Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

(TRIPHENYLPHOSPHINE)PLATINUM PHENYLACETYLIDES

I. COLLAMATI AND A. FURLANI

Istituto di Chimica Generale ed Inorganica dell'Università di Roma, Centro di Chimica dei Composti di Coordinazione del C.N.R., Rome (Italy)

(Received August 15th, 1968; in revised form October 14th, 1968; final edited form February 24th, 1969)

SUMMARY

Some new Pt acetylides have been made from *cis*- and *trans*-$(PPh_3)_2PtCl_2$ and NaC≡CPh in liquid ammonia. Both *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ are obtained if the reaction is carried out in the presence of an excess of NaC≡CPh. The *cis* complex is the first example of a *cis* platinum acetylide. The complex $(PPh_3)_2$-PtCl(C≡CPh), probably in the *trans* form, is obtained when the reaction is carried out in a 1 : 1 molar ratio. Chemical and physical properties of compounds are described.

INTRODUCTION

In connection with a study of the polymerization of phenylacetylene in the presence of some bis(triphenylphosphine)platinum(II) complexes (see ref. 13) we have synthesized some new bis(triphenylphosphine)platinum(II) phenylacetylides. Ethynyl derivatives of Pt^{II}, such as $L_2Pt(C{\equiv}CR)_2$ ($L = PEt_3, AsEt_3$; $R = H, CH_3, C_6H_5$) have been prepared previously from the corresponding dichlorides L_2PtCl_2 and sodium acetylides NaC≡CR in liquid ammonia[1]. Other ethynylplatinum derivatives have been obtained by using lithium acetylides in ethyl ether[2] or ethynylmagnesium iodide[3]. The alkynyl complexes are stable crystalline compounds. They are characterized by an IR band at about 2100 cm^{-1}, due to the C≡C stretching vibrations. Until now ethynylnickel and -platinum complexes have been obtained exclusively in the *trans* form, regardless of the preparation method and starting from both the *cis* or the *trans* dichlorides. We have for the first time obtained both *cis* and *trans* diphenylacetylides.

EXPERIMENTAL

Apparatus

IR spectra were measured on nujol mulls using a Beckman IR 7 spectrophotometer. UV spectra were run on a Beckman DK 2 instrument.

Differential thermal analyses were carried out with a Geb Metrisch apparatus with platinum, platinum–rhodium thermocouples.

Molecular weights were measured with $CHCl_3$ solutions using a Mechrolab model 301-A osmometer. Fractionations of crude mixtures were carried out on silica gel columns, using C_6H_6 and $CHCl_3$ as eluents. The complexes were identified in the eluted fractions by means of their UV spectra.

Reactions

cis-Bis(triphenylphosphine)platinum dichloride, cis-$(PPh_3)_2PtCl_2$. This complex was prepared according to Jensen[4]. It was purified from $CHCl_3$/n-heptane. The white crystals were dried under vacuum to constant weight. (Found: C, 54.7; H, 3.6. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 54.7; H, 3.8%.)

trans-Bis(triphenylphosphine)platinum dichloride, trans-$(PPh_3)_2PtCl_2$. It was prepared from *trans*-$(PPh_3)_2PtHCl$ according to Allen[5]. A mixture of *cis* and *trans* dichlorides was always obtained. The *trans* isomer separated in pale yellow crystals on slow evaporation of a $CHCl_3$ solution. *Cis* and *trans* isomers were purified by chromatography on silica gel columns, using $CHCl_3$ as eluent.

UV spectroscopic data of both isomers are given in Table 1. IR spectra are identical in the 4000–650 cm^{-1} region. The two complexes are stable from room temperature to about 300°, at which partial isomerization takes place.

trans-Bis(triphenylphosphine)bis(phenylethynyl)platinum, trans-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (I). It was prepared according to Chatt[1].

A suspension of sodamide was prepared in a small Dewar vessel from sodium (0.23 g) and liquid ammonia (50 ml). Phenylacetylene (1 g) was added and then *cis*-$(PPh_3)_2PtCl_2$ (0.8 g). After 20 min of intermittent stirring, dry ammonium chloride (1 g) was added and ammonia was evaporated. The crude solid was treated with $CHCl_3$ and addition of CH_3OH afforded *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (I). The compound was crystallized from benzene. Two different crystalline modifications of (I) were observed, yellow hexagonal prisms or pale yellow needles. Both crystalline forms have the same X-ray powder spectrum and the same elemental analysis. (Found: C, 67.6; H, 4.3. $C_{52}H_{40}P_2Pt$ calcd.: C, 67.5; H, 4.3%.) M.p. 220–222°

TABLE 1

Complex	λ (mμ)	ν (cm^{-1})	ε	log ε
trans-$(PPh_3)_2PtCl_2$	320 (sh)	31200	1600	3.20
	283	35300	27600	4.44
	260	38500	16600	4.22
cis-$(PPh_3)_2PtCl_2$	328	30500	535	2.73
	275 (sh)	36400	8750	3.94
	267 (sh)	37400	10100	4.05
$(PPh_3)_2PtCl(C{\equiv}CPh)$	335 (sh)	29800	3980	3.60
	314	31850	13350	4.12
	264	37800	39900	4.60
trans-$(PPh_3)_2Pt(C{\equiv}CPh)_2$	348	28700	24800	4.39
	290 (sh)	34500	32600	4.51
	266	37600	49400	4.69
cis-$(PPh_3)_2Pt(C{\equiv}CPh)_2$	314	31850	26000	4.41
	254	39500	44000	4.64

(decompn.). The compound is stable in the solid state or in solution; it is soluble in CH_2Cl_2 and $CHCl_3$, less soluble in benzene, and insoluble in CH_3OH or hexane. It decomposes at about 200° with partial isomerization. UV data are given in Table 1.

