

Investigations on 1-Metallaindanes

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1-Mercuraindane (**6**) was prepared in three steps from 1-bromo-2-(2-bromoethyl)benzene (**3**) and converted into 1-magnesaindane (**1**) by reaction with magnesium. In solution, **6** was observed to occur in a remarkable dimer/trimer equilibrium, whereas **1** forms a dimer. From **1** and dichlorozirconocene, the 1-zirconaindane **2** was obtained, which reacted with B(C₆F₅)₃ to form the adduct **13**. According to spectro-

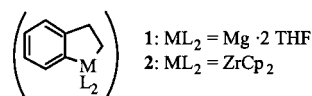
scopic data, **13** is formed by attack of the β -methylene carbon atom at the boron atom and has a zwitterionic structure with weak interactions between the zirconium ion and one of the *ortho*-fluorine atoms.

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Introduction

Cyclic diorganylmagnesium compounds^[1] often show interesting structural features.^[2,3] One aspect is the relatively large C–Mg–C bond angle, which for normal diorganylmagnesium compounds of the general type R₂MgL₂ (L = ligand, mostly an ether) is around 120–130°. This leads to considerable strain if the two R groups are connected such that magnesium is incorporated into a small ring. As the carbon–magnesium bonds undergo a rapid exchange in ethereal solution, the strained monomers can easily escape from this situation and thus tend to form more stable dimers or higher aggregates in which the large bond angle can be accommodated free of strain; sometimes an equilibrium between two oligomers is established. For the sake of simplicity, the oligomers are indicated by the names of the *monomeric* parent units where appropriate; furthermore, magnesium is assumed to be tetracoordinate including two solvent molecules,^[1–3] which in the present case is THF. We have previously reported the investigation of a number of such cyclic diorganylmagnesium compounds,^[3,4] and wanted to extend this study to 1-magnesaindane (**1**) (Scheme 1).

A further reason for our interest in **1** was that it is a difunctional organomagnesium compound and as such is attractive for the preparation of other metallacycles such as the corresponding 1-zirconaindane **2**, which is potentially



Scheme 1

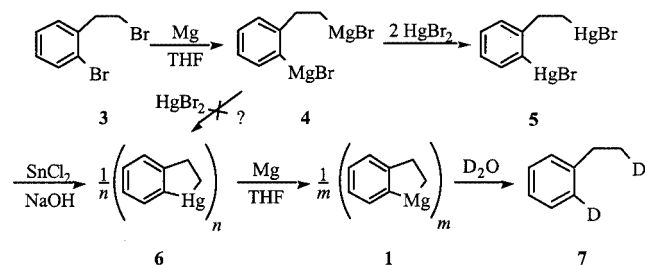
of interest as a precursor of a new class of single-site olefin polymerization catalysts.^[5–7]

Results and Discussion

Synthesis of Magnesaindane (**1**)

In order to obtain **1** in pure form, we decided to prepare it by transmetalation of the corresponding cyclic organomercury compound **6** with metallic magnesium, as shown in Scheme 2. For this purpose, the dibromide **3** was converted into **4**, which is the known^[8] di-Grignard reagent corresponding to the diorganylmagnesium **1**. In an attempt to obtain **6** from **4** directly, we treated **4** with 1 mol-equiv. of mercury dibromide but, according to the ¹⁹⁹Hg NMR spectrum, a mixture of organomercury compounds was formed which could not be separated. However, **6** was obtained by reduction^[9] of the corresponding organomercury halide **5** with stannous chloride in the presence of base. Reaction of **6** with metallic magnesium in THF furnished **1**, which was characterized spectroscopically by its ¹H and ¹³C NMR spectrum (see Exp. Sect.) and chemically by reaction with deuterium oxide which gave [D₂]ethylbenzene (**7**) exclusively.

