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Synthesis and Structural Studies of Ionic Monoorganopalladium(II) Complexes with Tridentate Nitrogen-Donor Ligands

Bertus A. Markies,[†] Peter Wijkens,[†] Jaap Boersma,*[,†] Huub Kooijman,[‡] Nora Veldman,[‡] Anthony L. Spek,[‡,§] and Gerard van Koten[†]

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and the Bijvoet Center for Biomolecular Research, Laboratory of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Ionic palladium(II) complexes of the types [PdCl(N-N′-N″)]Cl and [PdR(N-N′-N″)]OTf, with R = Me or aryl, N-N′-N″ = tridentate nitrogen donor ligand, and OTf = trifluoromethanesulfonate (triflate), have been prepared. The tridentate nitrogen-donor ligands used are 2,6-bis[(dimethylamino)methyl]pyridine (NN′N), *N,N,N′*-trimethyl-*N′*-(2-picolyl)ethylenediamine (pico), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdeta). The chloro derivatives (**3**–**5a**) were obtained as yellow ionic complexes in excellent yields (81–93%). Crystals of **4a** were obtained from methanol/diethyl ether and are monoclinic, space group $P2_1/c$ (No. 14), $a = 15.0760(7)$ Å, $b = 7.4468(8)$ Å, $c = 13.553(2)$ Å, $\beta = 115.653(6)°$, and $Z = 4$. Refinement converged at $R = 0.0325$ ($wR2 = 0.0663$). The molecular structure shows a four-coordinate palladium center surrounded by the terdentate bound pico ligand and a chloride anion. There is no interaction of the palladium center with the second chloride anion (Pd–Cl2 ≥ 4.2617 Å). The Pd–NMe bond distance (2.023(3) Å) is relatively short and is accompanied by a small trans N–Pd–N bond angle (168.03(12)°). The methyl derivatives (**3**–**5b**) were also obtained in good yield (79–91%) via reaction of PdIMe(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with silver trifluoromethanesulfonate and the ligand. An alternative route, starting from $PdMe_2$(tmeda), is reported for the synthesis of [PdMe(NN′N)OTf (**3b**). Crystals of **3b** were obtained from methanol/diethyl ether and are monoclinic, space group $P2_1/a$ (No. 14), $a = 7.738(1)$ Å, $b = 21.280(2)$ Å, $c = 11.399(1)$ Å, $\beta = 92.05(1)°$, and $Z = 4$. Refinement converged at $R = 0.066$ ($R_w = 0.065$). The molecular structure of **3b** shows a terdentate coordination of the NN′N ligand to the metal, with a relatively short Pd–N′ bond distance (1.996(8) Å) and small N–Pd–N bond angle (161.7(3)°). Yellow crystals of [PdMe(ONN′)(tmeda)]OTf (**8**), with ONN′ = 2-(hydroxymethyl)-6-[(dimethylamino)methyl]pyridine (**7**), were accidentally obtained from the reaction of [PdMe(MeCN)(tmeda)]OTf (**I**) with an impure sample of the NN′N ligand, containing the ONN′ ligand. The molecular structure of **8** shows the ONN′ ligand monodentate coordinated to the metal *via* its pyridyl nitrogen donor whereas the NMe_2 and OH functionalities are free. The triflate anion is hydrogen bonded to the hydroxymethyl group with OH⋯O-(SO_2CF_3) = 2.759(3) Å and O–H–O = 173(4)°. Crystals of [PdMe(ONN′)(tmeda)]OTf (**8**) are triclinic, space group $P\bar{1}$ (No. 2), $a = 9.7902(14)$ Å, $b = 10.0555(15)$ Å, $c = 12.362(2)$ Å, $\alpha = 75.828(12)°$, $\beta = 81.234(12)°$, $\gamma = 84.836(11)°$, and $Z = 2$. Refinement converged at $R = 0.032$ ($R_w = 0.040$). The first examples of simple arylpalladium(II) cations containing tridentate ligands were obtained in moderate to high yield (35–95%). The aryl groups studied differ in both steric and electronic properties. Conformational analysis by NMR of the NCCN moieties of the pico and pmdeta containing complexes showed the five-membered chelate rings in the complexes to occur selectively in one of the two possible conformations. The rotational-energy barriers of the aryl groups have been studied as a function of the ligand and were shown to increase in the order NN′N < pico < pmdeta. This is explained in terms of the positioning and orientation of the pyridyl and NMe_2 groups around the metal center. The aryl rotation is found to be blocked in ortho-substituted aryl complexes, leading to atropisomerism in the pmdeta complex.

