For example, H···Acc distances can be correlated with the nature and environment of the donor and acceptor groups; Don–H···Acc angles have an energetic preference for linearity or near-linearity; and there is a slight tendency for hydrogen bonds to form in the directions of the acceptor-atom lone pairs. The importance of these results is that they may be used to devise "rules" for rationalizing, or even predicting, crystal-structure hydrogen-bonding arrangements. Recent studies on simple molecules such as amides and monosaccharides suggest that this is already a profitable area of research. In fairness, though, we must quote from a reviewer's report on this paper: "There have been some heroic attempts and a few minor advances ... but [rationalization of crystal-structure hydrogen-bonding patterns] ... is still at the foot of the rainbow". The truth of this remark cannot be denied: we have come a long way, but there is much further to go. Still, it is encouraging to recall the conventional wisdom about rainbows: pots of gold are to be found at their ends!

New Synthetic Chemistry of Transition-Metal Trialkylsilane Complexes

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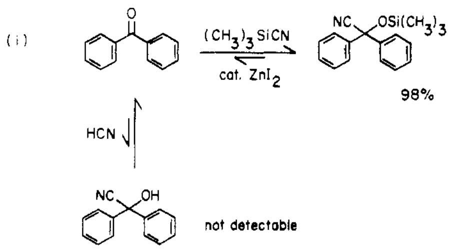
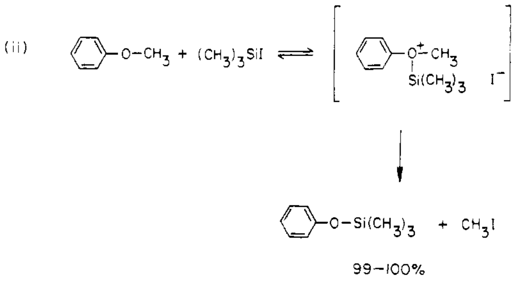
Many useful transformations, such as the Wittig reaction, are thermodynamically driven by the formation of strong heteroatom–oxygen or metal–oxygen bonds. Silicon makes an exceptionally strong single bond to oxygen (106–127 kcal/mol),[1] and this provides the basis for many of the applications of silicon reagents in organic synthesis.[2]

Our attention was drawn to trimethylsilyl (pseudo)halogen compounds, $(CH_3)_3SiX$,[2-4] by the elegant research of three Southern California colleagues: Evans, Jung, and Olah. These reagents are capable of effecting types of organic transformation (particularly with oxygen-containing substrates) which otherwise require harsh conditions or are impossible with the corresponding protic acids HX. A striking example is provided by the 1,2-addition of $(CH_3)_3SiCN$ to benzophenone to give a silylated cyanohydrin (eq i).[3a] No cyanohydrin is obtained when benzophenone is treated with HCN. Another example is the cleavage of ethers by $(CH_3)_3SiI$ (eq ii).[4b,d] This reaction is believed to involve the initial formation of an oxonium salt ion pair.





We sought to determine if reactivity patterns similar to eq i and ii might be exhibited by *transition-metal trialkylsilanes*, L_nMSiR_3.[5] In other words, can the –CN and –I in eq i and ii be replaced by metals? If so, it might be possible to achieve (1) conceptually new syntheses of organometallic complexes, (2) heretofore difficult or unprecedented organic transformations by elaboration of these organometallic complexes, and (3) stoichiometric analogues of postulated but yet unobserved steps in the catalytic hydrosilylation of unsaturated organic molecules. As precedent, we noted Ellis' observation that L_nM^- moieties often exhibit halide-like (X^-) reactivity.[6]

Examples of readily available transition-metal trialkylsilanes include $(CO)_4CoSi(CH_3)_3$,[7] $(CO)_5MnSi(C-$

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$H_3)_3$ (1),[8] $(CO)_5ReSi(CH_3)_3$,[9] $(\eta\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_3$,[8b,10] *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (2),[11] and $(CO)_4FeSi(CH_3)_2CH_2CH_2Si(CH_3)_2$ (3).[12] Such complexes are commonly prepared by two routes. The first is the thermal or photochemical addition of silanes, R_3SiH, to mono and bimetallic (L_nMML_n) complexes.[7,8a,9,12] The second is by attack of a metal anion, $M'^+ L_nM^-$, upon silicon electrophile R_3SiX.[8,10,11b] These latter reactions are best conducted in hydrocarbon solvents to avoid silane/solvent side reactions and precipitate the salt byproduct M'^+X^-. It is important that M'^+X^- have a strong lattice energy, since silane complex formation can be close to thermoneutral and reversed by solubilized X^-.[13]

At the time we initiated this research, there were several clues in the literature that silane complexes L_nMSiR_3 might react with organic substrates along the lines of eq i and ii. For instance, $(CO)_5MnSi(CH_3)_3$ (1) had been shown to silylate $(CH_3)_3N$ to give the isolable ion pair $(CH_3)_3N^+Si(CH_3)_3$ $(CO)_5Mn^-$.[8a] THF solutions of $(CO)_4CoSi(CH_3)_3$ rapidly decomposed to ring-opened silyloxy olefins plausibly derived from $(CH_3)_3SiOCH_2CH_2CH_2CH_2Co(CO)_4$.[14] These two transformations have strong parallels in eq ii. Murai had found that aldehydes RCHO could be homologated with CO (50 atm) and $HSi(CH_2CH_3)_2CH_3$ in the presence of a $Co_2(CO)_8/PPh_3$ catalyst at 100 °C to new aldehydes $RCH[OSi(CH_2CH_3)_2CH_3]CHO$.[15] These conditions likely generate an active $L_nCoSi(CH_2CH_3)_2CH_3$ catalyst which adds to aldehydes as in eq i.

