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^{7}Li solid-state NMR spectroscopic study of cyclopentadienyllithium complexes†

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ABSTRACT: Eighteen cyclopentadienyllithium complexes were studied by solid-state ^{7}Li NMR spectroscopy. It is shown that the chemical shift gives information on the type of complex, i.e. whether the complex is a contact ion pair, a solvent-separated ion pair, a sandwich structure or a polymeric material. These shift differences are due to the ring current of the aromatic anion. In order to obtain information about the solvation of the lithium cation, the quadrupolar coupling constant χ has to be determined. The χ value depends on the number and type of donor atoms in the ligand, where the nitrogen-containing ligands give rise to higher χ values than the oxygen analogues. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: ^{7}Li solid-state NMR; organolithium compounds; quadrupolar coupling constant; cyclopentadienyllithium complexes

INTRODUCTION

The structure and reactivity of organolithium compounds is an important topic because of the frequent use of these intermediates in organic and organometallic synthesis. Consequently, the structures of a large number of organolithium compounds have been studied in the solid state by x-ray crystallography[1] and in solution by different spectroscopic methods, mainly NMR spectroscopy.[2]

By correlating solution and solid-state NMR spectroscopic data with information from x-ray crystallography, we tried to clarify whether the solid structures are relevant models for the organolithium structures in solution. We also explored the possibility of using solid state NMR spectroscopy as a tool for selecting suitable candidates for x-ray analysis and to obtain direct structural information.

In previous papers, ^{13}C and ^{6,7}Li solid-state NMR investigations of organolithium complexes were presented with these aims.[3] In the ^{7}Li NMR studies, we measured the chemical shift under magic angle spinning (MAS) conditions and the quadrupolar coupling constant ($\chi = e^2qQ/h$) under static conditions. The small ^{7}Li chemical shift range restricts the usefulness of this parameter as it is known that the variation due to different ligands is of the same order of magnitude as the difference due to aggregation.[4] One exception is when the lithium cation is situated above an aromatic system, since the cation experiences the influence of the ring current in these cases. On the other hand, the χ value is sensitive to both aggregation and solvation.[3c,d]

In a ^{7}Li solid-state NMR investigation of different fluorenyllithium complexes,[3d] it was shown that the chemical shift reflects the position of the lithium cation relative to the aromatic framework. The χ value is also sensitive to changes in the cation–anion interaction and, further, to changes in ligation of the lithium cation. In order to characterize these complexes fully, both the chemical shifts and χ values should be measured.

However, to obtain a better understanding of the factors that affect χ, an investigation of a number of cyclopentadienyllithium derivatives (Cp*Li) with different carbanion substitutions and lithium ligands was undertaken. This was based on the fact that cyclopentadienyllithium derivatives are commonly used intermediates in organometallic syntheses for preparing transition metal metallocenes. Hence a number of solid-state structures have been determined both experimentally[5] and theoretically[5n,o,6] in recent decades.

In the solid state, these compounds have been shown to adopt at least six different structures: contact ion pairs (CIP) **A**,[5b–d,f–h,j,k] solvent-separated ion pairs (SSIP) **B**,[5h] sandwich structures **C**,[5k–m] inverted sandwich structures **D**,[5e] super-sandwich structures **E**[5n,o,q] and higher polymeric species **F**[5i,p] (Scheme 1).

