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SYNTHESIS AND VARIABLE TEMPERATURE ^{31}P NMR SPECTRA OF THE COBALT, RHODIUM AND IRIDIUM COMPLEXES $[M(P(O)(OMe)_2)(P(OMe)_3)_4]$ (M = Co, Rh, Ir)

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Summary

Syntheses of $[M(P(O)(OMe)_2)(P(OMe)_3)_4]$ (M = Co,Rh,Ir) and variable temperature ^{31}P NMR studies are described, and mechanistic implications discussed.

Introduction

Several years ago we reported [1,2] that in addition to olefin displacement both indenyl and cyclopentadienyl groups are displaced during reactions of an excess of trimethylphosphite with $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ and $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$. The only product from these reactions was originally formulated as the dinuclear complex $[Rh_2(P(OMe)_3)_8]$, largely on the basis of ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of the reaction product (Fig. 1), consisted of a doublet of doublets and a five line multiplet, (assigned as a superimposed doublet of quartets). The spectrum was consistent with a structure involving two trigonal bipyramids joined at axial positions, i.e. containing six equivalent equatorial (L_{eq}) and two axial (L_{ax}) phosphite groups, the doubleting in the ^{31}P NMR spectrum being due to the rhodium nucleus, (^{103}Rh, $I = \frac{1}{2}$, 100% abundance). It was suggested that $[Rh_2(P(OMe)_3)_8]$ was rigid at room temperature, but underwent an intermolecular ligand exchange process with free phosphite at 100°C.

Subsequently the dinuclear cobalt complex $[Co_2(P(OMe)_3)_8]$ was described by Muetterties and co-workers [3], who obtained it from the disproportionation of the unstable $[Co(SiMe_3)(P(OMe)_3)_4]$ compound, and it was also reported to be non-fluxional, due to severe steric crowding around each metal atom.

In order to extend the work, indenyl olefin complexes of iridium were reacted with $P(OMe)_3$, in reactions identical to those reported for the rhodium compounds. However the results obtained showed clearly that the reaction product was not

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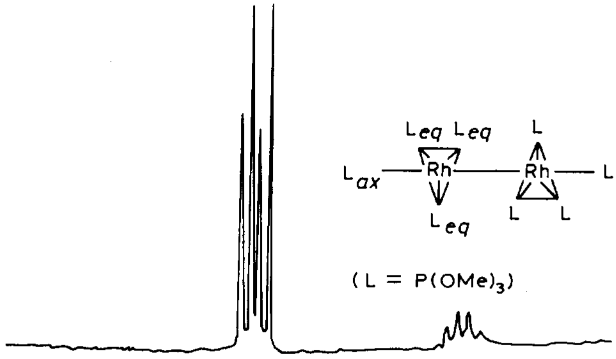


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum and proposed structure for the product from the reaction of $P(OMe)_3$ with $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ [1,2].

$[Ir_2(P(OMe)_3)_8]$ but instead the phosphonate compound $[IrP(O)(OMe)_2(P(OMe)_3)_4]$, (vide infra) thereby necessitating a reinvestigation of the earlier work. While this study was in progress, the cobalt phosphonate complex $[CoP(O)(OMe)_2(P(OMe)_3)_4]$ was reported using a different synthetic route involving sodium amalgam reduction of $CoCl_2$ in the presence of an excess of $P(OMe)_3$ [4–6].

Results and discussion

In contrast to the unreactive $[Ir(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ complex addition of $P(OMe)_3$ to the indenyl iridium alkene complexes $[Ir(\eta^5\text{-}C_9H_7)(L)_2]$ ($L = C_2H_4$, C_8H_{14}; $(L)_2 = C_8H_{12}$), leads to ready displacement of the alkene and the indenyl group. The product which is an off-white oily material, showed ^1H NMR resonances due only to coordinated phosphite groups. The IR spectrum of the metallic complex was uninformative but the $^{31}P\{^1H\}$ NMR of the complex at room temperature showed a pattern (Fig. 2) similar to that previously assigned to $[Rh_2(P(OMe)_3)_8]$, but with the multiplet consisting of five lines.

The quintet pattern in the $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2(P(OMe)_3)_8]$ (Fig. 1) had been originally assumed to be caused by the near coincidence of the values for the couplings $^1J(Rh\text{-}P_{ax})$ and $^2J(P_{eq}\text{-}P_{ax})$. However, the absence of any nuclear spin in the iridium nucleus, made inexplicable the presence of five lines (with second order splittings in the centre of the multiplet) in the spectrum of the iridium complex (Fig. 2). It was also noted that the relative intensity of the two types of phosphorus present in the $^{31}P\{^1H\}$ NMR spectrum of the iridium complex, was always significantly bigger than the expected ratio of 3/1 for $[Ir_2(P(OMe)_3)_8]$ in measurements made on a number of separate samples.

