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Hydrogallation of Alkynes with H−$GaCl_2$: Formation of Organoelement Dichlorogallium Compounds Potentially Applicable as Chelating Lewis Acids

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Treatment of trimethylsilylethynylbenzenes $C_6H_{6-x}(C{\equiv}C{-}SiMe_3)_x$ ($x = 1$–3) with the hydridodichlorogallium compound H−$GaCl_2$ afforded, almost quantitatively, the alkenylphenyl compounds $C_6H_{6-x}[C(H){=}C(SiMe_3){-}GaCl_2]_x$ [$x = 1$ (**6**), 2 (**7**), and 3 (**8**)] by hydrogallation. Only compound **6** was readily soluble in *n*-hexane; it formed dimers via Ga−Cl bridges. The bisalkenyl compound **7** was only sparingly soluble; its molecular structure consisted of a singular dimeric formula unit with a cyclophane-type constitution and two bridging Ga_2Cl_2 heterocycles. The overall structure may be described by a molecular box formed by a large macrocycle comprising 22 Ga, C, and Cl atoms. Compound **8** proved to be insoluble in hydrocarbon solvents. Its molecular structure could not be detected. Extraction of the solid raw products of **7** and **8** with diethyl ether yielded small quantities of the ether adducts $C_6H_{6-x}[C(H){=}C(SiMe_3){-}GaCl_2(OEt_2)]_x$ ($x = 2$, 3) [**7(OEt$_2$)$_2$** and **8(OEt$_2$)$_3$**], both of which are monomeric because of the coordinative saturation of their gallium atoms. The tetraalkyne 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene gave a different reaction course. Complete hydrogallation resulted in the release of 2 equiv of $GaCl_3$, and neighboring alkenyl groups of the product **9** were connected by GaCl bridges to form seven-membered heterocycles and an overall tricyclic compound. Compound **9** was characterized as a diethyl ether adduct.

Introduction

Hydroalumination is a powerful method for the reduction of organic compounds containing homo- or heteronuclear double or triple bonds.[1] The mechanisms of these reactions and the structures of the organoaluminum products remained unknown in most cases because usual workup included the hydrolysis of the intermediates with isolation of the respective hydrocarbons only. In some recent investigations, we found that the courses of these reactions and the compositions of the intermediate organoelement compounds are much more interesting than may be derived from textbook knowledge and that fast secondary reactions often yielded unprecedented products. Hydroalumination of dialkylaluminum alkynides gave, by the spontaneous release of trialkylaluminum, a novel class of carbaalanes possessing clusters of carbon and aluminum atoms and a delocalized bonding situation, that is, $(AlMe)_8(CCH_2C_6H_5)_5H$ (**1**, Scheme 1).[2] The spontaneous release of trialkylaluminum was also observed upon treatment of some alkyl−aryl−ethynes with dialkylaluminum hydrides; however, the course of these reactions could not be clarified completely until now. In contrast, the corresponding reactions of trimethylsilylethynes afforded the expected dialkylaluminumalkenyl compounds (**2**, Scheme 1) with the aluminum atoms exclusively bonded to those carbon atoms of the C═C double bonds that also are attached to the trimethylsilyl groups.[3] A *cis* arrangement of Al and H across the C═C double bonds resulted in the first step of all reactions. A rearrangement to form the *trans* products could

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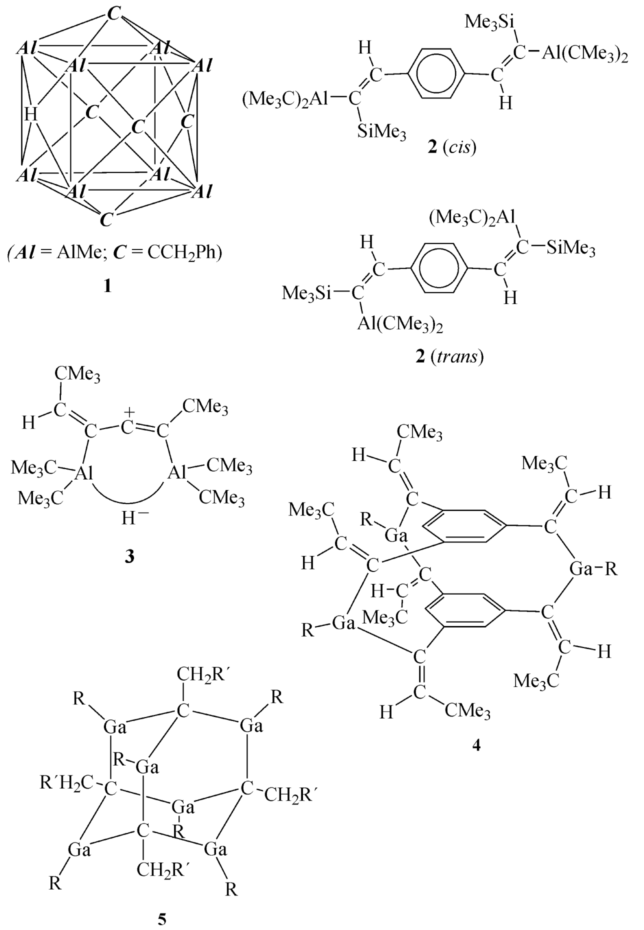
Scheme 1



be detected upon heating of one compound only [**2**(*trans*)], while in other cases, decomposition occurred.[3] Another unprecedented and fascinating product resulted from the double hydroalumination of di(*tert*-butyl)butadiyne with di(*tert*-butyl)aluminum hydride. C−H bond activation and the chelating coordination of a hydride ion yielded a remarkable compound containing a butadienyl cation as the organic backbone (**3**, Scheme 1).[4]

