Preparation and Fluxional Behaviour of 4-Substituted 2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane Hydride Complexes of the Cobalt Triad

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Caged phosphite complexes of the type $[MH\{P(OCH_2)CPr^n\}_4]$ (M = Co, Rh, or Ir) have been synthesized. These complexes are stereochemically non-rigid on the n.m.r. time scale at 25 °C. However, for the rhodium and iridium analogues, near-limiting and limiting slow-exchange spectra respectively, corresponding to a structure with C_{3v} symmetry, have been obtained at low temperatures. Activation parameters have been calculated from lineshape analyses. Mixed-ligand complexes of the types $[M(CO)H(PPh_3)_2\{P(OCH_2)_3CX\}]$ (M = Rh or Ir; X = Pr^n or NO_2) and $[M(CO)H(PPh_3)\{P(OCH_2)_3CX\}_2]$ (X = Pr^n, Ph, or NO_2) have also been prepared. For the latter complexes, n.m.r. evidence suggests that more than two isomers are involved.

THE synthesis and reactivity of trialkyl or triaryl phosphite hydride complexes of univalent cobalt, rhodium, and iridium have been widely reported in recent years.[1-6] In order to compare the behaviour of bicyclic phosphites in such complexes we have synthesized several five-co-ordinate hydride derivatives.

RESULTS AND DISCUSSION

Complexes of the type $[MH\{P(OCH_2)_3CPr^n\}_4]$ (M = Co, Rh, or Ir) were prepared by routes essentially similar to those reported previously.[1,4,6] Reaction of excess of bicyclic ligand with an ethanolic suspension of $[Rh(CO)H(PPh_3)_3]$ leads to formation of the white crystalline complex $[RhH\{P(OCH_2)_3CPr^n\}_4]$. Attempts

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[1] J. J. Levison and S. D. Robinson, *Chem. Comm.*, 1968, 1405.

[2] E. W. Ainscough and S. D. Robinson, *J. Chem. Soc.* (*A*), 1971, 3413.

[3] W. Kruse and R. H. Atalla, *Chem. Comm.*, 1968, 921.

[4] D. Guisto, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 767.

[5] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.

[6] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 96.

to prepare the iridium derivative in a similar manner resulted in substitution of only two PPh_3 ligands to give $[Ir(CO)H(PPh_3)\{P(OCH_2)_3CX\}_2]$ (X = Pr^n, Ph, or NO_2). These complexes were characterized by analyses and ^1H and ^{31}P n.m.r. spectra.

The analogous reaction of $P(OPh)_3$ with $[Ir(CO)H(PPh_3)_3]$ has been reported by Ainscough and Robinson[2] who obtained only oily mixtures which were shown by ^1H n.m.r. to contain only the mono- and tri-substituted aryl phosphite intermediates. The monosubstituted bicyclic phosphite complex $[Ir(CO)H(PPh_3)_2\{P(OCH_2)_3CX\}]$ (X = Pr^n or NO_2) can be isolated by the reaction of $[Ir(CO)H(PPh_3)_3]$ and ligand in a 1 : 1 ratio. The analogous reaction with $[Rh(CO)H(PPh_3)_3]$ and ligand in a 1 : 1 ratio yielded the monosubstituted rhodium complex $[Rh(CO)H(PPh_3)_2\{P(OCH_2)_3CPr^n\}]$. However, the product was shown by ^1H n.m.r. spectra to contain small amounts of starting material and another hydride complex, probably the disubstituted phosphite complex. Attempts to make this disubstituted complex in greater yield were unsuccessful, the fully substituted $[RhH\{P(OCH_2)_3CPr^n\}_4]$ being obtained instead. The hydridotetrakis(phosphite)iridium complex $[IrHP\{(OCH_2)_3CPr^n\}_4]$ was obtained by treating $[IrH_3(PPh_3)_3]$ with excess of ligand.[4]

It is well established from *X*-ray analyses [7-11] that transition-metal hydrides of the form MHL_4 (L = a phosphorus ligand) are neither trigonal bipyramidal nor square pyramidal but may be considered as pseudotetrahedral with an MP_4 skeleton in a nearly regular tetrahedral array. The hydrogen-atom position has been located on a face of the tetrahedron in two *X*-ray studies.[9,11] Stereochemical non-rigidity is a prominent feature of this class of complexes, and variable-temperature n.m.r. studies [12,13] led to the conclusion that they have C_{3v} symmetry in the low-temperature limit, suggesting that the hydrogen is on a tetrahedral face. On the basis of these experiments it has been proposed [13] that the lowest-energy path for interchanging the phosphorus environments involves a tetrahedral-jump rearrangement mechanism. Further evidence for these conclusions has been obtained from n.m.r. studies of the complexes $[MH\{P(OCH_2)_3Pr^n\}_4]$ (M = Co, Rh, or Ir).

