Correlating Pt-P Bond lengths and Pt-P Coupling Constants.

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Abstract: The X-Ray Structures of **(5)** *cis*-PtBr₂(P(OMe)₃)₂, **(6)** *cis*-PtBr₂(P(OMe)₂Ph)₂, **(7)** *cis*-PtBr₂(P(OMe)Ph₂)₂, **(8)** *cis*-PtBr₂(PPh₃)₂, **(9)** *cis*-PtI₂(P(OMe)₃)₂, **(10)** *cis*-PtI₂(P(OMe)₂Ph)₂, **(11)** *cis*-PtI₂(P(OMe)Ph₂)₂ and **(12)** *cis*-PtI₂(PPh₃)₂ are reported and compared with the previously reported chloride analogues. The magnitude of the J{Pt-P} varies linearly with the Pt-P bond length ($I_{\text{Pt-P}} = 2.421 - J/24255$) for these 12 complexes.

Introduction

As a consequence of their interesting reactivity and since the discovery of the anti-cancer action of *cis*-platin¹ the study of square planar platinum complexes has been of great interest. Platinum complexes containing phosphorus ligands are of particular interest as their ³¹P NMR spectra contain ¹⁹⁵Pt satellite peaks which allow the ³¹P-¹⁹⁵Pt coupling constant to be measured giving insight into the nature of bonding around the platinum centre². Previous studies have shown in a limited range of compounds that there is a crude correlation between the P-Pt bond length and the ³¹P-¹⁹⁵Pt coupling constant³⁻⁵. Here we report the crystal structures of a series of *cis*-PtX₂(P(OMe)_nPh_{3-n})₂ (X = Br or I; PR₃ = P(OMe)₃, P(OMe)₂Ph, P(OMe)Ph₂ or PPh₃) and compare them to their *cis*-PtCl₂(PR₃)₂ analogues to create a series with coupling constants in the range 3450-5750 Hz and show that the relationship between their ³¹P-¹⁹⁵Pt coupling constant and Pt-P bond length is linear.

Experimental

Unless otherwise stated all manipulations were performed under an oxygen-free nitrogen atmosphere, using standard Schlenk techniques and glassware. Solvents were dried and stored according to common procedures. Reagents were obtained from Aldrich and used without further purification. Solution state ³¹P-{¹H} (109 MHz) and ¹H (270 MHz) NMR spectra were recorded using a JEOL GSX Delta 270. IR spectra were recorded using KBr discs on a Perkin-Elmer System 2000 FT spectrometer. Microanalyses were performed by the University of St. Andrews microanalysis service.

cis-PtBr₂(P(OMe)₃)₂⁶, *cis*-PtBr₂(P(OMe)₂Ph)₂⁷, *cis*-PtBr₂(P(OMe)Ph₂)₂⁷ and *cis*-PtBr₂(PPh₃)₂⁸ were prepared in good yield from *trans*-PtBr₂(PhCN)₂ and two equivalents of the phosphite, phosphonite, phosphinite or phosphine in acetone. *cis*-PtI₂(P(OMe)₃)₂⁶ was prepared in good yield from *trans*-PtI₂(PhCN)₂ and two equivalents of trimethyl phosphite in acetone. *cis*-PI₂(PPh₃)₂⁸ was prepared by metathesis of *cis*-PtCl₂(PPh₃)₂ with excess sodium iodide in an equivolume mixture of water, ethanol, acetone and chloroform. All compounds were characterised using

NMR. Crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into a solution of the complex in dichloromethane for all except $\text{PtBr}_2(\text{PPh}_3)_2$ (grown by slow diffusion of hexane into a solution of the complex in chloroform).

Preparation of *cis*- $\text{PtI}_2(\text{P}(\text{OMe})_2\text{Ph})_2$: 1 g (1.53 mmol) of *trans*- $\text{PtI}_2(\text{PhCN})_2$ was vigorously stirred in 40 mL acetone to which 0.48 mL (3.05 mmol) of $\text{P}(\text{OMe})_2\text{Ph}$ was added affording a clear yellow solution. The volume of acetone was reduced to *ca.* 10 mL with a yellow precipitate of *cis*- $\text{PtI}_2(\text{P}(\text{OMe})_2\text{Ph})_2$ forming. The remaining product was precipitated upon addition of 50 mL diethyl ether. The solid was filtered and washed with diethyl ether to give a crystalline, yellow solid, mp 172-174°.

