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$_2$CHMePh[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 ^{1}H 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 ^{1}H 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.

References and Notes

(1) W. Knowles, *Ann. N.Y. Acad. Sci.*, **214,** 119 (1973)

(2) L. Markó and B. Heil, *Catal. Rev.*, **8,** 269 (1973).

(3) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971.

(4) E. Ruch and I. Ugi, *Top. Stereochem.*, **4,** 99 (1969).

(5) L. Salem, *J. Am. Chem. Soc.*, **95,** 94 (1973).

(6) K. Stanley and M. C. Baird, *Inorg. Nucl. Chem. Lett.*, **10,** 1111 (1974); *J. Am. Chem. Soc.*, **97,** 4292 (1975).

(7) Attempts to prepare the compounds by photolysis of solutions of η^5-$C_5H_5Fe(CO)_2CHPhSiMe_3$ and L resulted in considerable decomposition.

(8) A. Davison and D. L. Reger, *J. Am. Chem. Soc.*, **94,** 9237 (1972).

(9) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96,** 2814 (1974).

(10) D. Slack and M. C. Baird, unpublished results.

(11) P. Reich-Rohrwig and A. Wojcicki, *Inorg. Chem.*, **13,** 2457 (1974).

(12) We thank Professor A. Wojcicki for this suggestion, based on the premise that the SO_2 insertion reaction should be stereospecific. Thus reactions of SO_2 with η^5-$C_5H_5Fe(CO)_2R$ (R = *threo*-CHDCHDCMe$_3$,[9] *threo*-CHDCHDPh[10]) proceed with inversion of configuration at the α-carbon atom, while reaction of SO_2 with η^5-$C_5H_5FeCOPPh_3CH_2CO$mentholate[13] proceeds with retention of configuration at iron.

(13) T. C. Flood and D. L. Miles, *J. Am. Chem. Soc.*, **95,** 6460 (1973).

(14) K. Stanley, D. Groves, and M. C. Baird, *J. Am. Chem. Soc.*, following paper in this issue.

(15) *Pure Applied Chem.*, **28,** 1 (1971).

(16) A. Davison and N. Martinez, *J. Organomet. Chem.*, **74,** C17 (1974).

(17) H. Alt, M. Herberhold, C. G. Kreiter, and H. Strack, *J. Organomet. Chem.*, **77,** 353 (1974).

(18) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5,** 385 (1966).

(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.

K. Stanley, M. C. Baird*

Department of Chemistry, Queen's University
Kingston, Ontario, Canada K7L 3N6

Received July 3, 1975

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–

Table I. ^1H NMR Chemical Shift Data in SO_2

Compound	α-CH	η^5-C_5H_5	SiMe	Ph
3	δ 4.89	δ 4.32	δ −0.1	δ ~7.2
4	δ 5.27	δ 4.54	δ 0.07	δ ~7.2

carbon bonds are normally highly stereospecific, occurring with inversion of configuration at the α-carbon atom with the compounds η^5-$C_5H_5Fe(CO)_2R$ (R = *threo*-$CHDCHDCMe_3$,[4] *threo*-CHDCHDPh[5]), stereospecifically, at least, with $(+)_{546}$-η^5-$C_5H_5Fe(CO)_2CHMePh$,[6] and with retention of configuration at iron with η^5-$C_5H_5FeCOPPh_3CH_2CO$(mentholate).[7] Therefore the reaction of **1** with SO_2 was investigated in detail in an attempt to elucidate the mechanism of the epimerization reaction, which does not occur in a number of organic solvents in the absence of SO_2.

In accord with established procedures,[2,3] **1** was refluxed in SO_2 for 5 hr, the solvent was allowed to evaporate and the solid residue was extracted with methylene chloride and eluted on an alumina column. The product contained no SO_2 but was rather a 40:60 mixture of **1** and **2**. A similar result was obtained by bubbling SO_2 through a solution of **1** in methylene chloride, although slight paramagnetism of the solution precluded following the course of the reaction using NMR spectroscopy.

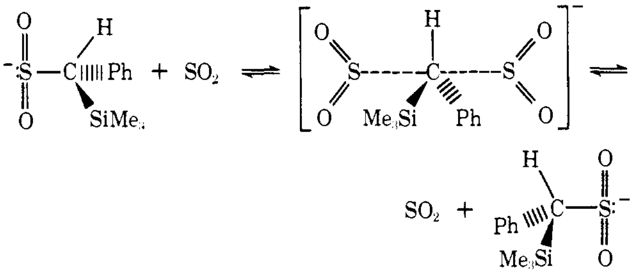
The reactions of **1** (and **2**) with SO_2 were, however, followed successfully using ^1H NMR spectroscopy in SO_2 solvent. Both **1** and **2** reacted essentially completely in neat SO_2 at 293 K, **2** faster than **1**, to form the corresponding *S*-sulfinates, **3** and **4**, respectively. Although the latter compounds lost SO_2 both in the solid state and in organic solvents too rapidly to be characterized properly, comparison of their NMR parameters (Table I) with those of similar complexes[2,3] permitted their identification. (Presumably **3** and **4** have the *RR-SS* and *RS-SR* configurations, respectively[1]). On standing in SO_2 for 1 hr, **3** and **4** equilibrated with each other such that, at equilibrium, [**3**]:[**4**] ≈ 3:1; these results can be summarized as follows:

