$^{69/71}$Ga and ^{115}In NMR Spectroscopy of Lithium Tetra(*tert*-butyl)gallate and -indate: Spin-Spin Coupling Constants $^1J(^{69/71}\mathrm{Ga},^{13}\mathrm{C})$ and $^1J(^{115}\mathrm{In},^{13}\mathrm{C})$

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The ^{13}C, $^{69/71}$Ga and ^{115}In NMR spectra of lithium tetra(*tert*-butyl)gallate and -indate were measured under various conditions. It proved possible to determine for the first time the coupling constants $^1J(^{69/71}\mathrm{Ga},^{13}\mathrm{C})$ = 182 Hz/232 Hz and $^1J(^{115}\mathrm{In},^{13}\mathrm{C}) = 310 \pm 10$ Hz for these metallates under conditions for solvent-separated ions. DFT calculations [B3LYP/6-311+G(d,p)] were carried out for organogallium compounds such as tri(*tert*-butyl)gallium, trimethylgallium and tetramethylgallate in order to predict and confirm coupling constants $^1J(\mathrm{Ga},^{13}\mathrm{C})$.

Key words: Tetra(*tert*-butyl)gallate, Tetra(*tert*-butyl)indate, ^{13}C, ^{69}Ga, ^{71}Ga, ^{115}In NMR, Coupling Constants, DFT Calculations

Introduction

Both NMR active isotopes of gallium, ^{69}Ga and ^{71}Ga, possess fairly large quadrupole moments (I = 3/2; Q = 0.17 and 0.11 [10^{-24} m^2]), and that of ^{115}In is even greater (I = 9/2, Q = 0.86 [10^{-24} m^2]; ^{113}In is of low natural abundance and has similar unfavorable nuclear properties). Therefore, with few exceptions for $^{69/71}$Ga, indirect nuclear Ga–X or ^{115}In–X spin-spin coupling is generally not resolved [1, 2]. So far particularly important data, like $^1J(^{69/71}\mathrm{Ga},^{13}\mathrm{C})$ or $^1J(^{115}\mathrm{In},^{13}\mathrm{C})$, for comparison with the wealth of other ^{13}C–X couplings [3], are missing. Recently we have found that the ^{27}Al NMR signal of lithium tetra(*tert*-butyl)alanate (**1Al**), dissolved in benzene in the presence of an excess of THF, is extremely narrow. Well resolved splitting due to ^{27}Al–^{13}C spin-spin coupling has been observed in $^{13}\mathrm{C}\{^1\mathrm{H}\}$ as well as in $^{27}\mathrm{Al}\{^1\mathrm{H}\}$ NMR spectra of **1Al** [4]. This prompted us to prepare the corresponding lithium tetra(*tert*-butyl)gallate (**1Ga**) and -indate (**1In**), and to study their NMR spectra under various conditions.

Results and Discussion

*Tri(tert-butyl)gallium (**2Ga**) and tri(tert-butyl)indium (**2In**)*

Tri(*tert*-butyl)gallium (**2Ga**) and -indium (**2In**) were prepared following literature procedures [5, 6]. They were characterized by ^{1}H and ^{13}C NMR spectra. Unlike the ^{13}C(Al–C) NMR signals of the aluminum analog **2Al** [4], the broadening of the ^{13}C(Ga–C) NMR signal of **2Ga** owing to partially relaxed $^{69/71}$Ga–^{13}C spin-spin coupling is fairly small, indicating extremely efficient quadrupole-induced $^{69/71}$Ga nuclear spin relaxation. This was confirmed by the measurement of the ^{71}Ga NMR spectrum of **2Ga**, which shows a very broad signal (full width at half height of about 50 ± 5 kHz). It was not possible with our equipment to record the ^{69}Ga NMR signal of **2Ga**. Expectedly, there is no appreciable broadening of the ^{13}C(In–C) NMR signal of **2In**, indicating complete averaging of the ^{115}In–^{13}C spin-spin coupling owing to fast relaxation of ^{115}In. Since the observed slight broadening of the ^{13}C(Ga–C) NMR signal in the case of **2Ga** results from both ^{69}Ga and ^{71}Ga in the neighborhood to this ^{13}C nucleus, the respective contributions are difficult to evaluate. Therefore, the use of Eq. 1 [7, 8], where $\Delta\nu_b$ is the broadening of the ^{13}C(Ga–C) NMR signal caused by scalar relaxation of the second kind, cannot give accurate results [S_X = 3/2 for ^{71}Ga; T^Q (^{71}Ga) = $6.4 \cdot 10^{-6}$ s].

