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Induction of Atropisomeric Chirality on Heavily Substituted Phosphametallocenes

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Summary: The solution behavior of the diphospha- and the monophosphametallocenes with (−)-menthyl substituents was investigated by variable-temperature NMR measurements in toluene-d_8. Because of the bulky and chiral (−)-menthyl substituents which restrict the rotation of the η^5-phospholyl/η^5-cyclopentadienyl ligands with respect to each other, the tetra[(−)-menthyl]phosphametallocenes were observed as mixtures of two slowly interconverting diastereomers.

Introduction. Rotation of a η^5-cyclopentadienyl ligand about the metal−cyclopentadienyl axis is a dynamic process that is characteristic of metallocene or half-metallocene species.[1] The energy barrier to the ring rotation in the (η^5-C_5H_5)-M species is generally very low. For example, the ring rotation barrier in Fe(η^5-C_5H_5)$_2$ was estimated to be 1−2 kcal/mol.[2] In 1981, Luke and Streitwieser demonstrated that the ring rotation in ferrocene and uranocene could be slowed by introducing bulky substituents in the metallocenes, the rotation barrier in (η^5-C_5H_3-1,3-^{t}Bu$_2$)$_2$Fe being 13.1 kcal/mol.[3] Following this report, analogous partially restricted rotations of η^5-cyclopentadienyl ligands about the Cp-M-Cp axes have been observed in many other metallocenes with bulky substituents.[4]

As illustrated in Figure 1 for (η^5-C_5H_3-R_2)$_2$Fe, if the ring rotation about Cp-Fe-Cp is frozen, the skewed orientation of the four R substituents breaks symmetry in the metallocene and generates an atropisomerically chiral environment around the iron center.[5] The energy barriers of Cp's rotation in heavily substituted metallocenes, however, are not large enough to freeze the rotation. These heavily substituted metallocenes exist as mixtures of equally populated enantiomers which are rapidly exchanging with each other in solution, i.e., they are *racemic*. With a proper artifice, as described in this report, restricted rotation of cyclopentadienyl ligands in metallocenes can be used as a source of *unequally populated* chirality. The species of our interest are diphosphaferrocene (**1**), diphospharuthenocene (**2**), and monophosphaferrocene (**3**), all of which have (−)-menthyl groups as bulky and *chiral* substituents (Figure 2).[6]

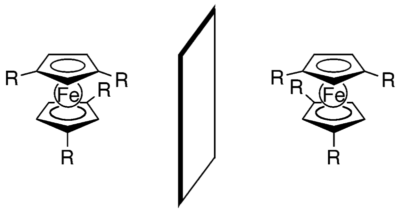
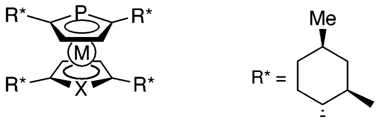


Figure 1. A pair of atropisomerically chiral enantiomers.



1: M = Fe, X = P
2: M = Ru, X = P
3: M = Fe, X = CH

Figure 2. Chiral phosphametallocenes with (−)-menthyl substituents.

In our phosphametallocenes, the bulky substituents are also chiral, and thus the complex exists in solution as a mixture of two atropisomerical *diastereomers* (not as enantiomers) which are different in energy (i.e. different in abundance). Here we wish to report our observations on the dynamic solution behavior of the phosphametallocenes **1**−**3**. To our best knowledge, this is the first NMR study pertaining to the solution behavior of metallocene species which possess chiral bulky substituents.

Results and Discussion. (a) ^{1}H and ^{31}P NMR Characteristics of Diphosphaferrocene (1) and Diphospharuthenocene (2). The ^{1}H NMR spectrum of Pp*$_2$Fe (**1**: Pp* = C_4P-2,5-((−)-menthyl)$_2$), which was prepared from 1-phenyl-2,5-di((−)-menthyl)phosphole,[7] in toluene-d_8 gave broad signals at room temperature.

