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SUPPORTING INFORMATION

Solution Structures of Alkali Metal Cyclopentadienides in THF estimated by ECC-DOSY NMR-Spectroscopy (incl. Software)

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Contents

I. Parameters and Methodology to Estimate Molecular Weights (*MW*s) from DOSY

Recently, our group could show that normalised logarithmic diffusion coefficients are independent of gradient and magnetic field strength, gradient pulse duration, and changes in temperature or viscosity. This creates comparability of diffusion coefficients and the creation of so called external calibration curves (ECCs) becomes possible, which will be explained herein. Equation **(S1)** was derived to normalise said diffusion coefficients:[1]

$$logD_{x,norm} = logD_{ref,fix} - logD_{ref} + logD_x \qquad \textbf{(S1)}$$

$logD_{ref,fix}$ is the fixed logarithmic diffusion coefficient of the reference, which was estimated for the original references by using the middle diffusion coefficient of multiple DOSY measurements of 15 mM solutions at 25 °C, $logD_{ref}$ is the measured logarithmic diffusion coefficient of the reference, $logD_x$ the measured logarithmic diffusion coefficient of analyte (x) and $logD_{x,norm}$ the relative logarithmic diffusion coefficient of the analyte x normalised to the reference, which will be used in ECCs as well as estimation of *MW*s.

In this article we used 1,2,3,4-tetraphenylnaphthalene (TPhN) or 2,2,3,3-tetramethylbutane (TMB) as internal references with the following fixed diffusion coefficients in THF-d_8:[1]

$$logD_{ref,fix}(TPhN) = -9.1054$$
$$logD_{ref,fix}(TMB) = -8.7749$$

With equation (**S2**) it is possible to estimate *MW*s (MW_{det}) with the help of ECC parameters (*K* and *α*) taken from our ECC establishing papers (see. Tab. S-1).[1] Most *MW*s were calculated with the ECCs for dissipated spheres and ellipsoidal (DSE) molecules, when no specific aggregate could be presented we used merged ECCs. Deuterated species diffuse like their protonated counterparts.[2]

$$MW_{det} = 10^{\left(\frac{logD_{x,norm} - logK}{\alpha}\right)} \qquad \textbf{(S2)}$$

Tab. S-1: Linear fit parameters for ECCs in THF-d_8. We used all normalised diffusion coefficients given in literature[1] to redo the merged ECC and got different ECC parameters, which were then used in this study. In literature the merged ECC was generated by averaging the ECC parameters of all shape optimized ECCs.

	log*K*	Δlog*K*	*α*	Δ*α*
ECC_{DSE}^{THF}	–7.54	0.0285	–0.582	0.0124
ECC_{merge}^{THF}	–7.60	0.0407	–0.553	0.0180

The accuracy of the ECCs are: MW_{dif} ≤ ±9 % (ECC_{DSE}^{THF}) and MW_{dif} ≤ ±30 % (ECC_{merge}^{THF}). The deviation is calculated by $MW_{dif} = [(MW_{calc} - MW_{det})/MW_{det}] \cdot 100\%$, where MW_{det} is the experimentally determined and MW_{calc} the calculated molecular weight of a hypothetical aggregate.

Furthermore, the theoretical error limits have been calculated for the ECC-methodology *via* the following formulae (**S3**) and (**S4**). Formula (**S3**) has been derived through error propagation:

$$\Delta MW_{det} = \sqrt{\begin{gathered}\left(-\frac{MW_{det}}{D_{ref}\alpha}\cdot\Delta D_{ref}\right)^2 + \left(-\frac{MW_{det}}{K\alpha}\cdot\Delta K\right)^2 + \left(\frac{MW_{det}}{D_x\alpha}\cdot\Delta D_x\right)^2 \\ + \left(\frac{MW_{det}}{D_{ref,fix}\alpha}\cdot\Delta D_{ref,fix}\right)^2 + \left(-\frac{MW_{det}log\left(\frac{D_x D_{ref,fix}}{D_{ref}K}\right)}{\alpha^2}\cdot\Delta\alpha\right)^2\end{gathered}} \tag{S3}$$

$$\Delta MW_{det,rel} = \frac{\Delta MW_{det}}{MW_{det}} \cdot 100\% \tag{S4}$$

Maximum deviations of logarithmic diffusion coefficients were around 0.075, which is approximately the width at half maximum of a DOSY signal. For all logarithmic diffusion coefficients an error of Δlog*D* of 0.015 (twice the mentioned deviations) was assumed. Theoretical errors are depending mostly on the linear fit parameters of the ECCs (listed further above; 99% of the final error), therefore utilizing individual errors for the diffusion coefficients did not seem necessary.

II. Preparation and NMR Assignment of Alkali Metal Cyclopentadienides (MCps)

All preparations were performed in a dry and O_2-free Ar atmosphere using Schlenk techniques.[3] Solvents were dried under reflux with appropriate drying agents in an Ar atmosphere. Dicyclopentadiene was purchased from Fluka and thermally cracked and distilled directly before use at 170 °C and ambient pressure (results in cyclopentadiene (CpH)). Other Chemicals were either purchased commercially or synthesised according to known literature procedures and stored under inert atmosphere. *n*Butyllithium (*n*BuLi) was kindly donated by Rockwood Lithium GmbH and was filtered through Celite© before use along with determination of the concentration.[4]

Cyclopentadienyllithium (CpLi) was prepared following a preparation route similar to *Olbrich*'s[5] and *Wagner*'s[6]. It was synthesised by lithiation of freshly distilled CpH (0.45 mL, 5.50 mmol, 1.16 eq.) with *n*BuLi (4.74 M in hexane, 1.00 mL, 4.74 mmol, 1.0 eq.) at 0 °C in THF (50 mL). The colorless reaction mixture was stirred for 10 h and after evaporation of the solvent CpLi was received as a white powder (0.34 g, 4.72 mmol, 99%) and dried *in vacuo*. For NMR measurements in NH_3, gaseous NH_3 was introduced into the NMR tube for one minute at –78 °C; afterwards 0.1 mL of toluene-d_8 was added for referencing and after sealing the NMR tube spectra were recorded at 25 °C.

(THF-d_8):
^{1}H-NMR (400.13 MHz, THF-d_8): δ = 5.69 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, THF-d_8): δ = 103.4 (s, 5 C, 5 CH) ppm.
^{7}Li-NMR (155.51 MHz, THF-d_8): δ = –7.75 (s) ppm.

(NH_3):
^{1}H-NMR (400.13 MHz, NH_3): δ = 5.89 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, NH_3): δ = 104.1 (s, 5 C, 5 CH) ppm.
^{7}Li-NMR (155.51 MHz, NH_3): δ = –0.59 (s) ppm.

Cyclopentadienylsodium (CpNa) was prepared following a preparation route similar to *Olbrich's*[5]. It was synthesised by addition of freshly distilled CpH (0.90 mL, 10.8 mmol, 1.08 eq.) to a suspension of NaH (0.24 g, 10.0 mmol, 1.00 eq.) in Et_2O (50 mL). The reaction mixture was stirred for 24 h and turned light pink in the process. After filtration, cyclopentane (10 mL) and pentane (20 mL) were added to the filtrate and the product was crystallised at –28 °C. The white crystals (0.64 g, 7.27 mmol, 73%) were filtered, washed with cold pentane and dried *in vacuo*.

(THF-d_8):
^{1}H-NMR (400.13 MHz, THF-d_8): δ = 5.72 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, THF-d_8): δ = 103.3 (s, 5 C, 5 CH) ppm.
^{23}Na-NMR (105.84 MHz, THF-d_8): δ = –28 to –31 (s_{br}) ppm.

Cyclopentadienylpotassium (CpK) was prepared by addition of freshly distilled CpH (0.96 g, 14.5 mmol, 1.00 eq.) to a solution of freshly cut potassium (2.3 g, 58.8 mmol, 4.10 eq.) in Et_2O (15 mL). After stirring the reaction mixture for 10 h and filtration of unreacted potassium, hexane (10 mL) was added. The product precipitated as a white solid (0.33 g, 3.17 mmol, 22%) and was filtered and dried *in vacuo*.

