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THE PREPARATION AND REARRANGEMENT OF HALOMETHYLSILYLIRON COMPLEXES. THE ANOMALOUS REACTION BETWEEN SODIUM η^5-CYCLOPENTADIENYLDICARBONYLFERRATE AND BROMOMETHYLDIMETHYLCHLOROSILANE

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Summary

The halomethylsilyl complexes $Cp(CO)_2FeSiMe_nCl_{2-n}CH_2X$ (I: X = Cl, n = 2; II: X = Cl, n = 1; III: X = Cl, n = 0; VIII: X = Br, n = 2) were prepared by the metathesis between $ClCH_2SiMe_nCl_{3-n}$, $ClCH_2SiMe_2Br$ or $BrCH_2SiMe_2Br$ and $NaFe(CO)_2Cp$. The reaction between $BrCH_2SiMe_3$ and $NaFe(CO)_2Cp$ afforded $Cp(CO)_2FeCH_2SiMe_3$ (IV). Complexes I and II undergo quantitative, thermal, unimolecular rearrangement to $Cp(CO)_2FeCH_2SiMe_2Cl$ (V) and $Cp(CO)_2FeCH_2SiMeCl_2$ (VI), respectively. III was rearranged catalytically by $AlCl_3$ to $Cp(CO)_2FeCH_2SiCl_3$. The binuclear complexes $Cp(CO)_2FeSiMe_nCl_{2-n}CH_2Fe(CO)_2Cp$ (n = 2, 1, 0) also were prepared and characterized.

The reaction between $NaFe(CO)_2Cp$ and $BrCH_2SiMe_2Cl$ afforded $BrCH_2SiMe_2CH_2SiMe_2Cl$ or $Cp(CO)_2FeSiMe_3$, depending on the reaction conditions. When the reaction was carried out in the presence of 1,3-diphenylisobenzofuran the Diels—Alder adduct of 1,1-dimethylsilaethylene and 1,3-diphenylisobenzofuran was not observed.

Introduction

Our interest in the chemistry of neutral alkyl and cationic alkene complexes of the type $Cp(CO)_2FeR$ and $[Cp(CO)_2Fe(alkene)]^+$ led us to prepare the chloromethylsilyl complexes ($Cp(CO)_2FeSiMe_nCl_{2-n}CH_2Cl$) with a view toward transforming these substances into cationic silaethylene complexes. Herein, we

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report the preparation, characterization and thermal rearrangement of the aforementioned chloromethylsilyliron complexes. In addition, we report the novel reduction of $BrCH_2SiMe_2Cl$ by $NaFe(CO)_2Cp$.

Results

The Fe—Si complexes I-III were obtained as orange crystalline solids in ca. 50% yield from the metathesis between $ClCH_2SiMe_nCl_{3-n}$ and $NaFe(CO)_2Cp$ (eqn. 1) when the reactants were mixed at 0°C, and the products isolated carefully by fractional crystallization. Complexes I and II were isomerized quantitatively when heated at 100°C, to the Fe—C isomers V and VI, which also were obtained directly by sublimation or distillation of the aforementioned reaction residue. Although complex III is thermally stable, it was isomerized by $AlCl_3$ at 24°C to the Fe—C isomer (VII) in 22% yield. Although III was completely consumed, the fate of the remainder of III is not known.

$$ClCH_2SiMe_nCl_{3-n} \xrightarrow{NaFe(CO)_2Cp} Cp(CO)_2FeSiMe_nCl_{2-n}CH_2Cl \qquad (1)$$

(I: $n = 2$;
II: $n = 1$;
III: $n = 0$)

$Cp(CO)_2FeCH_2SiMe_nCl_{3-n}$

(IV: $n = 3$; V: $n = 2$;
VI: $n = 1$; VII: $n = 0$)

The identities of the Fe—C and Fe—Si isomers were established by elemental analyses and by comparison of the spectroscopic and chemical properties of each type of complex. Thus, the methylene resonances of I-III were observed between τ 6.63 and 7.02 ppm, a region characteristic of a chloromethyl group. In addition, the diastereotopic methylene protons of II exhibited an AB resonance and, thereby, demonstrated the chirality of the adjacent silicon center. The methylene protons of V-VII were highly shielded by the adjacent silicon and iron groups and were observed between τ 9.87 and 10.21 ppm. The analogous resonance of IV has been reported at τ 10.28 ppm [1].

Although the IR spectra of the Fe—C and Fe—Si isomers were rather uninformative, there were observed for each of the Fe—Si isomers, II and III, four absorptions near 2000 cm^{-1} instead of the expected pair of absorptions typical of $Cp(CO)_2FeL$ complexes. A similar phenomenon has been reported previously and attributed to rotamers, the equilibration of which is relatively slow on the IR time scale [2]. All of the Fe—C isomers exhibited only two carbonyl absorptions near 2000 cm^{-1}.

The UV spectra of the Fe—C and Fe—Si isomers were distinctive. Each of the Fe—Si isomers exhibited a low frequency absorption near 31200 cm^{-1} typical of a silyl—iron complex [3], whereas each of the Fe—C isomers exhibited a low frequency absorption near 27600 cm^{-1} which is in good agreement with the value of 28300 cm^{-1} reported for $Cp(CO)_2FeMe$ [4].

The Fe—C isomers behave chemically in a manner typical of alkyl—iron complexes. For example, hydrogen chloride, which converts $Cp(CO)_2FeMe$ to $Cp(CO)_2FeCl$ and methane [4], cleaved the Fe—C bonds of IV-VI to form $Cp(CO)_2FeCl$ and the appropriate methylchlorosilane.

$$\underset{\text{(IV-VI)}}{Cp(CO)_2FeCH_2SiMe_nCl_{3-n}} \xrightarrow{HCl} Cp(CO)_2FeCl + Me_{n+1}SiCl_{3-n} \quad (n = 1, 2, 3) \qquad (2)$$

The Fe—Si bond is cleaved in the opposite manner to afford $Cp(CO)_2FeH$ and the appropriate chlorosilane [3].

The rate of rearrangement (determined by PMR spectroscopy) of I to V is first order in I and independent of the concentration of I. The rate of rearrangement is dependent on the solvent and becomes greater in more polar solvents. Thus, in cyclohexane $k = 0.038 \pm 0.004$, in tetrahydrofuran $k = 0.099 \pm 0.009$, and in methylene chloride $k = 0.53 \pm 0.05\ h^{-1}$.

