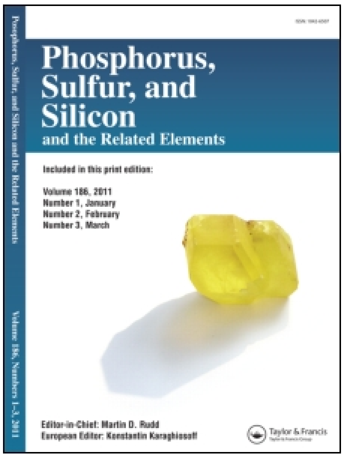

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Ionic Platinum(II)-Imidobis(diphenylthiophosphinato) Complexes: Preparation, Structure, and Thermal Behavior

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IONIC PLATINUM(II)–IMIDOBIS(DIPHENYLTHIOPHOSPHINATO) COMPLEXES: PREPARATION, STRUCTURE, AND THERMAL BEHAVIOR

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The $PPh_2P(S)NHP(S)PPh_2$ ($dppaS_2$) ligand reacts with the starting complexes $PtCl_2$(L-L) (L-L = $Ph_2PCH_2PPh_2$), (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), and $NaClO_4{\cdot}H_2O$. Final products are monomeric complexes, and their formulas are [Pt(L-L)($dppaS_2$-H)] [(L-L = dppm(1), dppe(2), dppp(3)]. All of these have been characterized by ^{1}H, ^{13}C,$^{31}P\{^{1}H\}$ NMR, FTIR, and elemental analysis. These complexes were also examined by TGA, DTA, and DSC analysis. Complexes 2 and 3 were crystallographically characterized.

Keywords Aminophosphine complexes; platinum complexes; phosphines; thermogravimetric analysis; X-ray crystal structures

INTRODUCTION

Recent results show that the coordination chemistry of [$R_2P(X)NHP(Y)R_2'$] (R = R′ = Me, Pr, Ph; X=Y=O, S, Se)–type ligands has been widely investigated. There are two possible structures on the coordination of these ligands: natural chelating ligands or a chelating anion. Anionic functional ligands of this type are analogues of the more familiar β-diketonate ligands, most notably aceylacetonate (acac).[1–4] On the other hand, dichalcogenoimidodiphosphinato anions $[R_2P(X)NP(Y)R_2']^-$ (R = R′ = Me, Pr, Ph; X=Y=O, S, Se) coordinate to the metals forming inorganic (carbon-free) chelate rings. Such chelates are widely used in metal extraction, catalytic, and medicinal applications. The interest in metal complexes of these ligands is mainly due to the unusual flexibility of the SPNPS system. This allows the formation of chelate rings in which the ligand usually exhibits a symmetrical coordination pattern through both sulfur atoms.[5,6]

Many current studies on metal complexes of these ligands have been reported.[7–9] Silvestru et al. have suggested a cobalt complex of the type $[Co\{(Me_2(S)P)_2N\}_2]$.[6] A manganese complex, in which $dppaS_2$ ligand forms a six-membered chelate ring, was reported

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by Simnan and Gray.[10] The structure consists of monomeric units of $Mn(SPPh_2NPPh_2S)_2$ in which the central metal is in approximately tetrahedral coordination to four sulfur atoms in this compound. Another example of the metal complexes of this type of ligand is also the gold complex that was synthesized by Laguna et al. in 1988.[11] The crystal and molecular structure of $Bi(SPPh_2NPh_2PS)_3$, which is the first structural example of a main group element coordinated to this particular ligand, was presented by Williams et al.[12] Furthermore, this is the first structural example of a tris complex of any metal with this ligand. $Ni[(OPR'_2)(SPR_2)N]_2$ (R, R′ = Ph, Me)–type complexes were obtained in good yields by reacting $NiCl_2{\cdot}6H_2O$ and the alkaline salts of the corresponding tetraorganomonothioimidodiphosphinic acids.[13] The reaction of $[Ru_3(CO)_{12}]$ with $(SPPh_2)_2NH$ produced two different complexes in which, for both of them, one of the P=S bonds of the ligand has been broken while other the P=S group is bonded through the sulfur atom to two ruthenium atoms.[14] Although a number of platinum, palladium, copper, cobalt, manganese, gold, and bismuth complexes have been reported, only a few of them are ionic complexes.[15–17]

