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Dialkylaluminium-, -Gallium-, and -Indium-Based Poly-Lewis Acids with a 1,8-Diethynylanthracene Backbone

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Dedicated to Professor Hans H. Karsch on the occasion of his 65th birthday

Abstract: Potential host systems based on a rigid 1,8-diethynylanthracendiyl backbone were synthesised by treatment of 1,8-diethynylanthracene with the Group 13 trialkyls $AlMe_3$, $GaMe_3$, $InMe_3$, $AlEt_3$ and $GaEt_3$. The resulting products were characterised by IR and multinuclear NMR spectroscopy, elemental analyses and determination of their crystal structures by X-ray diffraction. The compounds are dimeric in the solid state and comprise two M_2C_2 heterocycles. Depending on the steric demand of the alkyl substituents at the metal atom, different types of binding modes were observed, which can be classified to lie between the ideals of side-on coordination with almost linear primary M−C≡C units and the 3c–2e coordination with symmetrically bridging alkynyl units in M-C-M bonds. As a solution in THF the dimers are broken into monomers and some are found to undergo ligand scrambling reactions.

Keywords: alkynes · aluminum · anthracene · gallium · Lewis acids

Introduction

The field of σ-alkynyl complexes is well documented in organometallic chemistry, especially with respect to synthetic use such as stereoselective epoxide-opening reactions.[1] In 1956, Wilke and Müller reported the first synthesis of an alkynyl aluminium compound ($Et_2AlC{\equiv}CEt$) by salt elimination from diethylaluminium chloride and $NaC{\equiv}CEt$.[2] This initiated the preparation of several other alkynyl aluminium compounds through metallation of CH-acidic terminal alkynes with dialkylaluminium hydride and the formation of elemental hydrogen or with trialkyl- or triarylaluminium under evolution of the corresponding gaseous or liquid hydrocarbon.[3] Nevertheless, until 2003 only a few alkynyl derivatives of Group 13 elements were described in the literature.[4] In particular, the bonding situation between the metal centres and alkynyl groups remained poorly understood due to the fact that only a few derivatives of dialkyl or diaryl compounds of Group 13 metals have been structurally characterised so far.[5] This situation has changed during the last few years and new results in alkynyl aluminium and gallium chemistry now provide more detailed insights into the structures and bonding situations.[6a–d] Uhl et al. figured out that the metallation of terminal alkynes leads to alkynyl compounds with two different binding modes of the bridging alkynido groups. The motifs depend on the steric demand of the substituents terminally attached to the metal atoms.[6b] All the quoted examples are dimeric and the carbanionic carbon atoms of the alkynido groups assume bridging positions. Smaller substituents (like methyl) result in a side-on-type coordination with linear Al−C≡C groups and an interaction with a second aluminium atom through a π-orbital localised at the α-carbon atom (type **A**, Scheme 1). More bulky substituents like *tert*-butyl lead to structures in which the C≡C triple bonds are oriented perpendicularly to the M···M axis of the central M_2C_2 heterocycle (type **B**, Scheme 1). It has to be noted that the energy differences between these two idealised borderline cases are very small and thus the structures are expected to be dependent on various factors including the size of all substituents in the molecules and intermolecular forces in the case of solid-state investigations (crystal structures). Intermediate cases are known;[7] in particular, a gas-phase structure determination of $(Me_2Al{-}C{\equiv}CH)_2$ has demonstrated a preference for the C_{2h} symmetric form (**A**) over the D_{2h} symmetric case (**B**) in

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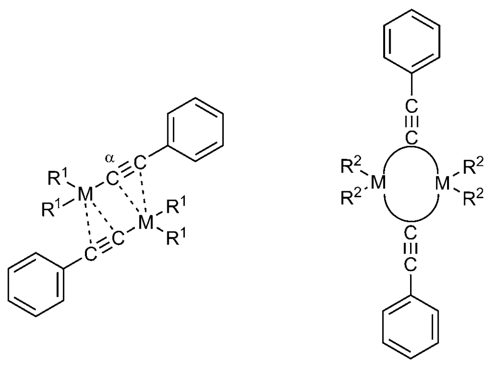


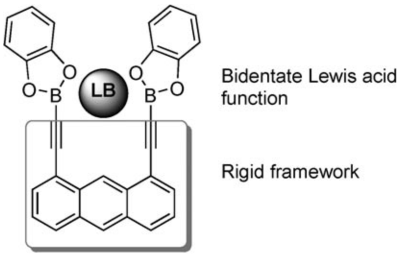
Type **A**
R^1= small substituent

Type **B**
R^2= bulky substituent

Scheme 1. Two different aggregation motifs found for dimeric σ-alkynyl complexes of the earth metals.

the absence of pronounced substituent or intermolecular interactions.[8]

There is still a distinct paucity of di- or oligometallated alkynyl frameworks with Group 13 elements, and in many of the few known cases the structural characterisation is missing. One of the earliest examples with non-metallic boron is 1,8-bis(catecholboranylethynyl)anthracene[9] (Scheme 2). The anthracenediethynyl unit incorporates the two rigid spacers (anthracene and acetylene) and is therefore a promising rigid framework with potential use in the field of host–guest chemistry. Both Lewis acidic boron functions are in close proximity to each other and offer a 5 Å bridging distance with minimal steric interference, which is advantageous in the synthesis of complexation agents for Lewis basic guests of suitable size.



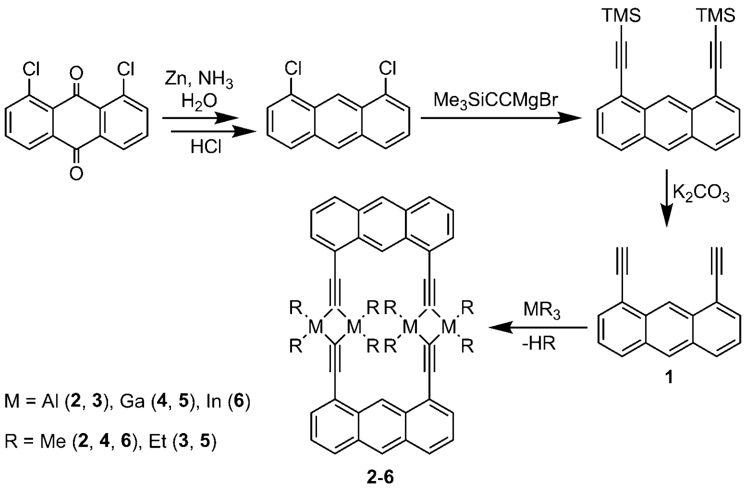
Scheme 2. Schematic representation of the functional units 1,8-bis(catecholboranylethynyl)anthracene.[7]