In order to try to resolve the problem the $^{31}P\{^1H\}$ NMR spectrum of the product of the reaction of $[Rh(\eta^5\text{-}C_9H_7(C_2H_4)_2]$ and $P(OMe)_3$ was re-examined at higher resolution (Fig. 3) and revealed an extra weak line in the spectrum. Thus both the $^{31}P\{^1H\}$ NMR spectra shown correspond with spin systems of the types $[A_4M]$ and $[A_4MX]$ respectively, (A, $M = {}^{31}P$; $X = {}^{103}Rh$), and indicate that both complexes contain one group which is different from the other four. Molecules of the type $[MX\{P(OMe)_3\}_4]$ have been synthesized by Muetterties and co-workers, (M = Co;

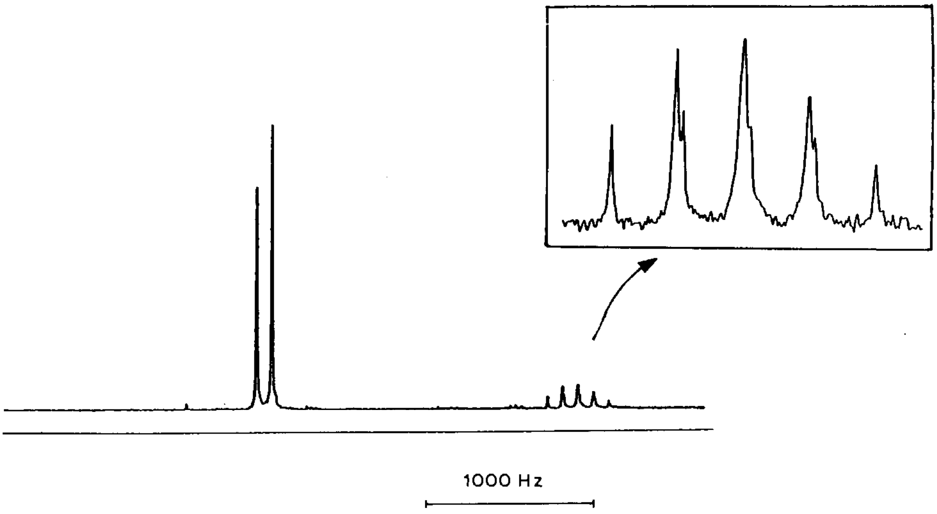


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of the sole metal-containing product of the reaction $[Ir(\eta^5-C_9H_7)(C_2H_4)_2] + P(OMe)_3$, excess.

X = a σ-bonded, one-electron donor ligand such as CH_3 and H) [3]. Two possibilities were considered for the $(MX(P(OMe)_3)_4]$; complexes in which the unique phosphorous containing group could be either a phosphido-type $(P(OMe)_2)$, or a phosphonate type $(P(O)(OMe)_2)$. Micro-analytical data for the iridium complex are summarized in Table 1, together with the values calculated for a phosphido and a phosphonate mononuclear compound, and for the dinuclear complex $[Ir_2(P(OMe)_3)_8]$.

It is clear from Table 1 that the analytical data for all three types of complexes

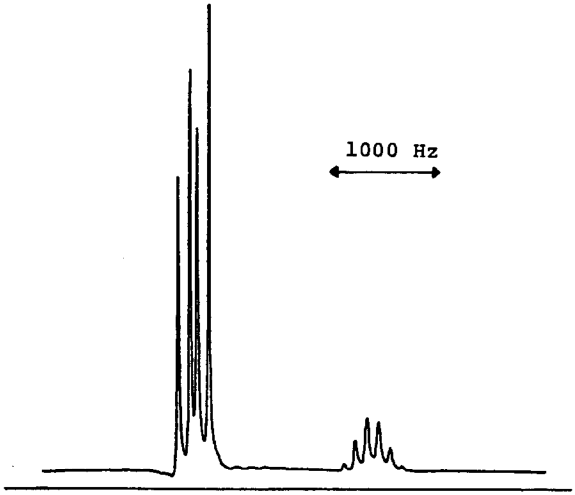


Fig. 3. The complete $^{31}P\{^1H\}$ NMR spectrum of the product of the reaction between $Rh(\eta^5-C_9H_7)(C_2H_4)_2]$ and $P(OMe)_3$.

TABLE 1

THEORETICAL ANALYTICAL DATA

Possible formula	%C	%H
$[Ir_2(P(OMe)_3)_8]$	20.93	5.27
$[IrP(OMe)_2(P(OMe)_3)_4]$	21.49	5.37
$[IrP(O)(OMe)_2(P(OMe)_3)_4]$	21.08	5.30
Found:	21.14	5.29

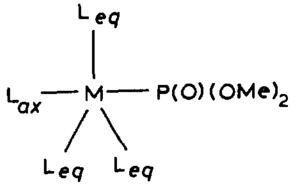
listed are very similar, with the best fit being the mononuclear iridium(I) complex $[IrP(O)(OMe)_2(P(OMe)_3)_4]$.

The presence of a σ-bonded phosphonate group in the iridium complex was not clearly indicated by IR spectroscopy. Infra-red data on transition-metal phosphonate complexes reported in the literature suggest that $\nu(P=O)$ usually lies in the range 1100–1200 cm^{-1} [7–9]. An analytically pure sample of $[IrP(O)(OMe)_2(P(OMe)_3)_4]$ showed a weak band at 1251 cm^{-1}, which is tentatively assigned to the $\nu(P=O)$ stretching mode.

