NMR Study on the Coordination Behavior of Dissymmetric Terdentate Trinitrogen Ligands on Methylpalladium(II) Compounds

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Neutral compounds of the type [(6-RC_5H_3N-2-C=NCH_2CH_2-2-C_5H_4N)Pd(CH_3)(Cl)] (R = H (MAP), CH_3 (6′-CH_3-MAP)) have been synthesized starting from [(cyclooctadiene)Pd(CH_3)(Cl)], while ionic compounds of the type [(6-RC_5H_3N-2-C=NCH_2CH_2-2-C_5H_4N)Pd(CH_3)]$^+$[(Y)]$^-$ (Y = Cl, CF_3SO_3, NO_3; R = H, CH_3) were formed by reacting the chlorides in a polar solvent with silver triflate and silver nitrate, respectively. An X-ray structure of the ionic compound [(C_5H_4N-2-C=NCH_2CH_2-2-C_5H_4N)Pd(CH_3)(CF_3SO_3)] is presented. The crystals are of the triclinic spacegroup $P\bar{1}$, with a = 7.690(1) Å, b = 8.653(2) Å, c = 13.888(1) Å, α = 98.01(1)°, β = 99.83(1)°, and γ = 95.55(1)°. The X-ray structure shows a square planar palladium complex in which the MAP ligand is terdentate coordinated to the palladium atom. The fourth coordination site is occupied by the methyl ligand. The triflate anion is not coordinating. The methyl–palladium distance is 2.024(8) Å; the lengths of the palladium–nitrogen bonds are 2.039(7), 2.058(7), and 2.024(8) Å for N(1), N(2), and N(3), respectively. The neutral compounds exist in various isomeric forms. In a noncoordinating solvent, a bidentate coordination of the α-diimine moiety is preferred at elevated temperatures. At lower temperatures, a terdentate coordination fashion of the ligands is preferred, resulting in five-coordinate compounds. For N-N-N = MAP, a square pyramidal five-coordinate configuration is observed, whereas for 6′-CH_3-MAP an initially formed ionic square planar configuration at 223 K isomerizes to a trigonal bipyramidal five-coordinate configuration. These isomerization reactions proved to be reversible. In a polar solvent both neutral and ionic compounds were observed in a varying ratio for both ligands. The neutral and the ionic compounds could reversibly be converted into each other by interchanging the solvent. Synthesis in benzene or diethyl ether of [(6-$CH_3C_5H_3N$-2-C=NCH_2CH_2-2-C_5H_4N)Pd(CH_3)(Cl)] resulted in the formation of two kinetic products. These consist of a bidentate coordination of the ligand with the nitrogen atoms of the $NCH_2CH_2C_5H_4N$ moiety, resulting in a six-membered ring, in a cis isomer, and in a trans isomer. The kinetic products could be converted into the mixture of thermodynamic isomers in which the ligand is bidentate coordinated with the α-diimine moiety, *vide supra*, upon heating. The mechanisms of the ligand rearrangements in the palladium complexes are discussed.

Introduction

As a result of the recently reported palladium(II)-catalyzed, perfectly alternating copolymerization of CO and ethene by Drent and co-workers,[1] our interest has been focused on the mechanistic aspects of CO insertion into palladium alkyl bonds and of alkene insertion into palladium acyl bonds. In previous articles we[2] and others[3] have reported about CO and alkene insertion reactions into methyl and acetyl palladium complexes, respectively, of the type (L-L)Pd(R)(Cl) (**A** in Figure 1) and {(L-L)Pd(R)(S)}$^+${Y}$^-$ (**B** in Figure 1), with L-L = diphosphine, P-P, and aminophosphine, P-N; R = CH_3 and $C(O)CH_3$; Y = CF_3SO_3, BF_4, and PF_6; and S = solvent.

Recently, we have investigated the formation and properties of palladium complexes of the composition σ^2-(N-N-N)Pd(CH_3)(Cl) (**C** in Figure 1) and {σ^3-(N-N-N)Pd(CH_3)}$^+${Y}$^-$ (**D** in Figure 1), in which N-N-N are terdentate ligands 2,6-bis(2-propanecarbaldimino)pyridine (iPr-DIP) and 2,2′:6′,2″-terpyridine (terpy); Y = Cl and CF_3SO_3.[4] These complexes turned out not only to be thermally very stable but also very reactive with respect to CO

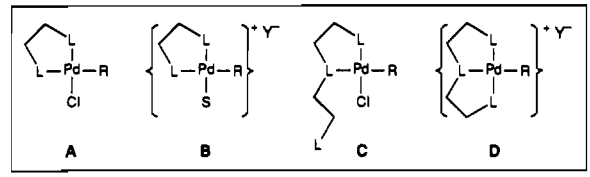

Figure 1.

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insertion, resulting in complexes of the type σ^2(N-N-N)Pd(C[O]-CH_3)(Cl) and $\{\sigma^3$(N-N-N)Pd(C[O]CH_3)$\}^+\{Y\}^-$.

Interestingly, these complexes also reacted rapidly with norbornene, norbornadiene, and dicyclopentadiene to give (N-N-N)Pd($C_nH_mC[O]CH_3$)(Cl) and $\{$(N-N-N)Pd-($C_nH_mC[O]CH_3$)$\}^+\{Y\}^-$ (where C_nH_m is the former alkene: n = 7, m = 8, norbornadiene; n = 7, m = 10, norbornene; n = 10, m = 12, dicyclopentadiene). These unusual reactions prompted us to address the perennial question whether the insertion proceeds via the well-known square planar intermediate[5] or via a five-coordinate intermediate.[6] One may imagine that in the case of the terpy compounds, one pyridyl group might become nonbonded and rotate into a perpendicular position with regard to the coordination plane as suggested by Abel et al.[7a] and as shown in the crystal structures of (terpy)Ru(CO)Br_2 and $\{$(terpy)(bipy)$_2$-Ru$\}Cl_2$.[7b] This seems possible for CO insertion into the Pd–CH_3 bond but rather unlikely for rapid insertion of the bulky alkenes in the palladium–acetyl bond of $\{$(terpy)Pd(C[O]CH_3)$\}^+\{Cl\}^-$.

The unexpected and very surprising results of this rapid norbornene and norbornadiene insertion into the terpy compounds prompted us to investigate in more depth the role of the type of (potentially) terdentate ligand on the type of isomer formed. We are therefore investigating a number of trinitrogen ligands which differ in their geometry, rigidity, and electronic properties. The rigidity is varied in the sequence 2-(2-((2′-pyridylmethylene)-amino)ethyl)pyridine (MAP) and 2-(2-(((6′-methyl-2-pyridyl)-methylene)amino)ethyl)pyridine (6′-CH_3-MAP), both in this article; iPr-DIP;[4] terpy,[4] [8,7-*b*:5,6]tetrahydroquino[8,7-*b*][1,-10]phenanthroline (TH-terphen); and quino[8,7-*b*][1,10]phenanthroline (terphen) in order of increasing rigidity.

In this article we present the synthesis and properties of methylpalladium complexes with the dissymmetric MAP and 6′-CH_3-MAP ligands. In subsequent articles we will report on the insertion reactions with CO and alkenes.

Experimental Section

Materials and Apparatus. All manipulations were carried out in an atmosphere of purified, dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen; acetonitrile was also dried over 3-Å molecular sieves. Starting chemicals were purchased from Aldrich Chemicals and were used without further purification except where mentioned explicitly. Silver trifluoromethanesulfonate (abbreviated as silver triflate or AgOTf) was stored at –20 °C under nitrogen and in the dark.

Elemental analyses were carried out by Dornis u. Kolbe Mikroanalytisches Laboratorium, Mühlheim a.d. Ruhr, Germany. ^{1}H-, ^{15}N-INEPT-,[10] and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker AMX 300 spectrometer. Mass spectra were recorded on a Hewlett-Packard HP 5790 gaschromatograph equiped with a HP 5971A mass selective detector in the EI-mode.

Synthesis of (η^2,η^2-Cycloocta-1,5-diene)chloromethylpalladium(II), (COD)Pd(CH_3)(Cl). In a 100-mL Schlenk tube, 2.0 g (7.0 mmol) of (COD)$PdCl_2$[22] was dissolved in 50 mL of dichloromethane. Then 1.16 mL (1.2 equiv) of tetramethyltin was added and stirred at room temperature until the bright yellow color of the precursor had vanished, which normally took ca. 1 day. The pale solution was filtered off Celite, and the solvent was then removed under reduced pressure from the nearly colorless solution, while the temperature was kept at 0 °C using an ice bath. The off-white powder was washed twice with a small amount of diethyl ether in order to remove the trimethyltin chloride formed. The compound can be crystallized from chloroform.

Yield: 1.7 g (6.4 mmol; 92%).

The product is air stable, but releases some COD upon longer standing, resulting in Pd(0). The impure compound however, can be easily purified by filtration through a 0.2-μm PTFE filter.

Synthesis of 2-(2-((2′-Pyridylmethylene)amino)ethyl)pyridine, MAP. In a 250-mL round-bottom flask, 4.00 g (32.8 mmol) of 2-(2-aminoethyl)-pyridine was dissolved in 100 mL of dry diethyl ether and 30 mL of 3-Å molecular sieves was added. While this mixture was being stirred, a 3.51-g (32.8-mmol) sample of 2-pyridinealdehyde, which was eluted over a small column containing activated basic alumina prior to use, was then added. After 2 days, 20 mL of fresh molecular sieves were added, and after 3 days the condensation was completed as could be judged from the absence of the aldehyde C=O stretching frequency in the IR spectrum. After filtration of the molecular sieves, washing with 2 × 20 mL of dry diethyl ether, and evaporation of the combined fractions, a bright orange oil of pure ligand was obtained which could be used immediately without further purification. When allowed to stand longer, the oil became darker, and it is advisable to purify the ligand over activated basic alumina prior to use.

