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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

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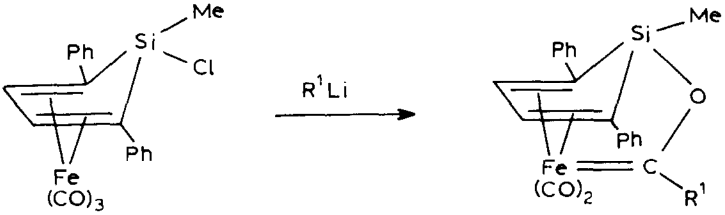
Abstract

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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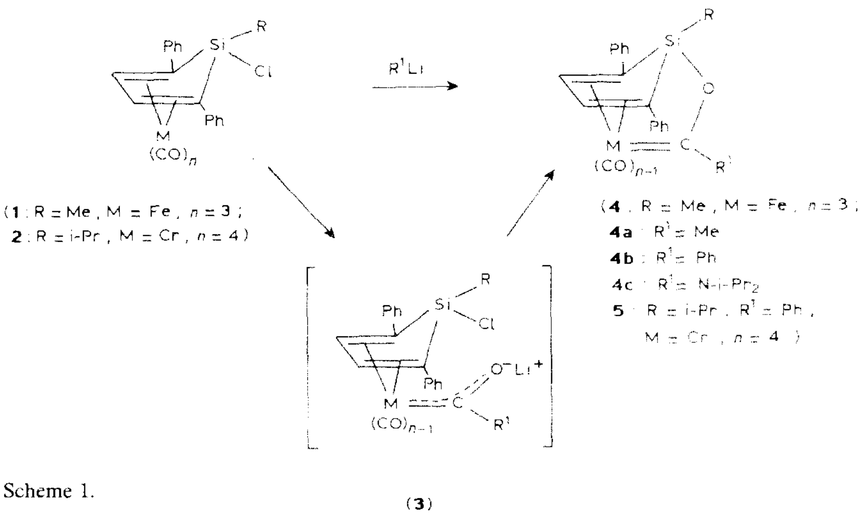

Scheme 1.

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].

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

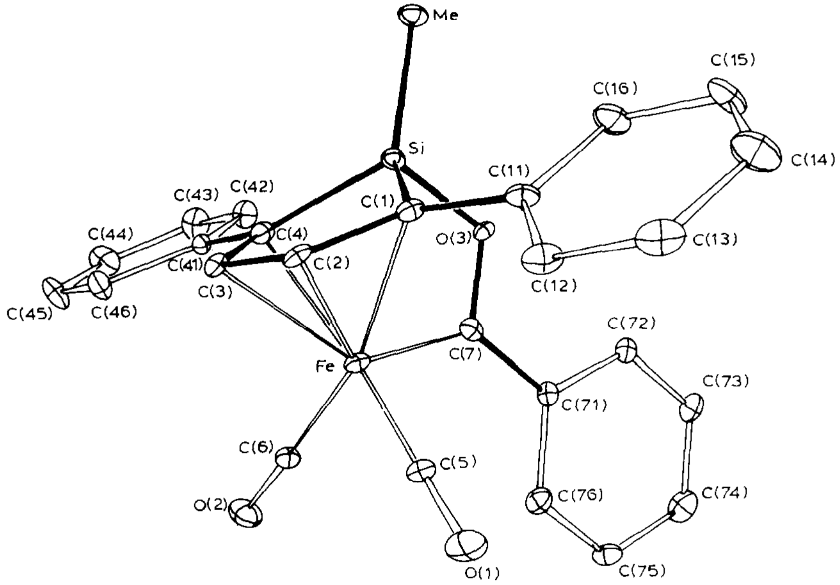
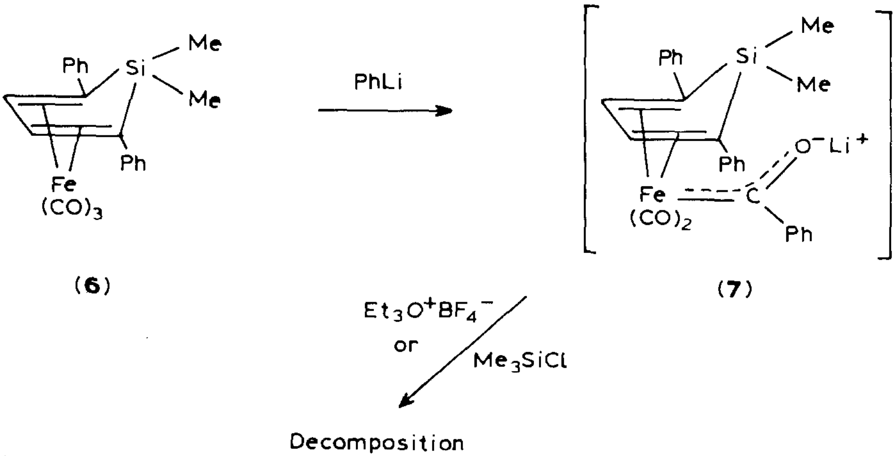


Fig. 1. ORTEP drawing of complex **4b**.

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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