

Note

Platinum(II) imidazo[4,5-*f*]-1,10-phenanthroline chloride and thiolate complexes: Synthesis and crystal structures

Nail M. Shavaleev, Harry Adams, Julia A. Weinstein *

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England, United Kingdom

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Abstract

The planar aromatic imidazo[4,5-*f*]-1,10-phenanthroline ligands have been used to prepare platinum(II) chloride and thiolate complexes. The X-ray structures of two thiolate compounds are reported, which show column-like packing in the solid state due to intermolecular aromatic π - π interactions. The compounds absorb moderately in the visible region, owing to {charge-transfer-to-diimine} electronic transition.

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1. Introduction

Platinum complexes with the diimine ligands are widely used as optical materials [1], DNA intercalators [2] and solar cell dyes [3]. We would like to introduce imidazo[4,5-*f*]-1,10-phenanthroline ligands (**imP**) to Pt(II) coordination chemistry, and illustrate it by synthesis of Pt(**imP**) chloride and thiolate complexes. The **imP** ligands are easy to prepare and modify and therefore have recently gained a lot of interest with respect to synthesis of novel metal compounds [4–11], amenable to the various applications stated above. In particular, the potential of flat extended aromatic system of **imP** ligands as a DNA intercalating unit has been exploited [4–6]. In order to increase solubility, and demonstrate synthetic versatility of the **imP** ligands, four new representatives of this class of diimines have also been prepared.

2. Results and discussion

The imidazo[4,5-*f*]-1,10-phenanthrolines were prepared by a reaction of 1,10-phenanthroline-5,6-dione with alde-

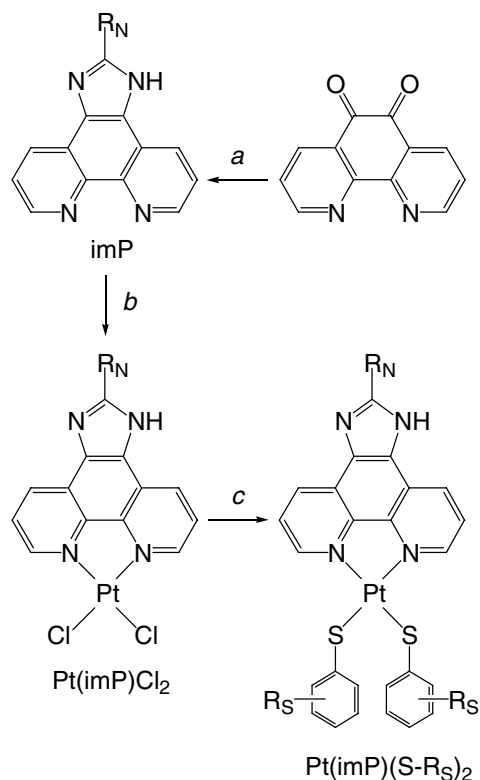
hyde in the presence of ammonium acetate in acetic acid [12] (Scheme 1). Four new ligands have been prepared, which contained either alkyl groups (**imP**-*t*Bu, **L**-*t*Bu) to improve solubility, or extended aromatic chromophore groups (**L**-Ph, **L**-Nap) to potentially modify spectroscopic properties (Scheme 2).

The ligands were refluxed with Pt(DMSO)₂Cl₂ [13] in alcohols to give Pt(**imP**)Cl₂ complexes that were then used as precursors to other Pt(**imP**) compounds.

