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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

IX *. INSERTION OF PLATINUM(0) IN THE NS BOND OF 2,1,3-BENZOTHIADIAZOLE WITH CONCOMITANT P—C BOND RUPTURE, YIELDING A NOVEL COMPLEX $[Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$. CRYSTAL AND MOLECULAR STRUCTURE AND ^{31}P NMR RESULTS

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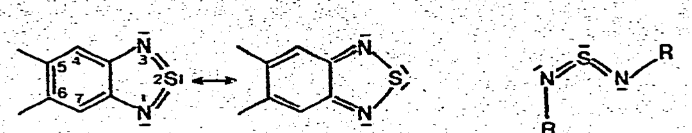
Summary

Reaction of $[(PPh_3)_2Pt(C_2H_4)]$ with 5,6-dimethyl-2,1,3-benzothiadiazole affords $[Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$. A crystal structure determination shows that one of the Pt-atoms is inserted into one of the N=S bonds. The two Pt-atoms are bridged by the amino groups produced by this insertion, and by a diphenylphosphido group which is formed by insertion of the other Pt-atom into a P—C bond. The bond distances in the six-membered heterocyclic PtSNCC-μ-N ring indicate an extensive electron delocalization. The ^{31}P-NMR spectrum reveals a large upfield shift for the bridging diphenylphosphido group, which is consistent with its presence in a four-membered ring.

Introduction

An X-ray structure determination of 2,1,3-benzothiadiazole, $C_6H_4N_2S$, indicated that there is an extended π-delocalization in the heterocyclic ring [1] (See Fig. 1). This is confirmed by photoelectron spectra and ab initio calculations, which were published recently [2]. Furthermore, it has been shown that 2,1,3-benzothiadiazole may coordinate via one nitrogen to metal atoms such as Pt^{II}

* For part VIII see ref. 8.



A B C

Fig. 1. Two possible resonance structures of 5,6-dimethyl-2,1,3-benzothiadiazole (A and B) and the most common configuration of sulfurdiimines (C).

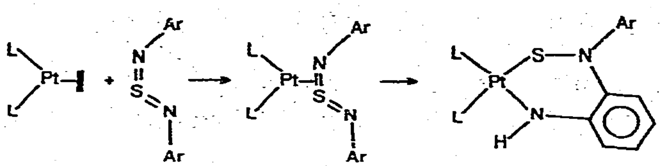


Fig. 2. The reaction of Pt^0 with arylsulfurdiimines [8], L = PPh_3.

[3], Cr^0, Mo^0 and W^0 [4]. Complexes have also been reported of Hg^{II}, Ag^{II}, Cu^{II}, Cd^{II} [5], Co^{II}, Ni^{II} and Fe^{III} [6], but for these, the mode of bonding of the ligand to the metal was not discussed. Because of the close relation of this ligand to R—N=S=N—R [3,4,7] (see Fig. 1), of which we established the interesting rearrangement of arylsulfurdiimines with Pt^0 as shown in Fig. 2 [8,9,10,11], the reactivity of 2,1,3-benzothiadiazole towards Pt^0 has been investigated.

In this paper we describe crystallographic and NMR (^1H and ^{31}P) studies on $[\overline{Pt_2S\{N(6\text{-}\mu\text{-}N}\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$.

Experimental

Preparation of $[\overline{Pt_2S\{N(6\text{-}\mu\text{-}N}\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$

The reaction was carried out under dry oxygen-free nitrogen. Solvents were dried over sodium wire and distilled under nitrogen before use. $[Pt(PPh_3)_2(C_2H_4)]$ [12] and 5,6-dimethyl-2,1,3-benzothiadiazole [13] were prepared by published methods.

0.5 mmol 5,6-dimethyl-2,1,3-benzothiadiazole (85 mg) was added to a stirred suspension of 0.5 mmol $[Pt(PPh_3)_2(C_2H_4)]$ (374 mg) in 20 ml ether. The solution darkened slowly. After stirring for four days at ambient temperature the mixture was refluxed during 2 h. The mixture was set aside at room temperature and after three days 0.09 mmol (121 mg) of black crystals were obtained. Yield 36%.

