^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX500 NMR spectrometer at 500 and 125 MHz, respectively. The experimental conditions were similar to those reported previously.[14] The ^{1}H NMR reference was endogenous formate ($\delta = 8.465$ at pH* > 7.0 relative to trimethylsilyl propionate (TSP)), which was always present in transferrin samples as a minor impurity. The ^{13}C NMR reference was added dioxane ($\delta = 67.4$ relative to TSP).

The titanium content of transferrin was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Jarrell Ash IRIS, at 323.40 nm). The Ti$_2$-hTF samples for ICP-AES were prepared as follows: titanium(IV) citrate (2.2 molequiv) was added to apo-hTF (in 10 mM Hepes buffer, pH 7.4, 10 mM bicarbonate) and left to equilibrate for over 24 h at 310 K. The protein was then purified by ultrafiltration (Centricon30, Amicon), washing four times with 0.1 M KCl and twice with water. An aliquot of the final solution was diluted with concentrated HNO$_3$ (ca. 6 M) and the titanium content was measured without any digestion of the sample.[20] The transferrin concentration in this sample was determined by titrating with Fe^{III} ions (added as [Fe(NTA)$_2$]) by measuring the absorbance at 465 nm ($\Delta\varepsilon = 4950\,\text{M}^{-1}\,\text{cm}^{-1}$ for diferric transferrin).[21]

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Platinum(II) Complexes with Constructive and Destructive Interaction of Diphosphane and Binaphthol Ligands**

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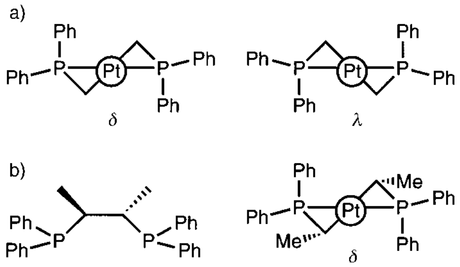
Michel R. Gagné*

(*S*,*S*)-2,3-Bis(diphenylphosphanyl)butane ((*S*,*S*)-Chiraphos) and its achiral analogue 1,2-bis(diphenylphosphanyl)ethane (dppe) belong to a class of chelating diphosphanes that form five-membered rings with late transition metals. These diphosphanes usually adopt a δ- or λ-*skew* conformation (Scheme 1a).[1] With the achiral dppe, the two conformers are equally favorable; however, backbone modification of chiral diphosphanes makes one conformer more stable than the other.[2] For example, the *trans*-methyl substituents of (*S*,*S*)-Chiraphos favor the δ conformer (pseudoequatorial versus



Scheme 1. a) *skew* conformations of dppe in platinum complexes. b) (*S*,*S*)-Chiraphos and its preferred δ conformation in the complex.

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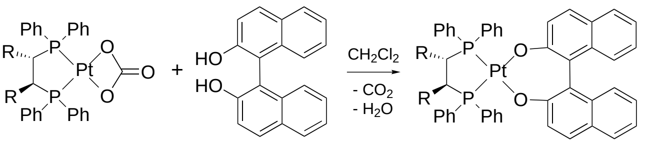
pseudoaxial methyl groups, Scheme 1b).[3] Because of this conformational preference, (*S*,*S*)-Chiraphos and similar ligands have been used extensively in asymmetric catalysis.[4] The chelate ring fixes the positions of the phenyl groups of the phosphane such that their stereochemistry influences other bound ligands.[2, 5] Although the effect of diphosphane conformation on the stereoselectivity with which ligands are bound has been studied in detail, the reciprocal effect of coordinating ligands on the conformation of the diphosphane has received little attention.

To investigate the magnitude of this type of interaction, the square-planar platinum(II) complex [(dppe)Pt{(*R*)-Binol}] (**2a**) was synthesized by the method of Andrews et al. (Scheme 2, H_2Binol = 1,1′-bi-2-naphthol).[6] The single-crystal X-ray structure of **2a** indicates that the chelating diphosphane adopts only the *λ-skew* conformation in the solid state.[7] Since dppe has no inherent conformational preference, the *λ* conformation must be imposed on the diphosphane by the bulky (*R*)-Binol ligand, which interacts with the phenyl groups of dppe.



