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Sub Room Temperature Differential Vapor Pressure Osmometry: A Method for the Determination of the Aggregation Number of α-Heterosubstituted Organolithium Compounds and Lithium Amides in Solution

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Differential Vapor Pressure Osmometry / Aggregation /
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The aggregation number of α-Selenium- and α-Sulfur-substituted organolithium compounds, lithium amides, and transition metal complexes in solution has been determined by sub room temperature differential vapor pressure osmometry. This novel method allows measurements of oxygen, moisture, and temperature sensitive compounds. The aggregation number of these compounds can be determined in THF solutions at 0 °C and in diethyl ether solutions at −35 °C.

1. Sub Room Temperature Differential Vapor Pressure Osmometry

Introduction

Lithium organyls, lithium amides, and transition metal complexes have a strong tendency to form aggregates. This behavior has a major impact on the reactivity and mechanistic pathways of these reagents [1–9]. Their aggregation number in solution depends strongly on factors like the concentration, the solvent, and the temperature [18]. In addition, many of these compounds are sensitive towards moisture, oxygen, and heat. In order to

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obtain data relevant for the conditions under which organometallic reagents are utilized their aggregation number should be determined under similar conditions.

For determining the aggregation number in solution methods based on colligative properties like ebullioscopy [10, 11], cryoscopy [12, 13], differential vapor pressure barometry [14–17], as well as standard differential vapor pressure osmometry [18–22] have been employed. Except cryoscopy all these methods are carried out at room temperature or above limiting their use to only such organometallic compounds, which do not decompose at these temperatures.

Cryoscopy, as developed by Funk [13], Bauer, and Seebach [12], has two other major limitations:

(i) It can only be performed in well crystallizing solvents like THF and benzene, but not in solvents like diethyl ether or pentane which are often used in organometallic chemistry.

(ii) Measurements can only be carried out at the freezing temperature of the solvent, e.g. −108 °C for THF, whereas most reactions of or with organometallic reagents are carried out at temperatures higher than the solvent's freezing point. As the aggregation number can change with the solvent and the temperature, the degree detected by cryoscopy does not necessarily match with the aggregation number under the conditions during mechanistic studies of these reagents.

In order to circumvent these limitations, we developed a sub room temperature differential vapor pressure osmometry instrument as a novel and flexible tool to determine the aggregation number. A wide range of different solvents and temperatures high enough for kinetic studies and low enough to prevent the decomposition of sensitive compounds can be employed. The method is based on the colligative property of vapor pressure depression of solutions [23, 24] (Fig. 1).

The principle of vapor pressure depression of solutions can be illustrated as follows: In a saturated gas phase of the solvent at a constant temperature, one drop of the pure solvent (Drop 1) and one drop of the solution (Drop 2) are positioned opposite to each other, covering the surface of two thermoresistors NTC1 and NTC2. Drop 2 has a lower vapor pressure than the pure solvent. As a consequence, solvent molecules condense on Drop 2, release their condensation enthalpy, and thus cause a rise of temperature. Drop 1 is in equilibrium with the gas phase, so its temperature remains constant. The temperature difference between Drop 1 and Drop 2 can be evaluated by measuring the difference in resistance (ΔR, $\Delta R = R_{\mathrm{NTC1}} - R_{\mathrm{NTC2}}$) of the two NTC's [23–31]. ΔR is directly proportional to the concentration of the solution forming Drop 2[1]. The proportionality factor K is a function of the

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[1] In fact, linearity of ΔR is given for a small ΔR only. Nevertheless, this applies in the technical setup for the SRTDVPO.

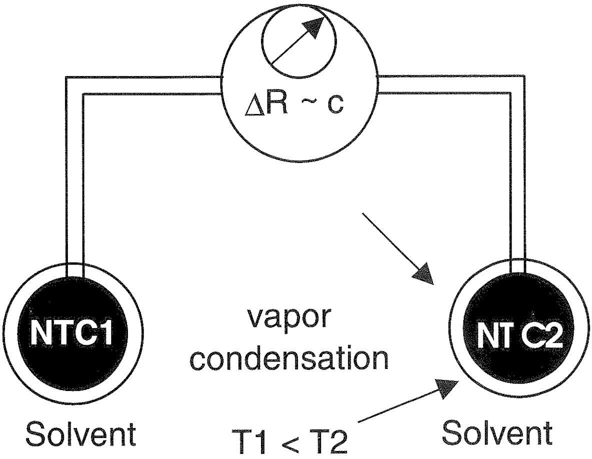

Fig. 1. Principle of a differential vapor pressure osmometer.

solvent, the temperature, and the apparatus itself. Therefore, K must be calibrated in advance of each measurement with stock solutions of known concentrations.

