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INTRAMOLECULAR METAL—DOUBLE BOND INTERACTIONS

V. ^{1}H NMR INVESTIGATION OF GROUP II METAL—ALKENE COMPOUNDS

J.St. DENIS and J.P. OLIVER*
Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)

T.W. DOLZINE and J.B. SMART
Department of Chemistry, Xavier University, Cincinnati, Ohio 45207 (U.S.A.)

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Summary

^{1}H NMR data are presented for a series of terminal alkenes and their respective halogen and Group II metal derivatives. The NMR parameters of the olefin functionality, with the exception of di-4-pentenylzinc, generally vary with the electron-donating or -attracting ability of the terminal substituent. The NMR parameters of di-4-pentenylzinc are interpreted in terms of an internal metal—double bond interaction. This direct interaction leads to intramolecular cyclization in the di-5-hexenylmagnesium and -zinc derivatives.

Introduction

It has been shown recently that a number of unsaturated main group organometallic compounds may exhibit intramolecular interactions between the metal center and the olefinic site which, under favorable circumstances, lead to intramolecular cyclization. This type of interaction has been clearly demonstrated for aluminum derivatives in several studies [1—5] and has been suggested for other species including derivatives of lithium [3, 6—9], magnesium [3, 10, 11], zinc [12], gallium [3—5] and indium [3]. With the exception of the studies on aluminum compounds, in which the degree of aggregation and NMR parameters have been correlated with the metal—olefin interaction, little quantitative information is available on the nature or magnitude of the metal—olefin interaction.

In an effort to provide some of the necessary information regarding the factors which influence this metal—olefin interaction the present study on the ^{1}H NMR spectra of a series of unsaturated Group II organometallic derivatives was undertaken. It has been shown in these studies that the NMR parameters of

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*Author to whom inquiries should be addressed.

those species studied, with the exception of those for di-4-pentenylzinc, vary, predictably with the electron-releasing or -withdrawing ability of the substituent occupying the terminal position.

The perturbation of the NMR parameters of the pentenylzinc system are interpreted in terms of a direct metal—olefin interaction which leads, under special conditions to the facile internal cyclization of the organometallic derivative. Preliminary accounts of this work have appeared previously [3, 12].

Experimental

The preparation of air sensitive organometallic derivatives were carried out under high vacuum conditions with subsequent handling performed in a Na/K alloy scavenged dry box with an argon atmosphere. All solvents were rigorously dried over Na/K alloy.

NMR spectra were recorded on a Varian Associates HA-60 IL spectrometer operating with a probe temperature of 25°C. Precise line positions were determined using a calibration technique previously described [13]. The 1-chloro, l-iodo and l-mercury derivatives of 4-pentene and 5-hexene were calibrated by linear interpolation between audio frequency side bands. For all measurements a minimum of three scans was recorded and the average chemical shifts and coupling constants are reported. Chemical shift data are referenced to internal TMS = 0.0 ppm and coupling constants are given in Hz.

Computer simulated spectra were obtained from calculations using LACOON-3 [14] and are reproducible to 0.002 ppm for chemical shifts and to 0.05 Hz for coupling constants. Parameters derived from first order analysis are less precise and are certainly not reliable to more than ± 0.01 ppm and ± 0.25 Hz respectively.

IR measurements were obtained using either a Perkin—Elmer 237B or 621 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. 1-Bromo-3-butene and the alcohol derivatives were obtained from Chemical Samples Company and used as received.

Syntheses

The chloroalkene derivatives were prepared from the alcohols by reaction with thionyl chloride as described by Roberts et al. [15] and were characterized by their NMR and IR spectra. The analogous iodo compounds were prepared by reaction between the chloro compounds and NaI in acetone [16]. In addition to the IR data, the NMR spectral properties are consistent with terminal halogen substitution. Triplet resonance absorptions were observed at δ_α 3.50 and δ_α 3.13 ppm for the choro and iodo derivatives, respectively. The purity of these derivatives was confirmed by gas-chromatographic analysis.

