

Articles

**³¹P NMR and X-ray Crystallographic Study of
Atropisomerism in *cis*-Tetracarbonylmolybdenum(0) and
cis-Dichloroplatinum(II) Complexes of
(±)-6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*]-
[1,3,2]dioxaphosphepin) and (±)-6,6'-[[1,1'-Binaphthyl]-
2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)
Ligands**

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Both *cis*-tetracarbonylmolybdenum(0) and *cis*-dichloroplatinum(II) complexes of {(±)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo [*d,f*][1,3,2]dioxaphosphepin)}, **1**, and {(±)-6,6'-[[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo [*d,f*][1,3,2]dioxaphosphepin)}, **2**, have been prepared. Atropisomerism of the ligands in these complexes has been investigated by variable-temperature ³¹P{¹H} NMR spectroscopy. These studies demonstrate that all three diastereomers are present in solutions of the *cis*-tetracarbonylmolybdenum(0) complexes of both ligands in the slow exchange region, although the distribution of the diastereomers is strongly dependent on the nature of the ligand. The conformations proposed for the major complexes in solution are consistent with the solid-state conformations of the complexes, as determined by X-ray crystallography. Only two species are present in solutions of the *cis*-dichloroplatinum(II) complexes, and surprisingly, both appear to have the *R***R***S**(*S***S***R**) configuration. The different conformations of the *R***R***S**(*S***S***R**) diastereomers may arise from different interplanar angles of the biaryl group in the nine-membered chelate ring.

Introduction

Bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligands, such as those shown in Figure 1, are of interest because of their applications in asymmetric catalysis.^{1–5} As shown in Figure 1, these ligands possess endocyclic phosphorus-donor groups in a *C*₂-symmetric environment created

by an axially chiral diaryl backbone. This combination of structural elements results in excellent stereoselectivities in the asymmetric hydroformylations of olefins catalyzed by rhodium complexes of these ligands.^{1–5}

The bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligands, **1** and **2**, exhibit atropisomerism in solution because of hindered rotation around the σ -bond connecting the axially chiral diaryl groups.⁶ Both **1** and **2** have three possible diastereomers, each of which differs in the ab-

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(2) Recent examples with Rh(I)-chiral bisphosphite complexes: (a) Wink, D. J.; Kwok, T. J. Yee, A. *Inorg. Chem.* **1990**, *29*, 5006. (b) Kwok, J.; Wink, D. J. *Organometallics* **1993**, *12*, 1954. (c) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625. (d) Buisman, G. J. H.; van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kramer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929. (e) Babin, J. E.; Whiteker, G. T. WO 93/03839, U.S. Pat. US 911,518,1992; *Chem. Abstr.* **1993**, *119*, 159872h. (f) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijk, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719.

(3) Hybrid-type phosphite ligands for asymmetric hydroformylation, for example: (a) Pottier, Y.; Mortreux, A.; Petit, F. *J. Organomet. Chem.* **1989**, *370*, 333. (b) Arena, C. G.; Nicoló, F.; Drommi, D.; Bruno, G.; Faraone, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2251. (c) Sakai, N.; Nozaki, K.; Mano, S.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033. (d) Sakai, N.; Nozaki, K.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1994**, 395. (e) Higashijima, T.; Sakai, N.; Nozaki, K.; Takaya, H. *Tetrahedron Lett.* **1994**, *35*, 2023. (f) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413.

(4) For recent advances in enantioselective hydroformylation, see: Gladioli, S.; Bayon, J. C.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1453, and references therein.

(5) (a) Rieu, J. P.; Bouchelere, A.; Cousse, H.; Mouzin, G. *Tetrahedron* **1986**, *42*, 4095. (b) Botteghi, C.; Paganelli, S.; Schionato, A.; Marchetti, M. *Chirality* **1991**, *3*, 355. (c) Botteghi, C.; Del Ponte, G.; Marchetti, M.; Paganelli, S. *J. Mol. Catal.* **1994**, *93*, 1.

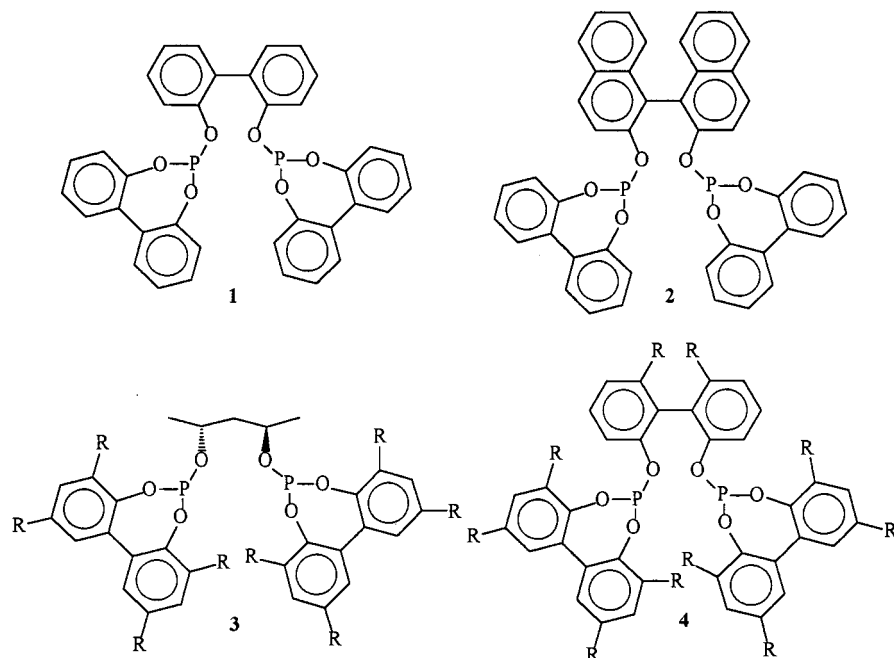


Figure 1. Chiral bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligands.

solute configurations of the three biaryl moieties. It is important to determine whether multiple diastereomers of **1** and **2** are present in complexes of these ligands, because complexes of the different diastereomers could exhibit quite different enantioselectivities as hydroformylation catalysts. Only one variable-temperature NMR study of complexes of these ligands, $[\text{Ni}(\mathbf{1})_2]$ and $[\text{Pt}(\mathbf{1})_2]$, has been reported.^{1b} The results from this study suggest that one major and one minor diastereomer were present at low temperatures in solutions of the complexes. Unfortunately, the presence of two ligands in the complexes prevented unambiguous assignment of the diastereomeric conformations. Also, $[\text{Ni}(\mathbf{1})_2]$ and $[\text{Pt}(\mathbf{1})_2]$ are poor models for asymmetric hydroformylation catalysts because all of the catalysts contain a single bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligand.

