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Syntheses and structures of palladium(II) and platinum(II) complexes with tridentate (Ph₂PCH₂CH₂CH₂)₂S and its arsenic analogue

C.R. Cheng, Pak-Hing Leung *, K.F. Mok

Department of Chemistry, National University of Singapore, Kent Ridge Crescent, 119260 Singapore, Singapore

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Abstract

A series of square-planar complexes [MLC1]ClO₄ (M=Pd(II), Pt(II); L=bis(3-(diphenylphosphino)propyl)sulfide (psp), bis(3-(diphenylphosphino)propyl)sulfide (asa)) have been prepared and characterized. The X-ray crystal structures of two of them have been determined: [Pd(psp)C1]ClO₄, P_{21}/c , a = 12.519(2), $b \approx 15.766(2)$, c = 16.501(2) Å, $\beta = 105.22(1)^\circ$, Z=4; and [Pt(asa)C1]ClO₄, P_{21}/c , a = 12.583(5), b = 16.007(6), c = 16.549(6) Å, $\beta = 104.89(3)^\circ$, Z=4. In both structures, there is a conformational disorder between the chair and skew-boat orientation in one of the two six-membered chelate rings. The C-H···O hydrogen bond between the hybrid ligand and the perchlorate counter ion that induces the conformational disorder is discussed.

Keywords: Platinum complexes; Palladium complexes; Six-membered chelate ring; C-H--O hydrogen bond; Phosphine; Arsine

1. Introduction

Transition metal complexes containing tertiary phosphine and arsine ligands have been increasingly investigated owing to their steric and electronic properties and their applications in homogeneous catalysis [1]. On the other hand, thiolate metal complexes have also been extensively studied because of their possible relevance to the biochemical function of active reaction centres in metalloproteins [2]. However, less attention has been paid to the arsine-thiolate and phosphinethiolate hybrid ligands [3], especially the multidentate ligands, and their complexes.

Our research efforts have been concentrated on the synthesis of tridentate ligands, which involve phosphines or arsines, sulfides or sulfoxides, and on the structural, catalytic properties and the coordination chemistry of the resulting nickel(II), palladium(II) and platinum(II) complexes. Recent studies in our group on the coordination behaviour of tridentate hybrid ligand ($Ph_2PCH_2CH_2CH_2)_2S$ (psp) to nickel(II) chloride reveals that the sulfur and both of the phosphorus coordinate to Ni(II) to form a five coordinated neutral complex [4]. In this paper, we report the synthesis of an analogous ligand ($Ph_2AsCH_2CH_2CH_2)_2S$ (asa), and the structural study on the palladium(II) and platinum(II) complexes of these two ligands.

2. Experimental

Bis(3-(diphenylphosphino)propyl)sulfide (psp) was synthesized as described previously [4]. Other chemicals were purchased from commercial sources and were used without further purification. All syntheses and manipulations involving air-sensitive materials were performed under nitrogen atmosphere by the use of standard Schlenk techniques. Routine ¹H and ³¹P NMR spectra were measured on a Bruker ACF 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer (PE) 2400 elemental analyzer by the Microanalytical Laboratory of the Department of Chemistry. Conductivities were measured with a STEM conductivity-1000 conductivity meter at 25°C.

Safety Note! Perchlorate salts are potentially explosive, only small amounts of materials should be used.

2.1. Bis(3-(diphenylarsino)propyl)sulfide (asa)

To a mixture of diphenylarsine (7.00 cm³, 40.0 mmol) in 40 cm³ of dry THF and *n*-BuLi in hexane (1.6 M, 25.0 cm³, 40.0 mmol), a solution of bis(3-(methylsulfonyloxy)propyl)sulfide (6.12 g, 20.0 mmol) in 10 cm³ of dry THF was added slowly at -78° C. The solution was stirred for 30 min at -78° C and then 2 h at room temperature. The crude product was isolated by extraction with diethyl ether (50 cm³ × 2) followed by the removal of solvents under

^{*} Corresponding author.

