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Coordination chemistry of perhalogenated cyclyopentadienes and alkynes—XXI.† Studies on the substitution reactions of $Pt(PPh_3)_2(C_2Cl_2)$ and *trans*-$Pt(PPh_3)_2(Cl)(C_2Cl)$ with triphenylphosphite

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Abstract—The reactions of the Pt(0) π-alkyne complex $Pt(PPh_3)_2(Cl\ C{\equiv}CCl)$ and the Pt^{II} alkynyl complex $Pt(PPh_3)_2(Cl)(C{\equiv}CCl)$ with $P(OPh)_3$ lead to either the π-alkyne complexes $Pt(PPh_3)_n(P(OPh)_3)_{2-n}(Cl\ C{\equiv}CCl)$ ($n = 0, 1$) or the *cis* and *trans* isomers of $Pt(PPh_3)_n[P(OPh)_3]_{2-n}(Cl)(C{\equiv}CCl)$ ($n = 0, 1$), depending on the reaction conditions. The course of the reaction was followed by ^{31}P-NMR spectroscopy, from which a plausible mechanism for the oxidative addition reaction can be derived: key steps are phosphine dissociation from the Pt(0) species to a two-coordinate intermediate, which undergoes oxidative addition of a C—Cl bond to give a three-coordinate Pt^{II} species, which might be stabilized by dimerization. © 1997 Elsevier Science Ltd

Keywords: platinum; dichloroethyne; alkyne complexes; oxidative addition.

Alkyne and alkynyl complexes of platinum have been the object of continuous interest for more than 30 years. The most common types of these compounds are $Pt(PR_3)_2(R'C{\equiv}CR'')$ and $Pt(PR_3)_2(X)(C{\equiv}CR'')$ [2]. Many representatives with alkyl or aryl phosphines are known, but there is only one report of an alkyne complex of platinum with a phosphite ligand [3]. We recently reported the synthesis of $Pt(PPh_3)_2(ClC{\equiv}CCl)$ (**1**) and *trans*-$Pt(PPh_3)_2(Cl)(C{\equiv}CCl)$ (**2**) as well as their reactivity towards phosphine or halide substitution reactions [4]. In extension of this work, we examined the reactivity of these compounds towards $P(OPh)_3$.

RESULTS

A few minutes after addition of $P(OPh)_3$ to a toluene solution of **1** the ^{31}P NMR spectrum of the reaction mixture shows the appearance of a signal due to free PPh_3 ($\delta \approx -5$ ppm) and of two doublets with ^{195}Pt satellites at $\delta = 24.2$ ($^2J_{PP} = 14$ Hz, $^1J_{PtP} = 3020$ Hz) and $\delta = 115.3$ ($^1J_{PtP} = 5466$ Hz). After about a 2 h reaction time, the NMR spectrum shows an additional singlet with ^{195}Pt satellites at $\delta = 116.5$ ($^1J_{PtP} = 5102$ Hz). Both signals appear when 1 or 2 equivalents of phosphite are added to the solution of **1**, but the intensity of the latter signal is higher for the 1 : 2 stoichiometry. From this observation and from the size of the coupling constants‡ we assign the former set of signals to $Pt(PPh_3)[P(OPh)_3](ClC{\equiv}CCl)$ (**3**) and the latter to the bis(phosphite) complex $Pt[P(OPh)_3]_2(ClC{\equiv}CCl)$ (**4**). After 24 h the signals of **1** have disappeared completely. From these solutions, analytically pure **3** can be isolated and characterised.

A ^{31}P NMR spectrum of a freshly prepared solution of **3** in dichloromethane shows, however, five different platinum species. The major component is still **3** (as can be seen from the very similar coupling constants in comparison to the toluene spectra) and one other component can be identified as the known [4] chloroethynyl complex *trans*-$Pt(PPh_3)_2(Cl)(C{\equiv}CCl)$ (**2**). But the occurrence of a number of signals at rather

† Part XX, see ref. [1].

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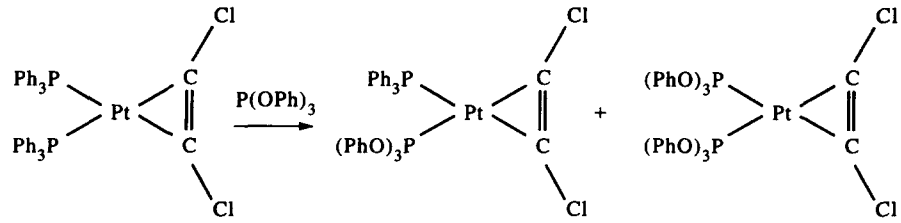
‡ Coupling constants J(Pt–P) are about 1.5 times larger for phosphite complexes than for phosphine complexes.



