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Journal of Organometallic Chemistry 570 (1998) 129–139

Journal of Organometallic Chemistry

Synthesis and characterization of novel dinuclear and cationic cyclobutadiene platinum complexes

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Received 18 June 1998

Abstract

Reactions of the cyclobutadiene platinum complexes $[PtCl_2(C_4R_4)]$ (R = Me **1a**, R = Et **1b**) with diphosphines $Ph_2P^{\cap}PPh_2$ ($^{\cap}$ = –C≡C– (dppa), $-CH_2-$ (dppm), $-(CH_2)_2-$ (dppe), $-(CH_2)_3-$ (dppp), $-(CH_2)_4-$ (dppb)) in a 2:1 molar ratio result in formation of novel binuclear cyclobutadiene platinum complexes $[\{PtCl_2(C_4R_4)\}_2(\mu\text{-}Ph_2P^{\cap}PPh_2)]$ (R = Me **2**, Et **3**). In contrast, reactions in equimolar ratio lead to formation of cationic complexes with dppe, dppp and dppb $[PtCl(C_4R_4)\{Ph_2P(CH_2)_nPPh_2\}]Cl$ (n = 2–4, R = Me **5**, Et **6**). Complexes **2**, **3** and **5**, **6** were fully characterized by microanalysis and by NMR and IR spectroscopies. Structural characterization of $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2b**) reveals a piano-stool coordination at each platinum center defined by the η^4-C_4Me_4 ligand, two Cl atoms and one P atom. The P–C–P angle of 131.0(4)° is larger than that expected for tetrahedral geometry. The X-ray structure of $[PtCl(C_4Me_4)\{Ph_2P(CH_2)_3PPh_2\}]Cl\cdot CH_2Cl_2$ (**5b**·CH_2Cl_2) reveals a Pt atom coordinated by the η^4-C_4Me_4 ligand, chloride and the two phosphorus donors in a piano-stool conformation. In the solid state, these cations are arranged to form channels with a diameter of 13.8 Å in which solvent molecules (CH_2Cl_2) are embedded. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Cyclobutadiene complexes; Phosphine complexes; X-ray diffraction

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1. Introduction

Cyclobutadiene platinum complexes first were prepared by reaction of $[PtCl_2(CO)_2]$ with diphenylacetylene by Canziani et al. [1]. During investigations of the platinum-catalyzed addition of alcohols to alkynes [2] we discovered a convenient synthesis of cyclobutadiene platinum complexes: Hexachloroplatinic(IV) acid reacts in n-butanol to give Zeise's acid with 1-butene as a ligand, $H[PtCl_3(\eta^2\text{-}C_4H_8)]$, and this complex reacts with dialkylsubstituted alkynes RC≡CR′ (R, R′ = Me, Et, n-Pr) to yield cyclobutadiene platinum complexes $[PtCl_2(C_4R_2R'_2)]$ [3,4]. The X-ray structures of $[PtCl_2(C_4R_4)]$ (R = Me **1a**, Et **1b**) revealed that these complexes are monomeric in the solid state [3,4]a. These 16-electron complexes react with donor ligands L to give 18-electron complexes of the type $[PtCl_2(C_4R_2R'_2)L]$ (L = PPh_3, $AsPh_3$, $SbPh_3$, py, p-tol ($para$-toluidine)) [4]b, [5]. Furthermore, reaction of $[PtCl_2(C_4Me_4)]$ (**1a**) with 2,2′-bipyridine (bpy) was shown to form a cationic complex $[PtCl(C_4Me_4)(bpy)]Cl$ [6].

We here report reactions of $[PtCl_2(C_4R_4)]$ (**1**) with diphosphines, which result in binuclear and cationic cyclobutadiene(diphosphine)platinum complexes.

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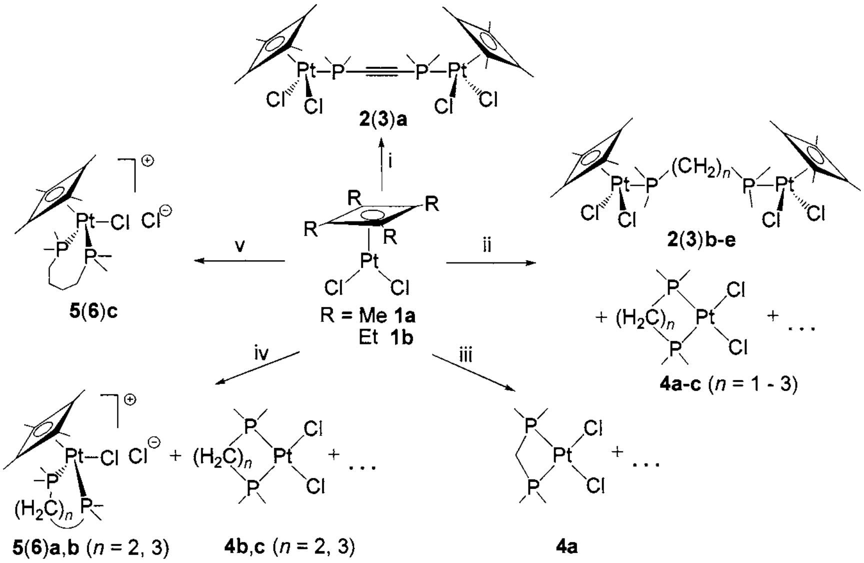
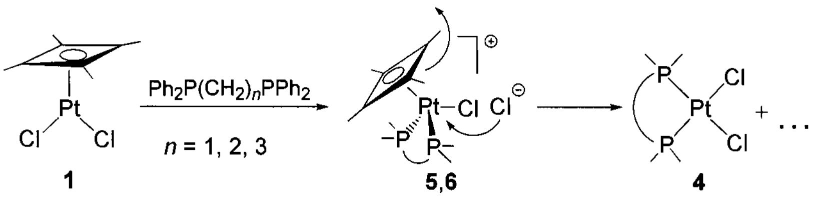
PII S0022-328X(98)00873-0



Scheme 1. i) dppa (2:1); ii) dppm, dppe, dppp, dppb (2:1); iii) dppm (1:1); iv) dppe, dppp (1:1); v) dppb (1:1).



Scheme 2.

2. Results and discussion

2.1. Syntheses

The complexes $[PtCl_2(C_4R_4)]$ (R = Me **1a**, Et **1b**) react in methylene chloride at ambient temperature with $Ph_2P^{\cap}PPh_2$ ($^{\cap}$ = $-C{\equiv}C-$ (dppa), $-CH_2-$ (dppm), $-(CH_2)_2-$ (dppe), $-(CH_2)_3-$ (dppp) and $-(CH_2)_4-$ (dppb)) in a 2:1 molar ratio to give binuclear complexes $[\{PtCl_2(C_4R_4)\}_2(\mu\text{-}Ph_2P^{\cap}PPh_2)]$ (R = Me **2**, Et **3**; $^{\cap}$ = $-C{\equiv}C-$ **a**, $-CH_2-$ **b**, $-(CH_2)_2-$ **c**, $-(CH_2)_3-$ **d**, $-(CH_2)_4-$ **e**) (Scheme 1(i, ii)). In reactions with dppm, dppe and dppp, the corresponding $[PtCl_2\{Ph_2P(CH_2)_nPPh_2\}]$ complexes (**4**) ($n = 1-3$) are formed as side products (ca. 5–20%). They were identified in solution by comparison of ^{31}P-NMR data with literature data [7]. The binuclear complexes **2** and **3** were isolated in high yields (65–93%) as yellow to yellow-orange crystals which are air-stable over several weeks.

With an equimolar ratio of **1** and $Ph_2P(CH_2)_nPPh_2$ ($n = 1-4$), the reactions yield cationic complexes $[PtCl(C_4R_4)\{Ph_2P(CH_2)_nPPh_2\}]Cl$ (R = Me **5**, Et **6**) and/or the corresponding complexes **4** by cleavage of cyclobutadiene (Scheme 1(iii–v)). The proposed pathway is shown in Scheme 2. In the case of dppb, cationic complexes **5(6)c** are the final products; formation of $[PtCl_2(dppb)]$ was not observed. In all other reactions the complexes **4** are the final products. With dppe and dppp, the intermediate cationic complexes could be isolated (**5(6)b**), or observed in solution (**5(6)a**) by NMR spectroscopy. With dppm, the cationic complexes could not be detected as intermediates at ambient temperatures. No identifiable products were obtained by reaction with dppa in equimolar ratio.

The cationic complexes **5(6)b** and **5(6)c** were obtained as well-shaped, yellow-orange crystals in 60–97% yields. They crystallized as methylene chloride solvates (**5(6)b**·CH_2Cl_2, **5(6)c**·CH_2Cl_2). Apart from aging, they were found to be air-stable over 2–3 weeks.

