Journal of Organometallic Chemistry, 376 (1989) 7–13
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20079

^{13}C NMR and Raman investigation of an intramolecular interaction between a zinc atom and a carbon–carbon triple bond in dihexyn-4-ylzinc

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(Received May 24th, 1989)

Abstract

Procedures to make the novel compounds of type $[CH_3C{\equiv}C(CH_2)_n]_2M$ (M = Hg, Zn and $n = 3, 4$) are described. The influence of the donor species on the ^{13}C NMR and Raman spectra of these compounds was examined. The low-temperature ^{13}C NMR spectra of hexyn-4-yl derivatives have been recorded. The presence of a relatively strong intramolecular ground state interaction between the zinc atom and the carbon–carbon triple bond in dihexyn-4-ylzinc has been confirmed.

In the case of both mercury compounds and diheptyn-5-ylzinc the experimental data did not indicate donation to a metal atom by π-orbitals of C≡C bonds.

Introduction

In typical organozinc compounds the ligands are bonded by two equivalent *sp*-hybrized molecular orbitals to the zinc atom. In this case there are two low-energy unoccupied *p* orbitals on a zinc atom which is coordinatively unsaturated and easily coordinates donors by intra- or inter-molecular complexation.

The ability of diorganozinc compounds having donor centres beyond the α position, to form intramolecular complexes depends on length of the carbon framework. The formation of five- or six-membered rings is preferred. Complexation by π-electron donors as well as by species containing π electrons is possible.

The structures of the complexes formulated as $Zn[(CH_2)_nX]_2$, where $n = 3$ or 4 for $X = OCH_3$ [1] and $n = 3$ for $X = N(CH_3)_2$, SCH_3 [2] and PPh_2 [3], were determined by gas electron diffraction or by X-ray crystallography. In these compounds the zinc atom occupies a *spiro* position and its surrounding is nearly square-planar for weak donors ($X = SCH_3$) or tetrahedral for stronger ones. Microwave titration of both oxygen compounds [4] indicates that the strength of the donor–acceptor bond is lower for $n = 4$, which suggests that a five-membered ring is more favourable than a six-membered ring.

0022-328X/89/$03.50

Three intramolecular organozinc complexes that show π-donation are known: dipenten-4-ylzinc [5–8], dibuten-3-ylzinc [8] and dihexyn-4-ylzinc [9]. Although an interaction between a zinc atom and C=C bond in dipenten-4-ylzinc was postulated on the basis of ^{1}H NMR [5,6] and ^{13}C NMR [7] studies there was no evidence of interaction in dibuten-3-ylzinc. On the other hand, gas electron diffraction data reveal the presence of an intramolecular complexation in both dialkenylzinc compounds [8]. In dipenten-4-ylzinc at least 80% of carbon chains are in a coiled-back conformation, to give a free energy of interaction $\Delta G^0 = -6$ kJ mol^{-1}, for dibuten-3-yl-zinc the obtained results are, 80% of the carbon chains are coiled back and $\Delta G^\circ = -4.5$ kJ mol^{-1}. For dihexyn-4-ylzinc an interaction between the zinc atom and the C≡C bond was present in the NMR as well as in the Raman spectra [9]. In compounds in which a zinc atom and a carbon–carbon multiple bond are separated by more than three methylene groups such as in dihexyn-5-ylzinc [5–7] and diheptyn-5-ylzinc [9], no interaction between these centres was observed, probably because of the large amount of strain energy required to form the associated complexes.

Here we describe the procedure to making dihexyn-4-yl and diheptyn-5-yl derivatives of mercury and zinc. A study of the influence of the type of donor and the temperature on the ^{13}C NMR and Raman spectra, as an extension of our preliminary studies [9], is also described.

Experimental

All operations with air-sensitive, organometallic compounds were carried out under dry, oxygen-free nitrogen on nitrogen–vacuum lines. All solvents were rigorously dried by distillation in the presence of complexes of potassium and sodium with benzophenone.

