Coordination Chemistry of Perhalogenated Cyclopentadienes and Alkynes, XXIX. The Reaction of Ni(0) and Pt(0) Phosphane Complexes with Trichloroethene, Hexachloro- and Hexabromocyclopentadiene

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

Trichloroethene reacts with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] at first to the π complex [Pt(PPh$_3$)$_2$(η^2-C$_2$HCl$_3$)] (**1a**), which isomerizes *via* the *cis*-isomer to the insoluble *trans*-[Pt(Cl)(η^1-CH=CCl$_2$)(PPh$_3$)$_2$] (**2a**). Both **1a** and **2a** react with PBu$_3$ to the corresponding tributylphosphane complexes **1b** and **2b**, respectively. From the reactions of [Ni(PR$_3$)$_2$(C$_2$H$_4$)] (R = Me, Et, Bu) and C$_2$HCl$_3$ only the products of oxidative addition *trans*-[Ni(Cl)(η^1-CH=CCl$_2$)(PR$_3$)$_2$] (**3a – c**) can be isolated. Hexachlorocyclopentadiene and hexabromocyclopentadiene react with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] or [Ni(PR$_3$)$_2$(C$_2$H$_4$)] (R = Ph, Me) to give highly colored solutions.

Key words: Oxidative Addition, Platinum Phosphane Complexes, Nickel Phosphane Complexes, Trichloroethene, Hexachlorocyclopentadiene

Introduction

The reactions of chloro-olefins and chloroalkanes with [Pt(PPh$_3$)$_4$] and [Pt(PMePh$_2$)$_4$] were first studied *ca*. fourty years ago [1]. These studies showed that while with tetrachloroethene a Pt(0) π complex could be isolated, trichloroethene or dichloroethene yielded only σ-vinyl complexes of Pt(II), and chloroalkanes like CHCl$_3$ or CCl$_4$ produced mainly [Pt(PPh$_3$)$_2$Cl$_2$]. Later on, the reactivity of the formed α-chlorovinyl complexes was studied by Chisholm *et al.* [2] and Otsuka *et al.* [3]. The oxidative addition of tetrachloroethene to Ni(0) phosphane complexes was examined by Wada *et al.* since 1979 [4], and the reactivity of σ-trichlorovinyl nickel complexes was studied by Muller *et al.* in 1985 [5]. The reactivity of some cyclic polyhaloolefins with Pt(0) was also studied in a few cases. Thus, reaction of 2,3-dihalobicyclo[2.2.1.]hept-2-ene with [Pt(PPh$_3$)$_3$] afforded π-alkene complexes which could be isomerized to the corresponding σ-vinyl complexes by heating [6]. Later on, Schubert reported the reaction of 3,3-dichloro-1,2-diphenylcyclopropene with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] to give the product of oxidative C-Cl addition [7]. Beck *et al.* studied the reaction of tetrachlorocyclopropene with the same Pt(0) compound and could isolate an unexpected σ-(3-triphenylphosphonio)-propenyl complex resulting from a ring-opening reaction [8]. The reaction of 5,5-dibromo-1,2,3,4-tetraphenylcyclopentadiene with [Ni(PEt$_3$)$_4$] led to [NiBr$_2$(PEt$_3$)$_2$] and triethylphosphonium tetraphenylcyclopentadienide [9]. Although the coordination chemistry of hexachlorocyclopentadiene apparently has not been studied in much detail, its reactivity toward low-valent transition metal complex seems to be governed by highly reactive carbene and radical intermediates, which in most cases allowed only the identification of organic products, but no metal-containing species [10 – 13].