(THF-d_8):
^{1}H-NMR (400.13 MHz, THF-d_8): δ = 5.63 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, THF-d_8): Due to low solubility no resonance could be detected.

Cyclopentadienylrubidium (CpRb) was prepared by addition of freshly distilled CpH (0.06 mL, 0.73 mmol, 1.06 eq.) to a stirred and cooled (0 °C) solution of RbHMDS[a] (0.17 g, 0.69 mmol, 1.00 eq.) in THF (10 mL). After heating to ambient temperature and stirring for another hour, pentane (15 mL) was added. The product precipitated as a light brown solid (0.09 g, 0.60 mmol, 87%) and was filtered and dried *in vacuo*.

(THF-d_8):
^{1}H-NMR (400.13 MHz, THF-d_8): δ = 5.61 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, THF-d_8): Due to low solubility no resonance could be detected.

Cyclopentadienylcaesium (CpCs) was prepared by addition of freshly distilled CpH (0.06 mL, 0.73 mmol, 1.06 eq.) to a stirred and cooled (0 °C) solution of CsHMDS[a] (0.20 g, 0.69 mmol, 1.00 eq.) in THF (10 mL). After heating to ambient temperature and stirring for another hour, pentane (15 mL) was added. The product precipitated as a light brown solid (0.11 g, 0.56 mmol, 81%) and was filtered and dried *in vacuo*.

(THF-d_8):
^{1}H-NMR (400.13 MHz, THF-d_8): δ = 5.55 (s, 5 H, 5 CH) ppm.
^{13}C{^{1}H}-NMR (100.62 MHz, THF-d_8): δ = 107.0 (s, 5 C, 5 CH) ppm.
^{133}Cs-NMR (52.48 MHz, THF-d_8): δ = –240.1 (s) ppm.

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[a] HMDS = hexamethyldisilazane (or Bis(trimethylsilyl)amine)

III. NMR Spectra

1. Cyclopentadienyllithium (CpLi)

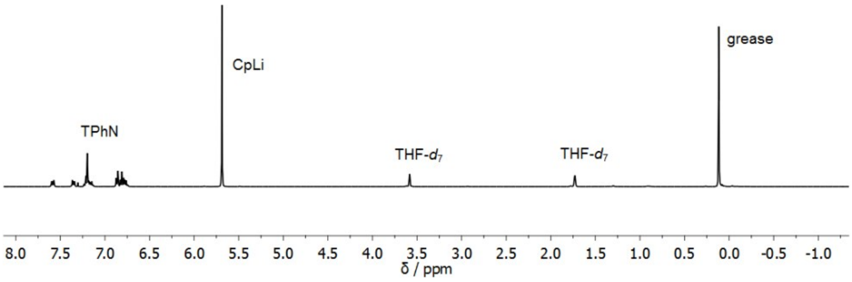


Fig. S-III-1: ^{1}H-NMR spectrum of CpLi in THF-d_8 at 25 °C.

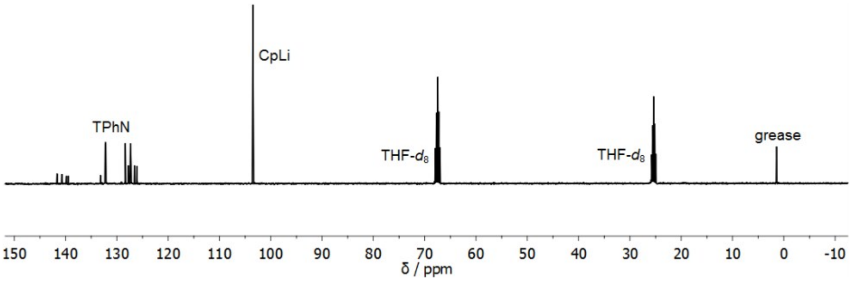


Fig. S-III-2: ^{13}C{^{1}H]-NMR spectrum of CpLi in THF-d_8 at 25 °C.

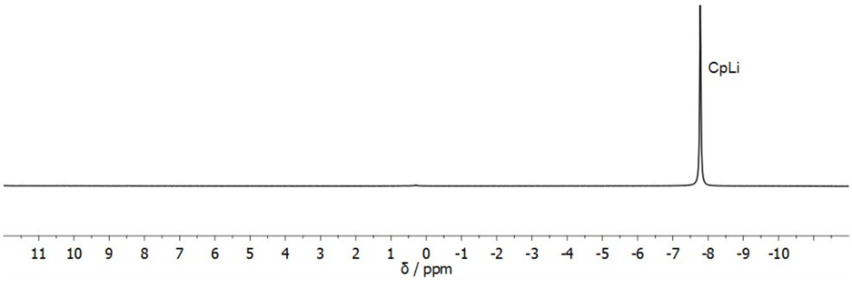


Fig. S-III-3: ^{7}Li-NMR spectrum of CpLi in THF-d_8 at 25 °C.

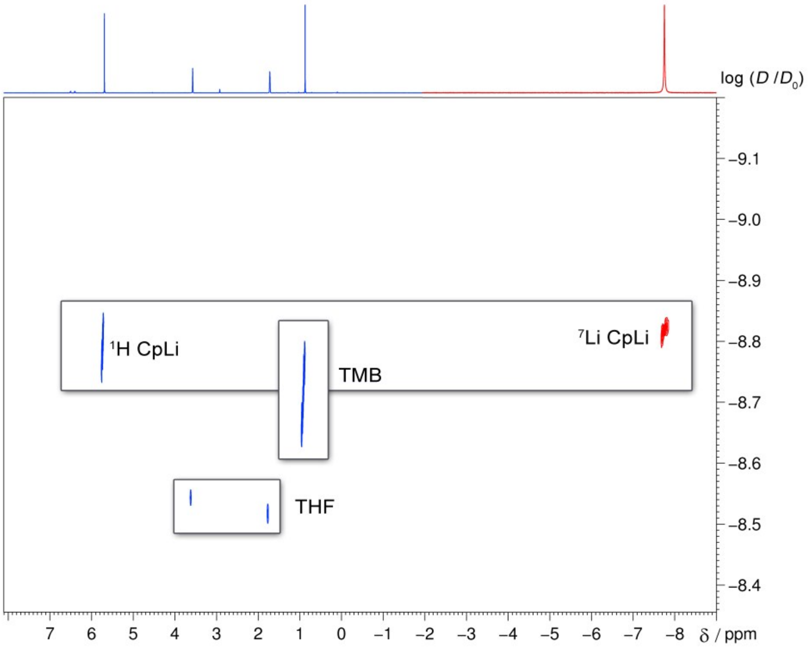


Fig. S-III-4: Superposition of ^{1}H- (blue) and ^{7}Li-DOSY-NMR (red) spectra of CpLi in THF-d_8 at 25 °C. Since only 15 mM solutions were used, not all THF is coordinated to CpLi and the diffusion coefficient is averaged with "free" THF.

