Table II. Comparison of the Rates of Hydrosilylation of Acrylonitrile with the Blustein Catalyst

catalyst	silane	conditns[a]	product	yield, %
Bluestein[7]	$HSiCl_3$	40 h, reflux	$Cl_3SiCH_2CH_2CN$	68
present work	$HSiCl_3$	1.5 h, reflux	$Cl_3SiCH_2CH_2CN$	90-95

[a] Both reactions were run by using a 7.5:1:1.2 mol ratio of acrylonitrile/copper catalyst/amine.

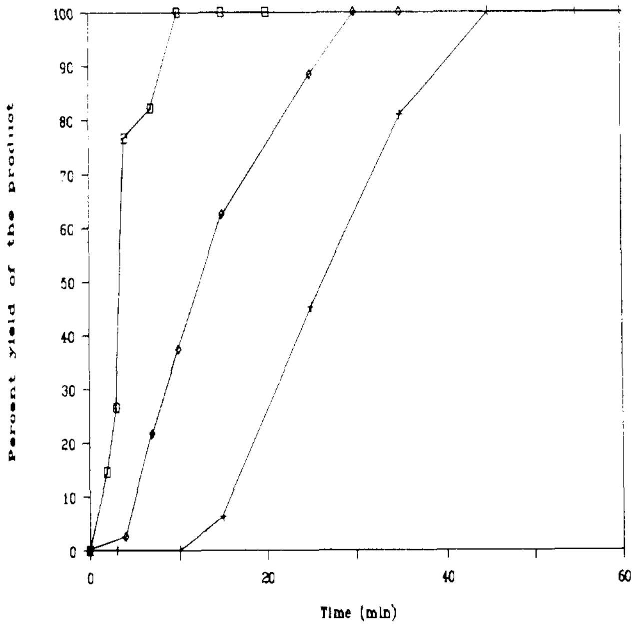

Figure 1. Hydrosilylation of acrylonitrile with $HSiCl_3$ (□), $HSiMeCl_2$ (+), and $HSiPhCl_2$ (◇) under refluxing conditions.

In a typical experiment, 1 g (0.0069 mol) of Cu_2O and 3 mL (0.019 mol) of TMEDA were placed in a 50-mL three-necked round-bottomed flask fitted with a dry ice condenser and a nitrogen inlet. The flask was cooled at 0 °C, and a mixture of 2.3 mL (0.04 mol) of acrylonitrile and 5.05 mL (0.05 mol) of trichlorosilane was added dropwise to the mixture. After the addition was complete, the reaction mixture was heated at reflux for 10 min. (β-Cyanoethyl)trichlorosilane was isolated by distillation (7.4 g, 98%; 60 °C (2 Torr)). The above reaction also was performed in a common ultrasonic laboratory cleaner (Bransonic Model 220), where the flask was positioned at a point that caused the most agitation in the flask. After 2 h of sonication, (β-cyanoethyl)trichlorosilane was collected by distillation (6.03 g, 80%; 60 °C (2 Torr)). Stirring at room temperature gave a 30% yield of (β-cyanoethyl)trichlorosilane (Table I).

To compare our catalyst more directly with the Bluestein catalyst system,[7] we used identical mole ratios of acrylonitrile, copper catalyst, and amine and found a >25-fold rate enhancement (Table II). The results summarized in Table II demonstrate that the functionalized silanes can add to acrylonitrile in good yield and the reactivity of silanes is in the order of $HSiCl_3 > HSiCl_2Ph$, $HSiCl_2Me \gg HSiClPh_2$. No product was observed when $HSiClMe_2$ was used as the silylating agent. Quantitative comparison is made in Figure 1 which shows that $HSiCl_3$ is 3 times more reactive than $HSiPhCl_2$ and 4 times as reactive as $HSiMeCl_2$ based on times required for completion of reaction. The effects of stirring at room temperature, refluxing at 70 °C, and ultrasonic irradiation at room temperature are compared in Figure 2 which shows that refluxing produces the fastest rates and that sonication is significantly faster than room-temperature stirring. Ultrasonic acceleration of reactions involving non-metals, while not as common as those examples in which metals are used, has been reported by several groups.[10] Increased reaction rates are attributed to increased surface area of the solid reagent from cavitation-induced particle size reduction and improved mass transport of liquid reagent to the solid surface via acoustic streaming. Reduction in catalyst affects the rate but not the yield. For example, when the Cu_2O/ TMEDA load is reduced to 10% of our normal runs, 4 h of refluxing are required to reach a 100% product yield.