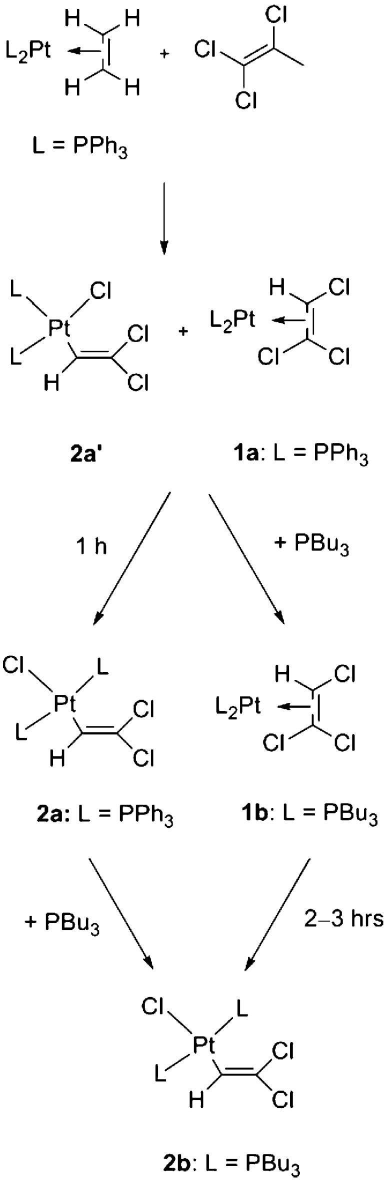
Since on one hand, trichloroethene is a starting material for the synthesis of dichloroethyne, the coordination chemistry of which was studied by us in some detail [14], and since on the other hand the special properties of the pentahalocyclopentadienyl ligand allowed us to develop a fascinating coordination chemistry [15], we found it worthwhile to look at the reactions of trichloroethene and hexachloro- and hexabromocyclopentadiene with Ni(0) and Pt(0) phosphane complexes.

Results and Discussion

A toluene solution of [Pt(PPh_3)$_2$(C_2H_4)] was treated with an excess of trichloroethene at room temperature. When the resulting solution was evaporated to dryness and the residue taken up in dichloromethane, a ^{31}P NMR spectrum of this solution showed the presence of two species in an approximate 4 : 1 ratio. The spectroscopic data (see Experimental Section) suggested that the major component is the π-olefin complex [Pt(PPh_3)$_2$(η^2-CHCl=CCl$_2$) (**1a**), while the minor compound is the σ-vinyl complex *cis*-[Pt(Cl)(CH=CCl$_2$)(PPh_3)$_2$] (**2a′**). From this solution a colorless precipitate began to form after *ca.* one hour, and after several hours precipitation was complete, and no signals could be seen in the NMR spectrum of the supernatant solution. The IR spectrum of this insoluble colorless powder agreed well with the data of *trans*-[Pt(Cl)(CH=CCl$_2$)(PPh_3)$_2$] (**2a**) reported by Kemmitt for the product of the reaction in benzene at 105 °C. Treatment of the freshly prepared NMR solution with PBu_3 produced a new species with NMR data indicative of a π complex, presumably [Pt(PBu_3)$_2$(η^2-CHCl=CCl$_2$)] (**1b**). After standing for several hours the solution contained a new species, now with data suggesting the formation of *trans*-[Pt(Cl)(CH=CCl$_2$)(PBu_3)$_2$] (**2b**). There was no sign of formation of an intermediate *cis*-σ-vinyl complex. The same spectrum of **2b** could be obtained after addition of PBu_3 to the CH_2Cl_2 suspension of **2a**, which led to complete dissolution of the solid (Scheme 1).

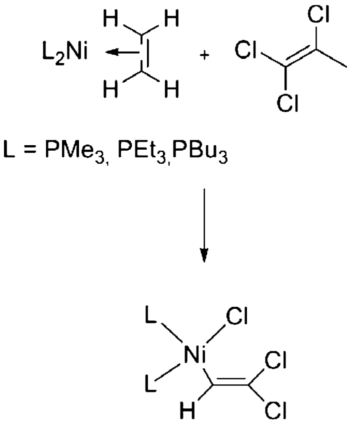
The observations made here for the isomerization process as well as for the phosphane substitution process are very similar to the ones made by us for the corresponding reactions of dichloroethyne with [Pt(PPh_3)$_2$(C_2H_4)], suggesting similar mechanisms [14]. It should also be mentioned that Kemmitt found strong solvent effects on the kinetics of the corresponding isomerization reaction of [Pt(PPh_3)$_2$(η^2-C_2Cl_4)] [16].