Crystals were grown for X-ray crystallography by slow diffusion of hexane into a solution of the product in dichloromethane. Yield: 0.632 g (0.8 mmol), 52 %.

Elemental Analysis (% , calculated in brackets): C, 24.65 (24.35); H, 2.51 (2.81). ^1H NMR (CDCl_3 , 291 K): $\delta_{(\text{ppm})} = 3.66$ (d, 12H, methyl, $^3J_{\text{PH}} = 12.9$ Hz), $\delta_{(\text{ppm})} = 7.41$ -7.77 (m, 10H, phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): $\delta_{(\text{ppm})} = 96.4$ ($^1J_{\text{P-Pt}} = 4618$ Hz). Infra Red: $\nu_{\text{Pt-I}}$ 163, 150 cm^{-1} , $\nu_{\text{Pt-P}}$ 202, 188 cm^{-1} , $\nu_{\text{P-O-alkyl}}$ 1045 cm^{-1} , $\nu_{\text{P-Ph}}$ 1434 cm^{-1} .

Preparation of *cis*- $\text{PtI}_2(\text{P}(\text{OMe})\text{Ph})_2$: 1 g (1.53 mmol) of *trans*- $\text{PtI}_2(\text{PhCN})_2$ was vigorously stirred in 40 mL acetone to which 0.61 mL (3.05 mmol) of $\text{P}(\text{OMe})\text{Ph}_2$ was added affording a clear yellow solution. The volume of acetone was reduced to *ca.* 10 mL with a yellow precipitate of *cis*- $\text{PtI}_2(\text{P}(\text{OMe})_2\text{Ph})_2$ forming. The solid was filtered and washed with diethyl ether to give a yellow powder, mp 182-186°. Crystals were grown for X-ray crystallography by slow diffusion of hexane into a solution of the product in dichloromethane. Yield: 1.255 g (1.43 mmol), 93 %. Elemental Analysis (% , calculated in brackets): C, 35.52 (35.42); H, 2.66 (2.97). ^1H NMR (CDCl_3 , 291 K): $\delta_{(\text{ppm})} = 3.31$ (d, 6H, methyl, $^3J_{\text{PH}} = 12.4$ Hz), $\delta_{(\text{ppm})} = 7.36$ -7.79 (m, 20H, phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): $\delta_{(\text{ppm})} = 83.5$ ($^1J_{\text{P-Pt}} = 3995$ Hz). Infra Red: $\nu_{\text{Pt-I}}$ 175, 167 cm^{-1} , $\nu_{\text{Pt-P}}$ 218, 206 cm^{-1} , $\nu_{\text{P-O-alkyl}}$ 1032 cm^{-1} , $\nu_{\text{P-Ph}}$ 1436 cm^{-1} .

Crystallography

Crystal structure data were collected for all complexes at 125 K using a Rigaku SCX-Mini, (Mo radiation). All data was corrected for absorption. The structures were

solved by direct methods and refined by full-matrix least-squares methods on F^2 values of all data⁹. Refinements were performed using SHELXL¹⁰.

Results and Discussion

The crystal structures and ^{31}P NMR for the dichloride complexes have been previously reported [(**1**) *cis*-PtCl₂(P(OMe)₃)₂]⁵, (**2**) *cis*-PtCl₂(P(OMe)₂Ph)₂¹¹, (**3**) *cis*-PtCl₂(P(OMe)Ph)₂¹² and (**4**) *cis*-PtCl₂(PPh₃)₂]¹³. The dibromide and diiodide analogues [(**5**) *cis*-PtBr₂(P(OMe)₃)₂, (**6**) *cis*-PtBr₂(P(OMe)₂Ph)₂, (**7**) *cis*-PtBr₂(P(OMe)Ph)₂, (**8**) *cis*-PtBr₂(PPh₃)₂, (**9**) *cis*-PtI₂(P(OMe)₃)₂, (**10**) *cis*-PtI₂(P(OMe)₂Ph)₂, (**11**) *cis*-PtI₂(P(OMe)Ph)₂ and (**12**) *cis*-PtI₂(PPh₃)₂] were characterised in this work.