In recent years, a number of cationic rhodium, iridium, and osmium complexes containing the phosphine and diphosphine ligands have been known as very active hydrogenation catalysts. The catalysis results show that the cationic complexes are more efficient catalyst precursors for the hydrogenation and intramolecular cycloaddition reactions.[18–20]

In this study, we report three cationic platinum(II) complexes containing diphosphine and $[Ph_2P(S)N(S)PPh_2]^-$ ligands of type $[Pt(L\text{-}L)(dppaS_2\text{-}H)]ClO_4$ [L-L = dppm(**1**), dppe(**2**), dppp(**3**)]. All of these complexes have been fully characterized by ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR, FTIR, and elemental analysis. In addition, complexes **2** and **3** were also crystallographically characterized. Thermal behavior of these complexes was investigated by TGA, DTG, and DSC methods.

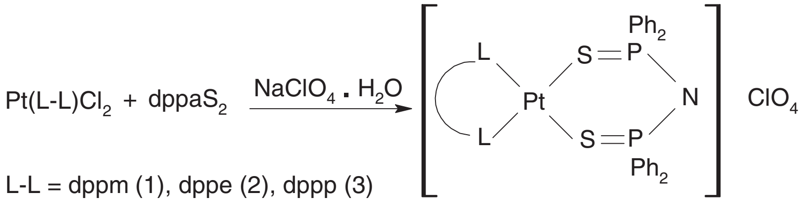
RESULTS AND DISCUSSION

NMR Spectral Studies

In this work, the starting complexes, $PtCl_2(L\text{-}L)$ (L-L = dppm, dppe, dppp) and $dppaS_2$ ligand were synthesized according to the literature (see the Experimental section). The starting complexes have only a singlet with ^{195}Pt satellites, the δP values of which are are −63.8, 43.2, −4.7, and 58.0 ppm, respectively, in $^{31}P\{^1H\}$ NMR spectra. The chemical shifts of phosphorus in dppm and dppp ligands are upfield of that of the free ligands, whereas the chemical shift of phosphorus in dppe is a large downfield shift relative to the free ligand in starting complexes.[21] In contrast with our results, a small downfield phosphorus shift should be observed in five-membered ring complexes, by the consideration of the C—P—C angle. So, it has been seen that the angle deformations are probably not responsible for the anomalous ^{31}P shift for five-membered ring complexes.[22] $^1J(P{-}Pt)$ values of starting complexes were 3078 Hz $[(PtCl_2(dppm)]$, 3606 Hz $[PtCl_2(dppe)]$, and 3400 Hz $[PtCl_2(dppp)]$. These obtained results were comparable with the literature.[23,24]

Three new ionic platinum(II) complexes, $[Pt(L\text{-}L)(dppaS_2\text{-}H)]ClO_4$ (**1**, **2**, **3**), were prepared by the mixing of solution of $PtCl_2(L\text{-}L)$ complexes in CH_2Cl_2 and $dppaS_2$ ligand and $NaClO_4$ H_2O salt in $(CH_3)_2CO$ (Scheme 1). (*Caution:* There is potential explosion hazard arising from the use of perchlorates in the presence of organic material, so quantities should be kept small and heating, especially to dryness, should be avoided.)

The $^{31}P\{^1H\}$ NMR spectra of these complexes show two doublets each with ^{195}Pt satellites. The phosphorus of the P=S groups experiences an increase in shielding upon



Scheme 1

coordination, while the value of δ for the free dppaS_2 ligand is indicated at 58.0 ppm. The δP values for the complexes are 32.8, 34.0, and 33.7 ppm in complexes **1**, **2**, and **3**, respectively. ^{2}J(P-Pt) values of the dppaS_2 ligand are suitable with the similar complexes in the literature.[25,26]

δP values of these diphosphines in complexes **1**, **2**, and **3** are −54.8 ppm (**1**), 53.6 ppm (**2**), and −0.8 ppm (**3**). These values are shifted to downfield according to the starting complexes. The phosphorus chemical shift in a five-membered ring is unusually large deshielding. This observation is not suitable according to bond angle consideration and ring strain. It has been seen that the phosphorus chemical shift values are invaluable according to structural assigments in phosphine-transition metal complexes.[22] ^{1}J(P-Pt) values of diphosphine ligands in complexes **1**, **2**, and **3** are smaller than that of the starting complexes, which are 2640.6, 2972.4, and 2985.3 Hz.

