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THE GEOMETRY OF ALLYL-ALKALI-METAL COMPOUNDS. A ^{13}C NMR REINVESTIGATION

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Summary

The spatial positions of the hydrogens in allyl-alkali-metal compounds are controversial: in agreement with the X-ray structures of those allyl compounds of which the positions of the hydrogen atoms have been determined, calculations predict strongly bent out inner hydrogens $H^{1(3)}$ and a weakly bent out central hydrogen H^2. On the other hand, since the coupling constant $^1J(^{13}CH^2)$ of allyl-alkali-metal compounds is even smaller than the already small coupling constant $^1J(^{13}CH^{1(3)})$, it has been proposed that H^2 is much more bent out than $H^{1(3)}$ [8]. We conclude from the essentially identical coupling constants $^1J(^{13}CH^2)$ (133 ± 2 Hz) in (1) the contact and the solvent-separated ion pair of phenylallyllithium (potassium), (2) allyllithium and 1,3-diphenylallyllithium, and (3) allyl-lithium, -sodium, -potassium, -rubidium, -cesium that this coupling constant is not a function of an out-of-plane distortion at C^2. A similar argument applies for $C^{1(3)}$. Rather, it is the angle widening at C^2 that causes the small coupling constants $^1J(^{13}CH^2)$, as supported by the larger coupling in 1-phenylcyclohexenyl- and, especially, 1,3-diphenylcyclopentenyl-lithium, and in agreement with both calculations and X-ray data for allyllithium.

Introduction and discussion

While ab initio calculations predict a planar structure with a CCC-angle α ~ 132° for the allyl anion $C_3H_5^-$ (**1a**) [1–3], the allyl part is distorted from planarity in allyllithium C_3H_5Li and the solvated allyllithium compounds $C_3H_5Li \cdot 2(3)H_2O$, e.g.

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** From the Diplomarbeit of G. Decher, Universität Marburg, 1983.

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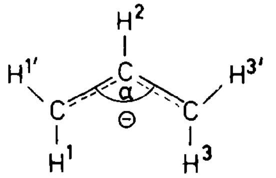
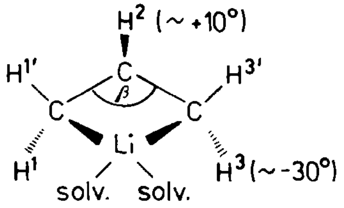
1b, according to both ab initio [4] and MNDO calculations [5]. The inner hydrogens H^1 and H^3 are strongly bent out of the plane of the carbon atoms and away from the bridging lithium atom (~ −30°); the central hydrogen H^2 is bent towards lithium (~ +10°), and the outer hydrogens $H^{1'}$ and $H^{3'}$ remain more or less in the plane of the carbon atoms. The CCC-angle β is also widened to 123–126°.



1a $\alpha \sim 132°$



1b $\beta = 123\text{-}126°$

Consequently, the hybridisation, especially of the $CH^{1(3)}$ bond, changes from sp^2 in the anion **1a** towards sp^3 in the lithium species **1b**.

Experimentally, the bridged structure of allyllithium (and allylpotassium) has been demonstrated unequivocally [6].

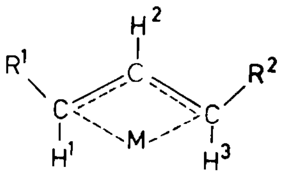
For the positions of the hydrogen atoms, however, ^{13}C NMR investigations have led to an interpretation [8] which disagrees with the results of the calculations [4,5], as well as the X-ray structure determinations of those allyl compounds of which the positions of the hydrogen atoms have been evaluated: the allyl nickel complex $(\eta^3\text{-}C_3H_5)_2NiP(CH_3)_3$ [9,5] and the hexatriene dianion $C_6H_8Li_2 \cdot 2TMEDA$ [10,5]. It has been suggested from the NMR data [8] that the rather small coupling constants of the inner hydrogens $^1J(^{13}CH^{1(3)})$ 142–147 Hz, and especially of the central hydrogens $^1J(^{13}CH^2)$ 128–134 Hz, found in various allyl-alkali-metal compounds (see Table 1, entries 2,7,8,10,11), parallel directly the increasing *p*-character of the corresponding carbon atoms. Thus, the central H^2 should be more bent out of the plane of the carbon atoms than the inner hydrogens H^1 and H^3. The coupling constants of the outer hydrogens $^1J(^{13}C\text{–}H^{1'(3')})$ 154–155 Hz (see Table 1) are regarded as normal [8,11]; these hydrogens should lie in the plane of the carbon atoms.