The presence of a σ-bonded phosphonate group in the rhodium and iridium complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$, (M = Rh, Ir) was more clearly indicated by ^{31}P NMR spectroscopy (see Table 2) by analogy with the work of Rowan [8], Malisch [10] and Haines [11] who all quote an upfield phosphorus chemical shift of at least 50 ppm for a transition-metal σ-bonded phosphonate group, in relation to the chemical shift of the remaining phosphites in the molecule. In addition, Muetterties and co-workers [12,13] quote a downfield shift of 50 ppm for the rather rare phosphido-type complex $[WP(OMe)_2(P(OMe)_3)_5]^+$, and a downfield shift of about 90 ppm for the axial phosphites in relation to the equatorial groups in $[Co_2(P(OMe)_3)_8]$ [3].

An important implication of mononuclear five coordinated complexes of the cobalt triad, $[MP(O)(OMe)_2(P(OMe)_3)_4]$, (M = Co, Rh, Ir), is that they should be stereochemically non-rigid. Extensive studies of the fluxional behaviour of structurally related five-coordinated complexes of the type $[MH(phosphite)_4]$ (M = Co, Rh) and $[M(phosphite)_5]^+ BPh_4^-$ (M = Co, Rh, Ir), have been carried out [14–16]. In the latter series fluxional mechanisms have been proposed. Accordingly, in the present work all three complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$, (M = Co, Rh, Ir), were found to be fluxional on the NMR time scale, and Figs. 5 and 6 show the changes in the $^{31}P\{^1H\}$ NMR spectrum for the Rh and Ir complexes respectively, at different temperatures. The $^{31}P\{^1H\}$ NMR spectrum of the Co complex at room temperature consists of two broad singlets and the quadrupole effects associated with the cobalt nucleus (^{59}Co spin $\frac{7}{2}$, 100% abundant), leads to a featureless ^{31}P NMR spectrum at temperatures above the slow exchange limit of the complex. Figure 4 shows this slow exchange limit $^{31}P\{^1H\}$ NMR spectrum for the complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$, (M = Co, Rh, Ir), together with their calculated best fit spectra. The relevant chemical shift and coupling constant parameters are listed in Table 2.

The $^{31}P\{^1H\}$ NMR spectrum spectra of the phosphonate complexes of Co, Rh and Ir at their slow exchange limit can be explained assuming that the structure is based on a trigonal bipyramidal geometry of ligands around the central metal, with the phosphonate group occupying an axial position, (C_{3v} symmetry) shown below.



(M = Co, Rh, Ir)

The $^{31}P\{^1H\}$ NMR spectrum of the iridium complex at −70°C is particularly instructive (Fig. 6). The central large triplet is in fact a partially superimposed doublet of doublets and arises from the three equatorial L_{eq} ligands, the doubling being due to spin–spin coupling with the axial phosphite and phosphonate groups ($^2J(L_{ax}–L_{eq})$ 57.8, $^2J(L_{eq}–P(O)(OMe))$ 55.8 Hz). These two appear as a quartet, due to their coupling to the three equivalent *cis*-phosphite groups L_{eq}, which is further doubleted by a large *trans* coupling ($^2J(P_{ax}–P(O)(OMe)_2)$ −569.1 Hz). It is interest-

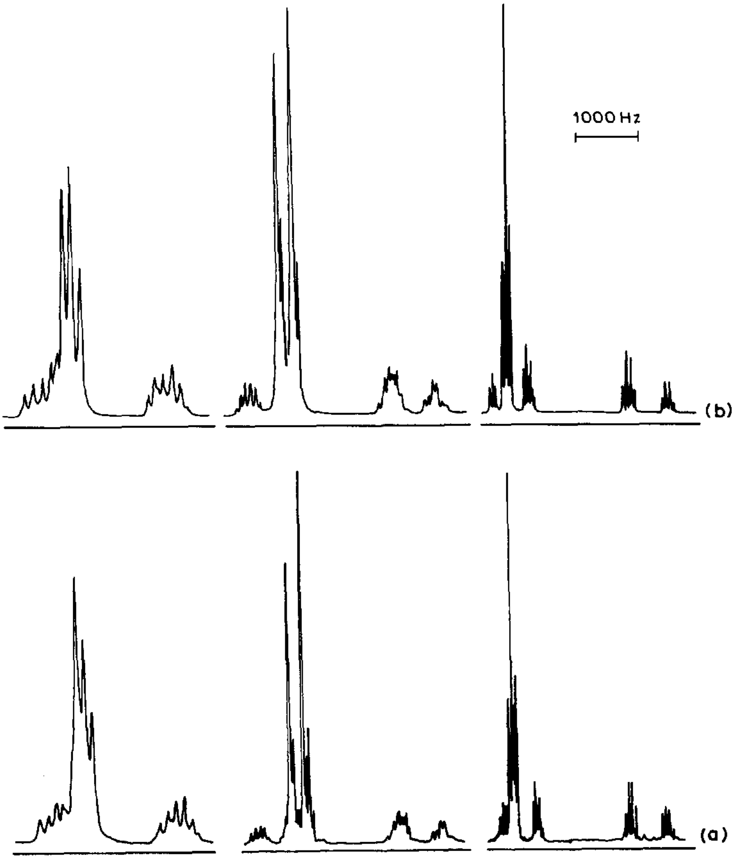


Fig. 4. Experimental (a) and calculated (b) slow-exchange limit $^{31}P\{^1H\}$ NMR spectra of $[MP(O)(OMe)_2(P(OMe)_3)_4]$ complexes. Left to right, M = Co, Rh, Ir. Spectroscopic data in Table 2.

