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Preliminary communication

Preparation and some properties of silacyclopentadiene complexes of cobalt

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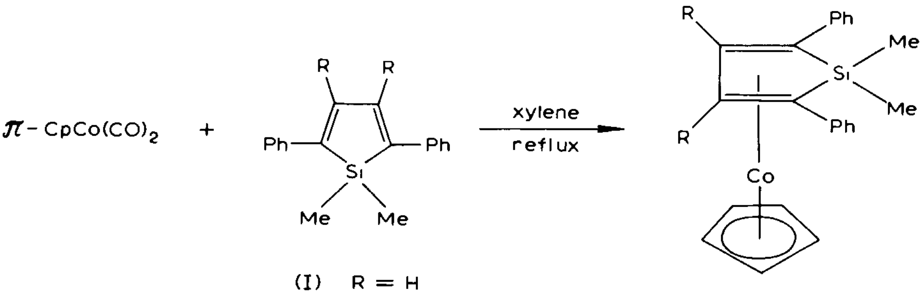
SUMMARY

New silacyclopentadiene cobalt complexes, (π-cyclopentadienyl)(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene)cobalt and (π-cyclopentadienyl)(1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)cobalt, have been prepared; they show strong peaks corresponding to (M^+ −15) in mass spectra, indicating the existence of silicon analogues of the cobalticenium cation.

Silacyclopentadienes are of interest in connection with the possibility of using silacyclopentadiene as a precursor to "π-silacyclopentadienyls" which might be stabilized by coordination to transition metals. However only iron tricarbonyl complexes of substituted silacyclopentadiene have been reported to date[1]. We have now prepared four new (π-cyclopentadienyl)cobalt complexes of substituted silacyclopentadiene; their properties are of special interest in view of the known instability of the corresponding (π-cyclopentadienyl)-(cyclopentadiene)cobalt.

Reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (I) or 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (II) with (π-cyclopentadienyl)cobalt dicarbonyl



(I) R = H
(II) R = Ph

(III) R = H
(IV) R = Ph

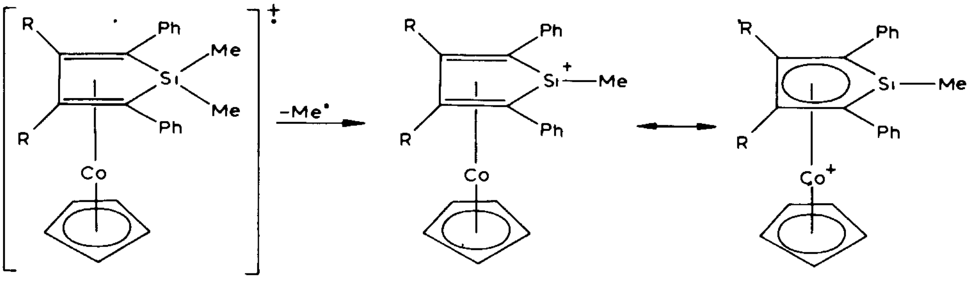
in refluxing xylene afforded the corresponding (π-cyclopentadienyl)cobalt complexes (III and IV) in 100 and 95% yield, respectively. Sublimation gave analytically pure crystals in each case. Physical properties including NMR and IR spectral data are listed in Table 1. The NMR spectra of (III) and (IV) showed two sharp singlets due to *exo* and *endo* methyl protons. Two Si–Me rocking frequencies were observed in the IR. The *exo* and *endo* methyl groups were assigned by comparing the spectral data with those of silanol complexes (*vide infra*).