Which structural type will prevail depends on the cyclopentadienyl (Cp) substitution pattern and lithium ligand used. Large substituents on the cyclopentadienyl ring will prevent the formation of polymeric chains or sandwich structures. The use of solvents and ligands with donor atoms, e.g. ethers or tertiary amines, will also prevent the formation of polymeric species since they will compete with the anion in the interaction with the lithium cation. Furthermore, the properties of the

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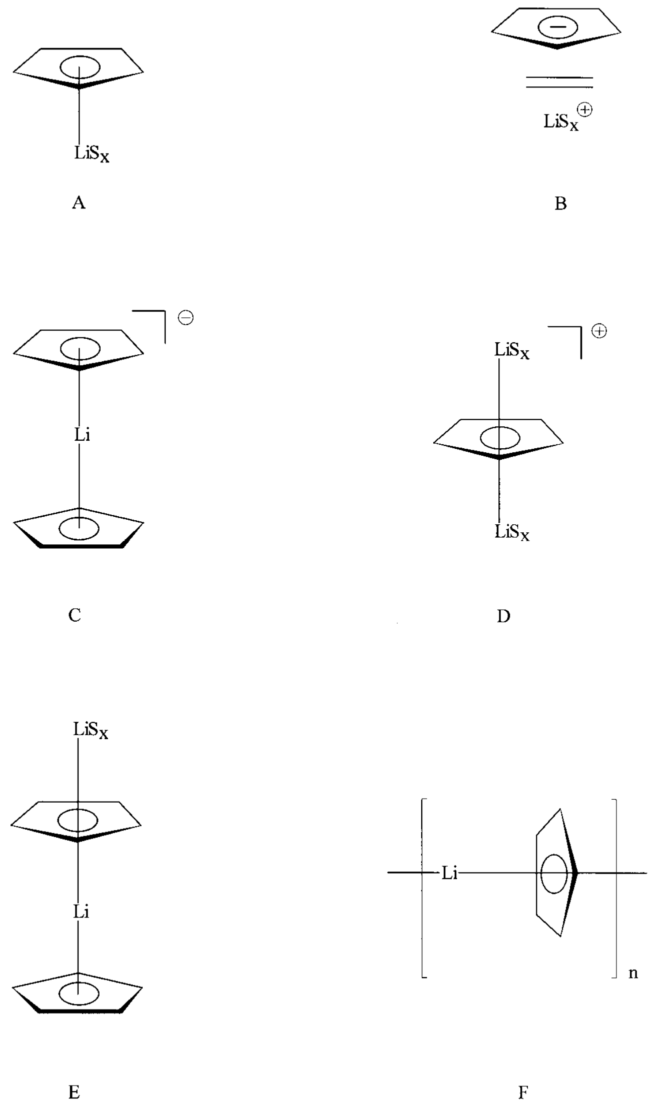

Scheme 1.

carbanion suggest that the cation will be coordinated to all five carbons and thus located above the five-membered ring in an η_5 fashion for all structural types except for SSIPs. In this work, complexes of type **A**–**C** and the polymer **F** were studied.

RESULTS AND DISCUSSION

The cyclopentadienyllithium derivatives investigated were various complexes of cyclopentadienyllithium (CpLi), methylcyclopentadienyllithium (Me-CpLi) and mono-, 1,3-bis- and 1,2,4-tris-trimethylsilylcyclopentadienyllithium (TMS-CpLi, bis-TMS-CpLi and tris-TMS-CpLi, respectively). The solid-state structures of half of the investigated complexes have been determined previously by x-ray diffraction techniques.[5]

The ^{7}Li solid-state NMR chemical shifts and χ, together with some relevant structural data, when known, are summarized in Table 1. The NMR data for three of the Cp*Li *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) complexes have been reported earlier.[3d]

^{7}Li chemical shifts

As can be seen from Table 1, the ^{7}Li chemical shifts for all CIP **A** structures are in the range -7 to -9 ppm regardless of the substitution pattern of the anion or the choice of ligand (entries 1–13) (given as **1**–**13** below). This is the expected chemical shift range for a lithium cation that is influenced by a ring current of an aromatic anion.[5d,f,j,6c,d,h,i,7] However, the ligation number of the neutral ligand does not seem to affect the chemical shift in any systematic way.