The ^{1}H and ^{13}C NMR spectra contains signals assigned to phenyl groups and $P(CH_2)_nP$ ($n = 1, 2, 3$) of diphosphines and dppaS_2-H. The values of these signals are in accordance with the chelate compounds in the literature.[27–31]

IR Spectral Studies

In solid state, the IR spectra of the complexes (**1**–**3**), the characteristic absorption of $\upsilon(P = S)$ groups are at 571.1, 576.1, and 570.5 cm^{-1}. These absorptions are shifted to the lower frequencies according to the free ligand, dppaS_2, absorption, which is at 612.9 cm^{-1}. This shows that the ligand is coordinating to the Pt(II) center via S donor atoms in the complexes. IR spectra of the free acid, dppaS_2, exhibits absorption of medium intensity at 2630.8 cm^{-1} and very strong absorption at 922.0 cm^{-1}, which were assigned to the υ_{sym}(N—H) stretching vibration and the $\upsilon_{as}(P_2NH)$ strecthing vibration, respectively. In IR spectra of complexes **1**, **2**, and **3**, the presence of strong absorptions in the regions 1000–1150 cm^{-1}, assigned to the $\upsilon_{as}(P_2N)$ stretching vibrations, indicates that the dppaS_2 ligand is coordinated to the palladium center in the deprotonated form.[9] The starting complexes $PtCl_2$(L-L) have two υ(Pt-Cl) stretching vibrations, which are 305.0 and 290.0 [$PtCl_2$(dppm)], 312.0 and 293.0 cm^{-1} [$PtCl_2$(dppe)], 314.0 and 288.0 cm^{-1} [$PtCl_2$(dppp)], respectively. The absence of these peaks from the complex spectra show that the starting complexes reacted with the dppaS_2 ligand.

X-Ray Structural Analysis

The structures of complexes **2** and **3** were determined by single crystal X-ray diffraction. Crystallization of **2** from $(CH_3)_2CO/C_6H_{14}$ gave single crystals of 2 $(CH_3)_2CO$. Complex **3** has also been crystallized from $(CH_3)_2CO/(C_2H_5)O$, but it has not solvent molecule in crystal. The perspective view of complexes **2** and **3** are given Figures 1 and 2, respectively. The selected bond distances and angles are listed in Table I, and crystal data,

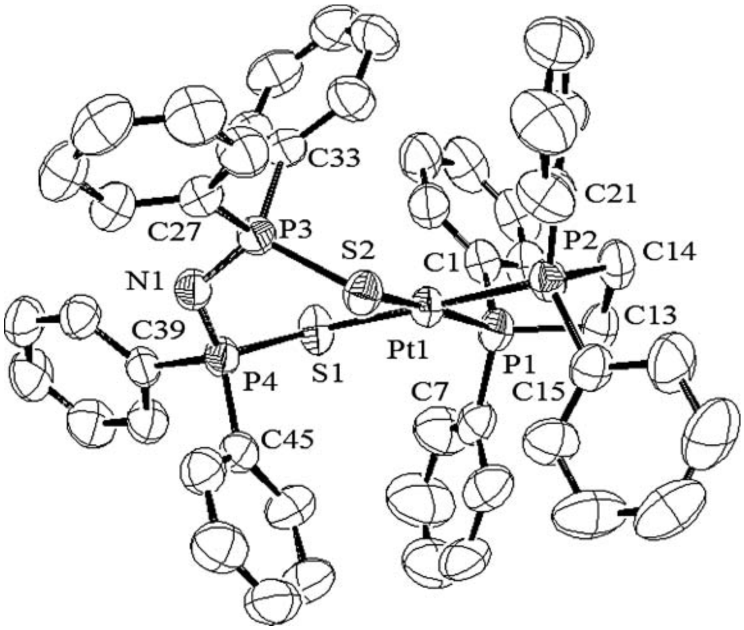


Figure 1 The perspective view of **2** (20% thermal probability). Hydrogen atoms, anions, and solvent molecules are omitted for clarity.

