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CONFORMATIONAL EQUILIBRIA IN 7-MEMBERED RING METAL CHELATE COMPLEXES

PENNY A. CHALONER *

Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY (Great Britain)

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Summary

Bis(diphosphine)metal and (diphosphine)(diene)metal (M = Rh, Ir) cationic complexes containing 7-membered chelate rings have been studied by low temperature ^{31}P and ^{1}H NMR spectroscopy. For cyclooctadiene-1,4-bis(diphenylphosphino)-butane- and -DIOP-rhodium, and cyclooctadiene-1,4-bis(diphenylphosphino)butane-iridium complexes, boat and chair conformations may be distinguished at low temperature. ^{1}H NMR spectra of these and analogous complexes suggest that both boat and chair conformers are significantly populated at room temperature. Bis(diphosphine) complexes of rhodium and iridium show very complex dynamic behaviour.

Introduction

Chelating diphosphine complexes of platinum group metals have been used as catalysts in a wide range of reactions including hydrogenation [1], hydroformylation [2], hydrosilylation [3] and Grignard coupling [4]. Our particular interest was in the use of diphosphines forming 7-membered chelate rings in rhodium complexes and their use in asymmetric hydrogenation [5]. Whilst 7-ring chelates such as DIOP, (**1**) rarely give the very high enantiomer excesses in the reduction of dehydroamino acids found for complexes of CHIRAPHOS (**2**) and DIPAMP, (**3**) which form 5-membered chelate rings, their range of substrates is much larger [6] **. It is considered

* Present address: School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ (Great Britain).

** DIOP = *RR*-4,5-bis(diphenylphosphino)methyl-2,2-dimethyldioxolane
CHIRAPHOS = *SS*-2,3-bis(diphenylphosphino)butane
DIPAMP = *RR*-bis(*o*-anisylphenylphosphino)ethane
COD = cyclooctadiene
dppb = 1,4-bis(diphenylphosphino)butane
dppp = 1,3-bis(diphenylphosphino)propane

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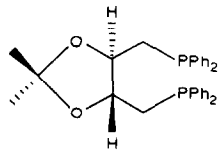

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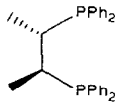

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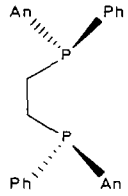

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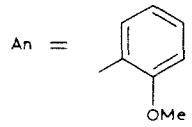

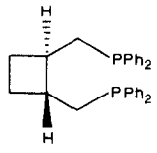

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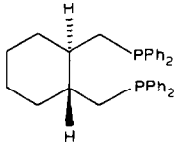

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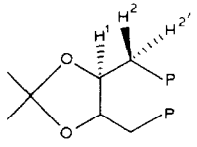

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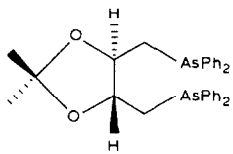

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that the flexibility, or otherwise, of the chelate ring is of considerable importance both in substrate binding and in hydrogen addition [7]. In this context Pignolet has studied the low temperature ^{31}P NMR spectra of bis(1,4-bis(diphenylphosphino)butane)rhodium tetrafluoroborate ($(dppb)_2RhBF_4$)) and bis(1.3-diphenylphosphinopropane) rhodium tetrafluoroborate ($(dppp)_2RhBF_4$) and has determined the crystal structures of $(dppb)_2RhBF_4$ and [(dppb)Rh-(1,5-cyclooctadiene) BF_4 [8]. The conformation of the chelate ring in DIOP complexes has been analysed by Kagan in the light of published X-ray structures [9]. Preliminary results describing the dynamic behaviour of $(DIOP)_2Pt$ and $(DIOP)_2Pd$ have been reported [10,11].

