Electronic Supporting Information

Vicinal dichlorine elimination at dichloroalkenes promoted by a well-defined iron(0) complex

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Preparation of [^{t}SiP$_3$(dmpm)Fe(C≡CCF$_3$)][Cl] (4)

Complex **4**, [^{t}SiP$_3$(dmpm)Fe(C≡CCF$_3$)][Cl], was readily prepared in quantitative yield at 100°C, using 3,3,3-trifluoropropyne and NEt$_3$. The characterization of **4** included ^{1}H, ^{31}P and ^{19}F NMR, ESI-HRMS, IR and X-Ray crystallography. The elemental composition of the **4** (595.1 *m/z*) was confirmed by ESI-HRMS with poly(ethylene glycol) exact mass internal standard. The ^{31}P{^{1}H} NMR pattern of **4** was consistent with an AA'BB'C spin system, as observed in the case of **2**.[1] The solid-state molecular structure of **4** (Fig. S-1) was determined by X-ray crystallography using crystals grown from toluene at room temperature. Numerous iron-σ-alkyne structures of the form (dppe)Cp*Fe(C≡CPh-R)[2-5] (dppe = Ph$_2$PCH$_2$CH$_2$Ph$_2$, Cp* = C$_5$Me$_5^-$) have been reported in addition to one example with a phosphorus atom *trans* to the acetylide, [(PP$_3$)Fe(C≡CPh)][BPh$_4$] (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$).[6] Comparison of the Fe–C and C≡C bond lengths of **4** with these iron-acetylides present no significant deviations. Crystallographic data and selected bond lengths and angles are presented in Tables S-1 and S-2.

Infrared characterization of **4** showed an absorbance corresponding to the C≡C stretch of the complexed propynyl ligand (2079 cm^{-1}), shifted -80 cm^{-1} from the free alkyne. This absorbance exhibited a shoulder at lower frequency (2044 cm^{-1}) which is similar to that observed with the free propyne. We assign this shoulder following Sanborn:[7] a combination band (C–C stretch + C–F stretch + C–C≡C bend) in Fermi resonance with the more intense C≡C fundamental mode. This phenomenon has also been observed in iron-(CF$_3$-phenyl)acetylide species.[6]

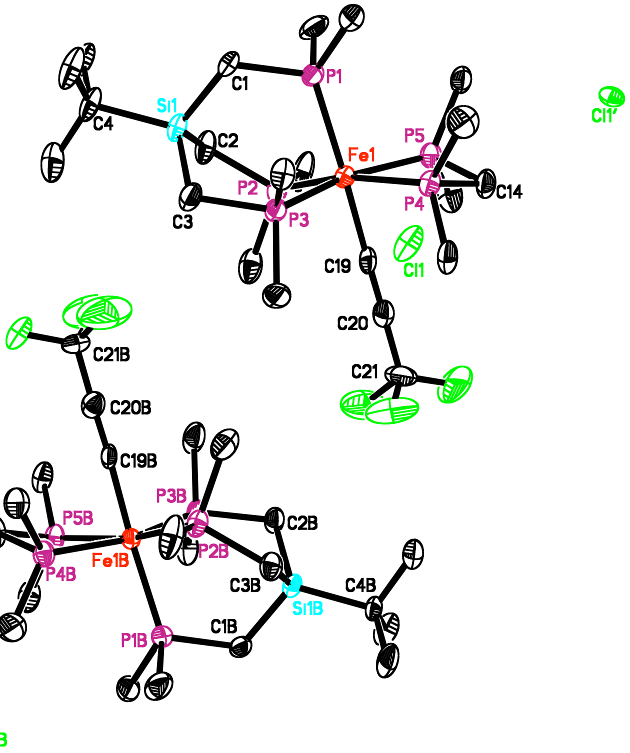

Fig. S-1. ORTEP diagram of complex **4**, $[^{t}\mathrm{SiP_3(dmpm)Fe(C{\equiv}CCF_3)}][\mathrm{Cl}]$, with thermal ellipsoids drawn at the 50% probability level. The outer-sphere chlorides in both molecules of the asymmetric unit are modeled as disordered over two positions.

Table S-1. X-ray crystallographic data.

