Dynamic Behavior and Crystal Structures of Pd₂(μ_{NS},η^2-L)₂Cl₂(PMe₃)₂ (L = Pyrimidine-2-thiolate, 4-Methylpyrimidine-2-thiolate, and Methylimidazole-2-thiolate): Influence of the N–C–S Bond Angle on the Stability of (Heterocyclic 2-thiolato)dipalladium Complexes

Glenn P. A. Yap[†] and Craig M. Jensen*

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

Received February 13, 1992

Dipalladium complexes Pd₂(μ_{NS},η^2-L)₂Cl₂(PMe₃)₂ (L = pyrimidine-2-thiolato, **2**; 4-methylpyrimidine-2-thiolato, **3**; and 1-methylimidazole-2-thiolato, **4**) were prepared by reaction of [PdCl(μ-Cl)(PMe₃)]₂ with the corresponding sodium heterocyclic thiolate. The molecular structures of **2**–**4** have been determined by X-ray diffraction. Crystallographic data: for **2** monoclinic *C2/c*, *Z* = 4, *a* = 19.857 (4) Å, *b* = 11.124 (2) Å, *c* = 12.054 (2) Å, β = 117.12 (1)°, *V* = 2369.9 (8) Å³; for **3** monoclinic *C2/c*, *Z* = 4, *a* = 19.616 (7) Å, *b* = 12.343 (4) Å, *c* = 11.886 (4) Å, β = 118.25 (3)°, *V* = 2535 (2) Å³; for **4**·(acetone) orthorhombic *Pbca*, *Z* = 8, *a* = 10.460 (3) Å, *b* 15.801 (4) Å, *c* = 32.17 (2) Å, *V* = 5316 (4) Å³. Variable-temperature ¹H NMR spectra of **2** indicate a temperature-dependent equilibrium is established with a second species in solution. From the changing ratios of the integrated intensities of the signals as associated with the two species over the range –40 to +50 °C, values of ΔH = 29 kJ mol⁻¹ and ΔS = 110 J K⁻¹ mol⁻¹ can be estimated for the equilibrium process. Carbon tetrachloride boiling point elevation experiments indicated that the predominant species in solutions of **2** and **3** at high temperatures have molecular weights of 340 ± 30 and 370 ± 30, respectively, and are monomeric species resulting from the cleavage of the parent dimeric complexes. The ³¹P{¹H} and ¹H NMR spectra of **3** dissolved in toluene-*d₈* are much more complicated than those of **1** and indicate that not only are both dimeric and monomeric species present in solution but also additional isomeric species are present. Variable-temperature ¹H NMR studies of **3** indicate interconversion of the isomers occurs in concert with the dimer–monomer interconversion and suggests that the dimer–monomer interconversion process involves Pd–N bond rupture. The variable-temperature ¹H NMR spectra of complex **4** over the –50 to +100 °C range are static, indicating the absence of any rapid equilibrium process on the NMR time scale. The molecular structures of **2** and **3** as well as that previously reported for Pd₂(μ-pyS)₂Cl₂(PMe₃)₂ (**1**) indicate no significant variation in the coordinative interaction of the $\mu_{NS}\eta^2$ bridging heterocyclic 2-thiolate ligands despite the differences in the basicities of the ligands. This suggests that the geometrical constraints of the N–C–S bond angles of the rigid six-membered heterocyclic restricts coordinative interaction and is responsible for the similar dynamic behavior observed for **1**–**3**. The five-membered heterocycle ring of **4** has larger N–C–S bond angles and contains Pd–N bond distances which are significantly shorter than those of **1**–**3**, demonstrating an enhanced Pd–N interaction and accounting for the static variable-temperature ¹H NMR spectra obtained for **4**.

Introduction

Recently, the bis(μ_{NS},η^2-pyridine-2-thiolato) (pyS) complex Pd₂(μ_{NS},η^2-pyS)₂Cl₂(PMe₃)₂ (**1**), was found to exhibit rapid equilibrium behavior in solution.[1] Variable-temperature ¹H, ¹³C-{¹H}, and ³¹P{¹H} NMR spectroscopic studies as well as a molecular weight determination at 77 °C indicated that **1** is in rapid equilibrium with monomeric Pd(pyS)Cl(PMe₃) in solution. Studies of the related μ_{NS},η^2-pyS complexes Pd₂[2-(dimethyl-amino)phenyl]₂(μ_{NS},η^2-pyS)₂[2] and Rh₂(pyS)₂(CO)₄[3] have indicated that other fluxional processes may account for the dynamic behavior observed for these complexes in solution. In order to investigate the generality of the reversible dimerization observed in solution for **1**, we have prepared the related pyrimidine-2-thiolate (primS) complexes Pd₂(μ_{NS},η^2-primS)₂Cl₂(PMe₃)₂ (**2**) and Pd₂(μ_{NS},η^2-4-MeprimS)₂Cl₂(PMe₃)₂ (**3**) as well as the 1-methylimidazole-2-thiolato (MeimidS) complex, Pd₂(μ_{NS},η^2-MeimidS)₂Cl₂(PMe₃)₂ (**4**), and examined their solution behavior by variable-temperature ¹H NMR spectroscopy. While the dynamic behavior of the primS derivatives was quite similar to that found for **1**, no rapid equilibrium behavior was observed for

the corresponding MeimidS complex on the NMR time scale. In order determine the origin of this surprising contrast between the five- and six-membered μ_{NS},η^2-heterocyclic 2-thiolato complexes, we have performed single-crystal structure determinations of **2**–**4**. We herein report the syntheses and molecular structures of the heterocyclic 2-thiolato dipalladium complexes along with the results of our variable-temperature ¹H NMR spectroscopic studies.

