associative bond formation process on introducing the stabilizing anions. This is most probably related to the totally different solvation shell in the case of NiL^{2+} and $\{NiL^{2+},X\}$ species, which assists the reaction with $HO_2^{\bullet}$ in a more associative way. As the redox potentials of the couples of $Ni^{III}LX_2/NiL^{2+}$ are only somewhat less anodic than that of the $O_2^{\bullet-}/H_2O_2$ couple, most of the oxidizing power of the free radical is maintained in these reactions. If such reactions occur also with transition-metal complexes present in biological systems, the high-valent complexes thus obtained might cause a deleterious process, thus explaining the toxicity of the superoxide.

The detailed mechanism study clearly indicates that the oxidations by $HO_2^{\bullet}$ occur as predicted via the inner-sphere mechanism.

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Supplementary Material Available: Figures 5 and 6, giving rates of formation of $Ni^{III}LX_2$ as a function of the concentrations of $Ni^{II}L(ClO_4)_2$ and HCO_2Na, respectively (2 pages). Ordering information is given on any current masthead page.

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Preparation and ^{31}P NMR Investigations of Monomeric and Dimeric Complexes of Platinum and Palladium with 1,5-Diphosphadithiatetrazocines: X-ray Structure of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)\cdot CH_2Cl_2$

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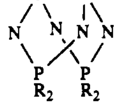
The reaction of $Pt(PPh_3)_2(C_2H_4)$ with $1,5\text{-}R_4P_2N_4S_2$ (R = Ph, Et, Me) in toluene at 23 °C produces the monomeric complexes $Pt(PPh_3)_2(1,5\text{-}R_4P_2N_4S_2)$ (**2a**, R = Ph; **2b**, R = Et; **2c**, R = Me) as air-stable yellow solids, which were characterized by ^{31}P NMR and, in the case of **2a**, ^{195}Pt NMR spectroscopy. The X-ray structure of **2a**$\cdot CH_2Cl_2$ shows that the heterocyclic ligand is bonded to platinum in an η^2-S,S′ fashion with Pt–S distances of 2.408 (4) and 2.341 (4) Å, respectively, and approximately square planar coordination at platinum. The crystals of **2a**$\cdot CH_2Cl_2$ are monoclinic, space group $P2_1/c$, with $a = 22.295$ (2) Å, $b = 10.500$ (1) Å, $c = 24.268$ (2) Å, $\beta = 101.10$ (1)°, $V = 5575$ (1) Å^3, and $Z = 4$. The final R and R_w values were 0.062 and 0.049, respectively. The reaction of $Pd(PPh_3)_4$ with $1,5\text{-}Ph_4P_2N_4S_2$ or $Pd(PPh_2Me)_4$ with $1,5\text{-}R_4P_2N_4S_2$ (R = Ph, Et) in toluene at 23 °C produces $Pd(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ or $Pd(PPh_2Me)_2(1,5\text{-}R_4P_2N_4S_2)$, respectively, which were characterized by ^{31}P NMR spectroscopy. Mild heating of the monomeric platinum or palladium complexes, either in solution or in the solid state, results in the dissociation of one of the phosphine ligands to give the dimers $[Pt(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$ (**5a**, R = Ph; **5b**, R = Et) or $[Pd(PPh_2R')(1,5\text{-}R_4P_2N_4S_2)]_2$ (R = R′ = Ph; R′ = Me, R = Ph, Et). The $P_2N_4S_2$ rings in **5a** act as chelating (N,S) ligands toward one platinum and form a bridge to the other platinum via the second sulfur atom to give a centrosymmetric dimeric structure. Variable-temperature ^{31}P NMR spectroscopic investigations of **5a** and **5b** reveal a fluxional process with an interconversion barrier of 10.2 ± 1.2 kcal mol^{-1} for **5a**. A [1,3]-metallotropic rearrangement is proposed to explain this behavior.

Introduction

The combination of hard (N) and soft (S) basic centers bestows upon binary sulfur-nitrogen (S–N) ligands a versatile coordination chemistry, as exemplified by the multifaceted behavior of tetrathiatetrazocine, S_4N_4.[1,2] With zerovalent complexes of the platinum group metals S_4N_4 produces both mono- and dinuclear complexes containing $\overline{\text{MSNSN}}$ rings (M = Pt, Pd, Ni)[3-5] via the unstable adduct $Pt(S_4N_4)(PPh_3)_2$ of unknown structure.[6] The related complexes $Ir(CO)Cl(S_4N_4)(PPh_3)$[7] and $Pt(S_4N_4)Cl_2(PMe_2Ph)_2$[8] incorporate the tridentate (N,S,S) $S_4N_4^{2-}$ ligand formed by insertion of the metal into an S–N bond. By contrast, we have shown that the integrity of 1,5-diphosphadithiatetrazocines (**1**) is retained in the formation of the 1:1 complex $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**2a**),[9] which loses PPh_3 reversibly upon heating in toluene at 105 °C to give the dimer $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$ (**5a**).[10] The structure of **5a** was shown to involve the ligand **1a** in an (η^2-N,S-μ, η^1-S′) bonding mode,[10] but the structure of **2a** was not established by X-ray crystallography.[9]



1a, R = Ph
1b, R = Et
1c, R = Me

In this account we provide the full details of these investigations, which include (a) the preparation and ^{31}P NMR characterization of monomeric platinum complexes $Pt(PPh_3)_2(1,5\text{-}R_4P_2N_4S_2)$ (R = Ph, Et, Me) and palladium complexes $Pd(PPh_2R')_2(1,5\text{-}R_4P_2N_4S_2)$ (R′ = R = Ph; R′ = Me, R = Ph, Et), (b) the preparation and ^{31}P NMR characterization of the corresponding dimers $[Pt(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$ (R = Ph, Et) and $[Pd(PPh_2R')(1,5\text{-}R_4P_2N_4S_2)]_2$, (c) the X-ray crystal structure of the monomer $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**2a**), and (d) a discussion

