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REACTIONS OF HYDRIDOSILACYCLOBUTANES WITH LOW-VALENT COMPLEXES OF IRON OR PLATINUM *

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Summary

Unstable transition metal compounds formed from hydridosilacyclobutanes are described: 1-methyl-1-silacyclobutane reacts with nonacarbonyldiiron to give the complexes $[Fe(CO)_4(H)\{\overline{Si(Me)CH_2CH_2CH_2}\}]$ and $[\overline{Fe\{CH_2CH_2CH_2Si}(H)Me\}(CO)_4]$, and with bis(triphenylphosphine)(ethylene)platinum(0) to give $[Pt(H)(PPh_3)_2\{\overline{Si(Me)CH_2CH_2CH_2}\}]$.

Introduction

In our investigations of the reactions of strained organosilicon heterocycles [1] with transition-metal complexes we have observed three modes of behaviour: (1) polymerisation of the heterocycle [2], (2) insertion to give a silaferracyclopentane [3], and (3) formation of a transition-metal-substituted silacyclobutane [4].

We now report on the silacyclobutane (I), characterised by having an Si—H bond, and find that this reacts in a complex manner, involving combinations of the reaction pathways 1—3.

Results and discussion

Treatment of a benzene suspension of $[Fe_2(CO)_9]$ with 1-methyl-1-silacyclobutane (I) under conditions which normally (e.g., [3] with $Me_2\overline{SiCH_2CH_2CH_2}$) give $[Fe(CO)_5]$, a (colourless) silaferracyclopentane, and some (green) $[Fe_3(CO)_{12}]$ by-product, gave a deep-yellow solution. Work-up afforded a volatile yellow liquid which decomposed rapidly above —30°C (extensive decomposition to a dark involatile gum occurred in a few minutes at 21°C) and ignited in air. Solutions appeared to be more stable thermally than the neat liquid, especially in

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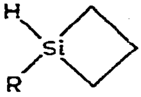
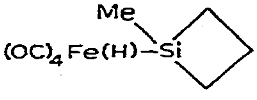
* No reprints available.

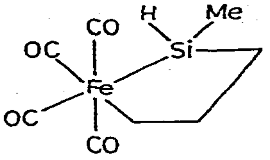
the absence of light. Comparison of the IR and NMR spectra of this material with those of compounds produced in our earlier studies [3] showed it to consist of a mixture of the silane oxidative adduct II and the silaferracyclopentane III in the ratio 2/1, together with traces of other unidentified materials.



(I)



(II)



(III)

(I: R= Me; IV: R=H)

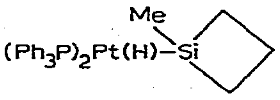
Complex II appears to be the first [M(CO)$_4$] (M = Fe, Ru) adduct of a trialkylsilane to be reported (see ref. 5 for details of complexes having Si—transition-metal bonds). Related derivatives [Fe(CO)$_4$(H)SiX$_3$] (X = Cl or Ph) have been made from [Fe(CO)$_5$] and the corresponding silane by irradiation at relatively low temperatures, while the silyl complex (X = H) was formed in low yield by the reaction of Na$_2$[Fe(CO)$_4$] with H$_3$SiI (the major product being [Fe(CO)$_4$(SiH$_3$)$_2$]).

The osmium hydrides [Os(CO)$_4$(H)SiR$_3$] (R = Me or Et) displayed sufficient thermal robustness to survive syntheses at 140°C/19 h, so that the present isolation of II provides evidence for the hypothesis that such silyl-transition-metal hydrides are the precursors of the family of interesting complexes isolable from the reactions between silanes and metal carbonyls. The resonance due to hydridic hydrogen in II was observed as a sharp singlet at τ 19.55 ppm in the PMR spectrum (cf. τ 19.00 ppm for [Fe(CO)$_4$(H)SiCl$_3$]). As with [Fe(CO)$_4$(H)SiX$_3$] (X = Cl or Ph), we are unable to assign a ν(Fe—H) IR stretch for compound II, although for X = H such a vibration was tentatively assigned to a weak absorption at 1880 cm^{-1}. The stereochemistry of II cannot be assigned with certainty. However, by analogy with [Fe(CO)$_4$(H)SiX$_3$] the compound is probably the *cis*-isomer.

