Preparation and Reactivity of the Optically Active Silicon–Manganese Compound (—)-[(π-Methylcyclopentadienyl) $Mn(CO)_2(H)SiMePh$(α-naphthyl)]

By Ernesto Colomer, Robert Corriu,* and André Vioux

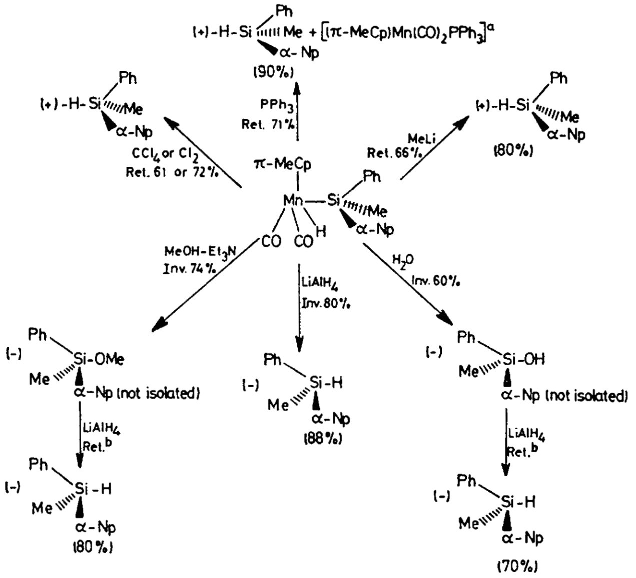
(*Laboratoire de Chimie des Organométalliques, Equipe de Recherche associée au C.N.R.S. N° 554, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France*)

Summary Cleavage of the complex (—)-[(π-MeCp)$Mn(CO)_2$(H)SiMePh(α-Np)] by electrophiles and nucleophiles may occur in three ways: electrophilic cleavage of the Mn–Si bond with retention of configuration at Si, nucleophilic attack at Mn also with retention of configuration, and nucleophilic attack at Si with inversion of configuration.

Compounds containing a transition metal bound to optically active silicon are currently of interest.[1,2] The photochemical reaction[3] of [(π-MeCp)$Mn(CO)_3$] (MeCp = methylcyclopentadienyl) with (+)-(α-Np)PhMeSiH yielded the new compound (—)-[(π-MeCp)$Mn(CO)_2$(H)SiMePh-(α–Np)], (I), $[\alpha]_D^{25}$ — 77·5° (*c* 0·2, C_6H_6), yellow crystals, m.p. 80—81 °C, ν_{CO} (C_6H_6) 1965 and 1903 cm^{-1}; satisfactory elemental analyses were obtained. The configuration around silicon was assumed to be the same as in the starting silane, resulting from insertion into the silicon–hydrogen bond.†

---

† This assumption is reasonable since it is well known that the Si–H bond always reacts with retention of configuration.[4]



[a] [(π-MeCp)Mn(CO)$_2$PPh$_3$] was isolated in 87% yield and compared with an authentic sample, m.p. 117—118 °C, prepared by the method of C. Barbeau, *Canad. J. Chem.*, 1967, **45**, 161.
[b] The Si–O bond is known to be cleaved with retention by LiAlH$_4$; see ref. 4, p. 73.

SCHEME.

Ret. = retention, Inv. = inversion; α-Np = α-naphthyl. Percentages under the silanes are chemical yields; percentages after Ret. or Inv. are stereoselectivities.

Our interest in the behaviour of silicon–transition metal bonds led us to study the reactions of (I) with several nucleophilic and electrophilic reagents. The results and stereochemical assignments are shown in the Scheme. We can distinguish three kinds of reagents: (a) electrophiles, which lead to silicon–transition metal bond cleavage with retention of configuration, (b) nucleophiles which attack manganese and lead to elimination with recovery of the starting silane with retention of configuration, and (c) nucleophiles which attack silicon by a normal S_N2-Si mechanism giving inversion of configuration.

Complex (II), [(π-MeCp)Mn(CO)$_2$(D)SiPh$_2$Me], yellow crystals, m.p. 86—87 °C, ν_{CO} (C_6H_6) 1975 and 1915 cm^{-1} was also prepared. It underwent elimination reactions leading to formation of Ph$_2$MeSiD when treated with MeLi or PPh$_3$,[5] and nucleophilic attack at Si leading to Ph$_2$MeSiH when treated with LiAlH$_4$. Reaction of (II) with H$_2$O or MeOH leads to recovery of the silanol or the methoxysilane.

Comparison of the behaviour of Mn–Si and Fe–Si[2,6] bonds is particularly interesting. With Mn–Si compounds it is not possible to replace a CO ligand by PPh$_3$ without breaking the Mn–Si bond. Furthermore nucleophilic attack on the Fe–Si bond leads to cleavage with retention of configuration at silicon, instead of inversion observed for the Mn–Si bond. This is probably due to the fact that the groups (π-Cp)Fe(CO)$_2$ and (π-Cp)Fe(CO)(PPh$_3$) are good nucleophiles[7] and poor leaving groups. In contrast, the corresponding manganese units seem to be good leaving groups.

(*Received*, 18*th December* 1975; *Com.* 1396.)

---

[1] L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1969, **91**, 7051; C. Eaborn, P. N. Kapoor, D. J. Tune, C. L. Turpin, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **34**, 153; R. J. P. Corriu and W. E. Douglas, *ibid.* 1973, **51**, C3; C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.
[2] G. Cerveau, E. Colomer, R. Corriu, and W. E. Douglas, *J.C.S. Chem. Comm.*, 1975, 410.
[3] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4.
[4] L. H. Sommer, 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965, p. 111.
[5] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1971, **94**, 4388.
[6] G. Cerveau, E. Colomer, and R. Corriu, unpublished results.
[7] R. B. King, *Accounts Chem. Res.*, 1970, **3**, 417.