Articles

NMR Studies of the Structures of *p*-Aryl-Substituted Chiral Ligands in Rhodium(I) and Platinum(II) Complexes

Imre Tóth† and Brian E. Hanson*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

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The solution-phase stereochemistry of the chelate rings and aryl group arrangement of some *p*-aryl-substituted DIOP, BDPP, and Chiraphos derivatives is studied in various complexes by ^1H, ^{13}C, and ^{31}P NMR. The complexes are of the general composition [Rh(diene)L_2] BF_4, PtL_2Cl_2, where L_2 = DIOP-($pNMe_2$)$_4$, **1a**, BDPP-($pNMe_2$)$_4$, **2a**, Chirophos-($pNMe_2$)$_4$, **3a**; diene = NBD or COD and [Rh(diene)L_2]$(BF_4)_5$ where L_2 = DIOP-($pNMe_3^+$)$_4$, **1b**, DIOP-($pNHMe_2^+$)$_4$, **1c**, BDPP-($pNMe_3^+$)$_4$, **2b**, BDPP-($pNHMe_2^+$)$_4$, **2c**, Chiraphos-($pNMe_3^+$)$_4$, **3b**; diene = NBD or COD. The characterization of complexes such as [Rh(**2b**)$(CH_3CN)_2$]$(BF_4)_5$, Ni(**3a**)$(SCN)_2$, and Pt(**2a**)Cl($SnCl_3$) is also included. With the exception of the latter, each complex shows C_2 symmetry; also, with the exception of Pt(**1a**)Cl_2, each complex shows two, different aryl group environments. The similarity in the aryl resonances of these complexes, the ^{13}C resonances and proton–proton couplings in the chelate rings, and variable-temperature measurements are consistent with the presence of rigid, or highly preferred, chelate ring conformations. Accordingly, the aryl groups of these complexes are fixed in a chiral quasi-axial quasi-equatorial arrangement in solution. The complex, Pt(**1a**)Cl_2 was found to be conformationally labile by NMR. The higher conformational stability of Rh–diene complexes of *p*-aryl-substituted DIOP derivatives compared to the ones with nonsubstituted DIOP ligand and to Pt(**1a**)Cl_2 is attributed to the stabilizing effect of the bulky diene ligands and the *p*-aryl substituents on the chelate conformation.

Introduction

It is generally accepted that the major source of discriminatory interaction in asymmetric hydrogenation arises from the chiral array of aryl groups on the chelating ligands complexed to rhodium.[1,2] Evidence for this is that those ligands which can present aryl groups in a C_2 fashion have proven to be effective in asymmetric hydrogenation.[3] The first step is discriminative coordination to yield diastereomeric intermediates and the final success of enantioselective hydrogenation is due to the rate differences between parallel reaction paths via the diastereomers.[4,5] The prevailing product enantiomer can be derived from the energetically unfavorable diastereomer. Thus, a chiral arrangement of the aryl groups is a necessary but not sufficient condition for successful enantioselective hydrogenation.

Different chiral ligands can provide the required arrangement of aryl groups in several ways. For example, in the rhodium(I) complexes of DIPAMP[6] the *o*-methoxy groups of the axial anisyl rings can weakly coordinate the metal.[7-8] In BPPFA[9] complexes the chiral aminoalkyl side chain can serve the same function.[3a,9] The ligands BINAP,[10] DIOP,[11] BPPM,[12] BDPP (Skewphos),[13] Chiraphos,[14] and Prophos[15] form complexes in which one chelate ring conformation is considered to be most stable; the arrangement of aryl groups, in turn, is fixed by the ligand conformation.[3a,8,13b,14,15] In the absence of functional groups on the chelate backbone, seven-, six-, and even five-member chelate rings can be flexible. However, when the chelate ring has a chirally disposed second ring as in BINAP, DIOP, and BPPM or methyl groups as in Prophos, Chiraphos, and BDPP a single conformation of the chelate

† Current address: Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Amsterdam, The Netherlands.

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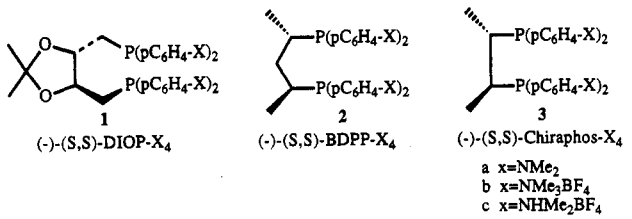
Chart I. Para-Substituted Chiral Ligands



ring may be preferred and may provide the asymmetric arrangement of phenyl rings.[8,12,13b,14-16]

Bosnich et al. have suggested that in Prophos, Chiraphos and BDPP complexes the conformational stability is due to the fact that the methyl groups on the chelate ring backbone prefer to be equatorially disposed.[13b,14,15] An equatorial position of cyclohexyl and phenyl groups in cycphos[17] and Phenphos[18] can fix the position of the phenyl rings in these ligands as well.

Crystallographic evidence[19] and solution NMR investigations[20,21] have provided support for the conformational flexibility of seven-member DIOP chelate rings. A recent X-ray crystallographic investigation of some BDPP complexes shows that this ligand can also adopt more than one ring conformation.[23]

Generally, speculations on the origin of stereoselectivity rely heavily on crystal structure determinations and ^{31}P NMR studies. Very few detailed solution ^{13}C or ^{1}H NMR studies on chiral chelate ring conformations are available.[24] The issue of chelate ring flexibility is crucial since ring flexibility necessitates a more complicated explanation for the mechanism of asymmetric induction.

The recently prepared complexes of *p*-aryl-substituted DIOP, BDPP, and Chiraphos derivatives[25,26] (ligands **1**, **2**, and **3** in Chart I) provide a good opportunity for a detailed ^{13}C and ^{1}H NMR study of chelate ring conformation since para substitution simplifies the spectra in the aryl region.