The complex is insoluble in hexane, soluble but not stable in chloroform, and slightly soluble in benzene. Analysis: Found: C, 55.74; H, 4.13; N, 2.08; S, 3.05; P, 6.74. $C_{38}H_{33}N_2P_3Pt_2S$ calcd.: C, 55.52; H, 3.98; N, 2.09; S, 2.39; P, 6.93%.

Spectroscopic measurements and analytical data

The ^1H-NMR spectra were recorded on a Varian T60 A and the ^{31}P-NMR spectrum was recorded on a Varian XL-100 spectrometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO, Utrecht.

Crystal data

Triclinic, cell constants $a = 11.1513(6)$, $b = 12.8134(6)$, $c = 19.109(1)$ Å, $\alpha = 75.601(3)$, $\beta = 88.97(1)$, $\gamma = 77.35(1)°$, $Z = 2$. Space group: $P\bar{1}$.

Intensity data, structure determination and refinement

4077 independent reflections (net intensity >2.5 σ(I)) were measured on a NONIUS CAD-4 automatic four circle diffractometer (Cu-K_α, θ-2θ scan). The structure was solved by locating the Pt-atoms from an E^2-Patterson synthesis. The next step was a difference Fourier, which revealed the three P-atoms and the S-atom. A subsequent difference Fourier gave us all the other atom positions. Refinement by block-diagonal least squares methods proceeded to a final R value of 6.4%.

The atomic coordinates are given in Table 1, the bond distances in Table 2 and the bond angles in Table 3. The positions of the carbon atoms in the phenyl rings, attached to P and Pt were refined in groups and so no standard deviations of the positions, not distances or angles for these phenyl rings are given.

Results and discussion

From the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with 5,6-dimethyl-2,1,3-benzothiadiazole black crystals were obtained, which dissolved to give a dark red colour. Analytical data, ^{31}P-NMR and ^{1}H-NMR spectra pointed to a dimeric complex, containing three phosphorous groups and one benzothiadiazole group. Single X-ray crystallography revealed that the complex must be formulated as $[\overline{\dot{P}t_2S\{N(6\text{-}\mu\text{-}\dot{N}}\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)Ph]$ (see Figs. 3 and 4).

The molecular structure

The molecular structure consists of a bimetallic molecule in which the

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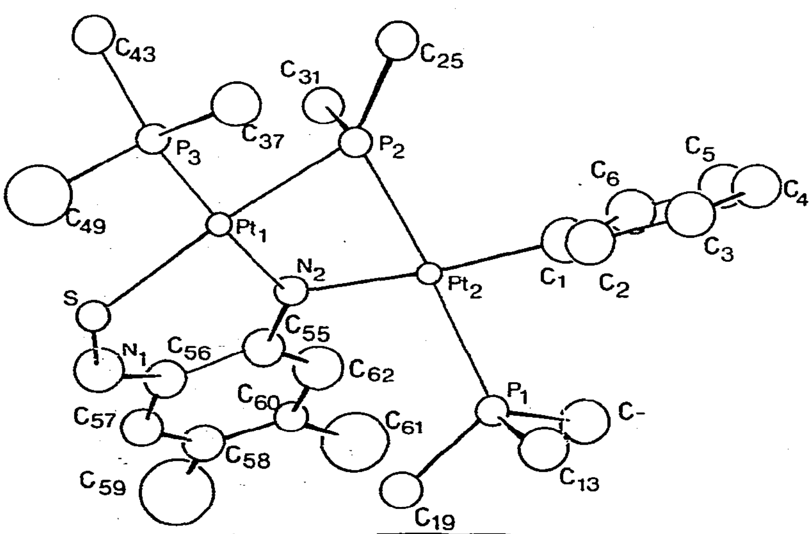

Fig. 3. The molecular structure of $[\overline{\dot{P}t_2S\{N(6\text{-}\mu\text{-}\dot{N}}\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$.of the phenyl groups attached to P, only the first C-atom is drawn.