The proton and phosphorus (with white-noise decoupling of protons) n.m.r. spectra of these complexes (Table 1) establish the magnetic equivalence of the phosphorus nuclei in the high-temperature limit. The proton spectrum consisted of a 1 : 4 : 6 : 4 : 1 quintet, with additional splitting due to $^1H-^{103}Rh$ coupling for the rhodium complex. The ^{31}P spectrum was a single resonance and again additional fine structure due to $^{31}P-^{103}Rh$ was observed. The complex $[CoH\{P(OCH_2)_3CPr^n\}_4]$ also showed line broadening at room temperature. Similar broadening has been reported for $[CoH\{P(OPh)_3\}_4]$,[1] $[CoH\{P(OEt)_3\}_4]$,[3] and $[CoH(PF_3)_4]$ [13,14] and is ascribable to the quadrupole moment of ^{59}Co. As the temperature was decreased, additional broadening of the hydride quintet occurred because of the exchange process and at −50 °C only a broad hump was observed. The only change that occurred on further cooling was a gradual broadening of the spectrum, and even at −100 °C the exchange process was still fast enough to broaden the spectrum. The complex was too insoluble to measure spectra at temperatures below −100 °C, thus precluding the acquisition of a low-temperature limiting spectrum. The temperature-dependent ^1H(hydride) n.m.r. spectra of the complex $[RhH\{P(OCH_2)_3CPr^n\}_4]$ from 0 to −80 °C are shown in Figure 1. In the low-temperature limit (below −60 °C) both the ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra can be analysed using an $AMXY_3$ model (A = ^1H, M = ^{103}Rh, X and Y = ^{31}P) indicating that the complex has C_{3v} symmetry on the n.m.r. time scale. The low-temperature-limit n.m.r. parameters are given in Table 1. As expected for a second-row transition-metal complex, the *trans* $^1H-^{31}P$ coupling constant is quite large (−180 Hz) and the low-temperature-limit hydride region of the ^1H n.m.r. spectrum appeared as a broad doublet since the small *cis* $^1H-^{31}P$ and the $^1H-^{103}Rh$ couplings were not resolved. As the temperature was increased the ^1H n.m.r. spectrum began to broaden (Figure 1), with the exception of two doublets at each end of the spectra which remained sharp. These sharp doublets correspond to transitions which are invariant of the exchange process and are characteristic of mutual exchange. At higher temperatures the spectrum coalesced into a binomial quintet of doublets indicating that the phosphorus spins have become equivalent on the n.m.r. time scale. The preservation of the $^1H-^{103}Rh$ and $^1H-^{31}P$ couplings in the high-temperature limit indicates that the H–Rh and Rh–P bonds are not broken during the exchange process. The observed spectra are complicated by the presence of a second hydride labelled I in the slow-exchange-limit spectrum. It is clear from the observed spectra that this impurity is not involved with the exchange process observed for the C_{3v} MHL_4 hydride since its resonances do not exchange with those of the C_{3v} MHL_4 complex.

The slow-exchange-limit $^{31}P-\{^1H\}$ n.m.r. spectra consisted of an AB_3X pattern which broadened and coalesced into a doublet in the fast-exchange limit, indicating that the environments of the phosphorus nuclei are averaged by the exchange process and that the exchange process is intramolecular. (The large $^{31}P-^{103}Rh$ coupling constants are averaged but not lost.) Similar temperature-dependent ^1H and $^{31}P-\{^1H\}$ spectra were observed for the complex $[RhH\{P(OEt)_3\}_4]$ [13] and,

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[7] R. W. Baker and P. Pauling, *Chem. Comm.*, 1969, 1495.

[8] R. W. Baker, B. Ilmaier, P. Pauling, and R. S. Nyholm, *Chem. Comm.*, 1970, 1077.

[9] D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Comm.*, 1971, 322.

[10] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 2403.

[11] D. W. H. Rankin, personal communication to J. F. Nixon and J. R. Swain; *Platinum Metals Rev.*, 1975, **19**, 1.

[12] P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 1797.

[13] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5271.

[14] Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1965, **4**, 870.