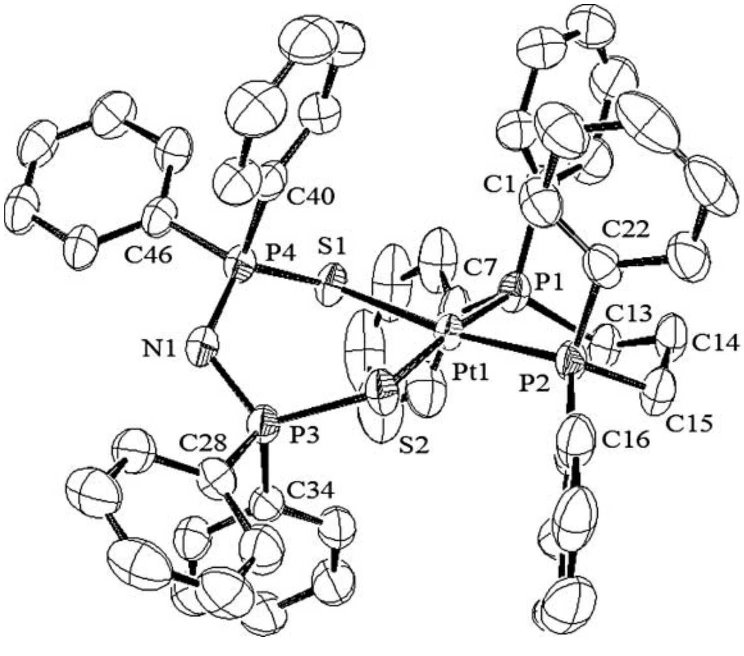


Figure 2 The perspective view of **3** (20% thermal probability). Hydrogen atoms, anions, and solvent molecules are omitted for clarity.

Table I Selected bond angles (°) and distances (Å) for [Pt(dppe)(dppaS$_2$-H)](ClO$_4$).(CH$_3$)$_2$CO (**2**) and [Pt(dppp)(dppaS$_2$-H)](ClO$_4$) (**3**)

	2	**3**
Bond distances		
Pt(1)-S(1)	2.3851 (8)	2.4136 (7)
Pt(1)-S(2)	2.4003 (8)	2.3682 (8)
P(3)-S(2)	2.0250 (11)	2.0260 (11)
P(4)-S(1)	2.0268 (11)	2.0357 (12)
Pt(1)-P(1)	2.2476 (9)	2.2625 (9)
Pt(1)-P(2)	2.2510 (8)	2.2872 (8)
Bond angles		
S(1)-Pt(1)-S(2)	101.19 (3)	98.14 (3)
P(1)-Pt(1)-S(2)	171.33 (3)	174.24 (3)
P(2)-Pt(1)-S(1)	170.21 (3)	172.28 (3)
P(1)-Pt(1)-P(2)	85.64 (3)	92.72 (3)
P(1)-Pt(1)-S(1)	85.16 (3)	85.32 (3)
P(2)-Pt(1)-S(2)	88.32 (3)	84.44 (3)

data collection, and structure-refinement parameters for complexes **2** and **3** are given in Table II. Complexes are colorless; complex **2** has a monoclinic crystal system, and complex **3** has a triclinic crystal system. Platinum atoms are distorted square-planar environments with from P(1)Pt(1)S(2) and P(2)Pt(1)S(1) are 171.33(3)° and 170.21(3)° for complex **2**, 174.24(3)° and 172.28(3)° for complex **3**.

In complex **3**, the six-membered dppp chelate ring has chair conformation with Pt(1)P(1)C(13)C(14) and Pt(1)P(2)C(15)C(14) torsion angles of −61.3(3)° and 47.3(3)°, respectively, and Pt(1) and C(14) atoms are located at −0.1585(12) ° below and 0.326(4) ° above the plane defined by the atoms P(3)-P(4)-C(13)-C(15).

