oxyethanol.[14] The dideuteride was synthesized in *ca.* 70% isotopic purity by refluxing a suspension of the dihydride in C_2H_5OD (9 days under N_2). The resonance interaction in this complex is analogous with that in I except that $\nu_{OsH(\beta)}$ is of lower energy than ν_{CO}. Accordingly, ν_{CO} shifts to a *lower* frequency in the dideuteride, and $\nu_{OsH(\beta)}/\nu_{OsD(\beta)}$ is *smaller* than $\nu_{OsH(\alpha)}/\nu_{OsD(\alpha)}$. On removing the interaction (as shown above for I, ref 9), and using the resultant ("unperturbed") $\nu_{OsH(\beta)}$, 1884 cm^{-1}, we obtain $\nu_{OsH(\beta)}(\text{calcd})/\nu_{OsD(\beta)}(\text{obsd}) = 1.396$, which is practically identical with the observed value of $\nu_{OsH(\alpha)}/\nu_{OsD(\alpha)}$.

The molecular configuration of this complex has been determined solely from the infrared spectral data given in Figure 1. There are three possible geometrical isomers, but the presence of the resonance is expected only in one, III.[15]

IV $[Os(H,D)Cl(CO)(Ph_3P)_3]$. The hydride,[13] pure deuteride,[16] and the structure[17] of the complex have been reported previously. The data are shown to substantiate[18] the interpretation of the spectra of III.

V $[Ir(H,D)(CO)(Ph_3P)_3]$ and VI $[Rh(H,D)(CO)(Ph_3P)_3]$. The hydrides[20] and their structures[20,21] have been previously described. The H–CO resonance interaction in these complexes was discovered after it became possible to prepare pure deuterides[7] by reaction with D_2.[16] The M–D stretching bands have not been definitely located because of an interfering spectral band of Ph_3P, the position of which suggests that $\nu_{MH}/\nu_{MD} > 1.4$.[4]

The results of the present study suggest that the vibrational interaction is likely to be present in all ternary carbonyl hydrides of transition metals,[22] *e.g.*, $FeH_2(CO)_4$[23] and $CoH(CO)_4$.[24] Because of their low thermal stability and high chemical reactivity, the spectra–structure correlations on these catalytically important compounds[25] have long been a subject of complications and an accompanying controversy.[22]

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[14] The colorless dihydride has been characterized by complete elemental analysis and magnetic (diamagnetic), molecular weight (monomeric in $CHCl_3$), conductivity (nonconducting in $C_6H_5NO_2$), and dipole moment (6.80 D. in benzene) measurements.

[15] In the remaining two isomers, (i) the hydrogens are *trans* to one another, and (ii) both hydrogens are *trans* to the Ph_3P ligands.

[16] L. Vaska, "Proceedings of the 8th International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer-Verlag, Vienna and New York, 1964, p 99.

[17] P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

[18] The bromo derivative of IV and the isostructural ruthenium compounds[19] show the same properties, *i.e.*, there is no H–CO interaction in these complexes.

[19] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 1262 (1961).

[20] S. S. Bath and L. Vaska, *ibid.*, **85**, 3500 (1963).

[21] S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

[22] There are two recent review articles which cover practically all the aspects of transition metal hydride complexes, including carbonyl hydrides: (a) A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3; this is the most comprehensive treatment of the subject to date. (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

[23] Isoelectronic (d^8) and probably isostructural with I and III.

[24] Isoelectronic (d^8) and probably isostructural with V and VI.[20]

[25] I. Wender, H. W. Sternberg, R. A. Friedel, S. J. Metlin, and R. E. Markby, "The Chemistry and Catalytic Properties of Cobalt and Iron Carbonyls," Bulletin 600, U. S. Bureau of Mines, U. S. Government Printing Office, Washington, D. C., 1962.

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Lithium–π-Electron Interactions in But-3-enyllithium[1]

Sir:

The structure, unique bonding, and ability of alkyllithium compounds to promote stereospecific polymerizations has caused considerable interest in these derivatives.[2] In particular, it has been shown that polymerizations of butadienes, initiated by alkyllithium compounds in polar solvents, yield polymers with a 1,4-*trans* configuration typical of anionic polymerization. However, when these same polymerizations are carried out in hydrocarbon solvents the 1,4-*cis* product is obtained in up to 95% yield.[3] It is this latter observation on which we wish to comment. The generally accepted interpretation of the kinetic data of these polymerizations in hydrocarbon solvents involves two steps: the dissociation of alkyllithium hexamer (or tetramer) into an "active monomer" (the rate-determining step), followed by addition of this moiety to the diene substrate. The stereospecificity of the reaction is said to be determined by an interaction of the lithium atom with the π electrons of the diene. The total reaction leaves a new organolithium compound which may either reassociate or undergo further reaction. It is significant that the critical step (the lithium–π-electron interaction) in the control of the stereochemistry of the reaction has never been experimentally observed.

