¹H, ³¹P and ¹⁹⁵Pt NMR characterization, and X-ray molecular structures of five- and six-membered platinum(II) and palladium(II) metallacycles from the alcoholysis of di- and triazaphosphole complexes

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Abstract

The 1,2,3-diazaphosphole P=C(H)C(Me)=NNMe (L$_A$) and the 1,2,4,3-triazaphospholes P=NC(Ph)=NNMe (L$_B$) and P=NN(Me)C(Me)=N (L$_C$) form Pt(II) and Pd(II) complexes of stoichiometry MX$_2$(PEt$_3$)L (X = Cl, Br) whose controlled reactions with alcohols, generally methanol, have been studied by ¹H, ³¹P and ¹⁹⁵Pt NMR spectroscopy. Discrete intermediate species and the final novel monomeric phosphito metallacycles (σ-P bonding of a {P(=O)(OR)R'}⁻ function and N-coordination of either an imine or amine function) have been identified by their characteristic multinuclear NMR data. These data allow a stepwise mechanism for the azaphosphole ring-opening to be proposed. Two representative products of the series derived from L$_B$ and L$_C$, namely [Pt{P(=O)(OMe)N(H)-C(Ph)=NN(H)Me}(Cl)(PEt$_3$)] (19c) and [Pt{P(=O)(OMe)N(H)N(Me)C(Me)=NH}(Cl)(PEt$_3$)] (20c) have been characterized by X-ray structure investigations. In the crystal the bonding of the P,N-chelating ligand in 19c is different to that identified in solution; the two ligand forms found can be described in terms of amidine tautomerism. (In this paper for simplicity we refer to a {P(=O)(OR)R'}⁻ ligand as a phosphite; this is strictly only correct if R is (bonded through) an electronegative element and in cases where R is C-bound the ligand is more properly a phosphinite.) © 1997 Elsevier Science S.A.

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1. Introduction

The azaphospholes [1,2] are heteroaromatic ring systems which contain a two-coordinate trivalent phosphorus atom; in these rings the P=C and P=N bonds are stabilized towards addition reactions by cyclic delocalization. While the synthesis of azaphospholes is well developed, their chemistry and in particular their complex chemistry has still not received much attention.

For the present investigation the 2,5-dimethyl-1,2,3-di-azaphosphole (L$_A$) (Scheme 1), the 2-methyl-5-phenyl-1,2,4,3-triazaphosphole (L$_B$) (Scheme 2) and the 1,5-dimethy-1,2,4,3-triazaphosphole (L$_C$) (Scheme 3) have

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been used. These three azaphospholes have a variety of potential ligating sites available. The phosphorus lone pair is common to all three systems and, in addition, L$_A$ has a single N coordination site (–N=C) whereas L$_B$ and L$_C$ both have two such sites (–N=C and –N=P). Through complexation to metal centres the properties of the azaphosphole will be modified in a way that is dependent on the coordination mode present [3]. In our research on platinum and palladium complexes [4–6] we have found ³¹P NMR spectroscopy to be a powerful tool for examining the interactions of these systems with the metal centres; particularly for platinum complexes which contain the ¹⁹⁵Pt nucleus ($I = 1/2$, 33.7% abundance) the combination of ³¹P shift data with coupling information and direct ¹⁹⁵Pt NMR observation of the metal coordination centre makes a unique analytical method. Previous studies of azaphosphosphole coordination chemistry have been reviewed [3].

In an earlier study employing primarily ^1H, ^{31}P and ^{195}Pt NMR spectroscopy, we identified and characterized the coordination complexes of $MX_2(PEt_3)L$ stoichiometry obtained from the reactions of L_A, L_B and L_C with halo-bridged dimers $[MX_2(PEt_3)]_2$ (M = Pt, Pd; X = Cl. M = Pt; X = Br) [6]. The majority of these Pt(II) and Pd(II) products (1–10) are monomeric and exhibit either σ-P or σ-N coordination modes, though the triazaphospholes L_B and L_C afford with $[PtCl_2(PEt_3)]_2$ more complex dinuclear species (11 and 12, respectively, whose structures are illustrated in Ref. [6]); the preparation of these complexes (with their schematic structures) is summarized in Schemes 1 (L_A), 2 (L_B) and 3 (L_C). The present paper is concerned with the unusual phosphito metallacycles products — characterized by multinuclear NMR and X-ray diffraction studies — arising from the reaction of these air-sensitive complexes with MeOH. These products and some observed intermediates provide insight into mechanistic aspects of this chemistry. Some preliminary findings from this study of selective ring-opening of coordinated azaphospholes have already been the subject of a communication [5].

2. Experimental

2.1. General

All preparations were carried out under oxygen-free dry nitrogen using carefully dried and distilled solvents. The dimers $[MX_2(PEt_3)]_2$ (M = Pt, X = Cl, Br; M = Pd, X = Cl) [7] and the azaphospholes L_A [8a,b], L_B [8a,b] and L_C [8c] were prepared by literature methods. Elemental microanalyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry, TNO, Zeist (Netherlands); data are collected in Table 1.

Table 1
Analytical data for complexes 19 and 20

Complex, formula	C	H	Cl/Br	N	P
19a. $C_{14}H_{28}ClN_3O_2P_2Pd$ Found	36.84	5.74	7.23	8.78	12.51
Calc.	37.05	5.80	7.29	8.64	12.75
19b. $C_{14}H_{28}BrN_3O_2P_2Pt$ Found	28.90	4.61	13.81	6.64	9.79
Calc.	29.09	4.56	12.90	6.78	10.00
19c. $C_{14}H_{28}ClN_3O_2P_2Pt$ Found	31.40	5.02	6.13	7.49	10.44
Calc.	31.34	4.91	6.17	7.13	10.78
20a. $C_{16}H_{28}ClN_3O_2P_2Pd$ Found	28.53	6.25	10.57	9.88	13.93
Calc.	28.32	6.18	8.36	9.91	14.60
20b. $C_{16}H_{28}BrN_3O_2P_2Pt$ Found	21.69	4.66	14.03	7.71	10.84
Calc.	21.55	4.70	14.34	7.54	11.12
20c. $C_{16}H_{28}ClN_3O_2P_2Pt$ Found	23.46	5.14	6.99	8.12	11.81
Calc.	23.42	5.11	6.91	8.19	12.09
20d. $C_{17}H_{28}ClN_3O_2P_2Pt$ Found	25.09	5.47	6.62	8.20	11.65
Calc.	25.08	5.36	6.73	7.98	11.76
20e. $C_{16}H_{10}ClN_3O_2P_2Pt$ Found	32.76	5.17	6.32	6.95	9.88
Calc.	32.63	5.14	6.02	7.14	10.52

2.2. Preparations of complexes 18–20

The preparations of the phosphito complexes 18, 19 and 20 are all very similar and start from the air-sensitive 1:1 azaphosphole-to-metal coordination complexes 1–12 described previously [5]; that of 20c is typical.

To a yellow solution of 12 (710 mg, 0.71 mmol) in CH_2Cl_2 (3 ml) was added MeOH (0.5 ml, excess) and the clear solution allowed to stand for 5 days. The solution was then concentrated in vacuo to ~0.5 ml and pentane (20 ml) added. The resulting white precipitate of the product was filtered off and recrystallized from a CH_2Cl_2/pentane mixture. Yield 530 mg of 20c (75%).