Treatment of solutions of the *in situ*-generated [Ni(PR_3)$_2$(C_2H_4)] (R = Me, Et, Bu) with trichloroethene apparently gives only the product of oxidative *trans*-addition [Ni(Cl)(CH=CCl$_2$)(PR_3)$_2$] (**3a**–**c**), except for R = Me, where a second species is present. (Scheme 2).



Scheme 1. Synthesis and reactivity of platinum trichloroethene complexes.

The regioselective addition of the (H)C–Cl bond and not of the (Cl)C–Cl bond can be proven by a ^{1}H-coupled ^{13}C NMR spectrum of **3c** and is in agreement with Muller's observation with the corresponding PPh_3 complex [17]. The NMR data of the second product in the reaction of the PMe_3 complex, however, indicate



3a–c

Scheme 2. Reaction of $[Ni(PR_3)_2(C_2H_4)]$ with trichloroethene.

that the alternative C–Cl bond can also undergo oxidative addition.

The reaction of hexachlorocyclopentadiene with Ni(0) complexes $[Ni(PR_3)_2(C_2H_4)]$ yielded no identifiable nickel compounds, as was reported for the corresponding reaction of the PEt_3 ethylene complex [13]. Mass spectral examination of the products showed all members of the series $C_{5n}Cl_{4n-(1,2,3)}$ for $n = 1-4$ as well as C_5Cl_6, C_5Cl_5, $C_{10}Cl_{10}$, and $C_{10}Cl_8$. These fragments are quite common in C_5Cl_6 chemistry [18] and were also observed in the reaction with $Fe(CO)_5$ [12]. The initially observed intense colors hint on the formation of the C_5Cl_5 radical [19].

The reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with C_5Cl_6 yielded a green-blue solid. However, the FAB$^+$-MS spectra showed no chlorine-containing species besides $[Pt(PPh_3)_2Cl]^+$ and the usual fragments of the $[Pt(PPh_3)_2]$ unit, including *e. g.* [20], $[Pt(PPh_3)(PPh_2)]^+$. The ^{31}P NMR spectrum showed, besides signals of PPh_3O, *cis*- and *trans*-$[Pt(PPh_3)_2Cl_2]$, and $[Pt(PPh_3)_2(CO_3)]$ (most likely an impurity in the starting ethylene complex), only an AX spin system with signals at $\delta = 22.8$ (d, $J_{PP} = 13$ Hz, $J_{PPt} = 4079$ Hz), and 26.5 (d, $J_{PP} = 13$ Hz, $J_{PPt} = 1710$ Hz). The size of the P_AP_X coupling constant suggests a *cis*-orientation of two PPh_3 ligands, and the values of J (P-Pt) hint on one chloride and one carbon ligand (compare data of **2a′**). When the reaction was carried out in an NMR tube, high field signals at $\delta < -60$ ppm appeared which are indicative of the formation of an orthometallated PPh_3 ligand [21]. Such a ligand might decompose *via* $[Pt(PPh_3)(PPh_2)(C_6H_5)]$ in CH_2Cl_2 with formation of *cis*-$[Pt(PPh_3)_2(Cl)(C_6H_5)]$, the *trans* isomer of which has been reported [22]. From the NMR tube solutions some colorless crystals precipitated, which were shown by X-ray crystallography to be a new modification of *trans*-$[Pt(PPh_3)_2Cl_2]$ (see Fig. 1 and discussion below).