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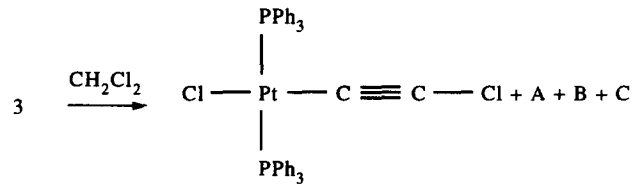

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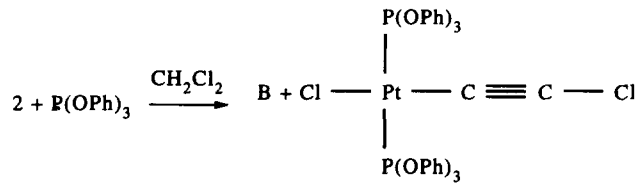

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Scheme 1.

low field with large Pt–P coupling constants suggests the presence of new $P(OPh)_3$ containing species. Careful analysis of the spectrum indicates three different compounds **A, B, C** (see Table 1) with the first two containing PPh_3 and $P(OPh)_3$ and the last only $P(OPh)_3$ ligands. Assuming that all products still contain the alkyne moiety it seems reasonable to assign these signals to the products of oxidative addition of one C—Cl bond. The data of **A** and **B** are consistent with *cis*- and *trans*- isomers of $Pt(PPh_3)[P(OPh)_3](Cl)(C{\equiv}CCl)$ (**5a, 6**),* while the latter, minor component, can be interpreted as *cis*-$Pt[P(OPh)_3]_2(Cl)(C{\equiv}CCl)$ (**7**). After prolonged standing of these solutions, the signals due to **3** disappear completely. At the same time, the amount of the *cis* complex **A** decreases, while the signals of **C** increase substantially. Parallel to this a white precipitate forms, which can be redissolved in CH_2Cl_2 and identified as pure **2**.

When the Pt^{II} complex **2** is treated with $P(OPh)_3$, and the reaction followed by ^{31}P NMR spectroscopy, the formation of two species can be observed. One of them is identical with the before-mentioned compound **B**, while the other (as it appears as a singlet with ^{195}Pt satellites) seems to be the *trans*-isomer **8** of **7**.

Table 1. ^{31}P NMR data (in CH_2Cl_2)

Compound	PR_3	δ (^{31}P)	$^2J_{PP}$ [Hz]	$^1J_{PtP}$ [Hz]
3	$P(OPh)_3$	115.3 d	13.5	5466
	PPh_3	24.1 d	13.5	3020
4	$P(OPh)_3$	116.5	—	5102
A	$P(OPh)_3$	57.7 d	22	6140
	PPh_3	24.0 d	22	2348
B	$P(OPh)_3$	85.6 d	697	4556
	PPh_3	21.2 d	697	2604
C	$P(OPh)_3$	93.4 d	27	3946
	$P(OPh)_3$	59.9 d	27	5880

DISCUSSION

Substitution reactions of Pt^{II} phosphine complexes have been performed mainly in connection with mechanistic studies on the so-called *trans*-effect and the *cis-trans*-isomerization reactions of square planar complexes [5]. Generally, substitution reactions occur stereospecifically with retention of configuration [6].

* Trans complexes $Pt(PR_3)(PR'_3)XY$ show a much larger coupling constant J(P–P) than the corresponding *cis* complexes: J.F. Nixon and A. Pidcock, *Ann. Rev. NMR Spectroscopy*, 1969, **2**, 346; J.G. Verkade, *Coord. Chem. Rev.*, 1972, **9**, 1.

The reaction of **2** with $P(OPh)_3$ seems to proceed in the expected manner: The *trans*- configured starting compound **2** leads exclusively to the *trans* complexes **6** and **8**. It is known from the literature that addition of phosphine ligands to complexes $ML_2(X)Cl$ leads first either to neutral five-coordinate species [7] or ionic four-coordinate complexes [8]. Depending on the polarity of the solvent, the nature of X and the basicity of the phosphine ligand, these intermediates are either stable or undergo further rearrangements. The final product distribution, if under thermodynamic control, will therefore be a manifestation of the best balance of the *trans* influences of the different ligands. The clean formation of *trans* complexes **6** and **8** from **2** and excess $P(OPh)_3$—which should lead to thermodynamically controlled products—therefore indicates that the *trans* influence of the chloroethynyl group is larger than that of $P(OPh)_3$.

