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Dimetallocenes Hot Paper

Heavy Pentaisopropylcyclopentadienyltriylenes and their Heterobimetallic Complexes

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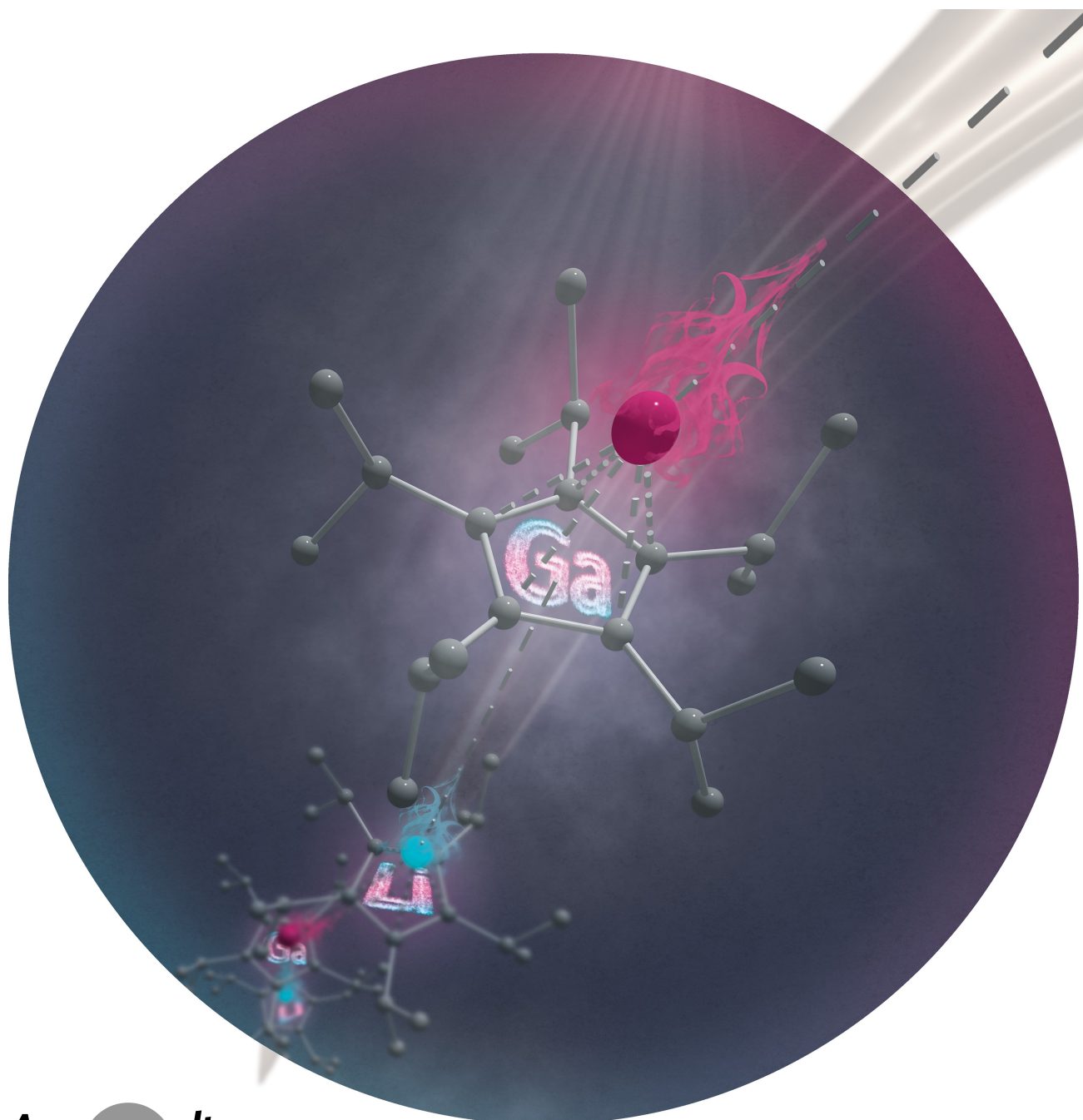
Abstract: A series of triylenes of the heavy group 13 elements gallium, indium and thallium, carrying the pentaisopropylcyclopentadienyl ligand is reported. The compounds were characterized in solution and in the solid-state and their donor ligand properties in hetero-bimetallic complexes were investigated, whereby a series of tungsten carbonyl complexes was isolated. Furthermore, a new synthetic route towards a previously described lithium-aluminum heterobimetallic dimetallo-cene is reported, which also enabled the isolation of a heterobimetallic polydecker of lithium and gallium.

Figure 1. Illustration of the frontier orbital configuration of a triylene (**A**) and of a triylene metal complex ([M] = metal fragment) (**B**).

Introduction

Metallylenes of the group 13 elements, so called "triylenes", are molecules of the general type "R–E" with the group 13 element in oxidation state +I, which formally feature a lone pair as well as two degenerate vacant p orbitals at the monovalent triel center (Figure 1).[1] While oxidation state +I is relatively common for the heavier group 13 elements due to the inert pair effect, it is rather rare in the chemistry of the lighter elements, in particular aluminum and gallium. Thus, the isolation of monovalent aluminylenes and gally-lenes remains challenging,[2] and bulky substituents for kinetic stabilization, and/or donor-type ligands that can compensate for the electron deficiency, are usually required. A major break-through in this field was the isolation and structural characterization of cyclopentadienyl (Cp) complexes of indium(I) and thallium(I), and later of the pentamethylcyclopentadienyl (Cp*) complexes of aluminum(I), gallium(I), indium(I) and thallium(I), which highlighted the fact that cyclopentadienyl ligands are very efficient at stabilizing low-valent heavy triel(I) centers.[3] Since then, a number of cyclopentadienyltriylenes, as well as triylenes with σ bonded substituents, have been reported.[2] The high stability of the cyclopentadienyl complexes origi-nates from the fact that the cyclopentadienyl ligand coor-dinates in an η⁵ fashion to the low-valent metal center, which compensates for electron deficiency, rendering the vacant p orbitals rather inert, and gives the complexes a *nido*-cluster-type structure, according to the Wade-Mingos rules.[4]

