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Reactions of Asymmetrical Organomercury Compounds of the Type $PhC{\equiv}CHgX$ ($X = Cl, CN$) with Tertiary Phosphines

E. DELGADO, M. CANO

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, Madrid -3, Spain

and A. SANTOS*

Instituto de Química Inorgánica 'Elhúyar', Consejo Superior de Investigaciones Científicas, Serrano, 113 bis, Madrid-6, Spain

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This work describes the reactions of asymmetrical alkynyl mercury compounds of general formula $PhC{\equiv}CHgX$ *(*$X = Cl, CN$*) with tertiary phosphines* PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, PBu_3 *and* $Ph_2PCH_2{\cdot}CH_2PPh_2$ *(dppe), which lead to symmetrization products (for* $X = CN$ *and monodentate phosphines and* $X = Cl$ *and dppe) or formation of adducts (for* $X = Cl$ *and* PPh_3 *or* PPh_2Et *and* $X = CN$ *and dppe). The reactions were studied on the basis of analytical and infrared spectral data of the isolated compounds. The preparation of a new compound* $PhC{\equiv}CHgCN$ *and the physical properties and* ^1H*-NMR-, infrared- and mass spectra of both asymmetrical starting compounds are also described.*

Introduction

The low tendency of the organomercury compounds to increase their coordination number by interaction with donor molecules [1–5] is well known, and it is accepted that a greater electronegativity of the groups bonded to metal increases acceptor capacity [6, 7]. Consequently, it can be expected that the asymmetrical derivatives of the type $PhC{\equiv}CHgX$ ($X = Cl, CN$) show an acceptor capacity intermediate between that of $(PhC{\equiv}C)_2Hg$ and those of the HgX_2 compounds. To date only a $PhC{\equiv}CHgX$ compound ($X = Cl$) has been described: for this reason we have considered it interesting to obtain new compounds of the type $PhC{\equiv}CHgX$, and to investigate coordinative ability against P-donor ligands. In this case we expected a relatively strong interaction Hg–P, owing to the soft nature of both atoms. On the other hand the tendency of some tertiary phosphines to give symmetrization reactions with organomercury compounds of the type RHgX is known [8]. This is the case of PhHgCl and PhHgCN, recently investigated by us [9].

The two possible reaction routes earlier mentioned have motivated our study on reactions of asymmetrical alkynyl compounds of the type $PhC{\equiv}CHgX$ ($X = Cl, CN$) with a series of tertiary phosphines: PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, PBu_3 and dppe.

Experimental

Materials

PPh_3, PBu_3 (Merck), PPh_2Et, $PPhEt_2$, PEt_3 and dppe (Maybridge) are commercially available in A.R. purity.

$PhC{\equiv}CHgCl$ was prepared according to the procedure previously described [10].

$PhC{\equiv}CHgCN$

$(PhC{\equiv}C)_2Hg$ (0.402 g, 1 mmol) and $Hg(CN)_2$ (0.256 g, 1 mmol) were mixed under stirring in 100 cm^3 of ethanol and refluxed for 8 hr. The solution obtained was concentrated until the apparition of a white precipitate, which was recrystallised from ethanol, yielding 0.13 g of the product (m.p. 162 °C). *Anal.* Calcd. for C_9H_5NHg: C, 33.02; H, 1.52; N, 4.28. Found.: C, 33.14; H, 1.61; N, 3.96%.

Reactions of $PhC{\equiv}CHgX$ ($X = Cl, CN$) with PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, PBu_3, and dppe

The general reaction consists of the addition of 2 mmol of a monodentate tertiary phosphine (or 1 mmol of dppe) to 1 mmol of $PhC{\equiv}CHgX$ in ethanol/ether, operating under a dry nitrogen atmosphere (except for the reaction with PPh_3). The reaction mixture was maintained under stirring for 24 hr. Solid products were isolated by partial evaporation of the solvent in the case of the reactions with PPh_3, PPh_2Et and dppe; which were filtered off, washed with a suitable solvent and dried under vacuum. The reactions of the cyano compound with the remaining phosphines lead to oils, from which in the case of

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*Author to whom correspondence should be addressed.

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PEt_3 a solid was isolated by addition of penthane. The analytical data of the isolated compounds and other properties are given in Table I.

Physical Measurements

Carbon, hydrogen and nitrogen were determined by the conventional organic microanalytical methods.

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 325 spectrophotometer, using Nujol mulls supported between CsI plates, KBr pellets or directly on the plates in the case of oils.

Conductometric measurements were performed with a Philips GM 4144/01 apparatus and a PR 9512/00 measurements cell in 10^{-3} *M* acetone solution.

^1H-NMR spectra were measured with a Perkin-Elmer R 12 spectrometer at 60 MHz, using TMS as internal standard.

