

Lithium 2-Lithio-1,1,3,3-tetraphenylpropenide¹

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The novel lithium 2-lithio-1,1,3,3-tetraphenylpropenide (**2**) is shown *via* ¹H, ¹³C, and ⁷Li n.m.r. spectroscopy and by chemical means to adopt an ionic allyl-lithium structure with C_{2v} symmetry; the second lithium is covalently bonded to the central (C-2) carbon.

The 1,2-addition of alkali metals to activated alkenes is well known.² Tetraphenylallene (**1**)³ is a particularly challenging substrate since its dimetal derivatives are synthetically useful intermediates⁴ and can adopt a variety of structures^{5,6} (linear or bent arrangement of C-1, C-2, C-3; sp- or sp²-hybridization of C-2). We have synthesised lithium 2-lithio-1,1,3,3-tetraphenylpropenide (**2**) and describe its unusual structure and reactivity.

The dilithium derivative of tetraphenylallene was prepared *via* reduction of (**1**) with highly active lithium at low temperatures in tetrahydrofuran (THF)[†] and its structure established from the following: (i) reoxidation with iodine gave the starting material (**1**) whilst protonation with alcohol afforded 1,1,3,3-tetraphenylpropene (**3**); (ii) alkylation of (**2**) with 1,3-dibromopropane, after aqueous work-up, gave (**4**) as the main product; (iii) reduction in liquid ammonia quantita-

tively transformed (**1**) into lithium 1,1,3,3-tetraphenylpropenide (**5**) which was identified by its ¹H and ¹³C n.m.r. spectra.[‡] Compound (**5**) was also accessible *via* deprotonation of (**3**) with *n*-butyl-lithium in tetrahydrofuran.⁷

[‡] ¹³C (75 MHz) and ¹H (300 MHz) N.m.r. spectroscopic data. δ_C (**2**) ([²H₈]THF-[²H₆]Me₂O, 1:2) -105 °C: 117.9 (C-1, C-3), 204.3 (C-2), 147.6, 150.4 (C-4, C-8), 118.4, 126.0, 126.5, 130.1 (C-5, C-5', C-6, C-6'), 116.6 (C-7), 129.4 (C-9), 126.5 (C-10), 119.2 (C-11); δ_H (**2**) ([²H₈]THF-[²H₆]Me₂O, 1:2) -120 °C: 7.24, 7.36 (H-5, H-5'), 6.66, 7.04 (H-6, H-6'), 6.43 (H-7), 6.76 (H-9), 6.43 (H-10), 6.22 (H-11); δ_C (**5**) (NH₃-THF) -60 °C: 105.0 (C-1, C-3), 132.1 (C-2), 143.8, 148.6 (C-4, C-8), 123.1, 126.6 (C-5, C-9), 125.5, 127.5 (C-6, C-10), 116.0, 117.9 (C-7, C-11); δ_H (**5**) ([²H₈]THF) +35 °C: 6.32 (H-2), 6.91 (H-5, H-9), 6.59 (H-6, H-10), 6.29 (H-7, H-11); δ_C (**6**) ([²H₈]THF) -70 °C: 112.3, 110.6, 107.1 (C-1, C-3, C-4), 43.9 (C-5), 76.2, 76.0 (C-6, C-8), 154.5 q, 150.7 q, 150.3 q, 147.5 q, 130.1, 129.4, 127.9, 127.5, 125.8, 125.4, 123.9, 121.9, 116.8, 116.5, 116.1, 111.9; δ_H (**6**) [²H₈]THF +25 °C: 3.10 (H-5), 3.78, 3.88 (H-6, H-8), 6.21 (H-7), 5.89 (H-9), 7.44 d 2H, 7.33 d 3H, 6.98 d 1H, 6.81 m 5H, 6.35 m 4H.

[†] According to the n.m.r. spectra (**2**) is accompanied by small amounts (3%) of (**5**).

