

Correspondence to:

Associate Professor W. Henderson,

Chemistry Department,

University of Waikato,

Private Bag 3105,

Hamilton,

New Zealand

e-mail w.henderson@waikato.ac.nz

FAX: (64) 7 838-4219

Platinum(II), palladium(II) and gold(III) complexes containing 1,1,4-trisubstituted thiosemicarbazide dianion ligands

William Henderson^{a,*} and Clifton E. F. Rickard^b

^a *Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand*

^b *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

Synopsis

The thiosemicarbazides Ph₂NNHC(S)NPh and Ph₂NNHC(S)NHMe form complexes as dianions with platinum(II), palladium(II) and gold(III); the two ligands bond in different modes to the Pt(PPh₃)₂ moiety, as shown by a crystal structure determination on [Pt{SC(=NPh)NNPh₂}(PPh₃)₂] and NMR spectroscopic data for [Pt{SC(=NNPh₂)NMe}(PPh₃)₂].

Abstract

Reactions of *cis*-[PtCl₂(PPh₃)₂] or [PdCl₂(PPh₃)₂] with Ph₂N-NHC(S)NPh and excess triethylamine, in refluxing methanol gave the complexes [M{SC(=NPh)NNPh₂}(PPh₃)₂] containing thiosemicarbazide dianion ligands. An analogous gold(III) complex containing the cyclo-aurated anilinopyridine ligand was also synthesised. A single crystal X-ray diffraction study was carried out on the complex [Pt{SC(=NPh)NNPh₂}(PPh₃)₂] which confirmed the bonding of the thiosemicarbazide dianion ligand *via* sulfur and the nitrogen bearing the NPh₂ substituent. In contrast, reaction of Ph₂N-NHC(S)NHMe with *cis*-[PtCl₂(PPh₃)₂] and excess triethylamine gave the complex [Pt{SC(=NNPh₂)NMe}(PPh₃)₂], containing a Pt-NMe group, characterized spectroscopically.

1. Introduction

A number of complexes are known which contain disubstituted thiourea dianion ligands, $[\text{RNHC}(\text{S})\text{NHR}]^{2-}$, coordinated to platinum(II) forming four-membered Pt-S-C-N ring systems. Examples include the complexes **1** formed from symmetrical thioureas $\text{RNHC}(\text{S})\text{NHR}$ [1–3] and **2**, formally derived from the cyanothiourea $\text{MeNHC}(\text{S})\text{NHCN}$. [4] Thiourea dianion complexes of other metals are also known, e.g. palladium(II) [5], molybdenum(IV) [6], rhodium(III) [7] and ruthenium(II). [7] In this paper we report the synthesis of platinum(II), palladium(II) and gold(III) complexes of the trisubstituted thiosemicarbazide ligands $\text{Ph}_2\text{N-NHC}(\text{S})\text{NHPH}$ **3a** and $\text{Ph}_2\text{N-NHC}(\text{S})\text{NHMe}$ **3b**, which form similar complexes to the thiourea analogues. While metal complexes of thiosemicarbazones have attracted much interest [8] there have been fewer studies on metal complexes of thiosemicarbazides, though supramolecular assembly of platinum thiosemicarbazide complexes *via* hydrogen bonding has attracted recent interest. [9]

2. Results and discussion

The reactions of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ or $[\text{PdCl}_2(\text{PPh}_3)_2]$ with 1,1,4-triphenylthiosemicarbazide $[\text{Ph}_2\text{N-NHC}(\text{S})\text{NHPH}]$ **3a** and triethylamine base in hot methanol gives high yields of the complexes **4a** and **4b** respectively, containing the thiosemicarbazide dianion ligand. The platinum complex is bright yellow in colour,

