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Preliminary communication

Intramolecular metal–double bond interaction
II. The interaction observed in di-4-pentenylzinc

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The interaction of metals with double bonds or other systems containing electron rich regions is of major importance in electrophilic addition reactions including polymerization and cyclization processes. The internal interaction or cyclization process has been suggested in 3-butenyllithium[1], several hexenylmetal derivatives[2], in some alkenylaluminum derivatives[3], and for some Grignard reagents[4] arising from unsaturated species. On the other hand, two independent studies[5,6] have shown that no interaction exists in alkenyltin compounds nor has evidence been found for interaction in alkenylmercury derivatives. In this paper we present evidence in support of internal interactions in di-4-pentenylzinc and present some additional preliminary arguments concerning the mechanism of interaction.

Di-3-butenyl and di-4-pentenylzinc were synthesized by reaction between the mercury analogs[1] and zinc dust in evacuated sealed tubes. The reactants were held at 120° for 20 h after which, nearly quantitative conversion to the organozinc derivative had occurred. (Found: C, 54.21; H, 7.95. $C_8H_{14}Zn$ calc.: C, 54.72; H, 8.03%. Found: C, 58.10; H, 8.80. $C_{10}H_{18}Zn$ calc.: C, 58.99; H, 8.91%.) The resulting compounds are colorless, high boiling liquids and may be distilled under high vacuum conditions (10^{-6} mm Hg/25°). Typically, they are moisture and oxygen sensitive and therefore all manipulations were carried out under an inert atmosphere. The IR spectrum of the butenyl compound in the gas phase showed peaks at 3083 m, 2971 m, 2907 st, 2861 (sh), 1634 m, 1406 w, 1310 w, 1249 w, 997 m, and 912 m. Likewise, the solution spectrum (C_5H_{10}) of di-4-pentenylzinc showed absorptions at 1823 w, 1637 m, 1400–1425 w, 1333 m, 1100 w, 1051 w, 993 st, 903 st, 805 (sh), 666 m, and 631 (sh)*.

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*Absorptions in the region of 3000 cm^{-1} were badly distorted due to the cyclopentane solvent and have not been determined accurately.

The NMR parameters for the alkenylzinc derivatives and their parent 1-alkenes are given in Table 1. The vinyl proton resonance absorptions, designated as δ_A and δ_B, for di-3-butenylzinc are similar to those in the butene parent; however, for di-4-pentenylzinc δ_B occurs significantly downfield from δ_B in 1-pentene and δ_A is also shifted slightly downfield*. The AB region of the spectrum for 1-pentene and di-4-pentenylzinc are reproduced in Fig. 1. It is also significant that the α protons in the di-4-pentenylzinc appear upfield (0.210 ppm) from the position normally associated with the absorption in saturated zinc organometallics (n-pentyl, 0.400 ppm; n-butyl, 0.425 ppm; n-heptyl, 0.383; ethyl, 0.400 ppm)[7]. The NMR spectra of both di-3-butenyl- and di-4-pentenylzinc are concentration independent but the latter shows a temperature dependence particularly for δ_α which shifts from 0.210 at 30° to 0.033 ppm at −70°.

Upon complexation with 2,2′-bipyridine[8] (Bipy) δ_α is shifted to 0.067 ppm in di-4-pentenylzinc and to 0.017 in dipentylzinc. Qualitative observations also show major changes occur in the vinyl region (Fig. 1) on complex formation which suggests the perturbing influence on the A and B protons has been removed.

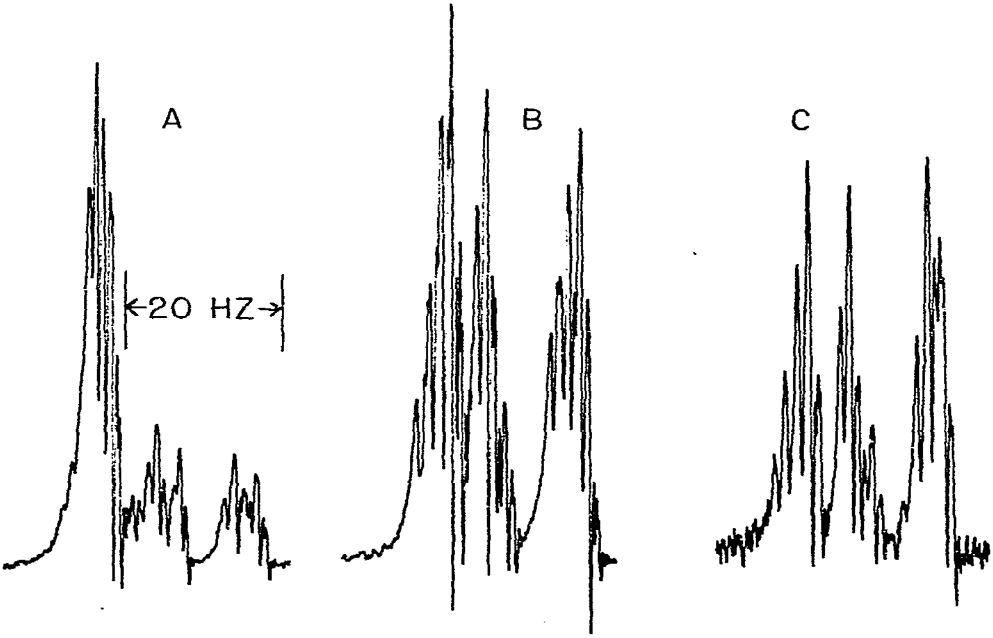

Fig. 1. The 60 MHz NMR spectra of the AB region of A, di-4-pentenylzinc; B, 1-pentene and C, di-4-pentenylzinc·2,2′-Bipy.