The mercury derivatives were synthesized by the method of Nesmeyanov [17]. Di-3-butenylmercury was purified by trap to trap distillation under high vacuum at room temperature. The pentenyl and hexenyl derivatives were purified by distillation in an apparatus modified for use under high vacuum. Elemental analyses and IR data for each of these derivatives are: $(CH_2{=}CHCH_2CH_2)_2$-Hg Anal.: Found: C, 31.15; H, 4.79; Hg, 64.27. $C_8H_{14}Hg$ calcd.: C, 30.91; H, 4.51; Hg, 64.58%. Principal IR bands*, 3080s, 3000(sh), 2980s, 2930(sh), 2910 vs, 2840s, 1825w, 1637s, 1445m, 1415m, 1310w, 1290w, 1245m, 990s, 906vs, 735w. $(CH_2=CHCH_2CH_2CH_2)_2Hg$ Anal. Found: C, 35.71; H, 5.47; Hg, 58.91. $C_{10}H_{15}Hg$ calcd.: C, 35.46; H, 5.31; Hg, 59.22%. Principal IR bands**, 3050s, 2970 (sh), 2950s, 2900vs, 2880(sh), 2820s, 1810w, 1640s, 1460(sh), 1455(sh), 1440s, 1420(sh), 1335s, 1255m, 1225w, 1125w, 1050—1075w, 990s, 908vs, 700 w. $(CH_2=CHCH_2CH_2CH_2CH_2)_2Hg$ Analysis by mass spectroscopy; parent ion $[CH_2=CH(CH_2)_4]_2Hg^+$, mass = 365 based on ^{199}Hg isotope; principal IR bands**, 3075s, 2975s, 2920vs, 2850s, 1825w, 1645(sh), 1640s, 1635(sh), 1455(sh), 1440s, 1435(sh), 1415(sh), 1335m, 1255(sh), 1247m, 1230(sh), 1180w, 1130w, 1150, 1175m, 995s, 910vs, 805w, 700→725m, 635m.

The organozinc derivatives were all prepared simialrly and the details given for di-3-butenylzinc are representative. An excess of zinc dust (99.9%, 5g, 0.077 mol) was added to a reaction vessel fitted with a magnetic stirring bar and a break seal side arm. The reaction vessel was evacuated and approximately 3g (0.01 mol) of di-3-butenylmercury distilled in and the tube sealed under vacuum. The reactants were placed in an oil bath at 120° for 24 h, after which the tube was attached to the high vacuum line via the break seal side arm. The volatile products were removed and separated by trap-to-trap distillation; the pure product was isolated in a 0° trap. Small amounts of highly volatile byproducts were isolated at —196°C but were not identified. $(CH_2=CHCH_2CH_2)_2Zn$ Anal. Found: C, 54.21; H, 7.95. $C_8H_{14}Zn$ calcd.: C, 54.72; H, 8.03%. Principal IR bands***, 3083m, 2971m, 2907s, 2861(sh), 1634m, 1406w, 1310w, 1249w, 997m, 912m. $(CH_2=CHCH_2CH_2CH_2)_2Zn$ Anal. Found: C, 58.10; H, 8.80. $C_{10}H_{18}Zn$ calcd.: C, 58.99; H, 8.91%. Principal IR bands***, 3071m, 3041→2831 br, 1823w, 1637m, 1400→1425w, 1333m, 1100w, 1051w, 993s, 903s, 805(sh), 666m, 631(sh).

