

The enigmatic $^1J(\text{CH})$ coupling constants of allyl-type organometallic compounds

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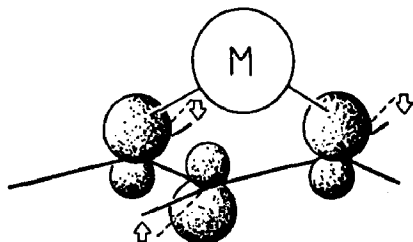
(Received November 13th, 1989)

Abstract

A new attempt has been made to identify the factors responsible for the abnormally small one-bond C, H coupling constants observed for allyl, pentadienyl and heptatrienylmetal compounds. In-plane deformations (widening of the central CCC angle) should have only a small, if not negligible effect. The out-of-plane bending of hydrogen atoms appears to contribute significantly, as probably also does accumulation or polarization of electron density in conjugated structures.

Introduction

A careful NMR investigation led us to assign bridged structures to allyl type organoalkali compounds whereas for the corresponding magnesium derivatives a monohapto σ -bond was favoured [1,2]. In the course of our studies we were puzzled by the observation of uncommonly small coupling constants for all C–H bonds in the allyl moiety. This issue had never been explicitly addressed before, and rather tentatively (the title of the communication ended with a question mark) we suggested that this unexpected behavior might reflect an out-of-plane distortion of the delocalized system. If the hydrogen atom at the nodal position bent over towards the metal in the centre while its two neighbours in the *endo* positions moved in the opposite direction, a better charge distribution and hence an improved binding should result [3].



This idea was challenged by Ahlbrecht et al. [4] as being incompatible with theoretical and experimental evidence. Moreover, those authors were impressed by finding almost identical coupling constants for the contact pair and the ion pair of

Table 1

Fraction of *s*-character in the hydrogen binding carbon orbital: allylpotassium (**1**, M = K) [3] and, in parentheses, allyllithium (**1**, M = Li) [11], *endo*-butenylpotassium (*endo*-**2**, M = K) [3], *exo*-butenylpotassium (*exo*-**2**, M = K) [3], 3-methylbutenylpotassium ("prenyl potassium", **3**, M = K) [1,12], 5-*t*-butyl-2-cyclohexenylpotassium (**4**, M = K) [12], "*U*"-2,4-pentadienylpotassium (*U*-**5**, M = K) [3], "*W*"-2,4-pentadienyllithium (*W*-**5**, M = Li) [3], *exo*-1-phenylallylpotassium (*exo*-**6**, M = K) [4], 1-phenyl-2-cyclohexenylpotassium (**7**, M = K) [4], *exo,exo*-2,4,6-heptatrienylpotassium (*exo,exo*-**8**, M = K) [12], *exo,exo*-1,3-diphenylallyllithium (*exo,exo*-**9**, M = Li) [4], 1,3-diphenyl-2-cyclopentenyllithium (**10**, M = Li) [4], *endo*-1-triphenylphosphonio-2-methyl-2-propenide (*endo*-**11**) [6,12] and *exo*-1-triphenylphosphonio-2-propenide (*exo*-**12**) [6,12]. The numbers shown were obtained by dividing the respective one-bond $^{13}\text{C}^1\text{H}$ coupling constants (Hz) by 500 (see text). The dots in the formule mark the centres of excess electron density.

<p>exo-2</p>	<p>U-5</p>		
<p>endo-2</p>	<p>W-5</p>	<p>exo,exo-8</p>	<p>endo-11</p>
<p>1</p>	<p>exo-6</p>	<p>exo,exo-9</p>	<p>exo-12</p>
<p>3</p>	<p>10</p>		
<p>4</p>	<p>7</p>		

Table 2

s-Characters of hydrogen bearing carbon orbitals as a function of the type of delocalization (numbers given are averaged over the most typical model compounds 1–6, 8–9 and 11–12, see Table 1)

Position	Allyl type	Pentadienyl type ^a	Heptatrienyl type ^b	Ylid type
<i>exo</i>	0.31	0.31	0.31	0.31
<i>endo</i>	0.28–0.29	0.29	0.29–0.30	0.30–0.32
nodal	0.26–0.27	0.27	0.27	0.29

^a Or phenylallyl type. ^b Or 1,3-diphenylallyl type.