while the palladium complex is deep maroon; the complexes give the expected intense $[M + H]^+$ ions in their ES mass spectra, and satisfactory microanalytical data.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **4a** showed the expected AB pattern for two inequivalent PPh_3 ligands coordinated to platinum, with phosphine resonances at δ 16.9 and 11.1 showing $^1\text{J}(\text{PtP})$ coupling constants of 3156 and 3147 Hz respectively. In comparison, the diphenylthiourea-derived analogue **1a** has similar coupling constants of 3261 and 3103 Hz.[1] Along with the major signals above, there was a minor species in the isolated product (*ca.* 5% relative intensity), which also appeared as an AB pattern, with coupling to ^{195}Pt of 3038 and 3330 Hz, consistent with S and N donor ligands. This species is tentatively assigned as the isomeric product **5a**, since in the ESMS spectrum of the crude complex only a single $[M + H]^+$ ion was observed in the ES spectrum (together with a very low intensity $[2M + H]^+$ ion). An alternative isomer, containing a five-membered ring with a coordinated NPh_2 group, is tentatively ruled out on the basis of poor coordinating ability of tertiary arylamines. Recrystallisation of the initially formed product by vapour diffusion of diethyl ether into a dichloromethane solution of the complex yielded bright yellow crystals of pure **4a**. Isolated samples of the palladium complex **4b** were pure by ^{31}P NMR, with no evidence for another isomer. Complex **4b** is assigned an analogous structure to **4a**, with a PdNNPh_2 group.

In order to unambiguously characterize the mode of bonding of the thiosemicarbazide ligand to the platinum centre a single-crystal X-ray diffraction study was carried out on complex **4a**. The molecular structure is shown in Figure 1, together with the atom numbering scheme, while selected bond lengths and angles are given in Table 1. The structure confirms the complex as a thiosemicarbazide dianion complex,

coordinated to platinum through the sulfur and the nitrogen bearing a substituted NPh₂ group, forming a four-membered ring, analogous to the previous structure of [Pt{SC(=NPh)NPh}(PPh₃)₂].[1] This isomer is presumably formed, as opposed to the alternative isomer [Pt{SC(=NNPh₂)NPh}(PPh₃)₂], because the NPh₂ group is sterically less bulky in the platinum coordination environment than the Ph group alone. Examination of the Cambridge Crystallographic Database (version 5.22, October 2001) revealed only five structures containing the M-S-C(N)-NN (M = transition metal) four-membered ring system, all being complexes of thiosemicarbazone monoanions.[10] Burrows *et al* have reported the structure of [(Ph₂PCH₂CH₂PPh₂)PtCl{S=C(NHNMe₂)(NHMe)]PF₆, containing a neutral, S-bonded trisubstituted thiosemicarbazide ligand.[9] The structure of **4a** thus appears to be first of a thiosemicarbazide bonded as a dianion to a transition metal centre.

Overall, the structural features of **4a** are very similar to the related diphenylthiourea dianion complex **1a**.[1] Thus, the Pt-S [**1a** 2.331(1), **4a** 2.3299(8) Å], S-C [**1a** 1.782(5), **4a** 1.798(3) Å] and C=N [**1a** 1.277(6), **4a** 1.281(4) Å] bonds are very comparable. However, the metallacyclic C-N and Pt-N bonds of **4a** [1.374(4) and 2.097(2) Å respectively] are both considerably longer than the corresponding bonds in **1a** [[C-N 1.348(7), Pt-N 2.054(3) Å]. Furthermore, the metallacyclic N in **4a** is less planar than its counterpart in **1a**, as shown by the bond angle sums [**1a** 357.1°, **4a** 352.3°]. The Pt-P bond distances of **4a** [*cis* to S 2.2614(7), *trans* to S 2.3158(7) Å] are both longer than their counterparts in **1a** [*cis* to S 2.247(1), *trans* to S 2.308(1) Å].

Using the same methodology as for the platinum and palladium complexes above, reaction of the gold(III) dichloride complex **6** with Ph₂NNHC(S)NHPPh and triethylamine