Experimental Section

General Details. The following were purchased from Aldrich Chemical Co. and used without further purification: 2-mercaptopyrimidine, 2-mercapto-4-methylpyrimidine hydrochloride, and 2-mercapto-1-methylimidazole. The complex [PdCl(PMe₃)(μ-Cl)]₂ was prepared by a method analogous to the Chatt and Venanzi[4] synthesis of [PdCl(PEt₃)-(μ-Cl)]₂.

The ¹H and ³¹P{¹H} NMR were recorded on a GN Omega 500 spectrometer at 500.1 and 202.4 MHz, respectively. The ¹H NMR data are listed in ppm downfield from TMS at 0.00 ppm. The ³¹P{¹H} NMR chemical shifts were measured relative to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H₃PO₄ centered in a 5-mm NMR tube containing the deuterated solvent appeared at 0.0 ppm at 20 °C. A preacquisition delay of 107 μs and a pulse delay of 1.3 s were used in the variable-temperature ¹H NMR studies.

Preparation of Pd₂(μ_{NS},η^2-primS)₂Cl₂(PMe₃)₂ (2). An ethanolic solution of sodium ethoxide (prepared by dissolving 26 mg (1 mmol) of

† J. J. Zuckerman Fellow, 1990.
(1) Yamamoto, J. H.; Yoshida, W.; Jensen, C. M. *Inorg. Chem.* **1991**, *30*, 1353–1357.
(2) Deeming, A. J.; Meah, M. N.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 2193–2199.
(3) Ciriano, M. A.; Viguri, F.; Torrente-Perez, J. J.; Lahoz, F. J.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 25–32.

(4) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2351–2356.

Table I. Summary of Crystal Data for **2**, **3**, and **4**·(acetone)

complex	1	3	4·(acetone)
formula	$Pd_2C_{14}H_{24}N_4P_2S_2Cl_2$	$Pd_2C_{16}H_{28}N_4P_2S_2Cl_2$	$Pd_2C_{17}H_{34}N_4OP_2S_2Cl_2$
fw	658.1	686.2	720.2
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$Pbca$ (No. 61)
a, Å	19.857 (4)	19.616 (7)	10.460 (3)
b, Å	11.124 (2)	12.343 (4)	15.801 (4)
c, Å	12.054 (2)	11.886 (4)	32.17 (2)
β, deg	117.12 (1)	118.25 (3)	90
V, Å^3	2369.9 (8)	2535 (2)	5316 (4)
Z	4	4	8
ρ_{calc}, g/cm^3	1.845	1.798	1.800
λ, Å (Mo Kα radiation)	0.710 73	0.710 73	0.710 73
T, K	298	298	298
μ, mm^{-1}	2.037	1.908	1.827
min, max transm coeff	0.8161, 0.9832	0.8791, 0.9151	0.6834, 0.8920
$R,^a$ %	2.43	2.60	3.78
$R_w,^b$ %	4.59	4.33	3.99

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

sodium in 25 mL of absolute ethanol) is treated with 2-mercaptopyrimidine (112 mg, 1 mmol). While the clear, yellow solution arising from the heterocyclic thiol deprotonation is stirred, [PdCl(PMe₃)(μ-Cl)]₂ (250 mg, 0.5 mmol) is added, and the resulting solution is allowed to stir for 24 h. The resulting orange precipitate is isolated by filtration, and purified **2** (110 mg, 33% yield) is obtained by recrystallization from chloroform. Anal. Calcd: C, 25.55; H, 3.68; N, 8.52. Found: C, 25.58; H, 3.39; N, 8.09.

Preparation of Pd₂(μ_NS,η²-MeprimS)₂Cl₂(PMe₃)₂ (3). An ethanolic solution of sodium ethoxide (prepared by dissolving 52 mg (2 mmol) of sodium in 25 mL of absolute ethanol) is treated with 2-mercapto-4-methylpyrimidine hydrochloride (163 mg, 1 mmol). While clear, yellow solution arising from the heterocyclic thiol deprotonation is stirred, [PdCl-(PMe₃)(μ-Cl)]₂ (250 mg, 0.5 mmol) is added, and the resulting solution is allowed to stir for 24 h. The resulting yellow-orange precipitate is isolated by filtration, and purified **3** (135 mg, 40% yield) is obtained by recrystallization from methylene chloride. Anal. Calcd: C, 28.00; H, 4.11; N, 8.17. Found: C, 27.98; H, 3.93; N, 8.03.

Preparation of Pd₂(μ_NS,η²-MeimidS)₂Cl₂(PMe₃) (4). An ethanolic solution of sodium ethoxide (prepared by dissolving 26 mg (1 mmol) of sodium in 25 mL of absolute ethanol) is treated with 2-mercapto-1-methylimidazole (114 mg, 1 mmol). While the clear, colorless solution arising from the heterocyclic thiol deprotonation is stirred, [PdCl(PMe₃)-(μ-Cl)]₂ (250 mg, 0.5 mmol) is added, and the resulting solution is allowed to stir for 24 h. The solvent is removed under vacuum, and the residue is extracted with chloroform. The resulting red-orange precipitate obtained by concentrating the chloroform extract is isolated by filtration. Purified **4** (301 mg, 91% yield) is obtained by recrystallization from chloroform. ¹H NMR (CD₂Cl₂): δ 6.87 (m), 6.66 (m) (4 H aromatic), 3.51 (s, 6 H, NCH₃), 1.47 (d, J_{P-H} = 12 Hz, 18 H, P(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂, 30 °C): δ 2.2 (s). Anal. Calcd: C, 25.39; H, 4.26; N, 8.46. Found: C, 25.54; H, 3.78; N, 7.66.

