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Interaction of Copper and Silver Alkynylides with Tertiary Phosphines

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The insolubility of alkynyl–copper and silver compounds in non-coordinating solvents has been cited by several authors as being an argument for a polymeric structure arising from intermolecular interaction of filled copper or silver d-orbital with antibonding π-orbitals of the acetilenic group [1].

Indeed, X-Ray analysis of $[Cu(C{\equiv}CPh)]_x$ indicates the presence of infinite zig-zag chains of copper atoms lying roughly in one plane. The phenylethynyl group seems to be σ-bonded to one copper atom, symmetrically π-bonded to a second one and asymmetrically π-bonded to a third copper atom [2].

These complexes all react with ligands such as ammonia and the tertiary phosphines. The ligands serve to de-polymerize the complexes by replacement of intermolecular π-bonds, forming complexes such as $(LMC{\equiv}CR)_n$, (L = amines, or tertiary phosphines; M = Cu, Ag) [3]. Cryoscopic studies suggest that the complexes have varying degrees of association. Most of them have PMe_3 as ligand and PPh_3 is used more or less as an extension. Only $PhC{\equiv}CCu{\cdot}PPh_3$ and p-$NO_2C_6H_4C{\equiv}CCu\ PPh_3$ have been reported previously [4].

Compounds of the type $CuC{\equiv}CR(PR_3)$ reported in the literature are stable only for a short time (1 or 2 days) and the tertiary phosphine complexes of silver ethynyls are sensible to light and air, so that they have not been studied extensively [5, 6].

Here we describe the reaction of some ethynyl complexes of Cu(I) and Ag(I) with $P(n\text{-}But)_3$, PEt_3 and PPh_3. The purpose of the study was to determine the degrees of association of these adducts in chloroform. We wanted to know if the complexes contain less associated species due to the addition of the tertiary phosphine.

Experimental

The preparation of the alkynyl–copper and silver compounds of cyclohexilethyne H(CHE), p-diethynylbenzene $H_2(p\text{-DEB})$ and octyne H(HE) have been reported in a previous publication [7]. The phosphines were obtained commercially. All reactions were carried out under nitrogen atmosphere. Organic solvents were purified by conventional methods and were saturated with nitrogen before use.

Microanalyses for C and H were carried out with a microanalytical Hewlett-Packard 185. Phosphorus was analyzed by an Elemental Micro-Analysis Laboratory. IR spectra were recorded on a Perkin Elmer 325 spectrophotometer with nujol mulls and KBr disks. Magnetic susceptibilities were determined by the Gouy method. Molecular weight determinations were performed with a Knawer Osmometer, using chloroform as solvent. Copper was determined by complexometry, and silver gravimetrically as chloride.

The adducts with $P(n\text{-}But)_3$ and PEt_3 were prepared by adding an equimolar amount of metal alkynylide to a magnetically-stirred solution of the phosphine in benzene. After additional stirring till all solid was dissolved the mixture of reaction was filtered and benzene was removed *in vacuo*. In all cases colored oils were isolated for copper compounds, and colourless oils for silver compounds.

The adducts of the same metal alkynylide with PPh_3 were prepared by mixing the starting compound and the phosphine in CCl_4 in molar ratios of 1:1 and 1:2. After stirring the copper derivatives yielded a microcrystalline powder which was then filtered, washed with ethanol and ethilic ether and dried under vacuum. The solvent of the mixture reaction of the silver derivatives was removed *in vacuo*. The solid residues were washed repeatedly with ethanol, filtered and dried. Tables I and II correlate all the isolated compounds.

Results and Discussion

We obtained a series of compounds of the type $RC{\equiv}CM{\cdot}(PR''_3)_x$ and $R'C{\equiv}CM_2(PR''_3)_x$ ($R = CH_3(CH_2)_5$, C_6H_{11}; $R' = C_6H_5(C{\equiv}C)$; $R'' = CH_3CH_2$, $CH_3(CH_2)_3$, C_6H_5; M = Cu, Ag) by reaction of the correspondent metal alkynylide with the phosphine in several molecular rates.

The reaction of the metal alkynylide with PPh_3 leads to a formation of solids adducts, with a 1:1 and 1:2 metal alkynylide: phosphine stoichiometry. The copper compounds are diamagnetic, which confirms the presence of Cu(I). The compounds are colored and soluble in organic solvents such as $CHCl_3$, CCl_4, and ethilic ether. Only $M_2(p\text{-DEB})(PPh_3)_2$ (M = Cu, Ag) and $HECu(PPh_3)_2$ are insoluble in any solvent.

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TABLE I. Analytical IR Spectra and Degree of Association Data of the Aryl Phosphine Complexes.

