

Chelate Compound with Silicon Atoms as 'Donors'

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Summary Chelate transition-metal compounds with two silicon atoms bound to the central metal are obtained from the reaction between $[\text{Ni}(\text{CO})_4]$ and the t-butyl substituted tetrafluorodisilacyclobutene $\text{C}_6\text{H}_{10}\text{F}_4\text{Si}_2$.

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 Balk⁴ have reported an unusual reaction between $[\text{Pt}(\text{PPh}_3)_4]$, Si_2Cl_6 , and acetylenes to give five-membered ring compounds $(\text{PPh}_3)_2\text{PtSiCl}_2\text{CR}^1\text{:CR}^2\text{SiCl}_2$.

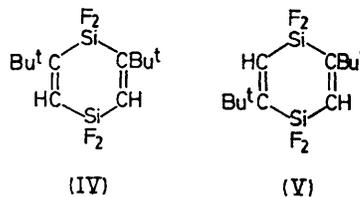
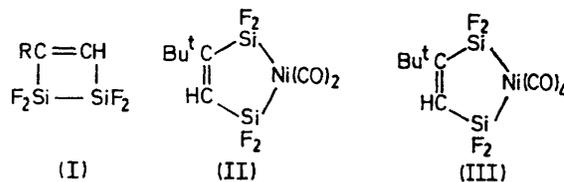
In view of the relative weakness of the Si-Si bond in (I) (Si-Si bond energy 54 kcal/mol in comparison with normal C-C bond 85 kcal/mol, some strain is also expected for such small ring compounds involving double bonds) and the electron-withdrawing ability of the fluorines, we tried to synthesize Si-chelate compounds by the reaction of (I; R = Bu^t) with $[\text{Ni}(\text{CO})_4]$. 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 resonances³. 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 $\nu(\text{C-H})$ (2970, 2910, and 2880 cm^{-1}), $\nu(\text{C}=\text{C})$ (1610 cm^{-1}), and $\nu(\text{Si-F})$ (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 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 187 ($\text{C}_4\text{H}_7\text{Si}_2\text{F}_4^+$), 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).

We thank the Chinese National Research Council for financial support.

(Received, 29th July, 1974; Com. 955.)

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