Molecular Weight Determinations. Molecular weights were determined by the literature[5] method using a Lauda RC6 temperature controller and Beckmann thermometer. Elevated boiling points of carbon tetrachloride solutions of compounds **2** (14 mg, CCl₄, 511 mg) and **3** (6 mg, CCl₄, 378 mg) in reference to pure solvent were consistently found to be 0.48 ± 0.02 and 0.21 ± 0.02 °C, respectively. On the basis of a value of 4.48 as the ebullioscopic constant of carbon tetrachloride,[6] molecular weights of 340 ± 30 and 370 ± 30 were determined for the species predominating at high temperature in solution of **2**, and **3**, respectively.

Crystallographic Studies. Crystals of complexes **2** and **3** suitable for X-ray diffraction were obtained by a slow evaporation of a chloroform solution of the corresponding complex. Single crystals of **4**·(acetone) were obtained by a slow evaporation of a solution of **4** in acetone. The crystals were mounted on glass fibers with epoxy. Centering and data collection were performed on a Nicolet P3 automated diffractometer for complexes **2** and **3** and on a Nicolet P1 automated diffractometer for **4**·(acetone). The unit cell parameters were obtained by least-squares refinement of the setting angles of 20 reflections. Crystal and instrument instability were monitored with a set of three standard reflections measured

(5) Pavia, D. L.; Lampman, G. M.; Krig, G. S. *Introduction to Organic Laboratory Techniques*, 3rd ed.; Saunders: Philadelphia, 1988; pp 552–554.

(6) Dean, J. A. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; p (10)73.

every 97 reflections; in all cases, no significant variations were found. Ellipsoid semiempirical absorption corrections were applied for complexes **2** and **3**. A laminar semiempirical absorption correction was applied for complex **4**·(acetone) using the prominent 010 crystal face. Details of other crystal data and relevant information are summarized in Table I.

The structures were solved by direct methods using SHELX PLUS computer programs (Nicolet Instrument Corp.) and refined by full-matrix least-squares procedures. During refinement of the structure of **4**·(acetone), a group of peaks, not associated with the palladium complex, became apparent in the difference Fourier maps. Initially, the peaks were refined with isotropic thermal parameters as an acetone solvate. Since the solvate atoms did not behave well during the initial isotropic refinement, the acetone solvate molecule which is 2-fold disordered about a C_2 rotation axis at the origin was refined as a rigid group with idealized geometry. All non-hydrogen atoms except those of the solvate were refined with anisotropic temperature coefficients. The aromatic hydrogen atoms of complexes **2** and **3** were allowed to refine isotropically. All other hydrogen atoms were introduced in fixed calculated positions, and their coordinates were allowed to vary in the final cycles of full-matrix least-squares refinement.

Results

The new dipalladium heterocyclic thiolate complexes were synthesized by a method analogous to the previously reported[1] synthesis of Pd₂(pyS)₂Cl₂(PMe₃)₂ (1) from [PdCl(PMe₃)(μ-Cl)]₂ with the corresponding heterocyclic thiolate ligands. The molecular structures of **2**, **3**, and **4**·(acetone) were determined by single-crystal X-ray diffraction studies. ORTEP projections with the atomic numbering schemes of the obtained molecular structures are presented in Figures 1–3. Selected bond distances
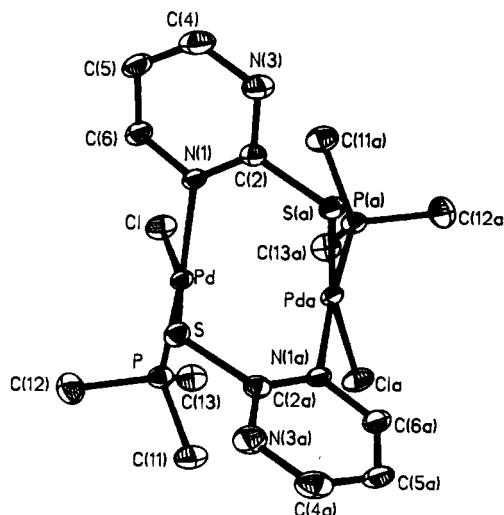