Differential vapor pressure osmometry is normally used at temperatures about 10°C below the boiling point of the solvent [21]. However, measurements can also be performed at much lower temperatures as long as

(i) the two thermoresistors have a deviation of less than 0.3% and

(ii) the vapor pressure of the solvent is $\geq$35 mbar at the measurement temperature. The latter condition is fulfilled by THF at 0°C and by diethyl ether at -35°C. At these temperatures most organometallic compounds remain stable for hours.

Commercially available differential vapor pressure osmometers are neither suitable for measurements at these temperatures nor for the study of oxygen- and moisture-sensitive compounds. Therefore, we designed and built a Sub Room Temperature Differential Vapor Pressure Osmometer (SRTDVPO) appropriate for this task.

2. Experimental

The SRTDVPO apparatus

The SRTDVPO is shown in Fig. 2. The main features of this novel apparatus are

(i) the exclusion of oxygen and moisture,

(ii) the construction of the apparatus, so it can be submerged in a cooling bath,

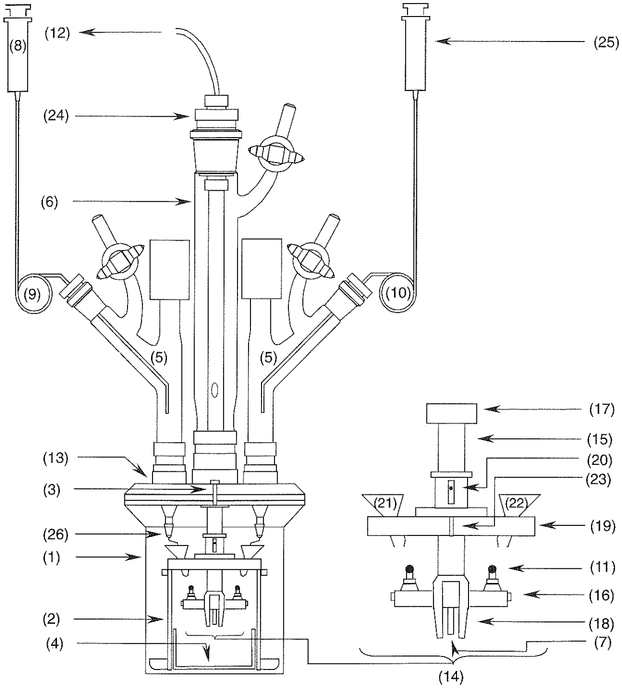

Fig. 2. The Sub Room Temperature Differential Vapor Pressure Osmometer.

(iii) the vertical upright orientation of the thermoresistors [25] for a reproducible drop size at low temperatures, and

(iv) the determination of the resistances of the NTC's as the voltage at constant current.

The latter reduces errors otherwise caused by electric heating and allows to set the amplification and the offset of the signal by a computer controlled circuit with minimal interference of the measurement.

Technical description of the SRTDVPO

A 1 L glass beaker (1) with a 100 mm flange connection (Normag) with a matching brass lid (13) was used as the measurement chamber. The flange connection was sealed with grease and an O-ring, and secured with a metal clamp. A cellulose cylinder (2, cut from a soxhlett thimble) guaranteed the saturation of the solvent vapor phase. A 80 mL glass beaker (4) with a stirring bar in the cylinder (2) contained an allylmagnesium chloride solution to trap traces of oxygen and moisture. It also prevented the solutions dropping from the NTC's to mix with the pure solvent placed outside the beaker (4) in the measurement chamber (1).