Empirical formula of the compound	Colour	Degree of association[a]	$\nu(C{\equiv}C)$ (cm^{-1})[b]	Analyses %[c]				Yield %
				M	C	H	P	
Cu_2p-DEB$(PPh_3)_2$	brown	i	2145w	16.38	71.20	4.72	7.90	90%
		(i)	(1920w)	(16.37)	(71.13)	(4.51)	(7.98)	
CuHe(PPh_3)	green	i		14.89	71.46	6.24	7.31	80%
		(i)		(14.62)	(71.80)	(6.44)	(7.12)	
CuHE$(PPh_3)_2$	white	1.06	2116s*	9.09	75.46	6.80	8.88	80%
		(i)	(1922w) (1930m, 1958m)*	(9.12)	(75.80)	(6.17)	(8.89)	
CuCHE(PPh_3)	green-yellow	1.02	2020w	14.65	72.30	5.56	7.76	85%
		(8.50, 5.36)	(2164m)	(14.69)	(72.13)	(6.01)	(7.16)	
CuCHE$(PPh_3)_2$	light yellow	0.99	2040w, 2025w	9.14	76.10	5.56	8.76	80%
		(8.50, 5.36)	(2164m)	(9.14)	(76.02)	(5.90)	(8.91)	
Ag_2p-DEB$(PPh_3)_2$	yellow	i	2020br	24.98	63.89	4.10	7.25	90%
		(i)	(2030m)	(24.86)	(63.83)	(4.04)	(7.16)	
AgHE(PPh_3)	brown	0.92	2070w	22.50	65.01	5.83	6.16	30%
		(3.00)	(2060m, 2040m)	(22.53)	(65.16)	(5.85)	(6.47)	
AgHE$(PPh_3)_2$	beige	0.75	2109w	14.56	71.00	6.00	8.38	30%
		(3.00)	(2060m, 2040m)	(14.56)	(71.35)	(5.80)	(8.36)	
AgCHE(PPh_3)	beige	0.91	2040br	22.61	65.41	5.50	6.50	50%
		(4.50)	(2028m, 1965s)	(22.70)	(65.55)	(5.46)	(6.50)	
AgCHE$(PPh_3)_2$	beige	0.71	2060sh, 2030m	14.57	71.45	5.00	8.28	45%
		(4.50)	(2028m, 1965s)	(14.60)	(71.46)	(5.55)	(8.38)	

[a,b] Values of starting metalalkynylide compounds are given in parentheses; i = insoluble; M = Cu, Ag. [c] Calculated values are in parentheses. *Obtained by Raman.

TABLE II. Colour and $\nu(C{\equiv}C)$ Stretching Frequencies of the Alkyl Phosphine Complexes.

Empirical formula of the compound	colour	$\nu(C{\equiv}C)$ (cm^{-1})
Cu_2p-DEB(PEt_3)	brown-gray	2050vs, 2090w, 2145w
Cu_2p-DEB P(n-But$)_3$	brown-gray	2090w, 2140br
CuHE(PEt_3)	brown-gray	2050w
CuHE P(n-But$)_3$	brown-gray	2065w, 2045m, 2025w
CuCHE(PEt_3)	green-yellow	2046m, 2020w
CuCHE P(n-But$)_3$	green-yellow	2040w, 2020w
Ag_2p-DEB(PEt_3)	yellow	2080m, 2060m
Ag_2p-DEB P(n-But$)_3$	yellow	2040m
AgHE(PEt_3)	brown	2070s
AgHE P(n-But$)_3$	brown	2070w, 2020vw
AgCHE(PEt_3)	colourless	2090vw
AgCHE P(n-But$)_3$	colourless	2098vw

Comparing the results of the association degree obtained in chloroform, for $RC{\equiv}CM(PPh_3)_x$ (R = $CH_3(CH_2)_5$, C_6H_{11}) compounds with the data of the correspondent alkynylides (Table I) shows that PPh_3 breaks the intermolecular interactions present in the original alkynylide when it is bonded to the metal.

Thus the majority of the adducts of PPh_3 are largely monomeric species in chloroform, whereas the metal alkynylides show values of association degree within 3 and 8.5 in this solvent.

The obtained compounds are air-stable for several weeks either in solution or in solid state. Also they show a great thermic stability: *e.g.* Pattern copper and silver derivatives of *p*-diethynylbenzene have lost their explosive and pyrophoric character and do not explode on heating by coordination to phosphine.

The IR spectra of the complexes differ from the starting metal alkynylides, showing the movement and splitting of ν(P–C) and δ(P–C) bands which are in accord with a coordination of the phosphine to the metal [8]. The majority of the bands related to the organic radical bonded to the ethylenic group could be not seen because of the coincidence of these bands with those of the phosphine that lies in the same range and are greater in intensity. The ν(C≡C) of the metal alkynylide as it would be expected is shifted to higher frequencies in the complexes. In the metal alkynylides the intermolecular interaction decreases the C≡C order bond that leads to a lowered value of ν(C≡C); when PPh_3 ligand breaks these interactions, the order bond increases as does ν(C≡C). This fact indicates that the PPh_3 constitutes a suitable ligand, capable of breaking the intermolecular bonds of the polymeric metal alkynylide leading to compounds with great stability and in general with high solubility.

Nevertheless, the adducts of the above metal alkynylides with alkyl phosphines are all oils and no solid could be isolated (Table II). The products obtained $RC{\equiv}CM(PR''_3)_x$ ($R'' = CH_3CH_2, CH_3(CH_2)_3$) have a good stability in N_2 atmosphere, but they lost phosphine by exposure to air, depositing the starting material. This enables us to measure their association. Here again the IR spectra indicate that phosphine is P-bounded. The complexes all show a shift of the ν(C≡C) bands to higher values, similar to that observed in PPh_3 adducts. These shifts suggest also that the intermolecular bonds of this adduct have been broken.

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