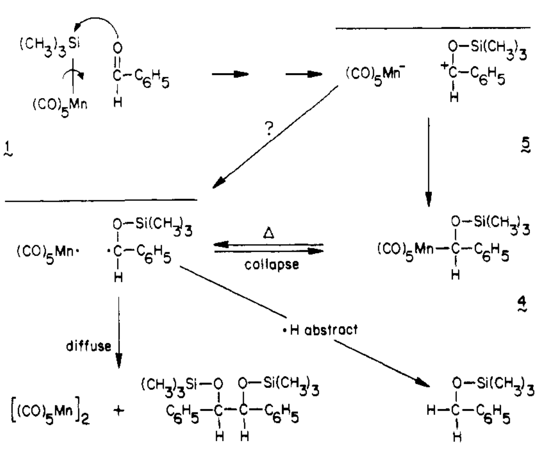
The two major variables in tailoring transition-metal silane reactivity are the silane ligand and the L_nM^- moiety. The studies summarized in this account have focused on *methylated* silanes for two reasons. First, methyl is less bulky than ethyl or phenyl and presents a minimum of steric hindrance to an attacking agent. Second, halide substituents on silicon increase the ligand π-acidity and hence the metal-silicon bond strength.[5b,8a,b]

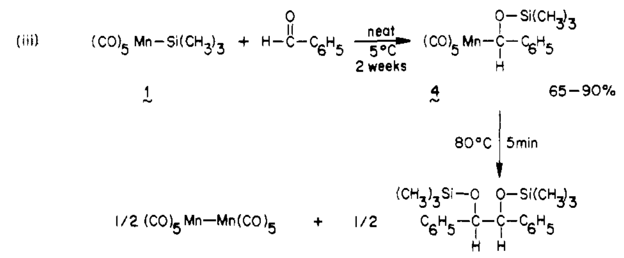
The studies that follow focus on the three representative, crystalline, coordinatively saturated silane complexes: $(CO)_5MnSi(CH_3)_3$ (1), *cis*-$(CO)_4Fe[Si(CH_3)_3]_2$ (2), and $(CO)_4FeSi(CH_3)_2CH_2CH_2Si(CH_3)_2$ (3). The first can be handled in air and is only moderately moisture sensitive. Both 2 and 3 are very air and water sensitive. All are thermally stable to ≳100 °C.

Reactions of Aldehydes and Ketones

Reactions of Aromatic Aldehydes with 1. When benzaldehyde and 1 are combined neat at 5 °C, a slow reaction occurs (eq iii). Over the course of 2 weeks, manganese α-(silyloxy)alkyl complex $(CO)_5MnCH(C_6H_5)OSi(CH_3)_3$ (4) forms in 65–90% yields.[16,17] Low temperatures are required because 4 undergoes facile homolysis ($t_{1/2}$ = 2.9 h, 38 °C).

Scheme I. Proposed Mechanism for the Reaction of 1 with Benzaldehyde





While the first stage of eq iii is too slow to be synthetically useful, several important mechanistic features can be discerned. First, the reaction is markedly slower in hexane, benzene, and CH_2Cl_2 but faster in CH_3CN. Second, added nucleophiles such as $(CO)_5Mn^-$ or Lewis acids such as $AlCl_3$ and ZnI_2 fail to accelerate the rate. Small amounts of oxygen neither accelerate nor inhibit the rate. These additives are potential initiators of chain mechanisms.[3] Third, *p*-methoxybenzaldehyde undergoes a much faster reaction with 1 to give α-(silyloxy)alkyl complex $(CO)_5MnCH(p\text{-}C_6H_4OCH_3)OSi(CH_3)_3$, which is less stable toward homolysis than 4. Reaction of 1 with *p*-(dimethylamino)benzaldehyde is faster still, but only homolysis products of presumed intermediate $(CO)_5MnCH[p\text{-}C_6H_4N(CH_3)_2]OSi(CH_3)_3$ are detected. Finally, no exchange of 1 with ^{13}CO occurs on the time scale of these faster reactions.

In view of the above solvent and substituent effects, we propose that the initial and rate-determining step of eq iii is the attack of benzaldehyde oxygen upon the trimethylsilyl group of 1. This would give the ion pair 5 shown in Scheme I. It is logical that the strongest bond formed in eq iii (Si–O) should be generated as early in the mechanism as possible.

