Covalent Carbon–Lithium Bridged Bonding in a Typical Alkynyl-lithium Compound

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Low temperature carbon-13 n.m.r. spectroscopy of 1-lithio-3,3-dimethylbut-1-yne in tetrahydrofuran solution shows this compound to exist as a nonfluxional cubic tetramer with $J[^{13}C(1), {}^{6}Li]$ 6 Hz; above 190 °C this scalar coupling is averaged by fast inter-aggregate exchange of alkynyl groups and/or lithium atoms at a rate which is fast relative to the n.m.r. time scale.

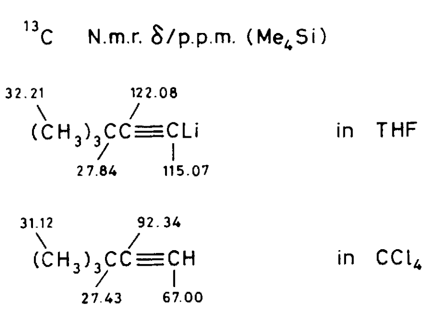
It is commonly claimed that alkynyl-lithium compounds should be regarded as carbanion salts (**1**) because sp hybridization at C(1) stabilizes the carbanion.[1] Streitwieser showed,

$$RC{\equiv}C{:}^{-}\ Li^{+}$$

(**1**)

from *ab initio* MO calculations for monomeric organolithium compounds, low electron density in the region between lithium and the α-carbon with minimum density in alkynyl-lithiums.[2] In a similar fashion Veillard found monomeric lithium acetylide to be ionic.[3]

We have chosen to investigate the structure and dynamic behaviour of 1-lithio-3,3-dimethylbut-1-yne (**2**). This compound is easily purified and since it has no prop-2-ynyl hydrogen atoms the system cannot rearrange to an allene. Compound (**2**) is obtained as a white precipitate by metallation of the corresponding butyne, (**3**), by n-butyl-lithium in



$$(CH_3)_3CC{\equiv}CLi \quad \text{in THF}$$
$$(CH_3)_3CC{\equiv}CH \quad \text{in } CCl_4$$

Figure 1

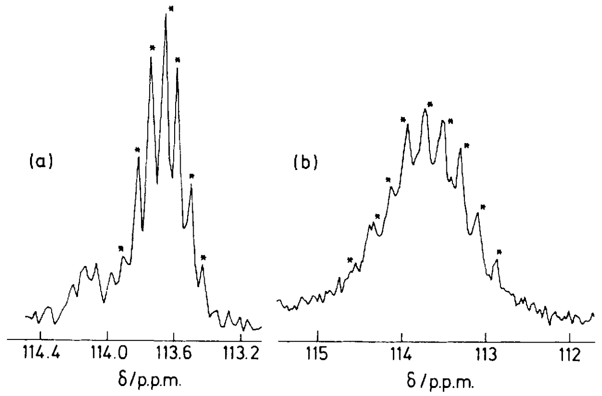


Figure 2. ^{13}C N.m.r. spectra, 75.47 MHz, C(1) of compound (**2**), 1.5 M in THF, 183 K, (a) $(\mathbf{2})^{6}Li$, (b) $(\mathbf{2})^{7}Li$.

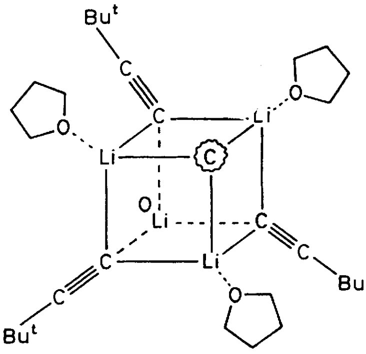


Figure 3. Cubic structure of (**2**) solvated by THF.