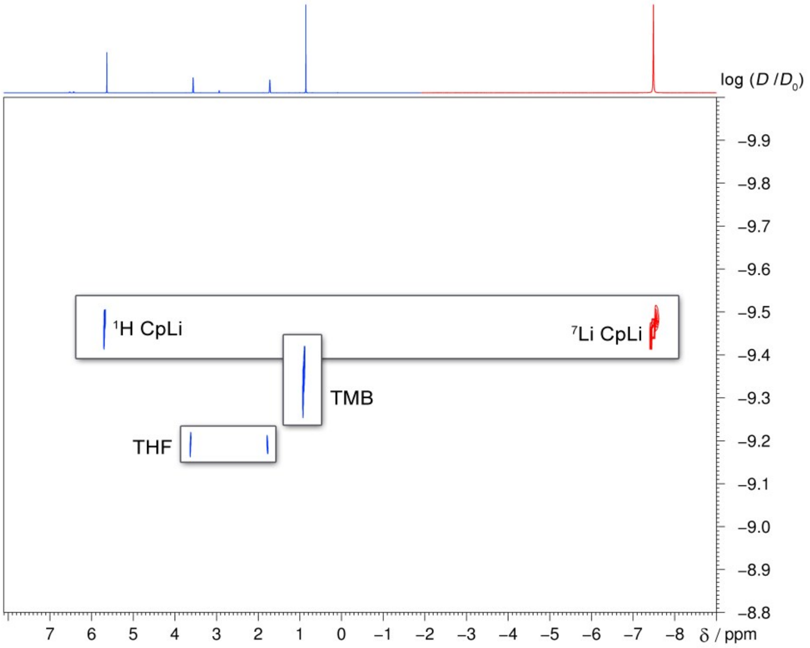


Fig. S-III-5: Superposition of ^{1}H- (blue) and ^{7}Li-DOSY-NMR (red) spectra of CpLi in THF-d_8 at –50 °C. Since only 15 mM solutions were used, not all THF is coordinated to CpLi and the diffusion coefficient is averaged with "free" THF.

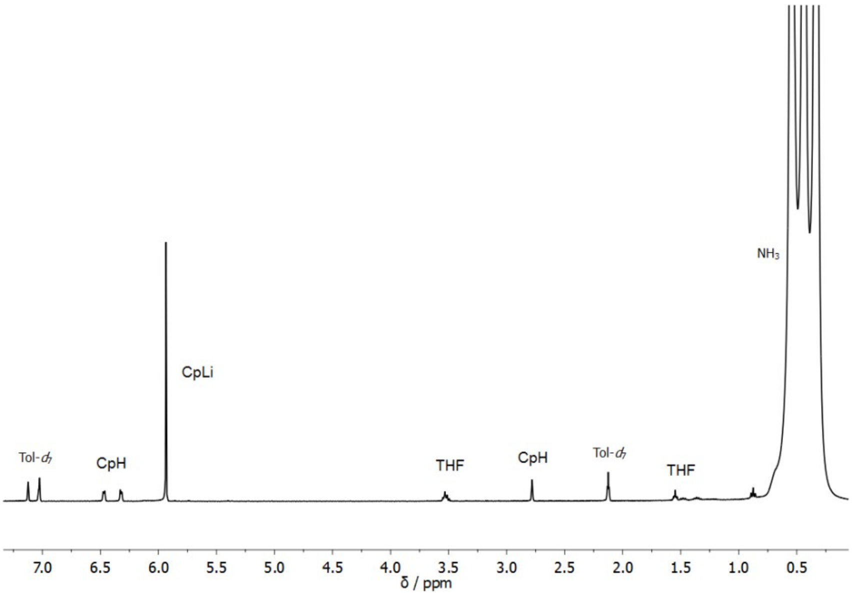


Fig. S-III-6: ^{1}H-NMR spectrum of CpLi in NH_3 with 0.1 mL toluene-d_8 at 25 °C.

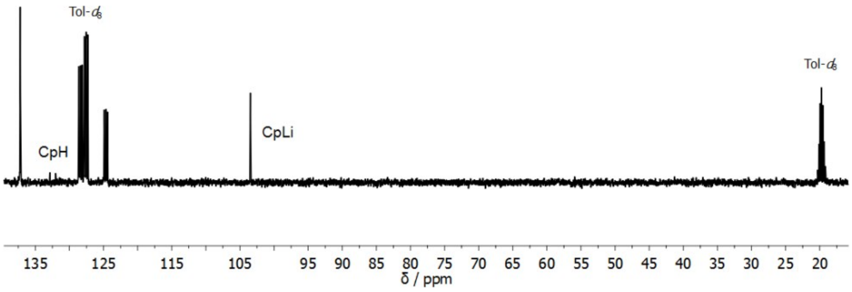


Fig. S-III-7: ^{13}C{^{1}H}-NMR spectrum of CpLi in NH_3 with 0.1 mL toluene-d_8 at 25 °C.

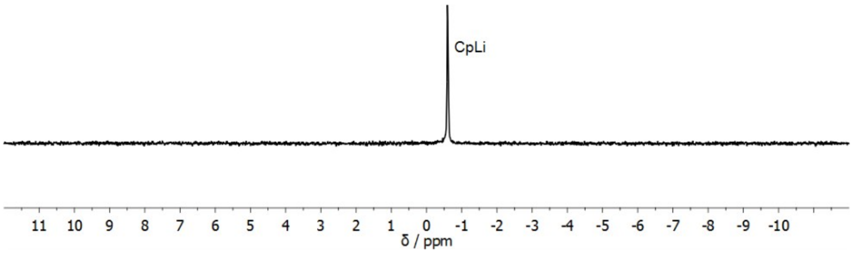


Fig. S-III-8: ^{7}Li-NMR spectrum of CpLi in NH_3 with 0.1 mL toluene-d_8 at 25 °C.

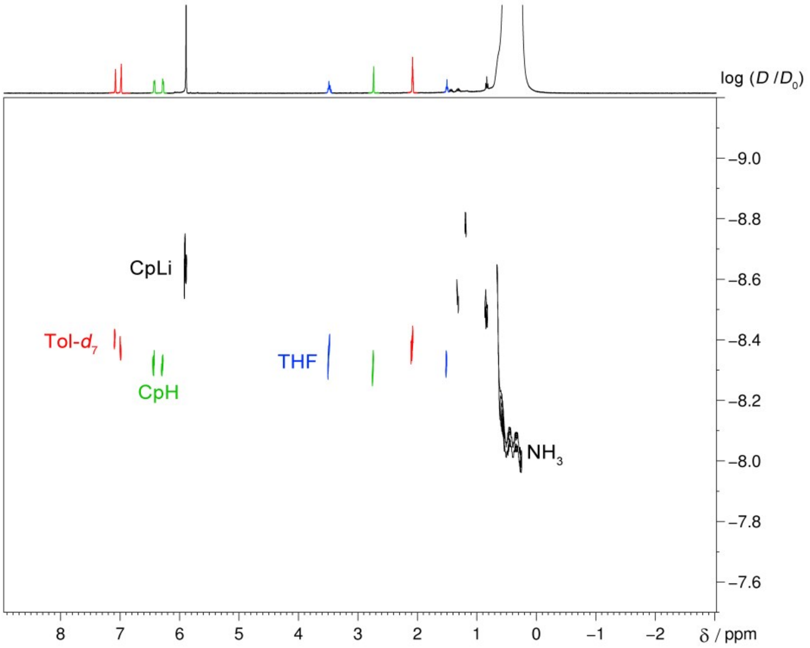


Fig. S-III-9: ^{1}H-DOSY-NMR spectrum of CpLi in NH_3 (with 0.1 mL toluene-d_8 (red)) at 25 °C. Cyclopentadiene (green) and THF (blue) remain from synthesis.

