

were first obtained by treating  $W(CO)_6$  with lithium alkyls<sup>6</sup>. The extension of reactions (1) and (2) initially using carbon monoxide, phosphines and amines, to other nucleophiles of completely different nature substantiates the generality of these reactions. The kinetic study of these new reactions should lead to a better understanding of the general problem of the carbon monoxide insertion reactions.

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- 1 F. CALDERAZZO AND F. A. COTTON, *Inorg. Chem.*, 1 (1962) 30.
- 2 F. CALDERAZZO AND F. A. COTTON, *Chim. Ind. (Milan)*, 46 (1964) 1165.
- 3 R. J. MAWBY, F. BASOLO AND R. PEARSON, *J. Am. Chem. Soc.*, 86 (1964) 3994.
- 4 F. CALDERAZZO AND K. NOACK, to be reported later.
- 5 F. CALDERAZZO AND K. NOACK, unpublished results.
- 6 E. O. FISCHER AND A. MAASBÖL, *Angew. Chem.*, 76 (1964) 645.

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### The ${}^7\text{Li}$ nuclear quadrupole coupling constants of methyl- and ethyllithium

The structures of crystalline ethyllithium<sup>1</sup> and methylithium<sup>2</sup> determined by X-ray crystallography show that the molecule is a tetramer in which, for the methyl compound, the lithium atoms lie at the apices of a regular tetrahedron and the four carbon atoms lie vertically above the center of each face. The structure of the ethyl compound is a distorted version of this in which one of the lithium-carbon distances is much longer than the other two while one of the lithium-lithium distances is much shorter.

In hydrocarbon solvents alkylolithiums are also associated, usually to tetramers and hexamers<sup>3</sup>. These molecules are thus electron-deficient and the electron distribution in them is of interest. In the hope that their  ${}^7\text{Li}$  nuclear quadrupole coupling constants would be relevant to this problem the  ${}^7\text{Li}$  nuclear magnetic resonance spectra of polycrystalline samples of these compounds have been measured and the results are reported here. The nuclear magnetic resonance spectrum of a polycrystalline sample of a compound in which the nucleus under study has a quadrupole coupling constant,  $eQq$ , is a central line flanked symmetrically by either two satellites whose separation in cycles/sec is approximately given by  $\frac{1}{2}eQq$  when the field gradient at the nucleus has cylindrical symmetry or, when the field gradient has an asymmetry parameter  $\eta$ , by two pairs of satellites separated by  $\frac{1}{2}eQq(1-\eta)$  and  $\frac{1}{2}eQq(1+\eta)$  (ref. 4). The  ${}^7\text{Li}$  nuclear magnetic resonance spectra of methyl- and ethyllithium at 14.7 kilogauss and 25° are shown in Figs. 1 (a) and (b) respectively.

The crystal structure of methylithium shows that there is only one kind of lithium atom in the crystal and that the field gradient tensor is necessarily cylindrically symmetric. Its spectrum shows no visible structure so that either the coupling

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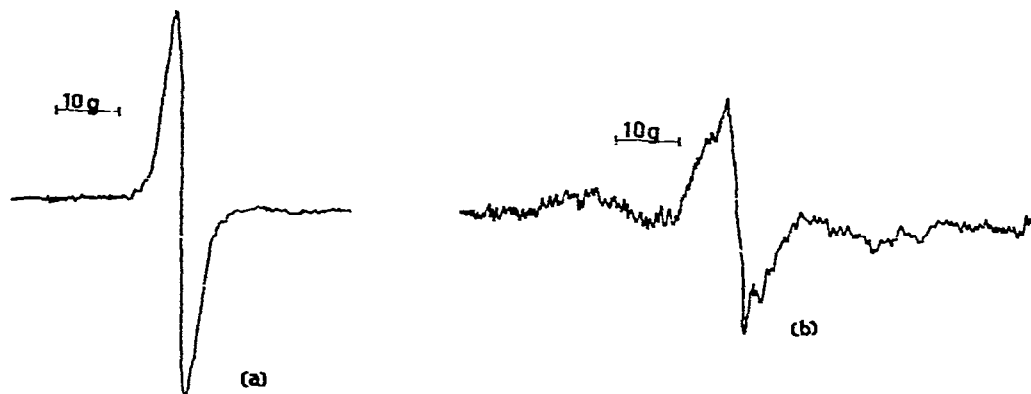


Fig. 1. The  ${}^7\text{Li}$  NMR spectrum at 14.7 kG and  $25^\circ$  of: (a), methyl lithium; (b), ethyl lithium.

constant is small and the satellites are hidden by the dipolar broadening or the coupling constant is very large and the satellites are too broad to be detectable. In this latter case, however, second-order quadrupole broadening of the central line should become significant and, as shown by Casabella<sup>5</sup>, its breadth should be dependent on the frequency at which the nuclear magnetic resonance spectrum is observed. However, both the peak to peak separation and the second moment of the methyl lithium spectrum remained constant within experimental error at  $(6.8 \pm 0.1 \text{ gauss})$  and  $(9.8 \pm 0.1 \text{ gauss}^2)$  respectively when measured at frequencies of 24.3, 16.0, 8.0 and 4.0 Megacycles/sec. It is estimated that on the one hand a coupling constant of 200 kc/s would have produced a detectable broadening of the line at 4.0 Mc/s and that on the other the first order satellites due to a coupling constant of less than 200 kc/s would have been readily visible. It is concluded that the coupling constant of methyl lithium is small. This conclusion is supported by the relative intensities of the nuclear magnetic resonance signals from methyl lithium and ethyl lithium, the peak height from methyl lithium under conditions in which saturation phenomena were having no effect on the spectra of either of the compounds being some 3-4 times greater than that from ethyl lithium under the same conditions.