gave **7**, which had a low solubility in common organic solvents. The complex is also tentatively assigned as having a coordinated NNPh₂ group, though the complex was too insoluble for NMR studies (which would probably be of limited usefulness) and single crystals could not be obtained. Gold(III) complexes containing thiosemicarbazones as ligands have been recently prepared by reaction of the gold(III) complex **8** with a variety of thiosemicarbazones; the resulting products contain five-membered Au-S-C-N-N rings, and the original Au-N bond is cleaved by protonation.[11] Diphenylthiocarbazono (dithizone) PhNHNHC(S)N=NPh behaves in the same way.[12] However, no gold(III) complexes of thiosemicarbazides appear to have been characterized previously. In the positive ion ES spectrum of **7** the [M + H]⁺ ion is essentially the only ion at low cone voltages (20 V) or very high cone voltages (140 V), while at intermediate cone voltages (e.g. 80 V), other fragment ions in the region *m/z* 400 - 566 are observed. These observations indicate the stability of the parent [M + H]⁺ ion, compared to the small number of fragment ions which are formed at elevated cone voltages. The stability of gold(III) metallacyclic complexes bearing cyclo-aured ligands in ES analysis has been noted previously.[13]

We subsequently wished to explore the effect of substituting the phenyl group with a sterically less bulky methyl, to provide an NMR spectroscopic handle upon which to characterize the coordination geometry (the presence of a Pt-NMe group can be readily determined by NMR spectroscopy due to the presence of ¹⁹⁵Pt and ³¹P couplings). Reaction of *cis*-[PtCl₂(PPh₃)₂] with a slight excess of Ph₂N-NHC(S)NHMe and triethylamine base in hot methanol gave complex **5b** as a yellow solid in high yield, which gave good microanalytical data, and a single [M + H]⁺ ion in the positive ion ES

mass spectrum. However, NMR spectroscopic analysis indicated that the opposite isomer to **4a** had formed. The presence of a Pt-NMe group was readily ascertained by a resonance at δ 2.43 in the ^1H NMR spectrum, showing coupling to both ^{31}P (4.1 Hz) and ^{195}Pt (29.9 Hz). These values compare very favourably with ^1H NMR data for other complexes with $(\text{Ph}_3\text{P})_2\text{Pt-NMe}$ groups, such as $[\text{Pt}\{\text{SC}(=\text{NMe})\text{NMe}\}(\text{PPh}_3)_2]$ **1b** [δ 2.27, $^4\text{J}(\text{PH})$ 4.29, $^3\text{J}(\text{PtH})$ 31.2] [**3**] and $[\text{Pt}\{\text{SC}(=\text{NCN})\text{NMe}\}(\text{PPh}_3)_2]$ **2** [δ 2.16, $^4\text{J}(\text{PH})$ 4.0, $^3\text{J}(\text{PtH})$ 31].[**4**] In the case of complex **5b**, the small size of the methyl group compared to NPh_2 appears to be effecting isomerisation.

In conclusion, trisubstituted thiosemicarbazide dianion ligands show strong similarities to the related thiourea dianion ligands, in bonding *via* S and N, forming four-membered metallacycles. The observation of isomerism dependent on ligand substituents suggests that this may also occur in the thiourea analogues, and this will be the topic of a subsequent investigation.

Experimental

3.1 General experimental procedures

Electrospray mass spectra were recorded in methanol solution on a VG Platform II instrument with nitrogen as the nebulising and drying gas. Identification of ions was aided by comparison of experimental and theoretical [**14**] isotope distribution patterns. NMR spectra were recorded on a Bruker AC300P instrument (^1H , 300.1 MHz, ^{13}C 75.5 MHz) or a Bruker DRX400 instrument (^1H , 400.1 MHz, ^{13}C 100 MHz) in CDCl_3 . Melting

points were recorded using a Reichert-Jung hotstage apparatus, and are uncorrected. Reactions were carried out in LR grade methanol without further purification, and without exclusion of air. Petroleum spirits refers to the fraction of boiling point 60 - 80 °C, and was used as supplied, while dichloromethane was distilled from calcium hydride prior to use.

