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ORGANOMETALLIC π-COMPLEXES OF SILACYCLES

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CONTENTS

A. INTRODUCTION

Ever since the structural elucidation of ferrocene in 1951, research concerning organometallic π-complexes has been a very active and fruitful field [1]. Innumerable π-complexes of many different transition metals have been prepared, and much interest has been directed toward heterocyclic π-ligands [2]. In view of the ability of transition metal complexes to stabilize otherwise unstable ligands (the iron tricarbonyl complex of cyclobutadiene [3], for example) it was believed that complexes of silacyclopentadienide anion might be isolable, even though the free anion is unknown [4]. Unfortunately, this has not been the case. We report here on the chemistry of organometallic complexes of sila-heterosubstituted π-ligands [5].

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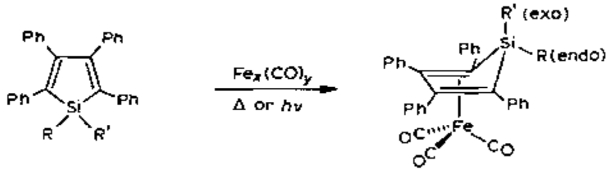
B. SILACYCLOPENTADIENES

(i) Complexes with iron

Brunet et al. reported the first transition metal complex of a silacycle in 1969 [6]. They allowed various 1,2-disubstituted-2,3,4,5-tetraphenyl-1-silacyclopentadienes (**1**) to react with iron carbonyls and isolated stable, high-melting, red-orange crystalline products which were characterized on the basis of elemental analysis and IR spectroscopy as η^4-silacyclopentadiene iron tricarbonyl complexes (**2**). These compounds are very similar to other non-aromatic conjugated diene complexes. Reactions with diiron nonacarbonyl or triiron dodecacarbonyl were carried out in ligroine, benzene, toluene or xylene at 60–100°C. Reactions with iron pentacarbonyl were carried out in benzene in a sealed tube at 150–200°C for 24 h. (No reaction occurred at temperatures less than 150°C.) The products were recrystallized from petroleum ether in 65–80% yield. The compounds are air-stable and soluble in organic solvents. Infrared CO stretching absorptions were observed at 1975, 1985 and 2080 cm^{-1} (KBr pellet) and were insensitive to the nature of the substituent at silicon.

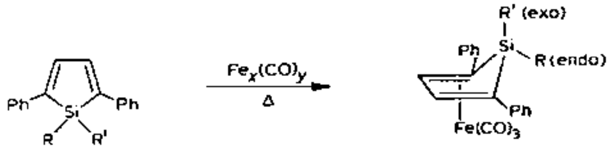


1 a R = R' = Me
b R = Me, R' = Ph
c R = R' = p-$CH_3C_6H_4$

2 a R = R' = Me
b R = Me, R' = Ph
c R = R' = p-$CH_3C_6H_4$

Jutzi and Karl [7] have developed a photochemical synthesis of 1,1-disubstituted-2,3,4,5-tetraphenyl-1-silacyclopentadiene iron tricarbonyl complexes (**2**). Irradiation of a benzene solution of 1,1-disubstituted tetraphenylsilacyclopentadiene (**1**) and iron pentacarbonyl with a 125 W high pressure mercury arc lamp for 72–100 h is reported to give a quantitative yield of the iron tricarbonyl adduct.

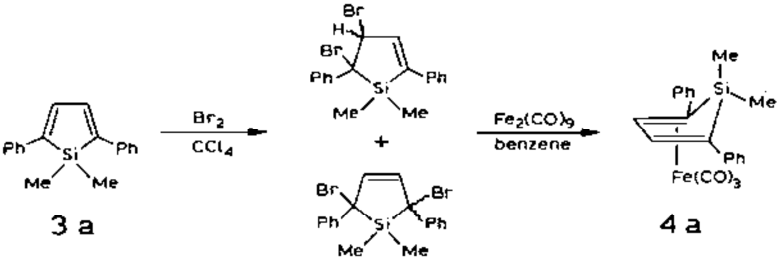
Brunet and Demey [8] have also prepared the analogous 1,1-disubstituted-2,5-diphenyl-1-silacyclopentadiene iron tricarbonyl complexes (**4**). The synthesis of these compounds proceeds in benzene under milder conditions; reactions occur with iron pentacarbonyl at 140°C in 12 h, diiron nonacarbonyl at 40°C in 1 h and triiron dodecacarbonyl at 80°C in 1 h. Yields ranged from 60–75% with iron pentacarbonyl to 40% with the other iron carbonyls. Fink [9] has employed similar conditions with iron pentacarbonyl and obtained yields of approximately 90%. These compounds exhibit IR



