Formation of the Digallium Compound $[(H_5C_6)_2N_3](R)Ga-Ga(R)[N_3(C_6H_5)_2]$ with Two Bis(trimethylsilyl)methyl Groups and Two Terminal Chelating Diphenyltriazenido Ligands

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Tetrakis[bis(trimethylsilyl)methyl]digallane(4) **1** reacts with 1,3-diphenyltriazene to yield two compounds, which were both characterized by a crystal structure determination. The gallium–gallium bond is retained in the yellow derivative $[(H_5C_6)_2N_3](R)Ga-Ga(R)[N_3(C_6H_5)_2]$ **2** [R = $CH(SiMe_3)_2$], which is formed by a ligand exchange reaction and shows two terminal chelating triazenido ligands besides two bis(trimethylsilyl)methyl groups; the Ga–Ga bond length is 245.79(6) pm. The second product is the orange dialkyl(diphenyltriazenido)gallium derivative $R_2Ga[N_3(C_6H_5)_2]$ **3**, where the triazene has reacted as an oxidant by the cleavage of the Ga–Ga bond and probably by release of elemental hydrogen.

Tetrakis[bis(trimethylsilyl)methyl]dialane(4)[1] with an Al–Al bond as well as the corresponding diindane(4) derivative[2] react with carboxylic acids by cleavage of the element–element bonds and the formation of carboxylato compounds of the trivalent elements[3]. The digallane(4) analog **1**[4] shows, however, a quite different chemical behavior, and dialkyldicarboxylatodigallane derivatives still exhibiting a Ga–Ga bond are formed in an almost quantitative yield by the release of two equivalents of bis(trimethylsilyl)methane[5]. The element-element bond of these products is bridged by two carboxylato groups, as has often been observed in transition metal compounds but not previously in main-group organic chemistry, and the small oxygen–oxygen distance of the bridging groups result in a very short Ga–Ga bond length of 238.5(2) pm. An even shorter distance between the coordinating atoms of a chelating ligand is observed in 1,3-diphenyltriazenide. Therefore, we treated the digallane(4) **1** with 1,3-diphenyltriazene in order to prevent the bridging and to realize an exclusively terminal coordination with a free Ga–Ga bond. Similar reactions of 1,3-diphenyltriazene with trialkyl derivatives of the trivalent elements aluminium, gallium, and indium have been reported in recent literature[6]; but it was uncertain whether the acidity of the N–H function was strong enough the initiate the substituent exchange with the digallium compound **1** and its divalent Ga atoms.

Reaction of 1,3-Diphenyltriazene with Digallane(4) 1

When the digallane(4) **1** is treated with an excess of 1,3-diphenyltriazene in boiling *n*-hexane over a period fo 24 h, a yellow-orange solution is formed, from which a mixture of yellow and orange crystals of two distinct products (**2** and **3**) in a molar ratio of 3:7 (determined by NMR spectroscopy) was isolated (eq. 1). These products could not be obtained in a pure form by repeated recrystallization, although we systematically employed solvents of different polarity (*n*-pentane, cyclopentane, toluene, diisopropyl ether, diethyl ether, THF). An attempt at sublimation in vacuo at 70–90 °C leads to the complete decomposition of **2**, and the starting compound 1,3-diphenyltriazene sublimes as the only volatile and isolable decomposition product. Almost pure **3** remains as a residue with a small impurity of $Ga[(CH(SiMe_3)_2]_3$[4] from a disproportionation reaction. **2** and **3** could however, easily be separated to give spectroscopically and analytically pure samples by manual sorting of the usually large crystals due to their different color. The reaction time is lengthened significantly to several days when using boiling diethyl ether as a solvent, and component **2** becomes a minor by-product with a molar ratio determined by NMR spectroscopy of 1:6 (**2**:**3**).

