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Reactions of Copper(I) and Zinc(II) Halides with Phenylacetylene

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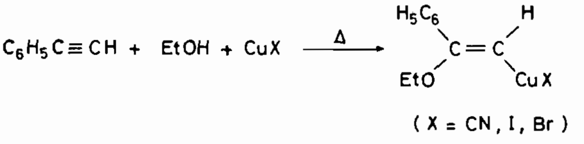
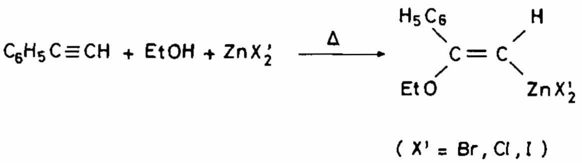
Two recent reports [1, 2] about the acetylenic π-bonding to copper(I) halides have prompted us to communicate some of our preliminary results on the reactions of phenylacetylene with copper(I) and zinc(II) halides.



$C_6H_5C{\equiv}CH + EtOH + CuX \xrightarrow{\Delta} C_6H_5(EtO)C{=}CH(CuX)$

(X = CN, I, Br)



$C_6H_5C{\equiv}CH + EtOH + ZnX'_2 \xrightarrow{\Delta} C_6H_5(EtO)C{=}CH(ZnX'_2)$

(X' = Br, Cl, I)

We had shown that the triple bond of disubstituted acetylenes is involved in pπ–dπ interaction with the central metal atom [1, 2]. However, the present work reveals that this interaction is not possible with phenylacetylene under the above experimental conditions. The analytical data (Table I) show that the ν(C≡C) absorption is absent in the infrared spectra of all the complexes. The presence of a strong band at the 1620–1640 cm^{-1} range is indicative of an olefinic bond. The absorption frequency of the acetylenic hydrogen bond, which usually appears at 3300 cm^{-1} as a sharp band in the IR spectrum of phenylacetylene, shifts to the 3400–3420 cm^{-1} region as a broad band in all the complexes. The characteristic ν(C–H) asymmetrical and symmetrical absorptions for the ethyl group occur at 2950 cm^{-1} and 2850 cm^{-1}, respectively. The addition products are characterised further by their ^{1}H NMR and UV absorptions. In the ^{1}H NMR spectra, a sharp band at δ 7.5 ppm corresponds to the resonance position of the aromatic ring protons. The ethyl protons resonate at δ = 2.9–2.6, while the olefinic proton has δ = 1.8 (relative to TMS). UV absorption bands are shown in Fig. 1. Phenylacetylene, as the figure indicates, has no characteristic UV absorption, but upon complexation the products absorb in this region. Puddephatt *et al.* [3] has

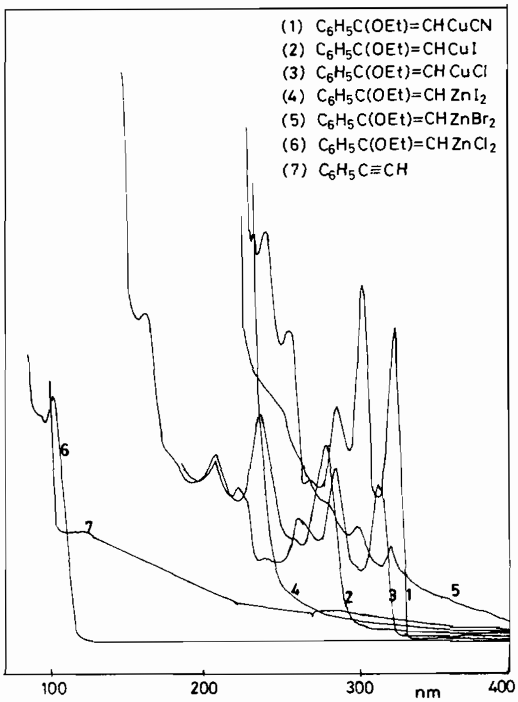


Fig. 1. UV Spectra of phenylacetylene complexes with Cu(I) and Zn(II) halides.

TABLE I. Analytical Data and Physical Properties of the Adducts of Phenylacetylene and Cu(I), Zn(II) Halides

Compound	Melting point (°C)	ν(C≡N)	ν(C=C)	ν(C–H)	Molecular weight	
					Found	Calc.
$C_6H_5C(OEt){=}CHCuCN$	261	2120	1630	3400	230.3	236.5
$C_6H_5C(OEt){=}CHCuBr$	255		1638	3410	287.1	290.4
$C_6H_5C(OEt){=}CHCuI$	253		1635	3420	341.5	337.4
$C_6H_5C(OEt){=}CHZnBr_2$	262		1635	3400	405.3	401.8
$C_6H_5C(OEt){=}CHZnCl_2$	270		1630	3410	280.5	283.4
$C_6H_5C(OEt){=}CHZnI_2$	260		1633	3410	462.5	466.2

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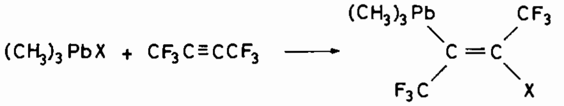
reported the possibility of an addition reaction between 3,3,3-trifluoropropyne and trimethyllead methoxide:

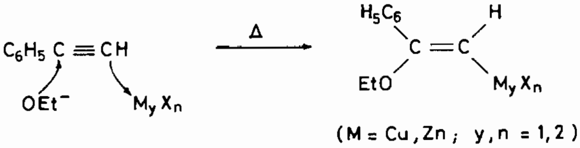
$$(CH_3)_3PbOCH_3 + CF_3C{\equiv}CH \longrightarrow (CH_3)_3PbC(CF_3){=}CHOCH_3$$

An analogous reaction was reported between trimethyllead dimethylamide and 3,3,3-trifluoropropyne [5]. A *trans*-addition across the triple bond was supposed to occur:



In the above addition reactions, an ionic mechanism was assumed to have occurred, and spectroscopic evidence revealed the presence of substitution products [4, 5].

The major point of interest in the work reported here is that a terminal acetylene having no heteroatom as a substituent reacts with copper(I) and zinc(II) halides in a synchronous four-centre transition state mechanism resulting in an addition product; no by-product could be identified.



References

1 A. C. Ukwueze and S. R. Landor, *Spectrochim. Acta, Part A, 40,* 5, 433 (1984).
2 A. C. Ukwueze and S. R. Landor, *Synth. React. Inorg. Met.-Org. Chem., 14,* 7; 1013 (1984).
3 R. J. Puddephatt and G. H. Thistlethwaite, *J. Organomet. Chem., 40,* 143 (1972).
4 A. G. Davies and R. J. Puddephatt, *J. Chem. Soc., C,* 317 (1968).
5 W. P. Neumann and K. Kuhlein, *Adv. Organomet. Chem., 7,* 241 (1968).