The discrepancy raises the question about the validity of the interpretation of the ^{13}CH NMR data [8]. A reexamination indicates that $^{13}C\text{–}H$ coupling constants do not necessarily parallel the distortions of the hydrogen atoms out of the plane of the carbon atoms in allyl-alkali-metal compounds. It is rather the widened CCC angle at C^2 which contributes decisively to the small coupling constant $^1J(^{13}CH^2)$. The following experimental and calculated data support these statements.

If the (differential) deformations of the allyl moieties in allyl-alkali-metal compounds would be revealed by the (gradually changing) $^{13}C\text{–}H$ coupling constants, one should be able to detect a change in the coupling constants on going from the contact ion pair (CIP) of a certain species to its solvent separated ion pair (SSIP). In contact ion pairs the metal atom is in close contact with the carbon atoms of the "anionic" part of the molecule, leading to structures like **1b**, as shown by solution and solid state investigations [12,13]. Solvent separated ion pairs, on the other hand, are characterized by little or no interaction of the "anion" with the alkali metal

TABLE 1

$^1J(^{13}CH)$ COUPLING CONSTANTS (Hz) OF VARIOUS ALLYL-ALKALI-METAL COMPOUNDS



Entry	R^1	R^2	M	Inner H		Outer H	Central H	Ref.
				$^1J(CH^1)$	$^1J(CH^3)$	$^1J(CH^3)$	$^1J(CH^2)$	
1	H	H	Li(CIP)	146	146	146	133	7,19
2	H	H	Li(CIP)	146.5	146.5	146.5	133.0	8
3	H	H	Li(CIP)	140.8	140.8	149.8	132.4	11
4	H	H	Na(CIP)	148	148	148	132	7
5	H	H	Na(CIP)	149.5	149.5	149.5	131.8	8
6	H	H	K(CIP)	148	148	148	131.8	7
7	H	H	K(CIP)	142.8	142.8	154.9	131.8	8
8	H	H	Rb(CIP)	143	143	154	131	7
9	H	H	Cs(CIP)	145	145	145	132	7
10	CH_3	H	K(CIP)	142.0	141.6	153.8	128.2	8
11	C_2H_3	H	Li(CIP?)	141.6	146.5	153.8	134.2	8
12	C_6H_5	H	Li(CIP)	145.2	150.7	150.7	134.0	[b]
13	C_6H_5	H	Li(SSIP)	146.4	148.4	154.9	132.9	[b]
14	C_6H_5	H	K(CIP)	145.4	148.4	157.2	134.2	[b]
15	C_6H_5	H[c]	K(CIP)	-	-	154.0	140.0	[b]
16	C_6H_5	C_6H_5	Li(SSIP)	145.6	145.6	-	132.8	[b]
17	C_6H_5	C_6H_5[d]	Li(SSIP)	-	-	-	144.8	[b]

[a] CIP = contact ion pair; SSIP = solvent separated ion pair. [b] This work. [c] **3**, $(CH_2)_3$ instead of $H^1(H^3)$. [d] **4**, $(CH_2)_2$ instead of $H^1(H^3)$.