In some recent investigations, we found facile access to a great variety of di(alkyl)gallium hydrides, which with the exception of dimethylgallium hydride are stable enough to be handled in boiling *n*-hexane without decomposition.[5,6] Hydrogallation reactions with alkynes involving these hydrides proved to be slower and more selective than hydroalumination reactions, which may depend on the lower polarity of the Ga−H bonds. Systematic investigations gave a concise insight into the course of these reactions. Ethynes bearing *tert*-butyl and phenyl substituents usually gave condensation reactions with the release of trialkylgallium and the formation of [3,3]- and [3,3,3]cyclophane-type molecules (**4**, Scheme 1).[6,7] Only 1,4-di(*tert*-butylethynyl)benzene and dialkylgallium hydrides bearing relatively small substituents (R = Et, *n*-Pr) yielded the stable addition products without condensation.[6,7] In these cases, the low steric shielding allowed for strong intermolecular interactions via the gallium atoms and the negatively charged carbon atoms of the ethenyl groups, which resulted in the formation of one-dimensional coordination polymers and prevented the substituent exchange processes. Dialkylgallium alkynides, $R_2Ga-C\equiv C-R'$, gave condensation reactions which afforded heteroadamantane type cages (**5**).[8] Although they are analogues of the above-mentioned carbaalanes and were generated on similar routes, the bonding situation of both types of cages is completely different with localized Ga−C bonds in the heteroadamantane systems. Trimethylsilylethynylbenzenes gave stable addition products with few exceptions only, for which, however, the reaction courses could not be clarified at all.[9] The gallium atoms attacked exclusively the carbon atoms in β-position to the phenyl rings, which also are attached to the trimethylsilyl groups. Spontaneous *cis*/*trans* isomerization occurred in most reactions, and the products of the *cis* addition were obtained for the sterically most shielded di(*tert*-butyl)gallium hydride only.[9]

Here, we report on hydrogallation reactions with the halide $H-GaCl_2$. This compound constitutes a very interesting starting compound and is available on a facile route by a procedure optimized in the group of Schmidbaur several years ago.[10] They also conducted a first hydrogallation reaction with an alkene derivative.[11] Investigations into the reactivity of $H-GaCl_2$ against trimethylsilylethynes seemed to be rather interesting because of the three most important reasons. (i) The products are expected to contain up to three $GaCl_2$ groups and, because of the enhanced Lewis-acidity compared to dialkylgallium groups, should form very effective chelating Lewis acids. (ii) In the absence of donor molecules, they should give interesting oligomers with the formation of macrocycles or cages via Ga−Cl bridges. (iii) These $GaCl_2$ derivatives seem to be very important starting compounds for application in secondary reactions, that is, alkylation reactions by salt elimination.

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Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane over $LiAlH_4$, diethyl ether and THF over Na/benzophenone). H−$GaCl_2$, 1,3,5-tris(trimethylsilylethynyl)benzene, and 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene were obtained according to literature procedures.[9,10,12] H−$GaCl_2$ is only sparingly soluble in *n*-hexane, and high dilution is necessary to obtain homogeneous mixtures. The commercially available alkynes (Aldrich), trimethylsilylethynylbenzene, and 1,4-bis(trimethylsilylethynyl)benzene were employed as purchased. Only the most intensive peaks of the mass spectra were given; the complete isotopic patterns are in accordance with the calculated ones. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Reaction of H−$GaCl_2$ with Trimethylsilylethynylbenzene. Synthesis of 6. H−$GaCl_2$ (1.05 g, 7.41 mmol, small excess) dissolved in 80 mL of *n*-hexane was treated with a solution of trimethylsilylethynylbenzene (1.15 g, 6.61 mmol) in 20 mL of *n*-hexane. The mixture was heated under reflux for 15 h. Small quantities of a colorless solid precipitated, which may result from a double hydrogallation, and were filtered off. The filtrate was concentrated and cooled to 4 °C to obtain colorless crystals of compound **6**. Yield: 1.72 g (82%). Mp (argon, closed capillary): 75 °C (dec). MS (EI, 70 eV): *m/z* 314 (28%), 316 (38%), 318 (17%) (M^+ of the monomeric formula unit); 299 (77%), 301 (100%), 303 (43%) ($^1/_2M^+ - CH_3$). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.84 (2 H, s, $^3J_{H-Si} \approx 10$ Hz, C=C−H), 7.24 (4 H, pseudo-d, *ortho*-H of phenyl), 7.05 (4 H, pseudo-t, *meta*-H of phenyl), 6.99 (2 H, pseudo-t, *para*-H of phenyl), 0.21 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 157.7 [*C*=C(Si)−Ga], 148.7 [C=*C*(Si)−Ga], 142.2 (*ipso*-C of phenyl), 129.3 (*meta*- and *para*-C of phenyl), 127.1 (*ortho*-C of phenyl), 0.2 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −1.3. IR (paraffin, CsBr plates, cm^{-1}): 1950 w, 1873 w, 1811 w, 1771 w, 1580 s, 1553 vs, 1489 vs phenyl, ν(C=C); 1456 vs paraffin; 1404 m $\delta(CH_3)$; 1377 vs paraffin; 1323 m, 1248 vs $\delta(CH_3)$; 1206 w, 1175 w, 1157 w, 1117 w, 1076 s, 1028 s, 986 w ν(CC), phenyl; 932 vs, 901 vs, 837 vs, 754 vs, 743 vs $\rho(CH_3(Si))$; 723 m paraffin; 700 vs ν_{as}(SiC); 621 s ν_s(SiC); 583 m, 532 m ν(GaC); 482 vs, 419 vs ν(GaCl), $\nu(Ga_2Cl_2)$. Anal. Calcd for $C_{22}H_{30}Si_2Cl_4Ga_2$ (631.9): Ga, 22.1; Cl, 22.4; C, 41.8; H, 4.79. Found: Ga, 22.1; Cl, 22.3; C, 41.4; H, 4.94.

Reaction of H−$GaCl_2$ with 1,4-Bis(trimethylsilylethynyl)-benzene. Synthesis of 7. A solution of 1,4-bis(trimethylsilylethynyl)benzene (0.39 g, 1.44 mmol) in 50 mL of *n*-hexane was added dropwise (3 h) to a cooled (−78 °C) solution of H−$GaCl_2$ (0.43 g, 3.03 mmol, small excess) in 300 mL of *n*-hexane. The mixture was warmed to room temperature and heated under reflux for 14 h. Small quantities of a colorless precipitate were filtered off. The product crystallized upon cooling of the reaction mixture to 4 °C. Yield: 0.55 g (66%); the crystals of **7** enclosed *n*-hexane (half a molecule to one molecule per formula unit of the dimer). The colorless product is soluble only in very dilute *n*-hexane or benzene solutions; however, it is readily soluble in THF. Solutions in THF were applied for the spectroscopic characterization. Adducts should be formed under these conditions. The solubility in diethyl ether is relatively low. Small quantities of **7$(Et_2O)_2$** crystallized from those solutions after filtration and cooling to 4 °C.

