Chiral effects on a fluxional ligand: chiral diphosphine platinum(II) complexes with thiacrowns †

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We report the syntheses, crystal structures, and spectroscopic properties for two new Pt(II) heteroleptic complexes containing the chiral diphosphine ligands R-BINAP and R,R-Chiraphos along with crown trithioether [9]aneS$_3$ (1,4,7-trithiacyclononane). The complexes have the general formula [Pt([9]aneS$_3$)(P$_2$)](PF$_6$)$_2$ (P$_2$ = R-BINAP or R,R-Chiraphos) and form similar structures in which the Pt(II) center is surrounded by a *cis* arrangement of the two P donors from the diphosphine chelate and two sulfur atoms from the trithioether macrocycle. The third sulfur in each complex shows a long distance interaction with the metal, resulting in an elongated square pyramidal structure with platinum–axial sulfur distances ranging from 2.695(3) to 2.802(2) Å with the Chiraphos complex showing the shorter distance. The X-ray crystal structure of the Chiraphos complex exhibits an unusual example of co-crystallization of solid state conformational diastereoisomers within the same unit cell. The unit cell consists of two crystallographically independent complex cations which are related by a conformational change around one carbon–carbon bond in the [9]aneS$_3$ ligand. The ^{195}Pt NMR chemical shifts for both complexes fall in the range of −4167 to −4452 ppm, consistent with a *cis*-PtS$_2$P$_2$ coordination sphere. The effects of chirality of the diphosphine are most notably seen in the ^{13}C NMR spectrum of the fluxional [9]aneS$_3$ ligand, resulting in two separate resonances as opposed to the single one which has always been observed in Pt complexes containing achiral diphosphines.

Introduction

Chiral diphosphine ligands have received considerable attention in large part due to their roles in enantioselective transformations.[1] Metal complexes containing well-designed C_2-symmetric diphosphines such as BINAP and Chiraphos (see Chart 1) have proven extremely useful in a variety of homogenous catalysis applications.[2] Our group is involved in the study of heteroleptic platinum(II) complexes containing both diphosphine and macrocyclic thioether ligands such as 1,4,7-trithiacyclononane ([9]aneS$_3$).[3] Although homoleptic Pt(II) crown thioether complexes have been well-characterized, research with heteroleptic thiacrown complexes containing phosphines and other ligands is far less developed.[4] The value of the P–M–P bite angle has been shown to correlate with the catalytic activity observed for a variety of diphosphine complexes,[5] and we recently examined this feature in the presence of a coordinated crown thioether for a number of achiral diphosphine complexes.[6] In the current study, we extend our work to include Pt(II) crown thioether complexes containing chiral diphosphine ligands such as those used in enantioselective catalysis. The trithioether [9]aneS$_3$ undergoes a rapid intramolecular ligand exchange process in virtually every one of its platinum and palladium complexes,[6–8] and we now report how the chiral environment of the diphosphine affects the dynamic NMR spectra of the fluxional coordinated thiacrown.
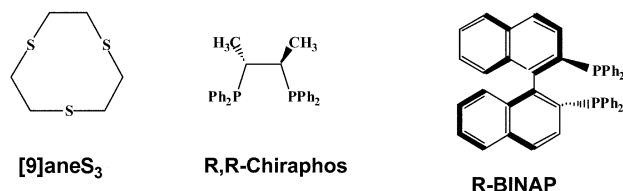

**Chart 1** Ligands used in this work.

Results and discussion

Syntheses and spectroscopy

The two complexes are readily prepared by a ligand substitution reaction using the appropriate stoichiometric equivalent of diphosphine and [Pt([9]aneS$_3$)Cl$_2$], resulting in chloride ion displacement by the diphosphine and subsequent isolation as the hexafluorophosphate salt. Their composition is confirmed using a variety of spectroscopic techniques and elemental analysis. The proton NMR spectra for the two complexes shows resonances for all types of protons associated with both the thioether and diphosphine ligands in their appropriate ratios and splittings. Furthermore, ^{13}C DEPT experiments confirm carbon connectivity. A distinct ABCD four peak splitting pattern of the twelve methylene protons of the [9]aneS$_3$ ligand is observed. This splitting pattern arises from the effects of the chiral diphosphine ligand since complexes involving achiral diphosphines such as dppe (1,2-bis(diphenylphosphino)ethane) display AA′BB′ patterns for [9]aneS$_3$ in their proton NMR spectra.[6,7] The ^{13}C peaks of the [9]aneS$_3$ ligand in the BINAP complex are shifted downfield compared to the Chiraphos complex.

