

The Organogallium Subhalide $R_2Ga_2I_2$ as Starting Compound for the Generation of a Transition Metal Gallium Complex – Synthesis of $Fe_2(CO)_6(\mu-GaR)_3$ [$R = C(SiMe_3)_3$]

Werner Uhl, Abdelhakim El-Hamdan, Wolfgang Petz, Gertraud Geiseler, and Klaus Harms

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

Reprint requests to Prof. Dr. W. Uhl. Fax ++49/(0)6421/2825653.

E-mail: uhl@chemie.uni-marburg.de

Z. Naturforsch. **59b**, 789 – 792 (2004); received April 2, 2004

Treatment of the monomeric organogallium subiodide $R(I)Ga-Ga(I)R$ **1** [$R = C(SiMe_3)_3$] with the diironcarbonylate anion $[Fe_2(CO)_8]^{2-}$ yielded the red iron gallium compound $Fe_2(CO)_6(\mu-GaR)_3$ **2** in moderate yield. **2** may be described as an analogue of enneacarbonyldiiron $Fe_2(CO)_9$, the three bridging carbonyl groups of which are replaced by GaR ligands.

Key words: Gallium, Iron, Coordination Compound

Introduction

Organometallic complexes of transition metals with third main-group elements found considerable interest in recent literature owing to their particular bonding situation and their potential applicability for the deposition of thin films of the corresponding alloys for electronic devices [1]. One facile route for the synthesis of those compounds comprises the treatment of carbonyl complexes with the tetraindium(I) cluster $In_4[C(SiMe_3)_3]_4$ [2, 3]. The monomeric fragments of this cluster InR possess highly unsaturated indium atoms in an oxidation state of +I with two empty p-orbitals perpendicular to the In-C bond axis and a lone electron pair. These monomeric fragments are isolobal to carbon monoxide, and indeed the replacement of bridging CO groups by InR could easily be achieved [2, 3]. However, this isolobal relationship was most impressively shown with the synthesis of the fascinating homoleptic compounds $M(ER)_4$ [$M = Ni, Pt$; $E = Ga, In$; $R = C(SiMe_3)_3, Cp^*$], which were obtained by treatment of the corresponding cyclooctadiene complexes $Ni(COD)_2$ and $Pt(COD)_2$ with the organoelement(I) clusters [4, 5]. A strong back-bonding of electron density from the central transition metal atoms into the empty π -orbitals of the third main-group atoms was verified for the alkyl derivatives by quantum-chemical calculations [4]. In contrast to the facile synthesis of heteroleptic transition metal indium complexes by the direct treatment of carbonyls with

the corresponding cluster, similar gallium compounds could be synthesized in very few cases only by employment of the cluster $Ga_4[C(SiMe_3)_3]_4$. Two compounds were published so far: $Mn_2(CO)_8(\mu-GaR)_2$ [6], in which the Mn-Mn bond is bridged by two GaR ligands, and $Fe_3(CO)_9(\mu-CO)(\mu-GaR)_2$ [6], in which all edges of the Fe_3 triangle are bridged (one by CO, two by GaR).

Recent investigations of our group showed that organoelement subhalides of gallium and indium are easily available by the careful oxidation of the tetrahedral tetraelement cluster compounds with halogens or halogen donors [7, 8]. These subhalides may be suitable starting materials for the generation of a broader variability of transition metal complexes by salt elimination reactions. Such a compound derived from an indium subhalide was published by our group only recently [9]. Here we report on the first successful synthesis of a transition metal gallium compound starting with an organogallium subhalide and a carbonylate anion. Organosilyl subhalides of gallium were obtained on other routes, which do not involve cluster compounds [10], and they had already been employed for the synthesis of transition metal complexes before [11].

Preparative Results

Treatment of a suspension of excess $Na_2[Fe_2(CO)_8] \cdot 4THF$ with a solution of the monomeric digal-