TABLE 2

^{31}P NMR DATA[a] FOR COMPLEXES [MP(O)(OMe)$_2$(P(OMe)$_3$)$_4$] (M = Co, Rh, Ir)

All NMR spectra run at 32.4 MHz, samples prepared in toluene with P(OMe)$_3$/C$_6$D$_6$ as reference and lock signal (external). Calculated parameters obtained with the use of PANIC·80 program from Bruker Spectrospin

M	$\delta(L_{ax})$	$\delta(L_{eq})$	δ(P(O)(OMe)$_2$)	$^3J(RhL_{ax})$	$^1J(RhL_{eq})$	^1J(RhP(O)(OMe)$_2$)	$^2J(L_{ax}L_{eq})$	$^2J(L_{ax}$P(O)(OMe)$_2$)[b]	$^2J(L_{eq}$P(O)(OMe)$_2$)	Temp. (°C)	Ref.
Co	+14.9	+14.9	−33.5	–	–	–	–	–	–	27	4,5
	28.0	13.0	−31.1	–	–	–	137.6	275.2	137.6	−70	4,5
	29.0	13.3	−33.4	–	–	–	151.5	−275.0	127.9	−70	This work
Rh				200	200	122	–	122	122	R.T.	1
	4.4	4.4	−53.8	200.2	200.2	219.7	–	119.6	119.6	36	This work
	12.7	5.3	−54.3	148.7	221.4	118.5	72.6	−647.2	58.3	−70	This work
Ir	−32.2	−32.2	−96.1	–	–	–	–	obs 102.5	obs 102.5	36	This work
								calcd. 99.9	calcd. 99.9	36	This work
	−31.0	−28.5	−93.1	–	–	–	57.8	−569.1	55.8	−70	This work

[a] Literature values corrected for P(OMe)$_3$ as standard. [b] Minus sign indicates the coupling differs in sign from the others, as indicated by spectrum calculation.

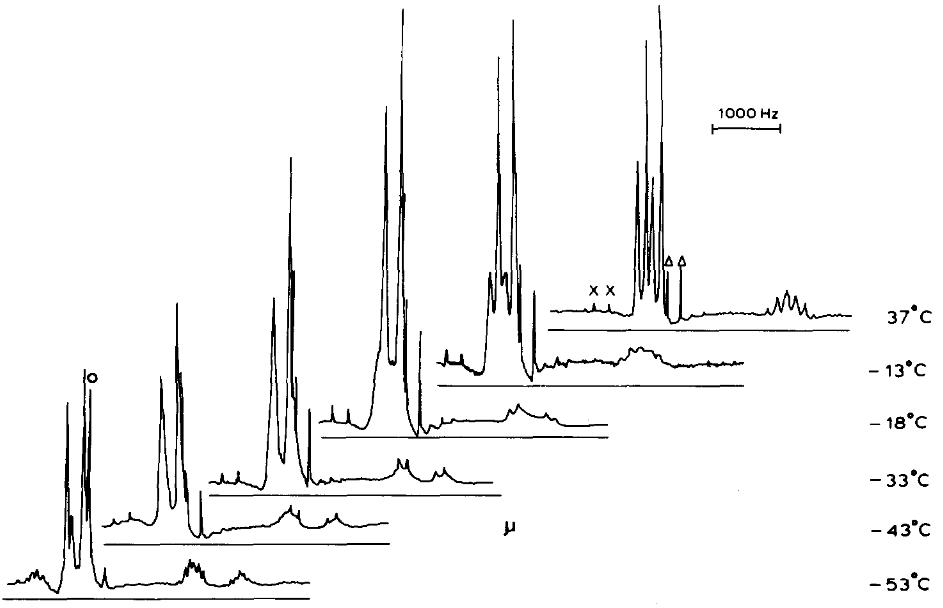


Fig. 5. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of $[RhP(O)(OMe)_2(P(OMe)_3)_4]$ at selected temperatures (°C). $\Delta = [Rh(P(OMe)_3)_5]^+ Cl^-$; $O = P(OMe)_3$; $\times = [RhH(P(OMe)_3)_4]$.

ing to compare the spectroscopic data of the phosphonate complexes of Co, Rh and Ir obtained after successful spectrum simulations (Table 2), with the data reported for the parent five-coordinate cationic complexes $[M(P(OMe)_3)_5]^+ BPh_4^-$ (M = Co, Rh, Ir), of similar low-temperature geometry [15]. In the latter compounds the *cis* ^2J(PP) coupling constants are 148, 68 and 59 Hz for Co, Rh, and Ir respectively, and these values agree well with the presently observed values of $^2J(L_{ax}-L_{eq})$ (151.5, 72.6 and 57.8 Hz) respectively. The *cis* couplings $^2J(L_{eq}-P(O)(OMe)_2)$ were found to be slightly smaller (127.9, 58.3 and 55.8 Hz), for the same sequence Co, Rh and Ir.