Stereochemical Considerations

Some of the possible chelate ring conformations for Chiraphos and BDPP and their derivatives are represented in Chart II. The twisted δ conformations with equatorially disposed Me groups are proposed to be most stable for rhodium complexes of Chiraphos and BDPP. The phenyl rings show C_2 symmetry as determined by X-ray analysis;[13b,27,28] also ^{1}H and ^{13}C NMR data are consistent with C_2 symmetry for the complexes.[13b,14] The alternative λ conformation of Chiraphos has diaxial Me groups and is sterically destabilized by cis 1,2-interactions of the methyl groups with the axial phenyl groups.[14] For Chiraphos and its derivatives then, it is reasonable to expect that only the δ conformation exists in solution.

Among the alternative conformations for BDPP and its derivatives the chair conformation contains one equatorial and one axial Me group (Chart II) while the λ conformation has two axial methyl groups. Thus the chair conformation should be more favorable than the λ conformation but less stable than the twisted δ conformation. The chair conformations of BDPP do not give a chiral arrangement of phenyl groups although the complexes themselves are chiral. The δ skew and chair conformations may be close in energy which may explain the fact that some substrates are hydrogenated with low enantioselectivity by BDPP.[13] The complex [Rh(NBD)(BDPP)]$^+$ exists in the chair form in the solid state,[13b,23] while in other BDPP complexes the δ-skew conformation was found[23,29] to be more consistent with solution NMR spectra. It was argued that the δ skew and chair conformations rapidly interconvert and that the δ skew conformation was favored.[23]

The number of possible conformations of a chelate ring increases with increasing ring size. In DIOP complexes two favorable conformations are possible, both of which provide a C_2 arrangement of quasi-axial, quasi-equatorial phenyl rings (Chart III).[30] Both conformations have been found in crystal structure determinations,[19] and it is reasonable to expect that they may be in an equilibrium in solution. In fact, many DIOP complexes show dynamic behavior by NMR.[20-22]

Results and Discussion

^{13}C NMR Spectra. The ^{13}C NMR data for rhodium(I) and platinum(II) complexes of **1a-c**, **2a-c**, and **3a-b** are summarized in Table I. Selected ^{13}C NMR spectra in the aromatic region are shown in Figure 1. The aryl groups of the free ligands are diastereotopic. The difference in chemical shift between two diastereotopic aryl carbons is generally small and in some cases is not resolved. The diastereotopic separation increases when the ligands are chelated to transition metals. For example, the difference between the C-4 and C-4′ carbons (see legend for Table I) in [Rh(COD)(**3a**)]$^+$ is 6 ppm.

If the chelate rings in derivatives of **1** and **2** are dynamic, a time-averaged C_2 structure is obtained (Chart IV). For the purpose of predicting expected NMR parameters the time-averaged structure can be considered to be a unique conformation. The observed chemical shift differences of 2.6-4.3 ppm between C-7 and C-7′, as well as the significant differences between C-5 and C-5′ (2.5-3.5 ppm) and H-4 and H-4′ are too large to be consistent with a time averaged conformation in [Rh(NBD)(**1a**)]$^+$.

The large differences between C-4 and C-4′, C-5 and C-5′, and C-7 and C-7′ in BDPP (**2a-c**) and Chiraphos (**3a-c**) derivatives (Table I, Figure 1) can be explained by assuming rigid twisted δ conformations (Chart II). The observed trends, COD > NBD > X_2, and **3a-b** > **2a-c** > **1a-c**, in the differences between C-4 and C-4′ are consistent

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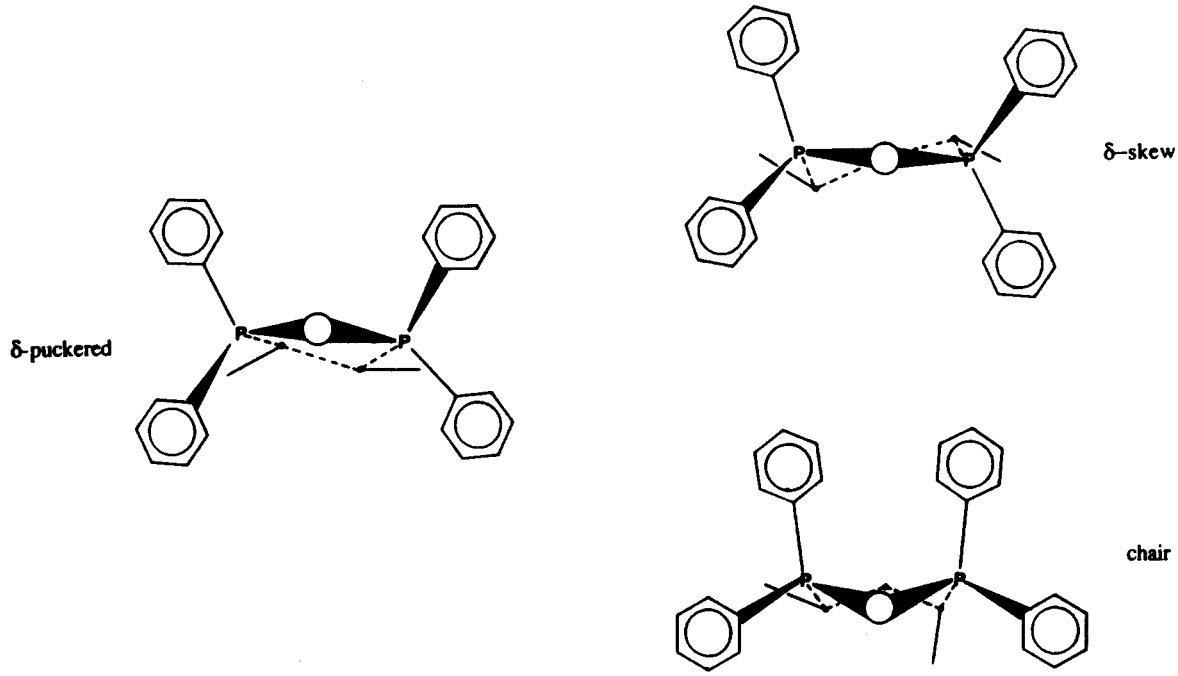
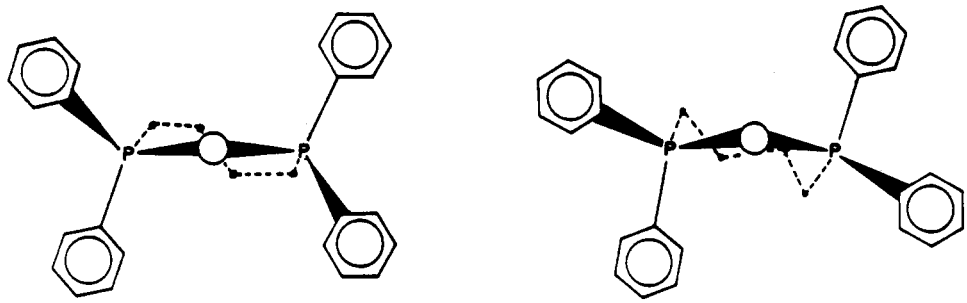
Chart II. Conformations in (*S,S*)-Chiraphos Complexes (Left) and (*S,S*)-Skewphos Complexes (Right)[a]