Results

^{31}P NMR studies

[(DIOP)Rh(COD)]BF_4. At room temperature in CH_2Cl_2 a sharp ^{31}P signal (δ 13.8 ppm, J(P,Rh) 143 Hz) is obtained for the complex. On cooling the signal broadens and splits into two rhodium coupled doublets of unequal intensity (Fig. 1, δ_1 15.8 ppm, J(RhP) 148 Hz; δ_2 11.8 ppm, J(RhP) 146 Hz). The spectra were simulated and $\Delta G^{\neq}$ found to be 34.6 $\pm$ 1.0 kJ mol^{-1} at 200 K. The ratio of the signal intensities varied with temperature, being 55/45 at 225 K and 64/36 at 163 K.

[(dppb)Rh(COD)]BF_4. The temperature dependence of the ^{31}P NMR spectrum of this complex was closely analogous to that observed for the DIOP species. At room temperature δ 25.6 ppm, J(RhP) 143 Hz whilst at low temperature signals at δ 27.5, J(RhP) 142 and δ 23.6 ppm, J(RhP) 139 Hz are distinguished. The limiting population ratio is approximately 2/1.

[(dppb)Ir(COD)]BF_4. The spectra of this species were very similar to those of the rhodium complexes, except for the absence of P–Rh coupling. Computer simulation of the spectra allowed $\Delta G^{\neq}$ to be determined as 36.6 $\pm$ 0.3 kJ mol^{-1} at 196 K. The populations of the two species were in the ratio 50/50 at 215 K and about 60/40 at 184 K. At room temperature δ 15.2 and at low temperature signals at δ 15.36 and δ 13.9 ppm were distinguished, the former predominating.

Other [diphosphinedienerhodium] BF_4 complexes. The ^{31}P NMR spectra of a

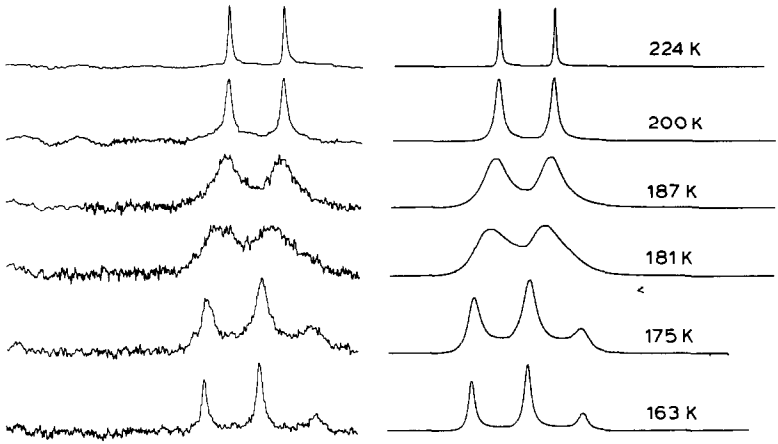

Fig. 1. Observed and calculated ^{31}P NMR spectra of bis(1,4-bis(diphenylphosphino)butane)rhodium tetrafluoroborate ($(dppb)_2RhBF_4$) and bis(1,3-bis(diphenylphosphino)propane)rhodium tetrafluoroborate ($(dppb)_2RhBF_4$).

number of other complexes were studied in the range 185–300 K. The cyclooctadienerhodium complexes of **4** and **5** showed no dynamic behaviour, nor did the bicyclo[2.2.1]heptadiene complexes of DIOP, dppb or **4**. In some cases temperature dependent chemical shifts were observed; whilst these might be due to a change in population of conformers, other explanations are also possible. The bicycloheptadiene complex of **5** shows broadened signals ($w_{1/2}$ 41 Hz) at 178 K but a limiting spectrum could not be obtained.

[(dppb)$_2$Rh]BF$_4$. The temperature variation of the ^{31}P spectrum of this species in CH_2Cl_2 showed very complex behaviour, broadly similar to that described by Pignolet in acetone. The low temperature limiting spectrum (Fig. 2) cannot be analysed but characteristic J(PP) *cis* and *trans* coupling constants can be discerned. In addition it is clear that there are several conformationally distinct species present.