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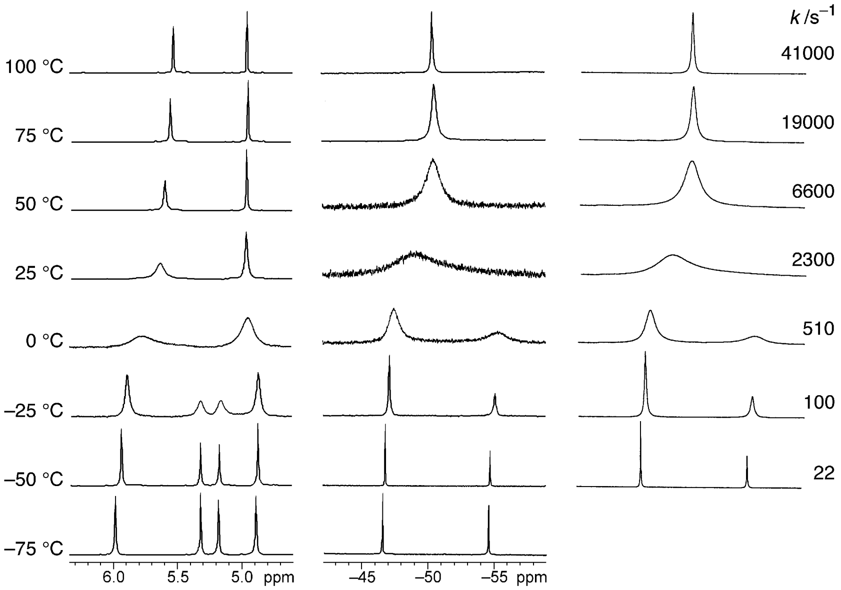
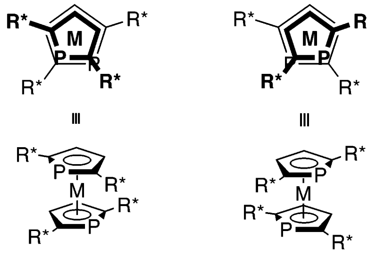


Figure 3. Experimental variable-temperature ^{1}H (in the phospholyl-*H* region at 500 MHz, left) and ^{31}P NMR (202 MHz, center) spectra of **1** in toluene-d_8, and computer simulation of ^{31}P NMR spectra with exchange rate constants (right).

The signals are sharpened at higher temperature, and the time-averaged signals were detected at 100 °C. On the other hand, at lower temperature, each of the broad resonances was split into a pair of signals with unequal intencity (ca. 54:46 molar ratio at −75 °C). The VT ^{1}H NMR signals of diastereotopic phospholyl β-hydrogens in **1** is characteristic of the dynamic process and the spectra are shown in Figure 3. The ^{31}P NMR spectrum of **1** at −75 °C gave two signals at δ −46.6 and −54.6 with a 54:46 integration ratio as well (Figure 3). The solution behavior of **1** observed by NMR was completely reversible and the relative molar ratios of the two isomers were temperature dependent. At lower temperature, the equilibrium was driven toward the isomer observed at the lower field in the ^{31}P NMR spectra. The equilibrium constants K_{eq} were calculated from the integration ratios of the two isomers in the ^{31}P or ^{1}H NMR spectra in the temperature range −25 to −75 °C. The plot of $1/T$ vs ln K_{eq} is linear, and the following thermodynamic parameters are given for **1**: $\Delta H° = 0.80 \pm 0.10$ kcal/mol and $\Delta S° = 4.4 \pm 0.4$ cal/(mol·K). The small $\Delta H°$ value indicates that difference in the relative stability between the two isomers is very small.

The origin of the two isomeric forms in **1** is restricted rotation of the two phosphacyclopentadienyl groups about the Pp*-Fe-Pp* axis. Because the diphosphaferrocene **1** possesses the chiral sidearms, it yielded a mixture of two diastereomers. The diastereomeric correlation between the two isomers is illustrated in Figure 4,[8] and the diastereomers are interchangeable as indicated in the VT NMR spectra.

