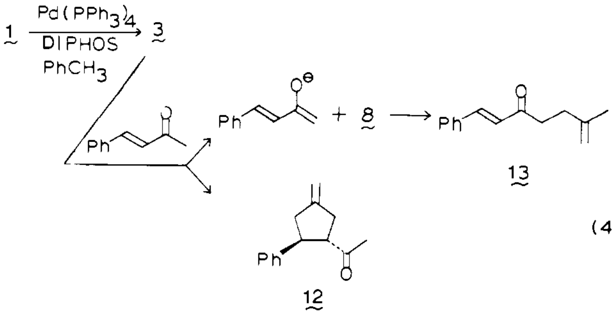
10 and **11** can compete with cyclization. In this case, starting olefin is not observed to isomerize under the reaction conditions. The ring closure of **10** and **11** is postulated in analogy to normal nucleophilic attack on π-allylpalladium cationic complexes.[7] Usually, simple enolates such as those from ketones and esters do not attack such complexes in good yield.[4,8] Presumably the intramolecularity of the cyclization reaction allows domination by the desired alkylation over the competing decomposition reactions observed in the intermolecular cases.

Further evidence of the behavior of **3** as a zwitterionic type species stems from the competing cycloaddition to give **12** and desilylative alkylation to give **13** when benzylideneacetone is employed as a trap (eq 4). Thus, with a trap that possesses an electrophilic unit and acidic protons, both the nucleophilicity and basicity of **3** is observed. Performing the reaction in refluxing THF leads almost exclusively to **12** which indicates that the nucleophilicity of **3** is enhanced at the expense of its basicity in this solvent.



(4)

The above results clearly show that the reaction of **1** and Pd(0) is initiated by ionization of acetate and that desilylation occurs before reaction with electron deficient olefins and some nucleophiles. Only a complex such as **3** appears compatible with these experimental observations.[9] Furthermore, this complex has the behavior of a zwitterion. It is interesting to contrast the complex with the free ligand which behaves more like a diradical.[10] These results can be contrasted to that of Binger and Schuchardt[3c] who claim to have generated this complex from methylenecyclopropane and a Pd(0) species generated in situ. While they report trapping with electron-deficient olefins in unstated yields and with E-Z isomerization, they also report trapping with norbornene—a reaction that we do not observe. In such a case, it is difficult to ascertain whether direct reaction of the highly reactive methylenecyclopropane with the olefins catalyzed by palladium occurred or whether opening to trimethylenemethane-palladium preceded reaction. By analogy to the nickel catalyzed reaction of methylenecyclopropane,[11] it appears that, at least for the norbornene case, the former appears more likely. Such an ambiguity does not exist for **1**. Thus, it may serve as a general entry into trimethylenemethane-transition metal complexes without the annoying self-oligomerization and direct condensation of methylenecyclopropane.[3]

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. We also thank Englehardt Industries and Mathey-Bishop for their generous gifts of palladium salts.

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(5) Generally, simple enolates react with π-allylpalladium cationic complexes in a stoichiometric reaction to give mainly decomposition. Recent work with the enol silyl ether of acetophenone as an enolate precursor and allyl acetate shows that C-alkylation occurs under palladium catalysis (E. Keinan, unpublished observations in these laboratories).

(6) This scheme represents a simplified version. Prior coordination of the electron-deficient olefin to palladium(0) may occur (Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375). Furthermore, an oxa-π-allyl-π-allyl sandwich complex may be the initial intermediate in lieu of **10** and **11** (for oxa-π-allyl complexes see Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494).

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(9) It should be noted that invoking a trimethylenemethane-palladium(0) complex does not make a statement regarding the symmetry of the complex. As represented in **3**, the complex has C_s symmetry. If the palladium rapidly migrates among the possible π-allyl units or effectively sets below the central carbon, then the complex would have (effective) C_{3v} symmetry. The nickel[3] and iron[2] complexes apparently have the latter symmetry. At this time, we do not differentiate between these possibilities.

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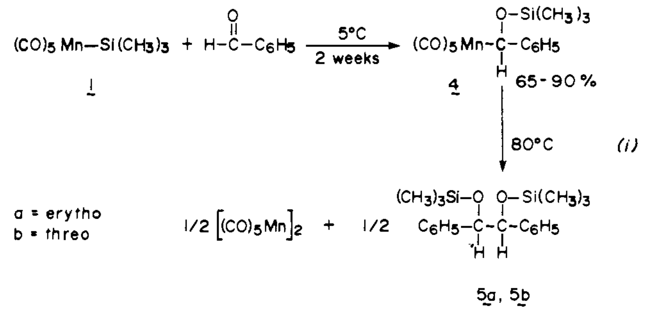
Reactions of Benzaldehyde with Trialkylsilyl Metal Carbonyl Complexes

Sir:

Our interest in new methodology for the formation of metal-carbon bonds[1] and the chemistry of the various oxidation states of metal-bound carbon[2] has led us to investigate the use of trialkylsilyl metal carbonyl complexes as reagents for organometallic synthesis. In this communication, we report that the metal silanes $(CO)_5MnSi(CH_3)_3$ (**1**),[3] $(CO)_4Fe[Si(CH_3)_3]_2$ (**2**),[4] and $(CO)_4\overline{FeSi(CH_3)_2CH_2CH_2Si}(CH_3)_2$ (**3**)[5] undergo reactions with benzaldehyde which result, under appropriate conditions, in the formation of α-silyloxybenzyl- and benzylidene-derived ligands.

