Base-promoted Cleavage of a P–C Bond in [$PtCl_2(Ph_2PCH_2PPh_2$-*PP'*)] under Mild Conditions

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The complex [$PtCl_2$(dppm-*PP'*)] (**4**) (dppm = $Ph_2PCH_2PPh_2$) reacts with NaOH under mild conditions in dmso, MeCN, or water to give *cis*- and *trans*- [$Pt_2(\mu\text{-}OH)_2(POPh_2)_2(PMePh_2)_2$] (**3a**) and (**3b**). The same products can be obtained from [PtI_2(dppm-*PP'*)] under similar conditions, or by base hydrolysis of [$PtCl_2(PClPh_2)(PMePh_2)$]. The products (**3a**) and (**3b**) have been characterised by a combination of molecular weight measurements and i.r., $^{31}P\text{-}\{^1H\}$, and particularly, ^1H n.m.r. spectroscopy; the ^1H signals for the μ-OH protons are high-field (0 to −2 p.p.m.) 1:8:18:8:1 multiplets due to coupling to two equivalent ^{195}Pt nuclei. The OH bridges are surprisingly stable but may be cleaved by aqueous HCl to give [$PtCl_2(PPh_2OH)(PMePh_2)$] (**6**), or by acetylacetone (Hacac) to give [$Pt(acac)(POPh_2)(PMePh_2)$] (**8**). Two mechanisms for the reaction of OH^- with the chelate (**4**) are considered: μ-OH formation followed by OH^- attack at P or OH^- attack at P followed by μ-OH formation. No intermediates have been identified but the feasibility of the latter mechanism is shown by the hydrolysis of [$PtMe_2$(dppm-*PP'*)] (**12**) to give [$PtMe_2(PPh_2OH)(PPh_2Me)$] (**13**).

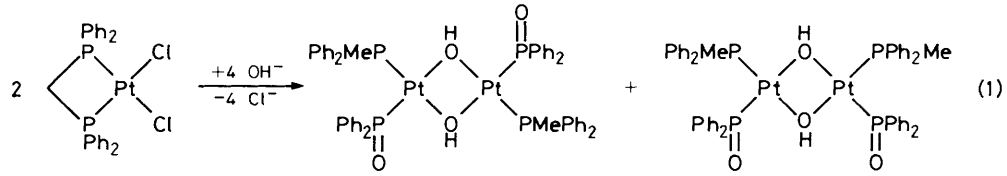
The chemistry of μ-hydroxo–platinum(II) complexes has assumed importance since oligomers $[\{Pt(NH_3)_2(\mu\text{-}OH)\}_n]^{n+}$ [n = 2(**1**) or 3(**2**)] have been identified as toxic *in vivo* side-products of *cis*-platin {*cis*-[$PtCl_2(NH_3)_2$]} cancer chemotherapy.[1] Few cationic or neutral platinum(II)–phosphine complexes containing μ-hydroxo ligands have been reported.[2] In this paper, we report the synthesis of the neutral μ-hydroxo-platinum(II) complexes (**3a**) and (**3b**) by two independent routes: base-induced P–C bond cleavage of the dppm [bis(diphenylphosphino)methane] chelate complex (**4**) [equation (1)] and base hydrolysis of the chlorophosphine complex (**5**) [equation (2)].

Results and Discussion

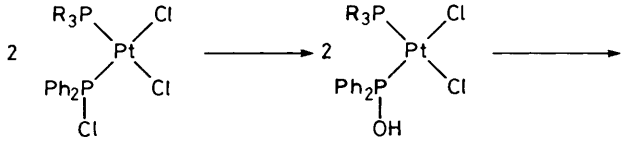
When a suspension of the chelate [$PtCl_2$(dppm-*PP'*)] (**4**) is boiled with aqueous sodium hydroxide for 16 h a remarkably specific reaction takes place to yield the products (**3a**) and (**3b**), as identified by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (see below). The same products are formed in minutes in high yields (>90%) at ambient temperatures when the chelate (**4**) is treated with NaOH in Me_2SO or MeCN.