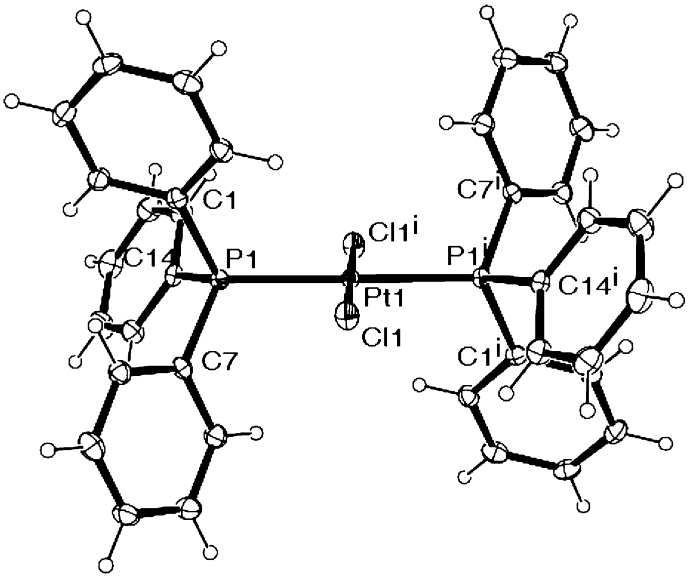


Fig. 1. ORTEP-III view of *trans*-$[Pt(PPh_3)_2Cl_2]$ (displacement ellipsoids are at the 30 % probability level; the H atoms are drawn as spheres with arbitrary radii).

The reaction of C_5Br_6 with $[Pt(PPh_3)_2(C_2H_4)]$ produced again an intensely colored solution from which a beige solid precipitated, which was isolated and examined. The FAB^+-MS spectrum showed the same fragments as the product of the C_5Cl_6 reaction in addition to $[Pt(PPh_3)_2Br]^+$. The ^{31}P NMR spectrum showed signals due to PPh_3O, *cis*-$[Pt(PPh_3)_2Br_2]$ and *cis*-$[Pt(PPh_3)_2(Br)(Cl)]$, which were identified by comparison with literature data [23]. About the origin of the chlorido ligand can only be speculated. An impurity in the starting ethylene complex seems to be the most plausible source. The reaction solution yielded after evaporation a dark brown solid. Its FAB^+-MS spectrum showed the presence of the dimer $[Pt(PPh_3)(Br)(\mu\text{-}Br)]_2$ and its fragments [24] together with two fragments apparently containing the (C_5Br_5) group $[Pt(PPh_3)_n(C_5Br_5)]^+$ with $m/e = 1179$ ($n = 2$) and 917 ($n = 1$). The ^{31}P NMR spectrum exhibited besides the signal of PPh_3O those of both *cis*- and *trans*-$[Pt(PPh_3)_2Br_2]$ [25] together with a very-low-intensity AMX (or two AA'XX') system(s) with $J_{PP} = 5$ Hz and $J_{PPt} = 2740$ and 2460 Hz. The small value of J (P-P) hints on a long range coupling, and therefore we assign these signals to the dimeric complexes *cis*- and *trans*-$[Pt(PPh_3)(Br)(\mu\text{-}Br)]_2$, the NMR data of which apparently have not been reported. However, for the analogous chlorido-complexes (*cis* and *trans*) $J_{PP'} = 5$ Hz has been reported [26].

Crystal structure determination of trans-[Pt(PPh₃)₂Cl₂]

The structure of a triclinic modification of *trans*-dichloridobis(triphenylphosphine) platinum was reported in 1999 [27]. The orthorhombic modification that we obtained crystallizes with two molecules of CH_2Cl_2 per formula unit, in space group *Pcab*. Similar to the triclinic form, the platinum atom also resides on an inversion center. The bond parameters around Pt are very similar to those in the triclinic modification: Pt–Cl 2.3086(7) *vs*. 2.2997(11) Å; Pt–P 2.3095(7) *vs*. 2.3163(11) Å, and Cl–Pt–P 86.62(3) and 93.38(3)° *vs*. 87.88(4) and 92.12(4)°.

Experimental Section

The reactions were performed under N_2 or Ar, using standard Schlenk techniques. Solvents were purified by standard procedures, saturated with N_2 or Ar and stored over molecular sieves. Trichloroethene and hexachlorocyclopentadiene were commercial products and used without further purification. $[Pt(PPh_3)_2(C_2H_4)]$, $[Ni(PR_3)_2Cl_2]$ and C_5Br_6 were prepared according to literature procedures [28–30]

Reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with trichloroethene

A solution of 130 mg $[Pt(PPh_3)_2(C_2H_4)]$ in 5 mL toluene was treated with *ca*. 0.12 mL C_2HCl_3 and then stirred for 90 min at r. t. Evaporation of the solvent *in vacuo* produced a colorless powder, which was dissolved in CH_2Cl_2 and examined by ^{31}P NMR: **1a**: $\delta = 22.0$ (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 3262$ Hz), 17.1 (d, $^2J_{PP} = 23$ Hz, $^1J_{PtP} = 3120$ Hz). **2a'**: $\delta = 12.4$ (d, $^2J_{PP} = 27$ Hz, $^1J_{PtP} = 1952$ Hz), 10.7 (d, $^2J_{PP} = 27$ Hz, $^1J_{PtP} = 4131$ Hz). This solution was stirred for 3 h at r. t. to produce a colorless precipitate which was isolated and identified by its IR spectrum ($\nu_{PtC=C} = 1550\ cm^{-1}$) as **2a**. A freshly prepared CH_2Cl_2 solution of **1a** was treated with several drops of PBu_3. A relatively broad ^{31}P NMR signal at $\delta = 0.2$ ($^1J_{PtP} = 3127$ Hz) indicated the formation of **1b**, but was gradually replaced by another singlet at $\delta = 7.2$ ($^1J_{PtP} = 2581$ Hz), which was also observed when the CH_2Cl_2 suspension of **2a** was treated with several drops of PBu_3: **2b**. Evaporation of the solution to dryness and dissolution of the residue in $CDCl_3$ allowed the measurement of the ^1H NMR spectrum. Besides the signals due to free PPh_3 and free and/or complexed PBu_3 only a triplet at $\delta = 5.52$ ($^3J_{HP} = 2$ Hz, $^2J_{HPt} = 32$ Hz) could be observed.

Reaction of $[Ni(PMe_3)_2(C_2H_4)]$ with trichloroethene

A red solution of $[NiCl_2(PMe_3)_2]$ (570 mg, 2.0 mmol) in 5 mL thf was treated under C_2H_4 with an excess of zinc powder for 30 min. The yellow solution was filtered, cooled to −30 °C and treated with *ca*. 0.1 mL C_2HCl_3. After warming to ambient temperature a black suspension had formed. Evaporation to dryness was followed by column chromatography on silica gel. A yellow band formed, which was collected, eluted with Et_2O and evaporated *in vacuo*. The residue was examined by NMR spectroscopy in C_6D_6 solution. – ^1H NMR: $\delta = 6.16$ (1H), 5.29 (1H), 1.08 (18H), 0.96 (18H) (broad signals). – ^{31}P NMR: $\delta = -12.8$ s, -13.4 s (relative intensities 1 : 1). – ^{13}C NMR: $\delta = 150.4$ (t, $J_{CP} = 42$ Hz), 144.7 (t, $J = 41$ Hz), 118.3 (t, $J = 8$ Hz), 102.7 (t, $J = 7$ Hz), 12.8 (t, $J = 14$ Hz), 12.2 (t, $J = 14$ Hz).

After standing for several days at r. t. a precipitate formed in the NMR tube, and the ^{31}P NMR spectrum showed a decrease in intensity of the signal at -12.8 ppm. Column chromatography of this solution on alumina, using Et_2O as eluent, produced a yellow band, from which, after dissolution and concentration *in vacuo* on cooling to −78 °C orange crystals of **3a'** could be obtained. – ^1H NMR ($CDCl_3$): $\delta = 6.11$ ("t", $J_{HP} = 6$ Hz, 1H), 1.35 ("t", $J_{HP} = 4$ Hz, 18H) ^{31}P NMR ($CDCl_3$): $\delta = -13.1$ s. – $C_8H_{19}Cl_3P_2Ni$: calcd. C 27.96, H 5.57; found C 28.95, H 6.16.

