

READY FORMATION OF PHOSPHONATE COMPLEXES OF RHODIUM AND IRIIDIUM FROM $[M(P(OMe)_3)_5]Cl$ COMPOUNDS ($M = Rh, Ir$). DIFFERENCES BETWEEN REACTIONS OF DIHYDROGEN WITH $[MP(O)(OMe)_2(P(OMe)_3)_4]$ COMPLEXES ($M = Co, Rh, Ir$), INCLUDING FACILE HYDROGENOLYSIS OF A RHODIUM-PHOSPHORUS BOND

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Summary

The ease of formation of the phosphonate complexes $[M(P(O)(OMe)_2(P(OMe)_3)_4]$ ($M = Rh, Ir$), from the pentakis-trimethylphosphite complexes $[M(P(OMe)_3)_5]Cl$ is reported. Differences in the interaction of H_2 with the complexes $[M'(P(O)(OMe)_2(P(OMe)_3)_4)]$, ($M' = Co, Rh, Ir$) are presented and discussed.

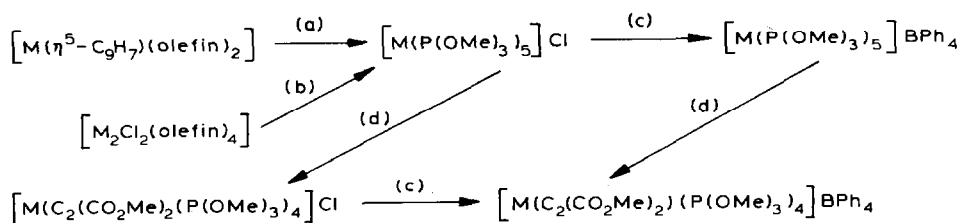
Results and discussion

In a previous paper [1] we described the synthesis of phosphonate complexes of the type $[MP(O)(OMe)_2(P(OMe)_3)_4]$, ($M = Rh, Ir$), from η^5 -cyclopentadienyl or η^5 -indenyl metal olefin precursors. $[M(\eta^5-L)(olefin)_2]$ ($M = Rh, Ir$), ($L = C_5H_5, C_9H_7$).

In the presence of chlorinated solvents however the yield of these phosphonate complexes decreases and the pentakis-trimethylphosphite complexes $[M(P(OMe)_3)_5]Cl$ ($M = Rh, Ir$) are then formed.

Mononuclear chloro complexes of Rh and Ir of the type $[M(\text{phosphite})_4]Cl$ have not been well established although recently Drago et al. [2] observed poorly defined cationic complexes resulting from the addition of $P(OMe)_3$ to chloro-bridged Rh olefin dimers. Pentakis-phosphite complexes containing non-coordinating anions such as $[BPh_4]$ have however been prepared, [3,4] usually by vigorous methods, using an excess of phosphite in boiling methanol containing the metal olefin chloro dimers [5,6]. However, we find that addition of an excess of $P(OMe)_3$ to chloro-bridged olefin dimers of Rh and Ir, in any solvent at room temperature, produces

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SCHEME 1. M = Rh, Ir; olefin = C₈H₁₂, C₂H₄. (a) excess P(OMe)₃, chlorinated solvent; (b) excess P(OMe)₃; (c) NaBPh₄; (d) C₂(CO₂Me)₂.

[M(P(OMe)₃)₅] Cl, (M = Rh, Ir). If the solvent is diethyl ether these white, microcrystalline, air and moisture sensitive pentakis complexes precipitate from solution in quantitative yields, and can be isolated. They are easily converted into known tetraphenylborate salts, and react with activated alkynes such as MeO₂CC≡CCO₂Me to produce the six-coordinated complexes [M(alkyne)(P(OMe)₃)₄] X, (X = Cl, BPh₄), which were fully characterized by microanalysis and their characteristic [A₂B₂] (Ir) or [A₂B₂X] (Rh) type ³¹P NMR spectra (see Scheme 1). A similar alkyne complex of Rh had already been prepared previously [7].

