Organometallics **2001,** *20,* 5492−5494

Photochemical Cleavage of Pentamethylcyclopentadienyl−Gallium Bonds: An Alternative Approach to the Formation of Digallanes

Thomas Pott, Peter Jutzi,* Wolfgang W. Schoeller, Anja Stammler, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, D-33615 Bielefeld, Germany

Received April 23, 2001

*Summary: The novel digallanes [GaN(Dipp)CH═CHN(Dipp)]$_2$ (**3**) (Dipp = 2,6-diisopropylphenyl) and [GaN(Dep)CH═CHN(Dep)]$_2$ (**4**) (Dep = 2,6-diethylphenyl) were obtained in quantitative yield by photolysis of the 1-galla-2,5-diazoles [(η^1-Cp*)GaN(Dipp)CH═CHN(Dipp)] (**1**) and [(η^1-Cp*)GaN(Dep)CH═CHN(Dep)] (**2**), respectively. This alternative approach to the synthesis of digallanes demonstrates the efficiency of the Cp* moiety as the leaving group in the formation of metal−metal bonds. Compounds **3** and **4** were characterized by spectroscopic and analytical data. Compound **3** could further be characterized by X-ray crystallography; its molecular structure is compared with the structures of some other digallanes. Density functional calculations for differently substituted digallanes are presented.*

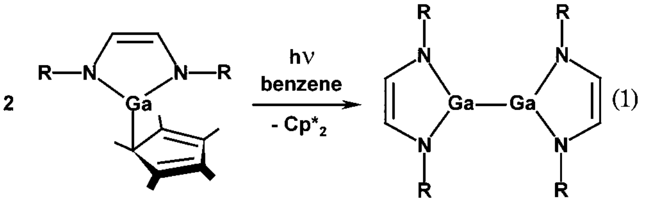
Introduction

The Cp* chemistry of main-group elements has experienced great progress, especially during the past 2 decades.[1−5] The versatile application of the Cp* moiety as ligand is based on its ability to adjust effectively to the electronic situation at the respective element center due to quite variable bonding modes ranging from mainly ionic to mainly covalent, and from η^1 to η^5. Furthermore, the steric requirements of the σ- or π-bound Cp* group enable the kinetic stabilization of otherwise highly reactive species such as compounds with monovalent group 13 elements, namely, Cp*Al and Cp*Ga.[6,7] Cp*−El σ-bonds are comparatively weak, thus allowing the application of the Cp* ligand as leaving group. Several examples from the chemistry of group 13, 14, and 15 elements support these statements.[5]

Only recently have we been successful with the synthesis of the novel 1-galla-2,5-diazoles [(η^1-Cp*)GaN(Dipp)CH═CHN(Dipp)] (**1**) and [(η^1-Cp*)GaN(Dep)CH═CHN(Dep)] (**2**) in the reaction of Cp*Ga with two differently *N*-substituted diazabutadienes (DABs).[8] Here we demonstrate the easy homolytic cleavage of the Cp*−Ga bonds in the above-mentioned compounds, opening an alternative way to the formation of gallium−gallium bonds.

Results and Discussion

Irradiation of a solution of compound **1** or **2** in benzene with a high-pressure mercury lamp for about 12 h led to the formation of the digallanes [GaN(Dipp)CH═CHN(Dipp)]$_2$ (**3**) and [GaN(Dep)CH═CHN(Dep)]$_2$ (**4**), respectively, in quantitative yield as verified by NMR spectroscopy. The reaction could be followed by a color change from initially orange to dark red (eq 1). After removal of nearly half of the solvent, **3** and **4** precipitated from solution, whereas Cp*$_2$ remained in solution as proven by NMR spectroscopy. Compounds **3** and **4** were obtained as red crystalline solids, which readily dissolve in aprotic organic solvents such as *n*-hexane, toluene, and tetrahydrofuran (THF). Single crystals of **3***1,5 THF suitable for X-ray crystallography were obtained from a concentrated solution of **3** in THF at room temperature.



R = 2,6-Diisopropylphenyl 3
2,6-Diethylphenyl 4

The molecular structure of compound **3** is shown in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles are collected in Table 2.

The molecular structure of **3** is asymmetric. This is mainly because the Ga−Ga bond does not lie in the planes spanned out by the two planar heterocycles: the angle between the average plane of the ligands and the Ga−Ga bond is 7.3° for the Ga(2), N(3), N(4), C(27),

---

* To whom correspondence should be addressed.