We also included the only SSIP type **B** Cp*Li complex known so far, where the lithium cation is complexed by two 12-crown-4 molecules. The chemical shift of the lithium cation is -2.4 ppm, as expected for a fully solvated lithium cation, **14**. ^{7}Li solid-state NMR data for lithium cations complexed by two 12-crown-4 ethers have been reported previously.[8] Our shift determination would, however, change the tentative shift assignment of the reported bis(12-crown-4)lithium bis[*N*,*N'*-bis(trimethylsilyl)benzenesulphinamidino]lithiate, where the solvated lithium was assigned to the signal with a chemical shift of 0.8 ppm.[8a] This change of signal assignment is also further strengthened by a later study of the bis(12-crown-4)lithium bis(pyridyl)methyllithiate complex.[8c]

The ^{7}Li chemical shift of one of the known sandwich structures **C**, i.e. the Cp_2Li with Ph_4P as a counterion,[5l] has a value of -12.9 ppm, i.e. in the range expected for a lithium cation between two aromatic systems, **15**. This assumption is supported by an earlier study where a ^{7}Li chemical shift of -12.78 was reported for the lithium cation sandwiched between two isodicyclopentadienyl units in THF-d_8.[6c] Interestingly, two of the diglyme complexes of Cp*Li give rise to two separate ^{7}Li signals of equal intensity, one signal at about -2 ppm and the other at about -12 ppm, **16** and **17**. This indicates that these complexes crystallize as a structure where one lithium is sandwiched between two Cp* systems and the other lithium cation is coordinated by the diglyme. This is unexpected since in C_6D_6 solution the bis-TMSCpLi diglyme complex shows only one resonance, indicating that this compound is a CIP of type **A** in solution.[5f] These diglyme structures presented above would represent the first complexes of type **C** in the solid state of a simple Cp*, with a solvated lithium cation as the counterion. It should be noted that a third Cp*Li diglyme complex, i.e. tris-TMS-CpLi, does not crystallize as a sandwich structure, but as a CIP of type **A**, possibly due to steric hindrance of the bulky substituents.

The polymeric CpLi of type **F**, also give a chemical shift within the expected shift range for lithium associated with two cyclopentadienyl rings, i.e. -13.1 ppm,[6c] **18**.

To conclude the chemical shift study, it is obvious that the ^{7}Li chemical shifts of Cp*Li complexes give direct information of the structural type, i.e. **A**, **B**, **C** or **F**, due to the aromatic character of the anion. However, as mentioned above, no information of the ligation

Table 1. ^{7}Li NMR spectroscopic parameters and some structural data for Cp*Li complexes

Entry	System	Structure	Ligand	Ligand No.[a]	δ[b] (ppm)	χ[c] (kHz)	η[d]	C—Li distance (Å)	S.D.[e] (Å)	Li—S[f] distance (Å)	S—Li—S angle(°)	Ref.	CCD ref. code[g]
1	Me-Cp	CIP	TMEDA	2 (N)	−7.1	156	0.05	2.257	0.020	2.125 2.230	87.44	5g	SIJNII
2	TMS-Cp	CIP	TMEDA	2 (N)	−7.5	156	0.10	2.267	0.012	2.119 2.142	84.92	5c	CEZTIK
3	Tris-TMS-Cp	CIP	TMEDA	2 (N)	−7.5	158	0.3	2.327	0.034	2.116 2.269	83.92	5d	COJRUO
4	Bis-TMS-Cp	CIP	TMEDA	2 (N)	−7.8	151	0.05						
5	Tris-TMS-Cp	CIP	PMDTA	2 (N)	−7.5	157	0.15	2.324	0.016	2.173 2.218	82.70	5b	COJROI
6	Bis-TMS-Cp	CIP	TMPDA	2 (N)	−8.9	150	0.20						
7	Tris-TMS-Cp	CIP	TMPDA	2 (N)	−7.7	155	0.05						
8	Tris-TMS-Cp	CIP	Quinuclidine	1 (N)	−7.7	172	0.05	2.157	0.013	2.012	—	5d	DECPOQ
9	Tris-TMS-Cp	CIP	THF	1 (O)	−9.1	125	0.10	2.161	0.022	1.882	—	5f	SEBHUC
10	Bis-TMS-Cp	CIP	DME	2 (O)	−8.4	98	0.05						
11	Tris-TMS-Cp	CIP	DME	2 (O)	−8.3	99	0.10						
12	Tris-TMS-Cp	CIP	Diglyme	2 (O)	−8.8	94	0.10						
13	Cp	CIP	12-Crown-4	4 (O)	−7.3	21	0.5	2.380	0.031	2.135 2.244 2.254 2.426	73.98 74.26 77.06	5h	VITKAK
14	Tris-TMS-Cp	SSIP	12-Crown-4	8 (O)	−2.4	39	0.3	—	—	2.343 2.371[h]		5h	VITJUD
15	Cp	Sandwich	PPh_4^+	η^{10}	−12.9	45	0.3	2.318	0.045	—	—	5l	HESJIY
16	Cp	Sandwich	Diglyme	η^{10}	−12.4 −1.6	26 51	0.20 0.20						
17	Bis-TMS-Cp	Sandwich	Diglyme	η^{10}	−12.2 −2.0	27 58	0.10 0.20						
18	Cp	Polymer		η^{10}	−13.1	small		2.307	—	—	—	5p	—

