Ni–$SiCl_3$ length of 2.286 (4) Å is within the range of reported values for Ni–Si[14] bonds. However, few structural data are available for Ni–$SiCl_3$ bonds. Interestingly, recent results in our laboratory[15] on the structure of $[\eta^6\text{-}C_6H_3(CH_3)_3]Ni(SiCl_3)_2$ reveal a considerably shorter Ni–Si distance of 2.194 (2) Å. Trigonal-bipyramidal complexes have been the subject of many studies. Several authors, including Osborn,[16] Churchill,[17] Dartiguenave,[11] and coworkers, have noted that strong π-acceptor ligands tend to occupy equatorial sites. Additionally, Rossi and Hoffmann[19] have considered a unified molecular orbital treatment of five-coordinate complexes in general. They concluded for the d^8 case that good σ-donor ligands will prefer axial sites while good π-acceptors will prefer the equatorial sites. The observed equatorial position of the three CO ligands in the present structure can be attributed to the better π-accepting ability of CO. This is supported by the fact that the Ni–CO bonds are typically short while the Ni–$SiCl_3$ bonds are ~0.09 Å longer than those in $[\eta^6\text{-}C_6H_3(CH_3)_3]Ni(SiCl_3)_2$[15] (where considerable π-backbonding to $SiCl_3$ is expected).

Acknowledgement is made to the University of North Dakota for a contribution of computer time, and the National Science Foundation for program support (K.J.K.).

Registry No. 2, 93921-98-3.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(14) See, for example: Von Werner, B.; Schuster, H. *Z. Anorg. Allg. Chem.* **1981**, *482*, 40–48. Herberich, G. E.; Thännessen, M.; Schmitz, D. *J. Organomet. Chem.* **1980**, *191*, 27–37.

(15) Radonovich, L. J.; Janikowski, S. K.; Klabunde, K. J.; Groshens, T. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; American Chemical Society: Washington, DC, 1982; INOR 1250

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Communications

A General Route to Novel Dinuclear Iron Carbonyl Complexes Containing Alkanethiolate and Bridging Organic Ligands†

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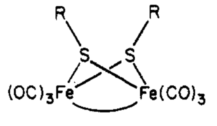
Received September 13, 1984

Summary: The reaction of $Fe_3(CO)_{12}$ with mercaptans (RSH, R = Et, Me_3C) in the presence of stoichiometric Et_3N in THF gives the reactive salt $[Et_3NH^+][(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6^-]$. Reactions of the latter with benzoyl and acetyl chloride, diphenylchlorophosphine, allyl chloride, and propargylic halides have been studied. New bridging ligands (μ-RC=O, μ-Ph_2P, μ-C_3H_6, μ-η^1,η^2-allenyl) were introduced between the iron atoms in all of these reactions. X-ray crystal structures of $(\mu\text{-EtS})(\mu\text{-}C_3H_6)Fe_2(CO)_6$ and $(\mu\text{-}Me_3CS)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CH_2)Fe(CO)_6$ were determined.

Reactions of organic thiols with iron carbonyls have received much attention, and the first report on this subject was published by Hieber and Spacu in 1939.[1] In general, complexes of type 1 are formed in such reactions.[2]



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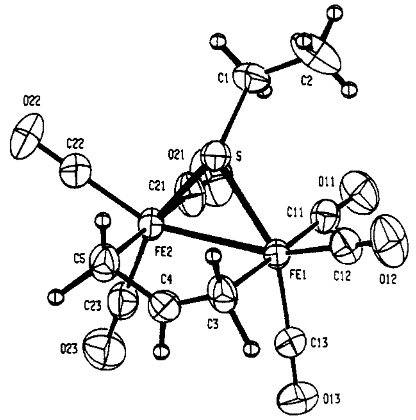

Figure 1. ORTEP diagram of 5 showing the 40% probability thermal ellipsoids and the atom labeling scheme. Hydrogen atoms are drawn as arbitrary spheres with B = 1.0 $Å^2$. Bond lengths (in Å) are as follows Fe(1)–Fe(2) = 2.675 (1), Fe(1)–S = 2.235 (2), Fe(1)–C(3) = 2.119 (5), Fe(1)···C(4) = 2.546 (4), Fe(2)–S = 2.251 (2), Fe(2)–C(5) = 2.139 (5), Fe(2)···C(4) = 2.445 (4), S–C(1) = 1.823 (5), C(1)–C(2) = 1.513 (9), C(3)–C(4) = 1.426 (8), C(4)–C(5) = 1.414 (8), Fe–CO(mean) = 1.784, C–O(mean) = 1.137.