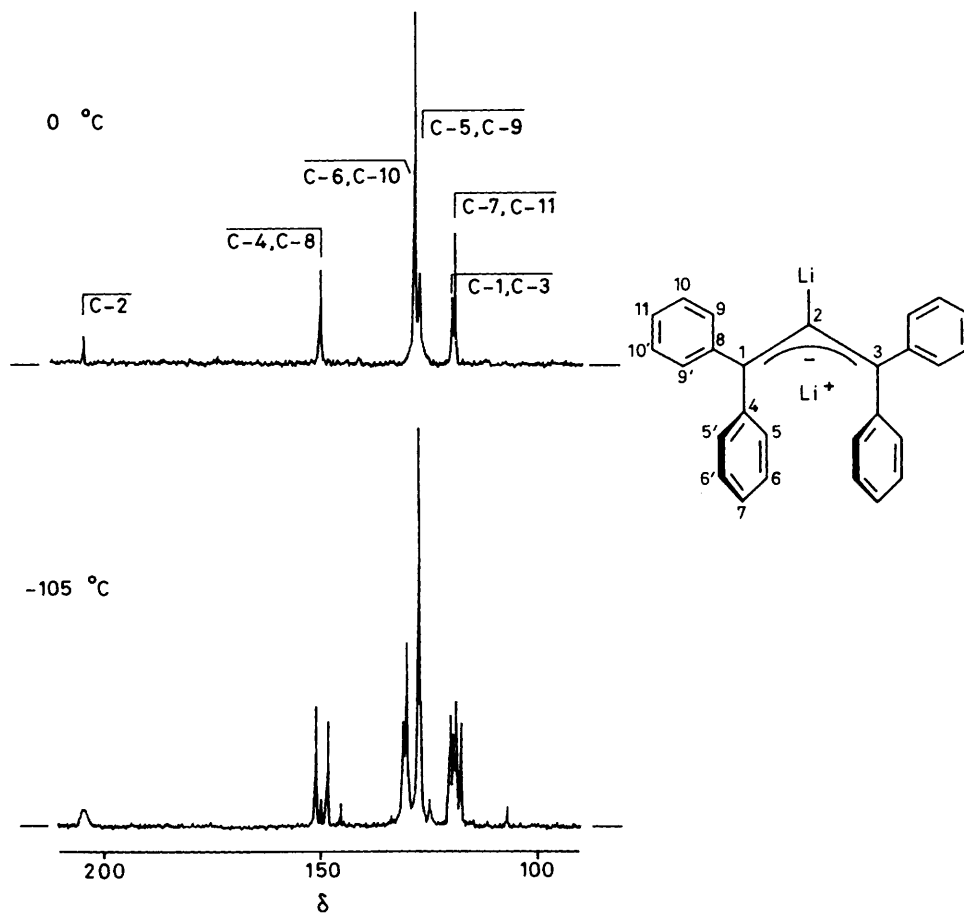
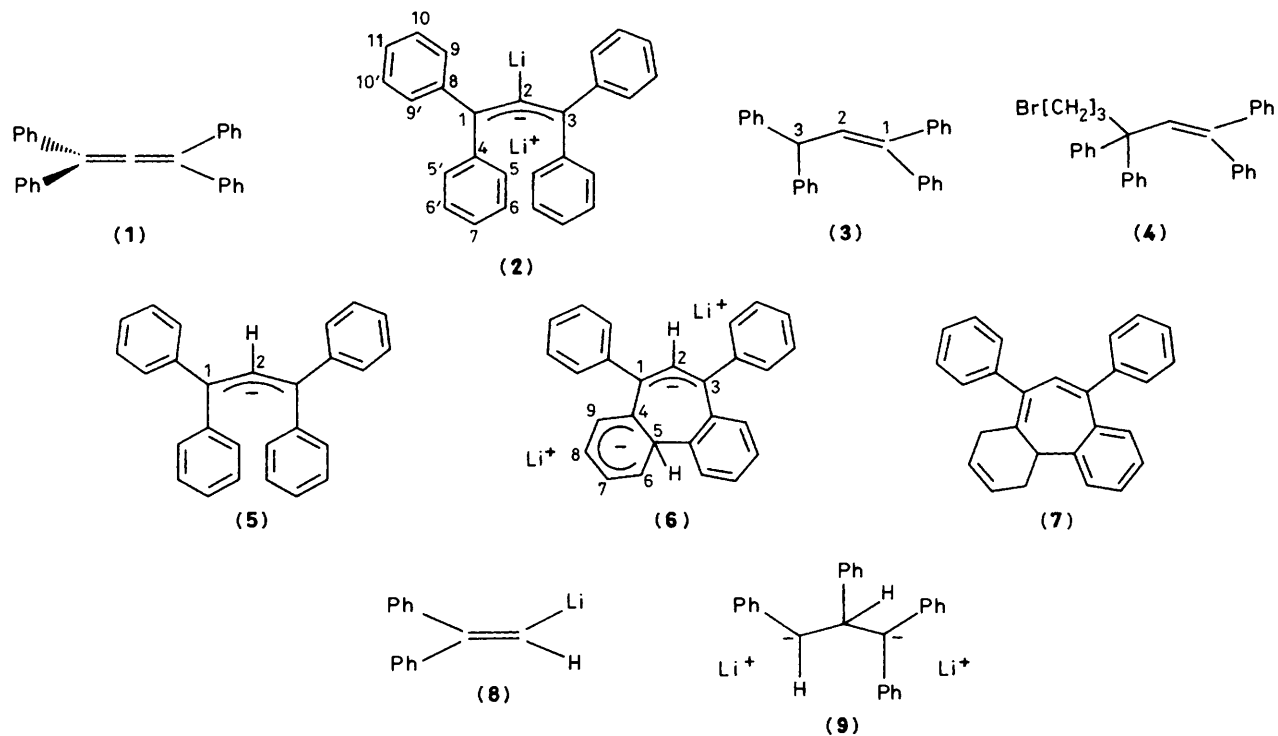