[a] Only one chair conformation is shown for Skewphos and energetically unfavorable conformations such as those with a diaxial arrangement of methyl groups (λ forms), an envelope conformation for Chiraphos, and boat forms for Skewphos are not shown.

Chart III. Possible Chiral Phenyl Group Arrangements in (*R,R*)-DIOP Derivatives[a]



[a] A twisted boat conformation is shown on the left, and a chair conformation is shown on the right.

with shielding of the axial aryl groups by the diene ligands and the chelate backbone substituents. This indicates a similarity in the phenyl group arrangement for all the complexes except the platinum complex Pt(**1a**)Cl_2 which shows little stereospecificity in its ^{13}C NMR spectrum.

For the complexes reported here the upfield C-5–C-5′ resonances are assigned to the axial phenyl groups, as the $^1J_{PC}$ couplings are consistently smaller on these signals.[32-37] The other phenyl carbons were assigned by the assumption that the $^2J_{PCC}$ and $^3J_{PCC}$ couplings keep the order observed for $^1J_{PC}$. Thus, when $^1J_{PC}$ is smaller in an axial than in an equatorial phenyl, then $^2J_{PCC}$ and $^3J_{PCC}$ are also expected to be smaller in the axial phenyl.[35,37] The C-3, C-3′ carbons can be assigned similarly, but due to the small differences in $^3J_{PCCC}$ couplings and C-3, C-3′ chemical shifts each case requires additional proof and further investigation. For example, in the spectrum of [Rh(NBD)(**2a**)]$^+$ complex (Table I, Figure 1) the higher field axial C-4–C-4′ resonance with the smaller $^2J_{PCC}$ coupling seems to match the lower field C-3–C-3′ resonance, which also has a smaller $^3J_{PCCC}$ coupling. This assignment is consistent with the observation that these patterns move together both as a function of temperature (vide infra) and upon protonation of the dimethylamino groups. The olefinic carbons (C-7, C-7′) are assigned on the assumption that the one close to the axial phenyl ring (particularly to C-4, C-4′ axial carbons) will be shielded and appear upfield to the others. Due to the small differences in C-1, C-1′ and C-2, C-2′ carbons and the lack of P–C couplings these signals cannot be assigned directly.

The C-5, C-5′, C-4, C-4′, and C-3, C-3′ resonances typically appear as pairs of pseudotriplets, whereas C-2, C-2′, C-1, C-1′ carbons give pairs of singlets (Figure 1, Table I) in most of the investigated complexes. The C-6 chelate carbons and the other chelate ring carbons also give pseudotriplets. When the overall C_2 symmetry is removed, for example, substitution of one Cl^- by $SnCl_3^-$ in Pt(**2a**)Cl_2, these patterns are typically doubled (Table I).

^{1}H NMR Spectra. The phenyl region of the 400-MHz proton NMR spectra for several of these complexes is shown in Figure 2. These spectra are consistent with the

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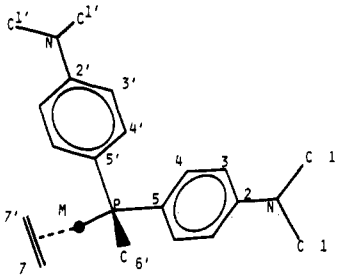
Table I