[1] Jutzi, P. *Chem. Rev.* **1986**, *86*, 983.

[2] Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969.

[3] Jutzi, P.; Burford, N. In *Metallocenes: Synthesis, Reactivity, and Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, pp 3−54.

[4] Jutzi, P. *Chem. Unserer Zeit* **1999**, *33*, 342.

[5] Jutzi, P.; Reumann, G. *J. Chem. Soc., Dalton Trans.* **2000**, 2237.

[6] Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.

[7] Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305.

[8] Pott, T.; Jutzi, P.; Neumann, B.; Stammler, H.-G. *Organometallics* **2001**, *20*, 1965.

10.1021/om0103310 CCC: $20.00
Publication on Web 11/10/2001

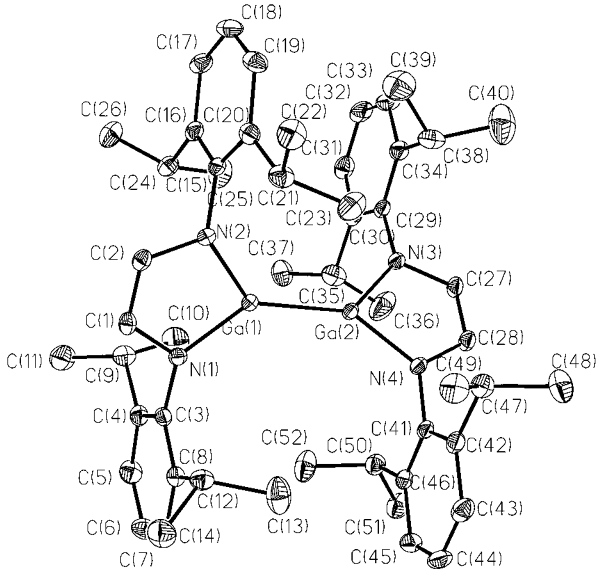


Figure 1. ORTEP plot of **3** with thermal ellipsoids at 50% probability.

Table 1. Crystallographic Data for 3

empirical formula	$C_{52}H_{72}Ga_2N_4 \cdot 1.5C_4H_8O$
fw	1000.73
temp, K	100(2)
wavelength, Å	0.71073
cryst syst, space group	triclinic $P\bar{1}$
unit cell dimens	
a, Å	11.0970(1)
b, Å	13.3750(1)
c, Å	19.5960(2)
α, deg	87.0380(3)
β, deg	79.2750(4)
γ, deg	75.2640(4)
vol, Å^3	2763.66(4)
Z	2
calcd dens, Mg/m^3	1.203
absorp coeff, mm^{-1}	1.017
F(000)	1068
cryst size (mm^3), color, and habit	0.26 × 0.24 × 0.20, red, irregular
θ range for data collection, deg	3.09−25.00
index ranges	$-13 \leq h \leq +13$, $-15 \leq k \leq +15$, $-23 \leq l \leq +23$
reflecns collected/unique	100381/9673 [$R_{\mathrm{int}} = 0.035$]
completeness to $\theta = 25.00$, %	99.5
Absorption correction	multi-scan
max and min transm	0.8225 and 0.7780
refinement method	full-matrix least-squares on F^2
data/restraints/params	9673/10/613
goodness-of-fit on F^2	1.014
final *R* indices [I > 2s(I)]	$R_1 = 0.0236$, $wR_2 = 0.0578$ [8773]
R indices (all data)	$R_1 = 0.0274$, $wR_2 = 0.0599$
largest diff peak and hole	0.439 and 0.449 e·A^{-3}

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

C(1)−C(2)	1.344(2)	C(27)−C(28)	1.347(2)
C(1)−N(1)	1.3970(19)	C(27)−N(3)	1.3983(19)
C(2)−N(2)	1.3955(19)	C(28)−N(4)	1.3938(19)
N(1)−Ga(1)	1.8470(12)	N(3)−Ga(2)	1.8507(12)
N(2)−Ga(1)	1.8525(12)	N(4)−Ga(2)	1.8466(12)
Ga(1)−Ga(2)	2.3482(2)		
N(1)−Ga(1)−N(2)	89.18(5)	N(3)−Ga(2)−N(4)	89.27(5)

