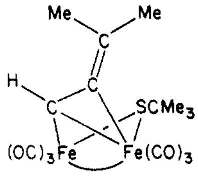
this question, an X-ray diffraction study was undertaken. Suitable crystals of the *tert*-butanethiolate analogue **8**, prepared by reaction of the $Me_3CSH/Fe_3(CO)_{12}/Et_3N$ system with propargyl bromide, were grown at −20 °C in pentane solution.[13]

The X-ray structure determination of **8** (Figure 2) shows that the propargyl bromide products have the structure **7**.[14] As in **5**, the alkanethiolate ligand bridges the two iron atoms slightly asymmetrically with Fe–S distances of 2.283 (2) and 2.250 (2) Å. However, instead of a three-carbon bridge as in **5**, an η^1,η^2-allenyl ligand is present. This compound has the same basic features reported for other η^1,η^2-vinyl-bridged $Fe_2(CO)_6$ systems.[15,16] The Fe–Fe bond length of 2.550 (1) Å is significantly shorter than the 2.675 (1) Å distance in **5**, but this probably reflects the difference in the bites of the two organic bridges. The C(6)–C(7) distance of 1.335 (9) Å is a standard C–C double bond length, while the C(5)–C(6) bond length of 1.363 (9) Å is slightly elongated as expected for a π-coordinated olefin.

These organic derivatives **5** and **7** most likely are formed in an S_N2' process, with initial attack by the iron nucleophile at C-3 of the allyl or propargyl halide. This was demonstrated by reactions in which $HC{\equiv}CCMe_2Br$ and $EtC{\equiv}CCH_2Cl$ were added to the $Me_3CSH/Fe_3(CO)_{12}/Et_3N$ system. In the former case the product was **9**;[17] in the latter it was **10**.[18]



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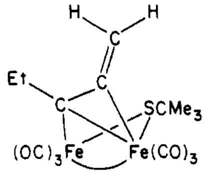

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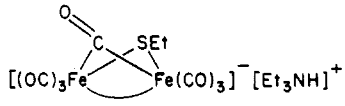
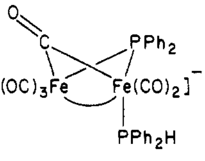
In conclusion, it is of interest to consider what the active reagent in the $EtSH/Et_3N/Fe_3(CO)_{12}$ system is. On the basis of the IR spectra of such solutions which show a band at 1743 cm^{-1} (in THF) which may be attributed to a μ-CO ligand, we suggest that the active reagent is **11** which reacts



11

with loss of one CO ligand. In support of this idea, we note that the closely related anionic species **12**[19] and **13**[20] showed



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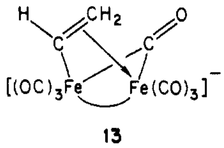

13

bridging CO frequencies at 1710 cm^{-1} (PPN^+ counterion, in THF) and 1735 cm^{-1} (Ph_4P^+ counterion, in CH_2Cl_2), respectively.

It is obvious that in **11** we have a new type of reactive dinuclear iron carbonyl species whose reactions should lead to many new and interesting $Fe_2(CO)_6$ complexes with two different bridges between the iron atoms. Our studies of the chemistry of **11** and of related species are continuing.

Acknowledgment. We are grateful to the National Science Foundation (Grant NSF CHE83-40747) for support of this work. We thank the biomedical research support shared instrumentation grant program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment, NIH Grant S10RR02243-01.

Registry No. **3a**, 93530-31-5; **3b**, 93602-99-4; **4**, 93564-55-7; **5**, 93530-32-6; **7**, 93530-33-7; **8**, 93530-34-8; **9**, 93530-35-9; **10**, 93530-36-0; **11**, 93530-38-2; (μ-CH_3CO)(μ-EtS)$Fe_2(CO)_6$ (e-Et isomer), 93530-39-3; (μ-CH_3CO)(μ-EtS)$Fe_2(CO)_6$ (a-Et isomer), 93603-00-0; $Fe_3(CO)_{12}$, 17685-52-8; $HC{\equiv}CCMe_2Br$, 6214-31-9; $EtC{\equiv}CCH_2Cl$, 22592-15-0; EtSH, 75-08-1; Et_3N, 121-44-8; Me_3CSH, 75-66-1; benzoyl chloride, 98-88-4; diphenylchlorophosphine, 1079-66-9; allyl chloride, 107-05-1; propargyl bromide, 106-96-7; acetyl chloride, 75-36-5.