1-phenylallyllithium [5*]**. This coincidence seems to argue against out-of-plane deformations as the origin of exceptionally small coupling constants if the plausible though unproven assumption is made that ion pairs have a perfectly planar delocalized skeleton. We wanted to eliminate metal effects even more rigorously by extending our study to allyl type phosphorus ylids. Since they do not show extensive charge delocalization they offer the advantage of well defined geometry and electron distribution [6].

We wish to compare now the spectral properties of these and a few more model compounds with those of the previously described species [1–4] (see Table 1). All chemical shifts and coupling constants are listed in the Experimental section (Table 3 and 4). In the compilation in Table 1 we specify the fraction of *s*-character in the corresponding carbon hybrid orbital of the C–H bonds. It has been suggested that there is a linear relationship between this parameter and the coupling constant [9], and according to a rule-of-thumb [10], the *s*-coefficient is equal to the ¹*J*(CH) value (in Hz) divided by 500. On this basis, C, H coupling constants of ca. 125, 167 and 250 Hz are predicted for aliphatic, olefins (or aromatic), and acetylenic carbon nuclei, in agreement with their approximate respective *s*^{0.25}*p*^{0.75}, *s*^{0.33}*p*^{0.67} and *s*^{0.50}*p*^{0.50} hybridizations. We refer to *s*-coefficients rather than to the coupling constants themselves for merely didactic reasons. The choice of a reduced scale is advisable when one wishes to focus on significantly large effects (in the given case, ≥ 5Hz) to the exclusion of minor perturbations.

Obviously the *s*-character of *exo*-oriented bonds is insensitive to structure. In all cases it is ca. 0.31 (see Table 2). In contrast, the *s*-character of the other bonds shows a clear trend, the value increases the more stable (i.e., the less basic) is the organometallic species. Up on going from allyl through pentadienyl- (or phenylallyl-) and heptatrienyl- (or 1,3-diphenylallyl-) type alkali metal compounds to allyl-type phosphorus ylids (i.e., from left to right in Table 1), the *s*-coefficients increase steadily from 0.28 to 0.31 at the *endo* positions and from 0.26 to 0.29 at the nodal points (see Table 2). We consider below with which structural changes these variations can be most convincingly correlated.

* Reference number with asterisk indicates a note in the list of references.

** Once again [7,8] we emphasize that “solvent separated ion pair” is a pleonasm while “contact ion pair” is a contradictio in adjecto. Avoiding misnomers may help to avoid misconceptions.

Angle widening

Having rejected the out-of-plane bending as a major contributor to the CH coupling anomalies, Ahlbrecht et al. [4] attribute the phenomenon to the well documented widening of the central CCC angle in electron-rich allyl compounds. They take as evidence the increased *s*-coefficients of 1-phenyl-2-cyclohexenyl potassium (7, 0.28 *s*) especially 1,3-diphenyl-2-cyclopentenyllithium (**10**, 0.29 *s*). But are these examples really conclusive? The allyl CCC angle in the five-membered ring species **10** can hardly exceed 120° (leaving on average no more than 105° for each of the other CCC angles). How much must the allyl moiety be still compressed and its CCC angle shortened to produce a “normal” *s*-coefficient of, say, 0.31 or 0.32?

The six-membered ring species provides a less biased case, since it can readily accommodate a 120° allyl angle but must be reluctant to increase it beyond 125°, while quantum chemical calculations indicate CCC angles of 126, 128 and 132° respectively, for allyllithium, allylsodium, and the free allyl anion [13]. We thus prepared 5-*t*-butyl-2-cyclohexenylpotassium (**4**) and characterized it by trapping it with a variety of electrophiles. The *s*-coefficients derived from its CH coupling constants were found to deviate only slightly from those for acyclic allylpotassium compounds, and were practically indistinguishable from those for *endo,endo*-2-cyclododecenylpotassium [14].

