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(4) Cf. Carlson, R. M. *Tetrahedron Lett.* **1978,** 111. Also see Sarkar, T. K.; Andersen, N. H. *Ibid.* **1978,** 3513.

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(8) A 12 ft × $^1/_4$ in. 15% Carbowax on Chromosorb W column was employed at 110 °C with a flow rate of 7 mL/min for this analysis.

(9) For reviews see: (a) Dowd, P. *Acc. Chem. Res.* **1972,** *5,* 242. (b) Berson, J. A.; *Ibid.* **1978,** *11,* 446.

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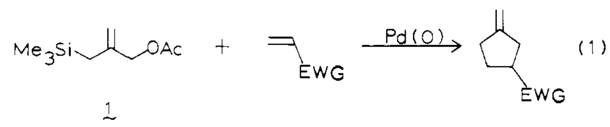
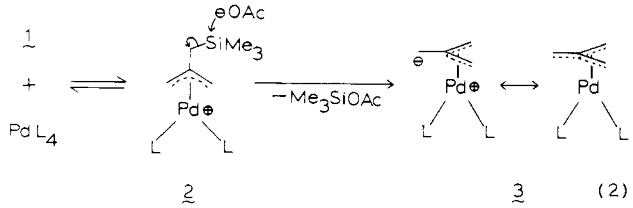
2-Acetoxymethyl-3-allyltrimethylsilane and Palladium(0): A Source of Trimethylenemethane-Palladium Complex?

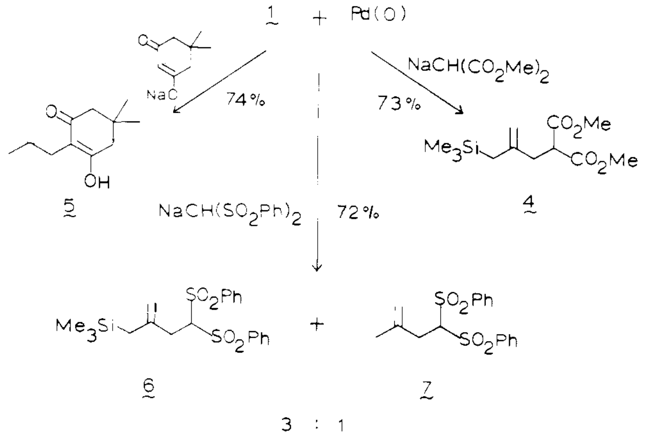
Sir:

In the previous paper,[1] we reported the cycloaddition of 2-acetoxymethyl-3-allyltrimethylsilane to electron-deficient olefins catalyzed by palladium(0) with formation of methylenecyclopentanes (eq 1). This rather surprising cycloaddition led us to propose the pathway in eq 2 as a working hypothesis. In this paper, we present evidence in support of this hypothesis—thus suggesting that **1** may be a valuable precursor to trimethylenemethane-metal complexes![2,3]

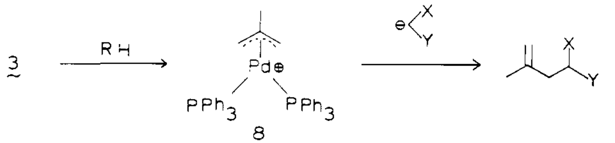




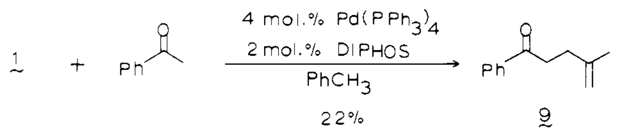
The initial formation of **2** is suggested by the reaction of **1** with dimethyl sodiomalonate to give the alkylated product **4.**[4] On the other hand, reaction with the anion of dimedone gave only the product of alkylation and desilylation, **5.** Interestingly, the anion of bis(benzenesulfonyl)methane leads to a mixture of **6** and **7.**



