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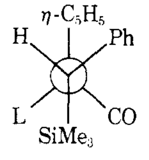
A Demonstration of Controlled Asymmetric Induction in Organoiron Chemistry. Suggestions Concerning the Specification of Chirality in Pseudotetrahedral Metal Complexes Containing Polyhapto Ligands

Sir:

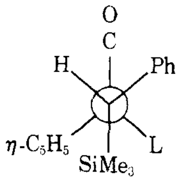
Catalysis by chiral transition metal complexes of the addition of, for instance, hydrogen and silanes to prochiral olefins and ketones often results in induction of asymmetry into the reaction products.[1,2] Although the reasons for such stereoselectivity are not, in general, understood, analogy with a number of well-studied, stoichiometric, stereoselective organic reactions[3-5] suggests that steric control may be very important in determining the relative free energies of formation of diastereomeric products, intermediates, and/or activated complexes.

We have recently shown,[6] using ^{1}H NMR spectroscopy, that steric effects strongly influence the relative energies of the staggered conformations of the compounds η^5-$C_5H_5FeCOLCH_2R$ (L = tertiary phosphine donors; R = Ph, $SiMe_3$). It was demonstrated that the order of decreasing ligand steric requirements is η^5-C_5H_5 > L > CO and $SiMe_3$ > Ph, and that the low energy rotamers, i.e., those in which the bulky η^5-C_5H_5 and R groups are mutually trans, are 550–700 cal mol^{-1} more stable than the other two rotamers when L = PPh_3 and R = Ph, 900–1500 cal mol^{-1} when L = PPh_3 and R = $SiMe_3$.

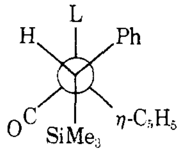
Armed with these data, we decided to study the diastereomeric relationships between a chiral metal entity, η^5-$C_5H_5Fe^*COL$–, and a chiral organic entity, –$C^*HPhSiMe_3$, both with ligands of quite different but clearly understood steric requirements. A compound of the type η^5-$C_5H_5FeCOLCHPhSiMe_3$ should exist as two diastereomerically related pairs of enantiomers, each diastereomer existing as three staggered rotamers.



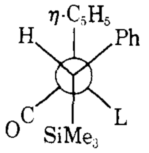
SR(*a*)



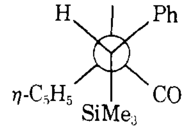
SR(*b*)



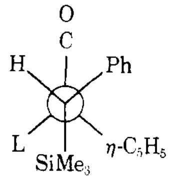
SR(*c*)



RR(*a*)



RR(*b*)



RR(*c*)

The enantiomeric *RS* and *SS* isomers would also exist, of course. (Suggestions concerning a convention for specifying the chirality of these stereoisomers will be discussed below.)

By analogy with similar primary alkyl complexes,[6] it is reasonable to expect that the most stable rotamer of each diastereomer would be that in which bulky η^5-C_5H_5 and $SiMe_3$ groups are mutually trans, i.e., *SR*(a) and *RR*(a) and their enantiomers. Furthermore, it is possible to predict that *SR*(a) should be somewhat more stable than *RR*(a), as the small CO is gauche to both the Ph and the $SiMe_3$ groups in the former, while L is gauche to Ph and $SiMe_3$ in the latter. Thus the *RS-SR* stereoisomers may be expected to be somewhat more stable than the *RR-SS* stereoisomers.