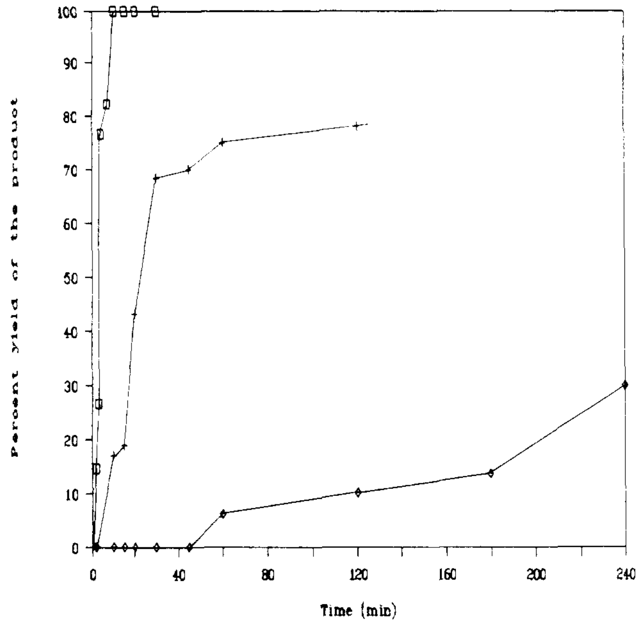

Figure 2. Hydrosilylation of acrylonitrile with $HSiCl_3$, Refluxing (□), ultrasound (+), and stirring (◇).

Cu_2O is recyclable. We found no decrease in the reactivity when product and TMEDA were removed from the flask by distillation, leaving Cu_2O, followed by recharging the vessel with TMEDA, silane, and acrylonitrile. The scope of this catalyst system can be extended to the hydrosilylation of acrylates.[11] We are pursuing that line of investigation and will report our progress in due course.

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Photochemical Skeletal Redistributions of Permethylated Linear and Cyclic Oligosilyl Groups in $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-Substituted Oligosilanes

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Summary: Photochemical treatment of oligosilyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–oligosilyl which contain at least four silicon atoms results in very high-yield formation of

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tris(silyl)silyl complexes. This result is in direct contrast to those obtained upon photolysis of the related di- and trisilyl complexes where monosilyl complexes are ultimately obtained involving expulsion of R_2Si fragments.

Studies on the chemistry of oligo- and polysilanes have recently flourished due to the discovery that polysilanes are useful materials in the area of photoresists, preceramics, photoconductors, etc.[2-7] We have been studying transition-metal-substituted oligosilanes[8-10] and polysilanes[11] and have shown that the transition-metal substituent can dramatically alter the chemical and physical properties of the silane chains. In particular we demonstrated that di- and trisilyl complexes of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–(Fp) readily photodegrade to monosilyl complexes. We have proposed a mechanism that involves initial photoelimination of CO followed by silyl group migration to form silyl (silylene) complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)(SiR_3)(=SiR_2)$, which exist as a dynamic equilibrium of complexes undergoing 1,3-alkyl and -aryl migrations. Upon recoordination of CO, loss of the silylene fragment results in the formation of monosilyl Fp complexes (eq 1 and 2).

$$\mathrm{Fp{-}SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{Fp{-}SiMe_3} + [\mathrm{SiMe_2}] \quad (1)$$

$$\mathrm{Fp{-}SiMe_2SiPh_3} \xrightarrow{h\nu} \mathrm{Fp{-}SiMe_2Ph} + \mathrm{Fp{-}SiMePh_2} + \mathrm{Fp{-}SiPh_3} \quad (2)$$

