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Synthesis and Characterization of $[Pt(COD)Cl(NO_3)]$ and $[Pt(COD)(NO_3)_2]$ and the Use of $[Pt(COD)Cl_x(NO_3)_{2-x}]$ in the Preparation of *cis*$[Pt(PPh_3)_2Cl_x(NO_3)_{2-x}]$ ($x = 0, 1, 2$) and $[Pt(PPh_3)_3L](NO_3)$ ($L = Cl, NO_3$)

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Abstract

$[Pt(COD)Cl_2]$ (COD = 1,5-cyclooctadiene) is a versatile starting material for the synthesis of Pt(II) compounds. The preparations of the new compounds $[Pt(COD)Cl(NO_3)]$, $[Pt(COD)(NO_3)_2]$ and $[Pt(PPh_3)_3(NO_3)](NO_3)$ and also of the known compounds *cis*$[Pt(PPh_3)_2Cl_2]$, *cis*$[Pt(PPh_3)_2Cl(NO_3)]$, *cis*$[Pt(PPh_3)_2(NO_3)_2]$ and $[Pt(PPh_3)_3Cl](NO_3)$ are reported. The compounds are characterized by elemental analysis, $^{31}P\{^1H\}$ NMR spectroscopy and IR spectroscopy.

Introduction

Metal compounds with good leaving groups are often used as starting materials for the synthesis of mixed-metal cluster compounds [1]. In the synthesis of mixed Pt–Au cluster compounds $[Pt(COD)(NO_3)_2]$ may be used as such [2]. In order to enrich the synthetic procedures for these cluster compounds, a number of compounds $[Pt(COD)Cl_x(NO_3)_{2-x}]$, *cis*$[Pt(PPh_3)_2Cl_x(NO_3)_{2-x}]$ ($x = 0, 1, 2$) and $[Pt(PPh_3)_3L](NO_3)$ ($L = Cl, NO_3$) were prepared and characterized.

Substitution of Pt-bonded Cl by NO_3 or PR_3 by means of $AgNO_3$ or $AgPR_3NO_3$ has been reported earlier, especially for R = alkyl. Species such as $[Pt(PR_3)_2X_2]$, $[Pt(PR_3)_3X]^+$ and $[Pt(PR_3)_4]^{2+}$ with R = alkyl [3–6] and with R = aryl [6, 7] were prepared in this way. Substitution of COD by phosphines has been applied previously [8, 9].

Experimental

General

$^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL100 FT at 40.5 MHz, in CH_2Cl_2 solution, with TMP in CH_2Cl_2 as external reference. Infra-red spectra were recorded on a Perkin-Elmer 283 spectrophotometer, in CsI pellets or in nujol between NaCl crystals. C, H and N analyses were carried out by the microanalytical department of this university.

Preparations

Starting materials

$[Pt(COD)Cl_2]$ was prepared according to the literature [10]. The COD used hereby was distilled over sodium under nitrogen. The white product was dried for 6 h at room temperature in vacuum. $AgPPh_3NO_3$ was prepared according to the literature [11]. All other chemicals were commercially available and were used without purification.

$[Pt(COD)Cl(NO_3)]$

A solution of 23.3 mg $AgNO_3$ (0.137 mmol) in 15 ml MeOH was added in 30 min to a stirred solution of 51.2 mg $[Pt(COD)Cl_2]$ (0.137 mmol) in 30 ml CH_2Cl_2. A white precipitate of AgCl was formed. The reaction mixture was evaporated to dryness at reduced pressure, at room temperature. AgCl was removed by adding 15 ml of CH_2Cl_2 and filtration. The volume of the filtrate was reduced to 5 ml by evaporation at reduced pressure at room temperature. Colourless needles were obtained by slow diffusion of diethylether in the solution. The product was filtered off, washed with diethylether and dried at room temperature in vacuum. Yield 41 mg (0.102 mmol = 75% based on Pt). Dec. 135–160 °C. *Anal.* Found (calc.): C, 23.75 (23.98); H, 2.98 (3.02); N, 3.33 (3.50)%. IR, apart from peaks due to COD: (nujol) bonded nitrate: 1520(s), 1510(s), 1270(s), 967(s), 793(w) cm^{-1}; (CsI) ν(Pt–Cl)/ν(Pt–O): 334(m), 308(m) cm^{-1}.