TABLE 1

PHYSICAL PROPERTIES OF NEW COBALT COMPLEXES

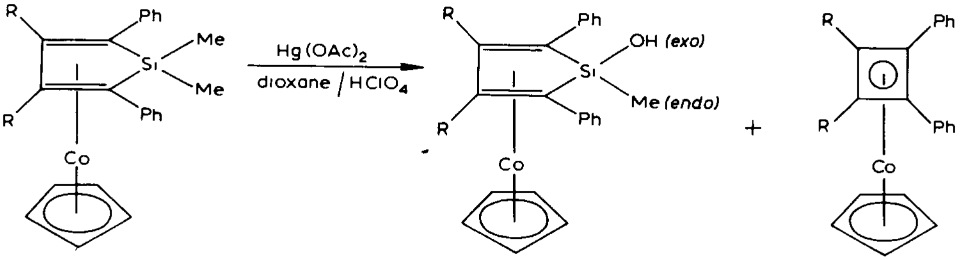
Compound	*m p. (°C)*	*NMR (CS_2, δ)*			*IR (CS_2, cm^{-1})*
		Me (exo)	*Me (endo)*	*π-Cp*	*δ($SiMe_3$)*
(III)	128–130	−0.18	1.20	4.25	1235, 1250
(IV)	174–175	−0.06	0.97	4.59	1237, 1250
(V)	decomp		1.11	4.29	– 1255
(VI)	162–164		0.91	4.57	– 1250

The most interesting properties of the complexes, however, appeared in their mass spectra. The mass spectrum of (III) revealed a very strong peak at *m/e* 371 (M^+ −15, 100%) in addition to the molecular ion (*m/e* 386, 36%). No other significant peak was observed. Exactly the same trend was observed in the mass spectrum of (IV), which showed only two significant peaks at *m/e* 538 (M^+, 74%) and 523 (M^+ −15, 100%). These facts suggest that the (M^+ −15) species must be stable at least in the mass-spectrometer.



In view of these results, it was of interest to examine electrophilic attack on the methyl groups bound to silicon, these groups are expected to be highly reactive toward electrophiles. Reaction of (III) with an equimolar amount of mercuric acetate in dioxane–70% perchloric acid (10/1) proceeds smoothly to give a silanol complex (V) and a π-cyclobutadiene complex (VII). The complex (IV) reacts similarly.

New ring-contraction reactions of the ligands resulted in the formation of π-cyclobutadiene complexes whose structures were verified by comparison with authentic samples[2].



(III) R = H
(IV) R = Ph

(V) R = H (22 5 %)
(VI) R = Ph (42 5 %)

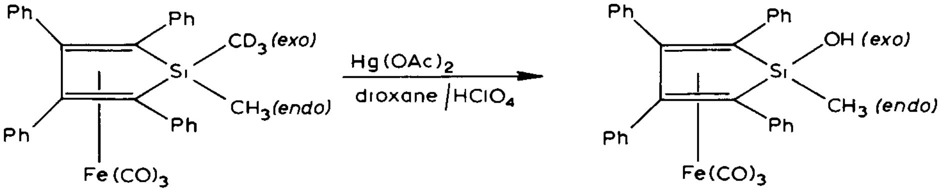
(VII) R = H (12.5 %)
(VIII) R = Ph (5 0 %)

The structures of (V) and (VI) were determined by NMR spectra with lanthanide shift reagent[3]. Of the chemical shifts due to the two methyl groups of (III) and (IV), the one with the higher NMR chemical shift and the lower Si–Me rocking frequency were not present in the spectra of (V) and (VI), respectively.

These silanol complexes are stable under acidic conditions, although a silanol is generally unstable toward acid.

Interestingly only a single isomer of the silanol complex with the hydroxyl group in *exo* position was obtained. It is not clear which methyl group of (III) and (IV) is replaced by the hydroxyl group. However a recent result[4] that the *exo*-CD_3 of (1-*exo*-trideuteromethyl-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (VII) was selectively replaced by OH with retention of configuration suggests that it is the *exo* methyl.

Reactions of these complexes open a new fascinating field in organosilicon chemistry. Further work in this field is in progress and results will be published soon.



(VII)

(VIII)

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3 H Sakurai and J. Hayashi, *J Organometal Chem* , 63 (1973) C7.
4 H Sakurai and J. Hayashi, unpublished results