Palladium(II)-Induced Activation of Carbon−Nitrogen Single Bond of Coordinated N_4S Ligand. Characterization of Product with Modified Ligand Structure: Kinetics versus Thermodynamic Considerations

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Received December 1, 1998

Introduction

The pentadentate N_4S ligands, methyl ((2-(*β*-bis((3,5-dimethylpyrazol-1-yl)methyl)amino)ethyl)amino)cyclopent-1-ene-1-dithiocarboxylate (**Hmmecd**) and its propyl homologue (**Hmmpcd**)[1] with pendent pyrazolyl groups, offer interesting variations in their coordination behavior with the available metal ion types. With copper(II), zinc(II), and cobalt(II) ions, the ligands use all five potential donor sites to form pentacoordination complexes of distorted geometries. Transformation from a tetragonal to trigonal structure becomes apparent when the copper(II) complex is doped (5%) into its zinc(II) counterpart as revealed from EPR and electronic spectral studies.[2] In the case of nickel(II), however, the ligand molecules undergo alcoholysis reaction through the activation of C−N single-bond linkage.[3] The products obtained are square planar complexes with modified ligand structures, involving N_3S donor set and a pendent arm that holds the alkoxy group provided by the solvent. When the complexation reaction with Ni(II) is carried out in solvents other than alcohol, the product obtained is intractable solid of unknown composition.

To gain further insight into the mechanistic aspect of this unprecedented alcoholysis reaction as observed earlier with nickel(II),[3] comparable studies have been extended to palladium(II) system. It was anticipated that palladium(II) being kinetically more inert, there would be opportunities for the isolation and characterization of the compound(s) formed during the alcoholysis process. Herein, we report the syntheses, crystal structure and spectroscopic characterization of square planar palladium(II) complexes obtained during this solvolysis process. Mechanistic implications of the formation of these products are also described.

Experimental Section

The pentadentate N_4S ligand **Hmmecd** was prepared as reported earlier[2] and $Pd(OAc)_2$ was obtained, following a literature method.[4] Solvents were purified and dried from appropriate reagents[5] and degassed prior to their use. All other chemicals were reagent grade, available commercially and used as received. Reactions were carried out under purified dinitrogen atmosphere unless stated otherwise.

Syntheses.[6] **[Pd(N$_3$S)-CH$_2$Me$_2$pz]ClO$_4$ (1) and [Pd(N$_3$S)-CH$_2$OMe]-ClO$_4$ (2). Method A.** To a stirred methanolic solution (30 mL) of **Hmmecd** (0.24 g, 0.56 mmol) was added an equimolar amount of $Pd(OAc)_2$ (0.12 g), in solid. Within 10 min, a clear red solution was formed. Addition of sodium perchlorate (0.1 g, 0.8 mmol) at this stage caused immediate precipitation of an orange solid (compound **1**), which was collected by filtration, and the filtrate was saved. The residue was recrystallized from hot methanol; yield, 0.1 g (28%). Anal. Calcd for $PdC_{21}H_{31}N_6S_2ClO_4$: C, 39.56; H, 4.87; N, 13.19. Found: C, 39.6; H, 4.7; N, 12.9. IR (KBr disk): ν(C⋯C) + ν(C⋯N)/pyrazole group, 1565 s; ν(C⋯N + C⋯C), 1460 s; ν_{as}(Cl−O), 1090 s; δ(O−Cl−O), 625 s cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN, 20 °C), δ/ppm: 6.07 and 5.92 (pair of s, 2H, pz rings), 5.76 and 5.24 (ABq, 2H, CH_2, J_{AB} = 11.4 Hz), 5.29 and 4.94 (ABq, 2H, CH_2, J_{AB} = 14.4 Hz), 4.51 and 4.09 (pair of m, 2H, CH_2), 3.71 and 3.11 (pair of m, 2H, CH_2), 2.78 (m, 4H, cyclopentene ring), 2.69 (s, 3H, SCH_3), 2.47−2.33 (3s, 12H, CH_3/ pz rings). Λ_M (CH_3CN): 116 Ω^{-1} cm^2 mol^{-1}. UV−vis (CH_3CN) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 450 (250), 394 (6 700), 379 (sh), 296 (11 400).