Compound	**4**
empirical formula	$C_{21}H_{47}ClF_3FeP_5Si$
fw, g mol^{-1}	630.83
color/habit	yellow/block
crystal system	monoclinic
space group	Cc
a, Å	16.1939(2)
b, Å	12.786(2)
c, Å	31.398(5)
α, degrees	90
β, degrees	104.475(2)
γ, degrees	90
V, Å^3	6294(2)
Z	8
D_{calc}, g cm^{-3}	1.331
F(000)	2656
reflns collect	32272
ind. reflns	10842
R_1, wR_2 ($I>2\sigma(I)$)	0.0633, 0.1654
GOF	1.021

Table S-2. Bond lengths (Å) and angles (º).

Bond/Angle	**4**
Fe-P1	2.288(2)Å
Fe-P2	2.252(2)Å
Fe-P3	2.236(2)Å
Fe-P4	2.282(2)Å
Fe-P5	2.270(2)Å
Fe-C	1.899(8)Å
C≡C	1.21(1)Å
≡C–CF_3	1.41(1)Å
P4-Fe-P5	72.72(8)°
P3-Fe-P5	164.21(9)°
P2-Fe-P4	166.23(9)°
P1-Fe-R	176.6(3)°

EXPERIMENTAL PROCEDURES

General considerations. All experiments were conducted under anhydrous and anaerobic (dinitrogen) conditions using a glove box or Schlenk line. All chemicals were purchased from chemical suppliers and used as received unless noted. Toluene was distilled from sodium metal. Acetonitrile, *d_6*-benzene and *d_3*-acetonitrile were dried over calcium hydride and distilled. Triethylamine was dried with calcium hydride, degassed and stored over 4Å molecular sieves. *E/Z*-1,2-dichloro-3,3,3-trifluoropropene (DCE-CF_3), *E*/*Z*-2,3-dichlorohexafluoro-2-butene (DCE-$(CF_3)_2$), (SynQuest Laboratories, Inc.), and 1-octyne (Alfa Aesar) were degassed and stored over 4Å molecular sieves. $^tSiP_3$(dmpm)Fe (**1**), [$^tSiP_3$(dmpm)FeCl][Cl] (**2**) and [$^tSiP_3$(dmpm)FeH][PF_6] (**3**) were prepared according to literature procedures.[1]

^1H NMR spectra were obtained on Varian Inova 300 MHz. $^{31}P\{^1H\}/^{31}P$ NMR and $^{19}F\{^1H\}$ NMR spectra were obtained at 121 MHz and 282 MHz, respectively. ^1H spectra were referenced to the residual solvent peak while ^{31}P and ^{19}F NMR spectra were referenced to external 85% H_3PO_4 and CF_3-toluene, respectively. Electrospray ionization high-resolution mass spectra (ESI-HRMS), in positive polarity, were collected on a Bruker II BioTOF mass spectrometer. Gas chromatography-mass spectrometry (GC/MS) data was collected on an Agilent 6890 gas chromatograph (Phenomenex ZB-624, 60 m x 0.32 mm i.d., 1.8 mm film thickness) coupled with an Agilent 5973 Mass Selective detector operated in selective ion mode. Infrared (IR) spectra were collected with a Midac M series spectrometer.

X-ray Crystallography. The crystal structure of **4** was collected using a Siemens SMART Platform CCD diffractometer at 173(2) K using a graphite monochromator and Mo Kα radiation. Structures were solved using SIR-97[8] and refined with SHELXL-97.[9] Crystallographic data for these complexes are given in Table S-1.

The crystal of complex **4** was modeled as a racemic twin with the SHELXL TWIN command as 50.3% of the opposite enantiomer. The outersphere chloride anion was modeled as disordered over two positions (74:26). Addsymm found a 93% detection of pseudo symmetry (inversion center) and suggested solving the structure in space group C2/c (centrosymmetric) rather than Cc (non-centrosymmetric). Attempts to refine the structure in C2/c were unsuccessful (R_1 = 19.15, ($I>2\sigma(I)$)). Overlaying the two asymmetric molecules in the unit cell displayed a slight difference in the twist of $^{t}SiP_3$, in addition to the disordered chlorides, signifying the non-centrosymmetric nature of this molecule.