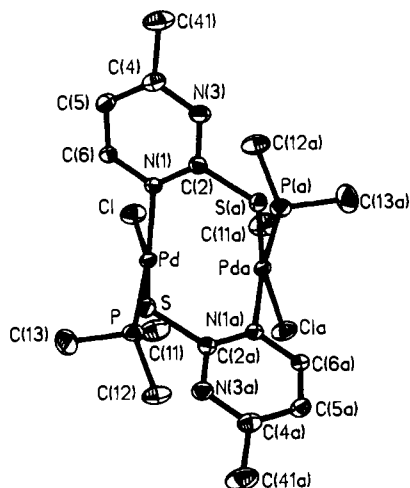**Figure 1.** ORTEP projection of Pd₂(μ_NS,η²-primS)₂Cl₂(PMe₃)₂ (2). Thermal ellipsoids are at 50% probability. The hydrogen atoms have been omitted for clarity.
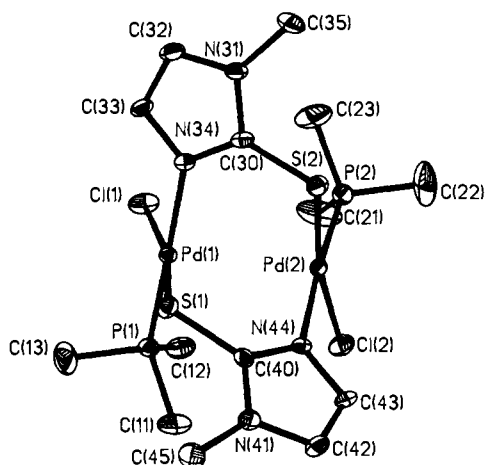
Figure 2. ORTEP projection of Pd$_2$(μ_{NS},η^2-MeprimS)$_2$Cl$_2$(PMe$_3$)$_2$ (3). Thermal ellipsoids are at 50% probability. The hydrogen atoms have been omitted for clarity.

Figure 3. ORTEP projection of Pd$_2$(μ_{NS},η^2-MeimidS)$_2$Cl$_2$(PMe$_3$)$_2$ (4). Thermal ellipsoids are at 50% probability. The hydrogen atoms have been omitted for clarity.

and angles for the new complexes as well as those previously determined[1,7] for **1** are listed in Tables II and III. The final fractional atomic coordinates are given in Tables IV–VI. Complexes **2** and **3** display C_2 symmetry, while **4·**(acetone) has an approximately C_2 symmetry with the two palladium atoms linked by the heterocyclic thiolate ligands through both the sulfur and one of the nitrogen atoms. The chlorine atoms are oriented trans to the sulfur atoms of the bridging ligands, while the phosphines are oriented trans to the coordinated nitrogen atoms of the bridging ligands. The coordination geometry about each of the palladium atoms is nearly square planar. The separations between the palladium atoms of **2**, **3**, and **4·**(acetone), 2.915 (1), 2.924 (1), and 3.104 (2) Å, respectively, are outside of the 2.594–2.848-Å range which has been found[8–10] for dipalladium complexes having strong Pd–Pd bonding interactions. The C–S bond lengths of **2** and **3**, 1.730 (5) and 1.732 (4) Å, respectively, and of **4·**(acetone), 1.729 (8) and 1.737 (9) Å, are within the 1.72–1.86-Å range that has been found[1–3,11–25] in pyS complexes, indicating that the bridging heterocyclic thiolate ligands have a significant amount of thione character. The C(2)–N(3)–C(4) angles of 116.3 (4) and 118.3 (3)° for **2** and **3**, respectively, are within the range expected[26] for deprotonated N-heterocycles.

As seen in Figure 4, the ^{31}P{^{1}H} NMR spectrum of **2** dissolved in toluene-d_8 at –50 °C contains a major singlet resonance at 7.7 ppm along with a minor singlet resonance at 2.7 ppm. Similarly, the ^{1}H NMR spectrum of complex **2** dissolved in toluene-d_8 at –40 °C contains a doublet resonance corresponding to the PMe$_3$ protons of **2** at 1.37 ppm (J_{P-H} = 13 Hz) along with multiplets at 8.46, 7.56, and 5.61 ppm corresponding to the aromatic protons. The spectrum is also seen to contain another much smaller set of resonances corresponding to PMe$_3$ (0.78 ppm, J_{P-H} = 13 Hz) and aromatic (7.56 (m), and 5.61 (m) ppm) protons in a 9:1:1 integrated intensity ratio. The third aromatic resonance of the minor species is presumably obscured due to accidental overlap with the corresponding resonance of **2**. The ^{1}H NMR signals are seen to gradually broaden as the temperature is eraised. Variable-temperature spectra of the region of the PMe$_3$ protons are seen in Figure 5. Additionally, there is a continuous increase in the relative intensity of the second set resonances, indicating a temperature-dependent shift in the equilibrium position. When the solution is cooled, the reverse trend is observed without loss of integrated intensity with an equal number of acquisitions. From the changing ratios of the integrated intensities of the two signals over the range –40 to +50 °C, values of ΔH = 29 kJ mol^{-1} and ΔS = 110 J K^{-1} mol^{-1} for the rapid equilibrium can be estimated. The energetics of this process are quite similar to that reported[1] for **1**: ΔH = 29 ± 1 kJ mol^{-1} and ΔS = 87 ± 4 J K^{-1} mol^{-1}. A molecular weight of 340 ± 30 was determined for the species predominating at high temperatures from carbon tetrachloride boiling point elevation experiments. This molecular weight is half of the 658 value expected for **2** and demonstrates that the high-temperature species is a monomeric complex, resulting from rupture of dimeric **2**. These results indicate that, in solution, **2** establishes an equilibrium with monomeric species containing chelating N-S-η^2 ligands, as has been reported[1] previously for **1**.