3 **a** R = R' = Me
b R = Me, R' = Ph

4 **a** R = R' = Me
b R = Me, R' = Ph
c R = Ph, R' = Me

bands at 1930 (shoulder), 1975 and 2080 cm^{-1}, as well as UV absorptions at 225–235 nm ($\epsilon = 13{,}000–20{,}000$) and 370–375 nm ($\epsilon = 13{,}200–18{,}000$; cyclohexane) and fluorescence at 490 nm ($\lambda_{exit} = 385$ nm; 2×10^{-5} M, cyclohexane). The complex **4a** is available from ligand precursors other than **3**; for instance, the mixture of isomers formed upon bromination of **3a** in



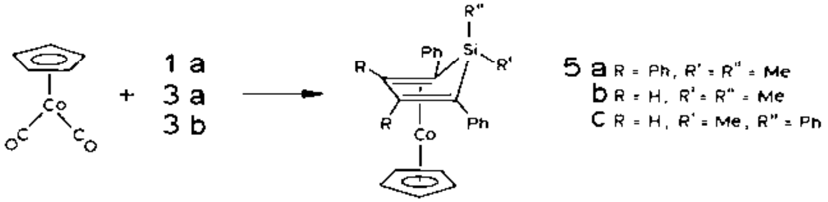
CCl_4 is debrominated by diiron nonacarbonyl in benzene to give a 30% yield of the iron tricarbonyl adduct [10].

If the silacycle is unsymmetrically disubstituted at silicon, as in **1b** and **3b**, then there is the possibility for *exo/endo* isomerism in the organotransition metal complex. The reaction of **3b** with iron pentacarbonyl gave a **4b**:**4c** ratio of 94:6 (94% overall yield) [9]. This ratio was determined by comparison of ^{1}H NMR spectra with model compounds in the literature. The *exo*-methyl substituent of **4c** appears at higher field ($\delta = 0.25$ ppm) than the *endo*-methyl substituent of **4b** ($\delta = 1.29$ ppm). The ratio is consistent with the more sterically demanding substituent occupying the less hindered axial (*exo*) position.

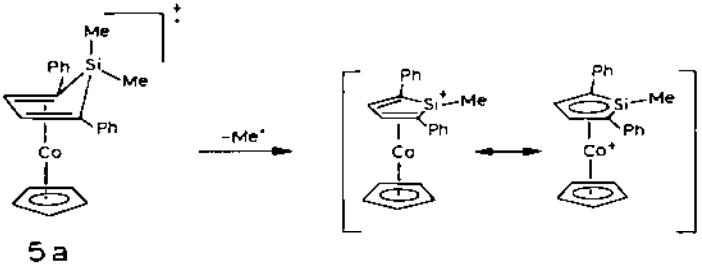
Earlier, Sakurai and Hayashi had employed a paramagnetic lanthanide shift reagent in the assignment of the stereochemistry of a silanol complex [11].

(ii) Complexes with other metals

Although the iron complexes of silacycles have been the most thoroughly investigated, the literature contains a few references to silacycle π-complexation with other transition metals as well. The first cobalt complex was reported by Sakurai and Hayashi, who have prepared 1,1-dimethyl-2,5-di-