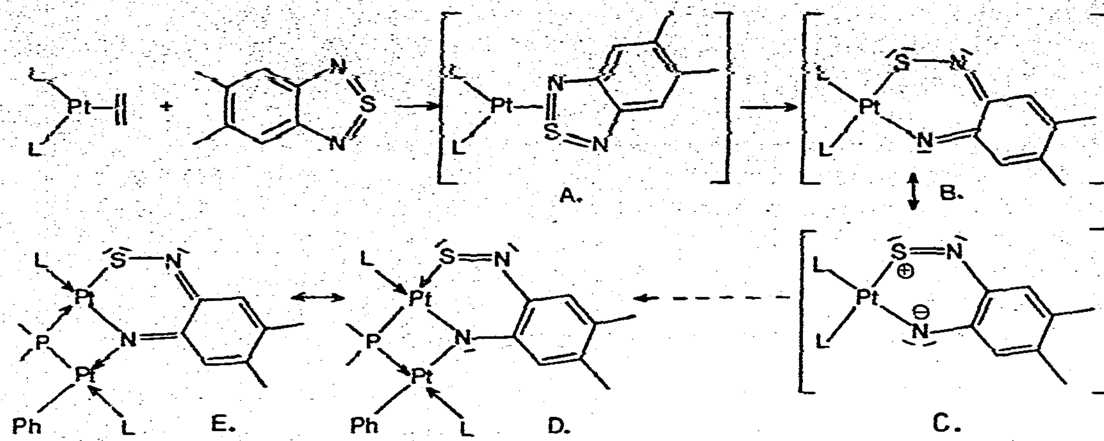

Fig. 4. A posible mechanism for the reaction between $Me_2C_6H_2N_2S$ and $[Pt(L_2)(C_2H_4)]$, L = PPh_3.

TABLE 1

ATOMIC COORDINATES (WITH STANDARD DEVIATIONS IN PARENTHESES) [a]

Atom	X	Y	Z	Atom	X	Y	Z
Pt_1	0.19858(9)	0.32866(8)	0.34720(6)	C_{21}	0.126	−0.057	0.340
Pt_2	0.16212(9)	0.32171(8)	0.18554(5)	C_{22}	0.053	−0.118	0.317
P_1	0.1819(6)	0.1600(5)	0.1508(3)	C_{23}	0.022	−0.097	0.243
P_2	0.1594(6)	0.4684(5)	0.2378(3)	C_{24}	0.064	−0.015	0.193
P_3	0.3395(6)	0.3805(5)	0.4034(3)	C_{25}	0.241	0.578	0.207
S	0.1806(7)	0.1923(6)	0.4454(3)	C_{26}	0.305	0.590	0.144
N_1	0.061(2)	0.147(1)	0.438(1)	C_{27}	0.365	0.676	0.123
N_2	0.084(1)	0.285(1)	0.288(1)	C_{28}	0.361	0.751	0.166
C_{55}	0.003(2)	0.226(1)	0.310(1)	C_{29}	0.298	0.734	0.230
C_{56}	−0.015(2)	0.168(2)	0.383(1)	C_{30}	0.238	0.652	0.250
C_{57}	−0.110(2)	0.109(2)	0.399(1)	C_{31}	0.010	0.551	0.241
C_{58}	−0.104(2)	0.111(2)	0.341(1)	C_{32}	−0.029	0.582	0.304
C_{59}	−0.279(3)	0.034(3)	0.358(2)	C_{33}	−0.141	0.652	0.304
C_{60}	−0.165(2)	0.165(2)	0.267(1)	C_{34}	−0.214	0.691	0.241
C_{61}	−0.245(3)	0.157(3)	0.207(2)	C_{35}	−0.175	0.661	0.178
C_{62}	−0.083(2)	0.220(2)	0.253(1)	C_{36}	0.063	0.591	0.177
C_1	0.249	0.375	0.093	C_{37}	0.469	0.403	0.351
C_2	0.184	0.436	0.029	C_{38}	0.474	0.392	0.280
C_3	0.244	0.460	−0.035	C_{39}	0.575	0.407	0.240
C_4	0.368	0.445	−0.034	C_{40}	0.671	0.433	0.271
C_5	0.434	0.384	0.030	C_{41}	0.665	0.445	0.342
C_6	0.374	0.350	0.093	C_{42}	0.564	0.429	0.382
C_7	0.102	0.172	0.066	C_{43}	0.410	0.278	0.486
C_8	−0.003	0.254	0.048	C_{44}	0.484	0.881	0.475
C_9	−0.074	0.261	−0.013	C_{45}	0.541	0.099	0.534
C_{10}	−0.039	0.187	−0.056	C_{46}	0.525	0.114	0.604
C_{11}	0.066	0.105	−0.038	C_{47}	0.451	0.210	0.615
C_{12}	0.136	0.098	0.023	C_{48}	0.393	0.293	0.556
C_{13}	0.339	0.102	0.134	C_{49}	0.278	0.502	0.435
C_{14}	0.384	0.129	0.065	C_{50}	0.174	0.503	0.474
C_{15}	0.504	0.086	0.054	C_{51}	0.122	0.560	0.500
C_{16}	0.578	0.016	0.112	C_{52}	0.174	0.688	0.486
C_{17}	0.533	−0.010	0.181	C_{53}	0.277	0.687	0.447
C_{18}	0.413	0.033	0.192	C_{54}	0.330	0.595	0.421
C_{19}	0.136	0.046	0.216				
C_{20}	0.167	0.025	0.289				