With respect to new insights into the field of host–guest systems of Group 13 elements aluminium, gallium and indium, with a tailor-made distribution of acceptor sites by a rigid backbone, we set out to functionalise the 1,8-anthracenediethynyl (**1**) backbone with Lewis acidic functionalities based on these elements. As for the above-mentioned boron compound, the new host molecules promise to be more highly associated towards a Lewis base than analogous complexes of simply monodentate chelating Lewis acid.[10] In this way we aim to contribute to the rapidly growing field of poly-Lewis acid chemistry.[11]

Results and Discussion

Synthesis of 1,8-diethynylanthracene (1): The synthesis of 1,8-diethynylanthracene (**1**) was performed by modified literature procedures: 1,8-dichloroanthraquinone was reduced to 1,8-dichloroanthracene[12] with zinc powder in aqueous ammonia, and the formed dihalide was coupled with a Grignard reagent (prepared by the reaction of trimethylsilylacetylene with ethynylmagnesium bromide) in the presence of a nickel catalyst.[13] Suitable reaction conditions had to be determined to prevent the formation of a monosubstituted byproduct and the homo-coupled 1,4-bis(trimethylsilyl)-1,3-butadiyne (TMS−C≡C−C≡C−TMS). In our hands, prolonged reaction times of the Kumada coupling to 48 h reflux were found to be advantageous, which is due to the fact that the substitution of the second chlorine functionalities takes place more slowly than that of the first. The homo-coupled byproduct was removed by sublimation (40 °C, 1 mbar). The last reaction step was a cleavage of the trimethylsilyl protecting groups by use of potassium carbonate (Scheme 3).

Reactions of 1 with trialkylaluminium, -gallium and -indium: Attempts to prepare a dilithiated 1,8-diethynylanthracene and to transmetallate this with dialkylmetal halides failed or did not turn out to afford suitable yields of doubly

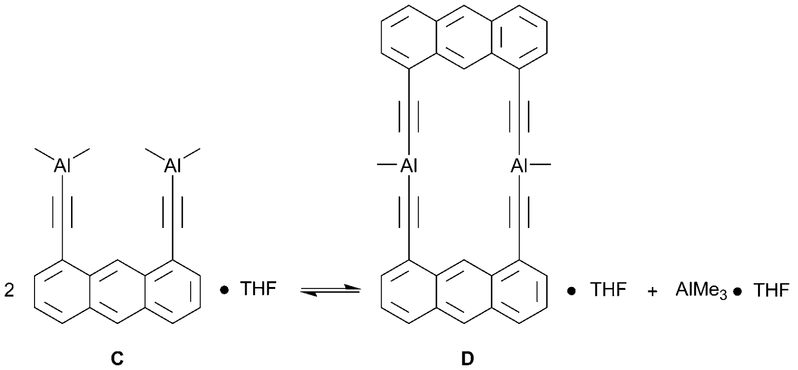


Scheme 3. General procedures for the syntheses of 1,8-bis(dialkylmetalethynyl)anthracenes.

metallated products. The successful dimetallation was achieved by treatment of 1,8-diethynylanthracene (**1**) with the metal trialkyls under evolution of the corresponding alkane (methane or ethane) in good yields (Scheme 3).[14] The products obtained in this way are bright yellow solids. They are virtually insoluble in non-polar solvents like toluene or hexane. Initiating the reactions requires temperatures of 50 to 75 °C. Catalytic amounts of auxiliary base (triethylamine) were employed in the reactions with aluminium trialkyls. The trialkylamine enhances the reactivity by decomplexation of AlR_3 and provides a reversible binding donor, which is important for later complexation of a Lewis base.[15]

IR and NMR spectroscopic studies: For all compounds, the triple-bond stretching frequencies measured in the solid state are close to 2054 cm^{-1}. This value is in accordance with literature-known triple-bond stretching frequencies of dimeric $Me_2PhCCAl$,[14a] $Me_2PhCCGa$[14a] and $Me_2PhCCIn$[14a] in benzene.

Due to the fact that the dimeric compounds **2**–**6** are insoluble in toluene or other hydrocarbon solvents, NMR spectroscopy experiments were carried out in $[D_8]$THF. The use of a donor solvent induces a disruption of the dimeric structure (see below for the solid-state structures). The ^{1}H NMR spectrum of **2** in $[D_8]$THF shows three singlets at $\delta = -0.67$, -0.70 and -0.96 ppm. These are characteristic for aluminium-bonded methyl groups and comply with the signals of the related compounds Me_3Al ($\delta = -0.96$ ppm), $(PhCC)AlMe_2$ ($\delta = -0.83$ ppm) and $(PhCC)_2AlMe$ ($\delta = -0.78$ ppm) in $[D_8]$THF.[14a] This might either be due to the simultaneous presence of monomers and dimers (see the crystal structures below) or due to possible redistribution reactions of ethynyl and methyl functionalities as depicted in Scheme 4. In addition, the number of signals and their relative intensities of the signals match the constitutions of the postulated products.



Scheme 4.

Further proof for the redistribution stems from the occurrence of two sets of signals for the protons of the anthracene backbone in the range between $\delta = 9.69$ and 7.34 ppm with the characteristic singlets at $\delta = 9.69$ and 9.56 ppm for protons bonded to C-9 (the position between the ethynyl groups). Note that such redistribution reactions have already been established for dimethyl(phenylethynyl)aluminium, -gallium or -indium. Their NMR spectra in $[D_8]$THF indicate such an equilibrium according to Equation (1).[14a]

$$2\,(PhCC)AlMe_2 \cdot THF \rightarrow Me_3Al \cdot THF + (PhCC)_2AlMe \cdot THF \qquad (1)$$

The spectrum of **3** shows the same features as the spectrum of **2**. A double set of signals is detected for the protons of the anthracene and two sets of signals for the ethyl substituents bonded to aluminium (two triplets at $\delta = 1.15$ and 0.99 ppm and two quartets at $\delta = 0.02$ and -0.12 ppm).

The spectra of compounds **4**, **5** and **6** do not indicate the occurrence of similar redistribution reactions as described above, as they show less signals for methyl or ethyl resonances in their ^{1}H NMR spectra. The proton signals of their ethyl or methyl substituents are found to be strongly shifted towards higher field ($\delta = -0.21$ ppm (**4**), 0.52 and 1.24 ppm (**5**), -0.23 ppm (**6**)), but only one set of signals is detected for each compound. The resonances of the protons attached to the anthracene backbone have similar shifts independent of the kind of metal atom and substituents attached to it. In this respect, the aluminium compounds **2** and **3** are thus clearly distinct in their behaviour from the gallium and indium compounds **4**, **5** and **6**.