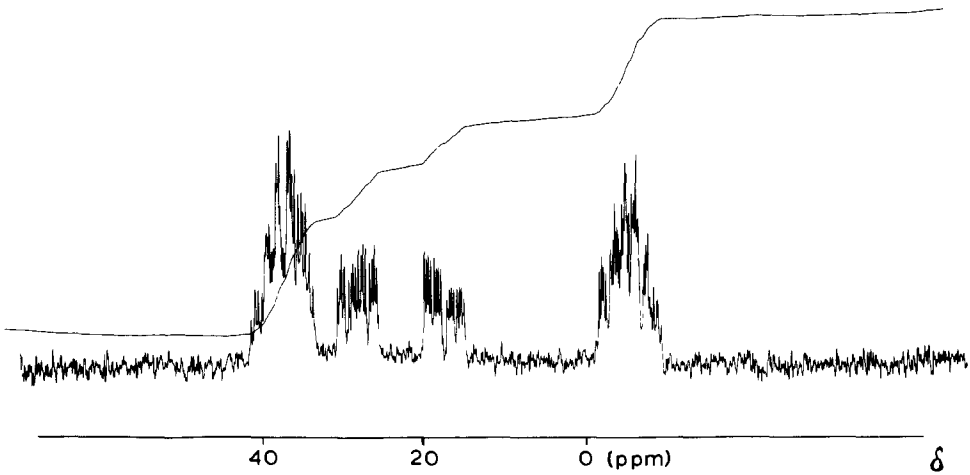

Fig. 2. ^{31}P NMR spectrum of $[(dppb)_2Rh]BF_4$ in CH_2Cl_2 at 178 K.

[(DIOP)$_2$Rh]BF$_4$. On cooling a sample of [(DIOP)$_2$Rh]BF$_4$ in CH_2Cl_2, complex behaviour is observed. At 273 K a fairly sharp rhodium coupled doublet is separated from a broader signal. By 243 K the broad signal is a doublet. At 228 K the sharp signals are broadening, a new upfield signal has appeared and there is a clear rhodium coupled triplet. In the limiting spectrum (Fig. 3) the lines are all fairly sharp and most can be analysed in terms of a non-symmetric structure with the following parameters: δ_1 23.1 ppm; J(RhP(1)) 140, J(P(1)P(2)) 40, J(P(1)P(3)) 40, J(P(1)P(4)) 260 Hz; $\delta_2 = \delta_3 = 16.6$ ppm; J(RhP(2)) 132, J(P(2)P(3)) 40, J(P(2)P(4)) 40 Hz; δ_4 −3.2 ppm, J(RhP(4)) 140 Hz. The small signal centred at δ 9.5 ppm, J(RhP) 135 Hz is not easy to interpret but its population is much reduced at this temperature.

[(dppb)$_2$Ir]BF$_4$. The dynamic behaviour of this complex is similar to its rhodium analogue with several distinguishable species. At the low temperature limit the signals are not amenable to analysis, but a *trans* J(PP) of 265 Hz is clearly discernible on the most upfield signal.

[((−)-DIOP)$_2$Ir]BF$_4$ and [((+)-DIOP)((−)-DIOP)Ir]BF$_4$ [12]. Whilst the spectra of these two species showed broadly similar changes on cooling, their low temperature limiting spectra were quite distinct. Unlike the rhodium analogue [13], [((−)-DIOP)$_2$Ir]BF$_4$ does not exchange with (+)-DIOP in 1 week at room temperature. If ((cyclooctene)$_2$IrCl)$_2$ was treated with a mixture of (+)-DIOP and (−)-DIOP the mixed complex was formed exclusively under conditions of kinetic control. The dynamic behaviour of [((−)-DIOP)$_2$Ir]BF$_4$ is shown in Fig. 4.