The direction of the equilibrium for the first stage of eq iii markedly contrasts with that of eq iv. Several attempts have been made to generate α-hydroxyalkyl complex $(CO)_5MnCH(C_6H_5)OH$ (6) from 4 and other precursors.[18] In each case, only $(CO)_5MnH$ and benzaldehyde are detected. However, $(CO)_5MnH$ can be

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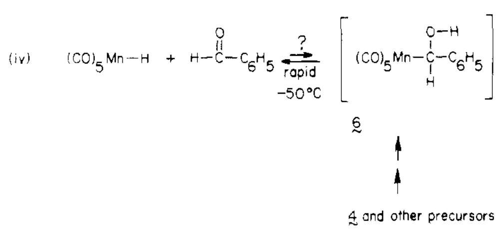
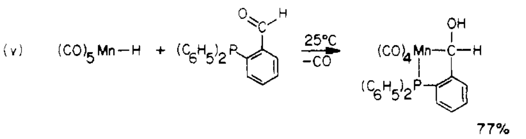
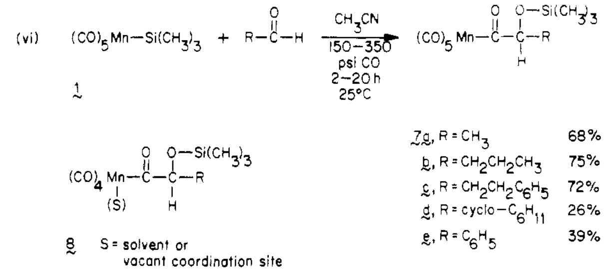
made to add to aromatic aldehydes under entropically favorable circumstances, as shown in eq v.[19]





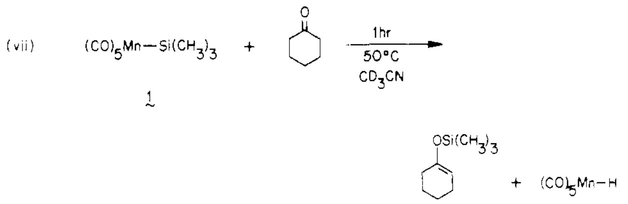
There are two principal reasons for the difference between eq iii and iv. The first is that the Si–O bond in **4** is much stronger than the O–H bond in **6**. Second, while highly accurate measurements of metal–trialkylsilyl bond strengths are not yet available, the iron–silicon bond in (η-C_5H_5)Fe(CO)$_2$Si(CH$_3$)$_2$CH$_2$Br has been shown to be no more than 5–7 kcal/mol stronger than the iron–carbon bond in (η-C_5H_5)Fe(CO)$_2$CH$_2$Si(CH$_3$)$_2$Br.[20] Since manganese–carbon bond strengths in alkyl complexes (CO)$_5$MnR fall in the 20–30 kcal/mol range,[21] it is unlikely that the manganese–silicon bond dissociation energy in **1** is much greater than 40 kcal/mol. In contrast, the manganese–hydrogen bond strength in (CO)$_5$MnH has been estimated to be as high as 60 kcal/mol.[21] Thus, a significantly stronger bond must be broken in eq iv.

Other Reactions of Aldehydes and Ketones with 1. When **1** is treated with aromatic or aliphatic aldehydes RCHO under 150–350 psi of CO, manganese acyl complexes (CO)$_5$MnCOCH(R)OSi(CH$_3$)$_3$ are obtained in fair to good yields as shown in eq vi.[22] These acyl



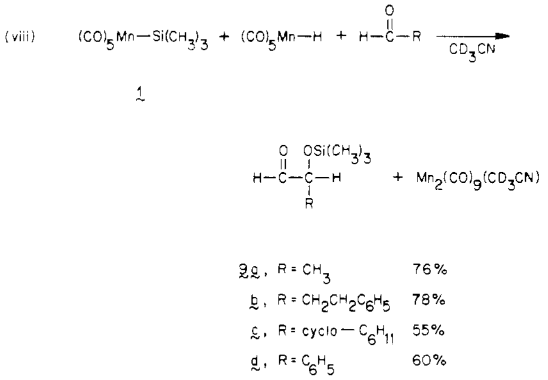
complexes are formed via the carbonylation of alkyl intermediates, (CO)$_5$MnCH(R)OSi(CH$_3$)$_3$, which are likely generated via a Scheme I type mechanism. Experiments with ^{13}CO-labeled **1** show that carbonylation occurs via a conventional Calderazzo mechanism,[23] i.e., first by alkyl migration to give the coordinatively unsaturated acyl intermediate **8** (eq vi) and then CO capture. Note that the CH$_3$CN solvent effects a substantial increase in the rate of eq vi over that of eq iii. Monomeric formaldehyde, however, repolymerizes faster than it reacts with **1**.[24]

Reaction of **1** with aliphatic aldehydes in the *absence* of CO—or with aliphatic ketones under any conditions—gives trimethylsilyl enol ethers and (CO)$_5$MnH in high yields (eq vii).[17] These products may



be viewed as net β-hydride elimination decomposition products of intermediate alkyls (CO)$_5$MnCR′(R)OSi(CH$_3$)$_3$, although other possible mechanisms for their formation exist.[17] Equation vii is noteworthy in that no acid or base is needed to effect enol ether formation. However, with less symmetrical organic substrates there is no pronounced regio- or stereocontrol, and the mildly acidic byproduct (CO)$_5$MnH (p$K_a \simeq 7$)[25,26] equilibrates all possible enol ether isomers upon standing.