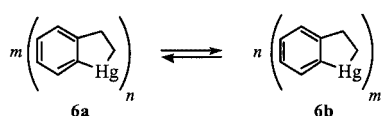
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Scheme 2

Structure of 1-Mercuraindane (6)

Although initially **6** was only of interest as an intermediate for the preparation of **1**, it showed spectral features which led to a closer investigation. The ^{13}C NMR spectrum of pure **6** in CDCl_3 shows evidence for the occurrence of two species **6a** and **6b**, presumably differing in their degree of oligomerization. For instance, four methylene carbon resonances were observed ($\delta = 41.5$ and 39.7 ppm for **6a**; $\delta = 41.7$ and 38.4 ppm for **6b**) as well as eight resonances of aromatic carbon atoms and two of ^{199}Hg ($\delta = -273.2$ ppm for **6a**; $\delta = -305.5$ ppm for **6b**). The signal integral ratio of the benzylic methylene protons of **6a** and **6b** in the ^1H NMR spectrum was found to be concentration-dependent, which suggests an equilibrium between them in solution (Scheme 3). From ^1H NMR spectroscopic data (Table 1), the equilibrium constant at room temperature was determined. As, according to HRMS spectroscopy, **6** has a dimeric structure ($m/z = 610.0642$) in the gas phase, one of the species involved in solution is presumably a dimer. Assuming a dimer/trimer equilibrium, the equilibrium constant was found to be in the range of $K = 0.4 \pm 0.2 \text{ L}\cdot\text{mol}^{-1}$.



Scheme 3

Table 1. Data on the equilibrium of **6** at room temperature [in 0.5 mL of CDCl_3 at room temperature; determined from the ratio of the benzylic protons at $\delta = 3.36$ ppm (**6a**) and 2.95 ppm (**6b**)]

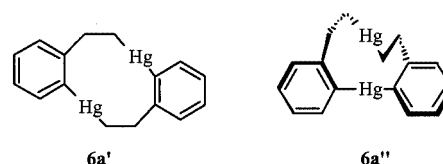
6a ^[a]	[6a] ^[b]	[6b] ^[b]	K ^[c]
1.5	$8.8 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$	0.49
4.1	$2.4 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	0.57
9.1	$5.2 \cdot 10^{-2}$	$7.6 \cdot 10^{-3}$	0.41
13.5	$7.6 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	0.33
17.8	$1.0 \cdot 10^{-1}$	$1.7 \cdot 10^{-2}$	0.30
21.5	$1.2 \cdot 10^{-1}$	$2.1 \cdot 10^{-2}$	0.26
25.4	$1.4 \cdot 10^{-1}$	$2.7 \cdot 10^{-2}$	0.24
31.0	$1.7 \cdot 10^{-1}$	$3.3 \cdot 10^{-2}$	0.22

[a] In mg. [b] In $\text{mol}\cdot\text{L}^{-1}$ (**6a** as dimer, **6b** as trimer). [c] In $\text{L}\cdot\text{mol}^{-1}$.

A dimer/trimer equilibrium is plausible since, in hypothetical monomeric **6**, the $\text{C}-\text{Hg}-\text{C}$ angle would deviate too much from the ideal value of 180° , making the ensuing ring strain prohibitive. This is less so for a dimeric species **6a**, while a trimeric species **6b** is strain-free as concluded from CPK model studies. Species higher than a trimer are not formed since oligomerization is entropically unfavorable.

The establishment of such an equilibrium is unexpected because, in contrast to the kinetically highly labile carbon–magnesium bond, the carbon–mercury bond is usually stable under ordinary conditions. Redistribution reactions of bifunctional organomercury compounds have been reported, but only in the presence of a catalyst such as AlCl_3 ^[10] or an organomercury halide (RHgX).^[10,11] For example, an equimolar mixture of Me_2Hg and Et_2Hg gives a random distribution of the three possible alkylmercury compounds, Me_2Hg , Et_2Hg and MeEtHg , upon standing at room temperature in the presence of AlCl_3 , but after removal of the catalyst, MeEtHg can be distilled at 127°C and is stable for months at room temperature.^[10] The presence of an organomercury halide, such as **5**, as an impurity, which might act as a catalyst, was excluded by a negative halide test performed by evaporation of the solvent from a sample followed by treatment with HNO_3 and AgNO_3 ; a precipitate of AgCl was not observed.