The ^{31}P -{ ^1H } NMR spectra of all the complexes (Table 1) exhibit singlets together with satellites due to $^1J_{\text{Pt-P}}$ couplings. For each of the three halides the coupling constant is observed to decrease in the order P(OMe)₃ > P(OMe)₂Ph > P(OMe)Ph₂ > PPh₃ (Figure 1) as the π -acidity of the phosphorus ligands decrease. In addition to this, for each of the four phosphorus ligands the coupling constant decreases in the order Cl > Br > I as the degree of π back-bonding between the platinum and the halide, and hence the halide's ability to compete with the phosphorus for the electron back-donation, increases. This can be interpreted as an increase in *trans*-influence as the coupling constant is an indication of bond strength and *trans*-influence is defined as the ability of a ligand to weaken the bond *trans* to it¹⁴. The chemical shifts are also seen to decrease in the order Cl > Br > I with the exception of the complexes containing P(OMe)₃ where the opposite is observed.

The X-ray crystal structures of the dibromide complexes **(5)**-**(8)** (Figure 2) were determined and refined to a good standard. All of the structures exhibit square planar geometry about the platinum and were observed to be isostructural to their dichloride analogues. The Pt-Br distances lie within the range 2.4696(4) Å to 2.4933(5) Å and exhibit no significant trend. The Pt-P bond lengths are within the range 2.207(2) Å to 2.2685(10) Å and, as was observed in the dichloride analogues, increase in the order $\text{P(OMe)}_3 < \text{P(OMe)}_2\text{Ph} < \text{P(OMe)Ph}_2 < \text{PPh}_3$. The P(1)-Pt-P(2) and Br(1)-Pt-Br(2) bond angles lie in the ranges $93.74(9)^\circ$ to $98.41(4)^\circ$ and $86.000(18)^\circ$ to $89.265(17)^\circ$ respectively with no significant trends apparent.

The X-ray crystal structures of the diiodide complexes **(9)**-**(12)** (Figure 3) were also determined and observed to be isostructural though not necessarily isomorphous to the dibromide structures. Similar trends in bond lengths and angles as those observed for the dibromides are also evident. Most significantly the Pt-P bond lengths (2.2214(14) Å to 2.295(2) Å) increase in the order $\text{P(OMe)}_3 < \text{P(OMe)}_2\text{Ph} < \text{P(OMe)Ph}_2 < \text{PPh}_3$. The Pt-I distances are in the range 2.6448(5) Å to 2.6814(5) Å and the P(1)-Pt-P(2) and Br(1)-Pt-Br(2) bond angles lie in the ranges $88.979(13)^\circ$ to $97.47(7)^\circ$ and $87.456(18)^\circ$ to $94.56(5)^\circ$ respectively with the latter decreasing in the order $\text{P(OMe)}_3 > \text{P(OMe)}_2\text{Ph} > \text{P(OMe)Ph}_2 > \text{PPh}_3$.

Comparing the structures of compounds **(1)**-**(12)** it can be seen that for each of the halides the Pt-P bond length is seen to increase in the order $\text{P(OMe)}_3 < \text{P(OMe)}_2\text{Ph} < \text{P(OMe)Ph}_2 < \text{PPh}_3$ with the PPh_3 complexes having Pt-P bond lengths *ca.* 0.06 Å longer than the P(OMe)_3 complexes (Table 2, Figure 4). For each of the phosphorus ligands the Pt-P bond length increases in the order $\text{Cl} < \text{Br} < \text{I}$ with Pt-P bond lengths

in the iodide complexes being *ca.* 0.03 Å longer than their dichloride equivalents. These two effects are in accord with [1] the π -acidity of the phosphorus ligands increasing as the oxygen content rises and [2] the heavier halogens being better π -acceptors and thus phosphorus *trans* to iodine is less strongly bound than phosphorus *trans* to chloride.