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reduced pressure. Pure as a was obtained as a colourless oil by silica column chromatography, yield 7.50 g (65%). ¹H NMR (CDCl₃): 7.37 (m, 20H, aromatics); 2.50 (t, 4H, 2SCH₂); 2.09 (t, 4H, 2AsCH₂); 1.74 ppm (m, 4H, 2CH₂). *Anal.* Calc. for $C_{30}H_{32}As_2S$: C, 62.7; H, 5.6. Found: C, 63.0; H, 5.6%.

2.2. [Pd(psp)Cl]ClO₄

To a solution of PdCl₂ (35 mg; 0.20 mmol) in 10 cm³ of acetonitrile, ligand psp (100 mg; 0.20 mmol) in 10 cm³ of dichloromethane was added. After refluxing the solution for half an hour, NaClO₄ (25 mg; 0.20 mmol) in a small amount of acetonitrile was added. Immediately, white precipitate of NaCl formed. After removing the solvents with rotary evaporator, the residue was dissolved in 10 cm³ of dichloromethane and 5 cm³ of ethyl acetate, and the resulting solution was filtered and set aside. Yellow prismatic crystals (yield 100 mg; 70%) formed after standing for a few hours. ¹H NMR (CD₂Cl₂): 7.71 (m, 8H, aromatics); 7.44 (m, 12H, aromatics); 3.31 (t, 4H, SCH₂); 2.65 (t, 4H, PCH₂); 2.17 ppm (m, 4H, CH₂). ³¹P NMR: δ – 0.82 (s). Anal. Calc. for C₃₀H₃₂Cl₂O₄P₂PdS: C, 49.5; H, 4.4. Found: C, 49.6; H, 4.4%.

The following compounds were similarly prepared.

2.3. [Pd(asa)Cl]ClO₄

The product prepared from asa (100 mg; 0.17 mmol) and PdCl₂ (31 mg; 0.17 mmol) was obtained as yellow prisms. Yield: 100 mg; 72%. 1H NMR (CD_2Cl_2): 7.72 (m, 8H, aromatics); 7.49 (m, 12H, aromatics); 3.35 (t, 4H, SCH₂); 2.66 (t, 4H, AsCH₂); 2.37 ppm (m, 4H, CH₂). Anal. Calc. for $C_{30}H_{32}As_2Cl_2O_4PdS$: C, 44.1; H, 3.9. Found: C, 44.1; H, 3.9%.

2.4. [Pt(psp)Cl]ClO4

The product was obtained as white prisms from psp (100 mg; 0.20 mmol) and PtCl₂ (55 mg; 0.20 mmol). Yield: 110 mg; 66%. ¹H NMR (CD₂Cl₂): 7.73 (s, 8H, aromatics); 7.52 (m, 12H, aromatics); 3.44 (s, 4H, ${}^{3}J_{Pt-H} = 69.3$ Hz, 2SCH₂); 2.79 (t, 4H, 2PCH₂); 2.31 ppm (s, 4H, 2CH₂). ³¹P NMR: -4.97 ppm (s, {}^{1}J_{Pt-P} = 2330 Hz). Anal. Calc. for C₃₀H₃₂Cl₂O₄P₂PtS: C, 44.1; H, 3.9. Found: C, 43.8; H, 4.1%.

2.5. [Pt(asa)Cl]ClO₄

The product was prepared from asa (100 mg; 0.17 mmol) and PtCl₂ (46 mg; 0.17 mmol) and was obtained as white prisms. Yield: 110 mg; 70%. Crystals suitable for X-ray analysis were recrystallized from dickloromethane–ethyl acetate solution. ¹H NMR (CD₂Cl₂): 7.68 (s, 8H, aromatics); 7.51 (s, 12H, aromatics); 3.44 (s, 4H, ³J_{Pt-H} = 66.2 Hz, 2SCH₂); 2.74 (t, 4H, 2AsCH₂); 2.50 ppm (m, 4H, 2CH₂). Anal. Calc. for C₁₀H₃₂As₂Cl₂O₄PtS: C, 39.8; H, 3.5. Found: C, 39.7; H, 3.6%.