To confirm the occurrence of an equilibrium for **6** and to estimate the exchange rates between both species, the magnetization-transfer NMR technique^[12] was applied between 25 and 95°C . Below 83°C , no transfer was observed, which indicates that the establishment of the equilibrium is relatively slow at these temperatures. At 83°C and 95°C , the (pseudo-first-order) rates obtained for the equilibrium $3 \text{ } \mathbf{6a} \rightleftharpoons 2 \text{ } \mathbf{6b}$ were in the range of $0.1\text{--}1 \text{ s}^{-1}$. Thus, the exchange between the two oligomers is rather fast, and even at room temperature, one can estimate that it will be sufficient to allow establishment of the equilibrium. However, it is a remarkable process, and it remains unclear whether it is caused by inherent structural features or by some kind of undetected catalyst present in the system. Compound **6a** is probably dimeric (vide supra) and CPK models show that, of the two possible structures, **6a'** is less strained than **6a''** due to the presence of the $\text{aryl}-\text{Hg}-\text{aryl}$ arrangement in the latter (Scheme 4).



Scheme 4

Structure of 1 in Solution

The appreciable solubility of **1** in THF (ca. 0.1 M at room temperature) allowed investigations concerning its structure in solution. The degree of association was determined by the stationary isothermal distillation method,^[13] which fur-

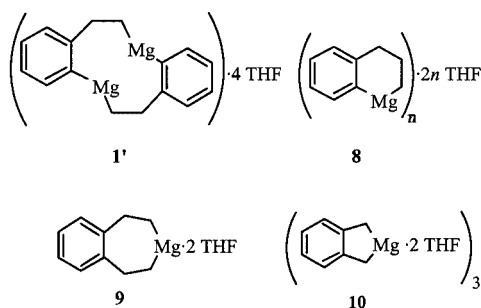
nished a concentration-independent degree of association of 2.08 (see Table 2).

Table 2. Degree of association of **1** in THF solution at 301 K^[13]

[Mg] ^[a]	S_{th} ^[b]	S_a ^[c]	i ^[d]
1.24	0.052	0.028	1.84
2.42	0.101	0.045	2.26
3.53	0.148	0.068	2.15
4.57	0.192	0.092	2.08
5.55	0.233	0.117	1.99
6.49	0.272	0.126	2.16

^[a] [Mg] = Formal concentration of magnesium in mmol·g⁻¹. ^[b] S_{th} = Theoretical rate of evaporation (in mm·h⁻¹) = [Mg]· S_s , where S_s (in mm·h⁻¹·mmol⁻¹·L) = standard rate of evaporation found by calibration of the apparatus with triphenylmethane, S_s (301 K) = 0.0119 mm·h⁻¹·mmol⁻¹·L. ^[c] S_a = Apparent rate of evaporation in mm·h⁻¹. ^[d] Association number $i = S_{th}/S_a$.

The structure of two benzomagnesacycloalkanes in solution has been investigated by Freijee et al., who determined the degree of association in solution of the 1-magnesatetralin **8** and the tetrahydrobenzomagnesepin **9** (Scheme 5).^[4] It was established that **8** was involved in a monomer/dimer equilibrium as its concentration-dependent degree of association was 1.26–1.49 in THF solution at room temperature, whereas the higher homologue **9** was completely monomeric. It was assumed that the higher ring strain in monomeric **8** (about 46 kJ·mol⁻¹) than in **9** (about 11 kJ·mol⁻¹) is largely responsible for the observed difference.



Scheme 5

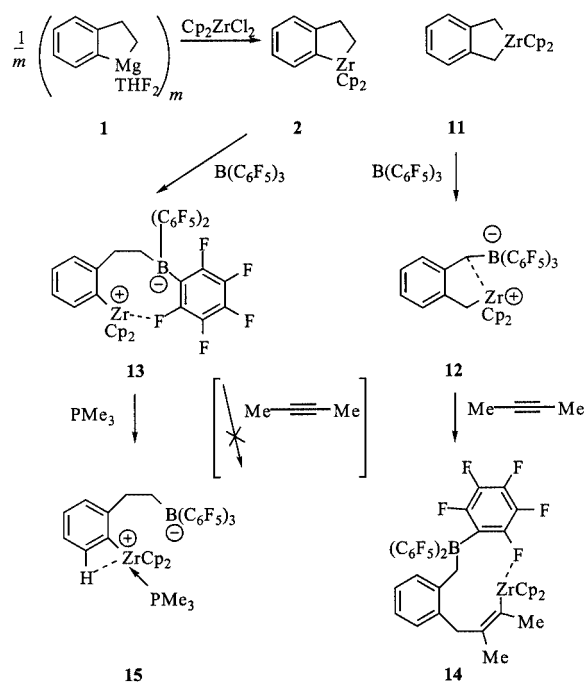
The fact that **1** is completely dimeric in THF solution at room temperature is in line with the results obtained from **8** and **9** since ring strain in the hypothetical monomer of **1**, with magnesium in a five-membered ring, will be even higher than in monomeric **8**. As the trimer of **1** is not observed, we assume that entropy protects the system from further oligomerization as is also the case for other cyclic organomagnesium compounds.^[3,4,14,15] Note, however, that the results presented so far pertain to the situation in solution where an equilibrium can be established; in the solid state, the degree of oligomerization may be different. Thus, Lappert et al. reported the crystal structure of 2-magnesaindane (**10**), the regioisomer of **1**, which turns out to be a trimer with a central fifteen-membered ring.^[16] Unfortu-

