

Synthesis and structure of an alkylgallium bridged [1,1]ferrocenophane

Werner Uhl *, Ingo Hahn, Andreas Jantschak, Thomas Spies

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Received 3 January 2001; received in revised form 12 February 2001; accepted 17 February 2001

Abstract

A gallium bridged [1,1]ferrocenophane (**2**) was obtained by the reaction of 1,1'-dilithio ferrocene with the alkyltrichlorogallate $[\text{Li}(\text{THF})]^+[\text{R}-\text{GaCl}_3]^-$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] (**1**). The crystal structure determination of the orange-red compound **2** revealed two trigonal planar coordinated, coordinatively unsaturated bridging gallium atoms, each of which is attached to two carbon atoms of different ferrocene molecules and the inner carbon atom of the bis(trimethylsilyl)methyl substituent. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gallium; Ferrocene; Ferrocenophane

1. Introduction

Polymeric ferrocenyl derivatives found considerable interest in recent literature [1] because they are potentially useful in material sciences, and, for instance, thin films of such an organometallic polymer were successfully produced in the last decade. These polymers were often prepared by the catalytic opening of [1]silaferrocenophane, which has an intramolecular bridging of both cyclopentadienyl ligands by one silicon atom. Interestingly, in the course of these processes the formation of the dimeric species, [1,1]silaferrocenophane, was observed in a single case only [2]. To the best of our knowledge, such dimeric [1,1]ferrocenophane structures have been observed in only few compounds with for instance carbon or silicon atoms in bridging positions [3–17], and no analogues bearing third main group elements were reported up to now. These derivatives may be of particular interest because owing to the coordinative and electronic unsaturation of their bridging atoms they may be suitable for an extensive information transfer between two or more ferrocene groups in the dimer or the one-dimensional

polymer. In the course of our investigations into the chemical properties of a compound possessing a Ga–Ga single bond [18] we also tried to synthesize ferrocenophanes bridged by digallium moieties, but in all reactions we observed the cleavage of the Ga–Ga bond. One of the products obtained in these reactions was a particular interesting one containing two ferrocene units bridged by two gallium atoms. We report here on the specific synthesis and the structure of that [1,1]digallaferrocenophane.

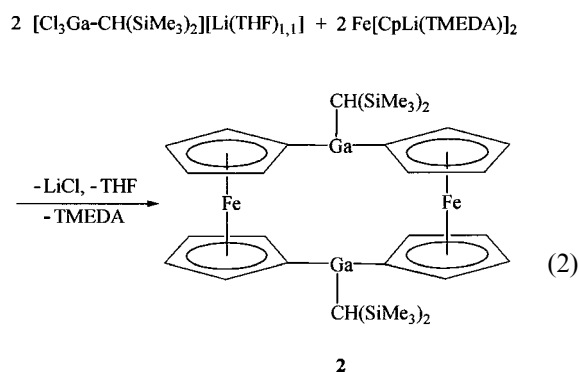
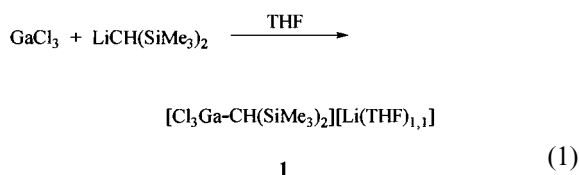
2. Synthesis and structure of the [1,1]digallaferrocenophane (**2**)

As a starting compound we employed the trichloroalkylgallate $[\text{Li}(\text{THF})_x]^+[\text{R}-\text{GaCl}_3]^-$ (**1**) [$\text{R} = \text{CH}(\text{SiMe}_3)_2$], which is easily available by the reaction of gallium trichloride with the lithium compound $\text{LiCH}(\text{SiMe}_3)_2$ in THF (Eq. (1)). According to this procedure some similar compounds were synthesized before in the group of Eaborn et al. [19] and our group [20]. Treatment of the adduct **1** with 1,1'-dilithioferrocene in *n*-hexane and recrystallization of the product from toluene afforded the orange-red compound **2** in 47% yield (Eq. (2)). The $^1\text{H-NMR}$ spectrum of the residue of the mother liquor showed resonances of

* Corresponding author. Tel.: +49-6421-282-5751; fax: +49-6421-282-5653.

