Cleavage of an Iron-Silicon Bond by Hexamethylphosphoric Triamide: Synthesis and Characterization of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$

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Z. Naturforsch. **2009**, *64b,* 1553 – 1557; received August 10, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Addition of excess hexamethylphosphoric triamide (HMPA) to *cis*-$Fe(CO)_4(SiCl_3)_2$ led to the exclusive formation of the new complex $[SiCl_3(HMPA)_3]^+$ $[Fe(CO)_4SiCl_3]^-$ by cleavage of an iron-silicon bond. A reaction mechanism is presented, based on density functional theory calculations.

Key words: Iron-Silicon Bond Cleavage, Anionic Metal Silyl Complex, Hexacoordinate Silicon, DFT Calculations

Introduction

Iron silyl complexes, especially $Fe(CO)_4(SiCl_3)_2$, were shown to be useful single-source precursors in CVD processes for iron silicide films [1], which are interesting for applications as semiconductors and in photonics [2]. Zybill *et al.* proposed a mechanism for the gas-phase decomposition of $Fe(CO)_4(SiCl_3)_2$ involving an intermediate silylene complex formed by $SiCl_4$ elimination [1, 3]. We were interested whether a similar mechanism would be feasible in solution, especially whether $Fe(CO)_4(SiCl_3)_2$ could be transformed to the known donor-stabilized silylene complex $(CO)_4Fe{=}SiCl_2(HMPA)$ [1] (HMPA = hexamethylphosphoric triamide) by reaction with HMPA. We report in this article the unexpected formation of the new ionic complex $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$ in this reaction and discuss a possible reaction mechanism.

Results and Discussions

Addition of an excess of HMPA to a $[D_8]$toluene solution of *cis*-$Fe(CO)_4(SiCl_3)_2$ and sonication at r. t. led to a single new product within 10 min, as evidenced by ^{31}P NMR spectroscopy. A peak at 18.4 ppm indicated the formation of a new phosphorus-containing species, differing from free HMPA (23.7 ppm). The ^{29}Si NMR spectrum exhibited two signals at 68.1 and −205.8 ppm. The signal at 47.4 ppm in *cis*-$Fe(CO)_4(SiCl_3)_2$ was shifted to 68.1 ppm attributed to the anionic complex $[Fe(CO)_4SiCl_3]^-$. The peak at −205.8 ppm is located in the range of six-coordinated silicon compounds and indicated the formation of the cationic species $[SiCl_3(HMPA)_3]^+$ [4]. The ^{13}C NMR data showed two signals for carbonyl carbons at 216.6 and 215.7 ppm, and a signal at 36.5 ppm attributed to the carbon atoms in HMPA. From the ^1H NMR experiment a conversion of 86 % was calculated. IR measurements in toluene solution showed four absorptions in the carbonyl region of the spectrum at 2029 (w), 1951 (w), 1923 (s), 1910 (s) cm^{-1}. Scaled frequencies obtained from calculations carried out as part of the computational study (*vide infra*) on $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$ reproduced the experimental results remarkably well and showed that the doubly degenerate E vibration of a trigonal bipyramidal $Fe(CO)_4X$ compound with C_{3v} symmetry is split into two energetically different vibrations (1923 and 1910 cm^{-1}, see Table 1).

Colorless crystals grown by slow diffusion of *n*-hexane into a saturated toluene solution were chosen for X-ray diffraction measurements, which revealed the ionic complex $[SiCl_3(HMPA)_3]^+$

Table 1. Comparison of experimental and calculated ν_{CO} values (scale factor 0.98) [4].

ν_{CO} (experimental) (cm^{-1})	ν_{CO} (calculated) (cm^{-1})
2029	2029
1951	1970
1923	1955
1910	1912

Table 2. Selected bond lengths (Å) and angles (deg) of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$.

Fe(1)–Si(1)	2.229(1)	Si(2)–Cl(5)	2.202(2)
Fe(1)–C(1)	1.779(4)	Si(2)–Cl(6)	2.211(2)
Fe(1)–C(2)	1.757(4)	Si(2)–O(5)	1.763(2)
Fe(1)–C(3)	1.789(4)	Si(2)–O(6)	1.755(2)
Fe(1)–C(4)	1.786(4)	Si(2)–O(7)	1.769(2)
Si(1)–Cl(1)	2.088(2)	P(1)–O(5)	1.512(2)
Si(1)–Cl(2)	2.089(2)	P(1)–N(1)	1.623(3)
Si(1)–Cl(3)	2.095(2)	P(1)–N(2)	1.629(3)
Si(2)–Cl(4)	2.211(2)	P(1)–N(3)	1.622(3)
C(1)–Fe(1)–Si(1)	85.83(2)	Cl(1)–Si(1)–Cl(3)	101.43(5)
C(2)–Fe(1)–Si(1)	85.83(2)	Cl(2)–Si(1)–Cl(3)	100.99(5)
C(3)–Fe(1)–Si(1)	86.76(2)	Cl(1)–Si(1)–Fe(1)	116.12(5)
C(4)–Fe(1)–Si(1)	179.78(2)	Cl(2)–Si(1)–Fe(1)	117.25(5)
Cl(1)–Si(1)–Cl(2)	101.36(6)	Cl(3)–Si(1)–Fe(1)	117.00(5)