Proton NMR studies

Coupling constants in the 7-membered ring. For complexes of DIOP we might expect substantial variations in dihedral angles around the ring on changing from the chair to the boat conformation. For example, application of the Karplus equation to H(1), H(2) and H(2′) in **6** gives $J_{1,2}$ 0–1.5 Hz for a chair and $J_{1,2}$ 2–4 Hz for a boat, whereas $J_{1,2'}$ 9–11 Hz in the chair and $J_{1,2'}$ 2–4 Hz in the boat. With this

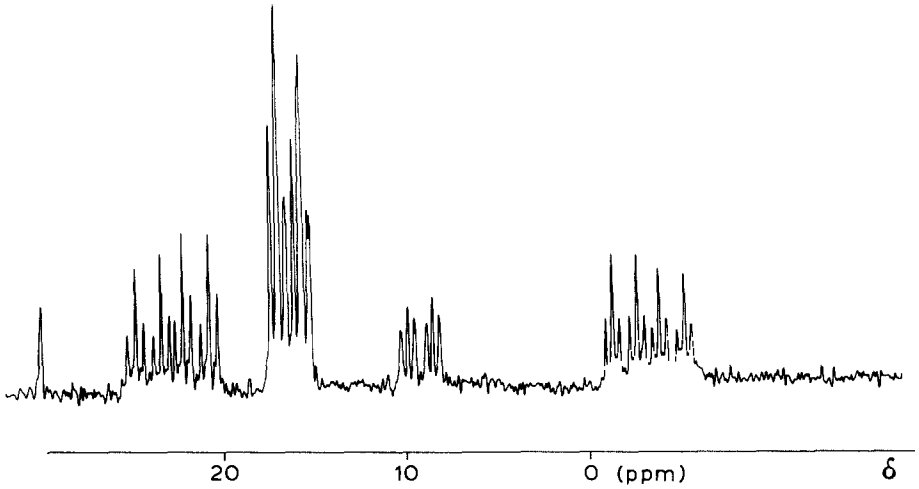

Fig. 3. ^{31}P NMR spectrum of [(DIOP)$_2$Rh]BF$_4$ in CH_2Cl_2 at 178 K.

in mind we determined the coupling constants in a range of DIOP and its arsine analogue complexes [14–16] (Table 1). Table 2 shows similar results for other phosphines which form 7-membered chelate rings. In this latter group assignments were more difficult because the bridgehead hydrogen was not shifted in such a distinctive manner as for DIOP.

Dynamic behaviour. The dynamic behaviour which gave such clear cut results in the ^{31}P NMR spectra gave ^{1}H spectra which were less easy to interpret. In the

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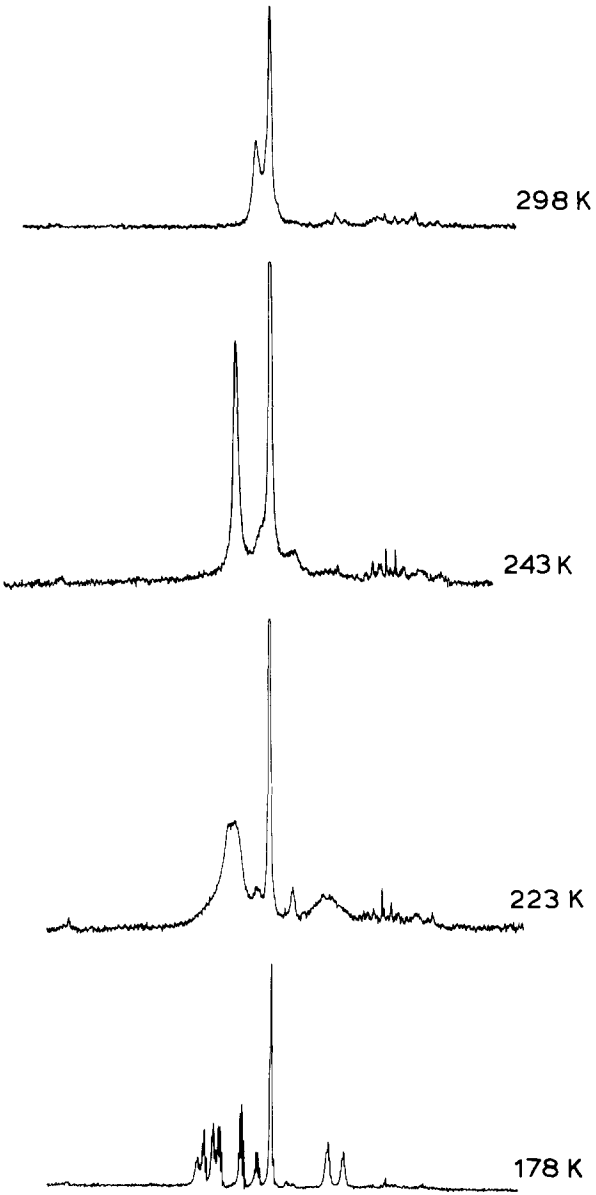