Spectroscopic studies

The ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. The compounds to be studied were in 30% cyclohexane solutions for measurements at room temperature and in 30% cyclopentane solutions for low-temperature recordings. Chemical shifts are referenced to solvent (for cyclohexane $\delta = 26.50$ ppm and for cyclopentane $\delta = 25.30$ ppm). The sealed tubes ($\varnothing = 8$ mm) containing the solutions were placed in tubes ($\varnothing = 10$ mm) filled with CH_3OD (for low-temperature measurements) or D_2O.

Raman spectra were recorded on a Coderg PHO spectrometer. The 30% cyclohexane solutions were placed in sealed, glass tubes.

Preparation of the compounds

Starting from either 1-bromo-3-chloropropane or 1-bromo-4-chlorobutane, 1-chlorohexyne-4 or 1-iodoheptyne-5, respectively, were prepared as described previously [10] and were characterized from their NMR and IR spectra. The purity of these derivatives was confirmed by gas chromatography.

Dihexyn-4-ylzinc was prepared in the following way (1):

Magnesium turnings (0.12 g-atom) in a reaction flask were heated for a few minutes and then cooled to room temperature in a stream of dry nitrogen. To the mixture was added 80 ml of THF. A portion (about 1/3 of the volume) of a mixture of 0.1 mol of 1-chlorohexyne-4 and 5 ml of 1,2-dibromomethane in 20 ml of THF was added to the reaction mixture, which was gently heated until the reaction started (other methods to activate the magnesium failed). Then the heating was stopped and the rest of the halide mixture was added dropwise at a rate so as to maintain gentle reflux. Once all the halide had been added, the mixture was refluxed for 2 h. Then 0.1 mol of mercuric chloride in 60 ml of THF was added dropwise during 1 h and the reaction mixture was refluxed for chloride solution which resulted in precipitation of organic salts. After filtration a two-phase liquid was obtained. Hexyn-4-ylmercury chloride was isolated from the brown greasy residue after removing the solvent from organic phase by periodic extraction with hexane. Each extract fraction was cooled to −70 ° C, filtered, and the solvent was recycled. Fine white crystals of the final product were obtained in 60% yield.

Dihexyn-4-ylmercury was prepared by the disproportionation of hexyn-4-ylmercury chloride using sodium stannite in the method developed by Nesmeyanov [11]. 0.04 mol of alkynylmercury halide placed in the reaction flask was dispersed in 125 ml of hexane and 200 ml of water and cooled to 0 ° C. 0.04 mol of $SnCl_2 \cdot H_2O$ in 125 ml of water was mixed with 0.54 mol of NaOH dissolved in 85 ml of water at 0 ° C. This mixture was added slowly (during about 1 h) to the reaction flask. The reaction mixture was stirred for 2.5 h at 0 ° C. After filtration the organic layer was separated and dried over $MgSO_4$. Dialkynylmercury was isolated by high vacuum distillation of the residue obtained after the removal of hexane from the organic layer. The final product was obtained in 85% yield and identified from its NMR and Raman spectra. The purity was confirmed by gas chromatographic.

Dihexyn-4-ylzinc was prepared by the transmetallation of dihexyn-4-ylmercury. An excess of zinc dust (0.115 g-atom) and 0.015 mol of dialkynylmercury were placed in a reaction flask fitted with a magnetic stirring bar and thermometer. The reaction was left to proceed for 10 h at 100 ° C. The pure organozinc compound was isolated from the reaction mixture by high-vacuum distillation in 80% yield. The product was identified from its NMR and Raman spectra. The purity was confirmed by elemental analysis and gas chromatography of the of hydrolysis product. Analysis: found Zn 28.50%, calcd. 28.75%.