Characterization of 7. Mp (argon, closed capillary): decomposition above 155 °C by formation of a black solid. MS (EI, 70 eV): *m/z* 515 (0.05%), 517 (0.2%), 519 (0.1%), 521 (0.1%) (M^+ of the monomeric formula unit − Cl), 441 (4%), 443 (10%), 445 (10%), 447 (7%) ($M^+ - HCl - SiMe_3$). ^{1}H NMR (very dilute solution in C_6D_6, 400 MHz, only two resonances could be identified unambiguously): δ 7.58 (phenyl?), 0.30 (18 H, s, $SiMe_3$). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.83 (2 H, s, $^3J_{Si-H} = 10.7$ Hz, C=C−H), 7.51 (4 H, s, phenyl), 0.25 (18 H, s, $SiMe_3$). ^{13}C NMR (THF-d_8, 100 MHz): δ 155.7 [*C*=C(Si)−Ga], 148.3 [C=*C*(Si)−Ga], 141.3 (*ipso*-C of phenyl), 128.4 (*ortho*-C of phenyl), 0.0 ($SiMe_3$). ^{29}Si NMR (THF-d_8, 79.5 MHz): δ 0.0. IR (paraffin, CsBr plates, cm^{-1}): 1578 s, 1557 s, 1462 vs phenyl, ν(*C*=C); 1455 vs paraffin; 1402 m $\delta(CH_3)$; 1377 s paraffin; 1306 m, 1254 vs $\delta(CH_3)$; 1209 w, 1155 w, 1115 w, 961 w ν(CC), phenyl; 901 s, 864 s, 841 s, 812 s, 791 m, 750 s $\rho(CH_3(Si))$; 719 s paraffin; 696 m, 667 w ν_{as}(SiC); 646 w, 621 w ν_s(SiC); 584 w, 540 w, 517 w, 507 w ν(GaC); 467 w, 438 w, 424 w ν(GaCl), $\nu(Ga_2Cl_2)$. Anal. Calcd for $C_{32}H_{48}Si_4Cl_8Ga_4 \cdot {}^1/_2C_6H_{14}$ (1150.6): Ga, 24.2; Cl, 24.6, C, 36.5; H, 4.82. Found: Ga, 24.0; Cl, 24.6; C, 36.3; H, 4.95.

Characterization of 7$(OEt_2)_2$. Mp (argon, closed capillary): decomposition above 155 °C by formation of black particles, no melting until 320 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.86 (2 H, s, $^3J_{Si-H} = 10.7$ Hz, C=C−H), 7.57 (4 H, s, phenyl), 3.44 (8 H, q, $^3J_{H-H} = 7.0$ Hz, OCH_2), 0.75 (12 H, t, $^3J_{H-H} = 7.0$ Hz, CH_3 of ether), 0.44 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 154.6 [*C*=C(Si)−Ga], 148.1 [C=*C*(Si)−Ga], 141.3 (*ipso*-C of phenyl), 128.3 (*ortho*-C of phenyl), 67.8 (OCH_2), 13.6 (CH_3 of ether), 0.0 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.0. IR (paraffin, CsBr plates, cm^{-1}): 1578 s, 1556 m, 1503 vw, 1462 s phenyl, ν(C=C); 1454 s paraffin; 1402 w $\delta(CH_3)$; 1375 m paraffin; 1338 vw, 1326 vw, 1290 w, 1266 w, 1254 w $\delta(CH_3)$; 1188 w, 1148 sh, 1024 vs ν(CC), ν(CO), phenyl; 918 w, 885 w, 837 w, 754 w $\rho(CH_3(Si))$; 719 w paraffin; 696 w ν_{as}(SiC); 621 w ν_s(SiC); 567 w, 561 w, 527 w, 517 m, 503 w ν(GaC), ν(GaO); 422 w ν(GaCl).

Reaction of H−$GaCl_2$ with 1,3,5-Tris(trimethylsilylethynyl)-benzene. Synthesis of 8. A solution of 1,3,5-tris(trimethylsilylethynyl)benzene (0.99 g, 2.70 mmol) in 25 mL of *n*-hexane was treated with H−$GaCl_2$ (1.38 g, 9.74 mmol, small excess) in 60 mL of *n*-hexane. The mixture was heated under reflux for 14 h. The colorless product precipitated. It was filtered off and washed with 10 mL of *n*-hexane. Yield: 1.65 g (77%). Compound **8** is insoluble in noncoordinating solvents, but it dissolved completely in THF. Solutions in THF were applied for its NMR spectroscopic characterization. Adducts with THF coordinated to the gallium atoms similar to compound **8$(OEt_2)_3$** may exist under these conditions. The solubility in diethyl ether is relatively poor. Small quantities of **8$(OEt_2)_3$** crystallized from these solutions after filtration and cooling to 4 °C.

Characterization of 8. Mp (argon, closed capillary): decomposition above 230 °C. MS (EI, 70 eV): *m/z* 687 (0.7%), 689 (0.9%), 691 (0.8%) ($M^+ - SiMe_3 - 2CH_3$). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.89 (3 H, s, $^3J_{Si-H} = 10.4$ Hz, C=C−H), 7.61 (3 H, s, phenyl), 0.27 (27 H, s, $SiMe_3$). ^{13}C NMR (THF-d_8, 100 MHz): δ 155.7 [*C*=C(Si)−Ga], 148.4 [C=*C*(Si)−Ga], 141.9 (*ipso*-C of phenyl), 127.7 (*ortho*-C of phenyl), 0.1 ($SiMe_3$). ^{29}Si NMR (THF-d_8, 79.5 MHz): δ 0.0. IR (paraffin, CsBr plates, cm^{-1}): 1589 m, 1566 vs, 1464 vs phenyl, ν(C=C); 1454 vs paraffin; 1423 m, 1402 m $\delta(CH_3)$; 1377 s paraffin; 1341 w, 1304 w, 1268 s, 1250 vs $\delta(CH_3)$; 1159 w ν(CC), phenyl; 916 vs, 903 vs, 887 vs, 876 vs, 857 vs, 833 vs, 752 s $\rho(CH_3(Si))$; 718 s paraffin; 692 m, 669 s ν_{as}(SiC); 635 m, 611 m ν_s(SiC); 565 m, 501 m ν(GaC); 424 vs ν(GaCl). Anal. Calcd for $C_{21}H_{33}Si_3Cl_6Ga_3$ (791.6 of the monomeric formula unit): Ga, 26.4; Cl, 26.9; C, 31.9; H, 4.20. Found: Ga, 27.0; Cl, 27.3; C, 30.9; H, 4.08.