The ^{31}P{^{1}H} NMR and ^{1}H spectra of **3** dissolved in toluene-d_8 are much more complicated than those of **2**. As seen in Figure 6, the ^{31}P{^{1}H} NMR spectrum at –50 °C contains a major singlet resonance at 7.3 ppm along with a minor singlet resonances at 9.1, 5.3, 3.5, and 2.4 ppm. Similarly, the ^{1}H NMR spectrum of **3** dissolved in toluene-d_8 at –50 °C is seen to contain a major set of resonances at 8.51 (m), 5.61 (m) (4 H aromatic), 1.78 (s, 6 H, CCH_3), and 1.42 (d, J_{P-H} = 13 Hz, 18 H, P(CH_3)$_3$) along with several minor aromatic multiplets, methyl singlets, and P(CH_3)$_3$) doublets. All signals in both the ^{31}P{^{1}H} NMR and ^{1}H spectra

(7) Yamamoto, J. H. M. S. Thesis, University of Hawaii, 1990.
(8) Kraft, T. E.; Hejna, C. I.; Smith, J. S. *Inorg. Chem.* **1990**, *29*, 2682–2688 and references therein.
(9) Wilson, W. L.; Nelson, J. H. *Organometallics* **1990**, *9*, 1699–1700.
(10) Micklitz, W.; Sheldrick, W. S.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 211–216.

(11) Fletcher, S. R.; Skapsi, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 635–639.
(12) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W. *Inorg. Chem.* **1978**, *17*, 3254–3257.
(13) Masaki, M.; Matsunami, S.; Ueda, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3298–3301.
(14) Kinoshita, I.; Yasuba, Y.; Matsumato, K.; Ooi, S. *Inorg. Chem. Acta* **1983**, *80*, L13–L14.
(15) Mura, P.; Olby, B. G.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2101–2112.
(16) Rosenfeld, S. G.; Swedberg, S. A.; Arora, S. K.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 2109–2114.
(17) Deeming, A. J.; Meah, M. N.; Dawes, H. M.; Hursthouse, M. B. *J. Organomet. Chem.* **1986**, *299*, C25–C28.
(18) Umakoshi, K.; Kinoshita, I.; Ooi, S. *Inorg. Chim. Acta* **1987**, *80*, L41–L42.
(19) Rosenfield, S. G.; Berends, H. P.; Gelmini, L.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 2792–2797.
(20) Deeming, A. J.; Meah, M. N.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 235–238.
(21) Deeming, A. J.; Karim, M.; Bates, P. A.; Hursthouse, M. B. *Polyhedron* **1988**, *7*, 1401–1403.
(22) Deeming, A. J.; Hardcastle, K. I.; Meah, M. N.; Bates, P. A.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 227–233.
(23) Deeming, A. J.; Meah, M. N.; Randle, N. P.; Hardcastle, K. I. *J. Chem. Soc., Dalton Trans.* **1989**, 2211–2216.
(24) Padilla, E. M.; Yamamoto, J. H.; Jensen, C. M. *Inorg. Chim. Acta* **1990**, *174*, 209–215.
(25) Ciriano, M. A.; Torrente-Perez, J. J.; Viguri, F.; Lahoz, F. J.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1493–1502.
(26) Singh, C. *Acta Crystallogr.* **1965**, *19*, 861–864.

Table II. Comparison of Selected Bond Distances of 1–3 and 4·(acetone)

1		2		3		4·(acetone)	
Pd(1)–N(2)	2.137 (9)	Pd–N(1)	2.143 (3)	Pd–N(1)	2.120 (2)	Pd(1)–N(34)	2.092 (7)
Pd(2)–N(1)	2.131 (8)					Pd(2)–N(44)	2.096 (7)
Pd(1)–S(1)	2.284 (3)	Pd–S	2.293 (1)	Pd–S	2.287 (1)	Pd(1)–S(1)	2.307 (3)
Pd(2)–S(2)	2.306 (3)					Pd(2)–S(2)	2.296 (3)
Pd(1)–P(1)	2.243 (4)	Pd–P	2.236 (1)	Pd–P	2.228 (1)	Pd(1)–P(1)	2.249 (3)
Pd(2)–P(2)	2.244 (3)					Pd(2)–P(2)	2.232 (3)
Pd(1)–Cl(1)	2.356 (3)	Pd–Cl	2.343 (1)	Pd–Cl	2.348 (1)	Pd(1)–Cl(1)	2.343 (3)
Pd(2)–Cl(2)	2.355 (3)					Pd(2)–Cl(2)	2.337 (3)
S(1)–C(11)	1.73 (1)	S–C(2A)	1.730 (5)	S–C(2A)	1.732 (4)	S(1)–C(40)	1.729 (8)
S(2)–C(21)	1.73 (1)					S(2)–C(30)	1.737 (9)

Table III. Comparison of Selected Coordinated Ligand Bond Angles of 1–3 and 4·(acetone)

complex	bond angle label	bond angle, deg
1	N(1)–C(11)–S(1)	123.2 (7)
	N(2)–C(21)–S(2)	124.5 (8)
2	N(1)–C(2)–S(A)	122.4 (3)
3	N(1)–C(2)–S(A)	121.9 (2)
4·(acetone)	N(44)–C(40)–S(1)	128.4 (6)
	N(34)–C(30)–S(2)	128.4 (7)