	C-1; C-1′	C-2; C-2′	C-3; C-3′ ($^3J_{PCCC}$)	C-4; C-4′ ($^2J_{PCC}$)	C-5; C-5′ ($^1J_{PC}$)	C-6 ($^1J_{PC}$)	C-7; C-7′ ($^1J_{RhC}$)
$C_6H_{13}P(pC_6H_4NMe_2)_2$[Ia]	40.2 s	150.42 s	112.3 d (7.3)	133.59 d (19)	125.06 d (7.6)*	26.06 d (7.6)*	
1a[Ia]	40.3 d	150.6 s; 150.3 s	112.3 d (8.1)	134.1; 133.6 d (20.6); (19.3)	124.7 d; 124.1 d (7.6); (8.8)*	32.87 d (17.0)*	
2a[Ia]	40.2 d	150.6 s; 150.5 s	112.6 d; 112.1 d (6.2)	134.6 d; 134.5 d (21); (20)	123.7 d; 122.9 d (8.5)*; (8.5)	27.93 dd (12.1)*	
3a[Ia]	40.3 s; 40.1 s	150.6 br s	112.2 d; 111.9 d (9.5)	134.9 br d (23)	123.8 d; 123.6 d (12)*; (12)	31.48 t (13.6)* J_{PCCC} = 13.6	
[Rh(NBD)(**1a**)]BF_4[IIa]	40.01 br s	152.50 s; 151.30 s	112.3 t; 112.0 t (5.3)	135.3 t; 131.8 t (7.2); (5.3)	115.8 t; 112.6 t (26.5); (23.1)	31.9 t (14.9)	87.2 br s; 82.36 q (4.6) $^2J_{PRhC}$ = 4.6
[Rh(NBD)(**1a**)]BF_4[IIb]	40.0 s	153.4 s; 152.5 s	113.1 br s; 112.8 br s	135.9 br s; 133.9 br s	116.9 t; 114.4 t (26.5); (24)	32.5 t (15.7)	86.6 br s, 82.9 br s
[Rh(NBD)(**2a**)]BF_4[IIIa]	40.0s; 39.9 s	152.1 s; 151.0 s	112.2 t; 111.6 t (4.6); (5.3)	136.6 t; 132.5 t (6.1); (4.6)	113.7 t; 111.0 t (25.3); (22.2)	26.4 t (17.5)	87.9 q; 83.9 q (5.3); (6.1) J_{PRhC} = 5.3; J_{PRhC} = 6
[Rh(NBD)(**2a**)]BF_4[IIb]	40.0 s; 39.9 s	153.2 s; 152.4 s	113.0 t; 112.4 t (4.6); (6.0)	137.4 t; 133.8 t (7.0); (4.8)	114.8 t; 112.3 t (25.5); (23.1)	27.2 t (17)	87.69 q; 84.7 q (6.1); (6.1) J_{PRhC} = 6.1
[Rh(NBD)(**3a**)]BF_4[IIIa]	40.0 s; 39.9 s	152.6 s; 151.5 s	112.5 t; 111.6 t (4.6); (5.3)	137.0 t; 131.6 t (6.8); (4.6)	111.8 t; 110.4 t (25.3); (24.0)	34.9 t (22.7)	91.6 q; 87.5 q (5.8); (6.1) J_{PRhC} = 5.8; J_{PRhC} = 6
[Rh(NBD)(**3a**)]BF_4[Ic]	40.3 s	154.2 s; 153.7 s	113.8 t; 112.8 t (4.5); (4.5)	138.2 t; 133.1 t (5.6); (5.6)	113.5 t; 112.1 t (24.2); (23.7)	36.5 t (25.1)	93.0 m; 88.4 m not res
[Rh(COD)(**2a**)]BF_4[Ic]	40.0 s	154.1 s; 152.5 s	113.1 br s; 112.9 br s not res	138.8 t; 133.6 t (7.5); (6.5)	115.3 t; 112.7 t (26.2); (25.0)	27.1 t (21.5)	101.7 q; 96.6 m (5.3); not res J_{PRhC} = 5.3;
[Rh(COD)(**3a**)]BF_4[Ia]	40.0 s	153.7 s; 152.6 s	113.3 t; 112.3 t (4.0); (5.1)	138.5 t; 132.6 t (8.5); (6.8)	113.6 t; 111.4 t (26.2); (19.2)	35.7 t (24.6)	102.4 q; 97.6 m (6.1); not res J_{PRhC} = 6.1
[Rh(**2b**)$(CH_3CN)_2$]$(BF_4)_5$[IId]	57.6 br s	149.6 s; 149.5 s	121.7 t; 120.9 t (4.5)	137.8 t; 135.9 t (6.4); (4.3)		26.1 t (19.6)	
[Rh(NBD)(**1b**)]$(BF_4)_5$[Ic]	58.3 br s	151.2 s; 148.5 s	122.8 br s; 122.3 t (5.5); (5.5)	137.6 br s; 135.0 t (7.5); (7.5)		31.5 dd (25.0) $^3J_{PC}$ = 12.1	91.7 q; 87.4 q (5.9); (6.1) J_{PRhC} = 5.9; J_{PRhC} = 6.1
[Rh(NBD)(**2b**)]$(BF_4)_5$[IIIc]	59.8 s; 59.7 s	152.1 s; 151.1 s	123.7 t; 123.4 t (4.8); (4.8)	140.6 t; 136.7 t (6.9); (5.3)	134.0 t; 132.3 t (20.9); (19.7)	28.4 t (18.0)	95.1 q; 90.1 q (4.8); (4.5) J_{PRhC} = 4.8; J_{PRhC} = 4.5
[Rh(NBD)(**3b**)]$(BF_4)_5$[Ic]	58.4 br s	151.1 s; 149.9 s	122.8 br s; 122.2 br s	139.7 t; 134.6 t (7.2); (6.0)	131.8 t; 130.9 t (23.2); (19.3)	35.9 t (23)	99.3 m; 92.7 m not res
[Rh(COD)(**3b**)]$(BF_4)_5$[Ic]	59.9 br s	152.6 s; 151.4 s	124.1 br s; 123.1 t (6.1); (6.1)	141.5 t; 135.9 br s (9.1)		37.9 t (24.5)	110.3 m; 103.8 m not res
[Rh(NBD)(**1c**)]$(BF_4)_5$[IIc]	46.9 s; 46.6 s	147.1 s; 146.0 s	122.2 br s	137.8 br s; 135.0 br s	133.3 t; 130.9 t (21); (21)	30.5	89.9 br s; 87.3 br s
[Rh(NBD)(**2c**)]$(BF_4)_5$[Ic]	47.0 s; 46.8 s	146.5 s; 145.5 s	122.8 br s; 122.4 br s	138.7 t; 135.4 t (6.2); (6.2)	132.7 t; 130.5 t (21); (20)	26.9 t (16.4)	92.3 m; 88.7 m not res
[Rh(COD)(**2c**)]$(BF_4)_5$[Ic]	46.8 s; 46.5 s	147.7 s; 145.4 s	122.5 br s; 122.4 br s	139.8 t; 135.2 t (6.0); (6.0)	132.6 t; – (22); –	28.2 t (17) 36.0 t (28.4)	106.7 br s; 100.7 br s
Ni(**3a**)$(SCN)_2$[Ib]	40.0 s	153.7 s; 153.1 s	113.0 t; 112.3 t (7.5); (6.2)	137.6 br s; 134.5 br s			
Pt(**1a**)Cl_2[IIIa]	40.1 s; 40.0 s	151.7 s; 151.5 s	111.2 t; 111.0 t (6.0); (6.0)	135.2 t; 134.2 t (5.7); (5.3)	116.4 m; 114.1 m	30.3 m	
Pt(**2a**)Cl_2[IIIa]	40.1 s; 40.0 s	151.7 s; 151.3 s	111.2 t; 111.1 t (6.1); (5.3)	136.3 t; 134.4 t (5.8); (4.7)	113.5 m; 110.5 m	27.1 m	
Pt(**2a**)Cl($SnCl_3$)[If]	40.2 s	153.2 s; 152.8 s	112.3 br d; 112.8 br dd	136.9 br d; 134.7 br d (11.5); (9.5)		27.2 m not res	
		152.9 s; 152.4 s	111.8 br d (12); (14)	136.4 br d; 134.1 br d (12.6); (11.5)			
Pt(**3a**)Cl_2[Ia]	40.1 s	152.4 s; 151.8	111.6 m; 111.2 t not res; (5.8)	138.0 t; 134.1 t (6.1); (4.8)	–; 109.2 m	36.2 m	