Due to their lone pair, triylenes are usually potent donor ligands and heterobimetallic complexes, featuring triylene ligands in combination with s-, p-, d-, and f-block fragments,
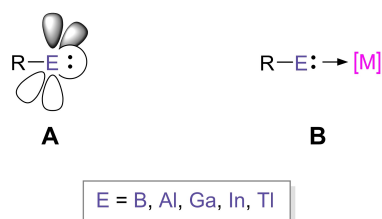
have been described (Figure 1).[5] Such complexes have gained much attention, due to the scarcity of some systems, the often unusual bond properties and potential applications as precursors in materials applications.[6]
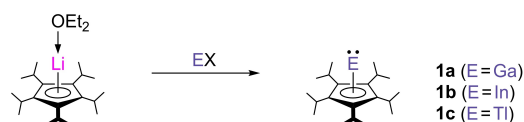
More recently, we have reported the application of the pentaisopropylcyclopentadienyl ligand, commonly referred to as "⁵Cp",[7] in the synthesis and isolation of the first monomeric crystalline cyclopentadienylaluminylene and demonstrated its capability to bind to different metal frag-ments, resulting in homo- as well as heterobimetallic complexes. Most significantly, we were able to isolate and characterize the first heterobimetallic dimetallocene,[8] fol-lowing the landmark reports of homobimetallic dizincocenes and diberyllocenes.[9]

We have now expanded our investigation towards the heavier group 13 analogues and herein report the isolation of ⁵Cp-gallylene, **1a**, ⁵Cp-indylene, **1b**, and ⁵Cp-thallylene, **1c**, as well as their application as ligands in heterobimetallic complexes.

Results and Discussion

Pentaisopropylcyclopentadienyltriylenes

For the syntheses of the ⁵Cp-triylenes **1a–c** appropriate triel(I) precursors were required. While simple salts of indium and thallium with the group 13 element in oxidation state +I are commercially available, the options available in case of gallium are much more limited. However, in analogy of our previous report of the preparation of ⁵CpAl from {Cp*Al}₄,[8] we found that in situ generated cyclopentadie-nylgallium (CpGa)[10] is a suitable candidate and selectively gives ⁵Cp-gallylene **1a**, when treated with ⁵CpLi·OEt₂. Likewise, starting from indium(I) chloride and thallium(I) sulfate, ⁵Cp-indylene **1b** and ⁵Cp-thallylene **1c** were acces-sible (Scheme 1).

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Scheme 1. Synthesis of gallylene **1a** (EX=CpGa), indylene **1b** (EX=InCl) and thallylene **1c** (EX=Tl₂SO₄).

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The ^{1}H NMR spectra of **1a,b** show the two typical pairs of doublets for the methyl groups between 1.30 ppm and 1.36 ppm, originating from a hindered rotation of the isopropyl groups and hence one set of methyl groups facing towards the metal and the other set facing away from the metal.[11] For **1c**, a similar set of signals is observed, yet with one methyl group resonance split into a doublet of doublet, presumably due to a $^{203/205}$Tl coupling ($J_{^1H-^{203/205}Tl} = 6.4$ Hz). This may be a result of a through-space coupling,[12] which only effects the methyl groups facing towards the thallium atom. The coupling is also observed in the ^{13}C{^{1}H} NMR spectrum of **1c**, in which all signals are split into doublets (Figures S8; S9).

Furthermore, **1a** was also characterized by ^{71}Ga NMR spectroscopy. In solution, for **1a** a broad resonance at -657 ppm is observed (Figure S3), which is in line with other cyclopentadienyl gallium(I) compounds (δ^{71}Ga(CpGa) $= -708.4$; δ^{71}Ga(Cp*Ga) $= -648$; δ^{71}Ga-(Cp'''Ga) $= -676.1$).[13] In the solid state, **1a** displays a similar ^{71}Ga NMR chemical shift of $\delta_{iso} = -664$ ppm (Figure S5), which suggests only weak intermolecular interactions. Single crystals of **1a–c**, suitable for XRD analysis, could be obtained from toluene solutions by slow evapo-ration of the solvent and allowed for the structural characterization in the solid state (Figures 2; S36; S37; S38).[14] **1a–c** are isostructural and crystallize in the ortho-rhombic space group *Pnma*. All three compounds form nearly linear polydecker chains, with shorter intramolecular bond lengths and longer intermolecular distances (Table 1).