For complexes of series 18 the reaction mixture was concentrated in vacuo to a viscous oil which upon standing afforded, often with difficulty, solid material. Because of their good solubility and air-sensitivity, recrystallization of these complexes was not successful and this has prevented us from obtaining satisfactory elemental analysis data.

2.3. NMR measurements

Typically ~200 mg of the metal complex in 0.5 ml $CDCl_3$ (~1 M solution) was measured in a 5 mm o.d. tube. The intermediates 13–17 were prepared in situ in the NMR tube by addition of MeOH by micro-syringe to a solution of the azaphosphole-to-metal coordination complexes 10, 11 and 12. The ^1H NMR spectra were recorded on Bruker WM-250 and Varian T-60 spectrometers. The $^{31}P\{H\}$ NMR spectra were recorded on Bruker WP-80 (32.4 MHz) and Varian XL-100 (40.5 MHz) spectrometers with chemical shifts referenced to external H_3PO_4 and with a positive value indicating a shift to lower field. The $^{195}Pt\{H\}$ NMR spectra were recorded at ~53.5 MHz on a Bruker WM-250 spectrometer for which the TMS ^1H resonance of a $CDCl_3$ solution is 250 132 847 Hz. The measured absolute frequency of a ^{195}Pt resonance was converted (making allowance for the various deuterium lock signals) to a standard frequency (TMS ^1H resonance at 100 MHz) [9]. Chemical shifts are reported relative to 21.4 MHz with a positive value being to higher frequency (cf. $PtCl_6^{2-}$; 21 496 770 Hz; δ = +4522) [10].

2.4. X-ray crystal structure determinations of 19c and 20c

Crystal data and numerical details of the structure determination are given in Table 2. Suitable colourless crystals of 19c and 20c were obtained by crystallization from warm ethanol and were used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα (λ = 1.5418 Å) radiation and θ–2θ scan. For both complexes the maximum value of (sinθ)/λ was 0.59 Å^{-1}. Unit-cell parameters were refined by a least-squares fitting procedure. For both complexes Lorentz and polarization effects were applied. The Pt atom was found by the Patterson method and the remainder of the non-H atoms were found in a ΔF synthesis. The hydrogen atom positions were calculated. The

Table 2
Crystal data and details of the structure determination for **19c** and **20c**

	19c	**20c**
Crystal data		
Formula	$C_{15}H_{28}ClN_3O_2P_2Pt$	$C_{10}H_{26}ClN_3O_2P_2Pt$
Molecular weight	574.9	512.83
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	15.924(2)	10.2230(7)
b (Å)	9.407(1)	21.720(2)
c (Å)	15.307(1)	7.9870(7)
β (°)	109.72(1)	102.30(1)
V (Å^3)	2158(2)	1732.8(3)
Z	4	4
D_{calc} (g cm^{-3})	1.77	1.96
$F(000)$, electrons	1120	992
$\mu(Cu\,K\alpha)$ (cm^{-1})	150.02	185.9
Crystal size (mm)	$0.23 \times 0.23 \times 0.33$	$0.20 \times 0.28 \times 0.38$
Data collection and refinement		
$\theta_{min}, \theta_{max}$ (°)	3.0, 64.8	4.1, 64.8
Radiation (Å)	Cu Kα (graphite-filtered), 1.5418	Cu Kα (graphite-filtered), 1.5418
Scan type	θ–2θ	θ–2θ
X-ray exposure time (h)	40	32
R to determine cell constants	23 with $78 < 2\theta < 90°$	23 with $80 < 2\theta < 86°$
DIFABS correction range		0.80–1.85
Data set	h –18:18, k 0:11, l 0:17	h –12:12, k 0:25, l 0:9
Total unique data	3642	3033
Observed data	2631 ($I > 2.5\sigma(I)$)	2705 ($I > 2.5\sigma(I)$)
Weighting scheme w^{-1}	$20.0 + 0.001\sigma^2(F_{obs})$ $+ 0.0001/\sigma(F_{obs})$	$10.0 + 0.0001\sigma^2(F_{obs})$ $+ 0.0001/\sigma(F_{obs})$
Final R, wR, S	0.041, 0.063, 0.95	0.035, 0.041, 1.02
Maximum (Δ/σ) in final cycle	0.44	0.41
Min. and max. residual density (e Å^{-3})	–1.7, 1.9 (near Pt)	–1.5, 1.7 (near Pt)

full-matrix refinement on F was anisotropic for the non-H atoms with the hydrogen atoms fixed at their calculated positions. For **20c** an empirical absorption correction (DIFABS) [11] was applied. The secondary isotropic extinction coefficient [12] refined to $g = 6.3(3) \times 10^2$ for **19c** and $g = 1.9(2) \times 10^2$ for **20c**. Weights were introduced in the final refinement cyles and convergence was reached at $R = 0.041$ (**19c**) and 0.035 (**20c**). Final heavy atom coordinates and equivalent isotropic thermal parameters are given in Tables 3 and 4 for **19c** and **20c**, respectively.

Neutral atom scattering factors were taken from Cromer and Mann [13]. The anomalous scattering of Pt, Cl and P was taken into account [14]. All calculations were performed with XTAL3.2 [15] with the exception of the illustrations which were performed with PLATON [16].

3. Results and discussion

3.1. Synthetic overview

In Schemes 1–3 are summarized the reactions of methanol with the previously described Pt(II) and Pd(II) azaphosphole coordination complexes **1–12** [6]. We find that in each case the addition of excess methanol affords a species whose

basic structure is determined solely by the azaphosphole ligand and not by the nature of the metal or of the halide. Thus, the coordination complexes of diazaphosphole L_A (i.e. **1**, **4**, **7** and **10**) provide the new metallacyclic products **18** (M = Pd, X = Cl (**18a**); M = Pt, X = Br (**18b**), Cl (**18c**)) which are isolated as air-sensitive yellow oils. The divalent platinum and palladium complexes of the triazaphospholes L_B (i.e. **2**, **5**, **8** and **11**) and L_C (i.e. **3**, **6**, **9** and **12**) afford with excess methanol the white solid complexes **19** (M = Pd, X = Cl (**19a**); M = Pt, X = Br (**19b**), Cl (**19c**)) and **20**, R is Me (M = Pd, X = Cl (**20a**); M = Pt, X = Br (**20b**), Cl (**20c**)), respectively. The reactions of excess ethanol and benzyl alcohol with **12** afford analogous metallacyclic species (M = Pt, X = Cl, R = Et (**20d**), PhCH$_2$ (**20e**)).

The complexes **18**, **19** and **20** are readily soluble in polar solvents such as CH$_2$Cl$_2$, CHCl$_3$ and MeOH, but have poor solubility in benzene and pentane.