To better understand the effects of the 2,2'-diaryl backbone and the coordination geometry of the metal on the atropisomerism of the coordinated bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligands, we have carried out variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR studies of *cis*-tetracarbonylmolybdenum(0) and *cis*-dichloroplatinum(II) complexes of **1** and **2**. The X-ray crystal structures of both *cis*-tetracarbonylmolybdenum(0) complexes have been determined to allow comparison of the solution and solid-state conformations of the complexes.

Experimental Section

General Remarks. The $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and ^1H NMR spectra of chloroform-*d* and dichloromethane-*d*₂ solutions of the complexes were recorded on a Bruker ARX-300 NMR spectrometer with a quad (^1H , ^{13}C , ^{19}F , ^{31}P) 5 mm probe. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external 85% phosphoric acid, while the $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra were

referenced to internal tetramethylsilane. In all cases, downfield was treated as positive. The temperature-dependent chemical shift differences between the OH and CH₃ resonances of methanol were used to calibrate the probe temperature for the variable-temperature studies.⁷ Atlantic Microlabs, Norcross, GA, performed all of the elemental analyses.

Materials All free ligands and tetrahydrofuran (THF) were handled under high-purity nitrogen, and all reactions and recrystallizations were carried out under high-purity nitrogen. All starting materials were reagent grade and were used as received. Tetrahydrofuran was distilled from sodium/benzophenone under high-purity nitrogen before use. Both chloroform-*d* and dichloromethane-*d*₂ were opened and handled under a nitrogen atmosphere at all times. The starting materials, *cis*-Mo(CO)₄(nbd),^{8a} 2,2'-biphenylene phosphorochloridite ester,^{8b} and *cis*-PtCl₂(cod)^{8c} were prepared by literature procedures. The ligands, **1** and **2** were prepared by the reactions of the 2,2'-biphenylene phosphorochloridite ester with 2,2'-biphenol and (±)-2,2'-binaphthol, respectively, using the procedure of Takaya.^{1d}

Preparation of *cis*-{6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), **5.** A mixture of 0.300 g (1.00 mmol) of *cis*-Mo(CO)₄(nbd) and 0.616 g (1.00 mmol) of **1** in 50 mL of degassed hexanes was stirred at room temperature for 24 h. The pale brown precipitate was collected and dissolved in 100 mL of a 1:1 dichloromethane–hexanes mixture. This solution was filtered through a short column of silica gel (25 g), and then the silica gel was washed with two, 50 mL portions of a 1:1 dichloromethane–hexanes mixture. The filtrate and washes were combined and evaporated to dryness to yield 0.786 g (95.3%) of **5** as a white powder. Recrystallization from dichloromethane–hexanes gave analytically pure **5** as colorless crystals. $^{31}\text{P}\{^1\text{H}\}$ NMR (295 K, dichloromethane-*d*₂): δ 179.87 (s). Carbonyl $^{13}\text{C}\{^1\text{H}\}$ NMR (295 K, dichloromethane-*d*₂): δ 210.18 (*trans*-carbonyls, A portion of an AXX' spin system, $|^2J(\text{PC}) + ^2J(\text{P}'\text{C})| = 34$ Hz); 206.10 (*cis*-carbonyls, A portion of an AX₂ spin system, $|^2J(\text{PC})| = 14$ Hz). ^1H NMR (295 K,

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chloroform-*d*): δ 7.40 (d, 4H), 7.35–7.05 (m, 16H), 6.95 (d, 2H), 6.65 (d, 2H). Anal. Calcd for $C_{40}H_{24}O_{10}P_2Mo$: C, 58.41; H, 2.94. Found: C, 58.27; H, 2.99.

Preparation of *cis*-{6,6'-[[1,1'-Binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), 6. Using the procedure for 5, 0.166 g (0.555 mmol) of *cis*-Mo(CO)₄(nbd) and 0.396 g (0.554 mmol) of 2 yielded 0.480 g (93.9%) of crude 6 as a white powder. Recrystallization from dichloromethane–hexanes gave analytically pure 6 as colorless crystals. ³¹P{¹H} NMR (295 K, dichloromethane-*d*₂): δ 181.88 (s). Carbonyl ¹³C{¹H} NMR (295 K, chloroform-*d*): δ 209.36 (*trans*-carbonyls, A portion of an AX'X' spin system, ²J(PC) + ²J(P'C) = 53 Hz); 205.62 (*cis*-carbonyls, A portion of an AX₂ spin system, ²J(PC) = 14 Hz). ¹H NMR (295 K, chloroform-*d*): δ 7.98 (d, 2H), 7.91 (d, 2H), 7.50–7.10 (m, 18H), 7.07 (t, 2H), 6.85 (m, 2H), 5.51 (d, 2H). Anal. Calcd for $C_{48}H_{28}O_{10}P_2Mo$: C, 62.49; H, 3.06. Found: C, 62.59; H, 2.97.