The complexes [M(P(OMe)₃)₅]Cl obtained by the above method or by addition of P(OMe)₃ to indenyl olefin complexes of Rh or Ir in chlorinated solvents have identical ³¹P NMR chemical shifts (Rh, Ir) and ¹J(RhP) coupling constant, (δ(P(Rh)) 5.9 ppm, ¹J(RhP) 181 Hz (lit. 182 Hz [8] δ(P(Ir)) -44.5 ppm).

It was also noted that the cationic chloro complexes [M(P(OMe)₃)₅]Cl, (M = Rh, Ir), and their corresponding phosphonates are readily interconverted, indeed traces of the iridium phosphonate compound were detected by ³¹P NMR spectroscopy even in freshly prepared solutions of [IrP(OMe)₃)₅]Cl in CH₂Cl₂. Moreover, solutions of [Rh(P(OMe)₃)₅]Cl in THF or warm acetone undergo readily conversion into [RhP(O)(OMe)₂(P(OMe)₃)₄], and the following equilibrium exists:



Since MeCl is a gas at room temperature it is conceivable that if it is allowed to escape from the reaction vessel, or to react further with other reagents, the conversion of the pentakis-phosphite complex into the phosphonate should be effected in high yields. In fact a number of such reagents were found useful for these transformations, and these are listed in Table 1. The most interesting way of displacing MeCl from [M(P(OMe)₃)₅]Cl involves purging a solution of the complex with N₂ or argon at or above room temperature and quantitative amounts of the phosphonate complexes can be obtained in this way. Obviously, the small amounts of MeCl present in those solutions are removed by the carrier gas, forcing the equilibrium in the above equation to the left. Further evidence for such transformations comes from the extreme reactivity of mixtures of all three phosphonate complexes of type [M(P(O)(OMe)₂(P(OMe)₃)₄] with MeI, and they are all rapidly converted into the corresponding pentakis complexes [M(P(OMe)₃)₅]I, (M = Co, Rh, Ir), which were characterized by their ³¹P NMR spectra. The ease of MeCl elimination from the [M(P(OMe)₃)₅]Cl complexes (M = Rh, Ir) results from initial nucleophilic attack by the chloride ion on the coordinated phosphite.

Similar behaviour, although not as facile, has been reported in a number of

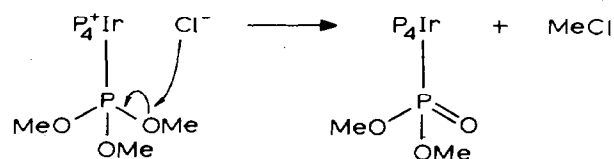
TABLE 1

REAGENTS AND CONDITIONS FOR THE CONVERSION $[ML_5]^+ Cl^- \rightarrow MP(O)(OMe)_2L_4$ ($L = P(OMe)_3$, $M = Rh$ or Ir)

Reagent ^a	<i>T</i> (°C)	Solvent	Time (h)	Yield (%)	Purification ^b
Na	RT	Et ₂ O	12	> 80	filtration, vac. dry ^c
Na/Hg ^c	RT	Et ₂ O	12	> 80	filtration, vac. dry
Acetone	+50	Acetone	~ 3	~ 50 ^d	vac. dry, Et ₂ O + filtration
dppm	RT	Toluene	12	> 90 ^d	inseparable mixture
NaBH ₄	RT	Et ₂ O	12	~ 5 ^d	not attempted
N ₂ or Argon flow (open system)	RT	Toluene (Ir) Toluene + THF (Rh)	5 ~ 5	100 ^d	vac. dry