3.2. Characterization of complexes 18, 19 and 20

The characterization of the new metallacyclic complexes **18**, **19** and **20** has been primarily based on elemental analysis and multinuclear NMR data; ^{1}H NMR data are given in Table 5 and ^{31}P and ^{195}Pt NMR data are collected together in Table 6. Because it was clear from these data that the skeleton

Table 3

Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for 19c [a]

Atom	x	y	z	U_{eq} [b] ($Å^2$)
Pt	0.26420(3)	0.05817(6)	0.05952(4)	0.0391(3)
Cl	0.1589(2)	0.0701(8)	0.1399(3)	0.101(3)
P1	0.1517(2)	0.0587(5)	−0.0777(3)	0.053(2)
P2	0.3719(2)	0.0470(3)	−0.0001(2)	0.032(1)
C1	0.4514(7)	0.052(1)	0.1851(7)	0.035(6)
C2	0.5347(7)	0.053(1)	0.2662(7)	0.033(6)
C3	0.5449(9)	0.143(1)	0.3403(8)	0.044(7)
C4	0.627(1)	0.152(1)	0.4115(9)	0.056(8)
C5	0.697(1)	0.069(2)	0.4099(9)	0.058(8)
C6	0.6865(9)	−0.025(2)	0.3383(9)	0.055(8)
C7	0.6062(8)	−0.033(1)	0.2644(8)	0.042(7)
C8	0.351(1)	−0.122(2)	0.290(1)	0.07(1)
C9	0.396(1)	0.319(2)	−0.010(1)	0.07(1)
C10	0.1778(9)	0.082(3)	−0.181(1)	0.09(1)
C11	0.100(1)	0.073(3)	−0.274(1)	0.13(2)
C12	0.067(1)	0.196(3)	−0.086(1)	0.11(1)
C13	0.099(2)	0.338(3)	−0.069(2)	0.17(2)
C14	0.090(1)	−0.106(2)	−0.095(2)	0.11(1)
C15	0.137(2)	−0.227(3)	−0.105(3)	0.24(3)
N1	0.3694(6)	0.051(1)	0.1839(6)	0.037(5)
N2	0.4626(5)	0.054(1)	0.1001(6)	0.036(5)
N3	0.3583(7)	0.031(1)	0.2722(7)	0.049(7)
O1	0.3799(5)	−0.0733(9)	−0.0587(5)	0.039(4)
O2	0.3860(5)	0.1858(9)	−0.0536(5)	0.039(4)

[a] E.s.d.s of the last significant digits are shown in parentheses.
[b] $U_{eq} = 1/3$ of the orthogonalized U tensor.

Table 4

Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of 20c [a]

| Atom	x	y	z	U_{eq} [b] ($Å^2$)
Pt	0.12733(3)	0.11743(2)	0.25112(4)	0.0215(2)
Cl	0.2808(2)	0.1221(1)	0.0618(3)	0.054(2)
P1	0.2629(2)	0.1678(1)	0.4648(3)	0.029(1)
P2	−0.0211(2)	0.10024(9)	0.4071(3)	0.025(1)
C1	0.186(1)	0.2194(5)	0.599(1)	0.049(6)
C2	0.107(1)	0.2723(6)	0.502(2)	0.077(9)
C3	0.382(1)	0.2159(5)	0.382(2)	0.057(7)
C4	0.473(1)	0.2557(7)	0.506(2)	0.09(1)
C5	0.358(1)	0.1167(5)	0.624(1)	0.047(6)
C6	0.432(1)	0.0660(6)	0.554(2)	0.067(8)
C7	−0.224(1)	0.1645(6)	0.473(2)	0.070(9)
C8	−0.1255(8)	0.0604(4)	0.014(1)	0.029(4)
C9	−0.205(1)	0.0526(5)	−0.167(1)	0.042(5)
C10	−0.3372(9)	0.0394(6)	0.112(1)	0.053(6)
N1	0.0001(7)	0.0766(3)	0.0436(9)	0.030(4)
N2	−0.1257(7)	0.0437(3)	0.3147(9)	0.032(4)
N3	−0.1908(7)	0.0497(4)	0.1411(9)	0.035(4)
O1	0.0211(6)	0.0817(3)	0.5902(7)	0.034(3)
O2	−0.1181(6)	0.1597(3)	0.3805(8)	0.040(4)

[a] E.s.d.s of the last significant digits are shown in parentheses.
[b] $U_{eq} = 1/3$ of the orthogonalized U tensor.

of the original azaphosphole ligand had been severely disrupted, X-ray crystallographic structural analysis of two representative platinum chloro complexes 19c and 20c was also carried out (vide infra).
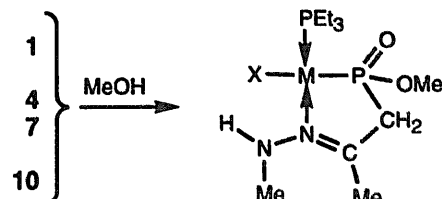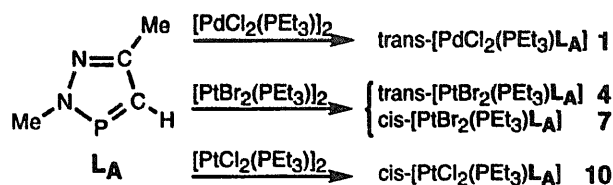
Scheme 1. Synthesis of metallacyclic complexes 18 from coordination complexes of 2H-1,2,3-diazaphosphole L_A.
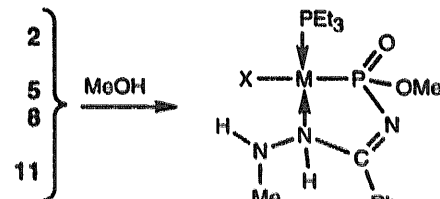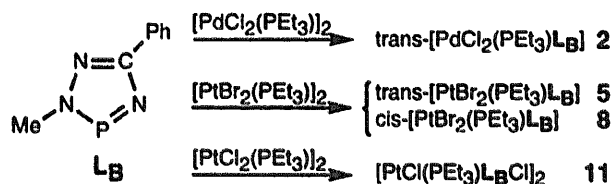
Scheme 2. Synthesis of metallacyclic complexes 19 from coordination complexes of 2H-1,2,4,3-triazaphosphole L_B.

3.3. NMR spectroscopic characterization

A comparison of the NMR data reflects a close inter-relationship of the three series derived from the three azaphosphole ligands used. For example, the individual $^{31}P\{^1H\}$ spectra of 18, 19 and 20 all show an AB resonance pattern for two signals with a coupling constant $J(PP)$ of either ~30 Hz (M = Pt) or <10 Hz (M = Pd) that is consistent with a common structural feature of two mutually cis-positioned P-donor sites. An illustrative spectrum of 20c is shown in Fig. 1. For platinum complexes the large $J(PtP)$ values confirm the direct coordination of both phosphorus sites to the metal centre. In all the species 18–20 the ^{31}P chemical shift for PEt$_3$ is consistent with, though not characteristic for, this phosphine being trans to an N-donor atom. The other ^{31}P resonance is at considerably lower frequency than that of either the parent azaphospholes ($\delta L_A = 228.9$; $\delta L_B = 253.3$; $\delta L_C =$
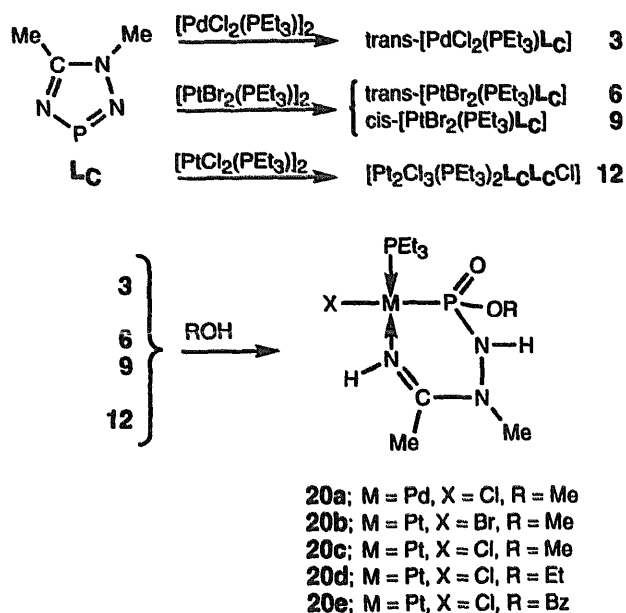
Scheme 3. Synthesis of metallacyclic complexes 20 from coordination complexes of 1H-1,2,4,3-triazaphosphole L$_C$.