Interestingly, **1a** is only the second solid-state structurally authenticated example of a cyclopentadienyl gallium(I) compound, as there are only a handful of cyclopentadienyl gallium(I) compounds known to the literature, with only Cp*Ga structurally characterized.[13a,15] While Cp*Ga is believed to be monomeric in solution, it possesses a hexameric structure in the solid state with the gallium atoms in an octahedral arrangement with Ga–Ga distances of 417.35(2) pm and Ga–Cp*^{cent} distances of 208.11(1) pm.[15,16] Such an aggregation is not possible for **1a**, due to the increased steric demand of the ^{5}Cp ligand, resulting in the formation of polydecker chains, a structural motif which had previously only been reported for heavier group 13 cyclopentadienyl compounds. In fact, there are several examples of cyclopentadienyl indium(I) and -thallium(I) compounds, which exhibit chain- and ring-type structures, in addition to hexameric {Cp*In}$_6$, dimeric arrangements with very long E···E contacts, as well as a monomeric example.[3,15,17] Note-worthy, when comparing the intramolecular E–^{5}Cp^{cent} distance in **1b,c**, they are significantly smaller than in other literature known analogues, in which they range from 253.74(1) pm to 272.64(7) pm for In–Cp^{cent} and 262.94(5) pm to 280.13(1) pm for thallium.[3a,d,f,g,1k,17b,d,e] This is a result of the more linear arrangement in **1a–c**, due to the high steric demand of the ^{5}Cp ligand, and possibly attractive dispersion interactions between the isopropyl groups, as previously shown.[8]

Interestingly, while the intramolecular E–Cp^{cent} distances increase from **1a** to **1b** to **1c**, as to be expected from the increasing ionic radii, the intermolecular E–Cp^{cent} actually decrease from **1a** to **1b** to **1c**. This indicates a weaker intermolecular interaction in the case of gallylene **1a**, which increases for the heavier elements indium and thallium. This may be a result of different factors. For one, the ionic character of the E–Cp bond increases from **1a** to **1b** to **1c**, giving the thallium atom in **1c** the most ionic character in the series, which will result in more pronounced intermolecular electrostatic interactions. Furthermore, while attractive lone pair π interactions are discussed for many heavy *p* block elements,[18] the repulsive character of the lone pair certainly decreases, as it gains higher *s* character going from lighter to heavier element. Therefore, a stronger intermolecular repulsion may occur between the molecules of **1a** and a weaker repulsion in case of **1c**.

This is supported by DFT calculations,[19] which reveal a lone pair at the group 13 element, in case of **1a** representing the HOMO and in case of **1b** and **1c** the HOMO-2. Additionally, two degenerated vacant *p* orbitals are found as LUMO and LUMO+1 (Figure S45). Derived from this triylene-typical frontier orbital configuration, **1a–c** could be expected to possess Lewis amphiphilic character. However, we found that **1a–c** as well as ^{5}CpAl do not form adducts
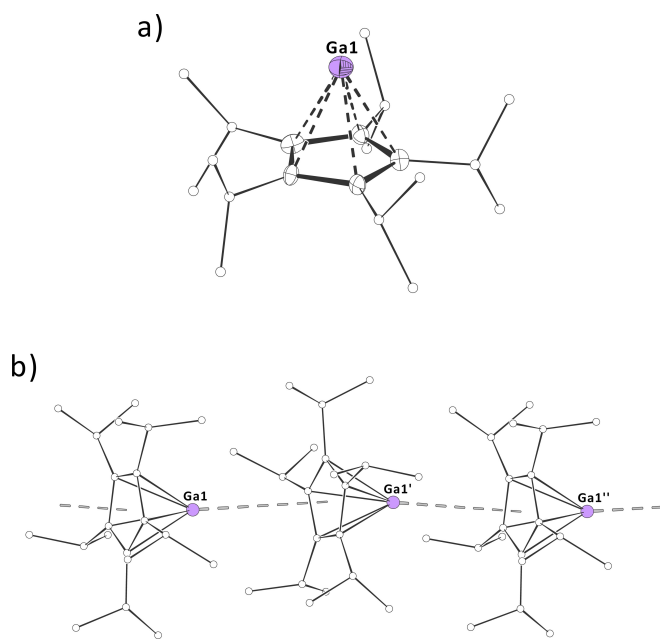

Figure 2. a) Molecular structure of **1a** in the crystal (displacement ellipsoids at 50% probability level; H atoms omitted for clarity, ^{i}Pr groups drawn as ball-and-stick models). b) Illustration of polydecker chain arrangement of **1a** in the crystal (hydrogen atoms omitted for clarity, all atoms drawn as ball-and-stick models).

Table 1: Selected bond lengths [pm] and angles [°] in **1a–c**.

	1a	1b	1c
E–^{5}Cp^{cent} (inter)	412.71(3)	388.21(3)	361.45(3)
E–^{5}Cp^{cent} (intra)	208.35(3)	233.51(3)	248.20(3)
^{5}Cp^{cent}–E–^{5}Cp^{cent}	175.85(1)	176.78(1)	177.54(9)
E–^{5}Cp^{cent}–E	175.08(8)	175.40(7)	175.37(7)

with NHCs, which indicates no significant Lewis acidic character.
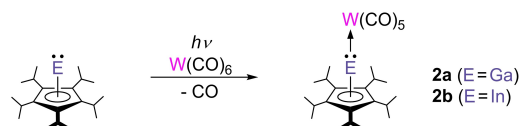
Triylene Tungsten Carbonyl Complexes

We had previously shown that the ^5Cp-aluminylene is a suitable ligand for different metal fragments, including $W(CO)_5$. Thus, we choose to investigate the ligand properties of **1a–c** towards $W(CO)_5$. Reactions of in situ generated $(thf)W(CO)_5$ with **1a** and **1b** in thf lead to the formation of the corresponding complexes **2a** and **2b** (Scheme 2), while the reaction with **1c** under identical conditions did not lead to the formation of a corresponding complex and only the starting materials were isolated.