As the temperature is increased (Figs. 5, 6), the axial phosphite resonances begin to merge into the resonances of the three equatorial groups, as an intramolecular pseudo-rotation of the groups around the metal sets in. At room temperature, this pseudo-rotation interconverts the sites of the ligands rapidly making all four phosphite groups appear equivalent. The $^{31}P\{^{1}H\}$ NMR spectrum thus simplifies into an $[A_4M]$ type, ($[A_4MX]$ for the Rh complex), with the A part being a simple doublet (doublet of doublets in the Rh compound) and the M part giving rise to a quintet (further doubleted by the ^{103}Rh nucleus in the Rh complex).

The variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of the complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$ are particularly important in relation to the interconversion of ligands in fluxional processes of other five-coordinated metal complexes. Meakin, Jesson, Muetterties and Tebbe [14–19], have studied extensively the intramolecular rearrangement of five- and six-coordinated transition-metal complexes, and this field has been reviewed by both Jesson and Muetterties [20], and Brocas et al. [21].

Stereochemical non-rigidity is a common feature of five-coordinated complexes particularly when all ligands are equivalent or relatively similar in electronic and steric character, or if only one ligating group is distinctly different, and barriers to

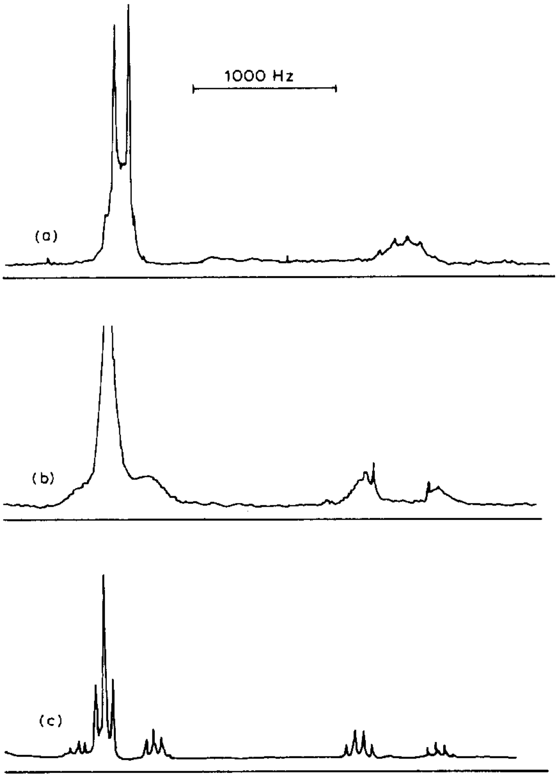


Fig. 6. Variable temperature $^{31}P\{^1H\}$ NMR spectra of $[IrP(O)(OMe)_2(P(OMe)_3)_4]$ at −10°C (a), −40°C (b) and −70°C (c).

rotation are sensitive to the steric bulk of ligands. Line-shape analysis of the NMR spectra for trigonal bipyramidal $[ML_5]^{n+}$ complexes where a low exchange limit has been observed, established conclusively that pseudo-rotation of ligating groups occurs via the Berry [22] mechanism involving the mutual exchange of two equatorial and two axial sites.

Likewise in $[MXL_4]$ complexes where the inter-ligand angles approach 90 and 120° (i.e., the molecule has trigonal bipyramidal geometry), and X is in an equatorial site (C_{2v} symmetry), barriers of rotation are low and rearrangements may be also explained assuming Berry's mechanism.

For $[MXL_4]$ complexes with X in an axial site (C_{3v} symmetry), the rearrangement barriers are high, if near trigonal bipyramidal angles are maintained and steric plus electronic characters of L and X are significantly different. The predominantly Berry-type rearrangement in such compounds populates a high energy C_{2v} transition state in which X occupies an equatorial position. If, however, complexes $[MXL_4]$ do not have trigonal bipyramidal or square pyramidal geometries the Berry mechanism is not feasible.

The lack of detailed mechanistic information resulting from NMR data for C_{3v} $[MXL_4]$ complexes, has led to mechanistic assumptions which were related to the physical aspects of the ligating groups. Since single crystal X-ray diffraction studies show that $[MHL_4]$ complexes adopt an almost tetrahedral arrangement of the L ligands, with the hydride occupying a position in the middle of a tetrahedral face a rearrangement pathway involving a "tetrahedral jump" mechanism, has been proposed. In this concerted process, one of the L–M–L angles increases as the hydride moves to this tetrahedral edge, and subsequently the L–M–L angle decreases as the hydride atom moves to a new tetrahedral face. In non-hydride $[MXL_4]$ complexes it is clear that as X grows in size, the arrangement of the remaining ligands gets more and more distorted from an ideal tetrahedron. In a limiting case, where $X = L$, the structure approaches a trigonal bipyramid. For intermediate systems a "tetrahedral edge transverse" mechanism [23] operates. In this mechanism, if the angle between the equatorial and axial ligands $\approx 90°$ and X and L have similar size and electronic properties, the transition state is a new trigonal bipyramid, and the process is indistinguishable from the Berry mechanism. If the angle gets smaller than 90°, because of the smaller steric requirements of X, then an idealised tetrahedral arrangement results, and the mechanism is indistinguishable from the tetrahedral jump.