(1) Measurement chamber	(14) NTC holder
(2) Cellulose cylinder	(15) Teflon shaft
(3) Screw-hole in lid (13)	(16) Side arms
(4) Glass beaker	(17) Plug holder
(5) Dropping funnels	(18) Teflon shields
(6) Central glass tube	(19) Teflon cover disk
(7) RTD	(20) Guide slot and pin
(8) Syringe	(21) Glass funnel
(9) Teflon tube	(22) Glass funnel
(10) Teflon tube	(23) Hole in cover disk (19)
(11) NTC's	(24) Electric supply pipe
(12) Computer	(25) Syringe
(13) Brass lid	(26) Bend tubes

The NTC-holder (14) was constructed as depicted in detail in Fig. 2. A teflon shaft (15) contained the extensions of the electric supply cable in a central drill hole. A Resistance Temperature Detector (7) monitored the temperature of the gas phase in chamber (1). Two horizontal side-arms (16) with plugs (17) were holding the two NTC's (11) in a vertical upright position. Two teflon shields (18) prevented the solutions from creeping from one NTC to the other. A vertical movable teflon disc (19) was used for covering the cellulose cylinder (2). A guide slot and pin (20) prevented the disc (19) from rotation relative to the central shaft (15). Two glass funnels (21) and (22) directed the solutions towards the NTC's. The cover disc had an additional small hole (23) to inject the allylmagnesium chloride solution into the glass beaker (4).

The NTC-holder (14) was connected to the electric supply pipe (24) containing the electric supply cable. The supply pipe (24) was located in the central glass tube (6). The pipe (24) was turned relative to the lid (13) so that the hole (23) of the coverdisc (19) matched with a screw hole (3) in the lid (13).

Coiled teflon tubes (9) and (10) with gas-tight syringes (8) and (25) were used to store the solutions for measurement. Like the apparatus, the coils were completely submerged in the cooling bath to keep the solutions at temperature. The free ends of the teflon tubes were inserted through septa into dropping funnels (5). Bent tubes (26) were placed on the exits of the dropping funnels to direct the out-coming solution to the funnels (21) and (22).

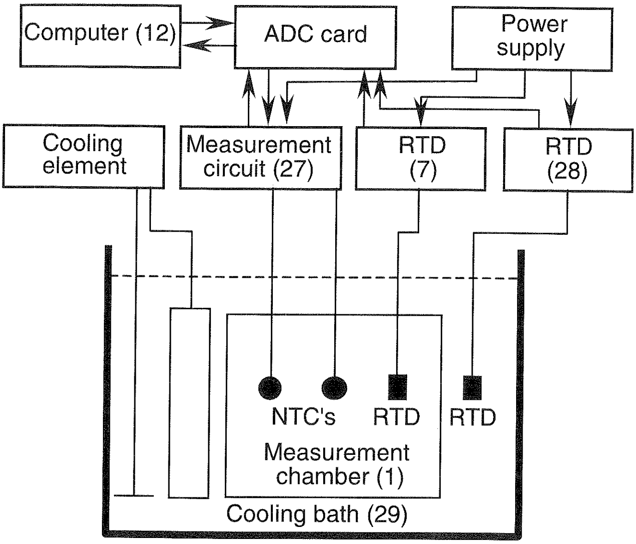

Fig. 3. The electronic components of the SRTDVPO.

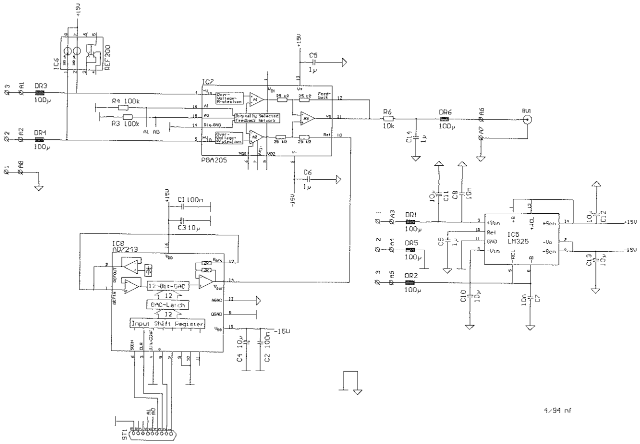

Fig. 4. Circuit (27) for the resistance voltage transformation.