2.2. NMR and IR spectra

Selected NMR data of the binuclear complexes **2** and **3** are given in Tables 1–3. In all complexes **2** and **3** the resonances due to the alkyl protons of the cyclobutadiene ligands are shifted upfield by 0.21–0.40 ppm with respect to those in **1**. In the tetramethyl-substituted complexes with dppa **2a**, dppp **2d** and dppb **2e**, the methyl protons appear as a doublet due to ^4J(P,H) coupling (5.1–6.1 Hz) with platinum satellites (^3J(Pt,H) = 14.3–16.4 Hz). The values of ^3J(Pt,H) are smaller than that found for **1a** (18.1 Hz) [4]a but are similar to those in $[PtCl_2(C_4Me_4)L]$ (**7**) (L = py, *p*-tol,

Table 1
Selected ^{1}H- and ^{13}C-NMR data (δ in ppm, J in Hz) for $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2P{\cap}PPh_2)]$ (**2**)

Complex	^{1}H-NMR					^{13}C-NMR			
	μ-L	$\delta(CH_3)$	$\Delta\delta$[a]	^{3}J(Pt,H)	$\Delta^{3}J$[b]	$\delta(C_4)$	$\Delta\delta$[a]	^{1}J(Pt,C)	$\Delta^{1}J$[b]
1a	—	1.60	—	18.1	—	103.8	—	143	—
2a	dppa	1.31	−0.29	14.3	−3.8	99.1	−4.7	123	−20
2b	dppm	1.25	−0.35	—	—	97.7	−6.1	127	−16
2c	dppe	1.26	−0.34	—	—	97.3	−6.5	124	−19
2d	dppp	1.20	−0.40	16.4	−1.7	96.7	−7.1	123	−20
2e	dppb	1.24	−0.36	16.0	−2.1	96.7	−7.1	[c]	

Data for $[PtCl_2(C_4Me_4)]$ (**1a**) are given for comparison.

[a] $\Delta\delta = \delta(\mathbf{2})-\delta(\mathbf{1a})$.

[b] $\Delta J = J(\mathbf{2})-J(\mathbf{1a})$.

[c] ^{195}Pt satellites could not be observed due to a poor signal-to-noise ratio.

Table 2
Selected ^{1}H- and ^{13}C-NMR data (δ in ppm, J in Hz) for $[\{PtCl_2(C_4Et_4)\}_2(\mu\text{-}Ph_2P{\cap}PPh_2)]$ (**3**)

Complex	^{1}H-NMR					^{13}C-NMR			
	μ-L	$\delta(CH_2)$	$\Delta\delta$ [a]	$\delta(CH_3)$	$\Delta\delta$[a]	$\delta(C_4)$	$\Delta\delta$[a]	^{1}J(Pt,C)	$\Delta^{1}J$[b]
1b	—	2.01	—	1.28	—	106.5	—	149	—
3a	dppa	1.77	−0.24	0.99	−0.29	102.2	−4.3	120	−29
3b	dppm	1.72	−0.29	1.07	−0.21	100.5	−6.0	122	−27
3c	dppe	1.63	−0.38	1.01	−0.27	101.2	−5.3	126	−23
3d	dppp	1.67	−0.34	1.02	−0.26	100.2	−6.3	128	−21
3e	dppb	1.69	−0.32	1.00	−0.28	100.1	−6.4	125	−24

Data for $[PtCl_2(C_4Et_4)]$ (**1b**) are given for comparison.

[a] $\Delta\delta = \delta(\mathbf{3})-\delta(\mathbf{1b})$.

[b] $\Delta J = J(\mathbf{3})-J(\mathbf{1b})$.

Table 3
^{31}P-NMR data (δ in ppm, J in Hz) for $[\{PtCl_2(C_4R_4)\}_2(\mu\text{-}Ph_2P{\cap}PPh_2)]$ (**2**/**3**)

Complex					Complex				
	μ-L	$\delta(^{31}P)$	$\Delta\delta(^{31}P)$[a]	^{1}J(Pt,P)		L	$\delta(^{31}P)$	$\Delta\delta(^{31}P)$[a]	^{1}J(Pt,P)
2a	dppa	−11.1	18.9	4225	**3a**	dppa	−14.6	15.4	4116
2b[b]	dppm	13.2[c]	34.8	4237[d]	**3b**[b]	dppm	11.3[g]	32.9	4132[h]
2c[b]	dppe	12.7[e]	24.5	4309[f]	**3c**[b]	dppe	11.8[i]	23.6	4241[j]
2d	dppp	13.4	30.1	4331	**3d**	dppp	11.6	28.3	4312
2e	dppb	13.0	28.3	4335	**3e**	dppb	11.5	26.8	3997

[a] $\Delta\delta = \delta(\mathbf{2}/\mathbf{3})-\delta$(free diphosphine).

[b] Coupling constants were obtained by simulation.

[c] $^{2}J(P,P) = 50.4$ Hz.

[d] $^{3}J(Pt,P) = 109.4$ Hz.

[e] $^{3}J(P,P) = 51.2$ Hz.

[f] $^{4}J(Pt,P) < 1$ Hz.

[g] $^{2}J(P,P) = 49.8$ Hz.

[h] $^{3}J(Pt,P) = 105.6$ Hz.

[i] $^{3}J(P,P) = 43.9$ Hz.

[j] $^{4}J(Pt,P) < 1$ Hz.

PPh_3, $AsPh_3$, $SbPh_3$) ($^{3}J(Pt,H) = 14.1$–16.3 Hz) [4]b. Due to the non-zero value of the $^{2/3}J(P,P)$ coupling and the superposition of the three subspectra of the platinum isotopomers (^{195}Pt: $I = \frac{1}{2}$, 33.8% abundance), the coupling constants ^{3}J(Pt,H) and ^{4}J(P,H) could not be calculated for the complexes **2b** and **2c**.

In **2** and **3**, the ^{13}C-NMR resonances of the cyclobutadiene carbon atoms are shifted upfield by 4–7 ppm compared with those in the 16-electron complexes **1a** and **1b**, respectively. Similar upfield shifts (4–11 ppm) were found in the mononuclear 18-electron complexes $[PtCl_2(C_4R_4)L]$ (R = Me **7**, Et **8**; L = py, *p*-tol, PPh_3,

Table 4
Selected ^{1}H- and ^{13}C-NMR data (δ in ppm, J in Hz) for $[PtCl(C_4Me_4)(Ph_2P(CH_2)_nPPh_2)]Cl$ (**5**)

Complex		^{1}H-NMR				^{13}C-NMR			
	L	$\delta(CH_3)$	$\Delta\delta$ [a]	$^{3}J(Pt,H)$	$\Delta^{3}J$ [b]	$\delta(C_4)$	$\Delta\delta$ [a]	$^{1}J(Pt,C)$	$\Delta^{1}J$ [b]
1a	—	1.60	—	18.1	—	103.8	—	143	—
5a	dppe	1.74	0.14	12.1	−6.0	[c]			
5b	dppp	1.54	−0.06	12.1	−6.0	102.3	−1.5	88	−55
5c	dppb	1.32	−0.28	12.5	−5.6	103.0	−0.8	88	−55

Data for $[PtCl_2(C_4Me_4)]$ (**1a**) are given for comparison.
[a] $\Delta\delta = \delta(\mathbf{5})–\delta(\mathbf{1a})$.
[b] $\Delta J = J(\mathbf{5})–J(\mathbf{1a})$.
[c] Due to the limited stability, a spectrum could not be obtained.

Table 5
Selected ^{1}H- and ^{13}C-NMR data (δ in ppm, J in Hz) for $[PtCl(C_4Et_4)(Ph_2P(CH_2)_nPPh_2)]Cl$ (**6**)

Complex		^{1}H-NMR				^{13}C-NMR			
	L	$\delta(CH_2)$	$\Delta\delta$[a]	$\delta(CH_3)$	$\Delta\delta$[a]	$\delta(C_4)$	$\Delta\delta$[a]	$^{1}J(Pt,C)$	$\Delta^{1}J$ [b]
1b	—	2.01	—	1.28	—	106.5	—	149	—
6a	dppe	1.94	−0.07	1.02	−0.26	[c]			
6b	dppp	1.87	−0.14	1.01	−0.27	105.0	−1.5	93	−56
6c	dppb	1.72	−0.29	1.00	−0.28	105.5	−1.0	[d]	

Data for $[PtCl_2(C_4Et_4)]$ (**1b**) are given for comparison.
[a] $\Delta\delta = \delta(\mathbf{6})–\delta(\mathbf{1b})$.
[b] $\Delta J = J(\mathbf{6})–J(\mathbf{1b})$.
[c] Due to the limited stability, a spectrum could not be obtained.
[d] ^{195}Pt satellites could not be observed due to a poor signal-to-noise ratio.