Complex III is the only known silaferracyclopentane bearing a hydrido substituent at silicon; its IR and PMR spectroscopic characteristics resembled quite closely those of the methyl analogue [3].

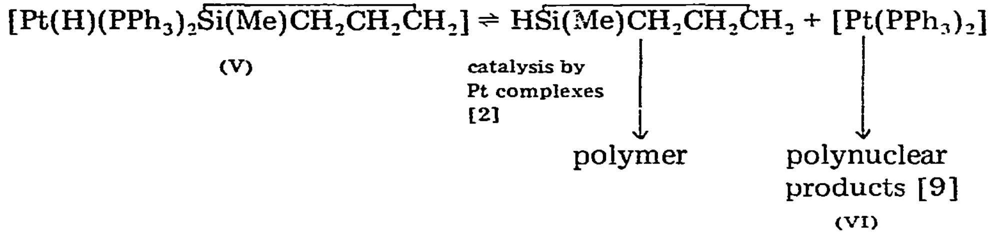
Reaction between the parent silacyclobutane IV and a [Fe$_2$(CO)$_9$] suspension in benzene gave a deep-orange solution which afforded only an involatile orange gum showing complex absorption in the carbonyl region of the IR spectrum (2120—1960 cm^{-1}) and having in its PMR spectrum, besides complex absorption in the τ 7—9 ppm region, at least three hydridic hydrogen signals (τ 19.5, 19.8, and 24.8 ppm, respectively).

Ethylenebis(triphenylphosphine)platinum(0) reacted rapidly with the silacyclobutane I in benzene, a gas (presumably ethylene) being evolved, and a labile material (Va) remaining. (Reaction without benzene, using excess of silacyclobutane as solvent, resulted in extensive polymerisation of the heterocycle.) The exact nature of the product Va was difficult to establish, but when first isolated the oxidative adduct (V) is probably the major component. Elemental analyses, although somewhat variable, supported this formulation. The IR spectrum



(V)

(Nujol mull) was typical of that of a [$Pt(PPh_3)_2XY$] complex, significant "XY"-assignable bands occurring at 2021 [ν(Pt—H)] and 1253 [δ((Si)CH_3)] cm^{-1}. Bands appeared at frequencies characteristic [1] of silacyclobutanes, but intensities were unusual. The PMR spectrum in the methylene region was complex and did not afford confirmation of the presence of an intact silacyclobutane ring. However, the $SiCH_3$ signal appeared as a well-defined sharp triplet (ca. 1/2/1) with ^{195}Pt satellites. This, together with the position of ν(Pt—H) suggests [6] that the complex may have the *trans* configuration. This would be unusual since [$Pt(H)(PPh_3)_2SiEt_3$] and related compounds [6] [with ν(Pt—H) in the range 2043—2105 cm^{-1}] are thought to be *cis*. A Pt—H signal was not found in the τ 15—35 ppm region [7], either in benzene (at room temperature) or in toluene (at —50°C) although sensitivity should have been sufficient for detection. Other specific searches have been equally unsuccessful [8]. Reaction between [$Pt(C_2H_4)(PPh_3)_2$] and the silacyclobutane I in hexane gave on filtration a yellow solution which rapidly decolourised and deposited a dull yellow precipitate VI. The IR spectrum of VI resembled that of [$Pt(PPh_3)_3$] and differed from that of Va principally in lacking the "XY" absorptions. Stirring Va with hexane gradually converted it to VI. Compound Va reacted with carbon tetrachloride in benzene to give *cis*-[$PtCl_2(PPh_3)_2$]; GLC analysis of the solution showed the formation of a small amount of $CHCl_3$, giving further indirect evidence for the hydridic nature of Va. The compound probably decomposes (particularly in hexane) as follows:



$$[Pt(H)(PPh_3)_2\overline{Si(Me)CH_2CH_2CH_2}] \rightleftharpoons H\overline{Si(Me)CH_2CH_2CH_2} + [Pt(PPh_3)_2]$$

(V)

(VI)

Experimental

Experimental procedures and instrumentation were as described previously [3]. Hydridosilacyclobutanes were prepared by published methods [1]. ^1H NMR integrated signal intensities were in the required formula ratio.