When considering the magnitude of the {Pt-P} coupling constant the s-character of the orbitals involved in the Pt-P bond is usually considered to be the most important variable.

$$^1J_{(M-P)} = \gamma_M \gamma_P \frac{64\pi^2}{9} \beta^2 \frac{|S_M(0)|^2}{\Delta E} |S_P(0)|^2 (P'_{S_M S_P})^2$$

Equation 1

Thus, to a good approximation, the coupling constant is given by equation 1³ where the s-characters of the orbitals is contained in the M.O. bond order between the s-orbitals, $(P'_{S_M S_P})^2$. The valence state s-orbital basis functions are given by the expressions $|S_P(0)|$ and $|S_M(0)|$, ΔE is the average excitation energy and γ_M and γ_P the magnetogyric constants for each nucleus. As is evident the principles involved are complex however for a given phosphorus ligand and metal centre $|S_P(0)|$ and $|S_M(0)|$ should remain relatively constant leaving $(P'_{S_M S_P})^2$ as the dominating factor in the magnitude of $^1J_{\text{Pt-P}}$. Clearly given equation 1 provided the nature of the bonding is not dramatically different there should be a good correlation between Pt-P bond length and $J\{\text{Pt-P}\}$.

We found that as the bond length increases the coupling constant decreases. The correlation between these two measurements in this series of compounds is rather good giving a reasonable straight line that can be fitted by equation 2 (Figure 5). We did consider that another way of gauging the s-character and hence the strength of the bond would be to look at the R-P-R, R-P-O and O-P-O bond angles in these complexes with larger values indicating a move towards more ideal sp^3 hybridisation however we did not observe any correlation in this regard.. It thus appears that in a narrow series of complexes the coupling constant could be used as a good indicator of bond length.

$$l_{(Pt-P)} = 2.421 - \frac{J}{24255}$$

Equation 2

To further test the principle we compared Pt-P bond lengths and $^1J_{Pt-P}$ coupling constants we examined $Pt(E_2N_2)(PR_3)_2$ ¹⁵⁻²² as well as their protonated equivalents that have been prepared in our and other labs^{18, 21-26}, corresponding *cis*- and *trans*-dihalides²⁷⁻⁴⁹ and $Pt(NSO)_2(PR_3)_2$ complexes.⁵⁰⁻⁵¹ This supports the assertion (Figure 6, Table 5 ESI) that the larger the coupling constant the shorter the Pt-P bond length. As can be seen in Figure 6 the correlation is not necessarily linear since at the extremes significant energetic stabilisation is needed in order to influence bond length and the magnitude of coupling constants is a better measure of s orbital overlap than of absolute bond length, however the best fit straight line is given by equation 3.

$$l_{(Pt-P)} = 2.422 - \frac{J}{21827}$$

Equation 3

Using equations 2 and 3 we tested the accuracy of the correlation as an indicator of bond length on a selection of compounds (Table 6). It is interesting to note that in most cases equation 2 tends to give a more accurate result than equation 3 the former being on average within 0.015 Å of the observed distance and the latter within 0.02 Å. The accuracy of equation 3 could potentially be improved with a more extensive literature search.

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Table 1: ^{31}P NMR chemical shifts and ^{195}Pt - ^{31}P coupling constants for (1)-(12)

Compound	δ_{ppm}	$J_{\text{P-Pt}}(\text{Hz})$
(1) <i>cis</i> -PtCl ₂ (P(OMe) ₃) ₂	73.7	5707
(2) <i>cis</i> -PtCl ₂ (P(OMe) ₂ Ph) ₂	97.2	4819
(3) <i>cis</i> -PtCl ₂ (P(OMe)Ph ₂) ₂	85.2	4183
(4) <i>cis</i> -PtCl ₂ (PPh ₃) ₂	14.5	3679
(5) <i>cis</i> -PtBr ₂ (P(OMe) ₃) ₂	75.2	5662
(6) <i>cis</i> -PtBr ₂ (P(OMe) ₂ Ph) ₂	97.0	4777
(7) <i>cis</i> -PtBr ₂ (P(OMe)Ph ₂) ₂	84.9	4141
(8) <i>cis</i> -PtBr ₂ (PPh ₃) ₂	14.0	3627
(9) <i>cis</i> -PtI ₂ (P(OMe) ₃) ₂	77.6	5477
(10) <i>cis</i> -PtI ₂ (P(OMe) ₂ Ph) ₂	96.4	4618
(11) <i>cis</i> -PtI ₂ (P(OMe)Ph ₂) ₂	83.5	3995
(12) <i>cis</i> -PtI ₂ (PPh ₃) ₂	11.6	3472

Figure 1: Variation of ^{195}Pt - ^{31}P coupling constants with phosphite/phosphine character

Table 2. Selected bond lengths (Å) and angles (°) for (1)-(12).