1a: R = H
1b: R = CH_3

(*R*)- or (*S*)-H_2Binol

2a: R = H; (*R*)-Binol
(*S*)-**2b**: R = CH_3; (*S*)-Binol
(*R*)-**2b**: R = CH_3; (*R*)-Binol

Scheme 2. Synthesis of **2**.

The strength of the Binol–diphosphane interaction was further probed by replacing dppe with the chiral diphosphane (*S*,*S*)-Chiraphos. Incorporation of two chiral ligands into a complex forces them to interact either constructively (matched) or destructively (mismatched).[8] (*S*,*S*)-Chiraphos prefers the *δ* conformation. Since the structure of **2a** indicates that (*R*)-Binol favors the *λ* chelate, it and (*S*,*S*)-Chiraphos are mismatched, whereas (*S*,*S*)-Chiraphos and (*S*)-Binol are matched.

The matched ((*S*)-**2b**) and mismatched ((*R*)-**2b**) complexes were prepared in the same way as **2a** (Scheme 2).[9] The X-ray structure of (*S*)-**2b** confirms that the diphosphane adopts the *δ* conformation that is favored by both (*S*,*S*)-Chiraphos and (*S*)-Binol (Figure 1).[10] The structure is otherwise unexceptional.[1, 3, 11] The unit cell of the mismatched complex, on the other hand, contains eight molecules of (*R*)-**2b** that differ in conformation.[12] Superposition of the conformers shows the significant conformational variability of both the Chiraphos and Binol ligands (Figure 2). Differences in the Pt–P bond lengths and P-Pt-P angles of the eight (*R*)-**2b** conformers are generally smaller than the differences in the Pt–O bond lengths and O-Pt-O angles (Table 1), but all bond lengths and angles are similar to those of related compounds.[11, 13, 14]

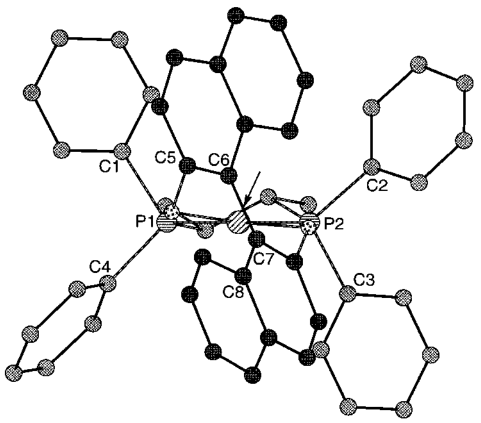


Figure 1. X-ray structure of (*S*)-**2b**. The arrow shows the center of the Binol 1,1′ bond: the distance from this point to the P-Pt-P plane is *ξ* (see Table 1).

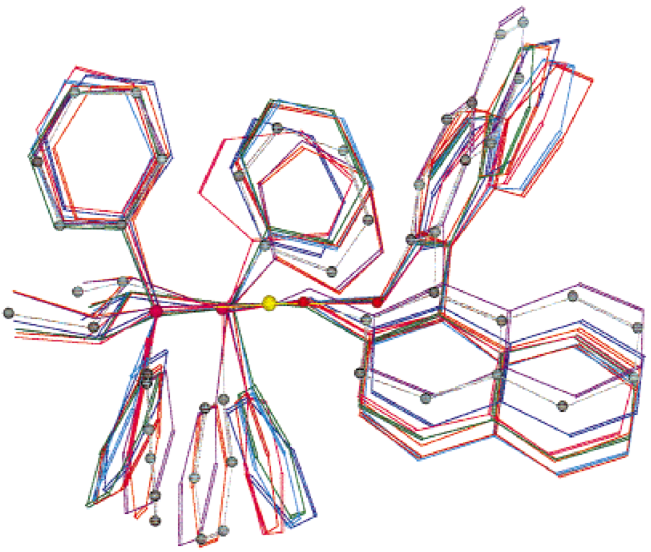


Figure 2. Superposition of the eight molecules of the unit cell of (*R*)-**2b**. The P-Pt-P planes are superimposed, and *ξ* is positive (the Binol units are skewed above the square plane).