The filtrate was rotary evaporated to a dense red oil. This was dissolved in acetone (20 mL) and filtered to obtain a clear orange solution, which was then layered with Et_2O (10 mL) and stored in a freezer (0 °C). The brick red microcrystals of **2** that deposited over 15 h were filtered and recrystallized from an acetone/*n*-hexane mixture, yield: 88 mg (27%). Anal. Calcd for $PdC_{17}H_{27}N_4S_2ClO_5$: C, 35.61; H, 4.71; N, 9.77. Found: C, 35.6; H, 4.7; N, 9.6. IR (KBr disk): ν(C⋯C), 1570 s; ν(C⋯N)/pyrazole ring, 1545 s; ν(C⋯N + C⋯C), 1460 s; ν_{as} (Cl−O), 1090 s; δ(O−Cl−O), 630 s cm^{-1}. ^{1}H NMR (300 MHz, CD_3-CN, 23 °C), δ/ppm: 5.97 (s, 1H, pz ring), 5.57 and 5.30 (ABq, 2H, CH_2, J_{AB} = 11.55 Hz), 4.44 (m, 2H, CH_2), 4.06 (m, 2H, CH_2), 3.80−3.60 (m, 2H, CH_2), 3.52 (s, 3H, OCH_3), 2.76 (m, 4H, cyclopentene ring), 2.66 (s, 3H, SCH_3), 2.40 and 2.35 (pair of s, 6H, CH_3/pz ring) and 2.01 (m, 2H, cyclopentene ring). Λ_M (CH_3CN): 128 Ω^{-1} cm^2 mol^{-1}. UV−vis (CH_3CN) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 450 (48), 395 (11 750), 377 (sh), 296 (21 600).

[Pd(N$_3$S)-CH$_2$Me$_2$pz]ClO$_4$ (1). Method B. To a stirred solution of **2** (50 mg, 0.1 mmol) in methanol (20 mL) was added a large excess of 3,5-dimethylpyrazole (50 mg, 0.5 mmol). The resulting reaction mixture was heated at reflux for ca. 1 h and then cooled to room temperature. The solution was rotary evaporated to ca. 10 mL volume and left standing in the air. Within 1 h, bright orange needles of **1** started to appear. The product was collected by filtration and recrystallized from acetone; yield, 25 mg, (45%).

Method C. To a stirred acetonitrile solution (30 mL) of **Hmmecd** (0.2 g, 0.46 mmol) was added a solid sample of $Pd(OAc)_2$ in equimolar amount (0.1 g, 0.45 mmol). The solids quickly dissolved and a clear red solution formed. The solution was heated at reflux for 30 min and then combined with a solution of sodium perchlorate (0.1 g, 0.8 mmol), also in acetonitrile (10 mL). Reducing the volume of the solution to ca. 15 mL and allowing it to stand for 10 h afforded orange crystals, which were collected by filtration and recrystallized from acetone; yield, 0.15 g (50%).

Safety Note! Perchlorate salts of metal complexes are potentially explosive[7] and should be handled only in small quantities with care.

Physical Measurements. Elemental analyses for (C, H, and N), IR, and electronic spectroscopic measurements were performed as described

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(1) Abbreviations used: **Hmmecd**, methyl ((2-(*β*-bis((3,5-dimethylpyrazol-1-yl)methyl)amino)ethyl)amino)cyclopent-1-ene-1-dithiocarboxylate; **Hmmpcd**, methyl ((2-(*β*-bis((3,5-dimethylpyrazol-1-yl)methyl)-amino)propyl)amino) cyclopent-1-ene-1-dithiocarboxylate; HOAc, acetic acid; Me_2pz, 3,5-dimethylpyrazole.