In reactions of bulky thiols with $Fe_3(CO)_{12}$ trinuclear iron products $(\mu_3\text{-RS})(\mu\text{-H})Fe_3(CO)_9(2\textit{Fe-Fe})$, 2, are formed instead.[2b,3] In related work, Takács and Markó carried out reactions of $Fe_3(CO)_{12}$ with sodium alkanethiolates, RSNa, in refluxing THF and obtained solutions containing $[Fe_3(CO)_9SR]^-$ anions which on acidification gave complexes of type 2.[4] We report here a new mode of reaction

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† Dedicated to Professor G. Wilke on the occasion of his 60th birthday.

(1) Hieber, W.; Spacu, P. *Z. Anorg. Allg. Chem.* **1937**, *233*, 353.

(2) (a) For other references see: "Gmelin Handbuch der Anorganischen Chemie", 8th ed.; Gmelin Institut für Anorganische Chemie and Springer-Verlag: Berlin, 1978; Part C1, pp 77–93. (b) Winter, A.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1982**, *115*, 1286. (c) Winter, A.; Zsolnai, L.; Huttner, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1430.

(3) de Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757; *J. Chem. Soc., Chem. Commun.* **1970**, 288.

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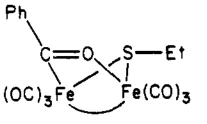
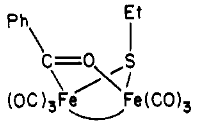
of thiolates with $Fe_3(CO)_{12}$ which permits the preparation of novel $Fe_2(CO)_6$ compounds which contain bridging organic ligands as well as bridging SR groups.

In a typical experiment, 3.38 mmol of ethanethiol and 3.50 mmol of triethylamine were added, with stirring under nitrogen, to a solution of 2.98 mmol of $Fe_3(CO)_{12}$ in 50 mL of THF. The resulting mixture was stirred at room temperature for 15 min. During this time a color change from green to red-brown was noted. To such a solution was added an excess (7.0 mmol) of benzoyl chloride, and the reaction mixture was stirred at room temperature for 23 h. A white solid ($[Et_3NH]Cl$) precipitated, and a dark red solution was formed. Filtration and removal of solvent at reduced pressure left a red oil. Filtration chromatography (silicic acid; pentane, then 1:9 CH_2Cl_2/pentane) gave 1.10 g (83% yield) of (μ-PhCO)(μ-EtS)$Fe_2(CO)_6$, red crystals, mp 81–86 °C, as a 2.3:1 mixture of isomers **3a** and **3b**.[5] A



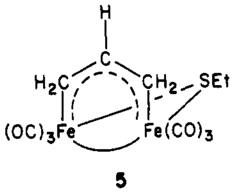
3a, e-Et isomer



3b, a-Et isomer

similar reaction in which acetyl chloride was used in place of benzoyl chloride gave a 52% yield of (μ-CH_3CO)(μ-EtS)$Fe_2(CO)_6$, a dark red oil, a 3.0:1 e-Et/a-Et isomer mixture. Addition of diphenylchlorophosphine to the EtSH/Et_3N/$Fe_3(CO)_{12}$ reaction mixture gave (μ-EtS)(μ-Ph_2P)$Fe_2(CO)_6$, **4**, as orange solid, mp 111–112 °C, in 80% yield.