Supplementary Material Available: Tables of final positional and thermal parameters and the final observed and calculated structure factors for **5** and **8** (18 pages). Ordering information is given on any current masthead page.

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[13] **8** was prepared by addition of propargyl bromide to the $Me_3CSH/Et_3N/Fe_3(CO)_{12}$ reaction mixture and has the same structure as **7** by NMR data. ^1H NMR (acetone-d_6, 90 MHz): δ 1.38 (s, 9 H, CH_3), 5.39 (d, $J = 4.4$ Hz, $={CH_2}$), 7.39 (t, $J = 4.4$ Hz, CH); ^{13}C NMR (C_6D_6, 67.9 MHz): δ_C 33.0 (q, $J = 129$ Hz, CH_3), 48.2 (s, CMe_3), 95.5 (t, $J = 166$ Hz, CH_2), 113.2 (d, $J = 162$ Hz, CH), 177.7 (s, C=), 210.2 (s, CO).

[14] Crystal data for compound **8**: $a = 8.455$ (1) Å, $b = 9.478$ (1) Å, $c = 10.926$ (2) Å, $\alpha = 90.95$ (1)°, $\beta = 97.44$ (1)°, $\gamma = 101.81$ (1)°, $V = 848.98$ Å^3, $Z = 2$, space group $P\bar{1}$. Data in the range $3° < 2\theta < 55°$ ($+h, +k, +l$) were collected by using Mo Kα radiation.[10a,b] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the *tert*-butyl group were placed in calculated positions. Hydrogen atoms of the allenyl group could not be located in difference Fourier maps and have been ignored. Final $R_1 = 0.048$ and $R_2 = 0.055$ for 2058 observed reflections [$F_o > 4\sigma(F_o)$] and 200 variables.

[15] Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 225.

[16] Krüger, C.; Tsay, Y. H.; Grevels, F. W.; Koerner von Gustorf, E. *Isr. J. Chem.* **1977**, *10*, 201.

[17] ^1H NMR (CD_2Cl_2): δ 1.34 (s, Me_3C), 1.96 (s, $={CMe_2}$), 7.36 (s, Fe_2CH). ^{13}C NMR (C_6D_6): δ_C 25.7 (q, $J = 128$ Hz, $={C(CH_3)_2}$), 32.7 (q, $J = 127$ Hz, (s, $={Me_3C}$), 47.4 (s, CMe_3), 115.4 (s, $={CMe_2}$), 119.6 (d, $J = 161$ Hz, Fe_2CH), 171.8 (s, $C{=}CMe_2$), 211.0 (s, CO). As the temperature was lowered when the ^1H NMR spectrum was measured, the $={C(CH_3)_2}$ singlet broadened until two peaks were observable below −23 °C. The limiting spectrum was obtained at −53 °C: two sharp singlets and δ 1.88 and 1.75.

[18] In the ^1H NMR spectrum $\delta(={CH_2})$ was observed at 5.20 ppm and in the ^{13}C NMR spectrum $\delta_C(={CH_2})$ at 94.7 ppm (t, $J = 163$ Hz).