When **1** and aldehydes RCHO are reacted in the presence of (CO)$_5$MnH, homologation to new aldehydes RCH(OSi(CH$_3$)$_3$)CHO occurs as shown in eq viii.[22] This "reductive formylation" requires several steps via conventional synthetic methodology. It is believed to occur via the trapping of coordinatively unsaturated intermediate **8** (eq vi) with (CO)$_5$MnH.[27]



Reactions of Aldehydes with Other Metal Silane Complexes. Relative Reactivity. Benzaldehyde does not react with (CO)$_5$ReSi(CH$_3$)$_3$ or (η-C_5H_5)Fe(CO)$_2$Si(CH$_3$)$_3$ over the course of 18 h in CD$_3$CN at 55 °C.[28] However, benzaldehyde and iron disilane complex **2** react rapidly in benzene at 5 °C (eq ix).[11b,16] Alkyl complex *cis*-(CO)$_4$Fe(Si(CH$_3$)$_3$)CH(C$_6$H$_5$)OSi(CH$_3$)$_3$ (**10**) can be observed in up to 65% spectrospcopic yield before competitive homolysis to pinacol ether dimers and the dinuclear silane *trans*-[-Fe(CO)$_4$Si(CH$_3$)$_3$]$_2$ (**11**) begins to dominate.

We presume that eq ix proceeds by a mechanism similar to eq iii (Scheme I). How can the greater reactivity of **2**—or the lack of reactivity of (CO)$_5$ReSi(CH$_3$)$_3$ and (η-C_5H_5)Fe(CO)$_2$Si(CH$_3$)$_3$—be accounted for? We consider the metal carbonyl moiety to act like a

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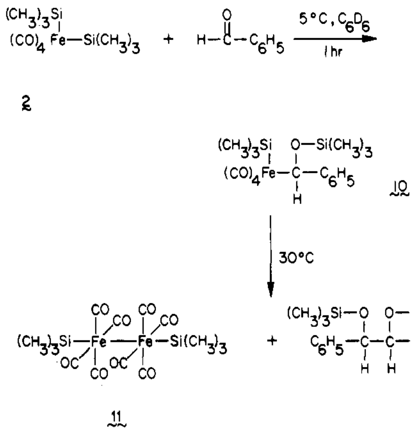
(ix)



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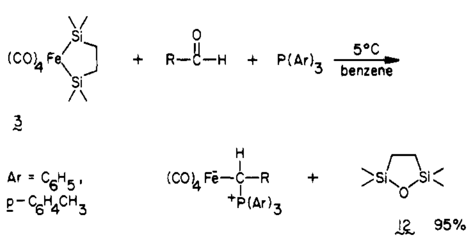

14a, $R = C_6H_5$, 99%
b, $R = p\text{-}C_6H_4OCH_3$, 99%
c, $R = p\text{-}C_6H_4N(CH_3)_2$, 50%
d, R = 2-naphthyl, 98%
e, $R = CH_2CH_3$, 70%
f, $R = CH_2CH_2CH_3$, 51%
g, $R = n\text{-}C_7H_{15}$, 85%
h, $R = \text{cyclo-}C_6H_{11}$, 42%
i, R = 2-furyl, 93%

"leaving group" in the first step of Scheme I. The leaving group abilities of L_nM^- species have not to our knowledge been measured but would be expected[29] to correlate roughly to acidities of the conjugate acids L_nMH. Metal hydride acidities are known to decrease in the order $(CO)_4CoH > (CO)_4FeH_2 > (CO)_5MnH > (CO)_5ReH \sim (\eta\text{-}C_5H_5)Fe(CO)_2H$.[24,25] Hence, the same order would be expected for the reactivity of the corresponding metal trialkylsilane complexes in reactions that entail initial and rate determining L_nM^- displacement. This is observed in the above reactions of benzaldehyde. Metal trialkylsilane complexes also commonly silylate methanol and other alcohols: $L_nMSiR_3 + CH_3OH \rightarrow L_nMH + CH_3OSiR_3$. Here, the parallel relative rates $(CO)_4CoSi(CH_3)_3$[7] > 1[30] >> $(\eta\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_3$[10b] have been found. In related reactions, Malish has observed the reactivity order $(\eta\text{-}C_5H_5)Mo(CO)_3Si(CH_3)_3 >> (\eta\text{-}C_5H_5)W(CO)_3Si(CH_3)_3 > 1 > (\eta\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_3$.[8b] Thus it is possible to rationally select a metal trialkylsilane complex with any desired degree of reactivity.

In a naive attempt to retard the homolysis of the iron-carbon bond of **10** in eq ix, we investigated the reaction of the chelated iron disilane complex **3** with benzaldehyde.[16,31] The cyclic siloxane $(CH_3)_2\overline{SiCH_2CH_2Si(CH_3)_2O}$ (**12**) rapidly forms in 95% yield, and some *trans*-stilbene (18–25%), $Fe(CO)_5$, and $Fe_3(CO)_{12}$ are detected. We thought that the oxygen atom of siloxane **12** was likely benzaldehyde derived. Alkylidene complexes $L_nM{=}CHR$ often couple to olefins,[32] so we proposed the intermediacy of benzylidene complex $(CO)_4Fe{=}CHC_6H_5$ (**13**). When this reaction is conducted in the presence of trapping agent $P(C_6H_5)_3$ (which does not alter the rate), a benzylidene adduct, ylide complex $(CO)_4Fe^-CH(C_6H_5)^+P(C_6H_5)_3$ (**14a**), is isolated in 99% yield (eq x).

This transformation is general for a variety of aromatic and aliphatic aldehydes, as summarized in eq x. Phosphine exchange experiments demonstrate that **14** is in equilibrium with the free alkylidene complex $(CO)_4Fe{=}CHR$. The mechanism suggested in Scheme II accounts for all of the above observations.