Of greater interest were those reactions of the RSH/Et_3N/$Fe_3(CO)_{12}$ reagent which introduced wholly organic ligands. The EtSH/Et_3N/$Fe_3(CO)_{12}$ system reacted readily with allyl chloride. The product, a red crystalline solid, mp 41–42 °C, obtained in 80% yield, had the composition $C_3H_5(EtS)Fe_2(CO)_6$ by analysis and mass spectroscopy. The NMR spectra indicated the allyl ligand to be symmetrically bridging.[6] The ^{13}C NMR spectrum showed a triplet (J = 154 Hz) at δ_C 20.9 for the allylic CH_2 groups, and the ^1H NMR spectrum showed the CH_2 proton signals of the allyl ligand as two doublets at δ 0.47 (J = 12.6 Hz) and 1.97 (J = 7.5 Hz), corresponding to the anti and syn hydrogens. This suggests a structure as shown in **5**,[7] which has been confirmed by an X-ray diffraction study (Figure 1).[10a] The product **5** is a diiron hexacarbonyl complex with both a bridging ethanethiolate ligand and a bridging allyl ligand. The SEt ligand is bound slightly asymmetrically across the two iron atoms [Fe(2)–S = 2.251 (2) Å; Fe(1)–S = 2.235 (2) Å] as is the allyl ligand [Fe(1)–C(3) = 2.119 (5) Å; Fe(2)–C(5) = 2.139 (5) Å], although this deviation from symmetry was not great enough to be detected spectroscopically. The plane of the allyl carbon atoms is tilted by 6.53° with respect to the Fe–Fe–S plane, with C(4) being tipped slightly toward the latter plane. The C–C distances of the allyl ligand [C(3)–C(4) = 1.426 (8) Å; C(4)–C(5) = 1.414 (3) Å] lie between the values reported for C–C single and double bonds, indicating that the ligand is best regarded as a delocalized π-allyl ligand.[11]



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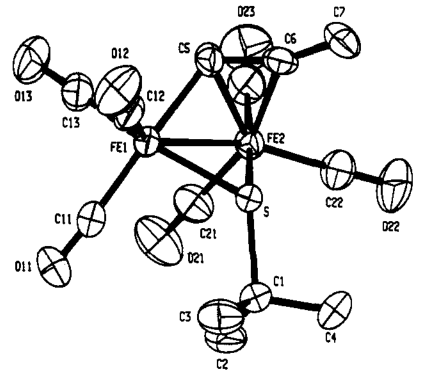
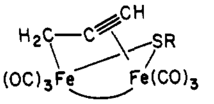


Figure 2. ORTEP diagram of **8** showing the 40% probability thermal ellipsoids and the atom labeling scheme. Hydrogen atoms have been omitted. Bond lengths (in Å) are as follows: Fe(1)–Fe(2) = 2.550 (1), Fe(1)–S = 2.250 (2), Fe(1)–C(5) = 1.982 (6), Fe(2)–S = 2.283 (2), Fe(2)–C(5) = 2.091 (6), Fe(2)–C(6) = 2.125 (6), S–C(1) = 1.867 (6), C(1)–CH_3(mean) = 1.522, C(5)–C(6) = 1.363 (9), C(6)–C(7) = 1.335 (9), Fe–CO(mean) = 1.780, C–O(mean) = 1.144.

The reaction of propargyl bromide with the EtSH/Et_3N/$Fe_3(CO)_{12}$ system gave a red crystalline solid, mp 39–41 °C, in 91% yield. If the propargyl ligand bridged the iron atoms in the same manner as the allyl group, the product would be **6** (R = Et). However, the NMR data[12] could not distinguish between **6** and a structural alternative **7**, which contains a μ-allenyl ligand. In order to resolve



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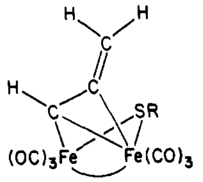

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[4] Takács, J.; Markó, L. *J. Organomet. Chem.* **1983**, *247*, 223.

[5] ^1H NMR (270 MHz, $CDCl_3$): δ 1.29 (t, J = 7.3 Hz, CH_3 of **3b**), 1.50 (t, J = 7.3 Hz, CH_3 of **3a**), 2.09, 2.29 (m, CH_2 of **3b**), 2.64 (m, CH_2 of **3a**), 7.5–7.3 (m, Ph). ^{13}C NMR ($CDCl_3$): δ_C 17.8 (q, J = 128 Hz, CH_3 of **3b**), 18.3 (q, J = 127 Hz, CH_3 of **3a**), 26.0 (t, J = 144 Hz, CH_2 of **3b**), 33.0 (t, J = 141 Hz, CH_2 of **3a**), 126.8, 127.2, 128.3, 128.6 (each d, J = 163 Hz, Ph), 133.4 (d, J = 160 Hz, Ph), 144.5 (s, ipso Ph of **3a**), 144.8 (s, ipso Ph of **3b**), 207.7, 209.5, 209.9, 210.3, 211.3, 212.0 (all s, Fe–CO), 289.0 (s, acyl of **3a**), 291.6 (s, acyl of **3b**). The 70-eV mass spectrum showed inter alia m/z corresponding to M^+ and $M^+ - n$CO (n = 1–7).