Electronic devices

The electronic components are schematically depicted in Fig. 3.

The resistance of the two NTC's (11) was measured by the circuit (27) in terms of the decrease of voltage across the NTC's at constant current (Fig. 4; [12]). By means of the RTD sensors and modules (7) and (28), the temperature of the cooling bath (29) and the measurement chamber (1) was recorded.

3. Measurement

All glass, teflon and brass parts of the apparatus were dried for 12 h at 75 °C. The assembled apparatus was evacuated (10^{-2} Torr) for 6 h, checked for tightness, and then refilled with argon. 40 mL of dry and pure solvent were placed between the glasswall of the measurement chamber (1) and the cellulose cylinder (2) through the lid screw hole (3). 30 mL of a 2 M allylmagnesium chloride solution were added into the glass beaker (4). All the taps of the dropping funnels (5) and the central glass tube (6) were connected to a single balloon filled with argon. The apparatus was placed on a magnetic stirrer, and the allylmagnesium chloride solution was slowly stirred for 12 h to remove the remaining traces of oxygen and moisture.

The apparatus and the coils of the teflon tubes were completely submerged in a vigorously stirred 60 L cooling bath for 12 h for temperature equilibration. The temperature in the measurement chamber was monitored with the RTD (7).

Using the syringe (8), the teflon-tube coil (9) was loaded with approximately 2 mL of either the calibration solutions or the solution of the organometallic compound to be investigated. 8 mL of dry solvent were injected into the remaining coil of the teflon tube coil (10). The solution for measurement and the pure solvent for reference were kept for at least 1 h in the teflon tube coils for thermal equilibration.

For each measurement about 0.5 mL of one of the solutions and 0.5 mL of the pure solvent for reference were released. The liquids went via the dropping funnels (5) and the directing glass funnels to the NTC's (11). The last drops covering the surface of the NTC's were used for measurement. A computer (12) recorded the evaluation of ΔU at constant current ΔI (ΔR proportional to ΔU) between the two NTC's over time. Examples of the curves obtained are shown in Fig. 5. After approximately 6 min the curves reached an almost constant value. After 10 min the value of ΔU was noted. Its dimensionless value SKT (Skalenteile) is proportional to the concentration of the solutions and was used for calculating the aggregation number.

For the calibration of the apparatus (4) biphenyl solutions of known concentration were prepared and measured[2]. A linear regression analysis was performed on ΔU vs. the known concentrations[3].

Now the ΔU of the solution of the compound in question was determined and the concentration of particles of this solution was calculated

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[2] The concentrations of the calibration solutions should be in range of the expected concentration of the solution of the organometallic compounds.

[3] If the correlation was below ±0.99, the calibration was repeated.

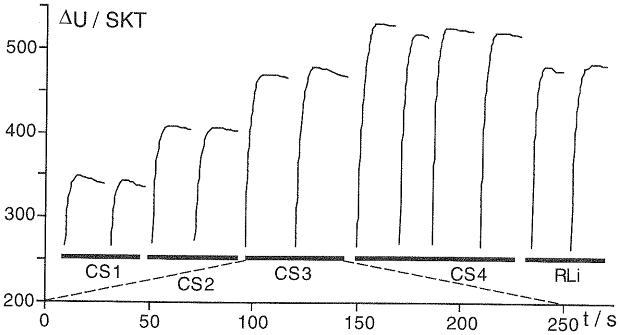


Fig. 5. Example of obtained curves. CS1 to CS4: curves of the calibration solutions (biphenyl in THF), RLi: curves of a $LiCH_2SePh$ solution in THF.

using the results from the linear regression. This in turn allowed to obtain its aggregation number depending on the way the organometallic compounds were prepared. For compounds that could be dissolved in the appropriate solvent (e.g. the transition metal complexes) or were generated by deprotonation releasing the volatile byproduct butane, the aggregation number is calculated using Eq. (1).

$$n = \frac{c_{\mathrm{nom}}}{c_{\mathrm{m}}} \tag{1}$$

with n = aggregation number; c_{nom} = nominal conc.; c_{m} = measured conc.