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Table I. ^{31}P NMR Data for Monomeric Platinum and Palladium Complexes of 1,5-Diphosphadithiatetrazocines

compd	$\delta^{a,b}$	$^1J(^{31}P-^{195}Pt)^c$	$\delta^{a,d}$	$^3J(^{31}P-^{195}Pt)^c$	$^4J(^{31}P-^{31}P)^c$	Δ^e
$Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**2a**)^{f,g}	18.3, t	2861	39.3, t	572		−74.9
$Pt(PPh_3)_2(1,5\text{-}Et_4P_2N_4S_2)$ (**2b**)^{h,i,j}	18.7, t	2820	60.6, t	579		−75.5
$Pt(PPh_3)_2(1,5\text{-}Me_4P_2N_4S_2)$ (**2c**)^f	18.7	2880	50.8	574		−69.2
$Pd(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**3a**)^f	25.4, t		53.9, t		12.5	−60.2
$Pd(PPh_2Me)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**4a**)^f	6.1, t		52.2, t		14.8	−61.9
$Pd(PPh_2Me)_2(1,5\text{-}Et_4P_2N_4S_2)$ (**4b**)^{f,j}	5.9, t		73.7, t		13.5	−62.4

[a] In ppm relative to external 85% H_3PO_4; t = triplet. [b] PPh_3 or PPh_2Me. [c] In Hz. [d] PR_2 of heterocyclic ligand. [e] $\Delta = \delta(^{31}P)$ of coordinated $1,5\text{-}R_4P_2N_4S_2 - \delta(^{31}P)$ of free $1,5\text{-}R_4P_2N_4S_2$. [f] In CH_2Cl_2. [g] $^4J(^{31}P-^{31}P) = 4.4$ Hz. [h] $^4J(^{31}P-^{31}P) = 4.5$ Hz. [i] In toluene. [j] Not isolated.

Table II. ^{31}P NMR Data for Dimeric Platinum and Palladium Complexes of 1,5-Diphosphadithiatetrazocines[a]

compd	$\delta^{b,c}$	$^1J(^{31}P-^{195}Pt)^d$	$\delta^{b,e}$	$^3J(^{31}P-^{195}Pt)^d$	$^4J(^{31}P-^{31}P)^d$	Δ^f
$[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$ (**5a**)^g	9.0	4160	31.1	170		−83.0
$[Pt(PPh_3)(1,5\text{-}Et_4P_2N_4S_2)]_2$ (**5b**)^g	15.3	4205	58.0	*h*		−78.1
$[Pd(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$ (**6a**)^g	24.7, t		57.0, d		11.1	−57.1
$[Pd(PPh_2Me)(1,5\text{-}Ph_4P_2N_4S_2)]_2$ (**7a**)^i	9.1, t		54.8, d		15.1	−59.3
$[Pd(PPh_2Me)(1,5\text{-}Et_4P_2N_4S_2)]_2$ (**7b**)^j	9.2, t		76.9, d		8.6	−59.2

[a] At 23 °C. [b] In ppm relative to external 85% H_3PO_4; d = doublet; t = triplet. [c] PPh_3 or PPh_2Me. [d] In Hz. [e] PR_2 of heterocyclic ligand. [f] $\Delta = \delta(^{31}P)$ of coordinated $1,5\text{-}R_4P_2N_4S_2 - \delta(^{31}P)$ of free $1,5\text{-}R_4P_2N_4S_2$. [g] In CH_2Cl_2. [h] Not resolved. [i] In CH_2Cl_2/toluene. [j] In CH_2Cl_2/hexanes.

of the fluxional behavior of the dimer $[Pt(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$ (R = Ph, Et).

Experimental Section

Reagents and General Procedures. All solvents were dried and distilled before use: tetrahydrofuran and toluene (Na); dichloromethane, chloroform, hexanes, and pentane (P_2O_5). All reactions and the manipulation of air- or moisture-sensitive products were carried out under an atmosphere of dry nitrogen (99.99% purity) by using Schlenk or drybox techniques. Commercial products were used as received: K_2PtCl_4 (Aldrich); $Pd(PPh_3)_4$, $Pd(PMePh_2)_4$, $(diphos)Ni(CO)_2$, $Ni(PPh_3)_4$ (all from Alfa); PPh_3 (Fisher); PPh_2Me (Aldrich); ethylene (Linde).

Literature procedures were used for the preparation of $1,5\text{-}R_4P_2N_4S_2$ (R = Ph,[11] Me,[11] Et[12]), $Pt(PPh_3)_4$,[13] and $Pt(PPh_3)_2(C_2H_4)$.[14]

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACE 200-MHz spectrometer. ^{31}P NMR spectra were obtained on a Varian XL 200-MHz or a Bruker AM 400-MHz spectrometer with 85% H_3PO_4 as an external reference. The lock signal for ^{31}P NMR was provided by sealed D_2O inserts or by using $CDCl_3$ as solvent. ^{195}Pt NMR spectra were obtained on a Bruker AM 400 spectrometer operating at 85.606 MHz in 10-mm NMR tubes equipped with a D_2O insert using a pulse length of 8 μs (ca. 60° flip angle), an acquisition time of 0.279 s, a spectral width of 100 000 Hz, a relaxation delay of 1.7 s, and a data collection size of 16 K (zero-filled to 32 K before transformation). ^{195}Pt chemical shifts are given with reference to 0.2 M H_2PtCl_6 in D_2O (0 ppm). Chemical analyses were performed by the Analytical Services of the Department of Chemistry, The University of Calgary, or by Canadian Microanalytical Service Ltd., Delta, BC, Canada. Molecular weight determinations were performed by Galbraith Laboratories Ltd., Knoxville, TN, by using the vapor-pressure osmometry method.

Preparation of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (2a). A solution of $Pt(PPh_3)_2(C_2H_4)$ (0.55 g, 0.74 mmol) in toluene (25 mL) was added dropwise (25 min), by transfer needle, to a stirred suspension of $1,5\text{-}Ph_4P_2N_4S_2$ (0.36 g, 0.73 mmol) in toluene (100 mL) at 23 °C. The solution immediately became a transparent yellow color, which darkened during the addition. After 17 h, the volume of the solvent was reduced by half under vacuum, and after 24 h at −25 °C the yellow precipitate was isolated by use of a filter needle. Recrystallization from CH_2Cl_2/hexane (1:10) yielded **2a** (0.66 g, 0.56 mmol). Anal. Calcd for $C_{60}H_{50}N_4P_4PtS_2$: C, 59.55; H, 4.16; N, 4.63. Found: C, 58.55; H, 4.03; N, 4.99. Mol wt (in $CHCl_3$, vapor-pressure osmometry): calcd, 1210; found, 1149. ^{31}P NMR data are given in Table I. The structure of **2a**·CH_2Cl_2 was determined by X-ray crystallography.