Bonding situations and molecular structures

*1,8-Diethynylanthracene (**1**)*: For comparison with the metallated compounds, we determined the crystal structure of 1,8-diethynylanthracene (**1**; Figure 1). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane. It crystallises in the monoclinic space group $P2_1/n$. Three molecules are found in the asymmetric unit. Important bond lengths and angles are listed in Table 1. Comparison of corresponding parameter values for the three independent molecules show impressively how structural parameter values of relatively rigid molecules may scatter for the same molecule. The reliability of the lengths and angles in terms of a determination of values independent of the surrounding is at best 0.01 Å and 1° in this case, which corresponds to about three estimated standard deviations of the individual parameters. Nevertheless, within this range one is able to recognise structural trends.

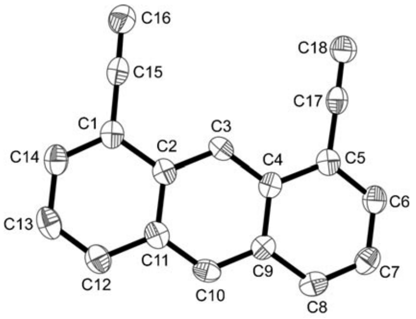


Figure 1. Molecular structure of 1,8-diethynylanthracene (**1**).

Table 1. Selected bond lengths [Å] and angles [°] of **1**.

	Molecule A	Molecule B[a]	Molecule C[a]
C1−C15	1.433(4)	1.436(3)	1.429(4)
C5−C17	1.431(4)	1.438(3)	1.433(4)
C15−C16	1.180(4)	1.174(3)	1.190(4)
C17−C18	1.188(4)	1.171(3)	1.185(4)
C14-C1-C15	120.1(2)	121.2(2)	120.7(3)
C2-C1-C14	119.7(2)	119.9(2)	120.1(3)
C2-C1-C15	120.2(2)	118.8(2)	119.2(2)
C6-C5-C17	120.5(2)	120.1(2)	120.8(2)
C4-C5-C6	119.8(2)	120.0(2)	120.1(3)
C4-C5-C17	119.7(2)	119.9(2)	119.1(2)
C1-C15-C16	179.4(3)	178.0(3)	179.3(3)
C5-C17-C18	179.0(3)	178.7(3)	178.1(3)

[a] The labelling scheme of molecule A is used. The other parameter values are the corresponding data from the other two molecules.

Due to the fact that all three structures are similar, only one of them is described in detail. The anthracene skeleton is planar with both alkyne substituents in plane. Only in molecule C is one alkyne group slightly displaced to one side of the anthracene plane by 1.4°.

The atoms C1 and C5 are trigonal-planar-coordinated with the three surrounding angles being close to 120°. The alkynyl groups are bonded to the anthracene skeleton with expectedly short bonds (sp−sp^2 bond); the bond C1−C15 measures 1.433(4) Å and C5−C17 measures 1.431(4) Å. These values are in the range observed for the corresponding ones in the free molecules of phenylacetylene (r_g = 1.400(3) Å by gas electron diffraction[16] and r_s = 1.448 Å by microwave spectroscopy[17]).

The alkynyl groups are almost linear (angles in molecule A: C1-C15-C16 179.4(3)° and C5-C17-C18 179.0(3)°), and the smallest of the six observed C−C≡C angles is 178.0(3)°, that is, is the largest deviation is 2°. The lengths of the bonds C15−C16 and C17−C18 are 1.180(4) and 1.188(4) Å, respectively. This is only slightly shorter than the standard length of a C≡C triple bond of 1.20 Å[18] and almost identical to the corresponding ones in gaseous phenylacetylene (r_g = 1.205(5) Å by gas electron diffraction[16] and r_s = 1.208 Å by microwave spectroscopy[17]). The bond lengths for the anthracene skeleton in **1** (1.36–1.45 Å) fall in the same range as for unsubstituted anthracene (1.37 to 1.43 Å)[19] and gaseous 1.392(6)–1437(4) Å[20]).

*1,8-Bis(dialkylmetalethynyl)anthracenes (**2**–**6**)*: Single crystals of compounds **2** to **6** were obtained by slowly cooling the reaction mixtures in toluene from around 50–70 °C to ambient temperature overnight. The molecular structures are shown in Figures 2 to 7. Due to structural similarities, compounds **2**, **4** and **6** (R = Me) and **3** and **5** (R = Et) are described together. Abnormalities or significant differences

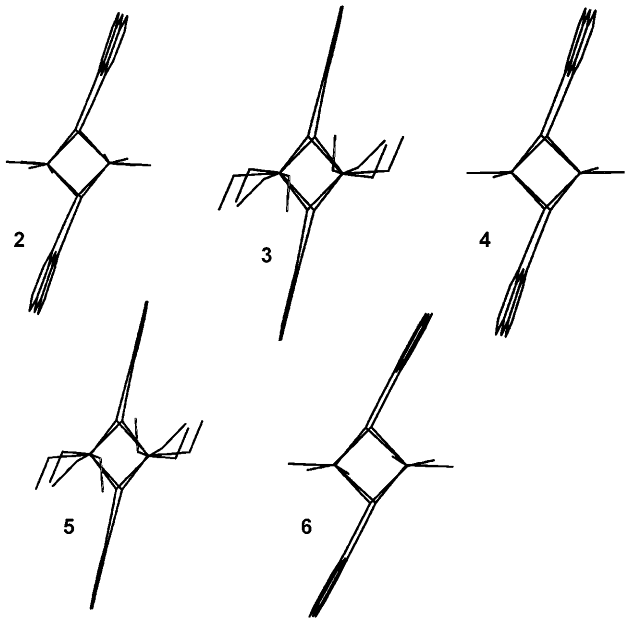


Figure 2. Wire models of compounds **2**–**6** in a view along the planes of the anthracene rings and on top of the M_2C_2 rings to illustrate the structural trends to the two binding modes shown in a general scheme in Scheme 5.