2.6. Crystallographic analyses

The crystals used for analyses were of approximate dimensions 0.22×0.30×0.44 mm and 0.22×0.30×0.36 mm for [Pd(psp)Cl]ClO₄ and [Pt(asa)Cl]ClO₄ respectively. Data were collected on a Siemens R3m/V four-circle diffractometer using graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Unit cell parameters were determined by least-squares fit of 25 independent reflections, which were obtained by an automatic random search routine. Intensities were measured by the $\omega/2\theta$ scan method in the index ranges $0 \le h \le 14$; $0 \le k \le 18$; $-19 \le l \le 18$ and $0 \le h \le 14$; $0 \le k \le 19$; $-19 \le l \le 19$ for complexes [Pd(psp)Cl]ClO₄ and [Pt(asa)Cl]ClO₄ respectively. Intensities of two standard reflections were measured after every 98 reflection data were collected. Semi-empirical absorption corrections were applied; minimum and maximum transmission coefficients were 0.763-0.828 and 0.622-0.825 for [Pd(psp)Cl1ClO₄ and [Pt(asa)Cl]ClO4 respectively.

The structure of $[Pd(psp)Cl]ClO_4$ was solved by a combination of Patterson and Fourier difference-map methods and was refined by full matrix least-squares. The structure of $[Pt(asa)Cl]ClO_4$ was solved by direct methods followed by Fourier syntheses. Structures were solved on a Digital Equipment Corporation MicroVax II computer, and full matrix least-squares refinements were done on a PC by using SHELXTL PC software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (C-H=0.96 Å) and given fixed thermal parameters.

When the structures were refined, difference electron density maps for both of the complexes clearly showed two peaks appropriate to the site for C7, which were respectively suitable for 'skew-boat' and 'chair' conformations for the corresponding chelate rings. The two peaks were incorporated in following least-squares refinement with the sum of the occupations for C7A and C7B constrained to unity. The appropriate constraint was applied to the correspond H atoms at C6, C7A, C7B and C8. The occupation of C7A converged to 0.68(1) for complex [Pd(psp)Cl]ClO₄ and 0.65(5) for complex [Pt(asa)Cl]ClO₄.

3. Results and discussion

All the complexes were obtained as highly crystalline perchlorate salts in high yields. In dichloromethane, they behave as 1:1 electrolytes, indicating that all the Pd(II) and Pt(II) complexes are four coordinated.

At room temperature, ¹H NMR spectra show simple resonance patterns for the three methylene groups for all the four complexes. The two protons in each methylene group are stereochemically identical due to the rapid conformational interconversion of the six-membered chelate rings. This interconversion can be hindered at low temperature as every resonance peak of the methylene groups splits into two sets at -35° C arising from non-equivalent axial and equatorial dispositions. The ¹H NMR spectra of both platinum complexes exhibit Pt-H coupling to SCH₂ protons with ³J_{Pt-H} = 69.3 Hz for [Pt(psp)Cl]ClO₄ and ³J_{Pt-H} = 66.2 Hz for [Pt(asa)Cl]-ClO₄ respectively. These values are significantly higher than those of the corresponding sulfoxide complexes previously observed (around 20 Hz) indicating that Pt-S bonds are stronger in the thioether complexes [5]. The ³¹P NMR spectra of [Pd(psp)Cl]ClO₄ and [Pt(psp)Cl]ClO₄ show only a singlet at $\delta 0.82$ and $\delta - 4.97$ respectively with coordination chemical shift $\Delta = 17.42$ and 11.63 ppm. The small ${}^{1}J_{Pt-P}$ value (2330 Hz) of [Pt(psp)Cl]ClO₄ indicates that the two phosphines coordinate to Pt(II) in a *trans* manner [6].

Crystallographic data of $[Pd(psp)Cl]ClO_4$ and $[Pt(asa)Cl]ClO_4$ are presented in Table 1. Final atomic positional and thermal parameters of these two complexes are given in Table 2. Fig. 1 is the stereoview of complex $[Pd(psp)Cl]ClO_4$, and Fig. 2 shows the structure of complex cation $[Pt(asa)Cl]^+$. The molecular geometry of these two

Table I		
Crystallographic and diffraction data for	[Pd(psp)Cl]ClQ, and]	Pt(asa)Cl1ClO