Table 6
^{31}P-NMR parameters for $[PtCl(C_4R_4)(Ph_2P(CH_2)_nPPh_2)]Cl$ (**5**/**6**)

Complex					Complex				
R = Me	L	$\delta(^{31}P)$	$\Delta\delta$ [a]	$^{1}J(Pt, P)$	R = Et	L	$\delta(^{31}P)$	$\Delta\delta$[a]	$^{1}J(Pt,P)$
5a	dppe	30.5	42.3	3322	**6a**	dppe	29.1	40.9	3262
5b	dppp	−6.9	9.8	3262	**6b**	dppp	−8.9	7.8	3224
5c	dppb	0.9	16.2	3462	**6c**	dppb	−1.3	14.0	3402

[a] $\Delta\delta = \delta(\mathbf{5}/\mathbf{6})–\delta$(free diphosphine).

$AsPh_3$, $SbPh_3$) [4]b. The appearance of only one resonance for the cyclobutadiene carbon atoms indicates free rotation of the ligand. Coordination of the diphosphine to platinum causes a decrease in $^{1}J(Pt,C)$ in **2** and **3** by 16–20 and 21–29 Hz, respectively. A similar decrease (19 Hz, 22 Hz) was found in $[PtCl_2(C_4R_4)(PPh_3)]$ (R = Me **7c**, Et **8c**).

In agreement with the structures shown in Scheme 1 ^{31}P-NMR spectra show singlet resonances with platinum satellites. Coordination of the diphosphine in **2** and **3** result in downfield shifts for the ^{31}P resonances ($\Delta\delta(^{31}P) = 15–35$ppm; Table 3). As no long-range couplings are observed in the ^{31}P-NMR spectra of the μ-dppa **2(3)a**, μ-dppp- **2(3)d** and μ-dppb complexes **2(3)e**, these spectra result from A and AX spin systems. However, ^{31}P-NMR spectra of μ-dppm **2(3)b** and μ-dppe complexes **2(3)c** are complex due to the non-zero, long-range couplings $^{2/3}J(P,P)$ and the presence of platinum isotopomers. Thus, these spectra result from superposition of A_2 (43.8%), ABX (44.8%) and AA′XX′ subspectra (11.4%) (A, B = ^{31}P; X = ^{195}Pt). Spectra were simulated using the program PERCH [8], Table 3. For example, Fig. 1 shows that the observed spectrum of $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2b**) was simulated adequately by superposition of the three calculated ABX, AA′XX′ and A_2 subspectra (the A_2 subspectrum exhibits only one singlet and is not shown in Fig. 1).

Selected ^{1}H- and ^{13}C-NMR parameters of the complexes **5** and **6** are given in Tables 4 and 5. The resonances of the alkyl protons of the cyclobutadiene

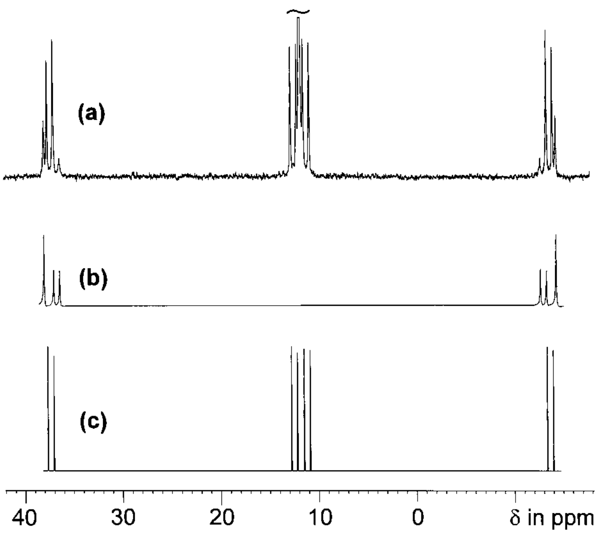


Fig. 1. Experimental (a) and simulated (b, c) ^{31}P-NMR spectra of $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2b**). The spectra b (AA′ part of the AA′XX′ subspectrum) and c (AB part of the ABX subspectrum; A, B = ^{31}P; X = ^{195}Pt) were separately calculated and are shown in the approximate ratio of their abundances (44.8% : 11.4%).

ligands in **5** and **6** are shifted upfield (0.06–0.29 ppm) with respect to those of **1**. Similar upfield shifts were observed for the binuclear complexes **2** and **3**. In contrast, a downfield shift of the methyl proton resonances was found ($\Delta\delta = 0.14$ ppm) for the complex $[PtCl(C_4Me_4)\{Ph_2P(CH_2)_2PPh_2\}]Cl$ (**5a**). A similar downfield shift ($\Delta\delta = 0.07$ ppm) was observed in the spectrum of $[PtCl(C_4Me_4)(bpy)]Cl$ ($\delta = 1.67$ ppm) [6]. In spectra of the tetramethyl-substituted complexes **5**, the methyl protons appear as 1:2:1 triplets (^4J(P,H) = 5.8–6.0 Hz) with platinum satellites (^3J(Pt,H) = 12.1–12.5 Hz). Similar to the case of the binuclear complexes **2** (ΔJ = 5.6–6.0 Hz), the ^3J(Pt,H) coupling constants in **5** are smaller than those in **1a** (18.1 Hz), which lacks a phosphine ligand.

The ^{13}C-NMR spectra of cationic dppp (**5**(**6**)**b**) and dppb (**5**(**6**)**c**) complexes reveal small upfield shifts of the cyclobutadiene ring carbon atoms by 0.8–1.5 ppm with respect to complexes **1** (cf. $\Delta\delta$ = 4–7 ppm in **2** and **3**). The values of ^1J(Pt,C) are more than 50 Hz smaller than those observed in **1** (cf. $\Delta J \approx -20$ to -30 Hz in **2** and **3**) and this may be due to a decrease in the s-electron density between platinum and the carbon atoms of the cyclobutadiene ring caused by coordination of an additional strong donor ligand to platinum.

The ^{31}P-NMR spectra of **5** and **6** show chemical and magnetic equivalence of both P atoms (superposition of A_2 and A_2X spin systems; A = ^{31}P, X = ^{195}Pt) and ^1J(Pt,P) can be obtained directly (Table 6). The values are about 600–1000 Hz smaller than those observed for **2** and **3**. The magnitudes of the downfield shift of the ^{31}P resonances in the five-, six- and seven-membered 1,3-diphospha-2-platina rings depend on the ring size and are about 42 ppm (**5**(**6**)**a**), 9 ppm (**5**(**6**)**b**) and 15 ppm (**5**(**6**)**c**), respectively. Similar values were also

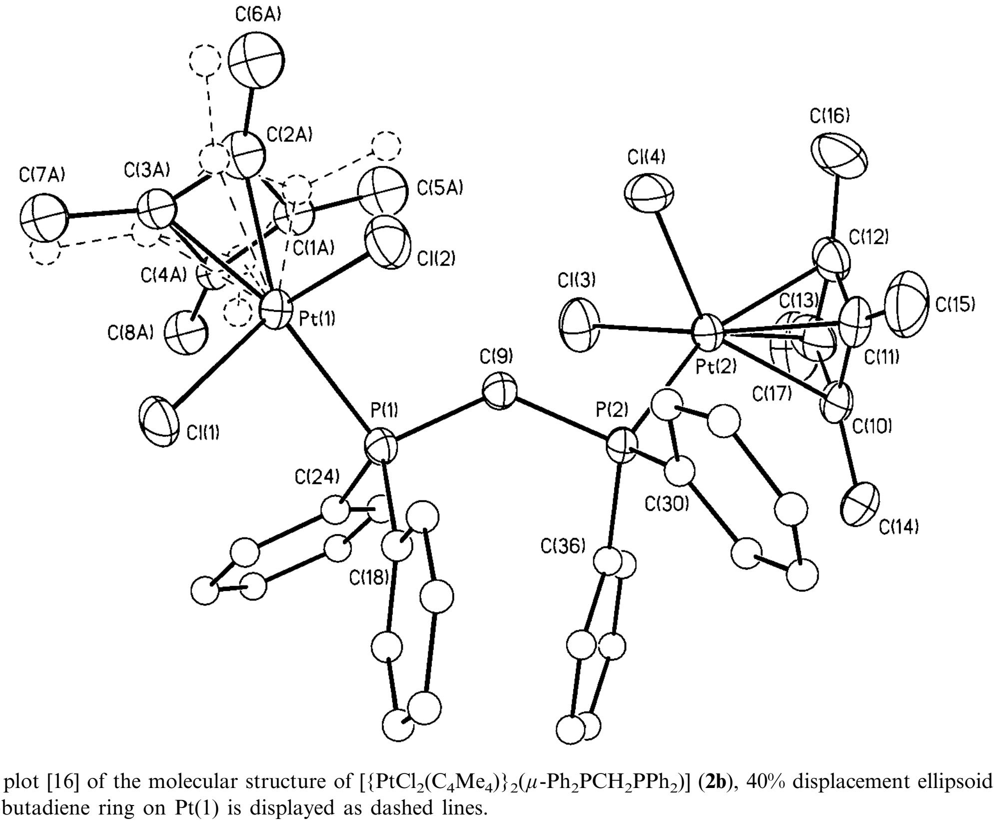


Fig. 2. ORTEP-III plot [16] of the molecular structure of $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2b**), 40% displacement ellipsoids. Second position of disordered cyclobutadiene ring on Pt(1) is displayed as dashed lines.