$[Pt(COD)(NO_3)_2]$

A solution of 250 mg $AgNO_3$ (1.47 mmol) in 50 ml MeOH was added to a stirred solution of 200 mg $[Pt(COD)Cl_2]$ (0.535 mmol) in 50 ml CH_2Cl_2. A white precipitate of AgCl was formed. The

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reaction mixture was evaporated to dryness at reduced pressure, at maximal 20 °C. AgCl and $AgNO_3$ were removed by adding 50 ml CH_2Cl_2 and filtration. The filtrate was diminished to 3 ml by evaporation at reduced pressure, at maximal 20 °C. A white precipitate was formed. After standing for 15 min, the precipitate was filtered off, washed with diethylether and dried at room temperature in vacuum. Yield 207 mg (0.484 mmol = 91% based on Pt). The product decomposes at room temperature within weeks, and at 50 °C within minutes, but is stable at 0 °C. The product does not explode when struck by a hammer and burns without exploding when ignited [2]. *Anal.* Found (calc.): C, 22.57 (22.49); H, 2.84 (2.83); N, 6.46 (6.56)%. IR (nujol) bonded nitrate: 1524(s), 1278(s), 972(s), 791(w) cm^{-1}; (CsI) ν(Pt–O): 310(m) cm^{-1}.

$[Pt(COD)(NO_3)_2]$ may be prepared from $[Pt(COD)Cl(NO_3)]$ in the same way (see Scheme 1).

cis[Pt(PPh₃)₂Cl₂]

A solution of 105 mg PPh_3 (0.400 mmol) in 2 ml CH_2Cl_2 was added to a stirred solution of 50 mg $[Pt(COD)Cl_2]$ (0.134 mmol) in 5 ml CH_2Cl_2. The white product was obtained by slow diffusion of diethylether in the CH_2Cl_2 solution. The product was filtered off, washed with diethylether and dried in vacuum at 70 °C. Yield 92 mg (116 mmol = 87% based on Pt). Melting point (m.p.) 298–302 °C (melting and decomposition). IR, apart from peaks due to triphenylphosphine: (CsI) ν(Pt–Cl): 317(m), 290(m) cm^{-1}, in accordance with the literature [12]. The $^{31}P\{^1H\}$ NMR spectrum of the product, a singlet with $^1J(^{195}Pt^{31}P)$ satellites (Table I) is identical to the spectrum of *cis*$[Pt(PPh_3)_2Cl_2]$ which was prepared according to the literature [13]. A solution of *cis*$[Pt(PPh_3)_2Cl_2]$ was prepared before in almost the same way [9].

TABLE I. $^{31}P\{^1H\}$ NMR Data Relative to TMP

Compound	δ (ppm)	$^1J(^{195}Pt^{31}P)$ (Hz)	$^2J(^{31}P^{31}P)$ (Hz)
cis$[Pt(PPh_3)_2Cl_2]$	11.7	3679	
cis$[Pt(PPh_3)_2(NO_3)_2]$	1.0	4012	
cis$[Pt(PPh_3)_2Cl(NO_3)]$	14.4[a]	3849[a]	19.0
	−0.3[b]	3863[b]	
$[Pt(PPh_3)_3Cl](NO_3)$	9.9[a]	3645[a]	18.7
	20.7	2486	
$[Pt(PPh_3)_3(NO_3)](NO_3)$	−0.2[b]	3726[b]	19.5
	19.5	2612	

[a] P *trans* to Cl. [b] P *trans* to NO_3.

cis[Pt(PPh₃)₂Cl(NO₃)]