Preparation of $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$ (5a). A slurry of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (0.30 g, 0.25 mmol) in toluene (30 mL) was heated at reflux. After 1 h the Pt complex had dissolved to give a yellow solution. After 6 h the reaction mixture was allowed to cool to 23 °C and a bright yellow precipitate was separated by filtration, washed with toluene (5 mL), and dried under vacuum to give the dimer **5a** (0.185 g, 0.098 mmol), which was recrystallized from CH_2Cl_2/pentane (5:2). Anal. Calcd for $C_{42}H_{35}N_4P_3PtS_2$: C, 53.22; H, 3.72; N, 5.91. Found: C, 52.92; H, 3.79; N, 5.59. The dimeric structure of the product was established by X-ray crystallography.[10] ^{31}P NMR data are given in Table II.

Preparation of $Pt(PPh_3)_2(1,5\text{-}Et_4P_2N_4S_2)$ (2b) and $[Pt(PPh_3)(1,5\text{-}Et_4P_2N_4S_2)]_2$ (5b). A solution of $Pt(PPh_3)_2(C_2H_4)$ (0.705 g, 0.943 mmol) in toluene (30 mL) was added dropwise (25 min) to a stirred solution of $1,5\text{-}Et_4P_2N_4S_2$ (0.281 g, 0.943 mmol) in toluene (40 mL) at 23 °C. The ^{31}P NMR spectrum of the clear orange solution so formed (Table I) was consistent with the formation of **2b**, but this monomer could not be isolated. After 5 days at −25 °C this solution produced an orange solid, which was recrystallized from CH_2Cl_2/hexanes (1:1) to give orange crystals of the dimer **5b** contaminated with an impurity, which cocrystallizes with **5b**. ^{31}P NMR data for **5b** are given in Table II.

Preparation of $Pt(PPh_3)_2(1,5\text{-}Me_4P_2N_4S_2)$ (2c). A solution of $Pt(PPh_3)_2(C_2H_4)$ (0.36 g, 0.48 mmol) in toluene (25 mL) was added dropwise to a stirred suspension of $1,5\text{-}Me_4P_2N_4S_2$ (0.12 g, 0.50 mmol) in toluene (25 mL) at 23 °C. The pale yellow solution became orange, and after 15 h a yellow precipitate was removed by filtration. Solvent was removed from the filtrate under vacuum to give a sticky orange solid (0.37 g), which was recrystallized twice from CH_2Cl_2/pentane (1:2) at −25 °C to give **2c** (0.12 g, 0.12 mmol) as a yellow powder. Anal. Calcd for $C_{40}H_{42}N_4P_4PtS_2\cdot CH_2Cl_2$: C, 47.00; H, 4.24; N, 5.35. Found: C, 47.85; H, 4.65; N, 5.42. ^1H NMR (in $CDCl_3$): 1.44 (6 H, CH_3, d, $^2J_{^1H-^{31}P} = 6.6$ Hz), 1.37 (6 H, CH_3, d, $^2J_{^1H-^{31}P} = 6.7$ Hz), 5.3 (2 H, CH_2Cl_2), 7.1–7.6 (30 H, C_6H_5, m). ^{31}P NMR data are given in Table I.

Preparation of $Pd(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (3a). A solution of $1,5\text{-}Ph_4P_2N_4S_2$ (0.484 g, 0.99 mmol) in toluene (40 mL)/THF (2 mL) was added dropwise (30 min) to a stirred suspension of $Pd(PPh_3)_4$ (1.14 g, 0.99 mmol) in toluene (75 mL) to give a clear yellow solution. After 3 h a yellow-green precipitate had formed. The solution was stored at −25 °C for 18 h, and then the yellow precipitate of **3a** (1.10 g, 0.98 mmol) was separated by use of a filter needle. Anal. Calcd for $C_{60}H_{50}N_4P_4PdS_2$: C, 64.26; H, 4.49; N, 5.00. Found: C, 63.71; H, 4.47; N, 4.61. ^{31}P NMR data, given in Table I, confirmed the purity of this product. Attempted recrystallization produced the dimer **6a**, which was characterized by ^{31}P NMR spectroscopy (Table II).

Preparation of $Pd(PPh_2Me)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (4a). A solution of $1,5\text{-}Ph_4P_2N_4S_2$ (0.114 g, 0.23 mmol) in toluene (25 mL) was added dropwise (15 min) to a stirred slurry of $Pd(PPh_2Me)_4$ (0.21 g, 0.23 mmol) in toluene (25 mL) to give a clear yellow solution. After 20 h the volume of the solution was reduced to 5 mL under vacuum. The resulting solution was stored at −25 °C for 18 h to yield a yellow-green precipitate, which was separated by filter needle and recrystallized from CH_2Cl_2/hexanes (1:5) to give **4a** (0.12 g, 0.12 mmol) as a lime green solid. Anal. Calcd for $C_{50}H_{46}N_4P_4PdS_2$: C, 60.21; H, 4.65; N, 5.62. Found: C, 60.30; H, 4.74; N, 5.43. ^{31}P NMR data are given in Table I.

Preparation of $Pd(PPh_2Me)_2(1,5\text{-}Et_4P_2N_4S_2)$ (4b). A solution of $1,5\text{-}Et_4P_2N_4S_2$ (0.145 g, 0.485 mmol) in toluene (40 mL) was added to an equimolar amount of $Pd(PPh_2Me)_4$ (0.440 g, 0.485 mmol) in toluene (40 mL) at 23 °C. After 18 h the resulting solution was filtered to remove a trace of a black precipitate. The removal of solvent under

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Table III. Crystallographic Data for $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (**2a**)

chem formula $C_{60}H_{50}PtN_4P_4S_2 \cdot CH_2Cl_2$	fw = 1295.11
a = 22.295 (2) Å	space group $P2_1/c$
b = 10.500 (1) Å	T = 25 (2) °C
c = 24.268 (3) Å	λ = 0.710 73 Å
β = 101.10 (1)°	ρ_{calcd} = 1.543 g cm^{-3}
V = 5575 (1) Å^3	μ = 28.7 cm^{-1}
Z = 4	R^a = 0.062
	$R_w{}^b$ = 0.049

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

vacuum followed by recrystallization from CH_2Cl_2/hexane (1:5) at −20 °C produced **4b** (0.28 g, 0.35 mmol). ^{31}P NMR data are given in Table I. An attempted second recrystallization produced a mixture of **4b** and the corresponding dimer, **7b**.