^a Tested for Rh and Ir, except for dppm where $M = Rh$ only. ^b Method stated is followed by extraction of soluble, filtered phase with petroleum ether 30–40°C. ^c Several Na/Hg ratios, (yield stated for $M = Ir$); reactions with $M = Rh$ slower. ^d As indicated by disappearance of $[ML_5Cl]^+$ ³¹P NMR resonance(s) from sampled solutions. ^e Occasionally, traces of $[IrH(P(OMe)_3)_4]$ are present, whereas the very stable $[RhH(P(OMe)_3)_4]$ is usually present, albeit in trace quantities, and their presence may be associated with the reduction of trace impurities of $[MCl(P(OMe)_3)_4]$ ($M = Rh, Ir$) by sodium metal [13].

related systems e.g. the formation of $[Rh(\eta^5-C_5H_5)Me(P(O)(OMe)_2(P(OMe)_3))]^+$ from $[Rh(\eta^5-C_5H_5)Me(P(OMe)_3)_2]^+$ at 50°C [9–12], and $[Co(\eta^5-C_5H_5)(P(O)(OMe)_2)_2P(OMe)_3]^+$ formation from $P(OMe)_3$ and $[Co(\eta^5-C_5H_5)I_2(P(OMe)_3)]^+$ [14,15]. Likewise the addition of MeI to phosphonate complexes has been utilised to generate Ru [16,17] and Re [18] cationic trimethylphosphite complexes.



Reactions of $[M(P(O)(OMe)_2(P(OMe)_3)_4)]$, ($M = Co, Rh, Ir$) with H_2

The phosphonate complexes $[MP(O)(OMe)_2(P(OMe)_3)_4]$, ($M = Co, Rh, Ir$), were found to behave differently in their reactions towards dihydrogen. $[CoP(O)(OMe)_2(P(OMe)_3)_4]$ does not react with H_2 at room temperature and this observation agrees with that reported independently by Muetterties et al. [19,20]. However at 100°C a reaction does occur leading to the formation of the hydride $[CoH(P(OMe)_3)_4]$. The fate of the phosphonate was not determined [19]. On the other hand $[RhP(O)(OMe)_2(P(OMe)_3)_4]$ reacts quickly with H_2 at room temperature producing the known hydride $[RhH(P(OMe)_3)_4]$ first reported in low yield by Muetterties et al. [21] from mixtures of $RhCl_3$, $NaBH_4$ and $P(OMe)_3$.

When the reaction of the Rh complex with H_2 is monitored by ³¹P NMR spectroscopy, (Fig. 1), the formation of $HP(O)(OMe)_2$ together with the metal hydride is clearly observed. The ³¹P NMR spectrum of $[RhH(P(OMe)_3)_4]$ showed

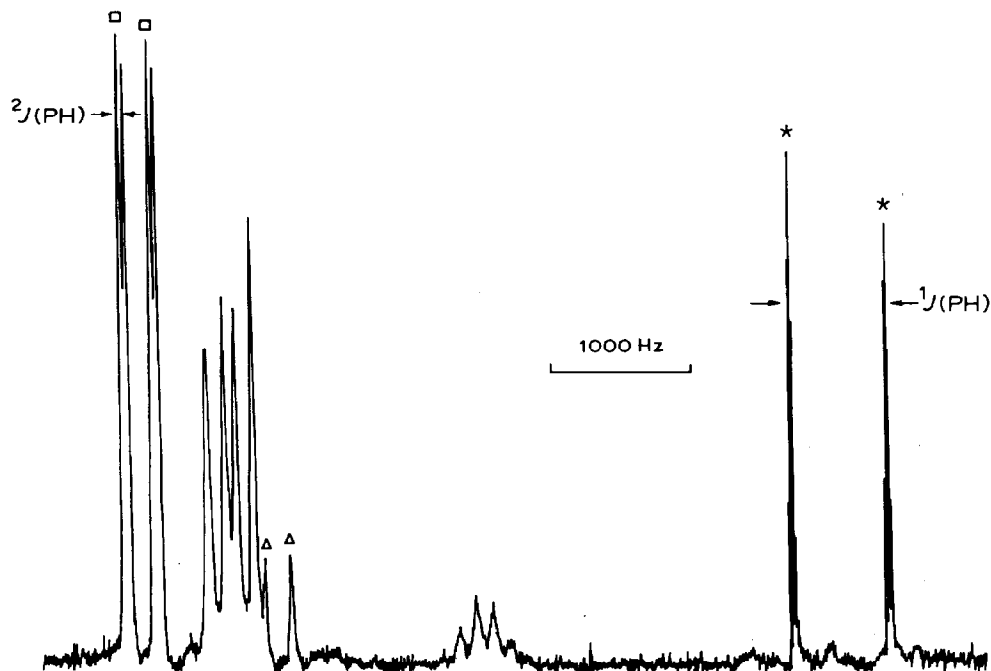
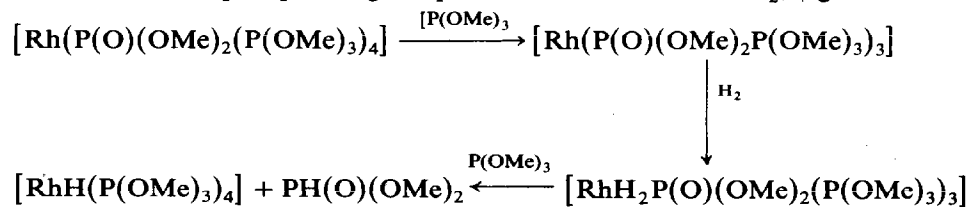


