Coordination Dynamics and Reactivity of Palladium(II) Complexes Containing the *N*-Thienylidene-L/D-methionine Methyl Ester Ligand

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Metathesis reactions of the *N*-thienylidene-L/D-methionine methyl ester ligand (th-metMe) with suitable palladium starting complexes afforded coordination complexes of the type PdX_2(th-metMe), PdX(Me)(th-metMe), and [Pd(Me)(th-metMe)(L″)](O_3SCF_3) (X = Cl, Br, I; and L″ = MeCN, pyridine, picoline, lutidine) which were studied by NMR with respect to the fluxional behavior of the diastereomeric PdNS six-membered ring chelates. The structure of $PdCl_2$(th-metMe) in the solid state (a = 13.318(5) Å, b = 11.365(2) Å, c = 13.579(5) Å, β = 96.66(4)°) showed a square planar coordination complex in which the ligand is chelating *via* the imine nitrogen (Pd−N = 2.030(7) Å) and the methionine sulfur donor atom (Pd−S^1 = 2.283(2) Å). The square planar geometry is completed by the chlorides (Pd−Cl^1 = 2.275(3) Å (*trans* to the imine nitrogen) and Pd−Cl^2 2.322(2) Å (*trans* to the sulfur donor)). The dimeric $[PdCl(L')]_2$ complex (L′ = anionic α-methoxycarbonyl, α-(2-thienylmethylidene)amine, α″-(methylthio)ethane) was formed by C−H activation of the chiral carbon atom of the α-amino acid moiety. The structure determination (a = 8.1887(7) Å, b = 20.507(2) Å, c = 34.079(3) Å, β = 91.220(7)°) revealed two stretched out ligands of which one is coordinating to Pd(1) *via* the methionine sulfur donor (2.268(2) Å) and σ-bonded *via* the stereogenic chiral carbon atom (2.068(6)) and to Pd(2) *via* the imine nitrogen (2.074(5) Å). The second ligand coordinates to Pd(1) *via* the imine donor (2.074(5) Å) and to Pd(2) *via* the methionine sulfur (2.276(1)) and the former stereogenic carbon atom (2.060(6)). Both square planar coordination sites are occupied by the chlorides which are positioned *trans* to the carbon atom (2.390(2) and 2.414(2) Å for Cl(1A) and Cl(2A)). Complexes of the type [PdX(C(O)Me)(th-metMe)] and [Pd(C(O)Me)(L″)(th-metMe)](O_3SCF_3) were obtained by reaction of CO with the corresponding methyl complexes. The rates of CO insertion into the methyl−palladium bond were investigated, and it was found that the rate decreases in the order [Pd(Me)(th-metMe)(CF_3SO_3)] > [Pd(Me)(I)(th-metMe)] > [Pd(Me)(Br)(th-metMe)] > [Pd(Me)(th-metMe)(MeCN)](CF_3SO_3) > [Pd(Me)(th-metMe)(2,6-lutidine)] (CF_3SO_3) > [Pd(Me)(Cl)(th-metMe)] > [Pd(Me)(th-metMe)(pyridine)](CF_3SO_3).

Introduction

In our laboratory the *N*-[*N*-((5-methyl-2-thienyl)methylidene)-L-methionyl]histamine ligand (Figure 1) was designed in order to mimic the active site of plastocyanine.[1] In the solid state this hemilabile ligand shows a polymeric structure which is formed by inter- and intramolecular hydrogen bonds.[2] The ethyl methyl sulfide arm connected to the central methionic carbon atom is stretched out and a helix geometry is formed. Upon coordination to a cationic silver(I) or copper(I) nucleus, again a helix geometry is created as each of the hemilabile ligand molecules bind to three metal ions while each metal center interacts with a suitable coordination site of three different hemilabile ligands. The geometry of the ligand backbone in the complex is only slightly changed when compared to the structure in the free ligand; this means that the tetrahedral geometry of the coordination site is mainly ligand controlled.[3]

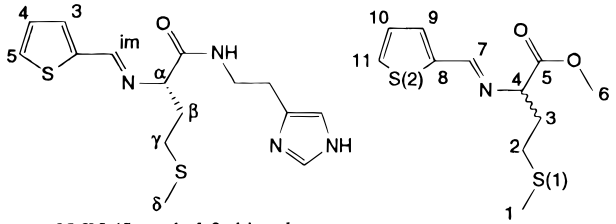

Figure 1. The th-met and D/L-th-metMe ligands.

This interesting feature initiated our interest in the coordination behavior of this ligand toward d^8 metal centers, which should force the ligand to assume a different configuration, because of the square planar geometry of the metal site. In order to gain understanding of the coordination properties of a potentially tetradentate ligand, the coordination behavior of a

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Table 1. Crystal Data for **1** and **12**

	1	**12**
formula	$C_{11}H_{15}NO_3S_2PdCl_2 \cdot CDCl_3$	$C_{22}H_{28}N_2O_4S_4Pd_2Cl_2$
mol wt	506.9	796.4
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, b, c (Å)	13.318(5), 11.365(2), 13.579(5)	8.1887(7), 20.507(2), 34.079(3)
β (deg)	96.66(4)	91.220(7)
V (Å^3)	2041(4)	5721(1)
Z	4	8
D_{calc} (g cm^{-3})	1.7	1.85
μ_{calc} (cm^{-1})	138.0	151.5
λ(Cu Kα) (Å)	1.5418 (graphite monochromated)	1.5418 (graphite monochromated)
T (K)	298	298
R^a	0.049 [for 2547 $F_o > 4\sigma(F_o)$]	0.042 [for 7941 $F_o > 4\sigma(F_o)$]
$R_w{}^b$	0.053	0.064

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

part of the latter ligand, *i.e.*, the *N*-thienylidene-L/D-methionyl part (Figure 1) was studied in more detail.

The coordination behavior of methionine toward platinum and palladium has already been studied extensively by various techniques.[4] On the basis of chemical reactivity, infrared data, and other measurements, complex structures in solution were assigned, while structures in the solid state were established for: [Pt(L-MetH-*S*,*N*)Cl_2], [Pt(L/D-MetH-*S*,*N*)Cl_2],[5] and [Pd(L/D-MetH-*S*,*N*)Cl_2].[6] These monomeric complexes show a chelating methionine ligand coordinating through the sulfur and amine nitrogen donor atoms.

Here we report the coordination behavior of the *N*-thienylidene-L/D-methionine methyl ester ligand (th-metMe), derived from methionine methyl ester and 2-thiophenecarbaldehyde, toward palladium(II), resulting in neutral and cationic complexes of the type PdXY(th-metMe). The methyl-containing complexes were investigated with respect to the reactivity toward CO insertion.

Experimental Section

Materials. All reactions were carried out in an atmosphere of purified nitrogen, using standard Schlenk techniques. Solvents were dried and distilled prior to use or stored under an inert atmosphere, unless noted otherwise. Ethyl acetate and triethylamine were of PA grade, $PdCl_2$(COD) and PdCl(Me)(COD) (COD = cycloocta-1,5-diene) were synthesized according to literature procedures.[7] 2-Thiophenecarbaldehyde was freshly distilled before use. Silica gel for column chromatography (Kieselgel 60, 70−330 mesh, E. Merck) was dried and activated prior to use.

Instrumentation. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on Bruker AMX300 and AC100 spectrometers. Chemical shift values are in ppm relative to Me_4Si (^{1}H and ^{13}C{^{1}H}) or $CFCl_3$ (^{19}F). Coupling constants are in Hz. Solid state magic angle spinning NMR experiments were performed on a Bruker AM500 using a DOTY probe (90° pulse was 5 μs). IR spectra were recorded on a Bio-Rad spectrophotometer in the range 1000−2200 cm^{-1}. Elemental analyses were carried out by Dornis und Kolbe.

The degree of association of **12** was calculated from vapor pressure measurements with a Hewlett-Packard 320B osmometer in dichloromethane (instrumental error amounts to 5%).

Conductivity experiments were carried out using a Consort K720 digital conductometer.

The CO insertion rates were determined using an electronic gas buret, which consists of an Inacom Instruments 5860E /1AB38 mass flowmeter (with a range of 0.06−9.00 mL/min) connected to a high-pressure 20 mL glass reaction vessel. In order to avoid CO pressure drop, a 300 cm^3 buffer flask was connected. Data points were sampled every 1 s and processed with TURBOKIN.[8]

Crystal Structure Determination of 1. A yellow crystal with approximate dimensions 0.20 × 0.25 × 0.35 mm was used for data collection, at room temperature, on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) and an $\omega-2\theta$ scan. A total of 3461 unique reflections were measured within the ranges $0 \le h \le 15$, $-13 \le k \le 0$, and $-15 \le l \le 15$; 2547 were above the significance level of 2.5σ(I). The maximum value of (sin θ)/λ was 0.59 Å^{-1}. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $72 < 2\theta < 80°$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods using the program SIMPEL.[9] After isotropic refinement of the model, a ΔF synthesis revealed four peaks which were interpreted as deuteriochloroform, one of the solvents used during the recrystallization. The hydrogens were calculated. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distances to their carrier atoms remained within 1.09(3) Å, converged to $R = 0.049$, $R_w = 0.053$, and $(\Delta/\sigma)_{max} = 0.70$. A weighting scheme $w = (5.02 + F_o + 0.029F_o^2)^{-1}$ was used. An empirical absorption correction[10] was applied, with coefficients in the range 0.74−1.50. A final difference Fourier map revealed a residual electron density between −1.1 and +0.8 e Å^{-3}. Scattering factors were taken from Cromer and Mann.[11] The anomalous dispersion of palladium and chlorine was taken into account. All calculations were performed with XTAL3.0,[12] unless stated otherwise. The crystal data are presented in Table 1, while the positional parameters are given in the Supporting Information.