The investigated α-selenium lithium compounds were generated by a selenium/lithium exchange reaction. One equivalent of the selenium ether *t*-BuSePh was formed as byproduct. This byproduct was not removed and its contribution to the total concentration of particles needs to be considered in the calculation of the aggregation number (Eq. (2)). (For an example using Eq. (2) cf. Table 1. Evaluation of the aggregation number of (1) in THF at 0 °C.)

$$n = \frac{c_{\mathrm{nom}}}{c_{\mathrm{m}} - c_{\mathrm{sp}}} \tag{2}$$

with n = aggregation number; c_{nom} = nominal conc.; c_{m} = measured conc.; c_{sp} = conc. of byproducts

4. Results and discussion

The aggregation numbers of lithium amides, α-selenyl-, and α-thio-substituted alkyllithium compounds were determined in THF at 0 °C and in diethyl ether at −30 °C or −35 °C (Table 2). In addition, the aggregation number of various complexes of Mn, Co, Ni, Cd, and Pt with phosphine,

Table 1. Evaluation of the aggregation number of $LiCH_2SePh$ (1) in THF at 0°C.

Calibration solutions	Biphenyl [g]	THF [g]	conc. [mol kg^{-1}]	ΔU^1 [SKT]
1	1.230	17.47	0.457	303 ± 4
2	1.488	17.40	0.555	370 ± 8
3	1.746	17.45	0.649	421 ± 4
4	2.004	17.40	0.747	470 ± 10

Calibration

slope [SKT kg mol^{-1}]	interception [SKT]	correlation
572.69 ± 30.31	46.23 ± 18.54	0.9972

$LiCH_2SePh$ solution	$(PhSe)_2CH_2$ ^{t}BuLi [g]	THF [g]	Total conc. [mol kg^{-1}]	ΔU [SKT]
1	1.983 0.399	18.24	0.670	460 ± 6

Aggregation number of $LiCH_2SePh$ (1)

Expected nominal conc. of particles^2	Measured total conc. of particles	Aggregation number (Eq. (2))
$c_{nom} = 0.335$ mol kg^{-1} $c_{sp} = 0.335$ mol kg^{-1}	$c_m = 0.724 \pm 0.07$ mol kg^{-1}	0.86 ± 0.15

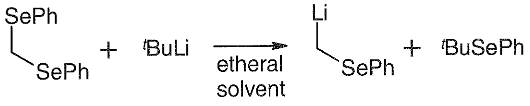
[1] Deviation of ΔU within 10 min ± 5 min; [2] if (1) is monomeric.

phosphoraneiminato, alkyne, or alkyl ligands were determined in THF at 0°C.

The lithium amides and the dithioacetals were prepared by deprotonation of the precursor compound with ^{n}butyllithium in etheral solvent.

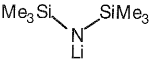
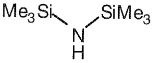
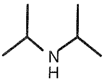
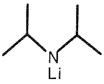
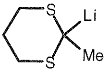
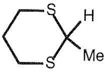
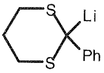
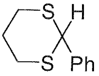
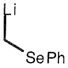
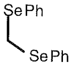
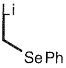
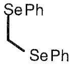
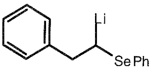
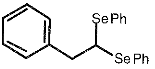
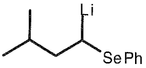
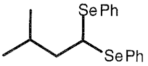
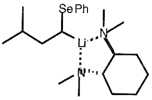
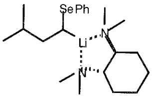
The α-seleno organolithiums were prepared from the corresponding diselenoacetals, which upon treatment with 1 equivalent of ^{t}butyllithium undergo an element lithium exchange (Scheme 1).

One equivalent of ^{t}butyl-seleno-phenyl is formed as byproduct. This has to be considered when calculating the aggregation number (Eq. (2)).



Scheme 1. Preparation of (1).

Table 2. Investigated lithium compounds and their precursors.