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10.1021/ic9813720 CCC: $18.00
Published on Web 10/29/1999

Table 1. Summary of Crystallographic Data for **1**

empirical formula	$PdC_{21}H_{31}N_6S_2ClO_4$
fw	637.49
space group	triclinic, $P\bar{1}$ (No. 2)
a, Å	8.8449 (5)
b, Å	11.2219 (8)
c, Å	14.466 (2)
α, deg	96.818 (7)
β, deg	107.649 (7)
γ, deg	104.520 (6)
V, Å^3	1294.3 (5)
Z	2
T, °C	20
λ(Mo Kα), Å	0.710 73
ρ_{calcd}, g cm^{-3}	1.636
μ, cm^{-1}	10.04
R^a(R_w^b)	0.029 (0.038)

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

elsewhere.[8] The ^{1}H NMR spectra were recorded on a Bruker model Avance DPX-300 spectrometer.

X-ray Crystallography. [Pd(N$_3$S)-CH$_2$Me$_2$pz]ClO$_4$ (1). Diffraction-quality crystals of **1** were grown by allowing *n*-hexane to diffuse into dichloromethane solution of the compound. Intensity data for a rose-pink plate (0.14 × 0.40 × 0.47 mm) were measured at room temperature (20 °C) on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromatized Mo Kα radiation, λ = 0.710 73 Å. The orientation matrix and cell dimensions were determined from the setting angles of 25 centered reflections (15° < θ < 16°). The $\omega-2\theta$ scan technique was employed to measure 4546 reflections ($2\theta_{max}$ = 50.0°). No decomposition of the crystal occurred during the data collection and 4100 data (range of absorption corrected[9] transmission factors: 0.595−0.860) which satisfied the $I \geq 3.0\sigma(I)$ criterion were used for subsequent analysis. Relevant crystal data are given in Table 1. The position of palladium was determined from the Patterson function. All other non-hydrogen atoms were located by means of a *DIRDIF*[10] calculation. Hydrogen atoms were included at updated calculated positions in the last cycles of refinement, with d(C−H) set at 0.95 Å and B(H) set at 1.2 B_{eq}(C). No solvent of crystallization was present, and the final difference map was featureless (maximum peak, 0.52 e Å^{-3}). Refinement with weights $1/\sigma^2(F)$ converged at R = 0.029 and wR = 0.038; final refinement details are given in Table 1. The *TEXSAN* program suit,[11] incorporating complex atomic scattering factors,[12] was used in all calculations. The crystallographic numbering scheme is shown in Figure 1, which was drawn with the ORTEP program at 30% probability ellipsoids.

Results and Discussion

Syntheses. The pentadentate N$_4$S ligand **Hmmecd** displays quite interesting variation in its coordination behavior with palladium(II) (Scheme 1). When palladium(II) acetate is stirred with stoichiometric amount (1:1) of the ligand in methanol at room temperature in the presence of added perchlorate ion (method A), the reaction seemingly proceeds in two parallel routes to generate structurally interesting products of differing solubilities that help in their isolations. Compound **1**, obtained as bright orange crystals, is relatively less soluble in methanol. It has the composition [Pd(mmecd)]ClO$_4$, with ligand structure remaining intact. As confirmed by X-ray crystal structure analysis (vide infra), **1** is a square-planar compound containing a N$_3$S chromophore with a free dangling pyrazolyl arm. The second product (compound **2**), isolated as a brick red crystalline solid, more soluble in methanol, appears to have generated by methanolysis reaction through a kinetically controlled path as observed with nickel(II) ion under identical situation.[3] It is also a planar molecule having a square base containing N$_3$S chromophore as in **1**, but unlike the former, the ligand structure here is modified by the incorporation of a methoxy group that replaces the pyrazolyl moiety of the dangling arm in **1**.[13]

