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A Model for Thiophene Chemisorption: A Stabilized, η^1 ,S-Thiophene Complex and Its Relationship to η^5 -Coordination

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Summary: The unstable species $[(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\eta^1\text{-S-C}_4\text{H}_4\text{S})]^+$ has been observed in solution and shown to convert to $[\text{Ru}(\text{C}_5\text{H}_5)(\eta^5\text{-C}_4\text{H}_4\text{S})]^+$. An η^1 ,S-thiophene complex has been stabilized in the form $[(\text{C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_3\text{S})\text{Ru}(\text{PPh}_3)_2]\text{X}$ (**2**). An X-ray structural study of **2** ($\text{X} = \text{BPh}_4$) confirms the structure and shows that the sulfur is pyramidal. Displacement reactions of **2** have been studied.

Although $\pi(\eta^5)$ -complexation of thiophenes has been recognized for many years,¹ it is only recently that η^1 ,S-coordination has been demonstrated for a dibenzothiophene derivative.² This report describes the characterization of a simple η^1 ,S-thiophene complex, its stabilization by chelation, and evidence that this type of complex is a precursor to η^5 -thiophene coordination. We suggest that the dynamics of thiophene coordination are relevant to the chemisorption of thiophene on metal surfaces.^{3,4}

Treatment of CD_2Cl_2 solutions of $(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ with AgBF_4 in the presence of thiophene gives a yellow, thermally unstable compound assigned as $[(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}_4\text{H}_4\text{S})]\text{BF}_4$ (**1**). The ^1H and ^{31}P NMR spectra show that **1** is a cyclopentadienyl complex ($\delta_{\text{Cp}} 4.52$) which contains equivalent phosphine ligands ($\delta_{\text{P}} 38.7$). Compound **1** could not be obtained in pure form, and the microanalytical data were generally low in carbon and high in sulfur. Both compound **1** and the recently reported $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_4\text{S})]\text{BF}_4$ are proposed to contain S-bound thiophene ligands.⁵ Upon standing in solution **1** steadily decomposed to give a new complex whose ^1H NMR spectrum was characterized by a Cp singlet ($\delta 5.40$) and a pair of multiplets (6.32, 6.16 ppm) in a 5:4 ratio