Mass spectra were recorded on a Varian MAT 711 apparatus, operating at 100 eV.

X-ray powder patterns were obtained using a Philips 1310/00 diffractometer and CuK radiation.

Results and Discussion

PhC≡CHgX Compounds

The synthesis and study by IR spectroscopy of the PhC≡CHgCl has already been described [10].

PhC≡CHgCN was isolated as a white solid, stable in air and soluble in DMSO and $CHCl_3$, by reaction of $Hg(CN)_2$ and $(PhC{\equiv}C)_2Hg$ in refluxing ethanol, by a route similar to the PhC≡CHgCl compound.

The infrared spectrum of this compound shows a band at 2137 cm^{-1}, assigned to the stretching vibration $\nu(C{\equiv}C)$. Two bands at 420 and 375 cm^{-1} were assigned to the stretching vibrations ν(Hg–CN) and $\nu(Hg{-}C{\equiv}C)$ respectively. All these bands appear at frequencies slightly different to those of the starting compounds $Hg(CN)_2$ and $(PhC{\equiv}C)_2Hg$.

The ^1H-NMR spectra of cyano- and chloro phenylethynyl mercury in DMSO show the resonance signals of the phenyl ring protons at δ values of 7.47 and 7.57 ppm, respectively.

The mass spectrum of PhC≡CHgCl shows a very well defined molecular ion at m/e 674, which can be explained by the presence of dimer units in the compound. This spectrum also exhibits numerous molecular ions in which the presence of two PhC≡C units bonded to a mercury atom confirms the dimeric structure of the compound. Table I gives the most representative fragmentations that appear in the spectrum.

The mass spectrum of PhC≡CHgCN is much more simple than that of PhC≡CHgCl, the molecular ion m/e 399 being the base peak. The most intense peaks of this spectrum correspond to the ions Hg^+ (m/e 202) and $C_6H_5C{\equiv}C^+$ (m/e 101).

TABLE I. Principal Fragmentations Appearing in the Mass Spectrum of PhC≡CHgCl.

m/e	Assignment
674	$(HgClC_6H_5C{\equiv}C)_2^+$
640	$Hg_2Cl(C_6H_5C{\equiv}C)_2^+$
474	$HgCl(C_6H_5C{\equiv}C)_2^+$
440	$HgHCl(C_6H_5C{\equiv}C)_2^+$
404	$Hg(C_6H_5C{\equiv}C)_2^+$
362	$HgCl_2C_7H_6^+$
338	$HgClC_6H_5C{\equiv}C^+$
316	$HgH_2ClC_6H_5^+$
272	$HgCl_2^+$
237	$HgCl^+$
202	Hg^+
136	$HgCl_2^{2+}$
101	$C_6H_5C{\equiv}C^+$

The X-ray diffraction pattern of PhC≡CHgCN was clearly different from those of the starting products.

Reactions of PhC≡CHgX Compounds with Tertiary Phosphines

On the basis of the analytical data of the isolated compounds (Table II), the reaction of PhC≡CHgCN with monodentate phosphines can be described as a symmetrization reaction, accordingly to the eqn. (1).

$$2PhC{\equiv}CHgCN + nPR_3 \xrightarrow[n\,=\,1,\,2]{} (PhC{\equiv}C)_2Hg + Hg(CN)_2(PR_3)_n \qquad (1)$$

In the case of $PPhEt_2$ and PBu_3 it was not possible to isolate solid substances from the oils obtained. However, dppe seems to yield an adduct of composition PhC≡CHgCN·dppe, which evolutes towards symmetrization products. This can account for the deviations founded in the analytical data of this product (Table II).

Contrarily, the reaction of PhC≡CHgCl with monodentate tertiary phosphines (PPh_3 and PPh_2Et) in ethanol/ether leads to the formation of crystalline 1:1 adducts, accordingly to the eqn. (2).

$$PhC{\equiv}CHgCl + PR_3 \longrightarrow PhC{\equiv}CHgCl{\cdot}PR_3 \qquad (2)$$

The reaction with $PPhEt_2$, PEt_3 and PBu_3 in ethanol/ether gives decomposition products only. However, dppe originates in a symmetrization reaction, with formation of the complex $HgCl_2{\cdot}$dppe, described in the literature [11].

Infrared Spectra

Table III gives the most significant frequencies and assignments of the infrared spectra of the complexes and adducts isolated in the reactions of PhC≡CHgX

TABLE II. Isolated Compounds from the Reactions of PhC≡CHgX Compounds with Tertiary Phosphines.