A larger central metal in a corresponding diphosphametallocene would widen the space between the two η^5-Pp* ligands[9] and should reduce the interannular steric interaction between the (−)-menthyl groups, which is the origin of the restricted rotation. The diphospharuthenocene Pp*$_2$Ru (**2**)[10] showed analogous NMR behavior to that of **1** (Figure 5), but the coalescence temperature of each signal in the ^{1}H and ^{31}P NMR spectra was significantly lower than that observed for **1**. The two diastereomeric isomers of **2** existed in a ratio of 82:18 at −75 °C. The equilibrium constants K_{eq} between the two isomers detected at lower temperatures were obtained in the temperature range −50 to −80 °C, and the thermodynamic parameters were calculated from the linear correlation between $1/T$ and ln K_{eq} as $\Delta H° = 1.68 \pm 0.20$ kcal/mol and $\Delta S° = 5.7 \pm 0.4$ cal/(mol·K). The positive entropy change value is larger than that of the exchange process in **1**. This may be a result of fluxionality of the menthyl groups, which is certainly less restricted in **2** due to larger separation of the two Pp* rings.[9]



R* = (−)-menthyl, M = Fe or Ru

Figure 4. Two atropisomeric diastereomers.

(b) Kinetic Parameters for the Equilibrium between the Atropisomeric Diastereomers of 1 and 2. For diphosphaferrocene (**1**), the rates of isomerization from the major diastereomer to the minor one were estimated in the temperature range between −50 and 100 °C by line-shape analysis[11] on the ^{31}P NMR spectra. For the line-shape analysis, it was required to determine the equilibrium constant between the two isomers at each temperature. At and below −25 °C, the

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(7) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 1014.

(8) The eclipse conformation (with respect to the phosphametallocene skeleton) for stable conformers has been proposed by Okuda (refs 4a and 4c) and Orrell (ref 4g).

(9) Although the complexes **1** and **2** were not crystalline and the structures could not be determined, the solid state structures of the closely related species, (η^5-PC$_4$-2,5-Cy$_2$)$_2$M where M = Fe and Ru, have been reported recently and the distances between the two phospholyl ligands in the disphosphametallocenes were 3.34 Å for M = Fe and 3.62 Å for M = Ru (see ref 10).

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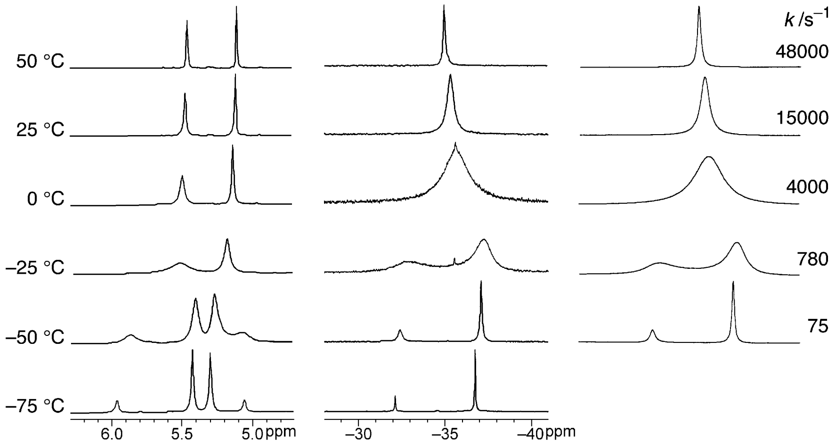

Figure 5. Experimental variable-temperature ^{1}H (in the phospholyl-*H* region at 500 MHz, left) and ^{31}P NMR (202 MHz, center) spectra of **2** in toluene-d_8, and computer simulation of ^{31}P NMR spectra with exchange rate constants (right).

