A linear relationship was observed between k_{obsd} and [L] where L is either CO or PPh_3 (Figure 2),[7] showing the observed rate law is first order in both transient and added ligand. The bimolecular rate constant for recombination with CO is 151 (10) $M^{-1}\ s^{-1}$ and with PPh_3 is 1.34 (5) × 10^3 $M^{-1}\ s^{-1}$. These rate constants are small compared to other processes involving Lewis base addition to a CO-deficient transient. For instance, addition of CO to $Cr(CO)_5(C_6H_{12})$ (C_6H_{12} = cyclohexane) has a rate constant of 3 × 10^6 $M^{-1}\ s^{-1}$.[8] Furthermore, flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in perfluorohexane under CO gives an observed rate constant only 5 times faster than that observed in hexane[9] showing that desolvation is not contributing to the activation barrier for CO addition. Thus the η^3-benzyl configuration is implicated as the observed transient.

A mechanism that satisfactorily accounts for this data is shown in Scheme I.[10] While there is no direct evidence in this study for either intermediate ($CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ is not an intermediate in this mechanism), NMR investigations demonstrate that the η^3-benzyl ligand rearranges via an η^1-intermediate.[1b,4,11] Furthermore, others have shown that 16-electron systems, such as $Cr(CO)_5$ and $W(CO)_5$, will be solvated in less than 100 ps[12] with a solvent molecule acting as a "token ligand".[13]

Assuming that the equilibria are rapid relative to the product forming step for the two intermediates in Scheme I, the derived rate law is $R = k_1k_L[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]/(k_{-1} + k_L[L])$. With $k_{-1} > k_L[L]$, the rate law, $R = k_{app}[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]$ is obtained with $k_{app} = k_1k_L/k_{-1}$. This is identical with the experimentally observed rate law. The ratio of the two rate constants, $k_{app(PPh_3)}/k_{app(CO)} = 8.9$.[14] Typically, competition ratios of 6 or less have been observed for various ligands competing with CO at organometallic metal centers following ligand loss.[15] A competition ratio of this magnitude is usually interpreted as indicating a high reactivity and low selectivity of a desolvated 16-electron species. It should be noted, however, that while this proposed mechanism is consistent with mechanisms proposed for comparable systems,[13,15e,16] no direct kinetic evidence is available demonstrating that ligand attack occurs on the desolvated 16-electron intermediate rather than on the solvated species or on the η^3-system.

Further studies on this system are currently in progress.

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(6) Determined by one flash of a Sunpak 321 S camera flash on a solution of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ and PPh_3 in hexane in an IR cell. $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$, produced by the literature method,[3] exhibits an identical IR spectrum.

(7) (a) The concentration of CO in hexane is obtained from P_{CO}, Henry's Law, and the solubility of CO in hexane. (b) Atwood, J. D. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1976.

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(9) (a) The solubility of CO in perfluorohexane under 1 atm of CO has not been reported. In perfluoroheptane it is 0.017 M which, for the observed rate constant of 14 (1) s^{-1}, corresponds to a bimolecular rate of 820 (60) $M^{-1}\ s^{-1}$. This is about 5 times larger than the rate in hexane but still 6 orders of magnitude smaller than the diffusion-controlled rate constant expected if solvation effects pertain. (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (c) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344. (d) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.

(10) NMR and other data[1b,4,11] show that the η^3-benzyl ligand exists as the endo form (benzo group trans to cyclopentadienyl) and rapidly fluctuates between enantiomers, and imply that α-H elimination from an η^1-intermediate forms a carbene hydride transient.[4a] This information does not need to be invoked to interpret the data presented here.

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Nucleophilic Catalysis of Organosilicon Substitution Reactions

Patrick J. Lennon,[*,†] **David P. Mack, and Quentin E. Thompson**

Monsanto Chemical Company
800 N. Lindbergh Blvd.
St. Louis, Missouri 63167

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Summary: Catalytic quantities of cyanide or thiocyanate ions are shown to facilitate the substitution of silyl chlorides by Grignard reagents and dialkylmagnesium reagents, to afford high yields of tetraalkyl- and tetraarylsilanes under extremely mild conditions.

Organolithium reagents are usually preferred to Grignard reagents for the synthesis of tetraorganosilanes. While Grignard reagents might otherwise be the reagents of choice because of greater availability, ease of formation, and cost, their reactions with triorganosilyl chlorides are so sluggish that only the simplest tetraorganosilanes can be obtained in satisfactory yields and purity.[1] We here report that cyanide and thiocyanate ions catalyze the reaction between organomagnesium reagents and chlorosilanes under extremely mild conditions affording tetraorganosilanes in high yield (eq 1).

$$RMgX + R'_nSiCl_{4-n} \xrightarrow[\leq 15\ °C]{5\%\ CN^-} R'_nSiR_{4-n} + ClMgX \tag{1}$$

For example, aryl Grignard reagents have been reported to yield tetraarylsilanes after reaction with $SiCl_4$ above 160 °C.[2] In contrast to these conditions, 5 mol % CuCN promotes the reaction of *p*-tolyltrichlorosilane with phenylmagnesium chloride at 10 °C to afford an 81% yield of *p*-tolyltriphenylsilane[3] after 1 h. This catalyst promotes reaction of both alkyl Grignards and dialkylmagnesium reagents. In the case of R_2Mg reagents, prepared by the excellent method of Bogdanovic,[4] this catalysis is partic-

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[†] Present address: Central Research Laboratories, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167.