It seems likely that the five-coordinate phosphonate complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$ (M = Co, Rh, Ir) reported in this paper will undergo an intramolecular rearrangement according to the more general tetrahedral edge transverse mechanism, in its limiting case where it becomes indistinguishable from the Berry process since the steric demands and electronic properties of the phosphonate group are essentially identical to those of the remaining phosphites. It is interesting however that the variable temperature $^{31}P\{^1H\}$ NMR spectrum of the phosphonate group in both

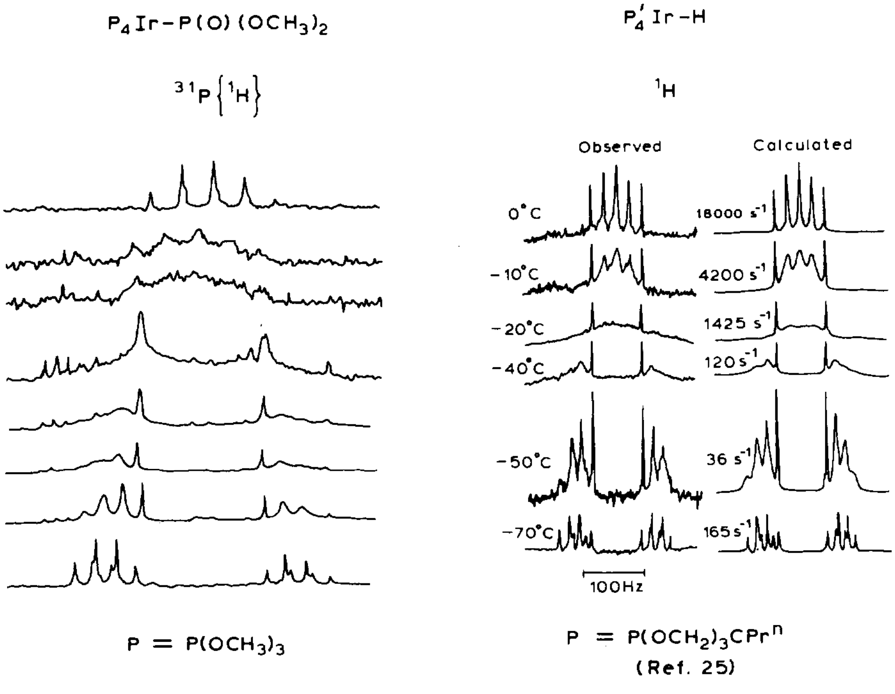


Fig. 7. NMR features for the X part of two $P_4Ir–X$ complexes.

$[MP(O)(OMe)_2(P(OMe)_3)_4]$ complexes (M = Rh, Ir) nevertheless closely resembles the ^1H NMR spectrum of the corresponding hydride in the hydride complexes $[MHL_4]$ [$L = P(OCH_2)_3CPr^n$, M = Rh, Ir; $L = P(OEt)_3$, M = Rh] [14,25]. The similarity of the spectra for the iridium complexes $[IrXL_4]$ ($X = P(O)(OMe)_2$, $L = P(OMe)_3$; X = H, $L = P(OCH_2)_3CPr^n$) is shown in Fig. 7, where the second order splittings of the inner lines of the quartets of the low temperature limit spectra differ from one complex to the other, because of the small *cis* coupling $^2J(HP)$ (13.9 Hz) compared to the larger *cis* $^2J(PP)$ (46.8 Hz) in $[IrH(P(OCH_2)_3CPr^n)_4]$. The corresponding values in the phosphonate complex are almost identical ($^2J(L_{eq}P(O)(OMe)_2)$ 55.8, $^2J(L_{ax}-L_{eq})$ 57.8 Hz). The barriers to rotation of the phosphonate complexes were not calculated, however, the high and the low temperature limit $^{31}P\{^1H\}$ NMR spectra lie within the same temperature range (ca. 30 to ca.