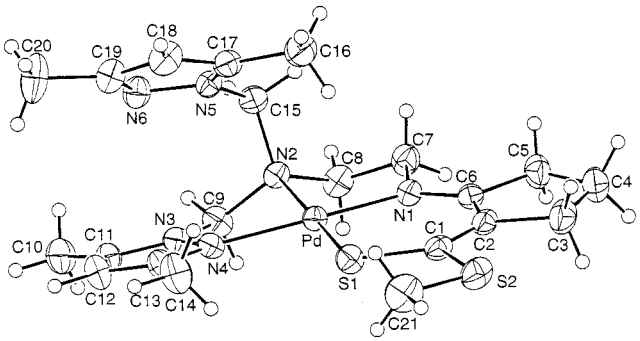
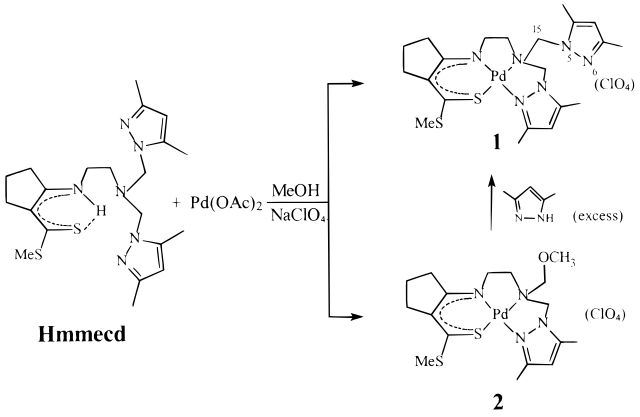


Figure 1. Molecular structure and atom numbering scheme for [Pd(N$_3$S)-CH$_2$Me$_2$pz]$^+$ (**1**$^+$) cation with thermal ellipsoids drawn at the 30% probability level.

Scheme 1



In refluxing methanol (or acetonitrile), **2** undergoes a simple condensation reaction with 3,5-dimethylpyrazole, taken in large excess (1:5 mole ratio) to produce compound **1** (Scheme 1) in 45% yield (method B). Identity of the product is established from elemental analyses and from its superimposing IR spectrum with that of compound **1** obtained by method A. Compound **1** is also obtained as the exclusive product when the solvent methanol in method A is replaced by acetonitrile (method C). Thus thermodynamically, **1** may be regarded as the favored product, while **2** is a kinetically favored one when methanol is used as solvent.

Synthesis of compound **2** thus involves C−N bond cleavage process. Controlled experiments have shown that the presence of palladium(II) ion is obligatory for this reaction to proceed.

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Table 2. Selected Bond Distances and Angles for $[Pd(N_3S)\text{-}CH_2Me_2Pz]ClO_4$ (**1**)

Distances (Å)			
Pd−S(1)	2.239 (1)	Pd−N(1)	1.970 (3)
Pd−N(2)	2.090 (2)	Pd−N(4)	2.039 (2)
S(1)−C(1)	1.709 (3)	C(1)−C(2)	1.361 (5)
C(2)−C(6)	1.419 (5)	C(6)−N(1)	1.315 (4)
Angles (deg)			
S(1)−Pd-N(1)	96.7 (1)	S(1)−Pd−N(2)	175.2 (1)
S(1)−Pd-N(4)	96.4 (1)	N(1)−Pd−N(2)	86.0 (1)
N(1)−Pd-N(4)	165.9 (1)	N(2)−Pd−N(4)	81.3 (1)
Pd−S(1)−C(1)	109.2 (1)	Pd−N(1)−C(6)	130.1 (2)
Pd−N(1)−C(7)	111.5 (2)	Pd−N(2)−C(8)	102.9 (2)
Pd−N(2)−C(9)	104.9 (2)	Pd−N(2)−C(15)	115.2 (2)
Pd−N(4)−N(3)	110.3 (2)	S(1)−C(1)−C(2)	128.7 (3)