Yield: 6.24 g (29.6 mmol; 90.2%). Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.21; N, 19.89. Found: C, 73.69; H, 6.32; N, 19.72. MS: m/z = 51 (27); 65 (37); 78 (37); 92 (69); 93 (69); 106 (44); 107 (40); 119 (100); 194 (1); 211 (1), M^+.

Synthesis of 2-(2-(((6-Methyl-2-pyridyl)methylene)amino)ethyl)pyridine, 6′-CH_3-MAP. The condensation was carried out according to the same procedure as for **1**. A 613-mg (5.06-mmol) sample of 6-methylpyridine-2-aldehyde was added to 618 mg (5.06 mmol) 2-(2-aminoethyl)-pyridine. Yield: 1.04 g (4.64 mmol; 91.6%). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.63; H, 6.72; N, 19.89. Found: C, 74.38; H, 6.79; N, 18.54. MS: m/z = 51 (15); 65 (23); 78 (27); 79 (27); 93 (49); 106 (87); 133 (100); 183 (1); 208 (1); 225 (2), M^+.

Synthesis in Dichloromethane or Chloroform of {2-(2-((2′-pyridylmethylene)amino)ethyl)pyridyl}chloromethylpalladium, (MAP)-Pd(CH_3)(Cl) (1). To a solution of 87.2 mg (0.33 mmol) of (COD)-Pd(CH_3)(Cl) in 1 mL of dichloromethane or chloroform at room temperature, 65 μL (69.4 mg; 0.33 mmol) of MAP was added. After 10 min, the solvent was removed under reduced pressure. The remaining orange oil was washed with a small volume of diethyl ether in order to remove small amounts of impurities. The yield was not determined, but was at least >90% according to the analysis of the washing fractions.

Synthesis in Acetonitrile of {2-(2-((2′-Pyridylmethylidene)amino)ethyl)-pyridyl}chloromethylpalladium(II), (MAP)Pd(CH_3)(Cl) (1). The synthesis was carried out according to the procedure followed above for **1** in dichloromethane or chloroform, except that acetonitrile was used instead of dichloromethane or chloroform. After removal of the acetonitrile an orange oil was formed.

Synthesis in Diethyl Ether or Benzene of {2-(2-((2′-Pyridylmethylene)-amino)ethyl)pyridyl}chloromethylpalladium(II), (MAP)Pd(CH_3)(Cl) (1). In a 25-mL Schlenk tube, 100.6 mg (0.477 mmol) of MAP was dissolved in 3 mL of diethyl ether or benzene. While the mixture was being stirred, 126.4 mg (0.477 mmol) of (COD)Pd(CH_3)(Cl) or its precursor dissolved in 2 mL of benzene was added, respectively. A pale yellow precipitate was formed which almost immediately coagulated into an orange oily fluid not soluble in diethyl ether or benzene. The solvent was decanted and the remaining oil dried *in vacuo*. The obtained compound could be dissolved in chloroform and dichloromethane for further use.

Synthesis of {2-(2-((2′-Pyridylmethylene)amino)ethyl)pyridyl}-methylpalladium(II) Triflate, $\{\sigma$3-(MAP)Pd(CH_3)$\}^+\{CF_3SO_3\}^-$ (1z). To a solution of 181.4 mg (0.493 mmol) of (MAP)Pd(CH_3)(Cl) in 1 mL

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Table I. Conductometric Data for **1** and **2**

compound, solvent	specific conductivity (temperature)[a]
1, $CHCl_3$	637 (317); 705 (295); 446 (239)
1, CH_2Cl_2	424 (295); 3740 (243); 2850 (222); 2350 (215); 2240 (212)
1, CH_3CN	42 800 (323); 42 360 (320); 41 500 (314); 39 150 (302); 36 460 (295); 34 560 (286); 28 740 (260); 26 870 (254); 24 630 (245); 20 450 (234)
1z, CH_3CN	111 200 (317); 91 100 (295); 5400 (240)
2, $CHCl_3$	84.1 (292); 98.9 (278); 112.9 (270); 126.1 (261); 131.3 (253); 131.3 (247); 109.2 (228); 82.6 (217)
2, CH_2Cl_2	2810 (293); 2862 (285); 3526 (278); 3696 (274); 3947 (270); 4389 (259); 4485 (255); 4588 (250); 4758 (243); 4670 (240); 4330 (233); 3039 (221); 2707 (217)
2, CH_3CN	28 700 (292); 27 100 (282); 26 850 (276); 25 900 (267); 25 500 (263); 22 350 (253); 20 800 (248)
2z, CH_3CN	87 150 (293); 72 350 (278); 66 700 (275); 60 600 (267); 54 950 (255); 50 200 (252); 44 550 (233)
$(bpy)Pd(CH_3)(Cl)$, $CHCl_3$	8.9 (324); 7.9 (317); 5.8 (295); 2.6 (240)
$\{(bpy)Pd(CH_3)\}OTf$, CH_3CN	86 900 (317); 74 500 (295); 37 800 (237)

[a] Specific conductivity is given in $\mu S \cdot M^{-1}$, and the temperature, in K.

of dichloromethane, was added 133.0 mg (1.05 equiv) of silver triflate. A white precipitate (AgCl) was formed instantaneously. The solution was filtered off glass wool immediately, and the solvent was removed at reduced pressure or stored at −20 °C to allow crystal growth. Yield: 83.1% of a pale yellow powder. Anal. Calcd for $C_{15}H_{16}F_3N_3O_3PdS$: C, 37.40; H, 3.35; N, 8.66; S, 6.66. Found: C, 37.33; H, 3.33; N, 8.69; S, 6.49.

Synthesis in Dichloromethane or Chloroform of {2-(2-(((6′-Methyl-2-pyridyl)methylene)amino)ethyl)pyridyl}chloromethylpalladium(II), (6′-Me-MAP)Pd(CH_3)(Cl) (2). The synthesis was carried out according to the procedure followed above for **1** in dichloromethane or chloroform except that 6′-CH_3-MAP was used as the ligand instead of MAP. After evaporation of the solvent, an orange oil was formed, which was soluble in dichloromethane, chloroform, and tetrachloroethane.

Synthesis in Diethyl Ether or Benzene of {2-(2-(((6′-methyl-2-pyridyl)methylene)amino)ethyl)pyridyl}chloromethylpalladium(II), (6′-Me-MAP)Pd(CH_3)(Cl) (2). The synthesis was carried out according to the procedure followed above for **1** in diethyl ether or benzene except that 6′-CH_3-MAP was used as the ligand instead of MAP. After evaporation of the solvent, a pale yellow powder was formed, which was soluble in dichloromethane, chloroform, and tetrachloroethane.

Yield: 161.0 mg (0.422 mmol; 88.4%).

Synthesis in Acetonitrile of {2-(2-(((6′-Methyl-2-pyridyl)methylene)amino)ethyl)pyridyl}chloromethylpalladium(II), (6′-Me-MAP)Pd(CH_3)(Cl) (2). The synthesis was carried out according to the procedure followed above for **2** in dichloromethane or chloroform, except that acetonitrile was used instead of dichloromethane or chloroform. After removal of the acetonitrile, a dark yellow gum was formed.

Synthesis of {2-(2-(((6′-Methyl-2′-pyridyl)methylene)amino)ethyl)pyridyl}methylpalladium(II) Triflate, $\{(6'\text{-Me-MAP})Pd(CH_3)\}^+\{CF_3SO_3\}^-$ (2z). Synthesis was carried out according to the procedure applied for **1z**. Yield: 92% of a pale yellow powder. The product is soluble in acetonitrile. Anal. Calcd for $C_{16}H_{18}F_3N_3O_3PdS$: C, 38.76; H, 3.66; N, 8.47; S, 6.47. Found: C, 38.20; H, 3.77; N, 8.13; S, 6.72.

Conductometry. The conductometric experiments were carried out with a Consort K 720 conductometer equipped with a Philips PW 9512/00 conductometrical cell in a closed glass vessel. For the experiments, ca. 20 mg of the complex was dissolved in 5.0 mL chloforom, dichloromethane or acetonitrile. The conductivities were not corrected for the temperature. The results of the conductometric experiments are presented in Table I. A graphical illustration of the conductivities of **2** in CH_2Cl_2 is presented in Figure 9.

Table II. Crystal and Refinement Data for $\{(MAP)Pd(CH_3)\}CF_3SO_3$ (**1z**)

chem formula	$C_{15}H_{16}F_3N_3O_3PdS$	T, K	295
fw	481.78	λ, Å	0.71073
a, Å	7.690(1)	space group	$P\bar{1}$
b, Å	8.653(2)	Z	2
c, Å	13.888(1)	d_x, g·cm^{-3}	1.788
α, deg	98.01(1)	μ, cm^{-1}	11.8
β, deg	99.83(1)	R^a	0.065
γ, deg	95.55(1)	$R_w{}^b$	0.076
V, Å^3	894.8(2)		

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{0.5}$; $w = 1/\sigma^2(F)$.

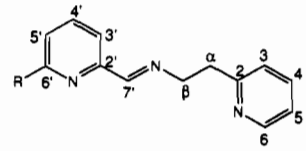

Figure 2. Numbering scheme for **1** and **2**.