	[Pd(psp)Cl]ClO₄	[Pt(asa)Cl]ClO₄	
Chemical formula	CanHanClaOaPaPdS	CinHinAs-CloQiPtS	
М.	727.9	904.4	
Crystal size (mm)	0.22×0.30×0.44	0.22×0.30×0.36	
Crystal system	Monoclinic	Monoclinic	
Space group	P2,/c	P2,/c	
a (Å)	12.519(2)	12.583(5)	
b (Å)	15.766(2)	16.007(6)	
c (Å)	16,501(2)	16.549(6)	
B(°)	105.22(1)	104.89(3)	
V (Å ³)	3143(2)	3221(2)	
Z	4	4	
- T(K)	298	298	
$D_{c} (g \text{ cm}^{-3})$	1.54	1.87	
λ (Μο Κα) (Å)	0.71073	0.71073	
μ (mm ⁻¹)	0.96	6.7	
Scan type	ω-2θ	ω-2 0	
20 range (°)	7.0-45.0	3.0-50.0	
F(000)	1480	1752	
Unique reflections	5565	5645	
Observed reflections a	4493	3883	
No. parameters	372	372	
R ^b	0.0395	0.0492	
R _w ^c	0.0461	0.0444	
Goodness-of-fit	1.46	1.22	
Residual density: min., max. (e Å ⁻³)	-0.47, 0.80	-0.92, 1.46	

* $[F>3\sigma(F)]$.

 ${}^{\mathrm{b}}R = \sum w |F_{\mathrm{o}} - F_{\mathrm{c}}| / \sum (F_{\mathrm{o}}).$

 $R_{w} = \{ [\Sigma w | F_{o} - F_{c}|^{2}] / [\Sigma w (F_{o})^{2}] \}^{1/2}.$



Fig. 1. Stereoview of the complex [Pd(psp)Cl]ClO₄.

Table 2
Atomic coordinates (×10 ⁴) and equivalent isotropic coefficients for [Pd(psp)Cl]ClO ₄ and [Pt(asa)Cl]ClO ₄

