Communications to the Editor

Germylenes Me_2Ge as Donors in [2 + 4] Cheletropic Cycloadditions to Conjugated Dienes

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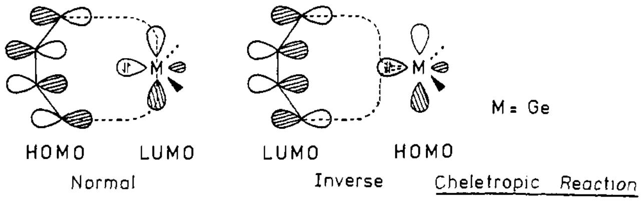
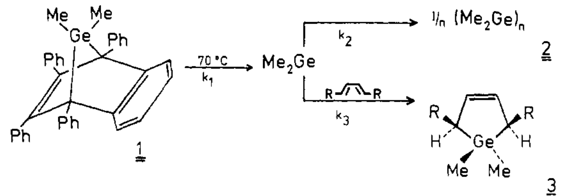
Thermal 1,4-additions of free germylenes Me_2Ge to a number of 1,3-dienes proceed concertedly via a [2 + 4] cheletropic mechanism, as reported recently.[1a,b] For a better understanding of these new pericyclic reactions the question has been raised[1a] whether in the transition state the $HOMO_{diene}$ interacts with the $LUMO_{germylene}$ ("normal" reaction) or the $LUMO_{diene}$ with the $HOMO_{germylene}$ ("inverse" reaction). This question is of general importance, since at present no information is available on the behavior of heavy carbene analogues—silylenes, germylenes, stannylenes—altogether.

We wish to report here that free Me_2Ge behaves as a donor toward 1,3-dienes, reacting faster with more electron-deficient ones thus exhibiting the "inverse" type of a cheletropic [2 + 4] addition, and not the "normal" one.



Following the thermal generation, k_1, of germylenes Me_2Ge in solution from **1**,[1a] the fast polymerization, k_2, of the latter is competing with the desired disrotatory ring closure with a diene, k_3.

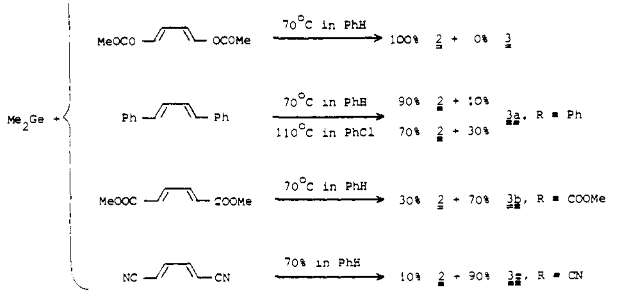


In the case of Diels–Alder reactions besides orbital energies (FMO concept) other factors are controlling the rate.[2] This can be concluded also for our cheletropic reaction: E.g., 2,3-substitution of the diene enhances the cycloaddition[1b] compared with 1,4-substitution, presumably by favoring the s-cis conformer. Thus, 2,3-dimethyl-[1a] and 2,3-diphenyl-1,3-butadiene yielded 80% of the expected cycloadduct. Unsymmetric substitution like in 1-phenyl-1,3-butadiene causes polarity of the diene, and a mixture of products is obtained containing not only cycloadducts. Therefore, in order to compare the reactivity of dienes and to control simultaneously the stereospecifity of the cycloaddition k_3, it is necessary to keep as many factors as possible constant thus restricting the changes in diene reactivity largely to changes in orbital energies.

Table I. ^1H NMR Data (δ) of Adducts **3a** (R = Ph), **3b** (R = COOMe), and **3c** (R = CN)

	Ge-CH_3	C=C-CH	C=CH	$COOCH_3$	C_6H_5
3a (in CCl_4)	−0.59, 0.55	3.32	6.10		6.70–7.40 m
3b (in CCl_4)	0.21, 0.79	3.03	6.03	3.62	
3c (in benzene)	−0.18, 0.54	1.92	5.31		

Having considered these factors, lastly we selected the *E,E* isomers of the following 1,4-disubstituted 1,3-dienes[3] exhibiting quite different π-electron densities for the desired estimation of diene reactivity. We have found the following results (yields, ±5%, estimated by ^1H NMR in the reaction mixture):



The 1,4-substituents of the dienes always are found in the syn position of the cycloadducts **3** giving two ^1H NMR Me–Ge singlets of equal intensity as to be expected;[4] see Table I.