The metathesis between $ClCH_2SiMe_2Br$ and $NaFe(CO)_2Cp$ afforded V (eqn. 3) when the product was isolated by sublimation. Bromomethyldimethylbromosilane afforded, after careful workup, the bromomethylsilyl complex VIII, which readily rearranged to the Fe—Si isomer IX at 0°C (eqn. 4). The spectroscopic properties of both VIII and IX are comparable to the analogous properties of I and V.

$$ClCH_2SiMe_2Br \xrightarrow{NaFe(CO)_2Cp} [ClCH_2SiMe_2Fe(CO)_2Cp] \rightarrow \underset{\text{(V)}}{ClSiMe_2CH_2Fe(CO)_2Cp} \qquad (3)$$

$$BrCH_2SiMe_2Br \xrightarrow[0^{\circ}C]{NaFe(CO)_2Cp} \underset{\text{(VIII)}}{BrCH_2SiMe_2Fe(CO)_2Cp} \xrightarrow{<24^{\circ}C} \underset{\text{(IX)}}{BrSiMe_2CH_2Fe(CO)_2Cp} \qquad (4)$$

The binuclear complexes, X and XI, were prepared by treatment of the appropriate chloromethylchlorosilane with two equivalents of $NaFe(CO)_2Cp$. Complex XII was obtained in low yield from VII.

$Cp(CO)_2FeSiMe_nCl_{2-n}CH_2Fe(CO)_2Cp$

(X: $n = 2$;
XI: $n = 1$;
XII: $n = 0$)

When equimolar amounts of $BrCH_2SiMe_2Cl$ and $NaFe(CO)_2Cp$ were mixed at —196°C and allowed to warm to 24°C, 1-bromo-4-chloro-2,2,4-trimethyl-2,4-disilapentane XIII was obtained as a major (45%) product (eqn. 5). The addition of 1 equivalent of $BrCH_2SiMe_2Cl$ to a solution of two equivalents of $NaFe(CO)_2Cp$

$$NaFe(CO)_2Cp + BrCH_2SiMe_2Cl \rightarrow \underset{\text{(XIII)}}{BrCH_2SiMe_2CH_2SiMe_2Cl} + [Cp(CO)_2Fe]_2 \qquad (5)$$

and 1 equivalent of 1,3-diphenylisobenzofuran (XIV) did not yield a Diels—Alder adduct of 1,1-dimethylsilaethylene and XIV. A number of mono- and binuclear complexes was obtained when the crude reaction product was chromatographed. Although $Cp(CO)_2FeSiMe_3$ was only observed in small yield in the latter reaction, this complex was obtained in 42% yield when moist tetrahydrofuran was substituted for the anhydrous solvent used in the preparation of $NaFe(CO)_2Cp$.

Discussion

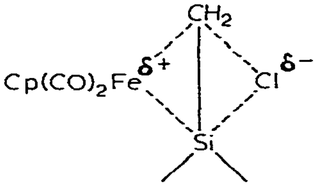
In view of the reported M—C and M—Si bond strengths, the rearrangement of the chloromethylsilyl complexes, I-III, to the chlorosilylmethyl complexes is surprising. The M—Si bond strengths for the series Cl_3Si— (126 ± 25), F_2MeSi— (127 ± 15), F_3Si—$Co(CO)_4$ (105 ± 12 kcal mol^{-1}), which were determined mass spectrometrically, are based on a rather uncertain value of ΔH_f^0 for $Co_2(CO)_8$ [5]. The value of ΔH_f^0 used to determine these bond strengths may be high and the reported bond strengths, therefore, may actually be some 30 kcal mol^{-1} lower. When the error in the determination is also considered, the Co—Si bond strengths may be as low as 71, 82, and 63 kcal mol^{-1}, respectively. The smaller bond energies are consonant with the recently reported Mn—Si bond strength of 54 kcal mol^{-1} [6] and are consistent with the reported bond strengths for M—Ge and M—Sn bonds [6]. When 53 kcal mol^{-1} is used as the upper limit for the reported M—C bond strengths ($(CO)_5Re$—Me) [7], the difference between the reported M—C and M—Si bond strengths is reduced to ~0-30 kcal mol^{-1}.

An upper limit on the difference between Fe—C and Fe—Si bond strengths can be estimated for the chloromethylsilyl and chlorosilylmethyl complexes. In particular, the quantitative rearrangements of I → V and II → VI demonstrate that the processes are exothermic by at least 2 kcal mol^{-1}, assuming that entropy changes are negligible. Using reported Si—Cl (96, [8a] or 88 ± 2 kcal mol^{-1} [8b]) and C—Cl (83.5 kcal mol^{-1} [9]) bond energies, the Fe—Si bond strengths in II and III are estimated to be no more than 10 kcal mol^{-1} greater than Fe—C bond strengths in V and VI. A similar analysis of bromomethylsilyl (VIII) and bromosilylmethyl (IX) complexes (taking the Si—Br [8c] and C—Br [9] energies as 69 and 79 kcal mol^{-1}, respectively) shows that the Fe—Si bond in VIII can be no more than 8 kcal mol^{-1} stronger than the Fe—C bond in IX. It appears that the Fe—Si and Fe—C bond strengths are similar and the possibility that the Fe—C bond is actually stronger than the Fe—Si bond cannot be excluded.

The reported values of M—C and M—Si bond strengths and the results of the work reported here make extremely tenuous the argument that the enhanced kinetic stability of silyl transition metal complexes, as compared to the iso-structural alkyl complexes, is a result of an inherently stronger M—Si bond [10]. Although a relatively strong M—Si bond has been attributed to partial multiple bonding via d_π—d_π interaction, there is evidence that supports the thesis that d_π—d_π bonding is not important in complexes with nonelectrophilic silyl ligands whereas such bonding becomes more important in halosilyl complexes. First, the photoelectron spectra of silyl complexes of the type H_3SiML_n show no evidence for d_π—d_π bonding between the metal and the silyl ligand [11]. Second, the rotational isomerism observed in chloro-, and dichlorosilyl complexes [2] but not in alkylsilyl complexes [3], suggests that d_π—d_π bonding is contributing to a rotational energy barrier in the first case but not in the second.