1,1-Diphenylhydrazine hydrochloride (Aldrich) and triethylamine (BDH) were used as supplied. The complexes [PtCl₂(cod)] [15] and [PdCl₂(cod)] [16] were synthesised by the literature procedures and the complexes *cis*-[PtCl₂(PPh₃)₂] and [PdCl₂(PPh₃)₂] synthesised from them by ligand substitution with a stoichiometric quantity of the phosphine in dichloromethane.[17] Complex 6 was prepared by the literature procedure.[18]

The thiosemicarbazides Ph₂NNHC(S)NHPH **3a** and Ph₂NNHC(S)NHMe **3b** were prepared by minor modification of the literature procedure [19] involving addition of Ph₂NNH₂ (prepared by treatment of the hydrochloride salt with aqueous KOH, and extraction of the hydrazine with ether) to diethyl ether solutions of PhNCS or MeNCS respectively. **3a**, m.p. 180-184 °C, lit. 181 °C; **3b**, m.p. 203-205 °C, lit. 203-204 °C.

3.2 Preparation of [Pt{SC(=NPh)NNPh₂}(PPh₃)₂] **4a**

To a pale yellow suspension of *cis*-[PtCl₂(PPh₃)₂] (400 mg, 0.506 mmol) and Ph₂NNHC(S)NHPH **3a** (168 mg, 0.527 mmol) in methanol (30 mL) was added triethylamine, immediately giving a bright yellow suspension. The mixture was refluxed for 10 min., water (10 mL) added and the mixture cooled to room temperature. The

bright yellow solid was filtered, washed with water (10 mL), cold methanol (10 mL) and diethyl ether (10 mL), and dried to give **4a** (484 mg, 92%). M.p. 270-274 °C. Found: C, 63.5; H, 4.5; N, 4.3. C₅₅H₄₅N₃P₂PtS requires C, 63.7; H, 4.4; N, 4.1%. ESMS (cone voltage 20 V) [M + H]⁺ (*m/z* 1037, 100%). The sample contained a small quantity (*ca.* 5% by ³¹P NMR) of another species, tentatively assigned as the isomer **5a** on the basis of ³¹P NMR data. Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution at room temperature gave pure **4a**.

³¹P-^{{1}H} NMR, **4a**: δ 16.9 [d, ¹J(PtP) 3156, ²J(PP) 23] and 11.1 [d, ¹J(PtP) 3147, ²J(PP) 23]. For isomer **5a**: δ 17.5 [¹J(PtP) 3038, ²J(PP) 21] and 12.8 [¹J(PtP) 3330, ²J(PP) 21].

3.3 Preparation of [Pd{SC(=NPh)NNPh₂}(PPh₃)₂] **4b**

[PdCl₂(PPh₃)₂] (371 mg, 0.529 mmol) with Ph₂NNHC(S)NHPPh **3a** (172 mg, 0.539 mmol) and excess triethylamine in methanol (30 mL) was refluxed for 15 min. to give a deep red solution, plus some red solid. The mixture was cooled to room temperature, the red solid filtered, washed with water (2 x 10 mL) and diethyl ether (10 mL) and dried to give **4b** as a deep maroon solid (280 mg, 56%). M.p. 190-192 °C. Found: C, 69.3; H, 4.7; N, 4.3. C₅₅H₄₅N₃P₂PdS requires C, 69.7; H, 4.8; N, 4.4%. ESMS (cone voltage 20 V) [M + H]⁺ (*m/z* 948, 100%). ³¹P-^{{1}H} NMR, δ 30.5 [d, ²J(PP) 46] and 23.7 [d, ²J(PP) 46].

3.4 Preparation of [Pt{SC(=NNPh₂)NMe}(PPh₃)₂] **5b**

cis-[PtCl₂(PPh₃)₂] (400 mg, 0.506 mmol) with Ph₂NNHC(S)NHMe (134 mg, 0.521 mmol) and triethylamine (1 mL) in methanol (30 mL) was refluxed for 20 min. to give a clear yellow solution. Water (40 mL) was added, the mixture cooled to room temperature, and the yellow solid filtered, washed with water (10 mL) and diethyl ether (2 x 10 mL) and dried to give **5b** (350 mg, 71%). M.p. 278-280 °C. Found: C, 61.0; H, 4.5; N, 4.5. C₅₀H₄₃N₃P₂PtS requires 61.6; H, 4.4; N, 4.3%. ESMS (cone voltage 20 V) [M + H]⁺ (*m/z* 975, 100%). ³¹P-¹H NMR, δ 18.8 [d, ¹J(PtP) 3044, ²J(PP) 20] and 14.8 [d, ¹J(PtP) 3213, ²J(PP) 20]. ¹H NMR, δ 7.66-6.85 (m, Ph) and 2.43 [d, PtNMe, ⁴J(PH) 4.1, ³J(PtH) 29.9].