Fig. 1. ^{31}P NMR spectrum of $[\text{RhP}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4] + \text{H}_2$, after 2.5 h of H_2 bubbling; \square , $[\text{RhH}(\text{P}(\text{OMe})_3)_4]$; Δ , $[\text{Rh}(\text{P}(\text{OMe})_3)_5]\text{Cl}$ impurity; *, $\text{HP}(\text{O})(\text{OMe})_2$.

the expected widely spaced doublet of doublets pattern ($^1J(\text{RhP})$ 209.9, $^2J(\text{PH})$ 34.2 Hz, δ 23.7 ppm) while a widely spaced doublet of septets arising from $\text{HP}(\text{O})(\text{OMe})_2$ ($\delta(\text{P})$ -129 ppm, $^1J(\text{PH})$ 710 Hz) is also clearly evident. The ^1H NMR spectrum of the Rh hydride showed the characteristic doublet of quintets pattern expected for a fluxional complex, arising from spin-spin coupling to the Rh atom and four equivalent phosphorus nuclei (δ 14.2 ppm; $^1J(\text{RhH})$ 9 Hz).

The mechanism of formation of the transition-metal hydrides of Co and Rh from the above reactions could conceivably involve either a four-coordinated $[\text{MP}(\text{O})(\text{OMe})_2\text{L}_3]$ or a seven-coordinated $[\text{M}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2\text{L}_4]$ intermediate. We described elsewhere [1] that whereas $[\text{Rh}(\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4)]$ undergoes intermolecular phosphite exchange at elevated temperatures the corresponding iridium complex does not. No data are available for the cobalt complex. The lability of the ligands in the Rh complex supports a mechanism in which the first step is dissociation of a phosphite ligand prior to interaction with H_2 , e.g.



Interestingly, addition of H_2 to the iridium phosphonate complex does not afford the analogous $[\text{IrH}(\text{P}(\text{OMe})_3)_4]$ complex but instead the reaction stops at the iridium(III) dihydrido phosphonate complex *cis*- $[\text{IrH}_2(\text{P}(\text{O})(\text{OMe})_2)(\text{P}(\text{OMe})_3)_3]$.