X-ray Analysis. A suitable, yellow block-shaped crystal of **2a**·CH_2Cl_2 0.075 × 0.12 × 0.22 mm, obtained by diffusion of diethyl ether into a dichloromethane solution, was glued on the top of a glass fiber and transferred to the goniometer mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a Micro VAX 2000 computer. The scattering power of the studied crystals was weak, and no observable intensities could be measured with $\theta > 24°$. Unit cell parameters were determined from a least-squares treatment of the SET4[15] setting angles of 20 reflections with $12.70° < \theta < 13.47$. The space group $P2_1/c$ was derived from the observed systematic extinctions $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. This choice was confirmed by the solution and the successful refinement of the structure. Reduced cell calculations did not indicate any higher metrical lattice symmetry,[16] and examination of the final atomic coordinates of the structure did not yield extra symmetry elements.[17]

Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 2 h of X-ray exposure time; these reflections exhibited a linear decay of 11% during the 142.1 h of X-ray exposure time. A 360° ψ-scan for a reflection close to axial $(10,\bar{2},\bar{4})$ showed an intensity variation up to 8% about the mean value. The intensity data were corrected for the decay, for Lorentz and polarization effects, but not for absorption. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance[18] of the three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.025I)^2$. Equivalent reflections were averaged ($\sum\sigma/\sum I = 0.075$) resulting in 4332 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[19] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ)[20] minimizing the function $Q = \sum_h[w(|F_o| - |F_c|)^2]$. Subsequent Fourier summations showed density which could be correlated to the solvent molecule of dichloromethane. After the inclusion of the positional parameters of dichloromethane, the remainder of the structure refined smoothly. The overall geometry of the solvent molecule appeared rather distorted, suggesting some degree of disorder, but no resolvable disorder could be stated. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp^2 or sp^3 hybridization at the C-atom as appropriate with a fixed C–H distance of 0.98 Å. Weights were introduced in the final refinement cycles. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged at R = 0.062 and R_w = 0.049. A final difference Fourier synthesis revealed residual densities between −1.31 and 1.51 e/Å^3. The CH_2Cl_2 solvent residue is probably disordered as indicated by the thermal displacement motion ellipsoids and geometry data. Crystal data and experimental details of the structure determination are compiled in Table III. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given in Table IV. Scattering factors were those given by Cromer and Mann,[21] and anomalous dispersion factors taken from Cromer and Liberman[22] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL[23] and PLATON[24] (calculation of geometric data).

Results and Discussion

Synthesis of Monomeric Platinum and Palladium Complexes of 1,5-Diphosphadithiatetrazocines. The reactions of $Pt(PPh_3)_2(C_2H_4)$ or $Pd(PPh_2R)_4$ (R = Me, Ph) with 1,5-diphosphadithiatetrazocines proceed rapidly in toluene at room temperature according to eqs 1 and 2.

$$Pt(PPh_3)_2(C_2H_4) + 1,5\text{-}R_4P_2N_4S_2 \xrightarrow{-C_2H_4} Pt(PPh_3)_2(1,5\text{-}R_4P_2N_4S_2) \qquad (1)$$

2a, R = Ph

2b, R = Et

2c, R = Me

$$Pd(PPh_2R')_4 + 1,5\text{-}R_4P_2N_4S_2 \xrightarrow{-2PPh_2R'} Pd(PPh_2R')_2(1,5\text{-}R_4P_2N_4S_2) \qquad (2)$$

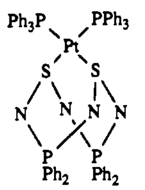
3a, R = R' = Ph

4a, R' = Me, R = Ph

4b, R' = Me, R = Et

Compounds **2a**, **2c**, **3a**, and **4a** were isolated as air-stable yellow solids that could be purified by recrystallization, whereas **2b** and **4b** were characterized by ^{31}P NMR spectroscopy in solution. Compound **2b** spontaneously loses a phosphine ligand in solution to give the corresponding dimer, **5b**, and **4b** undergoes a similar transformation to the dimer **7b** upon attempted recrystallization (vide infra).

The ^{31}P NMR spectra of **2a–c** consist of two equally intense signals at 18–19 and 40–60 ppm with ^{195}Pt satellites, which may be assigned to the Ph_3P ligands and the R_2P groups of coordinated 1,5-diphosphadithiatetrazocine, respectively, on the basis of the magnitude of the ^{31}P–^{195}Pt coupling constants. In the case of **2a,b**, these signals were resolved into 1:2:1 triplets that result from coupling between inequivalent pairs of phosphorus atoms, $^4J(^{31}P$–$^{31}P)$ = 4.4 Hz. The details are given in Table I. These assignments are confirmed by the ^{195}Pt NMR spectrum of **2a** (Figure 1), which consists of a 1:2:1 triplet of 1:2:1 triplets; i.e., the platinum nucleus is coupled to two pairs of equivalent phosphorus atoms with coupling constants of 2846 and 581 Hz, respectively. The NMR data for **2a–c** clearly indicate that the heterocyclic ligand is symmetrically bonded to platinum, and a molecular weight determination for **2a** by vapor-pressure osmometry in $CHCl_3$ was consistent with a monomeric structure. An X-ray structural determination of **2a** (vide infra) revealed that the heterocyclic ligand is bonded to platinum in an η^2-S,S' fashion.



