system crossing, following excitation of the first or second singlet levels.

However, energy transfer not involving triplet states cannot be excluded completely under our experimental conditions, and the large discrepancy between the present and previous results may have a deeper reason.

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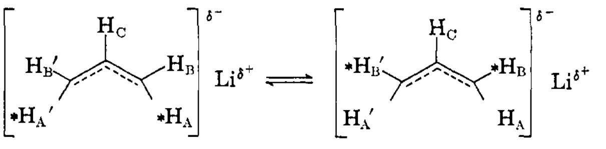
The Ionic Character of Allyllithium

Sir:

We have conducted variable-temperature nmr studies on allyllithium over the temperature range −100 to +60° in the donor solvents diethyl ether and tetrahydrofuran (THF). The data derived from these experiments demonstrate for the first time an AA'BB'C allyl → AB_4 allyl reversible transition in an unsubstituted allylorganometallic compound of a main group element. The nmr spectra of the systems (a) 1.5 *F* allyllithium in THF-d_8 (Figure 1) and (b) 1.5 *F* allyllithium in diethyl-d_{10} ether are very similar. They constitute the first direct evidence for a predominance in solution, at all temperatures studied, of an allyllithium species $[AA'BB'C]^{\delta -}Li^{\delta +}$ in which protons A and B (and at the same time A' and B') are exchanging environments at a temperature-dependent rate. At 37° all four terminal protons are equivalent in the recorded nmr spectrum, whereas at −87° two distinct types of terminal hydrogens are clearly observed.[1-3] These high- and low-temperature spectra are respectively almost pure AB_4 and AA'BB'C in nature. The data reported here are not consistent with the previously published conclusion that allyllithium in diethyl ether,[4] like allyl Grignard reagent,[5] is best described in terms of a rapid dynamic equilibrium between the two possible covalent forms of the compound, $LiC^*H_2CH{=}CH_2 \rightleftharpoons C^*H_2{=}CHCH_2Li$. Computer programs are being used to determine the temperature and allyllithium concentration dependencies of the A ⇄ B proton-exchange rate in various solvents. Preliminary activation energy (E_a) plots for exchange yield E_a = 10.5 ± 2.0 kcal mole^{-1} and $A = 10^{12.5 \pm 1.5}$ sec^{-1} for both systems a and b.



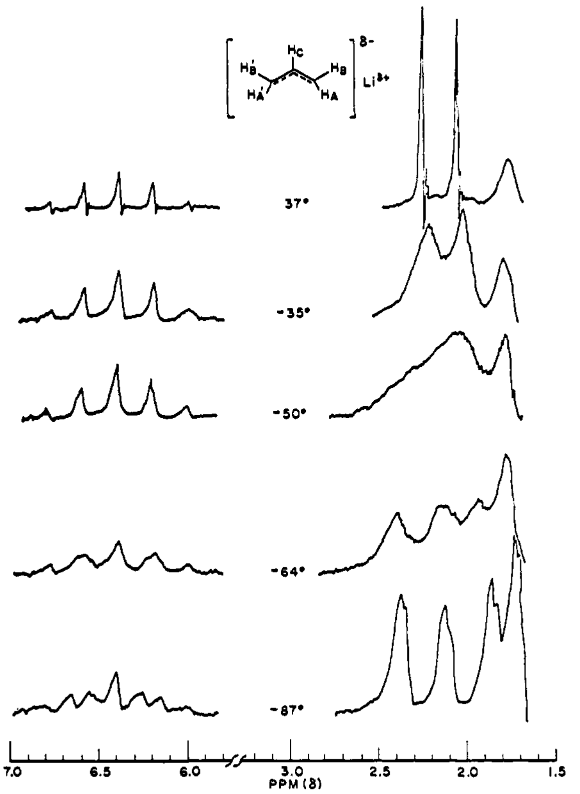


Figure 1. The temperature-dependent 60-MHz nmr spectrum of 1.5 *F* allyllithium in tetrahydrofuran-d_8. The β-CH_2 resonance of remnant protonated tetrahydrofuran appears at 1.77 ppm. Approximate spectral parameters are $\delta_A = \delta_{A'} = 2.24$ ppm, $\delta_B = \delta_{B'} = 1.78$ ppm, $\delta_C = 6.38$ ppm, $J_{AB} = J_{A'B'} = 1.6$ Hz, $J_{BC} = J_{B'C} = 8.6$ Hz, $J_{AC} = J_{A'C} = 15.2$ Hz, $J_{AA'} = J_{BB'} = J_{AB'} = J_{A'B} = 0$ Hz. The values of δ_A ($\delta_{A'}$) and δ_B ($\delta_{B'}$) are somewhat temperature dependent.