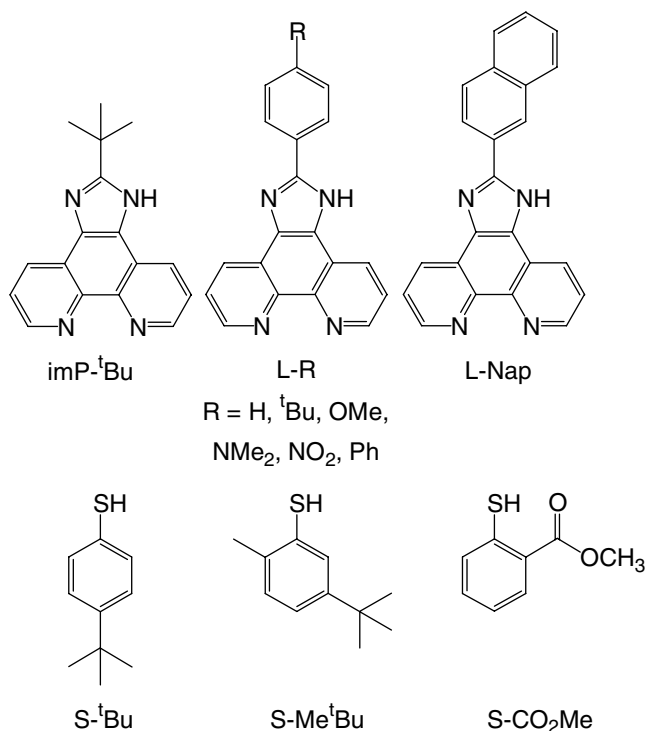
Reaction of Pt(**imP**)Cl₂ with thiophenols in methanol in the presence of a base gave thiolates Pt(**imP**)(S-R_S)₂ as coloured precipitates that were purified by column chromatography (Schemes 1 and 2). Sonication was used to increase the rate of this reaction and drive it to completion because both the precursor and the product Pt(II) complexes were only sparingly soluble in methanol.

All new compounds were identified by CHN data and ¹H NMR. In the ¹H NMR spectra, the NH proton of **imP** ligand was observed as either a broad or a sharp singlet, indicating respectively fast or slow exchange of a proton between the two nitrogens of the imidazole ring. The fast exchange of a proton resulted in the apparent C₂-symmetric structure of some ligands and complexes in the ¹H NMR spectra in solutions.

* Corresponding author. Tel.: +44 114 222 9408. fax: +44 114 222 9346.
E-mail address: julia.weinstein@sheffield.ac.uk (J.A. Weinstein).



Scheme 1. Synthesis of **imP** ligands and Pt^{2+} complexes: (a) aldehyde $\text{R}_\text{N}\text{CHO}$ (small excess), ammonium acetate (excess), acetic acid, N_2 , reflux, 3 h; (b) $\text{PtCl}_2(\text{DMSO})_2$, ethanol, N_2 , reflux, 24 h; (c) thiophenol HS-R_S and base (both in small excess), methanol, N_2 , sonication, rt, 24 h.



Scheme 2. **imP** Ligands and thiophenols used in the study.

The thiolate complexes $\text{Pt}(\text{imP})(\text{S-R}_\text{S})_2$ were obtained as red or brown solids. Their colour was determined by the broad and structureless absorption band in the visible region, centred at 503–526 nm, with the values of extinction coefficients of $(2.7\text{--}4.3) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (Table 1), typical for a charge-transfer transition. The negative solvatochromic behaviour (e.g., a shift of the absorption maximum from 498 nm in CH_3CN to 519 nm in CH_2Cl_2 for $\text{Pt}(\text{imP-}^t\text{Bu})(\text{S-Ph-}^t\text{Bu})_2$), typical for $\text{Pt}(\text{diimine})(\text{thiolate})_2$ complexes [1], also indicates the charge-transfer nature of the corresponding electronic transition. The energy of the lowest absorption band was red-shifted with the increase of the electron donating ability of thiophenols in the order $\text{S-Me}^t\text{Bu} > \text{S-}^t\text{Bu} > \text{S-CO}_2\text{Me}$, suggesting that the HOMO is largely localised on the thiolate part of the molecule. This assignment is in agreement with the absence of absorption bands at wavelengths >450 nm in the $\text{Pt}(\text{imP})\text{Cl}_2$ precursors. At the same time, the energy of the lowest absorption band of $\text{Pt}(\text{imP})(\text{S-R}_\text{S})_2$ was not very sensitive to the R_N group of **imP** ligand, and remains similar to that of $\text{Pt}(1,10\text{-phenanthroline})(\text{S-R}_\text{S})_2$ [1c]. These observations tentatively suggest that the corresponding electronic transition is mainly localised on the [phenanthroline–Pt–S– R_S] core with a rather limited R_N group participation. The lowest absorption band has therefore been assigned to a mainly thiolate-to-dimine charge-transfer transition.

The compounds were non-luminescent in degassed CH_2Cl_2 solutions at rt.