The *trans*-(**3a**) and *cis*-(**3b**) binuclear structures, containing phosphorus-(V), -(III), and μ-OH ligands, are assigned on the basis of elemental analysis, solution molecular weight measurement (see Experimental section for details), i.r., and, particularly, $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (see Figure 1 and Table 1) shows that two similar species are present. From the absence of signals at low frequency, it was deduced that four-membered chelates[3] were not present and signals at +25 to +27 p.p.m. indicated the presence of phosphorus(V) ligands. The small ^2J(PP) and large ^1J(PtP) values are consistent with mutually *cis* phosphorus nuclei which are *trans* to ligands of low *trans* influence. The i.r. spectrum has a sharp band at 3 590 cm^{-1} assigned to ν(μ-OH)[2] and several absorptions in the region of 1 100 cm^{-1} which may be associated with ν(P=O). The hydroxo ligands can be unambiguously assigned a bridging mode from the ^1H n.m.r. spectrum. The OH resonances (see Figure 2 and Table 2) are to high field of $SiMe_4$, as has been observed for other hydroxo complexes of the platinum-group metals.[4] The OH signal for the *trans* isomer (**3a**) is at −1.22 and is clearly a 1:8:18:8:1 multiplet, characteristic[5] of a nucleus coupled equally to two ^{195}Pt nuclei ($I = \frac{1}{2}$, 33.4%) and therefore consistent only with the OH ligand being bridging. The OH protons in the *cis* isomer (**3b**) are chemically inequivalent and resonate at −0.56 and −2.04; for these signals only the central three lines of the multiplets are resolved. The OH signals are sharp in both isomers showing that intramolecular and intermolecular proton exchange between the co-ordinated OH groups is slow on the n.m.r. time-scale. However, when D_2O is added the OH resonance disappears rapidly due to H/D exchange with the solvent.

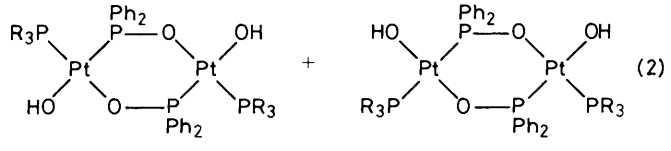
It has been reported[6] that complexes of type (**5**) can be hydrolysed to give hydroxyphosphine complexes (**6**) which, in turn, can be hydrolysed to give binuclear μ-phosphinito complexes (**7a**) and (**7b**) as a mixture of *cis* and *trans* isomers [equation (2)]; the reported structures were assigned on the basis of i.r. spectroscopy. Since (**7a**) and (**7b**), where PR_3 = $PMePh_2$, would be isomers of the μ-hydroxo complexes (**3a**) and (**3b**) above, we treated (**5a**) with NaOH. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the product clearly shows that μ-hydroxo complexes (**3a**) and (**3b**) are formed quantitatively. The reaction of (**5b**) with 3 equivalents of NaOH gave an impure mixture of the isomers (**3a'**) and (**3b'**) (as shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy), but upon addition of a slight excess of NaOH the single isomer (**3a'**) was formed quantitatively (see Tables 1 and 2 for characterising data). Hence hydrolysis of complexes (**5**) [equation (3)] is a convenient alternative route to (**3a**) and (**3b**) and is more general than the cleavage reaction (1). We conclude that the complexes assigned structures (**7a**) and (**7b**) should be reformulated as the μ-OH complexes (**3a**) and (**3b**).



