Reactivity of Organoelement Subhalides of Gallium and Indium — Ga−Ga and In−In Bonds Bridged by Carboxylato Ligands

Werner Uhl*[a] and Abdelhakim El-Hamdan[a]

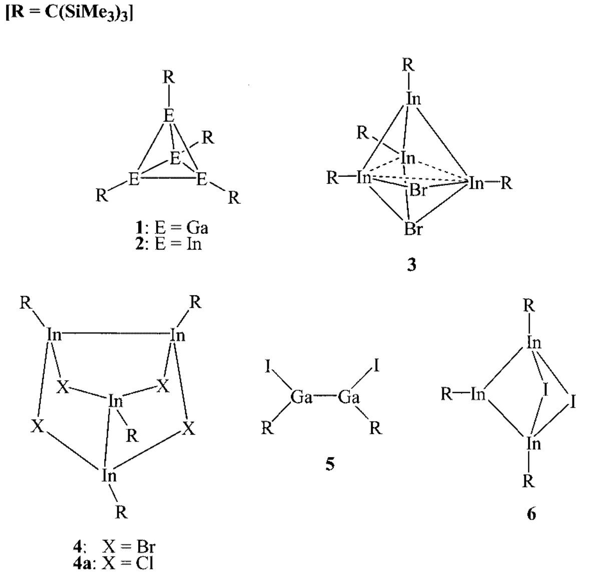
Keywords: Carboxylate ligands / Gallium / Indium / Subvalent compounds

The organoelement subhalides $R_2Ga_2I_2$ (**5**) and $R_3In_3I_2$ [**6**; R = $C(SiMe_3)_3$] reacted with silver benzoate $AgOOCC_6H_5$ to yield the dicarboxylato dielement compounds $R_2E_2(\mu\text{-}OOCC_6H_5\text{-}O,O')_2$ (**7**, E = Ga; **8**, E = In). Both compounds possess E–E single bonds bridged by the chelating carboxylato ligands. The chelating groups are arranged perpendicular to one another. Owing to the small bite of the carboxylato group very short E–E bond lengths of 240.5 pm (Ga–Ga) and 265.4 pm (In–In) were observed.

Introduction

Careful oxidation of the tetrahedral tetraelement clusters $Ga_4[C(SiMe_3)_3]_4$ (**1**)[1] and $In_4[C(SiMe_3)_3]_4$ (**2**)[2] (Scheme 1) with halogens or organic halogen donors yielded the corresponding subhalides still containing the elements gallium and indium in low oxidation states. The transfer of only one bromine molecule by the reaction of **2** with 1,2-dibromoethane gave the tetraindium compound **3** (Scheme 1), in which the overall tetrahedral arrangement of the In atoms is retained.[3] One face of the tetrahedron is bridged by a μ_3-Br atom, while the second Br atom is located above an edge of that particular face. Reaction with hexachloroethane, or mixtures of $AlBr_3$ and Br_2, yielded the diindium(II) compounds **4**, which contain localized In−In single bonds and form dimers through chlorine or bromine bridges.[3,4] The corresponding digallium(II) compound **5** was obtained by the reaction of **1** with ICl in the presence of AlI_3.[5] In contrast to the diindium compounds **4** it remains monomeric, even in the solid state. An average oxidation state of +1.66 was found for the central atoms of the triindium compound **6**, which possesses a chain of three In atoms connected by In−In single bonds and was obtained by the treatment of **2** with I_2/AlI_3.[6]

These subhalides should be suitable starting compounds for the generation of secondary products by salt-elimination reactions. In a first investigation, which is described here in detail, we employed silver benzoate as a reagent. The driving force of silver halide formation should favor these reactions, and the chelating carboxylato ligand should stabilize any secondary product by coordinative saturation of the Ga or In atoms. Dicarboxylatodigallium compounds containing a Ga−Ga single bond should result from the use of **5**.



Scheme 1

Similar products have previously been obtained in our group by another route when we treated tetraalkyldigallane(4) $R_2Ga{-}GaR_2$ [R = $CH(SiMe_3)_2$] with carboxylic acids. Two equivalents of bis(trimethylsilyl)methane were released in the course of these reactions, and two alkyl substituents were replaced by the chelating acid residues.[7,8] In contrast, similar diindium dicarboxylates are not accessible by such a reaction, which instead resulted in the quantitative cleavage of the In−In bond by oxidation of the In atoms.[9] Owing to the singular structure of the digallium compounds, which is discussed in detail below, the synthesis and characterization of the corresponding diindium derivatives was of particular interest. Indium subhalides seemed to be suitable starting compounds for their generation.

