Journal of Organometallic Chemistry, 57 (1973) C72–C74

Preliminary communication

1-[(π-Cyclopentadienyl)dicarbonyliron]-1-methylsilacyclobutane and related iron-substituted silacyclobutanes

C.S. CUNDY and M.F. LAPPERT

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received July 16th, 1973)

SUMMARY

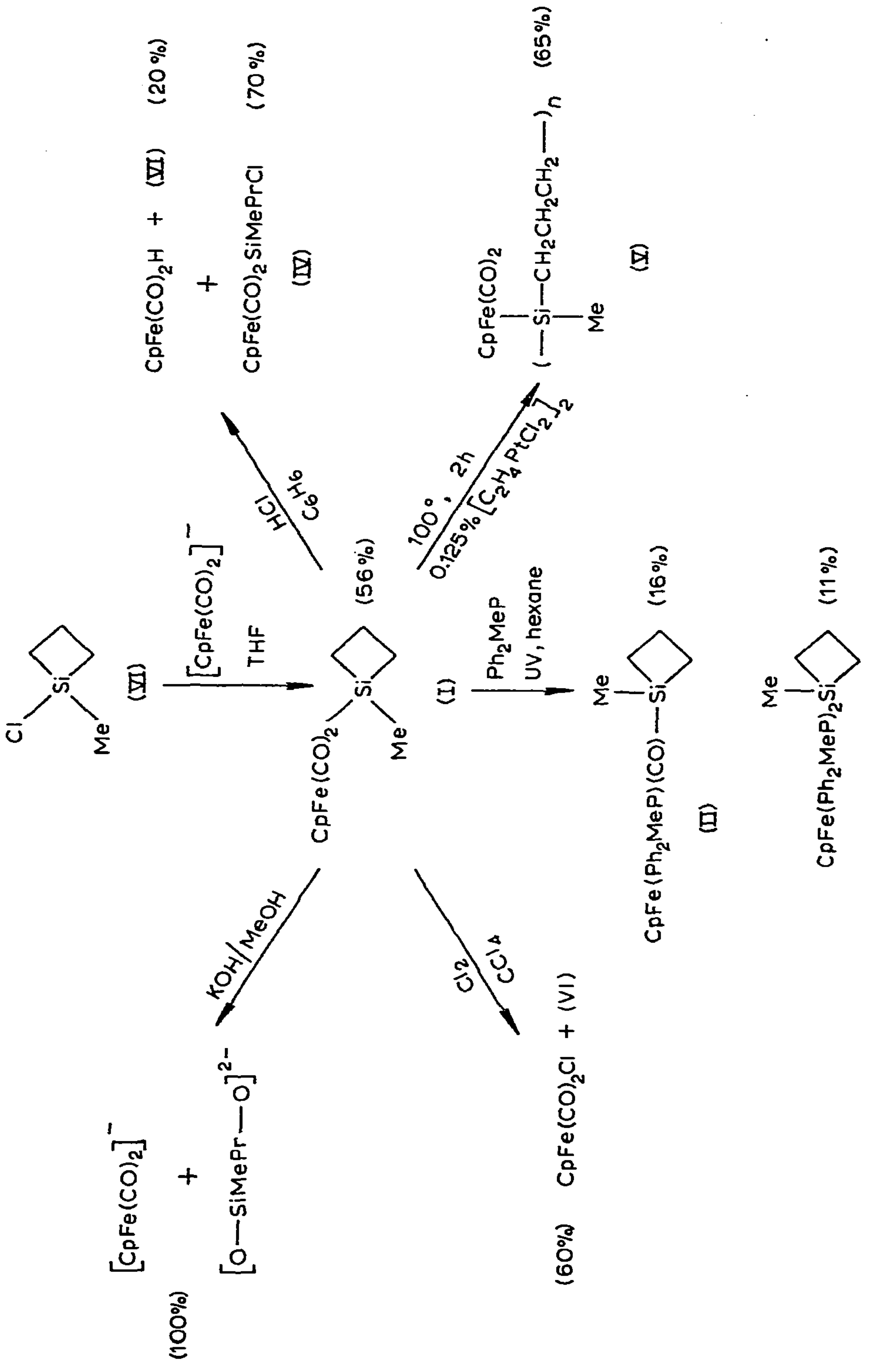
Silicon-transition metallic silacyclobutanes $CpFe(L_2)\overline{Si(Me)CH_2CH_2CH_2}$ [L = CO or Ph_2MeP; or $L_2 = (CO)(Ph_2MeP)$] have been prepared and their reactions (substitution at Si or Fe, Si–Fe cleavage, or ring-opening) studied.

Transition metal insertion and polymerisation reactions of the strained-ring silacyclobutanes have recently been studied[1,2]. We now report the first examples of compounds in which a transition metal is linked exocyclically through silicon to an intact silacyclobutane ring (see Scheme 1).