[6] ^1H NMR (250 MHz, $CDCl_3$): δ 0.47 (d, J = 12.6 Hz, 2 H, C*H*H), 1.29 (t, J = 7.4 Hz, 3 H, CH_3), 1.97 (d, J = 7.5 Hz, 2 H, CH*H*), 2.47 (q, J = 7.4 Hz, 2 H, SCH_2), 4.76 (m, 1 H allylic CH). ^{13}C NMR (C_6D_6): δ_C 18.1 (q, J = 130 Hz, CH_3), 20.9 (t, J = 154 Hz, allyl CH_2), 32.7 (t, J = 141 Hz, SCH_2), 88.5 (d, J = 158 Hz, allyl, CH), 211.2 (s, Fe–CO).

[7] Kobayashi, Iitaka, and Yamazaki[8] and Werner, Kühn, and Tune[9] have prepared dinuclear palladium complexes which contain bridging allyl ligands of this type. The values of J(HH anti) = 13 and 12 Hz and J(HH syn) = 6.5 and 8 Hz, respectively, which they reported are very similar to those found for the allyl ligand of **5**.

[8] Kobayashi, Y.; Iitaka, Y.; Yamazaki, H. *Acta Crystallogr., Sect. B* **1972**, *B28*, 899.

[9] Werner, H.; Kuhn, A.; Tune, D. J. *Chem. Ber.* **1977**, *110*, 1763.

[10] (a) Crystal data for compound **5**: a = 13.400 (2) Å, b = 6.958 (1) Å, c = 15.970 (2) Å, V = 1489.00 Å, Z = 4, space group $Pn2_1a$. Data in the range $3° < 2\theta < 55°$ ($+h,+k,+l$) were collected by using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[10b] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the ethyl group were placed in calculated positions while those of the bridging allyl group were located in a difference Fourier map. Final R_1 = 0.034 and R_2 = 0.037 for 1469 observed rereflections [$F_o > 4\sigma(F_o)$] and 185 variables. (b) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

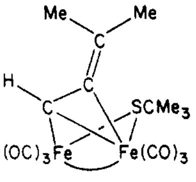
[11] MacGillavry, C. H.; Rieck, G. D., Ed. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. III, p 276.

[12] ^1H NMR (250 MHz, CD_2Cl_2): δ 1.29 (t, J = 7.4 Hz, 3 H, CH_3), 2.37 (q, J = 7.4 Hz, 2 H, SCH_2), 5.30 (d, J = 4.9 Hz, 2 H, Fe_2CH_2), 7.39 (t, J = 4.9 Hz, 1 H, CH). ^{13}C NMR (C_6D_6): δ 17.7 (q, J = 129 Hz, CH_3), 34.7 (t, J = 142 Hz, SCH_2), 93.4 (t, J = 167 Hz, $=CH_2$), 114.8 (d, J = 162 Hz, Fe_2CH), 176.6 (s, $C=CH_2$), 209.6 (s, Fe–CO).

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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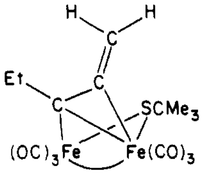

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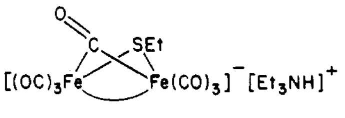
In conclusion, it is of interest to consider what the active reagent in the $EtSH/Et_3N/Fe_3(CO)_{12}$ system is. On the basis of the IR spectra of such solutions which show a band at 1743 cm^{-1} (in THF) which may be attributed to a μ-CO ligand, we suggest that the active reagent is **11** which reacts 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 bridging CO frequencies at 1710 cm^{-1} (PPN^+ counterion, in THF) and 1735 cm^{-1} (Ph_4P^+ counterion, in CH_2Cl_2), respectively.



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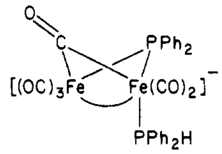

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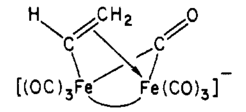

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It is obvious that in **11** we have a new type of reactive dinuclear iron carbonyl species whose reactions should lead to many new and interesting $Fe_2(CO)_6$ complexes with two different bridges between the iron atoms. Our studies of the chemistry 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, α = 90.95 (1)°, β = 97.44 (1)°, γ = 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[†]

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Received August 24, 1984

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 α_{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