nately, data on the degree of oligomerization of **10** in solution are not available.

In analogy to other magnesacycles,^[1–3] one may safely assume that the dimeric **1** has a ten-membered ring structure. As both the magnesium atom and the benzene ring prefer large bond angles ($\geq 120^\circ$), the structure of **1'** as shown in Scheme 5 (which is analogous to **6a'**, Scheme 4), is suggested to be energetically more favorable than the alternative arrangement **1''** (analogous to **6a''**) in which a C(Ar)–Mg–C(Ar) unit is present which probably would cause a higher ring strain in the molecule, as discussed for **6a**.

1,1-Dicyclopentadienyl-1-zirconaindane (**2**)

Having **1** available, it appeared to be an attractive starting material for the preparation of the 1-zirconaindane **2** which has previously been obtained by thermolysis of diphenylzirconocene in the presence of ethene.^[17] It has been shown that the reaction of **11**, the 2-zircona analogue of **2**, with B(C₆F₅)₃ furnished the intramolecular ion pair **12** (Scheme 6).^[5] It was therefore of interest to investigate the reaction of **2** with B(C₆F₅)₃ in order to generate the zwitterionic complex **13**. Study of the effect of anion–cation bonding interactions in **13** on the reactivity of unsaturated molecules was expected to improve our understanding of the factors influencing the activity of cationic metallocene catalysts in olefin polymerization.^[18–22]



Scheme 6

Compound **2** was treated with 1 equiv. of B(C₆F₅)₃ in bromobenzene at -30°C , and the product was isolated as a pale yellow powder in 81% yield by precipitation with *n*-pentane. Elemental analysis confirmed the composition of **13**. The ¹H NMR spectrum in C₂D₂Cl₄ shows a broad tri-

let signal at $\delta = 2.30$ ppm which was assigned to the methylene protons next to the borate group; in the ^{13}C NMR spectrum, a signal at $\delta = 178.2$ ppm indicates that the Zr–C(Ar) bond is still intact. Furthermore, the ^{19}F NMR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$, -25°C) shows three resonances at $\delta = -134.8$ (*o*-F), -160.1 (*p*-F), and -165.0 ppm (*m*-F). These data are in line with the presence of a tetracoordinate, negatively charged boron substituent^[5] $[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ in **13**. The presence of an anion–cation bonding interaction is indicated by the large value of $\Delta\delta(m,p\text{-F}) = 4.9$ (Scheme 6).^[23]

Solutions of **13** in tetrachloroethane are stable at room temperature for several hours. We ascribe this stabilization to intramolecular coordination of an *ortho*-fluoro substituent of one of the C_6F_5 groups to zirconium, as shown. This assumption was confirmed by variable-temperature ^{19}F NMR experiments in $\text{C}_6\text{D}_5\text{Br}/[\text{D}_8]\text{toluene}$. At -60°C , the ^{19}F NMR spectrum shows eight resonances (Table 3) as expected when one of the C_6F_5 groups is coordinating to the zirconium atom and hence becomes rigid and unsymmetrical. One fluorine resonance is shielded to $\delta = -180.2$ ppm, more than 50 ppm from the region typical for an *ortho*-fluorine nucleus in an $[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ anion. A similar shielding (to $\delta = -190.3$ ppm at -88°C) was observed for one of the *ortho*-fluorine nuclei in the zirconoxyborane $\text{Cp}^*_2\text{ZrOB}(\text{C}_6\text{F}_5)_3$ in which the C–F $\cdots$ Zr interaction was proven by X-ray analysis;^[24] more recently, a number of zwitterionic complexes with similar Zr $\cdots$ F bonding interactions have been spectroscopically and structurally characterized.^[6,7] The ^{19}F resonances of **13** broaden above -50°C , and at room temperature, only the initial three ^{19}F resonances are discernible. Note that, presumably for steric reasons, such a Zr $\cdots$ F interaction does not occur in **12**; instead, the X-ray structure reveals an interaction between the zirconium atom and the methylene group carrying the borate substituent.^[5]