^{31}P NMR spectra of **1** gave two clearly separated signals, and thus the molar ratios between the two isomers were directly obtained from the integration of the two resonances. Although the single coalesced signals was detected at higher temperature, the equilibrium constants K_{eq} were calculated from the following equation by using the $\Delta H°$ and $\Delta S°$ values.

$$\ln K_{eq} = -\Delta H°/RT + \Delta S°/R$$

The exchange rate constants k were determined over 25 °C increments between −50 and 100 °C and the values are shown in Figure 3. The Eyring plot ($\ln k/T$ vs $1/T$) is linear, and the activation parameters for the Pp* rotation in **1** are $\Delta H^{\ddagger} = 7.83 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -17.1 \pm 0.5$ cal/(mol·K), and the $\Delta G^{\ddagger}$(at 25 °C) = 12.9 ± 0.3 kcal/mol. The $\Delta G^{\ddagger}$ value is smaller than the rotation barrier in $(1,3\text{-}{}^{t}Bu_2C_5H_3)_2Fe$ (13.1−13.3 kcal/mol)[3,4g] but larger than that in $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Fe$ (11.0 kcal/mol).[4c]

The exchange rates of the two isomers in **2** were estimated in the temperature range between −50 and 50 °C by the analogous line-shape analysis[11] and are shown in Figure 5. The activation parameters of the Pp* ring rotation in **2**, $\Delta H^{\ddagger} = 8.7 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -10.2 \pm 0.5$ cal/(mol·K), were obtained from the linear correlation in the Eyring plot. The $\Delta G^{\ddagger}$ at 25 °C was calculated to be 11.8 ± 0.3 kcal/mol, significantly smaller than that of **1**.

Orrell reported the energy barriers of the hindered rotation in $Fe(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}R_2)_2$ and those in the isostructural ruthenocenes $Ru(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}R_2)_2$ (R = *tert*-butyl or *tert*-pentyl).[4g] The reported general trends are similar to those observed in this study. The rotation barriers are 2.6−3.8 kcal/mol lower for the ruthenocenes compared to the corresponding ferrocene derivatives,[4g] and the results are explained as the smaller interannular repulsions of the substituents in the ruthenocenes where the inter-ring distances are longer than those in the ferrocenes.[12]

(c) Solution Behavior of Monophosphaferrocene (3). The overall solution behavior of monophosphaferrocene (**3**) is very similar to that of **1** or **2**. The variable-temperature ^{1}H (in the phospholyl and the cyclopentadienyl region) and ^{31}P NMR spectra of **3** in toluene-d_8 are shown in Figure 6. Because monophosphaferrocene (**3**) has no molecular symmetry, all three C_5-*H* and the two β-phospholyl-*H* are inequivalent. Thus, as shown in Figure 6, the five time-averaged resonances were detected in the Cp and Pp* region in the ^{1}H NMR spectra at higher temperature (>0 °C) due to rapid rotation of the two η^5-ligands. The ring rotation was slowed at lower temperature and a pair of atropisomeric diastereomers (10 partially overlapped signals in the Cp and Pp* region) was observed in the ^{1}H NMR spectra at and below −50 °C. The VT-^{31}P NMR spectra were consistent with the ^{1}H NMR observation. The ratio of the two diastereomers was ca. 70/30 at −75 °C, and at higher temperature the equilibrium was driven toward the diastereomer detected at higher field in the ^{31}P NMR spectra. Because the two atropisomeric diastereomers of **3** gave the ^{31}P NMR resonances in a narrow region (δ −59.3 and −57.9 at −75 °C) and the

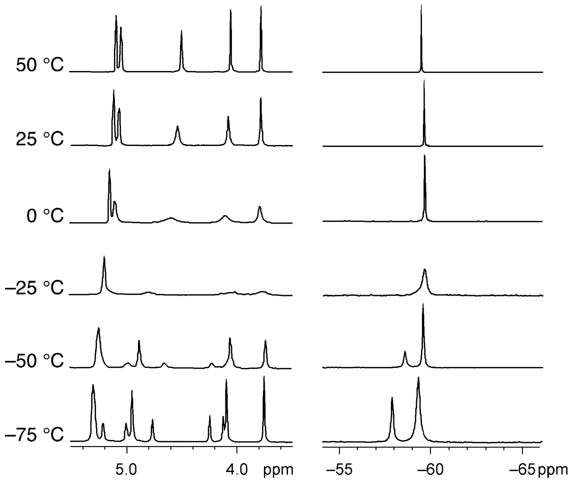

Figure 6. Experimental variable-temperature ^{1}H (in the phospholyl-*H* and cyclopentadienyl-*H* region at 500 MHz, left) and ^{31}P NMR (202 MHz, right) spectra of **3** in toluene-d_8.