The identification of both products succeeds simply by the integration of their ^{1}H-NMR spectra. The yellow compound **2** shows a ratio of two phenyl groups to one bis(trimethylsilyl)methyl group as expected for a digallium derivative with a Ga–Ga bond and one diphenyltriazenido and one alkyl substituent on each Ga atom. The second product **3** has a ratio of 1:1, which is consistent with the monogallium compound dialkyltriazenidogallium **3** (eq. 1). **3** might be formed by the oxidative addition of a N–H bond to the

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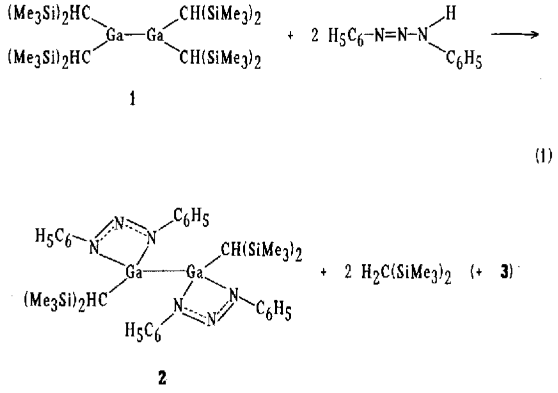


(1)

Ga atoms of **1** and the reaction of the Ga–H intermediate with a second molecule of triazene by the release of hydrogen. Thus, the less acidic starting compound diphenyltriazene shows a much more complicated reaction course than carboxylic acids, which gave the products of the ligand exchange without any by-products in a very high yield[5]. Compounds **2** and **3** are both readily soluble in organic solvents and exhibit very similar spectroscopic properties (see the Experimental Section). The most significant difference is the shift of the methine proton in the ^{1}H-NMR spectra, with $\delta = -0.06$ in **2** and $\delta = -0.23$ in **3**. The IR spectra show three absorptions between 1280 and 1325 cm^{-1}, which are characteristic of chelating triazene ligands[6].

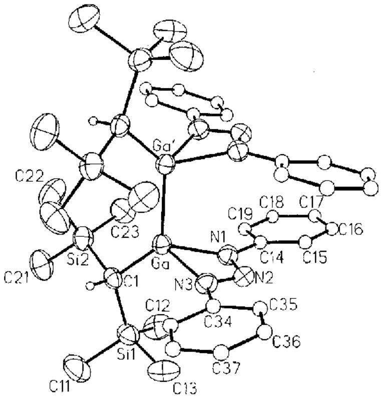
We succeeded in the synthesis of pure samples of **2** by another method. Treatment of the digallane(4) **1** with an excess of HCl dissolved in diethyl ether leads to the quantitative formation of two equivalents of bis(trimethylsilyl)methane without the precipitation of even traces of elemental gallium. The product is obtained in high purity (determined by NMR spectroscopy), but could not be recrystallized. Attempts at sublimation or distillation led to complete decomposition. We supposed that, like in the reactions with carboxylic acids[5] or 1,3-diphenyltriazene, a dialkyl digallium dichloride with a Ga–Ga bond might have formed; a similar derivative with $\text{Si(SiMe}_3)_3$ substituents was recently synthesized by another route by the group of Linti[7]. For the further characterization of the unknown product we used the reaction with lithium 1,3-diphenyltriazenide (eq. 2), which gives compound **2** in a yield of 84% with respect to **1** after recrystallization from *n*-pentane.

$$\mathbf{1} \xrightarrow[\text{2. 2 LiN}_3(\text{C}_6\text{H}_5)_2\cdot 2\text{Et}_2\text{O}]{\text{1. 2 HCl in Et}_2\text{O}} \mathbf{2} \qquad (2)$$