Third, the trend in Co—Si bond strengths [5] and lengths [12] is consonant with enhanced d_π—d_π bonding for the complexes with shorter and stronger bonds.

Enhanced Fe—Si d_π—d_π bonding in the complexes with the more electrophilic ligands is also consistent with the qualitative rates of rearrangement for the chloromethyl- and bromomethyl-silyl complexes. A kinetic study of the rearrangement of I to V demonstrated that this process is unimolecular and proceeds through a slightly polar transition state, which can be envisaged as one involving simultaneously migrating chloride and iron groups. The cleavage of the C—Cl bonds in I-III is probably not rate determining since these bonds should be energetically similar. The Fe—Si bond energy will vary greatly because of increased d_π—d_π bonding in the more highly chlorinated silyl complexes. Therefore, the cleavage of the Fe—Si bond is rate determining and the energy of this bond will strongly influence the activation energy of the rearrangement. Thus, the rate of rearrangement will decrease as d_π—d_π bonding becomes more important. Indeed, this appears to be the case. The relative electrophilicity, hence the extent of d_π—d_π bonding in the iron—silyl complexes, will increase in the following order: $SiMe_2CH_2Br < SiMe_2CH_2Cl < SiMeClCH_2Cl < SiCl_2CH_2Cl$. As predicted, the rate of rearrangement is opposite to this trend. Thus, VIII rearranged at 0°C. I and II rearranged near 100°C and III could only be rearranged catalytically. It is remarkable that III, which should exhibit the greatest d_π—d_π bonding and hence possess the strongest Fe—Si bond, still rearranged to the Fe—C isomer VII.

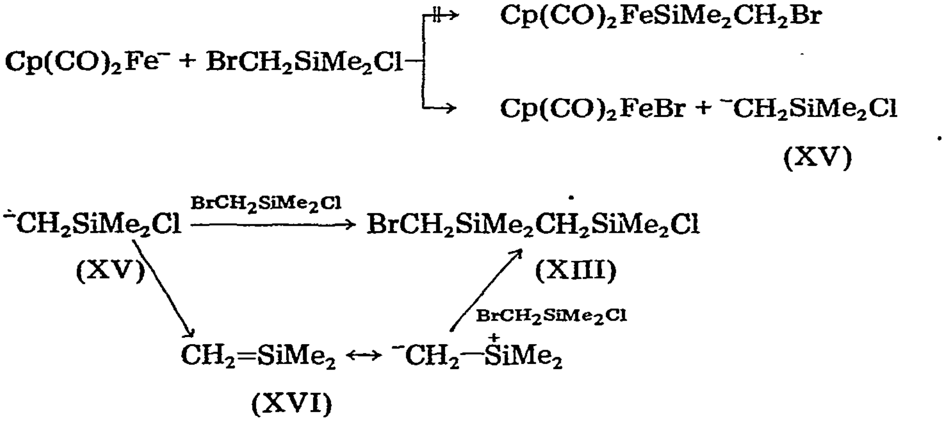


Certainly our results strongly support the contention that the kinetic stability of silyl transition metal complexes is attributable to the inaccessibility of a low energy degradative pathway (i.e. alkene formation via metal hydride elimination) and not because of an inherently more stable M—Si bond [13].

The anomalous reaction between $NaFe(CO)_2Cp$ and $BrCH_2SiMe_2Cl$

In the initial attempt to form the bromomethylsilyl complex VIII, $BrCH_2SiMe_2Cl$ was used. Surprisingly, when the reactants were mixed at —196°C and allowed to warm to 24°C, $NaFe(CO)_2Cp$ was quantitatively oxidized to $[Cp(CO)_2Fe]_2$. The other major product was 1-bromo-4-chloro-2,2,4-trimethyl-2,4-disilapentane (XIII). There are two reasonable pathways by which XIII could have been formed. Both pathways involve the initial formation of the chlorosilylcarbanion XV. The metathesis between XV and $BrCH_2SiMe_2Cl$ would yield XIII. Alternatively, XV may eliminate Cl^- to form 1,1-dimethylsilaethylene (XVI) (Scheme 1). Since the p_π—p_π bond of XVI is calculated to be strongly polarized toward carbon [14], XVI is expected to insert into the Si—Cl bond of $BrCH_2SiMe_2Cl$ to form XIII. In fact, this mode of reactivity has recently been reported for XVI [15].

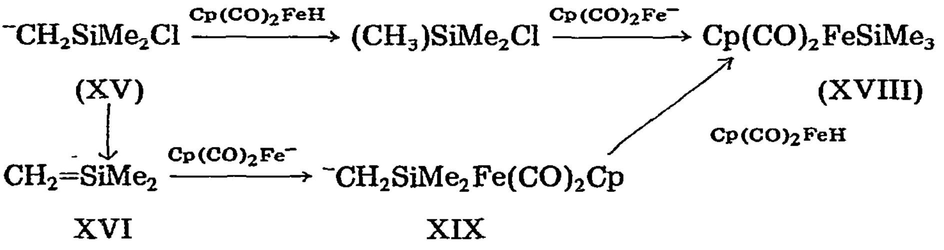
SCHEME 1



Strong but not conclusive experimental support for a silaethylene intermediate would have been provided by the formation of a silaethylene-1,3-diphenyl isobenzofuran Diels—Alder adduct (XVII). Recognizing that the reduction process is faster than nucleophilic addition of $Cp(CO)_2Fe^-$ to either $BrCH_2SiMe_2Cl$ or XIII (<2% yield of silyl complexes were formed in the aforementioned reduction), $BrCH_2SiMe_2Cl$ was slowly added to a tetrahydrofuran solution of $NaFe(CO)_2Cp$ and 1,3-diphenylisobenzofuran at 0°C, conditions that would minimize the formation of XIII and maximize the formation of XV. The Diels—Alder adduct XVII was not isolated nor observed in the reaction mixture.

