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Reactivity of $[Pt(CH_2X)_2(Ph_2PCH_2PPh_2\text{-}PP')]$ (X = Cl, Br, or I): Four- to Five-membered Ring Expansions. Crystal Structure of [Bis(diphenylphosphino)-methane-*PP'*]bis(chloromethyl)platinum(II) *

Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL
Paul G. Pringle
School of Chemistry, University of Bristol, Bristol BS8 1TS
Paola Bergamini, Silvana Sostero, and Orazio Traverso
Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy

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Addition of CH_2N_2 to the chelates $[PtX_2(dppm\text{-}PP')]$ (X = Cl, Br, or I; dppm = $Ph_2PCH_2PPh_2$) gives the complexes $[Pt(CH_2X)_2(dppm\text{-}PP')]$ **(2a)**—**(2c)** which have been fully characterised. The *X*-ray crystal structure of $[Pt(CH_2Cl)_2(dppm\text{-}PP')]$ **(2a)** has been determined in confirmation of its chemical identity (orthorhombic, space group *Pbca*, *R* = 0.053 for 2 499 observed reflections $[I/\sigma(I) \geqslant 2.0]$. Addition of HCl to complex **(2a)** gives $[PtCl(CH_2Cl)(dppm\text{-}PP')]$ **(3)**. Treatment of **(2a)** with phosphines or pyridine leads to a ring-expansion reaction to give $[PtL(CH_2Cl)(CH_2PPh_2CH_2PPh_2)]Cl$ [L = pyridine **(4a)**, PPh_3 **(4b)**, or PPh_2H **(4c)**]. With dppm, **(2a)** gives the bis chelate $[Pt(CH_2PPh_2CH_2PPh_2)_2]Cl_2$ **(5)**. The mechanism of these ligand-promoted ring expansions is discussed. The products have been fully characterised by a combination of elemental analysis, i.r., ^1H, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

The reactivity of $[PtCl_2(dppm\text{-}PP')]$ (1) is often very different from other $[PtCl_2(diphosphine)]$ complexes because of the ring strain inherent in the four-membered chelate.[1] Hence (1) readily ring opens at the Pt–P bond to give binuclear complexes containing bridging dppm ligands[1] and recently we have shown that P–C cleavage in (1) readily occurs in the presence of hydroxide.[2,3] In this paper we report a further manifestation of the tendency of (1) to relieve the ring strain: a four- to five-membered ring expansion which occurs in complexes of the type $[Pt(CH_2X)_2(dppm\text{-}PP')]$ (2a)—(2c).

Results and Discussion

McCrindle *et al.*[4,5] have reported the preparation of complexes of the type $[Pt(CH_2Cl)_2(PR_3)_2]$ by the addition of an excess of CH_2N_2 to the corresponding $[PtCl_2(PR_3)_2]$. In a similar manner, we have made the corresponding dppm complexes (2a)—(2c) and characterised them by elemental analysis, ^1H and ^{31}P n.m.r. spectroscopy (see Tables 1—3), and the crystal structure of (2a). The complex $[PtCl(CH_2Cl)(dppm\text{-}PP')]$ (3) was sometimes observed to contaminate the product (2a) but (3) was readily removed by recrystallisation; a convenient synthesis of (3) is by addition of 1 equivalent of HCl to (2a).

X-Ray Crystal Structure of Complex (2a).—The structure of complex (2a) (Figure, Tables 4 and 5) was undertaken primarily to confirm its chemical composition. The four-membered ring is clearly strained, with a P–Pt–P angle of only 73.4(1)°; repulsion between P and C is presumably responsible for the small C–Pt–C angle [84.2(4)°]. Both Cl atoms lie in the PtP_2 plane, perhaps as a result of van der Waals attraction to the phenyl group. No structures have been reported for other complexes containing terminal $PtCH_2Cl$ groups to show whether this orientation is normal.