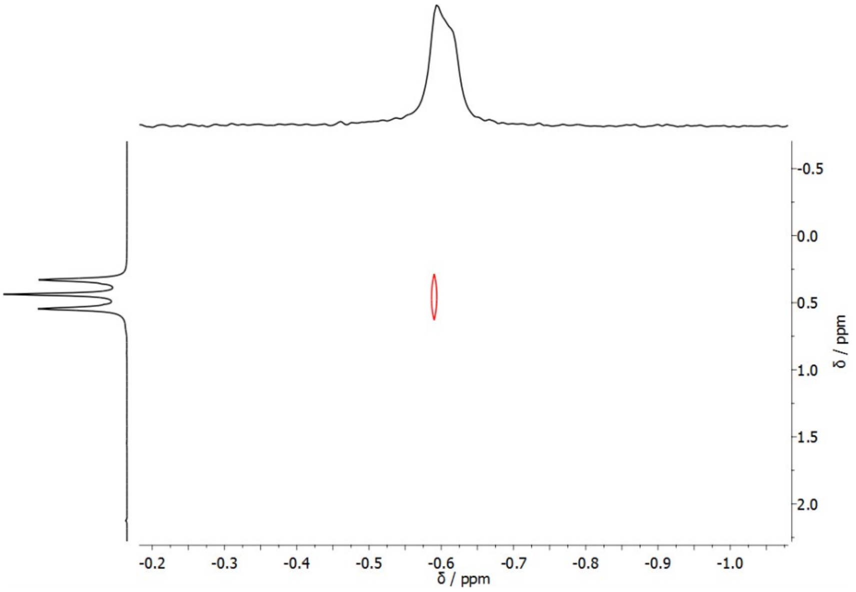


Fig. S-III-10: Excerpt of ^{7}Li-^{1}H-HOESY-NMR spectrum of CpLi in NH_3 with 0.1 mL toluene-d_8 at 25 °C. Shows coupling between NH_3 and lithium.

2. Cyclopentadienylsodium (CpNa)

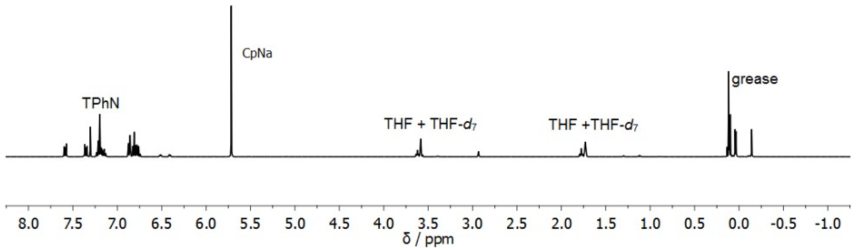


Fig. S-III-11: ^{1}H-NMR spectrum of CpNa in THF-d_8 at 25 °C.

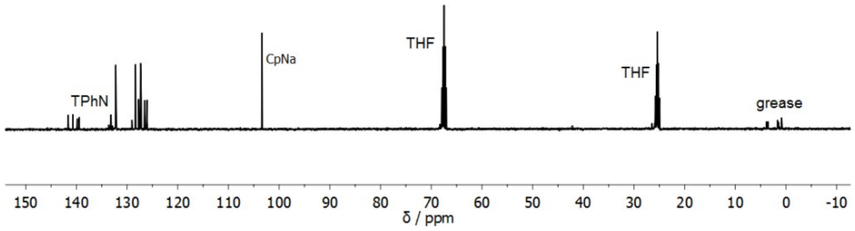


Fig. S-III-12: ^{13}C{^{1}H}-NMR spectrum of CpNa in THF-d_8 at 25 °C.

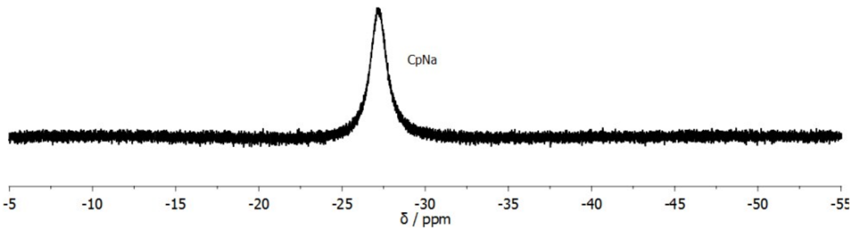


Fig. S-III-13: ^{23}Na-NMR spectrum of CpNa in THF-d_8 at 25 °C.

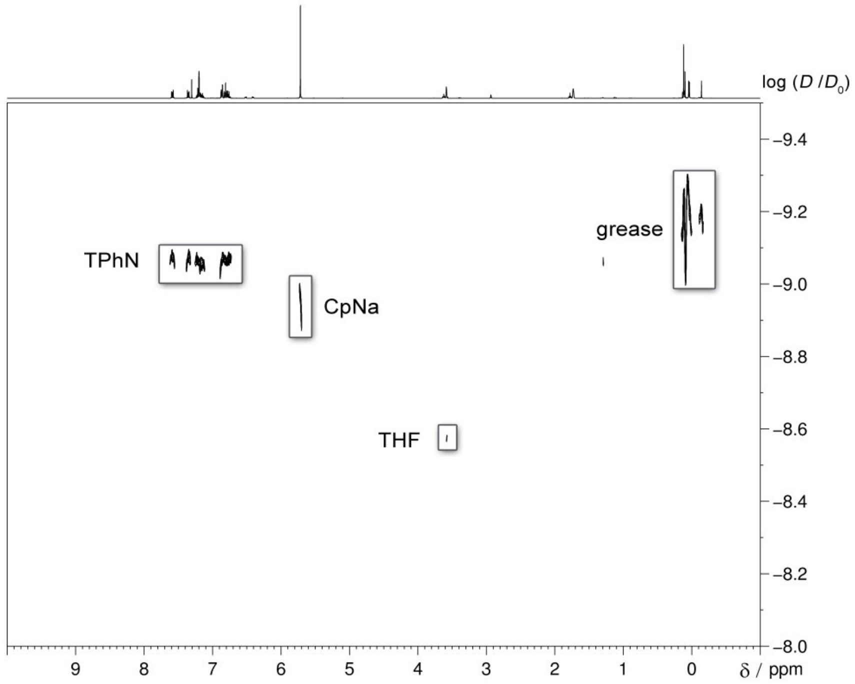


Fig. S-III-14: ^{1}H-DOSY-NMR spectrum of CpNa in THF-d_8 at 25 °C.

3. Cyclopentadienylpotassium (CpK)

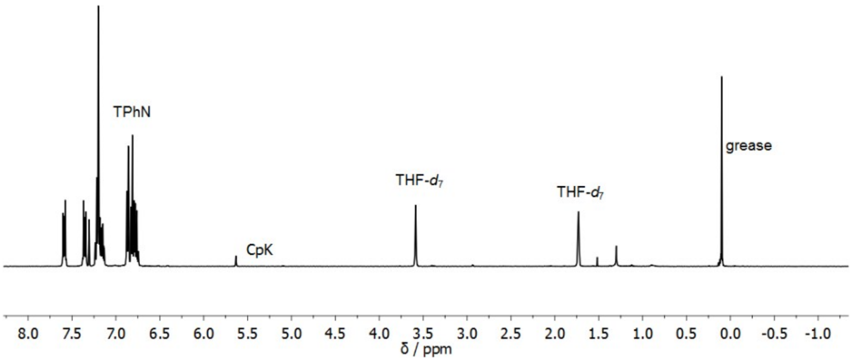


Fig. S-III-15: ^{1}H-NMR spectrum of CpK in THF-d_8 at 25 °C.

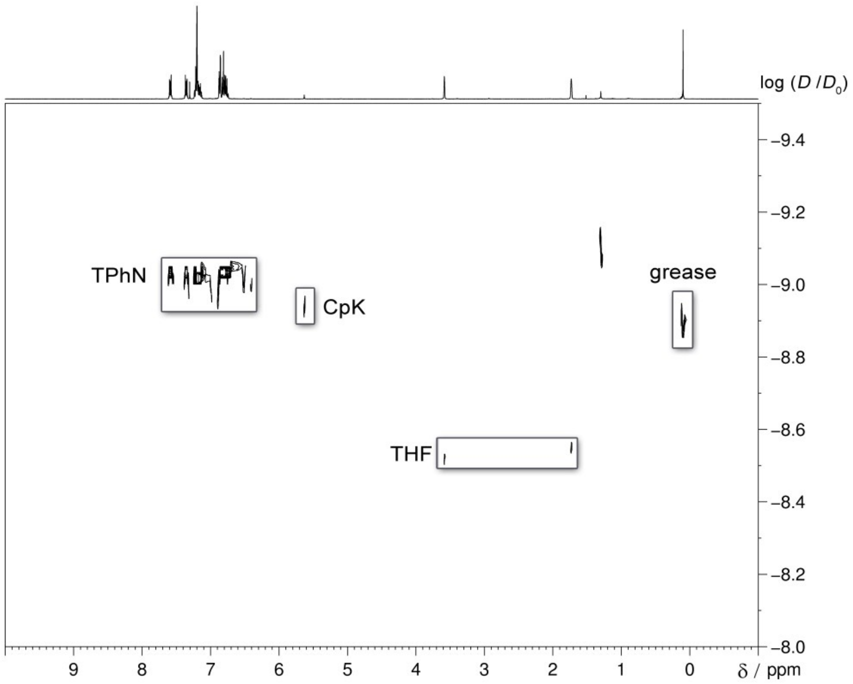


Fig. S-III-16: ^{1}H-DOSY-NMR spectrum of CpK in THF-d_8 at 25 °C.