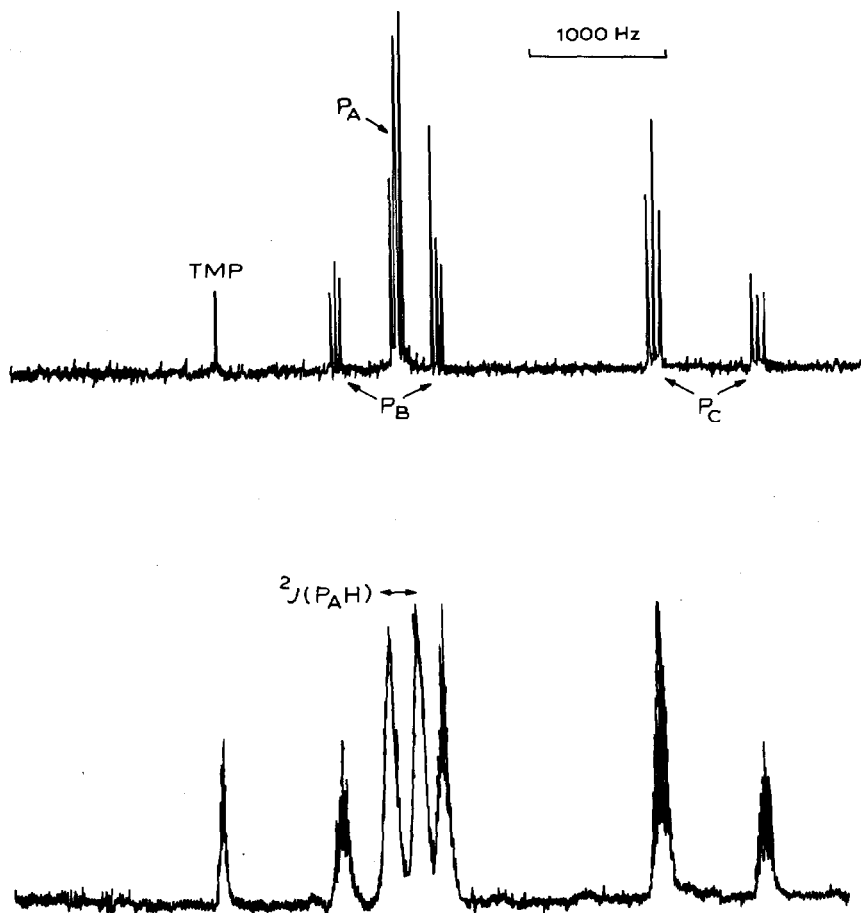


Fig. 2. (a) $^{31}\text{P}\{^1\text{H}\}$ and (b), ^{31}P NMR spectra of $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$.

Careful monitoring of this reaction by ^{31}P NMR spectroscopy showed that the iridium(III) dihydrido complex and free $\text{P}(\text{OMe})_3$ are the sole products. The $\nu(\text{Ir}-\text{H})$ band at 2085 cm^{-1} is typical for a hydride *trans* to a phosphite ligand [22]. The stereochemistry of the colourless oily dihydrido iridium(III) complex shown below was fully elucidated by ^1H and ^{31}P NMR spectroscopy (Figs. 2a, b and 3), likewise the mass spectrum showed a parent peak at m/e 676.

The structure of cis- $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$ as determined by ^1H NMR spectroscopy ($\text{P} = \text{P}(\text{OMe})_3$)

The spectroscopic parameters measured for (^1H NMR, $\delta(\text{H}) - 10.6$ ppm, $^2J(\text{HP}_{\text{cis}}) + ^2J(\text{HP}_{\text{trans}})$ 157 Hz. ^{31}P NMR, $\delta(\text{P}_\text{A}) - 34.3$, $\delta(\text{P}_\text{B}) - 33.6$, $\delta(\text{P}_\text{C}) - 90.2$ ppm, $^2J(\text{P}_\text{A}\text{P}_\text{C})$ 30.1, $^2J(\text{P}_\text{B}\text{P}_\text{C})$ 38.2, $^2J(\text{P}_\text{B}\text{P}_\text{C})$ 619.7 Hz.)

