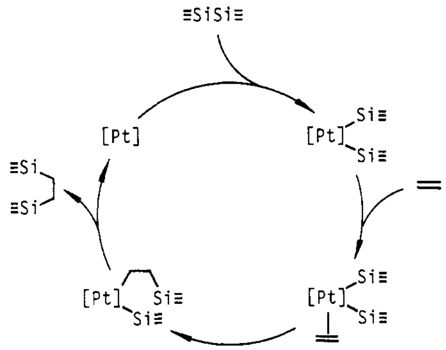
Organometallics **1990,** *9,* 281-284

Scheme I



the yield of 1,2-bis(dimethylphenylsilyl)ethane increased in the order $Pt(PPh_3)_4$ (yield 4.3%) < $Pt(PEt_3)_4$ (12.2%) < $Pt(PPhMe_2)_4$ (30.4%) < $Pt(PMe_3)_4$ (33.0%). Palladium complexes such as $Pd(PPh_3)_4$ and $PdCl_2(PhCN)_2$, which have been known to be active catalysts for double silylation of acetylenes and dienes, were inactive for the present reaction. Likewise, other complexes such as $PtCl_2(PPh_3)_2$, $PtCl_2(PhCN)_2$, $RhCl(PPh_3)_3$, $H_2Ru(CO)(PPh_3)_3$, and $Ru(CO)_3(PPh_3)_2$ were totally inactive.

As for the reaction mechanism, the following observations are worth noting. The Si–Si linkage in $FMe_2SiSiMe_2F$ and $ClMe_2SiSiMe_2Cl$ has been found to be readily cleaved when treated with $Pt(PEt_3)_3$ at room temperature to give *cis*-bis(silyl)bis(phosphine)platinum complexes. However, $PhMe_2SiSiMe_2Ph$ seemed unreactive.[5] Thus, the reactivities of disilanes toward $Pt(PEt_3)_3$ were in good agreement with those observed in the foregoing catalytic reactions. In addition to these, our previous paper[4] has communicated that *cis*-bis(dimethylphenylsilyl)bis(methyldiphenylphosphine)platinum readily reacts with ethylene at atmospheric pressure and room temperature to give the corresponding 1,2-bis(silyl)ethane. On the basis of all these facts combined together, the double silylation is envisaged to proceed via oxidative addition of the disilane, insertion of ethylene into one of the resulting Si–Pt bonds, and reductive elimination of 1,2-bis(silyl)ethane from the silyl(β-silylethyl)platinum intermediate as in Scheme I.

To see the stereochemistry of the addition, norbornene was allowed to react with 1,2-difluoro-1,1,2,2-tetramethyldisilane under the same conditions as above. 2,3-Bis(fluorodimethylsilyl)norbornane was formed in 26.0% yield, which was methylated with methyllithium to give 2-*exo*,3-*exo*-bis(trimethylsilyl)norbornane.[6] The result is rationalized by the cis addition of the disilane via coordination of the platinum center on the less hindered olefinic face.

In summary, this paper reports the first successful examples of double silylation of simple olefins, which offers a convenient way for the synthesis of silicon-containing polymers. For instance, 1,2-bis(chlorodimethylsilyl)ethane could be polymerized by Wurtz type condensation with sodium to give copoly(tetramethyldisilene–ethylene) with $\bar{M}_v = 192\,000$.[8] An investigation on reactivities of other types of olefins toward disilanes is now in progress.