Identification of *RS-SR* and *RR-SS* diastereomers should be possible using ^{1}H NMR spectroscopy, as the α-hydrogen of the coordinated alkyl group is gauche to L in *SR*(a) but trans to L in *RR*(a). Thus, if the barriers to rotation about the iron-carbon bonds are sufficiently high that individual rotamers can be distinguished in the NMR spectrum, then $^3J_{PH}$ for *SR*(a) should be less than $^3J_{PH}$ for *RR*(a).[6] If on the other hand, barriers to rotations are sufficiently low that time-averaged spectra are obtained, then the observed $^3J_{PH}$ of *SR* should decrease with decreasing temperature, while that of *RR* should increase.[6]

Treatment of racemic η^5-$C_5H_5FeCOLI$ (L = PPh_3, $P(OPh)_3$) with racemic $Me_3SiPhCHMgBr$ at 35° in 2:1 benzene-ethyl ether solution gave stable products of the formula η^5-$C_5H_5FeCOLCHPhSiMe_3$[7] (L = PPh_3 (**1**), $P(OPh)_3$ (**2**)). Surprisingly, the ^{1}H NMR spectra (Table I)

Table I. Chemical Shift and Coupling Constant Data

Compound		α-CH	η^5-C_5H_5	SiMe	Ph
1	^{1}H[a]	δ 1.40, $^3J_{PH}$ = 7.7 Hz	δ 4.37, J_{PH} = 1.5 Hz	δ 0.30	δ ~7.15
2		δ 2.24, $^3J_{PH}$ = 10.1 Hz	δ 4.07, J_{PH} = 1.0 Hz	δ 0.33	δ ~7.14
3		δ 2.13, $^3J_{PH}$ = 10.5 Hz	δ 4.30, J_{PH} = 1.0 Hz	δ 0.35	δ ~7.14
2	^{13}C[b]	δ 2.9, J_{PC} ≈ 18 Hz[c]	δ 82.84, J_{PC} = 1.5 Hz	δ 2.27	δ 121–157
3		δ 1.6, J_{PC} ≈ 18 Hz[c]	δ 82.70, J_{PC} = 1.4 Hz	δ 2.20	δ 121–157

[a] In C_6D_6 solution. [b] In $CDCl_3$ solution, in ppm downfield from internal TMS. [c] Doublet partially obscured by stronger MeSi resonance.

of each in C_6D_6 contained only one set of resonances, suggesting that, in each case, either only a single diastereomer was formed or that the diastereomers of each have completely coincident spectra. Either interpretation contrasts with the behavior of the compounds η^5-$C_5H_5FeCOPPh_3R$ (R = $CH(OEt)Me$,[8] *threo*-$CHDCHDCMe_3$,[9] *threo*-$CHDCHDPh$,[10] $CH_2CHMePh$[11]), for which the diastereomers are readily distinguishable by NMR spectroscopy and are formed in approximately equimolar quantities.

In an effort to settle the question of chemical shift coincidence, an attempt was made to insert SO_2 into the iron–carbon bonds of the complexes; it seemed very unlikely that the ^1H NMR spectra of the diastereomeric sulfinates would also be coincident.[12] Surprisingly, treatment of **2** with SO_2 under a variety of conditions did not result in the formation of a stable sulfinate but rather in epimerization of **2** to give mixtures of **2** and the *RR-SS* diastereomer **3**. As expected the ^1H and the ^{13}C NMR spectra of **2** and **3** are different (Table I). Identification of **2** and **3** as the *RS-SR* and *RR-SS* diastereomers, respectively, was tentatively made by studying the variation of $^3J_{PH}$ with temperature (see above); as expected, $^3J_{PH}$ of **2** (and **1**) decreased, that of **3** increased smoothly with decreasing temperature. Formation of **3** appeared to be kinetically controlled, as only **2** was obtained in significant quantities under conditions in which equilibrium between **2** and **3** appeared to have been reached in the presence of SO_2.[14] Thus, dramatic steric effects on the thermodynamically controlled stereoselective formation of these iron alkyl complexes has been demonstrated. Although it is not known whether the other, similar[8-11] diastereomeric iron complexes have been prepared under conditions in which the diastereomeric pairs had equilibrated with each other, it is probably significant that none of them is as crowded as are **1**, **2**, and **3**, and thus none of them would experience the same degree of steric control.