The IR spectrum of (I) is characterized by the C≡C stretching vibrations at 2110 cm^{-1}. X-ray measurements revealed a center of symmetry in the molecule; therefore (I) has a *trans* structure.

If (I) is treated with an excess of HCl (III) is formed (see below).

cis-Bis(triphenylphosphine)bis(phenylethynyl)platinum, *cis*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (*II*). Evaporation to dryness of the $CHCl_3/CH_3OH$ solution after separation of the *trans* isomer gives a crude solid which is purified by crystallization from hot acetone. The colorless crystals are recrystallized from chloroform/hexane and dried under vacuum. (Found: C, 67.8; H, 4.3; mol.wt., 915. $C_{52}H_{40}P_2Pt$ calcd.: C, 67.5; H, 4.3%; mol.wt., 921.) M.p. 206–208° (decompn.). When (II) was recrystallized from CH_3COCH_3, $CHCl_3$ or C_6H_6, the following adducts were obtained: $(PPh_3)_2Pt(C{\equiv}CPh)_2 \cdot CH_3COCH_3$. (Found: C, 67.5; H, 4.65. $C_{55}H_{46}O_2P_2Pt$ calcd.: C, 67.4; H, 4.69%.) $(PPh_3)_2Pt(C{\equiv}CPh)_2 \cdot CHCl_3$. (Found: C, 61.0; H, 3.8. $C_{53}H_{41}Cl_3P_2Pt$ calcd.: C, 61.1; H, 3.9%.) $(PPh_3)_2Pt(C{\equiv}CPh)_2 \cdot 2\,C_6H_6$. (Found: C, 72.5; H, 4.9. $C_{64}H_{52}P_2Pt$ calcd.: C, 71.0; H, 4.8%.) The solvent molecules are removed by drying under vacuum.

(II) and its adducts show an IR spectrum characterized by a band at 2125 cm^{-1}, due to the C≡C stretching vibrations. UV data are reported in Table 1.

Differential thermal analysis reveals that (II) undergoes an exothermic reaction at 160° with partial isomerization. Diphenylbutadiyne was identified among the decomposition products[6]. By treatment with HCl (II) is cleaved to *cis*-$(PPh_3)_2PtCl_2$.

Bis(triphenylphosphine)(phenylethynyl)platinum chloride, $(PPh_3)_2PtCl(C{\equiv}CPh)$ (*III*). *A.* A C_6H_6 or $CHCl_3$ solution of (I) is saturated with gaseous HCl. UV spectra of samples from the reaction solution are run periodically. When the maximum at 348 mμ (characteristic of the starting product) disappears, the reaction solution is evaporated to dryness. The crude solid is recrystallized from boiling acetone. $(PPh_3)_2PtCl(C{\equiv}CPh)$ separates in colorless crystals, which are dried under vacuum. (Found: C, 61.7; H, 4.2; Cl, 4.1. $C_{44}H_{35}ClP_2Pt$ calcd.: C, 61.75; H, 4.1; Cl, 4.15%.) M.p. 212–214° (decompn.). (III) is soluble in hot CH_3OH or CH_3COCH_3.

The IR C≡C stretching band of (III) is at 2125 cm^{-1}. UV spectroscopic data are given in Table 1.

B. (III) is also obtained starting from $(PPh_3)_2PtCl_2$ and NaC≡CPh in a 1 : 1 molar ratio, following the procedure given above for (I). After evaporation of liquid ammonia to dryness the crude product is dissolved in $CHCl_3$. The insoluble product is filtered off and the solution is chromatographed on a silica gel column. By using $C_6H_6/CHCl_3$ 1/1 as eluent the *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (I) is eluted in the first fractions, followed by the monochloro(phenylacetylide) (III) and then by the *cis*-bis(phenylacetylide) (II). Fractions containing (III) are evaporated to dryness and the product is purified as outlined above.

If (III) is treated with an excess of HCl the ethynyl–platinum bond is not cleaved. However some reaction does occur because UV and IR spectra are modified. This reaction is believed to be the formation of an adduct because treatment of the solution with silica gel results in the recovery of the original compound (III).

DISCUSSION

In order to investigate the influence of the configuration of the dihalides on the reaction products we also used *trans*-$(PPh_3)_2PtCl_2$ as starting material. This compound isomerizes in liquid ammonia to the *cis* form; therefore the same results were obtained from both isomers.