Crystal Structure Determination of 5a−c. Brown, blade-shaped crystals suitable for X-ray structure determination were mounted on a Lindemann glass capillary and transferred into a cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode (**5a** and **5c**) or to an Enraf-Nonius CAD4-F sealed tube diffractometer at room temperature (**5b**). Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections (set 4) in the ranges $11.5 < \theta < 14.0°$,

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Table 2. Crystal Data for **5a**−**c**

	5a	**5b**	**5c**
formula	$[C_{12}H_{18}NO_2S_2PdBr]_{0.229}$ $[C_{11}H_{15}NO_2S_2PdBr_2]_{0.771}\cdot CH_2Cl_2$	$[C_{12}H_{18}NO_2S_2PdBr]_{0.545}$ $[C_{11}H_{15}NO_2S_2PdBr_2]_{0.455}\cdot CHCl_3$	$[C_{12}H_{18}NO_2S_2PdBr]_{0.829}$ $[C_{11}H_{15}NO_2S_2PdBr_2]_{0.171}\cdot CH_2Cl_2$
mol wt	593.68	607.63	554.76
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, *b*, *c* (Å)	11.4256(7), 11.7188(7), 17.8751(8)	13.323(2), 11.6547(10), 18.014(2)	11.4677(8), 11.7543(6), 18.0255(10)
β (deg)	126.583(5)	130.731(12)	127.188(6)
V (Å^3)	1921.9(2)	2119.6(6)	1935.7(3)
Z	4	4	4
D_{calc} (g cm^{-3})	2.052	1.904	1.85
μ_{calc} (cm^{-1})	51.5	42.0	38.7
λ(Mo Kα) (Å)	0.710 73 (graphite monochromated)	0.710 73 (graphite monochromated)	0.710 73 (graphite monochromated)
T (K)	150	298	150
R1[a]	0.031 [for 3654 $F_o > 4\sigma(F_o)$]	0.053 [for 2415 $F_o > 4\sigma(F_o)$]	0.038 [for 3876 $F_o > 4\sigma(F_o)$]
wR2[b]	0.087	0.145	0.087

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = |\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

$9.79 < \theta < 13.9°$, and $11.5 < \theta < 14.0°$ (for **5a**−**c**, respectively). The unit-cell parameters were checked for the higher lattice symmetry.[13] Crystal data and details on data collection are presented in Table 2. Data were collected in the $\omega-2\theta$ scan mode. The scan width was $\Delta\omega = (a + 0.35 \tan \theta°)$ with $a = 0.55$, 0.78, and 0.71 for **5a**−**c**, respectively. Intensity data were collected up to $\theta = 27.50°$. Total data of 6189, 10 616, and 6079 reflections were collected, of which 4406, 4856, and 4432 were independent ($R_{int} = 0.027$, 0.047, and 0.035) for **5a**−**c** respectively. Data were corrected for Lp effects and for the linear decay of three periodically measured reference reflections during X-ray exposure time. An empirical absorption/extinction correction was applied (DIFABS,[14] correction ranges 0.72−161, 0.44−1.70, and 0.74−1.61 for **5a**−**c**, respectively). The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[15] Refinements on F^2 was carried out using full-matrix least-squares techniques (SHELXL-93);[16] no observance criterion was applied during refinement. The structures displayed substitutional disorder at the position of Br(2); *vide infra*. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl hydrogen atoms were refined as a rigid group, allowing for rotation around the O−C, Pd−S, or S−C bonds. For **5c** weak bond length restraints had to be used to prevent C(13) and Br(2) from merging. All non-hydrogen atoms, except for those of the disordered methyl atoms of **5a** and **5b**, were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with fixed isotropic thermal parameters related to the values of the equivalent isotropic thermal parameters of their carrier atoms by factors of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms. For **5a** convergence was reached at wR2 = 0.087, $w^{-1} = \sigma^2(F^2) + (0.0361P)^2 + 3.33P$, where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$, R1 = 0.031 for 3654 reflections with $F_o > 4\sigma(F_o)$, and $S = 1.19$ for 207 parameters. No residual density was found outside −1.08 and +0.68 e Å^{-3} (near Pd). For **5b** convergence was reached at wR2 = 0.145, $w^{-1} = \sigma^2(F^2) + (0.0667P)^2$, R1 = 0.053 for 2415 reflections with $F_o > 4\sigma(F_o)$, and $S = 1.03$ for 215 parameters. A final difference Fourier map showed no residual density outside −0.67 and +0.69 e Å^{-3} (near Pd). For **5c** convergence was reached at wR2 = 0.087, $w^{-1} = \sigma^2(F^2) + (0.0303P)^2 + 7.05P$, R1 = 0.038 for 3876 reflections with $F_o > 4\sigma(F_o)$, and $S = 1.08$ for 212 parameters. No residual density outside −1.44 and +1.44 e Å^{-3} (near Pd) was found. The crystal data of **5a**−**c** are presented in Table 2, and the positional parameters for **5a**−**c** are given in the Supporting Information. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 17. Geometrical calculations and illustrations were performed with PLATON.[18] All calculations were performed on a DEC5000 cluster.

Crystal Structure Determination of 12. An orange crystal with approximate dimensions 0.05 × 0.25 × 0.60 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and an $\omega-2\theta$ scan. A total of 9699 unique reflections were measured within the ranges $0 \le h \le 9$, $0 \le k \le 24$, and $-39 \le l \le 40$; of these, 7941 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0.59 Å^{-1}. Two reference reflections (110, 016) were measured hourly and showed no decrease during the 110 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $78 < 2\theta < 82°$. Corrections for Lorentz and polarization effects were applied. The asymmetric unit contains two independent molecules. The positions of the palladium atoms were found by direct methods. The remainder of the non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distances to their carrier atoms remained within 1.09 Å, converged to $R = 0.042$, $R_w = 0.064$, and $(\Delta/\sigma)_{max} = 0.51$. A weighting scheme $w = (5.8 + F_o + 0.0073F_{obs}^2)^{-1}$ was used. An empirical absorption correction[19] was applied, with coefficients in the range 0.61−1.55. The secondary isotropic extinction coefficient[20] refined to $G = 0.8(1)$. A final difference Fourier map revealed a residual electron density between −0.9 and +0.9 e Å^{-3}. Matching the two molecules resulted in an rms of 0.19 Å. Scattering factors were taken from Cromer and Mann.[21] The anomalous scattering of palladium, chlorine, and sulfur was taken into account. All calculations were performed with XTAL3.0,[22] unless stated otherwise. The crystal data are presented in Table 1, and the fractional coordinates are given in the Supporting Information.

Ligand Synthesis. L/D-Methionine Methyl Ester (L/D-HmetMe). According to the procedures described,[23] using L-methionine, the optically pure HCl salt of methionine methyl ester was obtained in 60% yield ($[\alpha]^{20} = +21.82$). By the reaction of HCl·L-HmetMe with Et_3N (1.5 equiv) in EtOH and subsequent evaporation of the solvent, followed by extraction of the resulting white sticky solid with CH_2Cl_2, L/D-HmetOme was obtained as a yellow oil in 60% yield ($[\alpha]^{20} = -2.43$).

***N*-(2-Thienylmethylidene)-L/D-methionine Methyl Ester (th-metMe).** This ligand was obtained by reacting 2-thiophenecarbalde-

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hyde (13.4 g; 120.0 mmol) with L/D-HmetMe (17.8 g; 109.1 mmol) in refluxing ethyl acetate (100 mL), on molecular sieves, for 18 h. After cooling of the yellow solution to room temperature and evaporation of the solvent, 28.5 g of a yellow oil was obtained. Purification was carried out by distillation of the 2-thiophenecarbaldehyde under reduced pressure (bp 373 K; 2 mmHg); yield 95% ($[\alpha]^{20} = +0.02$). Found (calc for $C_{11}H_{15}NO_2S_2$): C, 51.42 (51.33); H, 5.87 (5.88); N, 5.47 (5.44). IR (CH_2Cl_2, cm^{-1}): 1738 (C═O), 1632 (C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 10.8 (C^1); 26.0 (C^3); 27.7 (C^2); 47.9 (C^6); 66.3 (C^4); 123.4 (C^{10}); 125.7 (C^9); 127.6 (C^{11}); 137.5 (C^8); 153.2 (C^7); 167.5 (C^5). The ligand was stored under a nitrogen atmosphere at 273 K as a stock solution in CH_2Cl_2.

Synthesis of the Complexes. $PdCl_2$(th-metMe), 1. (A) To a stirred suspension of $PdCl_2$(COD) (1.44 g; 4.91 mmol) in CH_2Cl_2 (20 mL) was added a solution of th-metMe (1.33 g; 5.16 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for at least 3 h at room temperature, after which the solvent was evaporated. The resulting yellow sticky solid was washed with Et_2O (2 × 10 mL) and dried. A yellow solid was obtained in 92% yield. Slow diffusion of Et_2O into a solution of **1** in CH_2Cl_2 afforded yellow crystals.

(B) To a solution of Na_2PdCl_6 in CH_2Cl_2 (15 mL) was added th-metMe (1.1 equiv) in CH_2Cl_2 (10 mL). After 30 min, yellow solid **1** precipitated, which was isolated by filtration and subsequently dried *in vacuo*. Found (calc for $C_{11}H_{15}Cl_2NO_2S_2Pd{\cdot}CH_2Cl_2$): C, 27.31 (27.74); H, 3.32 (3.30); N, 2.87 (2.70). IR (KBr, cm^{-1}): 1740 (C═O), 1610 (C═N). $^{13}C\{^1H\}$ NMR (CD_3CN, 293 K, δ): 20.7, 20.5 (C^1); 28.7, 28.9 (C^3); 30.7, 30.8 (C^2); 52.6 (C^6); 69.3 (C^4); 128.0 (C^{10}); 137.3 (C^9); not obs (C^8); 141.7 (C^{11}); 168.3 (C^7); 170 (C^5). Solid state NMR (δ): 24.7 (C^1); 32.1 (C^3); not obs (C^2); 55.9 (C^6); 70.3 (C^4); 134.5 (C^{10}); 142.6 (C^9); 145.4 (C^8); 138.2 (C^{11}); 170.8 (C^7); not obs (C^5).