Characterization of 8$(OEt_2)_3$. Mp (argon, closed capillary): decomposition above 140 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.07 (3 H, s, $^3J_{Si-H} = 10.5$ Hz, C=C−H), 7.79 (3 H, s, phenyl), 3.59

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Table 1. Crystallographic Data for **6–9**

	6	**7**	**7**	**7(OEt$_2$)$_2$**	**8(OEt$_2$)$_3$**	**9**
empirical formula	$C_{28}H_{44}Cl_4Ga_2Si_2$	$C_{35}H_{55}Cl_8Ga_4Si_4$	$C_{35}H_{55}Cl_8Ga_4Si_4$	$C_{24}H_{44}Cl_4Ga_2O_2Si_2$	$C_{33}H_{63}Cl_6Ga_3O_3Si_3$	$C_{34}H_{62}Cl_2Ga_2O_2Si_4$
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$Pbca$	$P2_1/c$
a (pm)	961.2(1)	1774.7(1)	1063.2(2)	1028.4(1)	2514.2(10)	1373.0(3)
b (pm)	1582.5(2)	1059.99(9)	1554.6(3)	1537.4(2)	1355.9(5)	1034.5(2)
c (pm)	2263.8(2)	2986.6(2)	1736.8(4)	1088.1(1)	2825.9(11)	1689.7(4)
α (deg)	90	90	81.12(3)	90	90	90
β (deg)	92.645(2)	96.181(2)	83.96(3)	94.62(1)	90	112.335(4)
γ (deg)	90	90	70.71(3)	90	90	90
V (nm^3)	3.4398(6)	5.5855(8)	2.6725(9)	1.7148(4)	9.63(1)	2219.9(9)
Z	4	4	2	2	8	2
temp (K)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
D_{calcd} (g cm^{-3})	1.387	1.368	1.430	1.360	1.398	1.235
independent data	5316	17 181	15 853	3990	11 669	6441
observed data	4335	10 936	12 169	3193	7883	4946
params	167	471	473	180	506	218
μ (mm^{-1})	1.963	2.399	2.507	1.971	2.102	1.468
R1[a]	0.0360	0.0545	0.0372	0.0376	0.0510	0.0400
wR2 (all data)[b]	0.0880	0.1575	0.0966	0.0949	0.1026	0.1017
residual density (e nm^{-3})	+444/−347	+1394/−384	+735/−530	+935/−410	+586/−300	+751/−424

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

(12 H, q, $^3J_{H-H} = 7.2$ Hz, OCH_2), 0.84 (18 H, t, $^3J_{H-H} = 7.2$ Hz, CH_3 of ether), 0.44 (27 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 155.7 [*C*═C(Si)−Ga], 148.2 [C═*C*(Si)−Ga], 141.6 (*ipso*-C of phenyl), 127.5 (*ortho*-C of phenyl), 67.9 (OCH_2), 13.8 (CH_3 of ether), 0.1 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.1. IR (paraffin, CsBr plates, cm^{-1}): 1577 sh, 1570 sh, 1557 vs, br, 1472 sh, 1462 vs phenyl, ν(C═C); 1454 vs paraffin; 1447 vs, 1425 vs, 1402 s $\delta(CH_3)$; 1377 vs paraffin; 1339 m, 1323 m, 1306 m, 1292 m, 1244 s $\delta(CH_3)$; 1190 s, 1148 s, 1119 m, 1090 s, 1030 m, 989 sh ν(CC), ν(CO), phenyl; 930 m, 889 sh, 879 m, 845 s, 814 s, 785 m, 764 s, 741 s $\rho(CH_3(Si))$; 719 s paraffin; 698 sh, 671 m ν_{as}(SiC); 635 w, 604 w ν_s(SiC); 575 m, 560 w, 492 m, br, 467 m, br ν(GaC), ν(GaO); 437 s, 422 m ν(GaCl).

Reaction of H−GaCl$_2$ with 1,2,4,5-Tetrakis(trimethylsilylethynyl)benzene. Synthesis of 9. A solution of H−GaCl$_2$ (0.830 g, 5.86 mmol) in 50 mL of *n*-hexane was treated with a solution of the tetraalkyne, 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene (0.608 g, 1.32 mmol), in 50 mL of the same solvent at room temperature. The suspension adopted a red color, and small quantities of a colorless solid precipitated. Subsequently, the mixture was heated under reflux for 14 h. The product precipitated and was isolated by filtration. It was washed with 10 mL of *n*-hexane and treated with 50 mL of diethyl ether to yield a reddish suspension, which after filtration, concentration, and cooling to −45 °C yielded a colorless solid of the ether adduct **9**. Yield: 0.500 g (46%). Mp (argon, closed capillary): decomposition above 220 °C. MS (EI, 70 eV): *m*/*z* 787 (4%), 789 (5%), 791 (1%) ($M^+ - Cl$). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.02 (4 H, s, $^3J_{H-Si} = 11.3$ Hz, C═C−H), 7.68 (2 H, s, phenyl), 3.28 (8 H, q, $^3J_{H-H} = 7.6$ Hz; OCH_2), 0.65 (12 H, t, $^3J_{H-H} = 7.6$ Hz, CH_3 of ether), 0.43 (36 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 162.3 [C═*C*(Si)−Ga], 152.4 [*C*═C(Si)−Ga], 140.0 (*ipso*-C of phenyl), 138.8 (C−H of phenyl), 66.5 (OCH_2), 13.7 (CH_3 of ether), −0.2 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −3.2. IR (paraffin, CsBr plates, cm^{-1}): 1650 s, 1575 s, 1543 s phenyl, ν(C═C); 1456 vs, 1377 vs paraffin; 1315 w, 1285 w, 1242 m $\delta(CH_3)$; 1190 w, 1150 w, 1123 w, 1092 w, 1038 m, 995 w ν(CC), ν(CO), phenyl; 938 w, 918 m, 897 w, 878 w, 839 s, 773 m vs $\rho(CH_3(Si))$; 719 m paraffin; 687 m ν_{as}(SiC); 651 vw, 621 m ν_s(SiC); 567 m, 527 vw, 505 w, 470 m, 436 m ν(GaCl), ν(GaC), ν(GaO). Anal. Calcd for $C_{34}H_{62}O_2Si_4Cl_2Ga_2$ (825.5): Ga, 16.9; Cl, 8.6; C, 49.5; H, 7.6. Found: Ga, 17.5; Cl, 8.9; C, 48.9; H, 7.4.