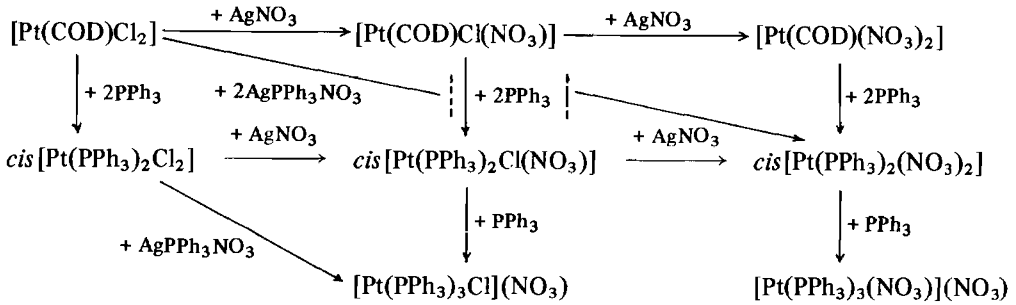
(a) From $[Pt(COD)Cl(NO_3)]$: in the same way as the preparation of *cis*$[Pt(PPh_3)_2Cl_2]$ from $[Pt(COD)Cl_2]$, with 2.00 equiv. PPh_3, which are added in 30 min.

(b) From *cis*$[Pt(PPh_3)_2Cl_2]$: in the same way as the preparation of $[Pt(COD)Cl(NO_3)]$ from $[Pt(COD)Cl_2]$.

(c) From *cis*$[Pt(PPh_3)_2Cl_2]$ and *cis*$[Pt(PPh_3)_2(NO_3)_2]$: 25.0 mg of *cis*$[Pt(PPh_3)_2Cl_2]$ (0.032 mmol) and 26.7 mg of *cis*$[Pt(PPh_3)_2(NO_3)_2]$ (0.032 mmol) were dissolved in 5 ml CH_2Cl_2. The solution was stirred for 1 h and allowed to stand for one night. Colourless crystals were obtained by slow diffusion of diethylether into the solution. The product was filtered off, washed with diethylether and dried at room temperature in vacuum. Yield 35 mg (0.043 mmol = 68% based on Pt). m.p. 218–226 °C (melting with decomposition). *Anal.* Found (calc.): C, 52.15 (52.92); H, 3.70 (3.70); N, 1.61 (1.71)%. IR (nujol) bonded nitrate: 1490(s), 1480(s), 1270(s), 990(s), 795(w) cm^{-1}; (CsI) ν(Pt–Cl)/ν(Pt–O): 308(m), 288(m) cm^{-1}. These data are in close accordance with the literature [14]. The $^{31}P\{^1H\}$ NMR spectrum consists of two doublets, intensity 1:1, both with $^1J(^{195}Pt^{31}P)$ satellites (Table I). The *cis*$[Pt(PPh_3)_2Cl(NO_3)]$ disproportionates in CH_2Cl_2 slightly, according to 2 *cis*$[Pt(PPh_3)_2Cl(NO_3)] \rightleftharpoons$ *cis*$[Pt(PPh_3)_2Cl_2]$ + *cis*$[Pt(PPh_3)_2(NO_3)_2]$. The disproportionation constant was calculated from $^{31}P\{^1H\}$ NMR data (see Table II).

cis[Pt(PPh₃)₂(NO₃)₂]

(a) From $[Pt(COD)(NO_3)_2]$: in the same way as the preparation of *cis*$[Pt(PPh_3)_2Cl(NO_3)]$ from $[Pt(COD)Cl(NO_3)]$. Yield 55% based on Pt.



Scheme 1.

TABLE II. Determination of the Disproportionation Constant of *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)] in CH$_2$Cl$_2$ Calculated from the Peak Heights in the ^{31}P{^{1}H} NMR Spectra[a]

Sample	h_1	h_2	h_3	K_{disp} ($\times 10^{-3}$) $= (h_1 - h_2)/h_3^2$
1	54	17	473	4.9
2	56	25	495	5.9
3	46	24	452	5.4
4	51	17	380	6.0
5	27	44	492	4.9
				Average: $(5.4 \pm 1)10^{-3}$

[a] h_1 = height of the central peak of *cis*[Pt(PPh$_3$)$_2$Cl$_2$]; h_2 = height of the central peak of *cis*[Pt(PPh$_3$)$_2$(NO$_3$)$_2$]; h_3 = sum of the heights of the four central peaks of *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)]. All peak heights are in relative units.

(b) From *cis*[Pt(PPh$_3$)$_2$Cl$_2$] or *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)]: in the same way as the preparation of [Pt(COD)(NO$_3$)$_2$] from [Pt(COD)Cl$_2$] or [Pt(COD)Cl(NO$_3$)]. Colourless crystals were obtained by slow diffusion of diethylether in the CH$_2$Cl$_2$ solution in the dark. Yield 83% based on Pt.