If CCC angles for a family of compounds are plotted against 1J values at the central carbon atom, a parabolic curve rather than a straight line results [15]. Ring strain does have an effect, beginning with the five- and steeply increasing towards the four- and three-membered rings (e.g., cyclooctene and cycloheptene 156, cyclohexene 158, cyclopentene 162, cyclobutene 169, and cyclopropene 228 Hz at the olefinic positions [9]). In contrast angle widening in saturated [15] or unsaturated [16*] hydrocarbons hardly affects the CH coupling constants. We suspect that this also holds for organometallic derivatives.

Out-of-plane deformation

Recently unequivocal evidence for the out-of-plane bending of hydrogen atoms has been provided by a low temperature X-ray crystallographic study of the first monomeric, and hence unperturbed, allyllithium complex [17]. Thus from now on the only question is whether one-bond CH coupling constants for allyl-type organometallic compounds reflect this structural deformation and, if so, to what extent.

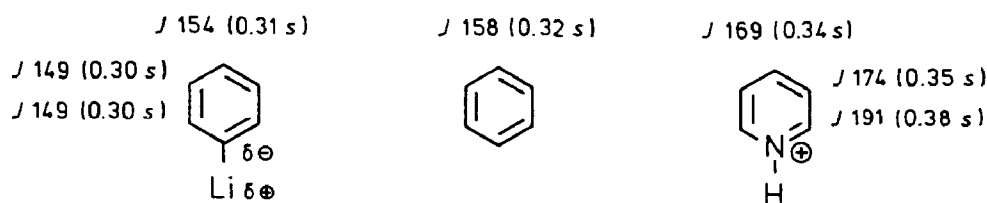
We believe that they do, at least qualitatively. We continue to associate the observed spectral peculiarities with metal-mediated out-of-plane bending of hydrogen atoms. This view is supported by the absence of such anomalies when the alkali metal to which the allyl group is attached is replaced by a triphenylphosphonio group, which acts as a built-in counter-ion (see model compounds **11** and **12**).

On the other hand, if the $^1J(\text{CH})$ values were exclusively dependent on out-of-plane geometries, the hydrogen at the inner, nodal position would have to lie much further from the plane than the *endo*-hydrogens, and these again much further than the *exo*-hydrogen atoms. This does not tally with the facts, as Ahlbrecht et al. [4] have correctly pointed out. The average out-of-plane bending in the slightly asymmetric allyllithium pentamethyldiethylenetriamine complex [17] is 6° (in the direc-

tion of the metal) at the inner and 7 and 12° at the outer *exo*- and *endo*-positions (with all the terminal hydrogen atoms moved away, from the metal). Thus, there must be at least one additional factor that contributes to the smallness of the coupling constants.

Other factors?

Further discussion must at present be speculative. We wonder, however, whether the accumulation of an electron excess does not cause a modulation of the transmission of spin-spin interactions. Such a phenomenon need not be restricted to allyl-, pentadienyl- and heptatrienyl-metal compounds with alternating crests and nodes of electron density, but could also operate in aromatic systems. The CH coupling constants for (undoubtedly planar) phenyllithium [18] are in fact substantially smaller than those for benzene, and on the other hand those for the pyridinium ion [19] are larger than those for benzene:



We conclude that the postulated linear correlation between one-band CH coupling constants and hybridization is an oversimplification, while acknowledging once again the difficulty of defining degrees of hybridization unambiguously [20*].

Experimental part

1. Generalities

Starting materials were purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details of the preparations are given. All commercial reagents were used without further purification. Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes and were protected by and handled under 99.995% pure nitrogen. Etheral extracts were dried over sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids, a little hydroquinone or potassium carbonate was added, as appropriate.

The temperature of dry ice-methanol baths is given as -75°C , and room temperature (22 – 26°C) as 25°C . If reduced pressure is not specified, boiling ranges were determined at atmospheric pressure (720 ± 25 mmHg). In the case of reaction products that were not isolated, yields were determined by gas chromatography by comparison of their peak areas with that for an internal standard after appropriate calibration. The purity of distilled compounds was checked by chromatography on at least two columns filled with stationary phases of different polarity. Chromosorb G-AW of 80–100 and, 60–80 mesh particle size was used respectively, as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). Packed columns

Table 3

¹³C-Chemical shifts δ [ppm] of resonance stabilized, organometallic or carbanionic species **1–12** in tetrahydrofuran solution.