The ^{195}Pt NMR spectra for the two complexes show the anticipated triplet splitting pattern and fall in the −4200 to −4600 ppm range previously observed for *cis*-PtP$_2$S$_2$ complexes.[3] The BINAP complex shows the more deshielded Pt, possibly due to the aromaticity of the BINAP ligand which results in enhanced Lewis acidity of its metal center. The values of the ^1J (^{195}Pt–^{31}P) coupling constants for the complexes occur in the range 3150 to 3300 Hz, typical values for diphosphine/thiacrown Pt complexes. The larger P–Pt–P chelate bite angle (89.66(5)° *vs.* 84.37(9)$_{ave}$ Å) is responsible for the increased coupling observed in the BINAP complex as we have previously noted a strong correlation between these two parameters in other diphosphine/thioether complexes.[3] The ^{31}P NMR spectra for the complexes show the expected single resonance, and the chemical shifts are highly deshielded (over 40 ppm) compared to the free ligands.

Both complexes display ^{13}C NMR spectra consistent with fluxional behavior of the [9]aneS$_3$ ligand in solution, and this fluxionality of the [9]aneS$_3$ ligand is a general property of the approximately 40 Pd(II) and Pt(II) complexes containing this ligand.[6] The fluxionality has been proposed to occur *via* rapid intramolecular exchanges of sulfur atoms (1,4-metallotropic shift).[7] However, for the first time, this fluxionality is observed in a chiral environment created by the coordinated diphosphine as shown in Fig. 1. Consequently, the six [9]aneS$_3$ methylene carbons do not appear as a singlet resonance, but rather as two peaks of equal intensity (three carbons each). We observe no significant change in the spectra upon cooling to −30 °C. The effect of the chirality of the diphosphine chelate is transferred through the Pt(II) center and can be observed in the ^{13}C NMR spectrum of the coordinated, fluxional trithioether ligand, an observation which further supports the intramolecular metallotropic shift mechanism.
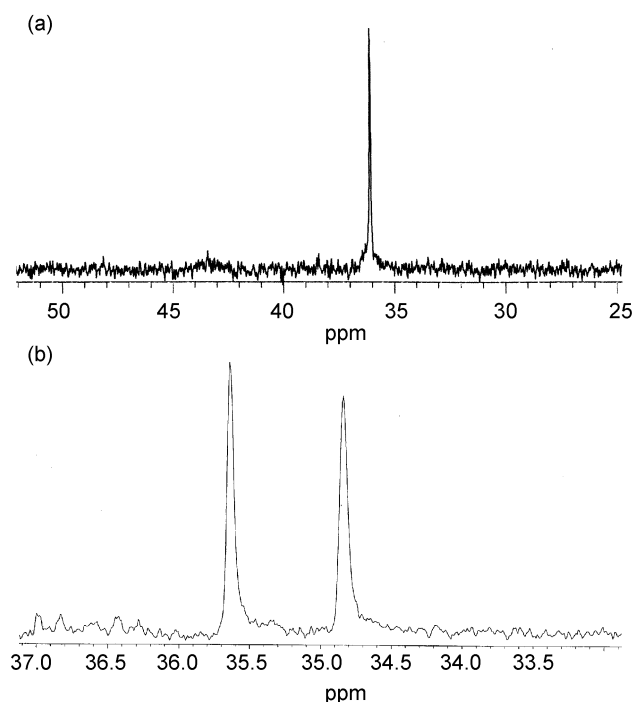
Fig. 1 ^{13}C NMR spectra, [9]aneS$_3$ region only. (a) [Pt([9]aneS$_3$)-(dppe)](PF$_6$)$_2$: fluxional [9]aneS$_3$ in an achiral diphosphine environment. (b) [Pt([9]aneS$_3$)(R,R-Chiraphos)](PF$_6$)$_2$: fluxional [9]aneS$_3$ in a chiral diphosphine environment.