While substitution reactions of Pt(0) complexes have been used extensively for preparative purposes, mechanistic studies have been performed to a much lesser extent. For systems $Pt(ER_3)_2(un)$, where E = P or As and 'un' stands for an alkene or alkyne ligand, addition of a phosphine ligand PR'_3 can either lead to substitution of ER_3 or the unsaturated organic ligand, depending on the relative bond strengths of Pt-ER_3 and Pt-(un). For instance, addition of $PMePh_2$ to $Pt(AsPh_3)_2(C_2F_4)$ leads to complete exchange of phosphine for arsine, while $P(OPh)_3$ displaces the olefin ligand [9]. Similarly, PCy_3 replaces one PPh_3 ligand in $Pt(PPh_3)_2(C_2H_4)$, while $P(OPh)_3$ yields $Pt(PPh_3)[P(OPh)_2]_2$ by substitution of one phosphine and olefin ligand each [10]. Mechanistic studies in the system Pt/PPh_3/alkyne showed that both *associative* and *dissociative* pathways contribute to the substitution reactions [11].

In our previous study [4] on substitution reactions of **1** and **2** with alkylphosphines we suggested the formation of a two-coordinate intermediate X from **1** *via* phosphine dissociation. Since we observed only products of an oxidative addition reaction, we further assumed that this intermediate X rapidly underwent oxidative addition of the C—Cl bond and excluded the formation of an intermediate 'mixed phosphine' π-complex. The results of the present study suggest, however, that formation of such an intermediate is a viable pathway, and the nature of the phosphine determines whether it can be detected or not. We therefore propose a mechanism for the phosphine–phosphite substitution reaction as outlined in Scheme 2.

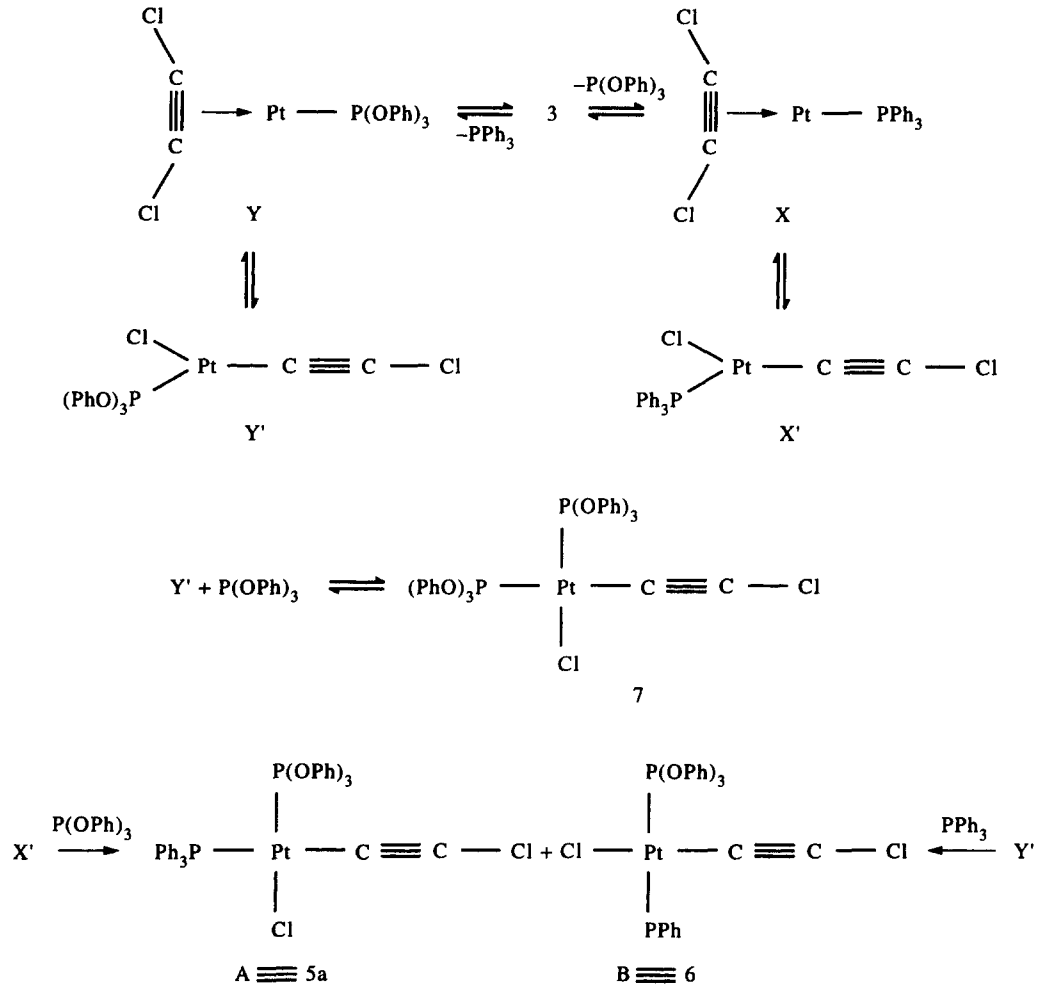
From the mixed phosphine–phosphite π-complex, **3**, either PPh_3 or $P(OPh)_3$ can dissociate with formation of two-coordinate intermediates Y or X, respectively. Y can add another molecule of $P(OPh)_3$ to yield **4**, while the other recombinations are 'unproductive' yielding only **1** or **3** again. When X or Y undergo an oxidative addition reaction, a three-coordinate species X′ or Y′, respectively, is formed, which in turn can either add PPh_3 or $P(OPh)_3$. The stereochemistry of the resulting products will be related to the relative *trans* effects of the three ligands coordinated to Pt, which can be assumed as $C{\equiv}CCl > P(OPh)_3 \approx PPh_3 > Cl^-$ [12]. There are contradictory reports in the literature about the relative *trans* effects of phosphines or phosphites [13], and the outcome of the reaction may as well be determined from effects in the transition state as from relative stabilities of the products. It seems reasonable to assume that the new ligand will primarily enter at a position *trans* to Cl, the ligand with the smallest *trans* effect. Thus, the primary products to be expected are: (a) *cis*-$Pt(PPh_3)_2(Cl)C{\equiv}CCl$ (**2′**) from X′ and PPh_3; (b) **5a** from X′ and $P(OPh)_3$; (c) **5b** (the "other" *cis*-chloro-chloroethynyl isomer) from Y′ and PPh_3; (d) **7** from Y′ and $P(OPh)_3$.