Compound ^a	M	Lit. ref.	$\delta(C^7)$	$\delta(C^6)$	$\delta(C^5)$	$\delta(C^4)$	$\delta(C^3)$	$\delta(C^2)$	$\delta(C^1)$
1	K	1	–	–	–	–	53	144	53
1	Li	1	–	–	–	–	51	147	51
<i>endo-2</i>	K	1	–	–	–	–	63	139	45
<i>exo-2</i>	K	1	–	–	–	–	64	142	43
3	K	1	–	–	–	–	69	136	39
4	K ^b	12	–	–	–	–	59	134	59
<i>U-5</i>	K	3	–	–	79	138	80	138	79
<i>W-5</i>	Li	3	–	–	66	144	87	144	66
<i>exo-6</i>	Li ^c	4	–	–	–	–	73	136	83
<i>exo-6</i>	Li	4	–	–	–	–	66	138	77
<i>exo-6</i>	K	4	–	–	–	–	73	136	80
7	K	4	–	–	–	–	93	128	81
<i>exo,exo-8</i>	K	12	81	143	91	142	91	143	81
<i>exo,exo-9</i>	Li ^d	4, 21	–	–	–	–	^e	^e	^e
10	Li	4	–	–	–	–	105	128	105
<i>endo-11</i>	–	6, 12	–	–	–	–	89	146	28
<i>exo-12</i>	–	6, 12	–	–	–	–	90	138	28

^a Contact pairs unless otherwise specified. ^b Exact data: δ 58.7 (*J* 154.4), δ 133.7 (*J* 134.6). ^c Ion pair after addition of hexamethylphosphorus triamide (HMPT). ^d Ion pair in neat tetrahydrofuran. ^e Not reported.

were made of glass, but coated SCOT-type capillary columns (≥ 10 m long) were of quartz. The stationary phases were SE-30 (silicone rubber), C-20M (polyethylene glycol of average molecular weight 20000) and Ap-L (Apiezon L hydrocarbon) type.

The ¹H NMR spectra were recorded at 360 MHz unless otherwise stated. Chemical shifts are relative to tetramethylsilane (δ 0 ppm). The chemical shifts of silylated compounds were determined relative to the residual solvent peak (CD₅H: δ 7.16 ppm, CHCl₃: δ 7.27 ppm). Coupling constants (*J*) are given in Hz. Abbreviations used for resonance patterns are: s, singlet; d, doublet; t, triplet; q, quadruplet; td, triplet of a doublet; m, multiplet.

Elementary analyses were performed in the laboratory of I. Beetz, D-8640 Kronach.

2. Spectroscopy

Samples were prepared and spectra recorded as described previously [2]. The data are listed in Tables 3 and 4.

3. 5-*t*-Butyl-2-cyclohexenylpotassium and derivatives thereof

(a) *4-t*-Butyl-1-cyclohexene. *p*-Toluenesulfonyl chloride (40 g, 0.21 mol) was added during 30 min to a solution of 4-*t*-butyl-1-cyclohexanol (commercial *cis/trans* mixture, 0.31 g, 0.20 mmol) in pyridine (200 ml) cooled in an ice bath. After 2 h stirring at 25 °C the mixture was added to water (0.5 l) and extracted with ether (5 \times 0.1 l). The combined organic layers were washed with 2 *N* hydrochloric acid (3 \times 0.1 l) and a 10% aqueous solution (2 \times 0.1 l) of cupric sulfate then dried. Evaporation of the solvent gave 50 g (81% of crude 4-*t*-butylcyclohexyl-*p*-toluene-

Table 4

 $J(\text{CH})$ coupling constants (Hz) of resonance stabilized, organometallic or carbanionic species 1–12 in tetrahydrofuran solution