Structures

The complex [Pt([9]aneS$_3$)(R-BINAP)](PF$_6$)$_2$ crystallizes in the chiral space group $P2_12_12_1$ and forms an elongated square pyramidal structure [*cis*-S$_2$P$_2$ + S$_1$]. An ORTEP[16] perspective is shown in Fig. 2 and bond lengths and distances presented in Table 1. One nitromethane solvent molecule is also incorporated into the crystal lattice. Here two sulfur atoms and two phosphorus atoms form a distorted *cis* square planar array around the Pt(II) while the third sulfur from the [9]aneS$_3$ (S1) interacts from a much longer distance of 2.8019(17) Å, over 0.45 Å greater than the two Pt–S equatorial distances, but still much less than the sum of the platinum(II) and sulfur van der Waals radii (3.50 Å).[9]

The complex [Pt([9]aneS$_3$)(R,R-Chiraphos)](PF$_6$)$_2$ also forms a similar elongated square pyramidal structure, crystallizing in the chiral space group $P2_1$. ORTEP perspectives of the two independent complex cations are shown in Fig. 3a and 3b and their bond lengths and distances are presented in Table 1. There are two independent cations per unit cell. The two complexes are related by a conformational change around the C–C bond in the five-membered chelate ring of the coordinated [9]aneS$_3$

Table 1   Selected bond distances (Å) and angles (°) for [Pt([9]aneS$_3$)-(R-BINAP)](PF$_6$)$_2$·CH$_3$NO$_2$ (**1**),   [Pt(δ-[9]aneS$_3$)(R,R-Chiraphos)]-(PF$_6$)$_2$ (**2a**), and [Pt(λ-[9]aneS$_3$)(R,R-Chiraphos)](PF$_6$)$_2$ (**2b**)

	(**1**)	(**2a**)	(**2b**)
Pt–S$_{eq}$	2.3740(16)	2.358(3)	2.355(2)
	2.3656(10)	2.383(2)	2.384(3)
Pt–S$_{axial}$	2.8019(17)	2.695(3)	2.703(3)
Pt–P$_{eq}$	2.2784(13)	2.259(2)	2.255(2)
	2.3082(13)	2.269(3)	2.270(3)
P–P distance	3.233(1)	3.037(2)	3.042(3)
S$_{eq}$–Pt–S$_{eq}$	87.13(6)	88.17(11)	88.04(10)
P(1)–Pt–P(2)	89.66(5)	84.22(9)	84.52(10)
P(1)–Pt–S$_{eq}$	86.07(4)	94.79(11)	91.90(9)
	161.28(6)	173.54(10)	170.50(11)
P(2)–Pt–S$_{eq}$	164.99(5)	166.07(9)	164.12(9)
	92.46(5)	109.38(8)	92.97(10)
S$_{eq}$–Pt–S$_{axial}$	83.04(6)	85.50(9)	85.25(10)
	81.69(5)	84.48(9)	83.63(9)
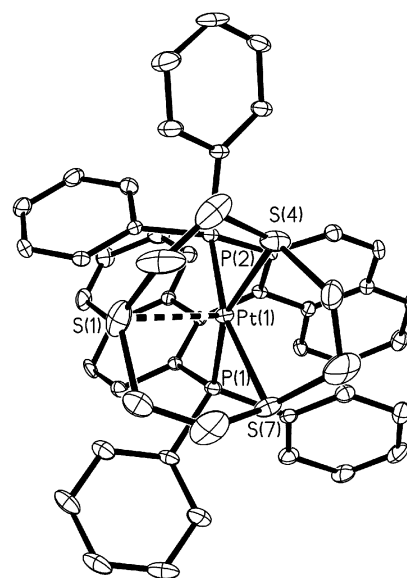
Fig. 2   ORTEP perspective of the cation in [Pt([9]aneS$_3$)(R-BINAP)]-(PF$_6$)$_2$·CH$_3$NO$_2$, (**1**).

ligand (carbons C5 and C6). We have used the δ and λ notation, originally developed for conformational stereoisomers of chelate rings, in Fig. 3a and 3b, respectively, to designate the two diastereoisomers.[10] The four phenyl rings of the R,R-Chiraphos are eclipsed, not staggered, as is commonly observed in other aryl diphosphine complexes.[6] The observed Pt–axial sulfur distances in the R,R-Chiraphos complexes are among the shortest Pt–S distances for this series of compounds, with values of 2.695(3) and 2.703(3) Å, and the values are considerably shorter than those found in the BINAP complex.

