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Article

Twofold Hydrogallation of $C{\equiv}C$ Triple Bonds by $H{-}GaCl_2$—Synthesis of Chelating Lewis Acids and Their Application in Adduct Formation

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The twofold addition of Ga–H to $C{\equiv}C$ triple bonds (hydrogallation) did not succeed by treatment of alkynes with an excess of dialkylgallium hydrides. In contrast, double hydrogallation was easily achieved by the reactions of $H{-}GaCl_2$ with trimethylsilyl-substituted alkynes [trimethylsilylphenylethyne and 1,4-bis(trimethylsilylethynyl)benzene] in appropriate stoichiometric ratios. The monoalkyne yielded the compound $[H_5C_6{-}CH_2{-}C(SiMe_3)(GaCl_2)_2]_2$, **1**, which was only sparingly soluble in *n*-hexane. Crystal structure determination revealed a dimeric formula unit possessing two parallel Ga_2Cl_2 heterocycles in the solid state. Treatment of the dialkyne with four equivalents of the hydride gave a colorless precipitate, which was completely insoluble in hydrocarbons. Addition of diethyl ether to both products afforded soluble and monomeric etherates **$1(OEt_2)_2$** and **2** in which the two or four gallium atoms, respectively, were coordinated by ether molecules. Preliminary experiments with simple Lewis bases showed the principle capability of **1** to act as an effective chelating Lewis acid. Adducts of the type $[H_5C_6{-}CH_2{-}C(SiMe_3)(GaCl_2)(GaClX)(\mu\text{-}Cl)]^-$ (**4**–**6**) resulted upon treatment with halide ions (X = Cl, Br, I).

Introduction

Chelating Lewis acids possessing more than one acceptor function in a single molecule form an interesting class of compounds which has found increasing attention in current research. Owing to their particular functionality they may be applicable in a broad variety of chemical processes such as catalysis, phase transfer, or anion recognition. Compounds containing coordinatively unsaturated aluminum, gallium, or indium atoms seem to be particularly suitable for the formation of those polyacceptors; however, their access is rather limited, and relatively inflexible organic backbones such as aromatic rings were often employed for their generation.[1] Furthermore, these compounds usually do not have more than two group 13 atoms in one molecule. Their real capability to act as a chelating Lewis acid was tested in rare cases only. An example is the methylene-bridged dialuminum compound $R_2Al{-}CH_2{-}AlR_2$ which is stabilized against dismutation processes by very bulky bis(trimethylsilyl)methyl groups.[2] It forms persistent and ether-soluble complexes by treatment with hydride, nitrate, nitrite, azide, acetate anions, etc. (examples are given in Scheme 1).[3]

Addition of Al–H or Ga–H bonds of easily accessible dialkylelement hydrides to the $C{\equiv}C$ triple bonds of polyalkynes (hydroalumination or hydrogallation) may be suitable to open a facile route for the generation of a broad variety of chelating Lewis acids. However, in contrast to general textbook knowledge, these reactions proved to be rather complicated in many cases, and very interesting and unprecedented products were obtained by secondary reactions. For instance, carbaalanes possessing clusters of aluminum and carbon atoms and a delocalized bonding situation resulted from the hydroalumination of aluminum alkynides

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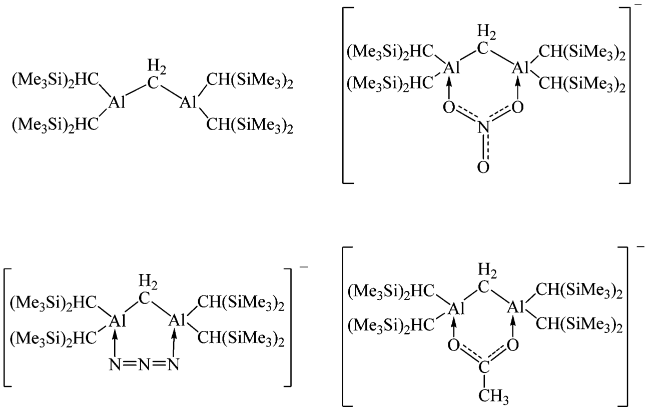
Scheme 1



by the release of trialkylaluminum derivatives.[4] The corresponding reactions of gallium alkynides afforded heteroadamantane structures with localized Ga−C bonds.[5] Di(*tert*-butyl)butadiyne and different dialkylaluminum hydrides yielded singular persistent carbocationic species by C−H bond activation and chelating coordination of the released hydride ion by two aluminum atoms.[6] *tert*-Butylethynylbenzenes gave cyclophane-type molecules with up to three bridging aluminum or gallium atoms by condensation. These secondary reactions were prevented by very bulky substituents attached to the aluminum or gallium atoms of the hydrides and unexpectedly also by application of very small groups.[7] Trimethylsilyl residues in the terminal position of the ethynes favored formation of the expected simple addition products, $R_2E{-}(Me_3Si)C{=}C(H){-}Aryl$ (E = Al, Ga). The gallium or aluminum atoms attacked selectively those carbon atoms which bear the trimethylsilyl groups.[8] Depending on the steric shielding and thermal conditions cis/trans-isomerization processes occurred which finally yielded the thermodynamically favored products with aluminum or gallium and the hydrogen atoms on different sides of the resulting C=C double bonds. In a recent publication we reported on hydrogallation reactions involving dichlorogallium hydride $H{-}GaCl_2$.[9] Monoaddition products, $Aryl{-}(H)C{=}C(SiMe_3){-}GaCl_2$, having exclusively a trans configuration were isolated. These compounds are of particular interest owing to several reasons: The chlorine atoms may be replaced by alkyl or aryl groups upon treatment with organolithium derivatives; the electronegative halogen atoms enhance the Lewis acidity of the gallium atoms; and they may exhibit interesting structural motifs by oligomerization via Ga−Cl bridges. So far twofold hydroalumination or hydrogallation reactions were only observed for aluminum or gallium alkynides under relatively drastic reaction conditions. We report here on attempts to realize double hydrogallation with other alkynes too.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane over $LiAlH_4$, toluene, diethyl ether, and THF over Na/benzophenone). $H{-}GaCl_2$ was obtained according to a literature procedure.[10] $H{-}GaCl_2$ is only sparingly soluble in *n*-hexane, and high dilution is necessary to obtain homogeneous mixtures. The commercially available alkynes (Aldrich) trimethylsilylphenylethyne and 1,4-bis(trimethylsilylethynyl)benzene were dried over molecular sieves. Only the most intensive peaks of the mass spectrum of **1** 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 Trimethylsilylphenylethyne in a Molar Ratio of 2 to 1: Synthesis of 1. $H{-}GaCl_2$ (1.16 g, 8.19 mmol) was suspended in 90 mL of *n*-hexane and treated with neat trimethylsilylphenylethyne (0.70 g, 0.79 mL, 4.02 mmol) at room temperature. The mixture was heated under reflux for 15 h. A colorless solid of **1** precipitated, which was filtered off and washed with 10 mL of *n*-hexane. Owing to its high purity, further purification of the product was unnecessary; recrystallization succeeded from toluene. Yield: 1.68 g (91%). Treatment with diethyl ether yielded quantitatively the etherate **$1(OEt_2)_2$**. It was recrystallized from diethyl ether (20/+4 °C).

