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Preliminary communication

Coordination chemistry of siloles: reaction of η^4-complexed *endo*-1-chloro-2,5-diphenylsilacyclopentadiene with lithium reagents. Synthesis of new carbenes, and the crystal structure of dicarbonylphenyl(η^4-*exo*-1-methyl-1-oxy-2,5-diphenylsilacyclopentadiene)carbene iron

Francis H. Carré, Robert J.P. Corriu, Christian Guerin, Bernard J.L. Henner and Wong Wee Choy Wong Chi Man

Institut de Chimie fine, U.A. CNRS 1097, Laboratoire "Hétérochimie et Amino-acides", Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, F-34060 Montpellier Cedex (France)

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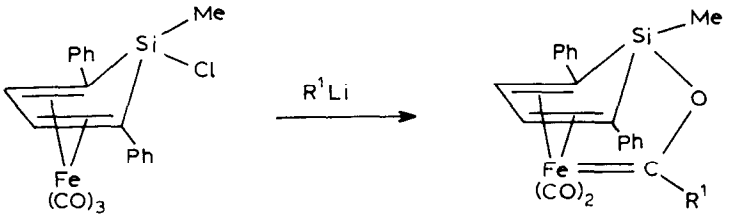
Abstract

The reaction of MeLi, PhLi and i-Pr_2NLi with (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**1**) has given a neutral carbene with an unusual cyclic structure. An X-ray structure determination was carried out in the case of the product, **4b**, from PhLi.



We previously reported the synthesis of functional-2,5-diphenylsilacyclopentadienes (siloles) and noted their ability to complex with transition metal moieties [1–5]. We observed that nucleophilic substitution at silicon in these derivatives always preceded retention of the configuration whatever the identity (F, Cl, OMe or H) or position (*exo* or *endo*) of the leaving group. However, as expected, the reactivity was greater for the *exo* position. The nucleophilic substitution at silicon is not controlled by the steric hindrance due to the metal and carbonyl ligands but by the angular strain, which favours retention of the configura-

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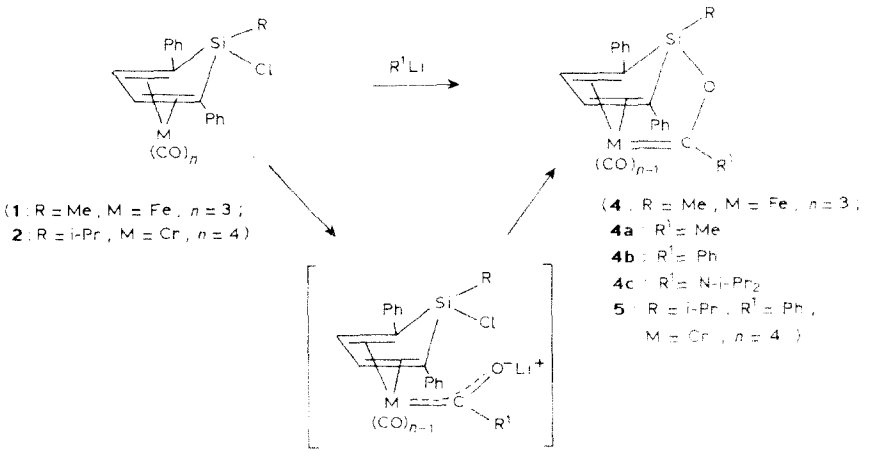


Scheme 1.

tion [6]. We describe here the use of this feature for the synthesis of intra-molecular carbene complexes with an unusual structure.

Lithium reagents R^1Li (R^1 = Me Ph) or $i\text{-}Pr_2NLi$, reacted with (η^4-*endo*-1-chloro-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyliron complex (**1**) (Scheme 1) to give the new cyclic carbenes **4** in good yields. The formation of complexes of type **4** can be accounted for in term of a Fischer-type attack [7] of the lithium reagent on a carbonyl group leading to the carbene **3** followed by an intramolecular attack at the Si–Cl bond in the *endo* position. There is retention of configuration, as observed before [4] (vide supra). The formation of the neutral carbene seems to be a general process, since the chromium complex **2** reacted with phenyllithium to give the expected carbene **5** (Scheme 1). The structures of complexes **4** and **5** were determined by ^1H and ^{13}C NMR, IR, analysis and by an X-ray diffraction study in the case of **4b** [8]. Figure 1 shows the ORTEP drawing of complex **4b**.

The X-ray study of complex **4b** confirmed the presence of a carbene moiety (Fig. 1) [8 *]. The sum of the angles around the carbene atom C(7) shows that the three bonds around this atom lie in a plane. The repulsion between the Fe and Si atoms (*d* 2.600(1) Å) causes the Si–O(3) bond length (1.721(2) Å) to be slightly longer than the Si–O bonds in $Ph_3SiOSiPh_3$ (1.616(1) Å) [9a] and $Me_3SiOSiMe_3$ (1.66(4) Å) [9b]. The C–O distance in the carbene moiety, 1.337(4) Å, is also slightly longer in other carbenic compounds, viz.: $(Ph_3Ge)(CO)_3Co(OEt)Et$ (1.29(1) Å) [10a] and $MePh(1\text{-}Np)Ge(CO)_4Mn\{C(OEt)Et\}$ (1.31(3) Å) [10b], but similar to that (1.33 Å) observed for $(CO)_5Cr\{C(OMe)Ph\}$ [11].

