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The pyrolysis of dimethyl-cis-1-propenylvinylsilane: a new source of dimethylsilylene and a new reaction for the formation of carbon-carbon double bonds

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by bridging ligands only.[14] The Os(1)–Os(4) bond which contains a bridging carbonyl ligand is significantly shorter than the Os(1)–Os(2) bond, 2.856 (1) Å vs. 2.937 (1) Å. The allene ligand C(19)–C(20)–C(21) is π-bonded to Os(4) and σ-bonded to Os(3) via the central carbon C(20). A similarly coordinated allene ligand was found in the molecule $Os_3(CO)_{11}(\mu_2\text{-}\eta^3\text{-}CH_2CCH_2)$.[15] The second allene molecule has been joined to the other alkyne ligand by the central carbon C(17), C(12)–C(17) = 1.43 (3) Å. This transforms the alkyne into an alkenyl group, C(12)–C(13) = 1.44 (3) Å, that is π-bonded to Os(1) and σ-bonded to Os(3). The allene molecule has become an allyl substituent of this alkenyl group, and it is π-bonded to Os(2). This transformation represents a new example of the coupling of allenes to hydrocarbon ligands.[16]

It is believed that the facile addition of ligands to 1 can be attributed to the "electron-deficient character" of the cluster. The cluster-opening processes can be attributed to the fact that the multiple-ligand additions produce a surfeit of electron donation that ultimately ruptures some of the metal–metal bonds. Efforts to obtain stepwise additions may provide further details about the cluster's transformations and these unusual ligand–ligand coupling processes. These studies are in progress.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy. We wish to thank Johnson-Matthey for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, selected interatomic distances and angles, and structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

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[14] Selected interatomic distances (Å) and angles (deg) for 3 are as follows: Os(1)–Os(2) = 2.937 (1), Os(1)–Os(4) = 2.856 (1), Os(1)···Os(3) = 3.692 (1), Os(3)···Os(4) = 3.551 (1), Os(1)–S = 2.408 (5), Os(3)–S = 2.452 (5), Os(4)–S = 2.442 (5), Os(1)–C(12) = 2.31 (2), Os(1)–C(13) = 2.40 (2), Os(2)–C(16) = 2.26 (2), Os(2)–C(17) = 2.20 (2), Os(2)–C(18) = 2.29 (2), Os(3)–C(13) = 2.17 (2), Os(3)–C(20) = 2.17 (2), Os(4)–C(20) = 2.23 (2), Os(4)–C(19) = 2.37 (2), Os(4)–C(21) = 2.25 (2), Os(2)–Os(1)–Os(4) = 141.22 (4).

[15] Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1982**, *231*, C65.

[16] (a) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Streib, W. E. *J. Chem., Soc., Chem. Commun.* **1985**, 1755. (b) Chisholm, M. H.; Johns, W. S. *Inorg. Chem.* **1975**, *14*, 1189. (c) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

The Pyrolysis of Dimethyl-*cis*-1-propenylvinylsilane: A New Source of Dimethylsilylene and a New Reaction for the Formation of Carbon–Carbon Double Bonds

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Summary: Pyrolysis of dimethyl-*cis*-1-propenylvinylsilane leads to the extrusion of dimethylsilylene and the formation of a mixture of *cis*- and *trans*-piperylenes. The reaction occurs via a sigmatropic hydrogen shift giving rise to a *cis*-1,1,2-trimethyl-3-vinylsilirane intermediate that releases Me_2Si: by a retro-1,2-cycloaddition. The overall transformation is a new reaction for the formation of carbon–carbon double bonds.

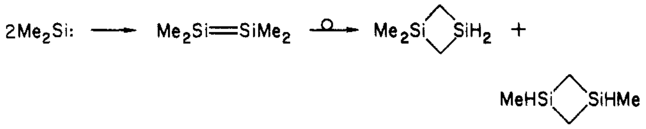
We have recently shown that a 1,5-sigmatropic shift, a homo-retro-ene reaction, is the dominant reaction channel for the silirane intermediate formed by cis addition of dimethylsilylene to *cis,cis*-2,4-hexadiene[1] (Scheme I).