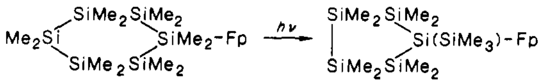
The recent isolation and X-ray structural analysis of such an $(\eta^5\text{-}C_5H_5)Fe(CO)$–silyl (silylene) complex by Ueno et al. from the photolysis of an Fp–disilyl complex has provided extra support for this proposed mechanism which was also favored by these investigators.[12] We now wish to report dramatic new photochemical transformations of related linear oligosilyl complexes of the Fp system that contain at least four Si atoms, as outlined in eq 3 and 4.

$$\mathrm{Fp{-}SiMe_2SiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{Fp{-}Si(SiMe_3)_3} \quad (3)$$

$$\mathrm{Fp{-}SiMe_2(SiMe_2)_4SiMe_3} \xrightarrow{h\nu} \mathrm{Fp{-}Si(SiMe_3)_2SiMe_2SiMe_2SiMe_3} \quad (4)$$

Continued photochemical treatment of the new tris(silyl)silyl–Fp complexes did not result in the formation of mono-, di-, or trisilyl complexes of the Fp system;[13a] prolonged photochemical treatment resulted in the cleavage of the Fe–Si bond and formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. The fate of the oligosilyl group is at present unknown.

An exactly analogous transformation occurs upon photochemical treatment of the silacyclohexyl Fp complex (eq 5).



(5)

The experimental procedure for this reaction was identical with that noted above.[13b] Analysis by ^{29}Si NMR spectroscopy was most useful for monitoring the reaction: $\mathrm{Fp\overline{SiMe(SiMe_2)_4Si}Me_2}$ (C_6D_6), δ(Si) −42.3, −39.7, −29.1, and −14.2 ppm; $\mathrm{Fp\overline{Si(SiMe_3)(SiMe_2)_3Si}Me_2}$ (C_6D_6), δ-(Si)−71.6, −41.0, −26.6, −4.62 ppm. The analysis of such data is facilitated by the following generalities in the chemical shift differences between Fp-substituted silanes and their methyl-substituted counterparts, i.e. δ(Fp–silyl) − δ(Me-silyl), $\Delta\delta$. This data, obtained from many varied complexes in our laboratory, may be summarized as follows: Si atoms attached directly to the Fe atom of the Fp system, Si_α, have $\Delta\delta$ values of $\simeq$40 ppm for $-\mathit{Si}\mathrm{Me_2R}$ groups, $\simeq$ 25 ppm for $-\mathit{Si}\mathrm{(Si)_2}$, and $\simeq$10 ppm for $-\mathit{Si}\mathrm{(Si)_3}$; Si atoms in the β-position to the metal have $\Delta\delta$ values of $\simeq$12 ppm for $-\mathit{Si}\mathrm{Me_2}-$ groups and $\simeq$7 ppm for $\mathit{Si}\mathrm{Me_3}$ groups; silicon atoms in the γ-position are generally shifted by 2 ppm.[8]

These results are reminiscent of the $AlCl_3$-catalyzed re-formation of oligopermethylated silanes reported by Kumada et al.[16,17] and the $AlCl_3/FeCl_3$-catalyzed ring contractions of cyclic polysilanes reported by West,[18] both of which occur without loss of silyl groups. For the cyclohexasilyl complex the new photochemistry is distinctive in that photochemical treatment of the parent $(SiMe_2)_6$ readily yields ring contraction to $(SiMe_2)_5$ with $SiMe_2$ expulsion.[19]

It is reasonable to suggest that the mechanism of the new photolytic rearrangements may related to that of the silylene expulsion reactions of the Fp–disilyl complexes involving not only 1,3-alkyl migrations between silyl and silylene groups but also 1,3-silyl migrations. A typical process, for the cyclic hexasilyl complex, is illustrated in Scheme I.