Table 7
Selected bond distances (Å) and bond angles (°) for $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}PPh_2CH_2PPh_2)]$ (**2b**)

Pt(1)–C(1)	2.06(2) [2.11(2)]	Pt(2)–C(10)	2.141(7)
Pt(1)–C(2)	2.19(2) [2.20(2)]	Pt(2)–C(11)	2.095(8)
Pt(1)–C(3)	2.21(2) [2.27(2)]	Pt(2)–C(12)	2.160(7)
Pt(1)–C(4)	2.10(1) [2.09(2)]	Pt(2)–C(13)	2.212(8)
Pt(1)–Cl(1)	2.448(2)	Pt(2)–Cl(3)	2.457(2)
Pt(1)–Cl(2)	2.470(2)	Pt(2)–Cl(4)	2.445(2)
Pt(1)–P(1)	2.331(2)	Pt(2)–P(2)	2.336(2)
C(1)–C(2)	1.42(3) [1.46(3)]	C(10)–C(11)	1.47(1)
C(2)–C(3)	1.35(3) [1.46(3)]	C(11)–C(12)	1.46(1)
C(3)–C(4)	1.56(2) [1.59(3)]	C(12)–C(13)	1.45(1)
C(1)–C(4)	1.40(3) [1.36(3)]	C(10)–C(13)	1.46(1)
P(1)–C(9)	1.824(7)	P(2)–C(9)	1.835(7)
Cl(1)–Pt(1)–Cl(2)	96.76(7)	Cl(3)–Pt(2)–Cl(4)	92.91(8)
Cl(1)–Pt(1)–P(1)	89.83(6)	Cl(3)–Pt(2)–P(2)	90.62(7)
Cl(2)–Pt(1)–P(1)	92.76(7)	Cl(4)–Pt(2)–P(2)	92.26(7)
C(1)–C(2)–C(3)	94(2) [94(2)]	C(10)–C(11)–C(12)	88.4(7)
C(2)–C(3)–Cl(4)	88(2) [82(2)]	C(11)–C(12)–Cl(13)	91.6(7)
C(1)–C(4)–C(3)	86(1) [93(2)]	C(10)–C(13)–C(12)	89.1(7)
C(2)–C(1)–C(4)	92(2) [91(2)]	C(11)–C(10)–C(13)	90.9(7)
P(1)–C(9)–P(2)	131.0(4)		

Values for the dashed cyclobutadiene moiety (Fig. 2) are given in square brackets.

found in other complexes with chelating $R_2P(CH_2)_nPR_2$ ($n = 2$–4) ligands [9].

The IR spectra of complexes **2**, **3**, **5** and **6** show that coordination of the diphosphine to platinum leads to a significant decrease in wavenumber of the Pt–Cl vibration. Thus, for **2** and **3**, v(Pt–Cl) appeared at ca. 260/230 cm^{-1} compared with 315/299 cm^{-1} in $[PtCl_2(C_4Me_4)]$ (**1a**) and 315/297 cm^{-1} in $[PtCl_2(C_4Et_4)]$ (**1b**) [4]. No Pt–Cl vibrations were observed above 200 cm^{-1} in the mononuclear cationic complexes **5** and **6** with two coordinated p-donors.

2.3. Structure of $[\{PtCl_2(C_4Me_4)\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (2b)

The molecular structure of **2b** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 7. The cyclobutadiene ligand on Pt(1) is disordered. The structure of **2b** reveals a piano-stool coordination at each platinum, similar to that found in $[PtCl_2(C_4Me_4)(SbPh_3)]$ (**7e**) [10].

The Pt–P distances are equal within 3σ (d(Pt–P) = 2.331(2)/2.336(2) Å) and are slightly shorter than that in $[PtCl_2(C_4Me_2Ph_2)(PPh_3)]$ (**9**) (d(Pt–P) = 2.353(2) Å) [5]. The distances between platinum atoms and the planes of the cyclobutadiene rings ($d[Pt(1)–C_4]$ = 1.88(1)/1.90(1) Å;[1] $d[Pt(2)–C_4]$ = 1.884(4) Å) are equal within 3σ and are similar to Pt–C_4 distances in the related complexes **1a**, **7e** and **9** (1.869(1) – 1.901(8) Å) [4]a, [5,10]. Remarkably, the two Cl–Pt–Cl angles differ significantly (96.76(7)° vs 92.91(8)°) for no obvious reason. The first value is comparable with that in **7e** (95.33(4)°) [10] and the second value with those in **1a** (92.3(1)°) and in **9** (92.30(9)°). As expected from Gutmann's bond length rules [11], the Pt–Cl bond lengths (2.445(2)–2.470(2) Å) are in the range of those found for the other 18-electron complexes **7e** and **9** (2.425(3)–2.458(1) Å) and are larger than those in the 16-electron complexes **1a** and **1b** (2.323(2)–2.339(6) Å) [3,4]a.

The cyclobutadiene ring on Pt(2) is square-planar; there is no significant deviation of the four endocyclic C–C–C angles (88.4(7)–91.6(7)°) from 90° and the four C–C bond lengths (1.45(1)–1.47(1) Å) are essentially equal. The disordered cyclobutadiene ring on Pt(1) seems to differ from the idealized square-planar geometry ($\angle$C–C–C = 86(1)–94(2)/82(1)–94(1)°; d(C–C) = 1.35(3)–1.56(2)/1.36(3)–1.59(3) Å). The Pt atoms are not symmetrically coordinated to the cyclobutadiene ligands as revealed by the large range of Pt–C bond lengths (at Pt(1): 2.06(2)–2.27(2) Å, at Pt(2): 2.095(8)–2.212(8) Å). This is in agreement with results found for **7e**, where a wide range of Pt–C bond lengths are also observed (2.105(4)–2.195(5) Å). The methyl substituents of the cyclobutadiene rings are displaced from the plane, defined by the four carbon atoms of the cyclobutadiene ring, away from platinum by 0.03(4)–0.40(4)/0.08(4)–0.37(4) Å at Pt(1) and 0.12(2)–0.30(2) Å at Pt(2). These values are similar to those observed in **7e** (0.083(6)–0.401(6) Å). It is noteworthy that coordination of dppm as a bridging ligand causes an increase in the P(1)–C(9)–P(2) angle (131.0(4)°) with respect to that typical of tetrahedral carbon.

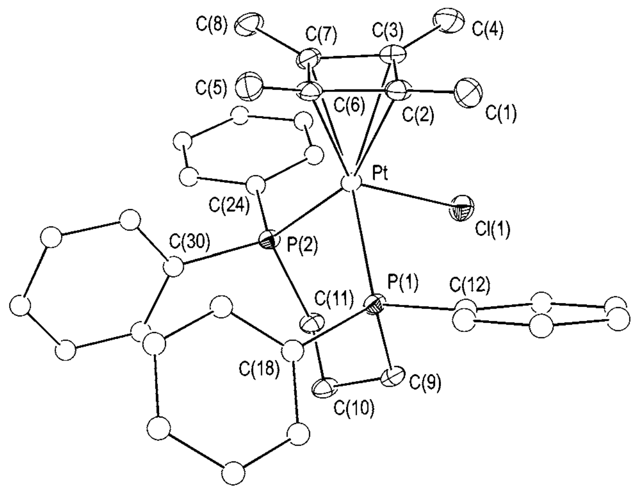


Fig. 3. ORTEP-III plot of the molecular structure of the cation in $[PtCl(C_4Me_4)\{Ph_2P(CH_2)_3PPh_2\}]Cl \cdot CH_2Cl_2$ (**5b**$\cdot CH_2Cl_2$), 30% displacement ellipsoids.

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[1] Here and following the first figure refers to one position (solid lines in Fig. 2) and the second to the other position (dashed lines) of the disordered η^4-C_4Me_4 ligand.

