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Preparation and NMR Characterization of η^1-N-Bonded Platinum(II) and Palladium(II) Adducts of Eight-Membered Heterocyclic Thiazenes

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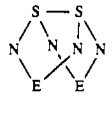
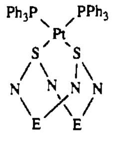
The reaction of the diphosphadithiatetrazocines 1,5-$R_4P_2N_4S_2$ with $[MCl_2(PEt_3)]_2$ (M = Pt, Pd) in a 2:1 molar ratio in CH_2Cl_2 or THF at 23 °C produces the 1:1 adducts *trans*-$[MCl_2(PEt_3)(R_4P_2N_4S_2)]$ (**5c**, M = Pt, R = Ph; **5d**, M = Pt, R = Et; **5e**, M = Pt, R = Me; **5f**, M = Pd, R = Et; **5g**, M = Pd, R = Me) in which the $P_2N_4S_2$ ligand is bound to either palladium or platinum via nitrogen. The dithiatetrazocine, 1,5-$(Me_2NC)_2N_4S_2$, and the trithiatetrazocine, $PhCN_4S_3NPPh_3$, react with $[PtCl_2(PEt_3)_2]_2$ to give the adducts $PtCl_2(PEt_3)[(Me_2NC)_2N_4S_2]$ (**6**) and $PtCl_2(PEt_3)(PhCN_4S_3NPPh_3)$ (**9**), respectively. The adduct **6** is obtained as a mixture of isomers, according to ^1H and ^{31}P NMR spectroscopic data, in which the platinum atom is bonded to either an exocyclic or an endocyclic nitrogen atom, **6a** and **6b**, respectively. Variable-temperature ^1H and ^{31}P NMR studies show that **6a** is converted into **6b** and indicate that the $PtCl_2(PEt_3)$ group is involved in a ring-whizzing process via a series of 1,3-shifts at higher temperatures. The adduct **9** is obtained as a single isomer in which the platinum atom is probably attached to an endocyclic nitrogen geminal to the $NPPh_3$ group. The heterocyclic ligands in **5c** and **6** are readily displaced by THF to give *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}O\text{-THF})]$ (**8**). In contrast, the adducts **5d** and **5e** do not dissociate in THF solution. The reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ with the N-bonded adducts $[Et_4P_2N_4S_2Me][CF_3SO_3]$, **5d** or **5e**, in toluene at 0 °C produces the complexes $Pt(PPh_3)_2(R_4P_2N_4S_2E)$ (**10a**, R = Et, E = Me^+; **10b**, R = Et, E = $PtCl_2(PEt_3)$; **10c**, R = Me, E = $PtCl_2(PEt_3)$) in good yield. The ^{31}P NMR spectrum of **10a** indicates that the $Et_4P_2N_4S_2Me^+$ ligand is bonded to platinum in a η^2-S,S′ mode, while the ^{31}P NMR spectra of the bimetallic complexes **10b** and **10c** are consistent with structures in which the $R_4P_2N_4S_2$ ligand is η^1-N-bonded to one platinum and η^2-S,S′-bonded to the other platinum atom. The decomposition of **10b** in THF at 23 °C produces $PtCl_2(PEt_3)(PPh_3)$ and the bimetallic dimer $[Pt(PPh_3)(Et_4P_2N_4S_2)]_2$. The reaction of equimolar amounts 1,5-$R_4P_2N_4S_2$ (R = Et, Ph) with $[PtCl_2(PEt_3)]_2$ in CH_2Cl_2 produces 2:1 and 3:1 η^1-N-bonded platinum(II) adducts, in addition to **5c**, on the basis of ^{31}P NMR spectroscopy.

Introduction

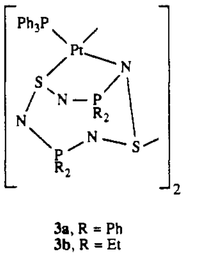
Although the coordination chemistry of binary sulfur–nitrogen (S–N) ligands derived from tetrathiatetrazocine (S_4N_4) is relatively well developed,[1,2] investigations of the interactions of metal centers with the dithiatetrazocines **1a** and **1d** commenced only recently as a test of the isolobal correspondence between the σ and σ^* orbitals of the S–S bonds in these heterocycles and the π and π^* orbitals of an electron-deficient alkene.[3] Support for this analogy was provided by the preparation of complexes of the type $Pt(PPh_3)_2(1,5\text{-}E_2N_4S_2)$, **2a** and **2d**, in which the ligands **1a** and **1d** are bonded to platinum in an η^2-S,S′ mode.[3,4] Relativistic density functional calculations confirmed the assertion that the bonding interactions between the S–S group and platinum in these complexes are comparable to those found in metal–alkene adducts.[3] Upon mild heating, complexes **2a** and **2b** are converted into the dimers $[Pt(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$, **3a** and **3b**, in which the $P_2N_4S_2$ ring acts as a tridentate ligand, chelating (N,S) toward one platinum atom and bridging (μ-S) toward the other.[5] Complexes **3a** and **3b** undergo a novel [1,3]-metallotropic rearrangement in solution involving a pendular movement of platinum between vicinal nitrogen atoms.[4,5]



1a, E = PPh_2
1b, E = PEt_2
1c, E = PMe_2
1d, E = $CNMe_2$



2a, E = PPh_2
2b, E = PEt_2
2c, E = PMe_2
2d, E = $CNMe_2$



3a, R = Ph
3b, R = Et

The reaction of strong electrophiles, e.g. BCl_3 and Me^+, with **1a** produces N-bonded adducts, e.g. **5a** and **5b**, and results in a contraction of the S–S interaction and a significant weakening of the P–N and, especially, the S–N bonds involving the coordinated nitrogen.[6] The heterocycle **1d**, however, shows no inclination to interact with Lewis or Brønsted acids[7,8] and η^1-N-bonded metal complexes of **1a** are unknown.

Significantly, the integrity of the eight-membered rings is retained in the complexes **2a–d**, **3a**, and **3b**. By contrast, the interaction of S_4N_4 with zerovalent complexes of the platinum group metals results in fragmentation of the ligand to give MS_2N_2 rings (M = Ni Pd, Pt),[9-12] while the treatment of S_4N_4 with dimeric platinum(II) complexes of the type $[PtCl_2(PR_3)]_2$ produces platinum(IV) complexes, **4**, that incorporate the

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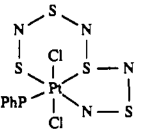
tridentate (N,S,S) ligand formed by insertion of the metal into an S-N bond as either *mer* or *fac* isomers.[13,14] It was, therefore, of considerable interest to investigate the interaction of the chloro-bridged platinum(II) dimers with **1a–d** in order to determine the mode of coordination and the fate of the heterocyclic ligand. The trithiatetrazocine $PhCN_4S_3NPPh_3$[15] was also included in this study as an example of an S–N ligand with inequivalent endocyclic nitrogen atoms.

The N-bonded adducts **5c–e**, obtained in this manner, retain the transannular S–S bond; cf. **5a**.[6] Consequently, we have investigated the reactions of **5a–e** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ to determine whether both η^1-N and η^2-S,S′ bonding modes can be incorporated in the same dithiatetrazocine complex.



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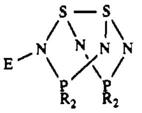

5a (R = Ph, E = Me^+)
5b (R = Et, E = Me^+)
5c [R = Ph, E = $PtCl_2(PEt_3)$]
5d [R = Et, E = $PtCl_2(PEt_3)$]
5e [R = Me, E = $PtCl_2(PEt_3)$]
5f [R = Et, E = $PdCl_2(PEt_3)$]
5g [R = Me, E = $PdCl_2(PEt_3)$]

Experimental Section

Reagents and General Procedures. All manipulations were carried out under dry nitrogen gas in Schlenk vessels using standard air-sensitive techniques. The solvents were deoxygenated and distilled immediately before their use. Sodium benzophenone was used as the drying agent for all solvents, except dichloromethane, which was distilled over P_2O_5. The compounds $Pt(CH_2{=}CH_2)(PPh_3)_2$,[16] $[PtCl_2(PEt_3)]_2$,[17] $[PdCl_2(PEt_3)]_2$,[17] 1,5-$R_4P_2N_4S_2$ (R = Me, Et, Ph),[18] 1,5-$R_2C_2N_4S_2$ (R = Me_2N, Ph),[7] and $PhCN_4S_3NPPh_3$[15] were prepared according to the published procedures. Methyl trifluoromethylsulfonate (Aldrich) was used as received. The elemental analyses were performed by the microanalytical service within the chemistry department at the University of Calgary.