In this paper evidence is presented for an interaction between the vacant orbitals on the hexameric lithium framework and the π orbitals on the butene moiety in but-3-enyllithium. A structure consistent with the observed nmr, ultraviolet, and infrared spectra of the hexamer and which is also consistent with all of the presently known structural details of lithium derivatives is given in Figure 1. This model also can explain the stereospecific addition in hydrocarbon solvents since the geometry of the hexameric lithium–π-complex would favor *cis* addition.

In order to prove that this interaction takes place a series of compounds of the type $H_2C{=}CHCH_2CH_2X$ (X = H, Cl, Br, HgCl, HgR, and Li) were prepared and their nmr spectra obtained (Table I). An examination of these data shows a regular variation of the chemical shift with the electronegativity of the substituent. The one exception to this trend is the lithium derivative. In this case, the protons are less shielded than expected, with the greatest discrepancy occurring for the vinyl

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[1] Taken in part from the Ph.D. dissertation of James B. Smart, Wayne State University, 1966.

[2] T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965).

[3] A. U. Tobolsky and G. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959); Yu. L. Spirin, D. K. Polyakov, A. R. Grantmakher, and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, **139**, 899 (1961).

Table I. Chemical Shifts of Several But-3-enyl Compounds[a]

Compound	δ_A[a]	δ_B	δ_C	δ_β	δ_α
$CH_2{=}CHCH_2CH_2Cl$	5.111	5.089	5.811	2.467	3.497
$CH_2{=}CHCH_2CH_2Br$	5.077	5.049	5.789	2.568	3.339
$CH_2{=}CHCH_2CH_2HgCl$	4.97	4.90	5.83	2.37	1.98
$CH_2{=}CHCH_2CH_3$	4.929	4.855	5.787	2.052	0.984
$(CH_2{=}CHCH_2CH_2)_2Hg$	4.975	4.860	5.881	2.555	1.110
$CH_2{=}CHCH_2CH_2Li$					
in cyclopentane	5.076	4.906	6.044	2.500	+0.847
in benzene	5.080	4.891	6.050	2.483	+0.908

[a] All chemical shift values in parts per million from tetramethylsilane and negative (lower field) with the exception of the α protons on the lithium derivative.

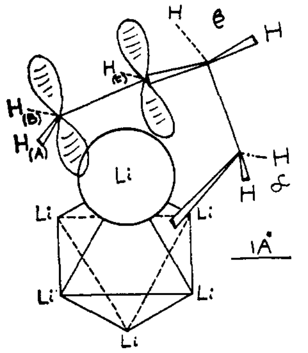

Figure 1. The proposed structure for but-3-enyllithium in cyclopentane.

protons. In order to interpret this result a model has been proposed (Figure 1) in which electron density is withdrawn from the vinyl portion of the molecule into the electron-deficient lithium framework, thus causing a decrease in shielding of these protons.

In order to provide corroborative evidence for this interaction a number of other experiments were carried out. It was noted that, if this interaction takes place, addition of a Lewis base to the system would either destroy the lithium–π interaction or add to the lithium framework with this interaction remaining. In either case the electron density on the butenyl moiety and particularly on the double bond would be increased.

To this end dimethyl ether was added to a solution of but-3-enyllithium (2:3 molar ratio) and the nmr parameters were determined. These were $\delta_\alpha = 0.983$, $\delta_\beta = -2.167$, $\delta_C = -5.933$, $\delta_B = -4.583$, and $\delta_A = -4.800$ ppm. A comparison of these with the values listed in Table I obtained for the same concentration of but-3-enyllithium in cyclopentane shows an upfield shift with base present. This was expected, but the large upfield shifts (5–20 cps) for the vinyl protons imply extensive electron donation into the double bond and supports the proposed model.