$PdBr_2$(th-metMe), 2. $PdBr_2$ (0.91g; 3.39 mmol) was suspended in a mixture of CH_2Cl_2 (15 mL) and MeCN (10 mL) followed by addition of a th-metMe solution in CH_2Cl_2 (13.2 mL of 0.26 M). The resulting purple suspension was stirred for at least 18 h at room temperature, during which the color of the mixture slowly changed to yellow. The yellow mixture was filtered and subsequently reduced to 5 mL by evaporation, after which Et_2O (20 mL) was added, causing a yellow solid to precipitate. Complex **2** was isolated in quantitative yield by filtration and subsequently dried in vacuo. Found (calc for $C_{11}H_{15}Br_2NO_2S_2Pd$): C, 25.08 (25.23); H, 2.81 (2.89); N, 2.74 (2.68). IR (KBr, cm^{-1}): 1737 (C═O), 1607 (C═N).

PdI_2(th-metMe), 3. To a suspension of **2** (0.36 g; 0.82 mmol) in CH_2Cl_2 (15 mL) was added NaI (0.25 g; 1.63 mmol), resulting in an immediate color change from yellow to purple. After 1 h, the solution was extracted with of H_2O (10 mL), and the organic layer was separated from the mixture and subsequently dried on Na_2SO_4. Filtration and evaporation of the solvent afforded **3** as an air-stable purple solid in 70% yield. Found (calc for $C_{11}H_{15}I_2NO_2S_2Pd$): C, 21.35 (21.39); H, 2.54 (2.45); N, 2.25 (2.27). IR (KBr, cm^{-1}): 1735 (C═O), 1605 (C═N).

PdCl(Me)(th-metMe), 4. (A) The same procedure as described for **1** was followed, using PdCl(Me)(COD) (1.40 g; 5.27 mmol). The yellow solid **4** was obtained in quantitative yield.

(B) Reaction of **1** (0.5g, 1.8 mmol) with of Me_4Sn (1.5 equiv) in CH_2Cl_2 (10 mL) for 18 h at room temperature resulted in the formation of a yellow suspension. After filtration and evaporation of the solvent, yellow solid **4** was obtained in 95% yield. Found (calc for $C_{12}H_{18}ClNO_2S_2Pd$): C, 34.65 (34.79); H, 4.38 (4.42); N, 3.38 (3.40). IR (KBr, cm^{-1}): 1742 (C═O), 1621 (C═N). IR (CH_2Cl_2, 293 K, cm^{-1}): 1743 (C═O), 1622 (C═N). IR (CH_2Cl_2, 243 K, cm^{-1}): 1732, 1742 (C═O), 1613, 1621 (C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 3.2, 4.4 (Pd−CH_3); 17.5, 20.4 (C^1); 30.1, 32.1 (C^3); 32.9, 35.5 (C^2); 55.3 (C^6); 73.1, 75.7 (C^4); 129.5 (C^{10}); 130.0 (C^9); not obs (C^8); 141.4 (C^{11}); 166.6, 166.7 (C^{10}); 170.9 (C^5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 263 K, δ): 1.6, 2.8 (Pd−CH_3); 18.7, 20.5, 21.3 (C^1); 30.8, 30.9, 31.0 (C^3); 31.7, 33.7 (C^2); 53.8, 55.4 (C^6); 71.3, 71.4, 73.8 (C^4); 127.9, 128.0, 128.4 (C^{10}); 135.1, 135.2, 136.6 (C^9); 138.3, 138.4, 138.6 (C^8); 139.0, 139.2, 140.0 (C^{11}); 163.3, 164.1, 165.1 (C^{10}); 169.1, 169.4, 169.8 (C^5). Solid state NMR (δ): 20.8 (C^1); not obs (C^3); 28.1 (C^2); 51.5 (C^6); 74.2 (C^4); not obs (C^{10}); not obs (C^9); not obs (C^8); 137.2 (C^{11}); 168 (C^{10}); not obs (C^5).

PdBr(Me)(th-metMe), 5. Reacting **2** (0.24 g; 0.55 mmol) with Me_4-Sn (0.15 g; 0.83 mmol) for 18 h at room temperature in CH_2Cl_2 (15 mL) resulted in a brownish solution. Evaporation of the solvent afforded a brown solid, which was purified by column chromatography (silica gel). Using CH_2Cl_2 as the eluent afforded a yellow fraction. Evaporation of the solvent and drying the product afforded yellow-orange complex **5** in 60% yield. Recrystallization was done in two different ways: (A) Slow diffusion of Et_2O into the reaction mixture of **5** in CH_2Cl_2 afforded yellow crystals of **5a** and **5c**. (B) Slow evaporation of $CHCl_3$ from a solution of the reaction mixture, afforded yellow crystals of **5b**. Attempts to recrystallize purified complex **5** failed. Found (calc for $C_{12}H_{18}BrNO_2S_2Pd{\cdot}CH_2Cl_2$): C, 28.69 (28.72); H, 3.88 (3.71); N, 2.79 (2.57). IR (KBr, cm^{-1}): 1744 (C═O), 1621 (C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 1.4, 2.3 (Pd−CH_3); 20.8, 21.1 (broad) (C^1); 31.8 (C^3); 32.0 (C^2); 54.3, 54.4 (C^6); 72.2 (broad), 74.3 (C^4); 128.5, 128.9 (C^{10}); 135.6, 137.0 (C^9); 139.2 (C^8); 139.7 (broad), 140.4 (C^{11}); 164.7 (broad), 165.7 (C^7); 170.0, 170.4 (C^5).

PdI(Me)(th-metMe), 6. Using the reaction conditions described for the synthesis of **3**, starting from **4** (0.7 g;1.48 mmol), a reddish-purple, sticky solid was obtained, which after washing with Et_2O (15 mL) afforded red solid **6** in 70% yield. Elemental analytical data were unreliable because of the presence of an unknown amount of NaI. IR (KBr, cm^{-1}): 1743 (C═O), 1617 (C═N).

[Pd(Me)(S)(th-metMe)](O_3SCF_3), 7 (S = Solvent). To a solution of $Ag(O_3SCF_3)$ (0.41 g; 1.60 mmol) in MeOH (10 mL), a solution of **4** (0.42 g; 1.60 mmol) in MeOH (10 mL). The resulting suspension was stirred for 1 h at room temperature and subsequently centrifuged. The MeOH layer was separated from the mixture by decantation, followed by evaporation, after which yellow-gray solid **7** was obtained.

The complex appeared to be too unstable to obtain reliable elemental analytical data. IR (CH_2Cl_2, cm^{-1}): 1740 (C═O), 1621 (C═N), 1250, 1030, 640 ($^-O_3SCF_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 0.8 (Pd−CH_3); 15.1 (C^1); 30.5 (C^3); 32 (broad) (C^2); 52.3 (C^6); 74.2 (C^4); 127.8 (C^{10}); 135.0 (C^9); 136.6 (C^8); 140.7 (C^{11}); 166.2 (C^7); 168.2 (C^5).

[Pd(Me)(th-metMe)(L″)](O_3SCF_3) (L″: MeCN, 8; Pyridine, 9; 2-Picoline, 10; 2,6-Lutidine, 11). **7** (0.03 g; 0.06 mmol) was dissolved in CD_2Cl_2 (0.5 mL), giving a clear yellow solution; addition of MeCN (0.06 mmol) afforded **8**. Complexes **9**−**11** were prepared as described for **8**. The complexes **8**−**11** were not isolated because of gradual degradation; *i.e.*, small amounts of colloidal palladium were formed on attempted isolation. $^{13}C\{^1H\}$ NMR for **10** ($CDCl_3$, 293 K, δ): 0.8 (Pd−CH_3); 20.3 (C^1); 29.5 (C^3); 33.9 (C^2); 53.1 (C^6); 74.9 (C^4); 128.1 (C^{10}); 135.8 (C^9); 137.7 (C^8); 138.2 (C^{11}); 166.9 (C^7); 168.9 (C^5); 31.3 (CH_3^{pic}); 122.5 ($C^{5,pic}$); 126.0 ($C^{3,pic}$); 135.8 ($C^{4,pic}$); 137.7 ($C^{2,pic}$); 144.9 ($C^{6,pic}$).

[PdCl(L′)]$_2$, 12. To a solution of $Pd(OAc)_2$ (0.78 g; 3.47 mmol) in CH_2Cl_2 (10 mL) were added th-metMe (0.86 g; 3.81 mmol) in CH_2Cl_2 (10 mL), Et_3N (0.92 g; 9.09 mmol), and NaCl (excess). The purple suspension was stirred for 18 h at room temperature, resulting in a brown solution, which was partly evaporated (CH_2Cl_2 volume of 5 mL). A brown solid was obtained after addition of Et_2O (15 mL) and hexane (5 mL) and subsequent filtration. Purification of the complex was achieved by column chromatography on silica gel. Using CH_2Cl_2 as the eluent caused a yellow band to run, which was not analyzed. Subsequent elution with CH_2Cl_2/MeOH (5:1) yielded, after evaporation of the solvent, the orange dimeric complex in 63%. Anal. Found (calc for $C_{22}H_{28}N_2O_4S_4Pd_2Cl_2$): C, 33.18 (32.99); H, 3.55 (3.45); N, 3.52 (3.52). IR (KBr, cm^{-1}): 1740 (C═O), 1620 (C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K, δ): 20.8 (C^1); 44 (C^3); 40 (C^2); 52 (C^6); 83 (C^4); 128 (C^{10}); 135 (C^9); 139 (C^8); 138 (C^{11}); 160 (C^7); 173 (C^5).