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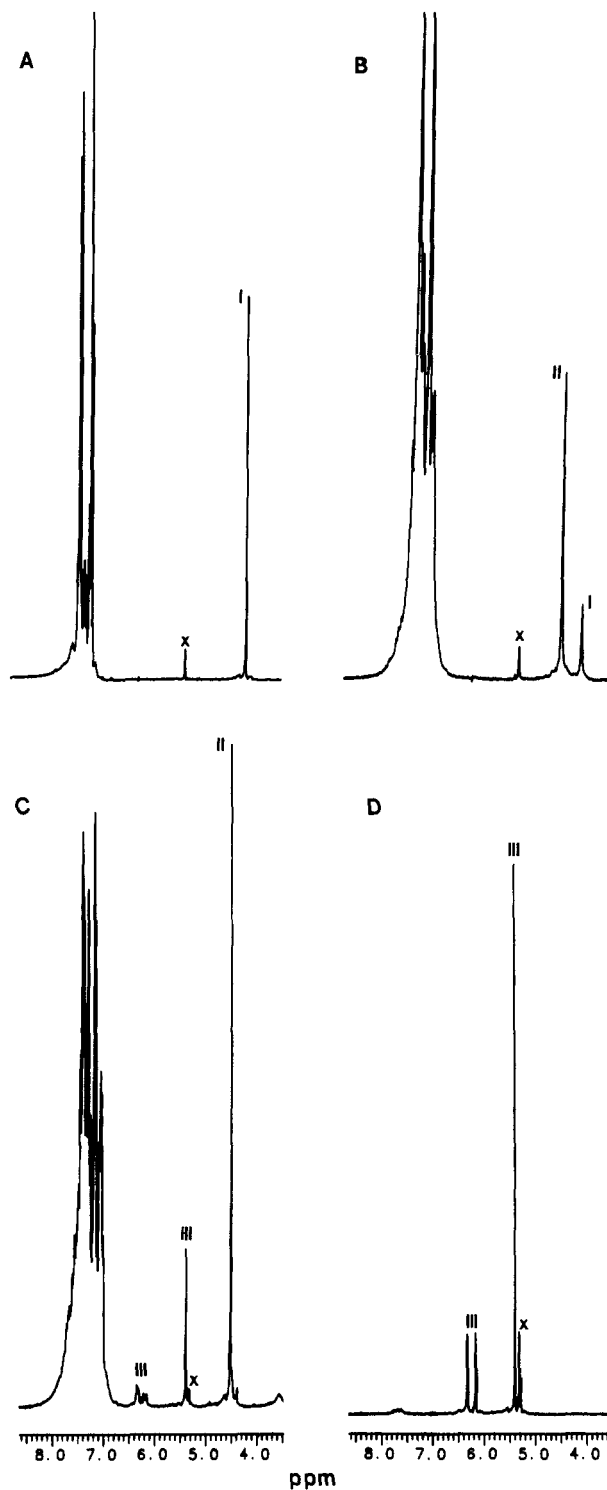
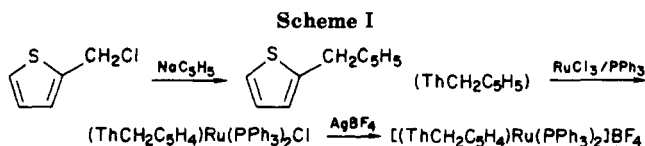
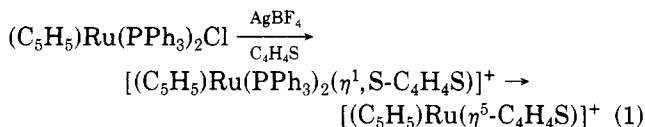


Figure 1. 200-MHz ^1H NMR spectra of $(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and thiophene (10 equiv) (spectrum A), the same solution 4 min after addition of 1 equiv of AgBF_4 (spectrum B), the same solution 30 min later (spectrum C), and purified $[(\text{C}_5\text{H}_5)\text{Ru}(\text{C}_4\text{H}_4\text{S})]\text{BF}_4$ in CD_2Cl_2 . Signals are labeled I for $(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$, II for $[(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}_4\text{H}_4\text{S})]^+$, III for $[(\text{C}_5\text{H}_5)\text{Ru}(\text{C}_4\text{H}_4\text{S})]^+$, and x for CH_2Cl_2 .



(Figure 1). This new complex has been identified as $[(\text{C}_5\text{H}_5)\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})]\text{BF}_4$ (eq 1).⁶



In order to stabilize the η^1 -S-thiophene adduct, we turned to chelation (Scheme 1). 2-(Thienylmethyl)cyclopentadiene, $\text{ThCH}_2\text{C}_5\text{H}_5$ (obtained from sodium cyclopentadienide and 2-(chloromethyl)thiophene⁷), was reacted with $\text{RuCl}_3(\text{H}_2\text{O})_x$ and PPh_3 in refluxing ethanol giving an 80% yield of $(\text{ThCH}_2\text{C}_5\text{H}_4)\text{Ru}(\text{PPh}_3)_2\text{Cl}$.⁸ The ^1H and ^{13}C NMR spectra of this neutral species indicated that the thiophene was not coordinated.⁹ Treatment of CH_2Cl_2 solutions of the chloro complex with AgBF_4 gave $[(\text{ThCH}_2\text{C}_5\text{H}_4)\text{Ru}(\text{PPh}_3)_2]\text{BF}_4$, **2**, which was isolated as analytically pure yellow crystals.¹⁰ The ^1H and ^{13}C NMR spectra of solutions of **2** indicated that the thiophene subunit was coordinated to the metal as evidenced by the shifts of the $\text{ThCH}_2\text{C}_5\text{H}_4$ resonances.