[a] Number and (type) of donor atom.

[b] Corrected for second-order quadrupolar interactions.

[c] Reproducibility *ca.* ± 2 kHz.

[d] Reproducibility *ca.* ± 0.05 for low η values (below 0.30) and *ca.* ± 0.1 for larger η values.

[e] Standard deviation of Li—C distance.

[f] Lithium—donor atom distance.

[g] Reference code for Cambridge Crystallographic Database.

[h] Mean value of the Li—O distances in the two crown ether ligands.

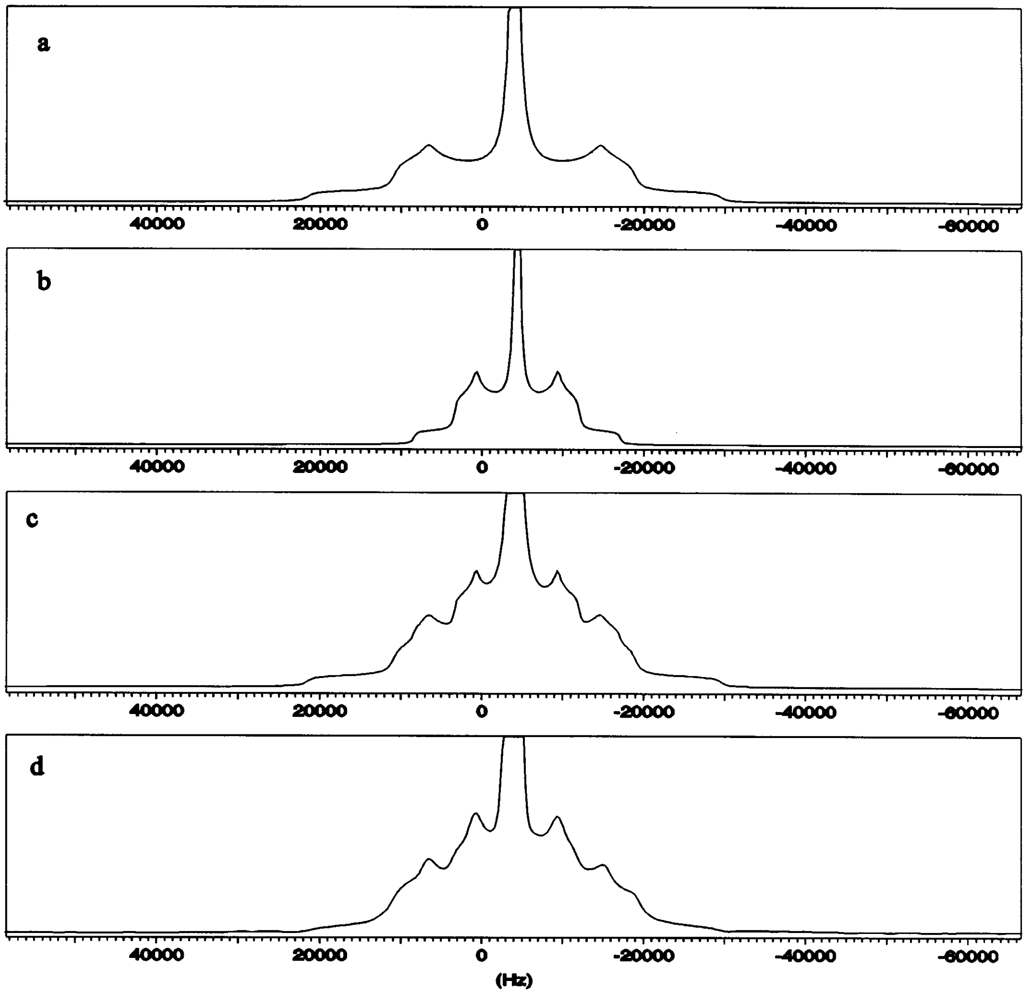

Figure 1. (a–c) Simulated and (d) experimental static ^{7}Li NMR spectrum of the diglyme complex of cyclopentadienyllithium at 38.92 MHz.

number of the neutral ligand can be obtained. In previous studies, the ^{7}Li χ proved to be sensitive to changes in solvation.[3] Hence, in order to probe the sensitivity of χ to other structural changes, the χ values of the various Cp*Li complexes were measured.

^{7}Li χ

The solid-state structures of a number of different TMEDA complexes have been determined by x-ray crystallography, (**1**–**3** in Table 1). As reported here, the χ values for these complexes range from 156 to 158 kHz, whereas the average Li—C distance varies from 2.257 to 2.327 Å. The χ values do not directly correlate with this distance or to the standard deviation of this distance, which gives an estimate of the symmetry of the η^5 Cp–Li interaction. The variations in the Li–N distance, changing by 0.048 Å for the shorter interaction and 0.127 Å for the longer distance, do not seem to have any simple correlation with the changes in χ. The N—Li—N angle also varies to some extent in this series, i.e. from 83.9° to 87.4°, but this change has no significant impact on χ either.