Table 1. Bond lengths [Å] as well as bond and dihedral angles [°] of **2a**, (*S*)-**2b**, and (*R*)-**2b**.

	2a	(*S*)-**2b**	(*R*)-**2b**	
			median	range
Pt–O	2.071(5)	2.072(6)	2.058	2.021(9)–2.091(8)
Pt–P	2.212(2)	2.203(3)	2.210	2.200(3)–2.222(4)
O-Pt-O	89.0(2)	90.3(3)	90.5	89.8(3)–92.6(3)
P-Pt-P	85.5(1)	87.3(9)	86.7	86.1(1)–87.2(1)
C_5-C_6-C_7-C_8	−62.9(1)	62.8(1)	−61.9	−58.6(2)–(−70.0)(2)
−(P_2-Pt-P_1-C_1)	142.5(6)	103.1(6)	106.7	98.2(8)–115.5(8)
P_1-Pt-P_2-C_2	113.5(6)	127.3(6)	131.8	125.6(9)–143.6(8)
−(P_1-Pt-P_2-C_3)	120.1(5)	111.0(6)	105.1	91.1(8)–113.0(9)
P_2-Pt-P_1-C_4	94.0(5)	135.2(6)	133.4	123.1(8)–138.7(9)
ξ	0.328	0.316	0.435	0.225–0.689

The extent of Binol distortion in each of the ten molecules (**2a**, (*S*)-**2b**, and eight (*R*)-**2b**) was quantified in terms of the distance *ξ* of the binaphthyl centroid from the P-Pt-P plane (Figure 1, Table 1). In an ideal C_2-symmetric molecule, $\xi = 0$ (the two naphthylene groups are symmetrically arranged above and below the square coordination plane of the Pt center). Nonzero values of *ξ* reflect twisting of Binol due to steric conflict with the phenyl groups of the phosphane.

1433-7851/98/3711-1580 $ 17.50+.50/0

Variations in diphosphane conformation were quantified by means of the four P-Pt-P-C_{ipso} torsional angles (Figure 1). These angles describe the degree to which each phenyl ring is pseudoaxial (ideal value: 90°) or pseudoequatorial (ideal value: 135°); together they define the λ and δ conformations (Scheme 1).[13] From the values in Table 1 it is apparent that all of the molecules deviate slightly from the ideal C_2 symmetry. The variation of ξ in the (*R*)-**2b** molecules (compared to $\xi_{\mathbf{2a}} \approx \xi_{(S)\text{-}\mathbf{2b}}$) shows the flexibility of the Binol unit in these complexes. The range of torsional angles in (*R*)-**2b** is also impressive, although **2a** and other Chiraphos compounds show similarly large deviations from ideal geometry.[11, 15] The most significant conclusion drawn from the torsional angle data is that each of the eight (*R*)-**2b** molecules adopts the δ conformation.[16] Comparison of the diphosphane conformations of **2a**, (*S*)-**2b**, and a representative molecule of (*R*)-**2b** reveals that (*R*)-**2b** more closely resembles (*S*)-**2b** than **2a** (Figure 3). Thus the *trans*-methyl groups of (*S*,*S*)-Chiraphos have a stronger influence on the diphosphane conformation than the Binol ligand.