Table 8
Selected bond distances (Å) and bond angles (°) for $[PtCl(C_4Me_4)(Ph_2P(CH_2)_3PPh_2)]Cl \cdot CH_2Cl_2$ (**5b** · CH_2Cl_2)

Pt–C(2)	2.135(5)	Pt–C(3)	2.273(5)
Pt–C(6)	2.140(5)	Pt–C(7)	2.221(5)
C(2)–C(3)	1.450(8)	C(6)–C(7)	1.469(8)
C(2)–C(6)	1.462(7)	C(3)–C(7)	1.427(7)
Pt–P(1)	2.330(1)	Pt–Cl(1)	2.509(1)
Pt–P(2)	2.348(1)		
P(1)–Pt–P(2)	91.85(5)	C(10)–C(11)–P(2)	114.1(3)
Cl(1)–Pt–P(1)	88.86(5)	C(2)–C(3)–C(7)	91.2(5)
Cl(1)–Pt–P(2)	90.73(5)	C(2)–C(6)–C(7)	89.1(4)
P(1)–C(9)–C(10)	113.9(4)	C(3)–C(7)–C(6)	90.1(4)
C(9)–C(10)–C(11)	115.6(4)	C(3)–C(2)–C(6)	89.5(4)

*2.4. Structure of $[PtCl(C_4Me_4)(Ph_2P(CH_2)_3PPh_2)]Cl \cdot CH_2Cl_2$ (**5b** · CH_2Cl_2)*

The molecular structure of the cation present in **5b** · CH_2Cl_2 is shown in Fig. 3. Selected bond lengths and angles are listed in Table 8. As found for **2b**, described previously, platinum exhibits a piano-stool coordination defined by the η^4-C_4Me_4 ligand, one chloride and two p-donors groups.

The Pt–Cl bond length (2.509(1) Å) is longer than those in **1a**, **2b**, **7e** and **9** (2.323(2)–2.470(2) Å). The Pt–P distances differ slightly from each other (2.330(1) vs 2.348(1) Å), and are comparable to those observed in **2b** and **9** (2.331(2)–2.353(2) Å). The P–Pt–P angle is 91.85(5)°. The Cl–Pt–P angles are also close to 90° (88.86(5)°, 90.73(5)°). The distance of Pt from the plane of the cyclobutadiene ligand is 1.930(2) Å.

The square-planar cyclobutadiene ring (d(C–C) = 1.427(7)–1.469(8) Å; ∠C–C–C = 89.1(4)–91.2(5)°) is not symmetrically bound to Pt: There are two shorter Pt–C bonds (2.135(5)/2.140(5) Å) and two longer Pt–C bonds (2.221(5)/2.273(5) Å). The methyl groups are displaced from the ring plane away from Pt by 0.22(1)–0.54(1) Å. The bond angles at the methylene carbon atoms C(9), C(10) and C(11) of the chelating diphosphine ligand are each slightly larger (113.9(4)–115.6(4)°) than that typical of tetrahedral carbon.

The complex **5b**·CH_2Cl_2 crystallizes in the trigonal space group $R\bar{3}$. The crystal structure (Fig. 4) reveals a trigonal arrangement of cations $[PtCl(C_4Me_4)\{Ph_2P(CH_2)_3PPh_2\}]^+$ such that channels are formed with a diameter of about 13.8 Å, parallel to the c-axis. The methylene chloride is embedded in these channels. The choride anions are positioned on other lattice sites such that short intermolecular Cl···H–C contacts (2.67 Å) to a hydrogen atom of a methylene bridge (C(11)) are observed (Cl···C = 3.53 Å; ∠(Cl–H–C) = 147.6°). However, it should be noted that all hydrogen atoms are placed in calculated positions. Nevertheless, these values are in the range of reported Cl···H–C hydrogen bonds distances (d(Cl···H) = 2.6–2.9 Å, d(Cl···C) = ca. 3.5 Å, ∠(Cl–H–C) > 90°) [12]. Thus, stabilization by hydrogen bonding in **5b**·CH_2Cl_2 may be present.

These results demonstrate the versatile reactivity of the electronically unsaturated 16-electron complexes $[PtCl_2(C_4R_4)]$ (**1**) towards diphosphines to give novel, neutral binuclear and cationic mononuclear cyclobutadiene platinum complexes, depending on the nature of the diphosphine used and the Pt:P molar ratio.

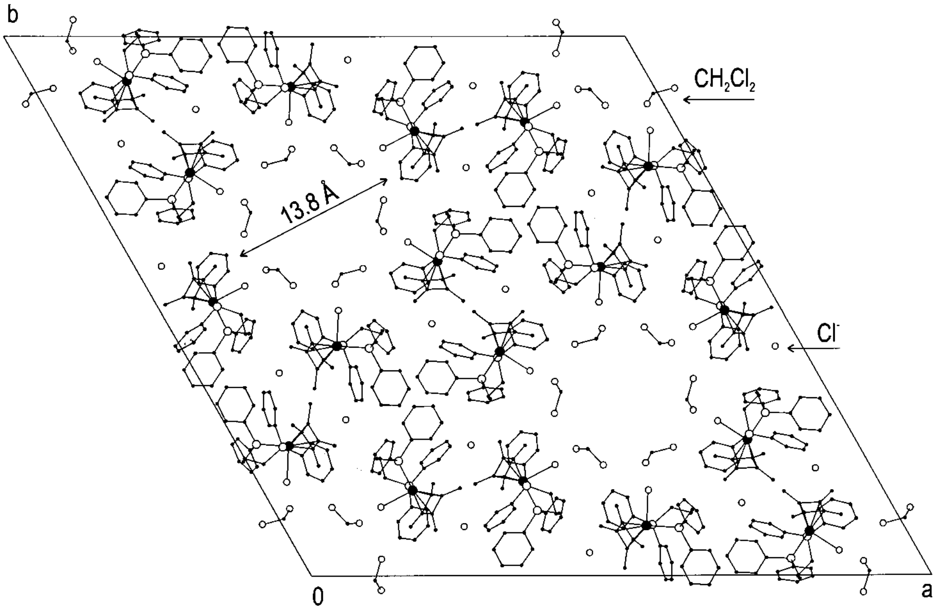

Fig. 4. View of the unit cell of $[PtCl(C_4Me_4)\{Ph_2P(CH_2)_3PPh_2\}]Cl \cdot CH_2Cl_2$ (**5b**·CH_2Cl_2) along the c-axis, only the major (70%) position of the solvate molecule is displayed.

3. Experimental section

All syntheses were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled prior to use. [PtCl$_2$(C$_4$Me$_4$)] (**1a**) and [PtCl$_2$(C$_4$Et$_4$)] (**1b**) were synthesized by literature methods [4]a. Other chemicals were commercial materials used without further purification.

Microanalyses (C, H, Cl) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. NMR spectra were obtained on Varian Gemini 200 and VXR 400 spectrometers. Chemical shifts are relative to C*H*DCl$_2$ (δ 5.32 ppm), *C*D$_2$Cl$_2$ (δ 53.8 ppm), C*H*Cl$_3$ (δ 7.24 ppm) and *C*DCl$_3$ (δ 77.0 ppm) as internal references; $\delta(^{31}P)$ is relative to external H$_3$PO$_4$ (85%). IR spectra were recorded on a Galaxy Mattson 5000 FT-IR spectrometer using CsBr pellets.

*3.1. Synthesis of [{PtCl$_2$(C$_4$R$_4$)}$_2$(μ-Ph$_2$P$^\frown$PPh$_2$)] (**2a–e**, **3a–e**)*

In a typical synthesis, [PtCl$_2$(C$_4$Me$_4$)] (**1a**) (75 mg, 0.20 mmol) or [PtCl$_2$(C$_4$Et$_4$)] (**1b**) (86 mg, 0.20 mmol) was placed into a Schlenk tube and dissolved in methylene chloride (3 ml) at r.t. After adding the corresponding diphosphine (0.10 mmol) the reaction solution was stirred for 5–10 h and diethyl ether (5 ml) was added. A precipitate formed which was filtered off, washed with diethyl ether and dried briefly in vacuo.