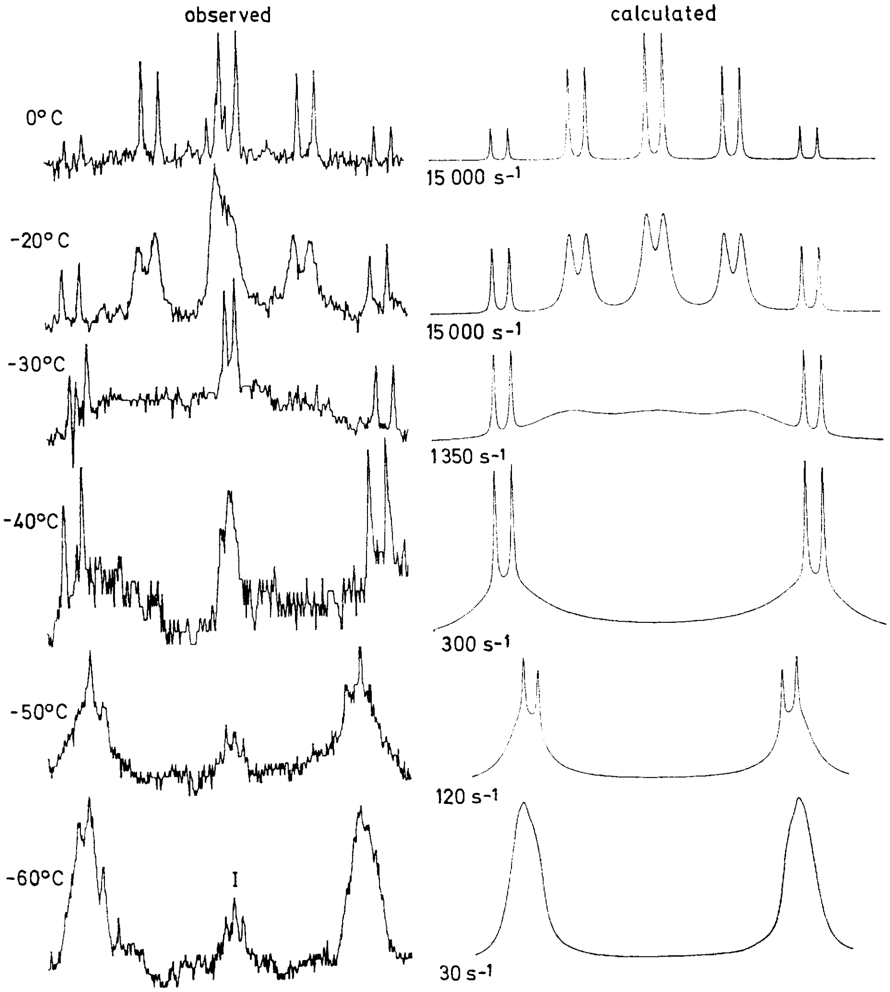

FIGURE 1 Observed and calculated temperature-dependent hydride region of the ^{1}H n.m.r. spectra (90 MHz) for a solution of $[RhH\{P(OCH_2)_3CPr^n\}_4]$

TABLE 1

Hydrogen-1 and ^{31}P n.m.r. data for the complexes $[MH\{P(OCH_2)_3CPr^n\}_4]$ [a]

	$[CoH\{P(OCH_2)_3CPr^n\}_4]$	$[RhH\{P(OCH_2)_3CPr^n\}_4]$	$[IrH\{P(OCH_2)_3CPr^n\}_4]$
	High-temperature limit [b]		
$\tau(M-H)$	24.44 (q)	20.75 (dq)	23.88 (q)
$\lvert{}^2J(P-H)\rvert$	12.1	44.12	21.12
$\lvert{}^1J(Rh-H)\rvert$		8.82	
$\delta(P)$	-142.73 [c]	-126.90	-89.76
$\lvert{}^1J(Rh-P)\rvert$		225.28	
	Data from lowest temperature reached [d]		Low-temperature limit [e]
$\tau(M-H)$	23.99 [f]	21.06 (d)	23.96
$^2J(P_{ax}-H)$		ca. 179	∓ 141.74
$^2J(P_{eq}-H)$			± 18.93
δP_{ax}	-142.18 [g]	-136.15	-93.41
δP_{eq}		-124.19	-87.36
$^2J(P_A-P_A)$		ca. 63	± 46.86
$^1J(Rh-P_B)$		ca. 241	

[a] d = Doublet, q = quintet, dq = doublet of quintets; δ in p.p.m., *J* in Hz. [b] 298 K. [c] Value at half-height, 93.7 Hz. [d] 173 K. [e] 203 K. [f] Value at half-height, 63 Hz. [g] Value at half-height, 78.7 Hz.

as in the present case, fully resolved low-temperature-limit spectra could not be obtained. The quality of the temperature-dependent n.m.r. spectra does not warrant an analysis of the rate data obtained from the n.m.r. spectra in terms of the Eyring or Arrhenius equations. The free energy of activation ($\Delta G^\ddagger$) at -35 °C is 10.5 kcal mol^{-1}.* This is considerably larger than the free energy of activation obtained for [RhH{P(OEt)$_3$}$_3$] [13] ($\Delta G_{175}^\ddagger = 7.25$ kcal mol^{-1}). We suggest that the larger steric size of the P(OEt)$_3$ ligand with respect to P(OCH$_2$)$_3$CPr (cone angles [15] of 109 and 101°, respectively) more strongly favours the pseudo-tetrahedral geometry in [RhH{P(OEt)$_3$}$_4$] thus facilitating the tetrahedral-jump process. It should be noted that there is no mechanistic information contained in the temperature n.m.r. lineshapes themselves since there is only one basic permutational set (apart from the identity) for a C_{3v} MHL$_4$ complex.[13] It is interesting to note that the free energy of activation for [RhH(PF$_3$)$_4$] is intermediate (9.0 kcal mol^{-1}) [13] between that of [RhH{P(OEt)$_3$}$_4$] and [RhH{P(OCH$_2$)$_3$CPr}$_4$] and the cone angle is also of intermediate size (104°).[15a] It is difficult to rationalize the activation-energy trend [RhH{P(OCH$_2$)$_3$CPr}$_4$] > [RhH(PF$_3$)$_4$] > [RhH{P(OEt)$_3$}$_4$] on the basis of the electronic characteristics of these three ligands.[15b]