Characterization of 1. Mp (argon, closed capillary): 204 °C. MS (EI, 70 eV): *m*/*z* 439 (3%), 441 (7%), 443 (8%), 445 (5%) M^+ of the monomer − Me; 419 (5%), 421 (14%), 423 (13%), 425 (5%) M^+ of the monomer − Cl. ^1H NMR (C_6D_6, saturated solution, low concentration, 400 MHz): δ 7.28 (4 H, *o*-H of phenyl), 7.05 (4 H, *m*-H of phenyl), 6.98 (2 H, *p*-H of phenyl), 3.18 (4 H, s, CH_2), 0.20 (18 H, s, $SiMe_3$). ^1H NMR (THF-d_8, 400 MHz): δ 7.57 (4 H, d, $^3J_{HH} = 7.6$ Hz, *o*-H of phenyl), 7.21 (4 H, m, *m*-H of phenyl), 7.14 (1 H, m, *p*-H of phenyl), 3.51 (4 H, s, CH_2), 0.17 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, saturated solution, low concentration, 100 MHz): δ 130.2 (*m*-C of phenyl), 129.2 (*o*-C of phenyl), 128.1 (*p*-C of phenyl), 36.1 (CH_2), 1.4 ($SiMe_3$); carbon atoms attached Ga and Si and the *ipso*-C atoms of the phenyl rings were not observed. ^{13}C NMR (THF-d_8, 100 MHz): δ 144.3 (*ipso*-C of phenyl), 131.2 (*o*-C of phenyl), 129.0 (*m*-C of phenyl), 127.3 (*p*-C of phenyl), 36.7 (CH_2), 2.3 ($SiMe_3$). ^{29}Si NMR (THF-d_8, 79.5 MHz): δ 2.0. IR (paraffin, CsBr plates, cm^{-1}): 1599 m, 1584 s, 1557 m, 1493 m (phenyl); 1465 vs (paraffin); 1408 m δ(CH); 1377 vs (paraffin); 1302 w, 1265 m, 1256 s $\delta(CH_3)$; 1209 w, 1175 m, 1153 w, 1123 w, 1080 s, 1028 m, 1003 w, 984 vw, 974 vw ν(CC), (phenyl); 947 m, 933 m, 912 s, 839 vs, 762 vs, 752 s $\rho(CH_3(Si))$; 729 vs (paraffin); 704 vs, 689 m, 667 s $\nu_{as}(SiC)$; 627 w $\nu_s(SiC)$; 561 s, 522 w, 424 m ν(GaC), ν(GaCl), $\nu(Ga_2Cl_2)$. Anal. Calcd for

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$C_{22}H_{32}Si_2Cl_8Ga_4$ (915.1): C, 28.9; H, 3.5; Cl, 31.0; Ga, 30.5. Found: C, 28.7; H, 3.7; Cl, 30.7; Ga, 30.4.

Characterization of $1(OEt_2)_2$. Mp (argon, closed capillary): 75 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.59 (2 H, d, $^3J_{HH} = 7.6$ Hz, *o*-H of phenyl), 7.09 (2 H, *pseudo*-t, $^3J_{HH} = 7.6$ Hz, *m*-H of phenyl), 6.98 (1 H, *pseudo*-t, $^3J_{HH} = 7.6$ Hz, *p*-H of phenyl), 3.62 (8 H, q, $^3J_{HH} = 6.8$ Hz, OCH_2), 3.59 (2 H, s, CH_2), 0.88 (12 H, t, $^3J_{HH} = 6.8$ Hz, CH_3 of ether), 0.37 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 143.5 (*ipso*-C of phenyl), 129.8 (*o*-C of phenyl), 129.0 (*m*-C of phenyl), 127.1 (*p*-C of phenyl), 67.5 (OCH_2), 36.2 (CH_2-Ph); 2.0 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.8. IR (paraffin, CsBr plates, cm^{-1}): 1600 w, 1582 w (phenyl); 1463 vs, 1377 s (paraffin); 1325 m, 1310 m, 1287 m, 1263 m, 1251 m $\delta(CH_3)$; 1223 w, 1184 w, 1149 m, 1120 w, 1090 m, 1022 m ν(CC), (phenyl); 937 w, 918 w, 889 w, 841 m $\rho(CH_3(Si))$; 721 m (paraffin); 657 w ν_{as}(SiC); 623 vw ν_s(SiC); 526 m, 457 m ν(GaC), ν(GaCl), ν(GaO).