Crystal Structure Determinations. Single crystals of compound **6** were obtained from the reaction mixture in *n*-hexane upon cooling to 4 °C. Crystals of **7** grew from the reaction mixture at 4 °C (monoclinic form) or at room temperature upon slow concentration (triclinic form). Crystals of the etherates **7(OEt$_2$)$_2$**, **8(OEt$_2$)$_3$**, and **9** were generated by the treatment of the corresponding solid reaction products with diethyl ether. After filtration, the crystals were obtained upon cooling of the filtrate to 4 °C. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo Kα radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1. All structures were solved by direct methods using the program system *SHELXTL-Plus*[13] and refined with the *SHELXL-97*[13] program via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}(C)$. Compound **6** crystallized with one molecule of *n*-hexane per formula unit of the dimer; the gallium compound was located on a crystallographic 2-fold rotation axis, and the solvent molecule was on a crystallographic center of symmetry. Compound **7** was isolated in a triclinic and a monoclinic form. The triclinic cell included half of a molecule of *n*-hexane (located on a crystallographic center of symmetry) per formula unit of dimeric **7**. The monoclinic form had a solvent molecule located on a general position. It showed some disorder and was refined with occupation factors of the carbon and hydrogen atoms of 0.5. The molecules of **7(OEt$_2$)$_2$** and **9** reside on crystallographic centers of symmetry. One methyl group of an ether ligand was disordered in both cases. Two ether ligands of **8(OEt$_2$)$_3$** were disordered (at OE1 and OE5); the carbon atoms were refined on split positions.

Results and Discussion

Because of the low solubility of the starting compound H−GaCl$_2$ in hydrocarbon solvents, the reactions with the corresponding alkynes were conducted in very dilute *n*-hexane solutions (eq 1). The reaction of the monoalkyne, trimethylsilylethynylbenzene, afforded a clear solution of the

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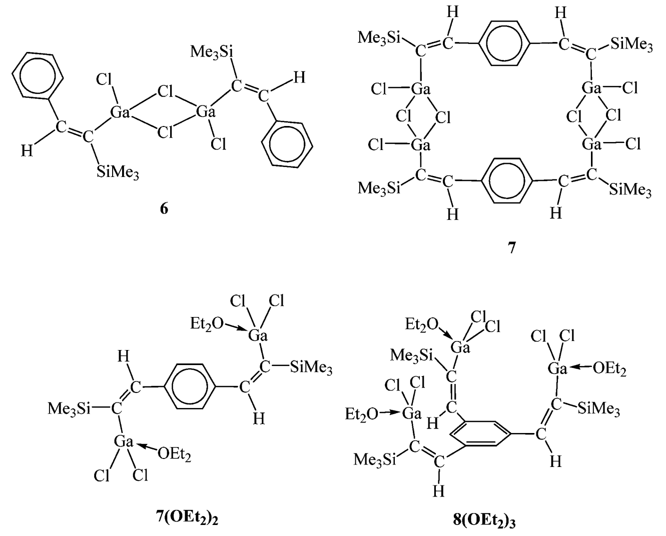
[13] (a) *SHELXTL-Plus*, release 4.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Structures*; Universität Göttingen: Göttingen, Germany, 1997.

Scheme 2. Schematic Drawings of Compounds **6**, **7**, **7(OEt$_2$)$_2$**, and **8(OEt$_2$)$_3$**

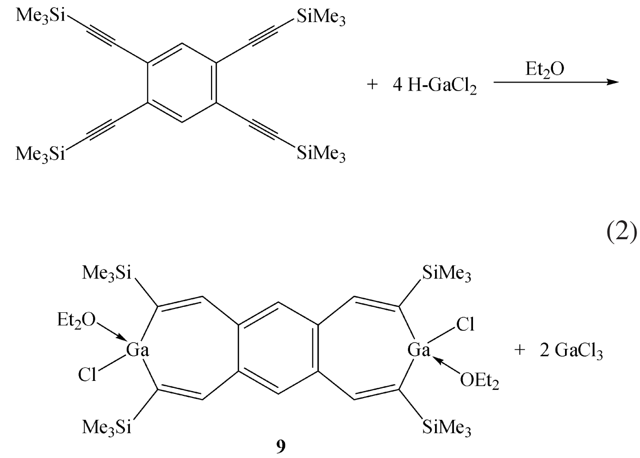


product in *n*-hexane. The colorless, crystalline compound **6** was isolated from the reaction mixture by concentration and cooling to 4 °C in 82% yield. In contrast, the product of the reaction with the bisalkyne, 1,4-bis(trimethylsilylethynyl)-benzene, was only sparingly soluble in *n*-hexane, and very dilute solutions were required to completely dissolve the colorless compound **7**. It possesses a dimeric formula unit in the solid state with a Ga−H group added to each C≡C triple bond of the starting compound. 1,3,5-Tris(trimethylsilylethynyl)benzene yielded a colorless solid (**8**) that was completely insoluble in *n*-hexane and was isolated by filtration of the reaction mixture in a yield of about 80%. The hexane solutions obtained from the syntheses of **8** gave small quantities of a colorless solid upon cooling; the NMR spectrum of which exhibited broad resonances of unknown products and did not show any resonance of aromatic protons. Partial dissolution occurred upon treatment of **7** and **8** with a few milliliters of diethyl ether. Filtration and cooling of the filtrates yielded relatively small quantities of the monomeric etherates **7(OEt$_2$)$_2$** and **8(OEt$_2$)$_3$**, in which each gallium atom was coordinated by an oxygen atom of an ether molecule. Complete dissolution of the solids occurred in THF only. Schematic drawings of the molecular structures of all isolated and characterized compounds are depicted in Scheme 2.

$$C_6H_{6-x}(C{\equiv}C{-}SiMe_3)_x + xH{-}GaCl_2 \rightarrow C_6H_{6-x}[C(H){=}C(SiMe_3){-}GaCl_2]_x \quad \mathbf{6}\ (x=1), \mathbf{7}\ (x=2), \mathbf{8}\ (x=3) \qquad (1)$$

The spectroscopic characterization of compounds **7** and **8** was conducted essentially with THF solutions, and the results are similar to those obtained for solutions of the etherates in C_6D_6. The integration ratios of the ^{1}H NMR spectra are in accordance with the structures obtained by crystal structure determinations (see below), which verify the geminal arrangement of Ga and Si atoms at one carbon atom of the C═C double bonds and the *trans* arrangement of Ga and H in the ethenyl groups (*Z* configuration). The vinyl protons in the ^{1}H NMR spectra resonate with relatively constant chemical shifts of δ 7.9 on average. The phenyl protons (*ortho*-protons in the case of the monoalkenyl derivative **6**) show a systematic shift to a lower field with the increasing number of alkenyl groups attached to the aromatic ring from δ 7.24 of **6** to δ 7.89 of **8**. The ^{13}C NMR resonances of the ethenyl carbon atoms occur at about δ 155 (attached to the aromatic rings) and 148 (attached to Ga and Si). They show a relatively strong difference from the corresponding chemical shifts of the addition products of dialkylgallium hydrides to silylalkynes, which contain coordinatively unsaturated, tricoordinated gallium atoms (δ 149 and 170, respectively).[9] NMR evidence for the particular *Z* configuration came from the coupling constants $^3J_{Si-H}$ across the C═C double bonds, which with about 10 Hz on average are in accordance with a coupling between atoms in a *cis* arrangement.