Introduction

Although neutral organometallic complexes of palladium(II) are well-known catalysts and intermediates in both organic synthesis and homogeneous catalysis,[1] the high reactivity of ionic organopalladium(II) complexes in organic transformations involving nucleophilic re-

* To whom correspondence should be addressed.
† Debye Institute.
‡ Bijvoet Center for Biomolecular Research.
§ To whom correspondence concerning crystallographic studies should be addressed.
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agents, such as carbon monoxide and alkenes, has been noticed only recently.[2,3] Examples of processes that are catalyzed by ionic palladium(II) complexes are the stereoselective arylation of alkenes using aryl triflates,[2] the alternating copolymerization of alkenes with carbon monoxide,[3a–n] the synthesis of methyl methacrylate from acetylene, CO, and methanol,[3o] and the anion controlled sequential insertion of norbornene and carbon monoxide.[4] These reports have in common that they all stress the importance of the influence the anions exert on the reactivity of the palladium(II) center toward nucleophiles. The complexes containing the more weakly coordinating anions have the strongest electrophilic character and show the higher reactivity in the arylation and copolymerization reactions.[2,3] Moreover, the anions have been shown to strongly control the stability of the insertion products.[4]

Neutral, square-planar complexes of palladium(II) contain, in most cases, one bidentate ligand or two unidentate ligands which are neutral.[1–5] Some of these complexes can be transformed into ionic monoorganopalladium complexes *via* substitution of a halide or an organic group, such as an alkyl or aryl group, for a more weakly coordinating anion. Examples of such complexes are [PdMe(MeCN)(tmeda)]OTf (tmeda = *N,N,N',N'*-tetramethylethylenediamine; OTf = trifluoromethanesulfonate),[5b] [Pd(CHMeCHMeNMe$_2$-*C,N*)(NHMe$_2$)$_2$]OTf,[6j] [PdMe(MeCN)(2,2'-bipyridyl)]BF$_4$,[7] and alkene inserted complexes like [Pd(C$_7$H$_{10}$COMe)(L$_2$)]OTf (C$_7$H$_{10}$ = *cis,exo*-norbornyl; L$_2$ = 2,2'-bipyridyl[4] or phosphine ligands[8]). The most stable ionic complexes contain a cyclometalated group[4,6,8] or an η^3-allyl group.[9] The objective of our studies is to obtain ionic monoorganopalladium(II) complexes with an organic group which is η^1-bound and is not contained within a chelating system. These complexes are generally less stable than those containing cyclometalated or η^3-allyl groups, with the exception of [PdMe(MeCN)(2,2'-bipyridyl)]BF$_4$ and related complexes.[7] An approach to this problem is to use tridentate ligands in which the three neutral ligands are linked *via* alkanediyl or arenediyl bridges, using the chelate effect to stabilize these complexes. A few complexes of this type have been reported, *e.g.* [PdMe(terpy)]I[7] and [PdMe(terpy)]Cl·2H$_2$O (terpy = 2,2':6',2''-terpyridyl).[10]

The availability of complexes containing neutral tridentate ligands is also of interest to us, as they can be compared to complexes of the anionic tridentate ligand 2,6-bis[(dimethylamino)methyl]phenyl (NCN) which has found many applications as a stabilizing ligand.[11] More recently, a variant on the NCN ligand, *i.e.* *N*-(2-benzyl)-

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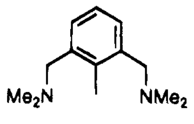
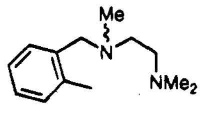


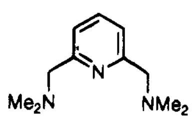
NCN



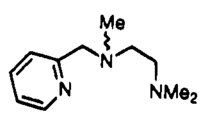
CNN

N,N',N'-trimethylethylenediamine (CNN), has been successfully applied in transition metal chemistry in our laboratory.[5h,12] For instance, NCN- and CNN-ligated late transition metal complexes have been used in the study of C–H activation processes[12] and in studies on oxidative addition of dihalides.[5h,13] Until now the chemistry of the NCN- and CNN-coordinated palladium(II) complexes has been restricted to the synthesis of the neutral complexes PdX(NCN)[14] and PdX(CNN)[5h] with X = halogen, the ionic complex $[Pd(H_2O)(NCN)]BF_4$,[14] and the chloro-bridged dinuclear complex $[(NCN)Pd(\mu\text{-}Cl)Pd(NCN)]BF_4$.[14] Attempts to replace the halide in PdX(NCN) by an organic ligand *via* transmetalation or reacting (NCN)Li with a monoorganopalladium(II) complex containing a readily displaceable ligand did not give the desired *trans*-diorganopalladium(II) complexes.