Crystal Structure Determination. Crystal data are presented in Table II. The X-ray data were collected [Zr-filtered Mo Kα radiation, (λ = 0.71073 Å); $\theta_{max} = 27.5°$; $\Delta\omega = 1.80 + 035 (\tan\theta)°$; $\omega/2\theta$ scan; 4276 reflections; $h = 0$ to 9, $k = -11$ to 10, $l = -18$ to 17] on an ENRAF NONIUS CAD4 diffractometer for a yellow crystal [0.25 × 0.33 × 0.67 mm] glued on top of a glass fiber. Unit cell dimensions were derived from the SET4 setting angles of 25 reflections in the range $14° < \theta < 20°$. The data were corrected for Lp, a small linear decay (3%), and absorption/extinction [DIFABS].[14] The structure was solved with SHELXS-86/TREF[15] and refined on F by full-matrix least-squares methods [SHELX-76][16] to $R = 0.065$. Hydrogens were taken into account at calculated positions and refined riding on their carrier atoms. In addition, the orientation of the methyl group was refined. Geometrical calculations were done with PLATON.[17]

Molecular Modeling Experiments. The molecular modelling on the MAP and the 6′-CH3-MAP ligands were performed on the Silicon Graphics Personal Iris, using Sybyl 5.5, Tripos Associates, Inc., St. Louis, MO. The standard Sybyl energy minimizer MAXIMIN 2 was used with the minimalization method "Conjugate Gradient" with default convergence criteria.

Results

The MAP and the 6′-CH_3-MAP ligands were obtained by condensation of 2-(2-aminoethyl)pyridine with pyridine-2-aldehyde and 6-methylpyridine-2-aldehyde by the published method of Nelson for the preparation of α-diimine ligands.[11] The structure and the atom labeling is presented in Figure 2.

The ligands contain on the one hand a pyridine–carbaldimine moiety similar to the well-known R-PyCa ligand[12] which has an α-diimine structure which will give rise to a five-membered ring upon coordination and on the other hand a more flexible imino–ethyl–pyridyl part which may result in a six-membered ring upon coordination. The ligands were characterized by different NMR techniques as shown in Tables V–VII.

(COD)Pd(CH_3)(Cl) was used as the precursor for the preparation of (chloro)methylpalladium compounds, and it has proved to be a most versatile one. The diene can be easily substituted by suitable ligands even at very low temperatures. The compound is soluble in benzene, toluene, dichloromethane and chloroform. Although (COD)Pd(CH_3)(Cl) was prepared before,[8] we report on a new and more facile synthetic route, which is a modified version of the methylation reaction as patented by van Leeuwen

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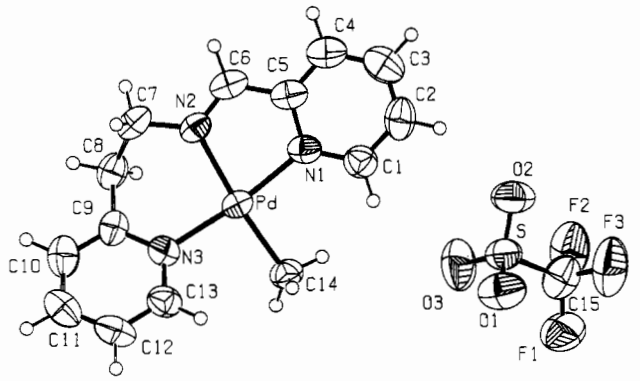

Figure 3. ORTEP plot (drawn at the 50% probability level) of the ionic compound **1z**.

Table III. Bond Distances (Å) for the Non-Hydrogen Atoms of $\{(MAP)Pd(CH_3)\}CF_3SO_3$ (**1z**) (with Esd's in Parentheses)

Pd–C14	2.024(8)	C3–C4	1.395(16)	C8–C9	1.501(11)
Pd–N1	2.039(7)	C4–C5	1.357(13)	C9–C10	1.363(13)
Pd–N2	2.074(6)	C5–N1	1.345(10)	C10–C11	1.371(14)
Pd–N3	2.058(7)	C5–C6	1.432(13)	C11–C12	1.363(15)
N1–C1	1.364(11)	C6–N2	1.285(11)	C12–C13	1.375(14)
C1–C2	1.409(13)	N2–C7	1.465(12)	C13–N3	1.330(11)
C2–C3	1.336(15)	C7–C8	1.541(12)	N3–C9	1.360(11)

Table IV. Bond Angles (deg) for the Non-Hydrogen Atoms of $\{(MAP)Pd(CH_3)\}CF_3SO_3$ (**1z**) (with Esd's in Parentheses)

N1–Pd–N2	78.7(3)	C1–N1–C5	117.7(7)	C8–C9)–C10	120.4(8)
N2–Pd–N3	93.4(3)	N1–C5–C6	115.1(8)	C9–C10–C11	122.0(9)
N3–Pd–C14	93.0(3)	C4–C5–C6	121.7(8)	C10–C11–C12	116.9(10)
N1–Pd–C14	95.6(3)	C5–C6–N2	117.8(7)	C11–C12–C13	120.6(9)
Pd–N1–C1	127.8(5)	Pd–N2–C6	113.8(6)	C12–C13–N	121.6(8)
N1–C1–C2	120.4(8)	Pd–N2–C7	123.1(5)	C9–N3–C13	119.0(7)
C1–C2–C3	120.6(9)	C6–N2–C7	122.6(7)	Pd–N3–C13	119.9(6)
C2–C3–C4	118.7(10)	N2–C7–C8	108.3(7)	N3–C9–C10	119.9(8)
C3–C4–C5	119.4(9)	C7–C8–C9	114.2(7)		
C4–C5–N1	123.2(8)	C8–C9–N3	119.7(8)	N1–Pd–N3	168.8(3)
Pd–N1–C5	114.2(6)	Pd–N3–C9	120.7(5)	N2–Pd–C14	171.8(3)

and Roobeek for diphosphine palladium compounds.[9] The method described here is, to our opinion, favored over the known routes[8] since the product is obtained in high yield, the use of tetramethyltin as the methylation agent allows one to use an excess of it, and the preparation can be carried out at room temperature. Besides, the trimethyltin chloride can be easily removed by washing the product with diethyl ether. The complex can be crystallized from chloroform, but several attempts to obtain a X-ray structure of $(COD)Pd(CH_3)(Cl)$ failed because of degradation of the compound during the measurement, even at 180 K.

Compounds of MAP are noted as **1**, 6′-CH_3-MAP compounds as **2**. The neutral complexes observed are given the suffixes **a**, **b**, etc., the ionic analogues, the suffixes **z**, **y**, etc.

The novel complexes $(MAP)Pd(CH_3)(Cl)$ **1** and $(6'\text{-}CH_3\text{-}MAP)Pd(CH_3)(Cl)$ **2** were obtained by substitution of the diene in $(COD)Pd(CH_3)(Cl)$ by the potentially terdentate trinitrogen ligands at room temperature in good yields.

The ionic complexes **1z** and **2z** were formed by metathesis of **1** and **2** with silver triflate, respectively. The same procedure performed with silver nitrate, resulted in the quantitative formation of **1x**.[13] The structures of **1z** and **1x** have been solved by X-ray crystallography. First the molecular structure of **1z** will be discussed, after which the structures of **1** and **2**, based on the spectroscopic data and the conductometrical experiments, will be described.

Molecular Structure of $\{(\sigma^3\text{-}MAP)Pd(CH_3)\}^+\{CF_3SO_3\}^-$ (1z). A view of the molecular structure of complex **1z** is shown in Figure 3 together with the atomic numbering. Tables III and IV contain the bond lengths and the bond angles of the non-hydrogen atoms of **1z** respectively.

The structure of **1z** displays an ionic methylpalladium complex in which the three nitrogen donor atoms of the MAP ligand are coordinating. The triflate anion has a closest Pd–O distance of 4.35[8] Å, indicating that it is not within the first coordination sphere of the palladium atom. The ligands around the palladium center are situated in a planar arrangement of N(1), N(2), N(3), and C(14). The pyridyl group of the ethylpyridyl part of the ligand is rotated 31° because of the 6-membered ring formed by the N(2)–Pd–N(3) moiety. However, a rotation of that extent is also found e.g. for $\{(bipy)(\alpha\text{-pic})Pd(CH_3)\}^+\{BF_4\}^-$ where the monodentate ligand α-picoline is not coplanar.[31] The pyridine–carbaldimine moiety of the ligand, defined by the chelate N(1)–C(5)–C(6)–N(2), is almost flat and coplanar with the coordination plane. The rotated pyridyl group makes the complex chiral, and indeed, the space group indicates a racemic mixture of the enantiomers. The bond lengths within the ligand are in agreement with the bond distances found for the analogous R-PyCa complexes of palladium and platinum.[12a,b,18] The palladium ligand distances of **1z**, however, differ to a small extent, compared with those of analogous palladium and platinum complexes.[12a,b,18] The Pd–N(2) distance of 2.07 Å is relatively short when one takes into account the strong trans influence of the methyl ligand, since it is scarcely longer than the Pd–N_{imine} distances of complexes containing a chloride ligand in a trans position, for which bond lengths of approximately 2.06 Å were found.[12a,b,18] The Pd–C(14) distance is 2.024 Å, being only slightly elongated when compared with R-PyCa complexes when the methyl ligand is in a position cis with regard to the imine nitrogen.[19] The Pd–N(1) and Pd–N(3) distances of 2.039 and 2.058 Å, respectively are short, probably due to the rather weak trans influence of the trans pyridyls.[20]