Molecular Structures of 2 and 3

Figure 1 shows the molecular structure of **2**. In contrast to the carboxylato derivatives with both RCOO groups bridging the Ga–Ga bond, the triazenido ligands in **2** occupy a terminal position and each chelating N_3 group is bound to only one Ga atom. The different coordination mode might, as mentioned above, be caused by the smaller "bite" of the triazenido ligand compared to that of the carboxylato group. The molecule resides on a crystallographic twofold rotation axis with an approximate *cis* arrangement of both bis(trimethylsilyl)methyl and both diphenyltriazenido groups. The molecular halves are, however, not synperiplanar, but significantly twisted with a torsion angle C1–Ga–Ga'–C1' of 45.1°. The Ga–Ga distance (245.79 pm) is shorter than in **1** [254.1(1) pm][4] or in tetraaryl[8], tetraamido[9] or silyl derivatives[7], but longer than in the carboxylato bridged derivative [238.5(2) pm][5]. Its very short Ga–Ga bond may result from the bridging of the Ga–Ga bond with two chelating ligands, and is possibly determined by the short O–O distance in the carboxylato group. Short bonds are observed in inorganic compounds with electronegative substituents like halides or chalcogenides (about 240 pm)[10,11], in an amide derivative with an unsaturated ligand [233.3(1) pm] and in a carbaborate derivative [234.0(1) pm][12,13]. A recently published triaryl cyclotrigallane dianion shows Ga–Ga bond lengths of 242–244 pm[14]; its bonding situation was described as a delocalized 3c-2e π bond similar to the cyclopropenyl cation. The shortening of the Ga–Ga bond in compound **2** compared to **1** is probably due to the coordination of electronegative atoms and less sterical interaction between the substituents.

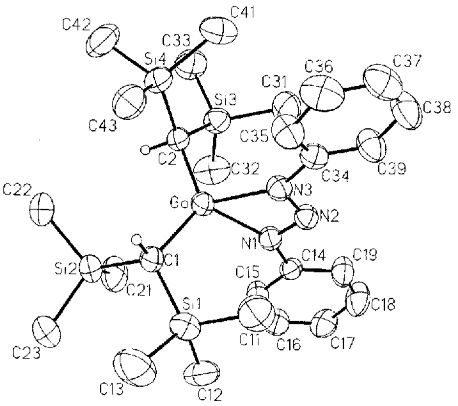
Figure 1. Molecular structure of **2**; the ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity, and the carbon atoms of the phenyl rings are drawn with an arbitrary radius to prevent overlapping. Selected bond lengths [pm] and angles [°]: Ga–Ga' 245.79(6), Ga–C1 197.7(2), Ga–N1 206.2(2), Ga–N3 203.8(2), N1–N2 131.6(2), N2–N3 130.6(2), Ga'–Ga–C1 132.63(5), Ga'–Ga–N1 103.78(4), Ga'–Ga–N3 102.66(5), Ga–N1–N2 95.2(1), N1–N2–N3 105.9(1), Ga–N3–N2 96.7(1), N1–Ga–N3 61.35(6), C1–Ga–N1 117.31(7), C1–Ga–N3 116.80(7); Ga' generated by −x, y, −z + 1/2



The molecular structure of the dialkyltriazenido gallium compound **3** is shown in Figure 2. Comparable gallane derivatives characterized by a crystal structure determination are to our knowledge not known in the literature, although several examples exist with aluminium or indium[6]. The gallium atom in **3** is bound to two carbon and two nitrogen atoms in a distorted tetrahedral environment, and as expected from alanate compounds with tetracoordinated Al atoms[15] the bis(trimethylsilyl)methyl groups stand perpendicular to one another so that one SiMe_3 group points between both SiMe_3 substituents of the second $\text{CH(SiMe}_3)_2$ group.

Despite their quite different molecular shapes and the different oxidation states of the Ga atoms of +II in **2** and

Figure 2. Molecular structure of **3**; the ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ga–C1 197.9(2), Ga–C2 196.7(3), Ga–N1 206.7(2), Ga–N2 204.8(2), N1–N2 130.3(3), N2–N3 131.3(3), C1–Ga–C2 124.0(1), C1–Ga–N1 113.63(9), C1–Ga–N3 117.7(1), C2–Ga–N1 114.9(1), C2–Ga–N3 109.03(9), N1–Ga–N3 61.31(8), Ga–N1–N2 95.7(2), N1–N2–N3 106.7(2), Ga–N3–N2 96.3(2)