Fig. 4. Temperature dependence of the ^{31}P NMR spectrum of $[((-)\text{-DIOP})_2Ir]BF_4$.

TABLE 1

^{1}H NMR SPECTRA OF DIOP COMPLEXES (δ, ppm; J, Hz)

Complex	δ(H(1))	δ(H(2))	δ(H(2'))	J(H(1)H(2))	J(H(1)H(2'))	J(H(2)H(2'))	J(H(1)P)	J(H(2)P)	J(H(2')P)
(DIOP)$PdCl_2$	3.91	2.83	2.56	2.3	7.0	14.5	7.0	10.5	5.0
$(DIOP)_2Pd$	3.62	2.94	2.01	0.0	11	15	1–2	0	?
[(DIOP)Rh-(bicycloheptadiene)]-BF_4	3.65	2.89	2.47	2.0	7.0	15	?	10.0	0.0
[(DIOP)Rh(1,5-cyclooctadiene)]BF_4	3.66	2.76	2.49	1.5	6.0	14	3.0	11	0.0
[(7)Rh(1,5-cyclooctadiene)]BF_4	3.88	2.69	2.52	1.8	8.0	13.5			
[(7)Rh(bicyclo-heptadiene)]BF_4	4.18	2.79	2.60	1.0	9.5	13			

TABLE 2

^{1}H NMR SPECTRA OF OTHER 7-RING DIPHOSPHINE-RHODIUM COMPLEXES (δ, ppm; J, Hz)

Complex	δ(H(2))	δ(H(2'))	J(H(1)H(2))	J(H(1)H(2'))	J(H(2)H(2'))	J(H(2)P)	J(H(2')P)
[(**4**)Rh(bicyclo-heptadiene)]BF_4 (**8**)	2.79	2.57	6.5	11	14	13	1.0
[(**4**)Rh(1,5-cyclooctadiene)]-BF_4 (**9**)	2.74	2.57	2.0	9.0	14.5	11.5	<1
[(**5**)Rh(bicyclo-heptadiene)]BF_4 (**10**)	2.43	2.19	3.0	8.0	15.5	7.5	0
[(**5**)Rh(1,5-cyclooctadiene)]-BF_4 (**11**)	2.40	2.25	3.0	8.8	15.0	10.5	0