This result encouraged us to examine such a reaction in the backward direction, both to determine whether it is indeed reversible and whether it can be used as a probe for contributions from diradical pathways.

Consider the related all-carbon system. Roth and König found that pyrolysis of *cis*-1,4-hexadiene in the gas phase at 410 °C for 16 h led to a mixture of 23% starting material, 9% of its trans isomer, and 68% 4-methylcyclopentene.[2] For the formation of the methylcyclopentene a pathway was proposed, shown in Scheme II, that is initiated by a step (d) analogous to the reversal of step b of Scheme I. This is followed by cleavage (step e) to a diradical that can cyclize (step f) to the observed product.

We have subjected dimethyl-*cis*-propenylvinylsilane (2),[4] a compound closely analogous to product 1 of Scheme I and of the starting compound in Scheme II, to vacuum flow pyrolysis at 610 °C (0.6 torr) (residence time ca. 5 ms). The results, given in Table I, suggest that both steps a and b of Scheme I are reversible.

As in the hydrocarbon case, the starting material undergoes cis–trans isomerization, and the trans isomer is the most abundant product. The piperylenes are also major products, formed in 36% yield (64% based on unisomerized starting material), and the disilacyclobutanes formed in 19% yield (35% based on unisomerized starting material) are known to be due to isomerization of the tetramethyldisilene dimer of Me_2Si.[3]



When the pyrolysis is carried out in the presence of a 5:1 excess of an efficient trapping agent for silylenes, 2,3-dimethylbutadiene, the adduct of Me_2Si, is formed in 29% yield (50% when corrected for isomerization, 79% based on the piperylenes). It is thus clear that extrusion of dimethylsilylene has occurred. Scheme III is proposed to account for the observed results including the formation in low yields of trimethylsilacyclopentenes 4 and 5.

Here we see a homo-ene reaction, a sigmatropic hydrogen shift, step h, that converts 2 into *cis*-1,1,2-trimethyl-2-vinylsilirane (3) that extrudes Me_2Si:.

That extrusion of Me_2Si does *not* occur directly from 2 is clear from the pyrolysis of its trans isomer reported in Table I. The conversion of trans is much lower than that of cis (by a factor of 3:1), trans to cis isomerization is the major process, and the low yield of piperylenes indicates that only the cis isomer extrudes Me_2Si.

The low yields of trimethylsilacyclopentenes 4 and 5

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[1] Lei, D.; Gaspar, P. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1149.

[2] Roth, W. R.; König, J. *Justus Liebigs Ann. Chem.* **1965**, *688*, 28.

[3] Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 868.

[4] Synthesized by coupling the Grignard reagent from 1-bromopropene with chlorodimethylvinylsilane by a procedure reported by Seyferth: Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* **1963**, *1*, 138.

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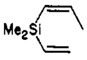
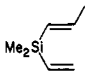
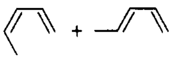
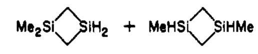
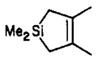
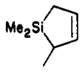
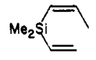
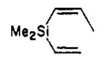
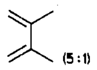
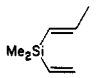
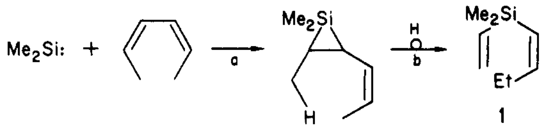
Table I. Product Yields (% Absolute) from Flow Pyrolyses of Dimethyl-1-propenylvinylsilanes[a,b]