Di-5-hexenylzinc was prepared by an identical procedure. However, an organozinc impurity was found to be present and identified as bis(cyclopentylmethyl)zinc by NMR analysis of the hydrolysis products which were methylcyclopentane and 1-hexene (from the noncyclic organozinc product). Integration of the NMR spectrum of the product mixture indicated a 10% impurity of bis(cyclopentylmethyl)zinc after a 24 h reaction time. However, by extending the reaction time to 84 h, the cyclopentylmethyl derivative made up approximately 90% of the product mixture. The NMR parameters for bis(cyclopentylmethyl)zinc consist of a high field doublet centered at 0.47 ppm and a multiplet centered at 1.67 ppm. It proved impossible to separate the mixture; therefore, NMR measurements of the hexenyl derivative were taken with the 10% impurity present. There is no evidence for exchange between the two compounds and the cylcopentylmethyl species has no resonance absorption in the olefin region. For these reasons, we feel the presence of the impurity does not affect the NMR parameters.

The organomagnesium compounds were also prepared by a mercury exchange reaction. All derivatives were prepared similarly. A reaction vessel with stirring bar and a break seal side arm was loaded with triply sublimed magne-

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*Gas cell, NaCl, 10.0 cm, calibrated against polystyrene film (± 4 cm^{-1}).

**Liquid film, calibrated against polystyrene film (± 4 cm^{-1}).

***C_5H_{10} solution, KBr cell, 0.25 mm, calibrated against polystyrene film (± 4 cm^{-1}).

sium (approximately 2.0 g). Diethyl ether (10 ml) and a small quantity of bromoethane (1 ml) were distilled into the reaction vessel. The vessel was closed off under vacuum and warmed to room temperature. The Grignard reaction started at room temperature and was allowed to continue until the magnesium metal chips darkened (approximately 5 min). At this time all solvent and volatile components were quickly removed on the vacuum line leaving the activated magnesium and dry Grignard. The vessel was transferred to a dry box and the Grignard reagent washed out of the reaction vessel with diethyl ether. The vessel was then reattached to the vacuum line and residual ether removed. Di-3-butenylmercury was subsequently distilled into the vessel and the tube was sealed under high vacuum. Reaction was allowed to proceed for 24 h at 120°C, after which time a white solid had formed and elemental mercury was deposited. The reaction tube was attached to a vacuum line via the side arm and all volatile components removed. To insure complete removal of any residual mercury compounds, the tube was heated to 100°C and pumping was continued for 24 h after which the tube was resealed and removed to a dry box. The magnesium compound was dissolved in diethyl ether and then transferred to another vessel. The ethereal solution was put under high vacuum and the ether removed and a second heating and pumping cycle maintained for another 24 h. Subsequent NMR spectra of ethereal solutions exhibited characteristic resonance absorptions and no mercury compound could be detected.

No straight chain hex-5-enylmagnesium compound could be isolated. After 24 h only bis(cyclopentylmethyl)magnesium was isolated as determined by NMR (—0.50 ppm, doublet; 1.65, multiplet) and hydrolysis experiments. An NMR tube reaction involving the di-5-hexenylmercury and -magnesium exchange was conducted and the presence of a straight chain derivative was indicated by the initial appearance of a high field triplet resonance (—0.60 ppm). After about 3 h of reaction time a new high field doublet resonance (—0.50 ppm) appeared and continued to increase in intensity as the triplet resonance disappeared. Isolation of the noncyclized product from this reaction is impractical because the rate of cyclization is comparable to the rate of metal exchange.

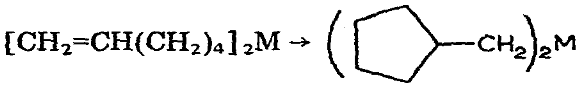
A complete workup of the hydrolysis residue of the cyclic magnesium compound indicated the presence of bis(cyclopentylmethyl)mercury. The identity of this compound was established by NMR (1.20 ppm, doublet; 1.65 ppm, multiplet; $J(^{199}\text{Hg}—\text{H})$ 95.7 Hz) and mass spectral analysis. The origin of this compound in the reaction will be discussed below.