2a

The three platinum complexes **2a–c** exhibit very similar coupling constants for both the one-bond Ph_3P–Pt interaction (2820–2880 Hz) and the three-bond R_2P–Pt interaction (572–580 Hz), and so their structures are probably identical. The values of $^3J(^{195}Pt$–$^{31}P)$ for **2a–c** are remarkably large (570–580 Hz), but we have been unable to unearth appropriate literature data for comparison. We note, however, that $^2J(^{195}Pt$–$^{31}P)$ for the bidentate $(EtO)_2PS_2^-$ ligand in Pt(II) complexes falls in the range 336–445 Hz.[25] The effect of coordination on the characteristically low-field

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Table IV. Atomic Coordinates and Isotropic Thermal Parameters for Non-H Atoms of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)\cdot CH_2Cl_2$

	x	y	z	U_{eq},^{a} Å^2
Pt(1)	0.21143 (3)	0.03309 (6)	0.15549 (2)	0.0330 (2)
S(1)	0.19238 (18)	0.1100 (4)	0.06022 (15)	0.0395 (16)
S(2)	0.30183 (18)	−0.0536 (4)	0.13605 (15)	0.0456 (14)
P(1)	0.2413 (2)	−0.1281 (4)	0.02765 (17)	0.0400 (17)
P(2)	0.3160 (2)	0.1917 (5)	0.09129 (19)	0.0508 (19)
P(3)	0.24270 (18)	−0.0217 (5)	0.24998 (15)	0.0413 (16)
P(4)	0.11196 (19)	0.1026 (4)	0.15753 (16)	0.0371 (16)
N(1)	0.1972 (5)	−0.0071 (11)	0.0164 (4)	0.045 (5)
N(2)	0.2465 (6)	0.2150 (11)	0.0620 (5)	0.044 (5)
N(3)	0.3407 (5)	0.0509 (13)	0.1079 (5)	0.054 (5)
N(4)	0.2742 (6)	−0.1653 (11)	0.0914 (5)	0.046 (5)
C(1)	0.1955 (7)	−0.2670 (15)	0.0013 (6)	0.041 (7)
C(2)	0.2128 (8)	−0.3861 (17)	0.0243 (6)	0.050 (7)
C(3)	0.1785 (8)	−0.4935 (15)	0.0024 (7)	0.059 (8)
C(4)	0.1312 (7)	−0.4806 (19)	−0.0415 (7)	0.061 (8)
C(5)	0.1149 (8)	−0.3616 (18)	−0.0645 (7)	0.065 (8)
C(6)	0.1470 (8)	−0.2574 (16)	−0.0423 (6)	0.053 (7)
C(7)	0.2967 (7)	−0.1223 (18)	−0.0189 (6)	0.048 (7)
C(8)	0.3130 (8)	−0.0052 (17)	−0.0377 (6)	0.062 (9)
C(9)	0.3557 (9)	0.0026 (18)	−0.0731 (7)	0.074 (9)
C(10)	0.3818 (9)	−0.107 (2)	−0.0881 (7)	0.068 (8)
C(11)	0.3657 (8)	−0.224 (2)	−0.0696 (7)	0.069 (9)
C(12)	0.3239 (8)	−0.2285 (18)	−0.0351 (7)	0.061 (8)
C(13)	0.3645 (8)	0.2555 (17)	0.0486 (7)	0.050 (7)
C(14)	0.4262 (9)	0.232 (2)	0.0576 (9)	0.102 (10)
C(15)	0.4613 (9)	0.290 (2)	0.0224 (9)	0.108 (12)
C(16)	0.4363 (12)	0.369 (2)	−0.0197 (9)	0.104 (11)
C(17)	0.3745 (11)	0.392 (2)	−0.0307 (9)	0.099 (11)
C(18)	0.3403 (9)	0.3359 (18)	0.0037 (8)	0.075 (9)
C(19)	0.3342 (9)	0.293 (2)	0.1540 (7)	0.057 (8)
C(20)	0.3754 (10)	0.255 (2)	0.1992 (9)	0.085 (10)
C(21)	0.3883 (13)	0.335 (3)	0.2435 (10)	0.111 (13)
C(22)	0.3619 (15)	0.450 (3)	0.2468 (12)	0.140 (15)
C(23)	0.3208 (13)	0.485 (2)	0.1998 (11)	0.131 (13)
C(24)	0.3049 (11)	0.409 (2)	0.1535 (8)	0.092 (10)
C(25)	0.3243 (7)	−0.0541 (16)	0.2746 (5)	0.040 (6)
C(26)	0.3625 (7)	0.0293 (18)	0.3079 (6)	0.054 (6)
C(27)	0.4232 (9)	0.000 (2)	0.3220 (7)	0.088 (12)
C(28)	0.4480 (9)	−0.108 (3)	0.3061 (8)	0.085 (10)
C(29)	0.4085 (9)	−0.1951 (18)	0.2758 (8)	0.062 (8)
C(30)	0.3470 (7)	−0.1694 (16)	0.2601 (6)	0.052 (7)
C(31)	0.2280 (6)	0.1070 (15)	0.2955 (6)	0.037 (6)
C(32)	0.2444 (7)	0.2325 (16)	0.2819 (7)	0.055 (7)
C(33)	0.2382 (7)	0.3349 (14)	0.3149 (7)	0.044 (7)
C(34)	0.2170 (8)	0.3128 (18)	0.3637 (7)	0.060 (8)
C(35)	0.2004 (8)	0.1934 (19)	0.3782 (7)	0.063 (8)
C(36)	0.2066 (7)	0.0894 (15)	0.3444 (7)	0.047 (7)
C(37)	0.2055 (7)	−0.1642 (15)	0.2696 (7)	0.042 (7)
C(38)	0.1584 (8)	−0.2197 (16)	0.2319 (7)	0.052 (7)
C(39)	0.1304 (8)	−0.3284 (16)	0.2468 (7)	0.057 (7)
C(40)	0.1483 (9)	−0.3837 (16)	0.2994 (8)	0.063 (8)
C(41)	0.1976 (9)	−0.3326 (17)	0.3351 (7)	0.068 (9)
C(42)	0.2263 (8)	−0.2212 (15)	0.3202 (8)	0.054 (8)
C(43)	0.0541 (7)	0.0067 (13)	0.1143 (6)	0.039 (6)
C(44)	0.0713 (8)	−0.0846 (15)	0.0787 (6)	0.048 (6)
C(45)	0.0279 (8)	−0.1556 (15)	0.0445 (6)	0.047 (7)
C(46)	−0.0341 (7)	−0.1415 (15)	0.0423 (6)	0.048 (7)
C(47)	−0.0503 (6)	−0.0490 (16)	0.0779 (6)	0.040 (6)
C(48)	−0.0081 (7)	0.0235 (16)	0.1136 (5)	0.045 (6)
C(49)	0.0804 (6)	0.1145 (16)	0.2218 (6)	0.038 (6)
C(50)	0.0573 (6)	0.0087 (15)	0.2436 (6)	0.046 (7)
C(51)	0.0340 (7)	0.0158 (19)	0.2925 (6)	0.060 (8)
C(52)	0.0339 (7)	0.131 (2)	0.3199 (7)	0.060 (8)
C(53)	0.0588 (8)	0.2371 (17)	0.2996 (7)	0.054 (7)
C(54)	0.0826 (7)	0.2305 (16)	0.2502 (7)	0.052 (7)
C(55)	0.1032 (8)	0.2666 (15)	0.1306 (6)	0.040 (6)
C(56)	0.1491 (8)	0.3488 (17)	0.1497 (7)	0.061 (8)
C(57)	0.1466 (8)	0.475 (2)	0.1364 (7)	0.070 (8)
C(58)	0.0938 (10)	0.5170 (17)	0.1014 (8)	0.070 (9)
C(59)	0.0457 (9)	0.4369 (16)	0.0791 (6)	0.056 (8)
C(60)	0.0497 (8)	0.3082 (17)	0.0956 (7)	0.056 (8)
Cl(1)	0.4231 (4)	0.6493 (11)	0.1017 (4)	0.226 (6)
Cl(2)	0.4968 (4)	0.8753 (13)	0.1228 (5)	0.278 (8)
C(61)	0.4409 (16)	0.807 (3)	0.1080 (16)	0.27 (3)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