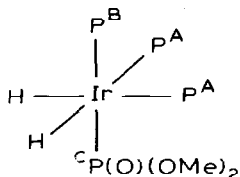




Fig. 3. ^1H NMR spectrum of $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$, hydride region.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$ (Fig. 2a) is particularly informative. The resonance of the two equivalent $\text{P}_\text{A}\text{P}(\text{OMe})_3$ ligands is split into a doublet of doublets due to the P_C phosphonate and the P_B phosphite group. Both P_C and P_B show the equivalent triplet structure (due to spin-spin coupling to the two equivalent P_A , doubled by a large phosphite-phosphonate *trans* coupling, $^2J(\text{P}_\text{C}\text{P}_\text{B})$). The $^2J(\text{PP})$ couplings in the complex are not exceptional, their values being $^2J(\text{P}_\text{A}\text{P}_\text{B})$ 30.2, $^2J(\text{P}_\text{A}\text{P}_\text{C})$ 38.3; $^2J(\text{P}_\text{B}\text{P}_\text{C})$ 619.7 Hz, but are substantially smaller than those found for the parent Ir^{I} complex $[\text{IrP}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4]$.

Particularly revealing is the proton coupled ^{31}P NMR spectrum (Fig. 2b) which shows a large doublet pattern for the P_A resonance indicating that the hydride ligands are both *trans* to P_A . The ^1H NMR spectrum (Fig. 3) of $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$ ($\delta(\text{H}) - 10.6$ ppm) in the hydride region, although not fully analysed, supports the stereochemical assignment and is as expected for a $[\text{AA}'\text{XX}']$ spin system formed by the *trans* H^1 , H^2 and P_A , which has been superimposed with further doubling patterns due to $^2J(\text{HP}_\text{B})$ and $^2J(\text{HP}_\text{C})$. We

have estimated these *cis* couplings, which can be unambiguously assigned as $^2J(\text{HP}_B)$ 18.6 and $^2J(\text{HP}_C)$ 12.8 Hz on the basis of the change in the ^1H NMR hydride resonances of $[\text{Ir}(\text{H})_2\text{P}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_3]$ upon acidification [13].

The formation of the bis(hydrido)iridium(III) complex may conceivably involve a different mechanistic route to that described for the formation of the cobalt(I) and rhodium(I) hydrides since $[\text{IrP}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4]$ does not exchange with free phosphite.

The non-isolation of $[\text{IrH}(\text{P}(\text{OMe})_3)_4]$ from the above reactions may reflect the known greater tendency for oxidative addition of Ir complexes, as compared with Co and Rh compounds. It is interesting to point out that even if reductive elimination of a neutral molecule, e.g. H_2 or $\text{HP}(\text{O})(\text{OMe})_2$, from any seven-coordinated intermediate occurred, the equilibrium could still lie well on the side of the Ir^{III} complex, since it is known that iridium(I) compounds generate hydridophosphonateiridium(III) complexes by oxidative addition of $\text{HP}(\text{O})(\text{OMe})_2$ [23–25]. The iridium(I) hydrido complex $[\text{IrH}(\text{P}(\text{OMe})_3)_4]$ could not be detected even after boiling a solution of the iridium(III) dihydride compounds with an excess of $\text{P}(\text{OMe})_3$, in an attempt to force a reductive elimination. $[\text{IrH}(\text{P}(\text{OMe})_3)_4]$ was however detected as a minor impurity in some preparations of $[\text{IrP}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4]$ and it has recently been described by Muetterties [26] from addition of dihydrogen to $[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\text{P}(\text{OMe})_3)_3]$ in the presence of $\text{P}(\text{OMe})_3$. It is however, present in varying quantities in reduction reactions of $[\text{Ir}(\text{P}(\text{OMe})_3)_4\text{Cl}]$ with potassium amalgam, reactions which will be described in detail later [13]. Its ^1H NMR spectrum showed the typical quintet pattern in the hydride region, ($\delta(\text{H})$ –14.2 ppm, $^2J(\text{PH})$ 18.5 Hz) expected for a fluxional molecule containing four approximately equivalent phosphite groups in its high temperature limiting spectrum, and the values presently found for the coupling constants agree precisely with those reported by Muetterties [26]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature showed a singlet at $\delta(\text{P})$ –15.1 ppm, (lit. –16 ppm). With the synthesis of the iridium complex, all three $[\text{MH}(\text{P}(\text{OMe})_3)_4]$ compounds (M = Co, Rh, Ir) are therefore now known.