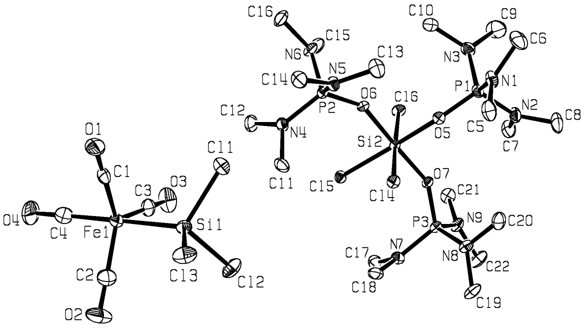

Fig. 1. ORTEP plot and crystallographic numbering scheme adopted of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$.

$[Fe(CO)_4SiCl_3]^-$. This compound is formed by cleavage of an Fe–Si bond and stabilization of the cleaved $SiCl_3^-$ ligand by three HMPA molecules, resulting in a cationic hexacoordinate silicon compound (Fig. 1, Table 2). The structural data thus confirmed the spectroscopic studies. The anionic iron complex has a trigonal-bipyramidal geometry (idealized point group C_{3v}) with the $SiCl_3^-$ ligand in an apical position. The chlorine substituents in the cationic, octahedral silicon compound have a meridional orientation. Its structure is closely related to the known $[SiCl_3(HMPA)_3]^+[HCl_2]^-$ [5]. In comparison with non-coordinated HMPA, a lengthening of the P–O bond and a concomitant shortening of the P–N bond was observed [6].

The cleavage reaction of an Fe–Si bond by hexamethylphosphoric triamide leading to the new ionic complex $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$ was additionally investigated by density functional calculations. Two possible pathways can be imagined (Fig. 2), *viz.* a mechanism involving an intermediate silylene complex or direct Fe–Si bond cleavage.

Due to steric constraints imposed by the size of HMPA and the octahedral geometry of *cis*-$Fe(CO)_4(SiCl_3)_2$, an approach to one of the equivalent iron-bonded $SiCl_3$ ligands is only possible opposite to the iron atom. Consequently, only one ground state was located for a *cis*-$Fe(CO)_4(SiCl_3)_2$-HMPA adduct (**B**, see Fig. 3). The formation of **B** is slightly endergonic at 298.15 K by $+5.9$ kcal mol^{-1} after inclusion of thermal corrections, but it is exothermic in terms of enthalpy by -10.5 kcal mol^{-1}, and no barrier was found. Slight elongation of the Fe–Si bond by 0.08 Å is concomitant with the formation of a Si–O single bond (1.71 Å). All attempts to locate a transition state leading to the formation of an intermediate silylene complex by subsequent $SiCl_4$ elimination from **B** were unsuccessful: one Si–Cl bond in **B** is significantly elongated (2.50 Å *vs.* 2.12 Å in **A**) but cannot participate in a chloride transfer because of its orientation away from the other $SiCl_3$ group. Additionally, visual inspection of the Kohn-Sham orbitals revealed an anti-bonding relationship between a region of the LUMO with *s* character on the silicon atom of the trichlorosilyl group and an orbital of the HOMO with p_z character on the chloride atom in closest proximity. Furthermore, the overall difference in Gibbs Free Energy for the alternative reaction is $+48.5$ kcal mol^{-1}, rendering this pathway thermodynamically unfavorable. In contrast, the transition state for direct bond cleavage (**TS**) exhibits an energy barrier of 14.2 kcal mol^{-1} at 298.15 K. In the transition state, the Fe–Si bond length is already dramatically increased (3.89 Å). The adjacent ground state (**C**) shows two separate species which are further stabilized by two additional HMPA groups, leading to product **D**. The overall reaction is exergonic by -10.1 kcal mol^{-1}. Values in parentheses show Gibbs Free Energies for the gas phase. Relative energies of **A**, **B**, **TS**, and **C** are similar but coordination of additional HMPA (**D**) would be unfavorable.