4. Cyclopentadienylrubidium (CpRb)

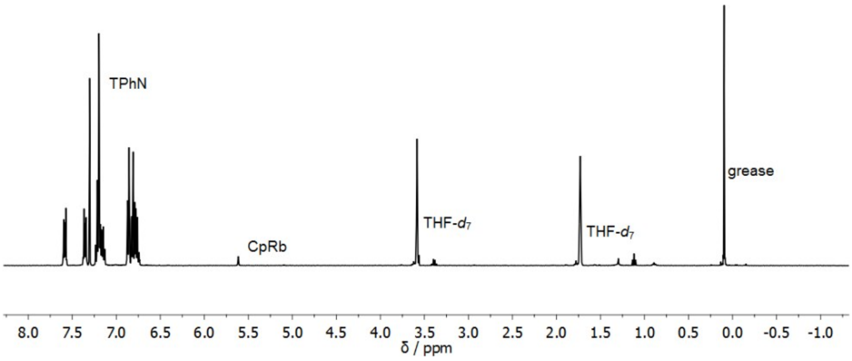


Fig. S-III-17: ^{1}H-NMR spectrum of CpRb in THF-d_8 at 25 °C.

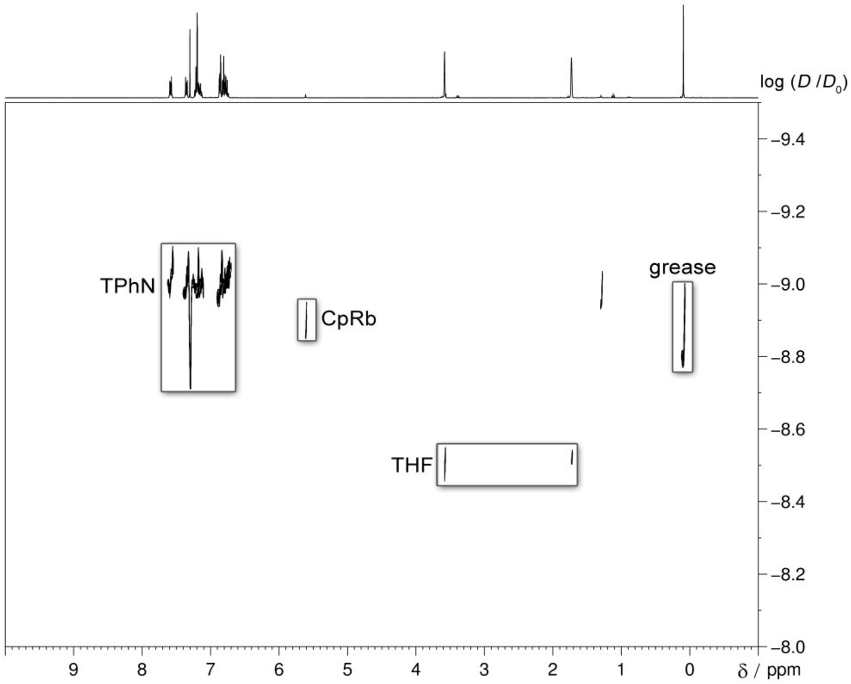


Fig. S-III-18: ^{1}H-DOSY-NMR spectrum of CpRb in THF-d_8 at 25 °C.

5. Cyclopentadienylcaesium (CpCs)

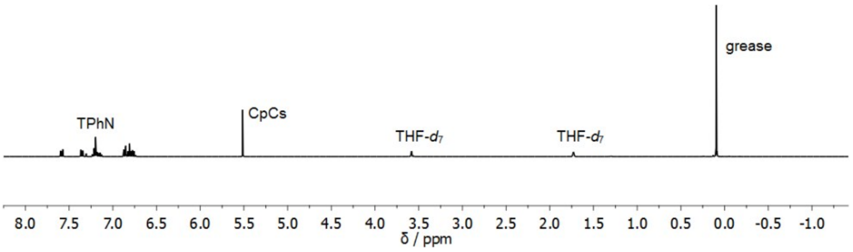


Fig. S-III-19: ^{1}H-NMR spectrum of CpCs in THF-d_8 at 25 °C.

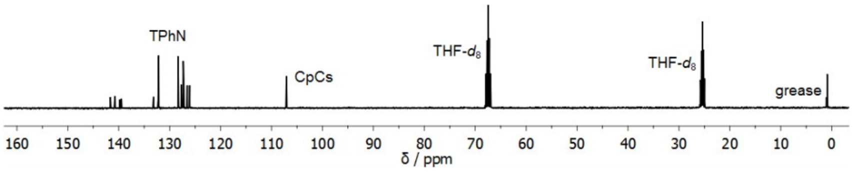


Fig. S-III-20: ^{13}C{^{1}H}-NMR spectrum of CpCs in THF-d_8 at 25 °C.

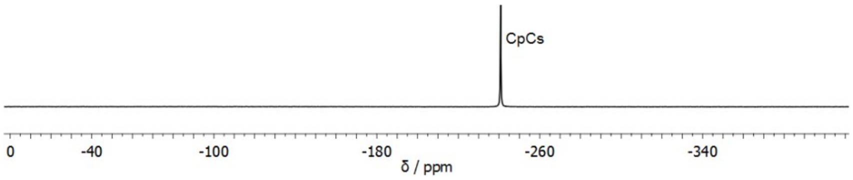


Fig. S-III-21: ^{133}Cs-NMR spectrum of CpCs in THF-d_8 at 25 °C.

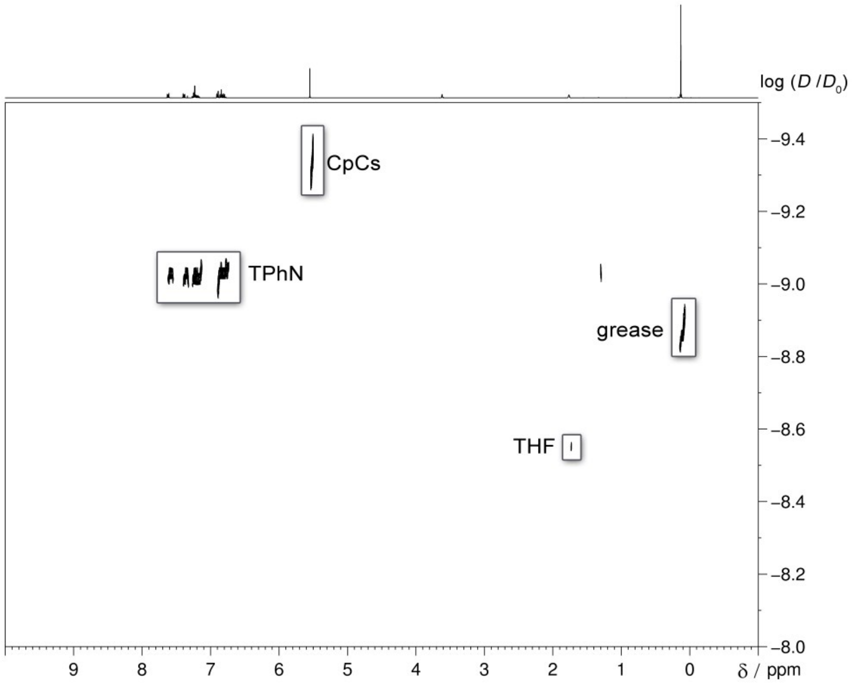


Fig. S-III-22: ^{1}H-DOSY-NMR spectrum of CpCs in THF-d_8 at 25 °C.