A small amount of the trimethylsilyl complex XVIII was observed among a relatively large number of mono- and binuclear complexes formed in this reaction. The yield of XVIII was increased to 42% when $NaFe(CO)_2Cp$ was prepared in moist tetrahydrofuran rather than the anhydrous solvent. Recently, it has been shown that $Cp(CO)_2FeH$ is the source of hydrogen in reductions of this type [16]. Thus, the formation of XVIII may be envisioned as occurring by protonation of XV by $Cp(CO)_2FeH$ and subsequent metathesis of the resulting

SCHEME 2



trimethylchlorosilane with $NaFe(CO)_2Cp$. Alternatively, XVIII could have been formed by addition of $Cp(CO)_2Fe^-$ to XVI followed by protonation of the resulting carbanion XIX by $Cp(CO)_2FeH$ (Scheme 2). Since XVI has been shown to be a potent electrophile [17], the addition of $Cp(CO)_2Fe^-$ to XVI would not be unexpected.

It is interesting to note here that the reductions of 1,2-dihalobenzocyclobutenes [16] and 1,4-dibromo-2-butyne [18] by $NaFe(CO)_2Cp$ and $Cp(CO)_2FeH$ apparently involve the initial generation of benzocyclobutadiene and butatriene, respectively. These two reactive hydrocarbons subsequently react with $Cp(CO)_2Fe^{\bullet}$ and/or $Cp(CO)_2FeH$ to afford mononuclear products via radical pathways. The formation of XIII in the reaction between $BrCH_2SiMe_2Cl$ and $NaFe(CO)_2Cp$ militates against a radical mechanism in this instance.

The reduction of $BrCH_2SiMe_2Cl$ is significant for two reasons. To our knowledge, this is the first example of nucleophilic attack on a reactive and unencumbered chlorosilyl substrate not occurring at silicon. Secondly, this is the first example of $^-Fe(CO)_2Cp$ effecting a two electron reduction of a primary carbon that is normally highly susceptible to nucleophilic substitution.

The nature of the reactive intermediate (XV or XVI) in this reduction is still unknown. A solution of this problem must await the development of an experimental test that will be uniquely diagnostic of XV or XVI.

Experimental

Materials

Chloromethyldimethylchlorosilane, chloromethylmethyldichlorosilane, bromomethyldimethylchlorosilane, and chloromethyltrichlorosilane (Pierce Chemical Company) were distilled in the vacuum line and trapped at —78°C. Methylene chloride (Fisher Chemical Company) was distilled from phosphorous pentoxide (Fisher). Tetrahydrofuran (Fisher) was stored over lithium aluminum hydride (Alfa Inorganics, Inc.) and was distilled in the vacuum line prior to use. Pyridine and acetone (Fisher) were dried over activated Linde 4A Molecular Sieves. Aluminum chloride (Hall Chemical Company) was sublimed prior to use. Dicyclopentadiene (Eastman), cyclohexane (J.T. Baker Chemical Company), hexane (Fisher), iron pentacarbonyl (GAF), neutral alumina (Fisher), carbon tetrachloride (Fisher), and sodium (Alfa) were used as received. All manipulations of the iron complexes were performed under nitrogen or in a nitrogen-flushed dry box. Solutions (nitrogen-saturated) were handled using nitrogen-flushed syringes.

Part of the experimental work was carried out in a vacuum line using standard techniques: IR spectra were recorded on a Perkin—Elmer 521 Grating Infrared Spectrometer, which was calibrated with deuterium chloride (2100-1900 cm^{-1}) or polystyrene. Concentrations of the samples used for the determination of the carbonyl stretching frequencies were 0.4 mg ml^{-1}. Potassium bromide cells, 0.1 mm, were used. To determine the positions of the carbonyl stretching frequencies, the range 2100-1900 cm^{-1} was expanded four times over the normal instrument settings and a scanning rate of 60 cm^{-1} min^{-1} was used. PMR spectra were recorded on a Varian Associates Model A-60 Nuclear Magnetic Resonance Spectrometer on a JEOL JNM-MH-100 Nuclear Magnetic Resonance Spectrometer, calibrated with a 12% chloroform solution of tetramethylsilane. PMR spectra of the silanes and iron compounds were determined on 0.5 *M* or saturated, when the complexes were less soluble, solutions. The solvent was cyclohexane unless otherwise specified. UV spectra were obtained on a Cary 14 Double Beam Spectrometer in hexane using matched quartz cells. Melting points were done in evacuated or nitrogen filled tubes and are uncorrected.

Unless otherwise stated, the reaction mixtures were worked up immediately after the reactants had been mixed and the mixture warmed to 24°C.

Kinetic measurements

The samples were prepared by dissolving about 0.1 g of a complex in 1 ml of the solvent, filtering into an NMR tube, and sealing off the tube under vacuum. The measurements were performed by inserting the samples into a thermostated water bath (±0.05°C) and recording PMR spectra of the samples at specified intervals. When the samples were not in the bath or spectrometer, they were kept at 0°C to minimize isomerisation. First order rate constants were obtained by plotting A/A_0 vs. time (h). When decomposition was observed, the samples were centrifuged to obtain sharp spectra. Changes in the rates were not observed over a two-fold change in the initial concentrations of the complexes. Data used in the analyses were the result of at least two experiments.

Thermal isomerizations

Isomerizations were carried out using 0.1 to 0.3 g of a complex at the specified conditions in evacuated ampules. Analyses of the products were performed by comparing the IR and/or PMR spectra of these substances with the spectra of authentic samples.

Analyses

Hydrolyzable halides were determined by hydrolyzing the compounds in an acetone/water solution and titrating with standardized sodium hydroxyde solution using phenolphthalein as an indicator.

Iron was determined by oxidizing carefully a complex with 40% nitric acid, evaporating to dryness, and dissolving the residue in 6 *M* hydrochloric acid. Concentrated sulfuric acid, 15 ml, was added carefully and the hydrochloric acid was boiled off. Water, 25 ml, was added, and the mixture was warmed to dissolve the solids to yield a yellow solution. The iron was reduced by heating with aluminum wire until the yellow color disappeared. The excess wire was removed and the solution titrated immediately with standardized potassium permanganate solution to a pink endpoint.

Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of chloromethyldimethylbromosilane

1,3-Bis(chloromethyl)-1,1,3,3-tetramethyldisilazane, 12 g (0.0524 mol) and 100 ml of dry pentane were placed in a 500 ml three-necked flask equipped with a mechanical stirrer, gas addition tube and reflux condenser attached to a Nujol bubbler. Hydrogen bromide was added to the solution at a rate sufficient to maintain reflux. Copious amounts of a white solid precipitated from the reaction mixture. The addition of hydrogen bromide was discontinued when the reaction mixture had cooled to room temperature. The volatile products and solvent were separated from the ammonium bromide by vacuum distillation.