Table 3. Central Bond Distances (Angstroms), Relative Energies (kilocalories per mole), and Populations (Charge and s/p/d Ratio) of Digallanes R_2GaGaR_2, Obtained at the B3LYP/6-31++G(d,p) Level

substituent	sym-metry	*d* (Ga−Ga)	Δ*E* [NIMAG]^a	q^b	*x* (*y*) [sp^{x}d^y]
H	D_{2h}	2.501	0.0 [1]	0.613	2.08 (0.0)
	D_{2d}	2.440	−3.0 [0]	0.576	2.01 (0.0)
CH_3	D_{2h}	2.514	0.0 [1]	1.056	2.36 (0.01)
	D_{2d}	2.474	−2.8 [0]	1.035	2.30 (0.01)
SiH_3	D_{2h}	2.540	0.0 [1]	0.379	2.15 (0.0)
	D_{2d}	2.451	−4.8 [0]	0.329	2.00 (0.0)
NH_2	D_{2h}	2.391	0.0 [1]	1.131	1.83 (0.0)
	D_{2d}	2.380	−1.7 [0]	1.130	1.83 (0.0)
HNCH═CHNH	D_{2h}	2.305	0.0 [0]	0.946	1.50 (0.0)
	D_{2d}	2.298	−0.7 [0]		

^{a} Number of imaginary frequences in brackets; NIMAG = 0 ground state, NIMAG = 1 transition state. ^{b} Natural charge.

C(28) unit, whereas it is only 1.8° for the Ga(1), N(1), N(2), C(1), C(2) unit. The bond lengths of these heterocycles are identical within the limit of experimental error. The average distances are as follows: C−C, 1.346(2) Å; C−N, 1.3962(13) Å; Ga−N, 1.8492(12) Å. The observed data correspond to those obtained for the precursor molecule **1** (C−C, 1.343(5) Å; C−N, 1.399(5) Å; Ga−N, 1.850(3) Å).[8] The Ga−Ga distance (2.3482(2) Å) is shorter than that in most other organodigallanes ($Ga_2[CH(SiMe_3)_2]_4$ (2.541(1) Å),[9] $Ga_2(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4$ (2.513(3) Å),[10] and $Ga_2(2,4,6\text{-}(CF_3)_3C_6H_2)_4$ (2.479(1) Å)[11]) but slightly longer than that in $[\overline{\mathrm{GaN(Bu^{t})CH{=}CHN}}\text{-}(\mathrm{Bu}^{t})]_2$ (2.333(1) Å),[11] the only other structurally characterized digallane of the DAB type.

The large variation of Ga−Ga bond lengths in dependence of the substituents at the gallium atoms prompted us to investigate this effect by quantum chemical calculations. Density functional calculations (B3LYP/6-31++g(d,p))[12] at a variety of differently substituted digallanes yield the following picture (Table 3).

The Ga−Ga bond distance is shortened by approximately 10% in the order $SiH_3 < CH_3 < H < NH_2 <$ HNCH═CHNH. At the same time the barriers for rotation around the central Ga−Ga bond are fairly small and diminish in nearly the same order. The vibrational analyses identify almost for all cases the planar geometries (D_{2h} symmetry) as transition states for rotation and the orthogonal geometries (D_{2d} symmetry) as corresponding energy minima.

It is of further interest to inspect the results of the population analyses at the NBO level[13] of sophistication.

---

(9) (a) Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1376. (b) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

(10) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717.

(11) Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421.

(12) All calculations were performed with the Gaussian set of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Methyl and amino substitutents attached at the gallium atoms strongly increase their positive charges. In other words, the electronegative substituents at the gallium atoms exert a $-I$ effect. Gallium is a higher main group element; thus, it suffers from *orbital nonhybridization*.[14] Consequently the p-electron density of the Ga−Ga bond will be exploited. This effect causes an increase of the relative s-content of the Ga−Ga bond, as seen by the calculated sp^x ratio, with concomitant shrinking of the bonding distance. The d-orbital participation towards Ga−Ga bonding is nihil. Since the rotational barriers around the Ga−Ga bond are negligibly small, π-contributions by back-donation of the adjacent 1,4-diazabutene-diyl ligand toward the Ga−Ga bond are also negligible. In fact, the heterocycles in **3** are twisted against each other by 51.3°. For $[\overline{\mathrm{GaN(Bu^t)CH{=}CHN}}(\mathrm{Bu}^t)]_2$ an orthogonal orientation of the heterocycles is observed.[11]

The NMR spectra of **3** and **4** indicate a hindered rotation of the aryl substituents in solution. In the ^{1}H NMR spectrum (benzene-d_6) of **3** two doublets are detected at 0.91 and 1.14 ppm for the methyl protons due to the presence of diastereomeric isopropyl groups. Similarly the ^{1}H NMR spectrum of **4** is characterized by two quartets at 2.38 and 2.50 ppm for the methylene protons within the ethyl groups.