E-mail address: uhl@chemie.uni-marburg.de (W. Uhl).

several unknown by-products none of which could be isolated in a pure form by crystallization.



(TMEDA = N,N,N',N'-tetramethylethylenediamine)

Compound **2** has two resonances of the cyclopentadienyl ligands and a sharp singlet of the SiMe_3 groups in the $^1\text{H-NMR}$ spectrum. The chemical shift of the methine proton and the inner carbon atom of bis(trimethylsilyl)methyl groups attached to aluminium or gallium is very sensitive to the coordination number

of those atoms, and resonances at a lower field [$\delta \sim 0$ to 0.5 (^1H) and > 10 (^{13}C)] verify coordinatively unsaturated central atoms [21]. Compound **2** showed values of $\delta = 0.41$ and 12.2 in the ^1H - and ^{13}C -NMR spectra, respectively, which gave a clear evidence for the coordination number three at gallium. Two absorptions were observed in the UV–vis spectrum at 340 and 465 nm, which may be caused by the ferrocene moieties of the molecule only and are similarly observed in free ferrocene (327 and 440 nm) [22].

The molecular structure of the [1,1]di(alkylgalla)ferrocenophane (**2**) is depicted in Fig. 1. One carbon atom of each cyclopentadienyl group is attached to a bis(trimethylsilyl)methyl gallium bridge with a coordinatively unsaturated, tricoordinated gallium atom. To the best of our knowledge, it is the first compound in which two ferrocene units are bridged by third main-group elements. Some [1,1]ferrocenophane derivatives are known from literature in which elements of the fourth main group (carbon to tin) are in bridging positions [3–17]. Both cyclopentadienyl ligands of each iron atom are not exactly parallel, however the angle between them is very small (5.2°). The atoms of both cyclopentadienyl groups of one dicyclopentadienyl-alkylgallium ligand, the gallium atom and the alkyl carbon atoms attached to gallium are almost ideally in a plane. Between both Cp substituents we observed an angle of 5.2° , while values of only 2.3 (Cp1 to Cp5) and 4.9° (Cp6' to Cp10'), respectively, were found between the cyclopentadienyl rings and the GaC_3 group. The Ga atom deviates from the plane of the neighboring carbon atoms (C1, Cp1, Cp6') by only 9.9 pm (sum of the angles 359.2°). Thus, the empty π -orbital at the Ga atom is in an ideal position to overlap with the π -orbitals of the cyclopentadienyl groups, such a conformation may open a facile route for the transfer of information between both halves of the molecule. The CSi_2 plane of the alkyl group attached to gallium is almost ideally perpendicular (94.6°) to the plane spanned by the atoms of both Cp rings and the Ga atom. The Fe–C distances [$202.8(4)$ – $207.4(4)$ pm] are as usual and similar to those observed for ferrocene (206 pm) [23]. The Ga–C bond length to the bis(trimethylsilyl)methyl substituent is quite normal [$196.9(4)$ pm], the Ga–C distances to the cyclopentadienyl carbon atoms are shorter [$193.3(4)$ and $193.4(4)$ pm]. Much longer Ga–C separations were observed in cyclopentadienylgallium derivatives, which usually have the Cp groups attached in an η^1 fashion with localized C=C double bonds [24] or which have one ferrocene carbon atom in a semi-bridging position between two gallium atoms [25]. The transannular metal–metal contacts are 354.0 and 351.3 (Fe–Ga), 532.5 (Fe–Fe) and 462.5 pm (Ga–Ga).