257.1) or of their coordination complexes [6], and this indicates that the original azaphosphole has been chemically modified. From the data of Table 5 there is a consistent pattern in which the ^{31}P NMR chemical shifts of the platinum com-

plexes, δP(Pt), are always to high field of those of the corresponding palladium complexes, δP(Pd); the shift difference Δ δ = δP(Pd) − δP(Pt) is ~20 ppm for PEt$_3$ (P$_E$) and ~28-26 ppm for the modified azaphosphole ligands (P$_L$). This is fully consistent with a fairly general rule that for analogous transition metal complexes containing a phosphorus-bonded ligand the δP values are usually found to increasingly higher field as one descends a triad [17]. Furthermore, linear relationships have been found between the the δP values of free phosphines and of their analogous complexes of a given metal [18,19]. Consequently, the phosphorus chemical shifts of two series of analogous metal complexes should also show a linear relationship. Using ^{31}P NMR literature data for complexes cis-[MX$_2$(phosphine)$_2$] (M = Pt, Pd) [18,20-26], collected in Table 7, the validity of this interrelationship for Pd(II)/Pt(II) is illustrated by Fig. 2 in which δP values for pairs of corresponding complexes are plotted against each other. Our own data for pairs of complexes (crosses) fit into this correlation; exactly for δP$_E$ and fairly well for δP$_L$. This not only confirms the cis structures of 18-20 but more importantly emphasizes that the palladium and platinum complexes derived from a specific azaphosphole do indeed have analogous structures.

Remarkably the linear correlation of Fig. 2 appears to hold for complexes in which the phosphorus containing ligand can

Table 5
^{1}H NMR data of complexes 13-20 [a]

Complex	OCH		CNH		N–NH		CH$_2$		NMe	CMe/Ph
	δ	J(PH)	δ	J(PtH)	δ	J(PH)	δ	J(PH)	δ	δ
18a	3.56	12			6.56		2.90	10 [b]	2.48	2.14
							2.98	16 [b]		
18b	3.46	12			6.60		2.85 [c]		2.4	2.14
18c	3.55	12			6.56		2.93 [c]		2.56	2.24
13	3.32	19					2.95	7 [d]	3.32	2.06
							3.90	≈0 [d]		
19a	3.67	14	8.39		5.57				2.22	7.3-7.7
19b	3.63	14	8.66	28	5.73				2.24	7.3-7.7
19c	3.63	14	8.49	28	5.73				2.27	7.3-7.8
14	3.47	9	8.51 [c]						3.30 [f]	7.3-8.0
20a	3.62	11	6.48		4.21	18			3.24	2.23
20b	3.60	12	6.78	46	4.54	16			3.23	2.26
20c	3.60	11	6.70	46	4.57	17			3.26	2.30
20d	3.92 [g]		6.69	46	4.35	16			3.22	2.24
	4.18 [g]									
20e	5.00 [h]		6.72	48	4.35	14			3.05	2.20
	5.14 [h]									
16	3.44	13	12.35 [i]						3.56	2.50

[a] In CDCl$_3$. Coupling constants in Hz. PEt$_3$: δ ≈ 2.0 (CH$_2$, m), ≈ 1.1 (CH$_3$, dt, ^{3}J(HH) ≈ 8 Hz, ^{3}J(PH) ≈ 18 Hz).
[b] ^{2}J(HH) 16 Hz.
[c] Complex signal not analysed.
[d] ^{2}J(HH) = 20 Hz. Signal at δ 3.9 shows non-resolved ^{195}Pt satellites.
[e] ^{2}J(PH) = 26 Hz.
[f] ^{3}J(PH) = 13 Hz.
[g] Complex signals, ^{2}J(HH) and ^{2}J(PH) not extracted; δ(CH$_3$CH$_2$O) = 1.21 (t, ^{3}J(HH) = 7 Hz).
[h] ^{2}J(HH) = 12 Hz.
[i] ^{2}J(PH) = 21 Hz.

Table 6
^{11}P and ^{195}Pt NMR data for complexes 13–20 [a]

Complex (M, X, azaphosphole)	P_L			P_E (PEt₃)		Pt
	δ	$^1J(PtP_L)$	$^3J(P_LP_E)$	δ	$^1J(PtP_E)$	δ
Phosphito complexes						
18a (Pd, Cl, L_A)	95.2		8	30.1		
18b (Pt, Br, L_A)	64.9	4434	20	9.0	3620	66
18c (Pt, Cl, L_A)	65.8	4453	23	9.4	3646	102
19a (Pd, Cl, L_B)	81.8		<4	27.9		
19b (Pt, Br, L_B)	53.4	5161	22	8.4	3318	−40
19c (Pt, Cl, L_B)	54.5	5155	25	9.5	3345	−44
20a (Pd, Cl, L_C)	72.3		9	30.4		
20b (Pt, Br, L_C)	37.2	5028	26	8.9	3535	−47
20c (Pt, Cl, L_C)	36.1	4974	29	9.6	3559	16
20d (Pt, Cl, L_C)	34.7	4999	29	9.2	3578	18
20e (Pt, Cl, L_C)	36.1	5054	28	9.2	3549	24
Intermediates						
13 (Pt, Cl, L_A)	86.9	4840	17	15.2	3403	
14 (Pt, Cl, L_B)	58.2	5615	20	15.8	3360	
15 (Pt, Cl, L_B)	88.8	5740	23	12.9	2979	
16 (Pt, Cl, L_C) [b]	63.4 [c]	5606 [d]	26 [e]	12.6 [c]	3122	21
17 (Pt, Cl, L_C)	75.7	5682	26	10.2	3045	

[a] In CDCl₃. Coupling constants in Hertz. See Section 2.
[b] Symmetric dimer.
[c] Main signal: A or B part of AA'BB' spin system.
[d] $^2J(PtP_L)$ 63 Hz.
[e] Simulation data: $^5J(P_BP_B')$ 0 Hz, $^2J(P_BP_L)$ +26 Hz, $^3J(P_BP_L')$ −6 Hz, $^4J(P_LP_L')$ −5 Hz.