The recorded allyllithium nmr spectra indicate a predominance of essentially delocalized symmetrical allyl anions between the temperatures −100 and +60°. This conclusion is substantiated by measurements of ultraviolet spectra of $\lesssim 0.05$ *F* allyllithium solutions in THF and diethyl ether over the temperature range −100 to 25°. An absorption peak falling within the range 310–320 mμ was observed at all temperatures (−100°, 310 mμ (log ε ~3.75); 25°, 315 mμ (log ε 3.66)),[6] in close agreement with the theoretical estimate of 326 mμ for the absorption of allylcarbanion.[7] In addition, measurements have been made at room temperature of infrared spectra of both allyllithium solutions in THF and diethyl ether and allyllithium mulls in Nujol. Each system showed an absorption in the region of 1525–1540 cm^{-1} assignable to the carbon–carbon stretching frequency in a symmetrical anionic allyl moiety. These findings are in agreement with the infrared absorptions reported in the range 1520–1560 cm^{-1} for mulls of other alkali metal allyl compounds.[8] They are also consistent with a trend observed among main group allyl compounds: those compounds that are expected to be more ionic have lower carbon–

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(1) Similar observations of magnetic nonequivalence of terminal protons have been reported for pentadienyllithium[2] and phenylallyllithium[3] systems.

(2) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 205 (1967).

(3) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Am. Chem. Soc.*, **90**, 495 (1968).

(4) (a) C. S. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *ibid.*, **83**, 1306 (1961); (b) D. Seyferth and T. F. Jula, *J. Organometal. Chem.* (Amsterdam), **8**, P13 (1967).

(5) (a) J. E. Nordlander, Ph.D. Thesis, California Institute of Technology, 1960; (b) J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 494 (1961); (c) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962).

(6) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

(7) K. Kuwata, *Bull. Chem. Soc. Japan*, **33**, 1091 (1960).

(8) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

carbon stretching frequencies[9,10] (allyl halides, 1640–1650 cm^{-1}; diallylzinc, 1610 cm^{-1}; diallylmagnesium, 1575 cm^{-1}).

Various allyl compounds of the main group elements Mg, Zn, and Cd have been investigated by nmr over a broad range of temperatures. With one exception, all the recorded allyl spectra have AB_4 character at every temperature studied.[11] It is conceivable, but not yet proven, that the magnetic equivalence of the C-1 and C-3 protons in these allyl systems occurs *via* intermolecular exchange of allyl groups; the greater the compound ionic character the larger the exchange rate.[15] Since the electropositive nature of the metal in main group allyl compounds would be expected to increase in the order Cd < Zn < Mg < Li,[16] one might anticipate that allyllithium in THF would likewise give an AB_4 allyl spectrum over the full temperature range -90 to $+40°$. Nevertheless, in practice this proves not to be the case. A possible explanation for the $AB_4 \rightarrow AA'BB'C$ allyl transition observed in the nmr of both THF and diethyl ether solutions of allyllithium is afforded by results of differential vapor-pressure measurements[17] on these systems.

From colligative property studies that we have carried out on allyllithium in donor solvents at 25° it can be inferred that allyllithium is aggregated in both THF and diethyl ether at concentrations similar to those employed in the nmr investigations. At a formal allyllithium concentration of 1.5 *M* in diethyl ether the apparent degree of allyllithium aggregation is $n_{\text{app}} > 10$. With 0.8 *M* allyllithium in THF, the maximum concentration amenable to colligative property measurements, $n_{\text{app}} > 1.4$. It is suggested, therefore, that the apparent substantial increase in lifetime of the allyllithium species $[AA'BB'C]^{\delta-}Li^{\delta+}$ in these solvents with decrease in temperature might be related to its propensity to self-associate.

An extended comparison is being made between allyllithium and the allyl compounds $(C_3H_5)_2M$, M = Mg. Zn Cd, and Hg. The relationship between proton chemical shifts and ionic character and the effect of strong bases (*e.g.*, N,N,N′,N′-tetramethylethylenediamine, sparteine, and hexamethylphosphoramide) are under investigation.