Diheptyn-5-ylzinc was obtained by reaction 2:

$$2RI \xrightarrow[CH_3COOEt]{Hg/Na} R_2Hg \xrightarrow{Zn} R_2Zn \qquad (2)$$

$$R = (CH_2)_4C{\equiv}CH_3$$

Diheptyn-5-ylmercury was prepared by the procedure described by Frankland [12]. Sodium amalgam (2% of Na) was prepared in a reaction flask made in a shaker from 3.67 g-atom of mercury and 0.08 g-atom of sodium under dry nitrogen. Small pieces of sodium were added to the mercury in the flask and the mixture was shaked for a few minutes after each piece of Na was added. The mixture of 0.067 mol of 1-iodoheptyne-5 and 0.036 mol of ethylacetate was added batchwise to the reaction flask and mixture was shaken and cooled to 35–50 ° C after each portion had been added. The reaction mixture was shaken for 2 h at room temperature after all the reactants had been added. Then the reaction mixture was hydrolyzed with water to give three layers: metallic mercury, water, and an organic layer. The organic layer, containing the crude product, that was separated off was found to contain about 10% of a by-product, viz., 2,12-tetradecadiyn (identified from its NMR spectra).

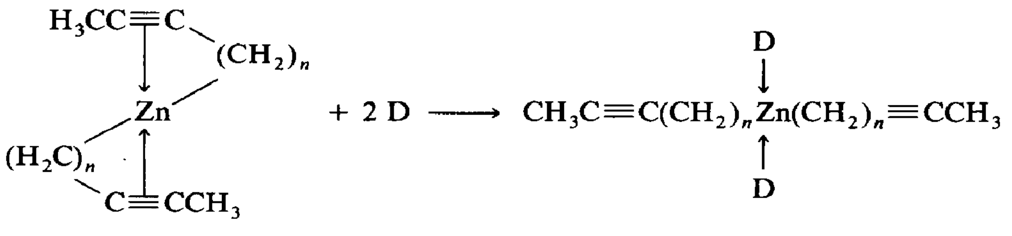
We have established that the yield of the by-product increased with rise in temperature, as well as with an increase in the molar ratio Na : RI. The best results were obtained for an Na : RI ratio of 0.5 : 1 at a temperature of 35–40 ° C. Mercury and the water layer were extracted three times with 15-ml portions of hexane, which were then added to the crude product. The hexane solution was dried over $MgSO_4$. After filtration the hexane was removed from the product. The product was purified by distillation in a vacuum system followed by vacuum transport to a trap cooled in liquid nitrogen. Diheptyn-5-ylmercury solidified at the bottom while 2,12-tetradecadiyn crystallized in the upper part of the trap. The bottom of the trap was heated to 10 ° C, the melting point of the organomercury compounds so that it could be separated from the by-product which is still solid at this temperature. Diheptyn-5-ylmercury was transferred by pipette to another flask. The product was obtained in 60% yield and identified from its NMR and Raman spectra. The purity was confirmed by gas chromatography.

Diheptyn-5-ylzinc was obtained in a 85% yield by the transmetallation of diheptyn-5-ylmercury by a procedure analogous to that described for dihexyn-4-ylzinc. The product was identified by NMR and Raman spectra. The purity was confirmed by elemental analysis and gas chromatography of the hydrolysis product. Analysis: found Zn 25.41%, calcd. 25.61%.

Results and discussion

In a previous paper [9] we demonstrated that ^{13}C NMR parameters and Raman spectra of dihexyn-4-ylzinc showed an intramolecular interaction between the zinc atom and the π orbitals of the C≡C bond. The C(α) signal was shifted upfield relative to that of the C(α) in dialkylzinc, which is in accord with the effect of complex formation between dialkylzinc and a donor [4]. The signals of the carbon atoms of C≡C bonds are shifted downfield relative to the position of the signals from analogous carbon atoms in simple alkyne-2. In the Raman spectra of dihexyn-4-ylzinc ν(C≡C) occurs at a lower position than that in the spectra of the parent alkyne, and is attributed to the attraction of π-electrons by the zinc atom.