The N(1)–Pd–N(2) angle is 78.8°, which is the normal bite angle for α-diimine complexes.[10a,b] The other angles, N(2)–Pd–N(3), N(3)–Pd–C(14), and C(14)–Pd–N(1), are between 93.0 and 95.6°; as a result, the bite angle of the terdentate ligand N(1)–Pd–N(3) is ca. 172°. The results of the X-ray structure of **1z** have been confirmed by one of the **1x**.[13]

NMR Spectroscopy. The ^1H-, ^{13}C-, and ^{15}N-NMR data have been listed in Tables V–VII, respectively. In order to establish the mode of coordination of the ligands on the metal center, ^1H-NMR proved to be very useful. The assignment of the aromatic region has been mainly carried out by means of the chemical shift of relevant protons, i.e. protons whose chemical shift and their mutual relations are very indicative for the coordination mode of the ligand. As relevant protons, the hydrogens 3′,6,6′, and 7′ have been used (see Figure 2 for the numbering of the positions on the ligands); the other resonances are relatively unaffected by the mode of coordination. The

(18) Goubitz, K.; Rülke, R. E.; Vrieze, K. To be submitted for publication in *Acta Crystallogr.*

(19) The terms *cis* and *trans* are often used to assign the relative positions on a square planar metal complex of the two strongest donors. In ref 12a,b the term is derived from the positions of the methyl ligand and the imino nitrogen since it is believed that those are the strongest donors. Although this might not be true in some cases, we will also use the terms *cis* and *trans* for the position of the imino nitrogen with regard to the position of the methyl ligand for clarity.

(20) The trans influence of a ligand is often found in the decreasing order: $R_3Si^- > C(O)CH_3^- > PH^- \approx CH_3^- \gg H^- > PR_3 \geq CN^- > AsR_3 > NO_2^- > EtNH_2 > Et_2NH > PyN_3^- \approx NCO^- \approx NCS^- > Cl^- \approx Br^- \approx I^- > NO_3^-$. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(21) Nitromethane is preferred by us as internal standard to the recommended internal standard, liquid anhydrous ammonia, because of the relative temperature independence of the first and its widespread use in articles about ^{15}N-NMR in organic and organometallic compounds.[23] Conversion to the recommended ammonia standard by adding 380 ppm to the nitromethane standard only gives a rough indication.

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(23) (a) von Philipsborn, W.; Müller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383–413. (b) Pregosin, P. S.; Rüedi, R.; Anklin, C. *Magn. Reson. Chem.* **1986**, *24*, 255–258. (c) Glemarec, C.; Remaud, G.; Chattopadhyaya, J. *Magn. Reson. Chem.* **1988**, *26*, 307–310. (d) Schumacher, M.; Günther, H. *Chem. Ber.* **1983**, *116*, 2001–2014. (e) Städeli, W.; von Philipsborn, W.; Wick, A.; Kompis, I. *Helv. Chim. Acta* **1980**, *63*, 504–522.

Table V. ^{1}H-NMR Data for the Ligands and Their Palladium Complexes

	Pd-CH_3	α-CH_2	β-CH_2	$H^{3'}$	$H^{6'}$	H^6	$H^{7'}$	
MAP[a]		2.83 (t)	3.69 (t)	7.54 (dd)	8.17 (dd)	8.12 (dd)	7.94 (s)	6.65 (ddd) H^5; 6.76 (dd) H^3; 6.82 (ddd) $H^{5'}$; 7.11 (dt) H^4; 7.25 (dt) $H^{4'}$
1a[b]	0.71 (s)	3.14 (t)	4.10 (t)	7.91 (d)	8.54 (d)	8.58 (d)	8.74 (s)	7.04 (t) H5; 7.11 (d) H^3; 7.49 (m) $H^{3'}$ and H^4; 7.93 (t) H4′
1b[c]	0.78 (s)	3.05 (t) 3.40 (d)	3.54 (t) 4.22 (d)	8.58 (d)	8.41 (d)	8.37 (d)	9.79 (s)	7.38 (t) H^5; 7.56 (d) H^3; 7.70 (t) $H^{5'}$; 7.93 (t) H^4; 8.10 (t) $H^{4'}$
1x,[h] **1y**,[h] **1z**[d]	1.02 (s)	3.18 (t) 3.44 (d)	3.69 (t) 4.28 (d)	8.10 (dd)	8.69 (dd)	8.61 (dd)	8.79 (t)	7.56 (ddd) H^5; 7.72 (dd) H^3; 7.85 (ddd) $H^{5'}$; 8.12 (dt) H^4; 8.32 (dt) $H^{4'}$
6′-CH_3-MAP[e]		3.15 (t)	4.01 (t)	7.69 (d)	2.50 (s)	8.47 (d)	8.24 (s)	7.03 (dd) H^5; 7.08 (d) $H^{5'}$; 7.11 (d) H^3; 7.49 (dt) H^4; 7.53 (t) $H^{4'}$
2a[f]	1.14 (s)	3.25 (t)	4.14 (t)	7.71 (d)	2.89 (s)	8.52 (d)	8.38 (s)	6.99 (t) H^5; 7.20 (d) $H^{5'}$; 7.33 (t) H^3; 7.58 (t) H^4; 7.77 (t) $H^{4'}$
2b[g]	1.52 (s)	3.61 (t)	4.24 (m)	8.79 (d)	2.74 (s)	8.59 (d)	10.51 (s)	7.3*, 7.49 (dd) H^5 and $H^{5'}$; 7.70*, 7.90 (t) H^4 and $H^{4'}$; 8.09 (d) H^3
2c[c]	0.04 (s)	3.72 (m) 4.07 (m)	4.58 (m) 5.12 (m)	7.4*	2.95 (s)	9.01 (d)	8.55 (s)	7.2* H^5 and $H^{5'}$; 7.4* H^3; 7.5* H^4; 7.71 (t) $H^{4'}$
2d[c]	1.02 (s)	3.72 (m) 4.07 (m)	4.33 (m) 4.84 (m)	7.4*	2.95 (s)	9.07 (d)	8.34 (s)	7.2* H^5 and $H^{5'}$; 7.4* H^3; 7.64 (t) $H^{4'}$; 7.68 (dt) H^4
2y,[h] **2z**[e]	0.97 (s)	3.38 (t)	4.02 (t)	8.05 (dd)	2.83 (s)	8.53 (dd)	9.23 (s)	7.42 (ddd) H^5; 7.49 (dd) H^3; 7.53 (dd) $H^{5'}$; 7.96 (dt) H^4; 7.97 (t) $H^{4'}$

[a] $CDCl_3$ solution, 293 K. [b] $CDCl_3$ solution, 353 K. [c] CD_2Cl_2 solution, 223 K. [d] $CDCl_3$ solution, 253 K. [e] $CDCl_3$ solution, 293 K. [f] $C_2D_2Cl_4$ solution, 363 K. [g] CD_2Cl_2 solution, 203 K. [h] CD_3CN solution, 293 K. An asterisk denotes a concealed peak.

Table VI. Selected ^{13}C-NMR Data for MAP and 6′-CH_3-MAP and the Complexes **1b**, **1z**, **2a**, **2b**, and **2z**

	Pd-CH_3	C^α	C^β	$C^{6'}$ or 6′-CH_3	$C^{7'}$
MAP[a]		38.4	59.8	148.4	161.5
1b[b]	8.2	39.8	52.7	149.4	164.7
1z[c]	6.8	39.4	52.4	150.4	163.5
6′-CH_3-MAP[a]		39.3	60.9	24.2	162.6
2a[a]	3.8	41.9	60.8	26.8	concealed
2b[b]	9.4	42.7	60.8	25.7	165.3
2c[b]	−7.5	39.2	66.7	26.4	169.6
2d[b]	−4.0	41.1	68.7	27.9	166.7
2z[c]	7.0	39.8	53.4	26.3	164.6

[a] $CDCl_3$, 293 K. [b] CD_2Cl_2, 223 K. [c] CD_3CN, 293 K.

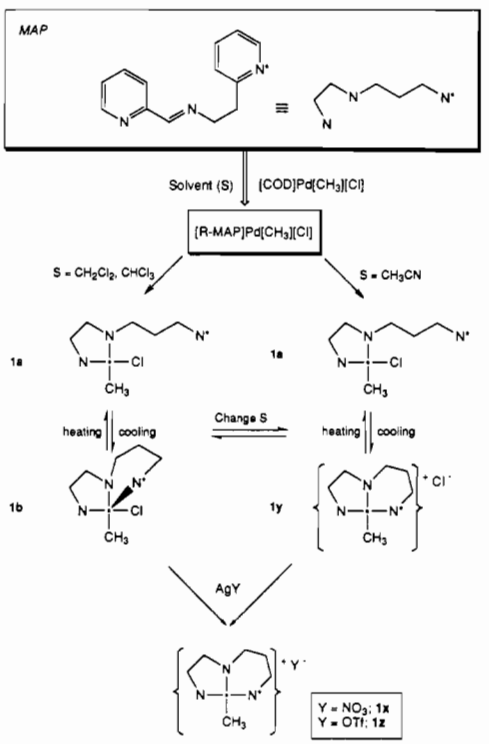
Table VII. ^{15}N-NMR Data for MAP and Its Complexes **1b** and **1z**[a]

compound	T_{evo} (τ), ms[g]	N^1 ($J_{N-H\alpha}$)[b]	N^2 ($J_{N-H\alpha}$)[b]	N^3 ($J_{N-H\alpha}$)[b]
MAP[c]	22.7	−61.0 (11.3)	−36.0 (4.4)	−63.2 (11.4)
1b[d,f]	30.0	−151.3	−92.0	−151.0
1z[e,f]	30.0	−152.3	−89.8	−152.1

[a] As determined by ^{1}H, ^{15}N-INEPT on a 300-MHz spectrometer, chemical shifts are in ppm relative to CH_3NO_2,[18] coupling constants in Hz. [b] For the labeling of the nitrogen atoms, see Figure 3. [c] In C_6D_6 at 32.4 MHz and 293 K. [d] In CD_2Cl_2 at 32.4 MHz and 223 K. [e] In CD_3CN at 32.4 MHz and 293 K. [f] Only broad-band decoupled spectra were recorded. [g] $\tau = {}^1/_4\,{}^2J(N-H)$.

assignment of the coordination mode was assisted by comparison with the NMR spectra of R-PyCa[12] and R_E,R_Z-IEP complexes[24] and by use of ^{15}N-INEPT.[10] Although the S/N enhancement of the INEPT technique made it possible to record the spectra without taking recourse to ^{15}N-enriched ligands, the lack of a hydrogen atom with a sufficiently large N–H coupling constant in the 6′-CH_3-MAP complexes and the interconversion of the observed coordination isomers even at very low temperatures made it impossible to record the ^{15}N-shift of all the 6′-CH_3-MAP complexes.