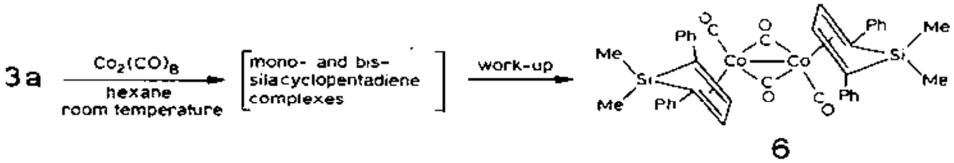


phenyl-1-silacyclopentadiene (**3a**) and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silicyclopentadiene (**1a**) complexes (**5a** and **5b**) of π-cyclopentadienyl cobalt dicarbonyl in high yield (> 95%) by refluxing in xylene [12]. The ^{1}H NMR spectra of these compounds show the *exo*-methyl substituent of **5a** at very high field ($\delta = -0.18$ ppm). This reaction is of interest because of the known instability of the (π-cyclopentadienyl) (cyclopentadiene) cobalt analog of the product. Fink has carried out a similar reaction of 1-methyl-1,2,5-triphenyl-1-silacyclopentadiene (**3b**) and cyclopentadienyl cobalt dicarbonyl, and has isolated the *endo*-methyl isomer (**5c**) (< 3% *exo* by NMR) in 86% yield [9]. The mass spectra of these complexes show very strong peaks at $M^{+\cdot} - 15$(100%), which indicate that the transient η^5-silacyclopentadienyl

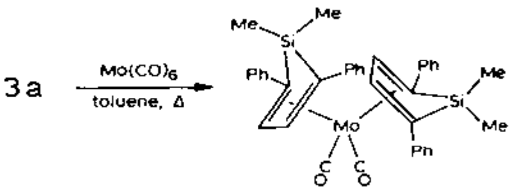


species is formed in the mass spectrometer [9,12]. Analogous species have been observed in mass spectra of other silacyclic π-complexes as well [13,23].

Abel et al. [13] have allowed **3a** to react with dicobalt octacarbonyl in hexane at room temperature. IR evidence was obtained for both $[Co_2(C_4Ph_2H_2SiMe_2)(CO)_6]$ and $[Co_2(C_4Ph_2H_2SiMe_2)_2(CO)_4]$ (**6**) in the reaction mixture, but upon work-up, only the bis-silacyclopentadiene species **6** was isolable (52% yield) [13].



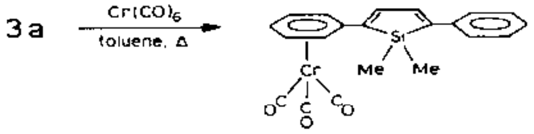
Abel et al. have also prepared 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**3a**) complexes of molybdenum, chromium, ruthenium and rhodium, in addition to iron and cobalt [13]. Reaction with molybdenum hexacarbonyl



7

$$3a \xrightarrow[\text{toluene, }\Delta]{W(CO)_6} \text{no reaction}$$

in refluxing toluene for 40 h gave a 44% yield (based on limiting **3a**) of bis(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene) molybdenum dicarbonyl (**7**) in a reaction analogous to other molybdenum carbonyl reactions with dienes [14]. In addition, a small amount of (toluene) molybdenum tricarbonyl was isolated. No reaction occurred with tungsten hexacarbonyl. A similar reaction employing chromium hexacarbonyl gave the arene adduct (**8**) (58% yield) rather than the silacyclopentadiene adduct, which is not an unexpected reaction of chromium compounds [15].



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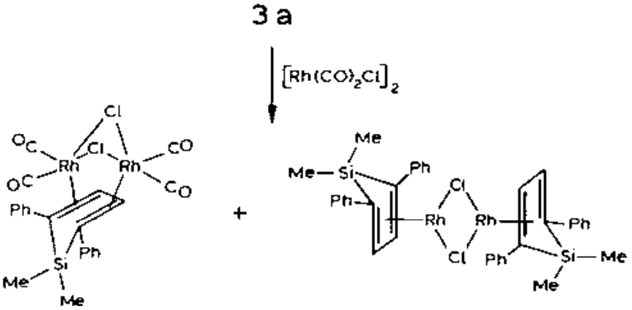
The primary product upon reaction of **3a** with bis(dicarbonylchlororhodium), a 16 electron species, is the addition product **9** (57% yield). A small amount (10%) of **10** was obtained. Finally, reaction of **3a** with triruthenium dodecacarbonyl in refluxing toluene gave the expected (silacyclopentadiene)ruthenium tricarbonyl (**11**), which has been characterized by X-ray crystallography [16]. The structure shows that the silicon atom, which is displaced only 0.08 Å from the plane in the non-com-