Registry No. $FMe_2SiSiMe_2F$, 661-68-7; $(MeO)Me_2SiSiMe_2(OMe)$, 10124-62-6; $ClMe_2SiSiMe_2Cl$, 4342-61-4; $Me_3SiSiMe_3$, 1450-14-2; $(p\text{-}CF_3C_6H_4)Me_2SiSiMe_2(p\text{-}CF_3C_6H_4)$, 36112-13-7; $PhMe_2SiSiMe_2Ph$, 1145-98-8; $(p\text{-}CH_3C_6H_4)Me_2SiSiMe_2(p\text{-}CH_3C_6H_4)$, 5971-96-0; $CH_2{=}CH_2$, 74-85-1; $Pt(PPh_3)_4$, 14221-02-4; $FMe_2SiCH_2CH_2SiMe_2F$, 2251-44-7; $(MeO)Me_2SiCH_2CH_2SiMe_2(OMe)$, 76490-69-2; $ClMe_2SiCH_2CH_2SiMe_2Cl$, 13528-93-3; $Me_3SiCH_2CH_2SiMe_3$, 6231-76-1; $(p\text{-}CF_3C_6H_4)Me_2SiCH_2CH_2SiMe_2(p\text{-}CF_3C_6H_4)$, 123857-50-1; $PhMe_2SiCH_2CH_2SiMe_2Ph$, 15527-45-4; $(p\text{-}CH_3C_6H_4)Me_2SiCH_2CH_2SiMe_2(p\text{-}CH_3C_6H_4)$, 123857-51-2; $Pt(PEt_3)_4$, 33937-26-7; $Pt(PPhMe_2)_4$, 33361-89-6; $Pt(PMe_3)_4$, 33937-27-8; norbornene, 498-66-8; 2-*exo*-3-*exo*-bis(fluorodimethylsilyl)norbornane, 123857-52-3; 2-*exo*-3-*exo*-bis(trimethylsilyl)norbornane, 123857-53-4.

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[5] Details will be published elsewhere.

[6] High-resolution MS: found M^+, 240.1736; calcd for $C_{13}H_{28}Si_2$, 240.1729. MS (EI, m/z (relative intensity)): 240 (M^+, 2), 167 (11), 151 (3), 131 (6), 124 (5), 109 (3), 101 (2), 73 (100). ^1H NMR (200 MHz, C_6D_6): δ 0.14 (s, 18 H, $SiCH_3$), 0.89 (d, $J = 1.7$ Hz, 2 H, SiCH), 1.05–1.38 (m, 4 H, methylene CH_2, ethylene CH (endo)), 1.61–1.73 (m, 2 H, ethylene CH (exo)), 2.25–2.33 (m, 2 H, bridgehead CH) ppm. ^{13}C NMR (C_6D_6): δ 0.5 ($SiCH_3$), 34.3, 36.0, 38.4, 40.1 (norbornane) ppm. ^1H COSY measurement revealed that the splitting of the silyl-substituted methine proton signal into a doublet was due to the coupling with the anti proton at the bridging methylene and that its coupling with the bridgehead proton was not observed. These results combined with precedents[7] verify the 2-*exo*,3-*exo* geometry of the bis(silyl) groups.

[7] (a) Laszlo, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1964**, *86*, 1171 and references cited therein. (b) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845.

[8] Tverdokhlebova, I. I.; Sutkevich, O. I.; Ronova, I. A.; Polyakov, Yu. P.; Gusel'nikov, L. Ye.; Pavlova, S. A. *Vysokomol. Soedin., Ser. A* **1988**, *30*, 1070.

Formation of Cyclic Carbosilanes in the Pyrolysis of Octamethyltrisilane

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Received May 19, 1989

Summary: Prominent products in the pyrolysis of the title compound are cyclic carbosilanes; evidence is presented that one of these is formed in a novel and potentially useful elimination reaction.

The mechanism of breakdown of polysilanes is of interest because of their importance as photoresists[1] and as potential precursors to new polycarbosilane polymers. Accordingly, we are undertaking a study of the gas-phase pyrolysis of volatile permethylated polysilanes as model compounds and now report our initial results with octamethyltrisilane, Me_8Si_3 (**1**).

Me_8Si_3 was pyrolyzed by our stirred-flow (SFR) technique[2] between 558 and 655 °C with partial pressures of 0.25–0.9 mmHg in helium or nitrogen carrier gas. The SFR apparatus attached to a GC/mass spectrometer (HP5995C)[2] was used for identification of products. The major product was Me_3SiH, with smaller quantities of other monosilanes (Me_2SiH_2 and Me_4Si), but the main