Results and discussion

In our investigation of terminal unsaturated organometallic derivatives of Group II, we have observed that cyclization of di-5-hexenylzinc and -magnesium occurs during the preparation of these compounds via the metal exchange indicated in eqn. 1. The cyclization is more easily achieved for the magnesium deriva-

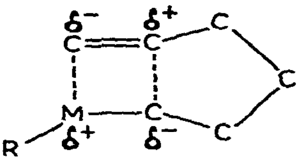
$$[\text{CH}_2\text{=CH(CH}_2)_4]_2\text{Hg} + \text{M} \rightleftharpoons \text{Hg} + [\text{CH}_2\text{=CH(CH}_2)_4]_2\text{M} \qquad (1)$$

tive and the isolation of a hexenyl derivative of magnesium is not possible by this synthetic method. The existence of such a derivative is indicated, however, by the high field triplet absorption in the NMR which is dominant in the initial stages of reaction. On the other hand, during the course of the mercury—zinc exchange only a small amount of cyclic product is produced before the metal—metal exchange is complete and isolation of di-5-hexenylzinc is possible. For both magnesium and zinc these observations demonstrate that metal exchange occurs prior to cyclization, as given by eqn. 1, followed by intramolecular cyclization indicated by eqn. 2.



(2)

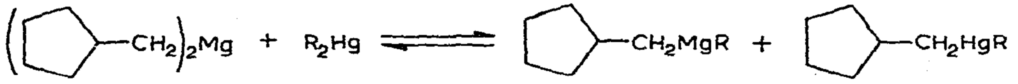
The cyclization is believed to occur via an internal addition to the double bond and to proceed through the transition state or activated complex indicated in I. The proposed path and transition state are based in part on analogy with the corresponding aluminium systems [2, 5] and previous detailed studies on Grignard cyclizations [11, 18].



(I)

The ease of cyclization of the hexenyl metal derivatives follows the order Al > Mg > Li > Zn ≫ Hg = 0. This order appears to be determined by (1) the availability of a vacant orbital on the metal center and (2) the polarity of the metal—carbon bond. The rate of cyclization is also dramatically effected by the chain length of the olefin moiety and is greatest when the conformation indicated in I can be obtained relatively strain-free [5].

The magnitude of the intramolecular interaction varies greatly from the aluminium systems, in which a strong interaction has been demonstrated, to the mercury species, in which no evidence for interaction has been obtained. In the latter system, cyclopentylmethylmercury species have been observed but these are formed by the slow exchange shown in eqn. 3 and not by cyclization as shown by prolonged heating of the pentenyl-, hexenyl- and heptenyl-mercury derivatives in the absence of other metals.

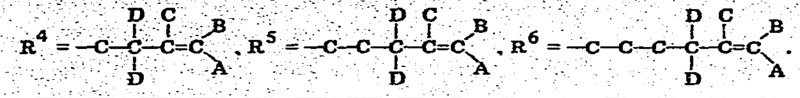


(3)

In an effort to provide additional information about the systems in which weaker interactions occur, i.e. the Group II metal derivatives, an investigation of their PMR spectra was undertaken. The results are listed in Tables 1—4 and the NMR parameters for the parent olefins are given in Table 5 to provide a reference. The NMR spectrum for 1-pentene has been determined to complete this sequence of compounds and is in full agreement with the approximately con-

TABLE 1

NMR PARAMETERS FOR ALKENYL DERIVATIVES OF CHLORINE, BROMINE AND IODINE[a]



	R^4Cl	R^5Cl	R^6Cl	$R^4Br^{b,c}$	R^4I^b	R^5I	R^6I
δ_A	5.11	5.01	4.97	5.090	5.069	5.03	4.96
δ_B	5.09	4.96	4.92	5.061	5.082	4.98	4.92
δ_C	5.81	5.78	5.79	5.765	5.728	5.75	5.78
J_{AB}	2.2	2.5	2.5	1.77	1.69	2.5	2.4
J_{AC}	16.9	17.4	17.4	17.11	17.1	17.4	17.3
J_{AD}	−1.1	−1.2	−1.3	−1.47	−1.49	−1.3	−1.3
J_{BC}	9.9	9.3	9.4	10.3	10.1	9.3	9.3
J_{BD}	−0.9	−1.1	−1.1	−1.19	−1.15	−0.9	−1.0
J_{CD}	7.0	6.1	6.2	6.67	6.63	6.1	6.2