3.5 Preparation of [Au{SC(=NPh)NNPh₂}(2-anp)] **7**

Complex **6** (300 mg, 0.686 mmol) with Ph₂NNHC(S)NHPh (219 mg, 0.687 mmol) and excess triethylamine in methanol (40 mL) was refluxed for 30 min., giving an orange suspension. The mixture was cooled to room temperature, the solid filtered, washed with water (10 mL), methanol (10 mL) and diethyl ether (10 mL) and dried to give **7** as an orange solid (426 mg, 91%). M.p. 192-194 °C (decomp.). Found: C, 52.1; H, 3.5; N, 10.3. C₃₀H₂₄N₅AuS requires C, 52.7; H, 3.5; N, 10.3%. ESMS (cone voltage 20 V) [M + H]⁺ (*m/z* 684, 100%). The complex had insufficient solubility in common solvents to allow characterization by NMR spectroscopy.

3.6 Crystal structure determination of [Pt{SC(=NPh)NNPh₂}(PPh₃)₂] **4a**

Bright yellow crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature.

Crystal data. C₅₅H₄₅N₃P₂PtS, M = 1037.03, monoclinic, space group P2₁, *a* = 9.9066(1), *b* = 18.4790(2), *c* = 13.0065(2) Å, β = 105.844(1)°, *U* = 2290.56(5) Å³, T = 150(2) K, Z = 2, ρ_{calc} = 1.504 g cm⁻³, μ(Mo-Kα) = 3.219 mm⁻¹, F(000) = 1040.

A total of 13920 reflections were measured, 7441 unique (*R*_{int} = 0.0211) which were all used in the refinement. A semi-empirical absorption correction was carried out, *T*_{max} and *T*_{min} 0.5377 and 0.4999. Final R indices: [*I* > 2σ(*I*)] *R*₁ = 0.0180, *wR*₂ = 0.0379. All data: *R*₁ = 0.0196, *wR*₂ = 0.0391. The largest residuals in the electron density map were 0.541 and -0.396 e Å⁻³. The SHELX programs were used for all calculations.[20]

4. Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. XXXXXX. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [FAX +44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Acknowledgements

We thank the University of Waikato for financial support of this work, together with the New Zealand Lottery Grants Board for a grant-in-aid for the purchase of the mass spectrometer, and for the purchase of precious metals. A generous loan of platinum from Johnson Matthey plc is acknowledged. WH thanks Pat Gread and Wendy Jackson for technical support and Dr. Ralph Thomson for some of the NMR spectra.

References

- [1] W. Henderson, R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1992, 59.
- [2] S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimomura and Y. Kushi, *Chem. Lett.*, 1992, 1823.
- [3] M. B. Dinger, W. Henderson, B. K. Nicholson and W. T. Robinson, *J. Organomet. Chem.*, 1998, **560**, 169.
- [4] W. Henderson and B. K. Nicholson, *Polyhedron*, 1996, **15**, 4015.
- [5] S. Okeya, H. Kameda, H. Kawashima, H. Shimomura, T. Nishioka and K. Isobe, *Chem. Lett.*, 1995, 501.
- [6] R. S. Pilato, K. A. Eriksen, E. I. Stiefel and A. L. Rheingold, *Inorg. Chem.*, 1993, **32**, 3799.
- [7] W. Henderson, B. K. Nicholson, M. B. Dinger and R. L. Bennett, submitted to *Inorg. Chim. Acta*.