$$\begin{tikzcd}
\mathbf{1} + SO_2 \arrow[r, shift left, "k_1"] & \mathbf{3} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift right, "k_3"'] & k_2 > k_1 \\
\mathbf{2} + SO_2 \arrow[r, shift left, "k_2"] & \mathbf{4} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift right, "k_4"'] & k_4 > k_3
\end{tikzcd}$$

If the reaction of **1** with liquid SO_2 were halted after the conversion to **3** was completed but before significant amounts of **4** were formed, solid **3** could be obtained by quickly removing the SO_2 at reduced pressure. While extrusion of SO_2 from solid **3** *in vacuo* at 328 K yielded pure **1**, loss of SO_2 from **3** in CD_2Cl_2 solution at 283 K in a sealed NMR tube initially yielded **2** faster than **1**, although **1** dominated as equilibrium was approached. In the latter reaction, no **4** could be detected. Also relevant are the observations that SO_2 did not induce epimerization of a solution of **1** in the nonpolar petroleum ether, that rapid removal by pumping of the extruded SO_2 during the decomposition of **3** at room temperature in methylene chloride, chloroform, or benzene resulted in [**2**]:[**1**] ratios as high as 4:1, but that heating a solution of **3** during extrusion or preventing the SO_2 from escaping until the system had approached equilibrium resulted in [**1**]:[**2**] ratios of 3:1 or higher.

The facile formation of the thermodynamically less stable **2** on decomposition of **3** presumably occurs via **4**, and must occur because the **3** → **4** → **2** sequence is favored kinetically over the **3** → **1** path; certainly the free energy of activation for the conversion of **1** to **3** is greater than that for **2** → **4**.[8] Thus, the rate of formation of **1** becomes competitive when sufficient heat is supplied to overcome the **3** → **1** activation barrier, while retention of SO_2 in solution allows the system to eventually equilibrate to the thermodynamically preferred **1**. On the other hand, cooling the system would make the **3** → **4** → **2** conversion kinetically more viable, while rapid removal of SO_2 from a solution containing predominantly **2** would prevent equilibration to **1**.

The hypothesis requires a mechanism for the interconversion of **3** and **4** which also involves epimerization at one of the chiral centers, a reaction which does not occur significantly with the compounds η^5-$C_5H_5Fe(CO)_2R$ (R = *threo*-$CHDCHDCMe_3$,[4] *threo*-CHDCHDPh,[5] and CHMePh[6]). We suggest that, because of greater strain, **3** and **4** dissociate to some extent in polar solvents to give the ions $[\eta^5$-$C_5H_5FeCOP(OPh)_3(\text{solvent})]^+$ and $[SO_2CHPhSiMe_3]^-$. The latter would then be susceptible to electrophilic attack by a second molecule of SO_2, resulting in a Walden-like inversion, i.e.



Ions such as the above are believed to be intermediates in the reactions of metal-alkyl complexes with SO_2 to give sulfinates.[9] The mechanism is also consistent with the observations that SO_2 does not induce epimerization of **1** in a poorly ionizing solvent such as petroleum ether. Experiments are now underway to determine if the epimerization does indeed take place at the α-carbon atom.

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

References and Notes

(1) K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, **4**, 347 (1970).
(3) S. R. Su and A. Wojcicki, *J. Organomet. Chem.*, **27**, 231 (1971).
(4) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974).
(5) D. Slack and M. C. Baird, unpublished results.
(6) J. J. Alexander and A. Wojcicki, *Inorg. Chim. Acta*, **5**, 655 (1971).
(7) T. C. Flood and D. L. Miles, *J. Am. Chem. Soc.*, **95**, 6460 (1973).
(8) Kinetic and equilibrium studies suggest that the difference in activation energies of the **3** → **1** and **4** → **2** conversions is about 2.8 kcal.
(9) A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974).

K. Stanley, D. Groves, M. C. Baird*
Department of Chemistry, Queen's University
Kingston, Ontario, Canada K7L3N6

Received July 3, 1975

Biosynthetic Studies Using ^{13}C Enriched Precursors on the 16-Membered Macrolide Antibiotic Leucomycin A_3

Sir:

According to previous reports[1] the aglycone carbons of the 16-membered macrolide antibiotic magnamycin B (Ia) are derived, as shown in Figure 1, from nine acetates, one propionate, and one methionine. As an application of a recent systematic ^{13}C NMR study of 16-membered macrolide antibiotics[2] the validity of these investigations was reexam-