The clear, colorless distillate was redistilled at atmospheric pressure through an 8 cm Vigreux column and 12 g of a fraction boiling between 128 and 140°C, the bulk of it boiling at 135°C, was collected; PMR (cyclohexane) τ (ppm) 7.07 (s, 2, CH_2), 9.38 (s, 6, Me); IR (10 cm CsI cell) 2975m, 2940w, 1490m, 1250s, 1160w, 1070w, 840w(sh), 810vs, 740m, 670w, 620m, 490m, 400s cm^{-1}. (Found: C, 19.49; H, 4.34; Br, 42.53; Cl, 18.62. $C_3H_8BrClSi$ calcd.: C, 19.09; H, 4.26; Br, 42.44; Cl, 18.83%.)

Preparation of bromomethyldimethylbromosilane

To 17.4 g (0.114 mol) of $BrCH_2SiMe_2H$ in 50 ml of carbon tetrachloride was added slowly 18.2 g (0.14 mol) of bromine in 25 ml of carbon tetrachloride. After the mixture had been stirred for 1 h, the excess bromine was destroyed by the addition of mercury. The mixture was filtered and the carbon tetrachloride was removed from the filtrate by distillation at 760 Torr. The high boiling residue was vacuum distilled (24°C/10^{-5} Torr) into a —45°C trap to yield 11.6 g (45%) of $BrCH_2SiMe_2Br$; PMR (cyclohexane) τ (ppm) 7.38 (s, 2, CH_2), 9.32 (s, 6, Me); IR (10 cm CsI cell) 2980w, 2920vs, 1138w, 1258m, 1115w, 1080w, 840s, 785m, 635w, 565w, 480w, 390w cm^{-1}. (Hydrolyzable bromine found: 34.40. $C_3H_8Br_2Si$ calcd.: 34.33%.)

Preparation of $Cp(CO)_2FeCH_2SiMe_3$

Chloromethyltrimethylsilane, 13.5 g (0.11 mol), in 50 ml of tetrahydrofuran, was added to a solution of 0.01 mol of $NaFe(CO)_2Cp$ in 300 ml of tetrahydrofuran. After 1 h at 24°C, the solvent was rotary evaporated. Distillation (65°C/10^{-2} Torr) of the resulting red oil afforded 15.0 g (57%) of $Cp(CO)_2FeCH_2SiMe_3$. Although initially a liquid at room temperature, the product crystallized rapidly forming large dark orange-red crystals which were air stable for extended periods. M.p. 28-30°C; PMR (cyclohexane) τ 5.28 (s, 5, Cp), 9.94 (s, 9, Me), 10.28 (s, 2, CH_2); IR (hexane) 2013, 1963 cm^{-1} (C≡O). (Found: C, 50.13; H, 6.45. $C_{11}H_{16}FeO_2Si$ calcd.: C, 49.81; H, 6.03%.)

Preparation of $Cp(CO)_2FeSiMe_2CH_2Cl$

Into a filtered solution of $NaFe(CO)_2Cp$ (0.02 mol) in 50 ml of tetrahydrofuran was distilled 2.82 g (0.02 mol) of $ClCH_2SiMe_2Cl$. After the mixture had been stirred for 20 min at 0°C, 30 ml of the solvent was removed in vacuo and 30 ml of hexane was added. The mixture was centrifuged and the residue was extracted with two 30 ml portions of hexane. The extracts were combined with the supernatant liquid, concentrated to 20 ml at 0°C, and diluted to 60 ml with hexane. This solution was filtered through a fine sintered glass disk. The crystalline product, which was obtained by cooling the filtrate to —78°C and decanting the supernatant liquid, was dried in vacuo at 0°C, to yield 3.43 g (60%) of $Cp(CO)_2FeSiMe_2CH_2Cl$. M.p. 30-31°C; PMR (cyclohexane) τ (ppm) 5.30 (s, 5, Cp), 7.02 (s, 2, CH_2), 9.56 (s, 6, Me): IR (hexane) 2010(sh), 2004, 1951 cm^{-1} (C≡O); UV (hexane) (ϵ), 31400 (2400), 37000 (8260) (sh), 41700 (11200) (sh) cm^{-1}. The complex was further characterized by its quantitative isomerization to $Cp(CO)_2FeCH_2SiMe_2Cl$.

Preparation of $Cp(CO)_2FeCH_2SiMe_2Cl$

Chloromethyldimethylchlorosilane, 2.68 g (0.018 mol) was distilled into a solution of $NaFe(CO)_2Cp$ (0.02 mol) in 50 ml of tetrahydrofuran. After removal of the solvent (24°C/10^{-5} Torr), the remaining oil was distilled (120°C/10^{-2} Torr) to afford 3.8 g (71%) of $Cp(CO)_2FeCH_2SiMe_2Cl$. M.p. 38-40°C; PMR (cyclohexane) τ (ppm) 5.19 (s, 5, Cp), 9.59 (s, 6, Me), 10.21 (s, 2, CH_2); IR (hexane) 2015, 1965 cm^{-1} (C≡O); UV (hexane) (ϵ) 27700 (775), 37500 (8000) (sh), 41200 (13700) cm^{-1}. (Found: C, 41.79; H, 5.06; Cl, 12.39. $C_{10}H_{13}ClFeO_2Si$ calcd.: C, 42.03; H, 4.59; Cl, 12.44%.)