liumdiiodide $R(I)Ga-Ga(I)R$ **1** [$R = C(SiMe_3)_3$] in *n*-hexane at room temperature gave a very slow reaction only. A complicated mixture was formed, which contained a considerable quantity of the starting compound **1** beside several products of unknown composition. Recrystallization from cyclopentane yielded red crystals of the product **2** in trace quantities, which were characterized by a crystal structure determination. The yield of **2** was considerably enhanced to 33% (based on **1**) when the suspension of the starting compounds was heated to 60 °C for 3.5 hours (eq. (1)). The subhalide **1** was completely consumed, and the crude product of the reaction showed four singlets in the $SiMe_3$ region of the 1H NMR spectrum with chemical shifts of $\delta = 0.41, 0.32, 0.30$ and 0.16 . The first resonance was the most intensive one and belonged to the red product **2** isolated before in trace amounts. The IR spectrum of **2** showed absorptions in the range of 1922 to 1973 cm^{-1} only, thus, the occurrence of bridging CO groups could clearly be excluded. The resonance of the CO ligands in the ^{13}C NMR spectrum was observed at $\delta = 216.8$. The central carbon atom of the tris(trimethylsilyl)methyl group gave a signal with a chemical shift of $\delta = 45.1$. This is outside the range usually observed for carbon atoms attached to gallium atoms in oxidation states of +II or +III ($\delta < 30$) [12]. Similar shifts were observed for the related transition metal GaR complexes cited above [6]. An even stronger shift to lower field ($\delta > 62$) was detected for the tetrahedral clusters $E_4[C(SiMe_3)_3]_4$ ($E = Ga, In$) [13, 14], which was explained by the particular bonding situation with low lying magnetically allowed excited states and by a contribution of unusually large spin-orbit effects [14]. A yellow solid was isolated as the second fraction after concentration and cooling of the mother liquor. It showed a resonance at $\delta = 0.32$ in the 1H NMR spectrum, however, all attempts to grow single crystals suitable for a crystal structure determination failed up to now, and its constitution is unknown yet. We did not succeed in isolating one of the remaining components of the reaction mixture.

Molecular Structure

The molecular structure of compound **2** (Fig. 1) strongly resembles that of the pure carbonyl $Fe_2(CO)_9$, which contains three CO ligands bridging the Fe_2 couple and three terminal CO groups per each iron atom. All bridging CO ligands are replaced by GaR groups in compound **2**. Thus, the molecular core may be

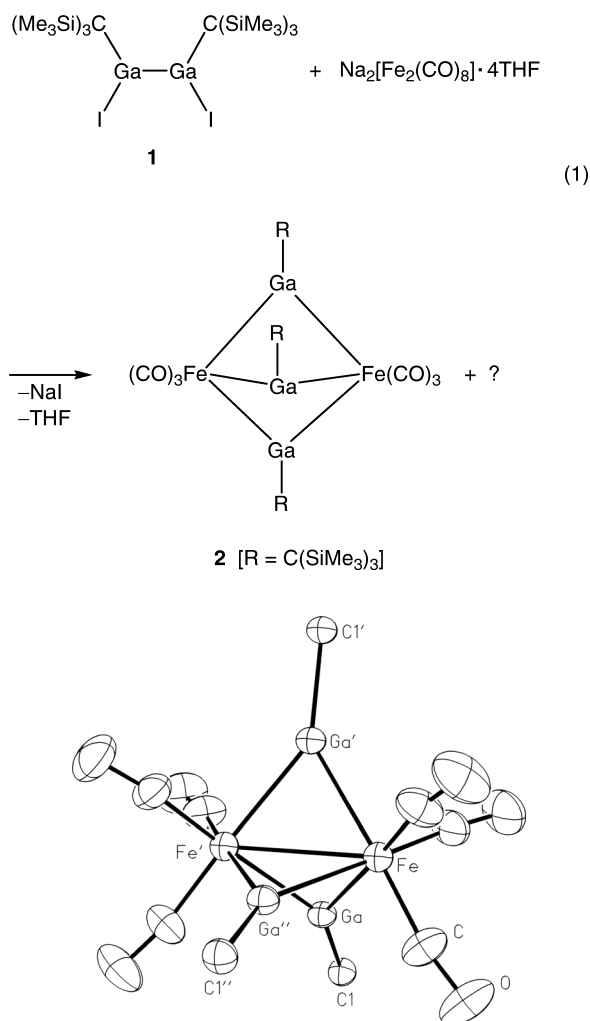


Fig. 1. Molecular structure of compound **2**. The ellipsoids are drawn at the 40% probability level; trimethylsilyl groups are omitted. Selected bond lengths [pm] and angles [°]: Ga-Fe 242.2(1), Ga-C1 199.7(7), Fe-C 174.6(6), C-O 116.4(8), Fe-Ga-C1 144.42(3), Fe-Ga-Fe' 71.16(5), C-Fe-C' 93.2(4), Ga-Fe-C 88.8(2), Ga-Fe-C' 88.4(2), Ga-Fe-C'' 177.4(3), Ga-Fe-Ga' 89.55(4), Fe-C-O 169.7(8); Fe' was generated by $x, y, -z + 0.5$; C' and Ga' by $-y + 1, x - y, z$; C'' by $-x + y + 1, -x + 1, z$.