Reaction of [Ni(PEt$_3$)$_2$(C$_2$H$_4$)] with trichloroethene

A solution of [NiCl$_2$(PEt$_3$)$_2$] (630 mg, 1.70 mmol) in 10 mL toluene was treated with sodium dust (300 mg, 13 mmol) under C_2H_4 for 20 h, filtered and cooled to -78 °C. After addition of 0.17 mL C_2HCl_3 (1.70 mmol) the reaction mixture was warmed to ambient temperature within two hours. Evaporation of the solvent *in vacuo* was followed by chromatography on Al_2O_3 using Et_2O as eluent. A yellow band developed, which was collected. Evaporation *in vacuo* produced **3b** as a yellow oil (350 mg, 47 % yield). Careful recrystallization from pentane at -30 °C gave **3b** as large red crystals. – ^{1}H NMR (CDCl$_3$): $\delta = 5.23$ (t, $J = 3$ Hz, 1H), 1.71 (m, 12H), 1.24 (m, 18H). – ^{31}P NMR (CDCl$_3$): $\delta = 13.5$ (s). – ^{13}C NMR (CDCl$_3$): $\delta = 143.4$ (t, $J = 39$ Hz) 103.6 (t, $J = 7$ Hz), 13.7 (“t”, $J = 13$ Hz), 7.9 (s). – $C_{14}H_{31}Cl_3NiP_2$: calcd. C 39.43, H 7.33; found C 39.99, H 7.44.

Reaction of [Ni(PBu$_3$)$_2$(C$_2$H$_4$)] with trichloroethene

A solution of [NiCl$_2$(PBu$_3$)$_2$] (800 mg, 1.50 mmol) in 10 mL toluene was stirred with 230 mg sodium dust (10.0 mmol) under C_2H_4 for 20 h, then cooled to -78 °C and treated with 0.15 mL C_2HCl_3 (1.50 mmol). Stirring was continued for 15 min at this temperature and then for 90 min at r. t. After evaporation of the solvent *in vacuo* the residue was taken up in a small amount of pentane and chromatographed on silica gel. Elution with Et_2O produced a yellow band from which after evaporation *in vacuo* a yellow oil could be isolated: **3c**. Recrystallization from MeOH at -78 °C gave a yellow flocculent precipitate, which was isolated. However, upon warming to r. t. the compound melted again. – ^{1}H NMR (C$_6$D$_6$): $\delta = 5.25$ (t, $J = 3$ Hz, 1H), 1.54 (m, 24H), 1.34 (m, 12H), 0.86 (“t”, 18H). – ^{31}P NMR (C$_6$D$_6$): $\delta = 6.4$ (s). – ^{13}C NMR (C$_6$D$_6$): $\delta = 143.7$ (dt, $^3J_{CP} = 39$ Hz, $^2J_{CH} = 21$ Hz), 103.5 (dt, $^2J_{CP} = 6$ Hz, $^1J_{CH} = 190$ Hz); 26.6 (s), 24.9 (“t”, $J_{CP} = 6$ Hz), 21.7 (“t”, $J_{CP} = 13$ Hz), 14.0 (s) ($PCH_2CH_2CH_2CH_3$). – $C_{26}H_{55}Cl_3P_2Ni$ (%): calcd. C 52.51, H 9.32; found C 50.08, H 9.27.

Reaction of C$_5$Cl$_6$ with [Ni(PPh$_3$)$_2$(C$_2$H$_4$)]

A suspension of [Ni(PPh$_3$)$_2$(C$_2$H$_4$)] (412 mg, 0.67 mmol) in toluene (10 mL) was treated at -78 °C with C_5Cl_6 (1.0 mL, 6.2 mmol) with stirring. The temperature raised to ambient overnight. The obtained dark-brown suspension was centrifuged and the supernatant discarded. The residue was washed three times with 20 mL portions of hexane, dried and extracted with 20 mL methanol. Evaporation of the extract left a light-green paramagnetic powder (228 mg). The IR spectrum showed bands which are attributable to the PPh$_3$ ligand.