[Pd(psp)Cl]ClO ₄		[Pt(asa)Cl]ClO ₄							
	x	у	z	B _{iso} ^a		x	у	Ζ	B _{iso} ª
Pd	2170(1)	3689(1)	6050(1)	40(1)	Pt	2089(1)	3738(1)	952(1)	46(1)
P(1)	1810(1)	2623(1)	5034(1)	38(1)	As(1)	1761(1)	2622(1)	-51(1)	44(1)
C(2)	2589(3)	2722(3)	4249(3)	54(2)	C(2)	2565(9)	2727(7)	- 900(6)	62(5)
C(3)	2473(5)	3563(3)	3802(3)	70(2)	C(3)	2564(12)	3549(7)	- 1252(7)	90(6)
C(4)	3027(5)	4267(4)	4287(3)	85(2)	C(4)	2981(12)	4255(9)	761(7)	106(7)
S(5)	2427(1)	4685(1)	5117(1)	76(1)	S(5)	2323(4)	4665(2)	-9(2)	103(2)
C(6)	3596(8)	5368(5)	5525(4)	149(5)	C(6)	3461(22)	5384(13)	412(10)	316(23)
C(7A)	4161(6)	5406(5)	6443(4)	88(4)	C(7A)	4083(22)	5477(16)	1282(14)	160(22)
C(7B)	3141(15)	5897(8)	6107(5)	133(15)	C(7B)	3436(36)	5968(17)	1062(14)	96(22)
C(8)	3413(5)	5569(3)	6980(3)	88(3)	C(8)	3465(12)	5681(8)	1895(8)	87(6)
P(9)	2645(1)	4643(1)	7173(1)	51(1)	As(9)	2609(1)	4711(1)	2093(1)	54(1)
CI(10)	1622(1)	2767(1)	6957(1)	54(1)	CI(10)	1564(2)	2844(2)	1878(2)	61(1)
Cl(11)	3880(1)	6838(1)	3638(1)	65(1)	Cl(11)	- 3938(3)	3129(2)	1295(2)	70(1)
O(12)	4030(4)	7548(3)	3169(3)	107(2)	O(12)	-4108(8)	2459(5)	1802(6)	105(4)
O(13)	3534(4)	6154(3)	3090(3)	118(2)	O(13)	- 3605(9)	3841(6)	1791(6)	121(5)
O(14)	3065(4)	7018(4)	4046(3)	148(3)	O(14)	- 3104(9)	2904(8)	929(7)	151(7)
O(15)	4875(4)	6636(3)	4227(3)	130(2)	O(15)	- 4905(9)	3293(7)	702(6)	147(6)
C(11A)	367(3)	2543(2)	4472(2)	41(1)	C(11A)	236(8)	2480(5)	- 633(6)	45(4)
C(12A)	24(4)	2334(3)	3626(3)	59(2)	C(12A)	-553(9)	2549(7)	- 195(7)	66(5)
C(13A)	- 1089(4)	2204(3)	3246(3)	68(2)	C(13A)	-1632(10)	2382(7)	- 579(8)	76(6)
C(14A)	- 1855(4)	2276(3)	3684(3)	70(2)	C(14A)	-1941(10)	2178(7)	- 1406(9)	73(5)
C(15A)	-1529(4)	2486(4)	4520(3)	76(2)	C(15A)	-1187(10)	2100(7)	- 1839(7)	67(5)
C(16A)	-431(3)	2626(3)	4910(3)	58(2)	C(16A)	- 74(9)	2259(7)	- 1459(6)	66(5)
C(11B)	2189(3)	1568(3)	5456(2)	46(1)	C(11B)	2196(8)	1526(6)	439(6)	47(4)
C(12B)	1568(4)	863(3)	5124(3)	60(2)	C(12B)	1657(10)	825(7)	115(7)	65(5)
C(13B)	1888(5)	69(3)	5448(4)	78(2)	C(13B)	1963(12)	66(8)	457(9)	87(6)
C(14B)	2800(5)	-30(4)	6113(4)	85(3)	C(14B)	2885(14)	19(9)	1138(10)	103(8)
C(15B)	3411(5)	661(4)	6442(3)	87(3)	C(15B)	3438(13)	703(10)	1435(9)	99(7)
C(16B)	3122(4)	1463(3)	6114(3)	67(2)	C(16B)	3107(10)	1452(8)	1102(7)	75(5)
C(91A)	1523(4)	5091(3)	7534(3)	58(2)	C(91A)	3616(8)	4188(6)	3037(6)	54(4)
C(92A)	529(5)	4677(3)	7401(4)	79(2)	C(92A)	3716(10)	4451(7)	3845(7)	70(5)
C(93A)	-318(5)	5013(4)	7702(4)	96(3)	C(93A)	4480(11)	4076(10)	4500(8)	87(6)
C(94A)	- 176(7)	5759(5)	8127(4)	103(4)	C(94A)	5127(12)	3442(10)	4336(11)	103(8)
C(95A)	781(7)	6181(4)	8255(4)	103(3)	C(95A)	5021(10)	3164(9)	3521(11)	90(7)
C(96A)	1625(5)	5857(3)	7964(3)	83(2)	C(96A)	4269(10)	3537(7)	2877(8)	76(6)
C(91B)	3591(3)	4147(3)	8063(3)	54(2)	C(91B)	1442(11)	5185(7)	2519(7)	68(5)
C(92B)	3716(4)	4407(3)	8881(3)	65(2)	C(92B)	484(12)	4772(8)	2434(8)	82(6)
C(93B)	4514(5)	4036(4)	9526(3)	90(3)	C(93B)	-314(12)	5092(9)	2765(9)	100(7)
C(94B)	5164(5)	3399(5)	9366(4)	99(3)	C(94B)	-192(15)	5821(11)	3182(9)	105(9)
C(95B)	5045(4)	3122(4)	8554(4)	89(3)	C(95B)	786(18)	6244(10)	3285(9)	117(9)
C(963)	4269(4)	3496(3)	7914(3)	71(2)	C(96B)	1604(13)	5933(8)	2956(8)	94(7)