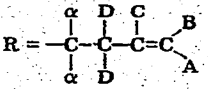
[a] Carbon tetrachloride solvent (~50/50 v/v) Positive values are downfield from TMS. [b] Computer simulated spectra. [c] Reference 7.

stant chemical shifts previously recorded for the vinyl protons of propene, 1-butene and 1-hexene [19]. These constant values for the chemical shifts establish the fact that the chain lenth has little influence on the olefin electronic environment. Substitution in the terminal position, however, alters the chemical shifts of the vinyl protons and, in general, a correlation with the electron-releasing or -withdrawing ability of the substituent exists. This can be established by examination of the data in Tables 1—4.

Di-4-pentenylzinc, however, exhibits anomalous behavior such that δ_β is shifted downfield with respect to the parent olefin. This behavior is contrary to

TABLE 2

NMR PARAMETERS FOR GROUP II METAL 3-BUTENYL COMPOUNDS[a]

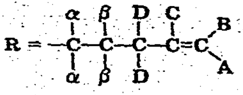


	R_2Mg^b	R_2Zn^c	R_2Hg^d
δ_A	4.761	4.940	4.976
δ_B	4.556	4.840	4.873
δ_C	5.895	5.938	5.888
δ_D	2.210	2.263	2.551
δ_α	−0.599	0.468	1.117
J_{AB}	2.78	1.92	2.00
J_{AC}	16.94	16.95	16.99
J_{AD}	−1.53	−1.72	−1.61
J_{BC}	9.89	10.09	10.07
J_{BD}	−1.19	−1.24	−1.24
J_{CD}	6.49	6.27	6.39
$J_{\alpha D}$	8.33	7.28	7.32

[a] Computer simulated spectra. Positive values are downfield from TMS. [b] Diethyl ether solvent. [c] Cyclopentane solvent (~50/50 v/v). [d] Carbon tetrachloride solvent (~50/50 v/v).

TABLE 3

NMR PARAMETERS FOR GROUP II METAL 4-PENTENYL COMPOUNDS[a]



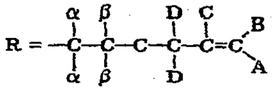
$R = -\overset{\alpha}{\underset{\alpha}{C}}-\overset{\beta}{\underset{\beta}{C}}-\overset{D}{\underset{D}{C}}-\overset{C}{C}=C\begin{smallmatrix}B\\A\end{smallmatrix}$

	R_2Mg[b]	R_2Zn	R_2Hg[c]	$R_2Zn{\cdot}DME$[d]	$R_2Zn{\cdot}2,2'$-bipy[e]
δ_A	4.84	4.98	4.92	4.95	4.80
δ_B	4.74	5.11	4.91	5.04	4.72
δ_C	5.84	5.74	5.75	5.79	5.78
δ_α	−0.58	0.21			0.07
J_{AB}	2.9	2.9	2.6	2.9	2.9
J_{AC}	17.2	15.9	17.9	15.2	17.3
J_{AD}	−1.4	−1.0	−1.3	−1.2	−1.4
J_{BC}	9.7	10.7	9.0	11.6	9.8
J_{BD}	−1.0	−1.0	−1.1	−1.0	−1.0
J_{CD}	6.3	6.4	6.3	6.5	6.4
$J_{\alpha\beta}$		7.0			7.8

[a] Cyclopentane solvent (~50/50 v/v) unless otherwise noted. Positive values are downfield from TMS. [b] Diethyl ether solvent. [c] Carbon tetrachloride solvent. [d] R_2Zn/DME molar ratio = 1.0. [e] R_2Zn/2,2'-bipy mole ratio = 1.0.