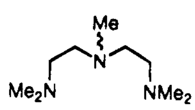
We recently reported on the use of the neutral tridentate nitrogen donor ligands 2,6-bis[(dimethylamino)methyl]pyridine (NN'N) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdeta) in the preparation



NN'N



pico



pmdeta

of ionic phenyl- and 1-naphthylpalladium(II) complexes.[15] In the present paper we describe the synthesis of complexes of the types [PdCl(N-N'-N'')]Cl and [PdR(N-N'-N'')]OTf, with R = Me or aryl and N-N'-N'' = NN'N, pmdeta, or *N,N,N'*-trimethyl-*N'*-(2-picolyl)ethylenediamine (pico). These complexes differ in flexibility of the five-membered chelate rings upon coordination to the metal and in the position and nature of the donor atoms.

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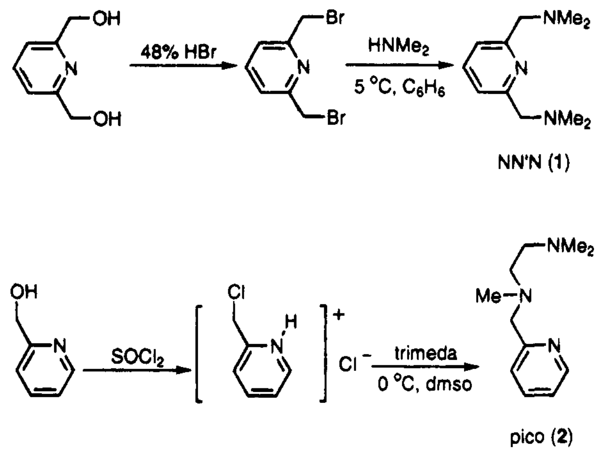
Scheme 1



trimeda = $Me_2NCH_2CH_2NHMe$

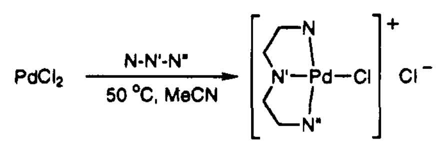
Results

In previous papers, we showed that organopalladium(II) complexes containing the chelating bis tertiary amine ligand *N,N,N',N'*-tetramethylethylenediamine (tmeda) easily undergo ligand exchange reactions.[4a,c,5a–e,i,j] A variety of $PdMe_2(L_2)$, $PdXMe(L_2)$, $PdX(COMe)(L_2)$, $PdXPh(L_2)$, and $PdMePh(L_2)$ complexes (L_2 = nitrogen and/or phosphorus donor ligands; X = Cl, Br, or I) were prepared, some of which are not currently accessible by other routes. The same method is applied here in the synthesis of the ionic complexes [PdR(N-N'-N'')]OTf, with the new tridentate nitrogen donor ligands 2,6-bis[(dimethylamino)methyl]pyridine (NN'N) and *N,N,N'*-trimethyl-*N'*-(2-picolyl)ethylenediamine (pico) and the commercially available ligand *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdeta).

Synthesis of the Ligands. The ligands NN'N (**1**) and pico (**2**) were prepared *via* the routes outlined in Scheme 1. Starting from 2,6-bis(hydroxymethyl)pyridine, we obtained NN'N (**1**) in two steps as a colorless oil in high yield (97%).

The pico ligand (**2**) was obtained in two steps, starting from 2-(hydroxymethyl)pyridine, as a colorless oil in 32% yield.