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(11) (a) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, UK, 1982. (b) The line-shape analyses were performed with the package software gNMR 5, v. 4.1 for Windows (Cherwell Scientific, 1999).

(12) It was reported that the distances between the two cyclopentadienyl rings in Cp_2Fe and Cp_2Ru are 3.32 and 3.68 Å, respectively. See: (a) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* 1**956**, *9*, 373. (b) Hardgrove, G. L.; Templeton, D. H. *Acta Crystallogr.* **1959**, *12*, 28.

temperature range detecting the two clearly separated ^{31}P NMR signals was narrow, the thermodynamic and the kinetic analysis of **3** encountered an accuracy problem. Thus, further detailed thermodynamic and kinetic analysis of the dynamic behavior of **3** was discontinued.[13]

In this study, we have demonstrated that fluxional conformations in the phosphametallocenes can be thermodynamically controlled by the chiral (−)-menthyl sidearms, which attach directly onto the phospholyl/cyclopentadienyl ligands. The rotation of the phospholyl ligands about the phospholyl−metal axis could not be frozen even at −75 °C because of the low energy barrier of the dynamic process, and thus the two atropisomeric forms in the phosphametallocene easily isomerize each other by ring rotation. Although the atropisomers are not separable in optically pure form for this reason, the thermodynamic discrimination between the two conformational atropisomers was achieved in diastereomeric fashion. For instance, the molar ratio between the two diastereomers of **2** is ca. 82:18 (64% de) at −75 °C (Figure 5). Although the diastereocontrol of 64% de is not high enough, the present study successfully demonstrates that the atropisomerism in the heavily substituted metallocenes is accessible as a source of unequally populated chirality. The atropisomeric chirality can be induced in metallocenes with symmetrically substituted cyclopentadienyl ligands.

Apparently, the methodology described here, the diastereomeric control of the atropisomeric chirality, can be applicable for metallocenes having no phosphorus as well as bent metallocenes of group III/IV.[14] The more precise thermodynamic control of the atropisomerism may be achieved with a proper choice of chiral bulky substituents on the cyclopentadienyl rings.

Experimental Section. (a) General. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. Tetra((−)-menthyl)diphospharuthenocene (**2**)[10] and 1-phenyl-2,5-di((−)-menthyl)phosphole[7] were synthesized as reported. Preparation of (η^6-mesitylene)[η^5-1,3-di((−)-menthyl)cyclopentadienyl]iron(II) hexafluorophosphate is described in the Supporting Information in detail. All other reagents were obtained from commercial sources. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz). ^{1}H and ^{13}C chemical shifts were referenced to the residual solvent (or the solvent) resonances and reported with respect to tetramethylsilane. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4.