Although π electron delocalization over the SPNPS fragment occurs upon chelation, the PtS$_2$P$_2$N rings are not planar. So, six-membered dppaS$_2$-H rings are twist-boat in two complexes, and are very similar to that observed in related platinum and palladium analogues in the literature.[15,17]

P-N bond lengths, N(1)-P(4) and N(1)-P(3), are 1.589(3) ° and 1.596(2) ° for **2** and 1.601(3) ° and 1.619(3) ° for **3**. P-N bond lengths show a shortening relative to the neutral ligand. This reflects partial double-bond character, and these values also are closer to those typically found for the P-N bond lengths in cyclic phosphazenes.[32,33] P—S bond lengths are 2.0250(11) and 2.0268(11) ° for complex **2** and 2.0260(11) and 2.0357(12) ° for complex **3**. These values are between single P—S and double P=S values.[6] P—S and P—N bond distances are suitable with the similar compounds in the literature.[17]

PNP bond angles are 122.36(16)° and 120.53(17)°, respectively, and the sum of the bond angles shows the trigonal planar geometry of nitrogen atoms.[17]

Pt-S bond lengths are slightly different from each other. Pt(1)-S(1) and Pt(1)-S(2) are 2.3851(8) and 2.4003(8) ° for complex **2**, and 2.4136(7) and 2.3682(8) ° for complex **3**.[17,34]

Thermogravimetric Analysis (TGA, DSC, DTG)

The thermal behavior of complexes was measured by the TGA, DSC, and DTG methods. The TGA curves corresponding to the complex **1**, **2**, and **3** are determined between the 0–1000°C temperature range. Before the thermal decomposition, melting of the complex

Table II Crystal data, data collection, and structure-refinement parameters for complexes **2** and **3**

	2	**3**
Emprical formula	$C_{50}H_{44}ClNO_4P_4PtS_2.(CH_3)_2CO$	$C_{51}H_{46}ClNO_4P_4PtS_2$
Formula weight	1199.48	1155.43
T (K)	296	296
Wavelength (A)	0.71073	0.71073
Color	Colorless	Colorless
Crystal size (mm)	0.67 × 0.34 × 0.12	0.62 × 0.46 × 0.29
Crystal system	Monoclinic	Triclinic
Space group	P21/c	P-1
Unit cell dimensions		
a (Å)	17.2855 (6)	10.9922 (4)
b (Å)	11.1696 (3)	13.1338 (5)
c (Å)	27.4448 (10)	20.8246 (7)
α (°)	90.00	72.501 (3)
β (°)	98.558 (3)	78.077 (3)
γ (°)	90.00	67.770 (3)
Vol ($Å^3$)	5239.8 (3)	2639.47 (16)
Z	4	2
D_{calc} ($Mg.m^{-3}$)	1.520	1.454
Absorption coeff. (mm^{-1})	2.978	2.951
F (0 0 0)	2408	1156
Index ranges	$-21 \leq h \leq 21$ $-13 \leq k \leq 13$ $-33 \leq l \leq 33$	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-25 \leq l \leq 25$
Theta range (°)	1.50–26.04	1.73–25.69
Goodness-of-fit on F^2	0.928	1.038
Number of data measured	10296	9819
Number of data with $[I>2\sigma(I)]$	7865	9278
$R_1[I>2\sigma(I)]$	0.0260	0.0273
$WR_2[I>2\sigma(I)]$	0.0506	0.0648

1 was observed at 290°C. From TGA, DTG, and DSC, thermal decomposition could be established in three steps for complex **1**. First step took place between 300–320°C with 40% weight loss. Second and third steps were between 325–436°C and 600–800°C with 12.7% and 8.0% weight loss, respectively. Unlike complex **1**, DSC curves of complexes **2** and **3** show vaporization peaks between 104–136°C and 107–136°C. These steps are endothermic and correspond to the moisture loss. Complex **2** was melted before decomposition at 294°C. TGA, DSC, and DTG curves indicate that thermal decomposition started at 325°C by a strong exothermal effect, and the next one took place between 680–780°C. Total weight loss was 60.0%. Decomposition of complex **3** starts at 205°C. Degradation steps are 205–266°C, 281–314°C, 314–570°C, and 660–780°C, with 67.0% total weight loss for complex **3**.