Reactivity of Complexes (2a)—(2c).—The complexes (2a)—(2c) are stable in the solid state but in solution they decompose slowly to a mixture of (1a)—(1c) and (3a)—(3c). The stability in solution is observed to be (2c) < (2b) < (2a). If $CDCl_3$ solutions of the di-iodo complex (2c) are irradiated (λ > 320 nm) decomposition to (1a) occurs rapidly (less than 10 min) and ethylene is detected by gas chromatography as a major product; the fate of the iodine ligands has not been determined.

Table 1. Elemental analyses (%)

Complex	C	H
(2a)	47.80 (47.80)	3.85 (3.85)
(2b)	42.20 (42.25)	3.30 (3.40)
(2c)	38.05 (37.65)	3.05 (3.05)
(4a)*	49.30 (50.70)	4.20 (4.10)
(4b)	57.60 (57.45)	4.30 (4.40)
(4c)$\cdot 0.5CH_2Cl_2$	52.05 (52.25)	4.05 (4.20)
(5)$\cdot 1.5CH_2Cl_2$	54.10 (54.00)	4.35 (4.30)

* N 1.45 (1.85%).

When $CDCl_3$ solutions of (2a) are treated with neutral ligands, L, a ring expansion occurs to give the cationic products (4a)—(4c) containing a novel phosphine–phosphorus ylide ligand. Their structures are assigned from elemental analysis, ^1H and particularly $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (see Tables 1—3). For example the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (4b) is an AMX pattern with associated ^{195}Pt satellites; the magnitudes of *J*(PP) and *J*(PtP) enable unambiguous assignments of the signals.

The bis(chloromethyl) complex (2a) reacts rapidly with 1 equivalent of dppm to give the bis chelate (5a). The structure is based on the highly symmetrical $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, and the observation of two ^1H n.m.r. signals in the ratio 1:1, assigned to the PCH_2P and the PCH_2Pt protons (see Tables 1—3).

Two possible mechanisms which may explain the ligand-promoted PPh_2 migration from Pt to CH_2 in the above reactions are shown in Schemes 1 and 2. In mechanism A an ylide complex is formed [step (i)] followed by migration of the PPh_2 to the CH_2 with concomitant migration of the ligand to Pt

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 2. Phosphorus-31 n.m.r. data*

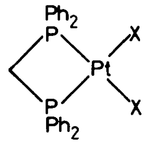
Complex	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^1J(PtP_B)$	$J(P_AP_B)$	$\delta(P_C)$	$^1J(PtP_C)$	$J(P_AP_C)$	$J(P_BP_C)$
(2a)	−33.8	1 636							
(2b)	−34.6	1 631							
(2c)	−35.1	1 643							
(4a)	9.8	2 280	45.4	56	66				
(4b)	16.4	1 884	44.1	50	61	22.3	2 600	15	5
(4c)	15.8	1 730	45.9	46	66	−5.6	2 540	18	5
(5)	15.5	2 350	45.6	42	54				

* Spectra measured at 36.4 MHz in $CDCl_3$. Chemical shift (δ) to high frequency of 85% H_3PO_4 in p.p.m. (±0.1) and coupling constants (J) in Hz (±3).

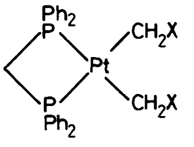
Table 3. Proton n.m.r. data* (J/Hz)

Complex	$\delta(PCH_2P)$	$J(PtH)$	$J(PH)$	$\delta(PtCH_2X)$	$J(PtH)$	$J(PH)$	$\delta(PtCH_2P)$	$J(PtH)$	$J(PH)$
(2a)	4.4	29.7	9.5	4.3	48.6	7.2			
(2b)	4.2	33.5	9.5	3.9	40.0	4.3			
(2c)	4.2	36.0	9.0	3.2	36.0	8.0			
(4a)	3.7	21.0	9.4	5.2	73.0	9.0	2.8	91.4	10, 2.7
(4b)	4.4	21.0	12.0	3.7	46.0	9.8, 2.0	3.0	72.0	10, 10, 3.4
(5)	4.5	22.0	11.0	3.6	68.0				

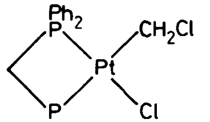
* Spectra measured at 80 MHz in $CDCl_3$. Chemical shifts (δ) to high frequency of $SiMe_4$ in p.p.m. (±0.05), and coupling constants (J) in Hz (±0.1).