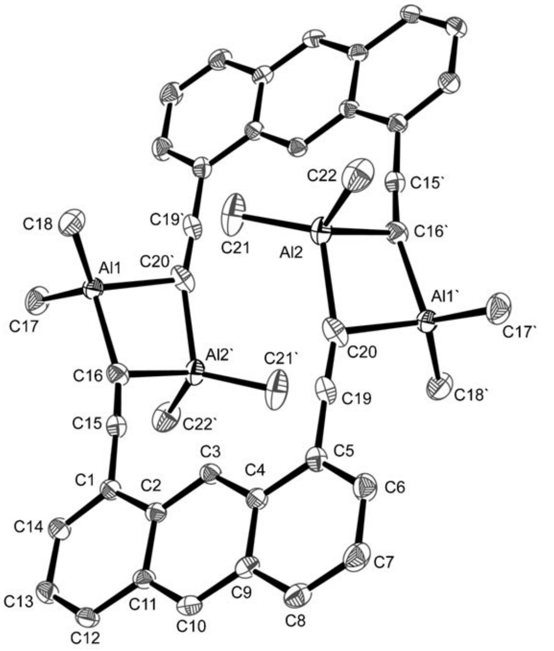


Figure 3. Molecular structure of dimeric 1,8-bis(dimethylalanylethynyl)anthracene (**2**).

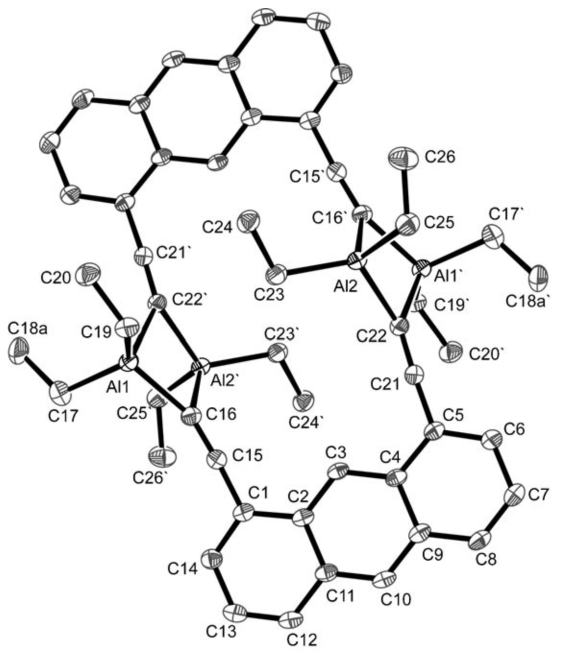


Figure 4. Molecular structure of dimeric 1,8-bis(diethylalanylethynyl)anthracene (**3**).

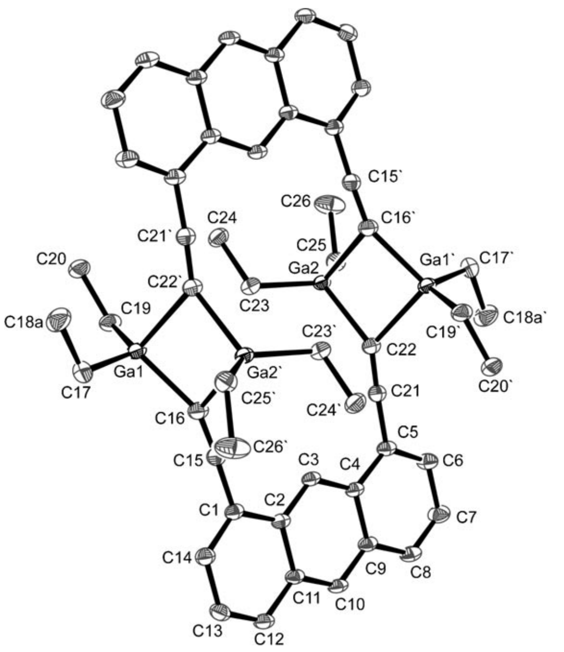


Figure 6. Molecular structure of dimeric 1,8-bis(diethylgallanylethynyl)anthracene (**5**).

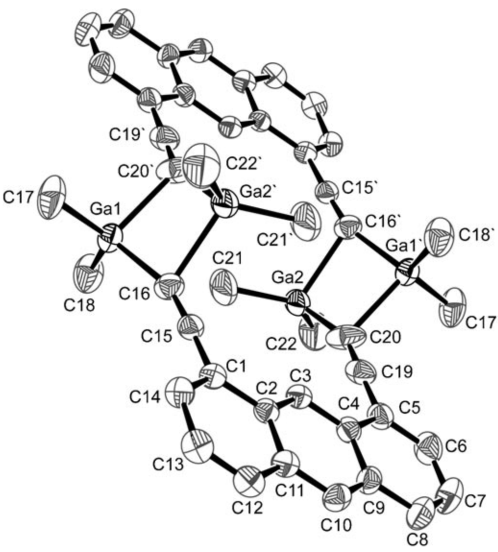


Figure 5. Molecular structure of dimeric 1,8-bis(dimethylgallanylethynyl)anthracene (**4**).

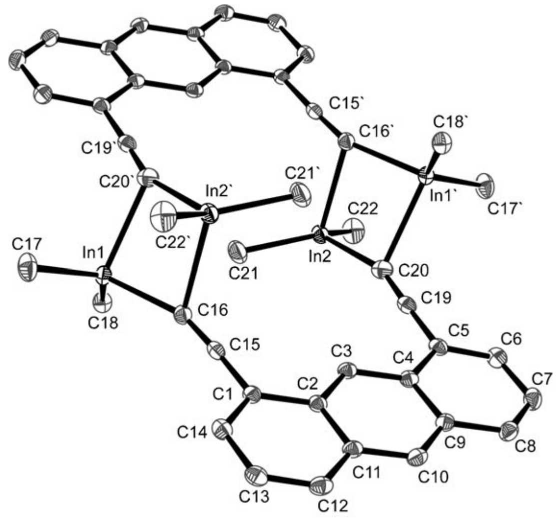
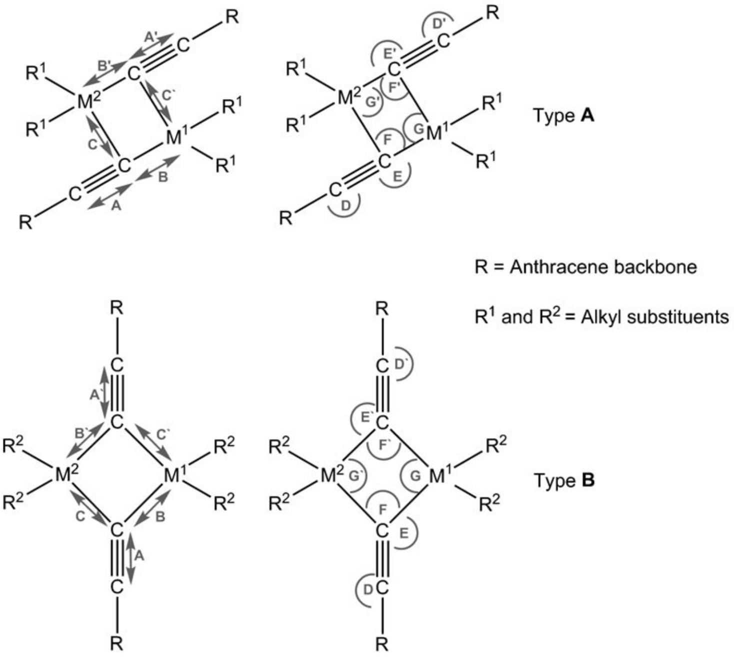


