# Molecular Asymmetry and Restricted Rotation in Transition-metal Complexes: Silylmethyl and Silylacetyl Derivatives of the π-Cyclopentadienyliron Carbonyl Phosphine System

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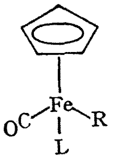
*Summary* I.r. and n.m.r. spectral data for new $\sigma$-silylacetyl- and $\sigma$-silylmethyl-$\pi$-cyclopentadienyliron carbonyl phosphine complexes are discussed and indicate that it should be possible to synthesize and resolve optically active organo-iron complexes from the general asymmetric system $\sigma$-R-$\pi$-$C_5H_5FeCO(L)$.

WE have recently prepared several new $\sigma$-silylacetyl and $\sigma$-silylmethyl derivatives of the $\pi$-cyclopentadienyliron carbonylphosphine system, these complexes being asymmetric at the iron centre.

The i.r. spectra (cyclohexane) of the silylacetyl complexes exhibit two ketonic carbonyl bands (1580—1599 cm.$^{-1}$) whose area ratios are temperature-dependent. A similar ketonic carbonyl band pattern is observed in the spectrum of $\sigma$-acetyl-$\pi$-cyclopentadienyliron carbonyl triphenylphosphine, $MeCOFeCOCpPPh_3$, whereas the related organic $\beta$-ketosilanes, $R^1{}_3Si{\cdot}CH_2{\cdot}CO{\cdot}R^2$, exhibit single ketonic carbonyl bands.[1] This indicates the presence of rotamers in the iron complexes resulting from restricted rotation about the transition-metal–carbon bond, a type of restriction predicted but not observed by Calderazzo during studies on halogenoacetylmanganese carbonyl complexes.[2]



R=Me$_3$SiCH$_2$
Me$_3$SiCH$_2$CO

L=PPh$_3$, PPh$_2$Me, PPh$_2$Et

The $^1$H n.m.r. spectra of the silylacetyl complexes show the methylene protons to be nonequivalent. For example, in the complex Me$_3$SiCH$_2$COFeCOCpPPh$_3$ the protons give rise to two doublets at $\tau$ 7·3 and 8·3, $J$ 12 Hz, when recorded on a Varian A-60 at 32°. Temperature variations from $-80°$ to $+110°$ do not remove this nonequivalence, neither do added phosphine ligand, nor Me$_2$SO in which the high-temperature studies were conducted. There is a variation in the $\Delta\tau$ values from 80 Hz at $-80°$ in CDCl$_3$ to 29 Hz at 110° in Me$_2$SO. This variation is expected, since increasing temperature permits more equal population of the staggered rotamers. We have not been able to observe the spectra of individual rotamers at the low temperatures (the two doublets each become broad and lack resolution) therefore it is not possible to calculate the contribution the intrinsic asymmetry of the iron atom makes to the $\Delta\tau$ value.[3] The low temperature ($-80°$) spectrum of $\sigma$-MeCOFeCOCpPPh$_3$ gives no indication for the presence of more than one molecular species, although two ketonic bands are observed in the i.r. spectrum. It thus seems probable that the nonequivalence observed for the silylacetyl methylene protons derives from the diastereotopic shielding by the asymmetric iron atom.[4] Similar nonequivalent methylene protons are observed in the $^1$H n.m.r. spectra of the related silylmethyl derivatives. In these complexes the protons are part of an ABX system where unequal coupling between the protons and the phosphorus atom is observed; *e.g.* for Me$_3$SiCH$_2$FeCOCpPPh$_3$ A, $\tau$ 10·2 $J_{AB}$ 12 Hz, $J_{AX}$ 2 Hz; M, $\tau$ 11·2 $J_{BX}$ 13 Hz.[5] In addition, the $^1$H n.m.r. spectra of the corresponding dimethylphenylsilylmethyl complexes exhibits two resonances for the silylmethyl groups. It is relevant that for the various silylmethyl-$\pi$-cyclopentadienyliron dicarbonyls, R$_3$SiCH$_2$Fe(CO)$_2$Cp, and silylmethylsulphinato-$\pi$-cyclopentadienyliron dicarbonyls, R$_3$SiCH$_2$SO$_2$Fe(CO)$_2$Cp, both of which lack asymmetric iron centres, the methylene protons appear in the n.m.r. spectra as singlets.

The observation of nonequivalent methylene and silicon methyl protons shows that the asymmetric iron complexes exist as enantiomeric pairs with finite lifetimes. No line-broadening is noted at elevated temperatures prior to product decomposition, and hence a minimum life time of the order of seconds may be placed upon the enantiomers at temperatures above 100°. We therefore believe that it should be possible, by judicious choice of $\sigma$-substituent, to resolve this asymmetric iron system.

Financial support from an S.R.C. Research Fellowship is acknowledged.

(*Received, September* 19*th*, **1969**; *Com.* 1420.)

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[1] A. G. Brook and J. B. Pierce, *Canad. J. Chem.*, 1964, **42**, 298., and personal communication from Professor Brook.

[2] F. Calderazzo, K. Noack, and U. Schaerer, *J. Organometallic Chem.*, 1966, **6**, 265.

[3] M. Raban, *Tetrahedron Letters*, 1966, 3105.

[4] *Note added in proof.* Spectral evidence for nonequivalent phosphorus methyl groups in MeCOFeCOCpPPhMe$_2$ due to similar asymmetry at iron has recently been reported. H. Brunner and E. Schmidt, *Angew. Chem. Internat. Edn.*, 1969, **8**, 616.

[5] A similar pattern is observed for the methylene protons in the $^1$H n.m.r. spectrum of PhCH$_2$FeCOCpPPh$_3$. J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1969, **9**, 1550.