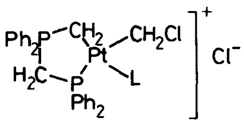
X
(1a) Cl
(1b) Br
(1c) I



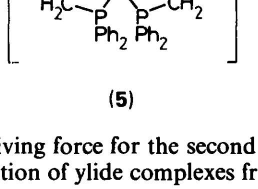
X
(2a) Cl
(2b) Br
(2c) I



(3)



L
(4a) C_5H_5N
(4b) PPh_3
(4c) PPh_2H



(5)

[step (ii)]; the driving force for the second step is relief of ring strain. The formation of ylide complexes from halogenomethyl complexes [step (i)] is now well established[6,7] but the proposed step (ii), involving P–C cleavage, has no precedent. An alternative mechanism B involves the transient formation of a five-co-ordinate intermediate [step (i)] followed by a migration of the PPh_2 to the CH_2 [step (ii)].

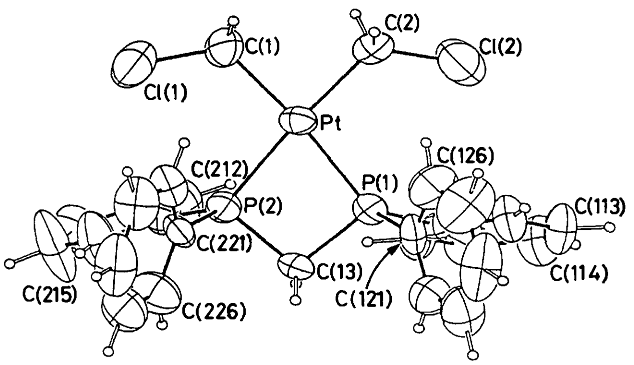


Figure. View of complex **(2a)** showing the atomic numbering

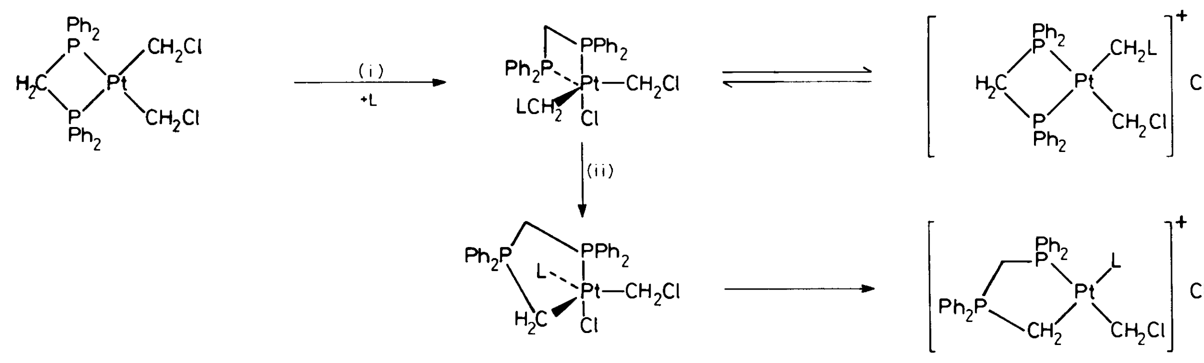
The ring expansions described above are peculiar to dppm chelates since analogous dppe chelates behave differently.[5] The driving force for the reaction is most probably relief of ring strain. The final result is the insertion of CH_2 into the Pt–P bond to give a new class of ligand.