The take-home lesson of eq x is that the two silicon-oxygen bonds in disiloxane **12** provide enough driving force to cleave the carbon–oxygen *double* bond of benzaldehyde (ca. 175 kcal/mol). This synthetic strategy can potentially be applied to the generation of other $(CO)_4Fe{=}XL_n$ compounds and species with multiple bonds to metals. Notably, eq x *and* vi provide the first general means for the direct incorporation of aldehydes into organometallic molecules.

Reactions of Ethers and Ketals

Reaction of Ethers with 1. Ethyl ether and other unstrained ethers do not react with **1** on the time scale of a few hours at room temperature. However, **1** does react with THF and strained cyclic ethers.[22,23] For instance, when **1** is treated with oxetane in CD_3CN, the labile alkyl complex $(CO)_5MnCH_2CH_2CH_2OSi(CH_3)_3$ forms in 55–80% spectroscopic yield.[22] When this reaction is conducted in ether under 320 psi of CO, the more robust acyl complex $(CO)_5MnCOCH_2CH_2CH_2OSi(CH_3)_3$ (**15b**) is isolated in 83% yield. Ethylene oxide and THF react with **1** and CO similarly, as outlined in Scheme III.

These reactions are proposed to occur via nucleophilic attack of $(CO)_5Mn^-$ upon silylated oxonium salts of the type **16** (step b, Scheme III). Reaction of propylene oxide with **1** and CO gives principally (>95%) the regioisomer that would be expected from S_N2 ring opening, $(CO)_5MnCOCH_2CH(CH_3)OSi(CH_3)_3$.[22] Similarly, cyclohexene oxide gives the manganese acyl derived from trans ring opening in 87% yield. No reaction is observed when **1** is dissolved in tetrahydropyran at room temperature.

Acyl ligands can be converted to a variety of different organic compounds. For instance, when acyl complexes **15b** and **15c** are treated with the fluoride ion source $[(CH_3CH_2)_2N]_3S^+Si(CH_3)_3F_2^-$, γ-butyrolactone and δ-valerolactone are obtained in 84–95% and 60–85% yields.[22] These transformations involve initial alkoxide generation, followed by intramolecular acylation and displacement of $(CO)_5Mn^-$. They constitute a net overall carbonylation of the cyclic ether precursors in Scheme III.

Reactions of Ethers with 2. Silane complex **2** is sufficiently reactive to attack unstrained, acyclic ethers. For instance, methyl and benzyl trimethylsilyl ether are deoxygenated (80 °C) to their respective alkyltrimethylsilanes, $RSi(CH_3)_3$.[34] These transformations are

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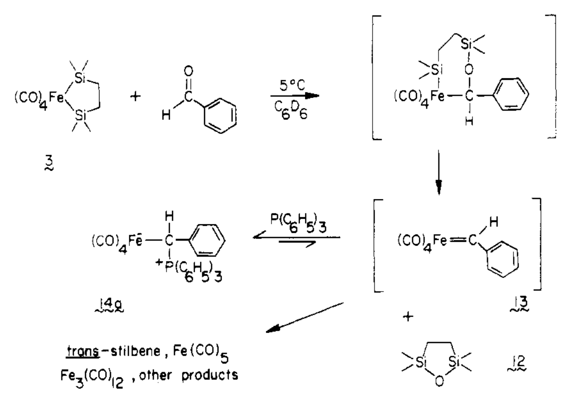
[30] Gladysz, J. A.; Tam, W.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163.

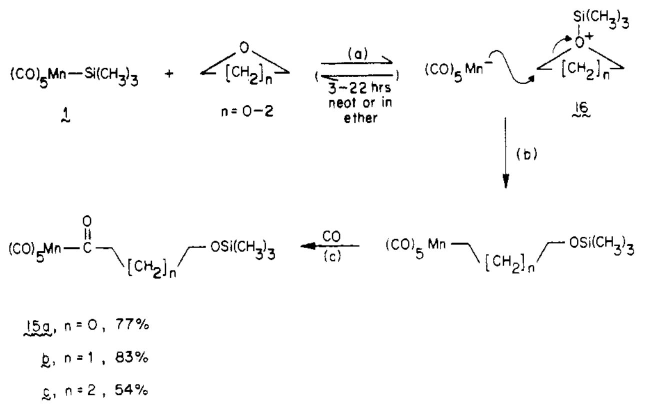
[31] Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846.

[32] (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *Ibid.* **1977**, *99*, 2127. (c) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *Ibid.* **1983**, *105*, 5811 and references therein.

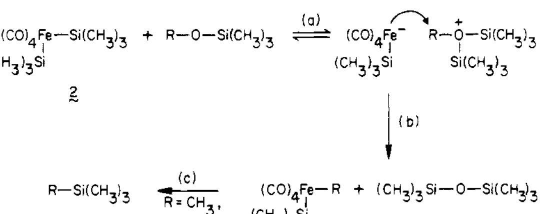
Scheme II. Proposed Pathway for the Reaction of 3 with Benzaldehyde



Scheme III. Proposed Mechanism for the Formation of Manganese Acyl Complexes $(CO)_5MnCOCH_2(CH_2)_nCH_2OSi(CH_3)_3$ from Cyclic Ethers, 1, and CO