Compound **2** was characterized by single-crystal X-ray diffraction (Figure 2).¹¹ The parameters associated with the $(\text{C}_5\text{H}_4\text{R})\text{Ru}(\text{PPh}_3)_2$ portion of the molecule are similar to other examples of this type.^{8,12} The Ru-S distance of 2.408 (1) Å is only slightly longer than that found in the mercaptan complex $[(\text{C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{HSC}_3\text{H}_7)]\text{BF}_4$ (2.377 (2) Å).¹² There are two features of this structure that merit special comment. First, the sulfur atom is clearly pyramidal as indicated by the angle defined by the Ru-S vector and the vector from S to the C(8), C(9) bisector. This bending angle of 126° compares favorably with the two independent angles of 130.1 and 132° found in the dibenzothiophene (DBT) complex $\text{RuCl}_2(p\text{-tol}_2\text{PDBT})_2$.² Although **2** contains nonequivalent phos-

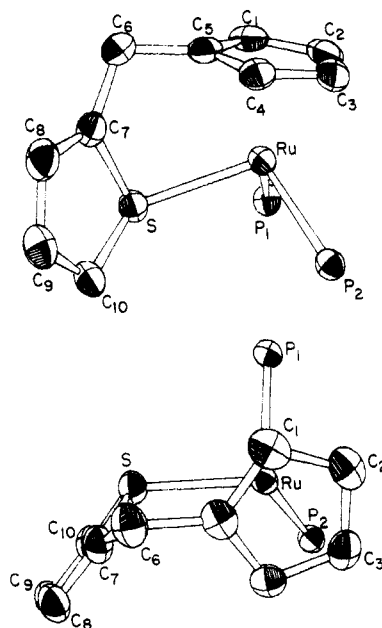


Figure 2. Two views of the cation in $[(\text{ThCH}_2\text{C}_5\text{H}_4)\text{Ru}(\text{PPh}_3)_2]\text{BPh}_4$ with hydrogen atoms and phenyl groups omitted for clarity. The thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (deg) are Ru-S = 2.408 (1), Ru-P = 2.358 (1), Ru-P₂ = 2.353 (1), Ru-C₅H₄ centroid = 1.855 (1), P₁-Ru-P₂ = 99.92 (5), S-Ru-P₁ = 91.03 (5), S-Ru-P₂ = 101.03 (5), and Ru-S-[C₄H₄S plane] = 126° .

phorus ligands in the solid state, the low-temperature (-80°C) ^{31}P NMR (101-MHz) spectrum showed only one resonance. Assuming the solid-state structure is retained in solution, either inversion about the coordinated sulfur atom¹³ or rapid reversible dissociation of the pendant thiophene ligand can explain the ^{31}P NMR result. This issue is the subject of further studies employing other complexes of chelated thiophenes. Changes in the aromaticity of thiophene upon complexation is relevant to the activation of this heterocycle by metallic desulfurization catalysts.¹⁴ The degree of alternation in the C-C distances in **2** (C(7)-C(8) = 1.344 (8), C(8)-C(9) = 1.409 (8), and C(9)-C(10) = 1.339 (8) Å) is similar to that in thiophene itself¹⁵ ($C_\alpha\text{-C}_\beta$ = 1.3696 (17) and $C_\beta\text{-C}_\gamma$ = 1.4232 (23) Å). For comparison the C-C distances are nearly equivalent in pyrrole, but a more noticeable deviation is observed in cyclopentadiene and benzylphosphole.¹⁶ The C-S distances in **2** are only very slightly elongated in comparison with those determined for thiophene in the gas phase.¹⁵ The C(7)-S-C(10) angle of 91.1 (3) $^\circ$ is within 1° of the corresponding angle in thiophene itself.