A different and unexpected reaction course was observed for the hydrogallation of the tetraalkyne 1,2,4,5-tetrakis-(trimethylsilylethynyl)benzene with H−GaCl$_2$ (eq 2). A colorless precipitate was formed under conditions similar to those described before. It dissolved completely upon treatment with diethyl ether. Cooling of the solution afforded colorless crystals of the product (**9**) in 46% yield. The ^{1}H NMR spectrum verified the formation of C═C double bonds by the characteristic resonances of the vinylic hydrogen atoms (δ 8.02). The integration ratio showed the presence of only two molecules of ether per formula unit of the product. A schematic drawing of the molecular structure is shown in eq 2. A novel tricyclic compound was formed by an intramolecular condensation reaction probably accompanied by the release of gallium trichloride. Seven-membered heterocycles resulted, in which the gallium atoms bridged the β-carbon atoms of the C═C double bonds. Further spectroscopic findings are similar to those discussed before, but the ^{13}C NMR resonance of the alkenyl carbon atoms attached to gallium and silicon (δ 162.3) is strongly shifted to a lower field compared to the corresponding signals of the GaCl$_2$ compounds. Particularly, the $^3J_{Si-H}$ coupling constant across the C═C double bond (11.3 Hz) verified the *cis* arrangement of hydrogen and silicon and the spontaneous *cis*/*trans* isomerization as discussed before.



(2)

Molecular structures were determined of the ether-free addition products of the mono- and bisalkyne (**6** and **7**) and

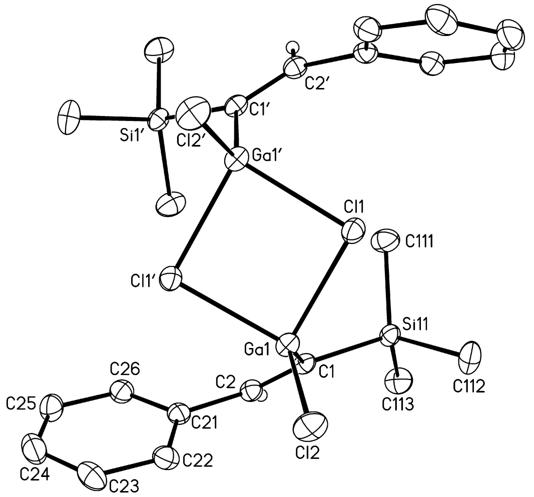


Figure 1. Molecular structure and numbering scheme of **6**; the thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms, with the exception of vinylic hydrogen atoms, are omitted for clarity. Important bond lengths (pm) and angles (deg): Ga1−C1 = 194.1(2), Ga1−Cl1 = 235.25(6), Ga1−Cl1′ = 233.31(5), Ga1−Cl2 = 214.96(6), C1−C2 = 133.6(3), Cl1−Ga1−Cl1′ = 87.59(2), Ga1−Cl1−Ga1′ = 91.39(2), C2−C1−Si11 = 122.0(2), C2−C1−Ga1 = 118.5(1), C1−C2−C21 = 127.3(2). Ga1′ and Cl1′ generated by $-x + 2$, y, $-z + 0.5$.

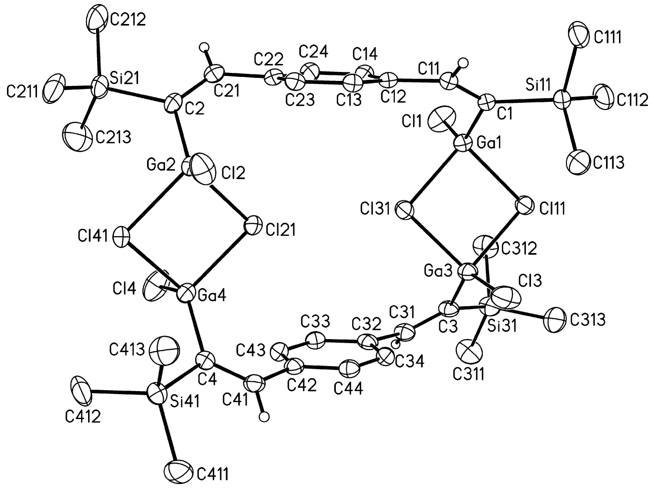


Figure 2. Molecular structure and numbering scheme of **7**; the thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms, with the exception of vinylic hydrogen atoms, are omitted for clarity. Important bond lengths (pm) and angles (deg) for the monoclinic form (the structural parameters of the triclinic system are almost identical): Ga1−C1 = 193.1(4), Ga1−Cl1 = 213.4(1), Ga1−Cl11 = 234.7(1), Ga1−Cl31 = 233.9(1), C1−C11 = 134.2(5), Ga2−C2 = 193.5(4), Ga2−Cl2 = 214.5(1), Ga2−Cl21 = 232.9(1), Ga2−Cl41 = 235.3(1), C2−C21 = 133.7(5), Ga3−C3 = 194.0(4), Ga3−Cl3 = 215.4(1), Ga3−Cl31 = 232.1(1), Ga3−Cl11 = 234.0(1), C3−C31 = 133.5(5), Ga4−C4 = 193.1(4), Ga4−Cl4 = 214.0(1), Ga4−Cl41 = 233.2(1), Ga4−Cl21 = 234.5(1), C4−C41 = 133.8(5), C−C−Si = 120.5 (av), C−C−Ga = 118.8 (av), C═C−C = 128.7 (av).