[19] Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

[20] Lourdichi, M. Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

Germacyclopentanes via Cycloadditions of Free Dimethylgermylene to Styrenes†

Jürgen Köcher and Wilhelm P. Neumann*

Lehrstuhl für Organische Chemie I
University of Dortmund, D-4600 Dortmund 50, Germany

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Summary: Free Me_2Ge gives cycloadditions with 2 mol of α-substituted styrenes via a regiospecific but not stereospecific mechanism. Equal amounts of syn/anti 3,4-diphenylgermacyclopentanes are formed in good yield, those arising from α-substituted styrenes bearing additional substituents in these positions, and no 2,5- or 2,4-substituted rings. The 4,4,5,5-Ph_4 derivative has an extraordinarily strained five-membered ring with a very long C_3–C_4 bond (1.626 Å) and $\alpha_{C-Ge-C} = 90.3°$. Styrenes without a $={CH_2}$ group as well as a number of other olefins do not react rapidly enough. A two-step mechanism involving an 1:1 adduct is suggested.

Free dimethylgermylene generated thermally from 7,7-dimethyl-7-germanobornadiene under mild conditions behaves as singlet heavy carbene analogue, undergoing in solution stereospecific (cheletropic) 1,4 cycloadditions to

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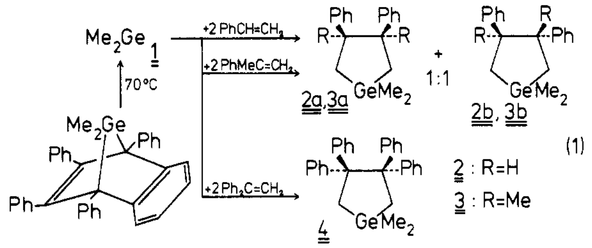
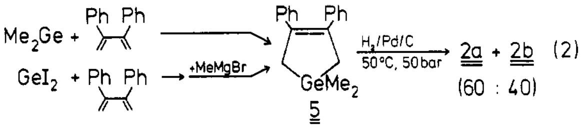
1,3-dienes[1] and typical insertions into σ bonds by way of both the one-step and the two-step (abstraction–recombination) mechanism.[2]

We report here concerning the behavior of monoolefins toward Me_2Ge under well established conditions where a free germylene 1 is the reactive species.[3-5] With styrene and α-methylstyrene we found in each case a 1:1 mixture of two isomers, whereas 1,1-diphenylethylene produced only one product. The product yields were good (60–85%). The isomers give identical elemental analyses, molecular weights, and MS data but have different ^1H and ^{13}C NMR spectra.[6] All facts are in accordance with the formation of 1,1-dimethyl-1-germacyclopentanes, which are unsubstituted in the 2- and 5-positions, rather are exclusively substituted in 3- and 4-positions (eq 1).



The ^{13}C NMR spectrum of 2 is very similar to that of the 3,4-Ph_2silacyclopentane and does not resemble that of 2,5-Ph_2silacyclopentane.[7]

In order to back up the structural conclusions by chemical evidence, we prepared 1,1-dimethyl-1-germa-3,4-diphenylcyclopent-3-ene (**5**) by two independent routes[8] (eq 2). The hydrogenation of **5** was very slow but produced exclusively small amounts of a mixture[9] of **2a** and **2b**.



As a final proof for the exclusion of 2,5 substitution,[3] the structure of 4 has been confirmed by X-ray analysis.[10] The five-membered ring is very strained due to the presence of the bulky phenyl groups. The C–C bond in 3–4-position is one of the longest known thus far (1.626 Å).[10] The bond angle at the ring C–Ge–C group is only 90.3°; the ring is markedly distorted.

The products **2a** and **2b** and **3a** and **3b** are, therefore, syn/anti isomers, whereas in the case of **4** only one product could be found. The unusual substitution pattern, avoiding the sterically less hindered 2,5-positions, must be governed by the mechanism of formation.

During the reaction (eq 1), no intermediates could be observed either by NMR or by ESR techniques. No polymers such as polystyrene were found, and also no polymers of type $(PhRCCH_2Me_2Ge)_n$. *tert*-Butyl bromide, a very efficient scavenger for Ge-centered radicals, does not influence the rate.