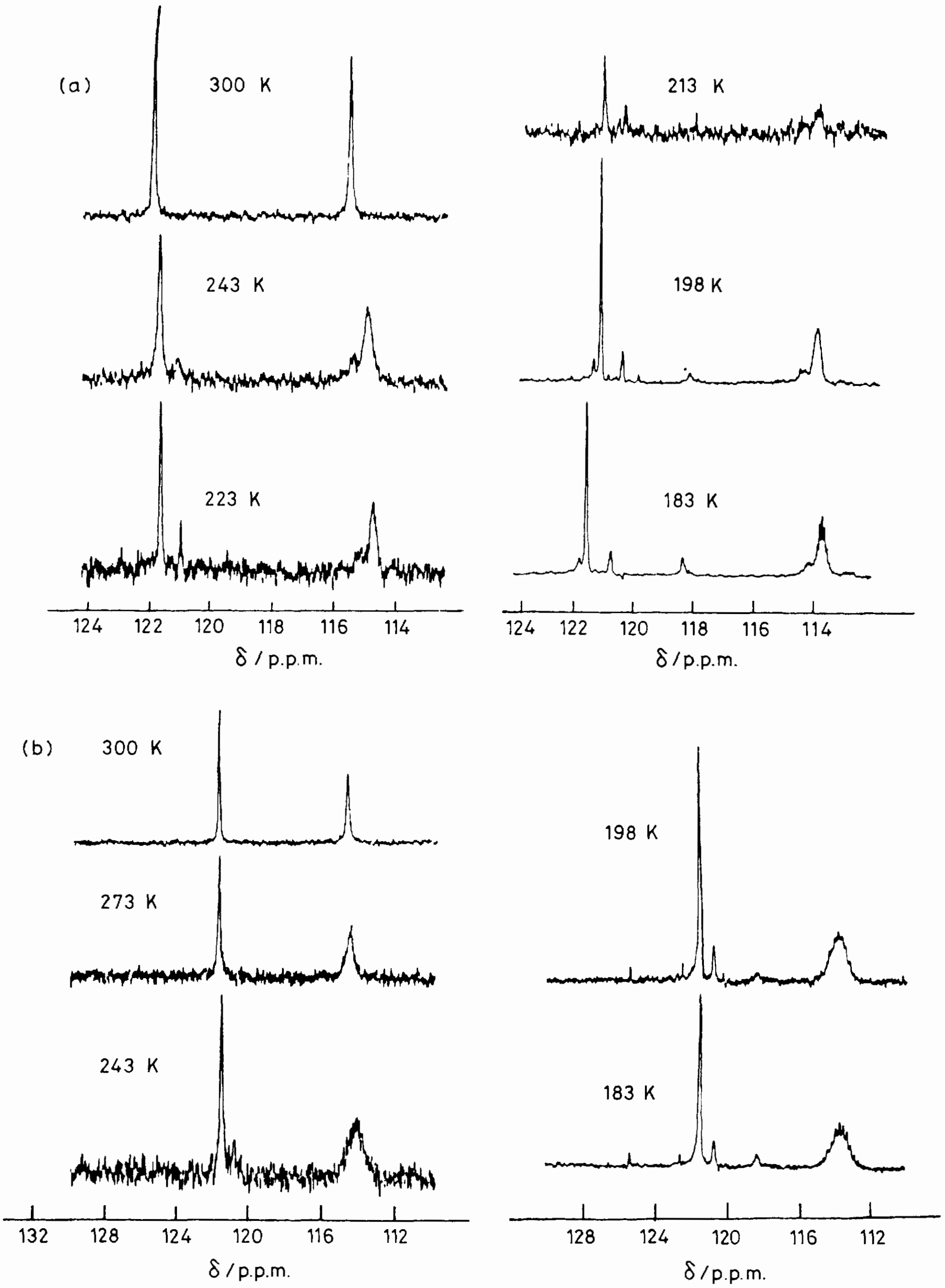


Figure 4. ^{13}C N.m.r. spectra, 75.47 MHz, C(1) and C(2) of (**2**), 1.5 M in THF, at different temperatures, (a) (**2**)^6Li, (b) (**2**)^7Li.

cyclohexane at 0 °C under an argon atmosphere [equation (1)]. The insoluble lithium compound (**2**) was separated by

$$\underset{(\mathbf{3})}{Me_3CC{\equiv}CH} \xrightarrow[Bu^nLi]{\text{Cyclohexane}} \underset{(\mathbf{2})}{Me_3CC{\equiv}CLi} \qquad (1)$$

filtration, washed with pure cyclohexane, dried *in vacuo* and then dissolved in dry tetrahydrofuran (THF).

Carbon-13 chemical shifts for (**2**) and (**3**) are shown around the formulae in Figure 1. Metallation of (**3**) brings about a striking deshielding by 48 p.p.m. at C(1). This is reminiscent of similar deshielding of the *ipso* carbon of phenyl-lithium compared with benzene. The latter effect comes from the mixing of ground with $\sigma_{C-Li} \rightarrow \pi^*$ excited states, resulting in a paramagnetic shift at C(1).[4]

The carbon-13 shifts of (**2**), 1.5 M in THF, change very little with temperature or lithium isotope. However with decreasing temperature the C(1) resonance broadens and by 183 K, in the case of the ^6Li compound, (**2**)^6Li, resolves into seven lines *ca.* 1:3:6:10:6:3:1, implying each ^{13}C is coupled to three equivalent ^6Li atoms with $J[^{13}C(1),^6Li]$ 6 Hz, Figure 2(a). This proposal is confirmed by the ^{13}C n.m.r. fine structure for C(1) of (**2**)^7Li at 183 K also 1.5 M in THF which shows nine of the expected ten lines, for three ^7Li atoms coupled to each C(**2**), with $J(^{13}C,^7Li)$ 16 Hz, Figure 2(b). It is unusual that ^7Li

quadrupole induced relaxation in (**2**)^{7}Li at 183 K is slow enough that the ^{13}C,^{7}Li coupling is not averaged at this temperature.[5] Finally the observed ratio $J[^{13}C(1),^7Li]/J(^{13}C,^6Li)$ of 2.67 is close to that of the ^{7}Li/^{6}Li resonance frequencies, 2.64.

^{6}Li and ^{7}Li N.m.r. spectra of (**2**) in THF consist each of a single narrow line whose shift and width changes little with temperature. This confirms, see above, that lithium quadrupole induced relaxation is not a significant feature of this species.

From the results described above it would appear that in THF (**2**) exists as a non-fluxional solvated cubic tetramer, Figure 3, in which each C(1) is strongly coupled to the three nearest lithium atoms and weakly ($\leqslant$0.5 Hz) to the fourth.

The cubic tetramer structure as detected by crystallography, and i.r. and n.m.r. spectroscopy is common but not exclusive to ether complexes of many organolithium compounds varying from alkyl-lithium compounds[6] to a lithium enolate salt.[7] The directly bonded lithium–carbon coupling constants for all these compounds are very similar, 6—9 Hz for $J(^{13}C,^6Li)$. This could imply similar carbon–lithium bonding throughout.

With increasing temperature above 190 K, the C(1),Li coupling is progressively averaged owing to exchange of alkynyl groups and/or lithium atoms from one aggregate to another at rates which lie on the n.m.r. time scale, Figure 4. The mechanism of this exchange process is under investigation, using the techniques of n.m.r. line-shape analysis.[8]

Interestingly, as recently described, 1-lithio-oct-1-yne in THF does not exhibit directly bonded ^{13}C(1),^{6}Li coupling, down to −126 K.[9] It may be that fast ^{6}Li relaxation at the lower temperatures averages out the coupling.[10]

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