TABLE 4

NMR PARAMETERS FOR GROUP II METAL 5-HEXENYL COMPOUNDS[a]



$R = -\overset{\alpha}{\underset{\alpha}{C}}-\overset{\beta}{\underset{\beta}{C}}-C-\overset{D}{\underset{D}{C}}-\overset{C}{C}=C\begin{smallmatrix}B\\A\end{smallmatrix}$

	R_2Zn[a]	$R_2Zn{\cdot}DME$[a,b]	R_2Hg[c]
δ_A	4.92	4.91	4.92
δ_B	4.86	4.84	4.87
δ_C	5.78	5.79	5.77
δ_α	0.39	0.17	1.05
J_{AB}	2.6	2.6	2.6
J_{AC}	18.2	17.2	17.4
J_{AD}	−1.3	−1.3	−1.3
J_{BC}	9.8	9.6	9.3
J_{BD}	−1.0	−1.1	−1.1
J_{CD}	6.6	6.3	6.2
$J_{\alpha\beta}$	6.8	7.0	7.0

[a] Cyclopentane solvent (~ 50/50 v/v). Positive values are downfield from TMS. [b] R_2Zn/DME mole ratio = 1.0. [c] Carbon tetrachloride solvent (~50/50 v/v).

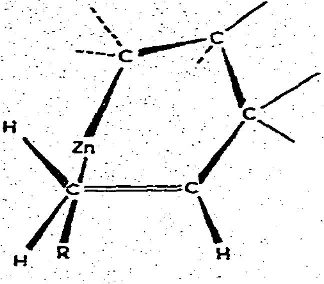
TABLE 5

NMR PARAMETERS FOR A SERIES OF 1-ALKENES[a]

	Propene[b]	1-Butene[b]	1-Pentene[c]	1-Hexene[b]
δ_A	4.963	4.939	4.945	4.941
δ_B	4.883	4.865	4.883	4.878
δ_C	5.734	5.780	5.733	5.724

[a] Computer simulated spectra. Positive values are downfield from TMS. [b] Ref. 19. [c] Cyclopentane solvent (~ 40% v/v).

the expected upfield shifts for an electropositive substituent. Along with other data this has been previously reported and interpreted in terms of a weak intramolecular interaction between the metal center and the terminal carbon as shown in II [12]. The interaction is interpreted in terms of a dipole—dipole association involving the polarized metal ($Zn^{\delta+}$) and the inherent dipole of the olefin [20, 21].



(II)

Di-3-butenyl- and di-5-hexenylzinc exhibit normal NMR parameters and the concept of metal—olefin association is not required to interpret their NMR parameters. Conceivably this is because the chain lengths are not appropriate to accomodate this ground-state interaction. Apparently the interaction does not stabilize the system sufficiently to overcome the strain energy involved to achieve the required conformation. A consideration of molecular models is consistent with this interpretation.

The extension of this research to the analogous compounds of magnesium and mercury provides further information regarding the requirements for the existence of the interaction. Di-4-pentenylmagnesium would presumably exhibit an interaction; however, the observation of this derivative in a two coordinate state has not been possible. The compound is insoluble in all solvents except coordinating solvents and by the very nature of the solvation, observation of the intramolecular interaction of interest is precluded. This behavior is quite similar to the 2,2′-bipyridine adduct of di-4-pentenylzinc [12].

The mercury derivatives, likewise, have been shown to be free of metal—olefin associations and this can be attributed to the lack of a sufficiently polar mercury—carbon bond.

In summary, the requirements for a ground state metal—olefin association and possible intramolecular cyclization appear to be: (1) a relatively strain-free conformation must be possible for the associated form (2) open coordination sites at the metal center and (3) a relatively polar metal—carbon bond.

Acknowledgements

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