described by a trigonal bipyramidal Fe_2Ga_3 cage, in which the Ga atoms occupy the equatorial positions. Owing to the long Fe-Ga distances (242.2 pm) compared to the Fe-C bond lengths in the homoleptic carbonyl complex (201.6 pm) [15], the Fe-Fe separation in **2** is elongated by about 30 pm (252.2 compared to 281.8 pm). An even longer Fe-Fe distance (299.2 pm) was observed for the isotopic triindium derivative $Fe_2(CO)_6(\mu-InR)_3$ [$R = C(SiMe_3)_3$] [3], which was

Table 1. Crystal data, data collection and structure refinement for compound **2**.

2	
<i>Crystal data</i>	
Empirical formula	$C_{36}H_{81}Fe_2Ga_3O_6Si_9$
M_r	1183.68
Crystal system	hexagonal
Space group	$P6_3/m$; no. 176 [22]
a, b [pm]	1446.90(8)
c [pm]	1568.48(10)
V [Å ³]	2843.7(3)
ρ_{calc} [g cm ⁻³]	1.382
Z	2
$F(000)$	1232
$\mu(Mo-K\alpha)$ [cm ⁻¹]	21.26; numerical absorption correction
<i>Data collection</i>	
T [K]	193(2)
Measured reflections	19204
Unique reflections	1981 [$R_{int} = 0.0917$]
Reflections $I > 2\sigma(I)$	1437
<i>Refinement</i>	
Refined parameters	227
Final R values [$I > 2\sigma(I)$]	
$R1^{[a]}$	0.0546
$wR2^{[b]}$ (all data)	0.1500
$\rho_{fin}(max/min)$ [eÅ ⁻³]	0.923/0.560
^[a] $R = \Sigma(F_o - F_c)/\Sigma F_o $; ^[b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.	

obtained by the direct reaction of the tetraindium cluster. Once again these data confirm the observation that the Fe-Fe distances of those dinuclear compounds are essentially determined by the covalent radius of the bridging atoms.

The Fe-Ga bond lengths (242.2 pm) are in the expected range [6, 11, 16, 17], shorter ones were observed for a few compounds containing terminal Fe-Ga bonds, in particular for those involving coordinatively unsaturated Ga atoms (< 222.5 pm) [17, 18]. The intramolecular Ga...Ga distances (341.2 pm) are very long and do not indicate any significant direct Ga-Ga interaction. Ga-Ga distances of 268 pm were observed for the tetrahedral compound $Ga_4[C(SiMe_3)_3]_4$ possessing a delocalized bonding in the cluster [13, 19]. The Ga-C distances (199.7 pm) are slightly lengthened compared to those of the starting compound **1** (196.2 pm), but are significantly shortened with respect to the bond lengths found in the corresponding tetrahedral cluster (208 pm on average). Gallium or indium compounds analogous to **2** are $Fe_2(CO)_6[\mu-GaSi(SiMe_3)_3]_3$ [11], $Fe_2(CO)_6(\mu-GaCp^*)_3$ [17], or $Fe_2(CO)_6(\mu-InR)_3$ [$R = C(SiMe_3)_3$] [3].

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-hexane and cyclopentane over $LiAlH_4$). $Ga_2I_2[C(SiMe_3)_3]_2$ **1** [7] and $[Na(THF)_2]_2[Fe_2(CO)_8]$ [20] were obtained according to literature procedures.