Figure 7. Molecular structure of dimeric 1,8-bis(dimethylindanylethynyl)anthracene (**6**).

will be mentioned separately. Figure 2 shows side views of compounds **2**–**6** that illustrate the two different types of binding modes. A general and ideal schematic representation of a side-on coordination (type **A**) and a 3c–2e bonding (type **B**) with important structural features is displayed in Scheme 5. Table 2 lists the corresponding bond lengths and angles of all compounds (**2**–**6**) for facilitated comparison and for a description of the bonding situations of methyl- and ethyl-substituted compounds. Additional structural parameter values of compounds **2**, **4** and **6** and **3** and **5** are compiled in Tables 3 and 4, respectively.

All compounds (**2**–**6**) crystallise in the triclinic system in the space group $P\bar{1}$. They form dimers linked by two M_2C_2 heterocycles. The carbanionic alkynyl carbon atoms thereby act as bridging units. The structural parameters listed in Table 2 indicate that **2**–**6** crystallise in aggregation modes, which differ from both the ideal side-on coordination and from geometries that representing 3c–2e bonding. The side-on coordination mode was earlier found for di(μ-phenylethynyl)bis(dimethylaluminium) or di(μ-phenylethynyl)bis(dimethylgallium).[6b] Close to ideal 3c–2e bonding was reported for di(μ-phenylethynyl)bis(di-*tert*-butylaluminium) and di(μ-phenylethynyl)bis(di-*tert*-butylgallium).[6b] Which of



Scheme 5. General schematic representation of important structural features of the central $M_2(C{\equiv}C)_2$ units of two different types of binding modes. The letters describe selected bond lengths (↔) and angles (∩) that emanate from side-on coordination (type **A**) and 3c–2e bonding (type **B**).

Table 2. Selected bond lengths [Å] and angles [°] of **2**–**6** (see Scheme 5 for an understanding of which bonds/angles the letters represent).

	2[a] (M = Al)	**3**[b] (M = Al)	**4**[a] (M = Ga)	**5**[b] (M = Ga)	**6**[a] (M = In)
A	1.219(2)	1.219(2)	1.209(3)	1.218(2)	1.219(3)
A′	1.217(2)	1.217(2)	1.209(3)	1.217(2)	1.218(3)
B	2.032(2)	2.044(2)	2.029(2)	2.056(2)	2.224(2)
B′	2.040(2)	2.053(1)	2.047(3)	2.072(1)	2.246(3)
C	2.141(1)	2.119(2)	2.237(3)	2.193(2)	2.437(2)
C′	2.129(2)	2.103(2)	2.203(2)	2.162(2)	2.430(2)
D	176.4(2)	176.3(1)	175.6(2)	176.2(2)	174.7(2)
D′	176.6(2)	177.2(1)	177.7(2)	177.0(2)	178.2(2)
E	162.2(1)	153.8(1)	160.7(2)	153.9(1)	161.4(2)
E′	159.8(1)	144.0(1)	157.2(2)	144.0(1)	159.4(2)
F	87.2(1)	84.9(1)	87.4(1)	84.4(1)	90.0(1)
F′	87.3(1)	85.1(1)	87.9(1)	84.8(1)	89.6(1)
G	90.7(1)	93.0(1)	90.4(1)	93.4(1)	87.8(1)
G′	90.2(1)	92.3(1)	89.0(1)	92.1(1)	87.2(1)

[a] Methyl as substituent. [b] Ethyl as substituent.

Table 3. Selected bond lengths [Å] and angles [°] of **2**, **4** and **6**.

	2[a] (M = Al)	**4**[a] (M = Ga)	**6**[a] (M = In)
M1−C16	2.032(2)	2.029(2)	2.224(2)
M1−C20′	2.129(2)	2.203(3)	2.430(2)
M1−C17	1.959(2)	1.966(2)	2.156(3)
M1−C18	1.954(2)	1.952(2)	2.150(2)
M2′−C20′	2.040(2)	2.047(3)	2.246(3)
M2′−C16	2.141(1)	2.237(2)	2.437(2)
M2′−C21′	1.948(2)	1.956(3)	2.144(3)
M2′−C22′	1.951(2)	1.960(3)	2.146(3)
C16−C15	1.219(2)	1.209(3)	1.219(3)
C20′−C19′	1.217(2)	1.209(3)	1.218(3)
M1−M2′	2.879(1)	2.951(1)	3.298(1)
M1-C16-M2′	87.2(1)	87.4(1)	90.0(1)
M1-C20′-M2′	87.3(1)	87.9(1)	89.6(1)
C16-M1-C20′	90.7(1)	90.4(1)	87.8(1)
C16-M2′-C20′	90.2(1)	89.0(1)	87.2(1)
C14-C1-C15	117.9(1)	118.4(2)	118.3(2)
C6′-C5′-C19′	119.0(1)	119.4(2)	119.9(2)

[a] Methyl as substituent.

Table 4. Selected bond lengths [Å] and angles [°] of **3** and **5**.

	3[a] (M = Al)	**5**[a] (M = Ga)
M1−C16	2.044(2)	2.056(2)
M1−C22′	2.103(1)	2.162(2)
M1−C17	1.970(2)	1.984(1)
M1−C19	1.963(2)	1.974(2)
M2′−C22′	2.053(1)	2.072(1)
M2′−C16	2.119(2)	2.193(1)
M2′−C23′	1.957(1)	1.962(2)
M2′−C25′	1.965(1)	1.974(2)
C16−C15	1.219(2)	1.218(2)
C22′−C21′	1.217(2)	1.217(2)
M1−M2′	2.811(1)	2.885(2)
M1-C16-M2′	84.9(1)	84.4(1)
M1-C22′-M2′	85.1(1)	84.8(1)
C16-M1-C22′	93.0(1)	93.4(1)
C16-M2′-C22′	92.3(1)	92.1(1)
M1-C16-C15	153.8(1)	153.9(1)
M1-C22′-C21′	130.4(1)	130.6(1)
M2′-C16-C15	120.3(1)	120.6(1)
M2′-C22′-C21′	144.0(1)	144.0(1)
C14-C1-C15	118.0(1)	118.4(1)
C6′-C5′-C21′	118.4(1)	118.6(1)

[a] Ethyl as substituent.

these modes is adopted depends primarily on the steric demand of the alkyl substituents.