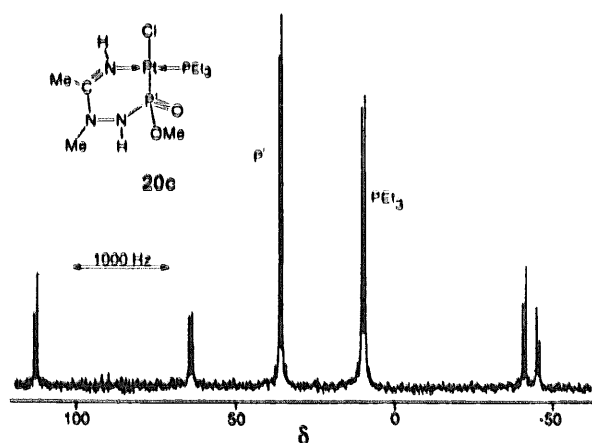

Fig. 1. 32.4 MHz ^{11}P NMR spectrum of 20c.

be of either phosphine or phosphito type. Including all values in a regression analysis ($r = 0.976$) gives:

$$\delta^{11}P(Pd) = 21.982 + 1.006\,\delta^{11}P(Pt)$$

For complexes 18 the ^{1}H NMR spectra show most directly the nature of the modified azaphosphole ligand. As well as the anticipated singlet CMe and NMe signals there are further signals attributable to a POMe unit at $\delta \approx 3.5$, an NH proton at $\delta \approx 6.65$ (not coupled to ^{195}Pt in 18b,c) and a complex resonance at $\delta \approx 2.95$ that corresponds to a CH₂ group rather than to an sp² CH as in L_A. As analyzed for 18a this latter resonance represents the AB part of an ABX spin system in which A and B are diastereotopic protons and X is phospho-

rus. Based on these data and likely reactions [2] of the diazaphosphole L_A with MeOH we deduce the presence of a P(=O)(OMe)CH₂CMe=NNH(Me) ligand which is chelating to the metal centre through P and the imine N. The postulated structure for 18, depicted in Scheme 1, provides these complexes with a novel five-membered metallacycle derived from ring-opening of coordinated L_A at the P–N bond. (Originally N¹-coordination resulting in a six-membered ring was assumed [5].) This structure with a phosphito ligand is of an unusual type but its credibility is strongly enhanced by the related, though different, arrangements identified in 19 and 20, vide infra.

The ^{1}H spectra for 19 show besides the NMe and CPh signals that are present in the parent triazaphosphole L_B a doublet for a POMe unit at $\delta \approx 3.5$ and two distinctly different NH protons, one at $\delta \approx 6$ and another, at $\delta \approx 8.5$. In the platinum complexes 19b and 19c the latter shows significant coupling to the metal centre ($^n J(Pt,H) = 28$ Hz). This latter coupling and the absence of a detectable coupling to phosphorus leads us to propose the five-membered metallacyclic structure and the specific tautomer shown in Scheme 2. In separate experiments we found that the ^{1}H NMR data of complex 19c, in particular those of the NH protons, were concentration (and temperature) dependent.

The ^{1}H NMR spectra of complexes 20a–e also show characteristic signals for the modified azaphosphole ligand. Together with the NMe and CMe singlet resonances of the original triazaphosphole L_C there are doublet signals, due to

Table 7
^{31}P chemical shifts of complexes cis-[MX$_2$(PRR'R")$_2$] (M = Pd, Pt)

R	R'	R"	X	δ^{31}P(Pd)	Ref.	δ^{31}P(Pt)	Ref.
Me	Me	Ph	Cl	6.4	[20]	−15.2	[21]
Me	Me	Ph	Br	3.9	[18]	−16.1	[22]
Me	Ph	Ph	Cl	19.1	[20]	−1.2	[21]
Et	Et	Et	Cl	34.1	[23]	9.3	[24]
Et	Et	Ph	Cl	25.4	[20]	3.3	[21]
Et	Ph	Ph	Cl	30.2	[20]	9.8	[21]
Pr	Pr	Pr	Cl	23.4	[25]	0.0	[24]
Pr	Ph	Ph	Cl	27.4	[20]	6.9	[21]
Bu	Bu	Ph	Cl	19.8	[20]	−2.3	[21]
Bu	Ph	Ph	Cl	27.1	[20]	7.0	[21]
F	F	O$^-$	Cl	58.8	[26]	32.4	[26]
F	F	F	Cl	81.2	[26]	69.6	[26]
F	F	OPh	Br	85.2	[26]	68.4	[26]
F	OPh	OPh	Cl	87.8	[26]	66.0	[16]
F	OPh	OPh	Br	87.2	[26]	66.0	[26]
F	OPh	OPh	I	86.8	[26]	65.9	[26]
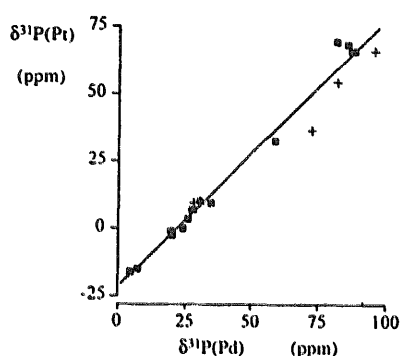
Fig. 2. Plot of the ^{31}P chemical shift of Pd(II) cis phosphine and phosphito complexes, δ^{31}P(Pd), against the ^{31}P chemical shift of analogous Pt(II) complexes, δ^{31}P(Pt). Full squares refer to data from Table 7; crosses refer to data for new complexes 18a/c, 19a/c, and 20a/c, from Table 6.
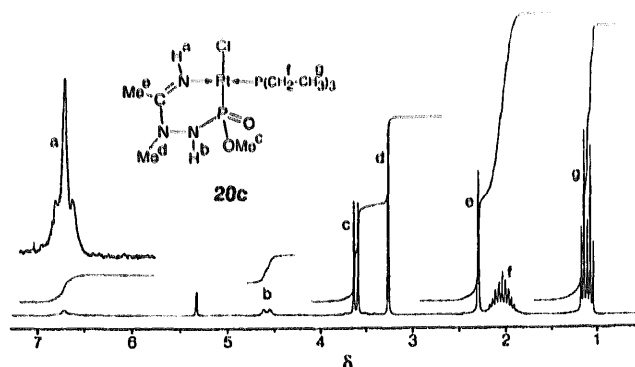

Fig. 3. 250 MHz ^{1}H NMR spectrum of 20c.

coupling to a nearby phosphorus centre, for both a POMe unit at $\delta \approx 3.6$ in 20a–c and a NNH proton in 20a–c at $\delta \approx 4.5$. There is also a C=NH proton signal at $\delta \approx 6.7$ that is coupled to ^{195}Pt in complexes 20b–e, see Fig. 3. For complexes 20d and 20e the spectra show that the two protons of the POCH$_2$ unit are diastereotopic, thereby indicating that the phosphorus atom is an asymmetric centre. On the basis of these data one can conclude that the structure of these complexes, shown in Scheme 3, contains a six-membered metallacycle

Pt{P(=O)(OR)N(H)N(Me)C(Me)=NH} in which there is coordination of an imine function to the metal centre.