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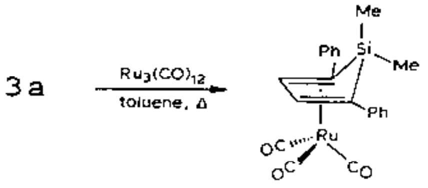
10



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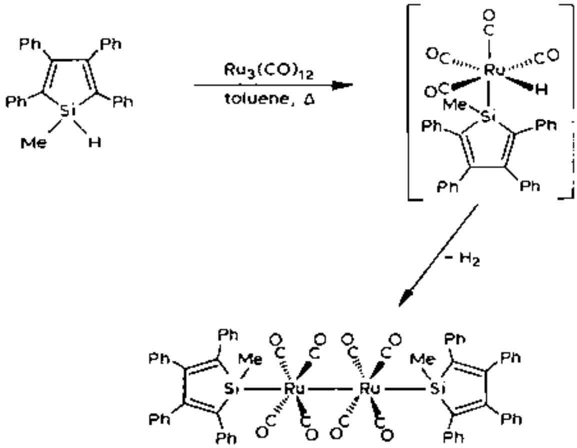
plexed material, is found to be 0.72 Å out of the plane in the complex. The Ru–Si bond distance is 2.992 Å, which is 0.56 Å longer than a Ru–Si covalent bond; therefore, direct bonding interaction between Ru and Si does not occur. Bond lengths in the cyclobutadiene unit are consistent with localized double bonds.

It should be noted that reactions of silacycles in which the silicon atom is



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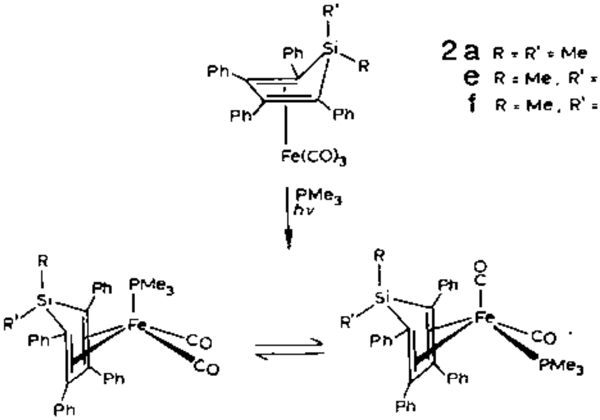
bonded to at least one hydrogen atom often do not give normal π-adducts, but rather, give coupled products (**12**, for example) or uncharacterized mixtures [6,13]. This is likely due to the ability of many transition metal complexes to insert into Si–H bonds, which is a key step in catalytic hydrosilylation [17].

(iii) Reactivity of complexes

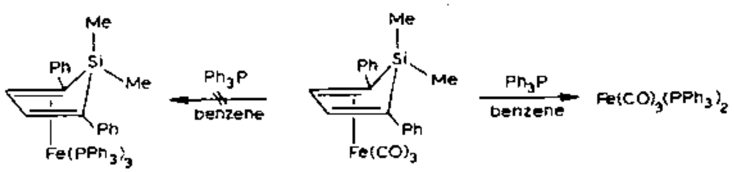
Very little of the chemistry of the organometallic silacyclic complexes has been explored. Jutzi and Karl have succeeded in photochemically replacing one CO ligand of **2a, e, f** with trimethylphosphine to give **13a, e, f** in 75–95% yield [29]. The presence of 4 C–O stretching absorptions in the IR have lead the authors to postulate two isomeric square pyramidal structures for the product which interconvert rapidly on the NMR time scale [29].