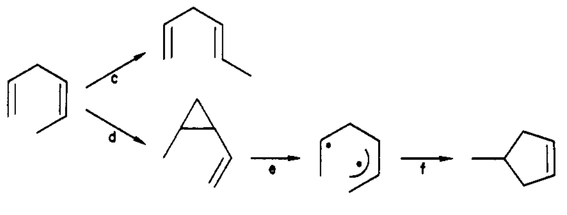
		products						
starting material	additive						 5	 4
 2	none	41.5[c]	44.2[d]	35.5[d,e]	19.6[d]		4.9[d]	4.2[d]
 2		45.1[c]	42.4[d]	36.8[d,e]		28.9[d]	2[d]	1.5[d]
	none	70[d]	84[c]	15.6[d,f]	trace			

[a] Hot zone 610 °C (0.6 torr); residence time ca. 5 ms. [b] All products have been previously characterized,[7] except for dimethyl-*trans*-1-propenylvinylsilane, whose spectral data are in accord with those expected based on its cis isomer. [c] Based on initial starting material. [d] Based on starting material converted. [e] Trans:cis = 56:44. [f] Trans:cis = 55:45.

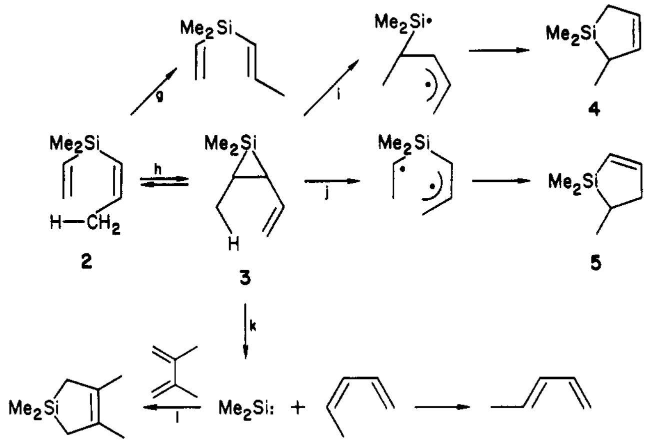
Scheme I



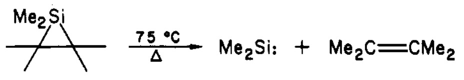
Scheme II



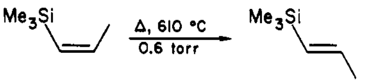
Scheme III



Scheme IV



Scheme V



relative to the products of silylene extrusion indicate that cleavage to diradicals, steps i and j of Scheme III, is unfavorable compared with extrusion step k. This is not surprising, considering the ease with which Me_2Si is lost from hexamethylsilirane[5] (Scheme IV).

While a mixture of piperylenes is found from decomposition of 2, it is believed that Me_2Si extrusion is stereospecific. The piperylene mixture obtained has the same composition as is found when pure *cis*-piperylene is subjected to the flow pyrolysis conditions and is much richer in the cis isomer than is the equilibrium mixture. Seyferth has found evidence that the silylene extrusion of Scheme IV is concerted.[6]

As a control experiment, it has been shown that cis–trans isomerization of the propenyl group in 2 and its trans isomer is a process not dependent on the presence of the additional vinyl substituent. When trimethyl-*cis*-propenylsilane was subjected to the pyrolysis conditions, a 23% yield of its trans isomer was the only observed product (Scheme V).

The drop in the yields of trimethylsilacyclopentenes 4 and 5 shown in Table I when 2 was pyrolyzed in the presence of 2,3-dimethylbutadiene indicates that in the absence of added silylene trapping agents readdition of Me_2Si to the piperylenes contributes to the yields of 4 and 5. These products have previously been obtained in this manner.[7]

It is now clear that, as in the hydrocarbon case, reversible sigmatropic hydrogen shifts interconvert *cis*-2-alkyl-3-alkenylsiliranes and *cis*-1-alkenylvinylsilanes. It is perhaps also worth noting that this process leads ultimately, via silylene extrusion from the silirane, to the formation of a new double bond. It is possible that with appropriate substituents on the vinyl and alkenyl groups, reaction conditions can be achieved that are sufficiently mild to make such a sequence a synthetically viable choice for the coupling of a vinyl and a *cis*-alkenyl halide to form a *cis*-1,3-diene unit.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant CHE-84-14358.