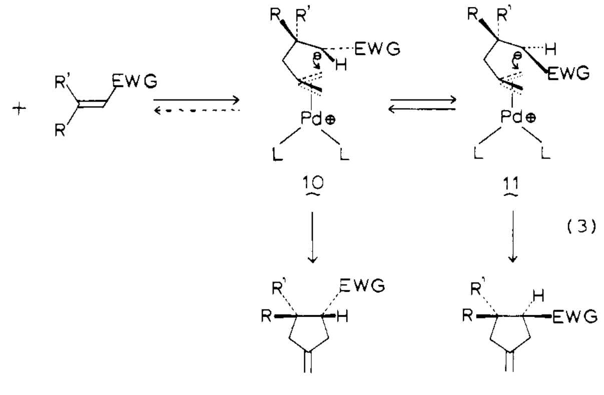
The formation of desilylated products does not arise from protodesilylation of the product or **1** under the reaction conditions as demonstrated by control experiments. Thus, some intermediate must be undergoing desilylation to lead to **5** and **7.** Apparently, if a nucleophile is kinetically slow in attacking **2, 2** lives long enough to suffer desilylation and generation of **3.** The latter is protonated by the excess dimedone or bis(benzenesulfonyl)methane or their alkylated products to give **8** which then reacts with starting nucleophile to give the desilylated product. Thus, the order of reactivity of the three nucleophiles toward **2** is malonate > bis(benzenesulfonyl)methane anion > dimedone anion—accounting for the straight alkylation with malonate, a competition of alkylation and desilylation with the sulfone system, and complete desilylation with dimedone.



To test this idea, **1** was reacted with acetophenone in the presence of the Pd(0) catalyst. Ketones do not react with allylic acetates in the presence of catalyst without a base.[4] The fact that desilylated-alkylated product **9** was obtained indicates that a base formed to generate the enolate of acetophenone and **8.**[5] This observation strongly implicates **3** as that base.



That the cycloaddition intermediate is a nucleophile and not an electrophile is indicated by its reaction with electron-deficient olefins and its failure to react with electron-rich ones. The reaction can be rationalized as shown in eq 3.[6] The partial loss of stereochemistry, i.e., methyl (*Z*)-cinnamate (*Z*:*E*, 10:1) gives a 1:1.3 ratio of *E* and *Z* isomers of methyl 2-phenyl-4-methylenecyclopentylcarboxylate, indicates equilibration of



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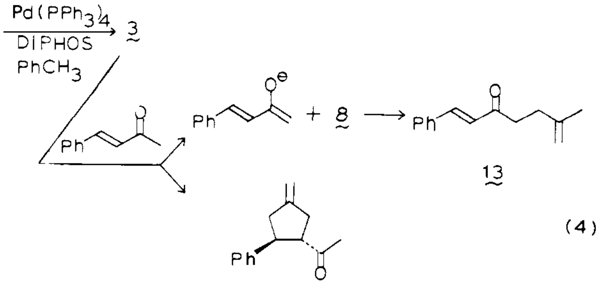
10 and **11** can compete with cyclization. In this case, starting olefin is not observed to isomerize under the reaction conditions. The ring closure of **10** and **11** is postulated in analogy to normal nucleophilic attack on π-allylpalladium cationic complexes.[7] Usually, simple enolates such as 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.



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]

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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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(8) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426.

(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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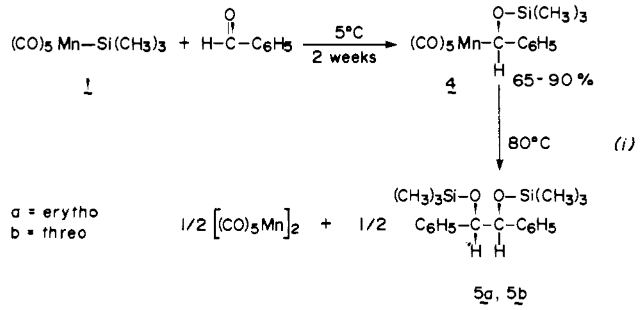
Reactions of Benzaldehyde with Trialkylsilyl Metal Carbonyl Complexes

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)$_5$MnSi(CH$_3$)$_3$ (**1**),[3] (CO)$_4$Fe[Si(CH$_3$)$_3$]$_2$ (**2**),[4] and (CO)$_4\overline{\text{FeSi(CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}}$(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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