Crystal structures of $\text{Pt}(\text{L-NMe}_2)(\text{S-}^t\text{Bu})_2$ and $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ complexes are shown in Figs. 1 and 2. The structural features are similar for both complexes. The Pt(II) is in a distorted square planar coordination environment. A particular distortion towards a tetrahedral coordination is observed for $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ with a dihedral angle of 7.32° between the planes defined by N(1) Pt(1) N(2) and S(1) Pt(1) S(2) atoms (Fig. 2).

The **imP** ligands are planar in both structures. The two thiol ligands are situated above the **imP** plane resulting in an overall L-shaped molecule. The *o*-hydrogen atoms of thiol ligands are located above the coordination plane of Pt(II). In the $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ structure such

Table 1
Absorption spectra of the $\text{Pt}(\text{imP})(\text{S-R}_\text{S})_2$ complexes

Complex	$\lambda_{\text{max}}/\text{nm}$ ($10^{-3}\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)
$\text{Pt}(\text{imP-}^t\text{Bu})(\text{S-CO}_2\text{Me})_2$	503 (2.9), 364 (11), 295 (38), 257 (68)
$\text{Pt}(\text{imP-}^t\text{Bu})(\text{S-}^t\text{Bu})_2$	519 (2.7), 402 (5.7), 386 (6.2), 288 (43), 258 (81)
$\text{Pt}(\text{L-H})(\text{S-Me}^t\text{Bu})_2$	523 (3.4), 394 (6.4), 279 (72)
$\text{Pt}(\text{L-}^t\text{Bu})(\text{S-}^t\text{Bu})_2$	510 (2.9), 394 (6.4), 283 (75)
$\text{Pt}(\text{L-}^t\text{Bu})(\text{S-CO}_2\text{Me})_2$	510 (3.7), 285 (62)
$\text{Pt}(\text{L-OMe})(\text{S-Me}^t\text{Bu})_2$	526 (2.8), 285 (62)
$\text{Pt}(\text{L-NMe}_2)(\text{S-}^t\text{Bu})_2$	507 (3.4), 349 (42), 287 (53), 257 (43)
$\text{Pt}(\text{L-NMe}_2)(\text{S-CO}_2\text{Me})_2$	505 (4.3), 353 (46), 290 (48)
$\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$	520 (3.5), 358 (30), 288 (42), 260 (55)
$\text{Pt}(\text{L-Ph})(\text{S-}^t\text{Bu})_2$	515 (2.9), 287 (67)
$\text{Pt}(\text{L-Nap})(\text{S-}^t\text{Bu})_2$	512 (3.1), 390 (7.8, sh), 274 (85)

In CH_2Cl_2 or $\text{CH}_2\text{Cl}_2 + 0.5\% \text{ CH}_3\text{OH}$.