PdCl(C(O)Me)(COD). According to literature procedures[24] using a 500 mL Schlenk flask, PdCl(Me)(COD) (0.09 g; 0.34 mmol) was dissolved in CH_2Cl_2 (10 mL) and brought to 223 K. The clear solution was put under CO atmosphere (5 bar) and stirred for 10 min. Releasing the pressure and addition of Et_2O (20 mL) resulted in precipitation of a very unstable off-white solid, which could be isolated by centrifugation and subsequent decantation. ^1H NMR ($CDCl_3$, 293 K, δ): 2.44 (Pd−COMe), 2.57 (CH_2), 5.16 (CH═CH, *trans* to Cl), 5.77 (CH═CH, *trans* to COMe). Elemental analysis was not performed due to fast degradation of the product; *i.e.*, colloidal palladium was formed upon isolation.

(24) Lapido, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.

PdCl(C(O)Me)(th-metMe), 13. A yellow solution of **4** (0.04 g; 0.16 mmol) in CD_2Cl_2 (2 mL), cooled to −78 °C, in a high-pressure tube, was put under 3 bar of CO atmosphere. The ^1H spectrum showed that the complex was formed quantitatively. Attempts to isolate the product were unsuccessful due to decomposition.

Addition of a stoichiometric amount of th-metMe to a PdCl(C(O)-Me)(COD) solution at 223 K, (*vide supra*) and stirring for 18 h at 223 K generated, after addition of Et_2O (25 mL), subsequent filtration, and drying *in vacuo*, a yellow solid quantitatively, which degraded slowly at room temperature. IR (CH_2Cl_2, 293 K, cm^{-1}): 1743 (C═O), 1622 (C═N), 1704 (Pd−COMe). IR (CH_2Cl_2, 243 K, cm^{-1}): 1739 (C═O), 1622 (C═N), 1704 (Pd−COMe).

PdX(C(O)Me)(th-metMe) (X: Br, 14; I, 15). Through a solution of **5** (0.03 g; 0.07 mmol) (or **6**) in $CDCl_3$ (0.5 mL) was bubbled CO for at least 15 min. A slight color change was observed. The product could not be isolated due to unstability. $^{13}C\{^1H\}$ NMR of **14** (CD_2Cl_2, 293 K, δ); 21.5 (C^1); 32.4 (C^3); 35.1 (C^2); 40.5 (Pd−$COCH_3$); 54.4 (C^6); 71.8 (C^4); 128 (C^{10}); 135 (C^9); 139 (C^8); , 139 (C^{11}); 164.3 (C^7); 170.9 (C^5).

[Pd(C(O)Me)(L″)(th-metMe)](O_3SCF_3) (L″: MeCN, 16; Pyridine, 17; Lutidine, 18). Using the corresponding starting complexes, *i.e.* **8, 9**, and **11**, *in situ* (*vide supra*), the products were obtained by bubbling CO through the cationic alkyl solution for 15 min or by pressurising the solution of the complex in a high pressure tube or by using a gas buret. The unstable products could not be isolated.

Results

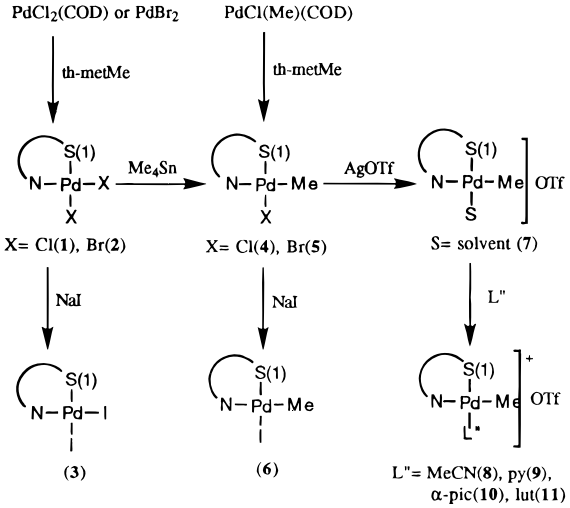
The first step in the ligand synthesis involves the formation of the optically active methyl ester of methionine. Reaction of this enantio pure ester with Et_3N resulted in the abstraction of the HCl but also in racemization of C4. After isolation of the HCl salt free racemic amine, the thiophene derivative was prepared by reacting the amine with 2-thiophenecarbaldehyde (eq 1).

$$\text{HCl.LHmetH} \xrightarrow[H^+]{\text{MeOH}} \text{HCl.LHmetMe} \xrightarrow[\text{thCHO}]{Et_3N} \text{D/L-th-metMe} \quad (1)$$

Reaction of th-metMe with $PdCl_2$(COD) or $PdBr_2$ afforded **1** or **2**, respectively, while compound **3** was obtained by reacting **1** with NaI in acetone. Complexes **4** and **5** were obtained by reacting the dihalide with Me_4Sn, while **4** could also be obtained by the 1:1 reaction of th-metMe with PdCl(Me)(COD). The crystal structure determination of **5** clearly showed that the conversion of **2** into **5** was incomplete, as crystalline mixtures with different molar ratios of **2** and **5** were obtained. Attempts to recrystallize purified **2** or **5** failed. A substitution reaction of NaI with **4** resulted in the formation of **6**. The cationic palladium complexes were obtained by abstraction of the halide of **4** using Ag(O_3SCF_3); addition of the coligand, *i.e.* MeCN, pyridine, lutidine, and picoline, resulted in the formation of **8**−**11**, respectively. (See eq 2.)

These complexes could be easily isolated by precipitating the product by addition of Et_2O or hexane to a concentrated solution of the complex in CH_2Cl_2 or MeCN. The neutral complexes dissolve in polar solvents and can be stored in the open atmosphere for a prolonged period. Heating of solutions of the complexes in CH_2Cl_2 or $CDCl_3$ (T > 363 K, 18 h) causes slow decomposition as shown by the formation of traces of colloidal palladium. The cationic complexes are very hygroscopic and unstable and were therefore prepared *in situ*. Identification of the products as monomeric complexes was based on elemental analytical data as well as on ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data (see Experimental Section and Tables 5 and 7).

The structural characterization of the neutral and cationic complexes will be described below as well as the reactivity of



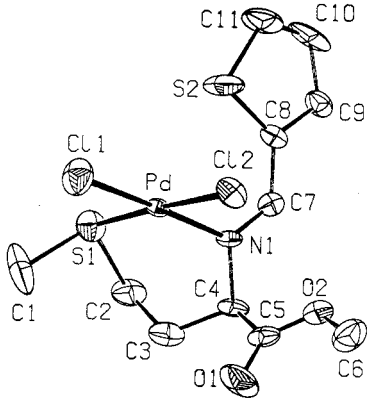
(2)

the ligand in a basic medium, resulting in a C−H activation, and of the methyl complexes toward CO.

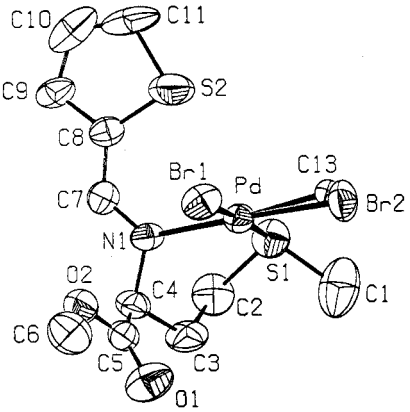
Neutral Complexes. PdX_2(th-metMe) (X = Cl, Br, I). The solid state structure of **1** (X = Cl) was determined by X-ray structure analysis. The molecular geometry of the mononuclear species comprises a square planar Pd center formed by to two halide atoms and the ligand. Coordination of the ligand *via* the imine nitrogen and the methionine sulfur donor atoms leads to a six-membered chelate ring having a boat configuration. The Pd−Cl, Pd−N, and Pd−S bond distances observed in **1** (Table 7) are all within the expected range for an imine N and a thioether sulfur coordination.[5,6,25] The methyl group on the sulfur donor in **1** is positioned quasi-axial, thus giving the sulfur atom either an *S* or *R* configuration. The thiophene moiety is positioned above the coordination plane, resulting in a Pd−S^2 distance of 3.11 Å, which points to a nonbonding interaction between the metal center and the thiophene sulfur donor (Figure 2).

The NMR spectra (Table 3) of the complexes in solution show that all the resonances are shifted to lower field as compared to the resonance values measured for the free ligand. The ^1H shift differences found for C^7H ($\Delta\delta$ = 0.09−0.72 ppm) and C^1H_3 ($\Delta\delta$ = 0.04−0.69 ppm) indicate that NS coordination occurs in solution, which is also supported by the downfield $^{13}C\{^1H\}$ shifts of C^1 ($\Delta\delta$ = 9.8 ppm) and C^7 ($\Delta\delta$ = 18.6 ppm) (Experimental Section). The fact that the ^1H NMR spectra of the neutral dihalopalladium complexes show a sharp as well as a broad set of resonance signals at room temperature indicates that exchange processes are occurring in solution. Unfortunately, the geometry of the isomers which are in the intermediate exchange at room temperature could not be elucidated; because of the low solubility of these complexes, low-temperature NMR could not be performed. Since no large shifts of C^9H are observed, isomerizations involving rotations around the C^7−C^8 bond, *i.e. s-cis*/*s-trans* conformations of the conjugated thienylideneamine moiety, can be excluded because an *s-cis* conformation would place C^9H in the vicinity of the palladium center. Addition of excess ligand to the complex in solution

(25) (a) Kubiak, M.; Allain, A.; Jezowska-Trzebiatowska, B.; Glowiak, T.; Kozlowski, H. *Acta Crystallogr.* **1980**, *B36*, 2246. (b) Byers, P. K.; Canty, A. J.; Engelhardt, L. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1731. (c) Byers, P. K.; Canty, A. J. *J. Organomet. Chem.* **1987**, *336*, C55. (d) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3363. (e) Albinati, A.; Kunz, R. W.; Amman, C. J.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800. (f) Butler, I. R. *Organometallics* **1992**, *11*, 74. (g) Abel, E. W.; Dormer, J. C.; Ellis, D.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1073. (h) Chooi, S. Y. M.; Hor, T. S. A.; Leung, P.-H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494.