Synthesis and Properties of Ionic [PdCl(terdentate)]Cl Complexes. Addition of the tridentate ligands (NN'N, pico, or pmdeta) to an acetonitrile solution of palladium dichloride (eq 1) resulted in the formation of

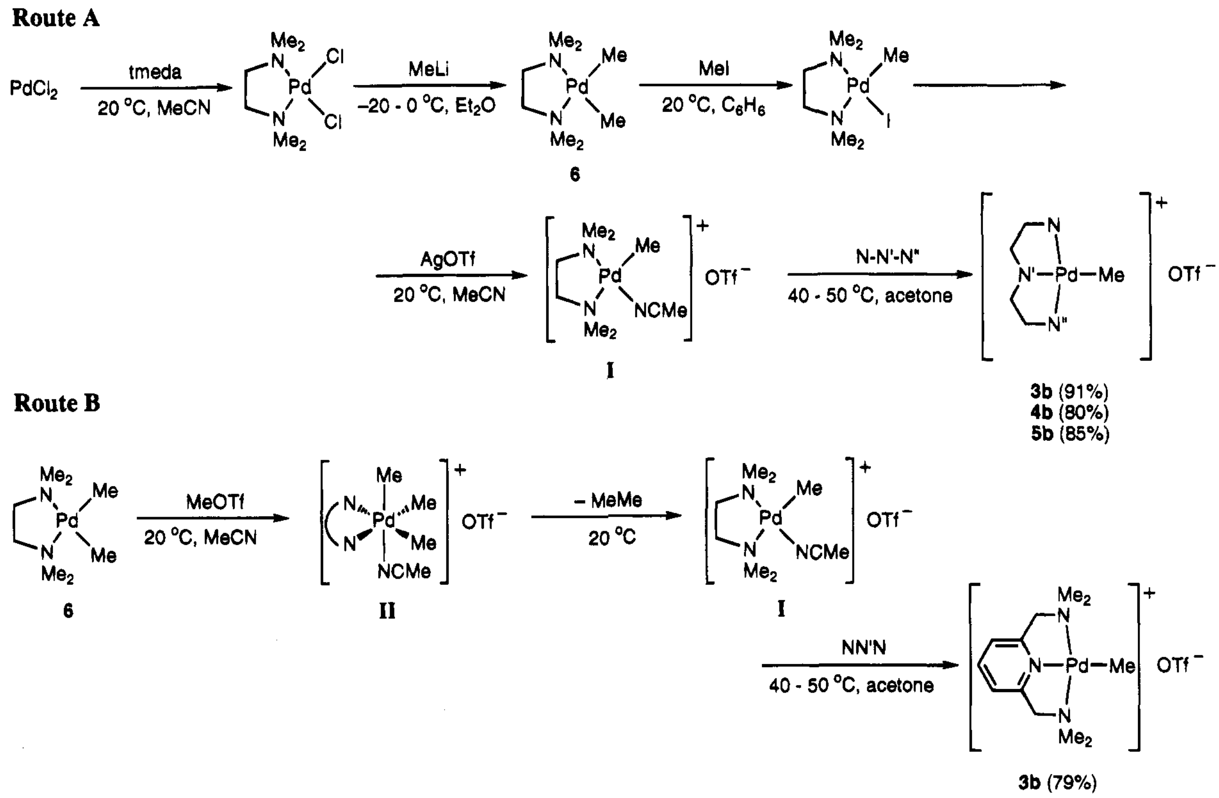


(1)

3a. N_3 = NN'N (81%)
4a. N_3 = pico (85%)
5a. N_3 = pmdta (93%)

the yellow complexes $[PdCl(NN'N)]Cl{\cdot}H_2O$ (**3a**, 81%), $[PdCl(pico)]Cl{\cdot}H_2O$ (**4a**, 85%), and [PdCl(pmdeta)]Cl (**5a**, 93%). These complexes are soluble only in strongly polar solvents like acetonitrile, methanol, or water, which is in accord with an ionic nature of **3–5a**, as neutral complexes of the type $PdCl_2$(N-N) are generally

Scheme 2



very insoluble in these solvents.[5a,b,16] The complexes were obtained in pure form by recrystallization from methanol/diethyl ether.

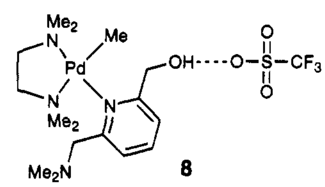
Attempts to prepare organopalladium complexes from the dichloro complexes *via* reaction with phenyl- or methyllithium in diethyl ether or tetrahydrofuran failed and gave, after aqueous workup, palladium metal, free ligand, and a quaternary ammonium salt of the ligand. An alternative method, *i.e.* substitution of one chloride by trifluoromethanesulfonate, and subsequent reaction with an organolithium reagent also was not successful.