Compound **2** is stable up to at least 150 °C and is not altered by KOH/EtOH at 90 °C during 24 h. Bromine slowly cleaves the ring to produce Me_2GeBr_2. In contrast, the tetraphenyl derivative **4** is much more reactive, obviously due to its ring strain. In chlorobenzene at 80 °C it has a half-life of 21 min forming poly(dimethylgermylene) and 2 molar equiv of $Ph_2C{=}CH_2$. No intermediates could be detected. A free germylene, **1**, is the reactive intermediate, as could be demonstrated, by use of typical Me_2Ge trapping reagents (eq 3). Both the stereospecificity of the 1,4 addition[1] and the well-known CIDNP pattern during the reaction with benzyl bromide[2] establish the singlet character of this germylene, Me_2Ge (**1**).

Using the same conditions as had been used with styrene and its analogues, similar reactions were sought with cyclohexene, 1-phenylcyclopentene, 3-phenylpropene, 4,4-dimethylpentene, (*E*)-β-methylstyrene, and (*E*)- and (*Z*)-stilbene. Only poly(dimethylgermylene) was found, and no products derived from the olefins. The configu-

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† Dedicated to Professor G. Wilke on the occasion of his 60th birthday. The first part of the following results has been reported under his chairmanship during the 29th IUPAC Congress, June 1983, in Köln, Germany.

(1) (a) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. (b) Köcher, J.; Neumann, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 3861.

(2) Köcher, J.; Lehnig, M. *Organometallics* **1984**, *3*, 937.

(3) In earlier attempts[4,5] a mixture of Me_2GeCl_2 and 2Na or 2Li was used, but the occurrence of a free germylene was not proven nor was the mechanism elucidated. Me_2Ge was suggested as the reactive intermediate in some cases, but initial electron transfer to the olefin and subsequent reaction with the germanium halide also has been proposed.[5] In most cases, moreover, it was not determined whether 2,5 or 3,4 substitution resulted.

(4) For reviews, see: Satgé, J; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1. Satgé, J. *Bull. Soc. Chim. Belg.* **1982**, *91*, 1019.

(5) Nefedov, O. M.; Manakov, M. N. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 226. Nefedov, O. M.; Manakov, M. N.; Petrov, A. D. *Sint. Svoistva Monomerov*, Sb. *Rab. Vysokomol. Soedin.* **1962**, 67. For experimental details see also: *Chem. Abstr.* **1965**, *62*, 6502; *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 1228; *Dokl. Akad. Nauk SSSR* **1962**, *147*, 1376. We repeated the experiment with Me_2GeCl_2, Li, and styrene and could isolate the reported germacyclopentane with unknown phenyl substitution pattern. To determine its structure, we recorded a ^{13}C NMR spectrum. This gives evidence for a syn/anti mixture of 2,5-diphenylgermacyclopentane, and not for **2**; the spectrum is also very similar to that of the analogous 2,5-diphenylsilacyclopentane.[13] ^{13}C NMR (decoupled) ($CDCl_3$) δ_C −6.40, −1.77 ($GeCH_3$, syn), −4.24 ($GeCH_3$, anti), 32.84, 33.13 (CH_2), 37.55, 39.17 (CHPh), 123.79, 123.96, 126.07, 126.32, 128.27, 144.92, 145.61 (phenyl C). Also the physical constants of this product differ markedly from those of **2**.