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(13) (a) In a typical reaction $\mathrm{Fp{-}SiMe_2(SiMe_2)_4SiMe_3}$ (30 mg, 0.055 mmol) in 300 mg of C_6D_6, was irradiated in a Pyrex NMR tube using a Hanovia 450-W medium-pressure mercury lamp at a distance of 10 cm from the lamp. The reaction was monitored by ^{29}Si NMR spectroscopy, and after 1.5 h no starting material was present. The initial ^{29}Si resonances at −42.6, −39.3, −37.4, −31.0, −14.7, and 23.3 ppm were replaced by five new resonances at −73.1, −39.6, −29.1, −13.3, and −5.4 ppm. The C_6D_6 was removed under vacuum and the residue placed upon a 1 × 5 cm silica gel column. Elution with hexane produced a yellow band that was collected to yield $\mathrm{Fp{-}Si(SiMe_3)_2SiMe_2SiMe_2SiMe_3}$: 15 mg (50%) as a yellow oils; *m/e* 540; IR (hexane) ν(CO) 1999, 1950. Anal. (Galbraith Labs. Inc., Knoxville, TN.) Calcd (Found): C, 44.1 (44.1); H, 8.19 (8.20). In the case of the $\mathrm{Fp{-}(SiMe_2)_3SiMe_3}$ to $\mathrm{FpSi(SiMe_3)_3}$ rearrangement a 70% yield was obtained. Both $\mathrm{Fp{-}Si_4}$ isomers are reported in the literature.[14,15] (b) The same procedure using $\mathrm{Fp\overline{SiMe_2(SiMe_2)_4Si}Me_2}$ as starting material produced a 73% yield of $\mathrm{Fp\overline{Si(SiMe_3)(SiMe_2)_3Si}Me_2}$. Anal. Calcd (Found): C, 43.3 (42.7); H, 7.50 (7.87).

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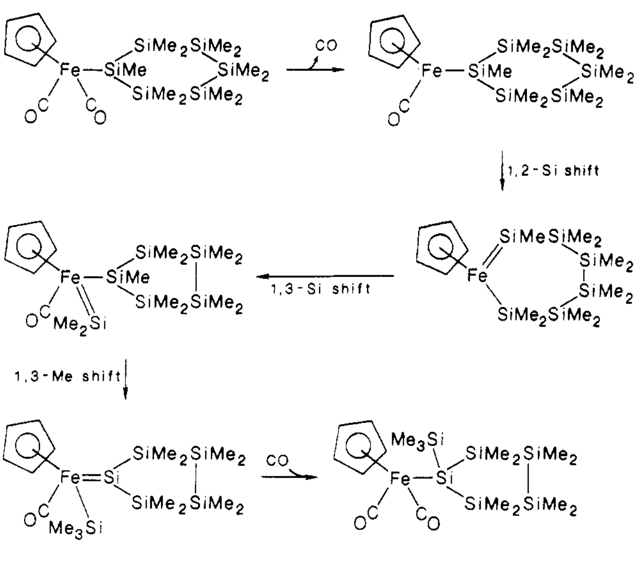
Scheme I



The key difference between the new rearrangements and the silylene expulsion reactions from the Fp-disilyl complexes is the lack of loss of Si fragments. If the above mechanism is operative, then recoordination of CO to silyl (silylene) Fp complexes where the silylene moiety contains silyl groups must cause re-formation of the Si-Si bond. Other mechanisms can be imagined, and our current studies are aimed at testing the various possibilities and discovering the extent to which other metals facilitate the skeletal rearrangements.

If the mechanism of the rearrangement of the linear $Fp(SiMe_2)_3SiMe_3$ and $Fp(SiMe_2)_5SiMe_3$ follows closely that of Scheme I, the intermediacy of various branched chain isomers; e.g., $FpSiMe(SiMe_3)SiMe_2SiMe_3$ is to be expected. At the present time we have not observed such transient species during the reaction of the tetrasilyl and hexasilyl Fp complexes. However, related to our suggestion is the direct transient formation of $FpSiMe(SiMe_3)_2$ upon irradiation of $FpSiMe_2SiMe_2SiMe_3$.[20] This rapidly further photodecomposes to form $Fp-SiMe_2SiMe_3$ and $Fp-SiMe_3$ with ultimate formation of only $Fp-SiMe_3$.