[$^{t}SiP_3$(dmpm)Fe(C≡CCF_3)][Cl] (4). Complex **4** was prepared by two methods. **Method A**: A solution of **2** (0.035 mmol) in 700 μL CD_3CN was placed in a sealable NMR tube with 5 equivalents of NEt_3 (26 μL, 0.18 mmol). A total of 1.2 equivalents of 3,3,3-trifluoropropyne were quantitatively gas transferred to the vessel in four separate events to avoid over pressurizing the tube. In between each addition, the reaction mixture was heated to 100°C for 0.5-2 hours. The solution was filtered and the solvent from the resulting filtrate was removed *in vacuo* to give a red-orange solid (0.034 mmol, 97% yield). Yellow, X-ray quality crystals were obtained from slow evaporation of toluene.

Method B: To a solution of **1** (13.6 μmol) in 700 μL C_6D_6 was added approximately one equivalent of 3,3,3-trifluoropropyne in a sealable NMR tube and mixed by inversion. Immediately following, 1.1 equivalents of **2** (stock solution in ACN, 15.1 μmol, 151 mM) was added to the reaction mixture and mixed. The solvent was removed under reduced pressure and the solid redissolved in 700 μL CD_3CN. Approximately 29% conversion to **4** was observed by NMR, as determined by integration to internal standard, diethylphenylphosphine (29 mM). ^1H NMR (300 MHz, CD_3CN, 25° C) δ ppm 0.86 (m, 2H, CH_2-$^tSiP_3$); 0.90 (s, 9H, ^tBu-Si); 0.93 (m, 4H, CH_2-$^tSiP_3$); 1.34 (m, 6H, Me-$^tSiP_3$); 1.54-1.70 (overlapping m, 24H, Me-$^tSiP_3$ and Me-dmpm); 2.68 (m, 1H, CH_2-dmpm); 3.49 (pseudo q, "J_{HP}" = 13 Hz, 1H, CH_2-dmpm). $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN, 25° C) δ ppm -3.6 (m, 2P, dmpm); 17.4 (tt, J_{PP} = 41, 52 Hz, 1P, $^tSiP_3$); 24.8 (m, 2P, $^tSiP_3$). $^{19}F\{^1H\}$ NMR (282 MHz, CD_3CN) δ ppm -45.3 (s, CF_3). IR (CH_2Cl_2 thin film, cm^{-1}) 2079, C≡C stretch. HRMS-TOF (*m/z*): $[M\text{-}Cl]^+$ calcd for $C_{21}H_{47}FeP_5SiF_3$, 595.1437; found, 595.1425.

Product ratio and mass balance determination: DCE-CF and DCE-(CF_3)$_2$. Addition of substrate to **1**: A solution of **1** in 2.15 mL toluene (24.0 μmol, 11.2 mM) was prepared in a 25 mL vial equipped with a stirbar and septum. 500 μL of an 48.0 mM stock solution of DCE-CF_3 or DCE-(CF_3)$_2$ solution was added dropwise (over approximately ~10 min) to the solution of **1**, through the septum. The solution was allowed to stir for 20 min before removing the volatiles *in vaccuo*. The resulting solid was carefully redissolved in 800 μL CD_3CN and transferred to an NMR tube. Tetrabutylammonium hexafluorophosphate was added as an internal standard (21 mM). Quantitative ^{31}P NMR was used to quantify each product and calculate the mass balance through integration of the well-resolved dmpm-^{31}P resonances of the products, referenced to the internal standard. Samples were conducted in triplicate. Addition of **1** to substrate: The same procedure was employed as described above except DCE-CF_3 or DCE-$(CF_3)_2$ (24.0 µmol, 11.2 mM) was in the original vial and a stock solution of **1** (500 µL, 48.0 mM) was added dropwise through the septum.

Volatile species analysis and reaction stoichiometry determination: DCE-CF and DCE-$(CF_3)_2$. Triplicate batches of five different volumes (0-200 µL) of a 136 mM stock solution of **1** in toluene was added dropwise, through a septum to 1.5 mL vials charged with 50 µL of 136 mM DCE-CF_3 or DCE-$(CF_3)_2$ and the appropriate amount of toluene such that the final volume totaled 1.1 mL. The solutions were allowed to stir for 20 min before analyzing them by headspace GC/MS. Concentrations were determined from calibration curves prepared from authentic standards in the same vials with identical head space volume.