CONCLUSION

In this study, it has been reported that three cationic platinum(II) complexes containing diphosphine and$[Ph_2P(S)N(S)PPh_2]^-$ ligands. All of these complexes have been fully characterized using ^1H, ^{13}C, $^{31}P\{^1H\}$-NMR, FTIR and elemental analysis. Complexes **2** and **3** were also crystallographically characterized. Platinum atoms are distorted, square-planar environments. Six- membered dppaS_2-H rings are twist-boat in two complexes. These complexes were also examined by TGA, DTA, and DSC analysis. While complexes **1** and **2** were stable at approximately 300°C, complex **3** decomposed at 205°C.

EXPERIMENTAL

Solvents were dried according to the methods given in the literature and were purified under inert conditions.[35] All syntheses were carried using standard Schlenk tube techniques under inert atmosphere.

Dichloromethane, toluene, methanol, hexane, and diethylether were purchased from Lab-Scan; dppm, dppe, dppp, $NaClO_4 \cdot H_2O$, and acetone were purchased from Merck Chemical. The starting complex, $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene), which is used for preparing the $[PtCI_2(L\text{-}L)]$ complexes,[36] dppa ($Ph_2PNHPPh_2$), and dppaS_2 were synthesized according to the method given in the literature.[37]

$^{31}P\{^1H\}$ NMR and ^1H NMR spectra were recorded on a Varian AS 400 MHz spectrometer, and ^{13}C NMR spectra were recorded on a Varian AS 100 MHz spectrometer, with chemical shifts, in ppm, related to external 85% H_3PO_4. Coupling constants are in Hz. IR spectra were recorded from 4000 to 200 cm^{-1} with a Perkin Elmer 100 FT-IR instrument. Melting points were determined by Electrothermal melting point detection apparatus. Elemental analyses were performed by the TÜBİTAK-Ankara Test and Analysis Laboratories. TGA, DSC, and DTG curves were obtained with a TG-DTA Perkin-Elmer diamond system apparatus.

[Pt(dppm)(dppaS_2-H)](ClO_4) (1)

$PtCl_2$(dppm) (0.15 mmol, 0.10 g) and dppaS_2 (0.15 mmol, 0.067 g) were placed in CH_2Cl_2 (30 mL) and stirred. The solution of $NaClO_4 \cdot H_2O$ (0.71 mmol, 0.10 g) in acetone (20 mL) was added dropwise to the stirring solution. Stirring was continued for 24 h at room temperature. After that, the solution was removed in vacuo. White solid was dissolved in CH_2CI_2, and then it was filtered through Celite in order to separate NaCI. The solution was removed in vacuo again. Yield: 0.089 g, 52.5%. mp = 288–290°C. Data for **1**: ^1H NMR ($CDCl_3$): δ 7.4–7.8 (m, 40 H, Ar), 5.0 (t, 2 H, PCH_2P) ($^2J_{P\text{-}H} = 23.6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 126–137 (Aromatic carbons), 44.1 P(CH_2), $^{31}P\{^1H\}$ NMR ($CDCl_3$): 32.8 ppm (dppaS_2) ($^2J_{P\text{-}Pt} = 44.4$ Hz); −54.8 ppm (dppm) ($^1J_{P\text{-}Pt} = 2640.6$ Hz). Selected IR data (CsI): ν(PS) 571.1 cm^{-1}, 1101.1, and 623.8 cm^{-1} (ClO_4^-). Anal. Calc. for $C_{49}H_{42}NClO_4P_4PtS_2$: C, 52.2; H, 3.7; S, 5.7; N, 1.2. Found: C, 52.0; H, 3.7; S, 5.5; N, 1.3%.