The TMEDA complex of trimethylsilylcyclopentadienyllithium has been investigated earlier.[9] It was shown that χ varied between 165 and 188 kHz depending on the temperature. It was assumed that the electric field gradient was of axial symmetry. The asymmetry parameter is, however, small but significant at ambient temperatures.[3d] A dynamic process of the TMEDA ligand is a reasonable explanation for this variation of χ at different temperatures. This process is reflected by large thermal factors of the TMEDA ligands reported in several x-ray studies.[5c,d,k,10] Similar results have been noted in ^{13}C CP/MAS studies of a number of TMEDA complexes of organolithium compounds.[3a,11] These dynamic processes were recently examined in more detail using ^{15}N and ^{7}Li solid-state NMR spectroscopy.[11] A χ value for the TMEDA complex of cyclopentadienyllithium of *ca.* 150 kHz and an η value close to 0 was obtained in that report, in agreement with the present study.

The χ of the *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA) complex of tris-TMS-CpLi also falls nicely in this range and it is known that only two of the three nitrogens are coordinated to the lithium cation.[5b] We included one additional TMEDA and two *N*,*N*,*N*′,*N*′-tetramethylpropane-1,3-diamine (TMPDA) complexes in this study, and the χ values of 150–155 indicate that also in these cases the ligands interact with the lithium cation in a bidentate fashion. The conclusion is that minor variations of the structural parameters do not influence the χ significantly, **1**–**7**.