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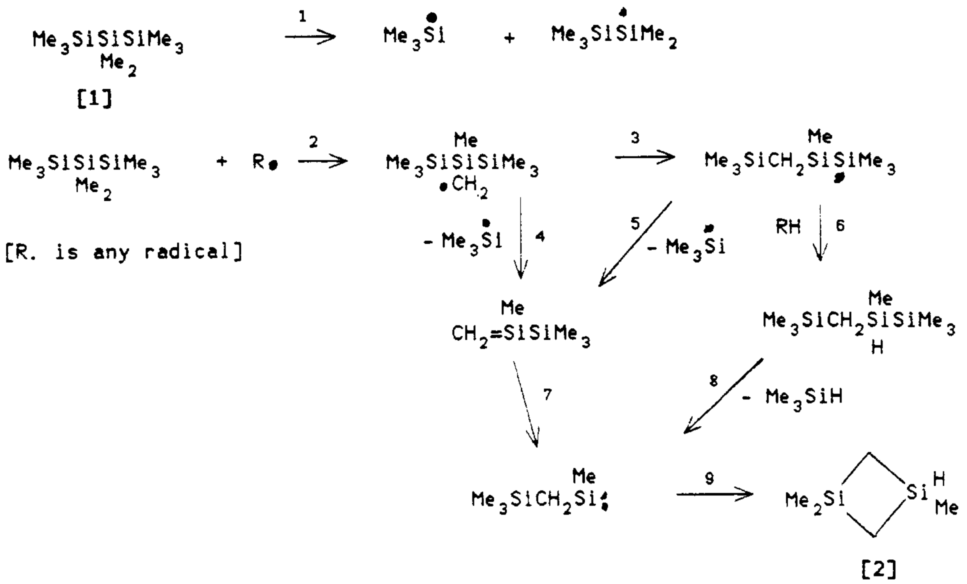
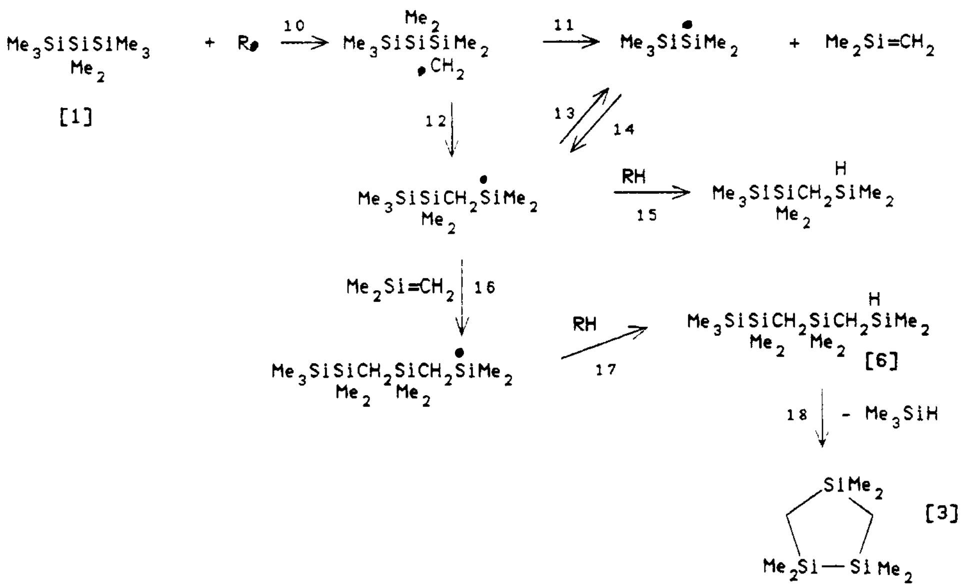
Scheme I



Scheme II



products containing more than one silicon atom per molecule were 1,1,3-trimethyl-1,3-disilacyclobutane (**2**), 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane (**3**), hexamethyldisilane (**4**), and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**5**). Mass spectrometric identification of these products was supplemented by comparison of GC retention times with authentic samples. Relative yields of products **2**–**4** showed little temperature dependence, but the yield of **5** relative to those of the others increased with temperature, corresponding to an activation energy differential of ca. 25 kcal·mol^{-1}. Relative yields of these products in the middle of the temperature range were **2**:**3**:**4**:**5** = 3.3:2:2:1. Copyrolysis of **1** with toluene or buta-1,3-diene reduced, but did not totally suppress, the production of these products; in the experiments with butadiene, cyclic adducts of Me$_2$Si: and Me$_2$Si=SiMe$_2$ were observed. Clearly, the product composition depends strongly on the experimental conditions, especially the pressure of **1**; Barton and co-workers[3] found that flash vacuum pyrolysis (FVP) of **1** at 860 °C and 10^{-3} mmHg gave **2** as the only significant product containing more than one silicon atom per molecule.