As noted, however, these two complexes are indeed diastereoisomers rather than enantiomers. The chirality of the R,R-Chiraphos ligand is fixed so that the conformational change within the [9]aneS$_3$ ligand results in conformational diastereoisomers. Accordingly, different values for the bond angles and distances are observed for each of the two cations. In solution, the two conformational diastereoisomers rapidly interconvert so their resolution is a result of their co-crystallization in the same lattice.[11] The equal co-crystallization of two conformational diastereoisomers within the same unit cell is unusual. Other examples of this phenomenon typically exhibit separate crystallization of the diastereoisomers, or, if both are present in the same unit cell, they are found in unequal amounts.[12] The importance of the chelate ring in Chiraphos and its influence on other bound ligands (constructive and destructive interactions) has recently been highlighted by Gangé and co-workers.[13] As
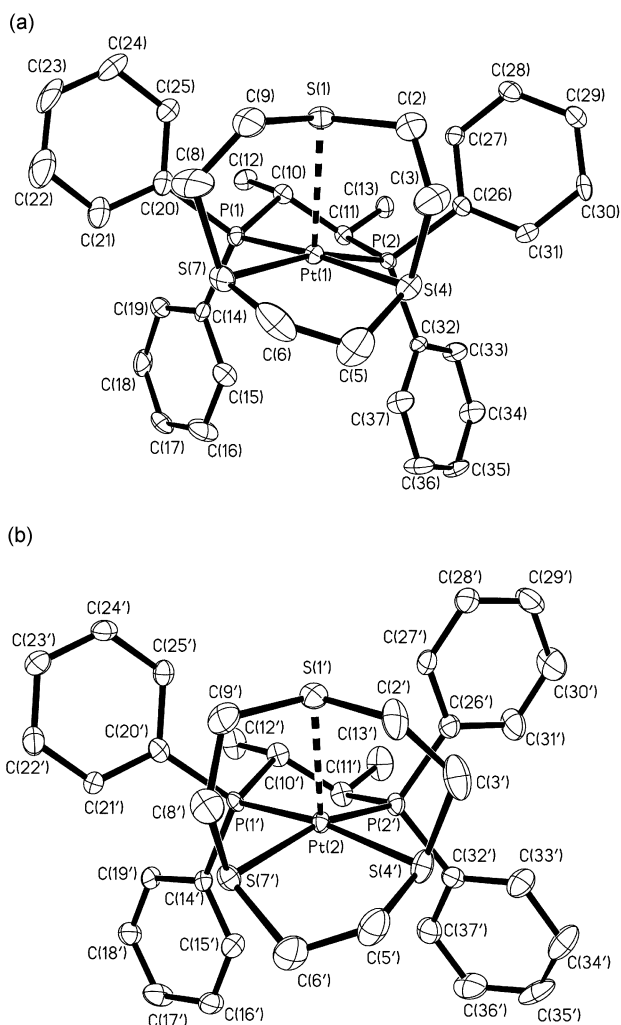
Fig. 3 (a) ORTEP perspective of the cation in [Pt(δ-[9]aneS₃)(R,R-Chiraphos)](PF₆)₂, (**2a**). (b) ORTEP perspective of the cation in [Pt(λ-[9]aneS₃)(R,R-Chiraphos)](PF₆)₂, (**2b**).

expected based upon its conformational preferences, the R,R-Chiraphos ligand adopts exclusively and rigidly the λ conformer in both structures. We would also like to note that the analogous complex ([Pt([9]aneS₃)(dppe)](PF₆) containing the achiral diphosphine, dppe, does not crystallize in this manner, but instead exclusively forms a racemic crystal.[3]

Conclusions

The two chiral diphosphine ligands, R-BINAP and R,R-Chiraphos, readily react with [Pt([9]aneS₃)Cl₂] to form heteroleptic thioether–phosphine complexes with elongated square pyramidal structures [S₂P₂ + S₁] in the solid state. The chiral effects of the diphosphines are seen in the ¹³C NMR spectra of the bound [9]aneS₃ ligand, resulting in two resonances for the fluxional ligand. The Chiraphos complex crystallizes in an unusual fashion to form two independent cations which are conformational diastereoisomers.