	(1) PtCl ₂ (P(OMe) ₃) ₂ ⁵	(2) PtCl ₂ (P(OMe) ₂ Ph) ₂ ¹¹	(3) PtCl ₂ (P(OMe)Ph) ₂ ¹²	(4) PtCl ₂ (PPh ₃) ₂ ¹³
Pt-Cl(1)	2.384(4)	2.3625(9)	2.3693(12)	2.3632(8)
Pt-Cl(2)	2.408(4)	2.3625(9)	2.3533(12)	2.3294(9)
Pt-P(1)	2.192(3)	2.2193(9)	2.2272(11)	2.2713(9)
Pt-P(2)	2.155(3)	2.2193(9)	2.2279(12)	2.2515(8)
P(1)-Pt-P(2)	95.5(1)	101.16(3)	98.14(4)	99.12(3)
Cl(1)-Pt-Cl(2)	85.8(1)	89.08(3)	89.37(4)	87.56(3)
	(5) PtBr ₂ (P(OMe) ₃) ₂	(6) PtBr ₂ (P(OMe) ₂ Ph) ₂	(7) PtBr ₂ (P(OMe)Ph) ₂	(8) PtBr ₂ (PPh ₃) ₂
Pt-Br(1)	2.4742(11)	2.4933(5)	2.4895(4)	2.4696(4)
Pt-Br(2)	2.4753(11)	2.4762(4)	2.4828(5)	2.4859(5)
Pt-P(1)	2.217(2)	2.2161(9)	2.2400(11)	2.2625(13)
Pt-P(2)	2.207(2)	2.2248(12)	2.2424(11)	2.2685(10)
P(1)-Pt-P(2)	93.74(9)	93.76(4)	98.41(4)	97.55(4)
Br(1)-Pt-Br(2)	88.54(3)	89.209(16)	89.265(17)	86.000(18)
	(9) PtI ₂ (P(OMe) ₃) ₂	(10) PtI ₂ (P(OMe) ₂ Ph) ₂	(11) PtI ₂ (P(OMe)Ph) ₂	(12) PtI ₂ (PPh ₃) ₂
Pt-I(1)	2.6587(4)	2.6608(5)	2.6814(5)	2.6647(6)
Pt-I(2)	2.6571(4)	2.6569(4)	2.6533(5)	2.6448(5)
Pt-P(1)	2.2214(14)	2.2360(14)	2.2481(19)	2.295(2)
Pt-P(2)	2.2248(16)	2.244(2)	2.2518(19)	2.277(2)
P(1)-Pt-P(2)	94.56(5)	93.84(6)	93.01(7)	97.47(7)
I(1)-Pt-I(2)	88.979(13)	88.836(17)	88.003(17)	87.456(18)

Table 3. Experimental and refinement details for the X-ray structures for (5)-(8)

Compound	(5)	(6)	(7)	(8)
Fw	C ₆ H ₁₈ O ₆ P ₂ Br ₂ Pt	C ₁₆ H ₂₂ O ₄ P ₂ Br ₂ Pt	C ₂₆ H ₂₆ O ₂ P ₂ Br ₂ Pt	C ₃₇ H ₃₁ P ₂ Cl ₃ Br ₂ Pt
M	603.05	695.19	787.34	998.86
Temperature (K)	125	125	125	125
Crystal System	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	Pna2 ₁	P-1	P 2 ₁ /n	P-1
a/ Å	12.6116(9)	9.1545(7)	12.675(3)	11.1265(7)
b/ Å	7.6773(6)	9.9510(8)	13.753(5)	11.7130(7)
c/ Å	16.0931(12)	13.1489(10)	14.938(10)	14.2633(10)
α/°	90	110.452(8)	90	90.826(6)
β/°	90	94.763(7)	93.283(9)	98.341(7)
γ/°	90	108.745(8)	90	106.986(8)
U/Å ³	1558.2(2)	1036.72(14)	2599.6(20)	1755.81(20)
Z	4	2	4	2
μ(Mo-Kα)mm ⁻¹	14.328	10.778	8.604	6.608
D _c /Mg m ⁻³	2.570	2.227	2.012	1.889
Total reflections	12415	3629	22176	15229
Independent	2730	3641	4568	6155
reflections (R _{int})	(0.085)	(0.026)	(0.050)	(0.036)
Max and min. transmission	0.4333, 0.2386	0.3575, 0.1904	0.2776, 0.2071	0.5297, 0.2587
Final R,R'	0.0335, 0.0664	0.0203, 0.0449	0.0265, 0.0624	0.0353, 0.0842
Largest difference peak, hole/e.Å ⁻³	1.36 -0.92	0.49 -0.69	1.16 -0.99	1.00 -0.88