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*Unpublished observation of the NMR spectra of Group I, II and III 3-butenyl metal derivatives show δ_C to consistently appear downfield of the position associated with this resonance in other derivatives. This observation is contrary to the result expected from purely inductive effects. These observations will be discussed in a forthcoming paper.

TABLE I

NMR PARAMETERS FOR SOME ORGANOZINC DERIVATIVES

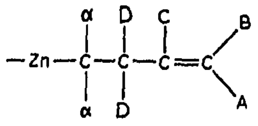
	1-Butene [b]	*Di-3-butenylzinc* [d]	*1-Pentene* [d]	*Di-4-pentenylzinc* [c]	*Di-4-pentenylzinc* [c]*·2,2'-Bipy*
δ_A [a]	4.939	4.940	4.945	4.98	4.80
δ_B	4.865	4.840	4.888	5.11	4.72
δ_C	5.780	5.938	5.733	5.74	5.78
δ_β	–	2.263	–	–	–
δ_α	–	0.468	–	0.21	0.07
J_{AB} [e]	1.96	1.92	2.03	2.9	2.9
J_{AC}	17.23	17.0	16.98	15.9	17.3
J_{AD}	−1.66	−1.7	−1.71	−1.0	−1.4
J_{BC}	10.32	10.1	10.12	10.7	9.8
J_{BD}	−1.26	−1.2	−1.31	−1.0	−1.0
J_{CD}	6.22	6.3	6.84	6.4	6.4
$J_{\alpha D}$	–	~7.3	–	7.0	7.8

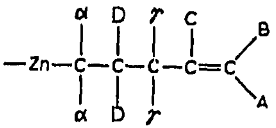
[a] Chemical shift data referenced to internal TMS = 0.0 ppm. All samples were degassed and sealed under vacuum.

[b] Ref. 13.

[c] C_8H_{10} solvent. δ and J values were obtained from multiple scans of the spectra by first order analysis and are deemed reliable to ±0.01 ppm and ±0.5 Hz respectively based on comparison between the first order and exact analysis of a series of butenyl metal derivatives.

[d] Computer simulated spectra, δ values are ±0.002 ppm and J values are ±0.01 Hz.

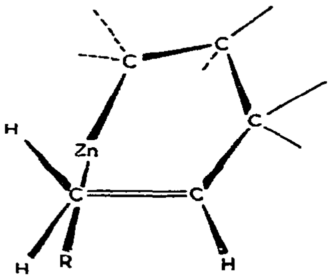




[e] All coupling constants are given in Hz.

The observed upfield shifts are in accord with the known inductive effects of complex formation[9]. The similarity observed in the values of δ_α in these complexes is a strong indication of the lack of influence which the double bond has on the α proton in the absence of an intramolecular interaction.

These data, taken together, strongly support an intramolecular interaction between the metal center and the double bond. The temperature dependence and upfield shift of δ_α are compatable with this type of interaction while the lack of change found in di-3-butenylzinc rules out intermolecular association. The model proposed for this interaction is given in I. The association between the terminal carbon and the zinc is weak but results in conformer I having the lowest energy of all possible orientations. This is consistent with the temperature dependence of the NMR spectrum which results from an average of all forms present. At room temperature a large portion of the molecules are present in the unfolded conformation and as the temperature is decreased a greater and greater proportion of the molecules exist in the associated form. This is reflected in the upfield shift of the α protons which results from the shielding arising from the anisotropic character of the double bond which is oriented, as shown in a molecular model, so that it results in shielding of the α protons[10]. Changes consistent with this, but less dramatic, are also observed in the vinyl portion of the spectrum.



(I)

The effects observed here do not represent stable adduct formation as observed in transition metal-olefin complexes because of the lack of change in ν(C=C)[11], but are primarily due to the weak dipole–dipole interaction implied in I. This dipolar interaction is the result of the inherent polarity of the $\overset{+}{\text{Zn}}-\overset{-}{\text{C}}$ bond and the polarity of the double bond which results in a partial negative charge on the terminal carbon[12].

The mechanism of interaction is of importance since it may play a role in polymerization reactions and takes on added significance in view of the cyclization reactions observed for di-5-hexenylorganometallic[2] compounds which may be accounted for in terms of the polarization suggested. For the pentenyl cases the chain length is not sufficiently long to achieve the requisite conformation for addition to the double bond; however, it is quite favorable for the terminal carbon–metal dipole–dipole association.

At this time sufficient data is not available to warrant a complete description of this model but currently this study is being extended to include other Group II and Group III metals and a more detailed description will be available at that time.

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