of the etherates of the bis- and trisalkenyl derivatives [**7(OEt$_2$)$_2$** and **8(OEt$_2$)$_3$**]. The solvent-free compounds give dimers via Ga−Cl bridges (Figures 1 and 2) and by the formation of Ga_2Cl_2 heterocycles as usually observed for organogallium halides.[14] However, that dimerization afforded an unprecedented nice molecular structure for compound **7**. A cagelike structure resulted, which in some respects resembles the one of cyclophane-type molecules and has two bridging Ga_2Cl_2 moieties almost perpendicularly arranged to the parallel organic backbones. In both compounds, an additional terminal chlorine atom is attached to each gallium atom. As expected the Ga−Cl distances differ strongly between the terminal and the bridging situation (214.6 vs 233.9 pm on average). The C═C double bond lengths correspond to standard values (133.8 pm). The gallium atoms exclusively attacked those carbon atoms which also bear the trimethylsilyl groups. This high regioselectivity may be caused by two effects. Because of the electronegativity difference between silicon and carbon, a small partial negative charge is induced at these carbon atoms, which then preferably may be attacked by the positively charged gallium atoms. Furthermore, that position allows for an effective hyperconjugation with the $SiMe_3$ group and an optimum stabilization of the negative charge, which in the products are enhanced at that position by the bonding to the more electropositive gallium atoms. Hydroalumination[3] and hydrogallation reactions[9] of trimethylsilylalkynes with dialkylelement hydrides show a comparable selectivity. The gallium and hydrogen atoms attached to the C═C double bonds adopt a *trans* arrangement and are located on different sides of the alkenyl groups. A *cis* arrangement may be expected as the first step of the insertion into the Ga−H bonds, as usually observed for the hydrogallation products obtained with *tert*-butyl(phenyl)ethynes.[6,7] A fast *cis*/*trans* rearrangement may occur here which is in accordance with similar reactions of dialkylgallium hydrides with trimethylsilylethynes.[9] The mechanism of the rearrangement process is not clear yet. It may depend on C−H bond activation, as recently observed for hydroalumination products (see Introduction). Further experimental work is necessary for a better understanding and is presently being conducted in our group. Two different crystal systems were observed for the crystals of compound **7** (triclinic and monoclinic). The structural parameters of the organogallium components are quite similar in both forms, but they differ with respect to the location of the enclosed *n*-hexane molecules. The triclinic form has one molecule of the solvent *n*-hexane per two formula units of the dimer. The solvent molecules are localized on a crystallographic center of symmetry between the trimethylsilyl groups of two different tetragallium molecules and are close to two Ga−Cl−Ga bridges. The monoclinic form has the *n*-hexane molecules above and below both Ga_2Cl_2 moieties of one formula unit and close to the sides of the bridging benzene rings. Thus, when these gallium compounds are considered

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[14] (a) Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1992**, *25*, 233. (b) Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron* **1992**, *11*, 477. (c) Schaller, F.; Schwarz, W.; Hausen, H.-D.; Klinkhammer, K. W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1455. (d) Crittendon, R. C.; Li, X.-W.; Su, J.; Robinson, G. H. *Organometallics* **1997**, *16*, 2443. (e) Beachley, O. T.; Hallock, R. B.; Zhang, H. M.; Atwood, J. L. *Organometallics* **1985**, *4*, 1675. (f) Carmalt, C. J.; Mileham, J. D.; White, A. J. P.; Williams, D. J.; Steed, J. W. *Inorg. Chem.* **2001**, *40*, 6035. (g) Lustig, C.; Mitzel, N. W. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 140. (h) Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1998**, 2015. (i) Gillan, E. G.; Bott, S. G.; Barron, A. R. *Chem. Mater.* **1997**, *9*, 796. (j) Neumüller, B.; Gahlmann, F. *Chem. Ber.* **1993**, *126*, 1579. (k) Uhl, W.; Cuypers, L.; Geiseler, G.; Harms, K.; Massa, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001. (l) Petrie, M. A.; Power, P. P.; Rasika Dias, H. V.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

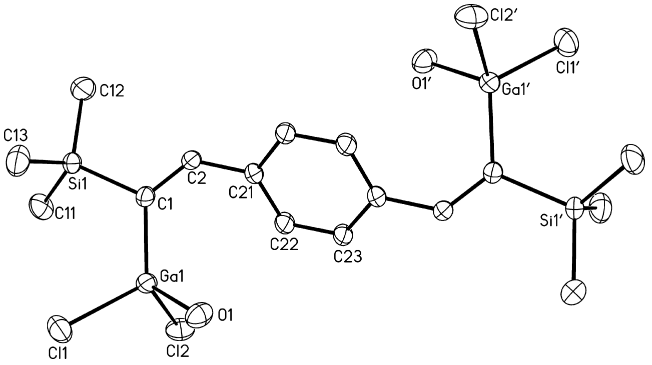

Figure 3. Molecular structure and numbering scheme of **$7(OEt_2)_2$**; the thermal ellipsoids are drawn at the 40% probability level. Ethyl groups of the ether ligands (O1) and hydrogen atoms are omitted for clarity. Important bond lengths (pm) and angles (deg): Ga1−C1 = 195.1(3), Ga1−O1 = 199.0(2), Ga1−Cl1 = 218.81(8), Ga1−Cl2 = 217.67(8), C1−C2 = 134.1(3), C2−C1−Si1 = 118.3(2), C2−C1−Ga1 = 125.4(2), C1−C2−C21 = 130.3(2).