Reaction of H−GaCl$_2$ with 1,4-Bis(trimethylsilylethynyl)benzene in a Molar Ratio of 4 to 1: Synthesis of 2. 1,4-Bis(trimethylsilylethynyl)benzene (0.503 mg, 1.86 mmol) dissolved in 30 mL of *n*-hexane was added to a suspension of H−GaCl$_2$ (1.058 g, 7.47 mmol) in 60 mL of *n*-hexane at room temperature. The mixture was heated under reflux for 16 h. A colorless solid precipitated, which was filtered off and washed with 10 mL of *n*-hexane. Diethyl ether (30 mL) was added. The clear solution obtained after filtration was concentrated in vacuum and cooled to 4 °C to yield colorless crystals of the product **2**. Yield: 0.832 g (39%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.53 (4 H, s, C_6H_4), 3.55 (4 H, s, $CH_2C_6H_4$), 3.48 (16 H, q, $^3J_{HH} = 7.2$ Hz, OCH_2), 0.91 (24 H, t, $^3J_{HH} = 7.2$ Hz, CH_3 of ether), 0.34 (18 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 142 (*ipso*-C of phenyl), 129.9 (*o*-C of phenyl), 67.7 (OCH_2), 42.5 (CGa_2Si), 35.7 ($CH_2C_6H_4$), 14.3 (CH_3 of ether), 1.9 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.6. IR (paraffin, CsBr plates, cm^{-1}): 1578 s (phenyl); 1460 vs (paraffin); 1404 w δCH; 1375 m (paraffin); 1304 vw, 1248 w $\delta(CH_3)$; 1186 w, 1146 m, 1113 s, br, 1094 m ν(CC), ν(CO); 934 w, 887 w, 845 w, 814 m $\rho(CH_3(Si))$; 721 m (paraffin); 662 vw ν_{as}(SiC); 621 vw ν_s(SiC); 588 w, 478 s, 448 m ν(GaC), ν(GaCl), ν(GaO). Anal. Calcd for $C_{32}H_{66}O_4Si_2Cl_8Ga_4$ (1133.6): C, 33.9; H, 5.9; Cl, 25.0; Ga, 24.6. Found: C, 35.0; H, 6.0; Cl, 24.5; Ga, 24.0.

General Procedure for the Synthesis of Adducts 4−6. A solution of the digallium compound **1** in toluene [**4**, 0.287 g (0.63 mmol, based on monomeric **1**) in 40 mL of toluene; **5**, 0.418 g, (0.91 mmol) in 45 mL of toluene; **6**, 0.190 g (0.42 mmol) in 50 mL of toluene] was added to the corresponding tetrabutylammonium halide [**4** (X = Cl), 0.174 g (0.63 mmol); **5** (X = Br), 0.294 g (0.91 mmol); **6** (X = I), 0.153 g (0.42 mmol)] at room temperature. After stirring for 16 h the reaction mixture was filtered, and the filtrate was concentrated in vacuum. Crystals of compounds **4**−**6** were obtained upon cooling to 4 °C. Yields: 0.300 g (65%) of **4**, 0.325 g (46%) of **5**, 0.160 g (47%) of **6**.

Characterization of Compound 4. Mp (argon, closed capillary): 142 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.68 (2 H, d, $^3J_{HH} = 7.6$ Hz, *o*-H of phenyl), 7.13 (2 H, t, $^3J_{HH} = 7.6$ Hz, *m*-H of phenyl), 7.01 (1 H, t, $^3J_{HH} = 7.6$ Hz, *p*-H of phenyl), 4.00 (2 H, s, CH_2), 2.56 (8 H, t, $^3J_{HH} = 7.6$ Hz, NCH_2), 1.21 (8 H, m, NCH_2CH_2), 1.17 (8 H, m, $NCH_2CH_2CH_2$), 0.92 (12 H, t, $^3J_{HH} = 7.2$ Hz, $NCH_2CH_2CH_2CH_3$), 0.44 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 144.6 (*ipso*-C of phenyl), 129.5 (*o*-C of phenyl), 129.0 (*m*-C of phenyl), 126.5 (*p*-C of phenyl), 58.8 (NCH_2), 47.4 (CGa_2Si), 37.4 ($CH_2-C_6H_5$), 23.9 (NCH_2CH_2), 19.9 ($NCH_2CH_2CH_2$), 13.9 ($NCH_2CH_2CH_2CH_3$), 1.7 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.2. IR (paraffin, CsBr plates, cm^{-1}): 1599 m, 1582 w, 1555 w, 1492 m (phenyl); 1454 vs (paraffin); 1400 w $\delta(CH_3)$; 1379 s (paraffin); 1339 vw, 1322 w, 1308 w, 1265 m, 1246 s $\delta(CH_3)$; 1169 m, 1109 w, 1080 w, 1057 w, 1030 w, 1008 m, 993 m ν(CC), ν(CO), ν(CN); 945 w, 926 w, 910 m, 895 m, 883 w, 839 vs, 772 m, 750 vs, 737 m $\rho(CH_3(Si))$; 698 s, 685 w, 654 m ν_{as}(SiC); 623 w, 617 w ν_s(SiC); 556 m, 529 w, 437 m ν(GaC), ν(GaCl), $\nu(Ga_2Cl)$. Anal. Calcd for $C_{27}H_{52}NSiCl_5Ga_2$ (735.5): C, 44.1; H, 7.1; C, 24.1; Ga, 19.0. Found: C, 44.1; H, 7.1; Cl, 24.2; Ga, 18.8.