(4) (3a) (3b)



(5a),(5b) (6)



(7a) (7b)

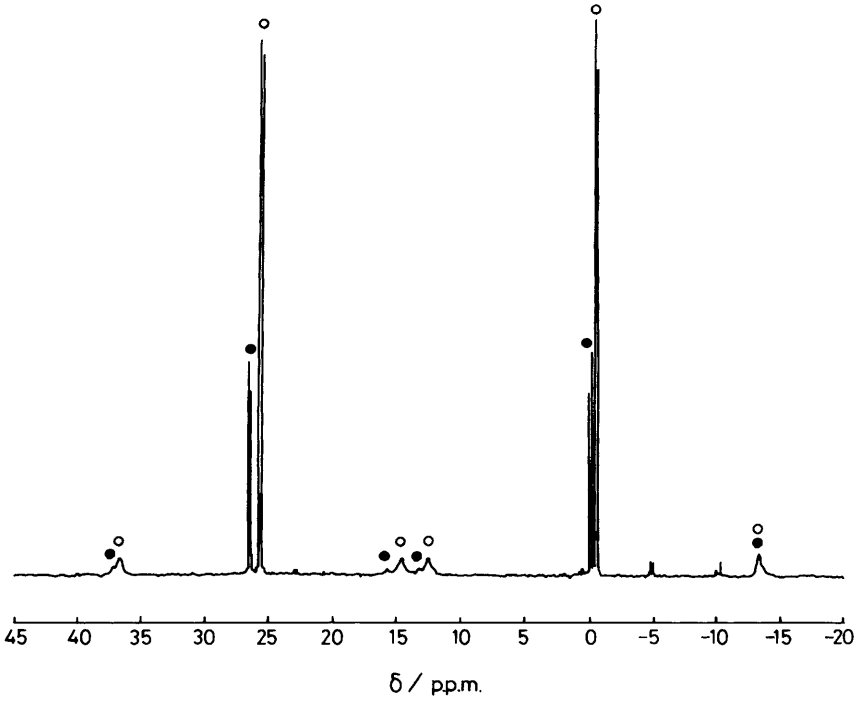


Figure 1. $^{31}P-\{^{1}H\}$ N.m.r. spectrum, 162 MHz, of $[Pt_2(\mu\text{-}OH)_2(POPh_2)_2(PMePh_2)_2]$ in $CDCl_3$ showing the mixture of *cis* (●) and *trans* (○) isomers. Note that the precise ^{31}P shifts are dependent on the amount of water present, presumably because of hydrogen bonding to P=O. The broadening of the satellites is due to chemical shift anisotropy

Table 1. ^{31}P-{^{1}H} N.m.r. data[a]

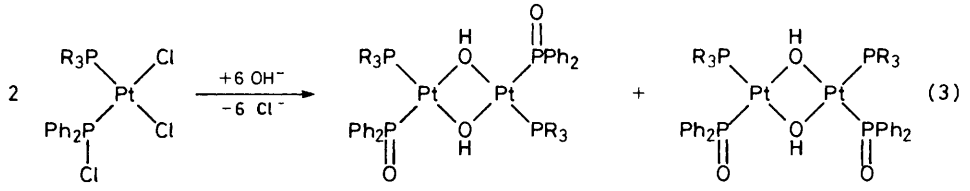
Complex	$\delta(P_A)$/p.p.m.	$^{1}J(PtP_A)$/Hz	$\delta(P_B)$/p.p.m.	$^{1}J(PtP_B)$/Hz	$^{2}J(P_AP_B)$/Hz
(**3a**)	−0.4	4 180	+25.6	3 570	28
(**3b**)	−0.1	4 240	+26.4	3 490	28
(**3a'**)	+12.0	3 989	+25.3	3 646	29
(**3b'**)	+10.0	4 100	+24.8	3 718	29
(**4**)[b]	−64.4	3 034			
(**5**)	+4.6	3 562	+69.6	4 242	14
(**6**)	+1.1	3 701	+73.5	3 823	16
(**8**)	+0.8	4 188	+24.2	3 417	32
(**12**)[b]	−40.5	1 453			
(**13**)[b]	+8.8	1 930	+72.4	2 405	10

[a] At 40.25 MHz and 28 °C. In $CDCl_3$ unless stated otherwise. Chemical shifts (±0.1 p.p.m.) to high frequency of 85% H_3PO_4. [b] In $(CD_3)_2SO$.