Description of Crystal Structure. Perspective view of the cation in $[Pd(N_3S)\text{-}CH_2Me_2pz]ClO_4$ (**1**) and the atom-labeling scheme are shown in Figure 1. Selected intramolecular distances and angles are given in Table 2. The ligand **Hmmecd** utilizes its four donor sites to bind the Pd atom in a square-planar geometry, leaving one of its pyrazolyl group to stay away from coordination. The S(1), N(1), N(2), and N(4) atoms define a square plane around the Pd center. While the S(1)−Pd−N(2) bond angle 175.2(1)° is close to the one required for an ideal square-planar geometry, some distortion is manifested in the N(1)−Pd−N(4) angle of 165.9(1)°, due to restricted bite angle of the ligand. Of the three Pd−N distances, Pd−N(2) (2.090-(2) Å) and Pd−N(4) (2.039(2) Å) are in a close range, normally observed with similar complexes.[14,15] N(1), being the deprotonation site of the ligand, forms the shortest Pd−N contact of 1.970(3) Å. The short C(1)−S(1) distance of 1.709(3) Å indicates significant thiol-like character of this bond.[16,17] Observed Pd−S(1) distance 2.239(1) Å is in the expected range 2.227(2)−2.3259(9) Å, reported for palladium(II) complexes of anionic sulfur ligands.[14,18−20]

^{1}H NMR Spectroscopy. Figure S1 (Supporting Information) shows the ^{1}H NMR spectrum observed for **2** in $CDCl_3$ solution. On the basis of the signal intensities, the multiplets centered at 4.44 and 4.06 ppm are assigned to the methylene protons CH_2-(7) and CH_2(8), respectively (atom labelings are as shown in Figure 2). The H(9) methylene protons which appear as a singlet in the free **Hmmecd** ligand, become anisochronous in complex **2** due to rigidity of the coordinated pyrazolyl arm and appear as AB quartet with $\delta_A = 5.57$ and $\delta_B = 5.30$ ppm ($J_{AB} = 11.55$ Hz). The two protons in the C(15)H_2 group of the free alkoxy arm, due to their attachment to a chiral nitrogen center, are also diastereotopic for symmetry reasons and show a set of signals, in the region of $\delta = 3.6-3.8$ ppm, that can be analyzed as an AB spectrum modified by coupling(s) with the nearby methylene protons. As expected, two methyl groups of the pyrazolyl moiety appear as a pair of singlets with resonances shifted downfield at 2.40 and 2.35 ppm relative to those in the free **Hmmecd** ligand ($\delta = 2.20$ and 2.16 ppm). Other strong singlets at $\delta =$ 3.52 and 2.66 ppm are asignable to OCH_3 and SCH_3 methyl protons, respectively.

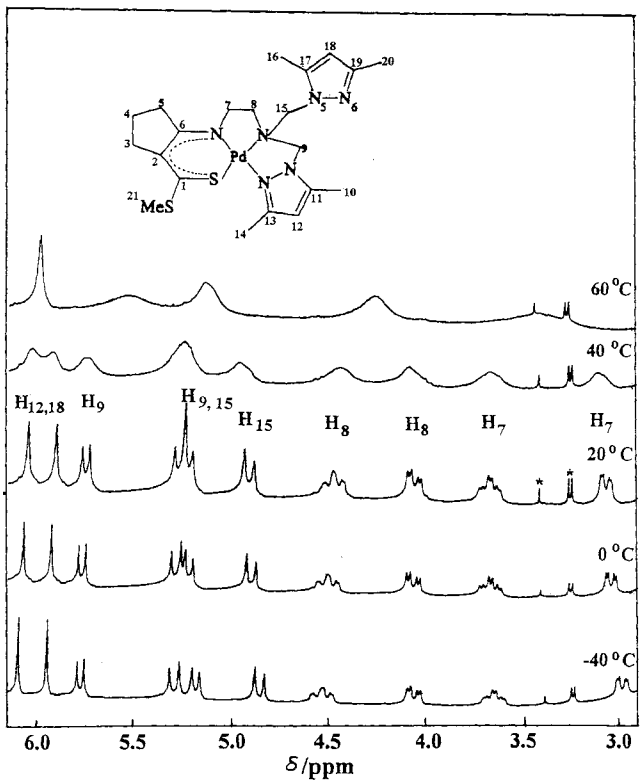

Figure 2. Variable temperature 300 MHz ^{1}H NMR spectra (δ, 2.8−6.3 ppm region) of $[Pd(N_3S)\text{-}CH_2Me_2pz]ClO_4$, (**1**) in acetonitrile-d_3. Asterisks indicate protio solvent impurities.