- [8] Selected recent refs: V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 2000, 335; D. Kovalá-Demertzi, J. R. Miller, N. Kourkoumelis, S. K. Hadjikakou and M. A. Demertzis, *Polyhedron*, 1999, **18**, 1005; J. M. Vila, M. T. Pereira, J. M. Ortigueira, M. Graña, D. Lata, A. Suárez, J. J. Fernández, A. Fernández, M. López-Torres and H. Adams, *J. Chem. Soc., Dalton Trans.*, 1999, 4193; E. W. Ainscough, A. M. Brodie, W. A. Denny, G. J. Finlay and J. D. Ranford, *J. Inorg. Biochem.*, 1998, **70**, 175; F. Basuli, S.-M. Peng, and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 1120; L. Ze-Hua, D. Chun-Ying, L. Ji-Hui, L. Yong-Jiang, M. Yu-Hua and Y. Xiao-Zeng, *New. J. Chem.*, 2000, **24**, 1057.
- [9] A. D. Burrows, M. D. Coleman and M. F. Mahon, *Polyhedron*, 1999, **18**, 2665.
- [10] F. Basuli, M. Ruf, C. G. Pierpont and S. Bhattacharya, *Inorg. Chem.*, 1998, **37**, 6113; A. Castineiras, E. Bermejo, D. X. West, A. K. El-Sawaf and J. K. Swearingen, *Polyhedron*, 1998, **17**, 2751; F. Basuli, S.-M. Peng, and S. Bhattacharya, *Inorg. Chem.*, 1997, **36**, 5645; A. Castineiras, M. Gil, E. Bermejo and D. X. West, *Z. Naturforsch., Teil B*, 2000, **55**, 863; F. Basuli, S.-M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 1120.
- [11] U. Abram, K. Ortner, R. Gust and K. Sommer, *J. Chem. Soc., Dalton Trans.*, 2000, 735.
- [12] K. Ortner and U. Abram, *Polyhedron*, 1999, **18**, 749.
- [13] M. B. Dinger and W. Henderson, *J. Organomet. Chem.*, 1999, **577**, 219.
- [14] L. J. Arnold, *J. Chem. Educ.*, 1992, **69**, 811.

- [15] J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
- [16] D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.
- [17] D. L. Oliver and G. K. Anderson, *Polyhedron*, 1992, **11**, 2415.
- [18] Y. Fuchita, H. Ieda, A. Kayama, J. Kinoshita-Nagaoka, H. Kawano, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1998, 4095.
- [19] W. Marckwald, *Berichte*, 1892, **25**, 3098.
- [20] G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467; G. M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.

Table 1. Selected bond lengths and angles for [Pt{SC(=NPh)NNPh₂}(PPh₃)₂] **4a** with estimated standard deviations in parentheses.

Pt-N(1)	2.097(2)	Pt-P(2)	2.2614(7)
Pt-P(1)	2.3158(7)	Pt-S	2.3299(8)
P(1)-C(31)	1.826(3)	P(1)-C(41)	1.848(3)
P(1)-C(51)	1.833(3)	P(2)-C(61)	1.833(3)
P(2)-C(71)	1.828(3)	P(2)-C(81)	1.832(3)
S-C	1.798(3)	N(1)-C	1.374(4)
N(1)-N(2)	1.412(3)	N(2)-C(1)	1.401(4)
N(2)-C(11)	1.432(3)	N(3)-C	1.281(4)
N(3)-C(21)	1.411(4)		
N(1)-Pt-P(2)	162.39(7)	N(1)-Pt-P(1)	99.47(7)
P(2)-Pt-P(1)	98.01(3)	N(1)-Pt-S	69.08(7)
P(2)-Pt-S	93.31(3)	P(1)-Pt-S	166.68(2)
C-S-Pt	82.96(10)	C-N(1)-N(2)	115.2(2)
C-N(1)-Pt	103.51(16)	N(2)-N(1)-Pt	133.59(19)
C(1)-N(2)-N(1)	119.2(2)	C(1)-N(2)-C(11)	123.9(2)
N(1)-N(2)-C(11)	115.4(2)	C-N(3)-C(21)	117.2(2)
N(3)-C-N(1)	127.0(3)	N(3)-C-S	128.8(2)
N(1)-C-S	104.25(18)		

Caption for Figure

Fig. 1. Molecular structure of $[\text{Pt}\{\text{SC}(=\text{NPh})\text{NNPh}_2\}(\text{PPh}_3)_2]$ **4a** with thermal ellipsoids at the 50% probability level.