As already outlined in the Introduction, in aggregation type **A** the metal atoms can be described as σ-bonded to one alkynyl group of one 1,8-anthracenediethynyl unit (stronger bond) and side-on coordinated to the alkynyl group of the other 1,8-anthracenediethynyl unit (weaker secondary interaction between the metal atom and the π-electrons of the C≡C bond). It may be seen as consisting of two distinct monomer units joined by long secondary bonds between the metal atom of one monomer unit and the α-C atom of the C≡C group in the other unit. In the case of the earlier reported di(μ-phenylethynyl)bis(dimethylaluminium) or di(μ-phenylethynyl)bis(dimethylgallium),[6] the M−C≡C groups are almost linear (173.7° and 173.5°) and have relatively short M−C bonds (1.994 and 2.001 Å). The C≡C bond lengths are close to the standard triple bond length of 1.20 Å. The remaining M−C distances of the asymmetric bridge perpendicular to the M−C≡C groups are strongly elongated to 2.224 and 2.378 Å.

Compared with these results, the new compounds with metal-bound methyl substituents, **2**, **4** and **6**, contain angles M−C≡C far away from the ideal 180° by 17.8° and 20.2° for **2**, by 19.3° and 22.8° for **4** and by 18.6° and 20.6° for **6**. The M1−C16 bonds (2.032(2) (**2**), 2.029(2) (**4**) and 2.224(2) Å (**6**)) are somewhat shorter than the M2′−C20′ bonds

(2.040(2) (**2**), 2.047(3) (**4**) and 2.246(3) Å (**6**)), but altogether longer than for the monodentate alkynides[6b] described above. Compared to this, the metal-to-bridging-carbon distances of M1−C20′ and M2′−C16 are elongated by 0.107 and 0.089 Å for **2**, by 0.208 and 0.156 Å for **4** and by 0.213 and 0.184 Å for **6**. This trend is approximately proportional to the widening of the M-C-M angles and to the compression of the C-M-C angles. The larger the radii of the metal atoms, the more widened are the angles M2′-C16-M1 and M2′-C20′-M1, which have nearly the same value for the three individual compounds (87.2° and 87.3° for **2**, 87.4° and 87.9° for **4** and 90.0° and 89.6° for **6**). In addition, the M1−M2′ distances are found to be elongated with increasing metal atom size (2.879(1) Å for Al1−Al2′, 2.951(1) Å for Ga1−Ga2′ in **4** and 3.298(1) Å for In1−In2′ in **6**). The C≡C bond lengths are in the range of 1.219 to 1.209 Å and thus nearly equal to the usual acetylenic bond length and the C≡C bond in $CH_3-C{\equiv}C-CH_3$ determined by gas-phase electron diffraction to 1.206(1) Å.[16b] This can be rationalised by the donation of π electrons into empty orbitals of the metal atoms. The four-membered rings formed by the metal atoms and the two bridging carbon atoms are not planar.

A representative structure for a 3c–2e bonding is the dimeric trimethylaluminium molecule with the bridging methyl group interacting equally with both Al atoms and an Al···Al distance of 2.619 Å. Two other examples on the basis of three-centre two-electron bonds are di(μ-phenylethynyl)-bis(di-*tert*-butylaluminium) and di(μ-phenylethynyl)bis(di-*tert*-butylgallium).[6b] The C≡C triple bonds in these complexes are oriented perpendicularly to the M···M axes of the central M_2C_2 heterocycles. For these established compounds, all four M−C distances of the central rings fall over a relatively narrow range between 2.063 and 2.097 Å for the aluminium compound and between 2.110 and 2.141 Å for the gallium compound. The M−C≡C angles are 136.4° and 135.6° for the gallium and 129.7° and 143.0° for the aluminium derivative. The C≡C triple bond lengths are close to the standard C≡C bond length (1.20 Å). The M···M distances are shorter (2.864 Å for Al···Al and 2.951 Å for Ga···Ga) than the ones in the side-on coordination type.

Compared to this, the new compounds with metal–ethyl substituents, **3** and **5**, with their slightly smaller ethyl substituents do not feature a pure 3c–2e bonding motif. The four-membered M_2C_2 rings are not planar and the M−C bond lengths are unequal. The distances M1−C16 and M2′−C22′ are 2.044(2) and 2.053(1) Å for **3** and 2.056(2) and 2.072(1) Å for **5**. M1−C22′ and M2′−C16 are 2.103(2) and 2.119(2) Å for **3** and 2.430(2) and 2.437(2) Å for **5**. In addition, the C≡C bonds are not perpendicular to the M···M axes and the M−C≡C angles are: M1-C16-C15 153.8(1)°, M2′-C16-C15 120.3(1)°, M1-C22′-C21′ 130.4(1)° and M2′-C22′-C21′ 144.0(1)° for **3**. The corresponding angles for compound **5** are M1-C16-C15 153.9(1)°, (M2′-C16-C15 120.6(1)°, M1-C22′-C21′ 130.6(1)° and 144.0(1)° M2′-C22′-C21′.

It is worth mentioning the deformation caused by a tilt of the ethynyl groups towards one metal atom of the rings. The C≡C triple bond lengths C16≡C15 and C22′≡C21′ of 1.217 to 1.219 Å are somewhat larger than the accepted standard value of 1.20 Å.

The non-bonded M···M distances are 2.811(1) Å for the Al···Al (**3**) and 2.951(1) Å for the Ga···Ga cases (**5**). This is comparable to the values in structures **2** and **4**, respectively. It is possible that these results indicate an attractive interaction between the π-bonding electrons of the C≡C bond and the metal atoms (side-on coordination). The facts outlined here illustrate that the metal–ethyl-substituted compounds adopt a kind of intermediate bonding situation between the side-on coordination and the 3c–2e bonding motif. This interpretation is also supported by the fact that the length M1−C22′ and M2−C16′ exceed that of M1−C16 and M2−C22′ by 0.05 and 0.08 Å in the case of **3** and 0.09 and 0.14 Å in the case of **5**.