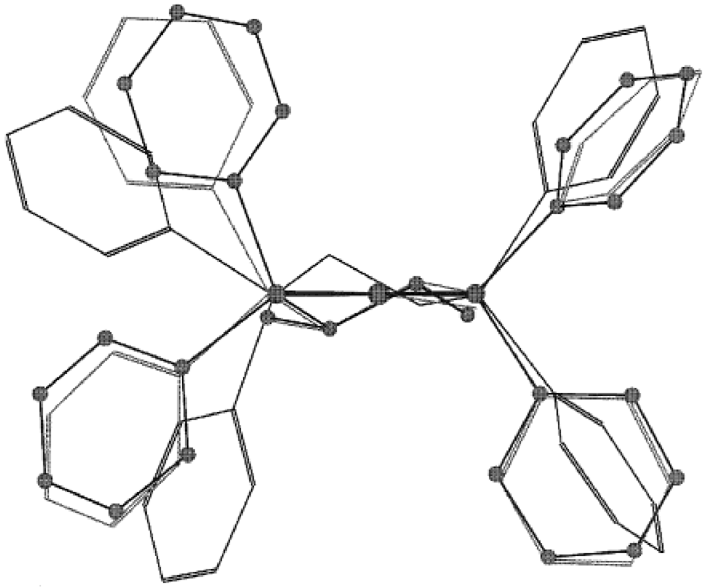


Figure 3. Comparison of the phosphane conformations of **2a** (black), (*S*)-**2b** (gray), and a typical molecule of (*R*)-**2b** (black, with atoms shown).

The influence of stereochemically matched and mismatched ligand pairs on the kinetics of complex formation was assessed by UV/Vis spectroscopy. Reactions with an excess of Binol (80 equiv) generated reproducible pseudo-first-order kinetic plots. Surprisingly, k_{obs} for the formation of the mismatched diastereomer (*R*)-**2b** is twice that of the matched diastereomer (*S*)-**2b** ($5.2(1) \times 10^{-3}\,s^{-1}$ versus $2.6(1) \times 10^{-3}\,s^{-1}$).[17]

The relative ground-state energies of the two diastereomers were determined by means of an exchange reaction of the binaphtholate ligands [Eq. (a)]. Integration of the ^{31}P NMR signals of the diastereomers at equilibrium afforded an equilibrium constant K_{eq} of 3.6 ± 0.3 at 25 °C [$\Delta G^{\ominus} = 0.76\ \text{kcal mol}^{-1}$ ($3.18\ \text{kJ mol}^{-1}$)]. As expected, the matched diastereomer (*S*)-**2b** is slightly more thermodynamically stable than the mismatched (*R*)-**2b**.

$$(R)\text{-}\mathbf{2b} + (S)\text{-}H_2\text{Binol} \rightleftharpoons (S)\text{-}\mathbf{2b} + (R)\text{-}H_2\text{Binol} \qquad \text{(a)}$$

The interaction of (*S*,*S*)-Chiraphos and Binol across the square coordination plane of the Pt^{II} center clearly has significant structural, kinetic, and thermodynamic consequences. Although the interactions observed are small, they are relevant, since high selectivities in asymmetric catalysis can be achieved with energy differences $\Delta\Delta G^{\ddagger}$ of only 2–3 kcal mol^{-1} for diastereomeric transition states. The conformational flexibilities of (*S*,*S*)-Chiraphos and Binol are noteworthy, as both ligands are widely used in asymmetric catalysis. This mobility is undoubtedly a general phenomenon that should be not be dismissed when correlating ground-state structural data with stereochemical models for reaction selectivities.[13]

Experimental Section

Racemic H_2Binol (Aldrich) was resolved into the enantiomers (> 95 % *ee*) with *N*-benzylcinchonidinium chloride.[18a] The starting materials [(dppe)$PtCl_2$], [(cod)$PtCl_2$], [(*S*,*S*)-Chiraphos)$PtCl_2$], **1a**, and **1b** were prepared according to literature procedures.[1a, 18b–d] A representative synthesis of a binaphtholate complex follows:[6]

(*S*)-**2b**: To a solution of [(*S*,*S*)-Chiraphos)$PtCO_3$] (125 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was added (*S*)-Binol (53 mg, 0.19 mmol). The reaction mixture immediately turned yellow, and the reaction was complete after 2 h according to ^{31}P NMR spectra. The solvent was evaporated in vacuo, and the yellow product was recrystallized from CH_2Cl_2/Et_2O to give 163 mg of (*S*)-**2b** (94 % yield).

UV/Vis spectra for the kinetic investigation were collected on an OLIS Cary-14 spectrometer interfaced to a computer for data collection. Reaction mixtures contained 0.16 mM **1a** or **1b** and 13.3 mM (*R*)- or (*S*)-Binol; k_{obs} is the average value from at least three experiments. Custom-made glass UV/Vis cells with screw-cap lids lined with PTFE-faced septa were used to prevent evaporative loss of CH_2Cl_2. The program Kaleidograph was used to determine k_{obs} by fitting a plot of absorbance ($\lambda = 410$ nm) versus time to the equation $A_t = A_\infty - A_\infty[\exp(-k_{obs}t)]$.