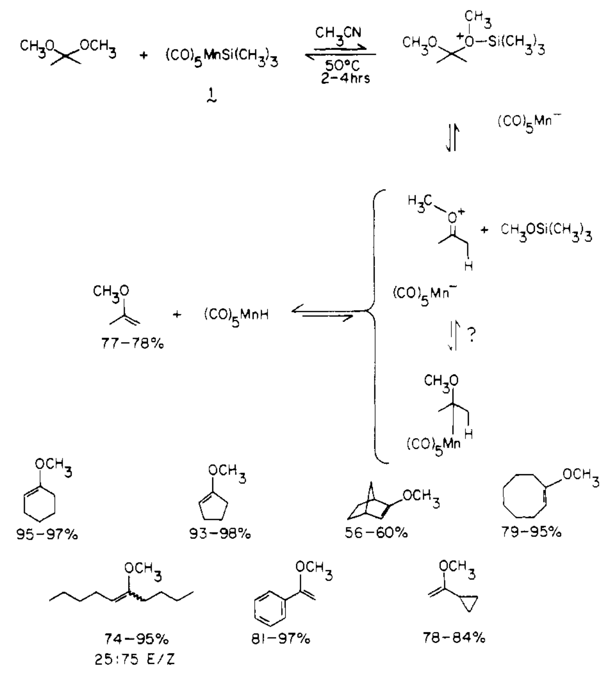
Scheme IV. Proposed Mechanism of Trimethylsilyl Ether Deoxygenation



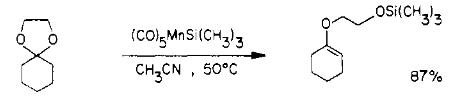
believed to occur as outlined in Scheme IV. Although the proposed $(CO)_4Fe(R)Si(CH_3)_3$ intermediates are not observed, they have been independently synthesized (see below) and reductively eliminate $RSi(CH_3)_3$ as shown in step c. Reaction of CH_3OCH_3 with **2** occurs at 5 °C, and the formation and subsequent decomposition of intermediate *cis*-$(CO)_4Fe(CH_3)Si(CH_3)_3$ is easily observed by ^1H NMR. Similar reactions of **2** with $(C_6H_5CH_2)_2O$ and $C_6H_5CH_2OCH_3$ have also been studied.[34] However, when there are C–H bonds *β* to the ether oxygen, complex reactions ensue.

Reactions of Ketals with 1. Enol ethers are conventionally synthesized by the reaction of ketals and acetals with protic acids at temperatures in the 100–200 °C range. However, we have found that enol ethers form in high yield when a variety of dimethyl ketals and **1** are combined at 50 °C in CH_3CN.[35] This transformation is believed to occur as outlined in Scheme V. The initial step, silylation of an "ether" oxygen, is analogous to those in Schemes III and IV. Some representative enol ethers that have been prepared by this route are shown in Scheme V. When regioisomers are possible, approximately thermodynamic mixtures are obtained. Cyclohexanone ethylene glycol ketal and **1** react to give the functionalized enol ether shown in eq xi.

Scheme V. Proposed Mechanism of Trimethylsilyl Enol Ether Formation



(xi)



Reactions of Other Organic Substrates

Reactions of Other Carbonyl Compound Derivatives with 1. The trimethylsilyl enol ether synthesis shown in eq vii, although mild, would be improved if the byproduct $(CO)_5MnH$ could be eliminated. It seemed to us that following initial O-silylation of an *α*-bromocarbonyl compound R′COCHBrR by **1**, subsequent formation of $(CO)_5MnBr$ would be favored over $(CO)_5MnH$. Concurrently, an enol ether would be regiospecifically generated. This prediction was based upon thermodynamic considerations: the Mn–Br bond of $(CO)_5MnBr$ and Mn–H bond of $(CO)_5Mn–H$ have comparable strengths (62 and ca. 55-60 kcal/mol),[21] but C–Br bonds are much weaker than C–H bonds.

In fact, *α*-bromocarbonyl compounds undergo preferential reductive dehalogenation to silyl enol ethers when treated with **1** at 25 °C in CH_3CN.[36] At most only a minor amount of proton abstraction occurs. In

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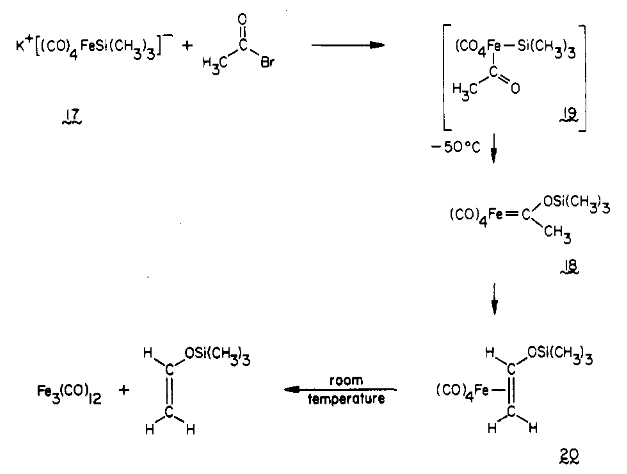
(33) Brinkman, K. C.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* 1980, 1260.

(34) Blakeney, A. J.; Gladysz, J. A. *J. Organomet. Chem.* 1981, *210*, 303.

(35) (a) Marsi, M.; Gladysz, J. A. *Tetrahedron Lett.* 1982, *23*, 631. (b) Marsi, M.; Gladysz, J. A. *Organometallics* 1982, *1*, 1467.

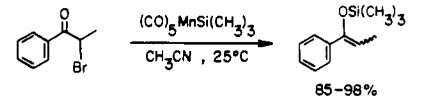
(36) Marsi, M.; Brinkman, K. C.; Lisensky, C. A.; Vaughn, G. D.; Gladysz, J. A., submitted for publication.