$$\Delta\nu_b = 4/3\pi S_\mathrm{X}(S_\mathrm{X}+1)[J(\mathrm{A},\mathrm{X})]^2[T^\mathrm{Q}(\mathrm{X})] \quad (1)$$

The line width of the ^{13}C(Ga–C) NMR signal of **2Ga** is close to 3 Hz, as measured from a refocused

Compound	^{71}Ga $\delta(h_{1/2}$(Hz))	^{69}Ga $\delta(h_{1/2}$(Hz))	^{13}C δ(Ga–C)	$\delta(CH_3)$
Bu^t_3Ga	900 (50000 ± 5000)	–	31.3[b]	30.8
$[Bu^t_4Ga]Li$	272 (8250 ± 250)	–	22.7 (br[c])	33.8
$[Bu^t_4Ga]Li$ (*n* py; *n* = 20)	271 (18 ± 0.5)	270 (42 ± 1)	24.2 $^1J(^{71}Ga,^{13}C)$ = 232 Hz $^1J(^{69}Ga,^{13}C)$ = 182 Hz	36.0
$[Bu^t_4Ga]Li$ (*n* THF; *n* = 9)	271 (22 ± 0.5)	270 (96 ± 1)	23.8 $^1J(^{71}Ga,^{13}C)$ = 232 Hz	35.4
$[Bu^t_4Ga]Li$ (*n* 12-crown-4; *n* = 20)	272 (58 ± 1)	270 (140 ± 2)	24.0 $^1J(^{71}Ga,^{13}C)$ = 232 Hz	35.8
$[Bu^t_4Ga]Li$ (*n* TMEDA; *n* = 18)	271 (85 ± 1)	270 (185 ± 2)	n. o.[d]	35.6

Table 1. ^{71}Ga, ^{69}Ga and ^{13}C NMR spectroscopic data[a] of Bu^t_3Ga (**2Ga**) and $[Bu^t_4Ga]Li$ (**1Ga**).

[a] In C_6D_6, at 298 K; [b] $h_{1/2}$ = 3.0 Hz; [c] exchange-broadened: $h_{1/2}$ = 12 Hz; [d] n. o. = not observed.