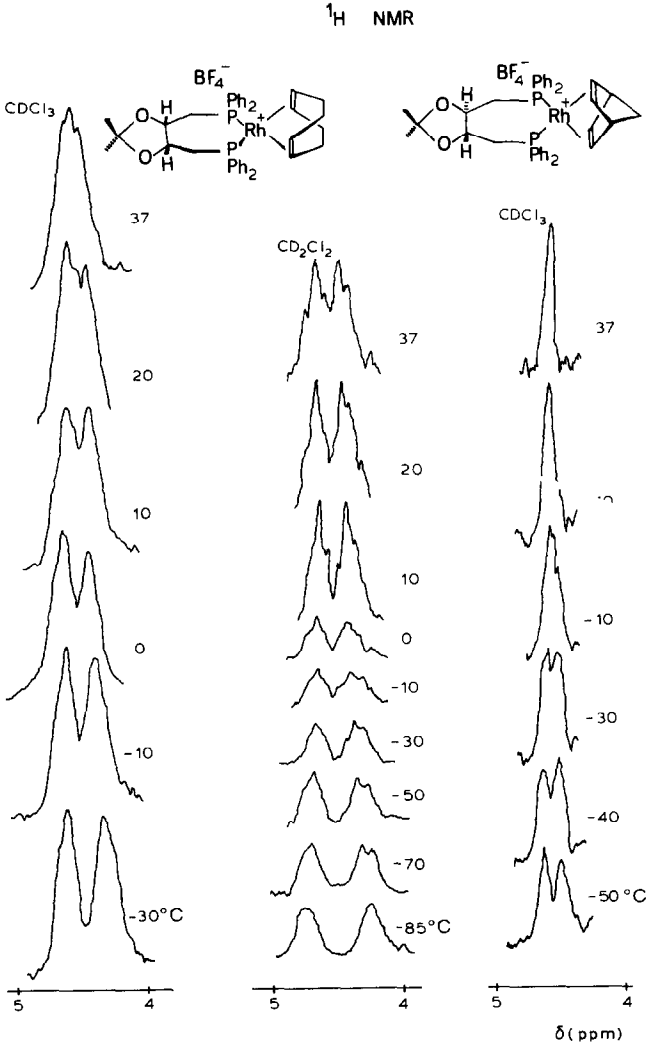

Fig. 5. Temperature dependent ^{1}H NMR spectrum of the diastereotopic vinyl hydrogens in DIOP rhodium diene complexes.

TABLE 3

TEMPERATURE DEPENDENCE OF THE CHEMICAL SHIFT[a] OF DIENE PROTONS IN RHODIUM COMPLEXES OF CHIRAL PHOSPHINES

Complex		Temperature (K)						
		310	289	260	241	223	206	183
8	δ_1	4.45	4.46	4.44	4.45	4.45	4.47	4.48
	δ_2	4.20	4.13	4.08	4.03	3.97	3.92	3.87
9	δ_1	[b]	[c]	4.44	4.44	4.45	4.47	4.50
	δ_2	[b]	[c]	4.27	4.22	4.18	4.10	4.04
10	δ_1	4.74	4.73	4.76	4.77	4.78	4.79	4.81
	δ_2	4.30	4.24	4.22	4.19	4.16	4.11	4.09
11	δ_1	4.61	4.73	4.78	4.78	4.79	4.79	4.80
	δ_2	4.03	3.88	3.95	3 92	3.85	3.80	3.77

[a] Solvent CD_2Cl_2, 90 MHz. [b] Signals not separated $\delta \sim 4.41$ ppm. $w_{1/2}$ 16 Hz. [c] Signals not separated $\delta \sim 4.40$ ppm. $w_{1/2}$ 27 Hz.

complex [(**5**)(COD)Rh]BF_4 there are substantial changes in the aromatic region on cooling. At 37°C there are four signals δ 7.4, 7.58, 7.88 and 8.21 ppm in the ratio 2/3/3/2. On cooling the signal at 8.21 ppm broadens and splits into two equal peaks at δ 8.8 and 7.7 ppm, as well as other changes. $\Delta G^{\neq}$ may be estimated only very approximately as 44 ± 5 kJ mol^{-1}. The analogous complex of **4** gives a similar result with $\Delta G^{\neq} \sim 40$ kJ mol^{-1}. Temperature dependent effects are also seen in the proton spectrum of [$(dppb)_2$Ir]BF_4; at 220 K a small signal at δ 9.63 ppm is sufficiently sharp to observe.