Additional evidence for the lithium–π interaction was obtained from infrared studies which showed several shifts in stretching and bending modes of but-3-enyllithium. In particular the C=C stretch was shifted 25 cm^{-1} lower, implying electron delocalization of the double bond. Several deformation modes of the vinyl group were also shifted to lower wavenumbers, which is in accord with weakened bonds in this region.

The ultraviolet spectra gives further support to the lithium–π-electron interaction. The low energy band normally associated with the butenyl group (λ_{max} 180–190 mμ) is absent in the lithium compound, and a new band at 251 mμ is observed, as seen in Figure 2. In addition, a band previously predicted from molecular orbital theory for the lithium framework[4] was observed in the 220-mμ region for both *n*-butyllithium and but-3-enyllithium. It can be seen that the framework transitions are much broader for the but-3-enyllithium than for the *n*-butyl derivative, suggesting the presence of additional or broadened energy levels. This is in accord with the π-interaction as is the appearance of the new band at lower energy.

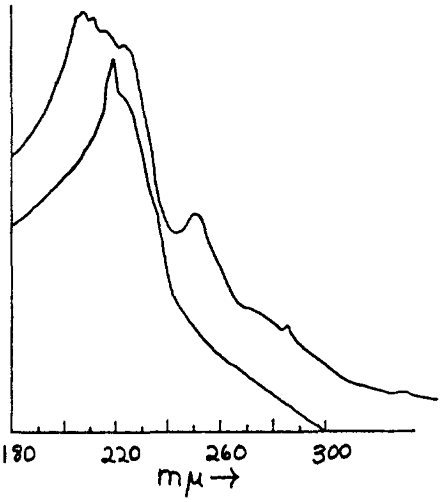

Figure 2. Comparison of the ultraviolet absorption spectra of but-3-enyllithium (upper) and *n*-butyllithium (lower).

All of these studies clearly indicate an interaction between the π electrons on the butenyl moiety and the lithium framework in the hexamer since they were carried out in cyclopentane or other noncoordinating hydrocarbon solvents in which but-3-enyllithium was shown to be hexameric by vapor-pressure lowering. This is in full accord with Brown's[5] calculations which indicate that the dissociation into monomer is far too small to account for the rates of the polymerization reactions or other properties of lithium alkyls in hydrocarbon solvents.

All compounds used in this work were prepared by standard methods and were handled either in a high vacuum system or in a drybox. The nmr spectra were obtained on a Varian DP-60 spectrometer with the chemical shifts determined by interpolation between audiofrequency side bands. The ultraviolet spectra were

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(4) E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197, (1964).

(5) T. L. Brown, *ibid.*, **5**, 191 (1966).

taken on a Cary 14 and the infrared spectra on a Perkin-Elmer 237-B spectrometer.

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The Structure of Boron Halide Complexes of α-Halo Ketones

Sir:

Molecular addition complexes between ketones and boron trihalides (BX_3) have been known since 1877;[1] however, the structures of the complexes have received limited attention. Infrared[2,3] and dipole moment[4] data on several adducts give evidence for oxygen–boron bonds. We wish to report detailed information regarding the geometry of the carbonyl carbon of boron halide complexes of α-chloropinacolone (Ia) and α-bromopinacolone (Ib) obtained by variable-temperature nuclear magnetic resonance (nmr) studies.

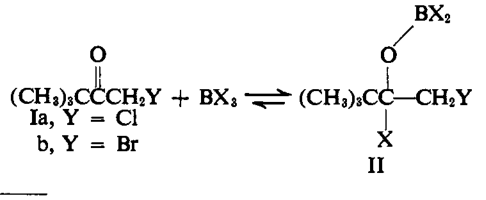
The nmr spectra[5] of Ia and Ib show sharp singlets for the methylene and *t*-butyl protons, which do not change as the temperature is lowered to −20°. On the other hand, the resonance of the methylene protons of complexes of Ia and Ib formed in the presence of excess BCl_3 and BBr_3 are temperature variant and generally appear as an AB pattern below 10°. Parameters describing nmr spectra at −10° are given in Table I.