Equilibrium experiments were carried out in dry CH_2Cl_2. One equivalent of (*R*)- or (*S*)-Binol was added to an NMR tube containing 15 mg (16 µmol) of (*S*)-**2b** or (*R*)-**2b**, respectively. The same equilibrium was reached from either side of Equation (a).

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[6] a) M. A. Andrews, E. J. Voss, G. L. Gould, W. T. Klooster, T. F. Koetzle, *J. Am. Chem. Soc.* **1994**, *116*, 5730–5740; b) ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 27.2$, $^{1}J_{P,Pt} = 3644$ Hz; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.98$ (m, 4H), 7.81 (m, 4H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.60 (m, 2H), 7.50 (m, 12H), 7.10 (t, 2H), 6.97 (t, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.51 (d, $J = 9$ Hz, 2H), 2.38 (m, 2H; CH_2), 2.05 (m, 2H; CH_2)

(1 equiv CH_2Cl_2 of crystallization also observed); $[\alpha]_D^{25.4} = -1.03$ ($c = 1.01$ in CH_2Cl_2); elemental analysis calcd for $C_{46}H_{36}O_2P_2Pt \cdot CH_2Cl_2$: C 58.6, H 4.0; found: C 58.2, H 4.0.

[7] Crystal data for **2a**: $a = 12.5114(7)$, $b = 17.0838(10)$, $c = 18.3107(10)$ Å, $V = 3913.8(4)$ Å^3, orthorhombic, space group $P2_12_12_1$, crystal dimensions $0.05 \times 0.05 \times 0.40$ mm, $\rho_{calc} = 1.634$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 50.0°$. X-ray data were collected at -100 °C on a Siemens SMART diffractometer with CCD detection and $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) in the ω scan mode. Of 20439 reflections collected, 6903 were unique and 5370 were included in subsequent calculations. Correction of the intensity data by using the SADABS program gave a range of relative corrections of 0.733–1.76 and an absorption correction of $\mu = 3.83$ mm^{-1}. The structure was solved by direct methods. In the final least-squares refinement cycle, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included with a riding model. The quantity minimized was SwD $|F|^2$. The model converged at $R = 0.042$, $wR = 0.042$, and GOF $= 1.15$ for 5335 reflections with $I_{net} > 2.5\sigma(I_{net})$ and 487 parameters. Calculations were performed with the program NRCVAX. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101092. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] (*S*)-**2b**: ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 30.3$, $^1J_{P,Pt} = 3547$ Hz; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.86$ (m, 8H), 7.66 (m, 4H), 7.51 (m, 12H), 7.05 (dd, $J = 7.7$, 6.9 Hz, 2H), 6.95 (dd, $J = 8.3$, 6.8 Hz, 2H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.59 (d, $J = 8.8$ Hz, 2H), 2.28 (m, 2H, CH), 1.05 (m, 2H, CH_3) (0.5 equiv Et_2O of crystallization also observed); $[\alpha]_D^{24.7} = -151.6$ ($c = 1.02$ in CH_2Cl_2); elemental analysis calcd for $C_{48}H_{40}O_2P_2Pt \cdot 0.5\,C_4H_{10}O$: C 63.7, H 4.8; found: C 63.9, H 4.9. (*R*)-**2b**: ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 31.8$, $^1J_{P,Pt} = 3562$ Hz; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.92$ (m, 4H), 7.83 (m, 4H), 7.74 (d, $J = 6.1$ Hz), 7.66 (m, 6H), 7.53 (m, 2H), 7.46 (m, 4H), 7.35 (d, $J = 8.8$ Hz, 2H), 7.03 (t, 2H), 6.90 (t, $J = 7.0$ Hz, 2H), 6.71 (d, $J = 8.6$ Hz, 2H), 6.00 (d, $J = 8.8$ Hz, 2H), 2.22 (m, 2H, CH), 1.04 (m, 6H, CH_3) (H_2O and Et_2O of crystallization also observed); $[\alpha]_D^{24.0} = +110.6$ ($c = 1.02$ in CH_2Cl_2); elemental analysis calcd for $C_{48}H_{40}O_2P_2Pt \cdot H_2O \cdot 0.375\,C_4H_{10}O$: C 62.5, H 4.85; found: C 61.9, H 4.55.