Pyrolysis of hexamethyldisilane (**4**) is initiated by Si–Si bond homolysis to form Me$_3$Si$^•$ radicals, with Me$_2$Si: formation as a minor process.[4] Although the latter might be less minor in the pyrolysis of **1**,[5] we believe that the radical-initiated sequence shown in Scheme I is a straightforward, well-precedented route to the cyclic product **3**. The radical produced in reaction 2 by hydrogen abstraction from one of the central methyl groups in **1** undergoes the isomerization reaction (3), well characterized

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(1) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. Elliot, D. J. *Integrated Circuit Fabrication Technology*; McGraw-Hill: New York, 1982.

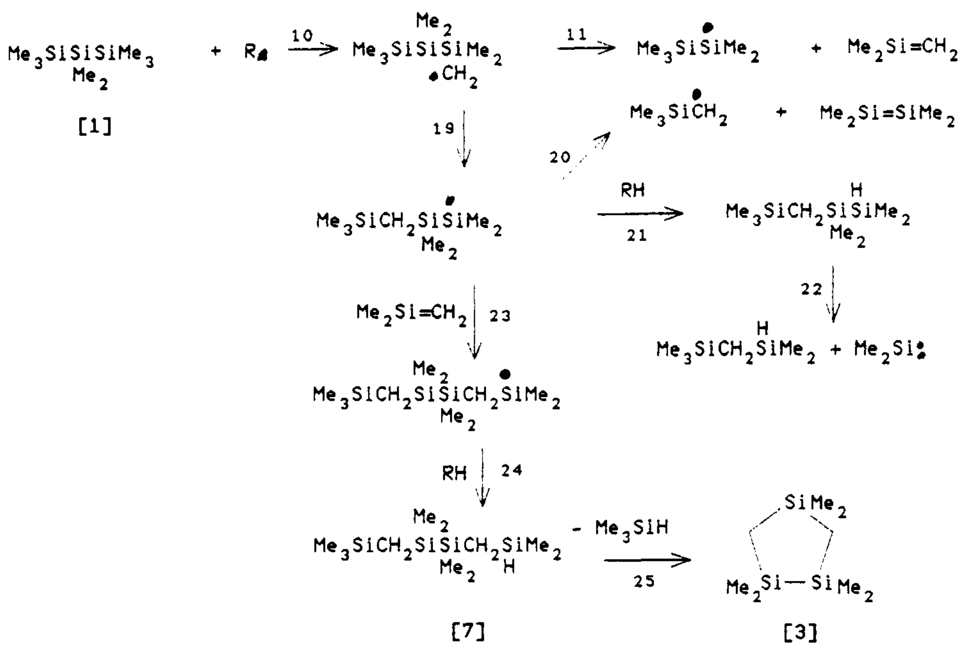
(2) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972. Davidson, I. M. T.; Eaton, G.; Hughes, K. J. *J. Organomet Chem.* **1988**, *347*, 17.

(3) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.

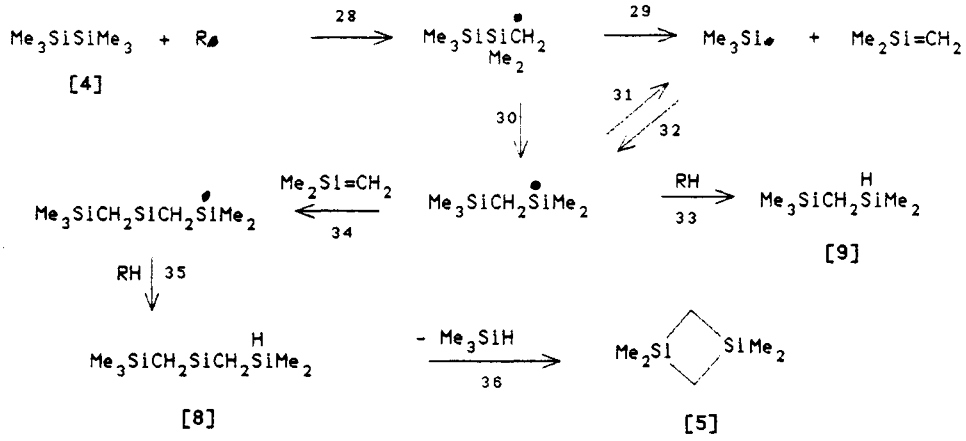
(4) Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 69.