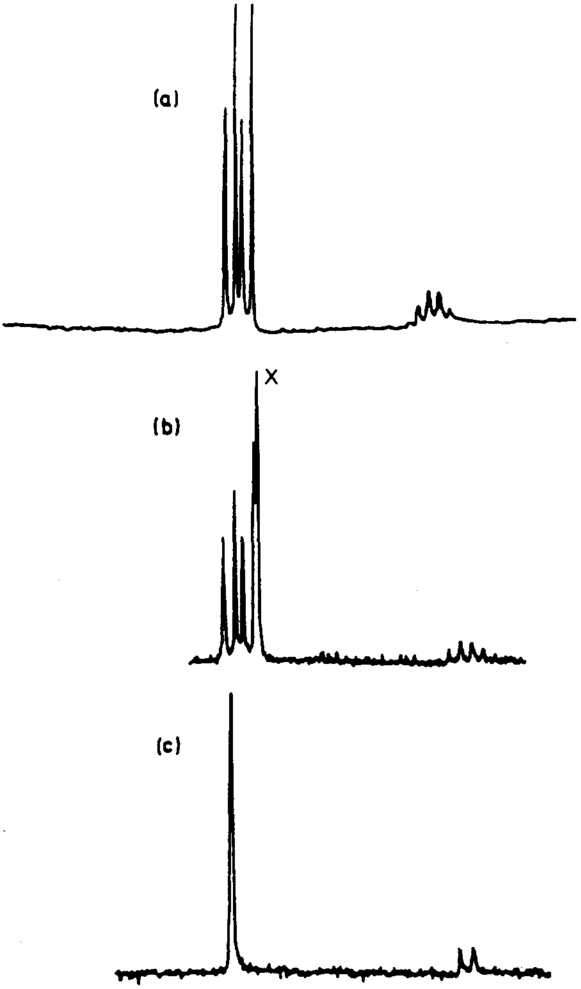


Fig. 8. (a) $^{31}P\{^1H\}$ NMR spectrum of $[RhP(O)(OMe)_2(P(OMe)_3)_4]$; With added $P(OMe)_3$: (b) at 32°C; (c) at 100°C (ref. 1).

$-70°$C) as the Co complex which reaches its slow exchange limit at the slightly higher temperature of $-66°$C. This indicates that the activation parameters for the rotation are quite similar and increase in the order Co < Rh ~ Ir. A similar trend was found by Verkade et al. [25] for the series of hydride complexes $[MH(P(OCH_2)_3CPr^n)_4]$ (M = Co, Rh, Ir). Unfortunately, no suitable quality crystals were obtained for a single crystal X-ray diffraction study of the complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$ (M = Co, Rh, Ir) to confirm its geometry.

The reformulation of the previously reported $[Rh_2(P(OMe)_3)_8]$ as the mononuclear phosphonate complex $[RhP(O)(OMe)_2(P(OMe)_3)_4]$, and the synthesis of its cobalt and iridium analogues also readily accounts for the observation [1] that in $[RhP(O)(OMe)_2(P(OMe)_3)_4]$ there is an intermolecular ligand exchange with free phosphite at temperatures approaching 100°C, as shown by the coalescence of the $P(OMe)_3$ and free phosphite (X) signals in the ^{31}P NMR spectrum of the mixture (Fig. 8), leaving the phosphonate resonance to appear as a simple doublet.

Interestingly the iridium phosphonate complex did not show evidence of any ligand exchange with free phosphite at room temperature, nor when a solution of $[IrP(O)(OMe)_2(P(OMe)_3)_4]$ in dimethylsulphoxide containing free $P(OMe)_3$ was heated up to the decomposition of the sample, (ca. 170°C).

Facile intermolecular ligand exchange reactions have been shown to occur in pentacoordinated rhodium complexes, e.g. $[Rh(P(OMe)_3)_5]^+$ BPh_4^- and free phosphite [15]. Likewise the cationic complexes $[Rh(P(OMe)_3)_4]^+$, undergo intermolecular exchange of $P(OMe)_3$ [15].

Alternative synthetic routes to phosphonate complexes and their chemical reactivity will be discussed in a later paper [30].

Experimental

All manipulations were carried out under dry nitrogen or argon, when stated, by standard Schlenk techniques. Solvents were dried by standard methods and distilled under dry nitrogen before use.

^1H NMR spectra were recorded on continuous wave spectrometers, either a Perkin-Elmer R32 operating at 90 MHz and a Perkin-Elmer R12 or Varian T60, both operating at 60 MHz. Variable temperature experiments were made on either the Perkin-Elmer R32 spectrometer or on a Bruker WP80 operating in the Fourier-transform mode. ^{31}P NMR were recorded in Fourier-transform mode on the following spectrometers: JEOL PF100 (40.5 MHz), Bruker WP80 (32.4 MHz) and Bruker W360 (145.8 MHz). The analysis of the NMR spectra was aided by the use of the computer program PANIC provided by Bruker Spectrospin, using the Adakos slave microcomputer of the Bruker WP80 spectrometer.

Infrared spectra in the range 4000–250 cm^{-1} were recorded on a Perkin-Elmer 457 spectrometer and are considered accurate to ±4 cm^{-1} in the region below 2000 cm^{-1}. Elemental analysis of stable complexes were performed by Mrs. A.G. Olney of these laboratories.

The following complexes were made by literature methods: $[Ir(C_8H_{14})_2Cl]_2$, $[Ir(C_2H_4)_2Cl]_2$ [26], $[Co_2(P(OMe)_3)_8]$ [27], $[CoP(O)(OMe)_2(P(OMe)_3)_4]$ [28], and $[Rh(C_6H_{10})Cl]_2$ [29].