$Fe_2(CO)_6[\mu-Ga-C(SiMe_3)_3]_3$ (**2**)

A suspension of $Na_2[Fe_2(CO)_8] \cdot 4THF$ (0.128 g, 0.191 mmol, excess) and the subhalide $R_2Ga_2I_2$ (0.134 g, 0.156 mmol) in 30 ml of *n*-hexane was warmed to 60 °C for 3.5 h. The mixture was filtered, and the solvent was removed in vacuum. The residue was recrystallized from cyclopentane (20/−30 °C, 10 d). Yield: 0.040 g (33% based on **1**). Dec. p. (under argon, sealed capillary) 312 °C. – UV/vis (*n*-hexane): λ_{max} ($\lg \epsilon$) = 240 nm (2.4), 310 nm (1.3), 405 nm (1.5). – IR (paraffin; CsBr plates): 1973 s, 1937 s, 1922 m νCO ; 1460 vs, 1377 vs paraffin; 1301 vw, 1257 s $\delta_s CH_3$; 1122 w, 1090 w, 1026 w; 845 vs, 778 m ρCH_3 ; 721 w paraffin; 678 w $\nu_{as} SiC_3$; 655 w, 615 w $\nu_s SiC_3$, νFeC ; 586 s, 535 vs, 525 vw, 462 vw cm⁻¹ νGaC . – ¹H NMR (300 MHz, C_6D_6): δ 0.42 (s, $SiMe_3$). – ¹³C NMR (100.6 MHz, C_6D_6): δ 6.7 ($SiMe_3$), 45.1 (GaC), 216.8 (CO).

Crystal structure determination

Single crystals of compound **2** were obtained by cooling of a saturated solution in cyclopentane to −35 °C. Data collections were performed on a STOE IPDS diffractometer employing graphite-monochromated $Mo-K\alpha$ radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 [21]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. The crystallographic data of **2** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre, CCDC-234514. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: file-serv@ccdc.cam.ac.uk). The molecules reside on crystallographic $\bar{6}$ axes. The tris(trimethylsilyl)methyl groups are rotationally disordered; the atoms of the trimethylsilyl groups were refined on split positions.