Table 2. Proton n.m.r.[a] and i.r. data[b]

Complex	$\delta(PCH_3)$	$J(PCH_3)$/Hz	$J(PtH)$/Hz	Other	I.r.
(**3a**)	2.10	45	12.5	δ(OH) −1.22; $J(PtH)$ 13.5	ν(OH) 3 590w (sharp); ν(PO) 1 088, 1 108, 1 134s
(**3b**)	2.20	45	11.2	δ(OH) −0.56, −2.04; $J(PtH)$ 20.3, 11.7	
(**3a'**), (**3b'**)[c]				δ(OH) −1.03; $\delta(CH_2)$ 1.1; $\delta(CH_3)$ 0.4	ν(OH) 3 600, 3 530w (sharp); ν(PO) not assigned
(**6**)	1.93	11.1	39		ν(OH) 3 420 (br); ν(PtCl) 315, 290s
(**8**)	2.38	11.8		$\delta[CH_3C(O)]$ 1.46, 1.65	ν(CO) 1 572, 1 595s; ν(PO) 1 092, 1 108, 1 135s

[a] At 80 MHz and 25 °C in $CDCl_3$. Chemical shifts (±0.01 p.p.m.) to high frequency of $SiMe_4$. [b] Given in cm^{-1}; CsI or CsCl discs. [c] Individual isomers not resolved.



(**5a**) PR_3 = $PMePh_2$
(**5b**) PR_3 = PEt_3

(**3a**)
(**3a'**)

(**3b**) PR_3 = $PMePh_2$
(**3b'**) PR_3 = PEt_3

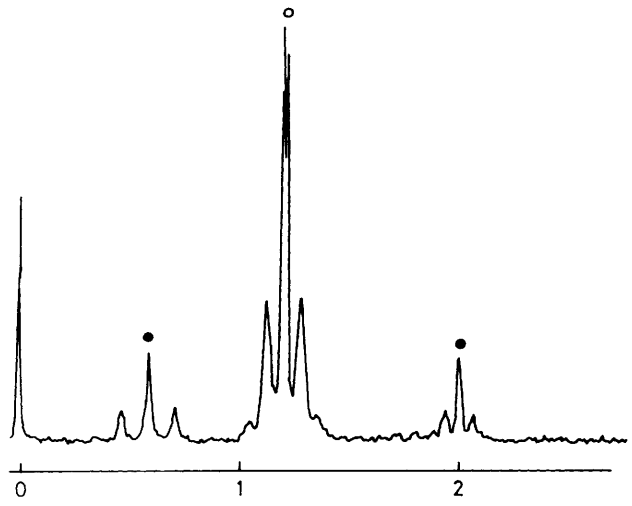
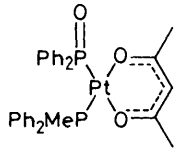


Figure 2. ^{1}H N.m.r. spectrum of $[Pt_2(\mu\text{-}OH)_2(POPh_2)_2(PMePh_2)_2]$ in $CDCl_3$ showing the high-field μ-OH signals of the *cis* (●) and *trans* (○) isomers. Note that the 1:8:18:8:1 multiplicity of the central signal shows further fine structure due to coupling to ^{31}P [$J(HP)$ 1.5 Hz]