The reaction of **1** with benzaldehyde was carried out at 5 °C in the absence of solvent. From an equimolar mixture of reactants, the insertion product **4** was formed in 65% yield after 2 weeks (eq i).[6a] Employing a twofold excess of benzaldehyde



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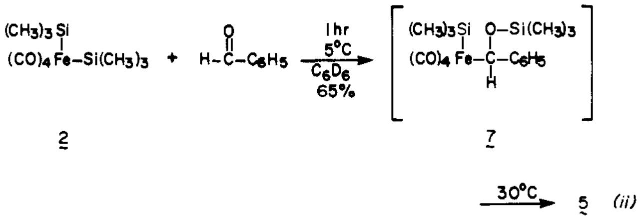
raised the yield of **4** to 90%. The identity of **4** was established by independent synthesis via an entirely different route.[2a]

The presence of small amounts of $[(C_6H_5)_3P]_2N^+$-$(CO)_5Mn^-$, $(CO)_5MnH$,[7] ZnI_2, or $AlCl_3$ had no effect on the rate of addition of **1** to benzaldehyde. In the cases of ZnI_2 and $AlCl_3$, $(CO)_5MnX$ and $[(CO)_4MnX]_2$ species were formed. Similar 1,2-addition reactions occur when aldehydes are reacted with $(CH_3)_3SiCN$ or $(CH_3)_3SiSCH_3$, but these can be catalyzed by both nucleophiles (e.g., ^-CN) and Lewis acids.[8] The reaction of **1** with benzaldehyde was slightly faster when carried out in acetonitrile solution (1 M).

Over the course of several hours at 25 °C or 5 min at 80 °C, **4** underwent homolytic decomposition to $[(CO)_5Mn]_2$ (100%) and a 1:1 mixture of the diastereomeric organic dimers **5a** and **5b** (eq i, 75-95%).[6] The hydrogen abstraction product benzyl trimethylsilyl ether (**6**) was also formed in 5-15% yield,[6] depending upon the presence and amount of any excess benzaldehyde. Benzylic radicals have been previously shown to efficiently abstract H· from $(CO)_5MnH$;[9] accordingly, when benzaldehyde was reacted in a 1:1:1 ratio with **2** and $(CO)_5MnH$[7] at 60 °C, **6** was the only organic product (100%).[6] The overall transformation depicted in eq i is reminiscent of the reduction of benzaldehyde to **5** by $Hg[Si(CH_3)_3]_2$, in which an organometallic intermediate was not detected.[10]

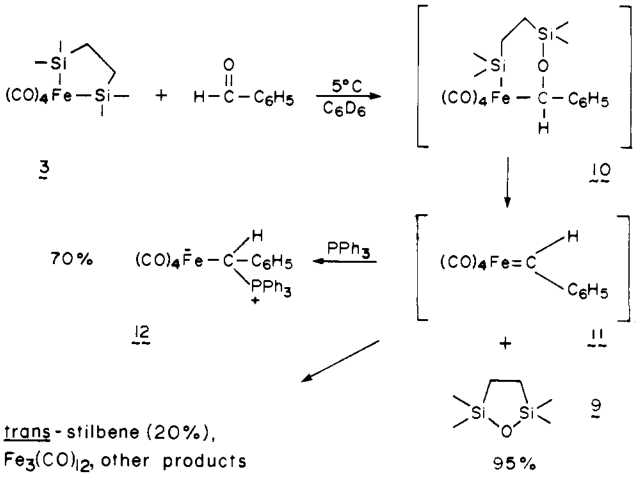
The iron silane **2** was considerably more reactive than **1**. When treated with 1 equiv of benzaldehyde at 5 °C in C_6D_6 solution (1 M), the adduct **7** was formed in 65% yield[6a] after 1 h (eq ii).[11] At this point, the unimolecular decomposition of **7** (to **5** and **6**) became as fast as its bimolecular formation. At 30 °C, **7** decomposed rapidly; the primary inorganic product showed a ^1H NMR resonance at δ 0.60, suggesting a metal-bound trimethylsilyl group; however, it decomposed upon attempted isolation.