Notable are the following: (1) Although silacyclobutanes are cleaved by many nucleophiles[3], (I), at least, is stable to excess of $[CpFe(CO)_2]^-$. However, (I) reacts rapidly with excess methanolic KOH. Comparison of the action of this reagent upon $CpFe(CO)_2SiMe_3$[4,5], $CpFe(CO)_2SiMe(n\text{-}Pr)OH$ [formed by hydrolysis of (IV)], and $\overline{CH_2CH_2CH_2Si}(Me)O(Me)\overline{SiCH_2CH_2CH_2}$[6] or I reveals that the Fe–Si bond in (I) is broken as a first step, with subsequent rapid cleavage of the 4-membered ring in the organosilicon residue $[\overline{CH_2CH_2CH_2Si}(Me)O^-]$. Furthermore, the observed enhancement in the rate of Fe–Si cleavage in (I) over that found for $CpFe(CO)_2SiMe_3$ is in accord with Sommer's observations on nucleophilic substitution (S_N2-Si) at constrained endocyclic silicon[7].

(2) Both Fe–Si in $CpFe(CO)_2SiMe_3$ and Si–C in $Me_2\overline{SiCH_2CH_2CH_2}$ are rapidly cleaved by anhydrous HCl[3,5]. Parallels to both these processes are found for (I), ring cleavage predominating. The substitution, in effect, of a chloride ligand for an alkyl group on passing from (I) to (IV) deactivates Fe–Si in (IV) towards HCl attack.

(3) Catalytic polymerisation of the silacyclobutane function in (I) occurs readily; (I) was recovered (96%) after similar heating in the absence of catalyst. Reactivity with



Scheme 1. Chemistry of 1-[(π-cyclopentadienyl)dicarbonyliron]-1-methylsilacyclobutane.

respect to the electrophilic reagents $[(C_2H_4)PtCl_2]_2$ [2] and $Fe_2(CO)_9$ [1] follows the sequence (III) > (II) > (I), *i.e.*, decreasing with decreasing electron density at Fe.

(4) The conversion of (I) to (IV) or (V) provides rare[8] examples of reactions at transition metal-coordinated silicon which leave the M–Si bond intact.

(5) Substitution of carbonyl groups at iron by tertiary phosphines $[Ph_2MeP$, Ph_3P, $n\text{-}Bu_3P$, or $Ph_2PCH_2CH_2PPh_2]$ occurs with retention of the silacyclobutane unit. This parallels the substitution pattern found[9] for $CpFe(CO)_2SiMe_3$, but contrasts with that for the endocyclic complex $(CO)_4\overline{FeSi(Me_2)CH_2CH_2CH_2}$ [1] where preferential loss of the organosilicon function took place. Only monosubstituted derivatives from PPh_3 and $P(OPh)_3$ were reported for $CpFe(CO)_2SiMe_3$ [9]; (I) is not exceptional [*viz.* (II) and (III)] since with PPh_3 only monosubstitution could be detected.

(6) In common with related $CpFe(CO)_2SiXY_2$ systems[8] ($XY_2 = ClMe_2$ or $MeCl_2$) the presence of more than two infrared carbonyl absorptions (see below) indicates the existence of conformers in solutions of (IV).

All compounds gave satisfactory analyses and (I) (monomeric in benzene)–(IV) showed molecular ions in their mass spectra. Physical properties [colour, m.p., ν(CO) cm^{-1}] are: (I): amber, −17 to −15°, 2002 + 1950; (II): yellow, 106–107°, 1916; (III): orange, 176–177°, –; (IV): amber, 17–18°, 2019 + 2012 + 1969 + 1958; (V): pale grey-brown, 110–115°, 1990 + 1931 (broad).

ACKNOWLEDGEMENT

We thank the S.R.C. for support.

REFERENCES

1 C.S. Cundy and M.F. Lappert, *Chem. Commun.*, (1972) 445.
2 C.S. Cundy, C. Eaborn and M.F. Lappert, *J. Organometal. Chem.*, 44 (1972) 291.
3 R. Damrauer, *Organometal. Chem. Rev. A*, 8 (1972) 67.
4 T.S. Piper, D. Lemal and G. Wilkinson, *Naturwissenschaften*, 43 (1956) 129.
5 M.A. Nasta and A.G. MacDiarmid, *J. Organometal. Chem.*, 18 (1969) P11.
6 J. Dubac, P. Mazerolles, M. Lesbre and M. Joly, *J. Organometal. Chem.*, 25 (1970) 367.
7 L.H. Sommer, O.F. Bennett, P.G. Campbell and D.R. Weyenberg, *J. Amer. Chem. Soc.*, 79 (1957) 3296, and ref. cited in ref. (3), pp. 87–88.
8 C.S. Cundy, B.M. Kingston and M.F. Lappert, *Advan. Organometal. Chem.*, 11 (1973) 253 [notably pp. 270–271, p. 286, and also ref. (164), therein].
9 R.B. King and K.H. Pannell, *Inorg. Chem.*, 7 (1968) 1510.