Complex **2** represents a stabilized version of **1**.¹⁷ Although **2** is an easily handled, thermally stable compound, the chelate effect does not appear to be great as the sulfur donor is easily displaced by carbon monoxide and acetonitrile as shown by ^1H NMR studies. Thus the salient aspect of **2** is that the methylene bridge prevents the formation of a η^5 -complex. As shown by the structural study, the pyramidal nature of the S-bound thiophene ligand lends itself to the $\eta^1 \rightarrow \eta^5$ changeover which is related to the dynamics of the $\eta^1\text{-C}_5\text{H}_5$ ligand.¹⁸ The facility

(6) This compound is spectroscopically identical with that prepared by Spies and Angelici (Spies, G. H.; Angelici, R. J., submitted for publication). ^1H NMR (CD_2Cl_2): 6.32 (m, 2 H), 6.16 (m, 2 H), 5.40 (s, 5 H). (The chemical shifts for this complex are highly solvent dependent.) FAB-MS: m/e 251 (M^+).

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(8) We used the procedure of Bruce and Windsor. Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* 1977, 30, 1601. For a review of cyclopentadienylruthenium chemistry see: Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982.

(9) Anal. Calcd for $\text{C}_{46}\text{H}_{39}\text{RuP}_2\text{S}$: C, 67.19; H, 4.74; P, 7.54. Found: C, 67.07; H, 4.74; P, 8.11. ^1H NMR (CDCl_3): 7.4 (m, 33 H); 4.10, 3.40 (d, 4 H); 3.80 ppm (s, 2 H). ^{13}C NMR (CDCl_3): 138 (t), 134, 129, 127 (C_6H_5); 144, 127, 125.4, 123.9 ($\text{C}_4\text{H}_4\text{S}$); 106.6, 80.6, 77.2 (C_5H_4); 27.6 ppm (CH_2). ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$): 39.79 ppm.

(10) Anal. Calcd for $\text{C}_{46}\text{H}_{39}\text{RuP}_2\text{S}$: C, 63.23; H, 4.46; P, 7.10; S, 3.66. Found: C, 62.59; H, 4.48; P, 7.95; S, 3.76. FAB-MS: m/z 787. ^1H NMR (CDCl_3): 7.0 (m, 33 H); 4.8, 3.5 (m, 4 H); 3.2 ppm (s, 2 H). ^{13}C NMR (CDCl_3): 135 (t), 133, 130, 128 (C_6H_5); 134, 130, 123 ($\text{C}_4\text{H}_4\text{S}$); 109.5, 82.6, 80.9 (C_5H_4); 25.6 ppm (CH_2). ^{31}P NMR ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$): 40.6 ppm.

(11) Crystal data for $[\text{Ru}(\text{ThCH}_2\text{C}_5\text{H}_4)(\text{PPh}_3)_2]\text{BPh}_4$: cell dimensions, $a = 14.846$ (4) Å, $b = 17.692$ (5) Å, $c = 11.218$ (3) Å, $\alpha = 104.02$ (2) $^\circ$, $\beta = 103.34$ (2) $^\circ$, $\gamma = 82.24$ (2) $^\circ$, $V = 2772$ (1) Å³, space group $P\bar{1}$, $Z = 2$; $d_{\text{calcd}} = 1.323$, $d_{\text{obsd}} = 1.319$ g/cm³; $\mu = 4.11$ cm⁻¹. Intensity data on a single crystal of **2** sealed in a glass capillary were collected on a Syntex P₂ automated four-circle diffractometer using the $2\theta/\theta$ scan technique and employing Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Lorentz-polarization and absorption corrections were applied to the data. The solution of the structure was obtained by conventional direct methods and Fourier techniques. Least-squares refinement (6052 unique reflections, $F > 2.58 \sigma(F)$) with anisotropic thermal parameters for the $\text{ThCH}_2\text{C}_5\text{H}_4\text{RuP}_2$ non-hydrogen atoms converged with a final R value of 5.26; $R_w = 6.26$. Hydrogen atoms were input at calculated positions (C-H = 0.95 Å) and were included in the structure factor calculations but were not refined. At this stage of refinement, disorder (resulting from a twist in the phenyl rings) of the carbon atoms in the BPh_4^- anion and the phenyl groups attached to P₁ was observed. The difference Fourier map revealed no peaks greater than $0.9 e \text{ \AA}^{-3}$. Refinement was discontinued at this point. The C-C distance was 1.381 (21) and 1.382 (28) Å for the PPh_3 and BPh_4^- carbon atoms, respectively, with the average angles being 120 (1) and 120 (3) $^\circ$ in the phosphine ligands and the anion, respectively. The structure was solved by using the SHELX programs.