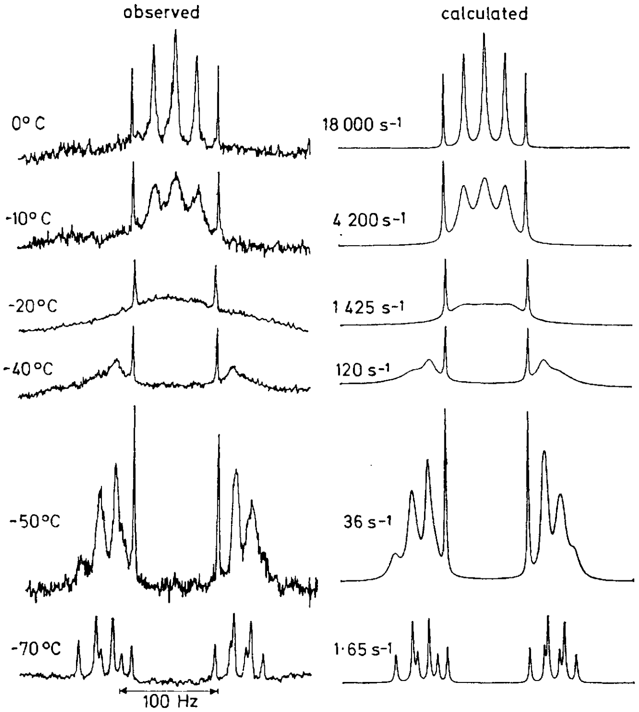

FIGURE 2 Observed and calculated hydride region of the ^{1}H n.m.r. spectra (90 MHz) for [IrH{P(OCH$_2$)$_3$CPr^n}$_4$] as a function of temperature

Low-temperature limiting ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra have been achieved for the iridium analogue [IrH{P(OCH$_2$)$_3$CPr^n}$_4$], however (Figures 2 and 3). The observed spectra at -70 °C show a good fit to a computer simulation using an AB$_3$X model, indicating that the structure in solution corresponds to a C_{3v} geometry with n.m.r. parameters J(P$_{ax}$–H) ± 141.74, J(P$_{eq}$–H) ∓ 18.93, and J(P$_{ax}$–P$_{eq}$) ± 46.86 Hz. Opposite signs for J(P$_{ax}$–H) and J(P$_{eq}$–H) have been observed previously in the low-temperature-limiting spectra of [Ir(CO)$_2$HL$_2$] [L = PPh$_3$ or P(C$_6$H$_4$Me-4)$_3$].[7] Calculated spectra correspond very well with the observed spectra (Figures 2 and 3) at all temperatures (exchange rates). The exchange rate is given as a function of temperature by the Eyring equation (1) with the activation parameters $\Delta H^\ddagger = 14.1$ kcal mol^{-1}, $\Delta S^\ddagger = 12.7$ cal K^{-1} mol^{-1}, $\Delta G_{298}^\ddagger = 10.3$ kcal mol^{-1}, $E_{298}^\ddagger = 14.7$ kcal mol^{-1}, and $\log_{10}(A_{298}) = 16.0$. The entropy of activation is rather large for a simple intramolecular process, but this is probably a result of errors in temperature calibration and fitting of the spectra, as indicated by discrepancies between rates obtained from the ^{1}H and ^{31}P-{^{1}H} spectra. The increase in rearrangement barrier for the compounds [MH(PF$_3$)$_4$] (M = Co, Rh, or Ir) on going down the

$$R(T) = (\boldsymbol{k}T/\boldsymbol{h})\exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT] \quad (1)$$