Table 4. Experimental and refinement details for the X-ray structures for **(9)**-(**12**)

Compound	(9)	(10)	(11)	(12)
Fw	C ₆ H ₁₈ O ₆ P ₂ I ₂ Pt	C ₁₆ H ₂₂ O ₄ P ₂ I ₂ Pt	C ₂₆ H ₂₆ O ₂ P ₂ I ₂ Pt	C ₃₆ H ₃₂ OP ₂ I ₂ Pt
M	697.05	789.19	881.34	991.49
Temperature (K)	125	125	125	125
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	P2 ₁ /n	P-1	Cc	P-1
a/ Å	9.0554(4)	9.496(3)	10.456(4)	9.8227(5)
b/ Å	14.7571(7)	10.044(3)	17.143(7)	10.4994(6)
c/ Å	12.8733(9)	13.743(4)	15.597(6)	17.7427(13)
α/°	90	66.910(15)	90	86.757(6)
β/°	98.251(7)	71.546(18)	104.500(3)	77.704(6)
γ/°	90	71.621(15)	90	70.376(5)
U/Å ³	1702.46(16)	1116.0(6)	2706.7(19)	1683.78(17)
Z	4	2	4	2
μ(Mo-Kα)mm ⁻¹	12.035	9.189	7.585	6.107
D _c /Mg m ⁻³	2.719	2.348	2.163	1.955
Total reflections	14469	9745	11522	14529
Independent	2993	3922	4748	5893
reflections (R _{int})	(0.051)	(0.035)	(0.035)	(0.046)
Max and min. transmission	0.5837, 0.2200	0.2602, 0.2062	0.7023, 0.4157	0.6088, 0.4408
Final R,R'	0.0276, 0.0472	0.0287, 0.0625	0.0267, 0.0467	0.0403, 0.0922
Largest difference	0.76	1.25	0.94	2.02
peak, hole/e.Å ⁻³	-0.93	-1.66	-1.00	-1.15

Figure 2: X-ray crystal structure of (7). The structures of (5), (6) and (8) are not illustrated as they are similar.

Figure 3: X-ray crystal structure of (10). The structures of (9), (11) and (12), are not illustrated as they are similar.

Figure 4: Variation of Pt-P in $\text{PtX}_2(\text{P}(\text{OMe})_n\text{Ph}_{3-n})_2$ complexes.

Figure 5: Correlation of $^1J_{\text{Pt-P}}$ with Pt-P bond length in $\text{PtX}_2(\text{P}(\text{OMe})_n\text{Ph}_{3-n})_2$ complexes.

Figure 6: Correlation of $^1J_{\text{Pt-P}}$ with Pt-P bond length in large range of Pt-Phosphorus complexes. Black line is best fit to the points in the graph equation 3. Red line is the line from equation 2.

Table 5: Pt-P distances and Coupling constants used in figure 6.