* $^1J_{PC}$ couplings are probably negative, as it generally is for P(III) compounds.[31,32,41] Observation frequencies: I 50.3 MHz, II 67.9 MHz, III 100.5 MHz. Solvent: a = $CDCl_3$, b = acetone-d_6, c = CD_3OD, d = CD_3CN, e = D_2O, f = CD_2Cl_2. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened, not res = not resolved.

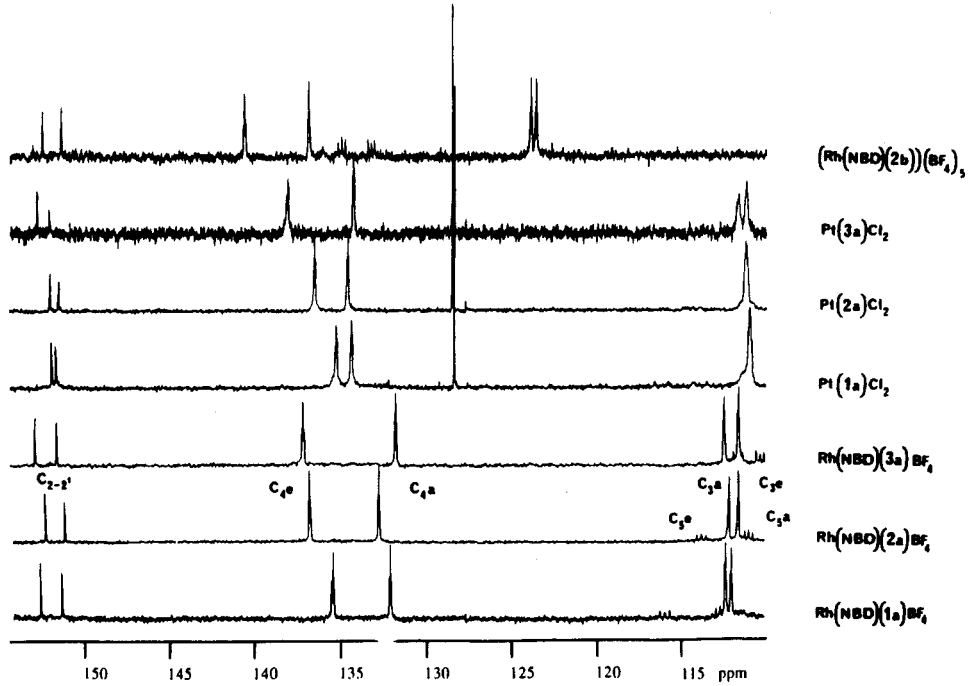
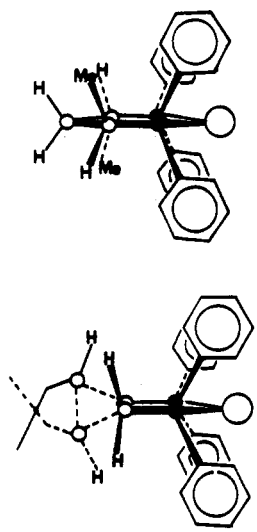


Figure 1. 100.3-MHz carbon-13 NMR spectra in the aromatic region of several complexes at in $CDCl_3$ at 293 K.