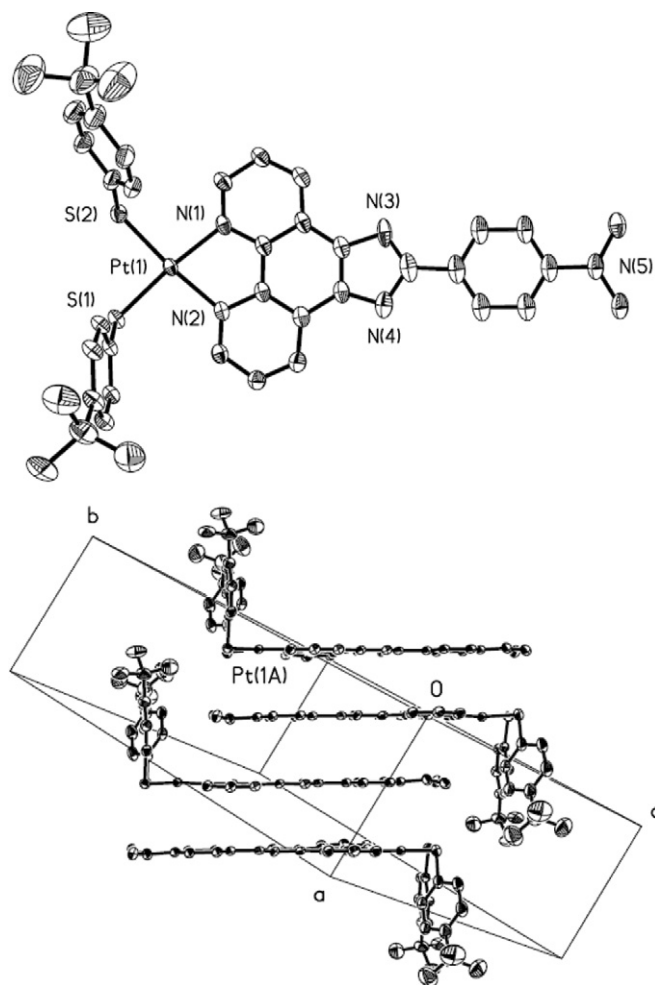


Fig. 1. Molecular structure of $\text{Pt}(\text{L-NMe}_2)(\text{S-}^t\text{Bu})_2$ (top-view) and packing of molecules into column of dimers (side-view) (50% probability ellipsoids, H atoms omitted). Selected bond lengths (Å) and angles ($^\circ$): Pt(1)–N(1) 2.062(5), Pt(1)–N(2) 2.066(5), Pt(1)–S(1) 2.2945(15), Pt(1)–S(2) 2.2822(16), N(1)–Pt(1)–N(2) 79.55(19), N(1)–Pt(1)–S(2) 95.44(15), N(2)–Pt(1)–S(1) 94.82(14), S(2)–Pt(1)–S(1) 90.03(6), N(1)–Pt(1)–S(1) 173.94(14), N(2)–Pt(1)–S(2) 173.86(14).

arrangement results in a short intramolecular Pt \cdots H–C contact (<2.9 Å) [14] with the Pt(1) \cdots H(21) and Pt(1) \cdots H(36) distances of 2.772 Å and 2.838 Å respectively and with the Pt \cdots H–C angles of *ca.* 122 $^\circ$.

The intermolecular aromatic π – π interactions of **imP** ligands result in the packing of their Pt(II) complexes into dimers (Figs. 1 and 2). The thiol ligands are pointing outwards from the centre of the dimer, thus allowing a closer approach and a better overlap between aromatic rings of **imP** ligands. The dimers are further packed into columns running along the *a*-axis. Each molecule within the column is related to the next one by a centre of inversion. The intra- and inter-dimer distances between **imP** ligands within the column are 3.364 Å and 3.453 Å for $\text{Pt}(\text{L-NMe}_2)(\text{S-}^t\text{Bu})_2$ and 3.360 Å and 3.374 Å for $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ (the distances were measured between the planes defined by all non-hydrogen atoms of **imP** ligand except the NO_2 or $\text{N}(\text{CH}_3)_2$ group).