Characterization of Compound 5. Mp (argon, closed capillary): 134 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.71 (2 H, m, *o*-H of phenyl), 7.14 (2 H, t, $^3J_{HH} = 7.6$ Hz, *m*-H of phenyl), 7.02 (1 H, t, $^3J_{HH} = 7.6$ Hz, *p*-H of phenyl), 3.98 (2 H, s, CH_2), 2.60 (8 H, t, NCH_2), 1.24 (8 H, m, NCH_2CH_2), 1.19 (8 H, m, $NCH_2CH_2CH_2$), 0.94 (12 H, t, $^3J_{HH} = 7.2$ Hz, $NCH_2CH_2CH_2CH_3$,), 0.46 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz): δ 144.5 (*ipso*-C of phenyl), 129.7 (*o*-C of phenyl), 129.0 (*m*-C of phenyl), 126.6 (*p*-C of phenyl), 58.8 (NCH_2), 47.8 (CGa_2Si), 37.8 ($CH_2C_6H_5$), 24.0 (NCH_2CH_2), 19.9 ($NCH_2CH_2CH_2$), 13.9 ($NCH_2CH_2CH_2CH_3$), 1.8 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 1.6. IR (paraffin, CsBr plates, cm^{-1}): 1601 m, 1582 m, 1555 m, 1497 m (phenyl); 1454 vs, 1447 vs (paraffin); 1402 w $\delta(CH_3)$; 1377 vs (paraffin); 1337 vw, 1319 w, 1308 w, 1258 m, 1244 m $\delta(CH_3)$; 1211 vw, 1169 m, 1155 m, 1120 w, 1078 w, 1057 w, 1048 w, 1005 w, 991 m, 945 w ν(CC), ν(CO), ν(CN); 925 w, 907 w, 897 w, 881 vw, 841 m, br, 772 w, 750 m $\rho(CH_3(Si))$; 721 m (paraffin); 702 m, 687 w, 654 m ν_{as}(SiC); 617 w ν_s(SiC); 588 vw, 556 m, 527 w, 469 vw, br, 438 m ν(GaC), ν(GaCl), $\nu(Ga_2Cl)$, ν(GaBr). Anal. Calcd for $C_{27}H_{52}NSiCl_4Ga_2Br$ (779.9): C, 41.6; H, 6.7; Cl, 18.2; Ga, 17.9; Br, 10.2. Found: C, 42,0; H, 6.8; Cl, 18.3; Ga, 17.9.

Characterization of Compound 6. Mp (argon, closed capillary): 124 °C. ^{1}H NMR (C_6D_6, 400 MHz, 350 K): δ 7.65 (2 H, d, $^3J_{HH} = 7.6$ Hz, *o*-H of phenyl), 7.14 (2 H, t, $^3J_{HH} = 7.6$ Hz, *m*-H of phenyl), 7.02 (1 H, t, $^3J_{HH} = 7.6$ Hz, *p*-H of phenyl), 3.94 (2 H, m, $CH_2C_6H_5$), 2.66 (8 H, t, NCH_2), 1.23 (8 H, m, $NCH_2CH_2CH_2$), 1.23 (8 H, m, NCH_2CH_2), 0.90 (12 H, t, $NCH_2CH_2CH_2CH_3$), 0.41 (9 H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 144.6 (br, *ipso*-C of phenyl), 129.5 (br, *o*-C of phenyl), 129.0 (br, *m*-C of phenyl), 126.6 (*p*-C of phenyl), 58.6 (NCH_2), 47.3 (CGa_2Si), 37.4 ($CH_2C_6H_5$), 23.8 (NCH_2CH_2), 19.8 ($NCH_2CH_2CH_2$), 13.9 ($NCH_2CH_2CH_2CH_3$), 1.7 ($SiMe_3$). IR (paraffin, CsBr plates, cm^{-1}): 1599 m, 1580 m, 1555 m, 1493 m (phenyl); 1466 vs (paraffin); 1402 w $\delta(CH_3)$; 1377 vs (paraffin); 1366 m, 1306 w, 1260 m, 1242 s $\delta(CH_3)$; 1204 vw, 1169 s, 1109 w, 1078 w, 1057 w, 1030 m, 1005 w, 982 m ν(CC), ν(CO), ν(CN); 941 m, 926 w, 912 w, 895 m, 885 w, 839 vs, 754 vs $\rho(CH_3(Si))$; 727 s (paraffin); 706 s, 684 s, 652 m ν_{as}(SiC); 621 w, 617 w ν_s(SiC); 551 s, 523 m, 463 m, 436 s ν(GaC), ν(GaCl), $\nu(Ga_2Cl)$. Anal. Calcd for $C_{27}H_{52}NSiCl_4Ga_2I$ (826.9): C, 39.2; H, 6.3; Cl, 17.1; Ga, 16.9; I, 15.3. Found: C, 39.1; H, 6.3; Cl, 17.5; Ga, 16.5; I, 14.7.

Crystal Structure Determinations. Single crystals of all compounds were obtained by cooling solutions (**1**, **4**, and **6** in toluene; $\mathbf{1(OEt_2)_2}$ and **2** in diethyl ether) to +4 °C. Crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo Kα radiation and a Bruker Smart 6000 diffractometer with Cu Kα radiation (**4**). 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[11] and refined

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Table 1. Crystallographic Data for **1**, **1(OEt$_2$)$_2$**, **2**, **4**, and **6**