---

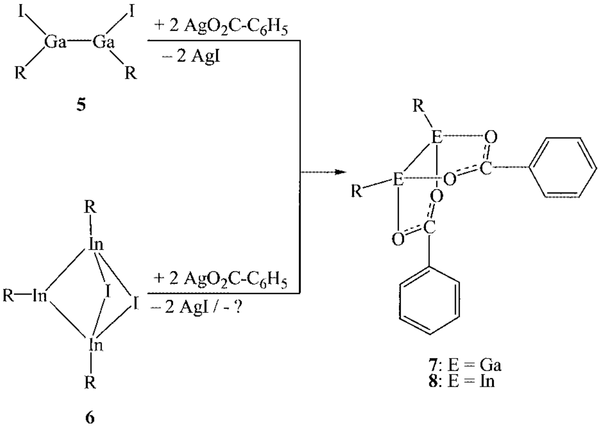
[a] Fachbereich Chemie der Philipps Universität,
Hans-Meerwein-Straße, 35032 Marburg, Germany
Fax: (internat.) +49-(0)6421-282-5653

DOI: 10.1002/ejic.200300640

Results and Discussion

Syntheses of the Dicarboxylatodigallium and -diindium Compounds 7 and 8

Treatment of the digallium(II) diiodide $R_2Ga_2I_2$ (**5**) with a suspension of silver benzoate in toluene at low temperature yielded colorless crystals of **7**, after recrystallization of the crude product from cyclopentane, in an almost quantitative yield. The integration ratio of the ^1H NMR spectrum showed one phenyl group per alkyl substituent, as expected for the complete replacement of both iodine atoms by benzoato groups. The resonance of the methyl protons appears at $\delta = 0.52$ ppm, which is in the characteristic range of compounds containing a Ga−Ga single bond. The molecular structure of **7**, possessing an intact Ga−Ga bond, was verified by an X-ray crystal-structure determination (see below) and is shown schematically in Equation (1). Compound **7** is thermally rather stable, with a melting point of 222 °C.



(1)

[R = C(SiMe3)3]

We hoped to synthesize the corresponding diindium(II) carboxylate **8** by the treatment of the dimeric subhalide $(R_2In_2Br_2)_2$ (**4**) with silver benzoate under similar reaction conditions. However, elemental indium precipitated, and the course of the reaction was more complicated. Crystals of the colorless product **8** could be obtained in very small quantities only. Interestingly, the diindium dicarboxylate **8** was finally isolated in 74% yield when we treated the triindium diiodide $R_3In_3I_2$ (**6**) with silver benzoate at low temperature [Equation (1)]. The silver iodide precipitate became black even at low temperature and in the dark, which may be caused by the formation of elemental indium as a by-product. However, tris(trimethylsilyl)methane, a possible second product of a disproportionation reaction, could not be detected by NMR spectroscopy. Formation of the tetraindium cluster **2** as another possible side product could not be verified by NMR spectroscopy or its characteristic violet color, either. The crude product of the reaction shows two further $SiMe_3$ resonances at $\delta = 0.45$ and 0.41 ppm, which may result from secondary products of the disproportionation but could not be assigned unambiguously.

Compound **8** is less stable than its digallium analogue and decomposes already at 158 °C with the formation of a red-brown solid.

Molecular Structures

Compounds **7** and **8** (Figure 1 and 2, respectively) contain a Ga−Ga or an In−In single bond terminally coordinated by two tris(trimethylsilyl)methyl groups and bridged by two carboxylato ligands. The bridging of metal-metal bonds by carboxylato groups is a quite common structural motif in transition metal compounds,[10] however, it is extraordinarily rare in main-group chemistry.[11] While Ga−Ga bonds bridged by carboxylato groups have been reported by our group previously,[7,8] the bridging of an In−In bond is observed for the first time in compound **8**. Owing to the relatively long In−In bonds compared to Ga−Ga distances, and the small bite of the chelating ligand, such a structure was totally unexpected. According to quantum-chemical calculations the terminal coordination of carboxylato groups is very unfavorable because of the rather high energy required for the deformation of the inner OCO angle.[8] Because of this inflexibility, a terminal arrangement, with the coordination of only one metal atom, leads to a relatively short distance between the inner carbon atom of the chelate and the Ga or In atoms, which results in considerable steric and electrostatic repulsion.