Compound ^a	M	lit. ref.	$J(\text{C}^5\text{H}^{\text{exo}})$	$J(\text{C}^5\text{H}^{\text{endo}})$	$J(\text{C}^4\text{H})$	$J(\text{C}^3\text{H})$	$J(\text{C}^2\text{H})$	$J(\text{C}^1\text{H}^{\text{endo}})$	$J(\text{C}^1\text{H}^{\text{exo}})$
1	K	1	—	—	—	—	132	143	155
1	Li	11	—	—	—	—	132	141	150
<i>endo</i> -2	K	3	—	—	—	159 ^b	134	145	153
<i>exo</i> -2	K	3	—	—	—	142 ^c	128	142	154
3	K	12	—	—	—	—	131	144	153
4	K ^d	12	—	—	—	154 ^{b,d}	135 ^d	—	154 ^d
<i>U</i> -5	K	3	154 ^e	154 ^e	137	156 ^{b,e}	137	154 ^e	154 ^e
<i>W</i> -5	Li	3	154	147	134	142 ^c	134	147	154
<i>exo</i> -6	Li ^f	4	—	—	—	155 ^b	134	145	—
<i>exo</i> -6	Li	4	—	—	—	148 ^c	134	145	—
<i>exo</i> -6	K	4	—	—	—	151 ^b	134	145	—
<i>exo</i> -6	K	4	—	—	—	145 ^c	134	145	—
<i>exo</i> -6	K	4	—	—	—	157 ^b	134	145	—
<i>exo</i> -6	K	4	—	—	—	148 ^c	140	154	—
7	K	4	—	—	—	154 ^b	140	154	—
<i>exo,exo</i> -8	K	4	—	—	134	143 ^b	137	149	156
<i>exo,exo</i> -9	Li ^c	12	—	—	—	146 ^c	133	146	—
10	Li	4	—	—	—	—	145	—	—
<i>endo</i> -11	—	6, 12	—	—	—	157	—	—	155
<i>exo</i> -12	—	6, 12	—	—	—	151	143	158	—
<i>exo</i> -12	—	6, 12	—	—	—	152	143	158	—
<i>exo</i> -12	—	6, 12	—	—	—	151	143	158	—

^a Contact pairs unless otherwise specified. ^b Hydrogen in *exo* position. ^c Hydrogen in *endo* position. ^d Exact data: δ 58.7 (J 154.4), δ 133.7 (J 134.6). ^e Number uncertain due to overlapping of signals. ^f Ion pair after addition of hexamethylphosphorus triamide (HMPT). ^g $\text{C}^5 \equiv \text{C}^3$, $\text{C}^6 \equiv \text{C}^2$, $\text{C}^7 \equiv \text{C}^1$. ^h Ion pair in neat tetrahydrofuran.

sulfonate, m.p. 50–54°C, which was added to a solution of potassium t-butoxide (18 g, 0.16 mol) in dimethyl sulfoxide (0.1 l). The mixture was kept for 90 min to 70°C then added to water (0.5 l). Extraction with hexane (3 × 0.1 l), evaporation of the solvent, and distillation of the residue gave 15.7 g (71%) of a colorless liquid; b.p. 161–163°C; n_D^{20} 1.4616; $^1\text{H NMR}$: 5.66 (2H, m, s-like), 2.1 (3H, m), 1.8 (2H, m), 1.29 (1H, tdd, J 11.3, 6.7, 2.1), 1.16 (1H, tdd, J 11.4, 10.8, 5.8), 0.86 (9H, s).

(b) *(5-t-Butyl-2-cyclohexenyl)trimethylsilane*. 4-t-Butyl-1-cyclohexene [22] (2.8 g, 20 mmol) was added to a suspension of trimethylsilylmethylpotassium (20 mmol) [2,23] in cyclopentane (0.1 l). After 80 h stirring, chlorotrimethylsilane (2.0 ml, 1.7 g, 16 mmol) was added at -75°C . Stirring was continued until the mixture had warmed to 25°C . The solvent was then rapidly evaporated off and the residue purified by bulb-to-bulb distillation to give a colorless liquid; 2.5 g (59%) b.p. 102–108°C/0.1 mmHg. Analysis. Found: C, 73.78; H, 12.17. $\text{C}_{13}\text{H}_{26}\text{Si}$ (210.43) calc.: C, 74.20; H, 12.45%.