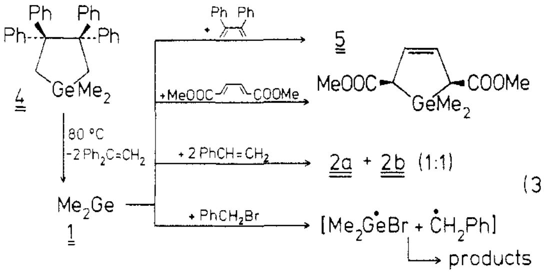
(6) Compounds **2**, **3**, and **4** were prepared by thermolysis of 7,7-dimethyl-7-germanorbornadiene in benzene at 70 °C[1] in the presence of a 2.5–7-fold molar excess of styrenes. The resulting germacyclopentanes can be isolated and purified by crystallization from EtOH, sublimation, or chromatography. **2a** and **2b** are separated by column chromatography (silica gel, hexane). Analytical data of **2**, **3**, and **4**: **2a**: 60-MHz ^1H NMR (CCl_4) δ 0.41 (s, 3 H, $GeCH_3$), 0.66 (s, 3 H, $GeCH_3$), 1.22 (wide d, 4 H, CH_2), 3.20–3.60 (m, 2 H, CHPh), 6.40–7.10 (m, 10 H, Ph). **2b**: 60-MHz ^1H NMR (CCl_4) δ 0.43 (s, 6 H, $GeCH_3$), 0.95–1.50 (m, 4 H, CH_2), 2.60–3.00 (m, 2 H, CHPh), 6.96 (s, 10 H, Ph). **2a + 2b**: ^{13}C NMR (decoupled) ($CDCl_3$) δ_C −1.85 ($GeCH_3$), 18.80, 25.63 (CH_2), 51.68, 53.85 (CHPh), 125.42, 125.64, 127.18, 127.92, 128.32, 143.79, 146.47 (phenyl C); MS (70 eV), *m/e* (relative intensity) 312 (1), 297 (2), 208 (95), 193 (13), 104 (100), 89 (47), 77 (9). **3a + 3b** (all data for a syn/anti mixture): 300-MHz ^1H NMR ($CDCl_3$) δ 0.44 (s, 3 H, syn $GeCH_3$), 0.45 (s, 3 H, syn $GeCH_3$), 0.57 (s, 6 H, anti $GeCH_3$), 1.06 (s, 6 H, CH_3), 1.40 (s, 6 H, CH_3), 0.98–1.85 ($2AB_q$, 4 H, CH_2), 6.72–7.13 (m, 10 H, Ph); ^{13}C NMR (decoupled) ($CDCl_3$) δ_C −0.52, −0.04, 1.40 ($GeCH_3$), 25.15, 26.15 (CH_3), 27.31, 28.54 (CH_2), 52.97, 53.19 ($C(CH_3)Ph$), 125.26, 125.50, 126.45, 126.48, 126.62, 127.92, 128.60, 145.97, 147.22 (phenyl C); MS (70 eV), *m/e* (relative intensity) 325 (1), 222 (88), 207 (35), 118 (22), 104 (100), 89 (76), 77 (20). **4**: 60-MHz ^1H NMR (CCl_4) δ −0.05 (s, 6 H, $GeCH_3$), 2.04 (s, 4 H, CH_2)e, 6.84 (s, 20 H, Ph); ^{13}C NMR (decoupled) ($CDCl_3$) δ_C −1.85 ($GeCH_3$), 33.48 (CH_2), 63.97 (CPh_2), 125.19, 125.59, 126.33, 131.16, 132.19, 147.60, 149.94 (phenyl C). We found correct (±0.3) elemental analyses for **2** and **4**. The carbon value of **3** was found 0.7 too low.

(7) Both silanes have been prepared following: Weyenberg, D. R.; Toporcer, L. H.; Bey, A. E. *J. Org. Chem.* **1965**, *30*, 4096. We recorded the following ^{13}C NMR spectra (decoupled) ($CDCl_3$): 3,4-Ph_2 derivative (syn/anti mixture), δ_C −1.32, −0.60 ($SiCH_3$, syn), −0.90 ($SiCH_3$, anti), 17.92, 25.00 (CH_2), 50.92, 53.24 (CHPh), 125.60, 125.80, 127.12, 127.44, 128.16, 128.52, 143.88, 146.32 (phenyl C); 2,5-Ph_2 derivative (syn/anti mixture) δ_C −5.95, −2.02 ($SiCH_3$, syn), 3.79 ($SiCH_3$, anti), 31.60, 31.94 (CH_2e, 35.59, 37.23 (CHPh), 123.94, 124.05, 126.10, 126.44, 128.26, 144.08, 144.87 (phenyl C). For the assignments, cf. ref 13.