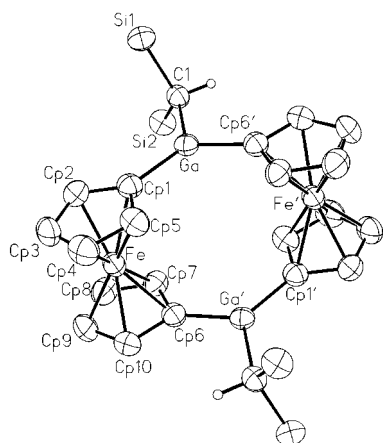


Fig. 1. Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (pm) and angles ($^\circ$): Ga–C1 $196.9(4)$, Ga–Cp1 $193.4(4)$, Ga–Cp6' $193.3(4)$, Fe–Cp1 $207.4(4)$, Fe–Cp2 $203.0(4)$, Fe–Cp3 $203.0(4)$, Fe–Cp4 $203.2(5)$, Fe–Cp5 $204.5(5)$, Fe–Cp6 $207.1(4)$, Fe–Cp7 $203.9(4)$, Fe–Cp8 $204.3(5)$, Fe–Cp9 $203.1(5)$, Fe–Cp10 $202.8(4)$, Cp1–Ga–Cp6' $117.9(2)$, C1–Ga–Cp6' $155.5(2)$, C1–Ga–Cp1 $125.8(2)$ (Cp6' was generated by $-x, -y+1, -z+1$).

3. Experimental

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over LiAlH₄; THF over Na/benzophenone). LiCH(SiMe₃)₂ [26] and Fe(C₅H₄Li)₂·2/3TMEDA [27] were synthesized according to literature procedures.

3.1. Synthesis of (tetrahydrofuran)lithium bis(trimethylsilyl)methyl-trichlorogallate

1: a solution of 2.13 g (12.1 mmol) of GaCl₃ in 70 ml of THF was treated with 18.7 ml (12.5 mmol) of a 0.67 M solution of LiCH(SiMe₃)₂ in diethyl ether at –10 °C. The mixture was warmed to room temperature (r.t.) and stirred for 17 h. All volatile components were distilled off in vacuum. The oily residue was treated with *n*-pentane, two phases were formed, and once again the solvent was distilled off in vacuum. Upon thorough evacuation a solid was obtained now, which was dissolved in 50 ml of toluene. After filtration and concentration to about 10 ml the product crystallized upon cooling of the solution to –50 °C. Yield: 3.14 g (62%); colorless crystals. The THF content was determined by the integration of the ¹H NMR resonances and varied between 1.1 and 1.3 molecules of THF per formula unit of **1**. M.p. (argon, sealed capillary): 97 °C. ¹H-NMR (C₆D₆, 300 MHz): δ = 3.53 (m, about 4H, OCH₂ of THF), 1.05 (m, about 4H, C₂H₄ of THF), 0.32 (s, 18H, SiMe₃), –0.43 (s, 1H, GaCH). ¹³C-NMR (C₆D₆, 75.5 MHz): δ = 70.6 (OCH₂), 24.8 (C₂H₄), 3.0 (SiMe₃); GaC not detected.

3.2. Synthesis of [1,1]bis[bis(trimethylsilyl)methylgalla]ferrocenophane

2: a suspension of 0.194 g (0.460 mmol) of Li[Cl₃Ga–CH(SiMe₃)₂]·THF **1** in 25 ml of *n*-hexane was cooled to –80 °C and treated with 0.137 g (0.499 mmol) of the solid dilithioferrocene TMEDA adduct. The mixture was warmed to room temperature and stirred for 15 h. The solvent was distilled off, and the residue was evacuated thoroughly (10^{–3} Torr). The residue was treated with 25 ml of toluene and filtrated. After concentration of the filtrate in vacuum and cooling to –50 °C orange–red crystals of the product **2** were isolated. Yield: 0.090 g (47%). M.p. (argon, sealed capillary): 186 °C (dec.). ¹H NMR (C₆D₆, 300 MHz): δ = 4.59 and 4.40 (each pseudo-t, 8H, cyclopentadienyl), 0.41 (s, 2H, GaCH), 0.28 (s, 36H, SiMe₃). ¹³C-NMR (C₆D₆, 75.5 MHz): δ = 74.5 and 72.7 (C–H of cyclopentadienyl), 71.2 (Ga–C of cyclopentadienyl), 12.2 (GaCH), 3.8 (SiMe₃). IR (CsBr plates, paraffin, cm^{–1}): ν = 1346 w, 1292 w, 1246 s δCH₃; 1177 w, 1167 vw, 1138 s, 1057 vw, 1028 s cyclopentadienyl; 1013 m δCHSi₂; 953 m, 864 s, 841 vs, 833 vs, 798 s, 770 s, 758

s, 725 m ρCH₃; 689 m, 669 s ν_{as}SiC; 627 w, 610 m ν_sSiC; 496 s, 480 m, 411 vw νGaC; 345 w, 330 w δSiC₃.