(c) From [Pt(COD)Cl$_2$]: a solution of 60.1 mg AgPPh$_3$NO$_3$ (0.139 mmol) in 10 ml CH$_2$Cl$_2$ was added to a stirred solution of 26.0 mg [Pt(COD)Cl$_2$] (0.0695 mmol) in 5 ml CH$_2$Cl$_2$. After stirring for 1 h and standing for 4 h the slowly precipitated AgCl was filtered off. The volume of the filtrate was reduced to 3 ml by evaporation at reduced pressure. Colourless crystals were obtained by slow diffusion of diethylether into the CH$_2$Cl$_2$ solution in the dark. The product was filtered off, washed with diethylether and dried at 70 °C in vacuum. Yield 49 mg (0.058 mmol = 84% based on Pt). m.p. 217–220 °C (melting and decomposition). *Anal.* Found (calc.): C, 51.34 (51.25); H, 3.57 (3.58); N, 3.26 (3.32)%. IR (nujol) bonded nitrate: 1504(s), 1497(s), 1282(s), 1263(s), 980(s), 792(w) cm^{-1}; (CsI) ν(Pt–O): 308(m), 290(m) cm^{-1}. These data are in close accordance with the literature [15–18]. The ^{31}P{^{1}H} NMR spectrum consists of a singlet with two ^1J(^{195}Pt^{31}P) satellites (Table I).

[Pt(PPh$_3$)$_3$Cl](NO$_3$)

(a) From *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)]: 35 mg of this (0.043 mmol) and 22 mg PPh$_3$ (0.084 mmol) were dissolved in 5 ml CH$_2$Cl$_2$. Slow diffusion of diethylether into the solution yielded colourless crystals. Yield 34 mg (0.031 mmol = 74% based on Pt).

(b) From *cis*[Pt(PPh$_3$)$_2$Cl$_2$]: a solution of 111.8 mg AgPPh$_3$NO$_3$ (0.259 mmol) in 30 ml CH$_2$Cl$_2$ was added in 45 min to a stirred solution of 204.5 mg *cis*[Pt(PPh$_3$)$_2$Cl$_2$] (0.259 mmol) in 30 ml CH$_2$Cl$_2$. After standing for one night the very slowly precipitated AgCl was filtered off. The volume of the filtrate was reduced to 3 ml by evaporation at reduced pressure. After standing for 2 h some AgCl was filtered off again. 14 mg PPh$_3$ (0.053 mmol) was added to the filtrate. Colourless crystals were formed by slow diffusion of diethylether into the solution. The product was recrystallized by slow diffusion of diethylether into a solution of the product in CH$_2$Cl$_2$. The product was filtered off, washed with diethylether and dried at 70 °C in vacuum. Yield: 112 mg (0.104 mmol = 40% based on Pt). m.p. 207–208 °C (decomposition at 210 °C). *Anal.* Found (calc.): C, 59.74 (60.09); H, 4.20 (4.20); N, 1.34 (1.30)%. IR (CsI) free nitrate: 1350(s), 830(w) cm^{-1}; ν(Pt–Cl): 315(m) cm^{-1}. The ^{31}P{^{1}H} NMR spectrum consists of a doublet and a triplet, intensity 2:1, both with ^1J(^{195}Pt^{31}P) satellites (Table I). It is identical to the spectrum of [Pt(PPh$_3$)$_3$Cl](BF$_4$) [19].

[Pt(PPh$_3$)$_3$(NO$_3$)](NO$_3$)

(a) From *cis*[Pt(PPh$_3$)$_2$(NO$_3$)$_2$]: in the same way as the preparation of [Pt(PPh$_3$)$_3$Cl](NO$_3$) from *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)]. The white product was dried at 70 °C in vacuum. Yield 80% based on Pt. m.p. 176–185 °C (melting and decomposition). *Anal.* Found (calc.): C, 58.55 (58.65); H, 4.10 (4.10); N, 2.34 (2.53)%. IR (nujol) bonded nitrate: 1514(s), 1268(s), 967(s), 784(w) cm^{-1}; free nitrate: 1355(s), 830(w) cm^{-1}; (CsI) ν(Pt–O): 293(w) cm^{-1}. The ^{31}P{^{1}H} NMR spectrum consists of a doublet and a triplet, intensity 2:1, both with ^1J(^{195}Pt^{31}P) satellites (Table I).