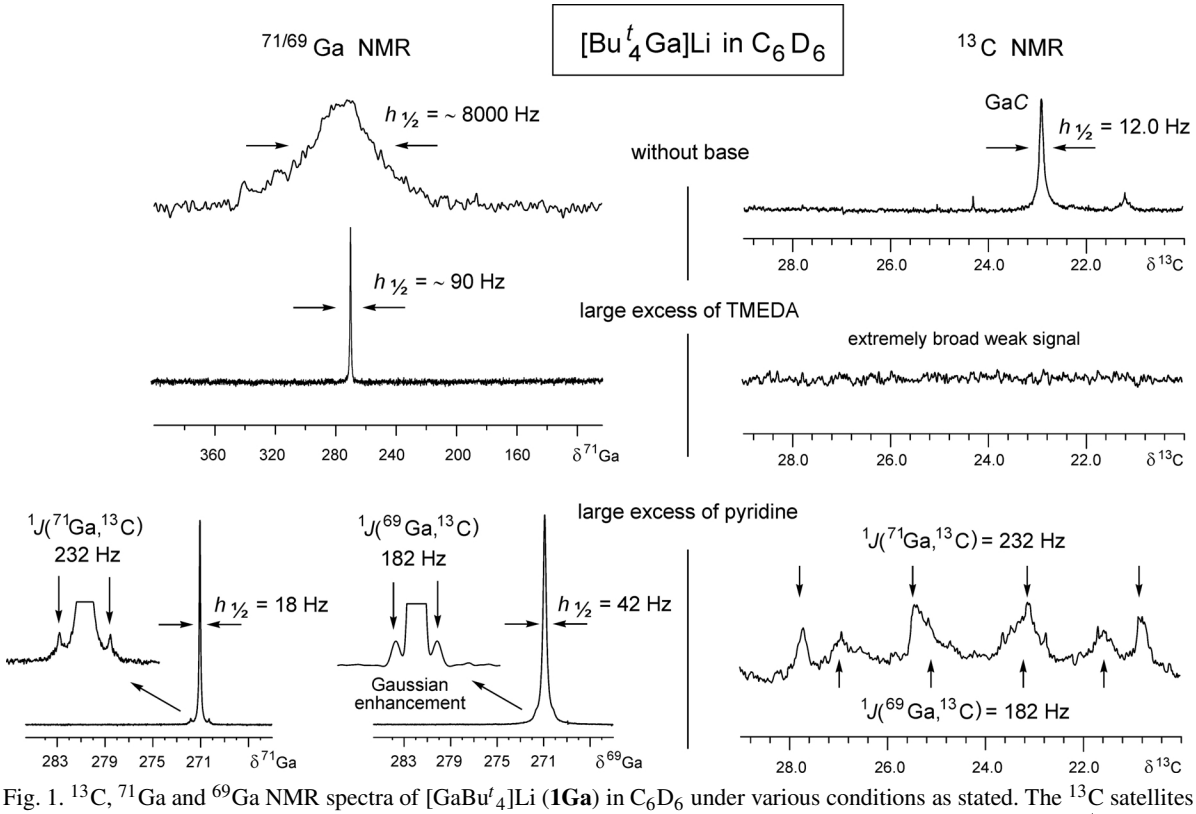


Fig. 1. ^{13}C, ^{71}Ga and ^{69}Ga NMR spectra of $[GaBu^t_4]Li$ (**1Ga**) in C_6D_6 under various conditions as stated. The ^{13}C satellites in the $^{71}Ga\{^1H\}$ and $^{69}Ga\{^1H\}$ NMR spectra do not show any appreciable isotope-induced chemical shift $^1\Delta^{12/13}C(^{71}Ga)$ and $^1\Delta^{12/13}C(^{69}Ga)$ (< 0.5 ppb).

INEPT experiment [9] with ^{1}H decoupling. This leaves a contribution between 3.5 and 5 Hz from ^{71}Ga (natural abundance 39.6 %) and gives a predicted coupling constant $^1J(^{71}Ga,^{13}C) = 205 \pm 30$ Hz for **2Ga**.

The yellow color of crystalline **2In** has been traced to $\sigma \rightarrow \pi$ transitions involving the In–C σ bonds and the In-p_z orbital. Although such transitions are also present in the case of the colorless homologs **2B**, **2Al** and **2Ga**, they are shifted to shorter wave lengths when compared with **2In**. Since these transitions are magnetic-dipole allowed, they cause an increase of the paramagnetic term of ^{13}C nuclear shielding of the ^{13}C nuclei directly linked to B, Al, Ga and In. Indeed, the ^{13}C(In–C) nuclei in

Compound	^{115}In $\delta(h_{1/2}$(Hz))	^{13}C δ(ln–C)	$\delta(CH_3)$
Bu^t_3In	–	40.4	32.6
$[Bu^t_4In]Li$	520 (38000 ± 2000)	25.5 (br[b])	34.4
$[Bu^t_4In]Li$ (*n* py; *n* = 15)	516 (530 ± 5)	n. o.[c]	36.4
$[Bu^t_4In]Li$ (*n* py; *n* = 100)	515 (130 ± 1)		
	$^1J(^{115}In,^{13}C)$ = 310 Hz	n. o.[c]	36.3
$[Bu^t_4In]Li$ (*n* THF; *n* = 100)	517 (192 ± 3)	n. o.[c]	35.9

Table 2. ^{115}In and ^{13}C NMR spectroscopic data[a] of Bu^t_3In (**2In**) and $[Bu^t_4In]Li$ (**1In**).