Scheme I. Presentation in Outline of the Proposed Reaction Routes to the Several Coordination Isomers of the Complexes Formed with MAP (Palladium Atom Label Omitted for Clarity)



It turns out that in solution **1** and **2** appear in various isomeric forms, depending on the solvent used and on the temperatures of the solutions of **1** and **2**. These isomeric structures are outlined in Schemes I and II for compounds **1** and **2**, respectively.

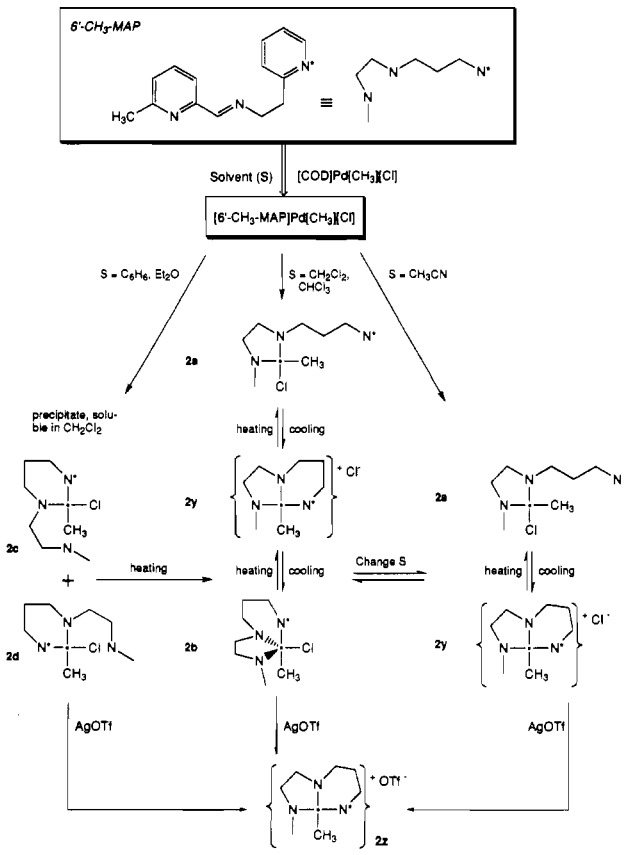
Characterization of NMR Data of 1z and 2z. The interpretation of the NMR data recorded of **1z** in acetonitrile is in agreement with the molecular structure. The bridging and the aromatic region of the ^{1}H-NMR spectrum of **1z** is presented in Figure 5. Compound **1z** and **2z** both contain a noncoordinating triflate

(24) R_E,R_Z-IEP = R_E,R_Z-1-(2-(methyleneamino)ethyl)pyridine, i.e. $(R_E)(R_Z)C{=}NCH_2$-2-$CH_2C_5H_4N$, in which the trans group R_E = alkyl, and aryl and the cis substituent R_Z = H and CH_3. Rülke, R. E.; de Wilde, J. C.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. to be submitted for publication.

(25) R-DAB = R,R-diazabutadiene, RN=C(H)(H)C=NR (with R = alkyl, aryl). (a) Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G.; Saporito, A. *Inorg. Chem.* **1985**, *24*, 2032–2039. (b) De Felice, V.; Ganis, P.; Vitagliano, A.; Valle, G. *Inorg. Chim. Acta* **1988**, *144*, 57–61. (c) van der Poel, H.; van Koten, G. *J. Organomet. Chem.* **1981**, *217*, 129–138. (d) van der Poel, H.; Kokkes, M.; Stam, C. H.; van Koten, G. *J. Organomet. Chem.* **1979**, *175*, C21–C4. (e) van der Poel, H.; van Koten, G. *J. Organomet. Chem.* **1980**, *187*, C17–C21. (f) van der Poel, H.; van Stein, G. C.; van Koten, G. *J. Chem. Soc. Dalton Trans.* **1981**, 2164–2171. (g) van der Poel, H.; Kokkes, M.; Stam, C. H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2941–2950. (h) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145.

(26) NMR data for *trans*-(lutidine)$_2$Pd(CH_3)(Cl). ^{1}H-NMR: 0.62 (s), Pd–CH_3; 3.35 (s) CH_3; 7.09 (d), H^3; 7.50 (t), H^4. ^{13}C-NMR: −8.6, Pd–CH_3; 28.4, CH_3; 122.9, C^3; 137.9, C^4; 160.6, C^2.

Scheme II. Presentation in Outline of the Proposed Reaction Routes to the Several Coordination Isomers of the Complexes Formed with 6′-CH3-MAP (Palladium Atom Label Omitted for Clarity)



anion as a counterion. Analogous complexes of **1z** and **2z** were prepared with a chloride (**1y**, **2y**) and a nitrate anion (**1x**). The chemical shift of the methyl ligand in ^{1}H-NMR at 0.98 ppm (**1z**) and 0.97 (**2z**) have often been encountered in R-PyCa-type complexes with the methyl ligand trans with regard to the imino-function.[12] The α-CH_2 and β-CH_2 signals (bridging region) are broadened at room temperature, probably because of a wagging motion due to the flexible six-membered ring structure of the Pd–iminoethyl–pyridyl moiety. This motion however, can easily be frozen out on the NMR time scale by cooling down the solution to 233 K. At this temperature, the bridging region shows four resonances, clearly indicating the inequivalence of the hydrogens involved. The resonances comprise a doublet and a triplet for both the α- and the β-hydrogens. This feature has also been found in the R_E,R_Z-IEP complexes[24] where the bridge is in a fixed conformation. The 6′-CH_3 substituent is found at 2.83 ppm. The aromatic region can easily be assigned by a COSY 45 spectrum in which the relevant proton signals occur in the sequence H$^{7'}$, H^6, H$^{6'}$, H$^{3'}$ (**1z**) and H$^{7'}$, H^6, H$^{3'}$ (**2z**), respectively.

The NMR data are supported by conductometric experiments (see Table I), since for **1z** and **2z** (Y = $CH_3SO_3^-$), **1y** and **2y** (Y = Cl^-), and **1x** (Y = NO_3^-) conductivity values typical for a 1:1 electrolyte were found in acetonitrile at all temperatures between 228 and 317 K. For **1x**, **1y**, and **2y**, *vide infra*, NMR spectra almost identical to the spectra found for **1z** and **2z** were obtained, indicating that the noncoordinated anion does not severely affect the position of the ligand shifts when recorded in the same solvent. The change of the solvent, however, proved to affect the chemical shifts of the hydrogens considerably.

Characterization of 1a and 2a. Upon synthesis of **1** and **2** in chloroform or dichloromethane, neutral complexes were formed, which we will denote **1a** and **2a**. After removal of the solvent, both compounds were isolated as an orange oil. These were very

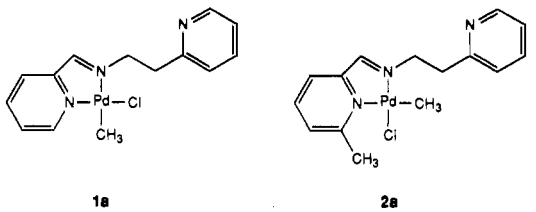


Figure 4. Structures of **1a** and **2a**.

soluble in dichloromethane, chloroform, and tetrachloroethane, but only moderately soluble in acetonitrile, whereas they are poorly soluble in diethyl ether, THF, benzene, and toluene.

Since the NMR spectra of **1a** and **2a** at room temperature show peak broadening, especially in the bridging region, both ligands are flexible upon coordination. The signals sharpen up by heating a solution of **1a** in dichloromethane to 353 K[33] and of **2a** in tetrachloroethane to 363 K, respectively. The relative positions of the methyl and the chloride ligands can be deduced from the chemical shift of the methyl ligand and the shift of H$^{6'}$. The chemical shifts of the methyl ligands have been found at 0.93 ppm and 1.14 ppm for **1a** and **2a**, respectively, in related trans and cis complexes respectively containing the R-PyCa ligand.[12b,d,27] The signal of H$^{6'}$ in **1a** has a small positive CIS value (CIS = coordination induced shift), indicating that H$^{6'}$ is in the vicinity of a methyl ligand rather than a chloride ligand since the relatively strong deshielding effects of a chloride should cause a much higher ppm value.