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr plates) on a Nicolet DX-5 FTIR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 161.978 MHz in either THF or CH_2Cl_2. A D_2O insert was used as the lock for the phosphorus spectra. Proton NMR spectra were run on either a Bruker AM-200 at 200.1 MHz or a Bruker AM-400 at 400.1 MHz, while carbon-13 NMR spectra were run on the AM-400 instrument at 100.614 MHz. For both the carbon-13 and proton NMR spectra the solvent deuterium resonance served as the lock. The $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker WM-250 spectrometer operating at 53.58 MHz. The ^{31}P chemical shifts are reported in ppm relative to 85% H_3PO_4; ^1H and ^{13}C chemical shifts are quoted relative to $SiMe_4$.

Preparation of [1,5-$Et_4P_2N_4S_2$Me][CF_3SO_3] (5b). Methyl trifluoromethylsulfonate (0.104 mL, 0.921 mmol) was added by syringe to a rapidly stirred, colorless solution of 1,5-$Et_4P_2N_4S_2$ (0.250 g, 0.838 mmol) in CH_2Cl_2 (30 mL) at 23 °C. After 12 h solvent was removed from the pale yellow solution under vacuum and the oily residue was washed with hexane to give $[Et_4P_2N_4S_2Me][CF_3SO_3]$ (**2b**) (0.381 g, 0.821 mmol) as a sticky yellow solid. Anal. Calcd for $C_{10}H_{23}F_3N_4O_3P_2S_3$: C, 25.97; H, 5.01; N, 12.11. Found: C, 26.30; H, 5.44; N, 11.36. ^1H NMR (in $CDCl_3$): 0.80–1.35 (overlapping multiplets, 12H, PCH_2CH_3), 1.70–2.45 (overlapping multiplets, 8H, PCH_2CH_3) and 3.32 (d, 3H, NCH_3) [$^3J(^{31}P-^1H)$ = 7.0 Hz]. $\delta(^{31}P)$ (in $CDCl_3$): +161.1 [d, $^4J(^{31}P-^{31}P)$ = 12.5 Hz] and +108.0 ppm [d, $^4J(^{31}P-^{31}P)$ = 12.5 Hz].

Table I. ^{31}P NMR Data for $MCl_2(PEt_3)(R_4P_2N_4S_2)$ (M = Pt, Pd; R = Ph, Et, Me)[a]

	$\delta(^{31}P)$[b,c]						
compd	P_A	P_B	P_C	$^3J(P_A-P_B)$[d]	$^4J(P_B-P_C)$[d]	$^1J(Pt-P_A)$[d]	$^2J(Pt-P_B)$[d]
5c[f]	3.2 (d)	117.0 (dd)	106.7 (d)	6	32	3739	50
5d[e]	4.5 (d)	123.2 (dd)	142.7 (d)	13	29	3663	~90
5e[f]	4.8 (d)	112.8 (dd)	127.3 (d)	12	34	3660	111
5f[g]	38.1 (d)	132.2 (dd)	135.2 (d)	12	29		
5g[g]	38.6 (d)	116.8 (dd)	124.3 (d)	10	34		

[a] Abbreviations used: (s) singlet, (d) doublet, (dd) doublet of doublets, (dt) doublet of triplets. [b] In ppm relative to 85% H_3PO_4. [c] See Figure 1 for assignments of P_A, P_B, and P_C. [d] In Hz. [e] In THF at 25 °C. [f] In CH_2Cl_2 at 25 °C. [g] In $CDCl_3$ at −55 °C.

Table II. ^{195}Pt NMR Data for $[PtCl_2(PEt_3)(R_4P_2N_4S_2)]$ (R = Et, Ph)[a]

compd	$\delta(^{195}Pt)$[b]	$\Xi(^{195}Pt)$[c]	$^1J(Pt-P_A)$[d,e]	$^2J(Pt-P_B)$[d,e]	$^4J(Pt-P_C)$[d,e]
5c[f]	410.6 (dd)	21.421 998	3743	44	~0
5d[f]	405.7 (dd)	21.421 747	3658	77	~0

[a] Abbreviations used: (dd) doublet of doublets. [b] In ppm relative to 21.400 000 MHz [c] Absolute frequency in MHz. [d] See Figure 1 for assignments of P_A, P_B, and P_C. [e] In Hz. [f] CH_2Cl_2 solution with external C_6D_6 lock at 25 °C.

Preparation of Dithiatetrazocine and Trithiatetrazocine Adducts. All of these adducts were prepared by using procedures similar to that described below for compound **5c**. $^{31}P\{^1H\}$ NMR data for the adducts **5c–g** are collected in Table I and $^{195}Pt\{^1H\}$ NMR data for **5c** and **5d** are given in Table II.

$PtCl_2(PEt_3)(\eta^1$-*N*-$Ph_4P_2N_4S_2)$ (5c). A solution of 1,5-$Ph_4P_2N_4S_2$ (0.127 g, 0.260 mmol) in THF (20 mL) was added to a rapidly stirred solution of $[PtCl_2(PEt_3)]_2$ (0.100 g, 0.130 mmol) in THF (20 mL) at 23 °C to give a pale yellow solution. After 3 h the solvent was removed under vacuum. The yellow residue was washed with Et_2O (3 × 20 mL), kept under dynamic vacuum for 12 h, and then recrystallized from CH_2Cl_2/Et_2O at 23 °C to give **5c**·$^1/_2CH_2Cl_2$ (0.117 g, 0.128 mmol) as yellow crystals. Anal. Calcd for $C_{30.5}H_{36}Cl_3N_4P_3PtS_2$: C, 39.94; H, 3.96; N, 6.11. Found: C, 39.63; H, 4.00; N, 6.27. ^1H NMR (in $CDCl_3$): 6.50–8.01 (m, C_6H_5, 20H), 1.54 (m, PCH_2CH_3, 6H), 0.61 (dt, PCH_2CH_3, 9H), $^3J(PH)$ = 17 Hz, $^3J(HH)$ = 8 Hz.

A similar procedure was used for the preparation of other N-bonded dithiatetrazocine adducts of Pt(II) and Pd(II) and the trithiatetrazocine adduct of Pt(II); the solvents used in the syntheses, the crystallization conditions, colors and yields are summarized below with CHN microanalytical and NMR data. The Pd(II) complexes were prepared by using $[PdCl_2(PEt_3)]_2$.

$PtCl_2(PEt_3)(\eta^1$-*N*-$Et_4P_2N_4S_2)$ (5d). This was prepared in THF at 23 °C, giving yellow crystals recrystallized from THF/Et_2O at −18 °C: yield 47%. Anal. Calcd for $C_{14}H_{35}N_4Cl_2P_3PtS_2$: C, 24.64; H, 5.17; N, 8.21. Found: C, 24.77; H, 5.24; N, 8.04.

$PtCl_2(PEt_3)(\eta^1$-*N*-$Me_4P_2N_4S_2)$ (5e). This was prepared in THF at 23 °C, giving yellow crystals: yield 83%. Anal. Calcd for $C_{10}H_{27}N_4Cl_2P_3PtS_2$: C, 19.17; H, 4.34; N, 8.95. Found: C, 19.35; H, 4.55; N, 9.57. ^1H NMR (in $CDCl_3$): 1.44–2.01 (overlapping multiplets, PCH_2CH_3 and PCH_3), 1.23 (dt, PCH_2CH_3), $^3J(PH)$ = 17 Hz, $^3J(HH)$ = 8 Hz.

$PdCl_2(PEt_3)(\eta^1$-*N*-$Et_4P_2N_4S_2)$ (5f). This was prepared in THF at 23 °C, giving orange-yellow crystals recrystallized from THF/Et_2O/pentane at −18 °C: yield 80%. Anal. Calcd for $C_{14}H_{35}Cl_2N_4P_3PdS_2$: C, 28.32; H, 5.94; N, 9.44. Found: C, 28.53; H, 6.07; N, 9.34. ^1H NMR (in $CDCl_3$ at −55 °C): 0.62–2.04 (overlapping multiplets, $P(CH_2CH_3)_3$ and $P(CH_2CH_3)_2$), 1.27 (dt, $P(CH_2CH_3)_3$), $^3J(PH)$ = 18 Hz, $^3J(HH)$ = 12 Hz.

$PdCl_2(PEt_3)(\eta^1$-*N*-$Me_4P_2N_4S_2)$ (5g). This was prepared in CH_2Cl_2 at 23 °C, giving orange-yellow crystals of **5g**·$^1/_2CH_2Cl_2$ obtained by recrystallization from CH_2Cl_2/pentane at −18 °C: yield 68%. Anal. Calcd for $C_{10.5}H_{28}N_4S_2Cl_3P_3Pd$: C, 21.74; H, 4.87; N, 9.66. Found: C, 21.17; H, 5.52; N, 9.78. ^1H NMR (in $CDCl_3$): 1.50–2.23 (overlapping multiplets, $P(CH_2CH_3)_3$ and $P(CH_3)_2$), 1.29 (dt, $P(CH_2CH_3)_3$), $^3J(PH)$ = 18 Hz, $^3J(HH)$ = 8 Hz.