Preparation of $Cp(CO)_2FeSiClMeCH_2Cl$

Into a solution of $NaFe(CO)_2Cp$ (0.02 mol) in 50 ml of tetrahydrofuran was distilled 3.26 g (0.02 mol) of $ClCH_2SiMeCl_2$. After the mixture had been stirred for 30 min at 23°C, approximately 30 ml of the solvent was removed in vacuo and 30 ml of hexane was added. The mixture was centrifuged and the residue was extracted with two 30 ml portions of hexane. The extracts were combined with the supernatant liquid, evaporated to 40 ml and filtered through a course sintered glass disk. The product was crystallized from this filtrate at —78°C to yield 4.08 g (68%) of $Cp(CO)_2FeSiClMeCH_2Cl$. M.p. 34-36°C; PMR (cyclohexane) τ (ppm) 5.15 (s, 5, Cp), 6.80 (AB, 2, $J = 12.2$ Hz, $v_0\delta = 3.3$ Hz, CH_2), 9.16 (s, 3, Me); IR (hexane) 2020, 2015 m(sh), 1972, 1965m(sh) cm^{-1} (C≡O); UV (hexane) (ϵ) 31000 (1060), 37000 (3300) (sh), 42000 (7000) (sh) cm^{-1}. The complex was further characterized by its quantitative isomerization to $Cp(CO)_2FeCH_2SiMeCl_2$.

Preparation of $Cp(CO)_2FeCH_2SiMeCl_2$

Chloromethylmethyldichlorosilane, 3.27 g (0.02 mol) was distilled into a solution of $NaFe(CO)_2Cp$ (0.02 mol) in 50 ml of tetrahydrofuran. After warming to 24°C and rotary evaporating the solvent, the residual oil was distilled (110°C/10^{-6} Torr) to yield 3.2 g (55%) of $Cp(CO)_2FeCH_2SiMeCl_2$; PMR (cyclohexane) τ (ppm) 5.15 (s, 5, Cp), 9.25 (s, 3, Me), 10.05 (s, 2, CH_2); IR (hexane) 2015, 1962 cm^{-1} (C≡O); UV (hexane) (ϵ) 276000 (925) cm^{-1}. (Found: C, 36.18; H, 3.54. $C_9H_{10}Cl_2FeO_2Si$ calcd.: C, 35.41; H, 3.28%.)

Preparation of $Cp(CO)_2FeSiCl_2CH_2Cl$

Chloromethyltrichlorosilane, 3.65 g (0.02 mol) was distilled into a solution of $NaFe(CO)_2Cp$ (0.02 mol) in 50 ml of tetrahydrofuran. After warming to 24°C the reaction mixture was transferred to a sublimator where the tetrahydrofuran was removed carefully in vacuo. The complex was sublimed three times (24°C/10^{-5} Torr) to yield 3.65 g (51%) of $Cp(CO)_2FeSiCl_2CH_2Cl$. M.p. 83-87°C; PMR (cyclohexane) τ (ppm) 5.04 (s, 5, Cp), 6.63 (s, 2, CH_2); IR (hexane) 2038w, 2034, 1992w, 1988 cm^{-1} (C≡O); UV (hexane) (ϵ) 31200 (1810), 37000 (5430) (sh), 41400 (13100) (sh) cm^{-1}. (Found: Cl, 42.89; Fe, 13.60. $C_8H_7Cl_3FeO_2Si$ calcd.: Cl, 43.25; Fe, 13.62%.)

Preparation of $Cp(CO)_2FeCH_2SiCl_3$

Into 0.4166 g (1.28 mmol) of $Cp(CO)_2FeSiCl_2CH_2Cl$ at —78°C was distilled approximately 0.06 g (0.04 mmol) of aluminum chloride and 8 ml of methylene chloride. After 12 h, the methylene chloride was removed in vacuo, and the residue was extracted with hexane. The residue resulting from the evaporation of the extract was sublimed for 18 h onto a water cooled probe. The sublimate was crystallized from hexane at —78°C to yield 0.0927 g (22%) of $Cp(CO)_2FeCH_2SiCl_3$. M.p. 23.5-24°C; PMR (cyclohexane) τ (ppm) 5.13 (s, 5, Cp); 9.87 (s, 2, CH_2); IR (hexane) 2030, 1983 cm^{-1} ($C\equiv O$). (Hydrolyzable chlorine found: 32.70. $C_8H_7Cl_3FeO_2Si$ calcd.: 32.61%.)

Preparation of $Cp(CO)_2FeSiMe_2CH_2Br$

Into a solution of $NaFe(CO)_2Cp$ (0.01 mol) in 25 ml of tetrahydrofuran was distilled 2.36 g (0.012 mol) of $BrCH_2SiMe_2Br$. The solution was warmed to —15°C and stirred for 30 min. Twenty ml of the solvent was removed in vacuo at —15°C and 20 ml of hexane was added. The resulting mixture was centrifuged; the precipitate was extracted with cold hexane; and the extracts were combined with the original supernatant liquid. This solution was concentrated to about 25 ml and filtered through a coarse sintered glass disk. The product, $Cp(CO)_2FeSiMe_2CH_2Br$, 1 g (30%), was isolated by crystallization from the filtrate at —78°C. Its extreme temperature sensitivity prevented a melting point from being taken. The material was stored at —78°C. PMR (cyclohexane) τ (ppm) 5.29 (s, 5, Cp), 7.22 (s, 2, CH_2), 9.51 (s, 6, Me); IR (hexane) 2010m(sh), 2003, 1949 ($C\equiv O$); UV (hexane) 31400, 37000(sh), 41700(sh) cm^{-1}. This complex was further characterized by its quantitative thermal isomerization to $Cp(CO)_2FeCH_2SiMe_2Br$.

Preparation of $Cp(CO)_2FeCH_2SiMe_2Br$

Into a solution of $NaFe(CO)_2Cp$ (0.012 mol) in 30 ml of tetrahydrofuran was distilled 2.8 g (0.012 mol) of $BrCH_2SiMe_2Br$. After the mixture had been stirred for 2 h at 23°C, the solvent was removed in vacuo and the residue distilled (80°C/10^{-5} Torr) for 2 days into a 0°C trap. The distillate was sublimed (70°C/10^{-5} Torr) onto a water cooled probe to afford 1.95 g (50%) of $Cp(CO)_2FeCH_2SiMe_2Br$. M.p. 43.5-45°C; PMR τ (ppm) 5.20 (s, 5, Cp), 9.45 (s, 6, Me), 10.02 (s, 2, CH_2); IR (hexane) 2018m(sh), 2014, 1968m(sh), 1962 cm^{-1} ($C\equiv O$); UV (hexane) (ϵ) 27500 (1340), 37500 (6800), 39200 (9800). (Found: Fe, 16.9. $C_{10}H_{13}BrFeO_2Si$ calcd.: Fe, 16.9%.)