[a] All carbon atoms of the phenyl groups attached to Pt and P have been refined in groups; no standard deviations can be given.

TABLE 2

BOND DISTANCES IN Å (WITH STANDARD DEVIATIONS IN PARENTHESES)

Pt_1—S	2.26(1)	N_1—C_{56}	1.32(3)	P_3—C_{49}	1.81(1)
Pt_1—P_2	2.36(1)	N_2—C_{55}	1.32(3)	C_{55}—C_{56}	1.44(3)
Pt_1—P_3	2.26(1)	P_1—C_7	1.83(1)	C_{56}—C_{57}	1.45(4)
Pt_1—N_2	2.01(3)	P_1—C_{13}	1.85(1)	C_{57}—C_{58}	1.40(4)
Pt_2—N_2	2.21(2)	P_1—C_{10}	1.83(1)	C_{58}—C_{59}	1.60(5)
Pt_2—P_1	2.29(1)	P_2—C_{25}	1.83(1)	C_{58}—C_{60}	1.43(4)
Pt_2—P_2	2.33(1)	P_2—C_{31}	1.82(1)	C_{60}—C_{61}	1.42(5)
Pt_2—C_1	2.062(8)	P_3—C_{37}	1.81(1)	C_{60}—C_{62}	1.28(4)
N_1—S	1.62(2)	P_3—C_{43}	1.84(1)	C_{62}—C_{55}	1.52(4)

TABLE 3

BOND ANGLES (°) (WITH STANDARD DEVIATIONS IN PARENTHESES)

P_3—Pt_1—S	92.7(3)	Pt_2—P_1—C_7	115.1(3)
S—Pt_1—N_2	91.9(6)	Pt_2—P_1—C_{13}	111.6(4)
N_2—Pt_1—P_2	73.6(6)	Pt_2—P_1—C_{19}	116.3(4)
P_2—Pt_1—P_3	102.4(3)	Pt_2—C_1—C_2	120.4(4)
P_2—Pt_2—N_2	72.5(7)	Pt_2—C_1—C_6	120.4(4)
N_2—Pt_2—P_1	102.3(7)	Pt_2—P_2—C_{25}	126.0(4)
P_1—Pt_2—C_1	85.9(2)	Pt_2—P_2—C_{31}	112.8(4)
C_1—Pt_2—P_2	98.9(2)	S—N_1—C_{56}	130.8(7)
Pt_1—S—N_1	111.5(8)	N_2—C_{55}—C_{56}	128(3)
Pt_1—N_2—C_{55}	129.2(7)	N_2—C_{55}—C_{62}	116(2)
Pt_1—N_2—Pt_2	99.1(9)	C_{55}—C_{62}—C_{60}	122(3)
Pt_1—P_2—Pt_2	84.2(3)	C_{62}—C_{60}—C_{58}	121(3)
Pt_1—P_2—C_{31}	107.9(3)	C_{62}—C_{60}—C_{61}	120(3)
Pt_1—P_2—C_{25}	125.4(4)	C_{60}—C_{58}—C_{59}	120(3)
Pt_1—P_3—C_{37}	115.6(4)	C_{60}—C_{58}—C_{57}	122(3)
Pt_1—P_3—C_{43}	114.7(3)	C_{58}—C_{57}—C_{56}	118(3)
Pt_1—P_3—C_{49}	111.9(4)	C_{57}—C_{56}—C_{55}	121(3)
Pt_2—N_2—C_{55}	130.1(7)		