Preparation of *cis*-{6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}-dichloroplatinum(II), 7. A solution of 0.122 g (0.325 mmol) of PtCl₂(cod) and 0.200 g (0.325 mmol) of 1 in 200 mL of dry THF was stirred overnight at ambient temperature. Then the THF was removed under vacuum to yield 0.267 g (93.0%) of crude 7 as a white powder. Recrystallization from dichloromethane–hexanes gave analytically pure 7. ³¹P{¹H} NMR (295 K, dichloromethane-*d*₂): δ 78.88 (s&d, ¹J(Pt–P)) = 5968 Hz). ¹H NMR (295 K, chloroform-*d*): δ 7.57 (d, 2H), 7.45–7.15 (m, 18H), 7.20 (d, 2H), 6.70 (d, 2H). Anal. Calcd for $C_{36}H_{24}O_6Cl_2Pt$: C, 49.11; H, 2.75. Found: C, 48.89; H, 2.83.

Preparation of *cis*-{6,6'-[[1,1'-Binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}-dichloroplatinum(II), 8. Using the procedure for 7, 0.208 g (0.555 mmol) of PtCl₂(cod) and 0.396 g (0.555 mmol) of 2 yielded 0.541 g (99.4%) of crude 8 as a white powder. Recrystallization from dichloromethane–hexanes gave analytically pure *cis*-8. ³¹P{¹H} NMR (295 K, dichloromethane-*d*₂): δ 82.87 (s&d, ¹J(Pt–P)) = 5740 Hz). ¹H NMR (295 K, dimethyl sulfoxide-*d*₆): δ 8.35 (d, 2H), 8.14 (d, 2H), 7.85–6.95 (m, 20H), 6.85 (d, 2H), 6.02 (broad s, 2H). Anal. Calcd for $C_{44}H_{28}O_6Cl_2Pt$: C, 53.89; H, 2.88. Found: C, 53.95; H, 2.91.

X-ray Structural Analyses. Hot, saturated dichloromethane–hexanes solutions of 5 and 6 were slowly cooled to –10 °C to yield X-ray quality single colorless crystals of each complex. A suitable crystal of 5 was mounted on a glass fiber with epoxy cement under aerobic conditions. A single crystal of 6 was mounted in a thin-walled glass capillary under aerobic conditions. Each crystal was mounted and aligned on an Enraf Nonius CAD4 single-crystal diffractometer. Details of the data collection of each complex are summarized in Table 1

Standard peak search and automatic indexing routines followed by least-squares fits of 25 accurately centered reflections resulted in accurate unit cell parameters for each complex.

The analytical scattering factors of each complex were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. Both structures were solved by the use of Patterson syntheses. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined. Hydrogen atoms were not located directly but were input in the calculated positions with the appropriate staggered geometry and with $d(C-H) = 0.96 \text{ \AA}$.⁹

***cis*-{6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), 5.** Unit cell parameters clearly indicated that the crystal belonged to the monoclinic crystal system. Intensity statistics clearly favored the noncentrosymmetric space group *P2*₁. This was confirmed by the successful solution and refinement of the crystal structure.

Table 1. Experimental Data for Crystallographic Studies of 5 and 6

	5	6
formula	C ₄₀ H ₂₄ O ₁₀ P ₂ Mo	C ₄₈ H ₂₈ O ₁₀ P ₂ Mo
MW, daltons	822.51	922.63
space group	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁ / <i>n</i>
<i>a</i> (Å)	10.808(2)	18.206(2)
<i>b</i> (Å)	15.694(2)	11.453(1)
<i>c</i> (Å)	12.039(2)	20.244(1)
α (deg)	90	90
β (deg)	102.42(3)	101.01(1)
γ (deg)	90	90
<i>Z</i>	2	4
<i>d</i> _{calc} (g/cm ³)	1.369	1.479
<i>h</i> _{max} , <i>h</i> _{min}	14, –14	19, 0
<i>k</i> _{max} , <i>k</i> _{min}	0, –20	12, 0
<i>l</i> _{max} , <i>l</i> _{min}	15, 0	21, –21
2 θ limits (deg)	0.0–55.0	5.0–45.0
no. of reflns measd	9765	5577
no. of ind reflns measd	4965	5378
no. of obsd reflns	3527 (<i>F</i> > 3 σ (<i>F</i>))	3288 (<i>F</i> > 6 σ (<i>F</i>))
<i>R</i> _{int} (%)		1.4
scan type	ω –2 θ	ω –2 θ
abs corr	empirical	empirical
abs coeff (mm ^{–1})	0.521	0.455
no. of variables	568	551
extinction coeff	4.4(2) × 10 ^{–7}	3.0(3) × 10 ^{–5}
<i>R</i> , %	6.8 (3 σ)	3.31 (6 σ)
<i>R</i> _w , %	8.0 (3 σ)	3.36 (6 σ)
GOF	1.77	0.97

Table 2. Selected Bond Distances (deg) with Their esds for 5 and 6

atom 1	atom 2	distance	atom 1	atom 2	distance
5					
Mo	P1	2.441(3)	Mo	P2	2.440(3)
C37	Mo	1.99(1)	C37	O7	1.14(2)
C38	Mo	1.96(1)	C38	O8	1.13(2)
C39	Mo	2.08(1)	C39	O9	1.10(1)
C40	Mo	2.02(1)	C40	O10	1.16(2)
P1	O1	1.615(7)	P2	O4	1.619(8)
P1	O2	1.625(8)	P2	O5	1.606(7)
P1	O3	1.618(8)	P2	O6	1.587(9)
6					
Mo1	P1	2.428(1)	Mo1	P2	2.452(1)
C1	Mo1	1.999(7)	C1	O1	1.138(9)
C2	Mo1	2.003(5)	C2	O2	1.146(6)
C3	Mo1	2.017(6)	C3	O3	1.123(8)
C4	Mo1	2.020(7)	C4	O4	1.124(9)
O10	P1	1.611(3)	O31	P2	1.603(4)
O60	P1	1.628(3)	O40	P2	1.608(3)
O73	P1	1.600(3)	O53	P2	1.611(3)

All crystallographic calculations were completed using the Enraf-Nonius MolEN series of programs. The isotropic thermal parameter of each hydrogen atom was set equal to 1.2 times the *U*_{eq} value of the carbon atom to which it was bonded. Refinement of the model converged with *R* = 6.8% and *R*_w = 8.0% for those 3527 reflections with $|F_o| > 3\sigma|F_o|$. Following refinement, the extreme features in the difference Fourier map were a peak of height 0.77 e Å^{–3} and a negative feature of –0.24 e Å^{–3}.