1, (D/L-th-metMe)PdCl$_2$



2/5, (D/L-th-metMe)PdBr$_2$/ (D/L-th-metMe)PdMeBr

Figure 2. Crystal structures of **1** and **5a**.

does not alter the appearance of the spectra, showing that intramolecular exchange processes are operating. Variation of the halide bonded to the palladium center influences the isomer ratio; an increase of the halide ion radius decreases the amount of complex responsible for the set of sharp resonance signals: **1** (22:78%), **2** (33:67%), **3** (100:0%).

PdX(Me)(th-metMe) (X = Cl, Br, I). The structure of compound **5** was established by a crystal structure determination. Three crystals of different batches were measured, each displaying a different ratio of compounds **5** and **2**. The fractions of compound **5** present in the crystals were 0.229(3), 0.545(4), and 0.829(3) for structure determinations on single crystals from batches **a**, **b**, and **c**, respectively. All crystals contained one solvent molecule per asymmetric unit, CH_2Cl_2 for batch **a** and batch **c** and $CHCl_3$ for batch **b**. The coordination of the ligand of complex **5** and **2** in all batches was found to be isostructural with that of **1**; *i.e.*, the ligand is chelate bonded *via* the N and S^1 donors. The Pd−N (2.043(4) Å) bond is relatively long when compared to this distance found in **1**, which can be ascribed to the larger *trans* influence of the methyl group. The Pd−S^1 bond (2.2782(11) Å) is within the expected range. In Figure 2 the *SS*-**5** configuration is shown, and again C^1H_3 is positioned under the coordination plane, *i.e.* directed away from the thiophene ring.

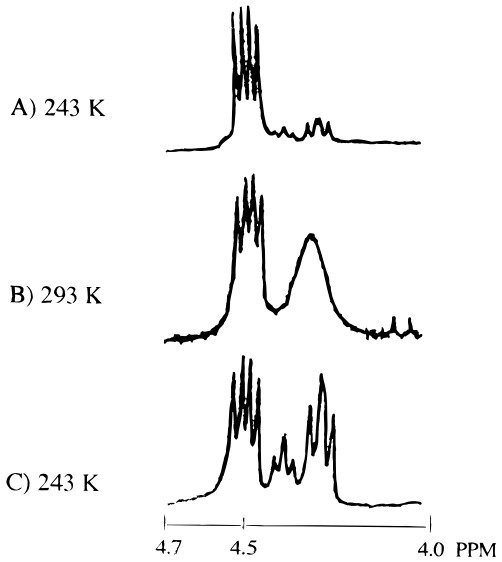


Figure 3. ^{1}H NMR spectra of the C^4H region of **4** in CD_2Cl_2.

In solution, coordination of the ligand in complexes **4**−**6** has been elucidated by ^{1}H (Table 3) and $^{13}C\{^1H\}$ NMR spectroscopy (Experimental Section). At room temperature the ^{1}H downfield shifts of the C^1H_3 ($\Delta\delta = 0.13-0.51$ ppm) and C^7H resonances ($\Delta\delta = 0.19-0.24$ ppm) confirm the expected NS^1 coordination, similar to that of **1**−**3**. At room temperature, the ^{1}H spectra have the same appearance as those of the dihalide complexes, *i.e.*, one set of sharp and one set of broad resonance signals, indicating that the methyl complexes (**4**−**6**) are isostructural with the dihalide compounds (**1**−**3**). Investigation of **4** (X = Cl) by variable-temperature ^{1}H NMR (Figure 3, in the range 243−348 K) shows an interesting dynamic behavior. Dissolving

Table 3. ^{1}H NMR Data for the Complexes Based on L, All Recorded at 293 K[a]

entry (solvent)	$C^6H_3{}^s$	C^4H^m	$C^1H_3{}^s$	C^7H^s	C^9H^d	$C^{10}H^{dd}$	$C^{11}H^d$	Pd−Me^s
L ($CDCl_3$)	3.69	4.14	2.04	8.38	7.34	7.04	7.41	
			Neutral PdX_2(L)					
1 (CD_3CN)	3.86, 3.85	4.40, 4.44	2.2, 2.67	8.71, 8.79	8.07	7.44	8.21	
2 (CD_3CN)	3.68, 3.70	4.50, 4.52	2.08, 2.10	8.80, 8.86*	8.10	7.38	8.32	
3 (CD_3CN)	3.86	4.27*	2.18	8.47*	7.86	7.23	7.93	
			Neutral $PtCl_2$(L)					
20 (CD_3CN)	3.85, 3.86	4.76	2.33, 2.73	9.02, 9.10	8.05	7.36	8.14	
			Neutral PdX(Me)(L)					
4 ($CDCl_3$)	3.78, 3.86	4.24*, 4.33	2.17, 2.45	8.58*, 8.62	7.7	7.14, 7.21	7.8	0.82*, 0.88
5 ($CDCl_3$)	3.79, 3.87	4.19*, 4.32	2.33*, 2.50	8.57, 8.61	7.71	7.15, 7.21	7.84, 7.78	0.82*, 0.90
6 ($CDCl_3$)	3.79, 3.87	4.27*, 4.36	2.33*, 2.55	8.57, 8.61	7.80, 7.88	7.14, 7.20	7.87, 7.91	0.79*, 0.88
			Cationic [Pd(Me)(L)(L″)](O_3SCF_3)					
7 (CD_2Cl_2)	3.72	4.50[d]	2.41	8.94	7.69	7.16	7.87	0.51
8 (CD_3CN)	3.81, 3.87	4.64*, 4.65	2.14, 2.44	8.87*, 8.93	7.95	7.37, 7.42	8.02	0.73*, 0.83*
9 (CD_3CN)	3.70, 3.77	4.35[d], 4.57[q], 4.71[q]	2.33, 2.42, 2.53	obsc	obsc	obsc	obsc	0.45, 0.59, 0.67
10 (CD_3CN)	3.65, 3.73*	4.45[d], 4.46*	2.24, 2.32	8.90	obsc	7.11	7.68	0.43, 0.66*
11 (CD_3CN)	3.72	4.45[d]	2.49	8.89	7.73	7.17	7.85	0.51

[a] m = multiplet, $^3J_{H^4H^3}$ = see Table 6; d = doublet, 3.4 Hz < $^3J_{H^9H^{10}}$ < 4.0 Hz; d = doublet, 4.8 Hz < $^3J_{H^{10}H^{11}}$ < 5.9 Hz; s = singlet; dd = double doublet. * = broad resonance; obsc = obscured by solvent or coligand resonance signals.

4 in CD_2Cl_2 at 243 K results in mainly one set of resonance signals, pointing to the existence of one diastereomer in the solid state, which is also confirmed by solid state NMR (Experimental Section). The coupling constants observed at 243 K for C^4H ($^3J_{H^4H^{3a}} = 5.28$ Hz, $^3J_{H^4H^{3b}} = 10.23$ Hz) point to a boat conformation of the six-membered ring, analogous to the crystal structures of **1** and **5**. However, heating of this solution to 348 K results in formation of a second set of isomers, in a 1:1 ratio. When the solution is cooled to 293 K, this second set of signals is broad. These spectral data indicate the occurrence of an exchange process. Subsequent cooling of the solution to 243 K results in a decoalescence of the broad set of resonance signals; the C^1H_3 singlet splits into two singlets and the C^4H resonance signal splits into two double doublets in a 3:1 ratio ($^3J_{H^4H^{3a}} = 5.7$ Hz (1) and 6.12 Hz (3), $^3J_{H^4H^{3b}} = 5.7$ Hz (1) and 8.01 Hz (3)). The free energy[26] associated with this process ($\Delta G^{\ddagger}_{293K} = 59.7 \pm 0.3$ kJ·mol^{-1} for **4**, $\Delta G^{\ddagger}_{298K} = 61.0 \pm 0.4$ kJ·mol^{-1} for **5**, and $\Delta G^{\ddagger}_{303K} = 61.8 \pm 0.4$ kJ·mol^{-1} for **6**) is comparable to the values found for monodentate thioethers such as *N*-acetyl-L-methionine bonded to Pt (63.7 kJ·mol^{-1}).[27] These results indicate that, in the case of the th-metMe palladium complexes, the inversion is accompanied by a change in the chelate ring conformation, since a much lower $\Delta G^{\ddagger}$ value, when compared to that of the (*N*-acetyl-L-methionine)platinum complex, is expected. The coupling constants of C^4H for the two diastereomers observed at 243 K indicate a conformational change of the chelate ring. Since for both a flattened boat and an envelope ring conformation different couplings would be observed,[28] two chair diastereomers are proposed that differ with respect to the position of C^1H_3.

These results suggest the presence of three discrete complexes of which two are in the intermediate-exchange region on the NMR time scale at 293 K. This is in accordance with the three sets of resonance signals observed in the $^{13}C\{^1H\}$ NMR at 263 K. Variation of the halide changes the ratio between the sets of isomers; the amount of complex in the intermediate exchange, at room temperature, increases as the ion radius increases: **4** (56:44%), **5** (49:51%), **6** (45:55%).