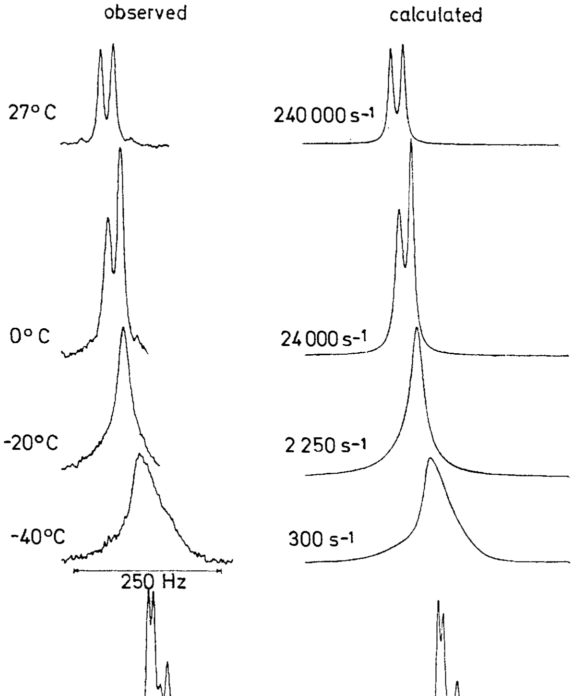

FIGURE 3 Observed and calculated proton-decoupled ^{31}P n.m.r. spectra of [IrH{P(OCH$_2$)$_3$CPr^n}$_4$] at various temperatures

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* 1 cal = 4.184 J.

[15] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, (*a*) 2956; (*b*) 2953.

Periodic Table has been rationalized [13] in terms of increased departure from pseudo-tetrahedral geometry as the size of the metal increases. For complexes of the type $[\mathrm{MH\{P(OCH_2)_3CPr^n\}_4}]$ we observe the barrier trend Co < Rh ≈ Ir. In this case with the very small $\mathrm{P(OCH_2)_3CPr^n}$ ligand the departure from pseudo-tetrahedral geometry may already be very large for the rhodium complex and little or no further change may occur on going from Rh to Ir. The $\mathrm{P(OCH_2)_3CPr^n}$ ligand may be sufficiently small that the $\mathrm{RhHL_4}$ and $\mathrm{IrHL_4}$ complexes can better be described in terms of trigonal-bipyramidal rather than pseudo-tetrahedral equilibrium geometries.

The ^{1}H and ^{31}P n.m.r. spectra of the complexes $[\mathrm{Ir(CO)H(PPh_3)\{P(OCH_2)_3CX\}_2}]$ (X = Pr^n, Ph, or NO$_2$) also show a temperature dependence. At room temperature the ^{1}H n.m.r. spectra consisted of a second-order triplet with a small $|^5J(\mathrm{PH}) + {}^3J(\mathrm{PH})|$ for the bridging methylene protons and a doublet of triplets at higher field for the hydride resonance. The ^{31}P-{^{1}H} n.m.r. spectra showed a doublet for the $\{\mathrm{P(OCH_2)_3CX}\}$ ^{31}P resonance and a triplet for the PPh$_3$ ^{31}P corresponding to an AX$_2$ system. For ^{1}H n.m.r. spectra in the range 283—313 K there was a marked change in coupling constants. Thus for $[\mathrm{Ir(CO)H(PPh_3)\{P'(OCH_2)_3CPr^n\}_2}]$ in CD$_2$Cl$_2$, J(P–H) 16.28—20.2 and J(P′–H) 6.1—8.55 Hz. Below 283 K, the ^{1}H n.m.r. spectrum started to collapse, the resolution of the CH_2 triplet was lost, and the doublet of triplets collapsed. The higher-field side triplet collapsed first followed by the lower-field region as the temperature was decreased further (*ca.* 233 K). At 213 K the broad signal for the methylene protons split to give two broad singlets. The intensity ratio of these signals changed from complex to complex and is shown in parentheses in Table 2. As this occurred a new hydride resonance centred *ca.* 0.5 p.p.m. toward higher field was observed with very different coupling constants (Table 2). Below this temperature the appearance of the spectra does not alter. It is of interest to note that the coupling constants do not change very much down the series X = Pr^n, Ph, NO$_2$ at −90 °C compared to the difference in coupling constants for the hydride resonance at room temperature. In addition to this well defined doublet of triplets there is a smaller resonance (most prominent in the X = Pr^n complex where the ratio of CH_2 signals is 1 : 1) centred at *ca.* τ 22.3. The multiplicity of this resonance cannot be determined unambiguously as it overlaps the larger doublet of triplets. However, we suggest that it is a pseudo-quartet.

TABLE 2

Hydrogen-1 and ^{31}P n.m.r. data for the complexes $[\mathrm{Ir(CO)H(PPh_3)\{P(OCH_2)_3CX\}_2}]$ [a]

(*a*) At 298 K

	Pr^n	Ph	NO$_2$
$\tau[\mathrm{P(OC}H_2\mathrm{)_3CX}]$	6.00 (t)	5.59 (t)	5.54 (t)
$\lvert {}^3J(\mathrm{P–H}) + {}^5J(\mathrm{P–H}) \rvert$	4.88	4.88	5.49
τ(Ir–H)	22.54 (dt)	22.46 (dt)	22.66 (dt)
^2J(P–H) [b]	17.42	22.79	35.20
^2J(P′–H) [b]	6.96	9.00	15.12
δP′	−88.26 (d)	−87.38 (d)	−85.92 (d)
δP	−9.28 (t)	−9.02 (t)	−7.47 [c]
J(P–P′)	71.62	64.36	50.05