***cis*-{6,6'-[[1,1'-Binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), 6.** The unit cell parameters clearly indicated that the crystal belonged to the monoclinic crystal system. The space group was determined unequivocally by the systematic absences *h* 0 *l* for *h* + *l* = 2*n* + 1 and 0 *k* 0 for *k* = 2*n* + 1 to be the centrosymmetric space group *P2*₁/*n*.

All crystallographic calculations were completed using the Siemens SHELXTL-PC program package.¹⁰ The isotropic

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(10) Siemens SHELXTL-PC Manual, Release 4.1; Siemens Analytical Instruments: Madison, WI, 1990.

Table 3. Selected Bond Angles (deg) with Their esds for 5 and 6

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
5							
P1	Mo	P2	84.7(1)	P2	Mo	C37	91.7(4)
P1	Mo	C37	175.8(4)	P2	Mo	C38	175.4(4)
P1	Mo	C38	95.2(4)	P2	Mo	C39	89.0(4)
P1	Mo	C39	91.9(3)	P2	Mo	C39	89.0(4)
P1	O1	C1	120.8(6)	P2	Mo	C40	97.2(4)
P1	O2	C12	120.0(6)	P2	O4	C13	122.2(7)
P1	O3	C25	124.3(7)	P2	O5	C24	119.1(7)
6							
P1	Mo1	P2	103.7(0)	P2	Mo1	C1	84.0(2)
P1	Mo1	C1	172.0(2)	P2	Mo1	C2	167.0(2)
P1	Mo1	C2	86.7(2)	P2	Mo1	C3	86.4(2)
P1	Mo1	C3	92.8(2)	P2	Mo1	C4	96.2(2)
P1	Mo1	C4	87.2(2)	P2	O40	C41	123.3(3)
P1	O60	C61	119.7(3)	P2	O53	C52	121.3(3)
P1	O73	C72	122.3(3)	P2	O31	C30	127.8(3)
P1	O10	O11	126.8(3)				

Table 4. Selected Torsion Angles (deg) for 5 and 6

atom 1	atom 2	atom 3	atom 4	angle (deg)
5				
Mo	P1	O1	C1	-172.68
Mo	P1	O2	C12	77.12
Mo	P1	O3	C25	53.52
Mo	P2	O4	C13	-173.30
Mo	P2	O5	C24	80.76
Mo	P2	O6	C36	128.91
C1	C6	C7	C12	-45.67
C13	C18	C19	C24	-43.24
C25	C30	C31	C36	69.73
6				
Mo1	P1	O60	C61	-72.8
Mo1	P1	O10	C11	-26.0
Mo1	P1	O73	C72	164.4
Mo1	P2	O53	C52	72.2
Mo1	P2	O40	C41	-174.7
Mo1	P2	O31	C30	-3.5
C52	C47	C46	C41	-38.4
C30	C21	C20	C11	-97.8
C61	C66	C67	C72	42.6

thermal parameter of each hydrogen atom was set equal to the U_{eq} value of the carbon atom to which it was bonded. Refinement of the model converged with $R = 3.31\%$ and $R_w = 3.36\%$ for those 3288 reflections with $|F_o| > 6.0\sigma|F_o|$ and $R = 6.93\%$ and $R_w = 4.98\%$ for all data. Following refinement, the extreme features in the difference Fourier map were a peak of height $0.44 \text{ e } \text{Å}^{-3}$ and a negative feature of $-0.51 \text{ e } \text{Å}^{-3}$.

Results and Discussion

Synthesis and Characterization. Complexes **5–8** were synthesized in high yields by the reactions of *cis*- $\text{Mo}(\text{CO})_4(\text{nbd})$ and *cis*- $\text{PtCl}_2(\text{cod})$ with the appropriate ligands as shown in Figure 2. All complexes were characterized by $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and ^1H NMR spectroscopy (vide infra), and the data are consistent with those reported for related complexes.¹¹ No attempt was made to assign the $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of the aromatic carbons of the complexes.

Variable-Temperature NMR Studies and the X-ray Crystal Structure of *cis*-{6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)} tetracarbonylmolybdenum-(0), 5. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a dichloromethane- d_2 solution of **5** are shown in Figure 3. At 295 K, a sharp singlet is observed at δ 179.87 ppm.

As the solution is cooled to 165 K, the singlet first broadens and then, below 216 K, splits into a doublet of doublets (AX pattern at δ 184.29 and 182.56 ppm, $|^2J(\text{PP})| = 38 \text{ Hz}$) and two singlets ($\delta = 185.69$ and 175.61 ppm), in a 2:2:3 ratio. This indicates that all three diastereomers of the complex are present at low temperatures. The doublet of doublets is assigned to the $R^*R^*S^*$ ($S^*S^*R^*$) diastereomer because it is the only diastereomer with inequivalent phosphorus nuclei.¹² The two singlets are due to the $R^*R^*R^*$ ($S^*S^*S^*$) and $S^*R^*S^*$ ($R^*S^*R^*$) diastereomers, but it is not possible to assign a particular resonance to a specific diastereomer. The dynamic behavior of **5** is consistent with a facile interconversion between the various diastereomers on the NMR time scale.¹³ This interconversion can be accomplished by epimerization of the dibenzo[*d,f*]-[1,3,2]dioxaphosphepin moieties in **5**.