Synthesis and Properties of the Methyl Derivatives. Scheme 2 outlines a general route for the synthesis of the complexes [PdMe(N-N′-N″)]OTf, with N-N′-N″ = NN′N (**3b**), pico (**4b**), or pmdeta (**5b**) and OTf = trifluoromethanesulfonate (triflate). These methyl complexes were obtained as beige, air-stable crystals which are soluble in polar solvents like acetone, methanol, and water. The complexes are insoluble in diethyl ether and hydrocarbon solvents. Complex **3b** could be recrystallized from methanol/diethyl ether to give crystals suitable for an X-ray structural analysis (*vide infra*).

Ionic [PdMe(MeCN)(tmeda)]OTf (**I**) is most conveniently prepared from $PdMe_2$(tmeda) (**6**) by reaction with methyl trifluoromethanesulfonate in acetonitrile solution (route B, Scheme 2).[5b] In this reaction an unstable palladium(IV) species is formed (**II**) which decomposes to **I** at −20 °C with elimination of ethane. Subsequent reaction of **I** with NN′N gives [PdMe(NN′N)]OTf (**3b**) in 79% yield. This route does not work for the other two ligands, and since PdIMe(tmeda) is more stable than **6** and can be kept without decomposition, the preferred way to prepare all of the methyl complexes is route A.

(16) Livingstone, S. E. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Exec. Ed.; Pergamon Press; Oxford, U.K., 1973; Vol 3.

As monodentate bound ligands are, in general, more easily displaced than bidentate ligands,[1] we anticipated the tridentate ligand to first substitute the MeCN ligand in **I**. By chance, we found evidence for this when we accidentally used nonpurified NN′N in the synthesis of **3b** (Scheme 2). The ligand mixture contained substantial amounts of 2-(hydroxymethyl)-6-[(dimethylamino)-methyl]pyridine (ONN′, **7**) which must have been formed *via* an incomplete bromination in the first step of the NN′N synthesis (Scheme 1). Using this NN′N/ONN′ mixture, we obtained yellow crystals of a complex with the formula [PdMe(ONN′)(tmeda)]OTf (**8**) in which the ONN′ ligand (**7**) is monodentate bound *via* the pyridyl N-donor atom. Moreover, the triflate anion is bound to the alcohol functionality on the ONN′ ligand *via* a hydrogen bond.



Solid State Structures of [PdCl(pico)]Cl (4a), [PdMe(NN′N)]OTf (3b), and [PdMe(ONN′)(tmeda)]-OTf (8). A thermal ellipsoid plot (ORTEP) of one of the two enantiomers of **4a** present in the unit cell is presented in Figure 1, with selected structural data in Table 1. The other enantiomer has identical bond distances and angles. The coordination sphere of the palladium(II) center of **4a** comprises the terdentate bound pico ligand and one of the chloride atoms. The chloride ion (C12) does not interact with the metal center, as the distance to the nearest palladium atom is 4.2617 Å.

An ORTEP representation of the cationic part of [PdMe(NN′N)]OTf (**3b**) is presented in Figure 2 with

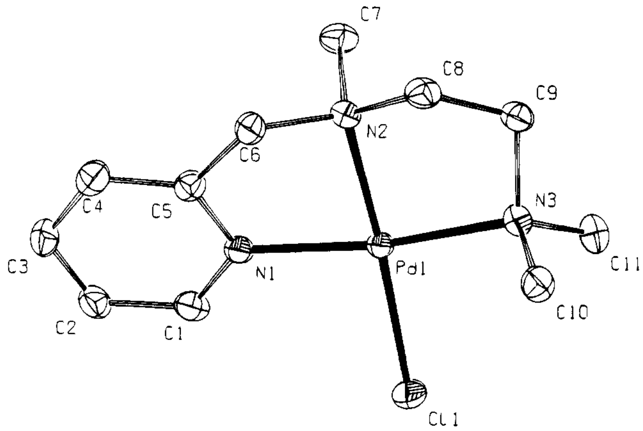


Figure 1. ORTEP drawing (50% probability level) of the cation $[PdCl(pico)]^+$ of **4a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 4a