2a ($^\frown$ = –C≡C–, dppa): Yield: 91 mg (80%). Anal. Found: C, 43.83; H, 3.97; Cl, 12.96. $C_{42}H_{44}Cl_4P_2Pt_2$ (1142.72). Calc.: C, 44.15; H, 3.88; Cl, 12.41. IR: ν(Pt–Cl) = 262 (m), 233 (sh), 229 (m) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): $\delta(CH_3)$ = 1.31 (24H, d + dd, ^3J(Pt,H) = 14.3 Hz, ^4J(P,H) = 6.0 Hz), (*m*-, *p*-C*H*) = 7.46 (12H, m), (*o*-C*H*) = 7.82 (8H, m). ^{13}C-NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): $\delta(CH_3)$ = 7.7 (s), (C_4) = 99.1 (d + dd, ^1J(Pt,C) = 123 Hz, ^2J(P,C) = 4.1 Hz), (*C*≡*C*) = 101.6 (dd + dd, ^1J(P,C) = 76 Hz, ^2J(P,C) = 4.6 Hz, ^2J(Pt,C) = 26 Hz), (*m*-*C*H) = 129.1 (d, ^3J(P,C) = 11.7 Hz), (*i*-*C*) = 129.5 (d + dd, ^1J(P,C) = 44 Hz, ^2J(Pt,C) = 27 Hz), (*p*-*C*H) = 131.9 (d, ^4J(P,C) = 2.6 Hz), (*o*-*C*H) = 134.1 (d, ^2J(P,C) = 12.9 Hz). ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P) = -11.1$ (s + d, ^1J(Pt,P) = 4225 Hz).

2b ($^\frown$ = –CH$_2$–, dppm): Yield: 85 mg (75%). Anal. Found: C, 43.19; H, 4.01; Cl, 12.85. $C_{41}H_{46}Cl_4P_2Pt_2$ (1132.72). Calc.: C, 43.48; H, 4.09; Cl, 12.52. IR: ν(Pt–Cl) = 260 (m), 229 (sh), 224 (m) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): $\delta(CH_3)$ = 1.25 (24H, m), (C*H*$_2$) = 5.04 (2H, t, ^2J(P,H) = 7.1 Hz), (*m*-, *p*-C*H*) = 7.21 (12H, m), (*o*-C*H*) = 7.61 (8H, m). ^{13}C-NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): $\delta(CH_3)$ = 7.7 (s), (*C*H$_2$) = 24.3 (m), (C_4) = 97.7 (s + d, ^1J(Pt,C) = 127 Hz), (*i*-*C*) = 127.3 ('d', *N* = 49 Hz), (*m*-*C*H) = 128.1 (s), (*p*-*C*H) = 131.2 (s), (*o*-*C*H) = 134.6 (s). ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P)$ = 13.2 (s + m, ^1J(Pt,P) = 4237 Hz, ^3J(Pt,P) = 109.4 Hz, ^2J(P,P) = 50.4 Hz).

2c ($^\frown$ = –(CH$_2$)$_2$–, dppe): Yield: 106 mg (93%). Anal. Found: C, 43.78; H, 4.03; Cl, 12.56. $C_{42}H_{48}Cl_4P_2Pt_2$ (1146.75). Calc.: C, 43.99; H, 4.22; Cl, 12.37. IR: ν(Pt–Cl) = 257 (w), 230 (m) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 400 MHz, 293 K): $\delta(CH_3)$ = 1.26 (24H, m), (C*H*$_2$) = 3.08 (4H, m), (*m*-, *p*-C*H*) = 7.40 (12H, m), (*o*-C*H*) = 7.68 (8H, m). ^{13}C-NMR (CDCl$_3$, 100 MHz, 293 K): $\delta(CH_3)$ = 7.3 (s), (*C*H$_2$) = 24.6 ('t', *N* = 30 Hz), (C_4) = 97.3 (d + dd, ^1J(Pt,C) = 124 Hz, ^2J(P,C) = 1.4 Hz), (*m*-*C*H) = 128.6 ('t', *N* = 10.4 Hz), (*i*-*C*) = 130.3 ('t', *N* = 50 Hz), (*p*-*C*H) = 130.7 (s), (*o*-*C*H) = 133.7 ('t', *N* = 10.2 Hz). ^{31}P-NMR (CDCl$_3$, 81 MHz, 293 K): $\delta(P)$ = 12.7 (s + m, ^1J(Pt,P) = 4309 Hz, ^4J(Pt,P) < 1 Hz, ^3J(P,P) = 51.2 Hz).

2d ($^\frown$ = –(CH$_2$)$_3$–, dppp): Yield: 98 mg (84%). Anal. Found: C, 44.48; H, 4.45; Cl, 12.39. $C_{43}H_{50}Cl_4P_2Pt_2$ (1160.78). Calc.: C, 44.49; H, 4.34; Cl, 12.22. IR: ν(Pt–Cl) = 260 (w), 255 (sh), 229 (sh), 225 (w) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): $\delta(CH_3)$ = 1.20 (24H, d + dd, ^3J(Pt,H) = 16.4 Hz, ^4J(P,H) = 5.1 Hz), (PCH$_2$C*H*$_2$) = 1.75 (2H, m), (PC*H*$_2$CH$_2$) = 2.88 (4H, m), (*m*-, *p*-C*H*) = 7.35 (12H, m), (*o*-C*H*) = 7.67 (8H, m). ^{13}C-NMR (CDCl$_3$, 100 MHz, 293 K): $\delta(CH_3)$ = 7.3 (s), (PCH$_2$*C*H$_2$) = 19.3 (s), (P*C*H$_2$CH$_2$) = 30.0 ('q', *N* = 32 Hz), (C_4) = 96.7 (d + dd, ^1J(Pt,C) = 123 Hz, ^2J(P,C) = 3.0 Hz), (*m*-*C*H) = 128.4 (d, ^3J(P,C) = 10.0 Hz), (*i*-*C*) = 129.2 (d, ^1J(P,C) = 48 Hz), (*p*-*C*H) = 130.7 (s), (*o*-*C*H) = 133.4 (d, ^2J(P,C) = 10.0 Hz). ^{31}P-NMR (CDCl$_3$, 81 MHz, 293 K): $\delta(P)$ = 13.4 (s + d, ^1J(Pt,P) = 4331 Hz).

2e ($^\frown$ = –(CH$_2$)$_4$–, dppb): Yield: 98 mg (84%). Anal. Found: C, 44.51; H, 4.26, Cl, 12.49. $C_{44}H_{52}Cl_4P_2Pt_2$ (1174.80). Calc.: C, 44.99; H, 4.46; Cl, 12.07. IR: ν(Pt–Cl) = 257 (m), 229 (sh), 225 (w) cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): $\delta(CH_3)$ = 1.24 (24H, d + dd, ^3J(Pt,H) = 16.0 Hz, ^4J(P,H) = 6.1 Hz), (PCH$_2$C*H*$_2$) = 1.41 (4H, m), (PC*H*$_2$CH$_2$) = 2.87 (4H, m), (*m*-, *p*-C*H*) = 7.41 (12H, m), (*o*-C*H*) = 7.74 (8H, m). ^{13}C-NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): $\delta(CH_3)$ = 7.4 (d, ^3J(P,C) = 2.2 Hz), (C_4) = 96.7 (s), (*m*-*C*H) = 128.6 (d, ^3J(P,C) = 10.2 Hz), (*p*-*C*H) = 130.9 (s), (*o*-*C*H) = 133.4 (d, ^2J(P,C) = 10.0 Hz), resonances for P*C*H$_2$CH$_2$, PCH$_2$*C*H$_2$ and *i*-*C* could not be observed due to a poor signal-to-noise ratio. ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P)$ = 13.0 (s + d, ^1J(Pt,P) = 4335 Hz).

3a ($^\frown$ = –C≡C–, dppa): Yield: 100 mg (80%). Anal. Found: C, 47.52; H, 4.85; Cl, 11.22. $C_{50}H_{60}Cl_4P_2Pt_2$ (1254.94). Calc.: C, 47.85; H, 4.82; Cl, 11.30. IR: ν(Pt–Cl) = 265 (m), 250 (m), 230 (m) cm^{-1}. ^{1}H-NMR (CDCl$_3$, 400 MHz, 293 K): $\delta(CH_3)$ = 0.99 (24H, t),

$(CH_2) = 1.77$ (16H, m), (m-, p-CH) = 7.43 (12H, m), (o-CH) = 8.05 (8H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz, 293 K): $\delta(CH_3) = 11.7$ (d, ^3J(P,C) = 2.9 Hz), $(CH_2) = 17.3$ (s), $(C_4) = 102.2$ (d + dd, ^1J(Pt,C) = 120 Hz, ^2J(P,C) = 4.0 Hz), (m-CH) = 129.0 (d, ^3J(P,C) = 11.5 Hz), (p-CH) = 131.7 (d, ^4J(P,C) = 2.3 Hz), (o-CH) = 134.2 (d, ^2J(P,C) = 12.1 Hz), resonances for $C{\equiv}C$ and i-C could not be observed due to a poor signal-to-noise ratio. ^{31}P-NMR ($CDCl_3$, 81 MHz, 293 K): $\delta(P) = -14.6$ (s + d, ^1J(Pt,P) = 4116 Hz).