[a] In C_6D_6, at 298 K; [b] exchange-broadened: $h_{1/2}$ = 30 Hz; [c] n. o. = not observed; extremely broad, ill-defined, weak and unresolved signal, partially overlapping with $^{13}C(CH_3)$ NMR signals from small amounts of impurities containing Bu^t groups.

2In are least shielded in this series with δ^{13}C(In–C) = 40.4.

*Lithium tetra(tert-butyl)gallate (**1Ga**) and lithium tetra(tert-butyl)indate (**1In**)*

Treatment of **2Ga** or **2In** with *tert*-butyllithium (Bu^tLi) afforded mainly the desired gallate **1Ga** or -indate **1In**, respectively, both soluble in benzene and also in mixtures of benzene with various donors such as an excess of pyridine, tmeda, THF, or 12-crown-4. Relevant NMR data are given in the Tables 1 and 2.

Very few examples of Ga–X spin-spin coupling have been reported, *viz.* for $[GaH_4]^-$ (X = ^{1}H [10]), $[Ga(NCS)_4]^-$ (X = ^{14}N [11]), and $\{Ga[OP(OMe)_3]_6\}^{3+}$ (X = ^{31}P [12]), whereas ^{115}In–X spin-spin couplings have not been detected so far. In the case of $[InH_4]^-$ a broad featureless ^{115}In NMR signal was measured which was described as the result of unresolved ^{115}In–^{1}H spin-spin coupling with $^1J(^{115}In,^1H) \approx 1000$ Hz [13]. From the present study of **1Ga** in benzene, in the presence of a large excess of pyridine (Fig. 1), we report the first examples of coupling constants $^1J(^{69,71}Ga,^{13}C)$ determined from the appropriate splitting in $^{69/71}$Ga and ^{13}C NMR spectra. Moreover, in the case of **1In**, we have observed the most narrow ^{115}In NMR signal reported so far which allowed to determine $^1J(^{115}In,^{13}C)$ from the ^{13}C satellites (Fig. 2).

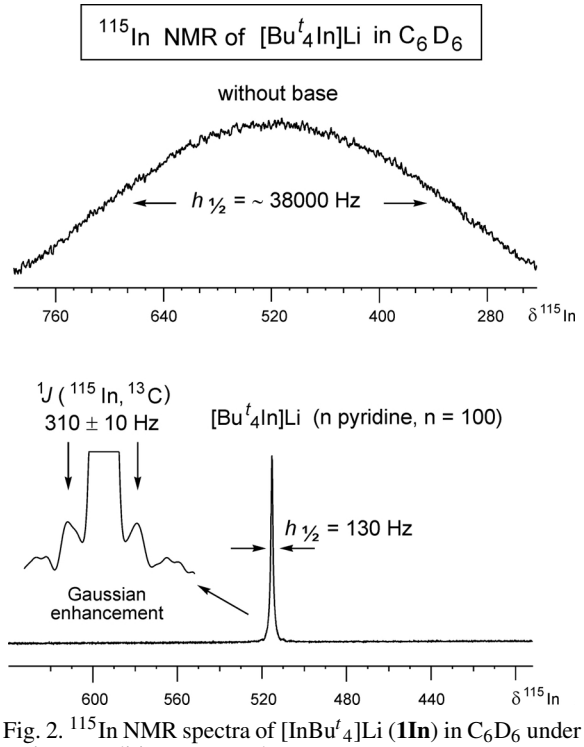


Fig. 2. ^{115}In NMR spectra of $[InBu^t_4]Li$ (**1In**) in C_6D_6 under various conditions as stated.