Cationic Complexes. [Pd(Me)(L″)(th-metMe)](O_3SCF_3) (L″ = CD_2Cl_2, MeCN, Pyridine, 2-Picoline, 2,6-Lutidine). In solution, the ^1H downfield shifts of the C^1H_3 ($\Delta\delta = 0.05-0.53$ ppm) and the C^7H resonances ($\Delta\delta = 0.39-0.56$ ppm) (Table 3) indicate NS^1 coordination for all the cationic complexes, while a ^{19}F singlet at −78.66 ppm, indicates that the triflate anion is not coordinated to the palladium atom.[29] The thienyl, *i.e.*, C^9H, $C^{10}H$, and $C^{11}H$, and the methyl ester resonance signals show no shift as compared to those of the neutral complexes, indicating that S^2 or carboxylic oxygen coordination does not occur.

The cationic complex **7** (L″ = CD_2Cl_2), prepared *in situ*, shows one set of resonance signals with pronounced couplings for the methionine backbone (Table 4), pointing to a rigid $C^4H-C^3H_2-C^2H_2$ moiety. Irradiation and COSY experiments clearly showed a specific coupling between C^4H and C^3H^a ($^3J_{H^4H^{3a}} = 11.4$ Hz) and the absence of coupling between C^4H and C^3H^b, giving an angle of either 0 or 180° between C^4H and C^3H^a and an angle of 90° between C^4H and C^3H^b. This vicinal coupling constant resembles quite closely the corresponding value found for chelated *N*,*N*′,2-Me_3tn in which Sadler[28] showed that the ring adopts an envelope conformation.

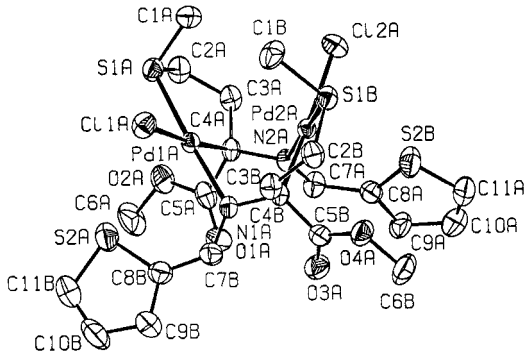


Figure 4. Crystal structure of **12**.

Table 4. Coupling Constants (Hz) of H^4 with H^{3a} and H^{3b} for the Complexes in Slow Exchange at Room Temperature[a]

	1	**2**	**3**	**4**	**4**^{243K}	**5**	**6**	**7**	**13**	**13**^{243K}	**14**	**15**
H^4-H^{3a}	6.4	6.4	6.3	5.0	5.3	5.0	5.1	0	br	5.6	br	br
H^4-H^{3b}	9.8	10.2	8.6^{vt}	9.8	10.2	9.6	9.6	11.6	br	6.6	br	br

*H^4 is observed at 4.5−3.8 ppm; the H^{β}'s are observed at 3.5−2.0 ppm; vt = virtual triplet; br = broad.

Addition of MeCN (**8**) enhances the flexibility of the methionine backbone, as can be seen from the existence of two sets of resonance signals in the ^1H NMR, which resembles the spectra observed for the neutral complexes (**1**−**6**). Conductivity measurements showed the existence of a cationic complex in solution [MeCN: 46 052 μS (253 K); 103 813 μS (293 K); 119 675 μS (313 K)]. An increase of the steric bulk of the coligand, *i.e.*, going from pyridine to 2,6-lutidine, changes the appearance of the ^1H NMR spectra notably. The pyridine-containing complex (**9**) shows three sets of resonance signals, in a ratio 4.5:1:4.5, whereas [Pd(Me)(2-picoline)(th-metMe)]-(O_3SCF_3) (**10**) shows a doublet and a broad resonance signal, in a 1:1 ratio, for C^4H in the ^1H NMR. Coordination of 2-picoline is indicated by the low-field shifts of the methyl substituent ($\Delta\delta = 0.33$ ppm), H^{3pic} and H^{4pic} ($\Delta\delta = 0.76$ ppm), H^{5pic} ($\Delta\delta = 0.94$ ppm), and H^{6pic} ($\Delta\delta = 0.32$ ppm) in the ^1H NMR and a low-field shift of the methyl group ($\Delta\delta = 7.0$ ppm) in the $^{13}C\{^1H\}$ NMR. The complex with the most bulky coligand, *i.e.* **11** (L″ = 2,6-lutidine) shows the exclusive formation of one isomer, which exhibits only a doublet multiplicity for the C^4H resonance signal, as has been found for **7** (L″ = CD_2Cl_2) (*vide supra*) indicating an envelope conformation of the six-membered NS chelate ring. Coordination of the 2,6-lutidine moiety is indicated by the low-field shifts of the methyl groups ($\Delta\delta = 0.93$ ppm), H^{3lut} ($\Delta\delta = 0.58$ ppm), and H^{4lut} ($\Delta\delta = 0.77$ ppm).

Reactivity of the Ligand and the Complexes. [PdCl(L′)]$_2$. The reactivity of the th-metMe ligand is highlighted by the acidity of C^4H, leading to racemization of the α-amino acid during isolation of the free amine after esterfication. This reactivity was also manifested during recrystallization of **4**; air stable orange crystals were obtained consisting of dimeric molecules, of which one is shown in Figure 4. Since this reaction could not be reproduced, a new synthetic route was developed, which involves reaction of the ligand with palladium acetate in a basic medium, leading to a high yield of the dimer (eq 3).

The structure of complex **12** in the solid state shows two monoanionic ligands coordinated to one palladium center *via* S^1 and anionic C^4, forming a five-membered ring with an envelope conformation, and to another metal nucleus *via* N,

(26) The free energies are calculated using $\Delta G^{\ddagger} = -RT_c \ln[(\pi(\Delta\omega)h)/\sqrt{2}kT_c]$ with $\Delta\omega = 61.98$ Hz and $T_c = 293$ K for **4**, $\Delta\omega = 57.59$ Hz and $T_c = 298$ K for **5**, and $\Delta\omega = 64.14$ and $T_c = 303$ K for **6**.

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Table 5. ^{1}H NMR Data for the Reaction Products, All Recorded at 293 K[a]

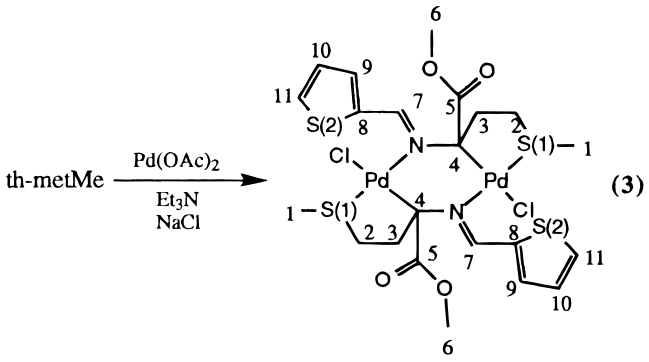
entry (solvent)	$C^6H_3{}^s$	C^4H^m	$C^1H_3{}^s$	C^7H^s	C^9H^d	$C^{10}H^{dd}$	$C^{11}H^d$	Pd−COMe^s
$[PdCl(L')]_2$								
12 ($CDCl_3$)	3.05		3.02	7.96	7.58	7.13	7.73	
			Neutral PdX(C(O)Me)(L)					
13 (CD_2Cl_2)	3.87	4.29*	2.60*	8.49	7.65	7.18	7.75	2.27*
14 ($CDCl_3$)	3.79	4.28*	2.58	8.52	7.67	7.13	7.71	2.22
15 (CD_2Cl_2)	3.69, 3.79	4.34, 4.78*	2.23, 2.27	8.90	*	*	*	2.35
			Cationic [Pd(C(O)Me)(L)(L'')](O_3SCF_3)					
16 ($CDCl_3$)	3.92*	4.53*	2.20*	8.75*	7.92*	7.42*	8.09*	2.65*
17 (CD_3CN)	3.68	4.12	2.30	obsc	obsc	obsc	obsc	obsc

[a] m = multiplet, $^3J_{H^4H^3}$ = see Table 6; d = doublet, 3.4 Hz < $^3J_{H^9H^{10}}$ < 4.0 Hz; *d* = doublet, 4.8 Hz < $^3J_{H^{10}H^{11}}$ < 5.9 Hz; s = singlet; dd = double doublet. * = broad resonance; obsc = obscured by solvent or coligand resonance signals.

Table 6. Half-Lives[a] for the CO Insertion Reaction

complex	**4**	**5**	**6**	**7**	**8**	**9**	**11**
$\tau_{1/2}$ (s)	64 + 3	59 + 4	40 + 3	28 + 3	58 + 3	75 + 6	66 + 5

[a] Defined as the time after which the amounts of starting complex and insertion product are equal, measured by gas buret techniques (5 bar of CO, room temperature, in 5 mL of solvent). The neutral complexes were studied in CH_2Cl_2 and the cationic compounds in MeCN.

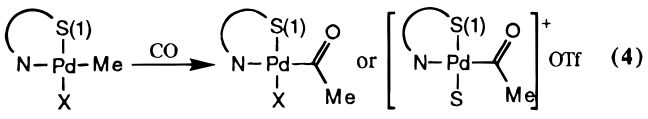


forming a six-membered ring with a boat conformation (Figure 4). This results in a dihedral angle of 73° between the coordination planes and a nonbonding interaction between the metal centers (Pd(1A)···Pd(2A) = 3.05 Å). The methyl ester moieties are positioned axially in the six-membered ring. The methyl groups on both methinic sulfur donors are again directed away from the thiophene rings, while these potential donors are again positioned above the coordination plane (Pd···S^{2A} = 3.23 Å), similar to the case of **1**.