X	Ligand	Compound	m.p. (°C)	Analyses (%)	Found (calcd.)		Λ_M (Ω^{-1}cm^2 mol^{-1})
				C	H	N	
CN	PPh_3	$Hg(CN)_2(PPh_3)_2$	240	59.0 (58.7)	3.9 (3.9)	3.5 (3.6)	5.38
CN	PPh_2Et	$Hg(CN)_2(PPh_2Et)_2$	166	53.1 (52.9)	4.6 (4.4)	4.3 (4.1)	0.73
CN	$PPhEt_2$	$Hg(CN)_2(PPhEt_2)_n$[a]					
CN	PEt_3	$Hg(CN)_2PEt_3$	113	25.8 (25.9)	4.0 (4.0)	7.4 (7.5)	2.38
CN	PBu_3	$Hg(CN)_2(PBu_3)_n$[a]					
CN	dppe	PhC≡CHgCN·dppe	205	54.2 (57.9)	3.6 (1.9)	3.9 (4.0)	
Cl	PPh_3	PhC≡CHgCl·PPh_3	165	49.5 (50.0)	3.4 (3.3)	5.2 (5.1)	1.81
Cl	PPh_2Et	PhC≡CHgCl·PPh_2Et	128	48.4 (47.9)	3.7 (3.6)	5.8 (5.6)	3.37
Cl	dppe	$HgCl_2$·dppe	323	46.6 (46.9)	3.6 (3.5)		

[a] Oil.

TABLE III. The Most Significative Infrared Frequencies (cm^{-1}) of the PhC≡CHgX (X = Cl, CN) Compounds and those of the Products Isolated from Their Reactions with Tertiary Phosphines.

Compounds	(C≡N)	(C≡C)	(Hg–C≡N)	(Hg–C≡C)	(Hg–X)
PhC≡CHgCN		2137	420	375	
PhC≡CHgCN·dppe			390	290, 250	
$Hg(CN)_2(PPh_3)_2$	2184		395		
$Hg(CN)_2(PPh_2Et)_2$	2130		345		
$Hg(CN)_2(PPhEt_2)_n$[a]	2138		370		
$Hg(CN)_2PEt_3$	2145		350		
$Hg(CN)_2(PBu_3)_n$[a]	2138, 2120		370		
PhC≡CHgCl		2195		360	345
PhC≡CHgCl·PPh_3		2170		395	
PhC≡CHgCl·PPh_2Et		2178		395	
$HgCl_2$·dppe					342

[a] Oil.

compounds with tertiary phosphines. The phenyl frequencies of the phenylethynyl ligand are excluded. The assignments were made by comparison of the spectra of $(PhC{\equiv}C)_2Hg$, $HgCl_2$ with those of the corresponding phosphine ligands [2, 12–16]. Shifts of the ν(Hg–C≡C), ν(Hg–CN) and ν(Hg–Cl) frequencies with respect to those of the related compounds were always observed. This the ν(C≡C) stretching frequency in the 2000–2200 cm^{-1} region shifts nearly 20 cm^{-1} towards lower frequency values in the adducts of PhC≡CHgCl with respect to that of the starting compound. The phosphine bands in the 700–400 cm^{-1} region show the shifts and splittings commonly observed in the phosphine complexes. The ν(Hg–Cl) stretching frequency, not observed in the spectrum, probably lay at a frequency value lower than 200 cm^{-1}.

In the infrared spectra of the $Hg(CN)_2(PR_3)_2$ compounds, obtained from PhC≡CHgCN, shifts in the bands assigned to the stretching frequencies ν(Hg–CN) and ν(CN) with respect to those of $Hg(CN)_2$ are observed. The position and shifts of these bands suggest a tetrahedral coordination and a metal–ligand interaction greater than those of analogous complexes with N-donor ligands [17].

The infrared spectrum of the compound isolated in the reaction of PhC≡CHgCN with dppe differs considerably from that of the symmetrical compound $Hg(CN)_2$dppe [18]. The complexity of the spectrum in the ν(Hg–CN) and ν(Hg–C≡C) region makes the assignment of these frequencies difficult*. However, the analytical data of this compound are only slightly lower than those expected for an adduct. This can be due to a partial decomposition, probably with evolution to the symmetrical compound $Hg(CN)_2$dppe.

The conductivity measurements correspond in all cases to non-electrolyte substances.

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*ν(CN) and ν(C≡C) do not appear. This fact has been frequently observed in cyano- and alkyl-mercury adducts [2, 3].

The evidently different behaviour of cyano- and chlorophenyl-ethynyl mercury in the reaction with tertiary phosphines can be due to the monomeric or dimeric nature, respectively, of the cyano- and chloro-compound.

The analogous behaviour of PhC≡CHgCN and PhHgCN, giving symmetrization products, was to be expected on the assumption that a lower difference of electronegativity between the substituents bonded to a mercury atom in an asymmetrical compound increases the tendency towards the symmetrization reaction in the presence of a P-donor ligand [9, 19].

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