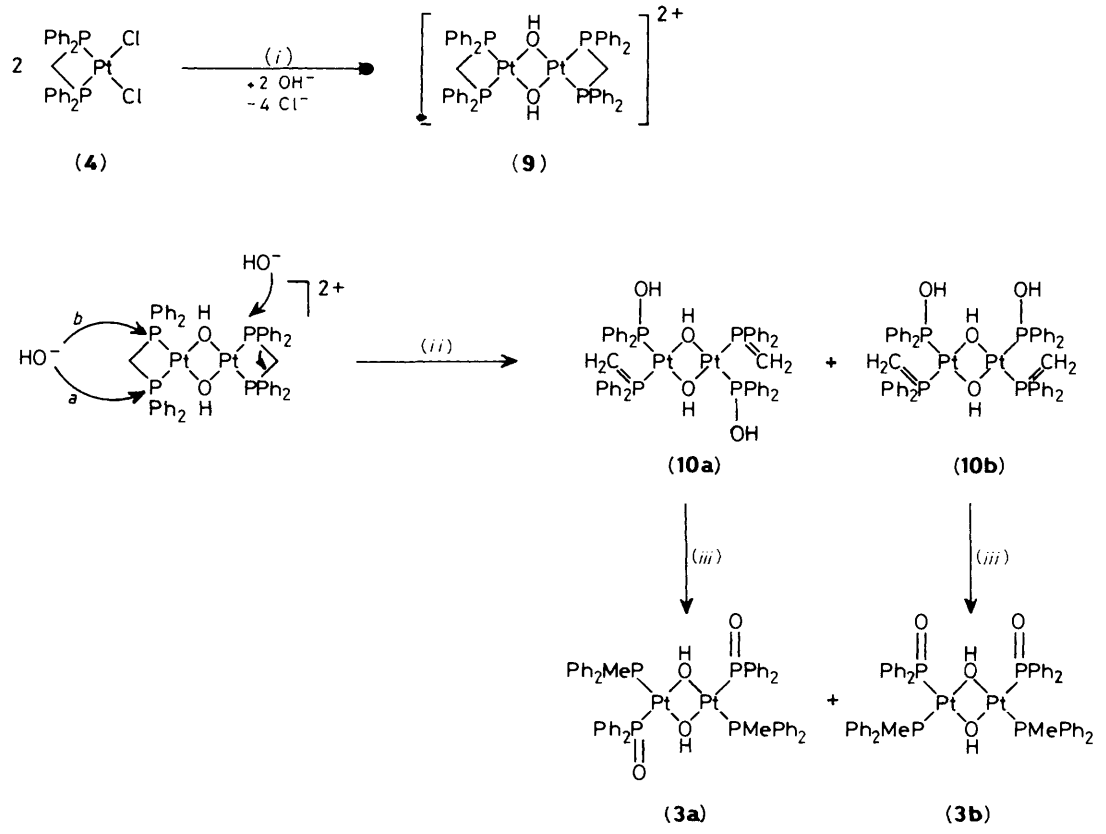


(**8**)

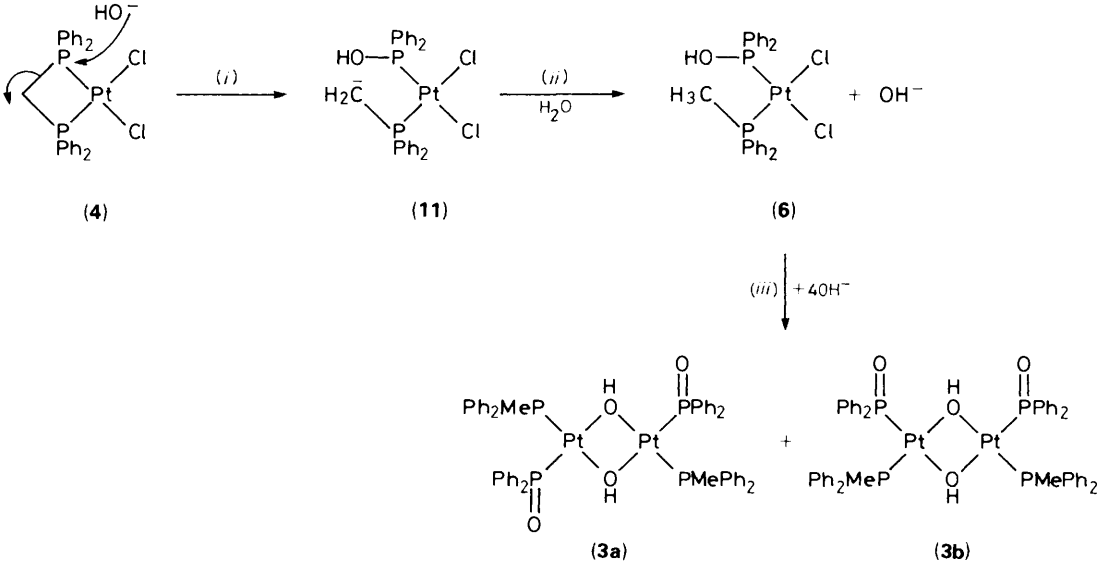
Some Reactions of the μ-*Hydroxo Complexes* (**3a**) and (**3b**).—The hydroxo bridges in (**3a**) and (**3b**) are surprisingly stable. For example, iodide is usually considered to be a good bridging ligand for platinum(II) and yet (**3a**) and (**3b**) are formed quantitatively upon treatment of $[PtI_2(dppm\text{-}PP')]$ with stoicheiometric amounts of OH^- in dmso. Furthermore, treatment of (**3a**) and (**3b**) with a large excess of LiI in dmso had no effect.