Compound (<i>trans</i> - atom in bold)	Pt-P Bond Length (Å)	$^1J_{\text{Pt-P}}$ (Hz)
Pt(S ₂ N ₂)(P(OPh) ₃) ₂ ¹⁵	2.221(3)	4634
Pt(S ₂ N ₂)(P(OPh) ₃) ₂	2.234(3)	4503
Pt(S ₂ N ₂)(P(OMe) ₃) ₂ ¹⁵	2.217(3)	4502
Pt(S ₂ N ₂)(P(OMe) ₃) ₂	2.246(3)	4395
Pt(S ₂ N ₂)(P(OEt) ₃) ₂ ¹⁵	2.239(2)	4498
Pt(S ₂ N ₂)(P(OEt) ₃) ₂	2.237(2)	4415
Pt(S ₂ N ₂)(P(OMe) ₂ Ph) ₂ ¹⁵	2.2175(15)	3864
Pt(S ₂ N ₂)(P(OMe) ₂ Ph) ₂	2.2407(15)	3761
Pt(S ₂ N ₂)(P(OMe)Ph ₂) ₂ ¹⁵	2.250(2)	3287
Pt(S ₂ N ₂)(P(OMe)Ph ₂) ₂	2.256(2)	3249
Pt(S ₂ N ₂)(PPh ₃) ₂ ¹⁶	2.263(4)	2994 ¹⁷
Pt(S ₂ N ₂)(PPh ₃) ₂	2.317(4)	2827
Pt(S ₂ N ₂)(PMe ₂ Ph) ₂ ¹⁸	2.265(3)	2799 ¹⁷
Pt(S ₂ N ₂)(PMe ₂ Ph) ₂	2.271(4)	2731
Pt(S ₂ N ₂)(PMePh ₂) ₂ ¹⁹	2.243(2)	2886 ¹⁷
Pt(S ₂ N ₂)(PMePh ₂) ₂	2.281(2)	2781
Pt(S ₂ N ₂)(PMe ₃) ₂ ¹⁷	2.261(6)	2748 ¹⁷
Pt(S ₂ N ₂)(PMe ₃) ₂	2.268(5)	2681
[Pt(S ₂ N ₂ H)(PMe ₂ Ph) ₂][PF ₆] ¹⁸	2.262(2)	3240 ²³
[Pt(S ₂ N ₂ H)(PMe ₂ Ph) ₂][PF ₆]	2.305(2)	2595
[Pt(S ₂ N ₂ H)(PMe ₃) ₂][PF ₆] ²⁴	2.249(1)	3130 ²³
[Pt(S ₂ N ₂ H)(PMe ₃) ₂][PF ₆]	2.263(1)	2566
[Pt(S ₂ N ₂ H)(PEt ₃) ₂][PF ₆] ²⁵	2.270(3)	3162 ²³
[Pt(S ₂ N ₂ H)(PEt ₃) ₂][PF ₆]	2.320(3)	2563
[Pt(S ₂ N ₂ H)(P ^{<i>n</i>} Bu ₃) ₂][PF ₆] ²³	2.2675(2)	3164
[Pt(S ₂ N ₂ H)(P ^{<i>n</i>} Bu ₃) ₂][PF ₆]	2.3145(2)	2561
Pt(SeSN ₂)(P(OMe) ₃) ₂ ²⁰	2.243(2)	4530
Pt(SeSN ₂)(P(OMe) ₃) ₂	2.214(2)	4571
Pt(SeSN ₂)(P(OMe) ₂ Ph) ₂ ²⁰	2.2480(14)	3868
Pt(SeSN ₂)(P(OMe) ₂ Ph) ₂	2.2266(13)	3900
Pt(SeSN ₂)(P(OMe)Ph ₂) ₂ ²⁰	2.260(3)	3309
Pt(SeSN ₂)(P(OMe)Ph ₂) ₂	2.253(4)	3391
Pt(SeSN ₂)(PPh ₃) ₂ ²⁰	2.3069(17)	2996
Pt(SeSN ₂)(PPh ₃) ₂	2.2664(12)	2948
Pt(SeSN ₂)(PMe ₂ Ph) ₂ ²¹	2.271(2)	2799 ²²
Pt(SeSN ₂)(PMe ₂ Ph) ₂	2.261(2)	2837
[Pt(SeSN ₂ H)(PMe ₂ Ph) ₂][BF ₄] ²¹	2.262(2)	2687 ²²
[Pt(SeSN ₂ H)(PMe ₂ Ph) ₂][BF ₄]	2.301(2)	3227
[Pt(TeSN ₂ H)(PMe ₂ Ph) ₂][BF ₄] ²⁶	2.257(3)	2645
[Pt(TeSN ₂ H)(PMe ₂ Ph) ₂][BF ₄]	2.313(3)	3171
<i>cis</i> -PtCl ₂ (P(OEt) ₃) ₂	2.2235	5697
<i>cis</i> -PtCl ₂ (P(O ^{<i>i</i>} Pr) ₃) ₂ ²⁷	2.21465	5812
<i>cis</i> -PtCl ₂ (P(OPh) ₃) ₂ ²⁸	2.19915	5793
<i>cis</i> -PtCl ₂ (P(OMe) ₃) ₂ ⁵	2.1735	5707
<i>cis</i> -PtCl ₂ (P(OMe) ₂ Ph) ₂ ¹¹	2.2190	4819
<i>cis</i> -PtCl ₂ (P(OMe)Ph ₂) ₂ ¹²	2.22755	4183
<i>cis</i> -PtCl ₂ (PPh ₃) ₂ ¹³	2.2614	3679
<i>cis</i> -PtCl ₂ (PMe ₃) ₂ ²⁹	2.238	3489 ³⁰
<i>cis</i> -PtCl ₂ (PMe ₂ Ph) ₂ ³¹	2.244	3549 ³²
<i>cis</i> -PtCl ₂ (PMePh ₂) ₂ ³³	2.24875	3616 ³²
<i>cis</i> -PtCl ₂ (PEt ₃) ₂ ³⁴	2.263	3520 ³²
<i>cis</i> -PtCl ₂ (PEt ₂ Ph) ₂ ³⁵	2.25295	3530 ³²
<i>cis</i> -PtCl ₂ (PEtPh ₂) ₂ ³⁶	2.25745	3640 ³²
<i>cis</i> -PtCl ₂ (dppe) ₂ ³⁷	2.208	3610