Reaction between $NaFe(CO)_2Cp$ and chloromethyldimethylbromosilane

Chloromethyldimethylbromosilane, 3.67 g (0.022 mol) was added to a solution of 0.02 mol of $NaFe(CO)_2Cp$ in 100 ml of tetrahydrofuran. Rotary evaporation of the solvent and distillation (65°C/10^{-2} Torr) of the resulting residue afforded 4.1 g (79%) of $Cp(CO)_2FeCH_2SiMe_2Cl$.

Preparation of $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$

Into a solution of $NaFe(CO)_2Cp$ (0.025 mol) in 50 ml of tetrahydrofuran was distilled 1.704 g (0.012 mol) of chloromethyldimethylchlorosilane. After the mixture had been stirrred for 12 h, nitrogen was admitted to the flask and 50 ml of hexane was added to the reaction mixture. The residue resulting from the filtration of the mixture and rotary evaporation of the filtrate was dissolved in 50 ml of benzene and chromatographed on 22 g (3 × 30 cm) of alumina. Elution with benzene and subsequent rotary evaporation of the yellow eluate afforded 2.3 g (45%) of $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$. M.p. 92-93°C; PMR (cyclohexane) τ (ppm) 5.21 (S, 5, Cp); 5.37 (s, 5, Cp); 9.67 (s, 6, Me); 9.86 (s, 2, CH_2); IR (hexane) 2012, 2008, 1990, 1959, 1938, 1934 cm^{-1} (C≡O). (Found: Fe, 25.98. $C_{17}H_{18}Fe_2O_4Si$ calcd.: Fe, 26.16%.)

Reaction between $NaFe(CO)_2Cp$ and $Cp(CO)_2FeCH_2SiMe_2Cl$

Into a solution of 0.74 g (2.6 mmol) of $Cp(CO)_2FeCH_2SiMe_2Cl$ in 5 ml of tetrahydrofuran at 0°C was added slowly 7.0 ml of a solution of $NaFe(CO)_2Cp$ (2.8 mmol) in tetrahydrofuran. After stirring for 20 h at 0°C, the solvent was removed in vacuo, and the residue extracted twice with 6 ml of hexane. Cooling the hexane extract to —78°C afforded a solid mixture of $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ and another species. It was not possible to separate these compounds by chromatography or fractional crystallization. In addition, upon passage through alumina, it appeared that $[CpFe(CO)_2]_2$ was being formed. The PMR spectrum of the mixture of complexes exhibited resonances, in addition to those assigned to $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ and $[Cp(CO)_2Fe]_2$, at τ (ppm) 5.13 (5), 5.26 (5), 6.4 [2, t(?)], 8.50 (6(br)), 9.95 (6), and 10.50 (2).

Preparation of $Cp(CO)_2FeSiClMeCH_2Fe(CO)_2Cp$

Into a solution of $NaFe(CO)_2Cp$ (10 mmol) in 25 ml of tetrahydrofuran was distilled 0.73 g (4.5 mmol) of $ClCH_2SiMeCl_2$. After the mixture had been stirred at 23°C for 20 h, the solvent was removed in vacuo and the residue extracted with hexane until $Cp(CO)_2FeSiClMeCH_2Cl$ was no longer observed in the IR spectrum of the extract. The residue was sublimed (100°C/10^{-5} Torr) for 1 day onto a water cooled probe. Despite repeated extractions with hexane and resublimations of the dark yellow solid, residual $(Cp(CO)_2Fe)_2$ could not be removed. Attempts to recrystallize the material from hexane were not successful. A total of 0.90 g (20%) of material was isolated and identified by its IR and PMR spectra as $Cp(CO)_2FeSiClMeCH_2Fe(CO)_2Cp$ contaminated with 5% $[Cp(CO)_2Fe]_2$; PMR (cyclohexane) τ (ppm) 4.91 (s, 5, Cp), 5.05 (s, 5, Cp), 9.10 (s, 3, Me), 9.48 (AB, 2, $J = 13$ Hz, CH_2 $v_0\delta = 35$ Hz); IR 2016 (sh), 2008, 2003, 1963, 1954 cm^{-1} (C≡O).

Reaction between $NaFe(CO)_2Cp$ and $Cp(CO)_2FeCH_2SiMeCl_2$

Into a solution of 0.78 g (2.5 mmol) of $Cp(CO)_2FeCH_2SiMeCl_2$ in 5 ml of tetrahydrofuran at 0°C was added slowly 6.5 ml of a tetrahydrofuran solution of $NaFe(CO)_2Cp$ (2.6 mmol). After the mixture had been stirred for 1 h, a PMR spectrum showed the presence of a major amount of $[CpFe(CO)_2]_2$ and a smaller amount of $Cp(CO)_2FeCH_2SiMeCl_2$. Vacuum distillation of the reaction mixture into a 0°C trap led to the recovery of 0.02 g (2%) $Cp(CO)_2FeCH_2SiCH_3Cl_2$.

Preparation of $Cp(CO)_2FeSiCl_2CH_2Fe(CO)_2Cp$

Into a solution of 0.253 g (0.78 mmol) of $Cp(CO)_2FeSiCl_2CH_2Cl$ in 2 ml of tetrahydrofuran at 0°C was added slowly 2 ml of a tetrahydrofuran solution of $NaFe(CO)_2Cp$ (0.8 mmol). After 20 h, the solvent was removed in vacuo and the residue sublimed (100°C/10^{-5} Torr) for 1 day onto a water cooled probe.

The sublimate was dissolved in a minimum amount of methylene chloride and diluted with 4 ml of hexane, thereby forming a precipitate. After the mixture had been centrifuged, the supernatant liquid was discarded. This procedure was repeated until $Cp(CO)_2FeSiCl_2CH_2Cl$ was not observed in the IR spectrum of the supernatant liquid. The precipitate was sublimed (105°C/10^{-5} Torr) for 1 day. The bottom of sublimator was changed and the sublimate on the probe was extracted by refluxing hexane off the cold finger. Yellow and red crystals formed on the walls of the sublimator. After the sublimate was removed from the probe, the hexane was removed in vacuo. The red and yellow solids were separated by hand. Crystallization of the yellow solid from hexane at —20°C afforded 0.01 g (4%) of $Cp(CO)_2FeSiCl_2CH_2Fe(CO)_2Cp$; which was characterized only by IR and PMR spectroscopy. PMR (cyclohexane) τ (ppm) 4.88 (s, 5, Cp), 4.97 (s, 5, Cp), 9.30 (s, 2, CH_2); IR (hexane) 2028, 2024, 2013, 1972, 1963 cm^{-1} (C≡O).