Chart IV. Side-On Views of the Time Averaged Interconversion of a Twisted Boat to Chair Conformation for both Skewphos Complexes (Top) and DIOP Complexes (Bottom)



^{13}C NMR data above. For example the H-4 and H-4′ protons generally show a large diastereotropic separation. The separation between H-4 and H-4′ in [Rh(NBD)(1a)]$^+$ is the largest among the NBD complexes. By analogy to the carbon assignments the upfield H-4, H-4′ resonance is attributed to the ortho protons in the axial phenyl rings.

The proton NMR spectra of the Chiraphos derivatives (**3a–b**) are consistent with the proposed rigid δ conformation[14] and C_2 symmetry (Chart II).[27] The ^1H NMR spectra of the alkyl protons in the complexes of BDPP derivatives (**2a–c**) show similar features to those presented with the nonfunctionalized ligand.[23]

The vicinal P–H coupling constants are dependent on the dihedral angle (Karplus relationship[38]), thus the two phosphorus atoms of a stable δ twisted boat conformation should give different couplings to the methylene protons as in Rh(COD) complexes. The equivalence of $^3J_{PCCH}$ couplings in BDPP complexes was interpreted as direct evidence for time-averaged C_2 symmetry.[23] We think that a time-averaged C_2 symmetry should provide unequal $^3J_{HH}$ couplings to the methine protons (Chart IV) ($^3J_{HH}$ vicinal couplings between the methine and methylene protons are not equivalent in a rigid δ skew conformation either, but they are similar due to their dihedral relationship[39]). A fast skew–chair interconversion with a more stable skew conformation should provide a spectroscopic picture similar to a rigid skew conformation. The virtual $^3J_{PCCH}$ couplings are probably the result of an averaging effect of two paths for coupling in a ring (i.e., $^3J_{PCCH}$, $^5J_{PRhPCCH}$). The two vicinal $^3J_{HH}$ couplings between the methine and methylene protons appear to be similar in all BDPP complexes. For example, Pt(**2a**)Cl_2, which exhibits a triplet of triplets for the methylene protons, gives a doublet of heptets for the methine protons. In rhodium complexes $^2J_{PCH}$ are different from the proton couplings; thus the resulting multiplets are more complicated. These are shown in Figure 3. The assumption of a conformationally rigid δ skew conformation for all complexes of **2a–c** is plausible as other details are consistent with it. Further indirect proof for the conformational stability of these chelates (**2a–c**, **3a–c**) comes from their catalytic use. The nature and position of aryl substituents (*m*-sulfonate, *p*-dimethylamino, *p*-trimethylammonium) on these ligands has little effect on the enantioselectivity in the asymmetric hydrogenation of prochiral dehydro amino acids.[26] This is not the case with the conformationally more labile aryl-substituted DIOP derivatives.[26,30] Finally, direct evidence for conformational stability is that the ^{31}P, ^{13}C, and ^1H NMR spectra of Pt(**2a**)Cl_2 and [Rh(NBD)(**2a**)]$^+$ show little temperature dependence in the range 177–393 K.

As cited above the nonsubstituted DIOP ligand shows dynamic behavior in several complexes. For instance, [Rh-

(38) Bentrude, W. G.; Setzer, W. N. in ref 34, p 365.

(39) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

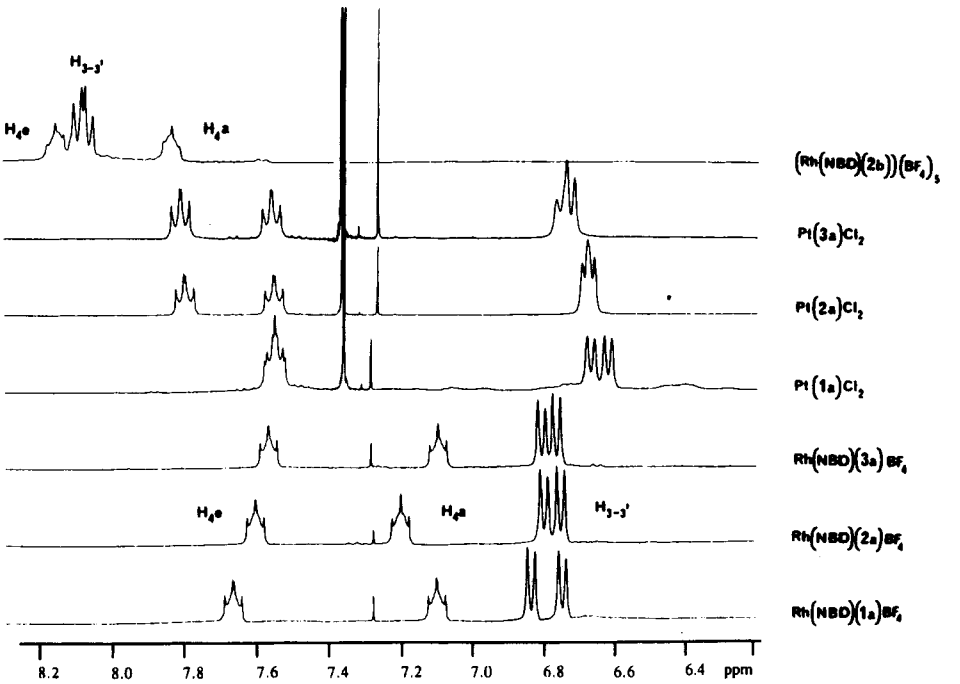


Figure 2. 400-MHz proton NMR of the aromatic protons of several complexes at in $CDCl_3$ at 293 K.