(b) Reaction of *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)] with 1.0 equiv. of AgPPh$_3$NO$_3$, in CH$_2$Cl$_2$, yielded a mixture of [Pt(PPh$_3$)$_3$(NO$_3$)](NO$_3$) and *cis*[Pt(PPh$_3$)$_2$(NO$_3$)$_2$], molar ratio approximately 1:2.

(c) Reaction of [Pt(PPh$_3$)$_3$Cl](NO$_3$) in CH$_2$Cl$_2$ with 1.0 equiv. of AgNO$_3$ in MeOH yielded after one day *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)]. After two days a mixture of [Pt(PPh$_3$)$_3$(NO$_3$)](NO$_3$) and *cis*[Pt(PPh$_3$)$_2$(NO$_3$)$_2$] was formed. With 2.0 equiv. of AgNO$_3$ only *cis*[Pt(PPh$_3$)$_2$(NO$_3$)$_2$] was formed.

Unsuccessful attempts to prepare [Pt(PPh$_3$)$_4$](NO$_3$)$_2$

Between [Pt(PPh$_3$)$_3$(NO$_3$)](NO$_3$) and excess of PPh$_3$ in CH$_2$Cl$_2$, or boiling MeOH under N$_2$, no reaction occurred. From [Pt(PPh$_3$)$_3$Cl](NO$_3$) and 1.0 equiv. of AgPPh$_3$NO$_3$ in CH$_2$Cl$_2$ some *cis*[Pt(PPh$_3$)$_2$Cl(NO$_3$)] was formed slowly.

Results and Discussion

The substitution of COD by two phosphines to yield *cis* bisphosphino Pt compounds is a fast and rather clean reaction. The *cis* configuration is retained. With only one equivalent of PPh_3, these reactions were incomplete.

The $^{31}P\{^1H\}$ NMR spectra of $[Pt(PPh_3)_2Cl(NO_3)]$ and $[Pt(PPh_3)_2(NO_3)_2]$ show that they are the *cis* compounds. The $^{31}P\{^1H\}$ NMR spectrum of $[Pt(PPh_3)_2Cl(NO_3)]$ contains two doublets, with different $^1J(^{195}Pt^{31}P)$ coupling, indicating that this compound contains two chemically non-equivalent phosphorus atoms. The magnitude of the $^2J(^{31}P^{31}P)$ coupling (19.0 Hz) lies in the region of compounds containing phosphines *cis* to each other [20] just as the $^2J(^{31}P^{31}P)$ coupling constants of $[Pt(PPh_3)_3Cl]^+$ (18.7 Hz) and $[Pt(PPh_3)_3(NO_3)]^+$ (19.5 Hz). Both $^1J(^{195}Pt^{31}P)$ coupling constants of $[Pt(PPh_3)_2Cl(NO_3)]$ (3849 and 3863 Hz) lie in the region of *cis* bisphosphino platinum complexes [20b]. The chemical shift of $[Pt(PPh_3)_2(NO_3)_2]$ (1.0 ppm) lies in the same region as the chemical shift of P *trans* to NO_3 in $[Pt(PPh_3)_3(NO_3)]^+$ (−0.2 ppm). The chemical shifts of P *trans* to P in $[Pt(PPh_3)_3Cl]^+$ (20.7 ppm) and $[Pt(PPh_3)_3(NO_3)]^+$ (19.5 ppm) lie at much higher field, in accordance with the literature [20c]. The $^1J(^{195}Pt^{31}P)$ coupling constant in $[Pt(PPh_3)_2(NO_3)_2]$ (4012 Hz) lies in the region of the *cis* bisphosphino platinum complexes [20b].