(8) Compound **5** can be prepared thermally from **1**, generated at 70–80 °C, in the presence of an excess 2,3-diphenylbutadiene in benzene, or from 2,3-diphenylbutadiene with excess GeI_2 in refluxing *n*-hexane and methylation of the resulting 1,1-diiodo-1-germacyclopent-3-ene. **5** has been characterized by ^1H NMR, MS, and elemental analysis.

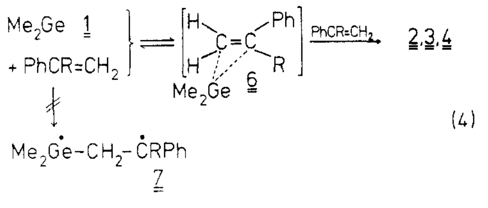
(9) Identified by capillary GLC (50-m OV 225 (43) quartz column).

(10) Preut, H.; Köcher, J.; Neumann, W. P., submitted for publication in Acta Crystallogr. Certain highly substituted ethanes sometimes have similar, extraordinary bond lengths: cf. Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 3235. Further references are given there.



ration of (*Z*)-stilbene remained unchanged, thus proving the absence of an transient, reversible addition reaction.

Clearly, a regiospecific but not stereospecific reaction of dimethylgermylene with 2 mol of the olefin takes place, presumably involving a short-lived 1:1 intermediate. All considerations concerning the mechanism have to take into account the competing, very rapid polymerization of **1**, giving $(Me_3Ge)_n$ which is diffusion controlled, $k \approx 10^9$ M^{-1} s^{-1}. Hence, only very rapid reactions with an olefin can compete. For this to be the case, two requirements are apparent: (a) An terminal olefin must be used. Whereas α-methylstyrene reacts, β-methylstyrene does not. 1,1-Diphenylethylene reacts readily but the two isomeric stilbenes do not. This suggests an unsymmetrical transition state (or π complex) **6** of a type which is known for the approach of a free radical toward an olefin.[11] This is in accordance with our earlier observation[1b] that terminal conjugated dienes react faster (giving cheletropic cycloadditions) than do nonterminal dienes. Thus 2,3-diphenyl-1,3-butadiene is more reactive than 1,4-diphenyl-1,3-butadiene. (b) The other end of the olefin has to be substituted by at least one aromatic ring.[12] All of the other olefins tested did not react rapidly enough under similar conditions to compete successfully with the polymerization of **1**. This stabilizing effect of the Ph group cannot involve the stabilization of a free benzyl radical **7**, because in this case polystyrene should be observed, and the *t*-BuBr added to the mixture should capture the Ge-centered radical. However, this is not observed. Whatever the nature of the 1:1 intermediate **6**—a question to be cleared up in more detailed investigations—it should have one stronger C–Ge bond, the CH_2–Ge bond, and one weaker, the benzyl–C bond, ready for the insertion of the second molecule of olefin, as indicated in eq 4, thus causing the regiospecificity of the overall reaction.[13]



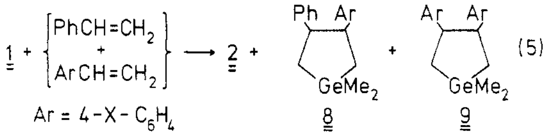
In a competition experiment, 2,3-diphenyl-1,3-butadiene undergoes a 1:1 reaction with **1** in the presence of an excess of styrene giving exclusively **5** (^1H NMR). Therefore, the cycloaddition is at least 10 times faster than the reaction with styrene. This could be an additional hint favoring the two-step mechanism of styrene, to be elucidated in the future.

Table I. Results of Competition Experiments with 1:1 Mixtures of Styrene and 4-X-Styrenes[a]

X	2	8	9
COMe	5	50	45
Cl	19	53	28
Me	26	51	24
OMe	30	52	18

[a] 2.0 mmol each + 0.6-mmol precursor of **1** in 5 mL of benzene at 80 °C. Total yields >80%; the relative distribution (SLC peak areas in percent, 2-m SE 30) is given.