Under identical conditions, **3** reacted with benzaldehyde to give disiloxane **9** (95%) and *trans*-stilbene (20-30%)[6b] as the only volatile organic products (Scheme I). Considerable insoluble material was also formed, of which $Fe_3(CO)_{12}$ was a major component. Although no intermediates could be detected in this reaction, initial formation of the cyclic 1,2 adduct **10** would be expected by analogy to eq ii. The high yield of **9** obtained suggests the concomitant formation of a species with the empirical formula $(CO)_4FeCHC_6H_5$, such as **11**. When **3** and benzaldehyde were reacted as above but in the presence of 1 equiv of triphenylphosphene, zwitterion **12** precipitated and was subsequently isolated in 70% yield.[12] Since triphenylphosphine has been shown to trap the unstable benzylidene complex $(CO)_5W{=}CHC_6H_5$ as a similar zwitterionic derivative,[13] the isolation of **12** can be taken as good evidence for the intermediacy of **11**. Disiloxane **9** (95%) and *trans*-stilbene (20%)[6b] were also formed in the reaction conducted with triphenylphosphine.

Several interesting points regarding the above reactions deserve mention. First, neither $(CO)_5MnH$ (2 months, 10 °C, or 1 day, 60 °C), $[(C_6H_5)_3P]_2N^+(CO)_5Mn^-$ (neat, 25 °C), nor $Li^+(CO)_5Mn^-$ (THF solution, 25 °C) undergoes reaction with benzaldehyde. Hence a strongly oxygenophilic group (e.g., Si) must be present on manganese (and presumably iron) in order for a benzaldehyde adduct to be detectably formed.

Scheme I. Proposed Pathway for the Formation of Products from 3 and Benzaldehyde



Secondly, the catalytic hydrosilylation of aldehydes and ketones has been postulated to involve a similar carbonyl group addition by a catalytically active $L_nM(H)SiR_3$ species.[14] Together, eq i and ii firmly establish the viability of such a step. The subsequent reductive elimination of alkyl silyl ether product from the hydride-bearing catalyst has abundant precedent.[15]

Finally, the presence of a chelating disilane ligand enables the chemistry of **3** to dramatically diverge from that of **2**. After **7** is formed from **2**, decomposition by simple iron-carbon bond homolysis is favored over disiloxane $((CH_3)_3SiOSi(CH_3)_3)$ elimination, which would require carbon-oxygen and iron-silicon bond cleavage. However, from **3** and benzaldehyde, analogous homolytic decomposition is surpressed relative the formation of the stable disiloxane **9**. Significantly, the deoxygenation step in the formation of alkanes from CO/H_2 gas mixtures by homogeneous catalyst systems[16] may also be promoted by strong interactions with ancillary or catalyst-bound oxygenophilic groups.

With aliphatic aldehydes and ketones, **1** and **2** react differently. For instance, cyclohexanone is quantitatively converted by **1** (25 °C, 7 days) or **2** (25 °C, 15 min) to its trimethylsilyl enol ether.[6] However, from the reaction of **3** with octanal in the presence of Ph_3P, a zwitterionic complex analogous to **12** can be isolated in 85% yield. Studies are in progress to clarify the mechanistic details of these reactions and those of **1-3** with benzaldehyde. These experiments, and additional novel reactions of trialkylsilyl metal carbonyl complexes with organic molecules, will be the subject of future reports from this laboratory.

Acknowledgment. We are grateful to the Department of Energy for financial support.

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(11) ^{1}H NMR (δ, C_6D_6): 7.00–7.30 (m, 5 H), 6.10 (s, 1 H), 0.55 (s, 9 H), 0.15 (s, 9 H).
(12) ^{1}H NMR (δ, $CDCl_3$): 7.09–7.71 (m, 20 H), 4.06 (d, 1 H, $J_{^{31}P-^1H}$ = 12.7 Hz). ^{13}C NMR (C_6D_6): 11.0 ppm (d, $J_{^{31}P-^{13}C}$ = 24.1 Hz), plus CO and phenyl resonances. IR (cm^{-1}, THF): 2023 (m), 1930 (m), 1905 (vs). A portion of **12** was recrystallized from benzene, mp 115–120 °C dec. Anal. Calcd for $C_{29}H_{21}FeO_4P$: C, 66.95; H, 4.07; Fe, 10.73; P, 5.95. Found: C, 67.07; H, 4.68; Fe, 11.33; P, 6.18.
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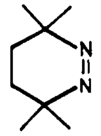
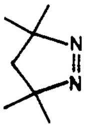
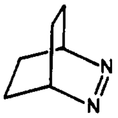
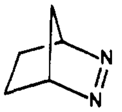
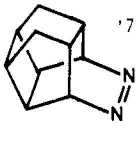
Enhancement of Decomposition Quantum Yields of "Reluctant" Azoalkanes