Reaction of C$_5$Cl$_6$ with [Ni(PMe$_3$)$_2$(C$_2$H$_4$)]

A mixture of [NiCl$_2$(PMe$_3$)$_2$] (0.29 g, 1.03 mmol), a small amount of zinc powder and C_5Cl_6 (0.17 mL, 1.06 mmol) was treated under an atmosphere of ethene with tetrahydrofuran (1.5 mL). Immediately a violet color developed. After stirring for 15 min the mixture was given on top of a short silica gel column and chromatographed using Et_2O as eluent. A red fraction was obtained which was evaporated to dryness. Yield: 0.19 g of a red-brown solid. The ^{31}P NMR spectrum in CDCl$_3$ showed only a weak, very broad absorption at *ca.* $\delta = 60$ ppm. – MS (DEI): $m/e = 473.6$ ($C_{10}Cl_{10}$), 403.7 ($C_{10}Cl_8$), 331.8 ($C_{10}Cl_6$), 308.7 (C_5Cl_7), 271.8 (C_5Cl_6), 236.8 (100 %, C_5Cl_5), 202.9 (C_5Cl_4), 166.9 (C_5Cl_3), 140.9 (C_3Cl_3), 129.9 (C_5Cl_2), 95.0 (C_5Cl), 60.0 (C_5); in addition, at very weak intensity, the complete series $C_{5n}Cl_{4n-(1,2,3)}$ with $n = 2,3,4,5$.

Reaction of C$_5$Cl$_6$ with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]

A solution of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (360 mg, 0.48 mmol) in toluene (10 mL) was treated at -40 °C with C_5Cl_6 (0.43 mL, 2.68 mmol). After keeping the reaction mixture at -78 °C for 16 h the precipitate was isolated by filtration, washed three times with 20 mL portions of pentane and dried *in vacuo*. Yield: 0.14 g of a green-blue solid. – MS ((+)-FAB): $m/e = 755.4$ ($PtP_2C_{36}H_{30}Cl$), 735.4 ($PtP_2C_{36}H_{31}O$), 719.4 ($PtP_2C_{36}H_{30}$), 642.3 ($PtP_2C_{30}H_{25}$), 455.2 ($PtPC_{18}H_{14}$), 378.1 ($PtPC_{12}H_8$), 279.3 ($PC_{18}H_{15}O$), 262.3 ($PC_{18}H_{15}$) plus numerous very weak unidentified peaks. – ^{31}P NMR (109.3 MHz, in CH$_2$Cl$_2$): $\delta = 8.2$ ($J_{\mathrm{PPt}} =$ 3700 Hz, [Pt(PPh$_3$)$_2$CO$_3$], impurity in the starting material), 15.6 ($J_{\mathrm{PPt}} = 3680$ Hz, *cis*-[Pt(PPh$_3$)$_2$Cl$_2$]), 22.1 ($J_{\mathrm{PPt}} =$ 2640 Hz, *trans*-[Pt(PPh$_3$)$_2$Cl$_2$]), 22.8 (d, $J_{\mathrm{PP}} = 13$ Hz, $J_{\mathrm{PPt}} =$ 4079 Hz), 26.5 (d, $J_{\mathrm{PP}} = 13$ Hz, $J_{\mathrm{PPt}} = 1710$ Hz), 29.0 (PPh$_3$O). From the NMR tube a few colorless crystals precipitated, which were used for a crystal structure determination (see below).

Reaction of C$_5$Br$_6$ with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]

