Chelate Compound with Silicon Atoms as 'Donors'

By CHI-WEN CHENG and CHAO-SHIVAN LIU*
(*Institute of Chemistry, National Tsing Hua University, Taiwan*)

Summary Chelate transition-metal compounds with two silicon atoms bound to the central metal are obtained from the reaction between $[Ni(CO)_4]$ and the t-butyl substituted tetrafluorodisilacyclobutene $C_6H_{10}F_4Si_2$.

RECENT interest in the synthetic use of thermally generated silicon difluoride species has resulted in a series of new fluorosilicon compounds.[1] We have found that the reactions between SiF_2 and alkyne systems give a four-membered ring disilacyclobutene product (I).[2,3]

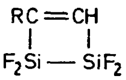
Schmid and Balk[4] have reported an unusual reaction between $[Pt(PPh_3)_4]$, Si_2Cl_6, and acetylenes to give five-membered ring compounds $(PPh_3)_2\overline{PtSiCl_2CR^1:CR^2Si}Cl_2$.

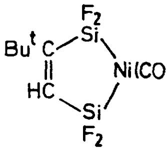
In view of the relative weakness of the Si–Si bond in (I) (Si–Si bond energy 54 kcal/mol in comparison with normal C–C bond 85 kcal/mol, some strain is also expected for such small ring compounds involving double bonds) and the electron-withdrawing ability of the fluorines, we tried to synthesize Si-chelate compounds by the reaction of (I; $R = Bu^t$) with $[Ni(CO)_4]$. Approximately equimolar proportions of the reactants were sealed in a tube and the reaction was carried out at room temperature. After fractionating the product solution, a portion contained mainly compound (II) and small amount of compound (III) was collected at 0 °C.

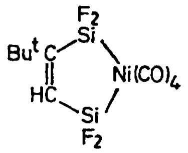
The brown liquid from this portion shows in its ^1H n.m.r. spectrum 2 sets of broad triplets at δ 6·64 and 7·27 [vinyl protons for (II) and (III)] and a singlet at δ 1·25 (Bu^t); the ratio of intensity of the triplets to that of the singlet is 1 : 9. The ^{19}F n.m.r. spectrum shows two broadened resonances at 136·4 and 137·1 upfield from internal CCl_3F, which are in the region typical of Si–F resonances[3]. The i.r. spectra of this portion, in both vapour and liquid phases, show characteristic CO stretching bands for CO bonded to nickel (2120, 2090, 2070, and 2040 cm^{-1}) as well as ν(C–H) (2970, 2910, and 2880 cm^{-1}), ν(C=C) (1610 cm^{-1}), and ν(Si–F) (960, 890, 840, and 810 cm^{-1}).

A relatively pure sample of (II) was obtained after exhaustive purification. The brown liquid is highly moisture-sensitive and decomposes at *ca.* 70 °C; its structure was further supported by elemental analysis and mass spectrometry [*m/e* 329 (M^+), 215 ($C_6H_{11}Si_2F_4^+$), 187 ($C_4H_7Si_2F_4^+$), 85 (SiF_3^+), 67 ($SiHF_2^+$), 57 ($C_4H_9^+$), and 28 (CO^+)]. The ^1H n.m.r. spectrum shows only one triplet at δ 7·27 and a singlet at δ 1·25 with intensity ratio 1 : 9. The ^{19}F n.m.r. spectrum shows resonances at 136·4 and 137·0. The i.r. spectrum is quite similar to that of the mixture except that 2 of the 4 CO stretching bands of the mixture decrease in intensity and apparently only 2 of them are seen (2090 cm^{-1} and 2040 cm^{-1}, with a small shoulder at 2120 cm^{-1}). All these features strongly support our structural assignment that the first portion is a mixture of (II) and (III) while the second portion contains mainly compound (II).

Structure (II) is further supported by a study of its reactivity. It reacts with t-butylacetylene to form two new compounds, (IV) and (V), which cannot be made under the same conditions by direct reaction of t-butylacetylene with the four-membered ring compound (I).


(I)


(II)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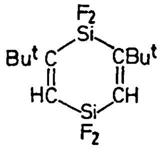
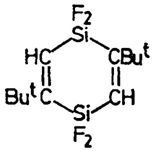

(IV)


(V)

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