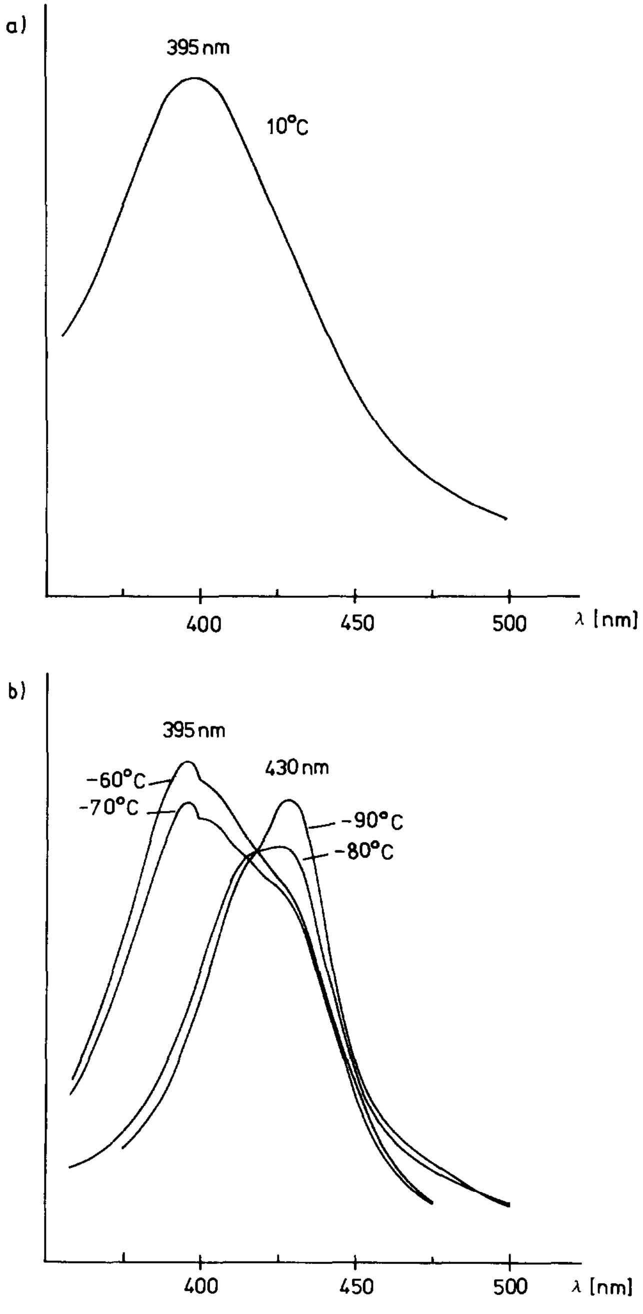
gegenion; therefore, the "anion" in these species is a good model for the properties of the corresponding free anion [12].

Since it is not possible to investigate these two ion pairs in the case of the parent allyl-alkali-metal compounds due to the instability of the solvent separated species [16], we have studied the phenylallyl system instead. Phenylallyllithium [17] (λ_{max} 395 nm, see Fig. 1a) and phenylallylpotassium [18] (λ_{max} 411 nm, see Fig. 2a) exist in tetrahydrofuran (THF) at room temperature as contact ion pairs.

When 6 mol equivalents of hexamethylphosphoric acid triamide (HMPT) are added to the THF solution of the lithium salt, or if the temperature of the THF solution is lowered to −90°C, the solvent separated ion pair is formed (λ_{max} 430 nm, see Fig. 1b,c). Under similar conditions, the potassium salt is only partially transformed into the solvent separated ion pair (see Fig. 2b): the transformation, however, is achieved by adding cryptand[2.2.2] to the THF solution (λ_{max} 430 nm). Cryptand[2.1.1] yields the solvent separated ion pair of the lithium species (λ_{max} 430 nm). These solutions decompose even at low temperatures within minutes.

The results of the visible spectra are supported by the ^{13}C NMR chemical shifts. In the lithium compound [19] the signals of C^1 and C^3 are strongly shifted towards lower, and of C^p towards higher fields on going from the contact to the solvent separated species (see Table 2, entries 1 and 2). The reduced polarization by the gegenion in the separated ion pair leads to enhanced delocalization of the negative charge into the phenyl ring (C^p!). The values of the potassium contact ion pair [20] lie between those of the lithium ion pairs, as expected (see Table 2, entry 3).

