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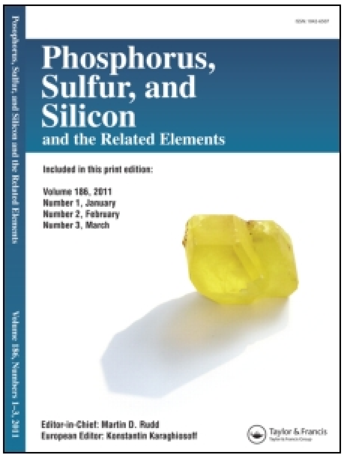

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GROUP 13 CLUSTER CHEMISTRY: ORGANOGALLIUM AND -INDIUM SUBHALIDES AND RADICALS

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GROUP 13 CLUSTER CHEMISTRY: ORGANOGALLIUM AND -INDIUM SUBHALIDES AND RADICALS

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(Received August 18, 2003; accepted October 3, 2003)

Organogallium or -indium subhalides are easily available by the halogenation of the corresponding tetrahedral clusters $E_4[C(SiMe_3)_3]_4$. *Three types of compounds are formed that retain the tetrahedral arrangement of In atoms or give chains with two or three Ga or In atoms connected by E—E bonds. These subhalides are suitable starting compounds for the synthesis of secondary products containing the elements in low oxidation states. Carboxylato derivatives or transition metal complexes were obtained on such a route. A persistent radical anion was formed on electron transfer to* $Ga_9(CMe_3)_9$.

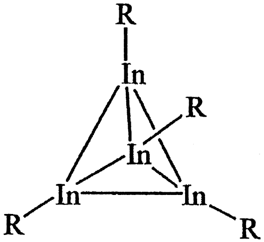
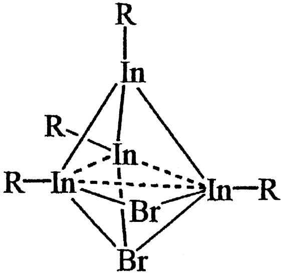
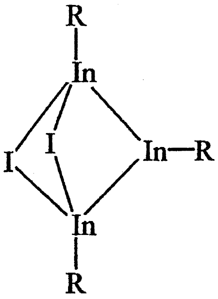
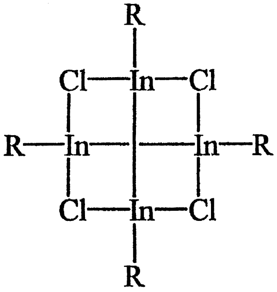
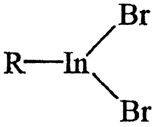
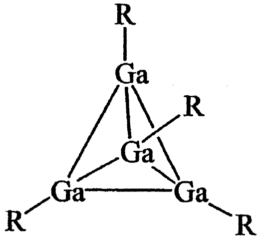
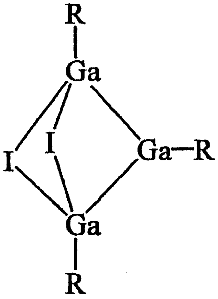
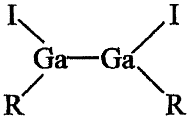
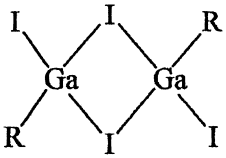
Keywords: Clusters; gallium; indium; subvalent compounds

Tetrahedral clusters of gallium or indium in an oxidation state of +1 E_4R_4 [E = Ga, In; R = $C(SiMe_3)_3$] are available by facile preparative routes.[1,2] They show an unprecedented chemical reactivity, and a broad variety of secondary products has been isolated.[3] At present, we are very interested in the syntheses of organogallium or organoindium subhalides derived from these clusters in order to obtain novel starting compounds suitable for the generation of cluster derivatives by salt elimination reactions. Another current topic is the electron transfer which, owing to results of cyclovoltammetry and EPR spectroscopy, should give persistent radical anions.[4]

I am very grateful to my coworkers Dr. Lars Cuypers, Abdel Hakim El-Hamdan, Andreas Lawerenz, and Dr. Sandra Melle. We all are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

Address correspondence to Werner Uhl, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany. E-mail: uhl@chemie.uni-marburg. de

TABLE I Organosubhalides of Gallium and Indium

	 **1**	 **5**	 **4**	 **3**	
average oxidation state	+1	+1.5	+1.66	+2	+3
	 **2** ($R = C(SiMe_3)_3$)		 **7**	 **6**	

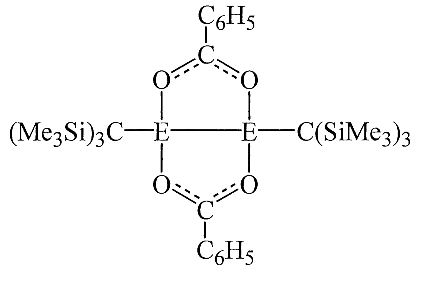
ORGANOGALLIUM AND ORGANOINDIUM SUBHALIDES

Alkylindium subhalides were obtained by treatment of the tetraindium cluster **1** with halogen donors such as C_2Cl_6 or $C_2H_4Br_2$. In the first case oxidation of all In atoms from +1 to +2 occurred, and a compound (**3**, Table I) was formed in which two In—In single bonds are bridged by four Cl atoms.[5] Partial oxidation to an average oxidation state of +1.5 gave compound **5**, in which the overall tetrahedral arrangement of the In atoms was retained.[5] One face is bridged by a Br atom, the second one bridges an edge of that particular face. The selectivity of the reactions with free halogens could be enhanced dramatically when mixtures with the corresponding aluminum trihalides were employed. Compound **4** was isolated by such a reaction. It possesses a chain of three In atoms connected by In—In single bonds.[6]