Reaction between $Cp(CO)_2FeCH_2SiMe_3$ and HCl

The following procedure was used for all the experiments involving the reactions between the silylmethyliron complexes and gaseous HCl.

Hydrogen chloride, 2.27 mmol, was distilled into an ampule containing 0.472 g (1.79 mmol) of $Cp(CO)_2FeCH_2SiMe_3$. The initial pressure of HCl in the ampule at 24°C was calculated to be 565 Torr. After 15 min at 24°C, the volatile material was removed in vacuo. Only a trace of noncondensible material was observed (<0.01 mmol). The condensible material was distilled twice through a —112°C trap into a —196°C trap. The material in the —196°C trap was redistilled through another —112°C trap into a —196°C trap. The highly volatile material in the —196°C trap was identified by its vapor pressure, 122 Torr/—112°C, (lit. [19] 125 Torr/—112°C) as HCl. Thus 1.75 mmol of HCl had been consumed. Tetramethylsilane, 1.68 mmol (94%), (obsrved v.p. 271.5 Torr/0°C; lit. [19] 271.5 Torr/0°C) was recovered from the —112°C traps. The red solid in the ampule was identified as $Cp(CO)_2FeCl$ (0.379 g). M.p. 85-88°C (lit. [20] 84-87°C).

Reaction between $Cp(CO)_2FeCH_2SiMe_2Cl$ and HCl

Hydrogen chloride, 2.02 mmol, was added to an ampule containing 0.1354 g (0.477 mmol) of $Cp(CO)_2FeCH_2SiMe_2Cl$. The calculated initial pressure of HCl at 24°C was 207 Torr. After 3 h at 24°C the volatile material was removed in vacuo. No noncondensible material was observed. The reaction consumed 0.49 mmol of HCl and formed 0.49 mmol of Me_3SiCl. (V.p. 72.5 Torr/0°C; lit. [19] 63.5 Torr/0°C; molecular weight found: 105 g mol^{-1}. Calcd.: 108.7 g mol^{-1}.)

Reaction between $Cp(CO)_2FeCH_2SiMeCl_2$ and HCl

Hydrogen chloride, 2.58 mmol, was added to an ampule containing 0.5040 g (1.65 mmol) of $Cp(CO)_2FeCH_2SiMeCl_2$. The calculated initial pressure of HCl in the ampule was 654 Torr. The mixture was allowed to stand for 20 h at 24°C. No noncondensible material was observed. The reaction consumed 1.60 mmol of HCl and formed 1.38 mmol (83%) of Me_2SiCl_2 which was identified by its vapour pressure (41 Torr/0°C; lit. [21] 40 Torr/0°C) and by comparison of its IR spectrum to the published spectrum [22]. Remaining in the ampule was $Cp(CO)_2FeCl$, 0.3680 g, M.p. 83-88°C (lit. [20] 84-87°C).

Reaction between $NaFe(CO)_2Cp$ and $BrCH_2SiMe_2Cl$

(A). Bromomethyldimethylchlorosilane, 1.87 g (0.01 mol) was added dropwise to a solution of $NaFe(CO)_2Cp$ (0.02 mol) and 2.70 g (0.01 mol) of 1,3-diphenylisobenzofuran in 100 ml of tetrahydrofuran at 10°C. After the mixture had been stirred for several minutes, 3 ml of dimethylacetylene dicarboxylate was added and the mixture was refluxed briefly. The residue resulting from the rotary evaporation of the reaction mixture was dissolved in a minimum amount of benzene and chromatographed on alumina (4 × 40 cm). Elution with petroleum ether afforded 0.191 g of a yellow oil which appeared to be in part $Cp(CO)_2FeSiMe_3$ as evidenced by singlets at τ 5.38 and 9.6 ppm in a 5/9 ratio in the PMR spectrum of the material. Several other singlets were also observed between τ 5.0-5.5 and 9.0-10.3 ppm. Further elution with petroleum ether afforded a second yellow band which yielded 0.821 g of a mixture of unidentified complexes. Finally elution with 1/1 petroleum ether/benzene afforded 0.525 g of a third yellow substance, the PMR spectrum of which exhibited, in addition to at least four singlets between τ 5.0-5.5 ppm and at least six singlets between τ 9.4-10.6 ppm a narrow multiplet at τ 8.6 ppm. An attempt to separate the components of each band by a second chromatography of each of unsuccessful.

When this reaction was repeated using moist tetrahydrofuran, a 42% yield of $Cp(CO)_2FeSiMe_3$ was isolated.

(B). Into a 120 ml of a solution of $NaFe(CO)_2Cp$ (0.06 mol) in tetrahydrofuran at —196°C was distilled 11.2 g (0.06 mol) of $BrCH_2Si(CH_3)_2Cl$. As the solution thawed, it was stirred vigorously and warmed slowly to 24°C. The solvent was removed in vacuo and the residue distilled (95°C/10^{-5} Torr) into —78°C trap for 18 h. The distillate was chromatographed twice on alumina (2 × 30 cm), which had been prepared by washing the alumina with a hexane/trimethylchlorosilane mixture. After elution with 400 ml of hexane and rotary evaporation of the eluate, the residue was twice distilled in the vacuum line into 0°C traps to yield 7.0 g (45%) $BrCH_2SiMe_2CH_2SiMe_2Cl$; PMR τ (ppm) 7.49 (s, 2, CH_2Br), 9.48 (s, 6, Me); 9.71 (s, 2, CH_2), 9.81 (s, 6, Me); IR (CS_2) 2965m, 2932wm, 2904w, 1785w, 1738w, 1255s, 1128w, 1058s, 810vs, 680w, 633w, 590w, 550w, 478vw, 460m, 380m cm^{-1}. (Found: Hydrolyzable chlorine, 13.42; Si, 21.55. $C_6H_{16}BrClSi_2$ calcd.: Cl, 13.59; Si, 21.17%.)

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