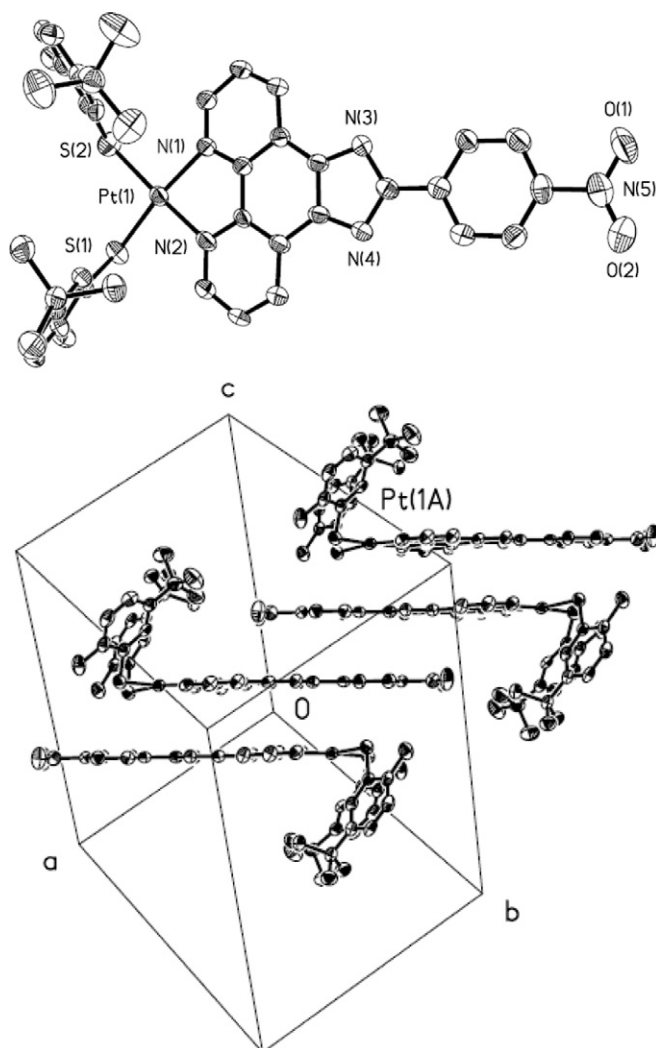


Fig. 2. Molecular structure of $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ (top-view) and packing of molecules into column of dimers (side-view) (50% probability ellipsoids, H atoms and co-crystallised molecule of DMSO omitted). Selected bond lengths (Å) and angles ($^\circ$): Pt(1)–N(1) 2.080(4), Pt(1)–N(2) 2.068(4), Pt(1)–S(1) 2.2996(14), Pt(1)–S(2) 2.2915(16), N(1)–Pt(1)–N(2) 79.71(16), N(1)–Pt(1)–S(2) 96.75(12), N(2)–Pt(1)–S(1) 96.00(12), S(2)–Pt(1)–S(1) 87.81(6), N(1)–Pt(1)–S(1) 172.05(12), N(2)–Pt(1)–S(2) 175.61(13).

The shortest Pt \cdots Pt distances are 8.035 Å for $\text{Pt}(\text{L-NMe}_2)(\text{S-}^t\text{Bu})_2$ and 8.923 Å for $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ indicating absence of metal–metal interaction.

The co-crystallised molecule of DMSO in the structure of $\text{Pt}(\text{L-NO}_2)(\text{S-Me}^t\text{Bu})_2$ forms a hydrogen bond through sulfoxide oxygen with NH proton of imidazole ring with O \cdots H distance 1.895 Å and O \cdots HN angle 165.28 $^\circ$.

In conclusion, this contribution has exploited synthetically versatile imidazo[4,5-*f*]-1,10-phenanthroline, **imP**, ligands to form a new series of stable Pt(II) chloride and thiolate complexes. The compounds absorb moderately in the visible region, owing to {charge-transfer-to-diimine} electronic transition. The X-ray crystallography has shown column-like packing in the solid state due to the intermolecular aromatic π – π interactions between the neighbouring **imP** ligands.

The extended planar aromatic system of the **imP** ligands renders their Pt(II) complexes potential intercalators into DNA. The notable lack of influence of the R_N substituent on the **imP** ligand on the electronic absorption spectra of these chromophores opens up future possibilities for altering their molecular properties, such as, for example, solubility, charge, or functionalisation required for incorporation into polynuclear assemblies and in solar cells, without altering absorption characteristics. These compounds thus offer a valuable alternative to the 2,2'-bipyridyl or 1,10-phenanthroline ligands that are widely used in Pt(II) chemistry.

3. Experimental

All reactions were carried out in the dark under N₂ using general grade solvents that were degassed by bubbling N₂ for 10 min. Purification, crystal growth and handling of all compounds were carried out under air with a minimum exposure to light. All products were air- and moisture-stable solids which were stored in the dark when not used.

3.1. Synthesis of **imP** ligands

1,10-Phenanthroline-5,6-dione, the corresponding aldehyde (small excess) and ammonium acetate (excess) were refluxed in degassed acetic acid (10 ml) under N₂ for 3 h. The reaction mixture was diluted with water (20 ml) and neutralized with NH₄OH to give a precipitate of the product which was filtered, washed with dilute NH₄OH (pH 8), water and ether and dried in vacuum. The compounds were often obtained as solvates with water and acetic acid. The amount of acetic acid was estimated by ¹H NMR. The ligands were soluble in alcohols, DMSO and mixtures of CH₂Cl₂ with alcohols but were insoluble in ether, hexane and CH₂Cl₂. The ligands L-H, L-NO₂, L-OMe and L-NMe₂ were known from previous studies [4]. The ligands imP-^tBu, L-^tBu, L-Ph and L-Nap are new.

3.2. Synthesis of complexes Pt(**imP**)Cl₂

PtCl₂(DMSO)₂ [13] and **imP** in 1:1 molar ratio (0.3–0.6 mmol scale) were refluxed in degassed ethanol (30 ml) under N₂ for 24 h to give a precipitate of the product that was filtered, washed with methanol and ether and dried in a vacuum. The yields were in the range 80–90%. The products were of yellow colour except for the deep red coloured Pt(L-NMe₂)Cl₂. The complexes Pt(L-^tBu)Cl₂ and Pt(L-NMe₂)Cl₂ were soluble in DMSO. Other complexes were insoluble in all common solvents.

