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NOTE

CHLOROSTYRYL DERIVATIVES OF PLATINUM(IV). AN UNUSUAL TYPE OF LIGAND ELIMINATION

RENATO ETTORRE
Istituto di Chimica Generale dell'Università, II Sezione, via Loredan 4, 35100 Padua (Italy)

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Recently, some chlorovinyl derivatives of platinum(II) have been reported[1]. They were obtained by isomerisation of chloro-olefin complexes of platinum(0). We report here a new route to chlorovinyl complexes of platinum, involving treatment of acetylide complexes with excess of chlorine in light petroleum. Thus the compound $[\mathrm{Pt(PPr_3)_2(CCl{=}CCl{-}Ph)_2Cl_2}]$ (I) was obtained from $[\mathrm{Pt(PPr_3)_2(C{\equiv}CPh)_2}]$ (II).

Formulation of (I) as a chlorostyryl derivative of platinum(IV) is based on the observation that the complex reacts with sodium iodide in methanol to give free iodine and that its infrared spectrum shows no bands in the region of the $\mathrm{C{\equiv}C}$ stretch. This indicates that two chlorine atoms were oxidatively added to the central metal and two other were added to the triple bond on each phenylethynyl group of (II).

In the region 1600–1500 $\mathrm{cm^{-1}}$ the spectrum of (I) shows three weak infrared bands at 1590, 1570 and 1540 $\mathrm{cm^{-1}}$. Bands at 1590 and 1570 $\mathrm{cm^{-1}}$ are present also in the spectra of complex (II) and of the platinum(IV) derivative $[\mathrm{Pt(PPr_3)_2(C{\equiv}CPh)_2I_2}]$, so the absorption at 1540 $\mathrm{cm^{-1}}$ may be tentatively assigned to the $\mathrm{C{=}C}$ stretch of the styryl groups. It is pertinent to note that the absorption assigned to the $\mathrm{C{=}C}$ stretch of the vinyl in complexes of the type $[\mathrm{Pt(PPh_3)_2(C_2Cl_nH_{3-n})Cl}]$ ($n=3, 2, 1$) occurs in the range 1560–1550 $\mathrm{cm^{-1}}$ (ref. 1).

Complex (I) undergoes an interesting ligand elimination reaction (1) when refluxed in methanol:

$$\underset{\text{(I)}}{[\mathrm{Pt(PPr_3)_2(CCl{=}CClPh)_2Cl_2}]} \rightarrow \underset{\text{(III)}}{[\mathrm{Pt(PPr_3)_2(CCl{=}CClPh)Cl_3}]} + \mathrm{PhC{\equiv}CCl} \qquad (1)$$

Structure of (III) as a chlorostyryl derivative of platinum(IV) has been assigned on the basis of the observation that this complex reacts with sodium iodide in methanol to give free iodine and remains unchanged upon standing 24 h in a solution of n-hexane saturated with chlorine, and despite the fact that we were not able to detect any appreciably absorption at 1540 $\mathrm{cm^{-1}}$.

The phenylchloroacetylene elimination reaction (1) involves a chlorine atom migration from an organic group to platinum and cleavage of a metal–carbon bond. It is noteworthy that the complex (I) reacts only to a small extent in refluxing n-hexane in the time required for reaction (1) to go to completion in refluxing methanol (20 min). Presumably the more polar methanol facilitates the dissociation of platinum-carbon and carbon–chlorine bonds involved in reaction (1). It is possible that dissociation of a platinum–chlorine bond is also involved as an initial step which makes a free site on platinum available to migrating chlorine.

EXPERIMENTAL

Materials

$[Pt(PPr_3)_2(C{\equiv}CPh)_2]$, m.p. 82–84°, was prepared by the method described for the analogous triethylphosphine derivative[2] (Found: C, 56.70, H, 7.42. $C_{34}H_{52}P_2Pt$ calcd.: C, 56.89; H, 7.30%.) The infrared spectrum has a strong band at 2100 cm^{-1} ($C{\equiv}C$ stretching).

$[Pt(PPr_3)_2(CCl{=}CClPh)_2Cl_2]$, m.p. 142–143°. (Found: C, 44.49; H, 5.88; Cl, 23.11; mol.wt., 930. $C_{34}H_{52}Cl_6P_2Pt$ calcd.: C, 43.88; H, 5.63; Cl, 22.86%; mol.wt., 930.)

$[Pt(PPr_3)_2(CCl{=}CClPh)Cl_3]$, m.p. 174–177° was prepared by reaction (1) and isolated by evaporating the reaction mixture under reduced pressure. (Found: C, 39.27; H, 6.14; Cl, 22.15; mol.wt., 776. $C_{26}H_{47}Cl_5P_2Pt$ calcd.: C, 39.33; H, 5.97; Cl, 22.33%; mol.wt., 794.)

The other product of reaction (1) was recognized by the identity of UV spectrum and retention times on vapor phase chromatography of the distillate from the reaction mixture with those of a methanol solution of authentic phenylchloroacetylene[3].

$[Pt(PPr_3)_2(C{\equiv}CPh)_2I_2]$, m.p. 131–133° separated as red crystals in few minutes when a solution of $[Pt(PPr_3)_2(C{\equiv}CPh)_2]$ in light petroleum was treated with iodine. (Found: C, 42.05; H, 5.24; I, 26.04. $C_{34}H_{52}I_2P_2Pt$ calcd.: C, 42.03; H, 5.39; I, 26.12%.) The infrared spectrum has a strong band at 2135 cm^{-1} ($C{\equiv}C$ stretching).

Physical measurements

Molecular weights were determined in 1,2-dichloroethane with a Mechrolab 301A osmometer.

Infrared spectra were measured in Nujol mulls using a Perkin–Elmer 257 spectrophotometer. The uncertainty in the wavenumbers is $\pm 5\ cm^{-1}$. UV spectra were measured with a Beckman DK-2A spectrophotometer.

GLC measurements were performed by means of a Hewlett–Packard 5750 Research Chromatograph.

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