(Continued on p. 7)



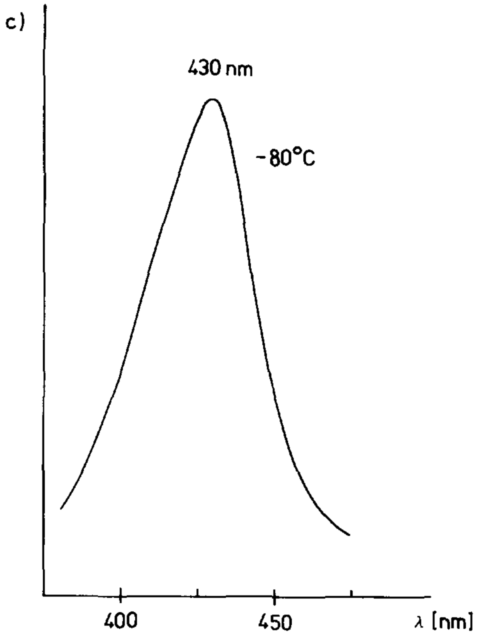
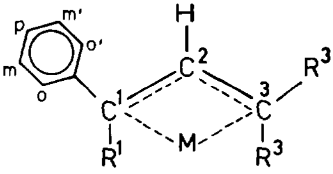


Fig. 1. Visible absorption spectra of 1-phenylallyllithium in (a) THF, (b) THF (c) THF, in the presence of 6 mol equiv. HMPT; the spectrum does not change with temperature. The marks at 400 nm in these (especially b) and the spectra shown in Fig. 2 are due to an automatic change of filters in the spectrometer.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS δ (ppm) OF (SUBSTITUTED) PHENYLALLYL-ALKALI-METAL COMPOUNDS



Entry	M	Solvent	T(°C)	C^1	C^2	C^3	C^i	C^o	$C^{o'}$	C^m	C^p
1 [a]	Li	THF-d_8	30	77.3	137.5	65.7	148.7	117.3	117.3	128.4	110.2 [f]
2 [a]	Li	THF-d_8 HMPT	−40	82.9	136.3	73.4	148.2	117.4	110.0	128.5 128.2	102.8
3 [a]	K	THF	−20	79.8	136.2	72.6	148.0	118.3	111.8	129.2	107.1 [g]
4 [b]	K	THF	−20	81.1	127.7	93.2 [c]	141.1	110.1 [d]	109.5 [d]	130.3 129.2	100.9
5 [b]	K	THF	0	81.2	127.6	95.1 [c]	140.9	109.9 [d]	109.7 [d]	130.8 129.8	101.3
6 [e]	Li	THF-d_8	0	104.9	128.2	104.9	141.2	116.5	116.5	127.9	109.5

[a] $R^1 = R^3 = R^{3'} = H$. [b] 3, $R^1 = R^3 = (CH_2)_3$, $R^{3'} = H$. [c] Assignment by means of deuteration. [d] Assignment uncertain. [e] 4, $R^1 = R^3 = (CH_2)_2$, $R^{3'} = C_6H_5$. [f] See ref. 19. [g] See ref. 20.