The ^{195}Pt NMR chemical shifts of complexes 18–20 fall in the range anticipated for Pt(II) species and this information usefully complements the ^{31}P NMR data. For complexes of both types 18 and 20 the chloro species has a ^{195}Pt chemical shift that is significantly more positive than that of the bromo analogue. In contrast the δ^{195}Pt values for 19b and 19c are very similar.

3.4. X-ray structure of 19c

The molecular structure of 19c is shown in Fig. 4 together with the adopted numbering scheme; bond lengths and angles are given in Table 8.

The geometrical description is based on a fairly regular square-planar Pt(II) centre. To this centre are coordinated a
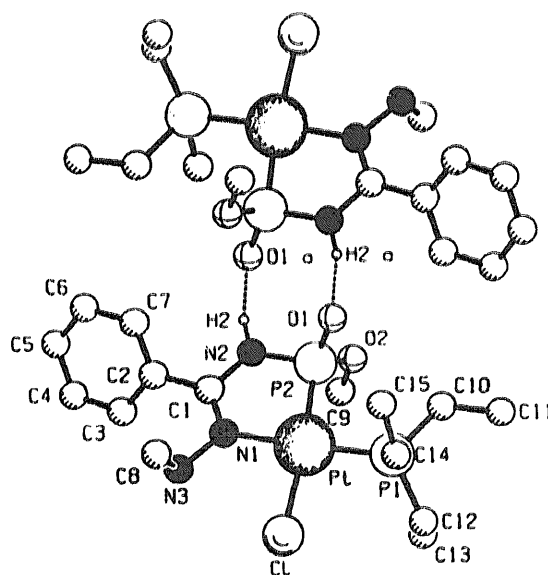

Fig. 4. PLUTO plot of the solid state structure of 19c with intermolecular NH···O interactions.

Table 8
Bond lengths (Å) and interbond angles (°) for **19c** with standard deviations in parentheses

Distances			
Pt–Cl	2.393(5)	C2–C3	1.38(2)
Pt–P1	2.254(3)	C2–C7	1.40(2)
Pt–P2	2.200(3)	C3–C4	1.39(2)
Pt–N1	2.069(8)	C4–C5	1.37(2)
P1–C10	1.77(2)	C5–C6	1.37(2)
P1–C12	1.84(2)	C6–C7	1.39(2)
P1–C14	1.81(2)	C8–N3	1.47(2)
P2–N2	1.717(7)	C9–O2	1.41(2)
P2–O1	1.477(9)	C10–C11	1.54(2)
P2–O2	1.598(9)	C12–C13	1.43(4)
C1–C2	1.48(1)	C14–C15	1.41(4)
C1–N1	1.30(2)	N1–N3	1.43(2)
C1–N2	1.37(2)		

Angles			
Cl–Pt–P1	90.31	C2–C1–N2	115(1)
Cl–Pt–P2	174.0(1)	N1–C1–N2	116.0(8)
Cl–Pt–N1	91.1(3)	C1–C2–C3	121(1)
P1–Pt–P2	95.7(1)	C1–C2–C7	119(1)
P1–Pt–N1	177.9(3)	C3–C2–C7	119.8(9)
P2–Pt–N1	83.0(3)	C2–C3–C4	120(1)
Pt–P1–C10	118.5(5)	C3–C4–C5	121(1)
Pt–P1–C12	113.5(6)	C4–C5–C6	120(1)
Pt–P1–C14	110.8(7)	C5–C6–C7	121(1)
C10–P1–C12	104(1)	C2–C7–C6	119(1)
C10–P1–C14	105(1)	P1–C10–C11	117(1)
C12–P1–C14	103.9(9)	P1–C12–C13	116(2)
Pt–P2–N2	99.6(4)	P1–C14–C15	115(2)
Pt–P2–O1	121.9(4)	Pt–N1–C1	120.7(8)
Pt–P2–O2	116.0(4)	Pt–N1–N3	123.6(7)
N2–P2–O1	110.8(5)	C1–N1–N3	115.5(8)
N2–P2–O2	101.7(5)	P2–N2–C1	120.4(7)
O1–P2–O2	105.0(5)	C8–N3–N1	110(1)
C2–C1–N1	129(1)	P2–O2–C9	119.8(9)

chloro atom, a triethylphosphine ligand and a P,N-chelating N^1-amidrazonylphosphito ligand derived from the original triazaphosphole L_B in an arrangement that affords mutually *cis*-positioned P atoms. Examination of bond lengths and angles within the five-membered metallacyclic ring lead us to believe that there is a donative bond from an imino nitrogen to the metal centre (Pt–N1 = 2.069(8) Å) and covalent bonding of the phosphorus to Pt(II) (Pt–P2 = 2.200(3) Å). The significant difference in the two C–N distances in the ring (C1–N1 = 1.30(2) Å, C1–N2 = 1.37(2) Å) is consistent with C1–N1 being a localized double bond and with N2 being an amine centre.

The solid state structure of **19c**, see schematic in Fig. 5, differs from that derived from solution NMR studies (shown
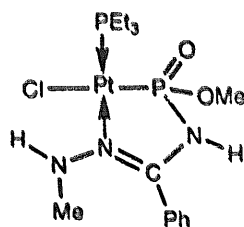
Fig. 5. Schematic structure of **19c** in the solid state.

in Scheme 2) by a proton shift in the amidrazone moiety from N^2 to N^3, i.e. these two structures are tautomers. Examples of amidine tautomerism in metal complexes are known and have been the subject of studies by several groups including our own [27].

In the crystal the molecules of **19c** form dimers through intermolecular NH···O bonding between aminophosphoryl entities (N2···O1a = 2.791(12) Å, ∠N2–H2···O1a = 165.3°). Similar hydrogen bonds are known for situations exemplified by $(H_2N)_3PO$, $(HNPO_2^-)_4$ and $R(H)NPO(OR)_2$ [28].

3.5. X-ray structure of 20c

The molecular structure of **20c** is shown in Fig. 6 together with the adopted numbering scheme; bond lengths and angles are given in Table 9. As with **19c** the geometrical description is based on a fairly regular square-planar Pt(II) centre. To this centre are bonded a chloro atom, a triethylphosphine ligand, and a P,N-chelating N^1-amidrazonylphosphito ligand derived from triazaphosphole L_C that are so arranged that the two phosphorus atoms are mutually *cis*-positioned. This P,N-chelating ligand and the platinum centre form an unusual puckered six-membered metallacycle in which there is a covalent Pt–P2 bond of 2.191(2) Å and a donative Pt–N1 bond of 2.075(6) Å involving an imine nitrogen atom (C8–N1 = 1.30(1) Å). This structure corresponds to that identified by our solution NMR studies. As was found for **19c** the crystal of **20c** contains dimeric units formed through intermolecular NH···O bonding between aminophosphoryl entities (N2···O1a = 2.965(9) Å, ∠N2–H2···O1a = 125.2°).