The linkage of the silicon atom down to the iron atom through atoms O(3) and C(7) results in a silole ring closer to being flat (the dihedral angle between the planar butadiene unit and the plane C(1)SiC(4) is 16.6°) than those in other coordinated silole complexes (20 to 37°) [12].

* Reference number with asterisk indicates a note in the list of references.

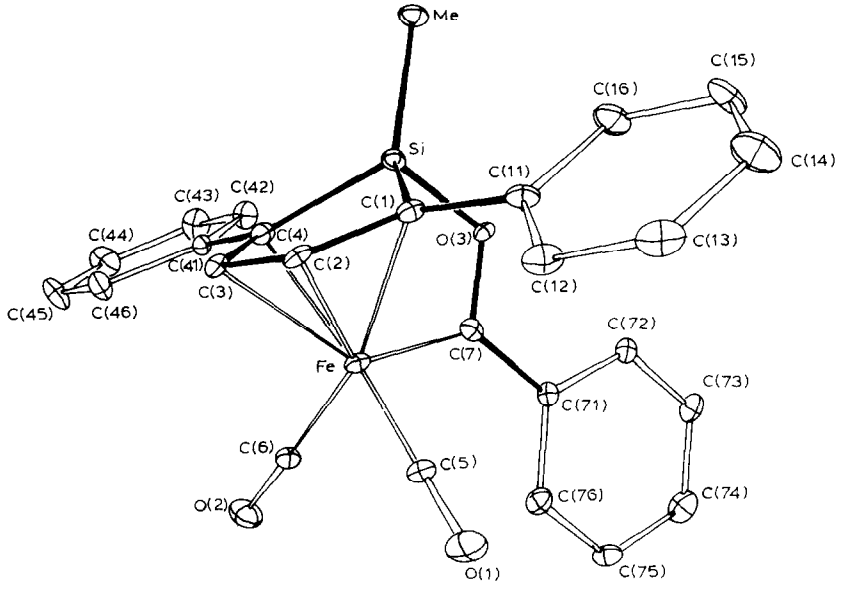
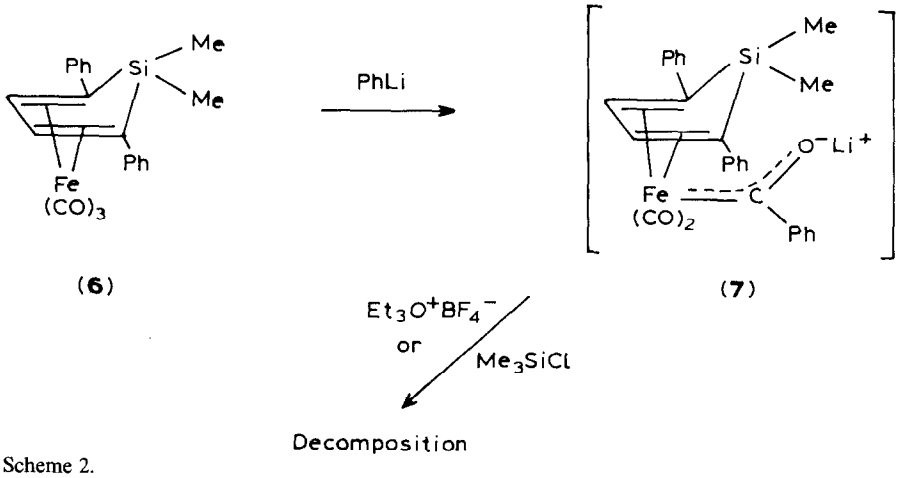


Fig. 1. ORTEP drawing of complex **4b**.

Interestingly, the neutral carbene was not obtained from the dimethylsilole complex **6** (Scheme 2); a reaction was noticed with PhLi but subsequent attempts to trap the expected charged carbene **7** with Me_3SiCl or $Et_3O^+BF_4^-$ resulted mainly in decomposition. In the case of $Et_3O^+BF_4^-$, 20% of the starting complex **6** was recovered as the only isolable compound.

Evidently, organolithium compounds attack complexed siloles at a carbonyl centre to give charged carbenes. The complexes are not very reactive, and give neutral carbenes only when intramolecular substitution at silicon is possible.



Scheme 2.

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8 Crystal structure analysis of **4b**: $P2_1/n$, a 15.054(3), b 15.104(2), c 9.630(2) Å, β 92.15(2)°, V 2188.0(4) Å^3, $Z = 4$, $R = 0.028$ for 1998 independent reflections with $F > 3\sigma(F)$ (Enraf–Nonius CAD-4 diffractometer, Mo-K_α). A list of atomic coordinates and tables of observed and calculated structure fraction may be obtained from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.
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