Currently we are engaged in the synthesis of further 1-galla-2,5-diazoles in order to examine their photolytic behavior.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled immediately prior to use. Compounds **1** and **2** were prepared according to the literature.[8] The melting point determinations were performed using a Büchi 510 melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. NMR spectra were recorded in benzene-d_6 using a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz; ^{13}C{^{1}H} 125.8 MHz). Chemical shifts are reported in parts per million and were referenced to the solvent resonances as internal standard. IR data were collected using a Bruker Vektor 22-FT spectrometer. The samples were measured as KBr pellets.

Preparation of 3. Compound **1** (0.58 g, 1.00 mmol) was dissolved in benzene (1 mL) in a glass tube (diameter 0.5 cm, length 21 cm). While the solution was irradiated with a high-pressure mercury lamp (model Hanau TQ 150) for 12 h, its color changed from initially orange to red. After removal of nearly half of the solvent in vacuo, 0.38 g of **3** (0.38 mmol, 76%) precipitated from solution as a red solid, whereas Cp^*_2 remained in solution. Single crystals of **3***1,5 THF suitable for X-ray crystallography were obtained by recrystallization from THF, slowly cooling a concentrated hot solution to room temperature, mp 156 °C.^{1}H NMR (benzene-d_6): δ 0.91 (d, 24 H, isopropyl), 1.14 (d, 24 H, isopropyl), 3.26 (sep, 8 H, isopropyl), 6.19 (s, 4 H, vinyl-H), 7.06 (m, 12 H, aryl-H). ^{13}C NMR (benzene-d_6): δ 24.47 (isopropyl), 25.03 (isopropyl), 28.51 (isopropyl), 119.95 (aryl), 123.18 (aryl), 126.56 (aryl), 144.34 (aryl), 145.08 (C═C). IR (cm^{-1}, KBr): 3062, 2962, 2865, 1669, 1626, 1465, 762. Anal. Calcd for $C_{52}H_{72}N_4Ga_2$ (M = 892.58 g·mol^{-1}): C, 69.97; H, 8.13; N, 6.28. Found: C, 69.76; H, 8.11; N, 6.26.

Cp^*_2: ^{1}H NMR (benzene-d_6): δ 1.22(s, 6 H, methyl), 1.66 (s, 12 H, methyl), 1.75 (s, 12 H, methyl).

Preparation of 4. The same procedure was used in the photoreaction of **2** (0.53 g, 1.00 mmol) in benzene (1 mL). A color change from orange to red was observed. Compound **4**, 0.28 g (0.36 mmol, 72%), was obtained as red crystals, mp 152 °C. ^{1}H NMR (benzene-d_6): δ 0.96 (t, 24 H, ethyl), 2.38 (q, 8 H, ethyl), 2.50 (q, 8 H, ethyl), 6.16 (s, 4 H, vinyl-H), 6.96 (m, 12 H, aryl-H). ^{13}C NMR (benzene-d_6): δ 11.20 (ethyl), 16.04 (ethyl), 25.48 (ethyl), 122.56 (aryl), 125.91 (aryl), 126.83 (aryl), 140.19 (aryl), 145.48 (C═C). IR (cm^{-1}, KBr): 3066, 2965, 2876, 1669, 1618, 1465, 759. Anal. Calcd for $C_{44}H_{56}N_4Ga_2$ (M = 780.39 g·mol^{-1}): C, 67.72; H, 7.23; N, 7.18. Found: C, 67.46; H, 7.21; N, 7.16.

Cp^*_2: ^{1}H NMR (benzene-d_6): δ 1.22(s, 6 H, methyl), 1.66 (s, 12 H, methyl), 1.75 (s, 12 H, methyl).

Supporting Information Available: Tables of crystal structure data, positional and thermal parameters, and selected bond lengths and angles of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0103310

---

[14] (a) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Schoeller, W. W. Bonding Properties of Low Coordinated Phosphorus Compounds. In *Multiple Bonding and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1989; p 5.