$$FpSiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe(SiMe_3)_2 \xrightarrow{h\nu} FpSiMe_2SiMe_3 + FpSiMe_3 \quad (6)$$

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(20) A concentrated solution of $Fp-SiMe_2SiMe_2SiMe_3$, 80 mg in 400 mg of C_6D_6, was irradiated in a Pyrex NMR tube with a 450-W medium-pressure mercury lamp for 20 min at a distance of 10 cm. A ^{13}C NMR spectrum was recorded, and in addition to the three SiMe ^{13}C resonances of the starting material at −4.26, −1.02, and 5.04 ppm we observed approximately 30% conversion to $FpSiMe(SiMe_3)_2$ as denoted by new resonances at −0.47 (SiMe) and 1.21 ($SiMe_3$) ppm. Trace (5%) amounts of $Fp-SiMe_3$, 7.57 ppm, and $Fp-SiMe_2SiMe_3$, −3.62 and 3.33 ppm, also were observed. Continued irradiation for 2 h led to formation of $Fp-SiMe_3$ as the ultimate iron-containing product, recovered in 66% yield.

Reactivity of Coordinated $[Ph_2PCHP(S)Ph_2]^-$ and $[Ph_2P(S)CHP(S)Ph_2]^-$: Two-Center, Regiospecific Reactivity in Rhodium and Iridium Complexes and Formation of a Disubstituted Methylene Bridge between Platinum Atoms

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Summary: Reaction of methyl iodide with $[Ir\{Ph_2P(S)CHP(S)Ph_2\}(cod)]$ occurs in a regiospecific sequence to form first $[Ir\{Ph_2P(S)CHMeP(S)Ph_2\}(cod)]I$ and only subsequently $[IrMeI\{Ph_2P(S)CHMeP(S)Ph_2\}(cod)]I$. For $[Rh\{Ph_2PCHP(S)Ph_2\}(cod)]$ the addition sequence is reversed. $[Pt\{Ph_2P(S)CHP(S)Ph_2\}(MeOcod)]$ shows both ligand and metal site reactivity in transforming to a novel dimer, $[Pt_2\{Ph_2P(S)CP(S)Ph_2\}(MeOcod)_2]$, containing a quaternary carbon bridge between two platinum centers. The bridging carbon is part of four-member C,S chelate rings at both platinums.

The coordination chemistry of bis(diphenylphosphino)methane ($dppCH_2$) is extensive and well-known.[1] Although the majority of studies have been concerned with reactivity at metal centers in dinuclear complexes bridged by $dppCH_2$,[1] reactivity at the methylene carbon has also attracted interest. Thus reactions of $M(CO)_4(dppCH_2)$ (M = Cr, Mo, or W) and $MCl_2(dppCH_2)$ (M = Pd or Pt) with bases followed by alkyl halides can result in either mono-or dialkylation at the methylene carbon.[2] Several complexes are known involving metalation at the methylene carbon of a coordinated $dppCH_2$,[3] including two examples of double metalation, $[(AcOHg)_2C(PPh_2HgOAc)_2]$[3a] and $[(PhNC)_4Fe\{(Ph_2P)_2C(AuPPh_3)_2\}]$,[3c] and a particularly unusual example involving carbene-like coordination in the polymer, $[Pt(\mu\text{-}Cl)_2Pd{=}C(PPh_2)_2]_n$.[4]

Corresponding work on $Ph_2PCH_2P(S)Ph_2$ ($dpp(S)CH_2$) and $Ph_2P(S)CH_2P(S)Ph_2$ ($dpp(S_2)CH_2$) has been much less extensive.[5] Coordination via (P,S) for $dpp(S)CH_2$ and $dpp(S)CH^-$,[5-7] via (S) or (S,S) for $dpp(S_2)CH_2$,[8-10] and via (S,S) or (S,C) for $dpp(S_2)CH^-$,[10-12] have all been reported but the ability of the sulfides to delocalize charge and enhance the acidity (reactivity) of the methylene protons relative to $dppCH_2$ has been little studied. We now report

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