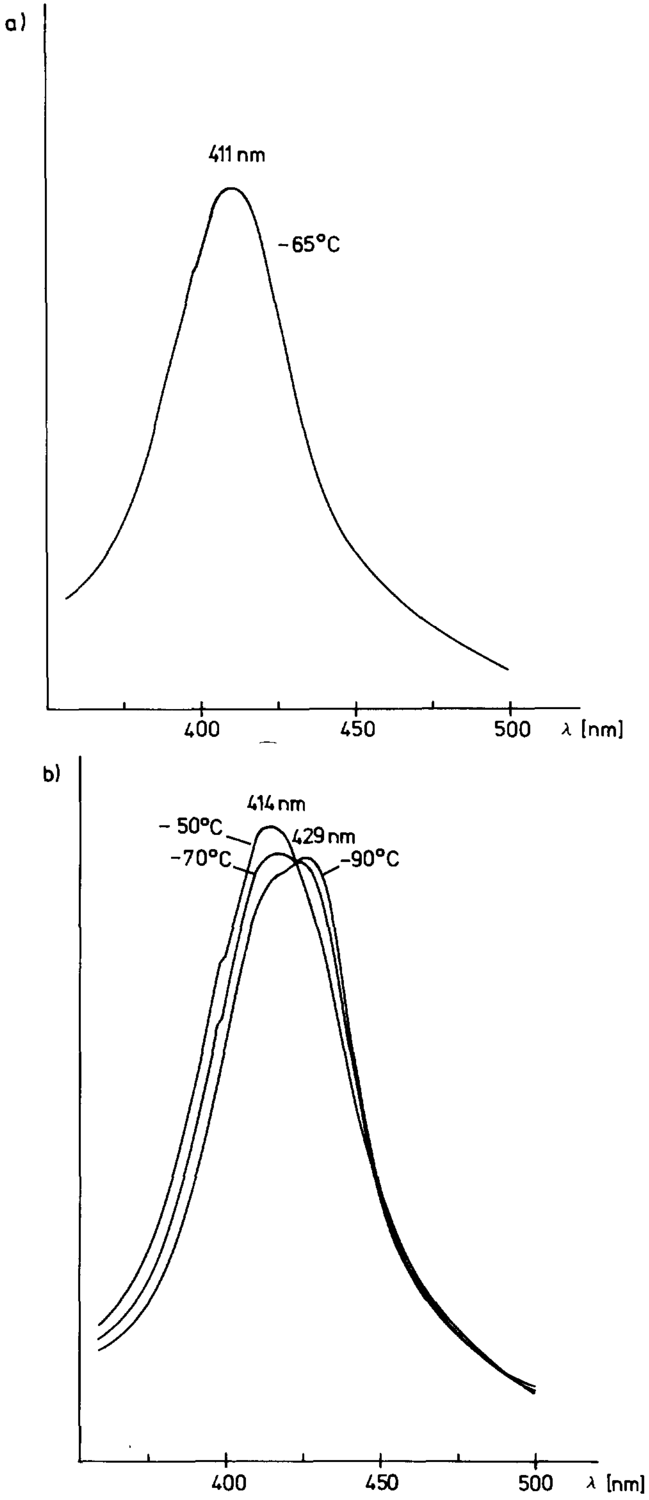
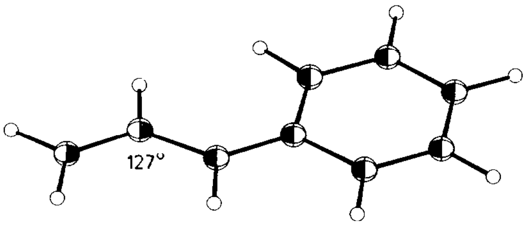


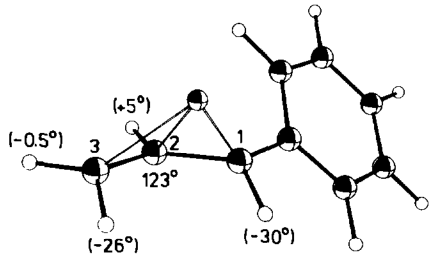
Fig. 2. Visible absorption spectra of 1-phenylallylpotassium in (a) THF, the spectrum does not change with temperature; and (b) THF in the presence of 6 mol equiv. HMPT.

Most remarkably, however, the changes in the ion pair structures are in our opinion not at all reflected in the ^{13}C–H coupling constants of the phenylallyl-alkali-metal compounds (see Table 1, entries 12–14)!

We would like to emphasize that the detailed structures of the phenylallyl-alkali-metal ion pairs are, unfortunately, not known to date. It is, therefore, not possible to exclude rigorously the possibility that a structural change within the phenylallyl "anion" framework, on going from the contact to the solvent separated ion pair, is marginal and thus not observable by means of the ^{13}C–H coupling constants. However, if the MNDO geometry optimized structures of the *planar* phenylallyl anion $C_6H_5{-}C_3H_4^-$ (**2a**) and of the *strongly distorted* phenylallyllithium $C_6H_5{-}C_3H_4Li$ (**2b**) [21] are reasonable models for the "anion" structure in the solvent separated and the contact ion pair, respectively, and if the ^{13}C–H coupling constants would depend largely on the hybridization of the corresponding carbon atoms in the two ion pairs, one should observe more pronounced differences!