In order to obtain an upper limit for the value of the coupling constant it is desirable to know the width the spectrum would have if magnetic dipole interactions were the only source of broadening. From the published interatomic distances the second moment has been calculated from the Van Vleck formula<sup>6</sup> as  $7.78 \pm 0.8 \text{ gauss}^2$ . In making this calculation account was taken of the fact that the methyl group is freely rotating at room temperature<sup>7</sup>. First-order quadrupole splitting increases the second moment of the satellites for a nucleus with spin  $\frac{3}{2}$  in a powder spectrum by  $0.05(eQq/g_N\beta_N)^2$ , where  $g_N$  is the nuclear  $g$  factor and  $\beta_N$  is the nuclear magneton, and since these represent 0.6 of the total intensity the contribution of quadrupole broadening to the total spectrum is  $0.03(eQq/g_N\beta_N)^2$ . If the maximum contribution that quadrupole broadening can have in this case is taken as  $3 \text{ gauss}^2$  then the upper limit for  $eQq$  is 16 kilocycles/sec.

The crystal structure of ethyl lithium shows that there is only one kind of environment for the lithium atoms in the crystal. The four satellites observed here are therefore due to an asymmetric field gradient. The separation of the inner pair is  $18 \pm 1 \text{ kc/s}$  and the outer pair  $80 \pm 1 \text{ kc/s}$  thus yielding  $98 \pm 2 \text{ kc/s}$  and 0.62 for the

coupling constant and asymmetry parameter respectively. The value for the coupling constant is much smaller than that (570 kc/s) estimated by Brown and Ladd for the quadrupole coupling constant of the  ${}^7\text{Li}$  nucleus in a toluene solution of ethyllithium<sup>8</sup>. The relatively large values of the coupling constant and asymmetry parameter for ethyllithium show that the small coupling constant for methyllithium is due to the cancelling out of large field gradients of opposite signs. Thus although a qualitative rationalisation of the difference between the two compounds presents no difficulty, a quantitative explanation on the basis of a simple model is not likely to be very successful. This task would be much simplified if the orientation of the field gradient axes in ethyllithium could be determined, however, the problem of growing a large single crystal of this compound is considerable.

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- 1 H. DIETRICH, *Acta Cryst.*, 16 (1963) 681.
- 2 E. WEISS AND E. A. C. LUCKEN, *J. Organometal. Chem.*, 2 (1964) 197.
- 3 T. L. BROWN, D. W. DICKERHOOF AND D. A. BAFUS, *J. Am. Chem. Soc.*, 84 (1962) 1371; R. WEST AND W. H. GLAZE, *J. Am. Chem. Soc.*, 83 (1961) 3580; M. WEINER, G. VOGEL AND R. WEST, *Inorg. Chem.*, 1 (1962) 654.
- 4 M. H. COHEN AND F. REIF, *Solid State Phys.*, 5 (1957) 332.
- 5 P. A. CASABELLA, *J. Chem. Phys.*, 40 (1964) 149.
- 6 J. H. VAN VLECK, *Phys. Rev.*, 74 (1948) 1168.
- 7 E. A. C. LUCKEN, unpublished observations.
- 8 T. L. BROWN AND J. A. LADD, *J. Organometal. Chem.*, 2 (1964) 373.

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## PRELIMINARY NOTES

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### Reactions of acetylenes with noble-metal halides.

#### III\*. Tetra-substituted cyclopentadienonerhodium chlorides

In connection with our interest in the reactions of acetylenes with palladium(II) halides<sup>1</sup>, we have also studied some reactions of acetylenes with a complex of another  $d^8$  ion, rhodium(I) dicarbonyl chloride dimer (I).

Reaction of (I) with a large excess of diphenylacetylene (II, R = C<sub>6</sub>H<sub>5</sub>) in refluxing benzene gave two soluble products and an insoluble polymer. The soluble materials were separated by chromatography on Florisil to give hexaphenylbenzene (V, R = C<sub>6</sub>H<sub>5</sub>; 9%) and orange-red 2,3,4,5-tetraphenylcyclopentadienonerhodium chloride (tetracyclonerhodium chloride) (III, R = C<sub>6</sub>H<sub>5</sub>) in 47% yield. The insoluble brown polymer, obtained in 12% yield, was identified by analysis and infra-red

\* Parts I and II of this series are entitled "Reactions of Palladium Compounds with Acetylenes" and are quoted in ref. 1.