When the ligation number is changed, however, as in the quinuclidine complex of tris-TMS-CpLi, where only one quinuclidine is involved in complexation of the lithium cation, χ is increased by *ca.* 20 kHz to 172 kHz, **8**.

When THF is used as a ligand, only one molecule is complexed with the lithium cation. The χ value is significantly reduced compared with the corresponding monodentate nitrogen (quinuclidine) complex, from 172 to 125 kHz, **9**. This is due to the change in donicity from a nitrogen to a oxygen donor, as the Cp*—Li distance is increased by only 0.004 Å and the Li—N/O distance is reduced by 0.13 Å. Comparable changes in the distances in the TMEDA complexes did not, as mentioned, have any notable effect on χ.

When the potentially bidentate O ligand DME is used as the complexing agent, a further reduction in χ is observed **10** and **11**. The reduction is of a similar magnitude to that observed in the nitrogen case when the number of complexing nitrogens is increased to two (20 kHz). The difference from the corresponding bidentate nitrogen complexes is again of the order of 50 kHz. The potentially terdentate ligand diglyme interacts only in a bidentate fashion in the CIP **A**-type structure, as does PMDTA, according to the χ value. This is valid even in solution, as determined earlier by solution NMR spectroscopy.[5f]

When 12-crown-4 is added as a ligand to cyclopentadienyllithium, a CIP is formed and there is a further decrease in χ to 21 kHz, **13**. In this complex the cation is coordinated to four oxygens in an asymmetric fashion. When tris-TMS-CpLi is complexed by 12-crown-4, however, an SSIP is formed. This is reflected, as mentioned, by the ^{7}Li chemical shift. The χ of this lithium cation coordinated by eight oxygens is also relatively low, **14**.

The χ value of the lithium cation in the Cp_2Li–Ph_4P sandwich structure is small, as would be expected. As mentioned previously, the diglyme complexes of Cp and bis-TMS-CpLi unexpectedly formed sandwich structures. As shown in Fig. 1, the obtained lineshape of the CpLi diglyme complex can be simulated by two overlapping signals of 51 and 26 kHz and η of 0.17 and 0.21, respectively [Fig. 1(a) and (b)], **16**. The 26 kHz χ value is assigned to the high-field signal, as this gives a better simulation of the experimental spectrum [Fig. 1(c) and (d)]. The diglyme complex of bis-TMS-CpLi can be analysed in a similar fashion, **17**.

The polymeric materials included in this study give such a low χ ($\leqslant 5$ kHz) that the influence of chemical shift anisotropy cannot be disregarded, preventing the exact determination of χ from the static or MAS spectra.

CONCLUSIONS

It has been shown that the ^{7}Li chemical shift is a sensitive probe for assigning the position of the lithium cation relative to the carbanionic framework, as expected. The chemical shifts are close to the values measured for the corresponding complexes in solution. However, in order to assess the coordination of the lithium cation, it is necessary to determine χ also. The χ value depends on the number and type of donor atoms in the ligand, where the nitrogen-containing ligands give rise to higher χ values than the oxygen analogues.

When the lithium cation is residing in a symmetric environment, e.g. in the CIP CpLi with 12-crown-4 as ligand or when the lithium cation is sandwiched between two Cp* rings, low χ values are obtained. In these cases the ^{7}Li shift information is needed in order to determine the actual structural type.

Introducing bulky substituents on the Cp* ring will weaken the Cp*–Li interaction and thus prevent the formation of CIPs, as in the previously reported case of the tris-TMS-CpLi 12-crown-4 SSIP structure,[5h] or the formation of sandwich structures, as in the tris-TMS-CpLi diglyme complex, where a CIP instead of a sandwich structure is formed.