(*b*) At 183 K

	Ratio of species present					
	1 : 1		1.5 : 1		2.5 : 1	
$\tau[(\mathrm{P(OC}H_2\mathrm{)_3CX}]$	6.07	5.77 (s)	5.66 (s) [d]	5.36 (s) [d]	5.58 (s)	5.25 (s)
τ(Ir–H)	23.15 (dt)	22.35 (q) [e]	23.07 (dt)	22.25 (q) [e]	23.17 (dt)	*f*
^2J(P–H)	86.47	18.86	85.65	19.55	83.01	
^2J(P′–H)	21.62		21.52		22.78	
δP′	−84.39 (d)	−89.72 (d)	−84.0 (d)	−89.0 (d)	−83.22 (d)	−88.20 (d)
δP	−8.34 (t) [g]	−10.18 (t) [g]	−7.86 (t) [g]	−10.23 (t) [g]	−5.29 (t)	−9.72 (t)
J(P–P′)	29.30	156.25	35.51	153.14	32.75	150.15

[a] s = Singlet, d = doublet, dt = doublet of triplets, q = quartet; δ in p.p.m., J in Hz. [b] P = PPh$_3$, P′ = $\mathrm{P(OCH_2)_3CX}$. [c] Value at half-height, 9.37. [d] Multiplicity uncertain because of overlap with other hydride resonance. [e] These two triplets overlap. [f] Not well resolved. [g] These two triplets overlap.

Similar phenomena are seen in the ^{31}P-{^{1}H} n.m.r. spectra. As in the ^{1}H n.m.r. spectra, the ^{31}P doublet and triplet started to collapse at *ca.* 283 K and a new spectrum was observed at 213 K. This consisted of two doublets for the phosphite ^{31}P signal and two triplets for the PPh$_3$ ^{31}P. However, these triplets overlap and in most cases it is difficult to obtain accurate J(P–P′) values from the PPh$_3$ resonance. This supports the ^{1}H n.m.r. evidence that two species are frozen out below 213 K. As in the ^{1}H n.m.r. spectra the two sets of resonances were of differing intensities, the ^{31}P doublet and triplet with the small coupling constant (*ca.* 35 Hz) corresponding to the hydride doublet of triplets, whereas the ^{31}P doublet and triplet with the large value (*ca.* 140 Hz) is connected with the small hydride resonance assigned as a quartet.

Attempts to carry out a quantitative lineshape analysis for this system were unsuccessful since the chemical shifts, coupling constants, and the relative populations, as well as the exchange rate, are all temperature dependent. The strong temperature dependence of the high-resolution n.m.r. parameters could imply that more than two isomers are involved, with exchange between two separate sets of isomers being fast on the n.m.r. time scale at −90 °C. The low solubility of these complexes precludes the recording of spectra at lower temperatures in order to obtain limiting conditions. The only conclusion permitted from the available data is that the doublet of triplets hydride resonance at −90 °C in which J(P–H) is large (*ca.* 81 Hz) is probably due to an isomer or isomers in which the H–Ir–PPh_3 angle is >90°.

It has also been found that the ^1H n.m.r. spectra of the complexes $[Ir(CO)H(PPh_3)_2\{P'(OCH_2)_3CX\}]$ (X = Pr^n or NO_2) show a doublet of triplets with comparable coupling constants for J(P–H) and J(P′–H) (see Table 3).

TABLE 3

Hydrogen-1 and ^{31}P n.m.r. data for the complexes $[Ir(CO)H(PPh_3)_2\{P(OCH_2)_3CX\}]$ [a]

	X	
	Pr^n	NO_2
(*a*) At 298 K		
$\tau[P(OCH_2)_3CX]$	5.94 (d)	5.39 (d)
^3J(P–H)	4.80	5.49
τ(Ir–*H*)	21.62 (dt)	21.49 (dt)
^2J(P–H) [b]	18.92	17.40
^2J(P′–H) [b]	15.26	20.75
δP′	−92.65	−89.94
δP	−12.73	−12.15
J(P–P′)	175.34	183.94
(*b*) At 273 K		
$\tau[P(OCH_2)_3CX]$	5.58 (s) [c]	5.14 (s) [d]
τ(Ir–*H*)	21.49 (q) [e]	21.44 (q) [e]
^2J(P–H)	19.71 [b]	20.19
δP′	−94.04	−92.16
δP	−14.02	−13.63
J(P–P′)	187.87	194.76

[a] s = Singlet, d = doublet, q = quartet, dt = doublet of tripets; δ in p.p.m., J in Hz. [b] P = PPh_3, P′ = $P(OCH_2)_3CX$. [c] Value at half-height, 12.5 Hz. [d] Value at half-height, 10.7 Hz. [e] Pseudoquartet.

