, *ibid.*, **13**, 3042 (1974).
(13) K. R. Aris, V. Aris, and J. M. Brown, *J. Organomet. Chem.*, **42**, C67 (1972).
(14) (a) C. D. M. Beverwijk and J. P. C. M. Van Dongen, *Tetrahedron Lett.*, 4291 (1972); (b) J. P. C. M. Van Dongen and C. D. M. Beverwijk, *J. Organomet. Chem.*, **51**, C36 (1973).
(15) D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J. Chem. Soc., Chem. Commun.*, 499 (1973).
(16) R. P. Hughes and J. Powell, *J. Organomet. Chem.*, **60**, 427 (1973).
(17) R. G. Solomon and J. K. Kochi, *J. Organomet. Chem.*, **64**, 135 (1974).
(18) L. Kruczynski, J. L. Martin, and J. Takats, *J. Organomet. Chem.*, **80**, C9 (1974).
(19) W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1405 (1974).
(20) C. A. Tolman, P. Z. Meakin, D. L. Linder, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
(21) C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, **14**, 2353 (1975).
(22) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **97**, 721 (1975).
(23) T. Iwayanagi and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **11**, 459 (1975).
(24) L. E. Manzer, *Inorg. Chem.*, **15**, 2354 (1976).
(25) P. W. Clark and A. J. Jones, *J. Organomet. Chem.*, **122**, C41 (1976).
(26) P. Powell and L. J. Russell, *J. Organomet. Chem.*, **129**, 415 (1977).
(27) D. G. Cooper and J. Powell, *Inorg. Chem.*, **16**, 142 (1977).
(28) R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, and G. Turner, *Inorg. Chem.*, **16**, 314 (1977).
(29) G. E. Hartwell and P. W. Clark, *Chem. Commun.*, 1115 (1970).
(30) P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, **9**, 1948 (1970).
(31) P. W. Clark, J. L. S. Curtis, P. E. Garrou, and G. E. Hartwell, *Can. J. Chem.*, **52**, 1711 (1974).
(32) P. W. Clark and G. W. Hartwell, *J. Organomet. Chem.*, **96**, 451 (1975).

(33) R. R. Ryan, R. Schaeffer, P. Clark, and G. E. Hartwell, *Inorg. Chem.*, **14**, 3039 (1975).
(34) P. W. Clark and G. E. Hartwell, *J. Organomet. Chem.*, **102**, 387 (1975).
(35) P. W. Clark, *J. Organomet. Chem.*, **137**, 235 (1977).
(36) P. W. Clark and G. E. Hartwell, *J. Organomet. Chem.*, **139**, 385 (1977).
(37) M. Orrico Vischer, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, **13**, 792 (1974).
(38) G. R. Clark, P. W. Clark, A. J. Jones, and D. Russell, *J. Organomet. Chem.*, **166**, 109 (1979).
(39) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(40) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966).
(41) A. van der Ent and A. L. Onderdelinden, *Inorg. Chim. Acta*, **7**, 203 (1973).
(42) G. R. Clark and P. W. Clark, *J. Organomet. Chem.*, in press.
(43) See, for example, A. J. Jones, J. A. Elix, and U. Engkaninan, *Aust. J. Chem.*, **29**, 1947 (1976).
(44) R. J. Restivo, G. Ferguson, T. L. Kelly, and C. V. Senoff, *J. Organomet. Chem.*, **90**, 101 (1975).
(45) B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, 30 (1972).
(46) J.-R. Llinas, E.-J. Vincent, and G. Peiffer, *Bull. Soc. Chim. Fr.*, 3209 (1973).
(47) P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1027 (1973).
(48) E. D. Becker, "High Resolution N.M.R. Spectroscopy", Academic Press, New York, 1969, p 163.
(49) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974).
(50) A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Commun.*, 712 (1971).
(51) F. Glockling and G. C. Hill, *J. Chem. Soc. A*, 2137 (1971).
(52) R. N. Haszeldine, R. J. Lunt, and R. V. Parish, *J. Chem. Soc. A*, 3711 (1971).
(53) M. A. Bennett, R. N. Johnson, and I. B. Tomkins, *J. Organomet. Chem.*, **118**, 205 (1976).
(54) The averaged value of $\Delta\Delta\delta(C)$ includes the values from [RhCl(C$_8$H$_{12}$)]$_2$ vs. [IrCl(C$_8$H$_{12}$)]$_2$ and RhCl(C$_2$H$_4$)(PPh$_3$)$_2$ vs. IrCl(C$_2$H$_4$)[P(p-tol)$_3$]$_2$.
(55) M. A. Bennett, P. W. Clark, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1011 (1972).
(56) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
(57) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747, 4583 (1964).