EXPERIMENTAL

All experiments were carried out under an argon atmosphere. Hexane and THF were dried by refluxing with potassium prior to use and diethyl ether was refluxed with a sodium–potassium alloy. Diglyme and DME were pre-dried over calcium hydride and distilled from sodium before use. TMEDA, PMDTA and TMPDA were distilled from $LiAlH_4$. Quinuclidine was sublimed twice and tetraphenylphosphonium chloride was dried in vacuum immediately before use. 1,1,3-Tris-trimethylsilylcyclopentadiene, 1,3-bistrimethylsilylcyclopentadiene and trimethylsilylcyclopentadiene were purchased from Aldrich and used without further purification. Methylcyclopentadiene and cyclopentadiene were purchased from Aldrich as dimers and cracked by distillation using a 35 cm Vigreux column. *n*-Butyllithium (2.5 M) was purchased from Acros Chimica and titrated with 1-pyreneacetic acid prior to use.[12] The organolithium compounds were isolated and dried *in vacuo* and transferred into 7 or 4 mm zirconia rotors with KelF caps for NMR measurements.

The NMR experiments were performed on Bruker MSL 100, Bruker AMX2-500 (at 38.92 and 194.37 MHz, respectively) and Chemagnetics CMX 100 (38.92 MHz) spectrometers. ^{1}H high-power decoupling was used both under MAS conditions for chemical shift determinations and under static conditions for χ measurements. The static spectra were obtained by a quadrupolar echo pulse sequence with a refocusing delay of 8–12 μs and a recycling delay of 15 s. The number of aquisitions varied between 6000 and 11 000 at low field and *ca.* 1000 at high field. The χ and η values were obtained from quadrupolar echo spectra. Chemical shifts are referred externally to 1 M aqueous LiCl and corrected for second-order quadrupolar interactions.[13]

Simulations of static quadrupolar spectra were made with WIN-FIT provided by Bruker. The simulations do not account for CSA or dipolar couplings. In the simulations presented in Fig. 1, a line broadening of 15 (arbitrary units) was used.

The complexes were prepared according to literature methods when available, with some modification such as substituting DEE–hexane solvent mixtures for pure hexane and working at higher concentrations. Examples are given below.

Diglyme complex of 1,3-bistrimethylsilylcyclopentadienyllitihum

To a mixture of 120 mg (0.57 mmol) of 1,3-bistrimethylsilylcyclopentadiene in 2 ml of hexane was added 0.25 ml (0.63 mmol) of 2.5 M *n*-BuLi at room temperature. After 30 min of stirring, the mixture became highly viscous and 77 mg (0.57 mmol) of diglyme were added at 0 °C. After a few hours in a freezer, orange prisms were formed.

TMEDA complex of methylcyclopentadienyllithium

To a solution of 170 mg (2.12 mmol) of methylcyclopentadiene in 4 ml of hexane and 246.5 mg (2.12 mmol) of TMEDA was added 0.93 ml (2.33 mmol) of 2.5 M *n*-BuLi in hexane. A dark yellow precipitate formed immediately.

Diglyme complex of cyclopentadienyllithium

To a solution of 120 mg (1.82 mmol) of cyclopentadiene and 1.5 ml (10.47 mmol) of diglyme was added 0.80 ml (2.0 mmol) of 2.5 M *n*-BuLi. To the resulting slightly coloured solution was added 3 ml of hexane, which immediately gave a massive white precipitate.

Tetraphenylphosphonium biscyclopentadienyllithiate

This compound was prepared with some modifications of the procedure in Ref. 5l. To a mixture of 200 mg (3.0 mmol) of cyclopentadiene in 8 ml of THF was added 1.3 ml (3.3 mmol) of 2.5 M *n*-BuLi. The resulting viscous solution was transferred via a cannula to a stirred suspension of 567 mg (1.5 mmol) of PPh_4Cl in 10 ml of THF. The resulting mixture became orange within a few seconds. The precipitated LiCl was removed by centrifugation followed by cannulation of the solution to a new flask. After a few days in a freezer, orange–brown prisms formed.

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