The hydroxo bridges are cleaved by acids. For example, aqueous HCl (2 mol dm^{-3}) reacts with (**3a**) and (**3b**) to give the hydroxyphosphine complex (**6**). Treatment of (**3a**) and (**3b**) with acetylacetone gave the mononuclear complex (**8**). (See Tables and Experimental section for characterising data.)

Some Observations on the Mechanism of the Chelate Ring Cleavage.—The ring cleavage reaction (1) is clearly complex but



Scheme 1. Mechanism A



Scheme 2. Mechanism B

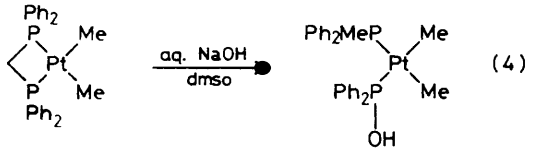
the observed high specificity prompted us to probe the mechanism of this process. The two mechanisms considered were (A) hydroxo bridge formation followed by ring cleavage (Scheme 1) and (B) ring cleavage followed by hydroxo bridge formation (Scheme 2).

In mechanism A (Scheme 1), step (*i*) is the substitution of the chloro ligands of the chelate complex (**4**) to give the binuclear dication (**9**), *i.e.* the dppm analogue of Dixon's[2] complexes $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$. Step (*ii*) is nucleophilic substitution at phosphorus by OH^- to give the ylide-like complexes (**10a**) and (**10b**) which then tautomerise [step (*iii*)] to give the observed products (**3a**) and (**3b**). In an attempt to make the cationic species (**9**), $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2$ was treated with dppm but the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this reaction mixture showed that a complex mixture of products had formed, none of which appeared to be the desired cation (**9**) or the cleavage products (**3a**) and (**3b**).

In mechanism B (Scheme 2), step (*i*) is nucleophilic substitution at P by OH^- to give the carbanion (**11**) followed by protonation [step (*ii*)] to give the previously characterised[6]

hydroxyphosphine complex (**6**). Steps (*i*) and (*ii*) amount to base-catalysed hydrolysis of the P–C bond in the dppm chelate ring. Step (*iii*) is substitution at Pt by OH^- to form the hydroxo bridges with concomitant elimination of HCl to give the observed products (**3a**) and (**3b**). Step (*iii*) in this mechanism is a known reaction,[6] so we need only justify steps (*i*) and (*ii*). We have never observed the intermediacy of complex (**6**) in any of the cleavage reactions followed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. This may be because (*a*) at low concentrations of OH^- (*i.e.* catalytic amounts) the base is consumed by deprotonation of the CH_2 group[7] and (*b*) at higher concentrations of OH^-, Pt–Cl substitution [step (*iii*)] is rapid and quantitative compared with the slow P–C cleavage [step (*i*)] so that build up of any significant concentration of intermediate (**6**) is not possible.