Table 3. ^{19}F NMR chemical shifts of **12** {in $\text{C}_6\text{D}_5\text{Br}/[\text{D}_8]\text{toluene}$ at -60°C (283.23 MHz; ref. $\text{CF}_3\text{C}_6\text{H}_5$ in C_6D_6 ; $\delta = -64$ ppm)}

	F(2) ^[a]	F(3) ^[b]	F(4) ^[b]	F(5) ^[b]	F(6) ^[b]
Ring A	–180.2	–155.6	–156.3	–161.8	–123.3
Ring B, C	–131.5	–162.6	–157.5	–162.6	–131.5

^[a] Fluorine positions are numbered clockwise, starting from the boron-substituted position.

The reactivity of **13** contrasts sharply with that of the related complex **12**. Whilst **12** inserts 2-butyne to furnish **14** (Scheme 6) and shows moderate catalytic activity in the polymerization of ethylene (about 20–40 times less active than simple cationic Group-4 catalysts^[18,19]), **13** is inactive in both types of reactions. This may be partly due to the low intrinsic reactivity of the metal–aryl bond towards insertion as compared to metal–alkyl bonds.^[25] Additionally, the fluorine–zirconium interaction in **13** (which is absent

in **12**) hinders coordination of the substrate. Nevertheless, the fluorine–zirconium interaction in **13** is not strong enough to resist cleavage by PMe_3 in CD_2Cl_4 with formation of **15**. The yellow color of **13** disappeared, and **15** was isolated as an off-white solid in 96% yield by precipitation with *n*-pentane. The structure of **15** was assigned on the basis of the ^1H and ^{19}F NMR spectra. In particular, the small value of $\Delta\delta(m,p\text{-F}) = 3.0$ ppm is consistent with the donor having displaced the anion–cation bonding interaction;^[23] an aromatic proton signal at $\delta = 4.48$ ppm strongly suggests an agostic Zr $\cdots$ H interaction.^[26]

Conclusion

1-Magnesaindane (**1**) was obtained via the corresponding 1-mercuraindane (**6**) and found to occur as a dimeric ten-membered ring species in THF solution; in line with the behavior of other magnesacycles, this is due to an interplay between ring strain and entropy. In contrast, intermediate **6** forms a dimer/trimer equilibrium, which is remarkable as, at room temperature and in the absence of a catalyst, diorganomercury compounds usually do not establish equilibria by exchanging ligands.

The 1-zirconaindane **2** was obtained from **1** and dichlorozirconocene. It reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to form the adduct **13** which, according to spectroscopic data, has a zwitterionic structure with transannular interactions between the zirconium atom and one of the *ortho*-fluorine atoms. Although this interaction may contribute to the inertness towards insertion of the zirconium–aryl bond in **13**, it is kinetically unstable at room temperature and is easily cleaved by the Lewis base trimethylphosphane, which coordinates to the zirconium atom with formation of **15**.