Single crystals of **2a** and **2b**, suitable for XRD analysis, could be obtained from toluene solutions at 248 K and enabled a structural characterization in the solid state (Figure 3).[14] Both complexes **2a** and **2b** are isostructural to each other and crystallize in the orthorhombic space group *Pbca*. Interestingly, while the E–$^5Cp^{cent}$ distances increase in length from previously reported $^5CpAl{\rightarrow}W(CO)_5$[8] to **2a** to **2b**, the Al–W and Ga–W bonds are almost identical in length (Table 2), which is a result of the very similar covalent radii of Al and Ga,[20] due to the *d*-block contraction. On the other hand, the E–^5Cp bonds may be less affected by this, as they have a higher ionic character. The IR stretching frequencies of the CO ligands in **2a**, **2b** and ^5CpAl[8] are relatively similar, indicating similar ligand strengths of the three congeners.[19] In comparison, higher wavenumbers have been reported for phosphane and amine tungsten pentacarbonyl complexes,[21] indicating that the ^5Cp-triylenes are weaker donors. Furthermore, there are no significant differences between the C≡O bond length of the axial/*trans* and the equatorial/*cis* CO ligands in **2a**, **2b** and ^5CpAl, indicating no substantial backbonding from the tungsten center to the triel centers in any of the complexes. On one occasion, serendipitous crystals of a bis(gallylene) tungsten tetracarbonyl complex of the type $(^5CpGa)_2{\rightarrow}W(CO)_4$ were obtained (Figure S40).[14] We had previously observed the formation of a by-product in the reaction of ^5CpAl with $(thf)W(CO)_5$ and speculated that it was the bis(aluminylene) complex,[8] which would be in line with reports of an analogues bis(triphenylphosphane) complex, obtained under similar conditions.[22] The isolation of the corresponding bis(gallylene) complex strongly supports this. Interestingly, literature known $(Cp^*Ga)_2{\rightarrow}Mo(CO)_4$ features the two gallylene ligands in equatorial *cis* position,

whereas the complex we isolated has them in axial *trans* position to each other. This is a result of the higher steric demand of the ^5Cp moiety, as steric effects have previously been discussed to be the main factor in *cis* versus *trans* coordination in $L_2W(CO)_4$ complexes.[23]

A Heterobimetallic Dimetallocene and Related Polydecker

We recently reported the isolation of the first heterobimetallic dimetallocene **3** by heterocoupling of ^5CpAl and ^5CpLi.[8] However, this coupling reaction is hampered by the presence of any donor molecules, thus has to be conducted in a non-donor solvent such as toluene. Because ^5CpLi is usually obtained in the form of its diethyl etherate,[7,24] an ether scavenger must be added to the reaction. To improve the synthetic access to heterobimetallic dimetallocene **3** and possibly other dimetallocenes, we investigated the possibility to synthesize an ether-free derivative of ^5CpLi. Although we were unsuccessful in obtaining solvent-free ^5CpLi, we successfully prepared and structurally authenticated a

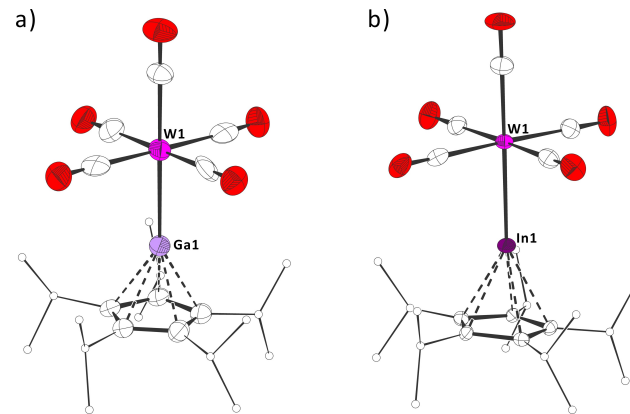**Scheme 2.** Synthesis of triylene tungsten pentacarbonyl complexes **2a,b**.

Figure 3. Molecular structure of a) **2a** and b) **2b** in the crystal (displacement ellipsoids at 50% probability level; H atoms omitted for clarity, ^iPr groups drawn as ball-and-stick models).
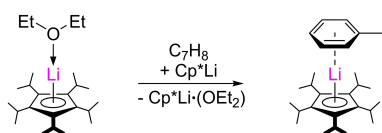
Table 2: Selected bond lengths [pm] in $^5CpAl{\rightarrow}W(CO)_5$,[8] **2a** and **2b**.

	$^5\mathbf{CpAl{\rightarrow}W(CO)_5}$	**2a**	**2b**
E–$^5Cp^{cent}$	183.54(6)	193.40(2)	214.44(3)
E–W	258.47(6)	257.10(2)	272.93(2)
W–C^{CO} (*cis*)	202.24(3)–204.54(3)	201.02(2)–206.64(2)	203.83(2)–205.14(2)
W–C^{CO} (*trans*)	199.74(3)	200.29(2)	198.71(2)
C–O (*cis*)	113.67(3)–114.98(3)	112.65(2)–117.83(2)	113.97(3)–114.51(3)
C–O (*trans*)	114.35(4)	112.94(2)	114.31(3)

toluene adduct (Scheme 3). X-ray quality crystals of ^{5}CpLi·(toluene) were obtained from a toluene solution by slow evaporation of the solvent. It crystallizes in the orthorhombic space group $Pca2_1$ with two molecules per asymmetric unit (Figures 4, S42).[14]

The Li atom is sandwiched between the ^{5}Cp ligand and the toluene molecule with a Li–^{5}Cp^{cent} bond length of 175.54(9) pm, which is slightly shorter than in ^{5}CpLi·OEt$_2$ (180.74(4) pm).[24] Furthermore, the Li atom coordinates in a distorted η^6 fashion to toluene with a Li–toluene^{cent} distance of 260.16(9) pm. Other lithium arene complexes in the literature exhibit Li–aryl^{cent} distances in the range of 186.13(2) pm to 224.54(2) pm,[25] which is much shorter, indicating an only weak interaction between the lithium atom and the toluene molecule in ^{5}CpLi·(toluene). Thus, this arene complex promised to be the perfect candidate for a straight forward synthesis of heterobimetallic dimetallocene 3. Indeed, stirring a solution of ^{5}CpAl and ^{5}CpLi·(toluene) in benzene or toluene selectively gives 3 (Scheme 4).