Compound		Precursor	Condition[1]	c_m[2]	T [°C]	n
	(2)		A	0.59	0	1.0 ± 0.1 (Eq. (1))
	(3)		A	0.37	0	2.1 ± 0.5 (Eq. (1))
	(4)		A	0.42	0	1.0 ± 0.1 (Eq. (1))
	(5)		A	0.29	0	0.9 ± 0.1 (Eq. (1))
	(1)		B	0.33	0	0.9 ± 0.1 (Eq. (2))
	(1)		C	0.25 0.26	0 −30	4.1 ± 1.2 2.9 ± 0.8
	(6)		C	0.29	−35	1.0 ± 0.1 (Eq. (2))
	(7)		C	0.30	−35	1.0 ± 0.1 (Eq. (2))
	(9)		C	0.23	−35	1.0 ± 0.2 (Eq. (2))

[1] A ^{n}BuLi, THF; B ^{t}BuLi, THF; C ^{t}BuLi, Et_2O; [2] [mol kg^{-1}].

Lithio-N,N-bis-(trimethylsilyl)-amide (2) and lithio-N,N-diisopropylamide (3): The two lithium amides were studied as reference compounds for evaluating the reliability of the SRTDVPO for determining the aggregation number of moisture- and oxygen-sensitive compounds. Kimura and Brown investigated the aggregation number of (2) in THF at RT (monomeric, n = 1.1) using differential vapor pressure barometry [17]. In accordance with their result, the aggregation number of (2) in THF at 0°C determined by SRTDVPO was also monomeric ($n = 1.0 \pm 0.1$, $c = 0.59$ mol kg^{-1}). Using cryoscopy in THF at −108°C, Bauer and Seebach determined the state of aggregation of (3) to be a monomer-dimer equilibrium ($n = 1.6$) [12].

Therefore, it was interesting to get an insight into the state of aggregation at higher temperatures. Comparable with the results obtained by Bauer and Seebach, the aggregation number in THF at 0 °C determined by SRTDVPO was found to be dimeric ($n = 2.1 \pm 0.5$, $c = 0.37$ mol kg^{-1}). The coherency of these results obtained by SRTDVPO on both lithium amides with the results obtained previously by other methods prooved the viability of SRTDVPO for determining the aggregation number of moisture- and oxygen-sensitive compounds. We therefore felt confident to measure the aggregation number of other sensitive lithium compounds.

2-Lithio-2-methyl-1,3-dithiane (4) and 2-lithio-2-phenyl-1,3-dithiane (5): aggregation numbers of these compounds in THF at 0 °C were measured because their crystal structures are known and because the aggregation number of (4) in THF at −108 °C had been investigated by cryoscopy [12, 32]. In the solid state, (5) as THF-TMEDA-complex is monomeric while (4) as TMEDA-complex is dimeric with a −[Li−C−S−Li−C−S]− six-membered ring-structure. The cryoscopically determined aggregation number in THF of (4) was $n = 1.2$, giving rise to the speculation that this might indicate an equilibrium between a monomer and a dimer in solution. However, when investigated by SRTDVPO in THF at 0 °C, (4) and (5) proved to be monomeric ($n = 1.0 \pm 0.1$, $c = 0.29$ mol kg^{-1} and $n = 0.9 \pm 0.1$, $c = 0.42$ mol kg^{-1}, respectively).

Lithio-phenylselenyl-methane (1): The aggregation behaviour of (1) was studied in diethyl ether at 0 °C and −30 °C and in THF at 0 °C. At 0 °C, the change in the polarity of the solvent altered the state of aggregation from monomeric ($n = 0.86 \pm 0.15$, $c = 0.31$ mol kg^{-1}) in the more polar THF to mainly tetrameric ($n = 4.1 \pm 1.2$, $c = 0.31$ mol kg^{-1})[4] in the less polar diethyl ether. Lowering the temperature from 0 °C to −30 °C in diethyl ether changed the aggregation number from $n = 4.1 \pm 1.2$ to $n = 2.9 \pm 0.8$ ($c = 0.26$ mol kg^{-1}). This result is consistent with the general finding that the degree of aggregation of organolithium compounds decreases at lower temperatures [12].