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(9) G. Wilke, B. Bogdanovič, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

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(11) AB_4 allyl spectra are observed with allylmagnesium bromide–diethyl ether[5] between -80 and $+33°$, diallylmagnesium–tetrahydrofuran (THF)[9,12] between -60 and $+37°$, and diallylcadmium–THF[13] between -100 and $-20°$, above which temperature it decomposes. Only with diallylzinc–THF[9,14] has a pronounced change been observed with variation in temperature; an AB_4 allyl $\rightarrow$ $ABCD_2$ σ-allyl transition is reported[9] to occur at $-100°$.

(12) P. West, unpublished data.

(13) K.-H. Thiele and J. Kohler, *J. Organometal Chem.* (Amsterdam), 7, 365 (1967).

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(15) Consistent with this idea is the broad $ABCD_2$ σ-allyl proton nmr spectrum observed for neat diallylmercury at 37°, which sharpens up dramatically on dilution with solvent and/or lowering the temperature.[12]

(16) (a) W. Strohmeier, *Z. Elektrochem.*, **60**, 58 (1956); (b) J. A. Ladd, *Spectrochim. Acta*, 22, 1157 (1966); (c) M. Witanowski and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 737 (1966), and references therein.

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The Crystal and Molecular Structure of a Tetracyanoethylene Complex of Platinum[1]

Sir:

The study of hydrocarbon complexes of transitional metals has contributed greatly to the advancement of coordination chemistry. More recently, investigations of fluorocarbon[2] derivatives of metals have provided deeper insight into the nature of the transitional metal–carbon bond. When H atoms in hydrocarbons are replaced by F atoms, a wider variety of more stable complexes may be prepared, and in many instances the nature of the bonding in the fluorocarbon complexes is significantly different from that in analogous hydrocarbon complexes.[3] A new class of metal–carbon bonded complexes has recently been reported[1c,d] where an olefinic cyanocarbon, tetracyanoethylene (TCNE), is covalently bonded to a transitional metal. These cyanocarbon complexes are noteworthy for being extremely stable relative to the hydrocarbon and fluorocarbon analogs. Heretofore, little could be said about the nature of bonding in these complexes because structural data were not available.

We report herein preliminary results of an X-ray analysis of the first example of a transitional metal–tetracyanoethylene complex, $Pt(Ph_3P)_2TCNE$. The molecular structure is unique in regard to the structural characteristics of the coordinated tetracyanoethylene and expands the concept of metal–olefin bonding.

Colorless crystals of $Pt(Ph_3P)_2TCNE$ suitable for crystallographic examination were obtained from the reaction of *trans*-$PtHCl(PPh_3)_2$ and tetracyanoethylene in benzene at room temperature, followed by slow recrystallization over a several day period from benzene–ethanol. The compound crystallizes in the monoclinic system with unit cell parameters $a = 17.506 \pm 0.009$ Å, $b = 11.234 \pm 0.008$ Å, $c = 18.521 \pm 0.013$ Å, and $\beta = 97° 10' \pm 10'$. The space group is $P2_1/c$ and $Z = 4$. The X-ray intensities were obtained (Cu $K\alpha$ radiation) with Weissenberg film methods (*h0l* through *h7l*) and recorded with a Joice–Loebl flying-spot microdensitometer. The structure was resolved by three-dimensional Patterson–Fourier methods and refined by isotropic least-squares block diagonal techniques. At the present stage of refinement, the *R* index calculated on 2042 observed reflections is 12%. The geometry of the metal coordination is shown in Figure 1, and the most important bond lengths and angles with their estimated standard deviations are listed.

Several salient features are to be noted. The dihedral angle between the planes P_1PtP_2 and C_1PtC_2 is 10°. The TCNE moiety is distorted from planarity upon coordination such that the angle between a line through C_1–CN and the plane which passes through C_1 and C_2, and which is perpendicular to the P_1PtP_2 plane, is about 10°. The C_1–C_2 bond length is 1.52 Å, which is close to that of a carbon–carbon single bond. The mean length of the carbon–carbon bonds of the C—CN

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(1) For W. H. B., this communication is part V in the series Metal Complexes of Cyanocarbons; (a) part IV, P. Uguagliati and W. H. Baddley, manuscript in preparation; (b) part III, W. H. Baddley, *J. Am. Chem. Soc.*, in press; (c) part II, *ibid.*, **88**, 4545 (1966); (d) part I, W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

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(3) See, for example, P. B. Hitchcock and R. Mason, *Chem. Commun.*, 242 (1967).