The ^{31}P NMR resonances of the $R^*R^*R^*$ ($S^*S^*S^*$) and $S^*R^*S^*$ ($R^*S^*R^*$) diastereomers are 10.0 ppm apart, but the two ^{31}P resonances of the $R^*R^*S^*$ ($S^*S^*R^*$) diastereomer are less than 3 ppm apart. This is somewhat surprising because the ^{31}P environment in half of the $R^*R^*S^*$ ($S^*S^*R^*$) diastereomer is like that in the $R^*R^*R^*$ ($S^*S^*S^*$) diastereomer, while the other half is like that in the $S^*R^*S^*$ ($R^*S^*R^*$) diastereomer. The most reasonable explanation for this behavior is that there are strong steric interactions between the dibenzo[*d,f*][1,3,2]dioxaphosphepin rings at the metal center. This further suggests that the various diastereomers could have quite different energies due to these steric interactions, although this does not appear to be the case for **5**.

The molecular structure of **5** has been determined and is shown in Figure 4. The coordination sphere of the molybdenum atom is composed of four carbonyl ligands and two phosphorus donor groups in a *cis*-octahedral geometry. The observed P1–Mo1–P2 angle of $84.71(1)^\circ$ is smaller than the ideal angle of 90° , indicating that ligand **1** has a small bite angle.

The space group of **5**, $P2_1$, is noncentrosymmetric, which indicates that a single enantiomeric conformation

(12) Throughout this paper, $R^*R^*S^*$ diastereomer refers to the relative configurations of 2,2'-biphenyl groups at P(1), chiral axis, and P(2), respectively. The configuration at P(1) is assigned R^* following the customary convention when the absolute configuration is unknown.

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(11) Pregosin, P. E.; Kunz, R. W. *NMR* **1979**, *16*, 1.

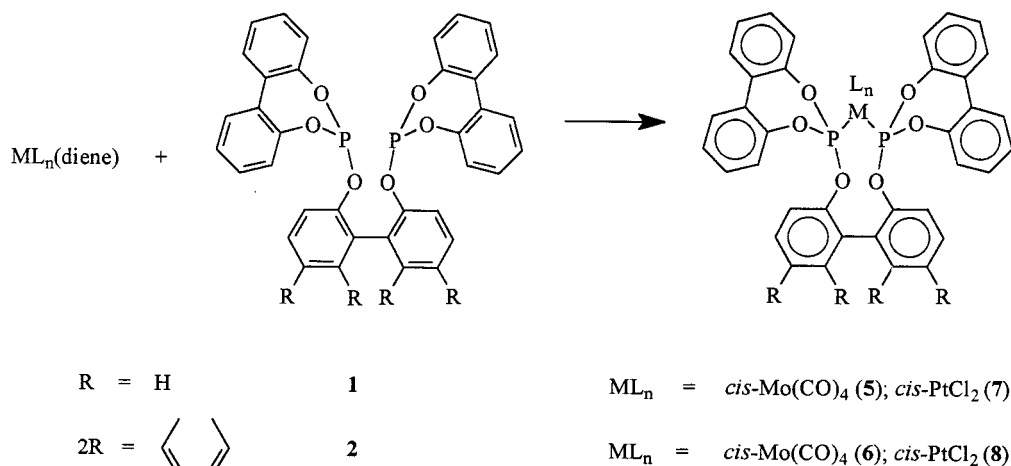


Figure 2. Scheme for the synthesis of the complexes *cis*-{(±)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)}tetracarbonylmolybdenum(0), **5**, *cis*-{(±)-6,6'-[[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)}tetracarbonylmolybdenum(0), **6**, *cis*-{(±)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)}dichloroplatinum(II), **7**, and *cis*-{(±)-6,6'-[[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)}dichloroplatinum(II), **8**.

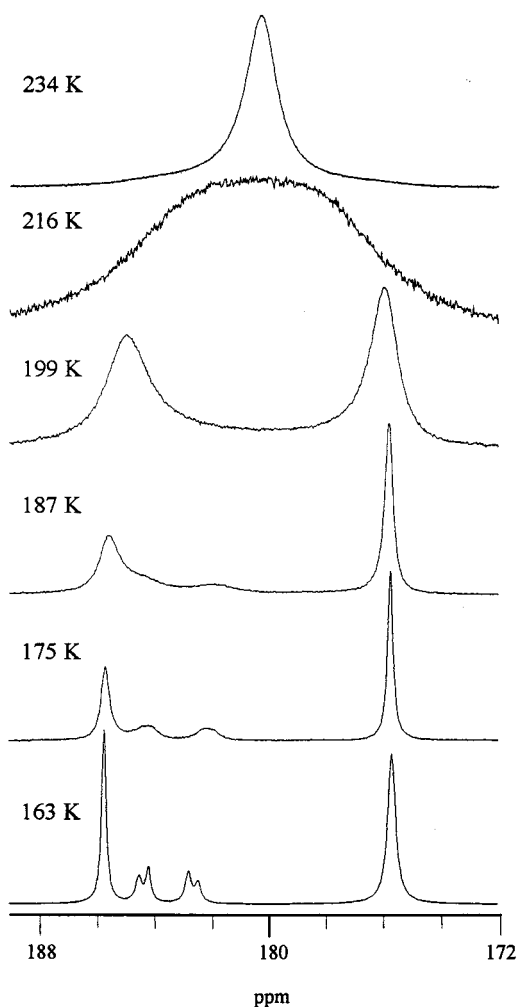


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of *cis*-{(±)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), **5**, in dichloromethane- d_2 .

of a diastereomer is present in the crystal. We have not carried out an η -refinement procedure with the molecular structure to determine the absolute conformation of the crystal structure. However, the twists about the