Analytical GLC (2 m, 5% C-20 M, 140°C), indicates that the material contained two components in the approximate ratio of 45/55, and there were separated by preparative GLC (3 m, 10% ApL, 180°C): *cis*-Isomer: n_D^{20} 1.4757; $^1\text{H NMR}$: 5.66 (1H, ddt, J 10.0, 5.8, 2.5), 5.61 (1H, d, broad, J 17), 2.05 (1H, dm, J 17), 1.83 (1H, dm, J 14), 1.7 (1H, m), 1.55 (1H, symm. m), 1.29 (1H, tdd, J 11.7, 4.7, 2.2), 1.00 (1H, q, J 12.2), 0.89 (9H, s), 0.01 (9H, s). *trans*-Isomer: n_D^{20} 1.4734; $^1\text{H NMR}$: 5.69 (1H, d, broad, J 10), 5.62 (1H, ddt, J 10.0, 5.0, 2.0), 2.00 (1H, dtq, J 17.0, 5.0, 1.3), 1.89 (1H, d, broad, J 12.8), 1.80 (1H, ddq, J 16.8, 11.1, 6.1), 1.64 (1H, symm. m), 1.46 (1H, ddd, J 19.0, 12.6, 6.2), 1.32 (1H, dddd, J 14.0, 10.8, 5.2, 2.2), 0.87 (9H, s), 0.03 (9H, s).

(c) *2-(5-t-Butyl-2-cyclohexenyl)ethanol*. After metalation (see Section 3(b)) of 4-t-butyl-1-cyclohexene (20 mmol), oxirane (1.2 ml, 1.1 g, 25 mmol) was added at -75°C . The mixture was allowed to warm to 25°C , then added to water (0.1 l), the organic layer was concentrated by evaporation and the product, again a *cis/trans* mixture, isolated by bulb-to-bulb distillation; 2.4 g (65%); b.p. 141–147°C/0.1 mmHg; n_D^{20} 1.4839; $^1\text{H NMR}$: 5.7 (2H, m), 3.75 (1H, td, J 7.2, 1.7), 3.72 (2H, t, J 6.6), 2.36 (0.5H, symm. m), 2.25 (0.5H, symm. m), 2.0 (1H, m), 1.6 (4H, m), 1.47 (1H, s, broad), 1.3 (1H, m), 0.87 (9H, s); Analysis: Found: C, 78.76; H, 11.95. $\text{C}_{12}\text{H}_{22}\text{O}$ (182.31) calcd.: C, 79.06; H, 12.16%.

(d) *5-t-Butyl-2-cyclohexen-1-ol*. After metalation (see Section 3(b)) of 4-t-butyl-1-cyclohexene (20 mmol) the mixture was treated successively with fluorodimethoxyboron diethyl etherate [24] (4.5 ml, 5.0 g, 30 mmol), 35% aqueous hydrogen peroxide (2.5 ml, 3.0 g, 30 mmol) and 3 M solution of sodium hydroxide (10 ml, 12 g, 30 mmol) in water. The product (1.7 g, 55%) was isolated as described in (c) above.

(e) *5-t-Butyl-2-cyclohexen-1-one*. Manganese dioxide (20 g) was added to the solution of 5-t-butyl-2-cyclohexene-1-ol (*cis/trans* mixture, 1.5 g, 10 mmol) in pentane (50 ml) and the suspension stirred 15 h at 25°C . After filtration and evaporation of the solvent the pure product (0.8 g, 53%) was obtained by bulb-to-bulb distillation; b.p. 122–126°C/0.1 mmHg; n_D^{20} 1.4806; IR (film; in cm^{-1}): 3050 (w, $\nu(\text{C-H})$), 2970 (s, $\nu(\text{C-H})$), 2890 (m, $\nu(\text{C-H})$), 1690 (s, $\nu(\text{C=O})$); $^1\text{H NMR}$ (80 MHz): 7.12 (1H, ddd, J 10, 6, 3), 6.12 (1H, d, J 10), 2.3 (5H, m, broad), 0.92 (9H, s); Analysis: Found: C, 76.68; H, 10.70. $\text{C}_{10}\text{H}_{16}\text{O}$ (152.24) calc.: C, 78.90; H, 10.59%.

Acknowledgment

The authors are indebted to the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung (grants no 2.885-0.80 and 2.635-0.82) for financial support.

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