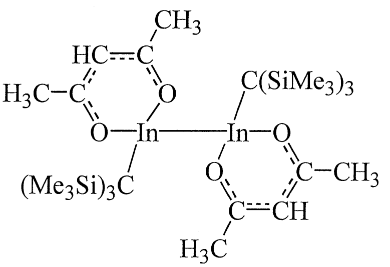
Ga subhalides derived from **2** are also summarized in Table I. Only the analogue of the tetrahedral In_4 compound **5** is missing, it may not be accessible at all owing to the instability of the tetrahedral arrangement of the Ga atoms in **2** with respect to dissociation. The compound R(I)Ga-Ga(I)R **6** was obtained by the reaction of the cluster with ICl in the presence of AlI_3.[7] In contrast to the corresponding diindium dihalides, compound **6** remains monomeric even in the solid state. The trigallium compound **7** was obtained by the reaction of **6** with $LiOCMe_3$, which did not result in substitution of halogen atoms (see next section), but initiates a partial disproportionation.

REACTIVITY OF SUBHALIDES

Replacement of the halogen atoms of these subhalides by other substituents may open the access to a broad variety of secondary products. However, the introduction of monodentate ligands such as amides or alcoholates (see above) did not succeed in any case. Chelating residues are required in order to isolate stable products still containing E—E bonds (Scheme 1). Schematic drawings of compounds derived from the subhalides are depicted in Scheme 2. The dibenzoato derivatives **8** were prepared by the treatment of **6** (E = Ga) and **3** (E = In) with silver benzoate. While facile routes for the synthesis of similar gallium species were reported in literature,[8] the method starting with organosubhalides is the only one to obtain those organoindium compounds. The E—E bonds are bridged by the carboxylato ligands. The molecules are not planar, but the chelating groups stand perpendicular to one another. A terminal coordination was observed for an acetylacetonato ligand (**9**).



8 (E = Ga, In)



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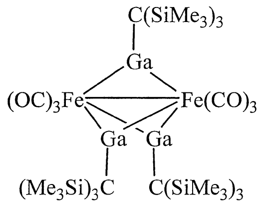
SCHEME 1

An interesting aspect of that chemistry is the synthesis of transition metal complexes containing Ga or In atoms. Such compounds were obtained by the reaction of the $R_2E_2X_2$ subhalides with $[Fe_2(CO)_8]^{2-}$ (Scheme 2). While numerous indium derivatives of transition metal carbonyls are available by the direct reaction of the tetraindium cluster **1** with binary carbonyls, the synthesis of corresponding gallium complexes requires other routes such as that one described here.



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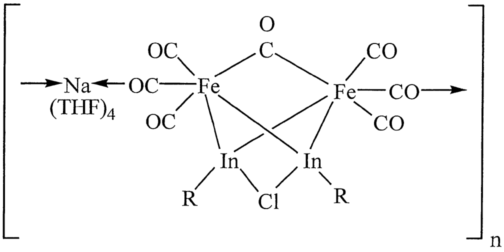


11

SCHEME 2

RADICAL ANIONS

Cyclovoltammetry revealed a reversible one-electron reduction for all clusters of the type E_nR_n to give relatively persistent radical anions. Up to now, we were not able to obtain these radicals in a preparative scale by starting with the tetrahedral clusters **1** or **2**. $Ga_9(CMe_3)_9$ **12** is another cluster of that type, which was formed as a by-product on treatment of $GaCl_3$ with $LiCMe_3$.[9] Its cluster may be described by a tricapped

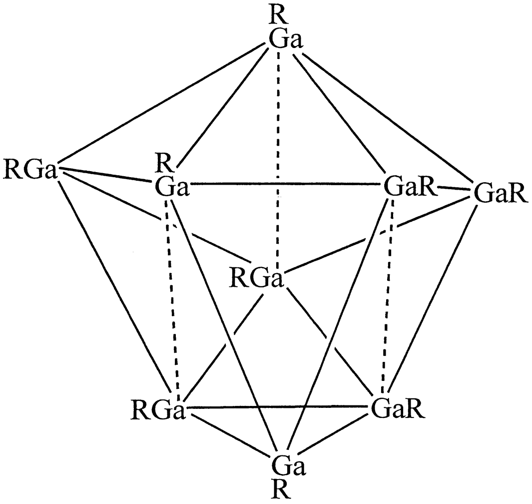
TABLE II Structural Parameters of $Ga_9(CMe_3)_9$ and its Radical Anion

	$Ga_9(CMe_3)_9$ experimental	$Ga_9(CMe_3)_9$ ab initio	$[Ga_9(CMe_3)_9]^{\cdot -}$ ab initio	$[Ga_9(CMe_3)_9]^{\cdot -}$ experimental
Ga—Ga[a]	258.8 pm	256.3 pm	254.4 pm	255.8 pm
Ga—Ga[b] (triangle)	267.0 pm	267.3 pm	275.1 pm	274.6 pm
Ga—Ga[c] (rectangle)	298.8 pm	298.2 pm	281.6 pm	281.9 pm

[a] Distances to the capping atoms.

[b] Distances along the edges of the triangles of the trigonal prism.

[c] Distances parallel to the threefold rotations axis (dashed lines in Scheme 3).



12,13 (R = CMe_3)

SCHEME 3

trigonal prism of Ga atoms (Scheme 3). The synthesis of its radical (**13**) succeeded by reduction with $Co(C_5Me_5)_2$.[10] Although the overall structure remained unchanged, the transfer of one electron resulted in some remarkable alterations of structural parameters, which are summarized in Table II.

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