In competition experiments with 1:1 mixtures of styrene and 4-X-styrenes, we found a rate sequence X = Me_2N (no yield) < OMe < Me ≈ H ≈ Cl < COMe with increasing yields of **8** and **9** (eq 5; Table I). Dimethylgermylene exhibits, therefore, *nucleophilic* behavior in these cycloadditions with styrenes, as it does toward conjugated dienes.[1b]



Acknowledgment. This work has been supported by the Minister für Wissenschaft und Forschung, Düsseldorf, and the Fonds der Chemischen Industrie.

Registry No. **1**, 74963-95-4; **2a**, 94070-43-6; **2b**, 94070-44-7; **3a**, 94070-45-8; **3b**, 94070-46-9; **4**, 94070-47-0; **5**, 94070-48-1; 4-$COMeC_6H_4CH{=}CH_2$, 10537-63-0; 4-$ClC_6H_4CH{=}CH_2$, 1073-67-2; 4-$MeC_6H_4CH{=}CH_2$, 622-97-9; 4-$OMeC_6H_4CH{=}CH_2$, 637-69-4; Me_2GeCl_2, 1529-48-2; GeI_2, 13573-08-5; Styrene, 100-42-5; α-methylstyrene, 98-83-9; 1,1-diphenylethylene, 530-48-3; cyclohexene, 110-83-8; 1-phenylcyclopentene, 825-54-7; 3-phenylpropene, 300-57-2; 4,4-dimethylpentene, 762-62-9; (*E*)-β-methylstyrene, 873-66-5; (*E*)-Stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; *cis*-2,5-diphenylgermacyclopentane, 26436-21-5; *trans*-2,5-diphenylgermacyclopentane, 26436-22-6; 7,7-dimethyl-7-germanorbornadiene, 76054-64-3; *cis*-3,4-diphenylsilacyclopentane, 94070-49-2; *trans*-3,4-diphenylsilacyclopentane, 88296-43-9; *iso*-2,5-diphenylsilacyclopentane, 26436-15-7; *trans*-2,5-diphenylsilacyclopentane, 26436-16-8; 2,3-diphenylbutadiene, 2548-47-2; 3,4-dimethyl-1,1-diiodo-1-germacyclopent-3-ene, 94234-81-8.

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(11) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753 and literature cited there.

(12) Other stabilizing groups such as CN or COOR in acrylic acid derivatives lead to other reactions outside the scope of this communication (work in progress).

(13) With a Si analogue, the isolated 1,1,2,2,3,3-hexamethylsilirane, a nonregiospecific two-atom insertion of styrene has been found, giving a mixture of 2-phenyl- and 3-phenylsilacyclopentanes. Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574. Earlier work is cited there.

Carbonylation of Metal–Oxygen Bonds. Formation of Carbalkoxydicarbonylbis(triphenylphosphine)iridium, $ROC(O)Ir(CO)_2(PPh_3)_2$, by Carbonylation of *trans*-Alkoxycarbonylbis(triphenylphosphine)iridium, *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, *n*-Pr, Ph)

Wayne M. Rees and Jim D. Atwood*[†]

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

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Summary: Carbonylation of the complexes *trans*-$MeOIr(CO)(PPh_3)_2$, *trans*-(*n*-PrO)$Ir(CO)(PPh_3)_2$, and *trans*-$PhOIr(CO)(PPh_3)_2$ leads to carboalkoxy complexes $ROC(O)Ir(CO)_2(PPh_3)_2$ in high yield. Identification of the intermediate $Ir(CO)_3(PPh_3)_2^+$ OR^- indicates a two-step mechanism—first displacement of the alkoxide from the coordination sphere and then nucleophilic attack on a carbon of the cationic carbonyl complex. The hydroxy complex did not undergo carbonylation under similar conditions.

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