The bridging region in the spectra show two sharp triplets which retain their pattern also upon cooling. This feature indicates that the ethyl–pyridyl group is not coordinating, which is supported by the observation that H^6 has almost no CIS effect. The aromatic region shows a decreasing chemical shift in the order H$^{7'}$, H^6, H$^{6'}$, and H$^{3'}$ for **1a** and H$^{7'}$, H^6, and H$^{3'}$ for **2a**. Indeed, the sequence determined is generally found in R-PyCa complexes,[12] which indicates that the MAP and the 6′-CH_3-MAP ligands in these compounds are bidentate coordinated in a R-PyCa-like coordination mode with a non-coordinating ethylpyridyl group, as is shown in Figure 4.

Characterization of 1b. When cooling down a solution of **1a**, we see that other isomers are formed. Cooling **1a** in CD_2Cl_2 to 223 K leads almost quantitatively to **1b**, which when isolated at low temperatures, turns out to be an orange oil which can be dissolved in the same solvents as used in the case of **1a**. We have

(27) Phenethyl-PyCa = $C_5H_4NC{=}NCH_2CH_2C_6H_5$. (Phe-PyCa)Pd($CH_3$)(Cl) occurs as 77% *cis* and 23% *trans* isomer. NMR data for *cis*-(Phe-PyCa)Pd(CH_3)(Cl). ^{1}H-NMR: 1.09, 3H, s, Pd-C*H*$_3$; 3.08, 2H, t, α-H; 4.01, 2H, t, β-H; 7.20, 5H, m, phenyl; 7.46, 1H, d, H^3; 7.60, 1H, ddd, H^5; 7.77, 1H, s, H^7; 7.91, 1H, dt, H^4; 9.05, 1H, d, H^6. ^{13}C-NMR: −2.4, Pd-*C*H3; 37.2, α-C; 62.2, β-C; 125.9, C^5; 127.5, C^3; 128.5, C^p; 129.3, C^m; 130.0, C^o; 137.8, C^i; 139.1, C^4; 150.0, C^6; 151.9, C^2; 166.9, C^7. NMR data for *trans*-(Phe-PyCa)Pd(CH_3)(Cl). ^{1}H-NMR: 1.07, 3H, s, Pd-C*H*$_3$; 3.25, 2H, t, α-H; 4.09, 2H, t, β-H; 7.20, 5H, m, phenyl: 7.52, 1H, d, H^3; 7.59, 1H, ddd, H^5; 7.77, 1H, s, H^7; 8.01, 1H, dt, H^4; 8.62, 1H, d, H^6.

(28) (a) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; De Felice, V. *Gazz. Chim. Ital.* **1989**, *119*, 461–462. (b) De Felice, V.; Albano, V. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem.* **1991**, *403*, 269–277. (c) Albano, V. G.; Castellari, C.; Morelli, G.; Vitagliano, A. *Gazz. Chim. Ital.* **1989**, *119*, 235–239.

(29) (a) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1155. (b) Okeya, S.; Miyamoto, T.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 395. (c) Sakai, T.; Taira, Z.; Yamazaki, S.; Ama, T. *Polyhedron* **1989**, *8*, 1989–1993. (d) Vicente, J.; Abad, J.-A.; Stiakaki, M.-A.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 137–139. (e) Vicente, J.; Abad, J-A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512–3517. (f) Villanueva, L. A.; Abboud, K.; Boncella, J. M. *Organometallics* **1991**, *10*, 2969–2972. (g) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785–1790. (h) Bushnell, G. W.; Dixon, K. R.; Khan, M. A. *Can. J. Chem.* **1974**, *52*, 1367–1376. (i) Wernberg, O.; Hazell, A. *J. Chem. Soc., Dalton Trans.* **1980**, 973–978. (j) Louw, W. J.; de Waal, D. J. A.; Kruger, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2364–2368. (k) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356–1365.

(30) Casarin, M.; Rülke, R. E. To be submitted for publication.

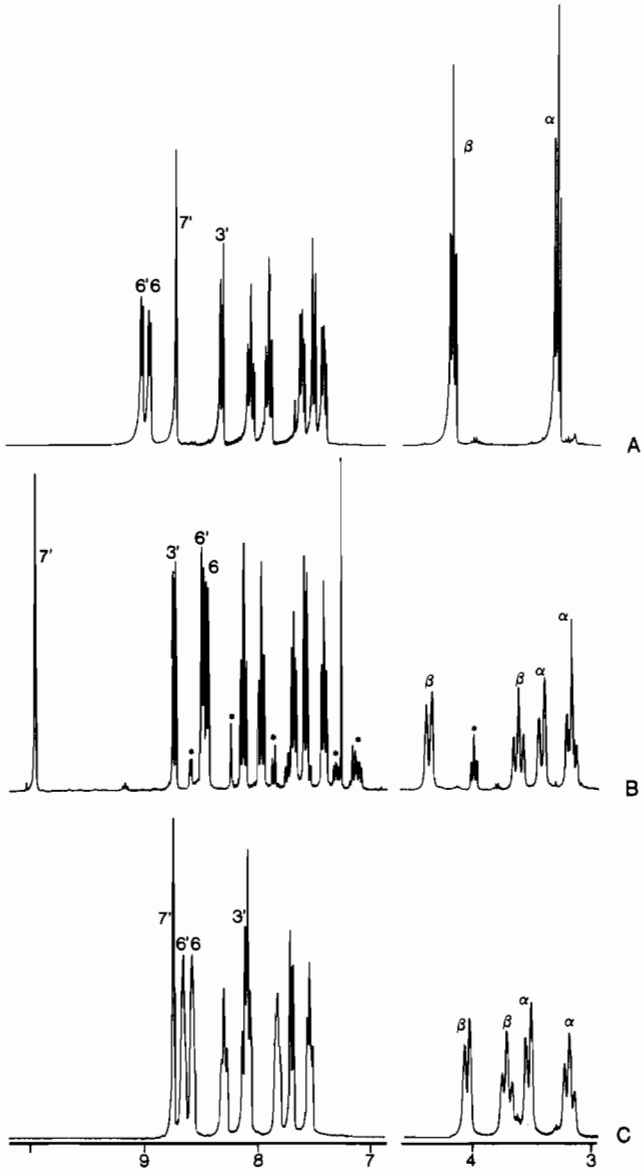


Figure 5. Bridging and aromatic regions of the ^{1}H-NMR spectra of MAP at 293 K in $CDCl_3$ (top, A), neutral σ^3-(MAP)Pd(CH_3)(Cl) (**1b**) at 233 K in $CDCl_3$ (signals with asterisks are MAP) (middle, B), and ionic [σ^3-(MAP)Pd(CH_3)]OTf (**1z**) at 233 K in CD_3CN (bottom, C).

been able to isolate **1b** as yellow crystals, which unfortunately were not suitable for X-ray determination and melt upon warming to room temperature.

Although the NMR spectra of **1b** are very well resolved, the assignment proved to be very difficult. The bridging and the aromatic region of the ^{1}H-NMR spectrum of **1b** is presented in Figure 5, together with those of MAP and **1z**.

The chemical shift of the methyl ligand occurs at 0.78 ppm, which indicates a position trans to the carbaldimino nitrogen, similar to **1a** and **1z**. Also similar to the ionic compound **1z**, the bridging region shows four resonances, indicating that all the bridging hydrogens are inequivalent with two doublets and two triplets for both the α- and the β-hydrogens respectively. This indicates that the ethylpyridyl group is coordinating to the palladium center. The aromatic part of the ^{1}H-NMR spectrum contain the signals of $H^{7'}$, $H^{3'}$, H^6, $H^{6'}$ in order of descending chemical shift, which is completely different from the ionic **1z**. The CIS values of H^6 and $H^{6'}$ are normal for a methyl ligand in the cis position (see also **1a**). The shifts of $H^{3'}$ at 8.58 ppm and $H^{7'}$ at 9.79 ppm are found at unexpectedly high ppm values.

^{15}N-NMR experiments (Table VII) clearly prove that all the nitrogen donor atoms of **1b** are coordinating, as is evident from

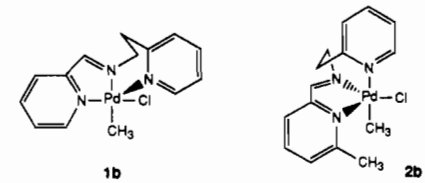


Figure 6. Structures of **1b** in a square pyramidal configuration and **2b** in a TBP configuration.

the dramatic high-field shift of the nitrogen nuclei of –50 to –90 ppm when compared to that of the free ligand. It is known that the CIS ($\Delta\delta$) of a nitrogen atom in palladium complexes is mainly dependent on the σ-donor capacities of a ligand that is in a *trans* position.[23b] For example when an alkyl or a phosphine ligand is in a trans position, an upfield shift of ca. –50 ppm is found, whereas values of –80 ppm have been observed for weakly σ-donating ligands in a trans position.[23b] Thus the CIS of –52 ppm as established for N2 clearly indicates a trans position of this nitrogen and the methyl ligand. The two pyridyl groups have CIS values of –90.3 and –87.8 ppm for N1 and N3, respectively, which points to weak trans ligands for both groups. Nitrogen NMR in this case, however, is incapable of differentiating between a halide, a nitrogen atom, or a solvent molecule as the weak donor in the trans position. It should be noted that the rather small differences in the CIS values in **1b** and the ionic **1z** do not imply that the ligands have the same coordination fashion since these two experiments were performed under totally different conditions; i.e., the temperature and the solvent differed, which has proved to be of considerable influence on the nitrogen shifts.