TABLE 4

Plane	Atoms defining the plane	Dihedral angles between planes (°)		Distances of atoms to plane 7 (Å) [a]	
1	S, Pt_1, P_3	2—1	9.7	S	0.00
2	N_2, Pt_1, P_2	3—2	53.2	N_1	0.00
3	N_2, Pt_2, P_2	3—4	8.1	C_{56}	0.04
4	P_1, Pt_2, C_1	5—6	57.1	C_{55}	−0.04
5	S, Pt_1, P_3, N_2, P_2	5—7	20.0	N_2	0.02
6	N_2, Pt_2, P_2, P_1, C_1	5—8	20.2		
7	S, N_1, C_{46}, C_{55}, N_2	6—7	62.1		
8	C_{55}, C_{56}, C_{57}, C_{58}, C_{60}, C_{62}	6—8	55.0		
9	Pt_1, N_2, C_{55}	7—8	7.3		
		9—3	29.3		

[a] The standard deviation is 0.03 Å.

Pt-atoms are bridged by a diphenylphosphido and by an amino group. There is no direct bond between the two Pt-atoms. Pt_1 and Pt_2 both have an approximately square planar coordination. The dihedral angle between plane 1 (S, Pt_1, P_3) and plane 2 (N_2, Pt_1, P_2) is 9.7°; the dihedral angle between plane 3 (N_2, Pt_2, P_2) and plane 4 (P_1, Pt_2, C_1) is 8.1°. The whole molecule does not have a planar geometry because the dihedral angle between the coordination planes of Pt_1 (S, Pt_1, P_3, N_2, P_2) (plane 5) and Pt_2 (N_2, Pt_2, P_2, P_1, C_1 (plane 6) is 57.1°. The atoms S, N_1, C_{56}, C_{55} and N_2 lie in one plane (see plane 7 in Table 4). The dihedral angle between this plane (7) and plane 5 is 20.0°.

The N_1—C_{56} and the N_2—C_{55} bond lengths are 1.32(4) Å. This value lies between a single NC (1.47 Å) and a double NC (1.22 Å) bond [8,11,14,15,16]. In the case of the NS distance (1.62(3) Å) the same conclusion can be drawn, since the value for a single bond is 1.74 Å and that for a double bond is 1.56 Å [8,14,15,17—20]. These NC and NS bond lengths are comparable to those found for the thiadiazole derivatives [1,13]. So the thiadiazole moiety in the free ligand and in the coordinated situation shows an extended π-delocalization, which may be rationalized in terms of the two resonance structures D and E in Fig. 4. In 4E the bridging nitrogen (N_2) atom has a sp^2 hybridisation and in 4D a sp^3 hybridisation. This is consistent with the observed spatial orientation of N_2, which is intermediate between a trigonal and a tetrahedral configuration. The displacement of the N_2-atom from the plane defined by the three surrounding atoms is 0.12 Å. The sum of the three angles around N_2 is 358° and the Newman projection along the C_{55}—N_2 bond reveals an angle of 162° between the two platinum nitrogen bonds.

The Pt—C, Pt—N, Pt—S and Pt—P bond lengths are consistent with values observed for other complexes [8,11,19,21—24]. The Pt—P bond lengths in the phosphido groups are longer (on average 0.07 Å) than the Pt—P distances of the Pt—phosphine bonds. This difference was also found for the Pt—P distances in $[Pt_2(PPh_3)_2(PPh_2)_2]$ [21]. The lengthening of the metal—phosphorus bond may be caused by electronic and steric effects [24].

Finally it should be noted that two C—C distances in the xylyl-ring, 152(4) and 1.28(4) Å, deviate from the ideal C—C distances in an aromatic ring. This may be due to an accidental error in the position of C_{62}.

Mechanism of the formation of the complex

A possible mechanism for the formation of this complex is given in Fig. 4. The first step is probably formation of a π-bonded complex (A), followed by insertion of Pt^0 in a N—S-bond (B and C). This type of reaction has been observed for the sulfurdiimines (Ar-N=S=N-Ar) (see Fig. 2) [8,9,10]. A rearrangement of the aryl-ring, however, is not necessary in the present case because the