Figure 2 shows spectra (δ, 2.8−6.3 ppm region) from variable temperature ^{1}H NMR study of **1** in acetonitrile-d_3. At 20 °C, the spectrum contains a pseudo-triplet (δ, 5.26 ppm) that breaks up into two well-resolved doublets at −40 °C. Each of these doublets is a part of two AB spectra. The one appearing at 5.24 ppm combines with the low-field doublet at 5.76 ppm to represent the diastereotopic methylenic C(9)H_2 protons (J_{AB}, 11.4 Hz) of the metal-bound rigid pyrazolyl arm. The remaining of these twin-doublets (at 5.29 ppm) together with the doublet at high-field (δ, 4.94 ppm) constitutes another AB spin system ($J_{AB} = 14.4$ Hz) due to protons of the C(15)H_2 methylene group which is sitting on a chiral N atom and are diastereotopic as observrd in **2**. The remaining C(7)H_2 and C(8)H_2 protons of the rigid ethylenic chain in **1** constitute an ABCD system and appear in the form of four multiplets with complex connectivities in the region 4.5−3.0 ppm. Spectrum at 20 °C also contains a pair of signals of identical nature due to C(12)H and C(18)H protons of the pyrazole rings at 6.07 and 5.92 ppm that coalesce into a singlet (δ, 5.99 ppm) at 60 °C as a consequence of a dynamic process that interchanges the two CH_2Me_2pz arms.

To gain further insight into the structural information of **1** and to resolve the complex couplings, ^{1}H−^{1}H COSY NMR experiment was performed in acetonitrile-d_3. Relevant section of the spectrum (δ, 3.0−6.2 ppm) at 22 °C is shown in Figure S2 (Supporting Information). Altogether eight cross-peaks are obtained. These include two strong peaks due to geminal couplings of C(9) and C(15) methylenic protons and a weak peak, due to their long-range interaction, all appearing above 4.6 ppm in the downfield. Analysis of the remaining connectivity pattern in the upfield region δ 4.6−3.0 ppm, reveals two strong geminal couplings, each corresponds to the nonequivalent C(7)-H_2 and C(8)H_2 methylene protons. Also the ABCD system here

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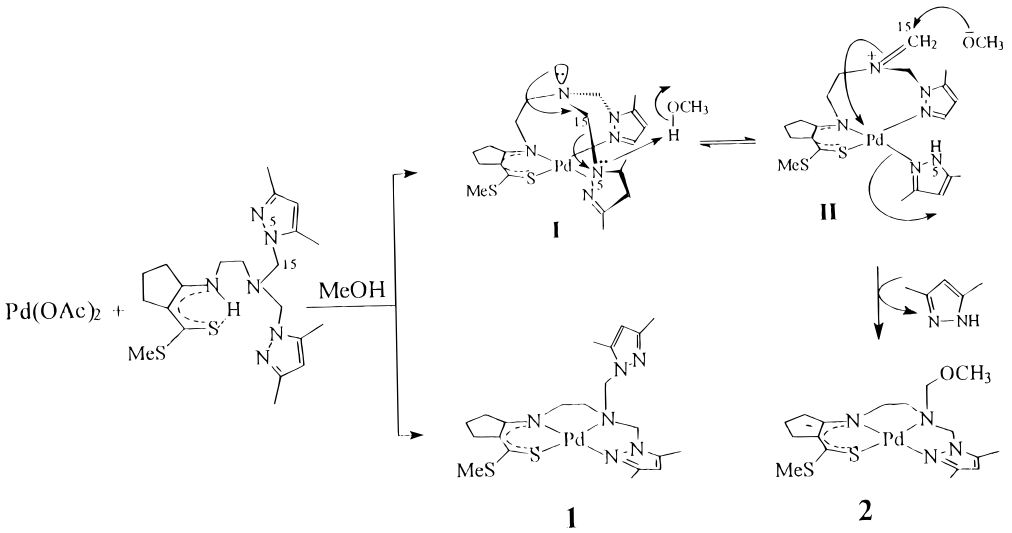
Scheme 2[a]