Since we have prepared the ionic isomer **1y**, we deduce from the ^{1}H-NMR data that **1b** is definitely not the ionic complex but rather the neutral five-coordinate one as stated above. This is supported by the conductometric data, which show no increase of the conductivity at decreasing temperatures.

In performing NOE-difference experiments, irradiation of the methyl ligand results in NOE-interactions on both H^6 and $H^{6'}$. In a second experiment, irradiation of the imine hydrogen shows an interaction with $H^{3'}$. These results support a square pyramidal structure and not a trigonal bipyramidal one.

Therefore structure **1b** probably is a (distorted) square pyramidal, five-coordinate complex with the ethylpyridyl group coordinating on the palladium center at an apical position as is shown in Figure 6 (see also Discussion) which is in an equilibrium with the four coordinate analogue **1a**, as shown by the completely reversible conversion of **1a** to **1b** and vice-versa.

Characterization of 2b. Compound **2b** is formed at temperatures below 233 K in a solution of **2a** and **2y** in dichloromethane. This interconversion could be followed down to 193 K, at which temperature ca. 60% of isomer **2b** is formed. Because of the presence of a reasonable amount of **2y**, some signals of **2b**, especially in the aromatic region between 6.5 and 8.0 ppm and the bridging region, are not completely resolved. Nevertheless, the ^{1}H-NMR spectrum of **2b** shows a few very characteristic signals. The chemical shift of the methyl ligand is found at 1.52 ppm, which is very high—in between the resonances of the palladium(II) and palladium(IV) complexes.[3d,e,g,4,12,24,31a] The imino hydrogen ($H^{7'}$) shift of 10.52 ppm is extremely high for an imine. Very high chemical shifts in imines are often found, for example, in complexes containing a non coordinating imine whose hydrogen is apically situated.[25c-h]

Although the briding region and the lower part of the aromatic region are interpreted with difficulty owing to the presence of the interfering aromatic signals of **2y**, no anomalies are observed for the hydrogens concerned.

With these characteristic NMR data several possible configurations were considered. One possibility that we thought of is

(31) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *393*, 299–306.

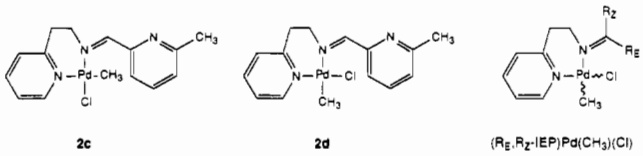


Figure 7. The structures of **2c**, **2d**, and $(R_E,R_Z\text{-IEP})Pd(CH_3)(Cl)$.[24]

the configuration in which the two pyridyl groups are found in a trans position and, as a result, the methyl ligand is trans with regard to the chloride ligand. However, comparing the spectra with the model system *trans*-$(lutidine)_2Pd(CH_3)(Cl)$[26] prompted us to reject this possibility. In this compound, the methyl signal resonates at 0.62 ppm, which is considerably lower than the methyl resonance of **2b**. The methyl substituents of *trans*-$(lutidine)_2Pd(CH_3)(Cl)$ are found at 3.35 ppm owing to the experienced strong deshielding effect of these protons in the axial positions of the square planar palladium coordination plane. In contrast, the methyl substituent of **2b** is found at 2.74 ppm, which is almost equal to those of **2a** and **2y**.

From both thermodynamic and spectroscopic points of view[32] the most probable configuration would be a five-coordinate complex, like **1b**, except that the palladium atom has changed from a square pyramidal conformation into a trigonal bipyramidal configuration. The α-diimine moiety and the methyl ligand are hence situated in an equatorial position, whereas the ethylpyridyl group and the chloride ligand are in axial positions, as presented in Figure 6.

Characterization of 2c and 2d. In the case of the synthesis of **2** in ether or benzene, a pale yellow precipitate is formed instantaneously. The precipitate contains two new isomeric forms of **2**, compounds **2c** and **2d**, in an approximate 40:50 ratio together with a minor amount (ca. 10%) of **2a**. It proved to be impossible to separate **2c** and **2d** by column chromatography or by selective crystallization. The ^{1}H-NMR spectra of **2c** and **2d** very much resemble the spectra we obtained from corresponding R_E,R_Z-IEP complexes.[24] The proposed structures are presented in Figure 7.

The palladium bonded methyl ligands of **2c** and **2d** resonate at 0.04 and 1.02 ppm, respectively. The high field value of 0.04 ppm of **2c** can be explained by assuming that the methyl ligand coordinates in a cis position with regard to the imino function. Since the 6′-CH_3-MAP ligand is coordinating with the imino–ethyl–pyridyl function in a six-membered ring, the noncoordinating picolyl group is situated in the vicinity of the methyl ligand. This will result in a strong shielding effect of the π-electrons of the picolylic group on the methyl ligand and, as a consequence, in a very low chemical shift of the methyl ligand of **2c**. The methyl resonance of 1.02 ppm of **2d** can be attributed to a methyl ligand in a position trans with regard to the imino function. In this position, the methyl ligand does not experience any shielding effects and the shift is normal for a trans configuration.

At room temperature the signals of the bridging region of both **2c** and **2d** are broadened because of inversion of the six-membered chelate ring occuring on the NMR time scale. At low temperatures, two sets of true AA′BB′ patterns emerge. In performing a COSY 45 spectrum, the bridging signals of **2c** and **2d** could be assigned to their corresponding isomers.

The signals of the bridging region are observed between 3.5 and 5.5 ppm, which is more than one ppm higher than the bridging signals of **1z**, **2z**, and **1b**. Since the two CH_2CH_2 groups are involved in the chelate rings, in a position between the two donor atoms, the inductive effect of the coordinating nitrogen atoms might be the reason for this high shift of the protons in the bridging region.

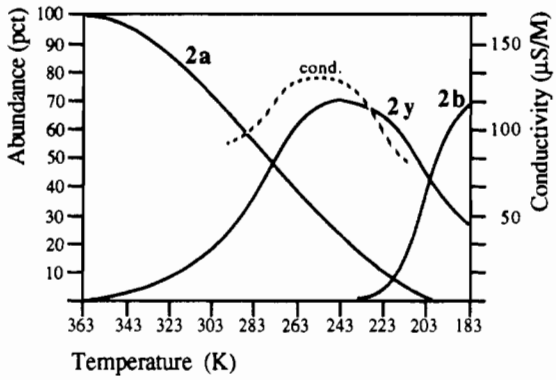


Figure 8. Temperature dependence of the abundance of **2a**, **2y** and **2b** (full lines) and of the conductivity of **2** (dashed line).

The aromatic part of the ^{1}H-NMR spectrum reveals the relevant protons in the sequence H^6, $H^{7'}$, $H^{3'}$ for both isomers. The H^6 of **2c** is found at a higher chemical shift than the H^6 of **2d**. This is caused by the presence of the chloride ligand in the cis position of the pyridyl group containing H^6 causing a deshielding effect on the hydrogen atom in question, in agreement with the proposed structures. The trans position of the methyl ligand with regard to the imine nitrogen in **2d** results in a lower chemical shift of $H^{7'}$ of **2d** due to the strong trans influence of a methyl ligand, compared to the situation in **2c** in which the chloride ligand is found in the trans position.

Intramolecular Ligand Rearrangements of 1 and 2. As we have seen, several coordination isomers of **1** and **2** can be obtained. This can be achieved by varying the solvent in which the substitution reaction is performed. The temperature of solutions of **1** and **2** proved to affect dramatically the relative ratio of the various coordination isomers.

When **1** is synthesized in dichloromethane or chloroform, a mixture of **1a** and **1b** is formed. The ratio of **1a** and **1b** varies reversibly with the temperature. While the ratio is approximately 1:1 at room temperature in dichloromethane, in chloroform at room temperature more **1b** is present. **1b** can be observed exclusively by cooling down to 233 K. By determining the K_{eq} of the equilibrium **1a** vs **1b** at different temperatures, we were able to calculate the ΔH and ΔS. In dichloromethane, ΔH^0 is −17.2 kJ/mol and ΔS is 54.5 J/(mol·K), whereas in chloroform ΔH^0 is −32.6 kJ/mol and ΔS is 91.0 J/(mol·K).

Upon synthesis of **1** in acetonitrile, however, a mixture of **1a** and **1y** is formed in an approximate 1:4 ratio at room temperature. When the mixture was cooled to 263 K, **1y** could be observed exclusively, while heating causes a slight increase of **1a** varying from 20% at room temperature to 25% at 323 K.

The mixture of **1a** and **1b** can be converted simply into a mixture of **1a** and **1y** by evaporation of the dichloromethane or chloroform and subsequent dissolution in acetonitrile and vice versa.

An analogous behavior was observed for **2**. Dissolving **2** in acetonitrile results in a mixture of the neutral compound **2a** and the ionic compound **2y**. The ratio is 4:1 at room temperature, which means that the ionic species is the minor component. This is in contrast to **1** however, for which the ionic species is the most abundant isomer.

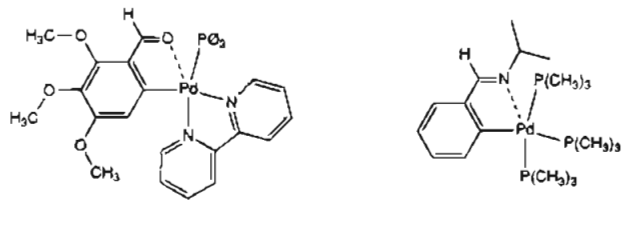
Synthesis of **2** in dichloromethane or chloroform also results in a mixture of **2a** and **2y**. The ratio of the mixture varies reversibly with the temperature (see Figure 8), while at 363 K **2a** is the only isomer present.