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients[a] for Pd₂(μₙₛ,η²-primS)₂Cl₂(PMe₃)₂ (2)

	x	y	z	U_{eq}, Å²
Pd	0.4772 (1)	0.3363 (1)	0.3491 (1)	0.030 (1)
S	0.5528 (1)	0.5032 (1)	0.4199 (1)	0.036 (1)
Cl	0.3916 (1)	0.1781 (1)	0.3106 (1)	0.052 (1)
P	0.5706 (1)	0.2201 (1)	0.4837 (1)	0.038 (1)
C(11)	0.6682 (2)	0.2597 (5)	0.5261 (5)	0.056 (2)
C(12)	0.5664 (3)	0.2162 (5)	0.6307 (4)	0.060 (2)
C(13)	0.5655 (3)	0.0664 (4)	0.4348 (5)	0.052 (2)
N(1)	0.3841 (2)	0.4480 (3)	0.2309 (3)	0.032 (1)
C(2)	0.3799 (2)	0.5135 (3)	0.1333 (3)	0.033 (1)
N(3)	0.3245 (2)	0.5921 (3)	0.0695 (3)	0.049 (2)
C(4)	0.2705 (3)	0.6035 (5)	0.1067 (5)	0.056 (2)
C(5)	0.2689 (2)	0.5349 (5)	0.2012 (4)	0.052 (2)
C(6)	0.3275 (2)	0.4604 (4)	0.2622 (4)	0.040 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients[a] for Pd₂(μₙₛ,η²-MeprimS)₂Cl₂(PMe₃)₂ (3)

	x	y	z	U_{eq}, Å²
Pd	0.0280 (1)	0.3406 (1)	0.1558 (1)	0.032 (1)
S	−0.0510 (1)	0.4878 (1)	0.0730 (1)	0.038 (1)
Cl	0.1178 (1)	0.1983 (1)	0.2122 (1)	0.060 (1)
P	−0.0629 (1)	0.2362 (1)	0.0078 (1)	0.048 (1)
C(11)	−0.0588 (3)	0.0956 (3)	0.0505 (5)	0.075 (2)
C(12)	−0.1636 (2)	0.2689 (4)	−0.0536 (4)	0.069 (2)
C(13)	−0.0500 (3)	0.2364 (5)	−0.1302 (4)	0.088 (3)
N(1)	0.1200 (1)	0.4414 (2)	0.2823 (2)	0.032 (1)
C(2)	0.1246 (2)	0.4941 (2)	0.3858 (3)	0.033 (1)
N(3)	0.1843 (2)	0.5563 (2)	0.4631 (3)	0.039 (1)
C(4)	0.2421 (2)	0.5708 (3)	0.4347 (3)	0.043 (1)
C(41)	0.3099 (2)	0.6349 (4)	0.5284 (5)	0.069 (2)
C(5)	0.2404 (2)	0.5236 (3)	0.3283 (3)	0.042 (1)
C(6)	0.1787 (2)	0.4581 (3)	0.2548 (3)	0.036 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients[a] for Pd₂(μₙₛ,η²-MeimidS)₂Cl₂(PMe₃)₂·(acetone) [4·(acetone)]

	x	y	z	U_{eq}, Å²
Pd(1)	0.0501 (1)	0.7081 (1)	0.3251 (1)	0.029 (1)
Pd(2)	0.1662 (1)	0.6712 (1)	0.4120 (1)	0.031 (1)
S(1)	0.2296 (2)	0.6397 (2)	0.3004 (1)	0.040 (1)
S(2)	0.1187 (2)	0.5326 (2)	0.3973 (1)	0.042 (1)
Cl(1)	−0.1497 (2)	0.7727 (2)	0.3339 (1)	0.064 (1)
Cl(2)	0.2378 (3)	0.8008 (2)	0.4381 (1)	0.058 (1)
P(1)	0.1354 (3)	0.8371 (2)	0.3152 (1)	0.045 (1)
C(11)	0.305 (1)	0.8504 (8)	0.3174 (4)	0.079 (5)
C(12)	0.082 (1)	0.9159 (7)	0.3512 (4)	0.068 (4)
C(13)	0.095 (2)	0.8755 (9)	0.2649 (4)	0.109 (7)
P(2)	−0.0072 (3)	0.6799 (2)	0.4522 (1)	0.044 (1)
C(21)	−0.073 (1)	0.7827 (9)	0.4578 (6)	0.127 (8)
C(22)	0.032 (2)	0.645 (1)	0.5038 (4)	0.15 (2)
C(23)	−0.149 (1)	0.622 (1)	0.4399 (4)	0.101 (7)
C(30)	−0.0070 (8)	0.5316 (6)	0.3619 (3)	0.036 (3)
N(31)	−0.0918 (8)	0.4669 (5)	0.3599 (2)	0.042 (3)
C(32)	−0.1773 (9)	0.4850 (7)	0.3293 (3)	0.050 (3)
C(33)	−0.1450 (9)	0.5605 (7)	0.3132 (3)	0.045 (3)
N(34)	−0.0385 (7)	0.5907 (4)	0.3339 (2)	0.034 (2)
C(35)	−0.096 (1)	0.3924 (7)	0.3865 (4)	0.068 (4)
C(40)	0.3488 (8)	0.6517 (6)	0.3372 (2)	0.035 (3)
N(41)	0.4753 (6)	0.6508 (5)	0.3266 (2)	0.037 (2)
C(42)	0.5435 (9)	0.6621 (6)	0.3631 (3)	0.047 (3)
C(43)	0.4594 (8)	0.6682 (6)	0.3935 (3)	0.042 (3)
N(44)	0.3366 (6)	0.6630 (5)	0.3780 (2)	0.035 (2)
C(45)	0.5275 (9)	0.6424 (8)	0.2848 (3)	0.066 (4)
O	0.605 (3)	0.001 (2)	−0.0431 (8)	0.19 (1)
C(97)	0.595	0.078	0.0308	0.12 (2)
C(98)	0.393	−0.011	−0.0166	0.13 (1)
C(99)	0.536	−0.002	−0.0120	0.15 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Figure 4. ³¹P{¹H} NMR spectrum (202.4 MHz) of Pd₂(μₙₛ,η²-primS)₂-Cl₂(PMe₃)₂ (2) dissolved in toluene-d_8 at −50 °C.
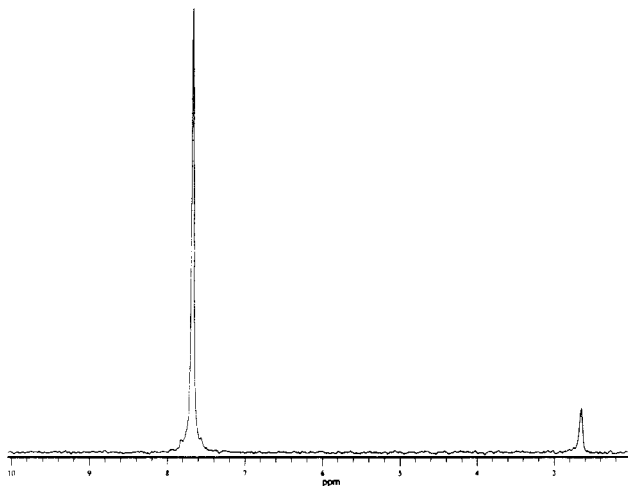
gradually broaden and marked changes are observed in their relative intensities as the temperature of the solution is increased. This behavior indicates that all of the species present in solution are involved in a temperature-dependent equilibrium.

