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BIS(TRIPHENYLPHOSPHINE)PLATINUM ACETYLIDES FROM FUNCTIONALLY SUBSTITUTED ACETYLENES. A NEW SYNTHESIS METHOD

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Summary

A general procedure, giving high yields for the synthesis of $(Ph_3P)_2Pt(C\equiv CR)_2$ complexes ($R = C_6H_5$, $C(CH_2)CH_3$, $(CH_2)_6C\equiv CH$, CH_2OH, $CH(OH)CH_3$, $CH(OH)C_6H_5$, $CH_2CH(OH)CH_3$, $C(OH)(CH_3)CH_3$, $C_6H_{10}OH$, $C(OH)(CH_3)CH_2CH_3$, CH_2NHCH_3, $CH_2NHCH_2C_6H_5$, $CH_2N(CH_3)_2$, $CH_2N(C_2H_5)_2$) is reported. On the basis of the low frequency IR spectra a *trans* structure is proposed for all complexes. UV spectra are also reported.

The methods of synthesis of platinum acetylides have been reviewed by Shaw et al. in their paper on bis(dimethylphenylphosphine)platinum acetylides formed from ethynylalcohols or ethers [1]. They observed that few complexes containing functionally substituted acetylide ligands have been synthesized, and proposed three different methods, each of which offered advantages for a given class of substituted alkynes.

The first method, which was previously used for the preparation of several acetylides of alkyl and aryl acetylenes [2,3] consists of a reaction of L_2PtCl_2 (L = tertiary phosphine) with the sodio derivative of the acetylene in liquid ammonia. This method was useful for the synthesis of acetylides of several tertiary ethynyl alcohols and of two alkynyl ethers $HC\equiv CCH_2OR$ (R = Me or Ph) but failed to give good results with propargyl alcohol $HC\equiv CCH_2OH$ and with secondary alkynyl alcohols.

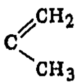
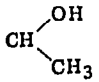
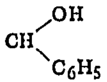
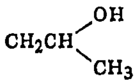
The second method proposed by Shaw et al., which consists in a reaction at reflux in ethanol between *cis*-$[PtCl_2(PMe_2Ph)_2]$ and $HC\equiv CR$ in the presence of hydrazine hydrate, gave good results for $R = C_6H_5$, *p*-tolyl, CH_2OH, CH_2OMe, CH_2OPh, but gave mixtures of products with tertiary ethynyl alcohols, which partly undergo dehydration under the conditions used.

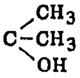
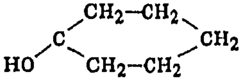
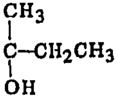
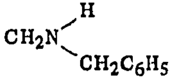
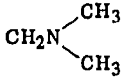
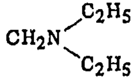
In the third method, analogous to the preceding one, concentrated aqueous ammonia was used instead of hydrazine hydrate. The method was successful

(continued on p. 104)

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF $(Ph_3P)_2Pt(C{\equiv}CR)_2$ COMPLEXES

R	Analysis found (calcd.) (%)		M.p. (°C)	Yield (%)	UV_{max} (nm) [a]	log ε	IR (cm^{-1}) [b]	
	C	H					$\nu(C{\equiv}C)$	$\nu(OH)$
C_6H_5	67.6 (67.5)	4.3 (4.3)	220—222	85	348	4.39	2120	
 $C(=CH_2)CH_3$	64.75 (65.40)	4.65 (4.71)	227—230	88	341	4.05	2090—2120	
$(CH_2)_6C{\equiv}CH$	67.89 (68.2)	5.81 (5.7)	114—116	69	323	3.76	2100—2140 [c]	
CH_2OH	61.29 (60.8)	4.55 (4.4)	194—197	48	316	3.65	2120	3430m
 $CH(OH)CH_3$	61.84 (61.6)	4.70 (4.7)	195—197	98	317	3.79	2120	3570m, 3450(br)
 $CH(OH)C_6H_5$	65.93 (66.1)	4.32 (4.5)	195—196	49	313	3.92	2135	3565s
 $CH_2CH(OH)CH_3$	62.36 (62.4)	4.98 (5.0)	199—202	98	319	3.77	2130—2140(sh)	3450(br), 3510w

 $\mathrm{C}\begin{smallmatrix}\diagup\mathrm{CH_3}\\ -\mathrm{CH_3}\\ \diagdown\mathrm{OH}\end{smallmatrix}$	62.6 (62.5)	5.04 (5.0)	247—250	72	322	3.76	2125	3580s
	64.93 (64.6)	5.31 (5.4)	238—241	85	322	3.83	2130	3560w(br)
 $\mathrm{\overset{CH_3}{\underset{OH}{C}}{-}CH_2CH_3}$	63.02 (63.07)	5.56 (5.26)	207—209	70	321	3.81	2120	3580w
$\mathrm{CH_2{-}NH{-}CH_3}$	58.94 (61.75)	4.83 (4.9)	166—168	77	318		2130	
 $\mathrm{CH_2N}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{CH_2C_6H_5}\end{smallmatrix}$	66.54 (66.7)	5.21 (4.96)	147—149	60	319	3.78	2130	
 $\mathrm{CH_2N}\begin{smallmatrix}\diagup\mathrm{CH_3}\\ \diagdown\mathrm{CH_3}\end{smallmatrix}$	61.75 (62.5)	5.23 (5.2)	200—201	77	318	3.79	2120—2130(sh)	
 $\mathrm{CH_2N}\begin{smallmatrix}\diagup\mathrm{C_2H_5}\\ \diagdown\mathrm{C_2H_5}\end{smallmatrix}$	63.65 (63.9)	5.95 (5.7)	174—175	77	322	3.79	2120	

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[a] Spectrum in $\mathrm{CHCl_3}$. [b] Nujol mulls. [c] $\nu(\mathrm{C{\equiv}C{-}H})$ 3290 $\mathrm{cm^{-1}}$. [d] s = strong, m = medium, w = weak, br = broad, sh = shoulder.

for the synthesis of complexes from unfunctionally substituted acetylenes. Secondary ethynyl alcohols did not give solid products with any of the proposed methods.