$PtCl_2(PEt_3)[\eta^1$-*N*-$(Me_2NC)_2N_4S_2]$ (6). (a) This method used CH_2Cl_2 at 0 °C, giving a dull yellow solid that was precipitated as **6**·$^1/_2CH_2Cl_2$ from CH_2Cl_2 by the addition of pentane: yield 68%. Anal. Calcd for $C_{12.5}H_{28}Cl_3N_6PPtS_2$: C, 22.78; H, 4.28; N, 12.76. Found: C, 23.28; H, 4.38; N, 12.04. ^{13}C NMR (in $CDCl_3$ at −65 °C): **6a**, N–CH_3: 40.74 (s), 40.54 (s); **6b**, N–CH_3: 40.96 (s), 40.30 (s), 39.23 (s), 38.93 (s). ^{31}P (in THF): **6a**, +3.2 ppm, $^1J(PtP)$ = 3729 Hz; **6b**, +2.2 ppm,

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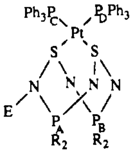
Table III. $^{31}P\{^1H\}$ NMR Parameters for η^2-S,S′-Bonded Complexes of Platinum with 1,5-Diphosphadithiatetrazocines[a,b]

	10a[c]	**10b**[c,d]	**10c**[c,e]	**2a**[f]	**2b**[f]	**2c**[f]
$\delta(P_A)$	52.0 (dd)	58.2 (dddd)	47.7 (dddd)	39.2 (t)	60.6 (t)	50.8 (t)
$\delta(P_B)$	64.3 (dd)	60.3 (ddd)	50.1 (ddd)	39.2 (t)	60.6 (t)	50.8 (t)
$\delta(P_C)$	18.9 (dd)	16.8 (dddd)	14.4 (dddd)	18.3 (t)	18.7 (t)	18.7 (t)
$\delta(P_D)$	12.0 (dd)	14.2 (ddd)	12.3 (ddd)	18.3 (t)	18.7 (t)	18.7 (t)
$^4J(P_A–P_B)$	21	30	34			
$^4J(P_A–P_C)$	~0	6	7	5	~0	~0
$^4J(P_A–P_D)$	12	6	7	5	~0	~0
$^4J(P_B–P_C)$	7	4	4	5	~0	~0
$^4J(P_B–P_D)$	~0	4	7	5	~0	~0
$^2J(P_C–P_D)$	32	25	27			
$^3J(Pt–P_A)$	261	377	388	572	578	574
$^3J(Pt–P_B)$	523	594	569	572	578	574
$^1J(Pt–P_C)$	3452	3008	3057	2861	2820	2880
$^1J(Pt–P_D)$	2315	2800	2816	2861	2820	2880

[a] Chemical shifts are quoted in ppm relative to 85% H_3PO_4. Coupling constants are in Hz. Abbreviations used: (dd) doublet of doublets, (ddd) doublet of doublets of doublets, (dddd) doublet of doublets of doublets of doublets, and (t) triplet. [b] The ^{31}P NMR spin labeling scheme is indicated in the following structure; E is defined in eq 4.



[c] $CDCl_3$ solution. [d] $\delta[PtCl_2(PEt_3)] = -1.6$ ppm (dd), $^3J(P_A–PEt_3) = 11$ Hz, $^5J(P_C–PEt_3) = 6$ Hz, and $^1J(Pt–PEt_3) = 3501$ Hz. [e] $\delta[PtCl_2(PEt_3)] = -3.6$ ppm (dd), $^3J(P_A–PEt_3) = 9$ Hz, $^5J(P_C–PEt_3) = 9$ Hz, and $^1J(Pt–PEt_3) = 3478$ Hz. [f] Data taken from ref 5.

$^1J(PtP) = 3719$ Hz. The variable-temperature ^1H NMR spectra of **6a** and **6b** are discussed in the text.

(b) This method used THF at 23 °C, producing a mixture of **6a** (ca. 20%) and *trans*-$PtCl_2(PEt_3)(\eta^1$-*O*-$C_4H_8O)$ (**7**) (*ca.* 80%), $^1J(PtP) = 4151$ Hz. Repeated recrystallizations of the mixture from THF/Et_2O gave essentially pure **7**.

$PtCl_2(PEt_3)(\eta^1$-*N*-$PhCN_4S_3NPPh_3)$ (9). This was prepared in THF at 23 °C, giving yellow crystals recrystallized as **9**$\cdot ^1/_2CH_2Cl_2$ from CH_2Cl_2/pentane at 23 °C: yield 60%. Anal. Calcd for $C_{31.5}H_{36}Cl_3N_5P_2PtS_3$: C, 40.07; H, 3.84; N, 7.42. Found: C, 40.26; H, 3.86; N, 7.35. ^1H NMR (in $CDCl_3$): 7.12–7.99 (m, C_6H_5, 20H), 1.61 (m, PCH_2CH_3, 6H), 1.11 (dt, PCH_2CH_3, 9H), $^3J(PH) = 17$ Hz, $^3J(HH) = 8$ Hz. ^{31}P NMR (in THF): +3.2 ppm (s, *P*Et_3), $^1J(PtP) = 3680$ Hz, +23.3 ppm (s, N*P*Ph_3).

Preparation of $[Pt(PPh_3)_2(Et_4P_2N_4S_2Me)][CF_3SO_3]$ (10a). A pale yellow solution of $[Et_4P_2N_4S_2Me][CF_3SO_3]$ (0.124 g, 0.267 mmol) in THF (20 mL) at 0 °C was transferred by cannula to a Schlenk tube containing a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.200 g, 0.267 mmol) in THF (20 mL) at 0 °C causing the immediate formation of a bright yellow solution. The mixture was stirred for 1.5 h at 0 °C and then solvent was removed under vacuum at 0 °C to give an oily yellow residue, which was recrystallized from CH_2Cl_2/pentane at −18 °C to give yellow crystals of **10a**$\cdot CH_2Cl_2$ (0.300 g, 0.237 mmol). Anal. Calcd for $C_{47}H_{55}Cl_2F_3N_4O_3P_4PtS_3$: C, 44.55; H, 4.38; N, 4.42. Found: C, 44.32; H, 4.51; N, 5.18. ^1H NMR (in $CDCl_3$): 1.00–1.29 (overlapping multiplets, 12H, PCH_2CH_3), 1.73–2.64 (overlapping multiplets,, 8H, PCH_2CH_3) and 2.69 (d, 3H, NCH_3) [$^3J(^{31}P\text{-}^1H) = 7.0$ Hz]. The ^{31}P NMR data for **10a** are given in Table III.

Preparation of $[Pt(PPh_3)_2(Et_4P_2N_4S_2)PtCl_2(PEt_3)]$ (10b). Toluene (30 mL) at 0 °C was added by cannula to an intimate mixture of *trans*-$[PtCl_2(PEt_3)(Et_4P_2N_4S_2)]$ (0.080 g, 0.117 mmol) and $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.088 g, 0.117 mmol). The resulting bright yellow solution was stirred for 3 h at 0 °C, and the solvent was removed under vacuum to give a yellow residue, which was dissolved in CH_2Cl_2 (5 mL). The slow addition of pentane (50 mL) produced **10b**$\cdot ^1/_2CH_2Cl_2$ (0.133 g, 0.092 mmol) as a yellow solid. Anal. Calcd for $C_{50.5}H_{66}Cl_3N_4P_5Pt_2S_2$: C, 41.99; H, 4.60; N, 3.88. Found: C, 41.79; H, 4.07; N, 3.87. The ^{31}P NMR data for **10b** are given in Table III.

Preparation of $[Pt(PPh_3)_2(Me_4P_2N_4S_2)PtCl_2(PEt_3)]$ (10c). The procedure was similar to that used for the preparation of **10b**. The product **10c**$\cdot ^1/_2CH_2Cl_2$ was obtained as a yellow crystalline solid in 82% yield. Anal. Calcd for $C_{46.5}H_{58}Cl_3N_4P_5Pt_2S_2$: C, 40.22; H, 4.21; N, 4.04. Found: C, 39.94; H, 4.19; N, 4.21. The ^{31}P NMR data for **10c** are given in Table III.

Table IV. $^{31}P\{^1H\}$ NMR Parameters for the η^1-N-Bonded Adducts $[PtCl_2(PEt_3)]_n(R_4P_2N_4S_2)$ [**11a**, R = Ph, *n* = 2; **11b**, R = Et, *n* = 2; **12a**, R = Ph, *n* = 3; **12b**, R = Et, *n* = 3][a]

	Et_3P			R_2P		
	$\delta(^{31}P)$	$J(P–P)$	$^1J(Pt–P)$	$\delta(^{31}P)$	$J(P–P)$	$^1J(Pt–P)$
11a	4.3 (s)		3789	114.2 (2)		
11b	3.2 (s)		3723	134.8 (s)		
12a	8.3 (d)	6	3716	57.5 (dd)	11, 6	95
	2.1 (d)	10	*b*	45.0 (d)	10	216
	1.2 (d)	12	*b*			
12b	8.9 (d)	7.7	3714	79.7 (dd)	16.5, 7	67
	2.8 (d)	17	3500	70.1 (d)	13	230
	2.5 (d)	13	3414			

[a] Chemical shifts are quoted relative to 85% H_3PO_4. Coupling constants are in Hz. Abbreviations used: (s) singlet, (d) doublet, and (dd) doublet of doublets. [b] Not resolved.