Experimental Section

General: All manipulations involving organometallic compounds were carried out in fully sealed glassware using standard high vacuum techniques. Solvents were dried by distillation from liquid Na/K alloy after predrying with NaOH. Magnesium was sublimed twice before use. NMR spectra were measured with a Bruker AC 200 spectrometer (^1H NMR: 200 MHz, ^{13}C NMR: 50.3 MHz), a Varian VXR-300 spectrometer (^1H NMR: 300 MHz, ^{13}C NMR: 75.4 MHz, ^{31}P NMR: 121.6 MHz, ^{19}F NMR: 283.23 MHz), or a Bruker MSL 400 spectrometer (^1H NMR: 400.1 MHz, ^{199}Hg NMR: 71.6 MHz). GCMS analyses were performed with an HP 5890 GC/5970 MS combination, operating at 70 eV and equipped with a Chrompack BP1 (QSGE) 50 m/0.25 mm column. HRMS measurements were performed with a Finnigan MAT 90 mass spectrometer under EI conditions using a direct introducing interface for the introduction of air- and moisture-sensitive compounds. Elemental analyses were carried out at the Microanalytical Laboratory, Rijksuniversiteit Groningen, The Netherlands.

1-(Bromomercurio)-2-[2-(bromomercurio)ethyl]benzene (5): In a Schlenk vessel, 1-bromo-2-(2-bromoethyl)benzene (**3**)^[8] (3.17 g, 12 mmol) in 20 mL of THF was slowly added during 5 h to a stirred suspension of magnesium (1.54 g, 64 mmol) in 60 mL of THF at room temperature. After the addition was complete, an

aliquot was hydrolyzed. Titration (HCl , EDTA)^[27] showed an $\text{Mg}^{2+}/\text{OH}^-$ ratio of 1.1:1 and 78% yield of 1-(bromomagnesio)-2-[2-(bromomagnesio)ethyl]benzene. Subsequently, mercury bromide (8.70 g, 24.2 mmol) in 30 mL of THF was added and the solution was stirred overnight, after which a grey suspension was obtained. After hydrolysis, the resulting suspension was filtered and the residue was washed twice with THF and H_2O and subsequently dried in vacuo to give **5** as a white powder. Yield: 6.0 g (75% based on **3**). ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$, ref. $[\text{D}_5]\text{DMSO}$: $\delta = 2.50$ ppm; NOESY): $\delta = 7.47$ (m, 1 H, 4-H), 7.30 (m, 1 H, 7-H), 7.21 (m, 2 H, 5,6-H), 3.00 (t, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, ArCH_2), 2.06 (t, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, CH_2Hg) ppm. ^{13}C NMR (50.3 MHz, $[\text{D}_6]\text{DMSO}$, ref. $[\text{D}_6]\text{DMSO}$: $\delta = 39.5$ ppm): $\delta = 154.0$ (br. s, C-1), 149.9 (s, C-2), 136.4 (dd, $^1J_{\text{C,H}} = 161.9$, $^3J_{\text{C,H}} = 5.6$ Hz, C-6), 128.1 (dd, $^1J_{\text{C,H}} = 159.6$, $^3J_{\text{C,H}} = 7.8$ Hz, C-4 or -5), 127.8 (dd, $^1J_{\text{C,H}} = 156.0$, $^3J_{\text{C,H}} = 5.8$ Hz, C-3), 125.5 (dd, $^1J_{\text{C,H}} = 159.6$, $^3J_{\text{C,H}} = 7.0$ Hz, C-4 or -5), 38.8 (t, $^1J_{\text{C,H}} = 126.1$ Hz, ArCH_2), 35.2 (bt, $^1J_{\text{C,H}} = 139.8$ Hz, CH_2Hg) ppm. ^{199}Hg NMR (71.6 MHz, DMSO , ref. $\text{Me}_2\text{Hg} = 0$): $\delta = -1107$, -1231 ppm.