[a] Net charges on the species are omitted for brevity.

comprising the above two methylene protons generates three more cross-peaks due to their mutual interactions involving one zero and three nonzero (one small) coupling constants. ^{1}H NMR spectrum thus clearly indicates in complex **2**, the presence of a pendent $-CH_2OCH_3$ group that replaces one of the pyrazolyl arms during the methanolysis reaction.

Mechanistic Implications of C−N Single Bond Cleavage Reaction: Structural Anomeric Effect. Isolation of two different products (**1** and **2**) in reasonable yields during the reaction of $Pd(OAc)_2$ with **Hmmecd** in methanol has some interesting mechanistic implications. As summarized in Scheme 2, the reaction proceeds through two simultaneous routes, each involving a square-planar Pd(II) center because of the preference of the metal ion to attain this geometry. To achieve that, Pd(II) has only two options to pick up a combination of four donor sites out of the available five in **Hmmecd**. Considering a strong affinity of the 2-aminocyclopent-1-ene-1-dithiocarboxylate moiety (providing bidentate N, S donor sites) to bind Pd(II),[21] two alternative donor set combinations are shown in Scheme 2. Compound **1** which is the thermodynamically favored product, involves a pyrazolyl arm nitrogen N(4) and the tertiary nitrogen N(2) bound to the Pd center along with the (N,S) donor sites from the cyclopentene moiety. In an alternative combination, the tertiary nitrogen N(2) itself stays away from coordination, and makes two pyrazolyl nitrogens N(4) and N(6) available for bonding to the metal center along with the cyclopentene-(N,S) sites. This generates a thermodynamically unstable reactive intermediate (**I**) because of its unfavorable chelate ring (eight-membered) size. Also, in this molecule the C(15)−N(5) bond is antiperiplanar to the loan pair of electrons on the N(2) nitrogen atom. Thus, in the presence of methanol, protonation of a pyrazolyl nitrogen N(5) triggers substantial structural anomeric effect,[22] leading to significant polarization of the C(15)−N(5) bond to render it susceptible to nucleophilic attack by methoxy group from the solvent. The product (compound **2**) is ultimately obtained by the cleavage of an otherwise unreactive C−N single bond, followed by ejection of the Me_2pz molecule from the metal coordination sphere (in **II**). Compound **2** when treated with excess 3,5-dimethylpyrazole (1:5 mole ratio) in methanol, generates compound **1** in 45% yield. Thus, of the two square-planar Pd(II) complexes of **Hmmecd** ligand compound **1** is thermodynamically more stable, while the second one (species **I**) with tertiary nitrogen atom N(2) staying away from coordination is believed to be the postulated intermediate that leads to compound **2** by a kinetically controlled solvolytic path (via **II**). Compound **1** once formed does not undergo methanolysis reaction further, for which antiperiplanar disposition of the C(15)−N(5) bond relative to the tertiary nitrogen N(2) loan pair is obligatory in order to induce bond activation through a structural anomeric effect.

Acknowledgment. Support of this work by the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. We thank Dr. B. Achari (Indian Institute of Chemical Biology, Calcutta) and Professor K. Nag for helpful discussions.

Supporting Information Available: One X-ray crystallographic file, in CIF format, a ^{1}H−^{1}H COSY NMR spectrum for **1**, and a ^{1}H NMR spectrum for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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