Preparation of $[Ir(\eta^5\text{-}C_9H_7)(C_8H_{14})_2]$

Distilled indene (260 mg, 22 mmol) was added to a diethyl ether solution containing 1.35 μl of a 1.6 *M* hexane solution of n-butyllithium (22 mmol), and the mixture was stirred overnight. Solid di-μ-chlorotetrakiscyclooctenediiridium(I) was then added (1 g, 1.1 mmol) and the resulting suspension was stirred for 24 h at room temperature, and then filtered through a porosity 2 frit. The excess solvent was removed under vacuum and the dark residue extracted with small portions of acetone, which yielded upon vacuum drying green crystals of the product, *η^5-indenylbiscycloocteneiridium(I)* (200 mg, 18%). The product is soluble in aromatic and chlorinated solvents, m.p. 148°C (dec.) (Found: C, 56.52; H, 6.6. $C_{25}H_{35}Ir$ calcd.: C, 56.89; H, 6.68%).

IR (KBr): 2930m,br, 2920m,br, 2840m,br, 2465s, 1445s, 1430s, 1355m, 1349m, 1323s, 1278m, 1235m, 1205m, 1146m, 1027m, 1005m, 972m, 955m,br, 910m, 895m, 818s, 805s, 798sh, 763w, 738ws, 640m,br, 587w,br, 566s, 555s, 548sh,sh, 440s cm^{-1}.

Preparation of [Ir(η^5-C_9H_7)(C_2H_4)$_2$]

25 mmol of indenyllithium, in THF (5 ml) prepared as above from 0.25 ml of indene and 2.57 ml of η-butyllithium 1.6 *M*, was cooled to 0°C and added to solid di-μ-chlorotetrakisethylenediiridium(I) (710 mg, 12 mmol), and the mixture stirred at 0°C for 5 h, then at room temperature for 12 h. Excess solvent was removed under vacuum at 0°C and residues extracted with 15 ml of petroleum ether (30–40°C). Golden-brown crystals of *η^5-indenylbisethyleneiridium(I)* (237 mg, 26%) was obtained by cooling the petroleum ether washings to −60°C. (Found: C, 43.36; H, 4.26; $C_{13}H_{15}Ir$ calcd.: C, 42.96; H, 4.15%). IR (KBr): 3662m, 3039m, 2962m, 1562w, 1482m, 1475m,sh, 1326s, 1330s, 1320w, 1205w, 1173s, 1169s, 1160vs, 1145w, 1025w, 1000s, 905w, 890w, 856w, 852w, 830m, 812m, 785m, 739vs, 732s, 725m, 720w, 590w, 550w, 445ms,br, 372w,br, 335w,br cm^{-1}.

Preparation of [Ir(η^5-C_5H_5)(C_2H_4)$_2$]

Cyclopentadienyllithium (20 mmol) was prepared by stirring a THF solution (10 ml of indene (0.13 g, 20 mmol) and n-butyllithium (1.2 ml of a hexane solution 1.6 *M*, 20 mmol) for 5 h at room temperature. The resulting mixture was cooled to 0°C and transferred via a long needle to a 0°C cold THF solution (15 ml) of di-μ-chlorotetrakisethylenediiridium(I) (370 mg, 10 mmol). The mixture was stirred at that temperature for ca. 5 h, then at room temperature overnight. The excess of solvent was reduced to ca. 5 ml under reduced pressure at 0°C and the residues extracted with 5 × 10 ml portions of pentane. White crystals of the product (410 mg, 56%) were obtained by cooling the pentane washings to −76°C. Analytically pure samples of the air stable *η^5-cyclopentadienylbisethyleneiridium(I)* were obtained by allowing the white crystals to sublime into long, thin colourless needles over the walls of the container vessel; by exposure to indirect sunlight. (Found: C, 42.31; H, 5.76. $C_{13}H_{21}Ir$ calcd.: C, 42.26; H, 5.73%). Sublimation (50°C) of the pentane insoluble residues from the mother liquor onto a cold finger yields a further, small amount of the product $\nu(C_2H_4)$ 1430, 1400 cm^{-1}, KBr disk.

Preparation of [Rh(η^5-C_9H_7)(C_6H_{10})]

A THF solution (20 ml) of di-μ-chlorobis-(1,5-hexadiene)dirhodium(I) (360 mg, 8 mmol) was transferred to a second flask containing 16 mmol of indenyllithium dissolved in 25 ml of THF (from an overnight stirring of 180 mg of indene and 1.01 ml of η-butyllithium (1.6 *M*, hexane), and the mixture was stirred at room temperature for 12 h. The resulting light caramel solution was reduced in volume under vacuum and the solid residues extracted with several small portions of toluene. Reduction of the volume of the toluene washing to ca. 4 ml and cooling separated the product η^5*-indenyl(1,5-hexadiene)rhodium(I)* as a caramel oil. The compound was shown to be pure by ^{1}H NMR spectroscopy.

Preparation of $[MP(O)(OMe)_2(P(OMe)_3)_4]$ *(M = Rh, Ir)*

All indenyl olefin complexes of rhodium tested (olefin = C_2H_4, C_8H_{12}, C_6H_{12}) and the iridium analogues (olefin = C_2H_4, C_8H_{14}, C_8H_{12}) reacted rapidly with trimethylphosphite to produce the corresponding metal phosphonate compound. At initial stages of the rection of η^5-indenyl-1,5-hexadienerhodium(I) with $P(OMe)_3$, the ^{31}P NMR resonances of η^5-indenylbis(trimethylphosphite)rhodium(I) were detected. These resonances disappear upon further addition of the phosphite ligand.

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