(5) Davidson, I. M. T.; Scampton, R. J. *J. Organomet. Chem.* **1984**, *271*, 249.

Scheme III



Scheme IV



in the pyrolysis of 4;[4,6] the resulting radical can dissociate by reaction 5, again by close analogy with the pyrolysis of 4, to produce a silylsilene that isomerizes by reaction 7 to a silylene, which ring closes to form product 2. The same silylene results from the alternative route, reactions 6 and 8, involving formation of a hydrido–disilane that would eliminate Me_3SiH rapidly at these temperatures.[7] Reactions 7 and 9, first suggested by Barton and co-workers,[3,8] are now well established in organosilicon chemistry.

The route to the cyclic product 3 is less obvious, but the likelihood that it resulted from radical attack on a terminal methyl group in compound 1 prompted the suggestions in Scheme II. Reactions 11–15 correspond closely to reactions in the pyrolysis of 4,[4,6] but we suggest that there is then a rapid addition reaction (16) involving the dimethylsilene formed in reactions 11 or 12; silenes are known to add rapidly to radicals.[9] The resulting radical then undergoes abstraction reaction 17, and the product of reaction 17 can then eliminate Me_3SiH to form the cyclic product 3. Reaction 18 may be thought of as being analogous to the elimination of Me_3SiH in the well-known[7] formation of a silylene from a hydrido–disilane (e.g., reaction 8 in Scheme I), the driving force in this case being the formation of a stable ring system in 3.

Reaction 12 is a 1,2-shift, just like the corresponding reaction in the pyrolysis of 4,[4,6] but in the pyrolysis of 1 a 1,3-shift might also be possible, with the consequences shown in Scheme III, the 1,3-shift being reaction 19.

We tested these ideas by synthesizing compounds 6 (Scheme II) and 7 (Scheme III) and pyrolyzing them under the same conditions as for 1. The main product of the pyrolysis of 6 at low partial pressures was indeed 3, providing good evidence in support of Scheme II and for reaction 18. Isomers of 6 became more important pyrolysis products at higher partial pressures but were substantially reduced in pyrolyses in the presence of toluene, confirming that they were formed in bimolecular radical reactions.[10]

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[6] Davidson, I. M. T.; Potzinger, P.; Reimann, B. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 13.

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[10] Davidson, I. M. T.; Eaborn, C.; Simmie, J. M. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 249.

3 was also a product of the pyrolysis of 7, but in that case 2 and 5 were more prominent products. In the pyrolysis of 1, trapping of $Me_2Si{=}SiMe_2$ by butadiene provides evidence for reaction 20 and, hence, for reaction 19 in Scheme III, but reaction 25 is clearly minor compared to reaction 18. A possible explanation of the difference is that elimination of Me_3SiH from 6 occurs entirely at silicon centers, as in reaction 8, whereas with 7 a carbon center is involved. Butadiene trapping also gave evidence for Me_2Si:, probably formed in reactions 26 and 27 as well as

$$Me_3SiSiMe_2^{\bullet} + RH \rightarrow Me_3SiSiMe_2H \rightarrow Me_2Si{:} + Me_3SiH \quad (26)$$

$$Me_3SiSi(Me_2)SiMe_3 \rightarrow Me_2Si{:} + Me_3SiSiMe_3 \quad (27)$$

reaction 22. Reaction 27 might also be a source of the product 4, but the main route to 4 is likely to be self-combination of $Me_3Si^{\bullet}$ radicals. We failed to trap $Me_2Si{=}CH_2$ with butadiene because reactions 16 and 23 are fast, whereas the rate constant for the reaction of $Me_2Si{=}CH_2$ with butadiene is relatively low.[5]

Our evidence in support of Scheme II prompted us to speculate that the similar reaction sequence shown in Scheme IV might be important in the pyrolysis of 4 as a route to the disilacyclobutane 5, which is a major product at low pressure.[4] However, on testing these ideas by synthesizing and pyrolyzing compound 8, we found that it was more stable thermally than compound 4 and gave little 5 when pyrolyzed under the conditions used for 4. Structurally, 8 resembles 7 rather than 6, with the additional drawback that a higher ring strain would have to be overcome in reaction 36 than in reaction 25 or 18. We conclude that elimination of Me_3SiH to form a stable cyclic product is a feasible and potentially important reaction in those polycarbosilanes that have the appropriate silicon-carbon skeleton, i.e. where the components of Me_3SiH are attached exclusively to silicon.