References

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STANDARD 1H OBSERVE

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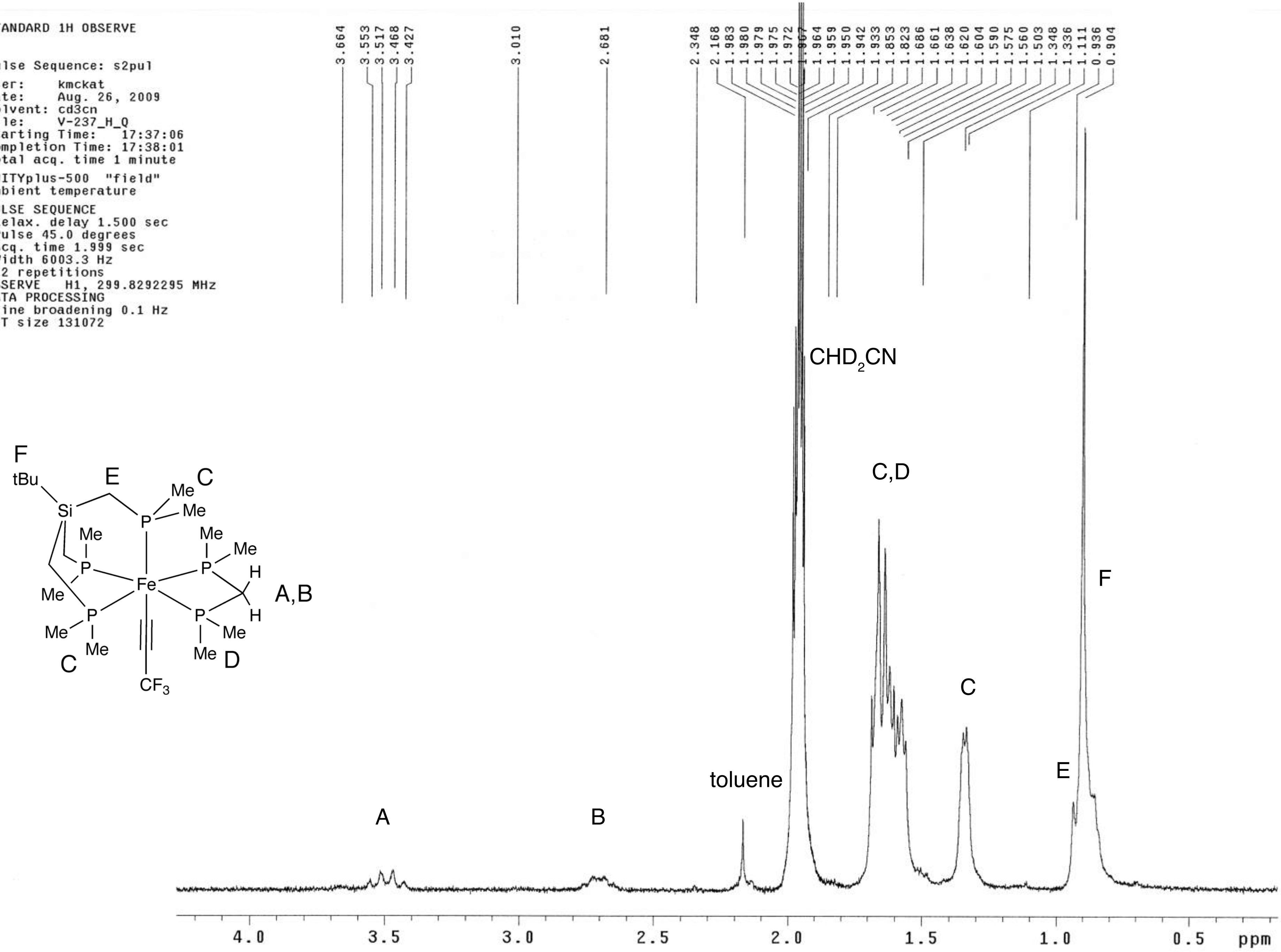

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P-31 STANDARD PARAMETERS
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