2a; ΔH_f = 22.7 kcal/mol



2b; ΔH_f = 23.8 kcal/mol

Likewise, a comparison of the coupling constants of 1,3-diphenylallyllithium, a solvent separated ion pair in THF [22] having most probably a planar 1,3-diphenylallyl "anion" structure (Table 1, entry 16) with those of allyllithium does not indicate remarkable differences!

The same, again, is observed if one compares allyl-sodium, -potassium, -rubidium and -cesium (Table 1, entries 4–9) with allyllithium! Undoubtedly, the large cesium atom is expected to influence the allyl moiety structurally much less than the small lithium atom, as similarly pointed out by Clark et al. for allylrubidium [4b].

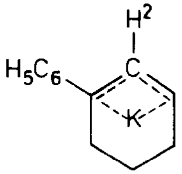
Two considerations, consequently, lead to the conclusion that the ^{13}CH coupling constants of allyl-alkali-metal compounds, and especially of allyllithium, do not reveal the amount of distortion out of the plane of the allyl carbon atoms of the corresponding hydrogen atoms:

(1) The variations within the ^{13}CH coupling constants of the inner *and* of the outer hydrogens are almost identical in the whole series of allyl "anion" species presented in Table 1. According to the calculations ([4,5], see **2a** and **2b**) and the X-ray data [9,10,5], however, the ^{13}CH coupling constants of the inner hydrogens should vary much more than those of the outer ones: the outer hydrogens, under any gegenion and ion pair conditions, should remain in the plane of the carbon atoms while the positions of the inner hydrogens, and thus their ^{13}CH coupling constants, should be a function of these conditions – provided the premise [8] is right.

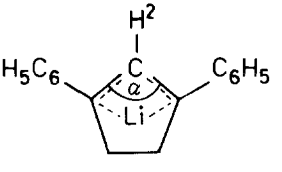
(2) The small values ($\sim 133 \pm 2$ Hz) of the ^{13}CH coupling constants of the central hydrogens are almost identical in all the allyl compounds and under any ion pair

conditions. This cannot mean that in any case (allyllithium, allylcesium, the solvent separated 1,3-diphenylallyllithium!) the central hydrogens H^2 are bent equally far out of the plane of the carbon atoms, as this is assumed to be so in allyllithium [8].

Therefore, a widening of the central CCC bond angle, as found (1) by the ab initio and MNDO calculations of the allyl anion and the allyl-alkali-metal compounds ([1–5] **2a**, **2b**; the angle $C^1C^2C^3$ of the 1,3-diphenylallyl anion is according to MNDO calculations 126.1°), and (2) by the X-ray structure determinations of crystalline allyllithium (angle $C^1C^2C^3$ 126.7°) [23] and of the hexatriene dianion $C_6H_8Li_2 \cdot 2TMEDA$ (angle $C^1C^2C^3$ = angle $C^4C^5C^6 = 130.1°$) [10], is much more likely to be the reason for a rehybridization at C^2, and thus for the small coupling constant $^1J(^{13}CH^2)$ [11,24]. This is strongly supported by the coupling in 1-phenylcyclohexenylpotassium (**3**) and 1,3-diphenylcyclopentenyllithium (**4**) in which the allyl systems are constrained in a 6- and 5-membered ring, respectively (Table 1, entries 15 and 17).



3 $^1J_{^{13}CH^2} = 140.0$ Hz



4 $^1J_{^{13}CH^2} = 144.8$ Hz

$\alpha_{MNDO} = 114.4°$

The ^{13}CH coupling of the central hydrogen H^2 increases to 140.0 Hz in the case of **3**. The 1,3-diphenylallyllithium system, forced into a 5-membered ring (**4**), results in an even higher coupling constant: 144.8 Hz (a MNDO calculation leads to α 114.4° for the CCC angle at the "central" carbon atom C^2).

Whether the central hydrogen is also somewhat bent out of the plane of the allyl carbon atoms, thus contributing to the small coupling constant $^{13}CH^2$, cannot be decided.

Interestingly, without considering charge effects [19, 28], and assuming a planar configuration at the central carbon C^2, the coupling constant $^1J(^{13}CH^2)$ 133 Hz leads to a CCC bond angle at C^2 in allyl "anions" of 125–126° [29] in (accidentally?) excellent agreement with calculations [4,5] and experiment [23].