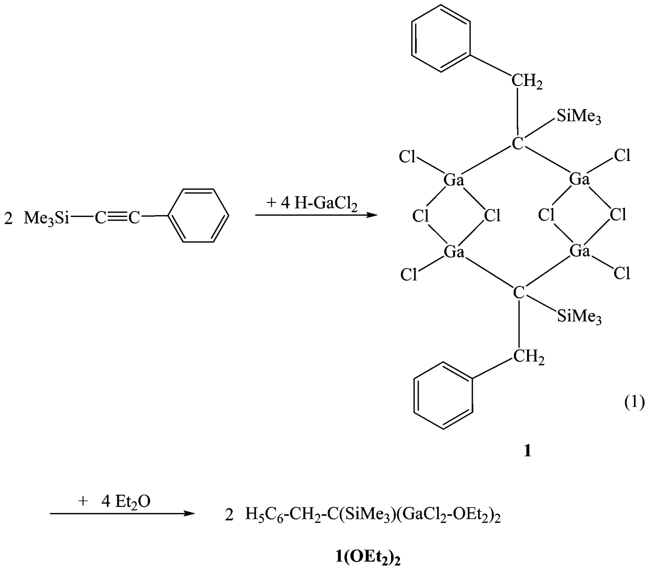
	1·toluene	**1(OEt$_2$)$_2$**	**2**	**4**	**6**
empirical formula	$C_{29}H_{40}Cl_8Ga_4Si_2$	$C_{19}H_{36}Cl_4Ga_2O_2Si$	$C_{32}H_{66}Cl_8Ga_4O_4Si_2$	$C_{27}H_{52}Cl_5Ga_2NSi$	$C_{27}H_{52}Cl_4Ga_2INSi$
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	P-1	$P1^c$	$P2_1/c$	$P2_1/c$	$P2_1^d$
a (pm)	859.8(2)	798.2(1)	1503.5(5)	1274.37(6)	1069.6(3)
b (pm)	1355.2(3)	913.4(1)	995.5(3)	1140.17(6)	1254.9(3)
c (pm)	1724.1(4)	1002.2(1)	1645.5(5)	2593.7(1)	1399.9(3)
α (deg)	101.698(4)	99.349(2)	90	90	90
β (deg)	93.413(4)	104.236(2)	92.985(5)	92.378(3)	95.701(5)
γ (deg)	91.305(4)	104.348(2)	90	90	90
V (nm^3)	1.9624(8)	0.6664(2)	2.460(1)	3.7653(3)	1.8697(8)
Z	2	1	2	4	2
temp (K)	153(2)	153(2)	153(2)	153(2)	153(2)
D_{calcd} (g cm^{-3})	1.705	1.510	1.531	1.297	1.469
independent data	11 234	6790	7134	6943	7293
obsd data	6693	6054	4900	5394	5744
params	395	260	233	332	368
μ (mm^{-1})	3.343	2.480	2.682	5.437	2.601
R1^a	0.0606	0.0423	0.0386	0.0446	0.0820
wR2 (all data)^b	0.1534	0.1036	0.0977	0.1245	0.2363
residual density (e nm^{-3})	+1378/−835	+912/−698	+959/−467	+901/−623	+1174/−1487

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Flack parameter: 0.01(1). [d] Flack parameter 0.04(3).

with the SHELXL-97[11] 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 **1** crystallized with one molecule of toluene per formula unit of the dimer. **2** is located on a crystallographic center of symmetry. The tetrabutylammonium ion of **6** is strongly disordered; the disorder was partially resolved by applying split positions for some carbon atoms.

Results and Discussion

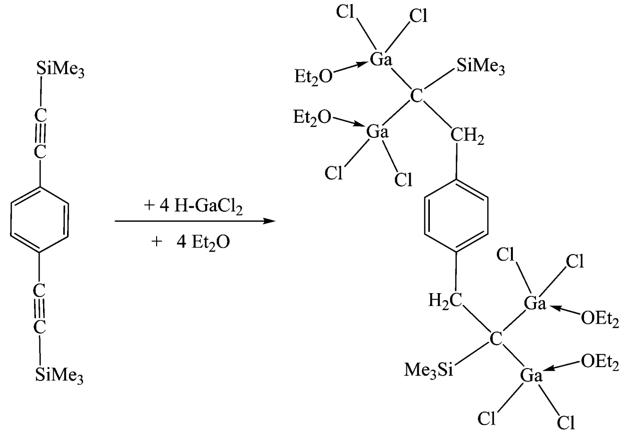
Hydrogallation Reactions. To date all experiments failed to achieve twofold hydrogallation of alkynes by application of an excess of different dialkylgallium hydrides under standard conditions in boiling *n*-hexane over several hours. As mentioned before, we recently reported the reaction of $H-GaCl_2$ with trimethylsilyl-substituted alkynes, which yielded the corresponding alkenes in high yields.[9] Only the monoalkyne $Me_3Si-C{\equiv}C-C_6H_5$ gave an addition product which was easily soluble in hydrocarbons. However, an only sparingly soluble byproduct precipitated in small quantities, which dissolved readily in diethyl ether. NMR spectroscopic characterization of the resulting etherate indicated the possible occurrence of twofold hydrogallation as a minor side reaction, which is in accordance with the application of a small excess of the hydride in all reactions. Thus, we treated the monoalkyne trimethylsilylphenylethyne with the hydride in a 1 to 2 molar ratio and isolated the colorless product of the twofold hydrogallation (**1**) in an almost quantitative yield (eq 1). A schematic drawing of the solid-state structure of **1** is depicted in eq 1. It formed dimeric formula units via Ga−Cl bridges. **1** precipitated from the reaction mixture and was obtained by filtration directly without further purification in high purity. It is only sparingly soluble in hydrocarbons such as *n*-hexane or benzene, and NMR characterization of the pure compound could only be conducted with some difficulties in saturated benzene solutions having a relatively low concentration of **1**. The most accurate data were obtained in THF. Complete dissolution occurred also in diethyl ether. The resulting etherate [**1(OEt$_2$)$_2$**] (eq 1) is soluble in benzene. The successful double hydrogallation of the C≡C triple bonds was easily established by a singlet at $\delta = 3.51$ in the ^{1}H NMR spectrum characteristic of a CH_2 group and the missing signals of alkene protons at a low field ($\delta > 6$). Similarly indicative were the data of the ^{13}C NMR spectra which had the resonance of the CH_2 group at $\delta = 36.7$.



(1)

Reaction of the dialkyne 1,4-bis(trimethylsilylethynyl)benzene with four equivalents of $H-GaCl_2$ afforded a colorless precipitate, which proved to be completely insoluble in hydrocarbon solvents. The solid dissolved partially upon treatment with diethyl ether. However, decomposition occurred by formation of a black precipitate, which probably contained elemental gallium. Filtration and cooling of the filtrate to +4 °C gave colorless crystals of the etherate **2** in 39% yield (eq 2). A gallium mirror was formed by decomposition in some cases during the purification process.