Reaction of 1-methyl-1-silacyclobutane with nonacarbonyldiiron(0)

To a stirred suspension of [$Fe_2(CO)_9$] (0.849 g, 2.33 mmol) in benzene (25 cm^3) held just above its freezing point was added the silacyclobutane I (0.220 g, 2.56 mmol). The mixture was allowed to warm to 21°C and was stirred for 16 h to give a deep-yellow solution. Solvent and [$Fe(CO)_5$] were then removed in vacuo, keeping the reaction flask contents as cold as possible without freezing. Molecular distillation of the resulting dark-orange oil gave the air- and thermally-sensitive product mixture as a yellow oil, stored in the dark at −30°C. IR spectrum (thin film, selected bands) cm^{-1}: 1253s (δ(Si)CH_3) + silaferracyclopentane vibration [3]); 1184w, 1120m, 929m (silacyclobutane [1]); 1213w, 1173w, 923w(sh) (silaferracyclopentane); 1050s(br) [ν(SiOSi) through decomposition during measurements]; ν(CO) + ν(Fe—H) + ν(Si—H) (cyclohexane) cm^{-1}; 2097m, 2083m, 2076w, 2043m, 2032s, 2024vs, 2011vs, 2007vs, 2000vs, 1988m. PMR spectrum (benzene, τ 2.73 ppm) τ 9.23 (s, $SiCH_3$), 8.54 (t, 2 α-CH_2, ^3J(HH) 7.5 Hz), 7.66 (quintet, β-CH_2, ^3J(HH) 7.5 Hz), 19.55 (s, FeH), [silacyclobutane (II)]; 9.40 (d, $SiCH_3$, ^3J(HH) 4.0 Hz), 8.8—9.1 (complex m, 1 ring CH_2), 8.05—8.35 ppm (complex m, 2 ring CH_2), [silaferracyclopentane(III)]. (N.B. The silacyclobutane PMR spectrum is interpreted in first-order terms; in practice, as with $Me_2\overline{SiCH_2CH_2C}H_2$, second-order interactions are clearly present; SiH was not located.)

Reaction of 1-methyl-1-silacyclobutane with ethylenebis(triphenylphosphine)-platinum(0)

To $[Pt(C_2H_4)(PPh_3)_2]$ (0.075 g, 0.100 mmol) was added benzene (0.25 cm^3) and then, with stirring, the silacyclobutane I (0.009 g, 0.100 mmol). Gas was evolved and a dark-brown solution formed. Further benzene (0.25 cm^3) was then added * and then, slowly, hexane (5 cm^3). Solvent volume reduction in vacuo gave a precipitate which was washed briefly with hexane to give the pale-brown product Va (0.059 g), >80°C dec. in vacuo (Found: C, 59.4—60.5; H, 5.1—5.5. $C_{40}H_{40}P_2PtSi$ calcd.: C, 59.6; H, 5.0%). IR spectrum (Nujol) cm^{-1}: the following bands disappeared on prolonged stirring of Va with hexane: 2021m, 1249w, 1222w, 918w, 872m, 841s, 831s, 774w, 622w; examination of ν(Pt—H) with scale expansion showed a shoulder at 2027 cm^{-1}. PMR spectrum (C_6H_6, τ 2.73 ppm) τ 6.6—ca. 9.5 (complex m, ring methylenes); 9.61 ppm (t of t; ^4J(PH) 15.4 Hz, ^3J(PtH) 3.7 Hz; $SiCH_3$). [N.B. The PMR spectrum was run as a separate experiment, using the solution at point *; subsequent recovery of the complex gave material of an essentially identical IR spectrum to the above, although ν(Pt—H) was broader.]

In a separate experiment, CCl_4 (0.015 g, 0.100 mmol) was added at point *. After 16 h, the precipitate formed was separated by decantation and washed (hexane) to yield *cis*-$[PtCl_2(PPh_3)_2]$ (0.058 g, 73%). GLC analysis of the decantate could not detect any $Me(Cl)\overline{SiCH_2CH_2C}H_2$ (polymerised? [2]), but did give a small peak corresponding to the retention time of $CHCl_3$.

Acknowledgement

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