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(17) Prolonged (>72 h) refluxing of methanol solutions of **2** does not result in decomposition (i.e., binuclear complexes such as $[(\text{ThCH}_2\text{C}_5\text{H}_4)_2\text{Ru}_2]^{2+}$ were not observed).

of this change in hapticity may explain the scarcity of η^1 , S-thiophene complexes and is of likely relevance to the dynamics of chemisorbed thiophene.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters, bond distances and angles, and structure factors (35 pages). Ordering information is given on any current masthead page.

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A New Cyclopalladation Reaction Involving Facile Chelated Transmetalation: Selective Cleavage of C-Sn and C-Si Bonds of Stannyl and Silyl Ketoximes

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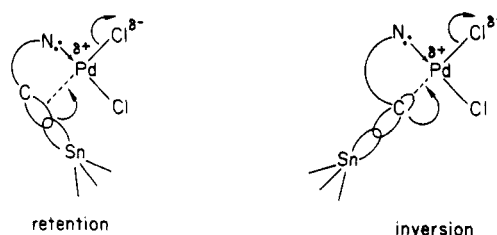
Summary: A new cyclopalladation involving a facile chelated transmetalation with the stannyl ketoximes 1-4 was found to form the five- and six-membered ring oxime complexes of palladium 5-8 in high yields. The silyl ketoxime 18 can react in a similar manner to give the complex of palladium 19 at higher temperature for longer reaction time than that of the stannyl derivatives.

Cyclopalladation has been well documented as a significant reaction in organometallic chemistry and has recently been examined from the view point of C-H bond activation of both aromatic and aliphatic hydrocarbons.¹ Although several cyclopalladation reactions have been reported in which a carbon-hydrogen bond on alkyl moiety is cleaved, the reactions are limited to substrates involving intramolecular coordinating compounds with sterically hindered alkyl groups or benzylic ones.² In this context, transmetalation by employing organostannyl or organosilyl functions as a selective electrophilic group may provide a new strategy for formation of a metal-carbon σ -bond in

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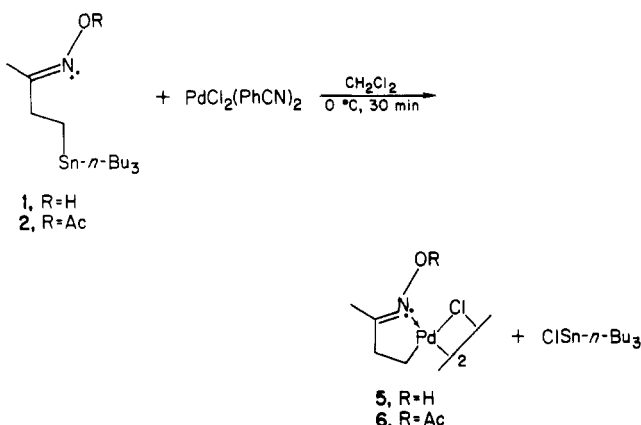
(2) For (oxime)palladium complexes, see: (a) Onoue, H.; Minami, K.; Nakagawa, K. *Bull. Chem. Soc. Jpn.* 1970, 43, 3480. (b) Grigor, B. A.; Nielson, A. J. *J. Organomet. Chem.* 1977, 132, 439. (c) Nielson, A. J. *J. Chem. Soc., Dalton Trans.* 1981, 205. (d) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Shaw, B. L. *Ibid.* 1980, 1992. (e) Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* 1984, 1227. (f) Baldwin, J. E.; Najera, C.; Yust, M. *Ibid.* 1985, 126. For other cycloalkylpalladium complexes, see: (g) Fuchita, Y.; Hiraki, K.; Uchiyama, T. *J. Chem. Soc., Dalton Trans.* 1983, 897. (h) Hartwell, G. E.; Lawrence, R. V.; Smas, M. *J. Chem. Soc., Chem. Commun.* 1970, 912. (i) Sokolov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. A. *J. Organomet. Chem.* 1972, 36, 389. (j) Mutet, C.; Pfeffer, M. *Ibid.* 1979, 171, C34.