3b ($\frown = -CH_2-$, dppm): Yield: 107 mg (86%). Anal. Found: C, 47.64; H, 4.87; Cl, 11.63. $C_{49}H_{62}Cl_4P_2Pt_2$ (1294.94). Calc.: C, 47.27; H, 5.02; Cl, 11.39. IR: ν(Pt–Cl) = 249 (w), 235 (w), 222 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta(CH_3) = 1.07$ (24H, t), $(CH_2) = 1.72$ (16H, m), $(PCH_2) = 5.03$ (2H, m), (m-, p-CH) = 7.18 (12H, m), (o-CH) = 7.63 (8H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz, 293 K): $\delta(CH_3) = 11.6$ (s), $(CH_2) = 17.3$ (s), $(PCH_2) = 22.9$ (m), $(C_4) = 100.5$ (s + d, ^1J(Pt,C) = 122 Hz), (i-C) = 127.1 (‘d’, $N = 41$ Hz), (m-CH) = 127.5 (‘t’, $N = 10.5$ Hz), (p-CH) = 130.7 (s), (o-CH) = 134.3 (br s). ^{31}P-NMR ($CDCl_3$, 81 MHz, 293 K): $\delta(P) = 11.3$ (s + m, ^1J(Pt,P) = 4132 Hz, ^3J(Pt,P) = 105.6 Hz, ^2J(P,P) = 49.8 Hz).

3c ($\frown = -(CH_2)_2-$, dppe): Yield: 113 mg (90%). Anal. Found: C, 47.68; H, 5.01; Cl, 11.53. $C_{50}H_{64}Cl_4P_2Pt_2$ (1258.97). Calc.: C, 47.70; H, 5.12; Cl, 11.26. IR: ν(Pt–Cl) = 267 (w), 249 (w), 229 (w), 225 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta(CH_3) = 1.01$ (24H, t), $(CH_2) = 1.63$ (16H, m), $(PCH_2) = 3.02$ (4H, m), (m-, p-CH) = 7.38 (12H, m), (o-CH) = 7.71 (8H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz, 293 K): $\delta(CH_3) = 11.7$ (d, ^3J(P,C) = 2.9 Hz), $(CH_2) = 17.5$ (s), $(PCH_2) = 24.4$ (m), $(C_4) = 101.2$ (‘t’ + d, ^1J(Pt,C) = 126 Hz, $N = 3.5$ Hz), (m-CH) = 128.4 (‘t’, $N = 10.6$ Hz), (i-C) = 129.9 (‘t’, $N = 49$ Hz), (p-CH) = 130.6 (s), (o-CH) = 133.7 (‘t’, $N = 9.9$ Hz). ^{31}P-NMR ($CDCl_3$, 81 MHz, 293 K): $\delta(P) = 11.8$ (s + m, ^1J(Pt,P) = 4241 Hz, ^4J(Pt,P) < 1 Hz, ^3J(P,P) = 43.9 Hz).

3d ($\frown = -(CH_2)_3-$, dppp): Yield: 82 mg (65%). Anal. Found: C, 47.84; H, 5.07; Cl, 11.34. $C_{51}H_{66}Cl_4P_2Pt_2$ (1273.00). Calc.: C, 48.12; H, 5.23; Cl, 11.14. IR: ν(Pt–Cl) = 258 (w), 250 (w), 232 (w), 216 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta(CH_3) = 1.02$ (24H, t), $(CH_2) = 1.67$ (16H, dq, ^4J(P,H) = 4.0 Hz), $(PCH_2CH_2) = 1.90$ (2H, m), $(PCH_2CH_2) = 2.85$ (4H, m), (m-, p-CH) = 7.38 (12H, m), (o-CH) = 7.70 (8H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz, 293 K): $\delta(CH_3) = 11.5$ (d, ^3J(P,C) = 2.3 Hz), $(CH_2) = 17.2$ (s), $(PCH_2CH_2) = 18.1$ (s), $(PCH_2CH_2) = 29.1$ (‘q’, $N = 45$ Hz), $(C_4) = 100.2$ (d + dd, ^1J(Pt,C) = 128 Hz, ^2J(P,C) = 3.8 Hz), (m-CH) = 128.3 (d, ^3J(P,C) = 10.7 Hz), (i-C) = 129.2 (d, ^1J(P,C) = 49 Hz), (p-CH) = 130.6 (s), (o-CH) = 133.4 (d, ^2J(P,C) = 10.0 Hz). ^{31}P-NMR ($CDCl_3$, 81 MHz, 293 K): $\delta(P) = 11.6$ (s + d, ^1J(Pt,P) = 4312 Hz).

3e ($\frown = -(CH_2)_4-$, dppb): Yield: 127 mg (97%). Anal. Found: C, 48.04; H, 5.15; Cl, 10.65. $C_{52}H_{68}Cl_4P_2Pt_2$ (1287.02). Calc.: C, 48.53; H, 5.33; Cl, 11.02. IR: ν(Pt–Cl) = 258 (w), 250 (w), 229 (w), 224 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta(CH_3) = 1.00$ (24H, t), $(PCH_2CH_2) = 1.32$ (4H, m), $(CH_2) = 1.69$ (16H, dq, ^4J(P,H) = 3.8 Hz), $(PCH_2CH_2) = 2.86$ (4H, m), (m-, p-CH) = 7.41 (12H, m), (o-CH) = 7.73 (8H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz, 293 K): $\delta(CH_3) = 11.5$ (s), $(CH_2) = 17.3$ (s), $(PCH_2CH_2) = 25.2$ (m), $(PCH_2CH_2) = 26.7$ (d, ^1J(P,C) = 32 Hz), $(C_4) = 100.1$ (d + dd, ^1J(Pt,C) = 125 Hz, ^2J(P,C) = 3.1 Hz), (i-C) = 128.2 (d, ^1J(P,C) = 51 Hz), (m-CH) = 128.5 (d, ^3J(P,C) = 10.6 Hz), (p-CH) = 130.8 (s), (o-CH) = 133.3 (d, ^2J(P,C) = 9.9 Hz). ^{31}P-NMR ($CDCl_3$, 81 MHz, 293 K): $\delta(P) = 11.5$ (s + d, ^1J(Pt,P) = 3997 Hz).

3.2. Synthesis of $[PtCl(C_4R_4)\{Ph_2P(CH_2)_nPPh_2\}]Cl$ (**5a–c**, **6a–c**)

In a typical synthesis, $[PtCl_2(C_4Me_4)]$ (**1a**) (75 mg, 0.20 mmol) or $[PtCl_2(C_4Et_4)]$ (**1b**) (86 mg, 0.20 mmol) was placed into a Schlenk tube and dissolved in methylene chloride (3 ml) at room temperature. After adding the corresponding diphosphine in an equimolar ratio (0.20 mmol) the reaction solution was stirred for 2–3 h and diethyl ether (5 ml) was added to induce precipitation. After standing over night the precipitate was filtered off, washed with diethyl ether and dried briefly in vacuo.

5a ($n = 2$, dppe): characterized only in solution. ^{1}H-NMR (CD_2Cl_2, 200 MHz, 293 K): $\delta(CH_3) = 1.74$ (12H, t + d, ^3J(Pt,H) = 12.1 Hz, ^4J(P,H) = 5.8 Hz), $(PCH_2) =$ 2.02–3.05 (4H, br m), $(CH) =$ 7.21–7.76 (20H, m). ^{31}P-NMR (CD_2Cl_2, 81 MHz, 293 K): $\delta(P) = 30.5$ (s + d, ^1J(Pt,P) = 3322 Hz).

5b·CH_2Cl_2 ($n = 3$, dppp): Yield: 126 mg (72%). Anal. Found: C, 49.88; H, 4.96; Cl, 15.77. $C_{35}H_{38}Cl_2P_2Pt \cdot CH_2Cl_2$ (871.55). Calc.: C, 49.61; H, 4.63; Cl, 16.27. ^{1}H-NMR (CD_2Cl_2, 200 MHz, 293 K): $\delta(CH_3) = 1.54$ (12H, t + dt, ^3J(Pt,H) = 12.1 Hz, ^4J(P,H) = 5.9 Hz), $(PCH_2CH_2) =$ 2.20–2.60 (2H, br m), $(PCH_2CH_2) =$ 3.14–3.62 (4H, br m), $(CH) =$ 7.02–7.58 (20H, m). ^{13}C-NMR (CD_2Cl_2, 100 MHz, 293 K): $\delta(CH_3) = 8.5$ (s), $(PCH_2CH_2) = 19.1$ (s), $(PCH_2CH_2) =$ 25.0 (‘quin’, $N = 18$ Hz), $(C_4) = 102.3$ (s + d, ^1J(Pt,C) = 88 Hz), (m-CH) = 128.3 (s), (p-CH) = 131.7 (s), (o-CH) = 133.5 (s), a resonance for i-C could not be observed due to a poor signal-to-noise ratio. ^{31}P-NMR (CD_2Cl_2, 81 MHz, 293 K): $\delta(P) = -6.9$ (s + d, ^1J(Pt,P) = 3262 Hz).