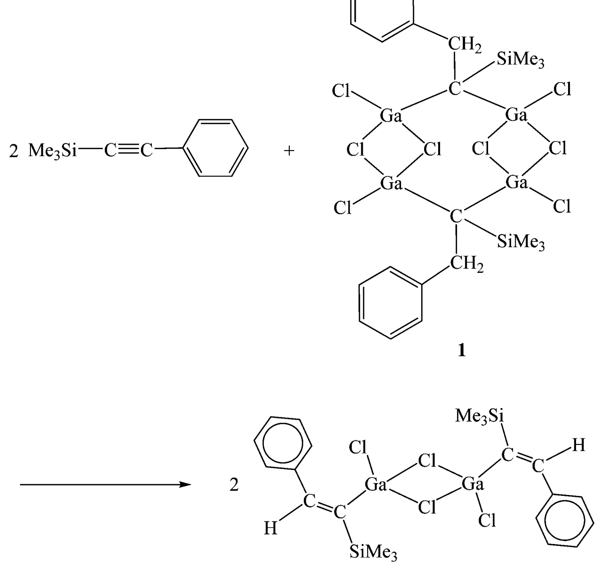
Compound **2** is soluble in benzene. It resulted from the twofold hydrogallation of both triple bonds of the starting dialkyne and has four dichlorogallium groups in one molecule. All gallium atoms are coordinated by a diethyl ether ligand. The spectroscopic findings are quite similar to those of the etherate **1(OEt$_2$)$_2$**.



(2)

2

At least the second hydrogallation step of the reaction described in eq 1 is reversible. We verified this in an NMR experiment when we mixed equimolar quantities of the hydrogallation product **1** and the starting alkyne $Me_3Si-C{\equiv}C-C_6H_5$ in benzene (eq 3). Quantitative formation of the alkenyl compound **3** occurred without NMR evidence of any byproduct within 16 h at room temperature. Compound **3** was described in a former publication.[9] It was obtained almost quantitatively by treatment of the starting monoalkyne with one equivalent of $H-GaCl_2$ and may be considered as a reasonable intermediate in the course of the formation of **1**.



1

(3)

3

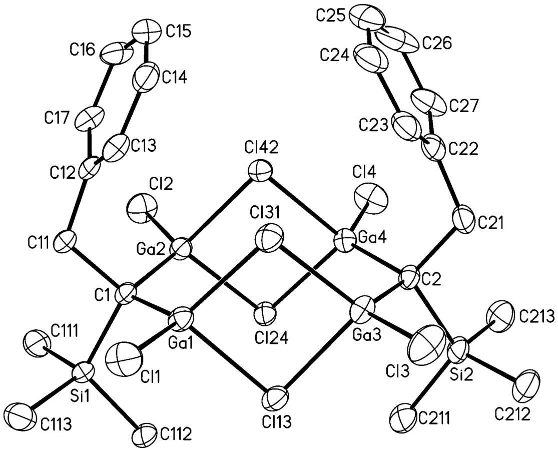


Figure 1. Molecular structure and numbering scheme of **1**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1 195.2(5), Ga2−C1 194.8(5), Ga3−C2 195.4(5), Ga4−C2 196.6(5), Ga1−Cl1 214.4(1), Ga1−Cl13 234.4(1), Ga1−Cl31 231.2(1), Ga2−Cl2 212.2(2), Ga2−Cl24 233.7(1), Ga2−Cl42 231.7(1), Ga3−Cl3 213.8(2), Ga3−Cl13 234.5(1), Ga3−Cl31 231.8(1), Ga4−Cl4 213.2(2), Ga4−Cl24 234.1(1), Ga4−Cl42 233.0(1), C1−Si1 192.2(5), Si2−C2 191.4(5), Ga1−C1−Ga2 112.1(2), Ga3−C2−Ga4 111.8(2), Cl13−Ga1−Cl31 87.42(5), Cl24−Ga2−Cl42 88.59(4), Cl13−Ga3−Cl31 87.24(5), Cl24−Ga4−Cl42 88.20(5), Ga1−Cl13−Ga3 91.12(4), Ga1−Cl31−Ga3 92.60(5), Ga2−Cl24−Ga4 91.14(4), Ga2−Cl42−Ga4 91.93(4).

The three hydrogallation products **1**, **1(OEt$_2$)$_2$**, and **2** were characterized by crystal structure determinations. The ether-free compound **1** possesses an unprecedented structure (Figure 1). By twofold hydrogallation two dichlorogallium groups were introduced per formula unit of the starting monoalkyne, and both gallium atoms are geminally attached to the same carbon atom. In accordance with the charge separation of the ethynyl moiety and the expected monogallium intermediate[9] both gallium atoms attacked exclusively that carbon atom which was attached to the trimethylsilyl group. The second carbon atom of the triple bond in the α position to the phenyl ring was transferred to a CH_2 group. Coordinative saturation of the metal atoms occurred by dimerization via Ga−Cl bridges and formation of two neighboring and almost ideally coplanar Ga_2Cl_2 heterocycles. Each gallium is further attached to a carbon and a terminal chlorine atom. Expectedly the Ga−Cl distances differ considerably with the different bonding situations and adopt values of 213.4 (terminal Ga−Cl) versus 233.1 pm (bridging Ga−Cl−Ga). Both are in the ranges usually observed.[12] Interestingly a centrosymmetric molecule did not form. Instead, the molecular structure approaches the point group