1-Lithio-2-phenyl-1-phenylselenyl-ethane (6): The aggregation number of (6) has already been determined by cryoscopy in THF at −108 °C to be monomeric ($n = 1.0 \pm 0.1$) [33]. Because the related compound (1) is aggregated in diethyl ether, the state of aggregation of (6) at −35 °C in diethyl ether was determined. Under these conditions, (6) was monomeric ($n = 1.0 \pm 0.1$, $c = 0.29$ mol kg^{-1}). This result demonstrates the effect of

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[4] The aggregation number is calculated from the total concentration of particles in the solution that can be determined with an accuracy of roughly ±0.03 to 0.06 mol kg^{-1} under the conditions of investigation. A higher aggregation number causes smaller absolute changes in the total concentration of particles and therefore causes a higher uncertainty.

the higher substituted α-carbon of (6). Steric hindrance leads to a decrease in the aggregation number relative to the sterically less hindered compound (1).

1-Lithio-3-methyl-1-phenylselenyl-butane (7): The reaction mechanism of the organolithium compound (7) with benzaldehyde in the presence of the chiral ligand trans-1,2-(Dimethylamino)-cyclohexane (8) has been studied in detail [35, 36]. The aggregation number in diethyl ether at −35 °C of the uncomplexed organolithium compound (7) and its complex (9) with the ligand (8) was investigated. Both the non-complexed organolithium compound (7) ($n = 1.0 \pm 0.1$, $c = 0.30$ mol kg^{-1}) and the complex (9) ($n = 1.0 \pm 0.2$, $c = 0.23$ mol kg^{-1}) were monomeric. According to these results, the diamine ligand has no influence on the aggregation number of the organolithium compound (7) in diethyl ether.

Bromo-μ_3-triethylphosphaniminato-manganese(II) [MnBr(NPEt$_3$)] (10) [40], bromo-μ_3-triethylphosphaniminato-cobalt(II) [CoBr(NPEt$_3$)] (11) [41], iodo-μ_3-triethylphosphaniminato-nickel(II) [NiI(NPEt$_3$)] (12) [42], and trimethylsilylethynyl-μ_3-triethylphosphaniminato-cadmium(II), [Cd(C≡CSiMe$_3$)(NPEt$_3$)] (13) [43]: The solid state structures of these complexes show tetrameric units of the heterocuban type. Their aggregation behavior was studied by SRTDVPO to determine if they maintain this aggregation or instead dissociate in solution. It was found that in THF at 0°C the aggregation number was dimeric for [MnBr(NPEt$_3$)] ($n = 2.15 \pm 0.27$, $c = 0.052$ mol kg^{-1}), between dimeric and monomeric for [CoBr(NPEt$_3$)] ($n = 1.58 \pm 0.12$; $c = 0.039$ mol kg^{-1}), and dimeric for [NiI(NPEt$_3$)] ($n = 1.92 \pm 0.09$; $c = 0.048$ mol kg^{-1}). This indicates the formation of complexes like [MnBr(NPEt$_3$)(solvent)]$_2$. However, [Cd(C≡CSiMe$_3$)(NPEt$_3$)] remained tetrameric ($n = 4.07 \pm 0.09$; $c = 0.061$ mol kg^{-1}) when dissolved in THF at 0°C.

Trimethyl-platinum-triflate (14) [44] and trimethyl-platinum-triflate · TMEDA (15) [45]: The aggregation numbers of (14) and (15) were investigated to determine if the TMEDA ligand of (15) remains bound to the metal center upon dissolution in THF at room temperature. Both complexes (14) and (15) are dissociated into two distinct species ($n = 0.54 \pm 0.07$; $c = 0.010$ mol kg^{-1} and $n = 0.45 \pm 0.02$; $c = 0.10$ mol kg^{-1}, respectively).

5. Conclusion

The novel instrument developed for sub room temperature differential vapor pressure osmometry enabled us to determine the aggregation number of sensitive compounds like lithium amides, lithium organyls, and transition metal complexes under the exclusion of oxygen and moisture in THF solutions at temperatures as low as 0°C and in diethyl ether solutions as low as −35 °C[5]. The instrument allows to determine the aggregation number under typical reaction conditions with these organometallic reagents.

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[5] At the measurement temperature, the solvent must have a vapor pressure of at least 35 mbar. Therefore, the determination of the aggregation numbers in a variaty of solvents such as methylene chloride, dimethylether, pentane or hexane at low temperatures is also possible.

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