Experimental

All reactions were performed under an inert atmosphere. The ^{13}CH NMR spectra were recorded on a Varian XL 100 FT or Bruker WH 400 FT machine, and the UV spectra on a Beckmann Acta III.

(1) Preparation of the solutions for ^{13}C NMR spectroscopy

(a) 1-Phenylallyllithium/THF-d_8. 0.19 g (1.60 mmol) 3-phenylpropene were dissolved in 1.0 ml THF-d_8 and metallated with 1.1 mol equiv. t-butyllithium at −20°C. The reaction was finished after 2 h and the solution transferred into an NMR tube.

(b) 1-Phenylallyllithium/THF-d_8/HMPT. HMPT was present in the THF-d_8 solution before the t-butyllithium was added; otherwise the details are as for reaction a.

(c) 1-Phenylallylpotassium. 48 mg (0.44 mmol) potassium t-butoxide and 47 mg (0.40 mmol) 3-phenylpropene were dissolved in 0.5 ml THF-d_8 in an NMR tube. Addition of 1.1 mol equiv. t-butyllithium led, after 1 h at -20°C, to the product.

(d) 1-Phenylcyclohexenylpotassium. 0.97 g (8.25 mmol) potassium t-butoxide and 1.19 g (7.50 mmol) 1-phenylcyclohexene in 20 ml petrol ether (50–70°C) were reacted with 1.1 mol equiv. t-butyllithium at 0°C. After 4 h the solid potassium salt was separated from the solvent and dissolved in THF-d_8 (4.5 ml) at -20°C. (If the deprotonation is performed in THF-d_8 the potassium salt is formed only in 70–80% yield.)

(e) 1,3-Diphenylcyclopentenyllithium. The lithium compound was prepared from 1,3-diphenylcyclopentene in the same way as in reaction a, n-butyllithium being used instead of t-butyllithium. ^{1}H NMR in THF-d_8, δ (ppm): 6.88 (s, 1H, H^2), 6.31–6.64 (m, 8H, $H^m + H^o$), 5.75 (t, 1H, H^p), 2.40 (s, 4H, $H^4 + H^5$).

At higher concentrations than mentioned in a–e the alkali metal compounds precipitated or separated into two phases.

(2) Preparation of the solutions for UV spectroscopy

The compounds were prepared as shown under 1 and then solvent was added to yield ca. 10^{-2} *M* solutions. The measurements were performed by means of a variable temperature cell. The temperature of the solutions was determined by means of a thermoelement.

Acknowledgements

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20 Phenylallylpotassium was first measured by D.H. O'Brien P.R. Russel and A.J. Hart, J. Am. Chem. Soc., 97 (1975) 4410. Their results agree with ours except for the values of C^1 and C^3. We have assigned C^1 and C^3 by means of an off-resonance experiment; compare D.H. O'Brien, in E. Buncel and T. Durst, Comprehensive Carbanion Chemistry, Part A, Elsevier, Amsterdam, 1980, p. 277.

21 The dihedral angle between the plane of the allyl carbon atoms C^1–C^3 and the plane through the phenyl carbon atoms is 50°; the bending of the allyl hydrogen atoms is similar to the bending of the hydrogen atoms in allyllithium [5].

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24 Nice examples of the dependence of the coupling constant $^1J(^{13}CH)$ on the corresponding CCC bond angle are provided by a series of benzo[1,2:4,5]dicycloalkanes [25] and by biphenylene (angle α 115.2° corresponds to $^1J(^{13}CH)$ 163.3 Hz; angle β 122.2° corresponds to $^1J(^{13}CH)$ 159.8 Hz) [26,27].

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Note added in proof. In $IrClH[\eta^3\text{-}C_3H_4(1\text{-}C_6H_5)][P(C_6H_5)_3]_2$ (T.H. Tulip and J.A. Ibers, J. Am. Chem. Soc., 101 (1979) 4201) and $\eta^3\text{-}C_3H_5V(CO)_3(Ph_2PCH_2CH_2PPh_2)$ (U. Franke and E. Weiss, J. Organomet. Chem., 139 (1977) 305) the positions of the hydrogens is also similar to that in **1b**.