Scheme VI. Proposed Mechanism for the Reaction of 17 with Acetyl Bromide

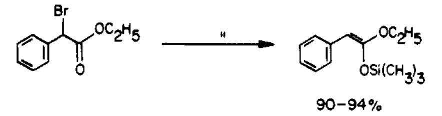


favorable cases, it is also possible to cleave other heteroatom–carbon bonds that are α to a carbonyl group. Representative examples are given in eq xxii–xiv.

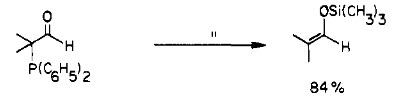
(xii)



(xiii)



(xiv)



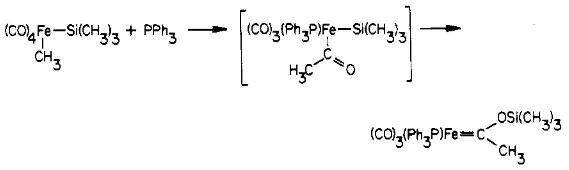
No reaction occurs upon heating CH_3CN solutions of 1 and ethyl acetate, methyl benzoate, and benzoic anhydride.[17] Benzoyl chloride and 1 give some $(CO)_5MnCOC_6H_5$ in CH_3CN, as assayed by IR spectroscopy. However, this product is not stable under the reaction conditions, probably due to further reaction with byproduct $(CH_3)_3SiCl$.[17]

Reactions of Alkylating and Acylating Agents with Silylated Iron Anions. We synthesized the new anionic iron silane complexes $M^+ [(CO)_4FeSi(CH_3)_3]^-$ (17, M = Na^+, K^+) by treating $(CO)_4Fe(H)Si(CH_3)_3$ with either NaH or KH.[10b,37] These react with strong alkylating agents such as CH_3SO_3F, $CH_3OSO_2CF_3$, $CH_3CH_2SO_3F$, $C_6H_5CH_2Br$, and $H_2C{=}CHCH_2Br$ to give labile alkyl complexes *cis*-$(CO)_4Fe(R)Si(CH_3)_3$ in 89–34% yields.[37] When R = CH_3 or $CH_2C_6H_5$, these alkyls eliminate $RSi(CH_3)_3$ as shown in Scheme IV.

An extraordinary transformation occurs when 17 and acetyl bromide are combined.[37b] Reaction occurs at −50 °C to give *silyloxycarbene* complex $(CO)_4Fe{=}C(CH_3)OSi(CH_3)_3$ (18) as the first detectable intermediate. This structural assignment is supported by low-temperature ^1H NMR, ^{13}C NMR, and IR spectroscopy and an independent synthesis from $(CO)_4Fe{=}C(CH_3)O^-$ and $(CH_3)_3SiBr$. Apparently, the initially formed iron acyl complex 19 (Scheme VI) undergoes a 1,3-silatropic rearrangement which is driven by formation of a silicon–oxygen bond. Upon warming, 18 rearranges to enol ether complex 20, which has been previously synthesiszed.[38] At room temperature, acetaldehyde trimethylsilyl enol ether, $H_2C{=}CHOSi(CH_3)_3$ is obtained in $\gtrsim$70% yield.

Transformations analogous to those in Scheme VI occur when 17 is treated with propionyl bromide and phenylacetyl bromide.[37b] Reaction of 17 with pivaloyl bromide, $(H_3C)_3CCOBr$, yields a stable silyloxycarbene complex, $(CO)_4Fe{=}C[C(CH_3)_3]OSi(CH_3)_3$. Finally, an alkyl migration/silatropic shift occurs when *cis*-$(CO)_4Fe(CH_3)Si(CH_3)_3$ and PPh_3 are reacted (Eq xv).[37b]

(xv)



Catalytic Hydrosilylation

The reactions described in the preceding sections provide explicit precedent for a number of proposed steps in the catalytic hydrosilylation of unsaturated organic molecules,[5,39,40] For instance, eq iii and ix constitute the first direct observations of the insertion of a carbonyl group into a transition metal–silicon bond. A similar step must occur in the metal-catalyzed addition of silanes R_3SiH to aldehydes and ketones.[39] However, most active hydrosilylation catalysts are coordinatively unsaturated and it is likely that the carbonyl group is bound prior to insertion. Step c of Scheme IV provides the first direct observation of alkylsilane reductive elimination. This is the final step in both metal-catalyzed alkene[40] and aldehyde/ketone hydrosilylation.[39] However, reactions of alkenes (and alkynes) with the types of metal carbonyl trialkylsilane complexes described in this Account are relatively uncommon, probably due to a requirement for a vacant coordination site. Finally, Murai has developed a number of cobalt-catalyzed reactions that entail the addition of CO and R_3SiH to organic substrates such as aldehydes, cyclic ethers, and alkenes.[15] Direct precedent for nearly all of the key proposed steps in these transformations is given above.