Experimental

All solvents and reagents including enantiomerically pure diphosphine ligands were purchased from Aldrich Chemical Company and used as received. The starting complex [Pt([9]-aneS₃)Cl₂] was prepared by the published methods.[8] Elemental analyses were performed by Atlantic Microlab, Inc. of Atlanta, Georgia. Fourier transform infrared spectra were obtained as KBr powders using a Galaxy FT IR 5000 spectrophotometer

equipped with an ATR accessory. Ultraviolet-visible spectra were obtained in acetonitrile using a Varian DMS 200 UV-visible spectrophotometer. $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CD_3NO_2 for both the deuterium lock and reference. All observed carbon resonance connectivity was confirmed *via* DEPT experiments. Platinum-195 NMR spectra (proton-decoupled) were recorded near 64.208 MHz using aqueous solutions of $[PtCl_6]^{2-}$ (0 ppm) as an external reference and delay time of 0.01 seconds. Referencing was verified *versus* authentic samples of $[PtCl_4]^{2-}$ which was found to have a chemical shift at −1626 ppm, in agreement with the reported value of −1624 ppm.[14] Phosphorus-31 NMR spectra (proton-decoupled) were measured at 121.470 MHz, and referencing was done using phosphoric acid (0 ppm) as an external standard.[15]

Syntheses

[Pt([9]aneS₃)(R-BINAP)](PF₆)₂·CH₃NO₂, (1). A mixture of [Pt([9]aneS₃)Cl₂] (36.0 mg, 0.0806 mmol) and (*R*)-2,2-bis(di-phenylphosphino)-1,1-binaphthyl (R-BINAP, 50.0 mg, 0.0803 mmol) was refluxed in 32 mL of CH₃NO₂ for 2 h. The resulting solution was allowed to cool slightly before NH₄PF₆ (39.3 mg, 0.241 mmol) was added and the mixture was refluxed for an additional 30 min. The solution was hot-filtered and concentrated on a rotary evaporator. Diethyl ether was diffused into this concentrated solution to form yellow crystals (75.0 mg, 69.2%) of [Pt([9]aneS₃)(R-BINAP)](PF₆)₂·CH₃NO₂ suitable for X-ray diffraction. Anal. Calcd for $C_{51}H_{47}F_{12}NO_2P_4PtS_3$: C, 45.36, H, 3.51, S, 7.13. Found: C, 45.48; H, 3.53, S, 7.15%. Electronic spectrum (MeCN): λ_{max} at 425 nm (ε = 550 dm³ mol⁻¹ cm⁻¹), and at 375 nm (ε = 23,500 dm³ mol⁻¹ cm⁻¹). FT-IR (KBr, cm⁻¹): 3056, 3012, 2961, 1948, 1571, 1507, 1482, 1438, 1375, 1313, 1261, 1224, 1192, 1167, 1105, 1029, 1004, 840 (s, PF₆⁻), 759, 701, 670, 626, 564, 500. ¹H-NMR (CD₃NO₂), δ (ppm): P*Ph₂*: 7.79–7.68 (m, 20 H); *BINAP*: six multiplets at 8.18, 7.99, 7.15, 6.95, 6.87, 6.64 (2 H each, 12 H); *[9]aneS₃*: multiplets at 3.33 (3 H), 3.08 (3 H), 2.83 (3 H), and 2.32 (3 H). $^{13}C\{^1H\}$-NMR (CD₃NO₂), δ (ppm): P*Ph₂* and *BINAP*: 135.9–128.0 (m, 44 C), *[9]aneS₃*: 37.60 (s, 3 C) and 36.34 (s, 3C). $^{195}Pt\{^1H\}$-NMR (CD₃NO₂), δ ($v_{1/2}$): triplet at −4167 ppm (52 Hz) ($^1J_{PtP}$ = 3296 Hz). $^{31}P\{^1H\}$-NMR (CD₃NO₂), δ: singlet at 5.78 ppm with ^{195}Pt satellites ($^1J_{PtP}$ = 3297 Hz).