2a R = R' = Me
e R = Me, R' = Cl
f R = Me, R' = F

13a R = R' = Me
e R = Me, R' = Cl
f R = Me, R' = F

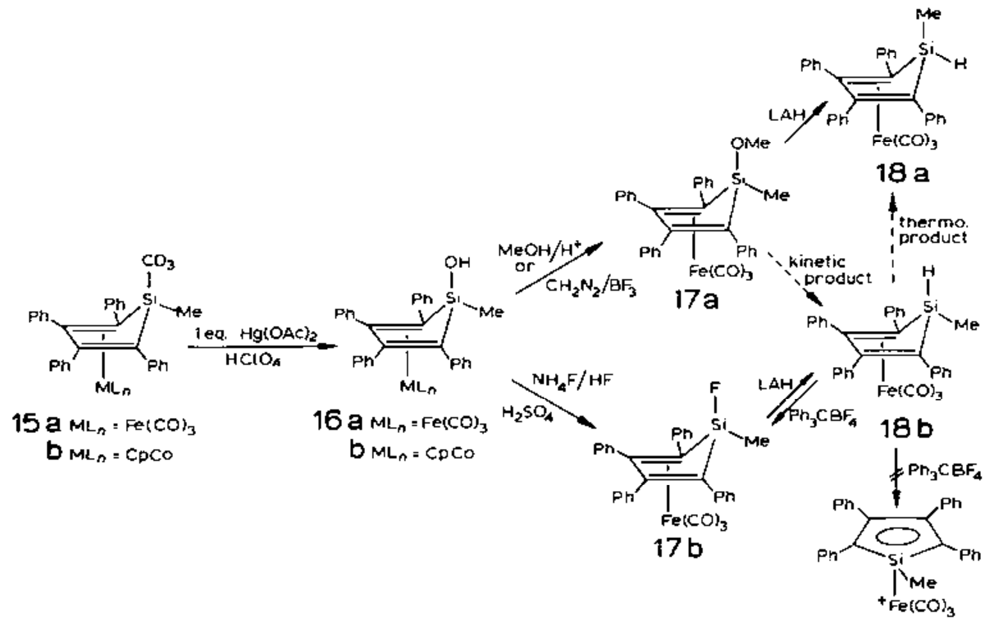
Brunet et al. have attempted to replace the CO ligands of **4a** with triphenylphosphine, but the bis(triphenylphosphine)iron tricarbonyl species **14** was obtained rather than the CO displacement product [6].



4a **14**

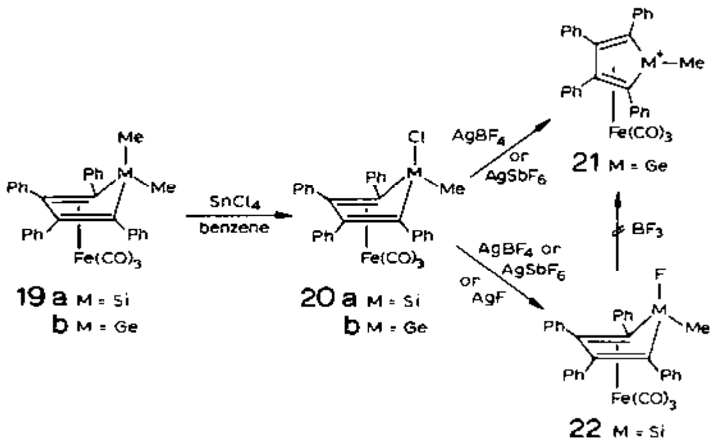
The majority of the work on reactivity of these species has been carried out by Sakurai and Hayashi, who have studied reactions that occur at the silicon atom. Reaction of **15** with mercuric acetate and perchloric acid in dioxane resulted in stereoselective replacement of the *exo*-substituent with retention of configuration [12]. Similar selectivity was observed in the reactions of **16a** [18]. Jutzi and Karl have also noted the lability of the *exo*-substituent in reactions of 1,1-disubstituted-2,3,4,5-tetraphenyl-1-sila or 1-germacyclopentadiene iron tricarbonyl complexes. Treatment of **19a** or **19b** with tin chloride in benzene gave 95% yields of the *exo*-chloro derivatives **20a** or **20b** [7,29].