Summary and Conclusions

We have made use of themes from physical organic, synthetic organic, and physical inorganic chemistry to systemize the reactivity of transition-metal trialkylsilane complexes. To date, two applications of metal trialkylsilane chemistry have received the most attention: (1) organic transformations and (2) the synthesis of organometallic compounds. However, we predict that there will also be exciting applications in the area of *inorganic synthesis*, i.e., the formation of metal–metal and metal–heteroatom bonds. Consider the possibility of substituting $L_nM{=}O$ or $RN{=}O$ substrates for aldehydes in eq x or metal phenoxides $M(OAr)_x$ for ethers in Scheme IV. Also, we feel that excellent opportunities for useful and unusual transformations are afforded by

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(37) (a) Blakeney, A. J.; Gladysz, J. A. *Inorg. Chim. Acta.* **1981**, *53*, L25. (b) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

(38) Thyret, H. *Angew. Chem., Int. Ed. Engl.* **1972**, 11, 520.

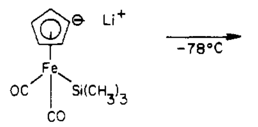
(39) (a) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. (b) Hayashi, T.; Yamamoto, K.; Kasuga, K.; Omizu, H.; Kumada, M. *Ibid.* **1976**, *113*, 127. (c) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chem.* **1978**, *2*, 211.

(40) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Harrod, J. F.; Chalk, A. J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 1, pp 673–704.

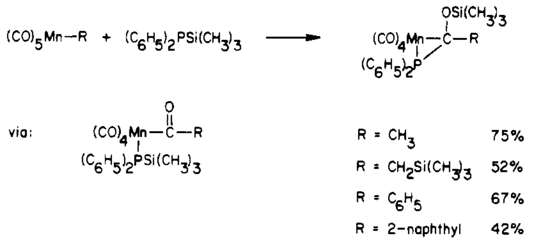
early transition metal[41] and coordinatively unsaturated[5] trialkylsilane complexes.

Mechanisticaly, we are coming to the realization that diverse types of organosilicon reactivity modes can manifest themselves within the coordination sphere of a transition metal. Striking examples include the silatropic shifts noted above and the Brook-like rearrangement (eq xvi) discovered by Berryhill.[42] Such reactions will be increasingly sought and exploited by synthetic organometallic and inorganic chemists. As an illustration, consider the recently reported $(C_6H_5)_2PSi(CH_3)_3$-induced CO insertion and cyclization shown in eq xvii.[43] We hope that this account has provided its readers with a firm basis for the rational design of such chemistry.

(xvi)



(xvii)



I express my sincere thanks to the research associates who collaborated on this project: Dennis L. Johnson, Dr. Andrew J. Blakeney, Kerry C. Brinkman, Marianne Marsi, Wilfried Krone-Schmidt, Patrick Donovan, George D. Vaughn, Dr. Hiroshi Nakazawa, Bill D. Zwick, K. Alex Krein, and Carol A. Lisensky. The National Science Foundation is gratefully acknowledged for suport of this research.

[41] Tilley, T. D., submitted for publication in *Organometallics*.

[42] Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* 1981, *221*, 143.

[43] Vaughn, G. D.; Krein, K. A.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 239.

Predicting Carcinogenicity of Polycyclic Aromatic Hydrocarbons

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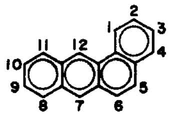
Polycyclic aromatic hydrocarbons (PAH) and related molecules display a wide range in cancer-inducing activity.[1] For instance, 1 is not carcinogenic, 2 is weakly carcinogenic, and 3 is very carcinogenic. 2 can be made much more carcinogenic by methylating position 6, 7, or 12, but methylation in any of the positions 1–5 causes complete loss of activity. Replacing a C–H in 2 by nitrogen to give 4 or 5 removes carcinogenic activity, but 4 can be more easily reactivated by methylation than can 5. 6 is extremely carcinogenic.


1



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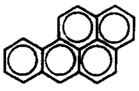
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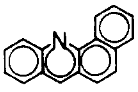

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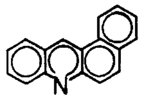

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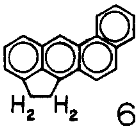

6

Why do these structural modifications cause these changes in carcinogenicity? Chemists have been intrigued by this question since such data began to become available in the 1930s. Physical properties, such as lipophilicity[2] and molecular shape,[3] appear to play a role, but these can only be expected to distinguish between molecules that differ in major ways. There must be other factors too, presumably having to do with chemical reactivity, and it is on these that chemists have focused their attention. In most cases, quantum chemical calculations have been used to generate re-

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B. David Silverman was born in 1931 and was educated at Brooklyn College, The University of Rochester, and Rutgers University. He is a research staff member at the IBM Thomas J. Watson Research Center, Yorktown Heights, NY. He is a theoretical solid-state physicist by training and has worked in such divergent areas as ferroelectrics, ultrasonics, quantum electronics, optical computer memories, organic metals, and chemical carcinogenesis.

[1] (a) Arcos, J. C.; Argus, M. F. "Chemical Induction of Cancer"; Academic Press: New York, 1974 (b) Dipple, A. In "Chemical Carcinogens"; Searle, C. E., Ed.; American Chemical Society: New York, 1976; pp 245–314. (c) Berenblum, I. In "Physico-Chemical Mechanisms of Carcinogenesis" (The Jersalem Symposia on Quantum Chemistry and Biochemistry); Academic Press: New York, 1969; Vol. 1, pp 321–324.

[2] Hansch, C.; Frijita, T. *J. Am. Chem. Soc.* 1964, *86*, 1616.

[3] Mohammad, S. N.; Hopfinger, A. J.; Bickers, D. R. *J. Theor. Biol.* 1983, *102*, 323–331.

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