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An intramolecular interaction between a zinc atom and a carbon–carbon triple bond in dihexyn-4-ylzinc

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Abstract

The new dialkynylmercury and dialkynylzinc compounds $[CH_3C{\equiv}C(CH_2)_n]_2M$ ($M = Hg$, Zn and $n = 3, 4$) have been synthesized. The presence of a ground-state intramolecular interaction between the zinc atom and a carbon–carbon triple bond in dihexyn-4-ylzinc was confirmed from ^{13}C NMR, ^1H NMR, and Raman spectra.

From the data there was no indication of a π-contribution to the metal atom by the $C{\equiv}C$ bond, in either mercury compound, or in diheptyn-5-ylzinc.

Synthesis of new alkynyl derivatives of mercury and zinc as well as spectral investigations were undertaken in order to provide evidence of intramolecular interactions between the metal atom and the carbon–carbon triple bond in these compounds.

Dihexyn-4-ylmercury- II, diheptyn-5-ylmercury- V, dihexyn-4-ylzinc- III, and diheptyn-5-ylzinc- VI, were synthesized according to Scheme 1.

We expected a metal to carbon–carbon triple bond interaction in dihexyn-4-ylzinc (III), a compound analogous to dipenten-4-ylzinc for which Oliver et al. proposed an intramolecularly associated form in which a zinc atom interacts weakly with the olefinic centre [1,2].

We demonstrated the presence of a zinc to carbon–carbon triple bond interaction in III on the basis of ^{13}C NMR and Raman spectra. The effects observed in ^1H NMR spectra were consistent with ^{13}C NMR results. They were however much weaker and therefore they are not discussed here.

In the ^{13}C NMR spectra, chemical shifts of the signals due to the carbon atoms in the α position vary with type of substituent (cf. Table 1).

Comparative analysis of the signals of diheptyn-5-ylzinc (VI) and dipentylzinc shows that the electronic environments of the $C(\alpha)$ atoms are similar. It also follows that in dihexyn-4-ylzinc (III) the $C(\alpha)$ atom has much more negative charge, which can be seen as being the result of the presence of a donor $C{\equiv}C$ bond in the coordination sphere of the zinc atom in III.

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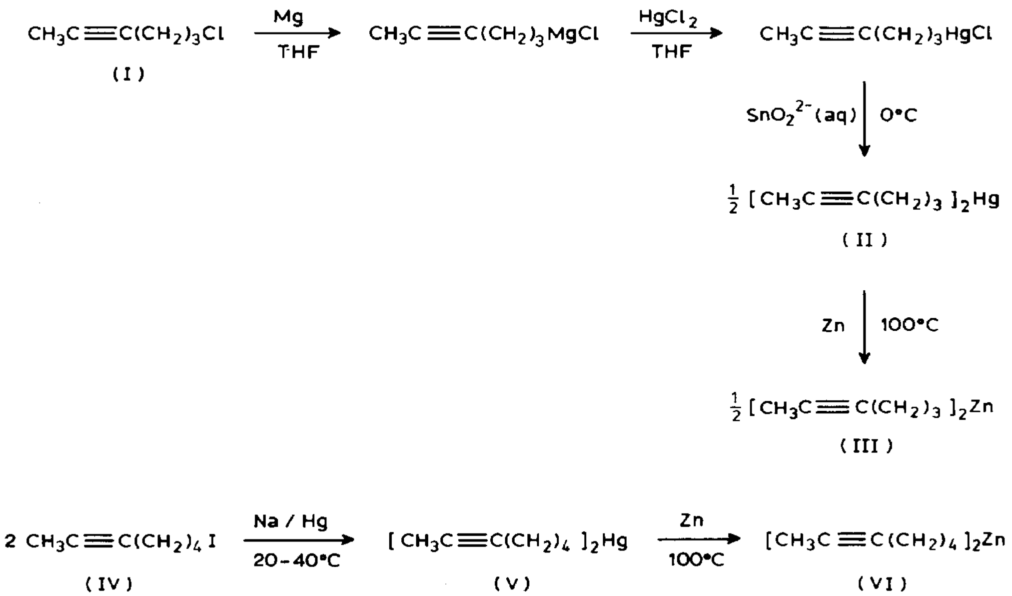

Scheme 1. Synthesis of dialkynyl derivatives of mercury (II and V) and of zinc (III and VI).

The influence of the substituents on the chemical shifts of the signals due to the carbon atoms of C≡C bond in the hexyn-4-yl derivatives (I–III) is significant, especially for dihexyn-4-ylzinc (III), whereas for the heptyn-5-yl compounds (IV–VI) it is much weaker. This influence is consistent with the electron-donating or -attracting ability of the substituent. The relatively large effect in III indicates that apart from a polarizing influence by zinc in the δ position there is also an interaction between the zinc atom and the C≡C bond. This conclusion is supported by Raman spectra (cf. Table 2).

There is no influence by the substituent on the ν(C≡C) frequency for heptyn-5-yl derivatives (IV–VI). For the hexyn-4-yl compounds I and II the influence is weak. In the case of III, the C≡C bond stretching frequency is shifted about 14 cm^{-1} to lower field with respect to the parent alkyne. This is because of the attraction to π-electrons by the zinc atom.

Table 1

^{13}C NMR parameters for the compounds $[CH_3C{\equiv}C(CH_2)_n]_2M$ [a] (M = Hg, Zn and $n = 3, 4$), their halogen derivatives [a], and for the reference compounds, dipentylzinc [a] and octyne-2 [b]

Compound [c]	C(α)	C(1)	C(2)
dihexyn-4-ylzinc	11.93	83.00	80.00
dihexyn-4-ylmercury	40.28	81.45	77.08
chlorohexyne-4	43.41	77.13	76.22
diheptyn-5-ylzinc	14.53	79.59	75.67
diheptyn-5-mercury	43.85	79.26	75.04
iodoheptyne-5	4.37	77.67	75.40
dipentylzinc	14.36	–	–
octyne-2	–	79.20	75.20

[a] Measured in cyclohexane. [b] Measured in dioxane [3]. [c] The carbon atoms were numbered thus: $CH_3\text{-}\underset{2}{C}{\equiv}\underset{1}{C}\text{-}(CH_2)_{n-1}\text{-}\underset{\alpha}{C}H_2\text{-}$.

Table 2

Triple bond stretching vibration frequencies for the compounds $[CH_3C{\equiv}C(CH_2)_n]_2M$ (M = Hg, Zn and $n = 3, 4$), their halogen derivatives, and hexyne-2 [a]

Compound		$\nu(C{\equiv}C)$ (cm^{-1})
dihexyn-4-ylzinc	2220	2287
dihexyn-4-ylmercury	2231	[b]
chlorohexyne-4	2238	2306
diheptyn-5-ylzinc	2235	2305
diheptyn-5-ylmercury	2236	2305
hexyne-2	2234	2300

[a] Measured in cyclohexane. [b] Not visible.

These results show that there is interaction between a zinc atom and a carbon–carbon triple bond in dihexyn-4-ylzinc III, an interaction which is stronger than that in dipenten-4-ylzinc [1], for which no effects were observed in the IR spectra. Lack of evidence for metal to C≡C bond interactions in diheptyn-5-ylzinc (VI) confirms the intramolecular character of the interactions in III (in the case of VI an energetically unfavourable seven-membered ring would have to be formed).

Mercury compounds II and V have normal spectra and hence the interpretation of the corresponding spectral data in terms of metal–alkynyl association is not necessary.

References

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