The small line widths of the $^{69/71}$Ga NMR signals of solutions containing **1Ga** with a large excess of pyridine suggest the presence of solvent-separated ion pairs and almost ideally tetrahedral surroundings of the gallium atom. The observed ratio of the line widths $[h_{1/2}(^{69}Ga)/h_{1/2}(^{71}Ga) = 2.4]$ is close to the theoretical value predicted from the square of the ratio of the quadrupole moments (2.5). It has been noted, in agreement with our own experience, that this is not always the case for unknown reasons [14]. In the case of **1In**, the line width of the ^{115}In NMR signal (Fig. 2, lower trace) corresponds to the lowest limit which can be achieved by dilution of the sample with pyridine. Nevertheless, the $^1H(Bu^t)$ NMR signal is broad (about 90 Hz in the top) and reminds of dynamic effects caused by exchange broadening. This signal becomes less broad in the presence of a small amount of pyridine or without pyridine, which indicates fast and random interaction of the lithium cation with the hydrocarbon framework around the indium atom. Thus, it is suggested that slow (on the NMR time scale) dynamic equilibria have to be considered for solutions containing **1In** and a large excess of pyridine, pointing towards ion pair interactions. More suitable donors or different cations (*e. g.* tetraalkylammonium) are required in order to enforce complete ion pair separation and to observe even sharper ^{115}In NMR signals. Heating of the sample containing **1In** and a large excess of pyridine induces decomposition as shown by several new fast growing ^{1}H NMR signals.

Table 3. Reduced coupling constants $^1J(M,^{13}C)$ and $^1K(M,^{13}C)$[a] for Me_4M (M = ^{29}Si, ^{73}Ge, ^{119}Sn[b]) and $[Bu^t{}_4M]^-$ (M = ^{27}Al, ^{71}Ga, ^{115}In).

Me_4M	$[Bu^t{}_4M]^-$
$^1J(M,^{13}C)$ (Hz) / $^1K(M,^{13}C)$ (nm^{-3})	$^1J(M,^{13}C)$ (Hz) / $^1K(M,^{13}C)$ (nm^{-3})
−52.0 / +8.65 (M = ^{29}Si)	+76.0 / +9.63 (M = ^{27}Al [4])
−18.7 / +17.67 (M = ^{73}Ge)	+232 / +25.09 (M = ^{71}Ga[c])
−352.0 / +31.04 (M = ^{119}Sn)	+310 / +46.5 (M = ^{115}In[c])

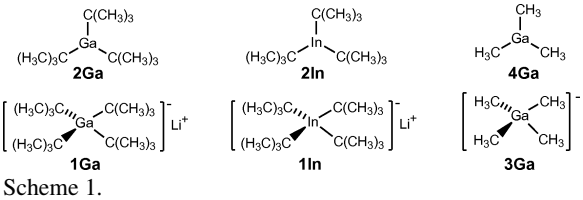
[a] $^1K(M,^{13}C) = 4\pi^2\ ^1J(M,^{13}C)$ (h $\gamma(M)$ $\gamma(^{13}C))^{-1}$; [b] R. K. Harris, B. E. Mann (Eds.), *NMR and the Periodic Table*, Academic Press, London, **1978**; [c] this work.

Changes in the magnitude of the coupling constants $^1J(M,^{13}C)$ are expected to be similar in comparable compounds for Group 13 and Group 14 nuclei, if the individual nuclear magnetic properties of M are eliminated. This is shown by a comparison of the reduced coupling constants $^1K(M,^{13}C) = 4\pi^2\ ^1J(M,^{13}C)$ (h $\gamma(M)$ $\gamma(^{13}C))^{-1}$, where M = ^{29}Si, ^{73}Ge, ^{119}Sn (in Me_4M), and M = ^{27}Al, ^{71}Ga and ^{115}In (in $[MBu^t{}_4]^-$) (Table 3).