Interesting stereoselectivity was observed in the lithium aluminum hydride reduction of **17a**. The initially formed product, as observed by NMR, is **18b**; however, by the time all of the starting material has reacted, **18a** is the only isolable product [18]. Interestingly, the $LiAlH_4$ reduction of **17b** gives only **18b** [31]. Therefore, both *exo*- and *endo*-hydrido isomers are available; each



is thermally stable, but the *exo*-isomer is more reactive, which is consistent with the previously cited reactivity patterns [18].

In view of its reactivity, the *exo*-hydrido isomer **18b** was treated with triphenylmethyl tetrafluoroborate in an attempt to abstract H^- and generate the (η^5-silacyclopentadienyl)iron tricarbonyl cation, but the observed product is the *exo*-fluoro derivative (**17b**) [18]. Jutzi et al. [30] have succeeded in abstracting chloride ion from **20b** with silver salts. However, they report that

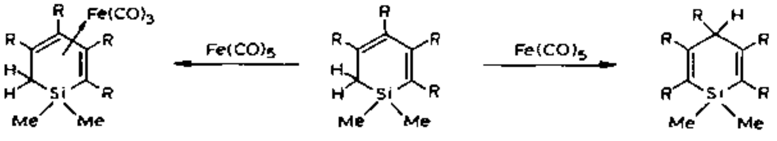


the positive charge of **21** resides almost exclusively on the germanium atom [30]. Their attempt to effect the transformation on the analogous silicon heterosubstituted compound **20a** failed, as simple halogen exchange took place to yield **22**. Treatment of **22** with boron trifluoride also failed to generate the desired product [29].

C. SILACYCLOHEXADIENES

(i) Complexes with iron

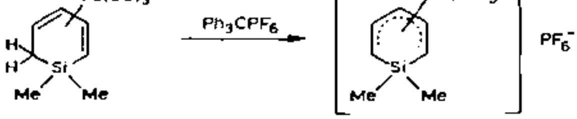
The π-complex chemistry of silacycles other than silacyclopentadiene has not received much attention in view of the fact that such compounds behave simply as olefinic π-ligands. One study in this area has shown that 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene (**23b**) is isomerized to the 2,5-diene (**24**) upon reaction with iron pentacarbonyl or diiron nonacarbonyl in benzene or hexane at 170–200°C [19]. No iron tricarbonyl adduct of the 2,5-diene was isolated. Reaction of the unsubstituted analog, 1,1-dimethyl-1-silacyclohexa-2,4-diene (**23a**) with iron pentacarbonyl in benzene at 150–160°C for 13 h gave the expected iron tricarbonyl adduct **25** in 69% yield [19] with no reported isomerization of the double bond. Treatment of the product with triphenylmethyl hexafluorophosphate in dichloromethane at 0–10°C resulted in hydride abstraction at the 6-position. Filtration gave an 80% yield of 1,1-dimethyl-1-silacyclohexadienyl tricarbonyl iron hexafluorophosphate (**26**), mp 175–177°C [20]. ^{1}H NMR (acetone-d_6: 60 MHz, internal TMS): δ (ppm) 0.075 (s, 3H, *exo*-CH_3); 0.96 (s, 3H, *endo*-CH_3); 3.89 (m, 2H, C-2 and C-6); 7.01 (m, 3 H, C-3, C-4 and C-5). Fink has interpreted these data in terms of a "pseudoaromatic" (6π electron) ligand on the basis of the lowfield chemical shifts observed for protons at C-3, C-4 and C-5. However, Birch et al. [21] and Pearson [22] have generated analogous tetrafluoroborate and hexafluorophosphate salts of non-hetero-



25 R = H

23 a R = H
b R = Ph

24 R = Ph



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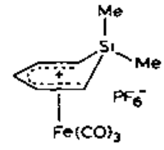
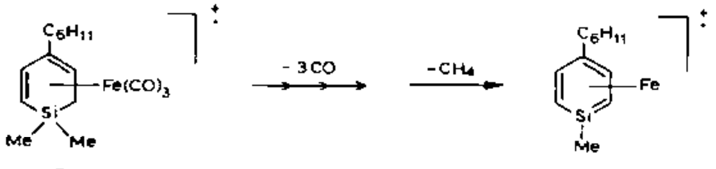


27

substituted cyclohexadiene iron tricarbonyl complexes and have observed nucleophilic attack on the ring, not at iron. This indicates that the electron deficiency is on the ring, which is acting as an η^5, 4 electron donor. Chemical shifts for the 3-proton of such a delocalized system (δ(ppm), internal TMS, CF_3CO_2H) were as low as 7.22 and consistently around 6.9–7.0. Fink's data are therefore also consistent with the structure **27**.