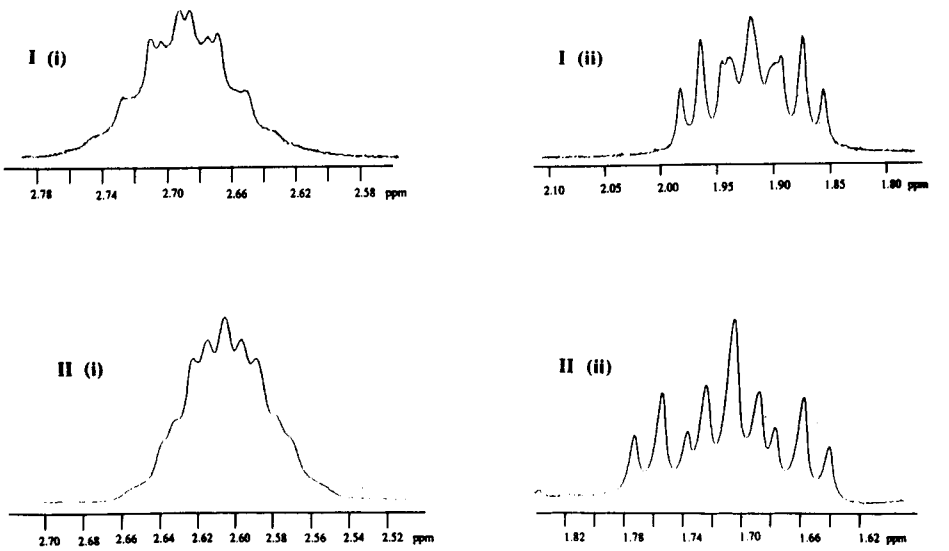


Figure 3. Methine (i) and methylene protons (ii) in the chelate rings of the complexes Pt(**2a**)Cl_2 (I) and [Rh(NBD)(**2a**)]BF_4 (II).

(COD)(DIOP)]$^+$ is reported to be fluxional.[21] In contrast, the ^{1}H NMR spectrum of the chelate ring in [Rh(NBD)-(**1a**)]BF_4, shown in Figure 4, is consistent with a rigid chair conformation of the ring. The diastereotropic methylene (H-6) protons of this complex exhibit two well-separated patterns centered at 2.73 and 2.36 ppm. The upfield doublet of doublets can be assigned to the axial H-6 proton (Figure 4).

Variable-Temperature NMR. Variable-temperature NMR measurements were made for four compounds: Pt-(**1a**)Cl_2, [Rh(NBD)(**1a**)]BF_4, Pt(**2a**)Cl_2, and [Rh(NBD)-(**2a**)]BF_4. Spectra were recorded from 393 K in DMSO-d_6 to 177 K in CD_2Cl_2. The ^{31}P, ^{13}C, and ^{1}H NMR spectra of Pt(**2a**)Cl_2 were not effected by temperature. The ^{31}P and ^{13}C NMR spectra of [Rh(NBD)(**2a**)]$^+$ also showed little change in this temperature range while the ^{1}H NMR spectrum was slightly influenced by temperature. Both the H-4 and H-4′ patterns were shifted by ~0.15 ppm, while the diastereotropic separation of the olefinic protons increased by 0.2 ppm, upon cooling to 177 K. The observed ^{1}H spectrum in DMSO at room temperature was almost identical with that in CD_2Cl_2 at 177 K. Similarly, the spectrum recorded at 393 K in DMSO resembles to the one in CD_2Cl_2 at room temperature. Since coalescence could not be observed (either by ^{1}H or ^{31}P NMR) the small shifts are partially attributed to a change in solvent viscosity and the diene motion in the complex. The X-ray structure of [Rh(COD)(BDPP)]$^+$ complex revealed two different orientations of COD;[23] thus the diene ligands probably rapidly rotate. The olefinic protons in [Rh-(NBD)(**1a**)]$^+$ showed similar changes, i.e. the separation increased with 0.2 ppm by cooling to 177 K. Other details of the proton spectrum or the ^{13}C, ^{31}P spectrum were not affected by the temperature.

The NMR spectra of Pt(**1a**)Cl_2 are highly temperature dependent. This is most evident in the ^{31}P NMR, shown in Figure 5. The sharp signal at −5.4 ppm in the room temperature spectrum undergoes coalescence at approx-

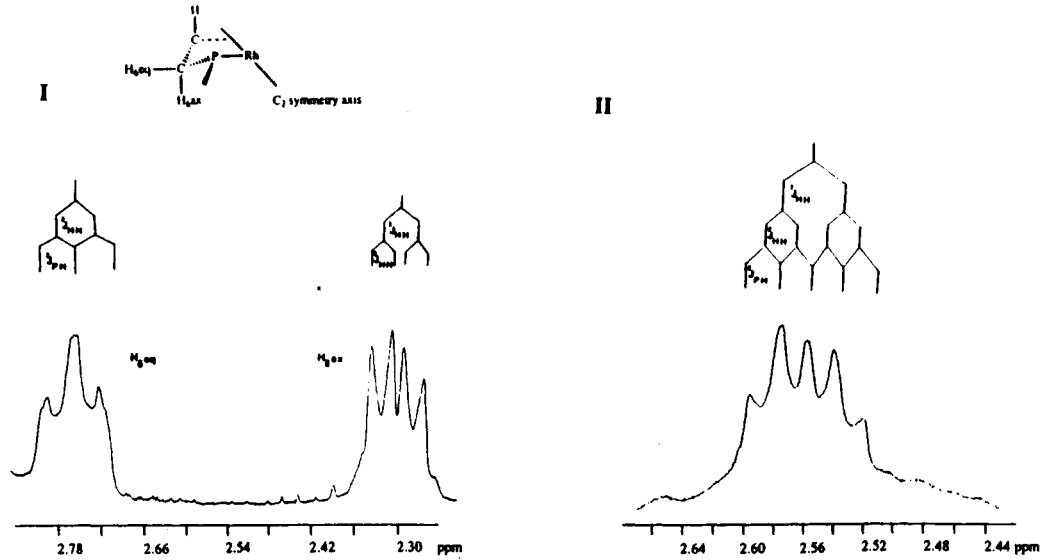


Figure 4. Methylene protons in [Rh(NBD)(**1a**)]BF_4 (I), upfield methylene protons in Pt(**1a**)Cl_2 (II).