These spectra did not change significantly as the temperature was decreased to −100 °C. The hydride region changed slightly to give the appearance of a quartet, but this is most likely due to loss of resolution with decreasing temperature. The only change in the ^{31}P-$\{^1H\}$ n.m.r. spectra was a gradual increase in J(P–P′) as the temperature was decreased. It is reasonable to assume therefore that the isomer present is a trigonal bipyramid with all three phosphorus nuclei in the equatorial plane. This is the known stereochemistry for $[Ir(CO)H(PPh_3)_3]$ [16] and substitution of one PPh_3 would not be expected to change the configuration significantly.

However, the ^1H n.m.r. spectrum of the rhodium analogue $[Rh(CO)H(PPh_3)_2\{P'(OCH_2)_3CPr^n\}]$ showed a marked dependence on temperature. The hydride region showed a triplet of double doublets at 25 °C [τ 20.16, J(P–H) 11.11, J(P′–H) 1.22, J(Rh–H) 2.89 Hz]. The latter two couplings were assigned by comparison with the ^1H n.m.r. spectrum with ^{31}P decoupling. This set of resonances broadened substantially as the temperature was decreased to give a triplet of triplets at 0 °C [J(P–H) 11.3, J(P′–H) 3.23, J(Rh–H) 2.93 Hz]; further cooling causes collapse at −40 °C, while down to −110 °C no further change was seen. Further cooling caused the precipitation of the complex and therefore a low-temperature-limiting spectrum was unobtainable.

The difference in temperature-dependent spectral behaviour between the monosubstituted derivatives $[M(CO)H(PPh_3)_2\{P(OCH_2)_3CX\}]$ (M = Rh or Ir) is possibly due to increased favourability of other isomers over the trigonal bipyramid with three equatorial P nuclei, due to the smaller size of the central metal atom.

EXPERIMENTAL

All preparations and handling were carried out in an atmosphere of dry nitrogen.

4-n-Propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was prepared by a method previously described.[17]

4-Phenyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]*octane*.— 2-Hydroxymethyl-2-phenylpropane-1,3-diol [18] (17.9 g, 98.3 mmol) and pyridine (23.8 ml, 2.96 mmol) were dissolved in tetrahydrofuran (thf) (100 cm^3) and placed in a dropping funnel. Phosphorus trichloride (8.6 ml, 98.5 mmol) in thf (100 cm^3) was placed in a second dropping funnel. The two solutions were slowly added dropwise over 1 h, to thf (100 cm^3), cooled to 0 °C, and stirred mechanically. The resulting white suspension was allowed to warm to room temperature over 3 h. The white precipitate was filtered off leaving a colourless filtrate. The solvent was removed by vacuum evaporation and the oily residue was sublimed at 80 °C and 0.01 mmHg pressure to give the white crystalline product (13.8 g, 67%). *4-Nitro-2,6,7-trioxa-1-phosphabicyclo*[2.2.2]*octane* was similarly prepared in 9% yield using phosphorus tribromide.

Hydridotetrakis(*4-n-propyl-2,6,7-trioxa-1-phosphabicyclo*-[2.2.2]*octane*)*cobalt*(I).—A solution of cobalt(II) nitrate hexahydrate (0.25 g, 0.86 mmol) in absolute ethanol (10 cm^3) and 2,2-dimethoxypropane (2 cm^3) was stirred for 1 h. The ligand 4-n-propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane (0.76 g, 4.3 mmol) was dissolved in this violet solution, followed by slow dropwise addition of sodium tetrahydridoborate (0.17 g, 4.49 mmol) in absolute ethanol (5 cm^3). The violet solution was rapidly decolourized and a white precipitate formed, which was recrystallized from chloroform–ethanol (1 : 3) giving the required product as white needles (0.176 g, 0.23 mmol, 27%) (Found: C, 43.05; H, 6.60; P, 18.7. Calc. for $C_{28}H_{53}CoO_{12}P_4$: C, 44.0; H, 6.95; P, 16.25%).

Hydridotetrakis(*4-n-propyl-2,6,7-trioxa-1-phosphabicyclo*-[2.2.2]*octane*)*rhodium*(I).—The ligand (0.48 g, 2.7 mmol) was added to a suspension of carbonylhydridotris(triphenylphosphine)rhodium(I) (0.50 g, 0.55 mmol) in absolute ethanol (10 cm^3) and the resulting yellow suspension was magnetically stirred for 2 h during which time the yellow colour slowly disappeared and a white suspension was obtained. The white precipitate was filtered off and washed several times with small portions of anhydrous diethyl ether to give the required product (0.21 g, 0.23 mmol, 42%) (Found: C, 41.5; H, 6.55; P, 15.6. Calc. for $C_{28}H_{53}O_{12}P_4Rh$: C, 41.6; H, 6.60; P, 15.3%).