Märkl et al. have obtained evidence for a truly aromatic silatoluene

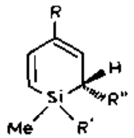


28 29

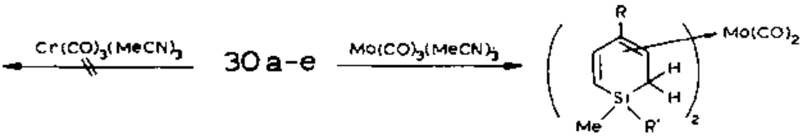
π-complex in the mass spectrum of **28**, which showed a peak corresponding to **29** at $m/e = 246(100\%)$ [23].

(ii) Complexes with other metals

Märkl and Hofmeister have studied the complexation of silacyclohexadienes with chromium, molybdenum and tungsten carbonyls. Reactions of **30a**–**e** with the tris(acetonitrile)tricarbonyl complexes of molybdenum or tungsten gave low yields (ca. 15%) of the bis(silacyclohexadiene) dicarbonyl adducts (**31**) [24] in a reaction completely analogous to the one previously

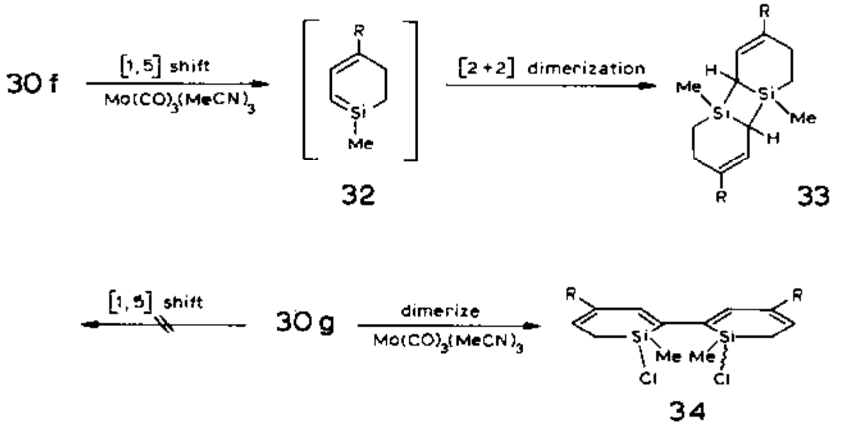


30 a R = *t*-Bu, R' = Me, R'' = H
b R = Ph, R' = Me, R'' = H
c R = R' = Ph, R'' = H
d R = *t*-Bu, R' = Cl, R'' = H
e R = C_6H_{11}, R' = Cl, R'' = H
f R = C_6H_{11}, R' = R'' = H
g R = C_6H_{11}, R' = R'' = Cl



31

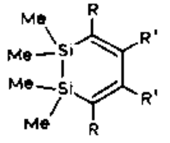
cited in the synthesis of **7** by Abel et al. [13]. No reaction was observed in the case of tris(acetonitrile)chromium tricarbonyl. Reaction of **30f** with tris(acetonitrile)molybdenum tricarbonyl gave the [2 + 2] dimer **33**. The mechanism postulated by the authors invokes an isomerization of the diene



system via a 1,5-hydride shift to give **32** as the reactive intermediate. The corresponding 1,6-dichloro species (**30g**) is unable to undergo this isomerization; it gives head to head dimerization at the 6 positions (**34**) [24].