+III in **3**, the bonding situation of the gallium triazenido groups are almost indistinguishable. The Ga–N bond lengths were found to be 205.0 (**2**) and 205.8 pm (**3**) on average, the N–N bond lengths 131.1 and 130.8 pm, respectively, similar to alane derivatives[6]. The angles N–Ga–N are very acute (61.35° and 61.31°), the angles N1–N2–N3 almost tetrahedral (105.9° and 106.7°), and the Ga–N–N angles close to square (96.0° in both **2** and **3**). The GaN_3 heterocycles deviate from planarity and are slightly folded across the Ga···N2 axis, by 10.5° and 13.0°, respectively; the phenyl groups are not exactly coplanar with the GaN_3 plane and the angles between the normals of the planes show values of 25.5 and 20.8° in **2** and 18.6 and 9.2° in **3**. The Ga–C distances are 197.7 in **2** and 197.3 pm on average in **3**, which is only a little shorter than in the starting compound **1** with 199.6 pm[4].

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Experimental Section

General: All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane with $LiAlH_4$). Compound **1** was prepared as described in ref.[4]; 1,3-diphenyltriazene from Aldrich was used without further purification.

Reaction of **1** *with Diphenyltriazene:* A solution of 0.36 g (1.83 mmol) 1,3-diphenyltriazene in 30 ml of *n*-hexane is added to a solution of digallane(4) **1** (0.71 g, 0.914 mmol) in 50 ml of *n*-hexane. The mixture is heated under reflux for 24 h. After evaporation of the solvent and bis(trimethylsilyl)methane a yellowish residue is obtained, which consists of two compounds (**2** and **3**) in a molar ratio of 3:7. Recrystallization from *n*-pentane gives a mixture of yellow (**2**) and orange (**3**) crystals.

Synthesis of **2** *via an R(Cl)Ga–Ga(Cl)R Intermediate:* The digallane(4) **1** (0.685 g, 0.883 mmol) dissolved in 50 ml of *n*-pentane is treated at −40 °C with 6.3 ml of a 0.42 M solution of HCl (2.646 mmol) in diethyl ether. The mixture is warmed to room temp., and the color changes from yellow to colorless. The solvents and bis(trimethylsilyl)methane are removed in vacuo. The residue (^1H NMR in C_6D_6: δ = 0.26 GaCH and 0.18 $SiMe_3$) is dissolved in 50 ml of *n*-pentane, cooled to −50 °C and treated with 0.619 g (1.76 mmol) bis(diethylether)lithium 1,3-diphenyltriazenide in 40 ml of diethyl ether (the Li compound is synthesized by treatment of 1,3-diphenyltriazene with the stoichiometric amount of n-butyllithium in diethyl ether; a solid remains after evaporation, which is used without further purification). The yellow-orange mixture is warmed to room temp., the solvents are evaporated, and the residue is treated with 20 ml of *n*-pentane. After filtration the solution is concentrated to about 5 ml; **2** crystallizes at −30 °C. Yield: 0.63 g (84%).

Characterization of **2**: Yellow, slightly air-sensitive crystals; m.p. (closed capillary, argon) 117–119 °C. – ^1H NMR (C_6D_6; 300 MHz): δ = 7.27 (8 H, pseudo-d, *o*-H of phenyl), 7.07 (8 H, pseudo-t, *m*-H of phenyl), 6.88 (4 H, pseudo-t, *p*-H of phenyl), 0.17 (36 H, $SiMe_3$), −0.06 (2 H, GaCH). – ^{13}C NMR (C_6D_6; 75.5 MHz): δ = 145.9 (*i*-C of phenyl), 129.2 and 118.7 (*o*/*m*-C of phenyl), 125.1 (*p*-C of phenyl), 11.9 ($GaCSi_2$), 3.8 ($SiMe_3$). – IR (CsBr): ṽ = 1593 cm^{-1} m (phenyl); 1460 vs, 1377 s (paraffin); 1325 w, 1300 vs, 1281 vs νN_3; 1258 s, 1248 s δCH_3; 1209 w, 1169 w, 1152 w, 1071 w νCN; 1001 s δCH; 961 vw, 928 s, 899 m, 839 vs, 783 s, 772 m, 754 vs, 723 s $\rho CH_3(Si)$; 689 vs, 667 vs $\nu_{as}SiC$; 623 w, 613 w ν_sSiC; 521 m, 513 m, 496 m, 488 m, 465 w νGaC,νGaN; 411 s; 359 vw δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 210 (4.7), 240 (4.7), 275 (4.2), 390 nm (4.6). – $C_{38}H_{58}Ga_2N_6Si_4$ (850.7): calcd. C 53.7, H 6.9, Ga 16.4; found C 53.2, H 7.0, Ga 16.2. – Mol. mass: 778 (cryoscopically in benzene).