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Table I. Reactions of Halosilanes and Organomagnesium Reagents Catalyzed by Cuprous Cyanide[a]

entry	organomagnesium reagent	halosilane	product	*T*, °C	yield,[b] %
1	$(C_8H_{17})_2Mg$	Cl_3SiCH_3	$(C_8H_{17})_3SiCH_3$	15	85 (96[c])
2	$C_8H_{17}MgBr$	Cl_3SiCH_3	$(C_8H_{17})_3SiCH_3$	0	90[c]
3	n-$C_{16}H_{33}MgBr$	$SiCl_4$	$(C_{16}H_{33})_4Si$	10	65
4	C_6H_5MgCl	p-$CH_3C_6H_4SiCl_3$	p-$CH_3C_6H_4Si(C_6H_5)_3$	−10	81
5	c-$C_6H_{11}MgBr$	$C_6H_5SiCl_3$	$C_6H_5Si(C_6H_{11})_2OH$	−30	83[d]

[a] General procedure: The organomagnesium reagent (from 0 to 36% excess) in tetrahydrofuran or ether–tetrahydrofuran was cooled to the indicated temperature under an inert atmosphere. The CuCN (5% based on Si) was added, followed immediately by the dropwise addition of the silyl halide at a rate which keeps the reaction temperature at or below the indicated temperature. After the reaction mixture had been allowed to warm to room temperature, it was carefully hydrolyzed with cooling, followed by ether extraction and distillation or recrystallization of the product. [b] Isolated yield, except where otherwise indicated. [c] Yield determined by gas chromatography using an internal standard. [d] Hydrolytic workup.

Table II. Yield of $(C_8H_{17})_3SiCH_3$ as a Function of Catalyst in the Reaction of $(C_8H_{17})_2Mg$ with Cl_3SiCH_3[a]

		% yield	
example	cat.	with cat.	without cat.
1	AgCN	80	16
2	$(C_4H_9)_3SnCN$	89	12
3	BrCN	94	12
4	$Hg(CN)_2$	97	12
5	$(CH_3)_3SiCN$	95	12
6	$(CH_3)_3SiNCS$	69	30
7	$Ca(SCN)_2$	73	12
8	AgSCN	79	31
9	$(C_4H_9)_4N^+SCN^-$	92	31

[a] These experiments were done by using several batches of $(C_8H_{17})_2Mg$ (molarity range, 0.45–0.78 in the THF/octene solution in which they were prepared). A reaction without catalyst was performed for each batch under conditions identical with those used with catalysts. These control reactions were allowed to proceed slightly longer than those containing catalysts. The catalyst, about 5 mol % with respect to chlorosilane, was added to a stirred solution of the organomagnesium reagent at 0 °C under argon; then the CH_3SiCl_3 was added in small portions over 2–3 min. After being stirred for 60–70 min, the reaction mixture was allowed to warm to room temperature (0.6–3.4 h). Docosane (internal standard) was added, and the amount of product present was determined by gas chromatography.

ularly important since the residual catalysts from R_2Mg preparation appear to promote formation of trialkylsilanes.[5] Yields of several representative reactions using catalytic quantities of CuCN are given in Table I. Earlier methods of preparation included 48 h at reflux in THF[7] (entry 2), high-temperature reactions[8,9] (entries 3 and 5), or the use of an organolithium reagent[3] (entry 4). That cyanide or thiocyanate are the necessary catalysts can be seen from Table II which shows the yields of methyltrioctylsilane, derived from dioctylmagnesium and methyltrichlorosilane, as a function of catalyst. It is apparent that these two pseudohalides are the important catalytic elements. Numerous other anions such as cyanate, iodide, and fluoride were inactive under these mild conditions. A few ions such as azide, nitrate, and phenylacetylide exhibited lesser degrees of catalytic activity. Other ions more closely related to cyanide such as dicyanamide and selenocyanate were good catalysts. Cuprous cyanide was generally used in preparative reactions since it is inexpensive and nonhygroscopic and generally gave good results, whether the scale was a few millimoles or several moles. It is quite possible that some of the other catalysts would be more useful in some cases.

Although the mechanism was not studied, several possibilities can be considered. Since many of the catalysts used in this work are known reagents[10] for the synthesis of silyl cyanides or silyl isothiocyanates, the intermediacy of such species is suggested. These silyl pseudohalides are known to react with Grignard reagents by displacement of the pseudohalide.[11] The possibility that a pentacoordinate species such as $R_3SiCl(CN)^-$ is the active intermediate is suggested by the findings of Corriu and coworkers who have shown that several types of pentacoordinated silicon anions have greatly enhanced tendencies to undergo nucleophilic substitution.[12] Finally, the possibility exists that complex anions such as R_2MgCN^-,[13] R_2MgSCN^-,[14] or $RMg(X)CN^-$ have enhanced nucleophilic properties. Regardless of mechanistic detail, the use of CN^- or NCS^- catalysts greatly increases the utility of organomagnesium reagents for the preparation of tetraorganosilanes.

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A Search for α-Hydrogen Migration in Iron–Alkyl Negative Ion Complexes in the Gas Phase

Richard N. McDonald,* Daniel J. Reed, and A. Kasem Chowdhury

*Department of Chemistry, Kansas State University
Manhattan, Kansas 66506*

Received September 27, 1988

Summary: The (adduct − H_2) product negative ion formed in the reaction of $(OC)_2Fe^{\bullet-}$ with $(CH_3)_2O$ was shown to be the carbene complex $(OC)_2Fe{=}CHOCH_3^{\bullet-}$, the product of C–H bond activation followed by α-hydrogen mi-

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