Diastereotopicity of diene protons. Significant temperature dependent chemical shifts were observed in the diastereotopic protons attached to the diene. The results for DIOP are shown in Fig. 5 and are detailed for other complexes in Table 3.

Discussion

The conformations of the 7-membered chelate ring in diphosphinemetal complexes may be modelled on cycloheptane. Four low energy conformations are accessible to cycloheptane, the chair, twist chair, boat, and twist boat, the chairs being somewhat more stable and the boat ⇌ chair barrier being approximately 34 kJ mol^{-1} [17]. In relating this barrier to that in metal chelates it must be noted that the bond length increase will tend to reduce the barrier but repulsions between the phenyl rings and other ligands will increase it. The available crystal structural data are summarised in Table 4.

Study of the coupling constants in the 7-membered ring and comparison with theoretical values from the Karplus equation lead to the conclusion that for most diphosphinedienerhodium complexes both chair and boat conformations are present in solution, with some preference for the chair form. At low temperature we believe that the ^{31}P NMR signals for the chair and boat form are distinct in some cases, and we may tentatively assign the one with the higher chemical shift to the predominant chair form in each case. That the barrier to interconversion of chair and boat forms is almost the same as for cycloheptane is probably fortuitous; a lowering of the barrier due to increased bond lengths is offset by interactions of the P-phenyl rings

TABLE 4

CONFORMATIONS OF 7-MEMBERED CHELATE RINGS IN DIPHOSPHINEMETAL COMPLEXES STUDIED BY X-RAY CRYSTALLOGRAPHY

Chair or Twist Chair	Boat or Twist Boat
(DIOP)$PtCl_2$ [a] [18]	(DIOP)$PtCl_2$ [a]
(DIOP)$PdCl_2$ [a]	(DIOP)$PdCl_2$ [a]
(DIOP)Ir(COD)Cl [19]	(dppb)Rh(COD)BF_4 [8]
(DIOP)$NiCl_2$ [18]	[(4)Rh(η^6-benzene)]ClO_4 [20]
$(dppb)_2RhBF_4$ [8]	
(DIOP)Rh(bicycloheptadiene)BF_4 [7]	
(DIOP)Fe(cyclopentadiene) [9]	
$HRh(DIOP)_2$ [21]	
$HRuCl(DIOP)_2$ [22]	

[a] Two molecules with distinct conformations exist in each unit cell.

with the cyclooctadiene ligands. Bicycloheptadiene is less sterically demanding and the barriers were not accessible to us in these complexes. The dynamic equilibria observed in the proton spectra are less easily interpreted. Whilst they may be connected with the boat chair equilibrium, an alternative explanation involves restricted rotation of one or more aromatic rings particularly where this would bring an *ortho*-hydrogen into close proximity to the metal. That the chemical shift difference between the diastereotopic alkene protons increases on cooling probably reflects the changing proportion of confomers but insufficient data are available for a more detailed explanation.

Bis(diphosphine)metal complexes may be expected to have higher barriers to boat $\rightleftharpoons$ chair interconversion than the (diphosphine)dienemetal complexes because of the increased Ph–Ph interactions at the transition state. This proved correct in the studies of $(DIOP)_2Pt$ and $(DIOP)_2Pd$ with barriers of 48 and 41 kJ mol^{-1} respectively. Whilst the dynamic spectra of $(DIOP)_2Ir^+$, $(dppb)_2Ir^+$ and their rhodium analogues could not be simulated, the line broadening is evident even at room temperature, indicating a fairly high barrier to conformational interconversion. Comparison of the NMR spectra of $(DIOP)_2Rh^+$ and $(dppb)_2Rh^+$ with the data reported by Pignolet is instructive. Particularly in $(DIOP)_2Rh^+$ some symmetry is retained and two mutually *trans*-phosphorus atoms are equivalent. These data may be related to the bond parameters in $(dppb)_2Rh^+$; one RhP distance is unusually long and may correspond to P(4) at δ −3.2 ppm, whilst the *trans*-phosphorus has a short Rh–P distance which may be related to P(1) at δ 23.1 ppm. The other two Rh–P distances are similar and intermediate, as is the chemical shift observed for them.