Decomposition of $[Pt(PPh_3)_2(Et_4P_2N_4S_2)PtCl_2(PEt_3)]$ (10b). A colorless solution of **10b** (0.100 g) in THF (2 mL) was layered with diethyl ether (5 mL). After 10 days white crystals were formed and identified as *cis*-$[PtCl_2(PPh_3)(PEt_3)]$ by $^{31}P\{^1H\}$ NMR spectroscopy. $\delta(^{31}P)$ (in CH_2Cl_2): 6.20 ppm [d, $^1J(^{31}P–^{195}Pt) = 3373$ Hz, $^2J(^{31}P–^{31}P) = 16$ Hz, *P*Et_3] and 13.4 ppm [d, $^1J(^{31}P–^{195}Pt) = 3816$ Hz, $^2J(^{31}P–^{31}P) = 16$ Hz, *P*Ph_3]. The $^{31}P\{^1H\}$ NMR spectrum (in CH_2Cl_2, 25 °C) of the yellow brown product isolated from the filtrate exhibits broad resonances at ca. 41 and 70 ppm, a sharp singlet at 11.9 ppm [$^1J(^{31}P–^{195}Pt) = 4167$ Hz] and another narrow singlet at 51.6 ppm, which exhibits coupling to two platinum atoms. In a separate experiment it was shown that a product with the same ^{31}P NMR resonances is formed by the decomposition of the bimetallic dimer **3b** in CH_2Cl_2 at 25 °C.

$[PtCl_2(PEt_3)]_3(Et_4P_2N_4S_2)$ (12). A colorless solution of 1,5-$Et_4P_2N_4S_2$ (0.080 g, 0.268 mmol) in CH_2Cl_2 (40 mL) was added dropwise (6 h) to a dark orange solution of $[PtCl_2(PEt_3)]_2$ (0.309 g, 0.402 mmol) in CH_2Cl_2 (30 mL) at 23 °C. Solvent was removed from the resulting yellow solution under vacuum to give a yellow solid. A solution of this solid in $CHCl_3$ (50 mL) was heated at reflux. Solvent was removed under vacuum and the residue was recrystallized from THF/pentane at −18 °C to give yellow crystals (0.211 g) tentatively identified as $[PtCl_2(PEt_3)]_3(Et_4P_2N_4S_2)$ (**12**) on the basis of the ^{31}P NMR data (see Table IV). Repeated attempts to obtain an analytically pure sample of **12**, uncontaminated with **5d**, were unsuccessful.

Results and Discussion

Preparation and NMR Characterization of 1:1 Platinum(II) and Palladium(II) Complexes of the 1,5-Diphosphadithiatetrazocines 1a, 1b, and 1c. The reaction of 2 molar equiv of **1a**, **1b**, or **1c** with $[MCl_2(PEt_3)]_2$ (M = Pt, Pd) in a polar solvent at 23 °C results in the cleavage of the chloro-bridged dimer to give the 1:1 adducts **5c–f** (eq 1) as air-stable yellow solids.

$$\begin{array}{l} 2R_4P_2N_4S_2 + [MCl_2(PEt_3)]_2 \xrightarrow[\text{or THF}]{CH_2Cl_2} \\ \qquad (M = Pt, Pd) \\ \qquad\qquad 2\ trans\text{-}[MCl_2(PEt_3)(\eta^1\text{-}N\text{-}R_4P_2N_4S_2)] \\ \qquad\qquad\qquad \mathbf{5c}\ (M = Pt, R = Ph) \\ \qquad\qquad\qquad \mathbf{5d}\ (M = Pt, R = Et) \\ \qquad\qquad\qquad \mathbf{5e}\ (M = Pt, R = Me) \\ \qquad\qquad\qquad \mathbf{5f}\ (M = Pd, R = Et) \\ \qquad\qquad\qquad \mathbf{5g}\ (M = Pd, R = Me) \end{array} \qquad (1)$$

These adducts have been characterized by microanalysis, by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy (Table I), and by an X-ray diffraction analysis of **5c**.[19]

The ^{31}P NMR spectrum of **5c** in THF is shown in Figure 1. The spectrum is readily interpreted as an equilibrium mixture of *trans*-$[PtCl_2(PEt_3)(\eta^1$-*N*-$Ph_4P_2N_4S_2)]$ (**5c**) with *trans*-$[PtCl_2$-

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(19) Parvez, M. Private communication. Problems have been encountered with the refinement of the X-ray structure of **5c** due to disorder of both the phenyl and ethyl groups. Nevertheless the structural determination shows clearly that the heterocyclic ring is attached to platinum via one of its nitrogen atoms in a position trans to PEt_3 and that the cross-ring S–S interaction is retained in **5c**, cf. 1,5-$Ph_4P_2N_4S_2Me^+$.[6]

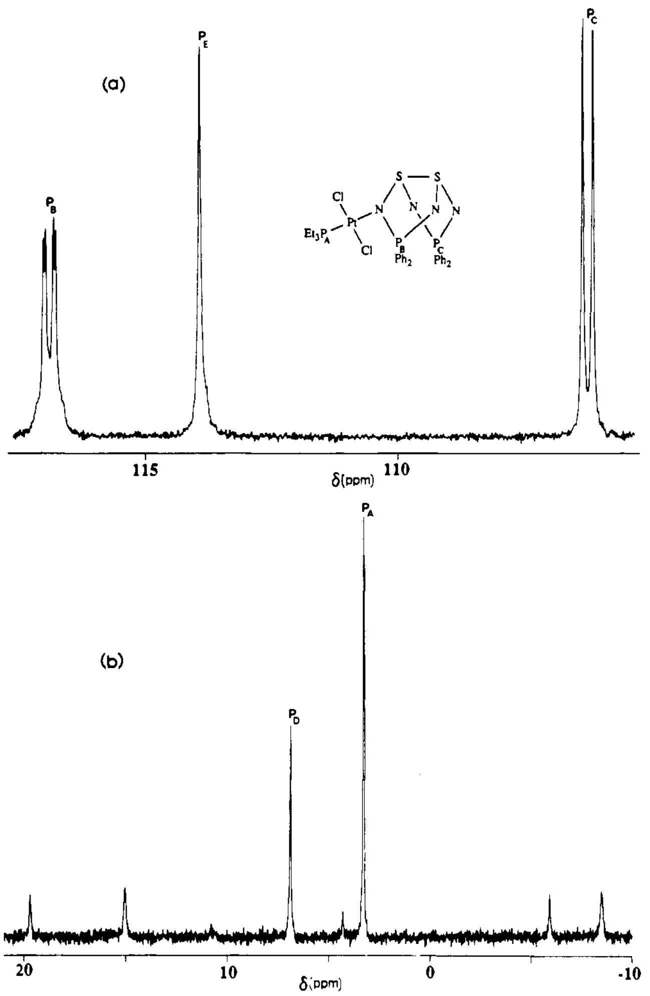


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}N\text{-}Ph_4P_2N_4S_2)]$ (**5c**) in THF at 23 °C: (a) low-field region; (b) high-field region. The assignments of P_A, P_B, and P_C to the inequivalent phosphorus atoms of **5c** are indicated. P_D = *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}O\text{-}THF)]$. P_E = 1,5-$Ph_4P_2N_4S_2$ (lit. $\delta(^{31}P)$ 113.9 ppm).[18]