 $B_{iso} = (1/3) \times (\text{trace of the orthogonalized } U_{ii}).$

complexes is very similar. Palladium(II) and platinum(II) atoms are normally four coordinated in a square-planar geometry and these two complexes are no exceptions. Both psp and asa coordinate to the central metal ion as a tridentate ligand to form two six-membered chelate rings. The *trans* position to the sulfur atom is occupied by a chloride atom. The metal ion deviates from the coordination least-squares plane by about 0.01 and 0.03 Å in [Pd(psp)Cl]⁺ and [Pt(asa)Cl]⁺ respectively. The geometry of the ClO₄⁻ ion shows no disorder probably due to the formation of C-H…O hydrogen bonds which will be discussed later in the text. Listed in Tables 3 and 4 are selected bond lengths and angles of the two complexes. Long Pd-P (~2.33 Å) and Pt-As $(\sim 2.40 \text{ Å})$ distances indicate high *trans* effect of phosphine and arsine. But the Pt-As distance is shorter than that in the complex [PtCl(CH₃)(PEt₃)(AsPh₃)] (2.423 Å) in which the arsine is *trans* to the phosphine [7], indicating that the *trans* effect of arsine is weaker than that of phosphine.

Perhaps the most interesting feature is that both of the compounds exhibit chair-skew boat disorder in one of the six-membered chelate rings, with the skew-boat form in 68% occupancy in [Pd(psp)Cl]ClO₄ and 65% in [Pt(asa)Cl]-ClO₄; whereas the other chelate ring adopts a definite chair conformation. The chair conformation of the M-E1-C2-C3-C4-S5 and M-S5-C6-C7B-C8-E9 rings are confirmed by the characteristic +g, -g alternate torsional angles



Fig. 2. ORTEP drawing of the complex cation [Pt(asa)Cl]⁺.

(Table 5) [8]. However, the boat form of the M–S5–C6– C7A–C8–E9 ring is highly distorted. Usually, the chair conformation is the most stable form for a six-membered chelate ring [9]. The existence of skew-boat conformation in one of the two six-membered chelate rings indicates forces other than those associated with crystal packing. The presence of the perchlorate ion is probably the influential factor that dictates different environments in the two chelate .ings. A detail examination of the stereo arrangement of the complex cation and the perchlorate ion indicates the presence of C–H···O hydrogen bonds between H4, H6 of the ligand and oxygen atoms of the perchlorate ion. The distances of C4–O13, C6–

Table 3 Selected bond lengths $(\overset{\bullet}{A})$ and bond angles $(\overset{\circ}{})$ for [Pd(nsn)C](C)(O, I)



Fig. 3. C-H...O hydrogen bonds between C6-H and the perchlorate ion in the two conformers of $[Pd(psp)C1]ClO_4$.

O14 and C6–O15, which are 3.716, 3.508 and 3.598 Å in $[Pd(psp)C1]ClO_4$ and 3.673, 3.483 and 3.593 Å in $[Pt(asa)C1]ClO_4$ respectively, fall within the range of C–H···O hydrogen bond formation of 3.30–3.80 Å [10,11]. Only one C4–H4···O13 hydrogen bond is formed as only one of the C4–H4 bonds points directly at O13. The formation of C6–H6···O hydrogen bonds depends on the directions of C6–H6 bonds which are changeable according to the conformation of the chelate ring. In the chair–chair (cc) form, only one of the C6–H bonds points to the centre of O14 and O15; while in the chair–skew boat (cb) form, both of the C6–H bonds can form hydrogen bond with O14 and O15 respectively as shown in Fig. 3.

Since a C-H···O hydrogen bond was first described by Sutor [12], it has played a significant role in molecular packing in crystals [13]. Usually, the energy of the C-H···O hydrogen bond $(4-8 \text{ kJ mol}^{-1})$ is just in the range where it