This reveals, using the Diels–Alder experience[2] and the Hammett σ-values,[5] a sequence of increasing reactivity k_3 with decreasing π-electron density in the diene. The donor systems NHCOOEt and OCOMe did not lead to detectable amounts of cycloadducts **3**, k_3, whereas the more electroneutral (*E,E*)-1,4-diphenylbutadiene competes with the polymerization k_2 and gives **3a**,[6] at 110 °C better than at 70 °C pointing to a considerable activation energy of this pericyclic reaction, k_3. The π-electron deficient *E,E* ester of muconic acid and its dinitrile[3] lastly give smooth cycloadditions k_3 yielding **3b**[7] or, respectively, **3c**.[8] The germylene Me_2Ge, thermally generated, k_1, behaves clearly as a nucleophile,[9] showing the "inverse" type of reaction indicated above.

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(1) (a) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897; *Angew. Chem.* **1981**, *93*, 1089; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1019. (b) Ma, E. C.-L.; Kobayashi, K.; Barzilai, M. W.; Gaspar, P. P. *J. Organomet. Chem.* **1982**, *224*, C13.

(2) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171. Sauer, J.; Sustmann, R. *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779. Further references are given there.

(3) The pure *E,E* isomers have been prepared by using known procedures. The purity of the *E,E* isomer of the dinitrile was only 97% (GC). Therefore, an unidentified 3% Me–Ge peak (0.20 ppm) could possibly represent the anti isomer of **3c**. Nitro or chloro substituents would also be desirable, but those dienes gave other reactions with Me_2Ge outside of cycloaddition.

(4) Anti isomers or other products are not present within the ^1H NMR accuracy (≤5, mostly ≤3%). The unreacted diene remained unchanged.

(5) Critically reviewed in: March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977.

(6) **3a**: for preparation and analysis see ref 1a, *m/e* 310 (M^+, 15), 206 (100), 178 (4), 91 (52), 89 (11).

(7) **3b**: preparation from 2 mmol of **1** + 6 mmol of the *E,E* diester in 25 mL of benzene, 4 h at 70 °C. Rapid decomposition of the isolated compound prevented analysis. *m/e* 274 (M^+, 18), 259 (5), 242 (21), 215 (32), 135 (67), 111 (100), 104(5) (93), 89 (31), 59 (27).

(8) **3c**: preparation as given for **3b** but with the dinitrile. Anal. Calcd for $C_8H_{10}N_2Ge$: C, 46.46; H, 4.87; N, 13.55. Found: C, 46.41; H, 4.91; N, 13.76. *m/e* 208 (M^+, 5), 193 (61), 104 (40), 89 (100).

(9) An analogue behavior is exhibited by several stannylenes R_2Sn: Marx, R.; Neumann, W. P.; Hillner, K. *Tetrahedron Lett.* **1984**, *25*, 625.

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This sequence is backed up by competition experiments: With a 1:1 mixture of the 1,4-diphenylbutadiene and the muconic acid ester at 70 °C as starting materials, exclusively **3b** could be detected, and no **3a**, whereas this ester and the dinitrile in a similar mixture showed comparable reactivities, k_3.

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Registry No. 1, 76054-64-3; **3a**, 80262-45-9; **3b**, 90195-45-2; **3c**, 90195-46-3; EtOOCHN—CH=CH—CH=CH—NHCOOEt, 78465-14-2; MeOCO—CH=CH—CH=CH—OCOMe, 15910-11-9; Ph—CH=CH—CH=CH—Ph, 538-81-8; MeOOC—CH=CH—CH=CH—COOMe, 1119-43-3; NC—CH=CH—CH=CH—CN, 5867-88-9; Me_2Ge, 74963-95-4.