Conclusions

The considerable conformational flexibility shown in complexes of diphosphines which form seven-membered chelate rings has important implications for their role in catalysis. The asymmetric environment in chiral phosphine complexes is controlled by the orientation of the phosphorus-bound phenyl rings and is substantially altered on interconversion of boat and chair rings. The dynamic behaviour of the systems we have studied suggests that the differences in energy between conforma-

tions is small, and barriers to their interconversion low. Thus many potential conformations are readily accessible to intermediates in catalysis by these complexes, and arguments based only on crystallographic studies must be treated with more caution than is warranted for the 5-ring chelate complexes.

Experimental

All manipulations involving air-sensitive species were carried out in Schlenk apparatus under an atmosphere of dry argon and solvents were thoroughly degassed before use according to standard vacuum line techniques. Melting points were recorded on a Reichert Köfler block and are uncorrected. ^{31}P NMR spectra were recorded on a Bruker WH90 or WH250 spectrometer and are reported relative to external H_3PO_4. ^1H NMR spectra were recorded on Perkin–Elmer R32, Varian XL300 and Bruker WA300 spectrometers. Optical rotations were measured on a Perkin–Elmer 141 polarimeter. Microanalyses were performed by Dr. F.B. Strauss, Oxford. All solvents employed were dried and distilled before use. Simulations of dynamic NMR spectra employed SHAPE using a Bruker WH90 spectrometer.

Diphosphinedienerhodium(I) tetrafluoroborate complexes

These were prepared as previously described [15] and the appropriate details of new complexes are collected in Table 5.

Bis(1,4-bis(diphenylphosphino)butane)iridium(I) tetrafluoroborate

A mixture of tetrakis(cyclooctene)-μ-dichlorodiiridium (179 mg, 0.2 mmol) and 1,4-bis(diphenylphosphino)butane (340.5 mg, 0.8 mmol) was stirred under argon in CH_2Cl_2 (2 ml). To the deep red solution was added silver tetrafluoroborate (80 mg, 0.4 mmol). The solution was filtered to remove precipitated silver chloride and slow addition of ether gave red crystals of bis(1,4-bis(diphenylphosphino)butane)iridium(I) tetrafluoroborate (430 mg, 95%). Found: C, 59.63; H, 5.12; P, 11.14. $C_{56}H_{56}P_4IrBF_4$ calcd.: C, 59.42; H, 4.99; P, 10.95%. Mass spectrum (field desorption, M^+) 1043, 1045 ($C_{56}H_{56}P_4Ir^+$, Ir 191, 193).

Bis(1,4-diphenylphosphino)butane-1,5-cyclooctadieneiridium(I) tetrafluoroborate

This complex was prepared according to Crabtree's method in 76% yield [23].

TABLE 5

ANALYTICAL DATA ON DIPHOSPHINEDIENERHODIUM(I) TETRAFLUOROBORATE COMPLEXES

Phosphine	Diene	Analysis (Found (calcd.) (%))				α_D (solvent)
		C	H	P	F	
4	Cyclooctadiene	60.49 (60.82)	5.64 (5.64)	8.15 (8.25)	9.91 (10.13)	+7.23 ($CHCl_3$)
5	Bicyclo[2.2.1]-heptadiene	61.48 (61.44)	5.55 (5.65)	7.86 (8.13)	10.19 (9.97)	−13.25 ($CHCl_3$)
7	Cyclooctadiene	53.15 (52.97)	5.28 (5.02)		8.79 (8.59)	+24.7 ($CHCl_3$)

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