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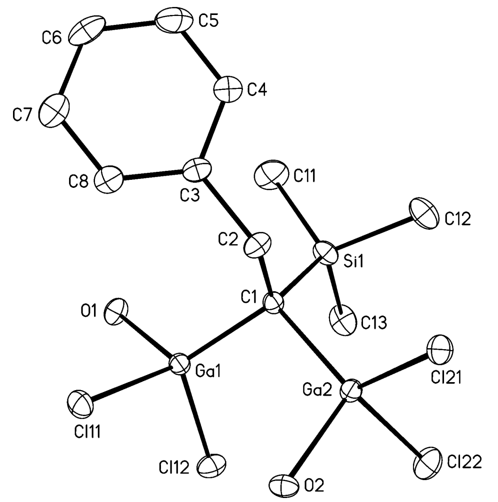


Figure 2. Molecular structure and numbering scheme of $\mathbf{1(OEt_2)_2}$; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and ethyl groups of the ether molecules are omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1 197.0(4), Ga1−Cl11 218.6(1), Ga1−Cl12 219.1(1), Ga2−C1 200.2(4), Ga2−Cl21 219.9(1), Ga2−Cl22 217.1(1), C1−Si1 189.6(4), Ga1−C1−Ga2 103.5(2), Cl11−Ga1−Cl12 106.35(4), Cl21−Ga2−Cl22 104.32(5), C1−C2−C3 119.9(3).

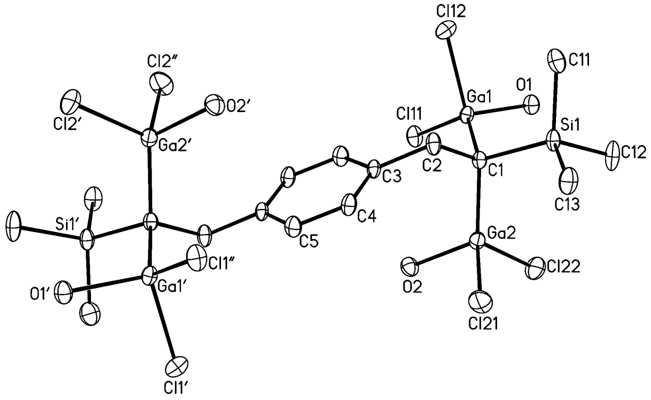
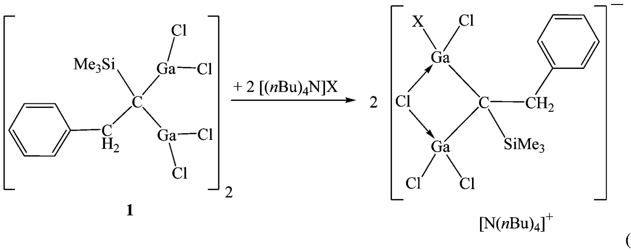


Figure 3. Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40% probability level; ethyl groups of the ether ligands and hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1 197.2(3), Ga1−Cl11 219.45(9), Ga1−Cl12 218.8(1), Ga2−C1 197.6(3), Ga2−Cl21 218.47(9), Ga2−Cl22 219.4(1), Ga1−C1−Ga2 114.2(1), Cl11−Ga1−Cl12 103.62(4), Cl21−Ga2−Cl22 107.46(4), C1−C2−C3 118.7(2).

C_{2v} with either trimethylsilyl or benzyl groups on the same sides of the average molecular plane.

The Ga−Cl−Ga bridges were opened upon formation of the monomeric etherates $\mathbf{1(OEt_2)_2}$ and **2** by dissociation and coordination of each gallium atom by an ether molecule. The molecular structures of both compounds are depicted in Figures 2 and 3. Their structural parameters are quite similar. The Ga−Cl distances (218.9 pm on average) correspond to the values expected for terminal Ga−Cl bonds, and the Ga−O distances (201.5 pm) are in the expected ranges of dative Ga−O interactions.

Application of Compound 1 as a Chelating Lewis Acid. The hypothetical, monomeric formula unit of compound **1** possesses two coordinatively unsaturated, tricoordinate gallium atoms. Hence, it should be able to act as a dipodal chelating Lewis acid upon treatment with suitable donor atoms or molecules. In order to test the principle capability of this class of hydrogallation products to act as bifunctional acceptors we treated **1** in some preliminary, simple experiments with tetrabutylammonium halides (X = Cl, Br, I) which have the considerable advantage of being soluble in noncoordinating solvents such as toluene. The reactions proceeded at room temperature overnight (eq 4). Suspensions were obtained in all cases, and small quantities of an unknown solid were removed by filtration. Colorless crystals of the three adducts (**4**, X = Cl; **5**, X = Br; **6**, X = I) were obtained in yields between 65% and 45% upon concentration and cooling of the filtrates to +4 °C. A liquid phase separated in some cases, which showed NMR parameters identical to those of the corresponding solid products and may be described as an ionic liquid. The ^{1}H NMR spectra of the chloride adduct **4** exhibited singlets of the trimethylsilyl and CH_2 groups, and the integration ratios gave the correct intensities. In contrast, the iodine product showed complicated NMR spectra with several signals in the range of the CH_2 and $SiMe_3$ groups, indicating the occurrence of several different species in solution. Heating to temperatures above 330 K was required to get the expected simple pattern of one singlet for each group. These observations verify a hindered exchange process in solution. In the solid state (see below) the iodine atom does not occupy the bridging position between both gallium atoms but is terminally arranged at one metal atom only. This particular molecular structure has a chiral gallium atom and, hence, should result in diastereotopic CH_2 protons with two different resonances in the ^{1}H NMR spectrum showing the characteristic shape of an AB spectrum. Although that particular pattern was not clearly resolved in the spectrum, it seems to be clear that the splitting is at least partially caused by this unsymmetric situation. The simple spectrum obtained at elevated temperature may be caused by a fast exchange process with iodine rapidly changing between terminal and bridging positions. The bromine compound **5** showed a similar splitting of resonances only when a solution in toluene was cooled to 280 K. Very broad signals were obtained at lower temperatures (below 240 K). Thus, a dynamic behavior occurred also in that case, but owing to the smaller size and molar mass of bromine compared to iodine the activation barrier seems to be lower for the exchange of chlorine and bromine positions.