Conclusions

Contrary to what has been postulated for the gas-phase decomposition of $Fe(CO)_4(SiCl_3)_2$ [1, 3], its reaction with HMPA does not result in $SiCl_4$ elimina-

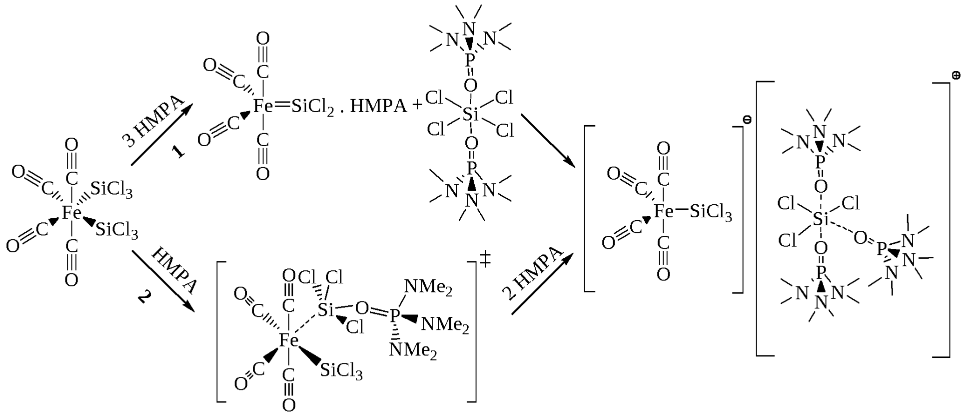

Fig. 2. Possible reaction pathways for the formation of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$.

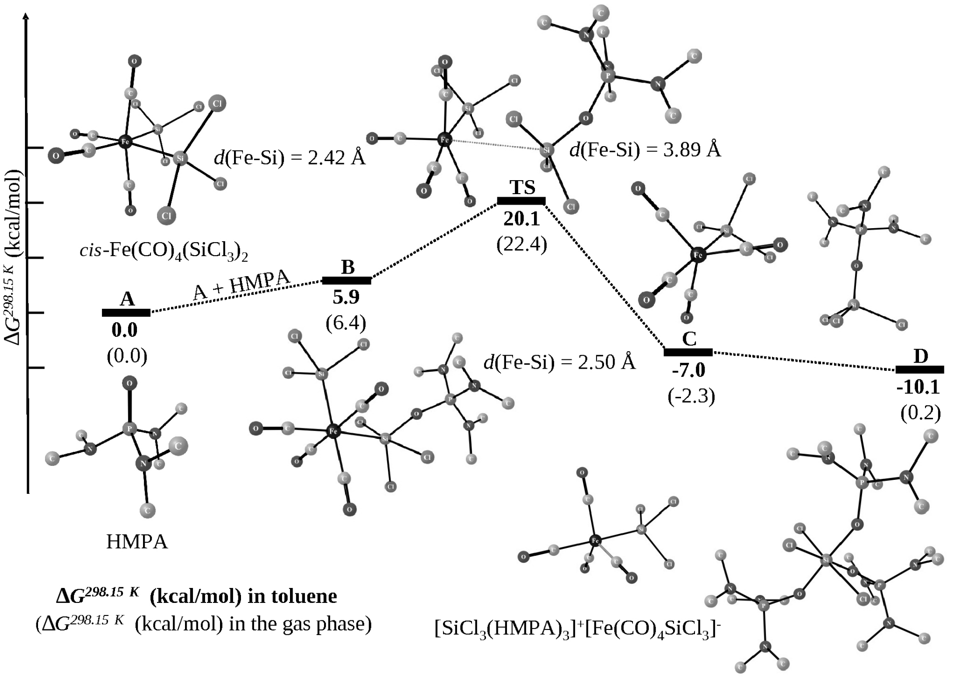

Fig. 3. Reaction profile for direct Fe–Si bond cleavage.

tion and formation of a (base-stabilized) metal silylene complex. Although one Fe–Si bond is broken, no transfer of Cl from the second $SiCl_3$ ligand is possible. This was confirmed by DFT calculations. Thus, the final product of this reaction is the new ionic complex $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon using Schlenk line techniques or a glove box. Triirondodecacarbonyl (Strem Chemicals, stabilized with 5 – 10 % methanol), trichlorosilane (Aldrich, 99 %) and hexamethylphosphoric triamide (Fluka, 98 %) were used as received. Hexane and toluene were distilled from CaH_2. $[D_8]$Toluene (99.6 %, euriso-top) used for the NMR experiments was dried over 3 Å molecular sieve and degassed. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 250 (250.13 MHz $\{^1H\}$, 62.86 MHz $\{^{13}C\}$, 100.13 MHz $\{^{31}P\}$) spectrometer. ^{29}Si NMR spectra were recorded on a Bruker Avance 300 (59.63 MHz $\{^{29}Si\}$) spectrometer. Infrared spectroscopy measurements were performed on Bruker Tensor 27 spectrometer (32 scans at resolution of 4 cm^{-1}) using a liquid cell with toluene as a sol-

Table 3. Crystal data and parameters pertinent to the structure determination of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$.