In the present work we studied the influence of various donor groups on ^{13}C NMR and Raman spectra of hexyn-4-yl derivatives of zinc, mercury, chloride and of diheptyn-5-ylzinc. In the case of π-complexes, the addition of strong n-electron donors should cause the replacement of an alkynyl group by a donor D (eq. 3) in the coordination sphere of the zinc atom, and return of the spectral parameters to values expected for non-interacting compounds.



$$\mathrm{+\ 2\,D \longrightarrow CH_3C{\equiv}C(CH_2)_n\underset{\underset{D}{\uparrow}}{\overset{\overset{D}{\downarrow}}{Zn}}(CH_2)_n{\equiv}CCH_3}$$

(3)

Table 1

The influence of the donors [a] on the chemical shifts of the carbon atoms [b] of hexyn-4-yl derivatives of zinc, mercury and chloride and of diheptyn-5-ylzinc

Compound	Donor	C(α)	C(χ)	C(ψ)
dihexyn-4-ylzinc	–	11.93	83.00	80.00
	Et_2O	11.89	82.93	79.99
	Et_3N	11.86	82.81	79.56
	pyridine	11.31	82.16	75.50
diheptyn-5-ylzinc	–	14.53	79.59	75.67
	pyridine	11.07	80.57	74.09
dihexyn-4-ylmercury	–	40.28	81.45	77.08
	pyridine	40.31	81.64	77.33
1-chlorohexyne-4	–	43.41	77.13	76.22
	pyridine	43.85	77.41	76.49

[a] Donors were added in molar ratio D:R = 1:1 (D = donor, R = alkynyl group). [b] The carbon atoms were numbered thus, $\overset{\alpha}{C}H_2(CH_2)_{n-1}\overset{\chi}{C}{\equiv}\overset{\psi}{C}CH_3$.

The ^{13}C NMR data are listed in Table 1. There is very weak effect by the addition of Et_2O and Et_3N to dihexyn-4-ylzinc on the ^{13}C NMR parameters of this compound. The change in the position of the signals is attributable to a change in the polarity of the solutions, and confirms the lack of complexation to dihexyn-4-ylzinc by these donors. Pyridine causes significant changes in the spectra of both dialkynylzinc compounds and displayed only small effects in the spectra of mercury and chloride compounds. For both dialkynylzinc compounds the effects observed after the addition of pyridine, though qualitatively different, may be explained in terms of complex formation with pyridine, which confirms the presence of an intramolecular π bond in dihexyn-4-ylzinc and the lack of intramolecular π interactions in diheptyn-5-ylzinc.

In the case of diheptyn-5-ylzinc complexed by pyridine there is a strong increase in the shielding of C(α) owing to the displacement of the electron pair of the Zn–C(α) bond in the direction of C(α). Such behaviour is characteristic for complexes of simple dialkylzinc with donor and confirms the lack of π interaction in diheptyn-5-ylzinc. Changes in positions of the signals of carbon atoms of C≡C bond are small and are probably caused by a transfer of the polarizing effect from C(α) by the carbon framework.

In the spectra of dihexyn-4-ylzinc complexed by pyridine very small upfield shift of the signal of C(α) and strong changes in positions of carbon atoms of C≡C bond to higher field are observed. The small effect on C(α) reflects the lack of the changes in the coordination sphere of zinc atom after complexation by pyridine: if a weak electron donor—an alkynyl group—is replaced by a stronger donor—pyridine—a small increase in the shielding of C(α) is observed. The complexation by pyridine breaks the zinc–C≡C bond interaction and the π-electron density in the alkynyl group is enhanced. The electron environment of carbon atoms of the C≡C bond becomes similar to that in non-interacting alkynyls.

The results discussed above indicate that interactions between the zinc atom and the carbon–carbon triple bond in dihexyn-4-ylzinc, are stable in the presence of Et_2O and Et_3N, and are broken only by strong electron donors, such as pyridine.

Table 2

Triple carbon–carbon bond stretching frequencies of hexyn-4-yl and heptyn-5-yl derivatives of zinc and mercury and of reference compounds

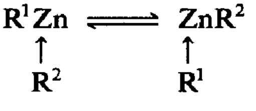
Compound	Donor	$\nu(C{\equiv}C)$ (cm^{-1})	
dihexyn-4-ylzinc	–	2220	2287
	Et_2O	2220	2287
	pyridine	2227	nv [a]
dihexyn-4-ylmercury	–	2231	2296
	pyridine	2228	nv [a]
1-chlorohexyne-4	–	2238	2306
	pyridine	2235	nv [a]
diheptyn-5-ylzinc	–	2235	2305
	pyridine	2234	2304
diheptyn-5-ylmercury	–	2236	2305
butyne-2 [b]	–	2236	2313
$RC{\equiv}CCH_3$ (R = n-alkyl) [b]		2239–2233	2316–2300

[a] Signals not detected because of fluorescence. [b] Ref. 13.