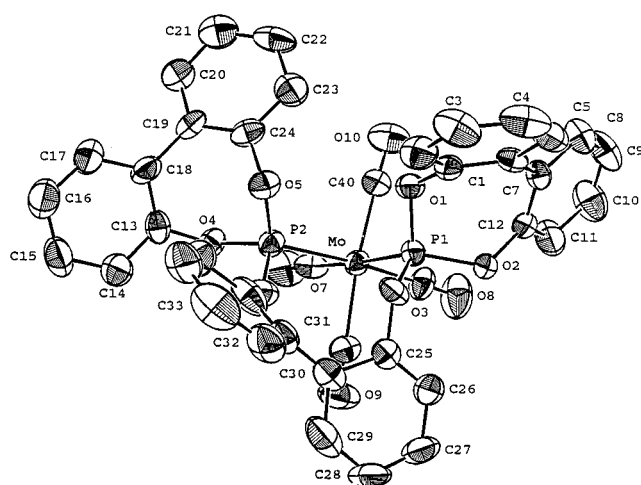


Figure 4. ORTEP diagram of *cis*-{(±)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), **5**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms attached to carbons are omitted for clarity.

C–C bond linking the two phenyl groups in the dibenzo[*d,f*][1,3,2]dioxaphosphepin groups, measured by the torsion angles C13–C18–C19–C24 = -43.2° and C1–C6–C7–C12 = -45.7° , demonstrate that **5** has either an *SRS* or *RSR* absolute configuration. Further, these results indicate that the two dibenzo[*d,f*][1,3,2]dioxaphosphepin groups in **5** are equivalent in the solid state. The fact that the two dibenzo[*d,f*][1,3,2]dioxaphosphepin groups are equivalent is also evident in the torsion angles about the phosphorus–oxygen bonds (Mo–P1–O1–C1, Mo–P1–O2–C12, Mo–P2–O4–C13, and Mo–P2–O5–C24) torsion angles of $-172.7(7)^\circ$, $77.1(7)^\circ$, $-173.3(7)^\circ$, and $80.8(8)^\circ$, respectively.

Variable-Temperature NMR Studies and the X-ray Crystal Structure of *cis*-{6,6'-[[1,1'-Binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]-dioxaphosphepin)}tetracarbonylmolybdenum(0), **6.** Variable-temperature $^{31}P\{^1H\}$ NMR spectra of dichloromethane- d_2 solutions of **6** are shown in Figure 5. At 295 K, a sharp singlet is observed at δ 181.88 ppm. As the temperature is lowered, this resonance first

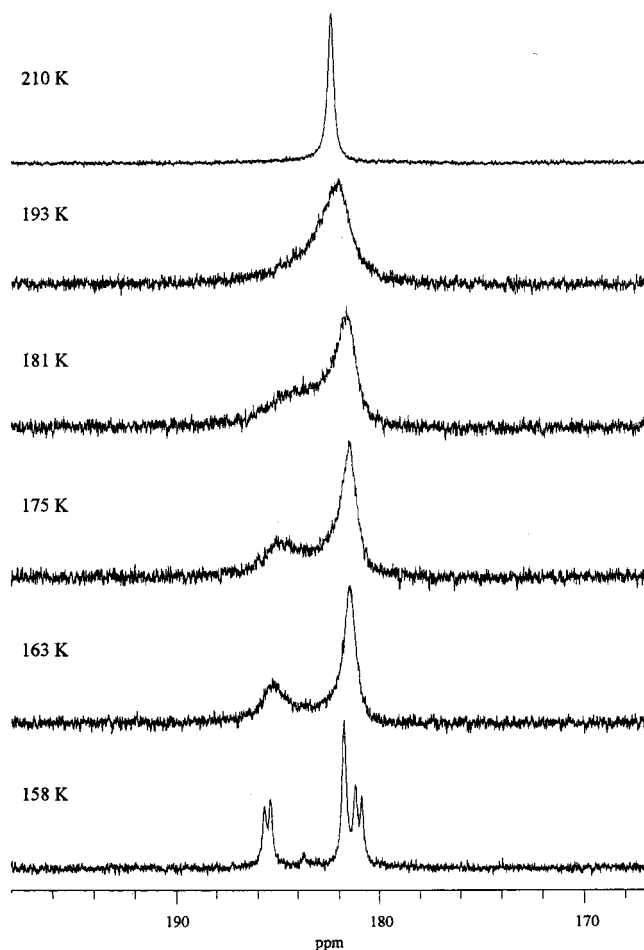


Figure 5. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *cis*-{ (\pm) -6,6'-[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), **6**, in dichloromethane- d_2 .

broadens and then, below 191 K, splits into a double of doublets (AX pattern at δ 185.52 and 181.04 with $|^2J(\text{PP})| = 35$ Hz) and two singlets (δ 183.70 and 181.74 ppm) in a 13:8:1 ratio. These resonances can be assigned to the $R^*R^*S^*$ ($S^*S^*R^*$) and $R^*R^*R^*$ ($S^*S^*S^*$)/ $S^*R^*S^*$ ($R^*S^*R^*$) diastereomers, respectively, consistent with the assignments previously made for **5**. As is the case for **5**, this behavior indicates that facile interconversion between various diastereomers occurs on the NMR time scale.¹³ As is also the case for **5**, this interconversion can be accomplished by epimerization at the 2,2'-biphenyl moieties without requiring epimerization of the 1,1'-bi-2-naphthylene moiety. The coalescence temperatures and the temperatures at which the slow exchange regions are reached are quite different for **5** and **6** even though this appears to be occurring via the epimerization of the 2,2'-biphenyl moieties in both molecules. Because of this, it seems unlikely that these differences are due to differences in the rates of the two processes. Instead, these differences are most likely due to the presence of different amounts of the diastereomers in solutions of **5** and **6** (see below) and to the quite different ^{31}P NMR chemical shifts of the diastereomers of **5** and **6**.