Empirical formula	$C_{22}H_{54}Cl_6FeN_9O_7P_3Si_2$
M_r	974.38
T, K	100
Crystal size, mm^3	$0.36 \times 0.29 \times 0.29$
Crystal system	orthorhombic
Space group	$Pca2_1$
a, Å	29.1479(2)
b, Å	11.4569(6)
c, Å	13.5927(7)
V, Å^3	4539.2(4)
Z	4
ρ_{calc}, g cm^{-3}	1.43
μ(MoK_α), mm^{-1}	0.9
θ range, deg	1.49 – 25.00
Reflections coll. / unique	45844/7983
Data / ref. parameters	7983/469
R [$I \geq 2\sigma(I)$]	0.031
$wR2$	0.060
GOF on F^2	1.023
Largest diff. peak / hole, e Å^{-3}	0.298 / −0.213

vent. $Fe(CO)_4SiCl_3$ was prepared by a modified procedure from literature [7].

Computations were carried out with the hybrid B3LYP density functional [8] in conjunction with double zeta basis sets 6-31G* (for N, O, P, and Si atoms), 6-31G (for C and H atoms) and the relativistic Stuttgart effective core potentials (large core for Cl atoms and small core for the Fe atom). Basis sets were retrieved from the EMSL Basis Set Exchange Library [9]. Geometry optimizations and transition state searches were carried out with the PC GAMESS version [10] of the GAMESS (US) QC package [11] without any symmetry constraints. Obtained geometries were additionally characterized by frequency calculations, exhibiting no imaginary frequencies for ground states and only one imaginary frequency for transition states. Energies include unscaled harmonic zero point energies and thermal corrections at T = 298.15 K and are therefore reported as Gibbs Free Energies. Solvent effects were computed using the Polarizable Continuum Model [12] with toluene as a solvent.

Synthesis of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$

HMPA (0.10 mL, 5.6 mmol) was added by a syringe to a solution of $Fe(CO)_4(SiCl_3)_2$ in 2 mL of [D$_8$]toluene. The reaction was continued for 10 min in an ultrasonic bath. Monitoring the reaction by ^{31}P NMR showed the reaction to be almost complete, also evidenced by almost quantitative disappearance of the starting materials in the ^{29}Si NMR spectrum. Yield 86 % (quantified by ^{1}H NMR). Slow addition of 1.5 mL of hexane gave colorless crystals of $[SiCl_3(HMPA)_3]^+[Fe(CO)_4SiCl_3]^-$. – ^{1}H NMR ([D$_8$]toluene): δ = 2.65 (54 H, CH_3). – ^{13}C NMR ([D$_8$]toluene): δ = 216.6 (CO), 215.7 (CO), 36.1 (CH_3). – ^{31}P NMR ([D$_8$]toluene): δ = 18.4 (s). – ^{29}Si NMR ([D$_8$]toluene): δ = 68.1 (Fe-$SiCl_3$), −205.8 ($Cl_3Si(HMPA)_3$). – IR (toluene): 2029 (w), 1951 (w), 1923 (s), 1910 (s) (CO) cm^{-1}.

X-Ray structure determination

Single crystal X-ray diffraction experiments were performed on a Bruker-AXS APEX diffractometer with a CCD area detector and a crystal-to-detector distance of 5.5 cm using graphite-monochromatized MoK_α radiation (λ = 71.073 pm) (Table 3). The data collection covered a full sphere of the reciprocal space by recording eight sets of exposures. Each exposure took 10 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS [13]) was applied. The cell dimensions were refined with all unique reflections. The structure was solved with Direct Methods (SHELXS-97) [14]. Refinement to convergence was carried out with the full-matrix least-squares method based on F^2 (SHELXL-97) [14] with anisotropic structure parameters for all non-hydrogen atoms. The hydrogen atoms were placed on calculated positions and refined riding on their parent atoms.

CCDC 740791 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by Shell Corp, The Netherlands. The authors thank Dr. Michael Puchberger for the NMR investigations.

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