The ³¹P{¹H} NMR spectrum at 80 °C contains only the two upfield resonances. Carbon tetrachloride boiling point elevation experiments indicated that the species corresponding to these resonances have molecular weights of 370 ± 30, rather than the 658 value expected for dimeric 3, and thus suggests the two high-temperature species to be isomeric monomeric species. Such isomeric complexes may result from coordination of the MePrimS

ligand through both nitrogens 1 and 3. Alternatively, isomeric species could also result from the two differing orientations of a ηₙₛ²-MeprimS ligand relative to the PMe₃ and Cl ligands.
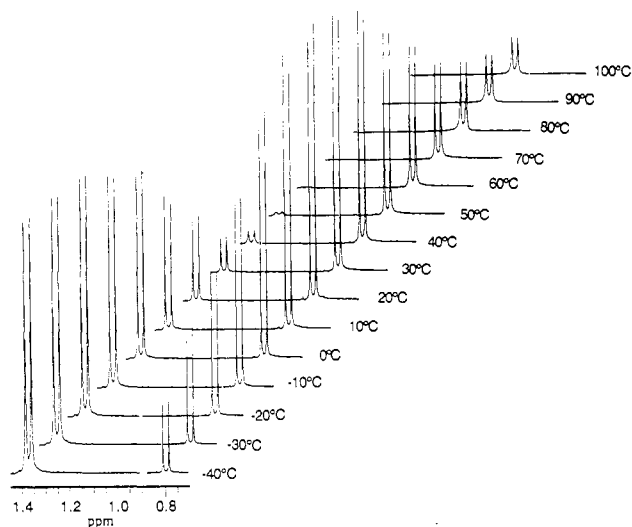
Figure 5. Variable-temperature ^{1}H NMR spectra (500 MHz) of the PMe$_3$ proton region of Pd$_2$(μ_{NS},η^2-primS)$_2$Cl$_2$(PMe$_3$)$_2$ (2) dissolved in toluene-d_8.
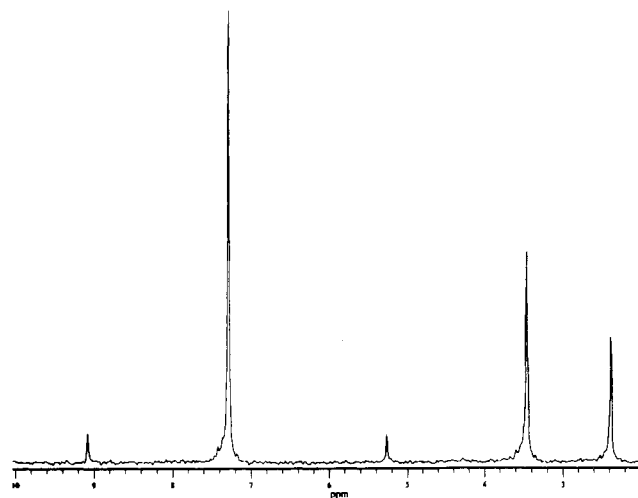
Figure 6. ^{31}P{^{1}H} NMR spectrum (202.4 MHz) of Pd$_2$(μ_{NS},η^2-MeprimS)$_2$Cl$_2$(PMe$_3$)$_2$ (3) dissolved in toluene-d_8 at -50 °C.

However, the second possibility would seem to be precluded by the observation of only one high-temperature form of **2**. We assign the major resonance observed at 7.3 ppm in the ^{31}P{^{1}H} NMR spectrum at low temperature to **3**. The minor, nearly 1:1 intensity resonances observed at 9.1 and 5.3 ppm may result from the asymmetric phosphorus atoms of the more sterically congested isomer containing both nitrogens 1 and 3 coordinated μ_s,η_{NS}^2-MeprimS ligands. Apparently, steric constraints prevent the formation of spectroscopically detectable amounts of a third possible isomer in which both μ_s,η_{NS}^2-MeprimS ligands are coordinated through nitrogen 3.