The relative amounts of the three diastereomers of **5** and **6** are quite different at low temperatures. All three diastereomers are approximately equally favored in **5**, while two of the three diastereomers are approximately

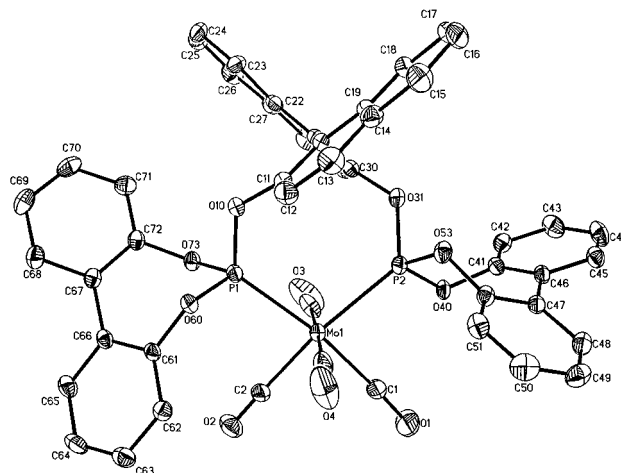


Figure 6. ORTEP diagram of *cis*-{ (\pm) -6,6'-[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}tetracarbonylmolybdenum(0), **6**. Thermal ellipsoids are drawn at the 25% probability level. The hydrogen atoms attached to carbons are omitted for clarity.

equally favored in **6**. The differences in the stabilities of the diastereomers of **5** and **6** clearly demonstrate that replacing the central 2,2'-biphenyl fragment in **5** with the more sterically demanding 1,1'-bi-2-naphthylene fragment in **6** reduces the number of low-energy conformations available.

The molecular structure of **6** has been determined and is presented in Figure 6. The coordination geometry of the molybdenum is a distorted octahedron. The distortion is most evident in the angle $\text{P1-Mo1-P2} = 103.7(1)^\circ$, which is significantly larger than both the ideal angle of 90° and the same angle in **5** ($\text{P1-Mo-P2} = 84.7(1)^\circ$). Because **5** and **6** differ only in bridging biaryl group in the ligand, this suggests that the 2,2'-binaphthyl group forces the bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligand in **6** (ligand **2**) to have a much larger bite angle that does the bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligand in **5** (ligand **1**). This conclusion is supported by fact that the twist about the C-C bond linking the naphthyl groups in **6** (torsion angle $\text{C11-C20-C21-C30} = -97.8^\circ$) is much closer to 90° than is the twist about the C-C bond linking the two biphenyl groups in **5** (torsion angle $\text{C25-C30-C31-C36} = 69.7^\circ$). The very different bite angles of the bridging biaryl groups in **5** and **6** are consistent with the different ratios of diastereomers that are observed in low-temperature solutions of the complexes.

Complex **6** crystallizes in the centrosymmetric space group, $P2_1/n$, which means that both enantiomers of **6** are present in the crystal. This is not unexpected because ligand **2** was prepared from racemic 2,2'-binaphthol. The twists about the C-C bond linking the two phenyl groups in the dibenzo[*d,f*][1,3,2]dioxaphosphepin groups (torsion angles $\text{C61-C66-C67-C72} = 42.6^\circ$ and $\text{C52-C47-C46-C41} = -38.4^\circ$) demonstrate that **1** has the $R^*R^*S^*/S^*S^*R^*$ configuration. The fact that the two dibenzo[*d,f*][1,3,2]dioxaphosphepin groups are inequivalent in the solid state is also evident in the torsion angles about the phosphorus-oxygen bonds (torsion angles $\text{Mo1-P1-O60-C61} = 72.2(1)^\circ$, $\text{Mo1-P1-O73-C72} = 164.4(2)^\circ$, $\text{Mo1-P2-O53-C52} = -77.8(1)^\circ$, and $\text{Mo1-P2-O40-C41} = -174.7(2)^\circ$). The solid-state conformation is also the preferred conforma-

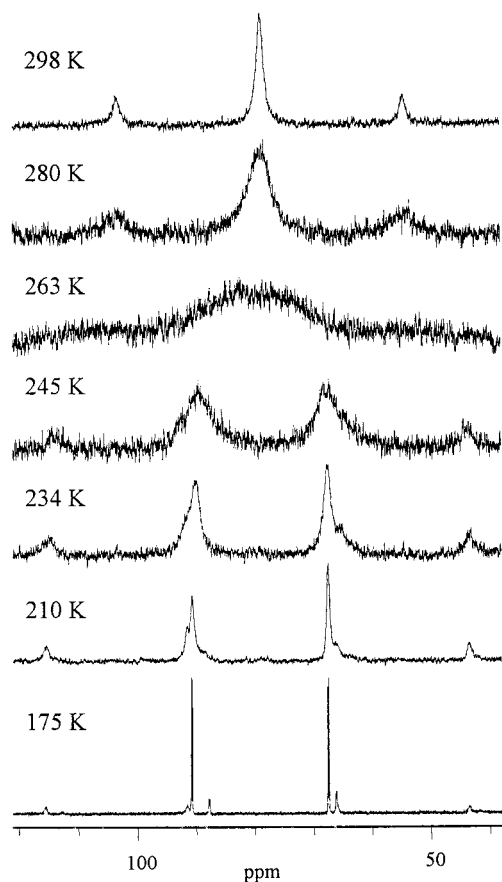


Figure 7. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *cis*-{(\pm)-6,6'-[[1,1'-biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}dichloroplatinum(II), **7**, in dichloromethane- d_2 .

tion in solution because the major conformer in the slow exchange region has inequivalent phosphorus environments (AX spectral pattern).

The configuration of ligand **2** in **6** is the same as that of ligand **1** in [Pt(**1**) $_2$] 1b but different from that of ligand **1** in **5**. This is surprising because the coordination geometries of the bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligands in **5** (*cis*-octahedral) and **6** (*cis*-square planar) are similar and quite different from that of the bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin) ligand in [Pt(**1**) $_2$] (tetrahedral). It is obvious that the ligand configuration is not solely determined either by the bridging biaryl group or by the coordination geometry of the ligand. This is consistent with the results from the variable-temperature NMR studies of **5** and **6**, which indicate that a number of the diastereomers of these complexes have similar energies.