Acknowledgements

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

- [1] R.A. Fischer, J. Weiß, *Angew. Chem.* **111**, 3002 (1999); *Angew. Chem. Int. Ed.* **38**, 2830 (1999).
- [2] W. Uhl, S.U. Keimling, W. Hiller, M. Neumayer, *Chem. Ber.* **128**, 1137 (1995); W. Uhl, S.U. Keimling, W. Hiller, M. Neumayer, *Chem. Ber.* **129**, 397 (1996); W. Uhl, S.U. Keimling, M. Pohlmann, S. Pohl, W. Saak, W. Hiller, M. Neumayer, *Inorg. Chem.* **36**, 5478 (1997); W. Uhl, S. Melle, G. Frenking, M. Hartmann, *Inorg. Chem.* **40**, 750 (2001); see also: C. Dohmeier, H. Krautscheid, H. Schnöckel, *Angew. Chem.* **106**, 2570 (1994); *Angew. Chem. Int. Ed.* **33**, 2482 (1994).
- [3] W. Uhl, M. Pohlmann, *Organometallics* **16**, 2478 (1997).
- [4] W. Uhl, M. Benter, S. Melle, W. Saak, G. Frenking, J. Uddin, *Organometallics* **18**, 3778 (1999).
- [5] W. Uhl, M. Pohlmann, R. Wartchow, *Angew. Chem.* **110**, 1007 (1998); *Angew. Chem. Int. Ed.* **37**, 961 (1998); W. Uhl, S. Melle, *Z. Anorg. Allg. Chem.* **626**, 2043 (2000); P. Jutzi, B. Neumann, L.O. Schebaum, A. Stammler, H.-G. Stammler, *Organometallics* **18**, 4462 (1999).
- [6] W. Uhl, M. Benter, M. Prött, *J. Chem. Soc., Dalton Trans.* 643 (2000).
- [7] W. Uhl, A. El-Hamdan, M. Prött, P. Spuhler, G. Frenking, *J. Chem. Soc., Dalton Trans.* 1360 (2003).
- [8] W. Uhl, S. Melle, G. Geiseler, K. Harms, *Organometallics* **20**, 3355 (2001); W. Uhl, S. Melle, *Chemistry Eur. J.* **7**, 4216 (2001); W. Uhl, A. El-Hamdan, G. Geiseler, K. Harms, *Z. Anorg. Allg. Chem.* **630**, 821 (2004).
- [9] W. Uhl, F. Schmock, W. Petz, *Z. Naturforsch.* **58b**, 385 (2003).
- [10] N. Wiberg, T. Blank, M. Westerhausen, S. Schneiderbauer, H. Schnöckel, I. Krossing, A. Schnepf, *Eur. J. Inorg. Chem.* 351 (2002); G. Linti, W. Köstler, *Angew. Chem.* **108**, 593 (1996); *Angew. Chem. Int. Ed.* **35**, 550 (1996); A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* **111**, 3578 (1999); *Angew. Chem. Int. Ed.* **38**, 3381 (1999); M. Kehrwald, W. Köstler, A. Rodig, G. Linti, T. Blank, N. Wiberg, *Organometallics* **20**, 860 (2001).
- [11] G. Linti, W. Köstler, *Chem. Eur. J.* 942 (1998); G. Linti, G. Li, H. Pritzkow, *J. Organomet. Chem.* **626**, 82 (2001).
- [12] See for instance: W. Uhl, M. Prött, *Z. Anorg. Allg. Chem.* **628**, 2259 (2002); W. Uhl, L. Cuyppers, K. Schüler, T. Spies, C. Strohmman, K. Lehmen, *Z. Anorg. Allg. Chem.* **626**, 1526 (2000); W. Uhl, T. Spies, *Z. Anorg. Allg. Chem.* **626**, 1059 (2000); W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* **364**, 289 (1989).
- [13] W. Uhl, A. Jantschak, *J. Organomet. Chem.* **555**, 263 (1998).
- [14] W. Uhl, A. Jantschak, W. Saak, M. Kaupp, R. Wartchow, *Organometallics* **17**, 5009 (1998).
- [15] F.A. Cotton, J.M. Troup, *J. Chem. Soc., Dalton Trans.* 800 (1974).
- [16] U. App, K. Merzweiler, *Z. Anorg. Allg. Chem.* **623**, 478 (1997); R.A. Fischer, A. Miehr, T. Priermeier, *Chem. Ber.* **128**, 831 (1995); R.A. Fischer, T. Priermeier, W. Scherer, *J. Organomet. Chem.* **459**, 65 (1993); X. He, R.A. Barlett, P.P. Power, *Organometallics* **13**, 548 (1994); R.A. Fischer, M.M. Schulte, E. Herdtweck, M.R. Mattner, *Inorg. Chem.* **36**, 2010 (1997); M.L.H. Green, P. Mountford, G.J. Smout, S.R. Speel, *Polyhedron* **9**, 2763 (1990); J.J. Schneider, U. Denninger, J. Hagen, C. Krüger, D. Bläser, R. Boese, *Chem. Ber.* **130**, 1433 (1997); R.M. Campbell, L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.L. Pickett, N.C. Norman, *Chem. Ber.* **125**, 55 (1992); J.C. Vanderhooft, R.D. Ernst, F.W. Cagle (Jr.), R.J. Neustadt, T.H. Cymbaluk, *Inorg. Chem.* **21**, 1876, (1982); D.L. Reger, D.G. Garza, A.L. Rheingold, G.P.A. Yap, *Organometallics* **17**, 3624 (1998); A.S. Borovik, S.G. Bott, A.R. Barron, *Organometallics* **18**, 2668 (1999); E. Leiner, M. Scheer, *Organometallics* **21**, 4448 (2002); P. Jutzi, B. Neumann, L.O. Schebaum, A. Stammler, H.-G. Stammler, *Organometallics* **19**, 1445 (2000); K. Ueno, T. Watanabe, H. Ogino, *Organometallics* **19**, 5679 (2000); T. Yamaguchi, K. Ueno, H. Ogino, *Organometallics* **20**, 501 (2001); E. Leiner, O. Hampe, M. Scheer, *Eur. J. Inorg. Chem.* **2002**, 584.
- [17] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **17**, 1305 (1998).
- [18] J. Su, X.-W. Li, R.C. Crittendon, C.F. Campana, G.H. Robinson, *Organometallics* **16**, 4511 (1997); C. Boehme, G. Frenking, *Chem. Eur. J.* **5**, 2184 (1999).
- [19] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **104**, 1378 (1992); *Angew. Chem. Int. Ed.* **31**, 1364 (1992).
- [20] J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, R.G. Komoto, J.I. Brauman, *J. Am. Chem. Soc.* **100**, 1119 (1978).
- [21] G.M. Sheldrick, SHELXTL-Plus REL. 4.1, Siemens Analytical X-RAY Instruments Inc., Madison, USA (1990); G.M. Sheldrick, SHELXL-97, Program for the Refinement of Structures, Universität Göttingen (1997).
- [22] T. Hahn (ed.): *International Tables for Crystallography, Space Group Symmetry*, Vol. A, Kluwer Academic Publishers, Dordrecht-Boston-London (1989).