Organosilyl Iron Carbonyl Complexes: Synthesis and Reactivity towards Alkynes and Nitriles

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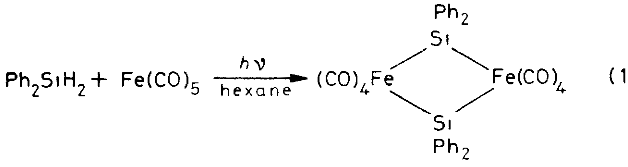
Summary The di-iron complex $[Fe(CO)_4SiPh_2]_2$ readily obtained from $Fe(CO)_5$ and Ph_2SiH_2 under photochemical conditions, reacts with the alkynes RC–CR to yield the new mono- and bi-metallic complexes $(CO)_4Fe\text{–}SiPh_2CR{=}CRSiPh_2$ (R = Ph, Me, or Et) and $(CO)_3Fe\text{–}CMe{=}CMe\text{–}SiPh_2\text{–}CMe{=}CMe\text{–}Fe(CO)_3$, the former complexes convert nitriles into aldehydes *via* disilylated enamines.

TRANSITION metal complexes containing alkylsilyl ligands are potential reagents for organometallic synthesis. While numerous silicon–transition metal compounds are known,[1] only a few complexes containing μ-SiR_2 ligands bridging two metal atoms have been reported[2,3] and little attention has been paid to their chemical reactivity. We report here our preliminary results concerning the synthesis and reactivity of arylsilyl iron carbonyls.

We synthesised μ-silanediyl-iron carbonyls by exposing hexane solutions of disubstituted silanes and pentacarbonyliron to u.v. light [equations (1) and (2)]. Compounds (**1**) and (**2**)† were obtained as yellow–orange crystals, in 54 and 22% yield respectively, having similar characteristics to those of known examples.[3]


(1)

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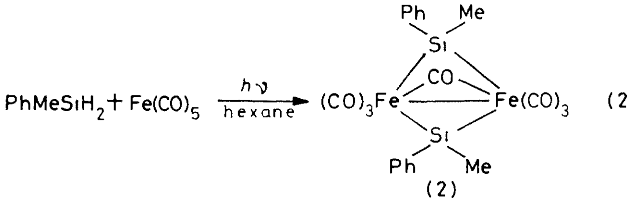
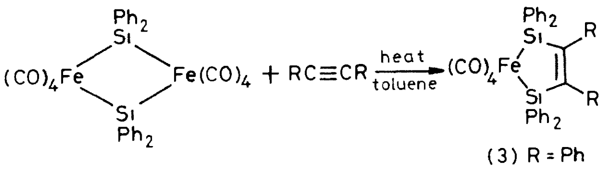

(2)

(2)

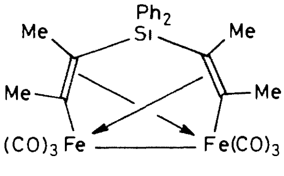
We examined the reaction of (**1**) with the disubstituted acetylenes RC≡CR, which led to the formation of the disilametallacyclopentenes (**3**)—(**5**)† [equation (3)], in 60, 65, and 30% yield, respectively.


(3)

(3) R = Ph
(4) R = Et
(5) R = Me

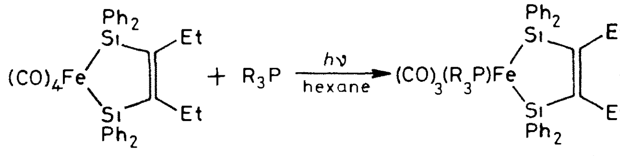
Analogous metallacycles have been reported recently arising from insertion of a tetracarbonyliron unit into disilacyclobutene.[4] A related reaction yielding similar platinum complexes has been mentioned by Eaborn and his coworkers.[5]

From reaction (3) the known acetylenic iron carbonyl complexes $[Fe_2(CO)_6(R_2C_2)_2]$ were also isolated. The reaction of but-2-yne also allowed recovery of an orange crystalline compound of stoicheiometry $[Fe_2(CO)_6(Me_2C_2)_2SiPh_2]$ (**6**),† in 11% yield. The analytical and spectroscopic data [i.r. ν_{CO} 2060, 2025, and 1980 cm^{-1}, ^{1}H n.m.r. (C_6D_6) δ 1.3 (3H, s), 3.0 (3H, s), 7.2 (3H, m), and 7.5 (2H, m), mass spectrum m/e 370 (M^+) followed by successive loss of 6 carbonyl groups and 2 iron atoms] suggested the structure shown.



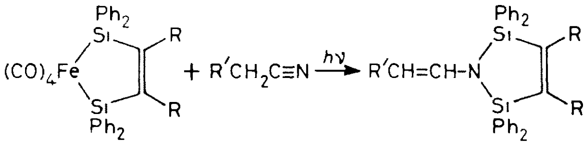
(6)

The disilylated iron complexes (**3**)—(**5**) are air stable white solids which do not exhibit thermal reactivity towards two-electron ligands. However, under photochemical conditions, substitution of one carbonyl group by a phosphine ligand can be achieved [equation (4)] *e.g.* from (**4**) compounds (**7**) and (**8**)† were obtained in 91 and 68% yield respectively.


(4)

(7) $R_3 = Ph_3$
(8) $R_3 = Me_2Ph$

An unexpected reaction was observed with the nitriles $R'CH_2CN$ using u.v. light. The disilylated enamines (**9**)—(**11**), a new class of compounds, were obtained in high


(5)

(9) R = Et, R′ = H (84% yield)
(10) R = Et, R′ = Ph (75%, *cis*:*trans* 55:45)
(11) R = R′ = Me (71%, *cis*:*trans* 58:42)

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† Satisfactory elemental analyses were obtained for all new compounds.

yields† by treating complexes (**3**)—(**5**) with the nitriles $R'CH_2CN$ [equation (5)].

It is noteworthy that upon hydrolysis the enamines yielded the corresponding aldehydes $R'CH_2CHO$. This reaction thus represents a potential way of converting nitriles into aldehydes. We are currently investigating the reactivity of other disilylated iron complexes and their use as reagents for organic syntheses.

The authors thank M. G. Guiraud who did part of the experimental work.

(*Received*, 6*th December* 1979; *Com.* 1274.)

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