3.3. Synthesis of complexes Pt(**imP**)(thiolate)₂

^tBuOK or triethylamine (0.31 mmol) and thiol (0.31 mmol) were stirred at rt for 5 min in degassed CH₃OH (15 ml) under N₂. Pt(**imP**)Cl₂ (0.15 mmol) was added to the resulting solution and the reaction mixture was sonicated for 8 h at rt and stirred overnight to give a

red, green or brown suspension of the product. The solid was filtered and washed with CH₃OH (10 ml). Purification by column chromatography (SiO₂, CH₃OH:CH₂Cl₂, 1:99–3:97) gave main coloured fraction that was reduced to 5 ml. Addition of hexane precipitated the product that was filtered, washed with hexane or a mixture of hexane and ether (50:50) and dried in vacuum. The yields were in the range 30–70%. The complexes were obtained as dark red or brown solids that were insoluble in alkanes and alcohols, soluble to various extents in CH₂Cl₂, and highly soluble in DMF, DMSO and in the mixtures of CH₂Cl₂ with alcohols.

3.4. X-ray crystallography

Single crystals were obtained by vapour diffusion of diethyl ether to DMF [Pt(L-NMe₂)(S-^tBu)₂] or DMSO [Pt(L-NO₂)(S-Me^tBu)₂] solutions of the complexes.

Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. All reflections were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods and refined by full matrix least squares methods on *F*². Complex scattering factors were taken from the program package SHELXTL (An integrated system for solving and refining crystal structures from diffraction data, Revision 5.1, Bruker AXS LTD) as implemented on the IBM PC. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with *U*_{iso} constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom. Data in common: T = 150(2) K, λ = 0.71073 Å.

Pt(L-NMe₂)(S-^tBu)₂. CCDC Ref. 607251; C₄₁H₄₃N₅PtS₂; *M*_w = 865.01; red plates; size (mm): 0.32 × 0.12 × 0.10; monoclinic; space group *P*2₁/*c* (*C*₂^h, No. 14); *a*/*b*/*c* (Å) = 8.0354(6)/23.8089(16)/21.3169(14); α/β/γ (°) = 90/95.276(3)/90; *V* = 4060.9(5) Å³; *Z* = 4; ρ_{calc} = 1.415 g cm⁻³; μ = 3.591 mm⁻¹; *F*(000) = 1736; θ range (°) = 1.29–29.05; reflections collected/*R*_{int}/data/restraints/parameters = 52304/0.0726/10698/323/443; goodness-of-fit on *F*² = 1.050; *R*(*I* > 2σ(*I*)): *R*₁ = 0.0487, *wR*₂ = 0.1199; *R* (all data): *R*₁ = 0.0746, *wR*₂ = 0.1288; Δρ_{min/max} (e Å⁻³) = -1.629/1.807.

Pt(L-NO₂)(S-Me^tBu)₂. CCDC Ref. 607252; C₄₁H₄₁N₅O₂PtS₂ · (C₂H₆OS); *M*_w = 973.14; red blocks; size (mm): 0.32 × 0.16 × 0.12; monoclinic; space group *P*2₁/*n* (a non-standard setting of *P*2₁/*c* *C*₂^h, No. 14); *a*/*b*/*c* (Å) = 12.4893(18)/20.476(3)/17.300(2); α/β/γ (°) = 90/105.269(2)/90; *V* = 4268.0(10) Å³; *Z* = 4; ρ_{calc} = 1.514 g cm⁻³; μ = 3.478 mm⁻¹; *F*(000) = 1960; θ range (°) = 1.57–27.55; reflections collected/*R*_{int}/data/restraints/parameters = 48169/0.1059/9689/6/514; goodness-of-fit on *F*² = 0.920; *R*(*I* > 2σ(*I*)): *R*₁ = 0.0425, *wR*₂ = 0.0861; *R*

(all data): $R_1 = 0.0874$, $wR_2 = 0.0999$; $\Delta\rho_{\min/\max}$ ($e \text{ \AA}^{-3}$) = $-0.997/2.209$.

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Appendix A. Supporting information

Additional experimental details are available as Supporting Information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.08.007.

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