In the synthetic reaction, formation of *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ [(II) and (III), respectively] predominates if a large excess of $NaC{\equiv}CPh$ is used. When the reaction between $(PPh_3)_2PtCl_2$ and $NaC{\equiv}CPh$ is carried out in a 1:1 molar ratio, the monochloro(phenylacetylide) $(PPh_3)_2PtCl(C{\equiv}CPh)$ (III) is obtained. Compound (III) exhibits IR and UV spectra very similar to those of (II); this led to considerable difficulty in the identification of (II) and (III), which are both formed in the reaction between $NaC{\equiv}CPh$ and $(PPh_3)_2PtCl_2$ although in amounts depending on the molar ratio of the starting products.

Some explanations have been offered for the differing stabilities of *cis* and *trans* dichloro complexes of platinum[7,12]. However, no discussion of the relative stabilities of the *cis* and *trans* diorganyl complexes L_2MR_2 (M = Ni, Pt; R = alkyl, aryl, ethynyl) or of *cis* and *trans* monoorganyl monohalides L_2MXR (X = Cl, Br, I) can be found in the literature.

From the literature data it is observed that until now all known organyl complexes of nickel have a *trans* structure[8]. The dialkylplatinum complexes are *cis*, while the diaryl and arylmonohalide complexes are *cis* and *trans*[1,9]. In the latter case the *cis* compounds are thermally less stable than the *trans* isomers. An aryl ethynyl complex of Pt was obtained by Parshall[2] in the *trans* form. The previously known diethynyl derivatives were always *trans*. We have now obtained the $(PPh_3)_2Pt(C{\equiv}CPh)_2$ complex in both *cis* and *trans* forms. The *cis* isomer is thermally less stable than the *trans* isomer.

Comparing structural data and thermal lability of some platinum–phosphine complexes, Davies and coworkers[10] observed that the Pt–P bond length decreases and the thermal stability increases as the ligand field strength increases. This observation is not confirmed by our results. Substitution of chlorine atoms of $(PPh_3)_2PtCl_2$ with strong field ligands such as acetylide groups gives rise to compounds less stable.

The monochloro phenylacetylide $(PPh_3)_2PtCl(C{\equiv}CPh)$ is probably the *trans* isomer. It can be obtained from the *trans* bis(phenylacetylide) and it does not react with gaseous HCl. The behaviour of (I) and (II) in the presence of HCl can be related to the *trans* effect. Both acetylide radicals are equally labilized by the two *trans* phosphine groups in the *cis* isomer, and they are easily replaced by two chlorine atoms giving *cis*-$(PPh_3)_2PtCl_2$. From *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$, $(PPh_3)_2PtCl(C{\equiv}CPh)$ is obtained. The Pt–C bond *trans* to a Cl atom is not cleaved, as a consequence of the lower *trans* effect of the Cl atom with respect to that of a phosphine ligand.

It is not yet clearly established whether the acetylide radicals act as pure σ or as σ and π ligands. According to Chatt[2] the M–C bond should have a considerable double bond character. NMR studies of Parshall[3] confirm the strong σ-donor and π-acceptor capacity of the acetylide group.

Two recent crystallographic studies on the structure of the same compound $(PPh_3)_2Ni(C{\equiv}CPh)_2$ do not clarify the problem because similar experimental data are interpreted in different ways[10,11]. The same Ni–C distance is given in the two papers but, on the basis of different evaluation of the Ni ionic radius, Davies[10] concludes that the Ni–C distance is characteristic of a single bond while Spofford[11] considers it characteristic of a partial double bond. Since some uncertainty exists in the evaluation of the ionic radius of Ni, the conclusions of Davies on the exclusively σ-donor character of the acetylide group seem premature. In order to clarify the problem an X-ray study of the structure of the *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ is in progress.

REFERENCES

1 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1959) 4020.
2 G. W. PARSHALL, *J. Amer. Chem. Soc.*, 88 (1966) 704.
3 M. I. BRUCE, D. A. HARBOURNE, F. WANGH AND F. G. A. STONE, *J. Chem. Soc., A*, (1968) 356.
4 K. A. JENSEN, *Z. Anorg. Allg. Chem.*, 229 (1936) 265.
5 A. D. ALLEN AND M. C. BAIRD, *Chem. Ind. (London)*, (1965) 139.
6 H: K. BLACK, D. H. SHORN AND B. C. WELDON, *J. Chem. Soc.*, (1954) 1704.
7 S. AHRLAND AND J. CHATT, *J. Chem. Soc.*, (1957) 1379.
8 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1960) 1718.
9 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1959) 705.
10 G. R. DAVIES, R. H. B. MAIS AND P. G. OWSTON, *J. Chem. Soc., A*, (1957) 1750.
11 W. A. SPOFFORD, P. D. CARFAGNA AND E. L. AMMA, *Inorg. Chem.*, (1967) 1553.
12 A. PIDCOCK, R. E. RICHARDS AND L. M. VENANZI, *J. Chem. Soc., A*, (1966) 1707.
13 A. FURLANI, I. COLLAMATI AND G. SARTORI, *J. Organometal. Chem.*, 17 (1969) 463.