$(PEt_3)(\eta^1\text{-}O\text{-}THF)]$ (**7**) and 1,5-$Ph_4P_2N_4S_2$ (**1a** (R = Ph)), apparently resulting from the displacement of coordinated **1a** (R = Ph) by THF. The singlet at 6.8 ppm (P_D) with ^{195}Pt satellites is attributed to *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}O\text{-}THF)]$ on the basis of the large one-bond ^{195}Pt–^{31}P coupling constant of 4147 Hz, which is typical for a trialkylphosphine ligand *trans* to a hard oxygen-bonded ligand in a platinum(II) complex.[20–22] The singlet at 113.9 ppm (P_E) is due to 1,5-$Ph_4P_2N_4S_2$ (**1a**),[18] displaced from Pt by coordination of THF. The remaining three resonances at 3.3, 106.2, and 116.9 ppm belong to the adduct **5c** and indicate the N-bonded structure shown in Figure 1. The former resonance $[^1J(^{195}Pt\text{–}^{31}P) = 3739\ \mathrm{Hz}]$ is assigned to the Et_3P ligand. In closely related complexes with strong Pt–N bonds, e.g. $[Pt(S_2N_2H)(PEt_3)_2][Me_2SnCl_3]$[23] and $[Pt(S_2N_2H)(PMe_3)Br]$,[24] the $^1J(^{195}Pt\text{–}^{31}P)$ coupling constants are substantially smaller (3176 and 3355 Hz, respectively). The large value of $^1J(^{195}Pt\text{–}^{31}PEt_3)$ for **5c** and the facile displacement of the heterocyclic ligand by THF suggest that the Pt–N bond is quite weak, and this conclusion was confirmed by the unusually long Pt–N bond distance [2.27 (4) Å].[19,25] The ^{31}P NMR resonances at 106.2 and 116.9 ppm for the two chemically inequivalent PPh_2 groups in the $Ph_4P_2N_4S_2$ ligand of **5c** fall on either side of the signal for the uncomplexed ligand at 113.9 ppm. This behavior resembles that observed for Lewis or Brønsted acid adducts of **1a**, for which chemical shifts in the range 83–95 and 125–129 ppm are observed for the inequivalent phosphorus atoms.[6] Furthermore it indicates strongly that the S–S bond is retained in **5c** since the disruption of this bond results in substantial (>90 ppm) upfield shifts of the ^{31}P NMR resonances.[6]

As indicated in Table I, the ^{31}P NMR spectra of **5d** and **5e** in THF at 23 °C exhibit features similar to that of **5c**. In particular, the signals for the inequivalent phosphorus atoms (P_B and P_C) of the $R_4P_2N_4S_2$ ligand fall on either side of those of the free ligands [cf. lit.[18] $\delta(^{31}P)$ 136.1 ppm for 1,5-$Et_4P_2N_4S_2$ and 119.7 ppm for 1,5-$Me_4P_2N_4S_2$].[18] Significantly, however, there was no evidence for dissociation of the adducts **5d** or **5e** into *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}O\text{-}THF)]$ (**7**) and **1b** or **1c** in THF. Furthermore, the three-bond coupling constants $^3J(^{31}PR_2\text{–}^{31}PEt_3)$ and $^3J(^{195}Pt\text{–}^{31}PR_2)$ in **5d** and **5e** are larger and the one-bond coupling $^1J(^{195}Pt\text{–}^{31}PEt_3)$ is smaller than the corresponding couplings in **5c** (see Table I). These observations are consistent with the ligand **1b** or **1c** being more strongly coordinated to platinum than **1a**; i.e., the replacement of phenyl groups attached to phosphorus by ethyl or methyl groups increases the Lewis basicity of the $P_2N_4S_2$ ring.

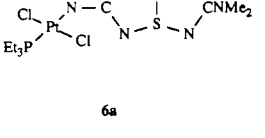
The large four-bond coupling of ca. 30 Hz between the inequivalent phosphorus atoms of the $P_2N_4S_2$ ring in **5c** and **5d** is comparable to that found for Lewis or Brønsted acid adducts of **1a** (16–23 Hz).[6]

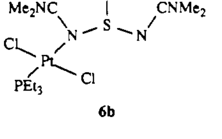
As indicated in Table I, the ^{31}P NMR spectra of the palladium derivatives **5f** and **5g** show similar features to those of the corresponding platinum complexes **5d** and **5e**, suggesting that their structures are also analogous.

Preparation and NMR Characterization of Platinum(II) Complexes of the Dithiatetrazocine 1d. The reaction of 2 molar equiv of **1d** with $[PtCl_2(PEt_3)]_2$ in CH_2Cl_2 at 0 °C produces complex **6** as a yellow solid in 68% yield. When this reaction is carried out in THF, the yield of **6** is much lower (*ca.* 30%) and the major product is *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-}O\text{-}THF)]$ (**7**). The facile displacement of the ligand **1d** in THF is presumably a reflection of the weak Pt–N bonds in **6**.

$$\underset{\mathbf{1d}}{2(Me_2NC)_2N_4S_2} + [PtCl_2(PEt_3)_2]_2 \rightarrow \underset{\mathbf{6}\ (R\ =\ NMe_2)}{2[PtCl_2(PEt_3)(R_2C_2N_4S_2)]} \qquad (2)$$

The ^1H, ^{13}C, and ^{31}P NMR spectra show that **6** is a mixture of two components, which are identified as the N-bonded exo and endo isomers **6a** and **6b**, respectively, on the basis of the low-temperature ^1H NMR spectrum.


6a


6b

At +25 °C the ^1H NMR spectrum of **6** in $CDCl_3$ shows broad, poorly defined resonances in the region 3.2–3.5 ppm for the $(CH_3)_2N$ groups. These signals are resolved into six sharp lines at −55 °C (Figure 2). The two most intense resonances at 3.62 and 3.23 ppm, which have twice the integrated intensity of each of the remaining four methyl signals, are attributed to the

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(21) Uson, R.; Royo, P.; Gimeno, J. *J. Organomet. Chem.* **1974**, *72*, 299.

(22) Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W. *Can. J. Chem.* **1988**, *66*, 1272.

(23) Jones, R.; Warrens, C. P.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 907.

(24) Jones, R.; Kelly, P. F.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1988**, 1569.

(25) A long Pt–N bond [2.122 (15) Å] and facile dissociation in THF have also been observed in the related complex *trans*-$PtCl_2(PEt_3)(\eta^1\text{-}N\text{-}Ph_2PS_2N_3)$. Chivers, T.; Hilts, R. W.; Krouse, I. H.; Cordes, A. W.; Hallford, R.; Scott, S. R. *Can. J. Chem.* **1992**, *70*, 2602.

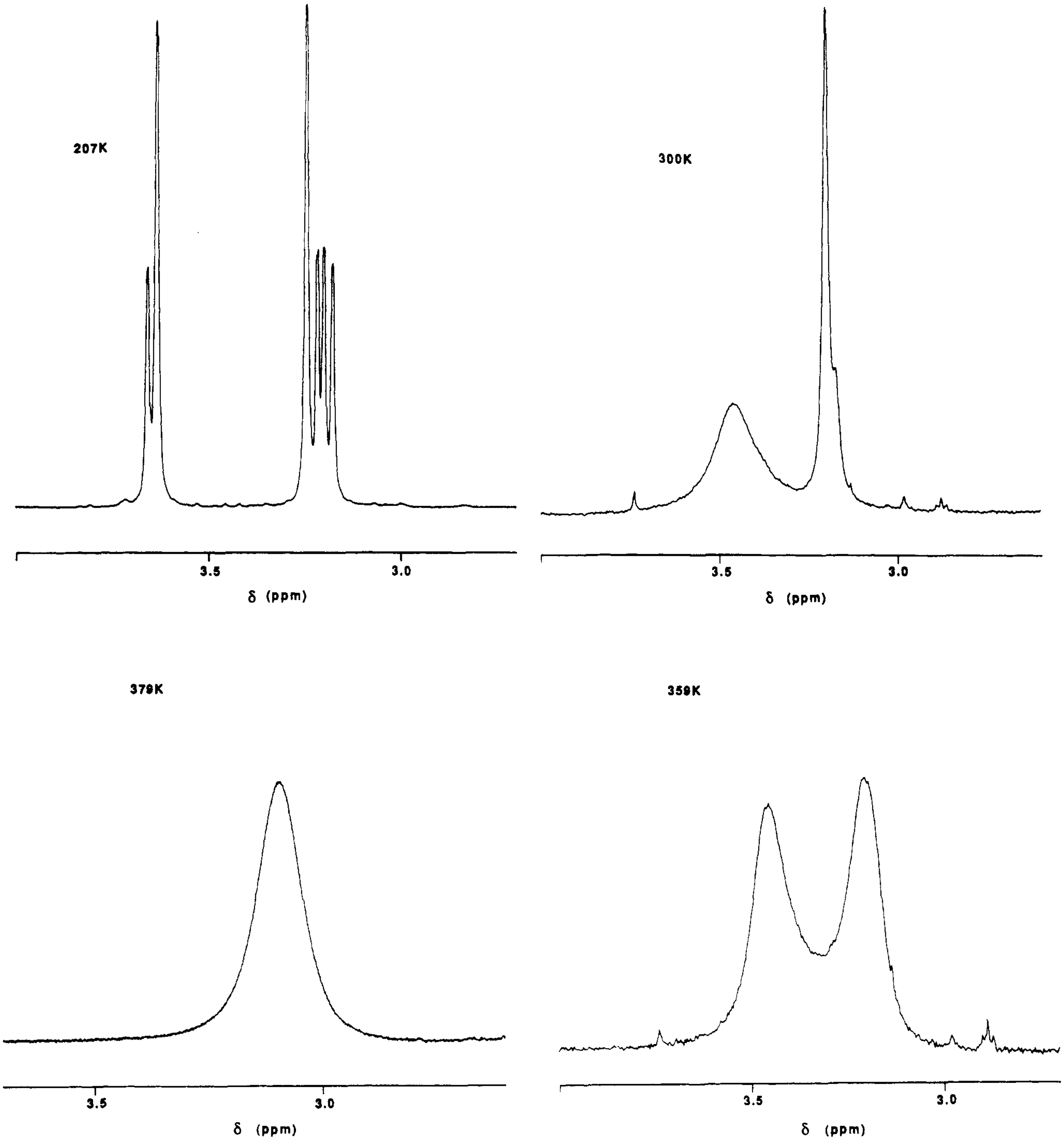

Figure 2. ^{1}H NMR spectra of a mixture of **6a** and **6b** in toluene-d_8.