2′ is known to isomerize rapidly to **2** in CH_2Cl_2, which may be due to the low solubility of the latter in this solvent [4]. But it is also possible that thermodynamic control leads to further isomerization of the primary products. The $C{\equiv}CCl$ group's strong *trans* influence should produce Y′ from **5a**, which in turn could react with $P(OPh)_3$ to yield **7**. Similarly, **5b** should lead *via* X′ to **6**, or by re-addition of $P(OPh)_3$ first to **5a** and finally to **7**. Following this argument, there is no analogous way for isomerization of **7** to the *trans*-isomer **8**. We note in this context an earlier statement that *cis* complexes $MRXL_2$ can 'not (be obtained) by the oxidative addition reactions' [8].

One objection to this mechanism might be the involvement of a three-coordinate Pt^{II} species. Such species were postulated as intermediates in the uncatalyzed *cis–trans* isomerization of complexes $PtX(R)(PR_3)_2$, but were later shown to be either solvated species $[Pt(R)(PR_3)_2(solv)]^+$ or dimers $[PtX(R)(PR_3)]_2$ formed *via* halide or phosphine dissociation [14]. A combination of phosphine dissociation and association processes was postulated in a recent study on intermolecular phosphine exchange reactions between $PtCl_2(PR_3)_2$ and $PtCl_2(PR'_3)_2$ [7]. Dimeric complexes $[Pt_2X_2(\mu\text{-}Cl)_2(ER_3)_2]$ have been used for the synthesis of mixed ligand complexes of Pt^{II} [15]. However, without isolation of any intermediates, there is no unambiguous way to decide in favour of one of the possibilities.

EXPERIMENTAL

The reactions were performed under nitrogen in deoxygenated solvents. Samples for NMR examinations were either taken directly from the reaction solutions, or after evaporation of solvent and dissolution in a deuterated solvent. **1** and **2** were prepared as described previously [4], $P(OPh)_3$ was commercially available and used as such. NMR spectra were recorded with a JEOL GSX 270 spectrometer, with external H_3PO_4 as reference for ^{31}P-, external $K_2Pt(CN)_6$ as reference for ^{195}Pt- and solvent signals for ^{13}C-NMR spectra.



Scheme 2.