3.3. Crystal structure determination of **2**

Single crystals of compound **2** were obtained by recrystallization from toluene (20/–50 °C), the molecules are located on crystallographic inversion centers. C₃₄H₅₄Fe₂Ga₂Si₄; monoclinic; space group *P*2₁/*c*, no. 14 [28]; *a* = 1269.3(3) pm, *b* = 894.1(2) pm, *c* = 1724.6(3) pm, β = 94.75(3)°; *V* = 1950.7(7); *T* = 20 °C; *Z* = 2; μ = 2.240; crystal dimensions 0.15 × 0.25 × 0.53 mm; four circle diffractometer AED2; Mo–K_α radiation; 2θ range 3–48°, –14 ≤ *h* ≤ 14, 0 ≤ *k* ≤ 10, 0 ≤ *l* ≤ 19; ω–2θ scan; 3054 independent reflections; 2451 reflections with *F* > 4σ(*F*); solution by direct methods; full-matrix refinement with all data; programs SHELXL-97 and SHELXTL plus [29]; 196 parameters; *R*₁ [*F* > 4σ(*F*)] = 0.042; *wR*₂ (all data) = 0.071; max./min. residual electron density 0.49/–0.25 × 10³⁰ e m^{–3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 155708 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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

References

- [1] (a) I. Manners, Chem. Commun. (1999) 857; (b) P. Nguyen, P. Gómez-Elipse, I. Manners, Chem. Rev. 99 (1999) 1515; (c) I. Manners, Polyhedron 15 (1996) 4311; (d) F. Jäkle, A. Berenbaum, A.J. Lough, I. Manners, Chem. Eur. J. 6 (2000) 2762.
- [2] Y. Ni, R. Rulkens, J.K. Pudelski, I. Manners, Makromol. Chem. Rapid Commun. 16 (1995) 637.
- [3] D.L. Zechel, D.A. Foucher, J.K. Pudelski, G.P.A. Yap, A.L. Rheingold, I. Manners, J. Chem. Soc. Dalton Trans. (1995) 1893.
- [4] J. Park, Y. Seo, S. Cho, D. Whang, K. Kim, T. Chang, J. Organomet. Chem. 489 (1995) 23.
- [5] A. Clearfield, C.J. Simmons, H.P. Withers Jr, D. Seyferth, Inorg. Chim. Acta 75 (1983) 139.