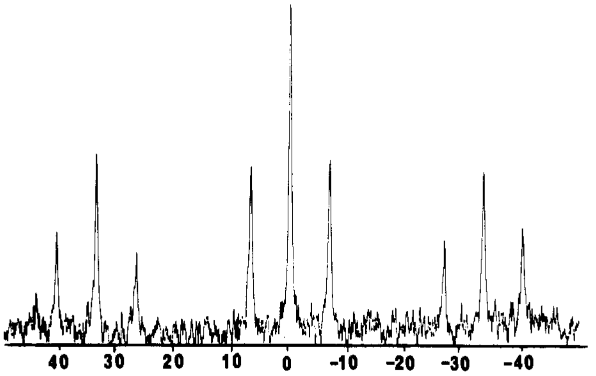

Figure 1. ^{195}Pt NMR spectrum of $Pt(PPh_3)_2[1,5\text{-}Ph_4P_2N_4S_2]$ (**2a**) in $CDCl_3$.

^{31}P NMR chemical shifts of 1,5-diphosphathiatetrazocines, which appear to be related in some way to the structural constraint imposed by the cross-ring S–S interaction,[11,26] is also noteworthy. Upfield shifts of the order 70–75 ppm are observed as a result of the loss of the transannular S--S interaction (Table I).

The reaction of $Pd(PPh_3)_4$ with **1a–c** in toluene was only successful for the preparation of **3a** (eq 2). The related complexes **4a,b** were obtained by the treatment of $Pd(PPh_2Me)_4$ with **1a,b**, respectively. As indicated in Table I, the ^{31}P NMR spectra of **3a**, **4a**, and **4b** exhibit two 1:2:1 triplets consistent with two pairs of inequivalent phosphorus atoms. The triplet structure is attributed to the four-bond $R'Ph_2P$–R_2P coupling of ca. 13–15 Hz, which is significantly larger than the value of 4.4 Hz observed for the platinum complexes, **2a,b**. Coordination to palladium causes a less pronounced (ca. 60 ppm) upfield shift of the ^{31}P NMR resonance of the 1,5-diphosphadithiatetrazocine ligand compared to the Pt complexes (70–75 ppm). The ^{31}P NMR data strongly suggest that the structures of **3a**, **4a**, and **4b** are analogous to that of **2a**.

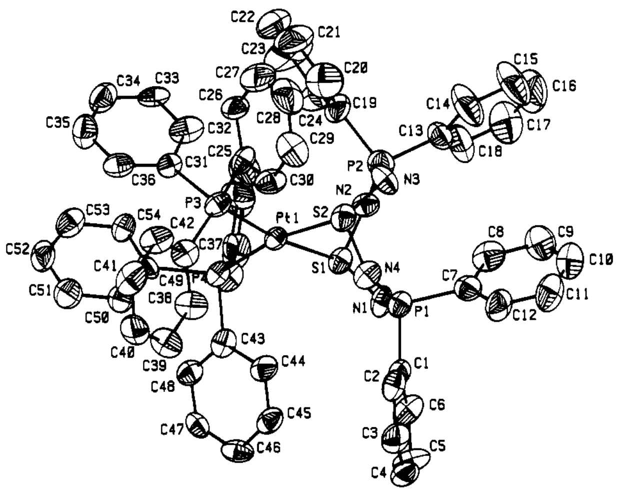

Figure 2. ORTEP plot of $Pt(PPh_3)_2[1,5\text{-}Ph_4P_2N_4S_2]$ (**2a**) (50% probability ellipsoids).

X-ray Structure of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)$ (2a). The structure of **2a** was determined by X-ray crystallography. The molecular geometry and atomic numbering scheme are given in Figure 2, and pertinent bond lengths and bond angles are listed in Table V. A better view of the conformation of the $P_2N_4S_2$

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Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $\mathrm{Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)\cdot CH_2Cl_2}$

Bond Distances			
Pt(1)-S(1)	2.408 (4)	S(2)-N(3)	1.628 (13)
Pt(1)-S(2)	2.341 (4)	S(2)-N(4)	1.635 (12)
Pt(1)-P(3)	2.337 (4)	P(1)-N(1)	1.598 (12)
Pt(1)-P(4)	2.344 (4)	P(1)-N(4)	1.627 (13)
S(1)-N(1)	1.643 (11)	P(2)-N(2)	1.594 (14)
S(1)-N(2)	1.629 (13)	P(2)-N(3)	1.602 (14)