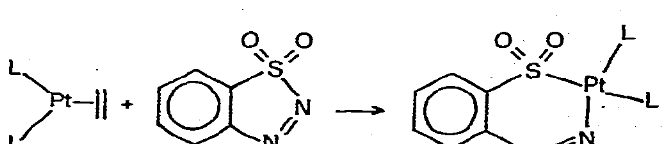

Fig. 5. The reaction of benzo-1,2,3-thiadiazole-1,1-dioxide with $[Pt(L_2)(C_2H_4)]$ [25], L = PPh_3.

aryl-ring in the benzothiadiazole is already in the *cis,cis* conformation. The subsequent steps appear much more complicated, since dimerization and rupture of a P—C bond of coordinated PPh_3 is also observed; it is worth noting that reactions of these types occur in the formation of $[Pt_2(PPh_3)_2(PPh_2)_2]$ from $[Pt(PPh_3)_2(C_2H_4)]$ [21]. The insertion of Pt^0 into a cyclic NS-bond was also proposed for the reaction of benzo-1,2,3-thiadiazole-1,1-dioxide with $[Pt(PPh_3)_2(C_2H_4)]$ [25] (see Fig. 5).

^1H and ^{31}P-NMR spectra

The ^{1}H-NMR spectrum shows that the two methyl groups in the xylyl-ring are inequivalent. The positions are (in C_6D_6) 1.57 and 1.03 ppm and (in $CDCl_3$) 1.78 and 1.18 ppm respectively. The proton decoupled ^{31}P-NMR spectrum in C_6D_6 belongs to an *ABCXY* system (*A* and *B* the PPh_3 groups, *X* and *Y* the Pt-atoms and *C* the PPh_2 group). $\delta P_1 = 20.1$ with $^1J(^{195}Pt—^{31}P) = 2662$ Hz., $\delta P_3 = 16.9$ with $^1J(^{195}Pt—^{31}P) = 3161$ Hz and $\delta P_2 = -68.6$ with $^1J(^{195}Pt—^{31}P) =$ 2016 and 2150 Hz relative to external H_3PO_4 (downfield shifts being positive). The $^{31}P—^{31}P$ coupling constants are typical for a *trans* and a *cis* coupling ($^2J(P_1—P_2) = 345$ Hz and $^2J(P_2—P_3) = 27$ Hz respectively). No coupling has been found between P_1 and P_3. So it may be concluded that the structure both in the solid state and in solution is similar.

It is worth noting that the platinum phosphorous coupling constants for the phosphido group (P_2) are on average lower than those for the phosphine groups. This is also reflected in a longer bond length of the $Pt—PPh_2$ bonds. This may be caused by the structural constraint in the bridging phosphido ligand as described by Tolman [24] for chelating phosphines. A second notable feature is the large upfield shift of about 90 ppm relative to values of coordinated phosphines. An even larger upfield shift was reported for the phosphido group in $[Pd_2Cl_2(PPh_2)_2(PPh_2H)_2]$ ($\delta = -132$ ppm) [26]. Recently the X-ray structure and the ^{31}P-NMR spectrum of $[Pd_3Cl(PPh_2)_2PEt_3)_3][BF_4]$ have been published [27]. The ^{31}P-NMR shift of the phosphido group in the latter compound had a very large downfield shift ($\delta = 225.4$) of about 200 ppm relative to values for monodentate coordinated phosphines. The upfield shifts refer to phosphides which are situated in a four membered ring, and the downfield shift to a phosphide which is situated in a three membered ring, and so it may be concluded

Fig. 6. The ^{31}P-NMR spectrum of $[Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$ in C_6D_6.

that the ring size is the decisive influence on the chemical shift, and not the difference in electronic properties between a phosphine and a phosphido group. Garrou [28] proposed empirical rules which involve a downfield shift for a five membered ring and upfield shifts for four and six membered rings. It appears that this rule can also be extended to four membered rings containing two metal atoms. However, the shifts found for ring s with one metal atom appear to be lower, e.g. $R_3P\text{-}\overline{Ir\text{-}PCH(CH_3)}CH_2$ ($\Delta(P_1{-}P_2) = 40$ ppm upfield for a four membered ring [29]), than for a ring as reported here with two metal atoms *. More experimental data are needed to check this hypothesis.

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* The $\delta(^{31}P)$ of PPh_2 in $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ [27] is the first published example of a phosphorus atom in a three membered ring. The enormous downfield shift can be explained by an extension of the "Garrou-rule" to three membered rings, which is in agreement with the alternation in this series.