[10] The crystal structure analysis of (*s*)-**2b** was carried out as described in ref. [7]. Crystal data: $a = 13.4508(6)$, $b = 17.5011(8)$, $c = 19.0202(9)$ Å, $V = 4477.4(4)$ Å^3, orthorhombic, space group $P22_12_1$, crystal dimensions $0.20 \times 0.20 \times 0.08$ mm, $\rho_{calcd} = 1.399$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 55.0°$. Of 36189 reflections collected, 10236 were unique and 9052 were included in the refinement. Correction of the intensity data by using the program SADABS gave a range of relative corrections of 0.816–1.136 and and an absorption correction $\mu = 3.23$ mm^{-1}. In the final least-squares cycle, the model converged at $R = 0.050$, $wR = 0.059$, and GOF $= 2.47$ for 9031 reflections with $I_{net} > 2.5\sigma(I_{net})$ and 538 parameters.

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[12] The crystal structure analysis of (*R*)-**2b** was carried out as described in ref. [7]. Crystal data: $a = b = 46.8015(23)$, $c = 16.1220(8)$ Å, $V = 35313(3)$ Å^3, tetragonal, space group $P4_3$, crystal dimensions $0.20 \times 0.20 \times 0.15$ mm, $\rho_{calcd} = 1.429$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 50.0°$. Of 319032 reflections collected, 62211 were unique and 45551 were included in the refinement. Correction of the intensity data by using the program SADABS gave a range of relative corrections of 0.700–1.223 with $\mu = 3.28$ mm^{-1}. In the final least-squares cycle, the model converged at $R = 0.065$, $wR = 0.060$, and GOF $= 1.91$ for 44970 reflections with $I_{net} > 3.0\sigma(I_{net})$ and 4023 parameters. Because of the unusual size of this structure, care was taken to ensure that the cell and symmetry were correct. The program MISSYM was used both on the completed structure and on the Pt positions alone. No additional crystallographic or noncrystallographic symmetry elements or translations were detected.

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[15] The magnitude of the variations in the torsional angles observed here is also similar to that of dppe fragments in multiple-molecule crystal structures: A. Martín, A. G. Orpen, *J. Am. Chem. Soc.* **1996**, *118*, 1464–1470.

[16] See Table 1. For **2a**, the torsional angles at C1 and C3 indicate pseudoequatorial, and those at C2 and C4 pseudoaxial phenyl groups. For (*S*)-**2b** and (*R*)-**2b**, the torsional angles at C1 and C3 indicate pseudoaxial, and those at C2 and C4 pseudoequatorial phenyl groups. Note that the lack of C_2 symmetry in these molecules makes each of the four torsional angles unique. All molecules are viewed with positive ξ so that intermolecular comparisons between phenyl groups in the same quadrant are possible.

[17] For comparison, k_{obs} for **2a** is $2.1(1) \times 10^{-3}$ s^{-1}.

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The Hexanitridodimanganate(IV) $Li_6Ca_2[Mn_2N_6]$: Preparation, Crystal Structure, and Chemical Bonding[**]

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While the ternary nitrides $Li_7[V^VN_4]$[1, 2] and $Li_6[Cr^{VI}N_4]$[3] contain the 3d metals in their highest oxidation states, only the oxidation state +5 is attained by manganese in $Li_7[Mn^VN_4]$[1]. In the ternary systems Ca/(V,Cr,Mn)/N, only intermediate transition metal(III) compounds occur: $Ca_3[V^{III}N_3]$[4], $Ca_3[Cr^{III}N_3]$[5], $Ca_3[Mn^{III}N_3]$,[6] and $(Ca_3N)_2[Mn^{III}N_3]$[7]. In the quaternary system Li/Ca/Mn/N, we have now obtained $Li_6Ca_2[Mn_2N_6]$, a hexanitridodimanganate(IV). This is the first nitridometalate of a transition metal with an unbridged

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