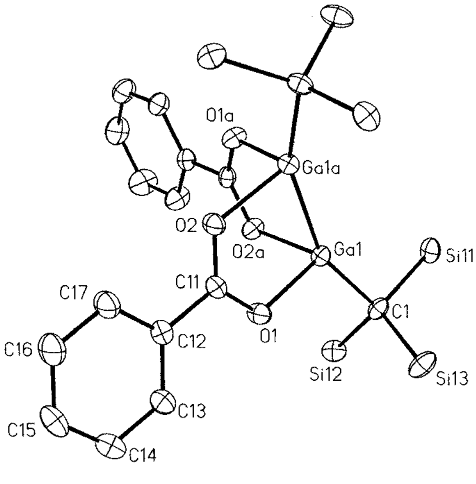


Figure 1. Molecular structure and numbering scheme of compound **7**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; selected bond lengths (pm) and angles (°): Ga1−Ga1′ 240.48(7), Ga1−C1 198.9(2), Ga1−O1 200.6(1), Ga1−O2′ 202.9(1); C1−Ga1−Ga1′ 156.38(6), O1−Ga1−O2′ 91.90(6), O1−Ga1−Ga1′ 88.95(4), O2′−Ga1−Ga1′ 85.95(4); Ga1′ and O2′ generated by $-x, y, -z + 3/2$

The rigidity of the CO_2 backbone results in almost indistinguishable C−O bond lengths [127.1 pm (**7**) and 126.8 pm (**8**), on average] and O−C−O bond angles [124.7° (**7**) and 124.9° (**8**)]. Thus, the bite of the carboxylato ligands [225.2 pm (**7**) and 224.9 pm (av., **8**)] is almost the same in both compounds despite the very different covalent radii of gallium and indium. A strong strain must result, which causes short E−E bond lengths. While that of the digallium compound **7** (240.5 pm) is in the lower range of Ga−Ga single-

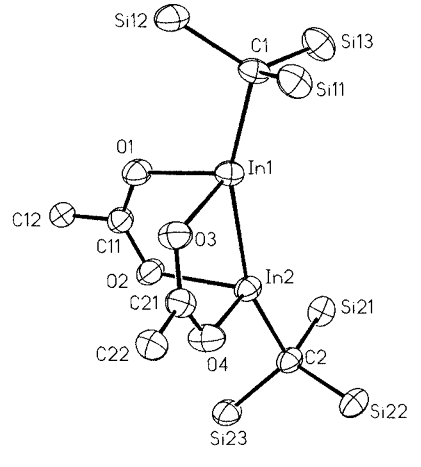


Figure 2. Molecular structure and numbering scheme of compound **8**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; only the *ipso*-carbon atoms of the phenyl groups are shown; selected bond lengths (pm) and angles (°) [the atoms In3, In4, C3, C4, O5, O6, O7 and O8 belong to the second independent molecule not shown here]: In1−In2 265.44(9), In3−In4 265.38(8), In1−C1 217.2(2), In2−C2 216.7(2), In3−C3 217.0(2), In4−C4 216.9(2), In1−O1 222.8(2), In1−O3 222.8(2), In2−O2 221.6(2), In2−O4 221.1(2), In3−O5 221.4(2), In3−O7 222.8(2), In4−O6 222.4(2), In4−O8 221.3(2); C1−In1−In2 158.74(6), C2−In2−In1 161.07(6), C3−In3−In4 160.43(6), C4−In4−In3 160.50(6), O1−In1−O3 89.93(6), O2−In2−O4 90.77(7), O5−In3−O7 90.38(7), O6−In4−O8 90.79(7), O1−In1−In2 85.13(4), O3−In1−In2 83.58(4), O2−In2−In1 83.99(4), O4−In2−In1 85.53(5), O5−In3−In4 85.15(4), O7−In3−In4 83.41(4), O6−In4−In3 84.01(4), O8−In4−In3 85.63(5)