With a more straight forward synthetic access to 3, we extended our investigation of its reactivity. Following previous investigations of its behavior towards heteroallenes, we continued these studies and reacted 3 with diisopropylcarbodiimide. Multinuclear NMR spectroscopy indicated an Al–Li bond cleavage and elimination of the ^{5}CpAl fragment, along with the formation of a new ^{5}CpLi complex. Colorless crystals, suitable for XRD analysis, could be obtained from a hexane/toluene solution at 248 K, which allowed for the product's structure to be determined (Scheme 5; Figure 5).[14] To the best of our knowledge, 4 is the first example of a carbodiimide coordinated cyclopentadienyllithium complex.

The lithium atom is coordinated by only one of the two nitrogen atoms of the diisopropylcarbodiimide, which preserves its near linear N=C=N assembly. The Li–^{5}Cp^{cent} bond length of 178.59(3) pm is similar to the one in ^{5}CpLi·OEt$_2$ (180.74(4) pm),[24] and the Li–N bond length is 200.66(4) pm, which is comparable to related lithium imine complexes.[26] The C1–N1 bond (123.14(9) pm) is slightly longer than the C1–N2 bond length (119.40(3) pm), which is a result of the asymmetric coordination, but both bond lengths are within normal lengths of C=N double bonds.

With the heavier ^{5}Cp-triylenes 1a–c and the ^{5}CpLi·(toluene) in hand, the synthesis of another heterobimetallic dimetallocene by heterocoupling seemed plausible. Thus, we attempted the synthesis of a lithium-gallium heterobimetallic dimetallocene by reacting ^{5}Cp-gallylene 1a with ^{5}CpLi·(toluene) in toluene. Inspection of the reaction mixture by multinuclear NMR spectroscopy indicated only marginal signal shifts compared to the starting materials, which points to a weak interaction between the two fragments. Nevertheless, we were able to obtain X-ray quality crystals from
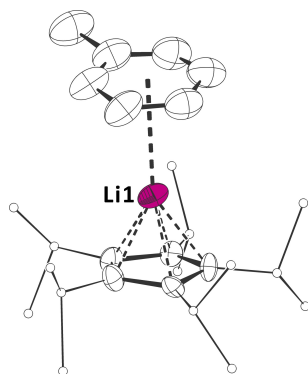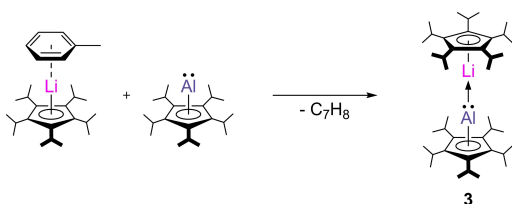

Scheme 3. Synthesis of ^{5}CpLi·(toluene).

Figure 4. Molecular structure of ^{5}CpLi·(toluene) in the solid state (displacement ellipsoids at 50% probability level; H atoms omitted for clarity, ^{i}Pr groups drawn as ball-and-stick models, only one of two molecules from the asymmetric unit shown).
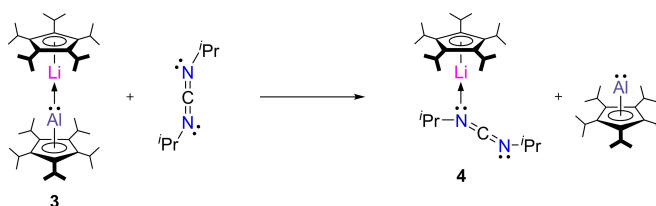

Scheme 4. Synthesis of heterobimetallic dimetallocene complex 3.

Scheme 5. Reaction of heterobimetallic dimetallocene 3 with diisopropylcarbodiimide.

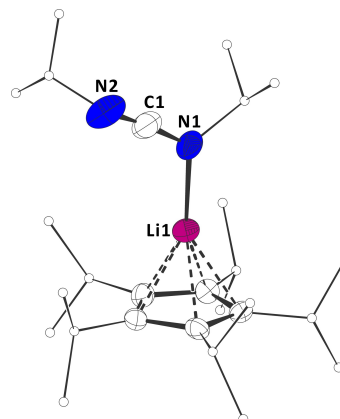**Figure 5.** Molecular structure of 4 in the solid state (displacement ellipsoids at 50% probability level; H atoms omitted for clarity, ^{i}Pr groups drawn as ball-and-stick models).

the reaction mixture by slow evaporation of the solvent. Single crystal X-ray diffraction indicated that this is neither the starting materials **1a** or ⁵CpLi·(toluene), nor a hetero-bimetallic dimetallocene of the type "⁵CpGa→Li⁵Cp", but in fact a heterobimetallic polydecker (Figures 6, S44).[14] To the best of our knowledge, **5** is the first example of a neutral heterobimetallic polydecker compound.[27]