When the mixture is cooled from room temperature, the amount of **2y** increases while below 233 K, **2b** emerges. At 193 K, the lowest temperature reached, **2b** is present in about 60%.

Synthesis of **2** in diethyl ether or benzene, however, results in the formation of **2c** and **2d**. Interestingly the ratio of **2c** and **2d** does not change upon variation of the temperature or the reaction conditions of the synthesis. Gentle heating of the mixture of **2c**

(32) (a) Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*, 3rd ed.; Harper Collins: New York, 1983; pp 471–484. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.

(33) This experiment was carried out in a single-crystal sapphire high-pressure NMR tube. Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388–91.



A B

Figure 9. Structures of $[(bipy)(P(C_6H_5)_3)Pd(C_6H(2\text{-}CHO)(3,4,5\text{-}(OCH_3)_3)]CF_3SO_3$, **A**, as published by Vicente et al.[29d,e] and $[(Me_3P)_3Pd(C_6H_4C(H)=NPr^i)]BF_4$, **B**, as published by Boncella et al.[29f]

and **2d** resulted in the conversion of **2c** and **2d** to a mixture of **2a** and **2y** at room temperature, while at low temperatures also **2b** is again observed, as expected.

Discussion

The inequivalence of all the three nitrogen functions of the MAP and 6′-CH_3-MAP ligands results in an unexpected and unique range of coordination isomers of (MAP)Pd(CH_3)(Cl) and (6′-CH_3-MAP)Pd(CH_3)(Cl). The rather minute differences in the donating properties of the three nitrogen atoms of both ligands play a subtle but nevertheless decisive part in the formation of the various isomers concerned including the temperature dependent choice between bidentate and terdentate coordination.

The four-coordinate complexes **1a** and **2a** both display the normal α-diimine coordination mode. The cis position of the methyl ligand and the imine nitrogen of **2a** agrees with the configuration found for analogous (tBu-6-CH_3-PyCa)Pd(CH_3)(Cl) and (iPr-6-CH_3-PyCa)Pd(CH_3)(Cl) complexes[12b,d] and is both sterically and electronically favored.

The trans configuration of **1a** is unexpected. In the known R-PyCa complexes, the R substituent on the imine function nearly always has a tertiary or a quarternary α-carbon atom, e.g. iPr, tBu, aryl. These complexes all show mainly cis arrangements. The presence of a secondary α-carbon atom on the imino nitrogen as in the MAP ligand should therefore normally also lead to mainly a cis configuration, as is supported by the synthesized bidentate analogue of **1a**, (Phe-PyCa)Pd(CH_3)(Cl),[27] where the cis isomer is the most favored isomer. The occurrence of this unexpected trans arrangement of **1a** must therefore be caused by the presence of the noncoordinating pyridyl group.

The most unusual isomers in our opinion are those displayed by the compounds **1b** and **2b**. In the literature only few examples have been reported in which five-coordinate palladium(II) complexes are involved. Many of these structures have the formula (α-diimine)$(L)_2$Pd(alkene) ($L = Cl^-, CH_3^-$) in a trigonal bipyramidal structure.[12d,25h,28a,b] However, it should be noted that analogous five-coordinate platinum complexes occur more frequently.[12a,e,f,25a,b,d-g,28a,c] The suggested TBP structure of **2b** is in agreement with this.

The equilibrium of the 4-coordinate **1a** with respect to **2a** and the 5-coordinate **1b** with respect to **2b** is probably forced by entropy, as the ΔS values of 54.5 and 91.0 J/(mol·K) for the reaction **1b** → **1a** (LT→HT) in, respectively, dichloromethane and chloroform indicate.

In the cases where the 5-coordinate complexes have a square pyramidal structure like **1b**,[29] five-coordination is sometimes imposed by the rigidity of the ligands concerned.[29a-c] Square pyramidal complexes in which the geometry is not imposed, are, e.g., found in the interesting work of Vicente[29d,e] and in the work of Boncella;[29f] see Figure 9.

Although Vicente et al. do not discuss into detail whether these complexes are five-coordinate ones, the apically situated aldehyde groups have Pd–O distances of 2.92 and 2.93 Å respectively and the oxygen atoms are definitely pointing toward the palladium atom. In the case of a noncoordinating oxygen atom, the aldehyde function is often pointed away from the metal, as examples in the same papers show.[29d,e] In the work of Boncella and others,[29f,g] apically coordinating nitrogen groups have also been found for which Pd–N distances of 2.779(3) and 2.710(6) Å have been found, respectively. These distances are considerably shorter than the Pd–O bonds Vicente has found. Analogous platinum complexes[29h,i] display Pt–N distances of 2.843(20) and 2.761(5) Å, respectively. Elongated C–N and C–O distances in these compounds imply real bonds, although the relatively long distances indicate that the interaction is rather weak. The square pyramidal five-coordinate geometry of **1b**, therefore, is not quite unexpected since the ligand is sufficiently flexible for five-coordination in a *fac* fashion.

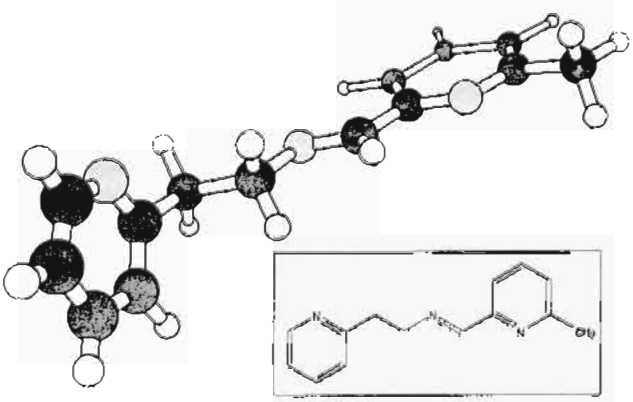


Figure 10. Lowest-energy configuration of 6′-CH_3-MAP as calculated with Sybyl. The left-hand pyridyl substituent is perpendicular to the α-diimine.

We now have to consider the rather intriguing phenomenon that at decreasing temperatures **2a** is converted into **2y** and subsequently into **2b** while cooling down **1a** results in the formation of **1b**. It is evident that the TBP conformation of **2b** must be caused by the presence of the 6′-CH_3 group in the 6′-CH_3-MAP ligand. It is very likely that **2y** must have a pronounced steric interaction between the 6′-CH_3 substituent and the methyl ligand. One may then envisage a facile change of the ligands in **2y** to a TBP configuration in **2b** since the steric interactions in **2b** are favorable, while this process lacks the steric driving force when starting with **1b**.

It should be clear that this rationalization of the observed phenomena is a tentative one. Studies are underway to investigate in more depth the influence of the type of terdentate ligand on these conversion processes, both experimentally and theoretically.[30]

The formation of a mixture of **1a** and the ionic **1y** and the analogous **2a** and **2y** in acetonitrile is not very surprising and it displays the hemilabile character of the five-coordinate complexes. The increased polarity of acetonitrile compared with dichloromethane or chloroform in the case of **1a,b** and **2a,b** in this reaction apparently stabilizes the formation of the ionic compounds **1y** and **2y**.

A salient feature is when one compares mixtures of **1** and **2** that in the case of **1**, ca. 80% of the ionic complex **1y** is formed whereas in the case of **2** only ca. 20% of the ionic complex **2y** is found. Whether this is caused by steric or electronic factors remains unclear at present.

The formation of **2c** and **2d** might be caused by the poor solubility of these complexes in diethyl ether or benzene. That these complexes are indeed kinetic products is confirmed by the observation (see results) that they are converted above 373 K to a mixture of **2a** and **2y**. It is of interest that these kinetic products are only formed for 6′-CH_3-MAP and not for MAP, from which we may conclude that steric factors are very important during the initial stages of the formation of **1** or **2**. Molecular modelling experiments (see Experimental Section) show that the most favored conformation of both ligands is a flat *E*-(s)-trans configuration for the diimine moiety with a perpendicular

arrangement of the ethylpyridyl group with regard to the diimine plane, as is shown in Figure 10 for 6′-CH_3-MAP.

In the case of 6′-CH_3-MAP it is difficult in this configuration for the metal to come close to the nitrogen atoms of the diimine moiety owing to the steric interactions of the palladium atom with the 6′-CH_3-group and the imino-hydrogen. Since the rotational barrier of the E-(s)-trans to the E-(s)-cis conformation of α-diimines[34] is ca. 20–25 kJ/mol at 90°, the calculated conformation is expected to be the most abundant one. One has to expect therefore that the most favorable point of attachment for the metal is the nitrogen atom N3 of the pyridyl group on the ethyl group. The resulting monodentate bonded 6′-CH_3-MAP ligand may now rotate 90° by which the nitrogen atom of the imine moiety is the first suitable coordination position, resulting in the kinetic products **2c** and **2d** with a six-membered ring.

(34) Crociani, B.; Granozzi, G. *Inorg. Chim. Acta* **1987**, *132*, 197–206.

Finally, we want to remark that the 1:1 ratio of cis to trans in the case of **2c** and **2d** is accidental since the analogous R_E,R_Z-IEP complexes show greatly varying cis to trans ratios dependent on the R_E and R_Z substituents.[24c]

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Supplementary Material Available: Tables of crystal data and details of the structure determination, final coordinates, thermal parameters, bond distances and angles, and torsion angles (9 pages). Ordering information is given on any current masthead page.