5c·CH_2Cl_2 ($n = 4$, dppb): Yield: 120 mg (68%). Anal. Found: C, 49.62; H, 4.93; Cl, 15.43. $C_{36}H_{40}Cl_2P_2Pt \cdot CH_2Cl_2$ (885.58). Calc.: C, 50.18; H, 4.78; Cl, 16.01. ^{1}H-NMR ($CDCl_3$, 200 MHz, 293 K): $\delta(CH_3) = 1.32$ (12H, t + dt, ^3J(Pt,H) = 12.5 Hz,

^4J(P,H) = 6.0 Hz), (PCH$_2$C*H*$_2$) = 2.32–2.64 (4H, br m), (PC*H*$_2$CH$_2$) = 3.36–3.79 (4H, br m), (C*H*) = 7.10–7.72 (20H, m). ^{13}C-NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): δ(*C*H$_3$) = 7.9 (s), (PCH$_2$*C*H$_2$) = 22.0 (s), (P*C*H$_2$CH$_2$) = 28.0 ('t', N = 32 Hz), (*C*$_4$) = 103.0 (s + d, ^1J(Pt,C) = 88 Hz), (*m*-*C*H) = 128.5 (m), (*p*-*C*H) = 129.5 (s), (*o*-*C*H) = 132.6 (m), a resonance for *i*-*C* could not be observed due to a poor signal-to-noise ratio. ^{31}P-NMR (CDCl$_3$, 81 MHz, 293 K): $\delta(P)$ = 0.9 (s + d, ^1J(Pt,P) = 3462 Hz).

6a (n = 2, dppe): characterized only in solution. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): δ(C*H*$_3$) = 1.02 (12H, t), (C*H*$_2$) = 1.94 (8H, m), (PC*H*$_2$) = 2.14–3.22 (4H, br m), (C*H*) = 7.08–7.74 (20H, br m). ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P)$ = 29.1 (s + d, ^1J(Pt,P) = 3262 Hz).

6b · CH$_2$Cl$_2$ (n = 3, dppp): Yield: 115 mg (60%). Anal. Found: C, 52.14; H, 5.34; Cl, 14.96. $C_{39}H_{46}Cl_2P_2Pt \cdot CH_2Cl_2$ (927.66). Calc.: C, 51.79; H, 5.22; Cl, 15.29. ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 293 K): δ(C*H*$_3$) = 1.01 (12H, t), (C*H*$_2$) = 1.87 (8H, m), (PCH$_2$C*H*$_2$) = 2.70–3.08 (2H, br m), (PC*H*$_2$CH$_2$) = 3.45–3.78 (4H, m), (C*H*) = 7.22–7.78 (20H, m). ^{13}C-NMR (CD$_2$Cl$_2$, 100 MHz, 293 K): δ(*C*H$_3$) = 12.4 (t, ^4J(P,C) = 4.1 Hz), (*C*H$_2$) = 17.7 (s), (PCH$_2$*C*H$_2$) = 18.8 (s), (P*C*H$_2$CH$_2$) = 25.2 ('quin', N = 17 Hz), (*C*$_4$) = 105.0 (s + d, ^1J(Pt,C) = 93 Hz), (phenyl-*C*) = 128.7–134.7 (m). ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P) = -8.9$ (s + d, ^1J(Pt,P) = 3224 Hz).

Table 9
Crystal data collection and processing parameters[a] for **2b** and **5b** · CH$_2$Cl$_2$

Complex	**2b**	**5b** · CH$_2$Cl$_2$
Formula	$C_{41}H_{46}Cl_4P_2Pt_2$	$C_{36}H_{40}Cl_4P_2Pt$
Molecular weight	1132.70	871.51
Temperature (K)	293(1)	240(2)
Crystal size (mm^3)	0.45 × 0.40 × 0.30	0.20 × 0.20 × 0.20
Crystal system	Monoclinic	Trigonal
Space group (number)	Cc/9	R$\bar{3}$/148
Z	4	18
Unit cell dimensions		
a (Å)	17.0855(4)	43.798(4)
b (Å)	15.4437(4)	43.798(4)
c (Å)	16.5379(5)	10.7773(9)
α (°)	90	90
β (°)	102.164(1)	90
γ (°)	90	120
V (Å^3)	4265.8(2)	17904(3)
D_{calc} (g cm^{-3})	1.764	1.455
μ(Mo–K_α) (mm^{-1})	6.904	3.898
F(000)	2184	7776
θ Range for data collection (°)	2.34–29.88	1.86–25.00
Total data	14894	19798
Total unique data	7896	6932
Observed data ($F > 2\sigma(F)$)	7050	5480
$R_{int.}$	0.0422	0.0538
wR_2, all data	0.0694	0.0846
R_1, observed data	0.0313	0.0330
Goodness of fit (S), all data	0.989	0.969
Parameters	434	400
Largest residual peak hole (e Å^{-3})	1.039/−1.329	1.387/−0.752

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, S (goodness of fit) $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$.

6c · CH$_2$Cl$_2$ (n = 4, dppb): Yield: 127 mg (97%). Anal. Found: C, 52.07; H, 5.17; Cl, 14.61. $C_{40}H_{48}Cl_2P_2Pt \cdot CH_2Cl_2$ (941.69). Calc.: C, 52.29; H, 5.35; Cl, 15.06. ^{1}H-NMR (CDCl$_3$, 200 MHz, 293 K): δ(C*H*$_3$) = 1.00 (12H, t), (C*H*$_2$) = 1.72 (8H, dq), (PCH$_2$C*H*$_2$) = 2.45–2.88 (4H, br m), (PC*H*$_2$CH$_2$) = 3.57–3.80 (4H, br m), (C*H*) = 7.28–7.82 (20H, m). ^{13}C-NMR (CDCl$_3$, 100 MHz, 293 K): δ(*C*H$_3$) = 11.8 (s), (*C*H$_2$) = 18.3 (s), (PCH$_2$*C*H$_2$) = 26.7 (m), (P*C*H$_2$CH$_2$) = 28.4 (m), (*C*$_4$) = 105.5 (s), (phenyl-*C*) = 129.0–134.4 (m). ^{31}P-NMR (CD$_2$Cl$_2$, 81 MHz, 293 K): $\delta(P) = -1.3$ (s + d, ^1J(Pt,P) = 3402 Hz).

3.3. X-ray structure determinations

Data collection for **2b** was performed on a SIEMENS Smart Platform diffractometer using three different φ settings and 0.3° increment scans, corresponding to a nominal hemisphere of data $2\theta < 59.76°$. Frame time was set to 10 s. Corrections for absorption and decay were applied using SADABS [13] (T_{min}/T_{max}: 0.42/0.80). X-ray measurement for **5b** · CH$_2$Cl$_2$ was carried out on a STOE IPDS image plate diffractometer. 133 frames were recorded oscillating the crystal 1.5° around the φ-axis. Absorption correction was applied to the data numerically (T_{min}/T_{max}: 0.50/0.66).

Intensities were collected using graphite monochromatized Mo–K_α radiation (λ_0 = 0.71073 Å). The structures were solved by direct methods (SHELXS-86) [14] and structure refinement was carried out by full-matrix least-squares procedures on F^2 (SHELXL-93 [15]). Crystal data and details of the data collections and refinements for **2b** and **5b** · CH$_2$Cl$_2$ are summarized in Table 9.

One of the two tetramethylcyclobutadiene units in **2b** is disordered. The model refined contains two positions with equal occupancies. All disordered carbon atoms were refined with isotropic thermal parameters, all other non-hydrogen atoms with anisotropic thermal parameters. The solvate molecule in **5b** · CH$_2$Cl$_2$ was included in two positions with probabilities of 70 and 30%, respectively. The Cl–C bond lengths were restrained to be equal with an effective S.D. of 0.03. The position with the lower probability was refined using isotropic displacement parameters. Hydrogen atoms were in both structures included in the refinement as riding atoms.

4. Supplementary material

Atomic coordinates, equivalent isotropic displacement parameters, hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, all bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number HE1027. They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK, citing the deposition no. 102184 (**2b**) and no. 102185 (**5b**·CH_2Cl_2), the authors and the reference.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the companies Merck and Degussa for gifts of chemicals. The authors thank Professor H.P. Abicht (Halle) for a gift of dppb. M.G. thanks the DAAD for a grant.

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