We attribute the isolation of polydecker **5** to the fact that the interaction between the ⁵Cp-gallylene **1a** and ⁵CpLi fragments is relatively weak and that the dimetallocene and its isomeric double-decker complexes are similar in energy, resulting in a corresponding equilibrium in solution (Scheme 6).
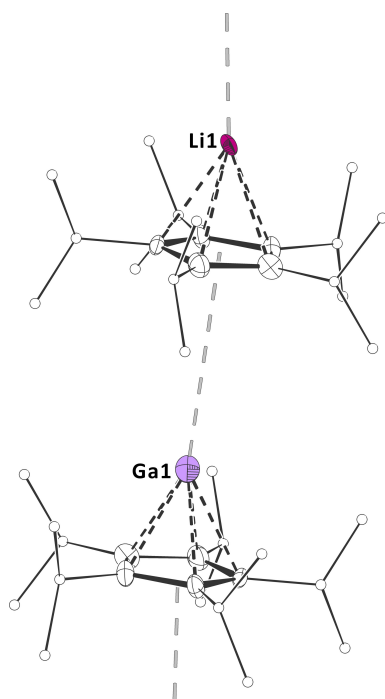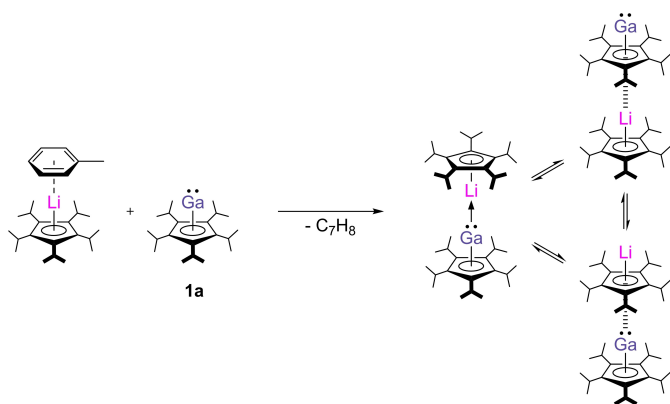

Figure 6. Molecular structure of ⁵CpLi···⁵CpGa polydecker **5** in the solid state (displacement ellipsoids at 50% probability level; H atoms omitted for clarity, ⁱPr groups drawn as ball-and-stick models).

Most importantly, theoretical studies had previously predicted that double-decker complexes can be energetically preferred over dimetallocene-type adducts.[28] To investigate this further, we performed DFT calculations and indeed, all three isomers are within 43.3 kJ mol⁻¹ (Figure 7). Interestingly, the dimetallocene is predicted to be the energetically favored ground state isomer, whereas the double-decker isomers are predicted to be higher in energy and within 7.8 kJ mol⁻¹ to each other.

However, it must be taken into consideration that the computational models are double-decker complexes and not polydeckers. In fact, the calculated intermolecular distances in the double-decker models are substantially shorter than what is observed in the solid-state structure of **5** (Li···⁵Cp: 393.8 pm (DFT) / 451.85(40) pm (XRD); Ga···⁵Cp: 370.4 pm (DFT) / 424.54(5) pm (XRD)), which, in case of gallium, is similar to the distance in **1a** (412.71(3) pm). This generally raises the question whether double-decker complexes are reasonable computational models, as has been suggested previously.[28] In principle, there can be no doubt that polydecker **5** possess a much larger lattice energy, respectively lower solubility, due to intermolecular interactions and its associated polymeric nature, than the molecular dimetallocene isomer. Therefore, the isolation of **5** does not allow to draw any conclusions about the situation in solution, where a weakly bonded ⁵CpGa→Li⁵Cp hetero-bimetallic dimetallocene may very well be present.

Conclusions

By utilizing the pentaisopropylcyclopentadienyl (⁵Cp) li-gand, a series of triylenes of gallium, indium and thallium could be accessed and isolated. The compounds **1a–c** were structurally authenticated by single crystal XRD and their properties as ligands were investigated, resulting in the isolation of tungsten carbonyl complexes **2a,b**. Furthermore, an improved synthetic route to a previously reported heterobimetallic dimetallocene **3** is presented, as well as investigations of its reactivity towards carbodiimides. More-over, making use of this new route, the preparation of a lithium-gallium dimetallocene was probed and lead to the isolation of a polydecker, exhibiting ⁵CpGa and ⁵CpLi units. This confirms previously made theoretical predictions and is supported by DFT calculations of a possible equilibrium

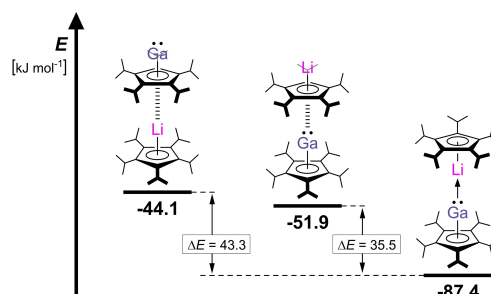**Scheme 6.** Reaction of **1a** with ⁵CpLi·(toluene) and proposed products equilibrium.

Figure 7. Energies (in kJ mol⁻¹) of a proposed Li–Ga-dimetallocene and its related double-decker complexes, relative to **1a** + ⁵CpLi.

between a dimetallocene arrangement and related double-decker complexes.

Supporting Information

Data that supports the findings of this study are available as Supporting Information. This includes experimental procedures, NMR, IR and UV/Vis spectra, X-ray crystallographic data, and computational details, as well as additional references cited by the authors [29–38].

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: group 13 · heterobimetallic · half-sandwich · double-decker · dimetallocene

[1] S. Aldridge, A. J. Downs, *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*, John Wiley & Sons, Ltd **2011**.

[2] M. He, C. Hu, R. Wei, X.-F. Wang, L. L. Liu, *Chem. Soc. Rev.* **2024**, *53*, 3896.