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μ-Ligand-μ-peroxo-dicobalt(III) Cations

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Potentiometric, ultraviolet–visible, and nuclear magnetic resonance studies of the oxygenation of aqueous solutions of 5:2 and 3:1 molar ratios of ethylenediamine (en) to Co(II) indicate that the equilibrium product is tetrakis(ethylenediamine)-μ-(ethylenediamine)-μ-peroxo-dicobalt(III) (I). The log of the overall formation constant of I is 37.1 (M^{-6} atm^{-1}). Studies also indicate the oxygenation of 2:2:1 and 2:1:3 Co(II) to triethylenetetramine (trien) to ethylenediamine solutions results in the formation of [Co$_2$trien(en)(O$_2$)$^{4+}$] (II) and of I and II, respectively.

Introduction

In biological systems iron(II) (e.g., hemoglobin and myoglobin) or copper(I) (hemocyanin) complexes serve as reversible oxygen carriers for transport and storage of oxygen. Simple low molecular weight metal chelates containing these ions seldom exhibit reversible oxygenation properties.[2] Cobalt(II), however, forms many simple complexes which react reversibly with oxygen to form 1:1 and 2:1 metal complex to oxygen adducts which have been widely studied as models for biological systems.[3] Although two reports[4,5] have invoked μ-ethylenediamine type linkages in μ-peroxo-dicobalt(III) cations, the evidence offered for their existence was not convincing. A third report,[6] however, on the isolation of a salt of the tetrakis(ethylenediamine)-μ-peroxo-μ-(ethylenediamine)-dicobalt(III) cation was more encouraging. We now report potentiometric, ultraviolet–visible, and nuclear magnetic resonance studies of the formation of μ-ethylenediamine bridges in addition to a μ-peroxo bridge in oxygenated Co(II) solutions containing ethylenediamine, diethylenetriamine, and triethylenetetramine. Before designing ligands to hold two

Co(II) centers that are favorably disposed for interaction, i.e., to bind 1 mol of O$_2$, it was necessary to examine the ability of μ-peroxo-dicobalt(III) cations to form μ-ligand bridges.

Experimental Section

Reagents. The hydrochloride salts of ethylenediamine (en), 3-azapentylene-1,5-diamine (diethylenetriamine, dien), and 3,6-diazaoctylene-1,8-diamine (triethylenetetramine, trien) were prepared in the usual manner.[7] Ethanolic water solutions of the ligands were cooled and stirred in a salt–ice bath. Six molar hydrochloric acid was added slowly to the solutions to prevent sudden increases in the temperatures of the solutions. Crystals of the dihydrochloride salt of ethylenediamine and the trihydrochloride of diethylenetriamine precipitated out of solution slowly. Second and third crops of the salts were obtained by successive additions of 95% ethanol. The polyamine salts were recrystallized from water–ethanol solutions three times and then dried.

The triethylenetetramine solution was cooled to 1 °C. The 6 M hydrochloric acid was added very slowly in order to keep the temperature of the solution below 10 °C. This was done to take advantage of the low solubility of the hydrochloride salt of β,β′,β″-triaminotriethylamine (tren), a major contaminant of triethylenetetramine.