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(5) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2273. Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *201*, 179.

(6) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 128.

(7) Lei, D.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1.

Registry No. (*Z*)-**2**, 93297-72-4; (*E*)-**2**, 100928-13-0; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; 1,1-dimethyl-1,3-disilacylobutane, 38512-90-2; 1,3-dimethyl-1,3-disilacyclobutane, 1628-01-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,1,3,4-tetramethylsilacyclopent-3-ene, 16109-39-0; diemthylsilylene, 6376-86-9.

Carbon–Carbon and Carbon–Nitrogen Bond Formation Induced by the Reaction of Diphenyldiazomethane with $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$

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Received February 20, 1986

Summary: The reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (**1**) with diphenyldiazomethane in refluxing benzene leads to the synthesis of $Fe_2(CO)_6(C_6H_5)_2CNNC(O)C(CH_3)C(OC_2H_5)$ (**2**), whose structure has been established by X-ray diffraction study: monoclinic, $P2_1/n$, a = 8.602 (1) Å, b = 10.916 (1) Å, c = 27.656 (3) Å, β = 94.74 (1)°; V = 2588.0 (9) Å^3; Z = 4; D_{calcd} = 1.504 g cm^{-3}; R = 0.034 for 3229 observations ($I \geq 4\sigma(I)$) and 334 variables. **2** contains two $Fe(CO)_3$ groups at bonding distance, bridged by a ligand resulting from the coupling of diphenyldiazomethane with carbon monoxide and the two alkylidyne ligands of **1**.

Pursuing our study about the reactivity of alkylidyne ligands bounded to three iron centers,[1] we were interested in the study of the possible coupling of alkylidyne with alkylidene ligands. Thus, we have studied the reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (1)[2] with diazoalkanes as a source of alkylidene ligands.[3] No reaction occurred with diazomethane either by thermal or by photochemical activation, and the ethyldiazoacetate gave an intractable mixture in refluxing toluene.

In the case of diphenyldiazomethane, the reaction was more successful. $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g, 1 mmol) and $N_2C(C_6H_5)_2$ (0.82 g, 4.2 mmol) were refluxed for 30 min in benzene. Evaporation of the solution and chromatography of the residue on a column of Florisil, eluting with benzene/diethyl ether with increasng concentration of diethyl ether, gave successively a red band of the starting material (0.070 g recovered), a brown band of an unidentified product, a yellow band of $C_2(C_6H_5)_4$, and an orange band. Crystallization of the orange band gave 0.058 g (12% yield) of orange crystals of **2** formulated as $Fe_2(CO)_7(N_2C(C_6H_5)_2)(C(OC_2H_5))(CCH_3)$ from the mass spectrum.[4] The ^1H and ^{13}C NMR spectra[4] confirm the presence of organic groups. Furthermore, the infrared spectrum in the $\nu(CO)$ stretching region show, except absorptions characteristic of terminal carbonyl groups, a weak band at 1695 cm^{-1} which could be attributed to a ketonic carbonyl group.