bond lengths reported for digallium(II) halides $Ga_2X_4(L)_2$,[12] for instance, and is similar to that of the starting subhalide **5** (240.1 pm), the bridging of the In−In bond forces a very close In−In contact in **8** of 265.4 pm, which, to the best of our knowledge, is the shortest value reported so far.[13] The In−In single bonds in the starting subhalides **4** and **6** (Scheme 1) are considerably longer (282 pm on average).[3,6] The longer E−E bond in **8** compared to **7** causes slightly more acute E−E−O angles of 84.6° (versus 87.5° in **7**) and larger E−O−C angles of 122.3° (119.3° in **7**). The carboxylato ligands of both compounds are arranged almost ideally perpendicular to one another (O−E−O 91.9° and 90.5°, respectively). In accordance with the almost linear C−E−E groups (156.4° and 160.2°), the particular bonding situation of these compounds is described by sp-hybridized Ga or In atoms[8] so that both E−O bonds are mainly formed by two *p*-orbitals of each central atom. The phenyl substituents in both compounds are almost ideally co-planar with the carboxylato groups (angles between the normals of the corresponding planes 2.1° in **7** and 1.4 to 6.9° in **8**).

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene and diisopropyl ether over Na/benzophenone; cyclopentane over $LiAlH_4$). The compounds $R_2Ga_2I_2$ (**5**)[5] and $R_3In_3I_2$ (**6**)[6] were synthesized according to literature procedures. Commercially available silver benzoate (99%; Aldrich) was employed without further purification.

Synthesis of $R_2Ga_2(\mu\text{-}O_2CC_6H_5\text{-}O,O')_2$ [7; R = $C(SiMe_3)_3$]: A suspension of silver benzoate (69 mg, 0.301 mmol) in 20 mL of toluene was cooled to −90 °C and treated with a solution of the diiodide **5** (129 mg, 0.151 mmol) in 10 mL of toluene. The mixture was stirred and slowly warmed to −65 °C. The precipitate was filtered off at −70 °C, and subsequently the solvent was removed in vacuo at room temperature. The yellowish solid residue was recrystallized from cyclopentane, cooling from 20 to −15 °C. Yield: 124 mg (97%), colorless crystals, m.p. (argon, sealed capillary): 222 °C. ^1H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.52 (s, 27 H, $SiMe_3$), 6.99 (m, 3 H, phenyl), 8.30 (m, 2 H, phenyl) ppm. ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ = 5.0 (GaC), 5.5 ($SiMe_3$), 128.7 and 130.8 (*m*- and *p*-C of phenyl), 131.4 and 133.7 (*ipso*- and *p*-C of phenyl), 177.6 (CO_2) ppm. IR (CsBr, nujol): $\tilde{\nu}$ = 1597 w phenyl; 1526 m νCO_2; 1462 vs. paraffin; 1411 s δCH_3; 1377 vs. paraffin; 1306 w, 1260 s δCH_3; 1174 vw, 1126 m, 1096 s, 1025 s δCH, νCC; 858 vs, 805 s, 754 vw, 718 m $\rho CH_3(Si)$; 699 w, 684 w $\nu_{as}SiC$; 639 vw, 625 vw $\nu_s SiC$; 513 w, 468 w, 373 vw νGaC, νGaO.