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Hydridotetrakis(4-*n-propyl*-2,6,7-*trioxa*-1-*phosphabicyclo*-[2.2.2]*octane*)*iridium*(I).—The ligand (2.04 g, 11.55 mmol) was added to a solution of *mer*-trihydridotris(triphenylphosphine)iridium(III) (2.27 g, 2.3 mmol) in benzene (60 cm^3) and the pale yellow solution was heated under reflux for 2 d. The resulting solution was evaporated to give a yellow oil, the extraction of which with methanol (20 cm^3) followed by the addition of diethyl ether (10 cm^3) gave the required product as white prisms (0.67 g, 0.75 mmol, 32.5%) (Found: C, 37.2; H, 5.95. Calc. for $C_{28}H_{53}IrO_{12}P_4$: C, 37.45; H, 5.80%).

Carbonylhydridobis(4-*n-propyl*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane*)(*triphenylphosphine*)*iridium*(I).— Carbonylhydridotris(triphenylphosphine)iridium (0.5 g, 0.5 mmol) and 4-n-propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane (0.44 g, 2.5 mmol) were dissolved in benzene (10 cm^3) and stirred magnetically at room temperature for 2 d. Diethyl ether (5 cm^3) was added to the resulting colourless solution which was cooled to -20 °C for several hours to give the required product as white crystals (0.31 g, 0.37 mmol; 73%) (Found: C, 47.2; H, 5.20. Calc. for $C_{33}H_{42}IrO_7P_3$: C, 47.4; H, 5.05%).

The following two complexes were similarly prepared: *carbonylhydridobis*(4-*phenyl*-2,6,7-*trioxa*-1-*phosphabicyclo*-[2.2.2]*octane*)(*triphenylphosphine*)*iridium*(I) (61%) (Found: C, 51.7; H, 4.35. Calc. for $C_{39}H_{38}IrO_7P_3$: C, 51.85; H, 4.25%); *carbonylhydridobis*(4-*nitro*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane*)(*triphenylphosphine*)*iridium*(I) (86.5%) (Found: C, 38.7; H, 3.50; N, 3.15. Calc. for $C_{27}H_{28}IrN_2O_{11}P_3$: C, 38.5; H, 3.35; N, 3.35%).

Carbonylhydrido(4-*propyl*-2,6,7-*trioxa*-1-*phosphabicyclo*-[2.2.2]*octane*)*bis*(*triphenylphosphine*)*iridium*(I).— Carbonylhydridotris(triphenylphosphine)iridium (0.83 g, 0.83 mmol) and 4-propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (0.15 g, 0.83 mmol) were added to absolute ethanol (20 cm^3). The yellow suspension was stirred magnetically at room temperature for 6 d. The resulting pale yellow suspension was filtered off and washed with diethyl ether (5 cm^3) to give the required pale yellow product (0.59 g, 0.64 mmol, 77%). *Carbonylhydrido*(4-*nitro*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane*)*bis*(*triphenylphosphine*)*iridium*(I) was similarly prepared in 82% yield (Found: C, 53.25; H, 4.05; N, 1.65. Calc. for $C_{41}H_{37}IrNO_6P_3$: C, 53.25; H, 4.05; N, 1.50%).

Carbonylhydrido(4-*propyl*-2,6,7-*trioxa*-1-*phosphabicyclo*-[2.2.2]*octane*)*bis*(*triphenylphosphine*)*rhodium*(I).— Carbonylhydridotris(triphenylphosphine)rhodium(I) (0.5 g, 0.55 mmol) and 4-n-propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane (0.12 g, 0.66 mmol) were added to absolute ethanol (20 cm^3) and stirred magnetically at room temperature for 7 h. The resulting pale yellow solution was filtered and washed with ethanol to give the required pale yellow product (0.38 g, 0.46 mmol, 84%). This product was shown by ^{1}H n.m.r. to be contaminated with starting material and another complex which was probably the monotriphenylphosphine derivative.

N.M.R. Procedure.—Hydrogen-1 and ^{31}P n.m.r. spectra were recorded on a Bruker HFX-90 spectrometer in the Fourier-transform mode at 90 and 36.43 MHz, respectively, using deuterium to provide the field–frequency lock. Hydrogen-1 chemical shifts were recorded using tetramethylsilane as internal standard, while ^{31}P chemical shifts are given with respect to external 85% phosphoric acid assuming that the ^{31}P chemical shift of trimethyl phosphite is -141.00 p.p.m. with respect to 85% H_3PO_4. Shifts to low field are negative. The n.m.r. samples were prepared in a nitrogen atmosphere. [$^2H_2$]Methylene chloride–methylene chloride and [$^2H_2$]methylene chloride–dichlorofluoromethane were used as low-temperature solvents.

Lineshape calculations. Complete n.m.r. lineshape calculations were made using the density-matrix method of Kaplan [19] and Alexander.[20] Details of the numerical methods used in the calculations are given in ref. 21. A double-precision version of the program described in ref. 21 was used. Unlike our earlier work [13] on $[RhH\{P(OEt)_3\}_4]$ where a first-order approximation was used to analyse the temperature-dependent n.m.r. spectra, a complete analysis was carried out in this work.

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