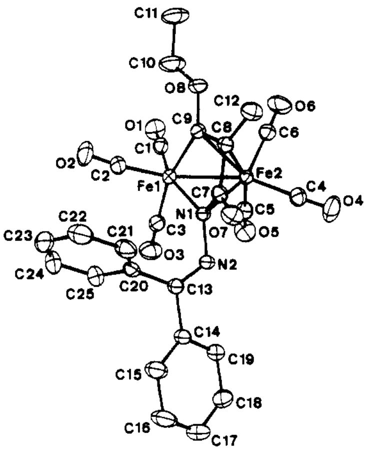

Figure 1. Ortep view of compound 2 showing the atomic numbering scheme. Selected bond distances (Å): Fe(1)–Fe(1)–Fe(2) = 2.4715 (9), Fe(1)–C(9) = 1.952 (4), Fe(2)–C(9) = 2.187 (4), C(8)–C(9) = 1.410 (6), C(7)–C(8) = 1.468 (6), N(1)–C(() = 1.409 (5), Fe(1)–N(1) = 1.979 (3), Fe(2)–N(1) = 2.014 (3)= N(1)–N2) = 1.436 (5), N(2)–C(13) = 1.267 (5). Selected angles (deg): Fe(1)–N(1)–Fe(2) = 76.5 (1), Fe(1)–C(9)–Fe(2) = 73.1 (1), N(1)–C(7)–C(8) = 105.7 (3), C(7)–C(8)–C(9) = 113.7 (4), Fe(1)–C(9)–C(8) = 116.7 (3), Fe(2)–C(9)–C(8) = 70.2 (2), Fe(2)–C(8)–C(7) = 79.5 (2), Fe(1)–N(1)–C(7) = 118.2 (3), Fe(2)–N(1)–C(7) 86.3 (2), Fe(1)–N(1)–N(2) = 126.4 (2), Fe(2)–N(1)–N(2) = 119.6 (2).

As it was difficult to ascertain the precise nature of **2** from spectroscopic data, an X-ray crystallographic study was carried out.[5] The resulting structure is shown in Figure 1. **2** consists of a dinuclear iron unit in which the Fe–Fe bond distance is in agreement with a single metal–metal bond.[6] Each iron atom is surrounded by three terminal carbonyl groups. The most salient feature of the structure is the nature of the ligand bridging the two $Fe(CO)_3$ units. It results from the coupling of diphenyldiazomethane with a carbonyl group and the two alkylidyne ligands of the starting complex **1**. This ligand is coordinated to iron atoms through the N(1), C(8), and C(9) atoms. The C(8)–C(9) group can be described as a vinyl group σ-bonded through C(9) to Fe(1) and η^2-bonded to Fe(2) by C(8)C(9). The conventional features of the bonding mode of this ligand[7] are observed. The C(9) atom is more tightly bonded to Fe(1) to which it is σ-bonded than to Fe(2). Further, the C(8)–C(9) bond distance is typical of a π-coordinated carbon–carbon double bond and corresponds to a bond order in the range 1–2. The N(1) atom bridges the two iron atoms and is at a slightly shorter distance from Fe(1) than from Fe(2). The length of the N(1)–N(2) bond is close to the expected single-bond value of 1.44 Å while the N(2)–C(13) distance is consistent with a C═N double bond. The bonding mode of the $(C_6H_5)_2CNN\text{-}C(O)$ fragment closely resembles that the $(C_6H_5)_2CNNH$ group in $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNC(C_6H_5)_2)$, the

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(1) (a) Dahan, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1984**, 432–433. (b) Nuel, D.; Dahan, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658–1664. (c) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436–1439.

(2) Lourdichi, M.; Mathieu, R. *Organometallics*, in press.

(3) Herrmann, W. A. *Angew, Chem., Int. Ed. Engl.* **1978**, 17, 800–812.

(4) **2**: mp 114 °C dec; mass spectrum, m/z 586; IR (C_6H_{14}) ν(CO) 2077 (m), 2044 (s), 2009 (s), 2001 (s), 1976 (m), 1695 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, ppm) 7.39 (m, C_6H_5), 3.87, 3.86 (q, J = 7 Hz, OCH_2CH_3), 2.05 (CH_3), 1.36 (t, J = 7 Hz, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2, ppm) 212.6, 211.4, 208.6, 208.4, 204.7 (CO + COC_2H_5), 174.1 (C═O), 166.5 (CCH_3), 137.9, 133.1, 131.2, 130.5, 129.1, 128.7, 128.3 (C_6H_5), 84.9 ($C(C_6H_5)_2$), 71.9 (OCH_2CH_3), 14.7 (OCH_2CH_3), 12.7 (CCH_3). Anal. Calcd for $C_{25}H_{18}Fe_2O_8N_2$: C, 51.23; H, 3.10; N, 4.78. Found: C, 48.85; H, 2.62; N, 4.58.

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