Synthesis of $R_2In_2(\mu\text{-}O_2CC_6H_5\text{-}O,O')_2$ [8; R = $C(SiMe_3)_3$]: Silver benzoate (50 mg, 0.218 mmol) was suspended in 20 mL of toluene and cooled to −90 °C. The suspension was treated with a solution of the triindium diiodide **6** (138 mg, 0.107 mmol) in 15 mL of toluene. A black precipitate was formed immediately, which was filtered off at −70 °C. The solvent was removed in vacuo at room temperature. The colorless residue was recrystallized from diisopropyl ether, cooling from 20 to 8 °C. Yield: 82 mg (74%; **8**·O*i*Pr_2); colorless crystals which include up to one molecule of diisopropyl ether per formula unit of **8**; m.p. (argon, sealed capillary): 158 °C (dec.). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.49 (s, 27 H, $SiMe_3$), 1.06 (d, $^3J_{H,H}$ = 6 Hz, 6 H, Me of *i*Pr_2O), 3.43 (sept, $^3J_{H,H}$ = 6 Hz, 1 H, CH of *i*Pr_2O), 7.03 (m, 3 H, phenyl), 8.33 (m, 2 H, phenyl) ppm. ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ = 5.6 ($SiMe_3$), 15.5 (InC), 23.0 (Me of *i*Pr_2O), 68.1 (CH of *i*Pr_2O), 128.5 and 130.6 (*m*- and *p*-C of phenyl), 132.8 and 133.1 (*ipso*- and *p*-C of phenyl), 176.6 (CO_2) ppm. IR (CsBr, paraffin): $\tilde{\nu}$ = 1592 w phenyl; 1528 m νCO_2; 1460 vs. paraffin; 1377 vs. paraffin; 1306 vw, 1260 s δCH_3; 1124 m, 1086 m, 1025 s δCH, νCC; 859 vs, 843 s, 804 m, 718 m $\rho CH_3(Si)$; 699 w, 680 w $\nu_{as}SiC$; 654 vw, 614 vw $\nu_s SiC$; 515 w, 460 m νGaC, νGaO.

Crystal-Structure Determinations: Single crystals of compounds **7** and **8** were obtained by cooling solutions in cyclopentane (−15 °C, **7**) or diisopropyl ether (8 °C, **8**). Crystal data and structure-refinement parameters are given in Table 1. The molecules of compound **7** reside on a crystallographic twofold rotation axis. They crystallize with two cyclopentane molecules per formula unit, which can easily be removed on evacuation. A slight disorder was observed for the $C(SiMe_3)_3$ group; owing to the small occupation factor of 0.055, only the silicon atoms were refined on split positions. Compound **8** crystallizes with two independent molecules in the asymmetric unit, which further comprises two diisopropyl ether molecules. A disorder was observed for the $C(SiMe_3)_3$ group at C4, all atoms were refined at split positions with occupation factors of 0.76 and 0.24. A minor disorder was further detected for the $C(SiMe_3)_3$ group at C2; owing to the small occupation of the second position (0.07), only the silicon atoms of the minor component were refined.

CCDC-218887 (**7**) and -218888 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cam-

Table 1. Crystal data, data collection parameters, and structure refinement of compounds **7** and **8**[a]

	7	**8**
Formula	$C_{34}H_{64}Ga_2O_4Si_6 \cdot 2C_5H_{10}$	$C_{34}H_{64}In_2O_4Si_6 \cdot OC_6H_{14}$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ no. 15[14]	$P2_1/c$ no. 14[14]
Z	4	8
Temperature [K]	193(2)	193(2)
$d_{\text{calcd.}}$ [g/cm^3]	1.211	1.295
a [pm]	2224.6(2)	2260.3(5)
b [pm]	1452.01(10)	2814.9(6)
c [pm]	1774.3(2)	1782.8(4)
β [°]	109.47(3)	110.31(3)
V [10^{-30} m^3]	5403.6(9)	10638(4)
μ [mm^{-1}]	1.166	1.037
Crystal size [mm]	0.4 × 0.3 × 0.3	0.4 × 0.3 × 0.12
Diffractometer	STOE IPDS	
Radiation	Mo-K_α radiation; graphite monochromator	
θ range [°]	1.90 to 25.93	1.42 to 26.24
Index ranges	$-27 \le h \le 27$ $-17 \le k \le 17$ $-21 \le l \le 21$	$-28 \le h \le 28$ $-34 \le k \le 32$ $-22 \le l \le 22$
Independent reflections	5238 [R(int) = 0.0495]	21356 [R(int) = 0.0415]
Reflections $I > 2\sigma(I)$	4040	16776
Parameters	275	1131
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$ [$I > 2\sigma(I)$]	0.0307	0.0272
$wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.0758	0.0863
Max./min. residual [10^{30} e/m^3]	0.604/−0.480	0.804/−0.783

[a] Program: SHELXTL-Plus, SHELXL-97;[15] solutions by direct methods; full-matrix refinement with all independent structure factors.

bridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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

---

[1] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364; W. Uhl, A. Jantschak, *J. Organomet. Chem.* **1998**, *555*, 263.