Bond Angles			
S(1)-Pt(1)-S(2)	86.36 (13)	Pt(1)-S(2)-N(4)	100.6 (5)
S(1)-Pt(1)-P(4)	85.59 (14)	N(3)-S(2)-N(4)	111.6 (7)
S(2)-Pt(1)-P(3)	89.79 (14)	N(1)-P(1)-N(4)	120.2 (6)
P(3)-Pt(1)-P(4)	99.25 (14)	N(2)-P(2)-N(3)	120.8 (7)
Pt(1)-S(1)-N(1)	110.4 (4)	S(1)-N(1)-P(1)	126.8 (7)
Pt(1)-S(1)-N(2)	102.0 (5)	S(1)-N(2)-P(2)	124.0 (8)
N(1)-S(1)-N(2)	112.5 (6)	S(2)-N(3)-P(2)	122.9 (8)
Pt(1)-S(2)-N(3)	111.8 (5)	S(2)-N(4)-P(1)	120.1 (7)

ring is provided in Figure 3. The asymmetric unit consists of a molecule of **2a** and a molecule of CH_2Cl_2 solvent, which is highly disordered. The eight-membered heterocyclic ligand in **2a** is attached to platinum by two Pt–S bonds with distances of 2.408 (4) and 2.341 (4) Å and ∠SPtS = 86.4 (1)°. The approximately square planar coordination sphere of Pt is completed by two PPh_3 groups with *d*(Pt–P) = 2.337 (4) and 2.344 (4) Å and ∠PPtP = 99.3 (1)°. The transannular S–S separation is opened up from 2.528 (1) Å in the free ligand, **1a**,[27] to 3.250 (6) Å in **2a**. The average S–N bond length increases slightly from 1.590 (3) to 1.634 (7) Å whereas the average P–N bond lengths are essentially unchanged at 1.621 (3) vs 1.605 (15) Å. The NSN angles are reduced from 116.1 (1)° in **1a** to an average value of 112.1 (6)° in **2a**, while the endocyclic bond angles at phosphorus increase from 110.8 (1) to 120.5 (5)° upon coordination to platinum. The endocyclic bond angles at nitrogen in **2a** are in the range 120.1–126.8 (7)° (cf. 120.7 (2) and 121.2 (2)° for **1a**).[27]

Synthesis of Dimeric Platinum and Palladium Complexes of 1,5-Diphosphadithiatetrazocines and the Structure of 5a. The monomeric platinum and palladium complexes described above form dimeric complexes via loss of a phosphine ligand upon mild heating according to eqs 3 and 4. In the case of the conversion

$$2\mathrm{Pt(PPh_3)_2(1,5\text{-}R_4P_2N_4S_2)} \xrightarrow{-2\mathrm{PPh_3}} [\mathrm{Pt(PPh_3)(1,5\text{-}R_4P_2N_4S_2)}]_2 \qquad (3)$$

2a or **2b** **5a**, R = Ph

5b, R = Et

$$2\mathrm{Pd(PPh_2R')_2(1,5\text{-}R_4P_2N_4S_2)} \xrightarrow{-2\mathrm{PPh_2R'}} [\mathrm{Pd(PPh_2R')(1,5\text{-}R_4P_2N_4S_2)}]_2 \qquad (4)$$

3a, **4a** or **4b** **6a**, R = R' = Ph

7a, R' = Me, R = Ph

7b, R' = Me, R = Et

of **2b** into **5b** and **4b** into **7b**, these reactions occur spontaneously in solution at 25 °C, whereas the formation of the other dimeric complexes requires heating either in solution (**5a**, toluene at reflux) or of the dry solid (**6a** and **7a**). This observation is consistent with our recent finding that $1,5\text{-}Et_4P_2N_4S_2$ binds more strongly than $1,5\text{-}Ph_4P_2N_4S_2$ to platinum(II) in N-bonded complexes of the type *trans*-$PtCl_2(PEt_3)(\eta^1\text{-}Et_4P_2N_4S_2)$.[28]

The reversibility of the transformations depicted in eqs 3 and 4 has been tested in two cases. The addition of 2 molar equiv of Ph_3P to a solution of **5a** in CH_2Cl_2 resulted in the regeneration of the monomer **2a** over the course of several days at room temperature as indicated by the ^{31}P NMR spectrum. The regeneration of **3a** from **6a** in a similar manner occurred within 2 h at 23 °C.

The structure of **5a** was shown by X-ray crystallography to consist of a centrosymmetric dimer in which the $P_2N_4S_2$ rings act as chelating (N,S) ligands toward one platinum atom and form a bridge to a second platinum via the other sulfur atom. The structural details are given in the preliminary communication.[10]

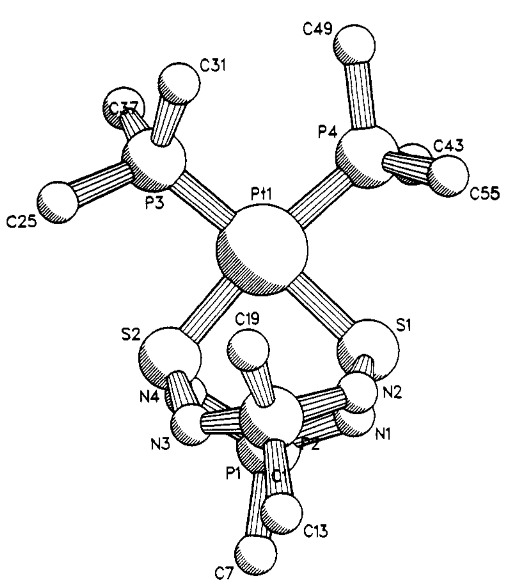


Figure 3. Conformation of the $P_2N_4S_2$ ring in **2a**.

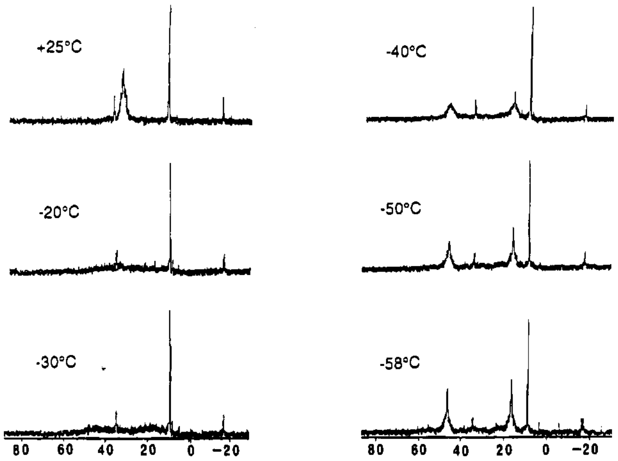
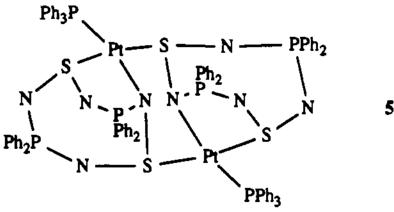


Figure 4. Variable-temperature 200-MHz $\{^1H\}^{31}P$ NMR spectra of $[\mathrm{Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)}]_2$ (**5a**) in $CH_2Cl_2/CDCl_3$ (1:1).