inequivalent $(CH_3)_2N$ groups of the isomer **6a**.[26] The resonance at 3.23 ppm is most likely due to the uncoordinated Me_2N group (cf. δ 3.15 for **1b**)[7] and that at 3.62 ppm is therefore attributed to the Pt-bonded Me_2N group. The remaining four resonances at 3.17, 3.19, 3.21, and 3.65 ppm are ascribed to isomer **6b** since, in the absence of free rotation about the $\mathrm{Me_2N \overset{\cdots}{-} C}$ bond [d(C–N) $\sim$ 1.35 Å in **1d**],[7] all four methyl groups in this isomer are inequivalent due to the lack of any molecular symmetry. In this isomer the resonance at 3.65 ppm is probably due to the methyl group closest to platinum. The ^{13}C NMR spectrum of **6** in $CDCl_3$ at −55 °C also shows six sharp resonances at 40.74 and 40.54 (**6a**) and at 40.96, 40.30, 39.23, and 38.93 (**6b**) consistent with this interpretation. Finally, the ^{31}P NMR spectrum of **6** exhibits two resonances at +3.2, $^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 3729 Hz, and +2.2 ppm, $^1J(^{195}\mathrm{P}-^{31}\mathrm{P})$ = 3719 Hz, attributed to **6a** and **6b**, respectively, on the basis of their relative intensities. Thus it appears that the endocyclic and exocyclic nitrogen atoms have similar basicities toward platinum(II). Surprisingly, previous investigations of the reactions of **1d** with electrophiles have revealed a lack of basic properties, e.g. no reaction with $HClO_4$.[7]

In order to probe the possible interconversion of **6a** and **6b**, variable-temperature NMR studies were carried out. At 23 °C the ^{31}P{^{1}H} NMR spectrum shows that the mixture is composed of ca. 40% of **6a** and ca. 60% of **6b**. When the solution is cooled to −55 °C, the composition changes to ca. 80% of **6a** and ca. 20% of **6b**. Above +55 °C, only isomer **6b** is observed in solution. Interestingly, when the temperature of a toluene-d_8 solution of **6b** is raised above room temperature, the two proton signals for the inequivalent NMe_2 groups broaden and eventually collapse to a singlet at 95 °C. These changes can be attributed to a

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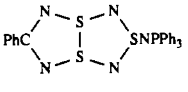
[26] Assuming C_s symmetry the CH_3 groups of each Me_2N group are related by a plane of symmetry.

"whizzing" of the $PtCl_2(PEt_3)$ group around the $C_2N_4S_2$ ring via a series of 1,3-metallatropic shifts, which may involve the exocyclic as well as the endocyclic nitrogen atoms. A gradual cooling of the hot toluene-d_8 solution from 100 °C down to -80 °C results in the exclusive formation of isomer **6b**.

Preparation and NMR Characterization of a Platinum(II) Complex of the Trithiatetrazocine $PhCN_4S_3NPPh_3$ (8). In contrast to the dithiatetrazocines **1a–d**, the trithiatetrazocine **8** has two pairs of inequivalent endocyclic nitrogen atoms in addition to the exocyclic nitrogen; i.e., there are three possible sites of electrophilic attack. The reaction of 2 molar equiv of **8** with $[PtCl_2(PEt_3)]_2$ in THF at 23 °C affords the 1:1 adduct **9** in essentially quantitative yield. The ^{31}P NMR spectrum of **9** in THF consists of only two resonances at +23.2 ($NPPh_3$) and +3.2 ppm (PEt_3) with $^1J(^{195}Pt-^{31}PEt_3)$ = 3680 Hz. This large value is indicative of an N-bonded ligand trans to PEt_3, but the ^{31}P NMR data do not distinguish between the three possible isomers **9a**, **9b**, and **9c**.

$$2PhCN_4S_3NPPh_3 + [PtCl_2(PEt_3)]_2 \rightarrow \underset{\mathbf{9}}{[PtCl_2(PEt_3)(PhCN_4S_3NPPh_3)]} \quad (3)$$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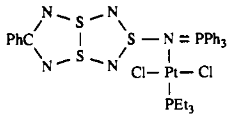
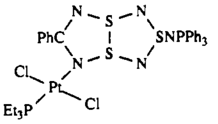
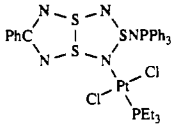

9a


9b


9c

Isomer **9b** can be ruled out on the grounds that the nitrogen atoms adjacent to the PhC groups are probably very weakly basic; cf. 1,5-$Ph_2C_2N_4S_2$.[7,27] Isomer **9a**, involving coordination to the exocyclic nitrogen atom, also seems unlikely because the ^{31}P NMR resonance for the Ph_3PN group is shifted by only 2.4 ppm relative to that for the uncoordinated ligand, and no coupling to platinum is observed for this signal. We conclude, therefore, that isomer **9c**, in which the platinum is bonded to a nitrogen atom closest to the electron-releasing Ph_3PN group,[28] is probably the correct structure for this adduct.

Preparation and ^{31}P NMR Spectra of η^2-S,S′ Platinum Complexes of 5b, 5d, and 5e. Since the transannular S–S bond is retained in the N-bonded adducts **5c–g**, (cf. **5a**[6]) it was of interest to investigate the possible incorporation of both η^1-N and η^2-S,S′ bonding modes (cf. **2a–c**) in the same complex via the oxidative-addition of these N-bonded adducts to a platinum(0) reagent.

The N-methylated derivative **5b** was included in this study because it was anticipated that **5b** would be less likely than **5a** to undergo N–CH_3 bond cleavage in view of the stronger Lewis basicity of **1b** compared to that of **1a** (vide supra).

The eight-membered ring **1b** reacts rapidly with methyl triflate in CH_2Cl_2 at 23 °C to afford the moisture-sensitive, yellow trifluoromethanesulfonate salt of **5b**. The ^{31}P NMR spectrum of **5b** shows two doublets at +161.1 and +108.0 ppm [cf. $\delta(^{31}P)$ +134.9 ppm for **1b**].[18] The four-bond coupling constant between the inequivalent phosphorus atoms is 12.5 Hz [cf. $^4J(^{31}P-^{31}P)$ = 23 Hz for **5a**].[6] These NMR data suggest strongly that the structure of **5b** is similar to that of **5a**.[6]

The reactions of **5b**, **5d**, and **5e** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ proceed cleanly at 0 °C in toluene to give the 1:1 adducts **10a**, **10b**, and **10c**.

$$\underset{\mathbf{5b},\ \mathbf{5d},\ \text{or}\ \mathbf{5e}}{R_4P_2N_4S_2E} + Pt(CH_2{=}CH_2)(PPh_3)_2 \xrightarrow{-CH_2=CH_2} \begin{array}{c} Pt(PPh_3)_2(R_4P_2N_4S_2E) \\ \mathbf{10a}\ (R = Et,\ E = Me^+) \\ \mathbf{10b}\ [R = Et,\ E = PtCl_2(PEt_3)] \\ \mathbf{10c}\ [R = Me,\ E = PtCl_2(PEt_3)] \end{array} \quad (4)$$

The composition of these adducts is indicated by chemical analyses and ^1H NMR spectra, which exhibit resonances for alkyl and aryl protons in the appropriate intensity ratios (see Experimental Section). ^{31}P NMR spectroscopic data are consistent with a μ^2,η^3-N,S,S′ bridging mode for the $P_2N_4S_2$ ring in **10a–c** (see Table III). Compound **10a** exhibits a first-order ^{31}P NMR spectrum in which two resonances are observed at 52.0 and 64.3 ppm for the Et_2P groups of the heterocyclic ring (cf. 108.0 and 161.1 ppm for **5b**). The large upfield shift of ca. 77 ppm in the mean value of these two chemical shifts is a strong indication that an S–S cross-ring bond is not present in **10a**.[4,6] The resonance at 64.3 ppm is assigned to P_A (i.e. the phosphorus atom adjacent to the methylated nitrogen), since the effect of electron withdrawal by the electrophile is expected to be greatest for that phosphorus atom.[6] The resonance at 52.0 ppm is, therefore, assigned to P_B. The values of the three-bond coupling constants, $^3J(^{31}P-^{195}Pt)$, are 261 and 523 Hz for P_A and P_B, respectively. The resonances for P_A and P_B are doublets of doublets due to the four-bond couplings $^4J(P_A-P_B)$ = 21 Hz and $^4J(P_A-P_D)$ = 12 Hz or $^4J(P_B-P_C)$ = 7 Hz. The resonances for the inequivalent Ph_3P groups attached to platinum in **10a** occur at 18.9 and 12.0 ppm with one-bond coupling constants, $^1J(^{31}P-^{195}Pt)$, of 3452 and 2315 Hz, respectively. The difference of >1100 Hz in these J values indicates that there is a substantial distinction between the trans effects of the two sulfur atoms. The former resonance is assigned to the PPh_3 group trans to the sulfur adjacent to the methylated nitrogen, since this is expected to form the weaker Pt–S bond. Finally, these two resonances are both doublets of doublets due to the two-bond coupling $^2J(P_C-P_D)$ = 32 Hz and the four-bond couplings $^4J(P_D-P_A)$ = 12 Hz or $^4J(P_C-P_B)$ = 7 Hz, respectively.