Sir:

Whereas irradiation of azoalkanes generally leads to efficient loss of nitrogen, six-membered azoalkanes decompose with low quantum yield (Φ_r).[1,2] This ring-size effect seems not to depend on whether the azo linkage is incorporated into a monocyclic or bicyclic system, as illustrated for compounds **1**, **2**, DBO, and DBH. Since analogues of DBO (e.g. compounds **3–6**) are also known to be photostable,[7–9] or to react slowly,[10] considerable interest has arisen[7,11] in finding methods for decomposing these "reluctant" azoalkanes. We report here that Φ_r for six-membered azoalkanes can be enhanced substantially either by modifying their structure so as to render them more labile thermally or by raising the temperature during photolysis. These measures are effective because the lowest excited singlet state encounters a barrier to loss of nitrogen.

	1	2	DBO[6]	DBH[6]
Φ_r	0.008	0.98	0.022	1.0



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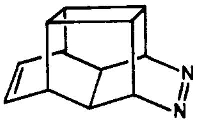

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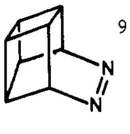

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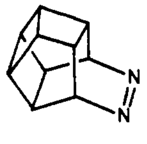


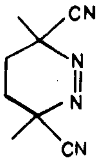
6[10]

Table I. Data for Photochemical and Thermal Decomposition of Azoalkanes

compd	Φ_r[a]	solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1	0.008[b]	benzene	36.3[c]	11.3
	0.0085[d]	*n*-butyl acetate		
7	0.2[d]	ethyl acetate	21.2[e]	5.9[e]
8	0.2[d]	ethyl acetate	(23)[f]	(7)[f]
DBO	0.022[g]	isooctane	44.3[c]	9.5[c]
9	0.014[h]	benzene	43.7[b]	11.4[b]
	0.0065[d]	*n*-butyl acetate		
10	0.3[d]	benzene	40.8[i]	10.3[i]
11	0.3[d]	benzene	38.6[i]	11[i]
	0.20[j]	hexane		
12	0.9[d]	benzene	34.2[k]	7.7[k]
13	0.8[d]	benzene	32.6[l]	(10)
14	0.9[d]	ethyl acetate	21.5[m]	4.1[m]

[a] Quantum yield for nitrogen formation. [b] Reference 3. [c] Average of values tabulated in ref 3. [d] This work. [e] Reference 12. [f] Calculated from data for the 3,6-dimethyl analogue[13] ($t_{1/2}$ = 30 min at −10 °C; calculated $\Delta G^{\ddagger}$ = 19.45 kcal mol^{-1}). $\Delta G^{\ddagger}$ for **8** is estimated[3] to be 21.15 kcal mol^{-1} and $\Delta S^{\ddagger}$ is assumed to be 7 eu. [g] Reference 4. [h] Reference 1. [i] Reference 14. [j] Reference 15. [k] Reference 16 [l] Based on our measured $k = 9.7 \times 10^{-5}$ s^{-1} at 100.2 °C and an assumed $\Delta S^{\ddagger}$ of 10 eu; cf. ref 17. [m] Reference 18.

As seen in Table I, the thermal lability of **1** and DBO was increased by two kinds of structural changes: placing radical-stabilizing groups at the α-carbon atoms or incorporating a strained ring into their structure. In the monocyclic series, Φ_r for **7** and **8** (determined at −78 °C) is 25-fold greater than for model compound **1**. Even larger effects are observed in the bicyclo[2.2.2] series, as demonstrated by comparison of DBO and **9** with **12–14**.



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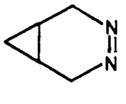

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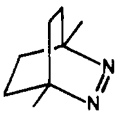

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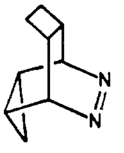

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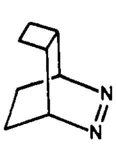

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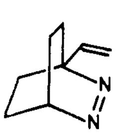

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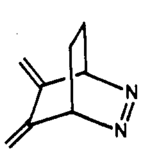

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Taking advantage of the fact that rigid cyclic azoalkanes fluoresce,[15] we studied the emission properties of DBO and **9–14** in hopes of clarifying the mechanism by which thermal lability influences Φ_r. All of these compounds exhibited fluorescence spectra of the same general shape and λ_{max}, but emission from **12–14** was much weaker than from DBO and **9–11**. Since the radiative rate constant k_f is safely assumed to be invariant for the series,[15] we conclude from the formula $\Phi_f = k_f\tau_f$ that **12–14** have a much shorter τ_f than DBO and **9–11**. This was verified experimentally for DBO, **11**, and **12**, whose measured lifetime in degassed benzene was 460, 330, and 0.5, respectively.[19] It follows that the *rate* of some excited singlet

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