In solution, one set of resonance signals is observed for **12** in both the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. The low-field shift of the C^1H_3 ($\Delta\delta$ = 0.98 ppm) and the high-field shifts of the C^7H ($\Delta\delta$ = 0.42 ppm) and the C^4 ($\Delta\delta$ = 0.64 ppm) resonance signals point to NC^4S coordination. The characteristic multiplicity, in the ^{1}H NMR, of the signals of the methionine $C^3H_2-C^2H_2$ backbone ($J_{H^{3a}H^{2a}}$ = 13.1 Hz, $J_{H^{3a}H^{2b}}$ = 14.3 Hz, $J_{H^{3b}H^{2a}}$ = 0 Hz, $J_{H^{3b}H^{2b}}$ = 6.2 Hz) indicates rigidity of this part of the ligand. Variable-temperature experiments did not reveal any dynamic behavior of the ligand backbone. The product is very stable, since no reactions were observed with CO, phosphines, alkylzinc, and several alkyllithium reagents.

CO Insertion. Reaction of the methyl complexes **4**−**11** with CO, either by pressurizing an evacuated reaction flask containing a solution of the methylpalladium complex or by bubbling CO through a solution of the alkyl complex, afforded the corresponding acyl complexes **13**−**18** (eq 4).

At room temperature, solutions of the neutral (**13**−**15**) and the cationic acyl products (**16**−**18**) in CH_2Cl_2, $CHCl_3$, or MeCN are unstable and colloidal palladium was formed immediately. The ^{1}H NMR of **13** (X = Cl, Table 5) and the $^{13}C\{^1H\}$ NMR



X= Cl (**13**), Br (**14**), I (**15**)

S= CD_2Cl_2 (**16**), MeCN (**17**), pyridine (**18**), lutidine (**19**)

of **14** (X = Br, Experimental Section) showed the formation of the acyl product (eq 4) in one isomeric form. A ^{1}H downfield shift of the C^7H ($\Delta\delta$ = 0.11−0.52 ppm) and C^1H_3 resonances ($\Delta\delta$ = 0.16−0.56 ppm) indicates coordination of the imine N and the methionine S^1 donors. The formed chelate ring probably has a boat conformation, as indicated by the coupling constants ($^3J_{H^4H^{3a}}$ = 5.6 Hz and $^3J_{H^4H^{3b}}$ = 6.6 Hz) of C^4H for **13** at 243 K (Table 4).

The reactivity of the neutral and cationic alkylpalladium complexes toward CO insertion was measured by using a low-temperature IR cell[30] and gas buret and high-pressure NMR techniques.[31] Half-lives were determined by pressurizing a flask filled with 0.02 mmol of the complex in 5 mL of solvent at room temperature, which was connected to a gas buret, using 5 bar of CO. The results are presented in Table 6.

The CO insertion rate, measured at room temperature (Table 6), increases upon going from chloride to iodide. Abstraction of the halide and replacement with a facile leaving group such as the triflate anion give a more reactive species. The cationic complexes to which a coligand was added, *i.e.*, MeCN (**8**), pyridine (**9**), or 2,6-lutidine (**11**), showed a lower reactivity toward CO than **7**, which lacks this coligand.

Discussion

Molecular System in the Solid State. It is clear from the comparison of the *N*-thienylidene-L-methionyl backbone of the *N*-[*N*-(5-methyl-2-thienylidene)-L-methionyl]histamine ligand[2] in the solid state with the backbone of the ligand in **1** that rotations around the $C^4-C^3-C^2$ axes in the ligand occurred. The dihedral angles within the $C^7-N^1-C^4-C^3-C^2-S^1-C^1$ chain are rotated 126, 138, 92, and 86°, respectively, compared to those of the free ligand. Since the use of excess ligand in the complexation reaction does not change the bidentate coordination mode of the ligand, the geometry of the ligand is dominated by the preferences of the metal and the chelating effect of the ligand. Otherwise, polymers would be formed by monodentate-bonded ligands, completely stretched out, coordinating to two palladium centers, as has been found for the

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Table 7. Selected Distances (Å) and Angles (deg) for **1**, **5a**, and **12**, with Esd's in Parentheses

Compound **1**	
Pd−Cl(1)	2.275(3)
Pd−Cl(2)	2.322(2)
Pd−S(1)	2.283(2)
Pd−N(1)	2.030(7)
Pd−S(2)	3.111
Cl(1)−Pd−Cl(2)	90.1(1)
Cl(1)−Pd−S(1)	92.7(1)
Cl(2)−Pd−N(1)	90.5(2)
S(2)−Pd−N(1)	86.7(2)
Compound **5a**	
Pd(1)−Br(1)	2.4464(6)
Pd(1)−Br(2)[C(13)]	2.3975(13)[2.08(5)]
Pd(1)−S(1)	2.2782(11)
Pd(1)−N(1)	2.043(4)
Pd(1)−S(2)	3.0568(15)
Br(1)−Pd(1)−Br(2)[C(13)]	90.56(3)[94.0(13)]
S(1)−Pd(1)−Br(2)[C(13)]	91.38(4)[87.9(13)]
N(1)−Pd(1)−Br(1)	90.50(10)
S(1)−Pd(1)−N(1)	87.66(10)
Compound **12**	
Pd(1A)-Pd(2A)	3.046(6)
Pd(1A)-Cl(1A)	2.390(2)
Pd(1A)-S(1A)	2.268(2)
Pd(1A)-C(4A)	2.068(6)
Pd(1A)-N(1A)	2.074(5)
Pd(1A)-S(2A)	3.234(2)
Pd(2A)-Cl(2A)	2.414(2)
Pd(2A)-S(1B)	2.276(1)
Pd(2A)-C(4B)	2.060(6)
Pd(2A)-N(2A)	2.087(5)
Pd(2A)-S(2B)	3.082(2)
Cl(1A)-Pd(1A)-S(1A)	87.45(6)
Cl(1A)-Pd(1A)-N(1A)	94.4(1)
S(1A)-Pd(1A)-C(4A)	88.0(2)
N(1A)-Pd(1A)-C(4A)	90.0(2)
Cl(2A)-Pd(2A)-S(1B)	88.74(5)
Cl(2A)-Pd(2A)-N(2A)	94.5(1)
S(1B)-Pd(2A)-C(4B)	87.6(2)
N(2A)-Pd(2A)-C(4B)	89.1(2)

{[Ag{*N*-[*N*-(5-methyl-2-thienylmethylidene)-L-methionyl]-histamine}]}(O_3SCF_3)·MeOH}$_\infty$ complex.

The most intriguing feature in complexes **1** and **5** is the configuration of the six-membered ring which is formed upon coordination. This ring has a twisted-boat geometry, which is in contrast to the perturbed chair conformation found in the corresponding [$PdCl_2$(MetH-*S*,*N*)] complex.[6] Both the relatively long Pd−S^1 distances (2.283(2) and 2.2782(11) Å) and the relative small N−Pd−S^1 angles (*i.e.*, 86.9 and 87.6°) cannot be explained by imine coordination compared to amine coordination and will therefore be caused by the rigidity of the backbone of the methionine moiety imposed by the position of the thiophenecarbaldimine unit (*vide infra*), similar to the case of [PtCl(Gly-MetH-*N*,*N*′,*S*)].[5] The methyl ester moiety is placed equatorially (C^4 has an *R* configuration), which is probably induced by the position of the thiophene ring of a neighboring molecule, because the groups are positioned parallel to each other with an average distance of 4 Å, thus forming a layer of alternating thienyl and ester groups. In Figure 2 the *RR*-**1** complex is shown, whereas the *SS*-**1** complex, also present in the unit cell, is omitted for clarity.

The thienylmethylidene moiety, in **1**, **5**, and **12**, is close to planar due to π-conjugation between the imine, which has the *E* configuration, and the thiophene ring system. As predicted by MNDO and AM1 calculations,[32] the *s-cis* configuration of the $S^2-C^8-C^7-N$ moiety is energetically favored over the *s-trans* form, which is confirmed by the crystal structures. The geometry of the methionine backbone in the solid state is fixed, because of the chelating effect, resulting in a fixed $C^7-N-C^4-C^3$ dihedral angle. Therefore, the thienyl sulfur atom is in the proximity of the metal center, having the ring almost perpendicular (**1**, 77.8°; **5**, 79.4°; **12**, 81.8 and 84.4°) to the coordination plane. The long Pd−S^2 distances (**1**, 3.111 Å; **5**, 3.107 Å; **12**, 3.234 and 3.082 Å) indicate a weak interaction with the central palladium ion.[33]

Molecular System in Solution. PdX_2(th-metMe) (X = Cl, Br, I), PdX(Me)(th-metMe) (X = Cl, Br, I), [Pd(Me)(L″)-(th-metMe)](O_3SCF_3) (L″ = CH_2Cl_2, MeCN, Pyridine, Picoline, Lutidine). The structure of the complexes in solution can be resolved by looking at the geometry of the methionine backbone, which can be elucidated by looking at the multiplicity of the C^4H resonance in the ^1H NMR. The coupling constants (Table 4) of the double doublet multiplicity observed for complex **1** (X = Cl) at room temperature, using the Karplus relation,[34] give dihedral angles of 38 and 160°, respectively. These angles are also found between $C^4H-C^3H^a$ and $C^4H-C^3H^b$ in the crystal structure. Therefore, the sharp set of resonance signals (approximately 25%) belongs to a structure in which the chelate backbone has a boat geometry, as was found in the solid state. Unfortunately the structures of the isomers, which are in the intermediate-exchange region at room temperature, could not be elucidated. However the solubility of **4** in CD_2Cl_2 enabled us to study all isomers.