- [6] N.J. Singletary, M. Hillman, H. Dauplaise, A. Kvik, R.C. Kerber, *Organometallics* 3 (1984) 1427.
- [7] M.F. Moore, S.R. Wilson, D.N. Hendrickson, U.T. Mueller-Westerhoff, *Inorg. Chem.* 23 (1984) 2918.
- [8] M.F. Moore, S.R. Wilson, M.J. Cohn, T.-Y. Dong, U.T. Mueller-Westerhoff, D.N. Hendrickson, *Inorg. Chem.* 24 (1985) 4559.
- [9] J.S. McKechnie, C.A. Maier, B. Bersted, I.C. Paul, *J. Chem. Soc. Perkin Trans. 2* (1973) 138.
- [10] F. Jäkle, R. Rulkens, G. Zech, D.A. Foucher, A.J. Lough, I. Manners, *Chem. Eur. J.* 4 (1998) 2117.
- [11] M. Watanabe, M. Sato, A. Nagasawa, I. Motoyama, T. Takayama, *Bull. Chem. Soc. Jpn.* 71 (1998) 2127.
- [12] P. Ahlberg, Ö. Davidsson, G. Hilmersson, M. Löwendahl, M. Håkansson, *J. Chem. Soc. Chem. Commun.* (1994) 1573.
- [13] A.L. Rheingold, U.T. Mueller-Westerhoff, G.F. Swiegers, T.J. Haas, *Organometallics* 11 (1992) 3411.
- [14] M. Håkansson, M. Löwendahl, Ö. Davidsson, P. Ahlberg, *Organometallics* 12 (1993) 2841.
- [15] T.-Y. Dong, M.-Y. Hwang, Y.-S. Wen, W.-S. Hwang, *J. Organomet. Chem.* 391 (1990) 377.
- [16] M. Löwendahl, Ö. Davidsson, P. Ahlberg, M. Håkansson, *Organometallics* 12 (1993) 2417.
- [17] J.-M. Löwendahl, M. Håkansson, *Organometallics* 14 (1995) 4736.
- [18] (a) W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* 364 (1989) 289;
(b) W. Uhl, *Coord. Chem. Rev.* 163 (1997) 1;
(c) W. Uhl, *Chem. Soc. Rev.* 29 (2000) 259.
- [19] J.L. Atwood, S.G. Bott, P.B. Hitchcock, C. Eaborn, R.S. Shariffudin, J.D. Smith, A.C. Sullivan, *J. Chem. Soc. Dalton Trans.* (1987) 747.
- [20] W. Uhl, A. Jantschak, *J. Organomet. Chem.* 555 (1998) 263.
- [21] (a) W. Uhl, I. Hahn, M. Koch, M. Layh, *Inorg. Chim. Acta* 249 (1996) 33;
(b) W. Uhl, R. Gerding, F. Hannemann, *Z. Anorg. Allg. Chem.* 624 (1998) 937;
- (c) W. Uhl, F. Hannemann, *Eur. J. Inorg. Chem.* (1999) 201;
(d) W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* (1999) 771.
- [22] DMS UV Atlas of Organic Compounds, vol. III, Butterworths/Verlag Chemie, London/Weinheim, 1967, F2T1.
- [23] (a) A. Haaland, *Acc. Chem. Res.* 12 (1979) 415;
(b) P. Seiler, J.D. Dunitz, *Acta Crystallogr. Sect. B* 38 (1982) 1741.
- [24] (a) O.T. Beachley Jr, T.D. Getman, R.U. Kirss, R.B. Hallock, W.E. Hunter, J.L. Atwood, *Organometallics* 4 (1985) 751;
(b) H. Schumann, S. Nickel, R. Weimann, *J. Organomet. Chem.* 468 (1994) 43;
(c) O.T. Beachley Jr, D.B. Rosenblum, M.R. Churchill, C.H. Lake, L.M. Krajowski, *Organometallics* 14 (1995) 4402;
(d) A.H. Cowley, S.K. Mehrotra, J.L. Atwood, W.E. Hunter, *Organometallics* 4 (1985) 1115.
- [25] B. Lee, W.T. Pennington, J.A. Laske, G.H. Robinson, *Organometallics* 9 (1990) 2864.
- [26] P.J. Davidson, D.H. Harris, M.F. Lappert, *J. Chem. Soc. Dalton Trans.* (1976) 2268.
- [27] (a) M.D. Rausch, D.J. Ciappenelli, *J. Organomet. Chem.* 10 (1967) 127;
(b) F.L. Hedberg, H. Rosenberg, *Tetrahedron Lett.* 46 (1969) 4011;
(c) M.S. Wrighton, M.C. Palazzotto, A.B. Bocarsly, J.M. Bolts, A.B. Fischer, L. Nadjó, *J. Am. Chem. Soc.* 100 (1978) 7264;
(d) J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenberg, R.E. Merrill, J.C. Smart, *J. Organomet. Chem.* 27 (1971) 241;
(e) I.R. Butler, W.R. Cullen, J. Ni, S.J. Rettig, *Organometallics* 4 (1985) 2196.
- [28] T. Hahn (Ed.), *International Tables for Crystallography, Space Group Symmetry*, vol. A, Kluwer Academic Publishers, Dordrecht, 1989.
- [29] (a) SHELXTL-plus REL. 4.1, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990;
(b) G.M. Sheldrick, SHELXL-97, Program for the Refinement of Structures, Universität Göttingen, Göttingen, Germany, 1997.