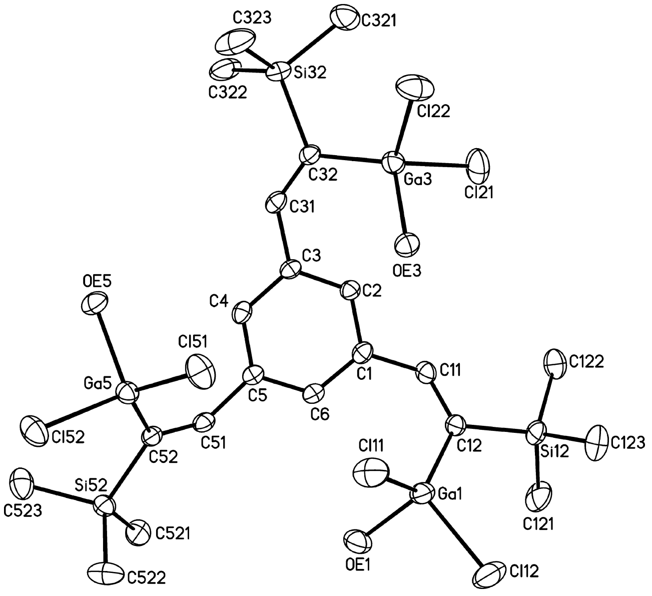

Figure 4. Molecular structure and numbering scheme of **$8(OEt_2)_3$**; the thermal ellipsoids are drawn at the 40% probability level. Ethyl groups of the ether ligands (OE1, OE3, OE5) and hydrogen atoms are omitted for clarity. Important bond lengths (pm) and angles (deg): Ga1−C12 = 195.0(3), Ga1−OE1 = 198.8(3), Ga1−Cl11 = 216.4(1), Ga1−Cl12 = 218.6(1), C11−C12 = 133.1(4), Ga3−C32 = 194.1(3), Ga3−OE3 = 196.8(2), Ga3−Cl21 = 217.0(1), Ga3−Cl22 = 219.3(1), C31−C32 = 134.4(4), Ga5−C52 = 194.4(3), Ga5−OE5 = 199.4(2), Ga5−Cl51 = 215.8(1), Ga5−Cl52 = 218.6(1), C51−C52 = 133.5(4), C−C−Si = 118.1 (av), C−C−Ga = 124.0 (av), C═C−C = 130.9 (av).

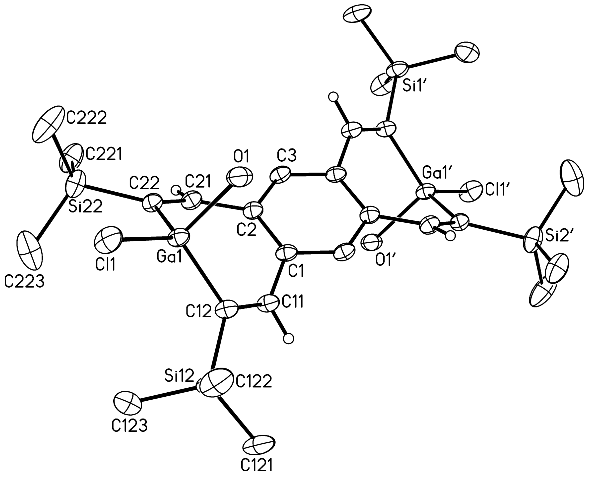

Figure 5. Molecular structure and numbering scheme of **9**; the thermal ellipsoids are drawn at the 40% probability level. Ethyl groups of the ether ligands and hydrogen atoms, with the exception of the vinylic hydrogen atoms, are omitted for clarity. Important bond lengths (pm) and angles (deg): Ga1−C12 = 194.0(2), Ga1−C22 = 194.0(2), Ga1−O1 = 202.6(2), Ga1−Cl1 = 220.80(7), C11−C12 = 134.6(3), C21−C22 = 134.5(2), C12−Ga1−C22 = 113.45(9), Ga1−C12−C11 = 115.7(2), Ga1−C22−C21 = 116.4(2), C12−C11−C1 = 131.8(2), C22−C21−C2 = 131.9(2). Symmetry equivalent atoms were generated by −*x*, −*y* + 2, −*z*.

to be cyclophane-type molecules, they cover the open faces of the resulting macrocycles.

Upon treatment with diethyl ether, the Ga−Cl bridges of the dimeric formula units are cleaved and monomeric fragments result, in which the gallium atoms are coordinatively saturated by interactions with the ether oxygen atoms. Two etherates were characterized by crystal structure determinations, which had two and three alkenyl groups (Figures 3 and 4). The molecules of **$7(OEt_2)_2$** reside on crystallographic centers of symmetry. Thus, the $GaCl_2$ groups are in an ideal *trans* arrangement on opposite sides of the central phenyl ring. In contrast, the alkenylgallium groups of the molecular structure of **$8(OEt_2)_3$** adopt a chalicelike arrangement with the $GaCl_2$ residues oriented to the same side of the molecule. With this particular orientation, they are nicely preorganized to potentially act as a chelating Lewis acid, if the diethyl ether molecules could be replaced by suitable multiple donors. The bond lengths are quite similar to those of the ether-free molecules and do not require a more detailed discussion. The Ga−O distances (198.5 pm on average) are in the expected range of donor−acceptor complexes.

The molecular structure of compound **9** is different from those of **6**–**8**. The tetraalkyne starting compound was successfully transformed into the corresponding tetraalkenyl derivative; however, the product did not possess $GaCl_2$ moieties as in the cases before. Instead intramolecular condensation reactions gave seven-membered heterocycles, in which Ga−Cl groups bridge two alkenyl groups (Figure 5). Each gallium atom is further coordinated by an ether molecule, which prevents polymerization by intermolecular Ga−Cl bridges. We did not observe a similar intramolecular process before. Instead condensation reactions by the release of trialkylgallium derivatives proceeded on intermolecular pathways in all cases and gave exclusively cyclophane-type molecules or heteroadamantane cages by oligomerization. A singular tricyclic, nonplanar molecular structure resulted for **9** which contains two GaC_6 heterocycles in addition to the inner benzene ring. The heterocycles deviate considerably from planarity. Their structures may be described by a boat conformation. The inner carbon atoms C1, C2, C3, C11, and C21 and the symmetry equivalent atoms are almost ideally in a plane with a maximum deviation of only 3.6 pm (C1). The normals of this plane and of the planes formed by the atoms C11, C12, Ga1, and Si12 or C21, C22, Ga1, and Si22 include angles of 35.2 and 52.1°, respectively. Finally, the gallium atoms are 67.8 pm above the plane formed by the alkenyl carbon atoms. All other structural parameters are quite similar to those of the other compounds described before and do not require a detailed discussion.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for the compounds $[C_6H_5{-}C(H){=}C(SiMe_3){-}GaCl_2]_2$ (**6**), $[C_6H_4\{C(H){=}C(SiMe_3){-}GaCl_2\}_2]_2$ (**7**; triclinic and monoclinic), $C_6H_4[C(H){=}C(SiMe_3){-}GaCl_2(OEt_2)]_2$ [**7(OEt$_2$)$_2$**], $C_6H_3[C(H){=}C(SiMe_3){-}GaCl_2(OEt_2)]_3$ [**8(OEt$_2$)$_3$**], and $C_6H_2[(CH{=}C{-}SiMe_3)_2GaCl(OEt_2)]_2$ (**9**). This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are also available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-642134 (**6**), -642135 (**7**, monoclinic), -642136 (**7**, triclinic), -642137 [**7(OEt$_2$)$_2$**], -642138 [**8(OEt$_2$)$_3$**], and -642139 (**9**).

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