Experimental

General procedures were as described in the previous paper of the series [1].

Preparation of $[\text{Ir}(\text{P}(\text{OMe})_3)_5]\text{Cl}$ and $[\text{Rh}(\text{P}(\text{OMe})_3)_5]\text{Cl}$

A 40 ml diethyl ether suspension of di- μ -chlorotetrakis-cyclooctenediiridium(I) (200 mg, 2 mmol) was vigorously stirred at room temperature while an excess of trimethylphosphite (6 ml) was added dropwise. The precipitation of a white, very air- and moisture-sensitive solid was immediate and quantitative. The ethereal supernatant was decanted and the solid washed with several portions of diethyl ether and dried under vacuum. Pentakis(trimethylphosphite)iridium(I) chloride is very soluble in chlorinated solvents from which it cannot be recrystallized due to its conversion into dimethylphosphonatotetrakis(trimethylphosphite)iridium(I). It is also moderately soluble in toluene, and very soluble in alcohols. (Found: C, 21.26; H, 5.85; $\text{C}_{15}\text{H}_{45}\text{ClIrO}_{15}\text{P}_5$ calcd.: C, 21.24; H, 5.35%). The IR spectrum of the complex is very similar to that of pure trimethylphosphite, (KBr): 2998s, 2945vs, 2822s, 1460br, 1180s,br, 1000–1100 vs,br, 770vs,br, 730 w, 710vs,br, 535vs,br,

450w,br, 400m cm^{-1} . ^1H NMR δ 3.4 ppm (m). ^{31}P NMR see text. The rhodium analogue is prepared similarly, as very sensitive white crystals which are also thermally unstable. Its IR spectrum is identical to the iridium complex.

Preparation of $[\text{Ir}(\text{P}(\text{OMe})_3)_5]\text{BPh}_4$

A methanol solution (8 ml) of pentakis(trimethylphosphite)iridium(I) chloride (100 mg, 1 mmol) and sodium tetraphenylborate (30 mg, slight excess) was stirred at room temperature for 5 h. The white, air-stable product crystallised on reduction of the solvent under low pressure and was filtered and washed with small portions of methanol. Pentakis(trimethylphosphite)iridium(I) tetraphenylborate has an identical ^{31}P NMR chemical shift to its chloride precursor, and its IR spectrum, exhibits enlargement of the strong band at ca. 1000 cm^{-1} due to the presence of the tetraphenylborate anion.

Preparation of $[\text{Ir}(\text{C}_2(\text{CO}_2\text{Me})_2(\text{P}(\text{OMe})_3)_4)]\text{X}$ ($\text{X} = \text{Cl}, \text{BPh}_4$)

Pentakis(trimethylphosphite)iridium(I) chloride (80 mg, 1 mmol) was stirred in 15 ml of diethyl ether. Dropwise addition of a solution of dimethylacetylenedicarboxylate (20 mg, excess) in diethylether (3 ml) caused the separation within a short period of a sticky red mass which is readily soluble in dichloromethane or acetone. Dimethylacetylenedicarboxylatotetrakis(trimethylphosphite)iridium(I) chloride showed a typical $[\text{A}_2\text{B}_2]$ ^{31}P NMR pattern, δ_{A} 51, δ_{B} 74.3 ppm, $^2J_{\text{AB}}$ 41 Hz. Addition of sodium tetraphenylborate (30 mg, excess) to an acetone solution of the complex followed by 2 h stirring, solvent evaporation, and recrystallization from a small portion of methanol (-20°C) afforded the red, moisture-sensitive crystalline complex dimethylacetylenedicarboxylatotetrakis(trimethylphosphite)iridium(I) tetraphenylborate (63 mg, 63%), m.p. 87°C (dec). (Found: C, 47.31; H, 5.43. $\text{C}_{36}\text{H}_{57}\text{IrP}_4\text{O}_{16}$ calcd.: C, 40.72; H, 5.41%). ^{31}P NMR spectrum is identical to its chloride analogue, ^1H NMR ($\delta(\text{CO}_2\text{Me})_2\text{C}_2$ 2.3 ppm). The IR spectrum of the compound showed the same bands due to the pentakisphosphite complexes, with additional sharp bands at 3030m, 3020m, 1580m, 1260m, 610m cm^{-1} .