The ^{31}P NMR spectrum of **10b** is illustrated in Figure 3 and the NMR data are summarized in Table III. Two pairs of resonances are observed for **10b** at 58.2 and 60.3 ppm and at 16.8 and 14.2 ppm, all of which exhibit ^{195}Pt satellites as expected for the structure depicted in Figure 3. These resonances are readily assigned to PEt_2 and PPh_3 groups, respectively, on the basis of the magnitude of the $^{195}Pt-^{31}P$ coupling constants. The values of $^3J(^{195}Pt-^{31}PEt_2)$ are 377 and 594 Hz, while $^1J(^{195}Pt-^{31}PPh_3)$ is equal to 3008 and 2800 Hz. Comparison of these J values with the corresponding data for **10a** indicates that the sulfur atom adjacent to the methylated nitrogen in **10a** has a weaker trans influence than the sulfur atom attached to the platinum(II)-bonded nitrogen atom in **10b**. The Et_2P resonances at 58.2 and 60.3 ppm are assigned to P_A and P_B, respectively. The former consists of a doublet of doublets of doublets of doublets while the latter is a doublet of doublets of doublets. Both P_A and P_B exhibit three four-bond couplings; viz. $^4J(P_A-P_B)$ = 30 Hz, $^4J(P_A-P_C)$ = 6 Hz, and $^4J(P_A-P_D)$ = 6 Hz for **10b**, and $^4J(P_B-P_A)$ = 30 Hz, $^4J(P_B-P_C)$ = 4 Hz and $^4J(P_B-P_D)$ = 4 Hz. In addition, P_A is involved in the three-bond coupling $^3J(P_A-PEt_3)$ = 11 Hz. The PPh_3 resonances at 16.8 and 14.2 ppm are assigned to P_C and P_D, respectively, since the latter has the smaller $^1J(^{195}Pt-P)$ value (2800 Hz vs 3008 Hz) and is, therefore, attributed to the phosphorus atom trans to the sulfur attached to the Pt(II)-bonded nitrogen. The resonance for P_C consists of a doublet of doublets

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[27] In a separate experiment 1,5-$Ph_2C_2N_4S_2$ was shown to be unreactive toward $[PtCl_2(PEt_3)]_2$.

[28] Bojes, J.; Chivers, T.; Cordes, A. W,; MacLean, G.; Oakley, R. T. *Inorg. Chem.* **1981**, *20*, 16.

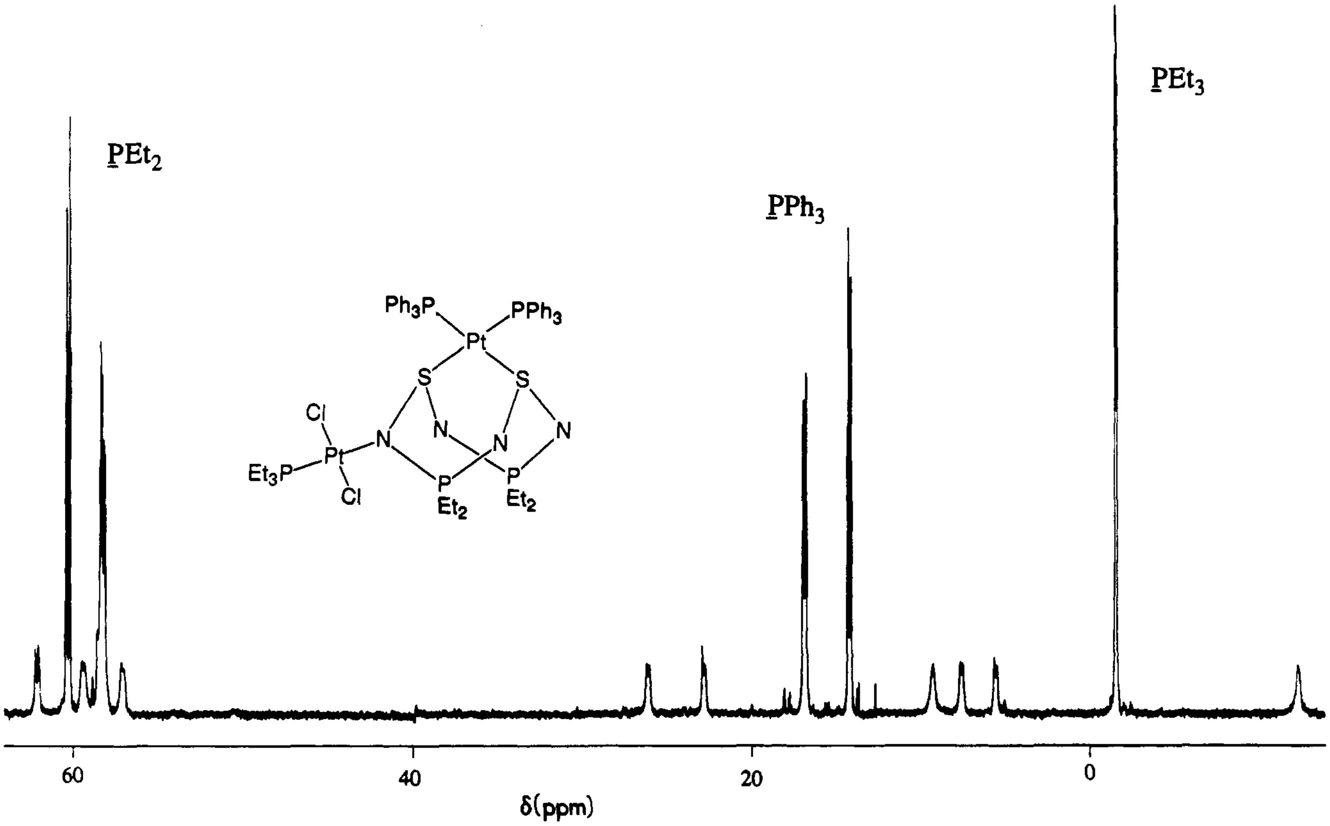


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Pt(PPh_3)_2(Et_4P_2N_4S_2)PtCl_2(PEt_3)]$ (**10b**) in CH_2Cl_2 at 23 °C.

of doublets of doublets due to the two-bond coupling $^2J(P_C–P_D)$ = 25 Hz, the four-bond couplings $^4J(P_C–P_A)$ = 6 Hz and $^4J(P_C–P_B)$ = 4 Hz, and the five-bond coupling $^5J(P_C–PEt_3)$ = 9 Hz. The resonance for P_D is a doublet of doublets of doublets comprising the following spin–spin interactions: $^2J(P_D–P_C)$ = 25 Hz, $^4J(P_D–P_A)$ = 6 Hz, and $^4J(P_D–P_B)$ = 4 Hz. The resonance for the (PEt$_3$)PtCl$_2$ group in **10b** consists of an doublet of doublets at −1.6 ppm with ^1J(Pt–P) = 3501 Hz, $^3J(PEt_3–P_A)$ = 11 Hz, and $^5J(PEt_3–P_C)$ = 6 Hz. The ^{31}P NMR spectrum of **10c** exhibits features similar to that of **10b**, indicating that these two complexes are structurally similar.