[3] a) E. Frasson, F. Menegus, C. Panattoni, *Nature* **1963**, *199*, 1087; b) O. T. Beachley Jr, M. R. Churchill, J. C. Fettinger, J. C. Pazik, L. Victoriano, *J. Am. Chem. Soc.* **1986**, *108*, 4666; c) O. T. Beachleay Jr, R. Blom, M. R. Churchill, K. Faegri Jr, J. C. Fettinger, J. C. Pazik, L. Victoriano, *Organometallics* **1989**, *8*, 346; d) H. Werner, H. Otto, H. J. Kraus, *J. Organomet. Chem.* **1986**, *315*, C57; e) H. Schumann, C. Janiak, F. Görlitz, J. Loebel, A. Dietrich, *J. Organomet. Chem.* **1989**, *363*, 243; f) O. T. Beachley Jr, J. C. Pazlik, T. E. Glassmann, M. R. Churchill, J. C. Fettinger, R. Blom, *Organometallics* **1988**, *7*, 1051; g) O. T. Beachley Jr, J. F. Lees, R. D. Rogers, *J. Organomet. Chem.* **1991**, *418*, 165; h) H. Schumann, T. Ghodsi, L. Esser, E. Hahn, *Chem. Ber.* **1993**, *126*, 591. i) H. Schumann, C. Janiak, M. A. Khan, J. J. Zuckerman, *J. Organomet. Chem.* **1988**, *354*, 7; j) H. Schumann, C. Janiak, J. Pickardt, U. Börner, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 789; k) S. Harvey, C. L. Raston, B. W. Skelton, A. H. White, M. F. Lappert, G. Srivastava, *J. Organomet. Chem.* **1987**, *328*, C1; l) A. Hofmann, T. Tröster, T. Kupfer, H. Braunschweig, *Chem. Sci.* **2019**, *10*, 3421; m) Y. Ding, P. N. Ruth, R. Herbst-Irmer, D. Stalke, Z. Yang, H. W. Roesky, *Dalton Trans.* **2021**, *50*, 2067; n) S. González-Gallardo, T. Bollermann, R. A. Fischer, R. Murugavel, *Chem. Rev.* **2012**, *112*, 3136.

[4] a) K. Wade, *J. Chem. Soc. D* **1971**, 792; b) D. M. P. Mingos, *Nat. Phys.* **1972**, *236*, 99; c) R. J. Gillespie, *Chem. Soc. Rev.* **1979**, *8*, 315; d) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311; e) A. J. Welch, *Chem. Commun.* **2013**, *49*, 3615.

[5] a) C. Gemel, T. Steinke, M. Cokoja, A. Kemper, R. A. Fischer, *Eur. J. Inorg. Chem.* **2004**, *21*, 4161; b) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354; c) S. T. Liddle, *Proc. Roy. Soc. A* **2009**, *465*, 1673; d) C.-S. Cao, Y. Shi, H. Xu, B. Zhao, *Coord. Chem. Rev.* **2018**, *365*, 122.

[6] a) J. T. Boronski, L. R. Thomas-Hargreaves, M. A. Ellwanger, A. E. Crumpton, J. Hicks, D. F. Bekiş, S. Aldridge, *J. Am. Chem. Soc.* **2023**, *145*, 4408; b) J. T. Boronski, L. P. Griffin, C. Conder, A. E. Crumpton, L. L. Wales, S. Aldridge, *Chem. Sci.* **2024**, *15*, 15377; c) L. P. Griffin, M. A. Ellwanger, J. Clark, W. K. Myers, A. F. Roper, A. Heilmann, S. Aldridge, *Angew. Chem. Int. Ed.* **2024**, *63*, e202405053; d) C. Berthold, J. Maurer, L. Klerner, S. Harder, M. R. Buchner, *Angew. Chem. Int. Ed.* **2024**, *63*, e202408422; e) C. L. Daniels, D. L. Mendivelso-Pérez, B. A. Rosales, D. You, S. Sahu, J. Stuart Jones, E. A. Smith, F. P. Gabbaï, J. Vela, *ACS Omega* **2019**, *4*, 5197; f) T. Büttner, O. Janka, V. Huch, D. Dhara, A. Jana, D. Scheschkewitz, *Eur. J. Inorg. Chem.* **2023**, *26*, e202300433; g) G. Karmakar, A. Tyagi, D. Tyagi, A. Y. Shah, A. P. Wadawale, H. Donthula, V. Singh, *New J. Chem.* **2024**, *48*, 11910.

[7] a) H. Sitzmann, *Z. Naturforsch.* **1989**, *44b*, 1293; b) T. Dezember, H. Sitzmann, *Z. Naturforsch.* **1997**, *52b*, 911; c) S. Lauk, A. Schäfer, *Eur. J. Inorg. Chem.* **2021**, *48*, 5026.

[8] I.-A. Bischoff, S. Danés, P. Thoni, B. Morgenstern, D. M. Andrada, C. Müller, J. Lambert, E. C. J. Gießelmann, M. Zimmer, A. Schäfer, *Nat. Chem.* **2024**, *16*, 1093.

[9] a) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136; b) A. Grirrane, I. Resa, A. Rodríguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* **2007**, *129*, 693; *J. Am. Chem. Soc.* **2007**, *129*, 14100; c) J. T. Boronski, A. E. Crumpton, L. L. Wales, S. Aldridge, *Science* **2024**, *380*, 1147; d) J. T. Boronski, A. E. Crumpton, A. F. Roper, S. Aldridge, *Nat. Chem.* **2024**, *16*, 1295.