Table I. Nmr Data of α-Halo Ketones and Complexes at −10°

System	δ_{H_a}, τ	δ_{H_b} τ	J_{ab}, cps	δ_{CH_3}, τ
$(CH_3)_3CCOCH_2Cl$	5.58[a]	....	..	8.80
$(CH)_3CCOCH_2Br$	5.77[a]	....	..	8.78
$(CH_3)_3CCOCH_2Cl + BF_3$ (excess)	5.53[a]	....	..	8.72
$(CH_3)_3CCOCH_2Cl + BCl_3$ (excess)	5.60	5.83	13	8.78
$(CH_3)_3CCOCH_2Cl + BBr_3$ (excess)	5.17	5.80	13	8.78
$(CH_3)_3CCOCH_2Br + BF_3$ (excess)	5.67[a]	....	..	8.63
$(CH_3)_3CCOCH_2Br + BCl_3$ (excess)	5.70	5.87	12	8.75
$(CH_3)_3CCOCH_2Br + BBr_3$ (excess)	5.23	5.85	12	8.72

[a] A singlet was observed for H_a and N_b.

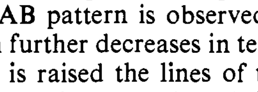
The observed AB pattern can be rationalized by addition of BCl_3 or BBr_3 across the carbon–oxygen double bond (eq 1) to yield II in which the methylene protons are adjacent to a magnetically asymmetric center[6] and are nonequivalent. An intermediate involving an sp^2-hybridized carbonyl carbon is highly unlikely since the energy required for the methylene protons to become magnetically equivalent, such as IIIa ⇄ IIIb,[7] would be small. *Therefore the carbon to which the oxygen is bonded must be tetrahedral.*



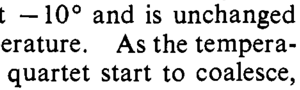
$$(CH_3)_3C\overset{\overset{O}{\|}}{C}CH_2Y + BX_3 \rightleftharpoons (CH_3)_3C\underset{\underset{X}{|}}{\overset{\overset{O-BX_2}{|}}{C}}-CH_2Y \qquad (1)$$

Ia, Y = Cl
b, Y = Br

II



IIIa



IIIb

Variable temperature spectra of the methylene region of α-bromopinacolone plus BBr_3 are shown in Figure 1. An AB pattern is observed at −10° and is unchanged with further decreases in temperature. As the temperature is raised the lines of the quartet start to coalesce, and at 56° a broad peak is observed in the methylene region. This change in absorption pattern is characteristic of two species in equilibrium (eq 1). When the rate of interconversion is rapid on the nmr time scale, the methylene protons can become equivalent. Reversible reactions involving starting material must account for this change in absorption since α-bromopinacolone can be recovered (91% by vpc analysis) by decomposition of the complex with sodium bicarbonate solution and extraction into methylene chloride.

In the spectrum of α-chloropinacolone plus BCl_3, the central lines of the quartet are distinguishable at tem-

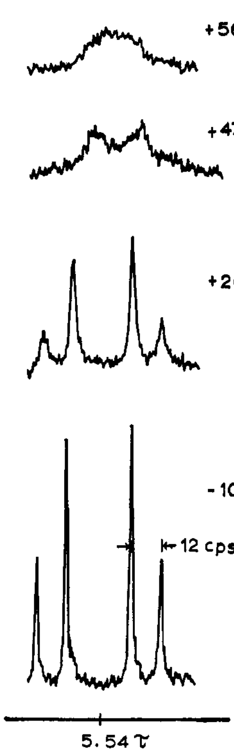


Figure 1. Temperature dependence of the nmr spectrum of the methylene protons of the α-bromopinacolone–boron tribromide complex.

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(1) D. Martin and J. Canon in "Friedel-Crafts and Related Reactions," Vol. I, G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter VI.

(2) B. Susz and P. Chalandon, *Helv. Chim. Acta*, **41**, 1332 (1958).

(3) M. Lappert, *J. Chem. Soc.*, 817 (1961).

(4) P. Chalandon and B. Susz, *Helv. Chim. Acta*, **41**, 697 (1958).

(5) Spectra were obtained on a Varian Associates A-60 spectrometer equipped with a variable temperature probe using 30% w/w solutions in carbon tetrachloride.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York N. Y., 1959 p 379.

(7) Mizushima, *et al.*,[8] have shown that chloroacetone exists in two molecular forms in solution. The dihedral angle between the C_1–Cl and the C_2–O planes in the less polar form is *ca.* 150° and that of the more polar form between 0 and 30°. Since rotation about the C_1–C_2 bond is likely to be rapid on the nmr scale, the methylene protons in either conformation will become magnetically equivalent.

(8) S. Mizashima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratuni, I. Nakagawa, and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).