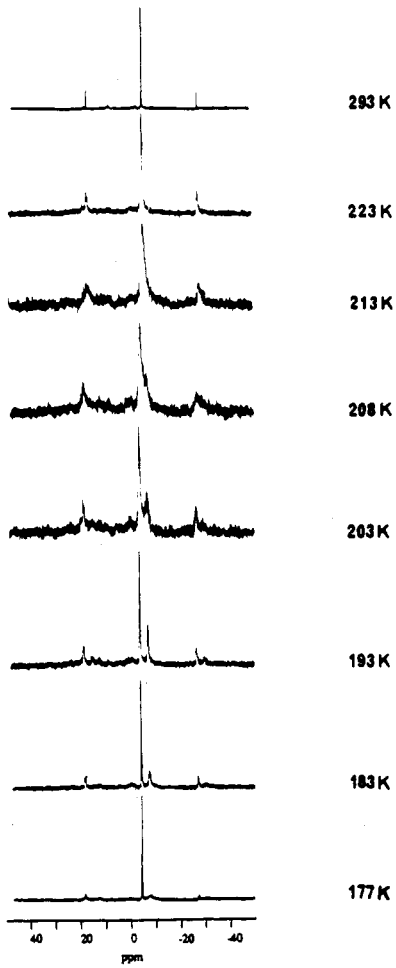


Figure 5. Phosphorus-31 NMR spectrum of Pt(**1a**)Cl_2 in $CDCl_2$ as a function of temperature. J_{Pt-P} satellites are also shown.

imately 213 K as the sample is cooled. At 193 K two signals separate, these are assigned to two isomers, both of which have equivalent phosphorus atoms. The downfield (−4.70 ppm) signal has twice the integrated intensity of the upfield (−7.8 ppm) signal. The downfield signal sharpens as the temperature is lowered further. This species probably has a rigid chelate ring with C_2 symmetry at low temperature. The upfield signal broadens significantly at 183 K. Unfortunately, a limiting spectrum could not be reached. This experiment proves that the observed C_2 symmetry assigned to Pt(**1a**)Cl_2 at room temperature (Figures 1, 2, and 4) must be a time-averaged C_2 symmetry based on at least two conformations.

Conclusion

With the exception of Pt(**2a**)Cl($SnCl_3$), each complex shows C_2 symmetry and, with the exception of Pt(**1a**)Cl_2, each complex examined shows two significantly different aryl group environments by NMR spectroscopy. The possibility of a time-averaged structure with C_2 symmetry is excluded since other details of the spectra, notably ^{13}C resonances and proton–proton coupling constants in the chelate rings, and the lack of change as a function of temperature, are not consistent with it. The observed C_2 symmetry must originate from rigid or highly preferential chelate ring conformations. Thus, the aryl groups possess chiral (alternating) quasi-axial quasi-equatorial aryl group arrangement in solution.

The observed similarity between the spectra of [Rh(diene)(**2–3a–c**)] complexes to those which do not contain diene ligands, (Pt (**2–3a,c**)Cl_2, Rh(**2c**)$(CH_3CN)_2$) Ni(**3a**)$(SCN)_2$ is consistent with the assumption that the chelate rings retain their preferred conformation when the diene ligands are absent. This may not be true, however, in all substrate complexes in which the phenyl rings express their discriminatory interaction. Unfortunately, due to the substrate dissociation process[5] and the extreme sensitivity of the intermediates, the substrate complexes are much more difficult to subject to a similar detailed NMR study. However, the catalytic results provide plausible support for the conformational stability of the bulk of substrate–metal complexes with para-substituted BDPP and Chiraphos derivatives.[26]

By the comparison of the NMR spectra of Rh(NBD)(**1a–c**) to those of Pt(**1a**)Cl_2 and also to those of [Rh(COD)(DIOP)]$^+$,[21] it is apparent that both the presence of the diene (or perhaps other bulky ligands)[29] and *p*-aryl substituents are required to prevent the flipping of the aryl groups, thus stabilizing the seven-membered chelate of DIOP complexes.

Experimental Section

All phosphines and complexes were synthesized as described elsewhere.[25,26,40] The NMR samples were prepared under argon from commercially available deuterated solvents in 5-mm-o.d. tubes. The concentrations in the samples were in the range of 30–70 mg/mL. All spectra were recorded with internal deuterium lock in FT mode. ^{1}H and ^{13}C spectra are referenced to tetramethylsilane; ^{31}P spectra are referenced to external 85% phosphoric acid.

The recording conditions for ^{13}C were as follows: frequency, 50.3 and 100.5 MHz; instrument, Bruker WP-200, Bruker WP-270, and Varian Unity 400. POWGATE AU optimized BB-decoupling (DP = 5H DO) and Waltz-16 modulated continuous high power BB-decoupling were used for proton decoupling on the Bruker and the Varian instrument, respectively. Data from the latter instrument were collected with double precision. Scans collected were in the range of 2000–10 000.

^{1}H: frequency, 399.9 MHz; instrument, Varian Unity 4000; scans, 32.

^{31}P: frequency, 81.0 MHz; instrument, Bruker WP-200; number of scans, 100–1000.

(40) Toth, I.; Guo, I.; Hanson, B. E.; Davis, M. E. Unpublished results.
(41) Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 125.

Acknowledgment. We thank Tom Glass for the ^{1}H and ^{13}C NMR spectra at 9.4 T. Support for this work was provided by the NSF.

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