Isolation of (π-dichloroethyne) (triphenylphosphine) (triphenylphosphite)platinum, $Pt(PPh_3)(P(OPh)_3)(\pi\text{-}Cl{-}C{\equiv}C{-}Cl)$, **3**

A solution of **1** (190 mg, 0.233 mmol) in 10 cm^3 toluene is treated with $P(OPh)_3$ (63 μl, 0.24 mmol). After stirring for 145 min at 45°C the solvent is stripped off *in vacuo*. The remaining oily residue is triturated with 20 cm^3 Et_2O, which generates a fine white powder and a colourless solution. The powder is identified as **2** by ^{31}P NMR spectroscopy. The ethereal solution is evaporated to dryness *in vacuo*, and the residue is taken up in ≈ 1 cm^3 toluene and treated with pentane until precipitation of a white powder starts. After standing overnight at −30°C, the precipitate is isolated by centrifugation, washed with 10 cm^3 pentane and dried *in vacuo*. Anal. $C_{38}H_{30}Cl_2O_3P_2Pt$ (M = 862.5): calc./found: C, 52.9/52.5; H, 3.5/3.9%.

^{13}C NMR (C_6D_6): δ = 110.0dd ($^2J(C{-}P_{trans})$ = 126 Hz; $^2J(C{-}P_{cis})$ = 32 Hz), 110.7dd ($^2J(C{-}P_{trans})$ = 231 Hz, $^2J(C{-}P_{cis})$ = 13 Hz). ^{195}Pt-NMR (CH_2Cl_2): δ = −759 dd ($^1J(Pt{-}P_{PPh})$ = 3020 Hz, $^1J(Pt{-}P_{P(OPh)})$ = 5466 Hz).

NMR Experiments

(i) *Isomerization and decomposition of* **3** *in* CH_2Cl_2. Approximately 100 mg of **3** are dissolved in the minimum amount of dichloromethane ($\approx$1–2 cm^3) and examined in a ^{31}P NMR spectrometer immediately. The spectrum shows besides the signals due to **3** also the signals of **A**, **B**, **C** and **2** in a ratio of approx. 70:10:10:5:5, but no free PPh_3 or $P(OPh)_3$. The solvent is evaporated *in vacuo*, and the residue is extracted with ≈ 2 cm^3 toluene. After filtration the toluene is removed again and replaced by ≈ 1 cm^3 CH_2Cl_2. A ^{31}P NMR spectrum of this solution shows no more signals of **3**, and only a small amount of **A** ($\approx$10%). The signals due to **B**, **C** and **2** integrate approximately 1:1:1.

(ii) *Addition of* $P(OPh)_3$ *to a toluene solution of* **1**. A solution of $\approx$100 mg of **1** (0.12 mmol) in 5 cm^3 toluene is treated with 63 mm^3 $P(OPh)_3$ (0.24 mmol). After stirring for 135 min at room temperature the toluene is evaporated *in vacuo* and the residue extracted with ≈ 1 cm^3 C_6D_6. The ^{31}P NMR spectrum shows signals due to PPh_3 (−4.9 ppm), $P(OPh)_3$

(128.5 ppm), **1** (24.3 ppm), **3** (24.0d/115.3d, $^2J_{PP}$ = 13 Hz, $^1J_{PtP}$ = 3022/5466 Hz) and **4** (116.5 ppm, $^1J_{PtP}$ = 5102 Hz). The low field signals of **3** and **4** integrate about 85:15. Further addition of ≈1 cm^3 $P(OPh)_3$ leads to disappearance of the signals due to **1** and a relative increase of the amount of **4** (integrals correspond now approx. to a 1:1 ratio). A ^{195}Pt NMR spectrum shows, besides the doublet of doublets due to **3** a triplet at δ −789 with $^1J_{PtP}$ 5102 Hz.

(iii) *Addition of* $P(OPh)_3$ *to a* CH_2Cl_2 *solution of* **2**. A solution of **2** (81 mg, 0.10 mmol) in 2 cm^3 CH_2Cl_2 is treated with an excess of $P(OPh)_3$ (≈5 drops from a Pasteur pipette). While a ^{31}P NMR spectrum recorded immediately after mixing shows only unreacted starting materials (plus a signal of an impurity present in commercial $P(OPh)_3$ at $\delta \approx 0.5$), a spectrum recorded after 24 h shows free PPh_3 (δ = −5.4 ppm), **8** (δ = 22.1, $^1J_{PtP}$ = 2927 Hz) and an AX system (δ = 21.3d, J = 656 Hz; 88.5d, J = 654 Hz, **B**?) plus several minor impurities. After a further 48 h, the spectrum shows only signals due to PPh_3, $P(OPh)_3$ and **8** (and still the 'impurity' at $\delta \approx 0.9$ ppm).

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