Again, the multiplicity of C^4H offered the opportunity of elucidating the structures of the isomers. In Scheme 1 the two possible diastereomers for the *SS*(*RR*) and *SR*(*RS*) complexes are depicted schematically. Complex **4A** is the isomer which is observed in the solid state (*SS*- or *RR*-**4A**) in which the six-membered ring has a twisted-boat geometry, similar to that of **1**. Puckering of the ring would place the ester as well as the methyl group in an axial position, which enhances steric hindrance between both groups (Scheme 1, **4B**). Inversion at the sulfur center,[35] *i.e.*, placing it axially, leads to the formation of the *RS* or *SR* isomer (Scheme 1, **4C**). The trend in the free energy associated with this inversion process, *i.e.*, $\Delta G^{\ddagger}_{Cl} < \Delta G^{\ddagger}_{I}$, cannot be explained by the *trans* influence of the halide, which would predict the opposite trend.[36] Since the differences are small and fall within the experimental error, no conclusions can be drawn. However the $\Delta G^{\ddagger}$ values measured are lower than those (approximately 72 kJ·mol^{-1}) found for the platinum methionine complexes investigated by Sadler,[31] which can be explained by the stronger bonding of the ligand to platinum compared to palladium.

When the mixture was heated to 363 K, the resonance signals belonging to the chair conformers were sharpened. However conversion of **4C** to **4D** could not be accomplished. After the mixture was cooled to room temperature, two sets of resonance signals were obtained in the same ratio as found in the spectrum after going from 243 to 293 K (*vide supra*.).

A change in the polarity of the solvent shows the existence

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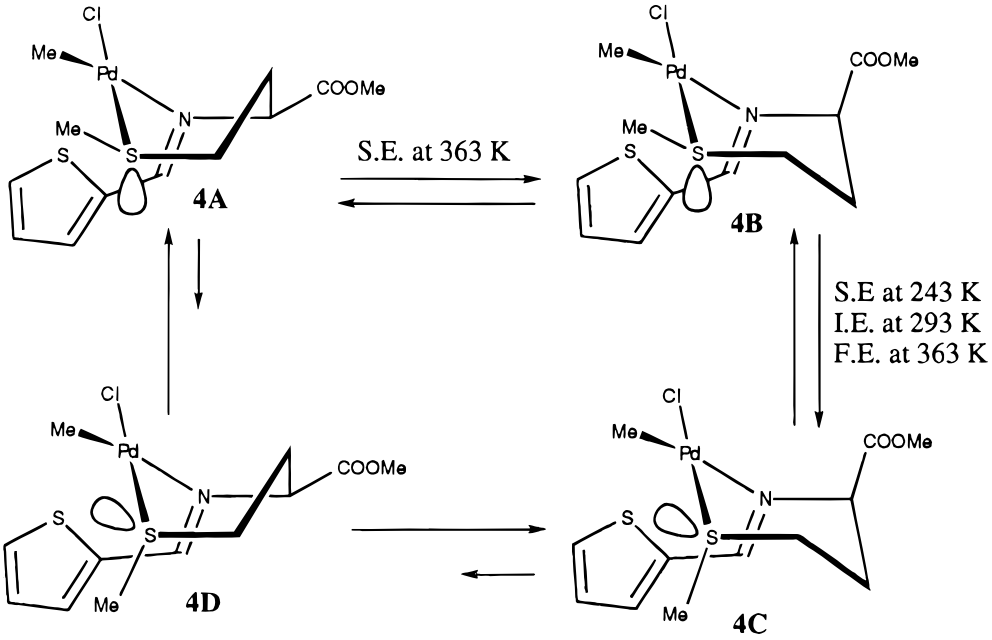
Scheme 1. Dynamic Behavior of Complex **4** in Solution

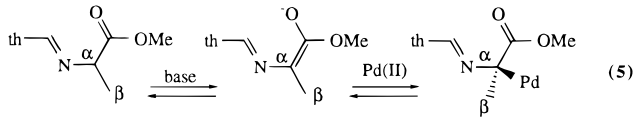


S.E.= slow exchange, I.E.= intermediate exchange, F.E.= fast exchange.

of the same isomers as were found in $CDCl_3$. In acetone, two sets of resonance signals are observed of which the C^7H resonance ($\Delta\delta$ = 0.46 and 0.34 ppm), the C^4H resonance ($\Delta\delta$ = 0.47 and 0.34 ppm), and one of the C^1H_3 signals ($\Delta\delta$ = 0.05 ppm) are shifted to low field and the other C^1H_3 signal ($\Delta\delta$ = 0.19 ppm) and the Pd−Me resonance signal are shifted to high field ($\Delta\delta$ = 0.16 and 0.13 ppm) when compared to the spectrum of **4** in $CDCl_3$. Conductivity experiments showed the existence of neutral monomeric species in solution. [CH_2Cl_2: 629 μS (253 K); 368 μS (293 K); 450 μS (313 K). Acetone: 2360 μS (253 K); 2050 μS (293 K); 2073 μS (313 K).]. The ratio of isomers of **4** at 293 K in acetone, *i.e.*, 1:0.5 between the boat and chair conformers, respectively, is different from the ratio found in $CDCl_3$. Heating of the sample to 348 K causes a conversion of the boat into the chair form, indicated by the ratio of 1:1 boat:chair ratio (at 348 K). Dissolving **4** in CD_3OD results, at room temperature, in three sets of signals having a ratio of approximately 1:0.2:0.1. The major component shows shifts to lower field compared to the case of **4** in $CDCl_3$. The imine proton signal is shifted to 9.01 ppm, and the C^4H signal is a doublet at 4.50 ppm ($^3J_{H^4H^3}$ = 11.4 Hz). The multiplicity of the C^4H resonance is due to coupling with C^3H^a and the absence of coupling with C^3H^b, indicating a rigid methionine backbone. At 293 K, dissociation of the chloride anion is probably involved, because the conductivity increases notably at 293 K [MeOH: 4600 μS (253 K); 15700 μS (293 K); 16700 μS (313 K)] and shows the same order of magnitude as the corresponding cationic complex (*vide infra*). The concentration of the chair conformers is increased upon raising the temperature, as was found for the complex in acetone.

The envelope conformation of the chelate ring in **7** is probably induced by the stronger bonding of the $N-S^1$ donors and the position of the thienyl ring. It is obvious that, upon addition of a coligand, the Pd−N and $Pd-S^1$ bonds are influenced as well as the position of the thienyl ring, resulting in the formation of several isomers in solution, which unfortunately could not be elucidated properly. However, it is clear that, upon addition of 2,6-lutidine, only the envelope conformation of the six-membered ring is formed, which is probably caused by steric interactions of the methyl substituents on the coligand and the thienyl ring.

[PdCl(th-metMe)]$_2$. The formation of **12** was followed by NMR spectroscopy. No precoordination of one of the donor atoms was observed, because all the resonance signals belonging to the dimeric product appeared simultaneously. In the presence of Et_3N base, an equilibrium between the O- and C-enolate anion occurs in which the C-enolate form binds to the palladium nucleus. This means that the reaction in which C^4 coordinates to the palladium center, *via* the preformed enolate structure, is fast (eq 5).



(5)

Osmometry experiments clearly proved the existence of dimeric molecules in solution. The ^1H NMR resonances of C^3H^a, C^3H^b, C^2H^a, and C^2H^b are a double triplet at 3.69 ppm, a double triplet at 3.50 ppm, a double doublet at 2.62 ppm, and a double doublet at 1.78 ppm. The coupling constants are $J_{H^{3a}H^{2a}}$ = 13.1 Hz, $J_{H^{3a}H^{2b}}$ = 14.3 Hz, $J_{H^{3b}H^{2a}}$ = 0 Hz, and $J_{H^{3b}H^{2b}}$ = 6.2 Hz, respectively, resulting in dihedral angles which correspond to the angles found in the crystal structure.

CO Insertion Reactions. The ^1H shifts of the C^7H and C^1H_3 and the multiplicity of $C^\alpha H$ of the acyl product indicate that the ligand is chelating and that the six-membered ring has a chair conformation. The puckering of the ring upon substitution of a methyl group with an acyl group is probably determined by the position of the thiophene unit determined by a steric interaction of the acyl group with the ring. This interaction is also highlighted by the observation of a hydrolysis of the imine

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bond of the acyl complex, similar to the hydrolysis of peptides in $[Pd(H_2O)(OH)(AcMet\text{-}Gly)]^+$ reported by Kostic.[37] The hydrolysis product is the stable complex PdCl(C(O)Me)-(HmetMe-*N*,*S*), whereas the fate of the thienyl moiety could not be determined.[38]

The half-lives measured for this reaction (Table 6) show the following trend: **7** > **6** > **8** ≥ **5** ≥ **4** ≥ **11** > **9**. The cationic complex is the most reactive, while the chloride is slower than the corresponding bromide, which in turn is slower than the iodide complex. This trend can be explained by the existence of open sites during the insertion process,[39] formed by dissociation of the halide or one of the ligand donors. It is evident that addition of coligand (MeCN, pyridine, or 2,6-lutidine) reduces the reaction rate by blocking the open site. It is striking, however, that the 2,6-lutidine complex reacts faster than the pyridine-containing complex. This can be explained by the less strongly bonded 2,6-lutidine on the palladium center, because of steric interactions, when compared to the MeCN or pyridine ligand, which enhances dissociation of the bulky coligand.

The instability of the acyl product obtained after the reaction of CO with the palladium methyl species can be explained by assuming the formation of palladium carbonyl complexes, which are unstable and will give dissociation of the CO ligand and colloidal palladium.

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Supporting Information Available: Tables giving further details of the structure determinations for **5a**−**c** and atomic coordinates, bond lengths and angles, and thermal parameters for **1**, **5a**−**c**, and **12** (45 pages). Ordering information is given on any current masthead page.

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