Conclusion

Alkane elimination is a process efficient enough to be employed to prepare dimetallated alkynyl complexes of Group 13 elements, that is, to affect both subsequent metallation steps in reasonable to high yields. The new poly-Lewis acids with a 1,8-diethynylanthracenediyl backbone form dimers with different types of molecular structures. In the solid state, tetranuclear compounds with a relatively fixed arrangement of the four metal atoms are present. Their structural motifs depend in a subtle way on the steric demand of the alkyl groups attached to the Group 13 metal atoms. A motif closer to side-on coordination was found for the dimers **2**, **4** and **6** with small methyl substituents, whereas with the only slightly larger ethyl substituents the structural motif tends more toward a 3c–2e bonding situation (compounds **3** and **5**). In a solution of the donor solvent THF, the dimers are broken into solvated monomers that are bidentate Lewis acids; some of these undergo ligand-scrambling reactions.

Experimental Section

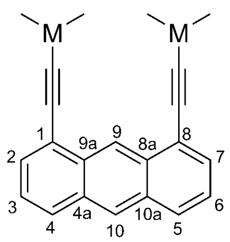
General: 1,8-Diethynylanthracene (**1**) was synthesised by modified literature-known procedures.[12,13] Its purification was performed by column chromatography on silica gel 60 (0.04–0.063 mm mesh) with pentane as the mobile phase to separate the monosubstituted byproduct in the first fraction. All metallation reactions were carried out under an anhydrous, inert atmosphere of nitrogen or argon using standard Schlenk and glovebox techniques in dried solvents (THF and toluene were dried over potassium and sodium and were freshly condensed before being used for the reactions). [D$_8$]THF was dried over Na/K alloy and the auxiliary base triethylamine was dried over CaH_2 and degassed. Trimethylaluminium, triethylaluminium, trimethylgallium, triethylgallium and trimethylindium were commercially available. NMR spectroscopic measurements were recorded using a Bruker DRX 500 and a Bruker Avance 600 at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ([D$_8$]THF, ^{1}H: $\delta = 1.73$ and 3.58 ppm, ^{13}C: $\delta = 25.5$ and 67.7 ppm). Elemental analyses were performed using a Leco CHNS 932 instrument.

Table 5. Crystallographic data for **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{18}H_{10}$	$C_{44}H_{40}Al_4$	$C_{52}H_{56}Al_4$	$C_{44}H_{40}Ga_4$	$C_{52}H_{56}Ga_4$	$C_{44}H_{40}In_4$
M_r	226.26	676.68	788.89	847.64	959.85	1028.04
crystal	yellow plates	yellow fragment	yellow fragment	yellow fragment	yellow fragment	yellow fragment
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.343(2)	8.664(1)	9.901(1)	8.714(1)	9.913(1)	7.350(1)
b [Å]	11.545(1)	10.731(1)	10.457(1)	10.756(1)	10.394(1)	12.221(1)
c [Å]	23.693(3)	12.418(1)	12.904(1)	12.411(1)	12.880(1)	12.383(1)
α [°]	90	65.26(1)	67.07(1)	65.86(1)	66.53(1)	61.43(1)
β [°]	94.42(1)	81.69(1)	82.10(1)	81.89(2)	81.62(1)	88.00(1)
γ [°]	90	66.36(1)	64.17(1)	66.73(1)	64.62(1)	88.75(1)
V [Å^3]	3638.8(7)	960.2(1)	1106.5(1)	974.9(1)	1099.2(1)	970.9(2)
Z	12	1	1	1	1	1
ρ_{calcd} [g cm^{-3}]	1.239	1.170	1.184	1.444	1.450	1.758
μ [mm^{-1}]	0.070	0.151	0.140	2.763	2.459	2.374
$2\theta_{max}$ [°]	25	30	27.47	30	30	27.50
reflns collected	28692	21780	34117	35102	52593	25891
independent reflns	6402	5572	5059	5665	6398	4456
R_{int}	0.088	0.034	0.033	0.038	0.038	0.037
observed reflns	3421	4488	4254	4419	5603	3895
$\rho_{min/max}$ [e Å^{-3}]	−0.20/0.18	−0.29/0.31	−0.23/0.29	−0.95/0.56	−0.60/0.54	−0.65/0.44
data/restraints/params	6402/0/487	5572/0/221	5059/0/263	5665/0/221	6398/0/268	4456/0/221
R_1 ($I>2\sigma(I)$)	0.0508	0.0409	0.0361	0.0334	0.0242	0.0218
wR_2 ($I>2\sigma(I)$)	0.0976	0.1102	0.0980	0.0876	0.0614	0.0459
R_1 (all data)	0.1204	0.0538	0.0449	0.0471	0.0298	0.0289
wR_2 (all data)	0.1232	0.1186	0.1030	0.0958	0.0637	0.0485
GOF	0.968	1.027	1.058	0.965	1.058	1.039
F(000)	1416	356	420	428	492	500

Crystallographic structure determinations: Single crystals of **2**–**6** were prepared inside a glovebox by means of a suspension in a Paratone-N/paraffin oil mixture, fixed on a glass fibre and transferred onto the goniometer of the diffractometer. The data were collected with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares cycle programs SHELXS-97 and SHELXL-97.[21] Crystallographic data are provided in Table 5. CCDC-779257 (**1**), CCDC-779258 (**2**), CCDC-779259 (**3**), CCDC-779260 (**4**), CCDC-779261 (**5**) and CCDC-779263 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the synthesis of alkynides 2–6: The 1,8-diethynylanthracene (**1**) was dissolved in a small amount of toluene and an excess amount of the metal trialkyl (3 equiv) was slowly added. The reactions were initiated by heating the mixtures several times (to temperatures depending on the different metals and substituents) until gas evolution and the formation of a bright yellow precipitate was observed. The products were characterised without further purification. The numbering scheme for NMR spectroscopic assignments (Scheme 6) is based on IUPAC guidelines. Only the lower number descriptor is used for equal protons or carbon atoms.



Scheme 6. Numbering scheme for NMR spectroscopic assignments.

1,8-Bis(dimethylalanylethynyl)anthracene (2): Triethylamine (10% based on amount of trimethylaluminium) was added to a solution of **1** and trimethylaluminium in toluene. The reaction started after 6 h after heating to 72 °C. Yield: 108 mg (78 %) (corresponding to a mixture of product and byproduct (3:1)). ^{1}H NMR (600 MHz, [D$_8$]THF, 25 °C): δ = 9.56 (s, 1 H; H-9), 8.42 (s, 1 H; H-10), 7.91 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H; H-2/H-7), 7.62 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H; H-4/H-5), 7.36 (dd, $^3J_{H,H}$ = 6.9, 8.4 Hz, 2 H; H-3/H-6), −0.71 ppm (s, 12 H; (CH$_3$)$_4$); ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 133.0–125.3 (*C*-aryl), 105.3 (*C*≡C−Al), 83.0 (C≡*C*−Al), −8.9 ppm (*C*H$_3$); ^{27}Al NMR (130 MHz, [D$_8$]THF): δ = 182 ppm; IR (KBr plates): $\tilde{\nu}$ = 3053–2820 (s) (aryl-H), 2060 (vs) (C≡C), 1938–1672, 1604–1425 cm^{-1} (w) (C=C); elemental analysis calcd (%) for $C_{44}H_{40}Al_4$: C 78.37, H 5.96; found C 78.37, H 5.96.

