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

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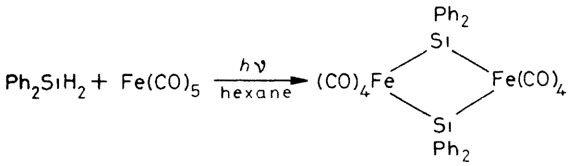
Summary The di-iron complex $[Fe(CO)_4SiPh_2]_2$ readily obtained from $Fe(CO)_5$ and Ph_2SiH_2 under photochemical conditions, reacts with the alkynes RC–CR to yield the new mono- and bi-metallic complexes $(CO)_4Fe–SiPh_2CR=CRSiPh_2$ (R = Ph, Me, or Et) and $(CO)_3Fe–CMe=CMe–SiPh_2–CMe=CMe–Fe(CO)_3$,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

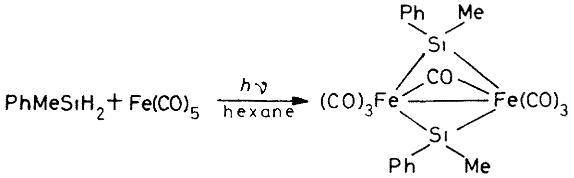
Transition metal complexes containing alkylsilyl ligands are potential reagents for organometallic synthesis While numerous silicon–transition metal compounds are known,[1] only a few complexes containing μ-SiR_2 ligands bridging two metal atoms have been reported[2,3] and little attention has been paid 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)

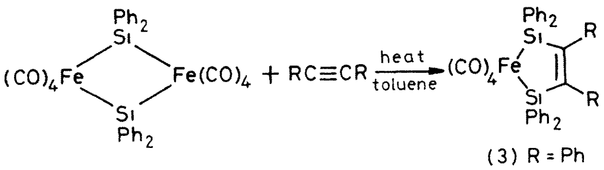
(**1**)



(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)

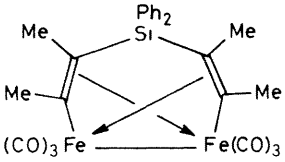
(**3**) R = Ph

(**4**) R = Et

(**5**) R = Me

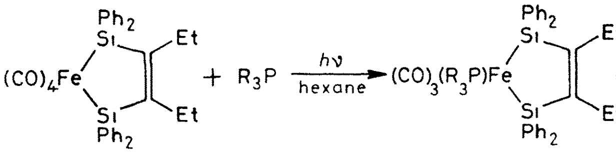
Analogous metallacycles have been reported recently arising from insertion of a tetracarbonyliron unit into disilacyclobutene[4] A related reaction yielding similar platinum complexes has been mentioned by Eaborn and his coworkers[5]

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 $[Fe_2(CO)_6(Me_2C_2)_2\text{-}SiPh_2]$ (**6**),† in 11% yield The analytical and spectroscopic data [i r ν_{CO} 2060 2025, and 1980 cm^{-1}, ^1H 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

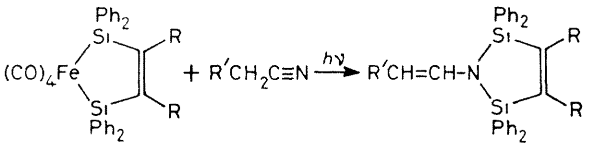


(4)

(**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.

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