Experimental

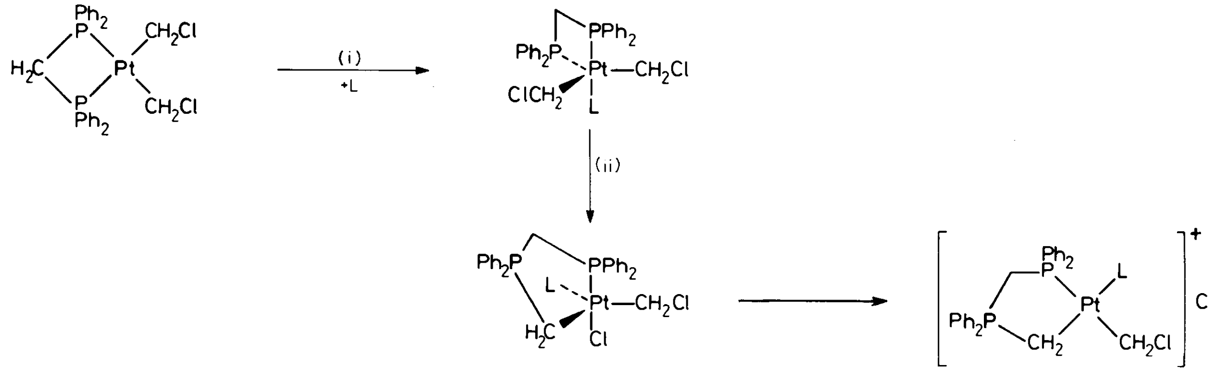
Diazomethane was prepared from *N*-methyl-*N*-nitrosourea and potassium hydroxide, following published procedures.[8] The starting material **(1a)** was prepared as previously reported.[9]

Preparation of $[Pt(CH_2X)_2(dppm\text{-}PP')]$ (X = Cl, Br, *or* I).—The complex $[PtX_2(dppm\text{-}PP')]$ [X = Cl **(1a)**, Br**(1b)**, or I **(1c)**] (1.5 mmol) was suspended in CH_2Cl_2 (200 cm^3) in a beaker in air. A solution containing a large excess (≈50 equiv.) of CH_2N_2 in Et_2O was slowly added to the suspension at 0 °C with vigorous stirring. After 8 h the solvent was evaporated *in vacuo* and the yellow solid residue was washed with diethyl ether (20 cm^3) and water (20 cm^3), to give a white solid. The yields were 77 (X = Cl), 65 (X = Br), and 84% (X = I).

Preparation of $[Pt(CH_2Cl)(py)(CH_2PPh_2CH_2PPh_2)]Cl$ **(4a)**.—Complex **(2a)** (100 mg, 0.147 mmol) was dissolved in dry CH_2Cl_2 (10 cm^3) and pyridine (0.1 cm^3) was added. The yellow solution was stirred for 2 h at room temperature, then



Scheme 1. Mechanism A; L = PPh_3, PPh_2H, or pyridine



Scheme 2. Mechanism B; L = PPh_3, PPh_2H, or pyridine

Table 4. Atom co-ordinates (× 10^4) for complex (**2a**)

Atom	*x*	*y*	*z*
Pt	1 427.0(2)	5 413.8(3)	6 150.4(2)
Cl(1)	−281(2)	5 512(3)	6 965(2)
C(1)	203(5)	5 465(8)	6 199(5)
Cl(2)	1 989(2)	5 080(3)	4 615(2)
C(2)	1 243(5)	5 418(7)	5 142(4)
P(1)	2 783.8(14)	5 345.6(23)	6 209.8(14)
P(2)	1 745.2(15)	5 424.7(25)	7 238.4(14)
C(3)	2 814(5)	5 185(7)	7 104(4)
C(111)	3 375(5)	4 448(7)	5 845(4)
C(112)	3 823(6)	4 603(8)	5 292(5)
C(113)	4 240(6)	3 927(8)	5 005(6)
C(114)	4 181(7)	3 069(8)	5 238(6)
C(115)	3 721(7)	2 917(8)	5 776(6)
C(116)	3 321(5)	3 593(7)	6 080(5)
C(121)	3 361(5)	6 341(7)	6 057(5)
C(122)	4 082(6)	6 495(8)	6 330(5)
C(123)	4 495(9)	7 251(10)	6 193(7)
C(124)	4 216(7)	7 862(7)	5 766(7)
C(125)	3 504(8)	7 720(9)	5 474(8)
C(126)	3 075(7)	6 949(7)	5 601(6)
C(211)	1 379(6)	4 542(9)	7 764(5)
C(212)	1 321(7)	3 687(8)	7 502(6)
C(213)	1 033(6)	2 987(8)	7 858(6)
C(214)	788(7)	3 113(8)	8 477(5)
C(215)	845(8)	3 932(9)	8 745(6)
C(216)	1 130(7)	4 639(10)	8 389(6)
C(221)	1 701(6)	6 462(8)	7 698(5)
C(222)	1 218(6)	7 133(7)	7 478(6)
C(223)	1 189(8)	7 951(9)	7 814(7)
C(224)	1 638(9)	8 077(11)	8 361(9)
C(225)	2 101(8)	7 397(11)	8 589(8)
C(226)	2 144(7)	6 607(8)	8 261(5)