Characterization of **3**: Orange, slightly air-sensitive crystals; m.p. (closed capillary, argon) 110–111 °C. – ^1H NMR (C_6D_6; 300 MHz): δ = 7.55 (4 H, pseudo-d, *o*-H of phenyl), 7.17 (4 H, pseudo-t, *m*-H of phenyl), 6.92 (2 H, pseudo-t, *p*-H of phenyl), 0.19 (36 H, $SiMe_3$), −0.23 (2 H, GaCH). – ^{13}C NMR (C_6D_6; 75.5 MHz): δ = 145.6 (*i*-C of phenyl), 129.4 and 119.4 (*o*/*m*-C of phenyl), 125.6 (*p*-C of phenyl), 9.0 ($GaCSi_2$), 3.9 ($SiMe_3$). – IR (CsBr): ṽ = 1595 cm^{-1} m (phenyl); 1460 vs, 1377 s (paraffin); 1350 w; 1325 s, 1306 vs, 1287 s νN_3; 1258 s, 1248 s δCH_3; 1167 w, 1154 w, 1072 w νCN;

Table 1. Crystal data and data collection parameters for **2** and **3**[18]

	2	**3**
Formula	$C_{38}H_{58}Ga_2N_6Si_4$	$C_{26}H_{48}GaN_3Si_4$
Crystal system	monoclinic	orthorhombic
Space group	*C*2/*c*; No.: 15 [16]	*Pbca*; Nr.: 61 [16]
Z	4	8
Temperature (K)	298(2)	298(2)
$d_{calc.}$ (g/cm³)	1.243	1.155
a (pm)	1781.2(4)	963.05(9)
b (pm)	1256.8(3)	2051.9(1)
c (pm)	2181.0(4)	3403.2(3)
β (°)	111.36(3)	90
V (10^{-30} m³)	4547(2)	6725.0(9)
μ (mm^{-1})	1.322	0.979
Crystal size (mm)	0.7 x 0.25 x 0.7	0.48 x 0.48 x 0.33
Diffractometer	Stoe-IPDS	Stoe-IPDS
Radiation: Mo-K_α graphite monochromator		
Range	$5 \le 2\Theta \le 56°$	$4 \le 2\Theta \le 48.2°$
Reciprocal space	$-23 \le h \le 23$ $-16 \le k \le 16$ $-28 \le l \le 28$	$-10 \le h \le 11$ $-21 \le k \le 22$ $-38 \le l \le 39$
Imaging plates , Δφ=1°	200	190
Independent reflections	5364	5170
Number of reflections with $F > 4\sigma(F)$	3787	3417
Program: SHELXTL, SHELXL-93 [17]; solutions by direct methods; full matrix refinement with all independent structure factors		
Parameters	232	319
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$ $(F > 4\sigma(F))$	0.0323	0.0353
$wR^2 = \{\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.0579	0.0577
Max. residual (10^{30} e/m³)	0.343	0.186
Min. residual (10^{30} e/m³)	-0.262	-0.195

1015 m, 997 m δCH; 963 m, 939 m, 893 w, 843 vs, 775 s, 754 vs, 721 s ρCH_3(Si); 687 s, 669 s ν_{as}SiC; 621 w, 611 w ν_sSiC; 515 m, 505 m, 465 w νGaC, νGaN; 413 m; 339 vw δSiC. – UV (*n*-hexane): λ_{max} (lg ε) = 210 (4.3), 240 (4.3), 290 (3.8), 380 nm (4.2). – $C_{26}H_{48}GaN_3Si_4$ (584.8): calcd. C 53.4, H 8.3, Ga 11.9; found C 53.0, H 8.1, Ga 11.5.