<i>cis</i> -PtCl ₂ (dppp) ₂ ³⁷	2.232	3408
<i>cis</i> -PtBr ₂ (P(OPh) ₃) ₂	2.205 ³⁸	5728 ³⁹
<i>cis</i> -PtI ₂ (PMe ₃) ₂	2.2575 ⁴⁰	3317 ³⁰
<i>cis</i> -PtI ₂ (dppe) ₂	2.2418 ⁴¹	3366 ⁴²
<i>trans</i> -PtCl ₂ (PEt ₃) ₂	2.298 ⁴³	2400 ³²
<i>trans</i> -PtCl ₂ (P ⁱ Pr ₃) ₂	2.3392 ⁴⁴	2417 ⁴⁵
<i>trans</i> -PtCl ₂ (PPh ₃) ₂	2.3186 ⁴⁶	2630 ⁴⁷
<i>trans</i> -PtI ₂ (PPh ₃) ₂	2.318 ⁴⁸	2496 ⁴⁷
<i>trans</i> -PtI ₂ (PMe ₃) ₂	2.315 ⁴⁹	2236 ³⁰
<i>cis</i> -Pt(NSO) ₂ (PPh ₃) ₂	2.3278 ⁵⁰	3027 ⁵¹
<i>cis</i> -Pt(NSO) ₂ (PMe ₃) ₂ ⁵¹	2.263	3190

Table 6: Coupling constants and calculated (using equation 2 or 3) and observed bond lengths for selected compounds

Compound	¹ J _{Pt-P} (Hz)	l _{Pt-P} (Å)	Eqn 2 (Å)	Eqn 3 (Å)
[Pt(9S3)(PPh ₃)Cl]PF ₆ ⁵²	3387	2.2838(8)	2.281	2.266
[Pt(10S3)(PPh ₃)Cl]PF ₆ ⁵²	3438	2.285(2)	2.279	2.264
[Pt(PMe ₃) ₂ {CS ₃ }] ⁵³	2969	2.265	2.298	2.285
[Pt(PPh ₃) ₂ {CS ₃ }] ⁵³	3145	2.2915	2.29	2.278
[Pt(dppp) ₂ {CS ₃ }] ⁵³	2881	2.263	2.302	2.289
[Pt(Se ₂ naph)(P(OPh) ₃) ₂] ⁵⁴	4711	2.231	2.227	2.208