1

$[N(nBu)_4]^+$

(4)

4: X = Cl
5: X = Br
6: X = I

Regrettably we did not succeed in growing single crystals of the bromine compound **5**. Crystal structures were determined for the chlorine and iodine products **4** and **6**. The most important anionic parts are depicted in Figures 4 and 5, while we abstain from a pictorial presentation of the tetrabutylam-

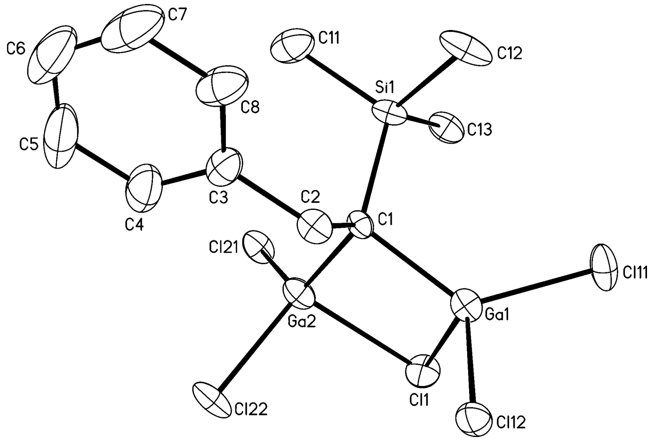


Figure 4. Molecular structure and numbering scheme of the anion of **4**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1 198.5(3), Ga1−Cl1 236.83(8), Ga1−Cl11 217.45(9), Ga1−Cl12 217.89(8), Ga2−C1 197.2(3), Ga2−Cl1 243.11(9), Ga2−Cl21 217.46(9), Ga2−Cl22 218.08(8), Ga1−Cl1−Ga2 74.02(2).

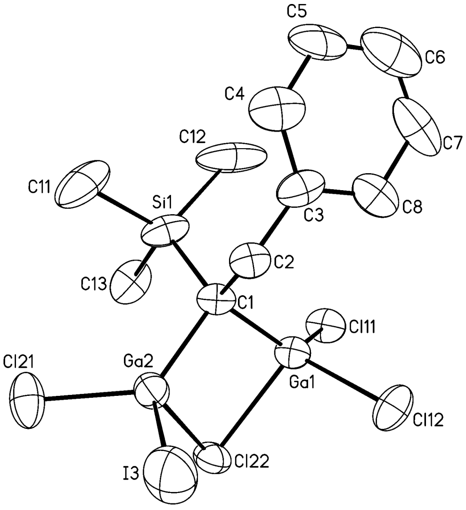


Figure 5. Molecular structure and numbering scheme of the anion of **6**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity. Important bond lengths [pm] and angles [deg]: Ga1−C1 196(1), Ga2−C1 196(1), Ga1−Cl22 244.7(3), Ga2−Cl22 243.3(3), Ga1−Cl11 223.1(3), Ga1−Cl12 223.4(3), Ga2−Cl21 223.7(4), Ga2−I3 249.2(2), Ga1−Cl22−Ga2 73.07(8).

monium counterions. Compound **4** has five chlorine atoms bonded to gallium; one of these (Cl1) is coordinated in a chelating manner by both metal atoms. A four-membered, nonplanar heterocycle results which consists of one carbon, one chlorine, and two gallium atoms. In accordance with the different bonding situation the Ga−Cl bond lengths differ with the shorter ones observed for the terminal Ga−Cl bonds (217.7 versus 240.0 pm). The molecular structure of compound **6** showed a severe disorder of the tetrabutylammonium ion. The relatively high displacement parameters observed even for the heavier atoms of the anionic part may be further caused by some intrinsic statistical disorder of the positions of the halogen atoms. However, we were not able to find any reasonable split position. An essential result is the terminal arrangement of the iodine atom and occupation of the bridging position between both chelating gallium atoms by chlorine. The Ga−Cl and Ga−I distances are in the expected ranges (223.4 and 244.0 pm for terminal and bridging Ga−Cl bonds,[12] 249.2 pm for terminal Ga−I bonds[13]). The angles Ga−Cl−Ga are much more acute (74° on average) in adducts **4** and **6** than in the Ga_2Cl_2 heterocycles of the dimeric compound **1** (92° on average). We suppose that the preferred chelating coordination of the chlorine atom compared to iodine does not depend on the different sizes with the larger iodine atom not fitting into the bite of the gallium atoms. Instead, that particular situation may be favored by the higher strength of the Ga−Cl interactions. These results show impressively the potential applicability of these gallium halides (**1** and **2**) as effective chelating Lewis acids. Preliminary experiments showed further that they are interesting starting compounds for generation of the corresponding alkyl derivatives, which are not accessible by direct hydrogallation with dialkylgallium hydrides and act as multiacceptors as well. Thus, these compounds are promising reagents for comprehensive future investigations.

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 compounds $[C_6H_5{-}CH_2{-}C(SiMe_3)(GaCl_2)_2]_2$ (**1**), $C_6H_5{-}CH_2{-}C(SiMe_3)(GaCl_2OEt_2)_2$ [**1(OEt$_2$)$_2$**], $C_6H_4[CH_2{-}C(SiMe_3)(GaCl_2OEt_2)_2]_2$ (**2**), $[C_6H_5{-}CH_2{-}C(SiMe_3)(GaCl_2)_2(\mu\text{-}Cl)]^-[NnBu_4]^+$ (**4**), and $[C_6H_5{-}CH_2{-}C(SiMe_3)(GaCl_2)(GaClI)(\mu\text{-}Cl)]^-[NnBu_4]^+$ (**6**). 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-662291 (**1**), -662292 [**1-(OEt$_2$)$_2$**], -662293 (**2**), -662294 (**4**), and -662295 (**6**).

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