In our earlier studies on the synthesis of bis(triphenylphosphine) platinum acetylides we used the first method for the synthesis of *trans*-$(Ph_3P)_2PtCl(C{\equiv}CPh)$ and of *cis*- and *trans*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2$ [3], but this method gave mixtures of products with $HC{\equiv}CC(OH)(CH_3)CH_3$.

Even under mild conditions dehydration of the tertiary alcoholic groups of the ethynyl alcohols can occur during the synthesis of platinum complexes, and this led us to an erroneous interpretation of the structure of some complexes of 2-methylbut-3-yn-2-ol [4]. The dehydration was discussed by us in a subsequent paper [5], in which for the preparation of *trans*-$(Ph_3P)_2Pt(C{\equiv}CC(OH)R_2)_2$ complexes, we proposed a method starting from $(Ph_3)_2Pt(HC{\equiv}CC(OH)(R^1)R^2)$ and $HC{\equiv}CC(OH)R^1R^2$.

Now we have examined a new method of preparation of *trans*-$(Ph_3P)_2Pt(C{\equiv}CR)_2$ complexes of more general applicability. A similar method has been used by Sonogashira et al. [6] for the synthesis of bis(phosphine)palladium acetylides.

Discussion of results

The reaction procedure is very simple and avoids all the practical difficulties required for the preparation of liquid ammonia and the sodio acetylides. *cis*-$(Ph_3P)_2PtCl_2$ is suspended in $NH(C_2H_5)_2$ containing a small amount of CuI (see Experimental) and the alkyne is added is small excess. The mixture is refluxed for a few minutes and the bis(acetylides) separate when the reaction mixtures are warmed to room temperature. The CuI exhibits a catalytic action and reduces the reaction time. The products obtained are shown in Table 1. Alsmost all the complexes, including those derived from secondary ethynyl alcohols, were obtained in very high yields. However, propargyl alcohol gave a mixture of products. The IR spectrum of the crude mixture revealed a band of medium-high intensity at 540 cm^{-1}, which suggested the presence of a bis(triphenylphosphine)platinum complex of *cis*-structure [5—7]. After chromatography on a silica gel column with $CHCl_3$ as eluent, or after successive crystallizations from C_6H_6/C_2H_5OH a pure product was obtained, in the IR spectrum the band at 540 cm^{-1} was absent. Probably a mixture of *cis*- and *trans*-$(Ph_3P)_2Pt(C{\equiv}CCH_2OH)_2$ is obtained, but the *cis* complex isomerizes to the *trans* form in solution. The other complexes showed no band at 540 ± 5 cm^{-1}. The more bulky substituents in the alkyne molecules favour direct formation of the *trans* complexes.

The IR spectra of the acetylide complexes prepared from hydroxyacetylenes showed one or two $\nu(OH)$ bands of various intensity and position as shown in Table 1. This is probably due to the existence in some cases of intermolecular hydrogen bonds, as suggested by Shaw et al. for similar complexes [1].

The UV spectra of the *trans*-bis(triphenylphosphine)platinum bisacetylides exhibit a maximum (in $CHCl_3$) in the range 313—323 nm. This band, which is due to an intramolecular charge transfer transition [8], undergoes a bathochromic shift when R = Ph or $C(=CH_2)CH_3$, that is when a long conjugated system involving the metal *d* orbitals is formed.

Unusual behaviour was observed for the complex obtained from the reaction with $HC{\equiv}CCH_2NHCH_3$. The crude complex showed UV and IR spectra in agreement with those of the other *trans*-bis(acetylide) complexes, but it was practically insoluble in most organic solvents and in water, and recrystallization could not be carried out. We tried to prepare the acetylides derived from $HC{\equiv}CCH_2Br$ and $HC{\equiv}CCH_2Cl$ by the same reaction procedure, but the two alkynes react with diethylamine giving $[HC{\equiv}CCH_2NH(C_2H_5)_2]^+ X^-$ (X = Br, Cl) and the complex *trans*-$(Ph_3P)_2Pt[C{\equiv}CCH_2N(C_2H_5)_2]_2$ is obtained.

Attempts of obtaining polynuclear complexes from $(Ph_3P)_2Pt[C{\equiv}C(CH_2)_6C{\equiv}CH]_2$ are currently under investigation.

Experimental

UV spectra were recorded on a Beckman DK 2-A spectrophotometer. IR spectra were recorded on a Perkin—Elmer 521 spectrophotometer. Melting points were determined on a Kofler apparatus and are uncorrected. The elemental analyses were carried out by Malissa and Reuter (Engelskirchen, Germany). Most products used were commercial grade and were not further purified. *cis*-$(Ph_3P)_2PtCl_2$ was synthesized and purified as previously reported [3].

General procedure for the synthesis of acetylide complexes. 0.25 mmol of *cis*-$(Ph_3P)_2PtCl_2$ are added to 20 ml of $NH(C_2H_5)_2$ containing 0.6 mmol of alkyne and 0.05 mmol of CuI. The mixture is stirred and refluxed for about ten minutes. Upon warming to room temperature the products separate as yellow-white crystals, which are purified by recrystallization from C_6H_6/C_2H_5OH or $CHCl_3/C_2H_5OH$.

Acknowledgements

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