Selected bond lengins (A) and bond angles () for [P0(psp)c1]ClO ₄				
Pd-P(1)	2.333(1)	C(4)-S(5)	1.848(6)	
Pd-S(5)	2.280(1)	S(5)-C(6)	1.799(8)	
Pd-P(9)	2.338(1)	C(6)-C(7A)	1.496(8)	
Pd-Cl(10)	2.316(1)	C(6)C(7B)	1.494(16)	
P(1)-C(2)	1.820(5)	C(7A)-C(8)	1.471(10)	
P(1)-C(11A)	1.805(4)	C(7B)-C(8)	1.484(11)	
P(1)-C(11B)	1.817(4)	C(8)-P(9)	1.821(6)	
C(2)-C(3)	1.506(6)	P(9)-C(91A)	1.809(5)	
C(3)-C(4)	1.437(7)	P(9)-C(91B)	1.805(4)	
P(1)-Pd-S(5)	92.6(1)	P(1)-Pd-P(9)	173.5(1)	
S(5)-Pd-P(9)	92.4(1)	P(1)-Pd-Cl(10)	88.8(1)	
S(5)-Pd-Cl(10)	170.7(1)	P(9)-Pd-Cl(10)	87.0(1)	
Pd-P(1)-C(2)	114.3(1)	Pd-P(1)-C(11A)	113.5(1)	
C(2)-P(1)-C(11A)	107.0(2)	Pd-P(1)-C(11B)	113.7(1)	
C(2)-P(1)-C(11B)	102.5(2)	C(11A)-P(1)-C(11B)	104.9(2)	
P(1)-C(2)-C(3)	115.0(3)	C(2)-C(3)-C(4)	115.9(4)	
C(3)-C(4)-S(5)	117.2(5)	Pd-S(5)-C(4)	114.3(2)	
Pd-S(5)-C(6)	113.9(2)	C(4)-S(5)-C(6)	92.3(3)	
S(5)-C(6)-C(7A)	121.6(6)	S(5)-C(6)-C(7B)	99.5(8)	
C(6)-C(7A)-C(8)	114.3(6)	C(6)-C(7B)-C(8)	113.6(10)	
C(7A)-C(8)-P(9)	114.5(5)	C(7B)-C(8)-P(9)	116.9(7)	
Pd-P(9)-C(8)	114.4(2)	Pd-P(9)-C(91A)	117.0(1)	
C(8)-P(9)-C(91A)	103.6(2)	Pd-P(9)-C(91B)	110.0(2)	
C(8)-P(9)-C(91B)	103.1(2)	C(91A)-P(9)-C(91B)	107.6(2)	
O(12)-Cl(11)-O(13)	108.7(3)	O(12)-Cl(11)-O(14)	109.1(3)	
O(13)-Cl(11)-O(14)	109.1(3)	O(12)-Cl(11)-O(15)	110.0(3)	
O(13)-Cl(11)-O(15)	109.9(3)	O(14)-Cl(11)-O(15)	110.0(3)	

Table 4		
Selected bond lengths (Å) and bond angles (°) for [Pt(asa)CI1CIO

2.402(1)	C(4)-S(5)	1,787(15)
2.249(4)	S(5)-C(6)	1.829(24)
2.404(1)	C(6)-C(7A)	1.458(26)
2.314(3)	C(6)-C(7B)	1.431(33)
1.940(12)	C(7A)-C(8)	1.465(31)
1.926(9)	C(7B)-C(8)	1.445(28)
1.950(10)	C(8)-As(9)	1.964(14)
1.439(16)	As(9)-C(91A)	1.930(9)
1.412(17)	As(9)-C(91B)	1.940(14)
91.9(1)	As(1)-Pt-As(9)	171.2(1)
94.U(1)	As(1)-Pt-Cl(10)	88.2(1)
171.1(1)	As(9)-Pt-Cl(10)	87.0(1)
114.0(3)	Pt-As(1)-C(11A)	114.0(3)
106.6(4)	Pt-As(1)-C(11B)	113.7(3)
103.7(5)	C(11A)-As(1)-C(11B)	103.8(4)
115.3(9)	C(2)-C(3)-C(4)	122.5(10)
121.6(12)	Pt-S(5)~C(4)	114.8(5)
112.1(6)	C(4)-S(5)-C(6)	92.2(9)
127.5(18)	S(5)-C(6)-C(7B)	122.1(25)
117.4(21)	C(6)-C(7B)-C(8)	120.6(21)
110.5(12)	C(7B)-C(8)-As(9)	122.0(15)
115.5(4)	Pt-As(9)-C(91A)	110.1(3)
101.8(5)	Pt-As(9)-C(91B)	117.4(3)
104.5(6)		
	2.402(1) 2.249(4) 2.404(1) 2.314(3) 1.940(12) 1.926(9) 1.950(10) 1.439(16) 1.412(17) 91.9(1) $\frac{9}{4.0}(1)$ 171.1(1) 171.1(1) 174.0(3) 106.6(4) 103.7(5) 115.3(9) 121.6(12) 112.1(6) 127.5(18) 117.4(21) 110.5(12) 115.5(4) 101.8(5) 104.5(6)	2.402(1) $C(4)-S(5)$ $2.249(4)$ $S(5)-C(6)$ $2.249(4)$ $S(5)-C(6)$ $2.404(1)$ $C(6)-C(7A)$ $2.314(3)$ $C(6)-C(7B)$ $1.940(12)$ $C(7A)-C(8)$ $1.926(9)$ $C(7B)-C(8)$ $1.926(9)$ $C(7B)-C(8)$ $1.950(10)$ $C(8)-As(9)$ $1.439(16)$ $As(9)-C(91A)$ $1.412(17)$ $As(9)-C(91B)$ $91.9(1)$ $As(1)-Pt-As(9)$ $9.4.0(1)$ $As(1)-Pt-Cl(10)$ $171.1(1)$ $As(9)-Pt-Cl(10)$ $174.0(3)$ $Pt-As(1)-C(11B)$ $103.7(5)$ $C(11A)-As(1)-C(11B)$ $103.7(5)$ $C(11A)-As(1)-C(11B)$ $115.3(9)$ $C(2)-C(3)-C(4)$ $112.1(6)$ $C(4)-S(5)-C(6)$ $127.5(18)$ $S(5)-C(6)-C(7B)$ $117.4(21)$ $C(6)-C(7B)-C(8)$ $110.5(12)$ $C(7B)-C(8)-As(9)$ $115.5(4)$ $Pt-As(9)-C(91B)$ $104.5(6)$ $21.5(9)$