[Pt(dppe)(dppaS_2-H)](ClO_4) (2)

The procedure used was the same as for **1** starting from $[PtCl_2(dppe)]$ (0.15 mmol, 0.10g), dppaS_2 (0.15 mmol, 0.067 g), and $NaClO_4 \cdot H_2O$ (0.71 mmol, 0.10 g). A cream-colored solid was obtained, and it was recrystallized from acetone/hexane (1:3 v/v). Yield: 0.074 g, 41.2%. mp = 285–288°C. Data for **2:** ^1H NMR (DMSO): δ 7.5–7.7 (m, 40 H, Ar), 2.6 (2 t, 4 H, PCH_2CH_2P) ($^2J_{P\text{-}H} = 42.4$ Hz). $^{13}C\{^1H\}$ NMR (DMSO): δ 126–137 (Aromatic carbons), 28.0 P(CH_2), $^{31}P\{^1H\}$ NMR (DMSO): 34.0 ppm (dppaS_2), ($^2J_{P\text{-}Pt} = 26.1$ Hz); 53.6 ppm (dppe) ($^1J_{P\text{-}Pt} = 2972.4$ Hz). Selected IR data (CsI): ν(PS) 576.1 cm^{-1}, 1104 and 624 cm^{-1} (ClO_4^-). Anal. Calc. for $C_{50}H_{44}NClO_4P_4PtS_2$: C, 52.6; H, 3.9; S, 5.6; N, 1.2. Found: C, 52.3; H, 3.9; S, 5.5; N, 1.3%.

[Pt(dppp)(dppaS$_2$-H)](ClO$_4$) (3)

This complex was obtained as a white solid, in a manner similar to **1** and **2**, from [PtCl$_2$(dppp)] (0.15 mmol, 0.10 g), dppaS$_2$ (0.15 mmol, 0.067 g), and NaClO$_4$·H$_2$O (0.71 mmol, 0.10 g). Colorless crystals, suitable for X-ray analysis, were obtained by slow diffusion of diethylether into acetone solution of **3** (1:3 v/v). Yield: 0.088 g, 50.9%. mp = 205°C (decomp.). Data for **3:** ^{1}H NMR (DMSO): δ7.4–7.8 (m, 40 H, Ar), 1.9 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.9 (m, 4H, PCH$_2$), $^3J_{\text{P-H}}$ value is unresolved. ^{13}C{^{1}H} NMR (DMSO): δ 128–137 (Aromatic carbons), 24.3 P(CH$_2$), 18.8 P(CH$_2$CH$_2$CH$_2$).^{31}P{^{1}H} NMR (DMSO): 33.7 ppm (dppaS$_2$) ($^2J_{\text{P-Pt}}$ = 72.9 Hz); −0.8 ppm (dppp) ($^1J_{\text{P-Pt}}$ = 2985.3 Hz). Selected IR data (CsI): ν(PS) 570.5 cm^{-1}, 1099 and 623.7 cm^{-1} (ClO$_4^-$). Anal. Calc. for C$_{51}$H$_{46}$NClO$_4$P$_4$PtS$_2$: C, 50.0; H, 4.0; S, 5.5; N, 1.2. Found: C, 50.6; H, 3.9; S, 5.2; N, 1.2%.

X-Ray Crystallographic Study of 2 and 3

The intensity data of the complexes **2** and **3** were collected using a STOE IPDS 2 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073) at 296 K. Details of crystal data, data collection, structure solution, and refinement are given in Table II. Data collection was as follows: Stoe X-AREA,[38] cell refinement: Stoe X-AREA,[38] data reduction: Stoe X-RED.[38] The structure was solved by direct-methods using SHELXS-97,[39] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97.[40] All hydrogen atoms were included using a riding model. Molecular drawings were obtained using ORTEP-III.[41]

Supplementary Material

Crystallographic data for C$_{50}$H$_{44}$ClNO$_4$P$_4$PtS$_2$·(CH$_3$)$_2$CO and C$_{51}$H$_{46}$ClNO$_4$P$_4$PtS$_2$ have been deposited with the Cambridge Crystallographic Data Center. Copies of available materials can be obtained, free of charge, upon application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336-033 or E-mail: deposit@ccdc.cam.ac.uk). Deposition numbers are CCDC 680784 and CCDC 687634, respectively.

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