Surprisingly, the variable-temperature ^{1}H NMR spectra of complex **4** over the -50 to $+100$ °C range were static, indicating the absence of any rapid equilibrium process on the NMR time scale.

Discussion

As seen in Table VII, the basicities of the six-membered heterocyclic 2-thiolate ligands are widely varied.[27,28] However, the Pd–S bond distances of 2.293 (1) and 2.287 (1) Å, found for **2** and **3**, respectively, are not significantly different from the Pd–S distances of 2.284 (3) and 2.306 (3) Å found[1] for **1**.

(27) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*, Butterworths: London, 1965; pp 164–226.
(28) Albert, A.; Barlin, G. B. *J. Chem. Soc.* **1959**, 2387.

Table VII. Comparison of Dissociation Constants (pK_a) for Uncoordinated Six-Membered Heterocyclothiolate ligands of 1–3

complex	ligand	pK_1	pK_2	ref
1	2-mercaptopyridine	−1.07	10.00	27
		−1.38	9.81	28
		−1.07	9.97	27
2	2-mercaptopyrimidine	1.35	7.10	27
		1.3	7.2	27
3	2-mercapto-4-methylpyrimidine	2.1	8.1	27

Scheme I
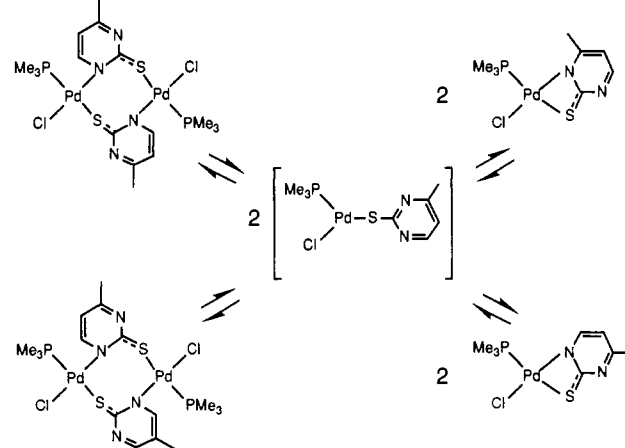
Similarly, the Pd–N bond distances of 2.143 (3) and 2.120 (2) Å, **2** and **3**, respectively, are not significantly different from the 2.137 (9)- and 2.131 (8)-Å distances found[1] for **1**. This is apparently the result of the geometrical constraints imposed by the rigid six-membered heterocycle rings resulting in the severe N–C–S bond angles of 123.2 (7), 124.5 (9), 122.4 (3), and 121.9 (2)°, of **1**,[1] **2**, and **3**, respectively. The limitation imposed by this geometric constraint on the ability of pyridinethiolate ligands to interact in a chelating fashion with monometal centers has been previously noted.[23] Our work demonstrates that these constraints also limit the interaction of six-membered heterocyclic 2-thiolates acting as N,S bridging ligands in dimetallic complexes. This conclusion is supported by the finding that **4**, which has a five-membered heterocycle ring and thus has significantly larger N–C–S bond angles of 128.4 (6) and 128.4 (7)°, also contains Pd–N bond distances of 2.092 (7) and 2.096 (7) Å, which are significantly shorter than those of the other three complexes.

The coordinative limitations imposed by the N–C–S angle of the six-membered heterocyclic 2-thiolate ligands are apparently responsible for the similar dynamic solution behavior observed for **1**,[1] **2**, and **3**. The large positive value of ΔS associated with the rapid equilibrium process observed for complex **2** in our variable-temperature ^{1}H NMR spectroscopic studies matches that reported[1] for **1** and suggests that these complexes undergo reversible dimer–monomer interconversion, as has been established for **1**. Our solution NMR studies of **3** indicate that interconversion of species bound through the inequivalent nitrogens of the MeprimS ligands occurs in concert with the dimer–monomer interconversion, as seen in Scheme I. This result strongly suggests that the dimer–monomer interconversion process involves Pd–N bond rupture. The enhanced Pd–N interaction indicated by the significantly shorter Pd–N bond distances of **4** is paralleled by the static variable-temperature ^{1}H NMR spectra of the complex over the -50 to $+100$ °C temperature range. Thus, the larger N–C–S bond angle in the five-membered heterocyclic 2-thiolate ligands results in enhanced Pd–N bonding and stabilization of the μ_{NS},η^2 bridges in the dimeric complex.

Conclusion

Our studies elucidate the dependence of the solution stability of dimeric complexes containing μ_{NS},η^2 bridging heterocyclic

2-thiolate ligands on the constraints of the S–C–N bond angles of these ligands. Reversible dimer–monomer interconversion can now be predicted for complexes containing six-membered heterocyclic 2-thiolate ligands, while complexes containing five-membered heterocyclic 2-thiolate ligands are expected to be highly stabilized as dimers. This understanding affords a method of tailoring rapid equilibrium behavior or dimeric stability in dimetallic complexes.

Supplementary Material Available: Table and plot of variable-temperature NMR data; tables of crystal data, anisotropic thermal parameters, bond distances, bond angles, hydrogen atom coordinates, and isotropic thermal parameters for **2**, **3**, and **4**-(acetone) (14 pages). Ordering information is given on any current masthead page.