Chart I



cyclic systems.³ We report here a new cyclopalladation reaction involving a chelated transmetalation with stannyl or silyl ketoximes.

Reaction of the (*E*)- β -tributylstannyl ketoxime 1⁴ with dichlorobis(benzonitrile)palladium (1 equiv) in dichloromethane at 0 °C for 30 min yielded 78% of the cyclopalladation product 5. Similarly, the stannyl ketoxime acetate 2 readily gave the corresponding complex 6. Interestingly, the six-membered ring complexes 7 and 8 were also obtained from the (*E*)- γ -tributylstannyl ketoxime derivatives (Table I).⁵



It is quite noteworthy that the transmetalation of the stannyl group by the palladium species takes place under such an extremely mild condition for short reaction time and that the C-Sn bond on the side chain of the oxime is cleaved exclusively and not Me or Bu groups. In contrast

(3) For transmetalation with alkenyl silanes and stannanes, see: (a) Kliegman, J. M. *J. Organomet. Chem.* 1971, 29, 73. (b) Itoh, K.; Fukui, M.; Kurachi, Y. *J. Chem. Soc., Chem. Commun.* 1977, 500. (c) Hayashi, T.; Konishi, M.; Kumada, M. *Ibid.* 1983, 736. (d) Abel, E. W.; Rowley, R. J. *J. Chem. Soc., Dalton Trans.* 1975, 1096. (e) Abel, E. W.; Moorhouse, S. *Ibid.* 1973, 1706. (f) Cardin, D. J.; Norton, R. J. *J. Chem. Soc., Chem. Commun.* 1979, 513.

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(5) Spectroscopic data. 5: IR (KBr) 3390, 2910, 1650 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz), 1.93 (s, 3 H, CH₃), 2.23 (t, 2 H), 2.63 (t, 2 H), 8.13 (s, 1 H, OH) ppm; ¹³C (CDCl₃) 13.96 (t, CPd), 21.30 (q, CH₂), 41.83 (t, CC=N), 172.06 (s, C=N) ppm. 6: IR (KBr) 2920, 1782, 1628 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz) 1.89 (s, 3 H, CH₃CN), 2.15 (s, 3 H, CH₃C=O), 2.40 (m, 4 H), CH₂CH₂ ppm. 7: IR (KBr) 3390, 1650 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz) 0.69 (quintet, 2 H, CH₂CPd), 2.04 (s, 3 H), 2.28 (t, 2 H, CH₂C=N), 2.49 (t, 2 H, CH₂Pd), 8.93 (s, 1 H, OH) ppm; ¹³C NMR (CDCl₃) 19.08 (q, CH₃), 22.01 (t, CH₂Pd), 23.47 (t, CCPd), 38.00 (t, CC=N), 160.40 (s) ppm. 8: IR (KBr) 1780, 1630 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz) 0.93 (quintet, 2 H, CH₂CPd), 2.30 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 2.38 (t, 2 H, CH₂Pd), 2.70 (t, 2 H, CH₂C=N) ppm. The acetate complex 7 isomerized to the five-membered ring complex 20 in a chloroform solution at 20 °C for ca 2 h.