(b) Bis[η^5-2,5-di((−)-menthyl)phosphacyclopentadienyl]iron(II) (1).[15] A THF solution of 1-phenyl-2,5-di((−)-menthyl)phosphole (437 mg, 1.00 mmol) was treated with lithium metal (69.4 mg, 10.0 mmol) and the mixture was stirred at room temperature until the phosphole was completely consumed (checked by TLC). The mixture was filtered through a glass filter and the filtrate was added to anhydrous $AlCl_3$ (44.0 mg, 0.333 mmol) at 0 °C. After being stirred for 30 min, the resulting mixture was added to anhydrous $FeCl_2$ (63.4 mg, 0.50 mmol) at 0 °C and stirred for 1.5 h at 60 °C. The mixture was cooled and evaporated to dryness under reduced pressure. The crude product was purified by preparative TLC on silica gel (elution with hexane) under an argon atmosphere to give the title compound in pure form. Yield: 337 mg (0.435 mmol, 87%). Mp 100−103 °C. ^{1}H NMR (toluene-d_8, 100 °C): δ 0.75−0.77 (m, 12H), 0.81 (d, J = 7.0 Hz, 6H), 0.85−1.03 (m, 30H), 1.30 (q, J = 12.0 Hz, 2H), 1.35−1.44 (m, 6H), 1.58−1.67 (m, 4H), 1.69−1.72 (m, 4H), 1.83−2.01 (m, 6H), 2.04−2.12 (m, 2H), 2.34−2.37 (m, 2H), 2.64−2.66 (m, 2H), 4.71 (br, 2H), 5.53 (br, 2H). ^{31}P{^{1}H} NMR (toluene-d_8, 100 °C): δ −50.5 (s). $[\alpha]^{20}_D$ −331 (c 0.670, $CHCl_3$). Anal. Calcd for $C_{48}H_{80}FeP_2$: C, 74.39; H, 10.41. Found: C, 74.10; H, 10.60.

(c) [η^5-1,3-Di((−)-menthyl)cyclopentadienyl][η^5-2,5-di((−)-menthyl)phosphacyclopentadienyl]iron(II) (3).[16] Lithium metal (13.9 mg, 2.00 mmol) was added to a solution of 1-phenyl-2,5-di((−)-menthyl)phosphole (87.3 mg, 0.200 mmol) in THF at room temperature. The mixture was stirred at this temperature until the phosphole was completely consumed (checked by TLC). The mixture was filtered with a glass filter and the filtrate was added to a solution of (η^6-mesitylene)[η^5-1,3-di((−)-menthyl)cyclopentadienyl]iron(II) hexafluorophosphate (265 mg, 0.400 mmol) in THF. The resulting mixture was refluxed for 2 h with stirring. The reaction mixture was passed through a short pad of silica gel (elution with Et_2O) under a nitrogen atmosphere. The filtrate was evaporated to dryness under reduced pressure and the resulting oily material was chromatographed on preparative TLC (elution with hexane) under an argon atmosphere to give the desired compound in pure form. Yield: 110.2 mg (0.146 mmol, 73%). Mp 95−97 °C. ^{1}H NMR (toluene-d_8, 50 °C): δ 0.72−2.26 (m, 74H), 2.87 (d, J = 11.8 Hz, 2H), 3.77 (s, 1H), 4.05 (s, 1H), 4.49 (s, 1H), 5.04 (dd, J = 5.0 and 2.7 Hz, 1H), 5.09 (dd, J = 4.5 and 2.7 Hz, 1H). ^{31}P{^{1}H} NMR (toluene-d_8, 50 °C): δ −59.4 (s). $[\alpha]^{20}_D$ −273 (c 0.600, $CHCl_3$). Anal. Calcd for $C_{49}H_{81}PFe$: C, 77.75; H, 10.79. Found: C, 77.47; H, 10.93.

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Supporting Information Available: Detailed experimental procedure for the preparation of (η^6-mesitylene)[η^5-1,3-di((−)-menthyl)cyclopentadienyl]iron(II) hexafluorophosphate and tables of crystallographic data for the complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The estimated thermodynamic and kinetic parameters of the Cp and Pp* rotation in **3** by the method used for the analyses of the dynamic behavior of **1** and **2** are the following: $\Delta H° = 0.49$ kcal/mol, $\Delta S° = 4.2$ cal/(mol·K), $\Delta H^\ddagger = 9.0$ kcal/mol, $\Delta S^\ddagger = -9.4$ cal/(mol·K), and $\Delta G^\ddagger$(at 25 °C) = 11.8 kcal/mol. However, these values contain a considerable amount of inaccuracy (ca. 10% or more) for the reasons described in the main text, thus we are very reluctant to have a discussion using these values.

[14] The restricted rotations of heavily substituted cyclopentadienyl ligands in the bent metallocenes of group IV metals are reported, see refs 4c and 4f.

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