A solution of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (360 mg, 0.48 mmol) in toluene (10 mL) was treated at -25 °C with C_5Br_6 (270 mg, 0.50 mmol). Under continuous stirring the temperature was raised to ambient within 16 h. The precipitate was isolated by filtration, washed with two 10 mL portions of toluene and dried *in vacuo*. Yield: 0.21 g of a beige solid. – MS ((+)-FAB): $m/e = 799.1$ ($PtP_2C_{36}H_{30}Br$), 755.2 ($PtP_2C_{36}H_{31}Cl$, from impurity in the starting material), 734.3 ($PtP_2C_{36}H_{30}O$), 718.3 ($PtP_2C_{36}H_{29}$), 455.2 ($PtPC_{18}H_{15}$), 378.1 ($PtPC_{12}H_{10}$), 279.2 ($PC_{18}H_{16}O$). – ^{31}P NMR (109.4 MHz, in CH$_2$Cl$_2$): $\delta = 14.0$ (d, $J_{\mathrm{PP}} = 14$ Hz, *cis*-Pt(PPh$_3$)$_2$BrCl), 15.0 ($J_{\mathrm{PPt}} = 3630$ Hz, *cis*-Pt(PPh$_3$)$_2$Br$_2$), 16.4 (d, $J_{\mathrm{PP}} = 14$ Hz, $J_{\mathrm{PPt}} = 3680$ Hz, *cis*-Pt(PPh_3)$_2$BrCl), 29.4 (PPh_3O). The filtrate was evaporated to dryness. Yield: 0.47 g of a dark-brown solid. – MS ((+)-FAB): m/e = 1257.2 ($Pt_2P_2C_{36}H_{30}Br_4$+Na), 1234.8 ($Pt_2P_2C_{36}H_{30}Br_4$), 1179 ($PtP_2C_{36}H_{30}C_5Br_5$), 1154.0 ($Pt_2P_2C_{36}H_{30}Br_3$), 1074.0 ($Pt_2P_2C_{36}H_{30}Br_2$), 993.1 ($Pt_2P_2C_{36}H_{29}Br$), 917 ($PtPC_{18}H_{15}C_5Br_5$), 799.2 ($PtP_2C_{36}H_{30}Br$), 755.9 ($PtP_2C_{36}H_{31}Cl$), 718.3 ($PtP_2C_{36}H_{29}$), 557.3 ($P_2C_{36}H_{31}O_2$), 537.9 ($PtPC_{18}H_{15}Br$), 456.1 ($PtPC_{18}H_{16}$), 279.2 ($PC_{18}H_{16}O$, 100 %). – ^{31}P NMR (109.4 MHz, in C_6D_6): δ = 7.9 (d, J_{PP} = 5 Hz, J_{PPt} = 2740 Hz), 9.4 (d, J_{PP} = 5 Hz, J_{PPt} = 2460 Hz), 15.8 (J_{PPt} = 3572 Hz, *cis*-[Pt(PPh_3)$_2Br_2$]), 21.2 (J_{PPt} = 2560 Hz, *trans*-[Pt(PPh_3)$_2Br_2$]), 28.0 (br, PPh_3O).

X-Ray structure determination

An X-ray quality single crystal was mounted on a glass fiber and cooled to 173(3) K for the measurements. The data were collected on a Nonius KappaCCD diffractometer using MoK_α radiation (λ = 0.71073 Å, graded multilayer X-ray optics). A multi-scan absorption correction was applied using the program SADABS [31a]. The structure was solved with SIR97 [31b] as implemented in the WINGX software package [31c]. Refinement (full-matrix least-squares on F^2) was carried out with SHELXL-97 [31d], also as implemented in WINGX. Molecular graphics: ORTEP-III [31e]. For crystallographic data and numbers pertinent to data collection and structure refinement see Table 1.

Table 1. Crystal data for trans-[Pt(PPh_3)$_2Cl_2$].

Empirical formula	$C_{36}H_{30}Cl_2P_2Pt \cdot 2CH_2Cl_2$
Formula weight	960.38
Crystal size, mm^3	0.09 × 0.07 × 0.05
Crystal system	orthorhombic
Space group	*Pcab*
Unit cell dimensions	
a, Å	8.0273(2)
b, Å	20.1801(3)
c, Å	23.0606(4)
Volume, Å^3	3735.63(13)
Z	4
Density (calculated), g cm^{-3}	1.71
Absorption coefficient, mm^{-1}	4.3
F(000), e	1888
θ range for data collection, deg	3.24 – 25.36
hkl ranges	±9, ±24, ±27
Reflections collected / unique / R_{int}	42311 / 3416 / 0.0394
Completeness to θ = 25.36°, %	99.9
Absorption correction	semi-empirical from equivalents
Max. / min. transmission	0.766 / 0.695
Data / ref. parameters	3416 / 215
Final $R1/wR2$ indices [$I > 2\sigma(I)$]	0.0219 / 0.0507
Final $R1/wR2$ indices (all data)	0.0324/ 0.0572
Goodness-of-fit on F^2	1.106
Extinction coefficient	0.00049(7)
Largest diff. peak / hole, e Å^{-3}	0.752 / −0.629

CCDC 873325 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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