IV. ^{1}H- and ^{7}Li-DOSY-ECC-*MW* estimation of CpLi at 50, 25, –50 and –80 °C in THF-d_8

Tab. S-2: ^{1}H- and ^{7}Li-DOSY-ECC-*MW* estimation of CpLi in THF-d_8 (15 mM) at different temperatures. TPhN or TMB were used as internal references with log$D_{ref,fix}$(TPhN) = –9.1054 or log$D_{ref,fix}$(TMB) = –8.7749. The accuracy of this method (DSE ECC) is in the range of MW_{dif} ≤ ±9%. Hypothetical aggregates are [CpLi · THF$_x$] (li1a to li1d) and [(CpLi)$_2$ · THF$_x$] (li2a to li2d) with a-d = x = 1-4. A trend is visible towards higher *MW*s and diffusion coefficients upon cooling, indicating the formation of a [Cp$_2$Li]$^-$ species proposed by *Paquette et al.*[7], but these changes are within the standard deviation of a DOSY signal and we therefore propose the monomeric aggregate to be dominating. Still, note that li1a has a similar *MW* as [Cp$_2$Li]$^-$, li1b as [Cp$_2$Li·THF]$^-$ and so on.

^{1}H-DOSY				**50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_x [m^2/s]	2.175E–09	li1a	144	–30
logD_x	–8.6625	li1b	216	5
log$D_{x,norm}$	–8.8855	li1c	288	41
D_{ref} (TMB) [m^2/s]	2.806E–09	li1d	360	76
logD_{ref}(TMB)	–8.5519	li2a	216	5
MW_{det} [g/mol]	205	li2b	288	41
ΔMW_{det} [g/mol] (%)	±10 (5)	li2c	360	76
		li2d	432	111

^{1}H-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_x [m^2/s]	1.407E–09	li1a	144	–34
logD_x	–8.8517	li1b	216	–1
log$D_{x,norm}$	–8.9012	li1c	288	32
D_{ref} (TPhN) [m^2/s]	8.791E–09	li1d	360	65
logD_{ref}(TPhN)	–9.0559	li2a	216	–1
MW_{det} [g/mol]	218	li2b	288	32
ΔMW_{det} [g/mol] (%)	±11 (5)	li2c	360	65
		li2d	432	98

^{1}H-DOSY				**–50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_x [m^2/s]	3.381E–10	li1a	144	–35
logD_x	–9.4710	li1b	216	–2
log$D_{x,norm}$	–8.9050	li1c	288	30
D_{ref} (TMB) [m^2/s]	4.562E–10	li1d	360	63
logD_{ref}(TMB)	–9.3408	li2a	216	–2
MW_{det} [g/mol]	222	li2b	288	30
ΔMW_{det} [g/mol] (%)	±11 (5)	li2c	360	63
		li2d	432	95

^{1}H-DOSY				**–80 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_x [m^2/s]	1.144E–10	li1a	144	–36
logD_x	–9.9416	li1b	216	–4
log$D_{x,norm}$	–8.9090	li1c	288	28
D_{ref} (TMB) [m^2/s]	1.558E–10	li1d	360	60
logD_{ref}(TMB)	–9.8074	li2a	216	–4
MW_{det} [g/mol]	225	li2b	288	28
ΔMW_{det} [g/mol] (%)	±11 (5)	li2c	360	60
		li2d	432	92

^{1}H-DOSY	**–100 °C**
No interpretable data	

^{7}Li-DOSY				**50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	2.085E−09	li1a	144	−35
logD_{x}	−8.6809	li1b	216	−2
log$D_{\mathrm{x,norm}}$	−8.9039	li1c	288	31
D_{ref} (TMB) [m^2/s]	2.806E−09	li1d	360	63
logD_{ref}(TMB)	−8.5519	li2a	216	−2
MW_{det} [g/mol]	221	li2b	288	31
ΔMW_{det} [g/mol] (%)	±11 (5)	li2c	360	63
		li2d	432	96

^{7}Li-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	1.519E−09	li1a	144	−30
logD_{x}	−8.8184	li1b	216	5
log$D_{\mathrm{x,norm}}$	−8.8874	li1c	288	40
D_{ref} (TMB) [m^2/s]	1.968E−09	li1d	360	74
logD_{ref}(TMB)	−8.7060	li2a	216	5
MW_{det} [g/mol]	207	li2b	288	40
ΔMW_{det} [g/mol] (%)	±10 (5)	li2c	360	74
		li2d	432	109

^{7}Li-DOSY				**−50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	3.369E−10	li1a	144	−35
logD_{x}	−9.4724	li1b	216	−3
log$D_{\mathrm{x,norm}}$	−8.9066	li1c	288	29
D_{ref} (TMB) [m^2/s]	4.562E−10	li1d	360	62
logD_{ref}(TMB)	−9.3408	li2a	216	−3
MW_{det} [g/mol]	223	li2b	288	29
ΔMW_{det} [g/mol] (%)	±11 (5)	li2c	360	62
		li2d	432	94

^{7}Li-DOSY	**−80 °C & −100 °C**
No interpretable data	

V. ^{1}H-DOSY-ECC-*MW* estimation of CpNa at 25 and –50 °C in THF-d_8

Tab. S-3: ^{1}H-DOSY-ECC-*MW* estimation of CpNa in THF-d_8 (15 mM) at different temperatures. TPhN or TMB were used as internal references with log$D_{\mathrm{ref,fix}}$(TPhN) = –9.1054 or log$D_{\mathrm{ref,fix}}$(TMB) = –8.7749. The accuracy of this method (DSE ECC) is in the range of $MW_{\mathrm{dif}} \leq \pm 9\%$. Hypothetical aggregates are [CpNa · THF$_x$] (na1a to na1d) and [(CpNa)$_2$ · THF$_x$] (na2a to na2d) with a-d = x = 1-4.

^{1}H-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	1.120E–09	na1a	160	–46
logD_{x}	–8.9508	na1b	232	–21
log$D_{\mathrm{x,norm}}$	–8.9778	na1c	304	3
D_{ref} (TPhN) [m^2/s]	8.3483E–09	na1d	376	27
logD_{ref}(TPhN)	–9.0784	na2a	248	–16
MW_{det} [g/mol]	295	na2b	320	8
ΔMW_{det} [g/mol] (%)	±16 (5)	na2c	392	33
		na2d	464	57

^{1}H-DOSY				**–50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	2.817E–10	na1a	160	–44
logD_{x}	–9.5502	na1b	232	–19
log$D_{\mathrm{x,norm}}$	–8.9705	na1c	304	6
D_{ref} (TMB) [m^2/s]	4.420E–10	na1d	376	31
logD_{ref}(TMB)	–9.3546	na2a	248	–14
MW_{det} [g/mol]	287	na2b	320	12
ΔMW_{det} [g/mol] (%)	±15 (5)	na2c	392	37
		na2d	464	62

VI. ^{1}H-DOSY-ECC-*MW* estimation of CpK at 25 in THF-d_8

Tab. S-4: ^{1}H-DOSY-ECC-*MW* estimation of CpK in THF-d_8 (15 mM) at 25 °C. TPhN was used as internal references with log$D_{\mathrm{ref,fix}}$(TPhN) = –9.1054. The accuracy of this method (DSE ECC) is in the range of $MW_{\mathrm{dif}} \leq \pm 9\%$. Hypothetical aggregates are [CpK · THF$_x$] (k1a to k1d) and [(CpK)$_2$ · THF$_x$] (k2a to k2d) with a-d = x = 1-4.