1,8-Bis(diethylalanylethynyl)anthracene (3): Triethylamine (10% based on amount of trimethylaluminium) was added to a solution of **1** and triethylaluminium in toluene. The reaction started at RT. For completion of the reaction the mixture was heated to 72 °C for 3 h. Yield: 170 mg (81 %) (corresponding to a mixture of product and by-product (3:1)). ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): δ = 9.56 (s, 1 H; H-9), 8.42 (s, 1 H; H-10), 7.91 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H; H-2/H-7), 7.65 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H; H-4/H-5), 7.37 (dd, $^3J_{H,H}$ = 7.0 Hz, 2 H; H-3/H-6), 1,15 (t, $^3J_{H,H}$ = 8.1 Hz, 12 H; (CH$_3$)$_4$), 0.02 ppm (q, $^3J_{H,H}$ = 8.1 Hz, 8 H; (CH$_2$)$_4$); ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 132.9–125.2 (*C*-aryl), 106.4 (C≡*C*), 10.1 (*C*H$_3$), 0.8 ppm (*C*H$_2$) (one signal missing due to overlapping or broadening); ^{27}Al NMR (130 MHz, [D$_8$]THF): δ = 178 ppm; IR (KBr plates): $\tilde{\nu}$ = 2933–2789 (s) (aryl-H), 2054 (vs) (C≡C), 1936–1658, 1604–1450 cm^{-1} (w) (C=C); elemental analysis calcd (%) for $C_{52}H_{56}Al_4$: C 79.17, H 7.15; found C 78.88, H 8.01 (an additional value of 0.341 % N indicates the presence of small amounts of triethylamine).

1,8-Bis(dimethylgallanylethynyl)anthracene (4): The product was obtained by heating the reaction mixture to 50 °C for 5 h. Yield: 123 mg (73 %). ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): δ = 9.59 (s, 1 H; H-9), 8.42 (s, 1 H; H-10), 7.92 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H; H-2/H-7), 7.62 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H; H-4/H-5), 7.38 (dd, $^3J_{H,H}$ = 7.1, 7.0 Hz, 2 H; H-3/H-6), −0.21 ppm (s, 12 H; (CH$_3$)$_3$); ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 132.8–125.1 (*C*-aryl), 114.2 (*C*≡C−Ga), 104.9 (C≡*C*−Ga), −5.3 ppm (*C*H$_3$); IR (KBr plates): $\tilde{\nu}$ = 3051–2895 (s) (aryl-H), 2065 (vs) (C≡C), 1930–1757, 1604–1442 cm^{-1} (w) (C=C); elemental analysis calcd (%) for $C_{44}H_{40}Ga_4$: C 62.34, H 4.76; found C 62.38, H 4.91.

1,8-Bis(diethylgallanylethynyl)anthracene (5): The product was obtained by heating the reaction mixture to 70 °C for 3 h. Yield: 366 mg (89 %). ^{1}H NMR (600 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=9.59$ (s, 1 H; H-9), 8.42 (s, 1 H; H-10), 7.91 (d, $^{3}J_{\mathrm{H,H}}=8.5$ Hz, 2 H; H-2/H-7), 7.63 (d, $^{3}J_{\mathrm{H,H}}=6.7$ Hz, 2 H; H-4/H-5), 7.37 (dd, $^{3}J_{\mathrm{H,H}}=7.1$, 7.0 Hz, 2 H; H-3/H-6), 1.24 (t, $^{3}J_{\mathrm{H,H}}=8.0$ Hz, 12 H; $(\mathrm{CH_3})_4$), 0.52 ppm (q, $^{3}J_{\mathrm{H,H}}=8.1$ Hz, 8 H; $(\mathrm{CH_2})_4$); ^{13}C NMR (125 MHz, $[\mathrm{D_8}]$THF): $\delta=132.6$–124.9 (C-aryl), 112.5 ($C{\equiv}\mathrm{C}{-}\mathrm{Ga}$), 106.1 ($\mathrm{C}{\equiv}C{-}\mathrm{Ga}$), 11.3 ($C\mathrm{H_3}$), 5.1 ppm ($C\mathrm{H_2}$) (one signal not observed due to overlapping or broadening); IR (KBr plates): $\tilde{\nu}=2943$–2812 (s) (aryl-H), 2054 (vs) ($\mathrm{C{\equiv}C}$), 1930–1753, 1604–1415 $\mathrm{cm^{-1}}$ (w) ($\mathrm{C{=}C}$); elemental analysis calcd (%) for $\mathrm{C_{52}H_{56}Ga_4}$: C 65.07, H 5.88; found C 64.25, H 5.69.

1,8-Bis(dimethylindanylethynyl)anthracene (6): Product **6** was obtained by heating the reaction mixture to 55 °C for 2 h. Yield: 179 mg (87 %). ^{1}H NMR (600 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=9.63$ (s, 1 H; H-9), 8.40 (s, 1 H; H-10), 7.88 (d, $^{3}J_{\mathrm{H,H}}=8.4$ Hz, 2 H; H-2/H-7), 7.61 (d, $^{3}J_{\mathrm{H,H}}=6.7$ Hz, 2 H; H-4/H-6), 7.36 (dd, $^{3}J_{\mathrm{H,H}}=7.5$, 7.6 Hz, 2 H; H-3/H-5), −0.23 ppm (s, 12 H; $(\mathrm{CH_3})_4$); ^{13}C NMR (150 MHz, $[\mathrm{D_8}]$THF): $\delta=132.9$–125.8 (C-aryl), 121.9 ($C{\equiv}\mathrm{C}{-}\mathrm{In}$), 107.4 ($\mathrm{C}{\equiv}C{-}\mathrm{In}$), −7.1 ppm ($C\mathrm{H_3}$); IR (KBr plates): $\tilde{\nu}=3049$–2874 (s) (aryl-H), 2054 (vs) ($\mathrm{C{\equiv}C}$), 1925–1672, 1604–1425 $\mathrm{cm^{-1}}$ (w) ($\mathrm{C{=}C}$); elemental analysis calcd (%) for $\mathrm{C_{44}H_{40}In_4}$: C 51.40, H 3.92; found C 52.64, H 4.40.

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