[2] W. Uhl, R. Graupner, M. Layh, U. Schütz, *J. Organomet. Chem.* **1995**, *493*, C1; W. Uhl, A. Jantschak, W. Saak, M. Kaupp, R. Wartchow, *Organometallics* **1998**, *17*, 5009.

[3] W. Uhl, S. Melle, *Chem. Eur. J.* **2001**, *7*, 4216.

[4] Similar dimeric silylgallium(II) halides have been reported: N. Wiberg, T. Blank, M. Westerhausen, S. Schneiderbauer, H. Schnöckel, I. Krossing, A. Schnepf, *Eur. J. Inorg. Chem.* **2002**, 351; G. Linti, W. Köstler, *Angew. Chem.* **1996**, *108*, 593; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 550; A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3578; *Angew. Chem. Int. Ed.* **1999**, *38*, 3381. See also: H. Schnöckel, C. Klemp, in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2002**, p. 245−257.

[5] W. Uhl, A. El-Hamdan, M. Prött, P. Spuhler, G. Frenking, *Dalton Trans.* **2003**, 1360.

[6] W. Uhl, S. Melle, G. Geiseler, K. Harms, *Organometallics* **2001**, *20*, 3355.

[7] W. Uhl, I. Hahn, H. Reuter, *Chem. Ber.* **1996**, *129*, 1425; W. Uhl, R. Graupner, I. Hahn, T. Spies, W. Frank, *Eur. J. Inorg. Chem.* **1998**, 355; W. Uhl, T. Spies, W. Saak, *Eur. J. Inorg. Chem.* **1998**, 1661; W. Uhl, T. Spies, D. Haase, R. Winter, W. Kaim, *Organometallics* **2000**, *19*, 1128; W. Uhl, L. Cuypers, M. Prött, K. Harms, *Polyhedron* **2002**, *21*, 511.

[8] W. Uhl, T. Spies, R. Koch, *J. Chem. Soc., Dalton Trans.* **1999**, 2385.

[9] W. Uhl, R. Graupner, S. Pohl, W. Saak, W. Hiller, M. Neumayer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 883.

[10] F. A. Cotton, L. M. Daniels, C. Lin, C. A. Murillo, *J. Am. Chem. Soc.* **1999**, *121*, 4538.

[11] H. Binder, B. Brellochs, B. Frei, A. Simon, B. Hettich, *Chem. Ber.* **1989**, *122*, 1049; S. Adams, M. Dräger, B. Mathiasch, *J. Organomet. Chem.* **1987**, *326*, 173.

[12] Some examples: J. C. Beamish, A. Boardman, R. W. H. Small, I. J. Worrall, *Polyhedron* **1985**, *4*, 983; C. E. F. Rickard, M. J. Taylor, M. Kilner, *Acta Crystallogr.* **1999**, *C55*, 1215; E. M. Gordon, A. F. Hepp, S. A. Duraj, T. S. Habash, P. E. Fanwick, J. D. Schupp, W. E. Eckles, S. Long, *Inorg. Chim. Acta* **1997**, *257*, 247; W. Hönle, G. Miller, A. Simon *J. Solid State Chem.* **1988**, *75*, 147; H. J. Cumming, D. Hall, C. E. Wright, *Cryst. Struct. Commun.* **1974**, *3*, 107.

[13] In_2X_4 adducts: F. P. Gabbaï, A. Schier, J. Riede, H. Schmidbaur, *Inorg. Chem.* **1995**, *34*, 3855; R. J. Baker, R. D. Farley, C. Jones, M. Kloth, D. M. Murphy, *Chem. Commun.* **2002**, 1196; S. M. Godfrey, K. J. Kelly, P. Kramkowski, C. A. McAuliffe, R. G. Pritchard, *Chem. Commun.* **1997**, 1001; M. Scholten, R. Dronskowski, T. Staffel, G. Meyer, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1741; H. Bärnighausen, *Z. Kristallogr.* **1989**, *186*, 16.

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

[15] *SHELXTL-Plus, Release 4.2* for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-ray Instruments Inc., Madison, USA, **1990**; G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Structures*, University of Göttingen, **1997**.

Received September 8, 2003
Early View Article
Published Online January 28, 2004