^{1}H-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	1.136E–09	k1a	176	–47
logD_{x}	–8.9446	k1b	248	–26
log$D_{\mathrm{x,norm}}$	–9.0098	k1c	320	–4
D_{ref} (TPhN) [m^2/s]	9.116E–09	k1d	392	17
logD_{ref}(TPhN)	–9.0402	k2a	280	–16
MW_{det} [g/mol]	335	k2b	353	5
ΔMW_{det} [g/mol] (%)	±18 (5)	k2c	425	27
		k2d	497	48

VII. ^{1}H-DOSY-ECC-*MW* estimation of CpRb at 25 °C in THF-d_8

Tab. S-5: ^{1}H-DOSY-ECC-*MW* estimation of CpRb in THF-d_8 (15 mM) at 25 °C. TPhN was used as internal references with log$D_{\mathrm{ref,fix}}$(TPhN) = –9.1054. The accuracy of this method (DSE ECC) is in the range of $MW_{\mathrm{dif}} \leq \pm 9\%$. Hypothetical aggregates are [CpRb · THF$_x$] (rb1a to rb1d) and [(CpRb)$_2$ · THF$_x$] (rb2a to rb2d) with a-d = x = 1-4.

^{1}H-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	1.272E–09	rb1a	223	–24
logD_{x}	–8.8955	rb1b	295	0
log$D_{\mathrm{x,norm}}$	–8.9770	rb1c	367	25
D_{ref} (TPhN) [m^2/s]	9.4637E–09	rb1d	439	49
logD_{ref}(TPhN)	–9.0239	rb2a	373	27
MW_{det} [g/mol]	294	rb2b	445	51
ΔMW_{det} [g/mol] (%)	±16 (5)	rb2c	517	76
		rb2d	589	100

VIII. ^{1}H-DOSY-ECC-*MW* estimation of CpCs at 25 and 50 °C in THF-d_8

Tab. S-6: ^{1}H-DOSY-ECC-*MW* estimation of CpCs in THF-d_8 (15 mM) at different temperatures. TPhN or TMB were used as internal references with log$D_{\mathrm{ref,fix}}$(TPhN) = –9.1054 or log$D_{\mathrm{ref,fix}}$(TMB) = –8.7749. The accuracy of this method (merged ECC) is in the range of $MW_{\mathrm{dif}} \leq \pm 18\%$. Exemplary hypothetical aggregates are [(CpCs)$_5$ · THF$_{10}$] (cs5j) or [(CpCs)$_6$ · THF$_{12}$] (cs6l), while other combinations may also be viable.

^{1}H-DOSY				**50 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	6.201E–09	cs5j	1710	–8
logD_{x}	–9.2076	cs6l	2053	10
log$D_{\mathrm{x,norm}}$	–9.4085			
D_{ref} (TMB) [m^2/s]	2.667E–09			
logD_{ref}(TMB)	–8.5740			
MW_{det} [g/mol]	1863			
ΔMW_{det} [g/mol] (%)	±199 (11)			
^{1}H-DOSY				**25 °C**
		Aggregate	MW_{calc} [g/mol]	MW_{dif} [%]
D_{x} [m^2/s]	4.595E–10	cs5j	1710	–8
logD_{x}	–9.3377	cs6l	2053	11
log$D_{\mathrm{x,norm}}$	–9.4072			
D_{ref} (TPhN) [m^2/s]	9.211E–09			
logD_{ref}(TPhN)	–9.0357			
MW_{det} [g/mol]	1855			
ΔMW_{det} [g/mol] (%)	±198 (11)			

IX. Calculation of the molar van-der-Waals density MD_W

The ECC-*MW* estimation works best with molecules that have a molar van-der-Waals density (see equation **S3**) between $MD_W = 4.3 \cdot 10^{29}$ g/(mol·m^3) and $MD_W = 5.9 \cdot 10^{29}$ g/(mol·m^3). If MD_W is bigger than $5.9 \cdot 10^{29}$ g/(mol·m^3), like for example for CpRb, CpCs or [CpCs · THF] then the determined *MW* would be underestimated, if the proposed aggregate would be estimated with ECC-DOSY.[1] We just listed calculations for monomeric species with 1 and 4 eq. of THF. All in between fit as well. For dimeric compounds only CpCs without THF would be underestimated.

Tab. S-7: Calculation of the molar van-der-Waals densities MD_W

	Formula	***MW***	**C**	**H**	**O**	**Li**	**Na**	**K**	**Rb**	**Cs**	**MD_W [g/(mol · m³)]**	**ΣV_W [m³]**
CpLi	C5H5Li	72	5	5	0	1	0	0	0	0	4.61E+29	1.56E–29
CpNa	C5H5Na	88	5	5	0	0	1	0	0	0	4.90E+29	1.80E–29
CpK	C5H5K	104	5	5	0	0	0	1	0	0	4.77E+29	2.18E–29
CpRb	C5H5Rb	151	5	5	0	0	0	0	1	0	6.23E+29	2.42E–29
CpCs	C5H5Cs	198	5	5	0	0	0	0	0	1	6.60E+29	3.00E–29
[CpLi · THF]	C9H13LiO	144	9	13	1	1	0	0	0	0	4.84E+29	2.98E–29
[CpNa · THF]	C9H13NaO	160	9	13	1	0	1	0	0	0	4.98E+29	3.21E–29
[CpK · THF]	C9H13KO	176	9	13	1	0	0	1	0	0	4.90E+29	3.60E–29
[CpRb · THF]	C9H13RbO	223	9	13	1	0	0	0	1	0	5.81E+29	3.84E–29
[CpCs · THF]	C9H13CsO	270	9	13	1	0	0	0	0	1	6.12E+29	4.41E–29
[CpLi · THF$_4$]	C21H37LiO4	360	21	37	4	1	0	0	0	0	4.98E+29	7.23E–29
[CpNa · THF$_4$]	C21H37NaO4	376	21	37	4	0	1	0	0	0	5.04E+29	7.46E–29
[CpK · THF$_4$]	C21H37KO4	392	21	37	4	0	0	1	0	0	5.00E+29	7.84E–29
[CpRb · THF$_4$]	C21H37RbO4	439	21	37	4	0	0	0	1	0	5.43E+29	8.09E–29
[CpCs · THF$_4$]	C21H37CsO4	486	21	37	4	0	0	0	0	1	5.61E+29	8.66E–29

$$MD_W = \frac{MW}{\sum V_W} = MW \Big/ \sum_{i=1}^{n} \frac{3}{4}\pi r_{W,i}^{3} \tag{S3}$$

Tab. S-8: Van-der-Waals volumina of selected elements.[8]

Element	V_W [m³]
H	5.575E–30
Li	2.525E–29
C	2.058E–29
Na	4.900E–29
K	8.711E–29
O	1.471E–29
Rb	1.117E–28
Cs	1.690E–28