[Pt([9]aneS₃)(R,R-Chiraphos)](PF₆)₂, (2). A mixture of [Pt([9]aneS₃)Cl₂] (52.0 mg, 0.117 mmol) and (2*R*,3*R*)-bis-(diphenylphosphino)butane (R,R-Chiraphos, 50.0 mg, 0.117 mmol) was refluxed in 46 mL of CH₃NO₂ for 2 h. The resulting solution was allowed to cool slightly before NH₄PF₆ (57.0 mg, 0.350 mmol) was added, and the mixture was refluxed for an additional 30 min. The solution was hot-filtered and concentrated on a rotary evaporator. Diethyl ether was then diffused into this concentrated solution to produce yellow crystals (33 mg, 25%) of [Pt([9]aneS₃)(R,R-Chiraphos)](PF₆)₂ suitable for X-ray diffraction. Anal. Calcd for $C_{34}H_{40}F_{12}P_4PtS_3$: C, 37.70, H, 3.69, S, 8.81. Found: C, 37.50; H, 3.77 S, 9.00%. Electronic spectrum (MeCN): λ_{max} at 376 nm (ε = 350 dm³ mol⁻¹ cm⁻¹) and at 266 nm (ε = 17,400 dm³ mol⁻¹ cm⁻¹). FT-IR (KBr, cm⁻¹): 3062, 2987, 2936, 2886, 1621, 1577, 1483, 1438, 1420, 1319, 1187, 1105, 1004, 935, 841 (s, PF₆⁻), 759, 703, 671, 620, 564. ¹H-NMR (CD₃NO₂), δ (ppm): P*Ph₂*: 7.82–7.70 (m, 20H); PC*H*(CH₃)C*H*(CH₃)P: 3.52 (m, 2 H); PCH(C*H₃*)CH(C*H₃*)P: 1.30 (m, 6 H); *[9]aneS₃*: 3.47 (m, 3 H), 3.01 (m, 3 H), 2.77 (m, 3 H), 2.41 (m, 3 H). $^{13}C\{^1H\}$-NMR (CD₃NO₂), δ (ppm) P*Ph₂*: multiplets at 136.9, 136.8, 135.2, 135.0, 134.0, 131.5, 131.2, 131.0 (20); P*C*H(CH₃)*C*H(CH₃)P: 39.6 (d ($^1J_{PC}$ = 52 Hz, 2C), PCH(*C*H₃)CH(*C*H₃)P: 13.6 (br s, 2C); *[9]aneS₃*: 36.4 (s, 3 C), 34.2 (s, 3 C). $^{195}Pt\{^1H\}$-NMR (CD₃NO₂), δ ($v_{1/2}$): triplet at

Table 2 Crystallographic data for [Pt([9]aneS$_3$)(R-BINAP)](PF$_6$)$_2\cdot$CH$_3$NO$_2$, (**1**) and [Pt([9]aneS$_3$)(R,R-Chiraphos)](PF$_6$)$_2$, (**2**)

	(**1**)	(**2**)
Empirical formula	C$_{51}$H$_{47}$F$_{12}$NO$_2$P$_4$PtS$_3$	C$_{34}$H$_{40}$F$_{12}$P$_4$PtS$_3$
M	1349.05	1091.81
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a/Å	11.2412(2)	10.5577(1)
b/Å	14.4595(2)	28.7620(4)
c/Å	31.3436(6)	13.8326(2)
β/°	90	102.457(1)
V/Å^3	5143.42(15)	4101.53(9)
Z	4	4
Radiation (λ/Å)	0.71073	0.71073
ρ_{calcd}/g cm^{-3}	1.742	1.768
μ/mm^{-1}	3.061	3.810
T/K	173(2)	173(2)
No. of reflns. collected	26846	24649
No. of unique reflns.	9043	13659
R^a	0.0282	0.0413
$R_w{}^b$	0.0379	0.0927
GOF	0.986	0.986

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}$.

−4452 (72 Hz) ppm ($^1J_{PtP}$ = 3144 Hz). ^{31}P{^{1}H}-NMR (CD$_3$NO$_2$), δ: singlet at 46.54 ppm with ^{195}Pt satellites ($^1J_{PtP}$ = 3141 Hz).

Crystallographic data collection and processing

The details of the data collection appear in Table 2 and selected bond distances and angles for both structures appear in Table 1. The intensity data for the two compounds were collected on a Siemens SMART 1K CCD diffractometer [16,17] and their structures were solved using direct methods.[16]

CCDC reference numbers 211787 and 211788.

See http://www.rsc.org/suppdata/dt/b3/b306663k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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