Figure 1. ^{13}C N.m.r. spectra (75 MHz, -105°C : $[\text{}^2\text{H}_8]\text{THF}-[\text{}^2\text{H}_6]\text{Me}_2\text{O}$, 1:2; 0°C : $[\text{}^2\text{H}_8]\text{THF}$) of (2).

Obviously, reduction of (1) in liquid ammonia was accompanied by protonation; (iv) anion (2) rearranged irreversibly into dianion (6) at temperatures above 0°C.‡ Protonation of (6) afforded the dihydroderivative (7).⁸

The n.m.r. spectroscopic description of (2) (see Figure 1)‡ leads us to the following conclusions. (i) Anion (2) is similar to (5) in that it possesses a bent (C_{2v}) structure in which the two *endo*- and *exo*-phenyl groups are pairwise equivalent. (ii) The broad resonance of C-2 (–105°C: $w_{1/2} = 130$ Hz) and the sharp resonance of C-1 (C-3) of the title compound (2) are downfield from those of (5) by 72.2 and 12.9 p.p.m., respectively. There is a coupling between C-2 and a quadrupolar ⁷Li-nucleus due to a covalent bond (see below). In dealing with the absorption of C-2 at such an extremely low field the structurally related 1,1-diphenyl-2-lithioethene (8) was prepared as a model compound by lithiation of the corresponding bromide with *t*-butyl-lithium.⁹ In (8) the metallated carbon atom resonates at δ 193.0, *i.e.* 78.9 p.p.m. downfield from the corresponding hydrocarbon resonance. (iii) The downfield (high field) absorptions of C-2 (C-1, C-3) together with the pronounced shielding of the *para*-carbon atoms of the phenyl groups (C-7, C-11) indicate a π -charge distribution to the non-bonding allyl π -orbital and a significant delocalization of the charge into the phenyl rings.

Thus, the reductive formation of the anion (2) can formally be described as the 1,2-addition of lithium to a C=C-double bond of the allene. One lithium becomes involved in an ionic allyl-lithium structure while the other is part of a strongly polar, covalent C-2–Li bond orthogonal to the π -system. An alternative C_{2v} -type structure with two 'Li-bridges' between C-1 and C-3 above and below the plane through C-1, C-2, C-3⁶ cannot be rigorously excluded, but appears much less likely because of the above spectroscopic findings.

Both (2) and the related anion (5) exhibit remarkable stereodynamic behaviour. It appears from the ¹³C n.m.r. spectra of (2) and (5) at –105°C (two pairs of phenyl groups) that the rotation about the C-1–C-2 (C-2–C-3) bond is slow on the n.m.r. time scale. Moreover, the *ortho*- (*meta*-) carbon atoms of two phenyl rings of (2) are no longer equivalent. This must be due to a slow rotation of these phenyl groups. It is reasonable to identify the two phenyl units as the *endo*- rings whose rotation is inhibited by considerable steric hindrance. The low-temperature spectra provide no evidence for a slow

rotation of the phenyl rings in (5) or for a non-equivalence of the position C-1 and C-3 in (2). The non-equivalence would result from a partial covalent bonding between the metal and one of the terminal carbon centres. The detection of one broad (–105°C: $w_{1/2} = 45$ Hz) ⁷Li signal at δ –0.1 (LiCl–H₂O, ext.) could be due to intra- or inter-molecular exchange effects. It is noteworthy that the ¹³C resonance of C-2 in (2) sharpened upon warming to 0°C.

The ¹³C and ¹H n.m.r. spectra of (2) and (5)⁷ at ambient temperatures [only three ¹H n.m.r. resonances due to the phenyl protons at 0°C (2) and 35°C (5), respectively] indicate the existence of four equivalent phenyl groups. We conclude that both the rotation of the phenyl rings around the C-1–C-4 and C-1–C-8 bonds and the rotation around C-1–C-2 (C-2–C-3) bond (with partial π -bond character) are rapid on the n.m.r. time scale.

In order to obtain another model compound for (2) we treated (3) with lithium at low temperatures. There is no cleavage of the C-3–H bond. However, the initially formed dianion undergoes a 1,2-migration of the phenyl group at C-3 to afford the dianion (9).

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