1-Mercuraindane (6): A solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (5.42 g, 24 mmol) in 120 mL of 20% aqueous NaOH was slowly added over 5 h to a suspension of **5** (8.0 g, 12 mmol) in a mixture of 120 mL of 10% aqueous NaOH and 24 mL of CHCl_3 at room temperature.^[9] After the addition was complete, a grey precipitate (Hg) was filtered off and the residue was extracted twice with CHCl_3 . The combined organic phases were dried with MgSO_4 and the solvents evaporated to give **6** as a light-grey solid (3.46 g, 95%). **6**: M.p. 71 °C. HRMS: ($^{12}\text{C}_{16}\text{H}_{16}^{200}\text{Hg}^{202}\text{Hg}$): calcd. 610.0642; found 610.0642. $\text{C}_8\text{H}_8\text{Hg}$ (304.74): calcd. C 31.53, H 2.65; found C 31.91, H 2.69. **6a**: ^1H NMR (200 MHz, CDCl_3 , ref. CHCl_3 : $\delta = 7.22$ ppm): $\delta = 7.30$ – 7.16 (m, 4 H, ArH), 3.36 (m, 2 H, ArCH_2), 1.73 (m, 2 H, CH_2Hg) ppm. ^{13}C NMR (50.3 MHz, CDCl_3 , ref. CDCl_3 : $\delta = 76.8$ ppm): $\delta = 180.1$, C-7a), 153.2 (s, C-3a), 136.7 (dd, $^1J_{\text{C,H}} = 158$, $^3J_{\text{C,H}} = 7$ Hz, C-3), 130.4 (dd, $^1J_{\text{C,H}} = 156$, $^3J_{\text{C,H}} = 6$ Hz, C-6), 127.7 (dd, $^1J_{\text{C,H}} = 159$, $^3J_{\text{C,H}} = 7$ Hz, C-5), 125.5 (dd, $^1J_{\text{C,H}} = 159$, $^3J_{\text{C,H}} = 7$ Hz, C-4), 41.5 (t, $^1J_{\text{C,H}} = 131$ Hz, C-3), 39.7 (t, $^1J_{\text{C,H}} = 125.5$ Hz, C-2) ppm. ^{199}Hg NMR (71.6 MHz, CDCl_3 , ref. Me_2Hg : $\delta = 0$): $\delta = -237.2$ ppm. **6b**: Due to the lower concentration of **6b** and to partial overlap of its NMR signals with those of **6a**, not all signals could be identified. ^1H NMR (200 MHz, CDCl_3 , ref. CHCl_3 : $\delta = 7.22$ ppm): $\delta = 7.30$ – 7.16 (undiscernible from those of **6a**, ArH), 2.95 (m, ArCH_2), 1.7 (shoulder on signal of **6a**, CH_2Hg) ppm. ^{13}C NMR (50.3 MHz, CDCl_3 , ref. CDCl_3 : $\delta = 76.8$ ppm): $\delta = 178.8$, C-7a), 154.5 (C-3a), 136.9 (C-3), 129.2 (C-6), 128.4 (C-5), 125.8 (C-4), 41.7 (C-3), 38.7 (C-2) ppm. ^{199}Hg NMR (71.6 MHz, CDCl_3 , ref. Me_2Hg : $\delta = 0$): $\delta = -305.5$ ppm.

1-Magnesaindane (1): Compound **6** (1.78 g, 5.9 mmol) and magnesium (2.5 g, 103 mmol) in 70 mL of THF were stirred for 4 d at 70 °C. A brown solution and a fine black precipitate were obtained. The excess magnesium and the black precipitate were removed by careful decantation. Crystallization by cooling a saturated THF solution gave **1** as colorless needles (4.1 mmol, 70% based on **6**; determined by titration^[27]). Attempts to obtain crystals suitable for an X-ray crystal structure determination were not successful. ^1H NMR (400 MHz, $[\text{D}_8]\text{THF}$, ref. $[\text{D}_7]\text{THF}$: $\delta = 1.75$ ppm): $\delta = 7.71$ (d, $^3J_{\text{H,H}} = 6.4$ Hz, 1 H), 6.73–6.86 (m, 3 H), 3.06 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, ArCH_2), 0.02 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, CH_2Mg) ppm. ^{13}C NMR (50.3 MHz, ref. $[\text{D}_8]\text{THF} = 67.4$): $\delta = 168.7$ (bs), 167.2 (bs), 142.2 (d, $^1J_{\text{C,H}} = 149.3$ Hz), 125.4 (d, $^1J_{\text{C,H}} = 154.5$ Hz), 124.9 (d, $^1J_{\text{C,H}} = 150.3$ Hz), 122.2 (d, $^1J_{\text{C,H}} = 153.6$ Hz), 43.3 (t, $^1J_{\text{C,H}} = 119.3$ Hz, C-3), 17.6 (t, $^1J_{\text{C,H}} = 108.6$ Hz, C-2) ppm.