3.6. NMR spectroscopic characterization of intermediate complexes 13–17 and the mechanism of azaphosphole alcoholysis

Controlled addition of methanol to the 1:1 azaphosphole-to-platinum(chloride) coordination complexes of L_A (**10**,
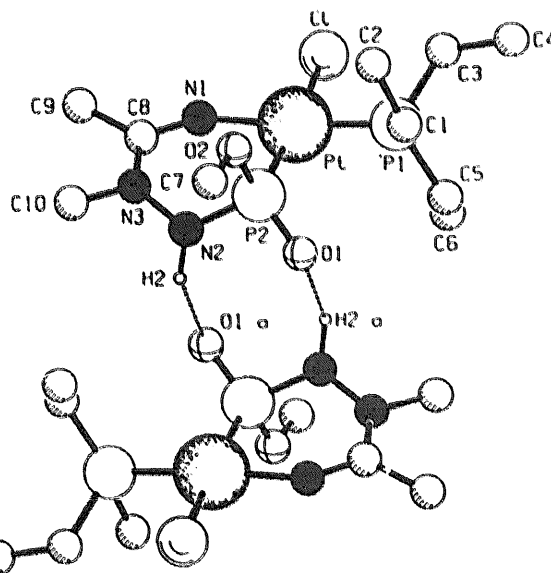
Fig. 6. PLUTO plot of the solid state structure of **20c** with intermolecular NH···O interactions.

Table 9

Bond lengths (Å) and interbond angles (°) for 20c with standard deviations in parentheses

Bond distances			
Pt–Cl	2.402(3)	C1–C2	1.52(2)
Pt–P1	2.241(2)	C3–C4	1.49(2)
Pt–P2	2.191(2)	C5–C6	1.51(2)
Pt–N1	2.075(6)	C7–O2	1.44(2)
P1–Cl	1.84(1)	C8–C9	1.51(1)
P1–C3	1.83(1)	C8–N1	1.30(1)
P1–C5	1.81(1)	C8–N3	1.35(1)
P2–N2	1.690(7)	C10–N3	1.48(1)
P2–O1	1.489(6)	N2–N3	1.410(9)
P2–O2	1.614(7)		

| Interbond angles			
Cl–Pt–P1	94.5(1)	N2–P2–O1	104.9(4)
Cl–Pt–P2	171.76(9)	N2–P2–O2	102.1(3)
Cl–Pt–N1	84.1(2)	O1–P2–O2	112.7(4)
P1–Pt–P2	92.34(9)	P1–C1–C2	114.3(9)
P1–Pt–N1	175.9(2)	P1–C3–C4	117(1)
P2–Pt–N1	89.4(2)	P1–C5–C6	115.2(8)
Pt–P1–Cl	118.1(3)	C9–C8–N1	120.8(8)
Pt–P1–C3	110.6(4)	C9–C8–N3	116.8(7)
Pt–P1–C5	112.8(3)	N1–C8–N3	122.4(7)
Cl–P1–C3	105.2(5)	Pt–N1–C8	133.3(6)
Cl–P1–C5	101.4(5)	P2–N2–N3	119.0(6)
C3–P1–C5	107.8(5)	C8–N3–C10	123.6(7)
Pt–P2–N2	109.0(3)	C8–N3–N2	123.4(7)
Pt–P2–O1	120.9(3)	C10–N3–N2	112.9(7)
Pt–P2–O2	105.7(3)	P2–O2–C7	120.0(7)

mononuclear, cis-[PtCl₂(PEt₃)Lₐ] [6]), Lₙ (11, symmetric, dinuclear, [PtCl(PEt₃)LₙCl]₂ [6]) and L_c (12, asymmetric, dinuclear [Pt₂Cl₃(PEt₃)₂L_c·L_c·Cl] [6]) provides interesting species 13–17, illustrated in Scheme 4–6, whose NMR data are sufficient to allow a considered judgement of their solution structures. From these structures it is possible to derive a description of the mechanism leading to the phosphito species 18, 19 and 20.

As shown in Scheme 4, the complex derived from the reaction of one equivalent of MeOH to the mononuclear diazaphosphole complex cis-[PtCl₂(PEt₃)Lₐ] (10), can be confidently identified as 13. This complex contains a monodentate P-coordinated ligand that is derived from Lₐ by simple addition of the MeO and H units of methanol across the original P=C bond. This addition is clearly reflected in the AB pattern of the ¹H NMR signal of the CH₂ unit of the ring (Table 5) and in the difference between the ³¹P NMR data of P₁ in 13 (Table 6) and in 10. In the next step towards the final product 18 the second equivalent of methanol probably adds to the P=N bond. The opened ring may then reclose while the imino nitrogen atom substitutes a chloride ion from the platinum centre. The resulting second intermediate contains a sort of methoxy phosphonium unit which is demethylated by the chloride ion to form 18c.

A similar mechanism, illustrated in Scheme 5, can account for the formation of 19 from dimeric 11, [PtCl(PEt₃)LₙCl]₂ [6]. The addition of two equivalents of methanol to 11 produces a species which we postulate to be mononuclear 14.
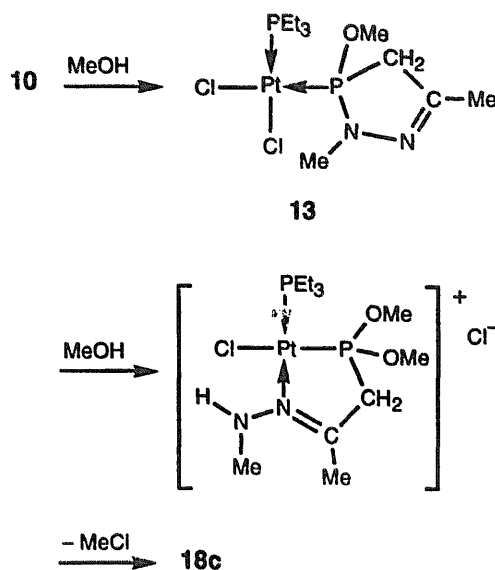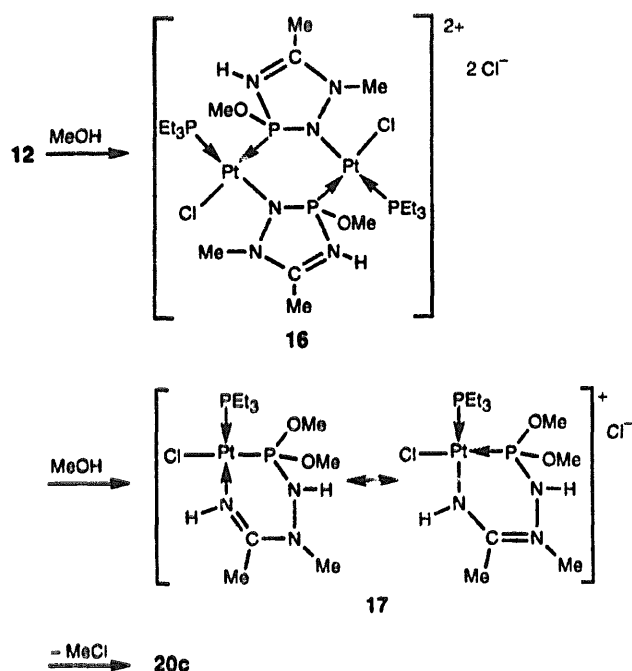

Scheme 4. Proposed mechanism for the formation of 18c from the 1:1 Lₐ/platinum chloride coordination complex (10, mononuclear) via the observed intermediate 13.
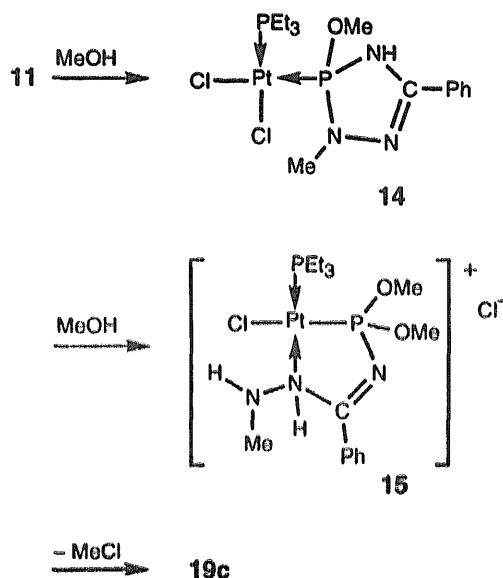
Scheme 5. Proposed mechanism for the formation of 19c from the 1:1 Lₙ/platinum chloride coordination complexes (11, dinuclear, symmetric) via the observed intermediates 14 and 15.