[10] D. Loos, H. Schnöckel, J. Gauss, U. Schneider, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1362.

[11] a) H. Sitzmann, R. Boese, P. Stellberg, *Z. Anorg. Allg. Chem.* **1996**, *622*, 751; b) H. Sitzmann, *Z. Anorg. Allg. Chem.* **1995**, *621*, 553; c) S. Lauk, M. Zimmer, B. Morgenstern, V. Huch, C. Müller, H. Sitzmann, A. Schäfer, *Organometallics* **2021**, *40*, 618.

[12] O. W. Howarth, J. Nelson, V. McKee, *Chem. Commun.* **2000**, 21.

[13] a) D. Loos, H. Schnöckel, *J. Organomet. Chem.* **1993**, *463*, 37; b) C. Schenk, R. Köppe, H. Schnöckel, A. Schnepf, *Eur. J. Inorg. Chem.* **2011**, *25*, 3681; c) Y. Ding, P. N. Ruth, R. Herbst-Irmer, D. Stalke, Z. Yang, H. W. Roesky, *Dalton Trans.* **2021**, *50*, 2067; d) J. L. Bourque, R. A. Nanni, M. C. Biesinger, K. M. Baines, *Inorg. Chem.* **2021**, *60*, 14713.

[14] Deposition numbers 2390255 (for **1a**), 2390256 (for **1b**), 2390260 (for **1c**) 2390261 (for **2a**), 2390267 (for (^{5}CpGa)$_2 \to$ W(CO)$_4$), 2390263 (for **2b**) 2390266 (for ^{5}CpLi·(toluene)) 2390268 (for **4**) and 2390270 (for **5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data

Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[15] D. Loos, E. Baum, A. Ecker, H. Schnöckel, A. J. Downs, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 860; *Angew. Chem.* **1997**, *109*, 894.

[16] A. Haaland, K.-G. Martinsen, H. V. Volden, D. Loos, H. Schnöckel, *Acta Chem. Scand.* **1994**, *48*, 172.

[17] a) E. O. Fischer, *Angew. Chem.* **1957**, *69*, 207; b) H. Schumann, H. Kucht, A. Dietrich, L. Esser, *Chem. Ber.* **1990**, *123*, 1811; c) H. Schumann, A. Lentz, R. Weimann, *J. Organomet. Chem.* **1995**, *487*, 245; d) G. Lin, W.-T. Wong, *J. Organomet. Chem.* **1995**, *495*, 203; e) O. T. Beachley Jr, J. F. Lees, T. E. Glassman, M. R. Churchill, L. A. Buttrey, *Organometallics* **1990**, *9*, 2488; f) H. Schumann, T. Ghodsi, L. Esser, *Acta Crystallogr.* **1992**, *C48*, 620; g) M. Enders, J. Fink, H. Pritzkow, *Eur. J. Inorg. Chem.* **2000**, *9*, 1923; h) M. B. Freeman, L. G. Sneddon, J. C. Huffman, *J. Am. Chem. Soc.* **1977**, *99*, 5194; i) G. A. Dushenko, I. E. Mikhailov, G. Reck, B. Schulz, A. Zschunke, V. I. Minkin, *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 890; j) H. Schumann, H. Kucht, A. Kucht, F. H. Görlitz, A. Dietrich, *Z. Naturforsch.* **1992**, *47b*, 1241.

[18] I. Caracelli, J. Zukerman-Schpector, I. Haiduc, E. R. T. Tiekink, *CrystEngComm* **2016**, *18*, 6960.

[19] See Supporting Information for further details.

[20] P. Pyykkö, *J. Phys. Chem. A* **2015**, *119*, 2326.

[21] a) J. F. Binder, S. C. Kosnik, C. L. B. Macdonald, *Chem. Eur. J.* **2018**, *24*, 3556; b) M. S. Davies, R. K. Pierens, M. J. Aroney, *J. Organomet. Chem.* **1993**, *458*, 141; c) G. M. Bancroft, L. Dignard-Bailey, R. J. Puddephatt, *Inorg. Chem.* **1986**, *25*, 3675.

[22] N. D. Silavwe, A. S. Goldman, R. Ritter, D. R. Tyler, *Inorg. Chem.* **1989**, *28*, 1231.

[23] I. M. Ounapu, J. A. Mosbo, J. M. Risley, B. N. Storhoff, *J. Organomet. Chem.* **1980**, *194*, 337.

[24] S. Lauk, M. Zimmer, B. Morgenstern, V. Huch, C. Müller, H. Sitzmann, A. Schäfer, *Organometallics* **2021**, *40*, 618.

[25] a) K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353; b) C. Uffing, R. Koppe, H. Schnöckel, *Organometallics* **1998**, *17*, 3512; c) B. Schiemenz, P. P. Power, *Angew. Chem. Int. Ed.* **1996**, *35*, 2150; d) R. E. Dinnebier, U. Behrens, F. Olbrich, *J. Am. Chem. Soc.* **1998**, *120*, 1430.

[26] a) X. Chen, X. Xue, L. Zhang, W.-H. Sun, *Inorg. Chem. Commun.* **2011**, *14*, 235; b) G. Sun, C. Tian, W. Nie, M. V. Borzov, *Acta Crystallogr.* **2009**, *E65*, m478; c) K. Kunz, G. Erker, G. Kehr, R. Fröhlich, *Organometallics* **2001**, *20*, 392.

[27] M. Schorpp, I. Krossing, *Chem. Eur. J.* **2020**, *26*, 14109.

[28] N. He, H.-b. Xie, Y.-h. Ding, *Organometallics* **2007**, *26*, 6839.