The chemical shift of phosphorus strongly depends on the ligand *trans* to the phosphine (Table I). The order $NO_3 > Cl > PPh_3$ holds, in accordance with the literature [20c]. The influence of the *trans* ligand can also be observed in the $^1J(^{195}Pt^{31}P)$ coupling constants. In $[Pt(PPh_3)_3X]^+$ and *cis*$[Pt(PPh_3)_2X_2]$ the coupling constant of Pt with P *trans* to X is smaller for X = Cl (3645 *versus* 3679 Hz) than for $X = NO_3$ (3726 *versus* 4012 Hz). Also, in *cis*-$[Pt(PPh_3)_2Cl(NO_3)]$ the coupling constant of Pt with P *trans* to Cl (3849 Hz) is smaller than the coupling constant of Pt with P *trans* to NO_3 (3863 Hz). The coupling constant of Pt with P *trans* to P in $[Pt(PPh_3)_3X]^+$ is much smaller (2486 Hz for X = Cl and 2612 Hz for $X = NO_3$), and lies in the region of the *trans* bisphosphino platinum complexes [20b]. When bond strength is decreased, the coupling constant decreases. So the order $PPh_3 > Cl > NO_3$ holds for the *trans* influence, in accordance with the literature [20d].

Obviously $AgPPh_3NO_3$ is not a very good phosphine donor, as more *cis*$[Pt(PPh_3)_2(NO_3)_2]$ than $[Pt(PPh_3)_3(NO_3)](NO_3)$ is formed in the reaction of *cis*$[Pt(PPh_3)_2Cl(NO_3)]$ with $AgPPh_3NO_3$. $AgNO_3$ can abstract PPh_3 from $[Pt(PPh_3)_3Cl]^+$, forming *cis*$[Pt(PPh_3)_2Cl(NO_3)]$. This is in contrast with trialkylphosphines where, from $[Pt(PR_3)_3Cl]^+$ and $AgNO_3$, $[Pt(PR_3)_3(NO_3)]^+$ is actually formed [3, 4]. $AgNO_3$ also abstracts PPh_3 from $[Pt(PPh_3)_3(NO_3)]^+$, forming *cis*$[Pt(PPh_3)_2(NO_3)_2]$. The *cis* compounds are formed during the phosphine abstractions because the X in $[Pt(PPh_3)_3X]^+$ ($X = Cl, NO_3$) effects a weaker *trans* influence than does PPh_3. We were unsuccessful in preparing $[Pt(PPh_3)_4](NO_3)_2$, in contrast with the literature [4], where $[Pt(PR_3)_4](NO_3)_2$ is reported, however, only for R = alkyl.

The reactions of $[Pt(COD)Cl_2]$ with $AgNO_3$, PPh_3 or $AgPPh_3NO_3$ form a quick synthesis pathway for the new compounds $[Pt(COD)Cl(NO_3)]$, $[Pt(COD)(NO_3)_2]$ and $[Pt(PPh_3)_3(NO_3)](NO_3)$. $[Pt(COD)Cl(NO_3)]$ and $[Pt(COD)(NO_3)_2]$ can be prepared in one step starting from $[Pt(COD)Cl_2]$. $[Pt(PPh_3)_3(NO_3)](NO_3)$ can be prepared in two steps, via *cis*$[Pt(PPh_3)_2(NO_3)_2$ (see Scheme 1). (The preparation of $[Pt(PPh_3)_3(NO_3)](NO_3)$ directly from $[Pt(COD)(NO_3)_2]$ with excess PPh_3 is not recommended; the product will be contaminated with an unidentified compound containing COD.)

The known compounds *cis*$[Pt(PPh_3)_2Cl_2]$, *cis*-$[Pt(PPh_3)_2Cl(NO_3)]$, *cis*$[Pt(PPh_3)_2(NO_3)_2]$ and $[Pt(PPh_3)_3Cl]^+$ can also be prepared in a simple way from $[Pt(COD)Cl_2]$: *cis*$[Pt(PPh_3)_2Cl_2]$ and *cis*$[Pt(PPh_3)_2(NO_3)_2]$ in one step; $[Pt(PPh_3)_3Cl](NO_3)$ in two steps, via *cis*$[Pt(PPh_3)_2Cl_2]$; and *cis*$[Pt(PPh_3)_2Cl(NO_3)]$ in two steps via *cis*$[Pt(PPh_3)_2Cl_2]$ or $[Pt(COD)Cl(NO_3)]$ (see Scheme 1).

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