Because of a dearth of information concerning the absolute configurations of pseudo-four-coordinate complexes containing polyhapto ligands, such as those discussed here, there has been little need for a systematic convention for the specification of chirality. The accepted IUPAC Rules for Nomenclature of Inorganic Chemistry[15] are not particularly applicable, and recourse has been made[16,17] to the widely accepted *R* and *S* conventions for tetrahedral compounds, as developed by Cahn, Ingold, and Prelog.[18] Unfortunately the latter conventions, while clearly specifying sequence priorities for monohapto and polydentate ligands, do not apply to polyhapto ligands, with the result that different extensions of the *R-S* conventions have already appeared in the organometallic literature.[16,17] Thus while both Davison and Martinez[16] and Alt et al.[17] arbitrarily choose to assign higher priorities to polyhapto than to monohapto ligands, i.e., η^5-C_5H_5 > η^2-C_2H_4 > η^1-CH_3, the former appear to prefer, in the case of monohapto ligands containing a donor atom of higher atomic weight than carbon, to assign such a ligand higher priority than η-C_5H_5. Alt et al., on the other hand, would appear to assign such a ligand lower priority. Besides the lack of consistency in the two approaches, both are also inconsistent with accepted priority rules,[18] which would assign lower priority to a hydrocarbon ligand than to a carbon-bonded ligand containing a β-oxygen or -nitrogen atom.

While any priority convention would be purely arbitrary and would undoubtedly evolve as inconsistencies appear, the present time is perhaps appropriate to suggest a more consistent approach. In keeping with the suggestion[16,17] that polyhapto ligands be assigned high priorities, we suggest that such ligands be considered *pseudo-atoms of atomic weight equal to the sum of the atomic weights of all the atoms bonded to the metal atom.* Thus the ligands η^7-C_7H_7, η^6-C_6H_6, η^5-C_5H_5, and η^3-C_3H_5 would be considered pseudo-atoms of atomic weights 84, 72, 60, and 36, respectively. The convention thus preserves the advantages of the topological approach of Cahn et al.[18] and, by retaining their sequence-rule procedure, at the same time allows distinction between, for instance, η^6-C_6H_6 and η^5-C_6H_7, η^5-C_6H_7, η^5-C_5H_4Me, and η^5-C_5H_5.[19]

Chirality of the complexes reported here has been assigned in accord with the above procedure, the iron designation preceding that of carbon as suggested by Reich-Rohrwig and Wojcicki.[11] We invite comment and suggestions concerning the pseudo-atom convention.

Acknowledgments. Financial assistance from Queen's University and the National Research Council of Canada made this research possible.

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(19) Attempts to apply the sequence rules rigorously would fail because unambiguous and widely-accepted valence bond structures for these delocalized structures do not exist. Cyclohexadienyl (η^5-C_6H_7) and methylcyclopentadienyl (η^5-C_5H_4Me) both contain "C_5" groups, the former with two C–C bonds to CH_2, the latter one C–C bond to methyl. Thus the former, containing in essence a "C_5" $=$ CH_2 group, would have priority over the latter, a "C_5"—CH_3 group.[18] Ambiguities may arise in the case of polyhapto ligands containing heteroatoms, as a η^6-C_6 ligand would have a higher pseudo-atomic weight than a η^5-C_4O ligand, although the sequence–rule procedures would probably assign the latter higher priority. The former approach would appear to be simpler.

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Novel Sulfur Dioxide-Induced Epimerization of Complexes of the Type η^5-$C_5H_5Fe^*COLC^*HRR'$

Sir:

We have recently shown[1] that (*RS-SR*)-η^5-$C_5H_5FeCOP(OPh)_3CHPhSiMe_3$ (**1**), obtained by treating racemic η^5-$C_5H_5FeCOP(OPh)_3I$ with racemic $Me_3SiPhCHMgBr$, reacts with SO_2 to form mixtures of **1** and its thermodynamically less stable diastereomer, (*RR-SS*)-η^5-$C_5H_5FeCOP(OPh)_3CHPhSiMe_3$ (**2**). The result was surprising because compounds such as **1** and **2** normally react very readily with SO_2 to form stable *S*-sulfinate complexes.[2,3] Furthermore, SO_2 insertion reactions into metal–