D. MISCELLANEOUS

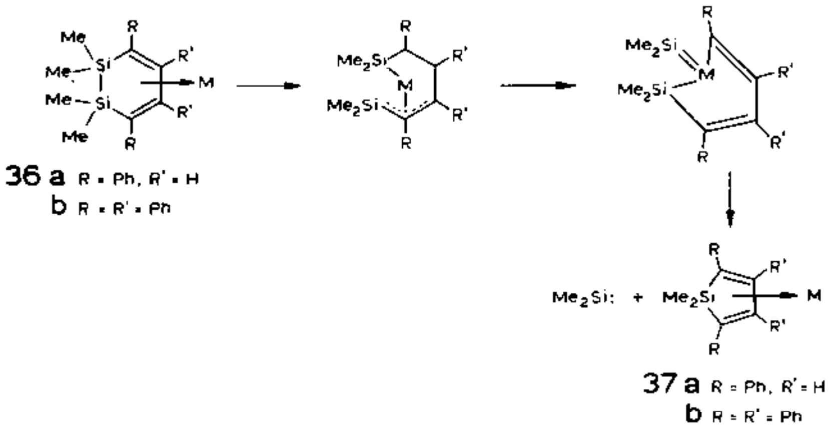
In their extensive studies of organosilicon chemistry, Sakurai and coworkers have examined the reactions of 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-disilacyclohexadiene (**35a**) and 1,1,2,2,-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexadiene (**35b**) with iron carbonyls [25]. Reaction of **35a** with



35 a R = Ph, R' = H
b R = R' = Ph

iron pentacarbonyl can give predominantly **36a** in refluxing xylene at 130°C for 16 h, or predominantly the ring contracted product in refluxing xylene at 160°C for 19 h. In the case of **35b**, only the ring contracted product is isolable. The authors have postulated a mechanism which invokes the intermediacy of an η^3-silaallyl species. However, efforts to trap the dimethylsilylene have been unsuccessful, and the reported isolation of an η^3-silaallyl complex [26] has been shown to be incorrect [32], so the basis for the mechanism is less firm than when the authors proposed it. Recently, these authors have also postulated η^3-silaallyl intermediates in the thermolysis and photolysis of vinyldisilanes in the presence of iron pentacarbonyl [27].

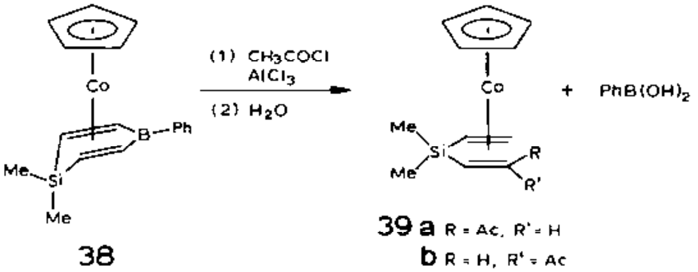
Herberich and coworkers have synthesized various 1-sila-4-bora-cyclohexadienes and studied their π-complexes with iron [28a], cobalt [28b],



36 a R = Ph, R' = H
b R = R' = Ph

37 a R = Ph, R' = H
b R = R' = Ph

nickel, palladium and platinum [28c]. In all cases, the heterosubstituted ring acts as an η^5-donor, with the silicon atom making an angle of 43.5° with the plane of the conjugated ring system in the iron tricarbonyl adduct [28a]. Attempted Friedel–Crafts acylation of **38** with acetyl chloride and aluminum chloride resulted in ring opening and loss of $PhB(OH)_2$ to give **39a** and **39b** as products [28b].



38

39 a R = Ac, R' = H
b R = H, R' = Ac

E. SUMMARY

Much research has focused on the synthesis of silacyclopentadiene π-complexes of transition metals. Various methods exist to give products in high yields. However, attempts to isolate a sila-substituted analog of the ubiquitous π-cyclopentadienyl ligand have not been successful, as these sila-compounds form η^4-complexes. The chemistry of such species is primarily reactivity at the silicon atom. Recent developments have indicated that η^3-silaallyl species may be important reactive intermediates in various mechanistic pathways, and research focusing on such species will probably be the most active sector of research concerning sila-substituted π-complexes in the near future.

ACKNOWLEDGEMENTS

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