In the pyrolysis of 1, the pronounced pressure dependence of product composition revealed by comparison of this work with that of Barton[3] has close parallels in similar organosilicon pyrolyses. In the pyrolysis of 4, product 5 was more important than product 9 (see Scheme IV) at low pressure,[4] but the position is totally reversed at high pressure,[10] because at low pressure the unimolecular radical dissociation reactions (29) and (31) are favored over the bimolecular reaction (33); increasing the pressure increases the relative importance of reaction 33. A similar situation arises in the pyrolysis of 3, where the main product at low pressure is 5,[11] while at high pressure it is 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane,[12] a product that bears the same relationship to 3 as 9 bears to 4. An explanation along similar lines, involving the balance between unimolecular reactions 4 and 5 on the one hand and bimolecular reactions 16 and 17 on the other, accounts for the different results observed by Barton[3] and by us.

Acknowledgment. We are most grateful to Dr. Peter Lo of Dow Corning Sussex Research for his generous help and encouragement. We thank Geraint H. Morgan for help with the pyrolysis experiments and the SERC for support.

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[11] Davidson, I. M. T.; Lawrence, F. T.; Fritz, G.; Matern, E. *Organometallics* **1982**, *1*, 1453.

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Regiospecific Nickel Cyanide and Phase Transfer Catalyzed Synthesis of β,γ-Unsaturated Acids from Allenes

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Received September 14, 1989

Summary: Allenes react with carbon monoxide in an aqueous base–toluene two-phase system, with cetyltrimethylammonium bromide as the phase-transfer agent and nickel cyanide as the metal catalyst, to give β,γ-unsaturated acids in 48–66% yields. This reaction proceeds under exceptionally mild conditions (90 °C, 1 atm), with the regiochemistry being opposite to that previously observed in hydrocarboxylation reactions.

A variety of metal-complex-catalyzed reduction, oxidation, and carbonylation reactions occur under remarkably mild conditions with use of phase-transfer catalysis.[1,2] Research in carbon monoxide phase-transfer processes has focused on the use of palladium, cobalt, and, to a lesser extent, iron complexes as catalysts for the conversion of halides to acids. More economical than any of these transition-metal complexes is the use of nickel compounds as catalysts. The cyanotricarbonylnickelate anion, generated by the phase-transfer-catalyzed reaction of nickel cyanide, carbon monoxide, and base, is an effective catalyst for the production of acids (eq 1) from allyl halides,[3] iodoarenes,[4] and benzyl chlorides (lanthanide salts promote this reaction).[5]

$$RX + CO \xrightarrow[C_6H_6,\ NaOH,\ 60\text{–}90\ ^\circ C,\ 1\ atm]{R_4N^+X^-,\ Ni(CN)_2{\cdot}4H_2O} RCOOH \quad (1)$$

A conceptually different type of carbonylation reaction is that which involves the addition of carbon monoxide and water (i.e., hydrocarboxylation) or alcohol (i.e. hydroesterification) to an unsaturated substrate. The homogeneous hydrocarboxylation and hydroesterification of allenes, catalyzed by a variety of metal complexes under stringent conditions, results in the formation of α,β-unsaturated acids or esters in low to moderate yields.[6,7] These reactions are believed to proceed via vinylmetallic complexes. Alkoxycarbonylation of allenes, which occurs under mild conditions with use of palladium chloride as the catalyst in alcohol solution, also affords the α,β-unsaturated carbonyl product.[8,9] To our knowledge there

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[9] For an intramolecular version, see footnote 4 of: Lathbury, D.; Vernon, P.; Gallagher, T. *Tetrahedron Lett.* **1986**, *27*, 6009.

0276-7333/90/2309-0284$02.50/0