Crystal Structure Determinations: Single crystals of the compounds **2** and **3** were grown from saturated pentane solutions by slow cooling to 0 °C. Details of the crystal structure determinations are given in Table 1[18].

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[1] W. Uhl, *Z. Naturforsch., B. Chem. Sci.* **1988**, *43*, 1113–1118.

[2] W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139–154.

[3] W. Uhl, R. Graupner, S. Pohl, W. Saak, W. Hiller, M. Neumayer, *Z. Anorg. Allg. Chem*, in press.

[4] W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* **1989**, *364*, 289–300.

[5] W. Uhl, I. Hahn, H. Reuter, *Chem. Ber.* **1996**, *129*, 1425–1428.

[6] J. T. Leman, A. R. Barron, J. W. Ziller, R. M. Kren, *Polyhedron* **1989**, *8*, 1909–1912. J. T. Leman, A. R. Barron, *Organometallics* **1989**, *8*, 1828–1829. J. Braddock-Wilking, J. T. Leman, C. T. Farrar, S. C. Larsen, D. J. Singel, A. R. Barron, *J. Am. Chem. Soc.* **1995**, *117*, 1736–1745. J. T. Leman, J. Braddock-Wilking, A. J. Coolong, A. R. Barron, *Inorg. Chem.* **1993**, *32*, 4324–4336. W. Uhl, R. Gerding, S. Pohl, W. Saak, *Chem. Ber.* **1995**, *128*, 81–85. Indium derivatives: J. T. Leman, H. A. Roman, A. R. Barron, *J. Chem. Soc., Dalton Trans.* **1992**, 2183–2191. J. T. Leman, H. A. Roman, A. R. Barron, *Organometallics* **1993**, *12*, 2986–2990.

[7] G. Linti, W. Köstler, *Angew. Chem.* **1996**, *108*, 593–595; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 550–552.

[8] X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem.* **1993**, *105*, 761–762; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717–718.

[9] G. Linti, R. Frey, M. Schmidt, *Z. Naturforsch., B. Chem. Sci.* **1994**, *49*, 958–962.

[10] D. Loos, H. Schnöckel, D. Fenske, *Angew. Chem.* **1993**, *105*, 1124–1125; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1059–1060. W. Hönle, G. Gerlach, W. Weppner, A. Simon, *J. Solid State Chem.* **1986**, *61*, 171–180. See also ref.[2] for further literature.

[11] M. Julien-Pouzol, S. Jaulmes, M. Guittard, F. Alapini, *Acta Crystallogr. B* **1979**, *35*, 2848–2851. A. Kuhn, A. Chevy, R. Chevalier, *Acta Crystallogr. B* **1976**, *32*, 983–984; cited lit. S. Paashaus, R. Kniep, *Z. Naturforsch. B. Chem. Sci.* **1990**, *45*, 667–678.

[12] D. S. Brown, A. Decken, A. H. Cowley, *J. Am. Chem. Soc.* **1995**, *117*, 5421–5422.

[13] A. K. Saxena, H. Zhang, J. A. Maguire, N. S. Hosmane, A. H. Cowley, *Angew. Chem.* **1995**, *107*, 378–380; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 332–334.

[14] X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578–7579. X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, G. H. Robinson, *Organometallics* **1996**, *15*, 3798–3803. For digallium radical anions with 1e π bonds see ref.[8] and W. Uhl, U. Schütz, W. Kaim, E. Waldhör, *J. Organomet. Chem.* **1995**, *501*, 79–85.

[15] W. Uhl, H. H. Karsch, U. Schütz, A. Vester, *Chem. Ber.* **1993**, *126*, 2637–2641.

[16] T. Hahn (Ed.), *International Tables for Crystallography, Space Group Symmetry*, Kluwer Academic Publishers, Dordrecht-Boston-London, **1989**, vol. A.

[17] *SHELXTL PLUS REL. 4.1*, Siemens Analytical X-RAY Instruments Inc., Madison, USA, **1990**; G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Structures*, Universität Göttingen, **1993**.

[18] Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406164 (**2**) and -406163 (**3**).

[96222]