Table 5

Torsional angles (°) around the six-membered chelate rings

Atoms	M = Pd, E = P	M = Pt, E = As
M-E(1)-C(2)-C(3)	- 54.4(4)	-44.3(7)
E(1)-C(2)-C(3)-C(4)	73.6(6)	60(1)
C(2)-C(3)-C(4)-S(5)	- 73.5(6)	-68(1)
C(3)-C(4)-S(5)-M	54.8(5)	56.6(9)
C(4)-S(5)-M-P(1)	-32.7(2)	-35.8(4)
S(5)-M-P(1)-C(2)	33.7(2)	32.4(3)
M-S(5)-C(6)-C(7A)	-15.3(9)	-7(2)
S(5)-C(6)-C(7A)-C(8)	-53(1)	-57(2)
C(6)-C(7A)-C(8)-E(9)	81.1(8)	71(2)
C(7A)-C(8)-E(9)-M	-34.9(6)	-26(1)
C(8)-E(9)-M-S(5)	-18.5(3)	-19.8(4)
E(9)-M-S(5)-C(6)	40.1(4)	33.6(8)
M-S(5)-C(6)-C(7B)	-74.1(5)	-63(2)
S(5)-C(6)-C(7B)-C(8)	94(1)	67(3)
C(6)-C(7B)-C(8)-E(9)	-76(1)	-42(3)
C(7B)-C(8)-E(9)-M	31.7(7)	23(2)

can compete with conformational forces [11]. The two different manners of forming C-H···O hydrogen bonds make the energy of the (cb) form close to that of the (cc) form. From the occupations of (cb) and (cc) sites, the equilibrium constants for the cc \Rightarrow cb interconversion can be deduced which allows values of ΔG° , -1.9 kJ mol⁻¹ and -1.5 kJ mol⁻¹ in the complexes [Pd(psp)Cl]ClO₄ and [Pt(asa)Cl]ClO₄ respectively, for the conformational interconversion to be calculated. During the cc \Rightarrow cb interconversion, the C(7) atom moves 1.47 Å in [Pd(psp)Cl]ClO₄ and 1.12 Å in [Pt(asa)Cl]ClO₄. There is less movement of the C(7) atom in [Pt(asa)Cl]ClO₄ because the longer Pt-As and As-C bonds force the chelate rings of $[Pt(asa)Cl]ClO_4$ to adopt a flatter conformation than in the case of $[Pd(psp)Cl]ClO_4$,

4. Supplementary material

Tables listing complete bond distances, bond angles and anisotropic parameters for $[Pd(psp)Cl]ClO_4$ and $[Pt(asa)-Cl]ClO_4$ are available from the authors on request.

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