DFT calculations

The DFT calculations of the NMR data were based on the optimized gas phase geometries for **2Ga**, $[GaMe_4]^-$ (**3Ga**), and $GaMe_3$ (**4Ga**) (Scheme 1).

The X-ray structural analysis has revealed negligible intermolecular interactions for **2Ga** [17], and also for **2In** [17], although the quality of the structure determination of the gallane suffered from disorder. Gas phase electron diffraction studies (GED) of **2Al** and **2Ga** have proven the strictly monomeric nature of these compounds and indicated closely related structural features [18]. As shown in Fig. 3, the atoms C1, C2 and C3 are coplanar with the central gallium atom and the carbon atoms linked directly to it. The difference in the respective calculated Ga–C–C bond angles indicates that in addition to steric effects hyperconjugation plays an important role [4, 17, 18]. The calculated bond length Ga–C in **4Ga** (199.2 pm) is shorter than in **2Ga** (206.4 pm), most likely because of the bulkiness of the *tert*-butyl groups. For $[GaMe_4]^-$ (**3Ga**), the bond length Ga–C is calculated as 208.1 pm.



Scheme 1.

Ga-C (pm)	calcd. 206.4; XRD: 199 – 202 (disorder); GED: 203.2
Ga-C-C1,2,3 (*deg*)	calcd. 114.9; XRD: 99 – 125 (disorder); GED: 109.2 (mean)
Ga-C-C (*deg*)	calcd. 107.8

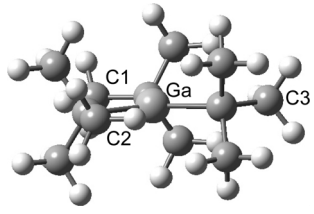


Fig. 3. Comparison of calculated [B3LYP/6-311+G(d,p)] [15, 16] and experimental (XRD [17] and GED [18]) structures of $GaBu^t{}_3$.

On the simple basis of the changes in the bond lengths Ga–C in **4Ga** and **3Ga** as well as of the concept of hybridization of the gallium atom (sp^2 and sp^3), one expects an increase in the magnitude of the coupling constant $^1J(^{71}Ga,^{13}C)$ in **4Ga** relative to **3Ga**. However, the calculated values are almost the same at 186.8 Hz (**4Ga**) and 185.5 Hz (**3Ga**). In **4Ga**, the gallium atom is three-coordinate and therefore, negative contributions to the Fermi contact term have to be taken into account owing to magnetic-field induced mixing of σ and π or σ and σ^* levels with small energy differences. The σ-π transitions are absent in **3Ga**, and the energy difference between the σ-σ^* transitions may be greater. The different electronic structure of **4Ga** and **3Ga** is also indicated by the calculated negative contributions from the paramagnetic spin-orbital term [19] (−11.6 Hz for **4Ga**; −2.8 Hz for **3Ga**). Usually, the calculations of coupling constants $^1J(M,^{13}C)$ (M = ^{29}Si [20], ^{73}Ge [21]) at the level of theory used here give values which are too small by about 20 %. Otherwise, calculated coupling constants appear to be fairly reliable [22 – 25]. In the case of **2Ga**, the calculated value $^1J(^{71}Ga,^{13}C)$ is 166.7 Hz which compares well with the estimated experimental value (205 ± 30 Hz), considering the systematic error in the calculations. The experimental value $^1J(^{71}Ga,^{13}C)$ for **1Ga** (232 Hz) is thus consistent, since negative contributions to the Fermi contact term and negative contributions arising from the paramagnetic spin-orbital term are not present or much smaller in the case of the gallate **1Ga**.

Experimental Section

The preparation and the handling of samples were carried out observing the necessary precautions to exclude air and traces of moisture. The solvents used were carefully dried by established methods. Starting materials such as LiBu^t (1.7 M in pentane) (Aldrich), gallium trichloride (anhydrous, beads, −10 mesh, 99.99 %) (Aldrich) and indium trichloride (anhydrous, powder, 99.999+ % metals basis) (Aldrich) were commercial products. Tri(*tert*-butyl)gallium (**2Ga**) [5c] [^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ ($^1J(^{13}C,^1H)$) = 1.17 (124.0) (s, 27H, CH_3)] and tri(*tert*-butyl)indium (**2In**) [6b] [^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ ($^1J(^{13}C,^1H)$) = 1.28 (123.5) (s, 27H, CH_3)] were prepared by literature procedures.