The Pt–C bonds in $[PtMe_2(PR_3)_2]$ are generally stable to hydrolysis. Hence, we reasoned that if $[PtMe_2(dppm\text{-}PP')]$ (**12**) reacted with OH^- *via* mechanism B then a hydroxyphosphine complex (**13**), analogous to the postulated intermediate (**6**),



(4)

(**12**) (**13**)

should be relatively stable. Treatment of complex (**12**) with NaOH in dmso does indeed result in the slow formation of the hydroxyphosphine complex (**13**) [equation (4)]. Complex (**13**) decomposes in solution over a period of a few hours and was thus not isolated in analytically pure form. It was identified in solution from its characteristic $^{31}P-\{^1H\}$ n.m.r. spectrum (see Table 1 for the data) which showed two signals with chemical shifts similar to those of the closely related dichloro derivative (**6**); the small $^2J(PP)$ and $^1J(PtP)$ values confirm that the P atoms are mutually *cis*, and are *trans* to the methyl ligands. The observation of cleavage of (**12**) by base to give (**13**) makes steps (*i*) and (*ii*) in mechanism B plausible.

Conclusions

Phosphorus–carbon bond cleavage in co-ordinated phosphines by radical mechanisms is well documented and of considerable importance in understanding the stability of homogeneous metal–phosphine catalysts.[8] To our knowledge, the reactions reported here are the first examples of base-induced P–C bond cleavage in a co-ordinated phosphine. The reaction is analogous to the well known, base-induced P–C cleavage in quaternary phosphonium salts [equation (5)].

$$PR_4^+ + OH^- \longrightarrow PR_3O + RH \qquad (5)$$

This reaction may be confined to dppm chelates, since attempts to cleave the P–C bonds in $[PtCl_2(dppe)]$ by treatment with NaOH under similar or more forcing conditions (*e.g.* boiling dmso) did not give products where the five-membered ring was cleaved. It is therefore likely that the reaction is another manifestation of the ring strain present in four-membered dppm chelate rings.

Experimental

All reactions were carried out under a nitrogen atmosphere although the products were, in general, air stable.

Preparation of $[Pt_2(\mu\text{-}OH)_2(POPh_2)_2(PMePh_2)_2]$ (**3a**) *and* (**3b**).—A solution of NaOH (0.30 g, 7.7 mmol) in water (1 cm^3) was added to a suspension of $[PtCl_2(dppm\text{-}PP')]$ (**4**) (1.00 g, 1.54 mmol) in MeCN (150 cm^3) and the mixture stirred for 30 min. The colourless solution was then concentrated under vacuum to 25 cm^3. Addition of water (100 cm^3) to the concentrate gave the white solid product which was then filtered off, washed with water (3 × 20 cm^3), and dried *in vacuo* to give 0.69 g (90%) of product. Crystalline material could be obtained from $CHCl_3$–diethyl ether (Found: C, 48.80; H, 4.15. *M* 1 135. Calc. for $C_{50}H_{48}O_4P_4Pt_2$; C, 48.95; H, 3.95%. *M* 1 226). The same products, (**3a**) and (**3b**), could be made using dmso instead of MeCN, the disadvantage being the involatility of this solvent. If the above reaction is carried out using water as solvent then the reaction mixture must be boiled for at least 16 h and even then the product may well be contaminated with the starting material (**4**). Finally, the products (**3a**) and (**3b**) may be made using the procedure described by Chatt and Heaton.[6]

Preparation of $[Pt(acac)(POPh_2)(PMePh_2)]$ (**8**).—Acetylacetone (Hacac) (170 mg, 1.70 mmol) and complexes (**3a**) and (**3b**) (207 mg, 0.17 mmol) were stirred in $CHCl_3$ (20 cm^3) for 1 h at 20 °C. The volume of the solution was then reduced to 5 cm^3 under vacuum and then, upon addition of light petroleum (b.p. 60—80 °C, 20 cm^3), the white product precipitated (140 mg, 59%) (Found: C, 51.75; H, 4.55. Calc. for $C_{30}H_{30}O_3P_2Pt$: C, 51.80; H, 4.35%).

N.M.R. Reactions.—In a typical experiment $[PtCl_2(dppm\text{-}PP')]$ (20 mg, 0.03 mmol) was dissolved in $[^2H_6]$ dmso (0.3 cm^3) and aliquots of 5 mol dm^{-3} aqueous KOH added and the mixture shaken in a 5-mm n.m.r. tube. The reaction was followed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy using a JEOL FX90Q spectrometer.

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