5a

^{31}P NMR Spectra and Fluxional Behavior of Dimeric Pt and Pd Complexes of 1,5-Diphosphatetrazocines. As illustrated in Table II, the ^{31}P NMR spectra of the dimeric Pt and Pd complexes **5a**, **5b**, **6a**, **7a**, and **7b** reveal equivalent environments for the R_2P groups of the heterocyclic ligand *at room temperature* indicative of a fluxional process. At −58 °C the ^{31}P NMR spectrum of **5a** exhibits two equally intense singlets at +46.3 and +16.3 ppm for the inequivalent Ph_2P groups (see Figure 4) consistent with the observed solid structure. When the temperature of the solution is gradually raised, these two singlets broaden and collapse until at +25 °C a new singlet is apparent at +31.1 ppm. The reverse of these changes is observed when the solution is cooled again to −60 °C. The coalescence temperature is ca. −30 °C, which corresponds to an interconversion barrier of 10.2 ± 1.2 kcal mol^{-1}.[29]

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Inorg. Chem. **1992**, *31*, 2161–2166

A [1,3]-metallotropic rearrangement involving a pendular movement of the Ph_3P–Pt groups between vicinal nitrogen atoms has been proposed to account for these observations (see Scheme I of ref 10). The Pt dimer, **5b**, exhibits similar fluxional behavior, At −71 °C the ^{31}P NMR spectrum of **5b** exhibits two equally intense signals at +73.8 and +40.2 ppm for the inequivalent Et_2P groups in addition to the signal for the two equivalent Ph_3P ligands at +12.9 ppm [$^1J(^{31}P-^{195}Pt) = 4140$ Hz]. The large value of $^1J(^{195}Pt-^{31}P)$ (ca. 4200 Hz) for the dimers **5a,b** compared with the values of ca. 2850 Hz observed for this interaction in the monomers **2a–c** is presumably a reflection of the weak trans influence of nitrogen in the dimers compared to sulfur in the monomers.[30-32]

When the temperature of the solution of **5b** is raised, the two signals for Et_2P groups broaden and collapse. However, an accurate coalescence temperature could not be obtained because **5b** cocrystallizes with another product, but it appears to be higher than that of **5a** consistent with stronger Pt–N bonding in **5b** compared to that in **5a**.[28] The ^{31}P NMR spectrum of the other product at −60 °C in CH_2Cl_2 exhibits four equally intense resonances at 62.8, 53.2, 51.6, and 20.9 ppm, which we attribute to *Et_2P* groups, and two singlets at 13.8 and 12.9 ppm with $^1J(^{31}P-^{195}Pt) = 3655$ and 4240 Hz, respectively, which we assigne to *Ph_3P* groups. Thus, the composition of the other product appears to be similar to that of the dimers **5a,b**, but it contains four inequivalent heterocyclic phosphorus atoms and two inequivalent, platinum-bound Ph_3P ligands. This product is also fluxional, and further studies are in progress in an attempt to isolate and structurally characterize it.

As indicated in Table II, the ^{31}P NMR spectra of the Pd dimers **6a**, **7a**, and **7b** at room temperature consist of a 1:1 doublet for the PR_2 groups and a 1:2:1 triplet for the PPh_2R' ligands with relative intensities of 2:1. The four-bond $^{31}P-^{31}P$ couplings, which are not observed for the Pt dimers, are in the range 9–15 Hz. In contrast to the Pt dimers, the resonances for the inequivalent PR_2 groups in the Pd dimers could not be resolved into the expected two components even at −90 °C. Thus, it appears that the energy barrier for the 1,3-shift is significantly lower when Pt is replaced by Pd in these dimers.

Conclusion. Zerovalent Pt or Pd complexes react readily with 1,5-diphosphadithiatetrazocines via insertion into the transannular S–S linkage to give mononuclear complexes of the type $M(PPh_2R')_2(1,5\text{-}R_4P_2N_4S_2)$ (M = Pt, Pd; R = Ph, Et, Me; R′ = Ph, Me) for which an η^2-S,S′ bonding mode has been established. These monomers readily lose one PR_3 molecule to give the dimers $[M(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$ in which the heterocyclic ligand exhibits an η^2-S,N-μ,η^1-S′ interaction with the metal centers. Both the Pt and Pd dimers undergo a facile fluxional process that probably involves a [1,3]-metallotropic rearrangement.

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Supplementary Material Available: Listings of crystal data and details of the structure determination, anisotropic thermal parameters, bond distances, bond angles, and torsion angles for non-hydrogen atoms (9 pages); a listing of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Experimental and Ab-Initio Stability Correlations among Isomeric Methyl Derivatives of *closo*- and *nido*-Monocarbahexaboranes

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The relative stabilities of the various isomeric methyl derivatives of *closo*-1-CB_5H_7 and *nido*-2-CB_5H_9, determined by both experimental and calculational (MP2/6-31G*//3-21G) methods, are compared. Calculational results indicate a 1.5 kcal/mol lowering of the activation energy for bridging hydrogen tautomerization of CB_5H_7 when the terminal hydrogen attached to the cage carbon is replaced by a methyl group; this is in excellent agreement with experimental observations. The calculated equilibrium ratio of 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 is compared to both past and recent experimental results. The relative stabilities of the four CH_3-*nido*-2-CB_5H_8 isomers are correlated to synthetic reaction results as well as with isomer interconversion observations at elevated temperatures; kinetic vs equilibrium conclusions are reached.

Introduction

The structures of *closo*-1-CB_5H_7[1-3] and *nido*-2-CB_5H_9[4] systems have been determined and found to be consistent with those previously proposed from the analyses of NMR data.[5-15] The (near) octahedral structure of *closo*-1-CB_5H_7 has also been examined by various calculational methods, PRDDO,[16] MNDO,[17] AM1 calculations,[18] and ab-initio (with full geometry optimization at the STO-3G level using the Gaussian-80 code)[19] MO calcu-

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