X. ECC-*MW* Estimation Software

To simplify the ECC-*MW* estimation process, minimize the possibility for errors and make the methodology more accessible: We developed a simple piece of software to apply and choose all current and up-coming ECC-*MW* estimation techniques. The software is available for download at:

http://www.stalke.chemie.uni-goettingen.de/mwestimation/

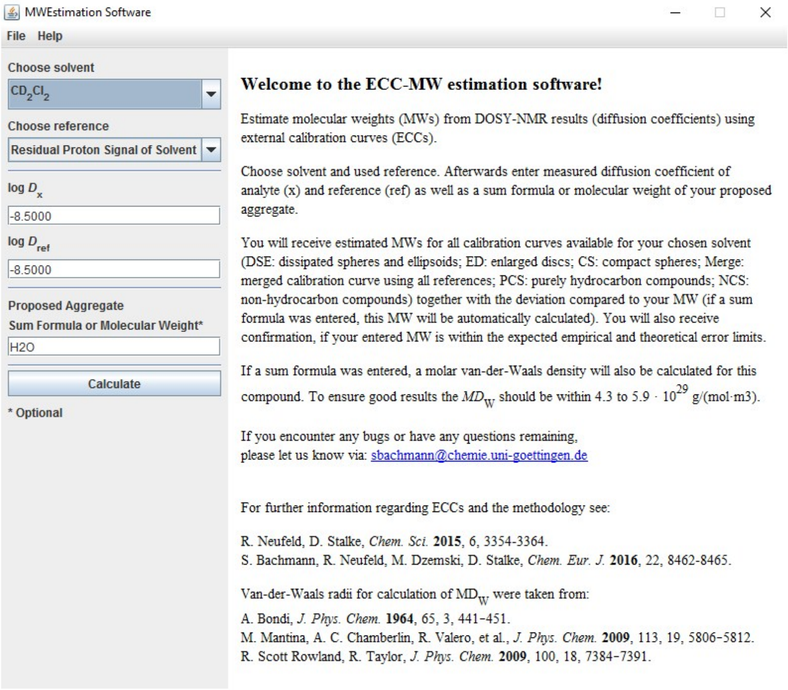
To achieve a maximum system interoperability the software was implemented in Oracle's object-oriented programming language "Java". Java uses a so called Java virtual machine (JVM), which is able to run bytecode and needs to be installed on the computer, which launches the software. The bytecode itself was created by compiling the Java code with the help of the Java compiler. With the combination of JVM and the system independent bytecode it is possible to run the software on a wide range of operating systems, including but not limited to Windows®, MacOS® and Linux.

As shown in Fig. S- X-1 and Fig. S- X-2 the application's main window was split into an input and output area. The user is able to select a wide range of solvents and references from the left-hand side of the window. The result will be shown on the right side after clicking the "calculate" button.

The program was written with the intention to support multiple languages. The default language setting is English. The program was also translated into German. During start, the program recognizes the locale setting on a user's computer and will automatically switch to the correct language.

As mentioned above you can choose the solvent and used reference within the software. Afterwards enter the measured diffusion coefficient of analyte (x) and reference (ref) as well as a sum formula or molecular weight of your proposed aggregate. You will receive estimated *MW*s for all ECCs available for your chosen solvent (DSE: dissipated spheres and ellipsoids; ED: enlarged discs; CS: compact spheres; Merge: merged calibration curve using all references; PCS: purely hydrocarbon compounds; NCS: non hydrocarbon compounds) together with the deviation compared to your *MW* (if a sum formula was entered, this *MW* will be automatically calculated). You will also receive confirmation, if your entered *MW* is within the expected empirical and theoretical error limits. If a sum formula was entered, a molar van-der-Waals density will also be calculated (based on a predefined list with van-der-Waals volumes of the elements, if no van-der-Waals volume is known, no molecular density will be calculated) for this compound. After estimation, saving or printing your results will also be possible, whereas copying your results is always a possibility.

Alongside with the download we offer the source code of the program, if you are interested. Please write an email to the author for receiving a copy. Note that this program may be subject to changes as it will be improved as deemed necessary.



Choose solvent: CD_2Cl_2

Choose reference: Residual Proton Signal of Solvent

log D_x: -8.5000

log D_{ref}: -8.5000

Proposed Aggregate
Sum Formula or Molecular Weight*: H2O

Welcome to the ECC-MW estimation software!

Estimate molecular weights (MWs) from DOSY-NMR results (diffusion coefficients) using external calibration curves (ECCs).

Choose solvent and used reference. Afterwards enter measured diffusion coefficient of analyte (x) and reference (ref) as well as a sum formula or molecular weight of your proposed aggregate.

You will receive estimated MWs for all calibration curves available for your chosen solvent (DSE: dissipated spheres and ellipsoids; ED: enlarged discs; CS: compact spheres; Merge: merged calibration curve using all references; PCS: purely hydrocarbon compounds; NCS: non-hydrocarbon compounds) together with the deviation compared to your MW (if a sum formula was entered, this MW will be automatically calculated). You will also receive confirmation, if your entered MW is within the expected empirical and theoretical error limits.

If a sum formula was entered, a molar van-der-Waals density will also be calculated for this compound. To ensure good results the MD_W should be within 4.3 to 5.9 · 10^{29} g/(mol·m3).

If you encounter any bugs or have any questions remaining,
please let us know via: sbachmann@chemie.uni-goettingen.de

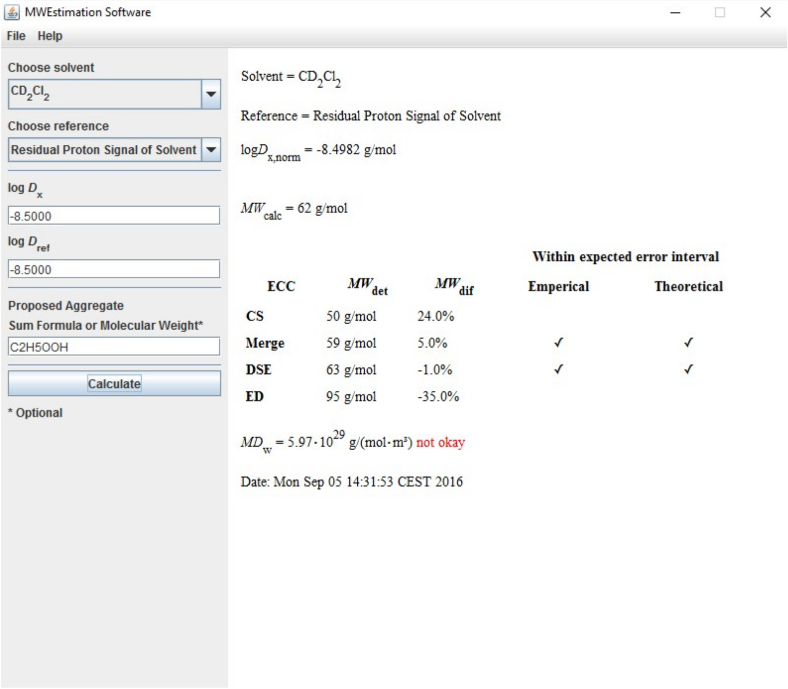
For further information regarding ECCs and the methodology see:

R. Neufeld, D. Stalke, *Chem. Sci.* **2015**, 6, 3354-3364.
S. Bachmann, R. Neufeld, M. Dzemski, D. Stalke, *Chem. Eur. J.* **2016**, 22, 8462-8465.

Van-der-Waals radii for calculation of MD_W were taken from:

A. Bondi, *J. Phys. Chem.* **1964**, 65, 3, 441-451.
M. Mantina, A. C. Chamberlin, R. Valero, et al., *J. Phys. Chem.* **2009**, 113, 19, 5806-5812.
R. Scott Rowland, R. Taylor, *J. Phys. Chem.* **2009**, 100, 18, 7384-7391.

Fig. S- X-1: Screenshot (1) of the ECC-*MW* estimation software – start screen.



Choose solvent: CD_2Cl_2

Choose reference: Residual Proton Signal of Solvent

log D_x: -8.5000

log D_{ref}: -8.5000

Proposed Aggregate
Sum Formula or Molecular Weight*: C2H5OOH

Solvent = CD_2Cl_2

Reference = Residual Proton Signal of Solvent

$\log D_{x,norm}$ = -8.4982 g/mol

MW_{calc} = 62 g/mol

ECC	MW_{det}	MW_{dif}	Within expected error interval Emperical	 Theoretical
CS	50 g/mol	24.0%		
Merge	59 g/mol	5.0%	✓	✓
DSE	63 g/mol	-1.0%	✓	✓
ED	95 g/mol	-35.0%		

$MD_w = 5.97 \cdot 10^{29}$ g/(mol·m³) not okay

Date: Mon Sep 05 14:31:53 CEST 2016

Fig. S- X-2: Screenshot (2) of the ECC-*MW* estimation software – after estimation.

XI. References

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8. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.