The influence of electron donors on $\nu(C{\equiv}C)$ stretching in the investigated compounds is presented in Table 2. It follows from the data obtained that only the addition of pyridine to dihexyn-4-ylzinc causes significant changes in the stretching frequency of the C≡C bond. The signal of the C≡C bond in this case is shifted to higher frequencies with respect to the signal from the non-uncomplexed compound, which implies increased bond strength. This observation is consistent with the effect expected for replacement of the C≡C bond with pyridine in the coordination sphere of the zinc atom. After complexation by pyridine the $\nu(C{\equiv}C)$ stretching is closer to the values characteristic for simple alkynes-2. That Et_2O has no effect on the Raman spectra of dihexyn-4-ylzinc, which indicates the stability of the π interactions in this compound in the presence of this donor. Small effects by the added donors on the $\nu(C{\equiv}C)$ stretching in other compounds are attributable to the changes in the polarity of the solutions. It is clear that the conclusions drawn from Raman spectra are consistent with those arising from the ^{13}C NMR spectra.

Further information about the stability of π interaction in dihexyn-4-ylzinc has been obtained from low-temperature ^{13}C NMR data. The spectra of dihexyn-4-ylzinc and dihexyn-4-ylmercury were measured at $-30°$, $0°C$, and room temperature (Table 3). The changes in the positions of the signals are not significant and are in the same direction as those for the analogous carbon atoms of both compounds. The effects are attributable to the increase in viscosity of the solutions. In conclusion, the interaction in dihexyn-4-ylzinc is so strong that at room temperature most if not all molecules have formed double intramolecular associations.

The Raman and low-temperature ^{13}C NMR data indicate that both the alkynyl groups of dihexyn-4-ylzinc simultaneously interact with the zinc atom. In the Raman spectra only one signal corresponding to the C≡C bond stretching is observed. In the ^{13}C NMR spectra of this compound measured at $-30°$ neither splitting nor broadening of the signals was observed. These facts exclude the dynamic equilibrium between the interacting alkynyl groups (4).



$$\underset{\overset{\uparrow}{R^2}}{R^1Zn} \rightleftharpoons \underset{\overset{\uparrow}{R^1}}{ZnR^2} \qquad (4)$$

Table 3

The influence of temperature on the ^{13}C NMR data for dihexyn-4-ylzinc and dihexyn-4-ylmercury

$R = -\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\chi}{C}\equiv\overset{\psi}{C}-\overset{\omega}{C}H_3$

Compound	Temperature (°C)	C(α)	C(β)	C(γ)	C(χ)	C(ψ)	C(ω)
R_2Zn	room	10.89	27.07	22.85	81.86	78.83	2.89
	0	10.64	27.27	22.67	81.93	79.10	3.13
	−30	10.58	27.30	22.64	81.94	79.10	3.17
Δδ [a]		0.31	−0.23	0.21	−0.08	−0.27	−0.28
R_2Hg	room	39.22	28.84	21.97	80.48	76.15	2.73
	0	38.59	28.99	21.71	80.70	76.38	2.58
	−30	38.45	29.02	21.65	80.75	76.43	2.61
Δδ [a]		0.77	−0.18	0.32	−0.27	−0.28	−0.24

[a] Δδ = difference between the chemical shifts of the signal, measured at room temperature and at −30°, respectively.

In summary, there is a relatively strong ground-state intramolecular interaction between the zinc atom and C≡C bond in dihexyn-4-ylzinc. This interaction is stable in the presence of Et_2O and Et_3N, but is broken by strong electron donors such as pyridine. Both alkynyl groups have a coiled-back conformation.

Acknowledgement

The authors thank the Institute of Low temperatures and Structural Investigations of the Polish Academy of Sciences for financial support of this work.

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