Table 5. Selected bond lengths (Å) and angles (°)

Pt–P(1)	2.296(2)	P(1)–C(3)	1.843(9)
Pt–P(2)	2.286(3)	P(2)–C(3)	1.859(9)
Pt–C(1)	2.069(8)	C(1)–Cl(1)	1.765(10)
Pt–C(2)	2.082(9)	C(2)–Cl(2)	1.733(9)
P(1)–Pt–P(2)	73.4(1)	P(2)–Pt–C(1)	100.8(3)
P(1)–C(3)–P(2)	95.4(4)	C(1)–Pt–C(2)	84.2(4)
P(1)–Pt–C(2)	101.6(2)		

evaporated to low volume and n-hexane (10 cm^3) slowly added. The off-white precipitate was filtered off and washed with n-hexane; yield 83 mg (75%).

The complexes (**4b**), (**4c**), and (**5**) were made similarly; (**4b**) was obtained in 84% yield after recrystallisation from $CHCl_3$ and Et_2O (**4c**) in 64% yield by precipitation from a CH_2Cl_2 solution with Et_2O, and (**5**) in 86% yield.

Crystal Structure Determination of Complex (**2a**).—*Crystal data.* $C_{27}H_{26}Cl_2Pt$, $M = 616.5$, orthorhombic, space group *Pbca*, $a = 16.881(4)$, $b = 14.924(4)$, $c = 20.425(4)$ Å, $U = 5\,146(2)$ Å^3, $Z = 8$, $D_c = 1.59$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 60.8 cm^{-1}, $T = 293$ K, $F(000) = 2\,400$.

Crystals were obtained from CH_2Cl_2–Et_2O as straw-yellow needles. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50, with scan range ±1.0 (2θ) around the K_{α_1}–K_{α_2} angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0—20, 0—17, 0—24. Three standard reflections were monitored every 200 reflections, and showed a slight decrease during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($23 < 2\theta < 25$). Reflections were processed using profile analysis to give 5 004 unique reflections; 2 499 were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Maximum and minimum transmission factors were 0.66 and 0.43. Crystal dimensions were $0.09 \times 0.10 \times 0.24$ mm. Systematic absences: $0kl, k \neq 2n$; $h0l, l \neq 2n$; $hk0, h \neq 2n$, indicating space group *Pbca* uniquely. The Pt atom was located by the Patterson interpretation section of SHELXTL.[10] A first Fourier synthesis showed the dppm ligand and the CH_2Cl groups. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined. Final refinement was on F by cascaded least-squares methods refining 289 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height 1.1 and -1.0 e Å^{-3}, in the neighbourhood of the Pt.

A weighting scheme of the form $w = 1/[(\sigma^2(F)]$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.053$, $R' = 0.036$. Maximum shift/error in final cycle 0.2. Computing with SHELXTL on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 11. Final atomic co-ordinates are given in Table 4 and selected bond lengths and angles in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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