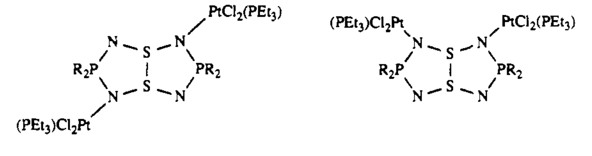
Decomposition of 10b. The complexes **10b** and **10c** are stable in the solid state in the absence of moisture, but they decompose slowly in THF at room temperature. The decomposition of **10b** results in the elimination of $PtCl_2(PEt_3)(PPh_3)$ and the formation of the bimetallic dimer **3b**.[4] The latter is presumably formed by dimerization of the coordinatively unsaturated platinum complex formed by dissociation of PPh_3 (cf. formation of **3a** and **3b** by the thermal decomposition of **2a** and **2b**, respectively) and the loss of a $PtCl_2(PEt_3)$ unit from **10b**. This facile decomposition of **10b** and **10c** in solution has thwarted attempts to obtain crystals suitable for an X-ray structural determination.

$$\mathbf{10b} \rightarrow PtCl_2(PEt_3)(PPh_3) + {}^1/_2\mathbf{3b} \qquad (5)$$

NMR Characterization of 2:1 and 3:1 Platinum(II) Complexes of a Diphosphadithiatetrazocine. The heterocycle **1a** (R = Ph) forms diprotonated or dimethylated derivatives, 1,5-$Ph_4P_2N_4S_2R'_2{}^{2+}$ (R′ = H, Me) which, on the basis of their ^{31}P NMR chemical shifts, no longer contain a transannular S–S bond.[6] The ^{31}P NMR chemical shift of 113.9 ppm for **1a** is displaced to 35–50 ppm in 1,5-$Ph_4P_2N_4S_2R'_2{}^{2+}$.[6] It was, therefore, of interest to determine whether more than one platinum(II) atom can be attached to the eight-membered ring.

Thus, **1a** and **1b** were treated with $[PtCl_2(PEt_3)]_2$ in a 1:1 molar ratio in CH_2Cl_2 giving rise, in each case, to a mixture of 1:1, 2:1, and 3:1 η^1-N bonded platinum(II) adducts. For both reactions, the 1:1 adduct is the preponderant product. The tetraethyl ring **1b**, however, produces a higher proportion of the 1:3 adduct in accordance with the stronger basicity of **1b** compared to **1a** (vide infra).

As indicated in Table IV the ^{31}P NMR spectra for the 2:1 adducts **11a** and **11b** contain only two resonances, attributable, on the basis of their chemical shifts, to pairs of equivalent PEt_3 ligands and PR_2 groups. Thus the structure of these adducts must be symmetrical, and we favor the isomer in which the $PtCl_2(PEt_3)$ groups are in distal rather than vicinal positions on steric grounds.[29] Evidently $^3J(PPh_2–PEt_3)$ is too small to introduce any significant magnetic inequivalence between the chemically equivalent pairs of phosphorus atoms.



Distal isomer   **11a** (R = Ph)   Vicinal isomer
11b (R = Et)

The reaction of **1b** with $[PtCl_2(PEt_3)]_2$ in a 2:3 ratio in CH_2Cl_2 produces mainly the 3:1 adduct $[(Et_3P)Cl_2Pt]_3(Et_4P_2N_4S_2)$ (**12b**). As indicated in Table IV, the ^{31}P NMR spectrum of **12b** exhibits three doublets, all with ^{195}Pt satellites, at +8.9, +2.8, and +2.5 ppm attributable to three inequivalent $PtCl_2(PEt_3)$ groups. Two other signals, both with ^{195}Pt satellites, are observed in the high-frequency region of the spectrum (see Figure 4). These signals can be assigned to the inequivalent phosphorus atoms of the heterocyclic ring and the shift of the ^{31}P NMR resonance from +134.9 ppm in **1b** to ca. 70 and ca. 80 ppm in the 1:3 adduct, **12b**, strongly suggests the loss of the cross-ring S–S bond in **12b**.[6] A comparable set of ^{31}P resonances is observed for the 1:3 adduct, **12a** (Table IV).

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(29) This structure has been confirmed by X-ray crystallography for the selenium analogue of **11a**. Chivers, T.; Doxsee, D. D.; Hilts, R. W.; Meersma, A.; Parvez, M.; van de Grampel, J. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1330.

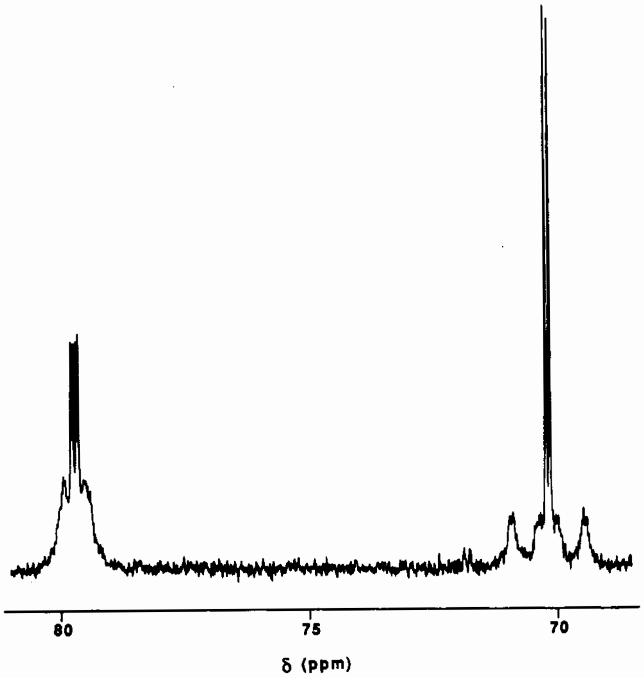
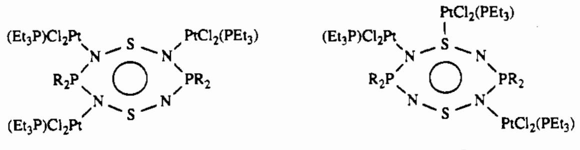


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $[PtCl_2(PEt_3)]_3(Et_4P_2N_4S_2)$ (**12b**) in CH_2Cl_2 at 23 °C showing the heterocyclic phosphorus resonances.

Inspection of the $^{31}P-^{31}P$ coupling constants for **12b**, which fall in the range 7–17 Hz [cf. $^3J(^{31}P-^{31}P)$ = 6–13 Hz for **5c–e**], reveals that the inequivalent phosphorus atoms of the $P_2N_4S_2$ ring are not coupled to each other. The resonance at +79.7 ppm is coupled to the two inequivalent $PtCl_2(PEt_3)$ groups with resonances at +8.9 and +2.8 ppm, and the resonance at +70.1 ppm is coupled to the third $PtCl_2(PEt_3)$ group [$\delta(^{31}P)$ = +2.5 ppm]. A similar pattern of coupling constants is observed for **12a** (Table IV). In view of the proposed bis(η^1-N) structure for the 2:1 adducts, the most likely structure of **12a** and **12b** involves either N,N,N or N,N,S bonding modes. However, the latter would involve a sterically unfavorable juxtaposition of $PtCl_2(PEt_3)$ groups and would give rise to more complex $^{31}P-^{31}P$ coupling patterns than observed. Consequently, we favor the tris(η^1-N) structure for **12a** and **12b**. Repeated attempts to obtain, pure crystalline samples of **12b**, uncontaminated with **5d**, and efforts to attach four $PtCl_2(PEt_3)$ groups to **1a** or **1b** were unsuccessful.



(N,N,N) **12a**, R = Ph
12b, R = Et (N,N,S)

Conclusion

Dithiatetrazocines, 1,5-$E_2N_4S_2$ [E = PR_2 (R = Me, Et, Ph), $CNMe_2$], and the trithiatetrazocine $PhCN_3S_3CNPPh_3$ react rapidly with $[PtCl_2(PEt_3)]_2$ in a polar solvent to give 1:1 adducts in which the heterocyclic ligand is attached to platinum by an endocyclic nitrogen atom. The weakness of the Pt–N bonds in these adducts is reflected in (a) the unusually long Pt–N distance in **5c**, (b) the facile displacement of the heterocyclic ligands by THF, and (c) the large values of $^1J(^{195}Pt-^{31}P)$ (>3600 Hz) for the trans PEt_3 ligands. In the case of 1,5-$(Me_2NC)_2N_4S_2$, the isomer in which an exocyclic nitrogen is bound to platinum is also produced, and variable-temperature NMR studies indicate the existence of a "ring-whizzing" process, involving [1,3]-metallatropic shifts.

Coordination of one platinum(II) atom to nitrogen in 1,5-$R_4P_2N_4S_2$, like N-methylation, results in retention of the cross-ring S–S interaction. These N-bonded adducts undergo oxidative addition to platinum(0) to give bimetallic complexes in which the $P_2N_4S_2$ ligands adopts a μ^2-η^3-N,S,S′ bridging mode. In common with monometallic η^2-S,S′ complexes, these bimetallic complexes are readily converted to dimers in which the $P_2N_4S_2$ ring functions as an η^2-S,N-μ^1-S′ bridging ligand.

Two or three $PtCl_2(PEt_3)$ groups can be attached to the $P_2N_4S_2$ ring in **1a** and **1b**, respectively. ^{31}P NMR data indicate that the Pt(II) atoms are all η^1-N bonded in these adducts and that, in contrast to dimethylation or diprotonation, the attachment of two $PtCl_2(PEt_3)$ groups to the $P_2N_4S_2$ ring in **1a** or **1b** preserves the transannular S–S bond. However, this interaction is apparently lost upon formation of a 3:1 adduct between Pt(II) and **1a** or **1b**.

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