Preparation of $[\text{RhC}_2(\text{CO}_2\text{Me})_2(\text{P}(\text{OMe})_3)_4]\text{BPh}_4$

This preparation followed closely that for the iridium compound, and the yellow, slightly hygroscopic solid dimethylacetylenedicarboxylatotetrakis(trimethylphosphite)rhodium(I) tetraphenylborate complex m.p. 106°C (dec.) (lit. 110°C [22]) showed an $[\text{A}_2\text{B}_2\text{X}]$ pattern in the ^{31}P NMR spectrum, δ_{A} 16.9, δ_{B} 42.4 ppm, $^2J_{\text{AB}}$ 43, $^1J_{\text{AX}}$ 137, $^1J_{\text{BX}}$ 198 Hz.

Preparation of $[\text{MP}(\text{O})(\text{OMe})_2(\text{P}(\text{OMe})_3)_4]$ ($\text{M} = \text{Rh}, \text{Ir}$)

Typically $[\text{Ir}(\text{P}(\text{OMe})_3)_5]\text{Cl}$ (300 mg, 4 mmol) was suspended in diethyl ether, and a large excess of small pieces of sodium metal (100 mg) was added. The mixture was stirred at room temperature for 12 – 14 h. The resulting colourless supernatant liquid was decanted, vacuum dried, and extracted with several small portions of pentane. Vacuum drying of the pentane washings gave the white, micro-crystalline solid complex dimethylphosphonatotetrakis(trimethylphosphite)iridium(I) (23 mg, 82%). The complex could be recrystallised from diethyl ether/pentane to give soft, colourless crystals. (Found: C, 21.14; H, 5.29, $\text{C}_{14}\text{H}_{42}\text{IrP}_5\text{O}_{15}$ calcd.: C, 21.08; H, 5.30%). ^1H NMR δ 3.4 ppm (m).

Dimethylphosphonatotetrakis(trimethylphosphite)rhodium(I) obtained similarly was shown to be contaminated with traces of hydridotetrakis(trimethylphosphite)rhodium(I) and the chloride precursor by low-temperature ^{31}P NMR spectroscopy. Details of the spectroscopic identification of this compound are in the text.

Preparation of $[\text{IrH}_2(\text{P}(\text{O})(\text{OMe})_2)(\text{P}(\text{OMe})_3)_3]$ and $[\text{RhH}(\text{P}(\text{OMe})_3)_4]$

These hydride complexes are obtained in quantitative yield by stirring a toluene solution of the appropriate $[\text{M}(\text{P}(\text{O})(\text{OMe})_2)(\text{P}(\text{OMe})_3)_4]$ ($\text{M} = \text{Rh}, \text{Ir}$) complex under an atmosphere of H_2 for ca. 72 h (Ir) or ca. 40 h (Rh). The iridium compound can also be obtained by bubbling H_2 through a stirred toluene solution of $[\text{Ir}(\text{P}(\text{OMe})_3)_5]\text{Cl}$ for several hours in an open flask. The compound could not be obtained in the solid state, but it was fully characterised by ^1H and ^{31}P NMR spectroscopy. This latter method did not produce $[\text{RhH}(\text{P}(\text{OMe})_3)_4]$ however it may be prepared in yields above 90% by sodium metal reduction of pentakis(trimethylphosphite)rhodium(I) chloride in THF at room temperature [12]. This method does not produce the iridium analogue. The monohydridorhodium complex had already been described [21].

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