Ferrocene-Containing Polyamides and Polyureas

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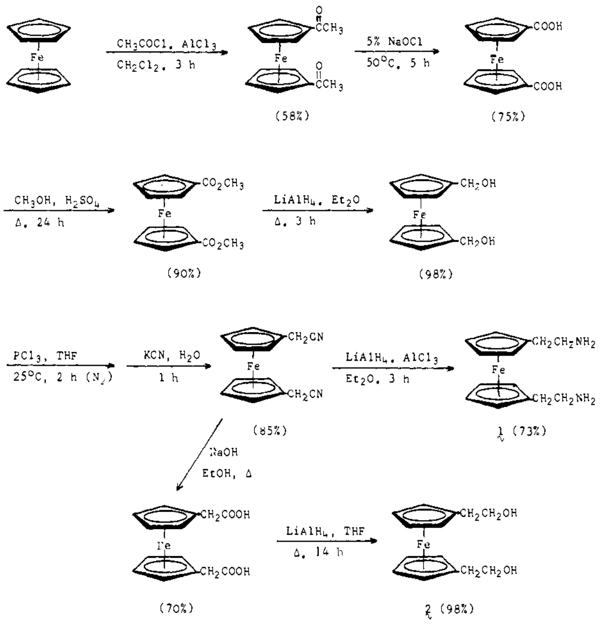
There is currently considerable interest in organometallic polymers, since polymers containing metals might be expected to possess properties different from those of conventional organic polymers.[1-4] Two major approaches to the formation of materials of this type have involved the derivatization of performed organic polymers with organometallic functions[5] and the synthesis and polymerization of organometallic monomers that contain vinyl substitutents.[6,7] For the transition metals, condensation polymerizations have also been investigated; however, the reactions have generally been conducted at elevated temperatures, and the resulting products have often not been well characterized.[4,8]

We now report a convenient method for the interfacial polycondensation of 1,1′-bis(β-aminoethyl)ferrocene (**1**) with a variety of diacid chlorides and diisocyanates, leading to ferrocene-containing polyamides and polyureas.[9] In some instances, we have been able to observe film formation at the interface. Moreover, the polymerization reactions can be conveniently conducted at ambient temperatures in contrast to earlier high-temperature organometallic condensation polymerizations, which frequently led to undesirable side reactions.[8] We also find that the related monomer 1,1′-bis(β-hydroxyethyl)ferrocene (**2**) reacts with diacid chlorides and diisocyanates to form ferrocene-containing polyesters and polyurethanes, respectively.

Scheme I



Monomers **1** and **2** have been synthesized starting from ferrocene, utilizing modifications of procedures outlined previously by Sonoda and Moritani[11] and by Ratajczak et al.[12] The intermediate diacid, 1,1′-ferrocenedicarboxylic acid, was synthesized according to the more convenient procedure of Knobloch and Rauscher.[10] Monomer **1** was vacuum distilled prior to use (bp 120 °C (1 mm Hg)). Details of the synthetic routes are given in Scheme I. It should be emphasized that in contrast to previous ferrocene-containing monomers,[13] **1** and **2** position the reactive amino and hydroxyl groups *two* methylene units removed from the ferrocene nucleus. This feature minimizes steric effects and also enables **1** and **2** to undergo the Schotten–Baumann reaction readily without the classical α-metallocenylcarbonium ion effect providing any constraints.[14,15] Polyamide formation is vigorous, exothermic, and instantaneous.

Interfacial or solution polycondensation, with or without stirring, was the general procedure utilized for the preparation of the polyamides and polyureas.[16a] Details are given in Table I. An important point to be noted is that, in the unstirred interfacial condensation polymerization of **1** with sebacoyl chloride or terephthaloyl chloride in the organic phase and triethylamine as the proton acceptor, immediate film formation took place at the interface. The polyamide films were removed after 1 h, dried, and utilized for taking electron micrographs.

Attempts to obtain molecular weights of these new iron-containing polyamides in *m*-cresol solution have not been successful, due to the very limited solubilities of the materials in organic solvents. Similar difficulties have previously been encountered in the molecular weight determination of nylon 66 (polyhexamethyleneadipamide).[17] However, the intrinsic viscosity values greater than 1.0 for the polyamides obtained from **1** and terephthaloyl chloride or sebacoyl chloride are comparable to intrisic viscosities of nylons having number average molecular weights between 10 000 and 18 000.[16b] The low [η] values obtained for the polyurethanes can be attributed to premature precipitation from solution and, in the case of polymers obtained from **1** and

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[2] Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. "Advances in Organometallic and Inorganic Polymer Science"; Marcel Dekker: New York, 1982.

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[8] Carraher, C. E., Jr. In "Interfacial Synthesis. Volume II. Polymer Applications and Technology"; Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker: New York, 1977; p 251.

[9] One previous synthesis of ferrocene-containing condensation polymers via interfacial methods at room temperature has been reported by Knobloch and Rauscher,[10] who formed low molecular weight polyamides and polyesters by reacting 1,1′-bis(chloroformyl)ferrocene with various diamines and diols. Further, Carraher and co-workers[8] have utilized interfacial techniques in the formation of other types of organometallic polymers.

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[16] (a) Morgan, P. W. "Condensation Polymers by Interfacial and Solution Methods"; Interscience: New York, 1965; (b) Chapter 10, p 446.

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