Variable-Temperature NMR Studies of *cis*-{6,6'-[[1,1'-Biphenyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}dichloroplatinum(II), **7, and *cis*-{6,6'-[[1,1'-Binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}dichloroplatinum(II), **8**.** The variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of dichloromethane- d_2 solutions of **7** and **8**, shown in Figures 7 and 8, are very similar. At 295 K, each $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet with ^{195}Pt satellites (**7**, δ 78.88 ppm, $|^1J_{\text{Pt-P}}| = 5968$ Hz; **8**, δ 82.87 ppm, $|^1J_{\text{Pt-P}}| = 5740$ Hz). The magnitudes of the one-bond platinum–phosphorus coupling constants are consistent with the proposed *cis* arrangement

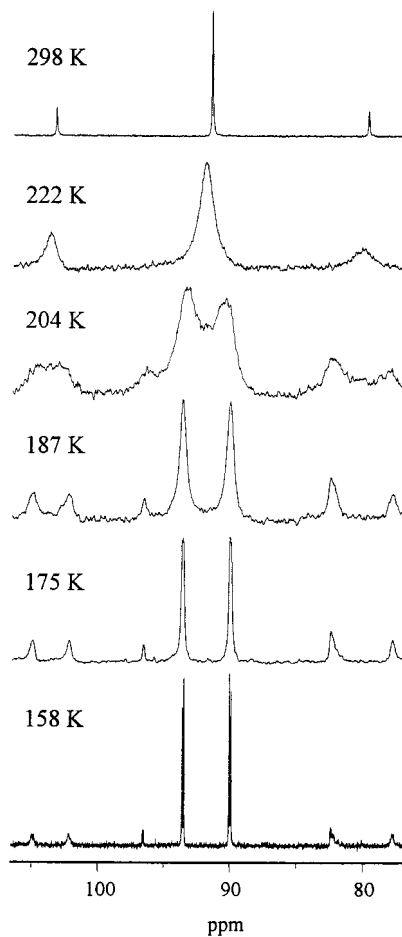


Figure 8. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *cis*-{(\pm)-6,6'-[[1,1'-binaphthyl]-2,2'-diylbis(oxy)]bis(dibenzo[*d,f*][1,3,2]dioxaphosphepin)}dichloroplatinum(II), **8**, in dichloromethane- d_2 .

of the phosphorus-donor groups. 11 As the temperature is decreased, the resonances in both solutions broaden and then split into two doublets of doublets with ^{195}Pt satellites (coalescence occurs at 256 K for **7** and at 211 K for **8**). The two doublets of doublets are in a 5:1 ratio for **7** (major, δ 90.77 and 67.51, $|^2J(\text{PP}')| = 21.4$ Hz, $|^1J(\text{PtP})| = 6009$ Hz, $|^1J(\text{PtP}')| = 5832$ Hz; minor, δ 87.82 and 66.17, $|^2J(\text{PP}')| = 18.3$ Hz, $|^1J(\text{PtP})| = 6104$ Hz, $|^1J(\text{PtP}')| = 5946$ Hz) and in a 10:1 ratio for **8** (major, δ 87.07 and 79.89, $|^2J(\text{PP}')| = 30.5$ Hz, $|^1J(\text{PtP})| = 6009$ Hz, $|^1J(\text{PtP}')| = 5832$ Hz; minor, δ 93.08 and 67.41, $|^2J(\text{PP}')| = 18.3$ Hz, $|^1J(\text{PtP})|$ and $|^1J(\text{PtP}')|$ not observed). This behavior is consistent with fast fluxional processes on the NMR time scale between the phosphorus resonances. 13 As is the case for *cis*-Mo(CO) $_4$ (bis(phosphite)) complexes, this interconversion can be accomplished by epimerization only of the dibenzo[*d,f*][1,3,2]dioxaphosphepin rings.

The observation of two species with inequivalent phosphorus nuclei at low temperatures for both **7** and **8** was unexpected. As previously discussed, only one diastereomer with inequivalent phosphorus nuclei, $R^*R^*S^*(S^*S^*R^*) \equiv S^*R^*R^*(R^*S^*S^*)$, is expected, and only one diastereomer with inequivalent phosphorus nuclei is observed for **5** and **6**. One possible explanation for the presence of two diastereomers with inequivalent phosphorus nuclei is that there are two low-energy conformations (with different interplanar angles) for the

nine-membered chelate ring in the $R^*R^*S^*(S^*S^*R^*)$ diastereomer. This suggestion is supported by the results from crystallographic studies of complexes of **1** in which very different interplanar angles were observed for the biphenyl group in the nine-membered chelate ring (-106.5° in $[\text{Pt}(\mathbf{1})_2]$ versus 69.7° in **5**). It seems less likely that the inequivalency of the phosphorus nuclei is due to different conformations of the dibenzo[d,f]-[1,3,2] dioxaphosphepin rings because their interplanar angles are always close to 45° . We would have liked to obtain the X-ray crystal structures of both **7** and **8** to better understand their solid-state conformational features, but we were unable to obtain stable crystals of these complexes.

Summary. The research described in paper clearly demonstrates that atropisomerism occurs in transition metal complexes of the bis(dibenzo[d,f][1,3,2]dioxaphosphepin) ligands **1** and **2**. The diastereomer distribution depends both on the nature of the transition metal center and on the biaryl group in the nine-membered chelate ring. These results indicate that ligands with

sterically locked dibenzo[d,f][1,3,2]dioxaphosphepin rings are the best candidates for use in enantioselective catalysis because only one diastereomer of these ligands will be present.

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Supporting Information Available: A discussion of atropisomerism in all of the complexes and tables of bond distances, bond angles, positional parameters, anisotropic thermal coordinates, and hydrogen atom coordinates for **5** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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