The ¹H NMR data (Table 5) are consistent with the presence of a heterocyclic ligand that is derived form the triazaphosphole Lₙ by addition of MeOH across the P=N bond. The ³¹P data for this species (Table 6) clearly indicate that this new ligand is monodentate P-bonded. A further equivalent of MeOH added to 14 produces a second intermediate. This complex, though not unambiguously identified, has ³¹P NMR data (Table 6) that are consistent with an ionic formulation 15. The most important feature of the cation is that the original triazaphosphole ring has been opened and the modified system is now forming a P,N-chelate with the platinum centre. This cation is converted by nucleophilic attack of the chloride ion and the loss of methyl chloride into the neutral product 19c.

Scheme 6. Proposed mechanism for the formation of 20c from the 1:1 L_C/platinum chloride coordination complexes (12, dinuclear, asymmetric) via the observed intermediates 16 and 17.

The addition of methanol to the coordination complex 12 eventually leads, via complexes 16 and 17, to complex 20c (Scheme 6). The path followed is similar to that described for 11 (leading to 19c) but the situation is complicated by the uncertainty as to the exact nature of the dinuclear starting material 12 formulated as $[Pt_2Cl_3(PEt_3)_2L_CL_CCl]$ [6]. With addition to 12 of one equivalent of MeOH per platinum centre the species formed, 16, has ^{31}P and ^{195}Pt NMR data (Table 6) that show it to be dinuclear with a symmetric structure; in the ^{31}P NMR spectrum the isotopomer without ^{195}Pt affords an AA'BB' spin system and the isotopomer with one ^{195}Pt shows the AB part of an AA'BB'X spin system. The ^{31}P data have clear parallels with those of dimeric 11 ($\delta(P_L) = 65.2$, $^{1,2}J(Pt,P) = 5728$, 124 Hz) [6]. The ^1H NMR spectrum shows a very characteristic resonance for the two NH protons per dimer at $\delta = 12.35$ which is split into a doublet by coupling to the phosphorus atom of P_L, but which is without platinum satellites. On this evidence we propose an ionic structure for 16 that contains a 3,4-dihydro-1,2,4,3-triazaphosphole ligand derived from the addition of MeOH to the triazaphosphole L_C. This new ligand functions as a bridging system, coordinating through the phosphite ring atom to one platinum centre and bonding by the nitrogen atom in the 2-position to the other; the cationic charge is distributed on the 4,5,1-ring fragment that is of an amidinium type. Further addition of methanol to reach two equivalents of MeOH per platinum affords 17, which appears to be a mononuclear ionic complex in which the modified triazaphosphole ligand now forms a six-membered chelate ring with the platinum centre. This ring may be written, as shown in Scheme 6, in two ways; either with a donating amidine moiety and a σ-bonded phosphorus

atom carrying the positive charge or with a donating phosphite moiety and a σ-bonded amidinium group. We anticipate the following intimate steps (not illustrated) to be the basis of the formation of 17 from 16. Within each modified ligand system of 16 the second equivalent of methanol adds to the platinum-coordinated phophorus centre and thereby substitutes N-4, i.e. the 3,4 bond of the bridging L_C ligand is opened to generate a free imino grouping. Each imino group can now attack a platinum centre in such a way that N-2 of the other ligand is substitued from the metal centre and a six-membered chelate ring is formed; the dicationic dimer has now become two identical monocations. As a final step within each monocation there is a 1,3 shift of the methanol proton to N-2 whereby 17 results.

The reaction pathways of Schemes 4–6 can be summarized as follows. The first equivalent of alcohol, ROH, adds directly to a P=C or P=N bond of the azaphosphole as is known for uncoordinated azaphospholes [1,2]. The addition yields cyclic phosphites and, since the donative coordination of phosphorus is retained, special representatives of the well-known class of PtX_2(phosphite) complexes result. Addition of a second equivalent of alcohol opens a PN bond of the formerly azaphosphole ring and thus yields either a hydrazonyl (L_A), a N^3-amidrazonyl (L_B) or a N^1-amidrazonyl (L_C) phosphite ligand. These ligands chelate to the Pt(II) centre by retaining the donative phosphorus coordination and by additionally coordinating one of the nitrogen atoms of the hydrazonyl or amidrazonyl chain. The result is ionic complexes with a PtX$^+$ coordinated $P(OR)_3$ unit (15 and 17; the equivalent complex for L_A was not seen). By nucleophilic attack of the halide ion onto this unit in the final stage (that affords the metallacycles 18, 19 and 20) alkyl halide is eliminated, in a Michaelis–Arbuzov type of reaction, to afford a $P(=O)(OR)$ unit covalently bonded to platinum. With the triazaphospholes L_B and L_C the original bond that is opened is the phosphorus bond with formal single bond character, i.e. that to N-2 in 2H-triazaphosphole L_B and that to N-4 in 1H-triazaphosphole L_C, and this results in a five-memberered metallacyclic ring in the former case but necessitates formation of a six-membered ring in the latter case.

4. Conclusions

The coordination chemistry of azaphosphole ligands has been extended through alcoholysis reactions to novel Pt(II) and Pd(II) products with metallacyclic rings, based on P,N chelation, which contain a phosphite type phosphorus centre. The use of P,N-chelating ligands, in particular for their potential in catalytic processes [29], is a topic of current interest and some of the new products described are examples of 'large ring' P,N metallacyles which have to date been little studied [30]. In representative crystal structures of these metallacyclic products the presence of intermolecular N–H···O bonding leads to dimeric formulations that illustrate how control of hydrogen bonding in organometallic species

can be used to tailor specific solid state architectures; this type of control has, for example, recently been employed by us to prepare one-dimensional organometallic polymers [31].

In conclusion, it is clear that the coordination chemistry of azaphospholes is, after many years of research [2], still proving to be a fascinating and relevant area of chemistry.

5. Supplementary material

Complete tables of fractional coordinates of all atoms, bond distances and bond angles, anisotropic thermal parameters and observed and calculated structure factors for **19c** and **20c** may be obtained from author K.G.

Acknowledgements

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[2] This publication marks the successful end of a very fruitful and enjoyable international collaboration that has lasted for more than 16 years and that has, remarkably, survived many changes in personal and professional circumstances of the authors.