NMR spectra were recorded at 23 °C on Bruker DRX 500 or Varian Inova 400 spectrometers (^{1}H, ^{13}C, ^{69}Ga, ^{71}Ga and ^{115}In NMR), all equipped with multinuclear units, using C_6D_6 solutions (*ca.* 5 %) in 5 mm tubes. Chemical shifts are given relative to Me_4Si [δ^1H (C_6D_5H) = 7.15, δ^{13}C (C_6D_6) = 128.0], external $GaCl_3$ in D_2O [δ^{71}Ga = 0 for $\Xi(^{71}Ga)$ = 30.496579 MHz and δ^{69}Ga = 0 for $\Xi(^{69}Ga)$ = 24.001317 MHz] and external $InCl_3$ in D_2O [δ^{115}In = 0 for $\Xi(^{115}In)$ = 21.914458 MHz].

*Lithium-tetra(tert-butyl)gallate (**1Ga**)*

A solution of **2Ga** (250 mg, 1.04 mmol) in C_6D_6 (1 mL) was cooled to 0 – 5 °C, and LiBu^t (0.61 mL of a 1.7 M solution in pentane, 1.04 mmol) was added. The mixture was warmed to r. t. and stirred for 1 h before all volatile materials were removed *in vacuo*. The remaining oil was dissolved in C_6D_6 (3 mL) and the mixture stirred for 4 h. Insoluble materials were filtered off, and the liquid was collected. Then pyridine, THF, 12-crown-4 or TMEDA were added in portions at 5 °C.

1Ga: ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = ($^1J(^{13}C,^1H)$) = 1.17 (122.6) (s, 36H, CH_3).

1Ga(*n* py; *n* = 20): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.66 (m, 36H, CH_3), 6.92, 7.31, 8.46 (m, m, m).

1Ga(*n* THF; *n* = 9): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.32 (br. m, 36H, CH_3), 1.56, 3.41 (m, m).

1Ga(*n* 12-crown-4; *n* = 20): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.35 (br. m, 36H, CH_3), 3.41 (m).

1Ga(*n* TMEDA; *n* = 18): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.35 (br. m, 36H, CH_3), 2.09 (s), 2.29 (m).

*Lithium-tetra(tert-butyl)indate (**1In**)*

A solution of **2In** (252 mg, 0.88 mmol) in C_6D_6 (3 mL) was cooled to 0 – 5 °C, and LiBu^t (0.52 mL of a 1.7 M solution in pentane, 0.88 mmol) was added drop wise and in the dark. The mixture was warmed to r. t., stirred for 1 h, and volatile materials were removed *in vacuo*. The remaining oily solid was dissolved in C_6D_6 (3 mL). Then pyridine (or THF) was added in portions at 5 °C.

1In: ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = ($^1J(^{13}C,^1H)$) = 1.22 (122.7) (s, 36H, CH_3).

1In(*n* py; *n* = 15): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.82 (m, 36H, CH_3), 6.75, 7.10, 8.44 (m, m, m).

1In(*n* py; *n* = 100): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.87 (very broad, 36H, CH_3), 7.23, 7.60, 8.76 (m, m, m).

1In(*n* THF, *n* = 100): ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.26 (very broad, 36H, CH_3), 1.57, 3.51 (m, m).

All calculations were performed using the GAUSSIAN03 program package [26]. Optimization of the gas phase geometries was carried out with DFT methods (B3LYP) [15] and the 6-311+G(d,p) basis set [16]. Frequencies were calculated analytically to characterize the stationary points of the optimized geometries as minima by the absence of imaginary frequencies.

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