Reaction of 1 with Deuterium Oxide: An excess of D_2O was added at room temperature to a solution of **1** (about 0.1 mmol) in THF. Diethyl ether and water were added and the organic layer was dried (MgSO_4). By GCMS, only $[\text{D}_2]\text{ethylbenzene}$ (**7**) was observed. GCMS: m/z (%) = 108 (100) $[\text{M}]^+$, 107 (18), 106 (6), 105 (7), 104 (6), 103 (2).

Formation of Zwitterion 13: The known complex **2**^[17] was obtained from the reaction of **1** with Cp_2ZrCl_2 . To a mixture of **2** (53.4 mg, 0.16 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (84.0 mg, 0.16 mmol), 1 mL of $\text{C}_6\text{H}_5\text{Br}$ was added at -30 °C. Addition of 3 mL of *n*-pentane gave a light yellow microcrystalline solid. The supernatant was pipetted off and the precipitate was washed twice with *n*-pentane (3 mL) and dried at 25 °C in the glovebox (1 h) to yield **13** (108.9 mg, 81%) as a pale yellow solid. ^1H NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. C_2DHCl_4 : $\delta = 5.91$ ppm; -25 °C): $\delta = 6.83$ (m, 3 H, ArH), 6.40 (s, 10 H, Cp), 6.32 (d, $^3J_{\text{H,H}} = 5.6$ Hz, 1 H, ArH), 2.70 (bt, $^3J_{\text{H,H}} = 7.5$ Hz, 2 H, ArCH_2), 2.30 (bm, 2 H, CH_2B) ppm. ^{13}C NMR (75.43 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. $\text{C}_2\text{D}_2\text{Cl}_4$: $\delta = 74.35$; -25 °C, cation signals only; those of the anion part were too broad for identification): $\delta = 178.2$ (CZr), 152.2, 138.7, 129.4, 125.3, 124.8 (d, $^1J_{\text{C,H}} = 157.9$ Hz), 116.5 (d, $^1J_{\text{C,H}} = 170.6$ Hz, Cp), 37.8 (t, $^1J_{\text{C,H}} = 126.5$ Hz, ArCH_2), 14.6 (CH_2B) ppm. ^{19}F NMR (283.23 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. $\text{CF}_3\text{C}_6\text{H}_5$ in C_6D_6 : $\delta = -64$; -25 °C): $\delta = -134.8$ (*o*-F), -160.1 (*p*-F), -165.0 (*m*-F) ppm. $\text{C}_{36}\text{H}_{18}\text{F}_{15}\text{Zr}$ (826.73): calcd. C 51.62, H 2.17; found C 52.02, H 2.37.

Reaction of 13 with PMe_3 . Formation of Adduct 15: PMe_3 was added (0.046 mmol, 4.8 μL) to a solution of **13** (38.5 mg, 0.046 mmol) in 0.5 mL of $\text{C}_2\text{D}_2\text{Cl}_4$ and an immediate color change from yellow to almost colorless was observed. After addition of 1 mL of *n*-pentane, a light yellow precipitate was obtained, which was filtered off and washed twice with *n*-pentane (2 mL). Evaporation of the *n*-pentane solution in the glovebox gave **15** as an off-white solid (40.2 mg, 96%). ^1H NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. C_2DHCl_4 : $\delta = 5.91$; -25 °C): $\delta = 7.09$ (d, $^3J_{\text{H,H}} = 7.1$ Hz, 1 H, ArH), 6.92 (m, 2 H, ArH), 5.53 (s, 10 H, Cp), 4.48 (dd, $^3J_{\text{H,H}} = 10.4$, $^4J_{\text{H,H}} = 7.0$ Hz, 1 H, $\text{ArH} \cdots \text{Zr}$), 2.06 (m, 2 H, ArCH_2), 1.35 (d, $^2J_{\text{P,H}} = 7.4$ Hz, 9 H, PMe_3), 1.06 (m, 2 H, CH_2B) ppm. ^{19}F NMR (283.23 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. $\text{CF}_3\text{C}_6\text{H}_5$ in C_6D_6 : $\delta = -64$ ppm; -25 °C): $\delta = -131.9$ (*o*-F), -163.0 (*p*-F), -166.0 (*m*-F) ppm. $^{31}\text{P}\{\text{H}\}$ NMR (121.6 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, ref. PPh_3 : $\delta = -6.0$ ppm): $\delta = -15.8$ ppm.

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