Pd−N1	2.009(3)	Pd−N3	2.061(3)
Pd−N2	2.023(3)	Pd−Cl1	2.2878(9)
		Pd−Cl2	5.6604(13)
Cl1−Pd−N1	94.83(8)	N1−Pd−N2	81.70(12)
Cl1−Pd−N2	176.25(8)	N1−Pd−N3	168.03(12)
Cl1−Pd−N3	95.94(8)	N2−Pd−N3	87.39(12)

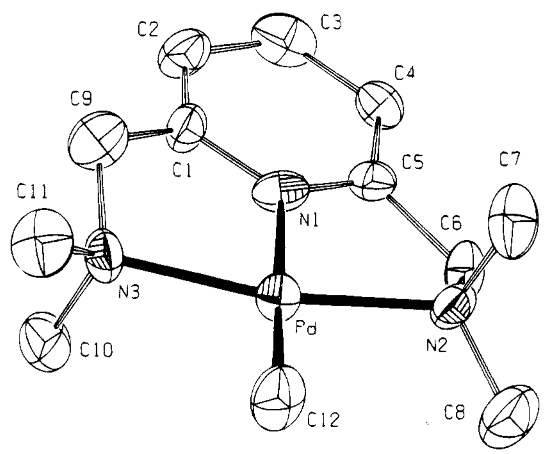


Figure 2. ORTEP drawing (30% probability level) of the cation $[PdMe(NN'N)]^+$ of **3b**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3b

Pd−N1	1.996(8)	Pd−N3	2.099(7)
Pd−N2	2.094(7)	Pd−C12	2.017(11)
N1−Pd−N2	80.9(3)	N1−Pd−N3	80.8(3)
N1−Pd−C12	177.3(4)	N2−Pd−N3	161.7(3)
N2−Pd−C12	98.9(4)	N3−Pd−C12	99.4(4)

selected structural data in Table 2. The four coordination sites in the square-planar structure are occupied by the NN′N ligand and the methyl group. The two five-membered chelate rings of the NN′N ligand are puckered with an angle of 10.4(5)° between the mean planes through N1, N2, N3, and C12 and the pyridine moiety.

In Figure 3 an ORTEP representation of the molecular structure of [PdMe(ONN′)(tmeda)]OTf (**8**) is shown. In this structure the square-planar coordination sites are occupied by the bidentate coordinated tmeda ligand, the methyl group, and the ONN′ ligand. The ONN′ ligand is clearly monodentate bound to the palladium center *via* the pyridyl nitrogen atom, with noncoordinating CH_2NMe_2 and CH_2OH groups. The triflate anion

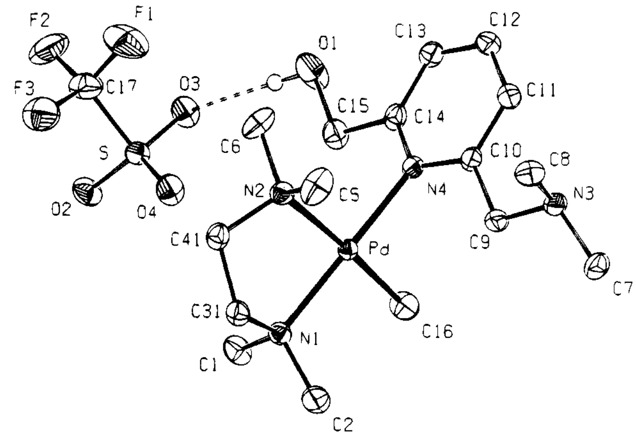


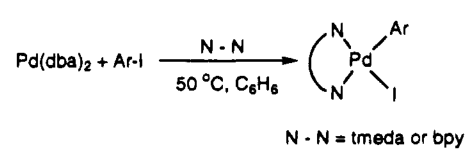
Figure 3. ORTEP drawing (50% probability level) of [PdMe(ONN′)(tmeda)]OTf (**8**). Only the major disorder component is shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 8

Pd−N1	2.087(2)	O1−O3	2.759(3)
Pd−N2	2.212(2)	O1−H14	0.83(4)
Pd−N4	2.047(2)	H14−O3	1.93(4)
Pd−C16	2.022(2)		
N1−Pd−N2	84.54(7)	N1−Pd−C16	92.82(10)
N2−Pd−N4	94.08(7)	N4−Pd−C16	88.55(10)
N1−Pd−N4	178.62(8)	N2−Pd−C16	177.25(10)
O1−H14−O3	173(4)		

is not bound to the metal but is kept in its vicinity *via* a hydrogen bond between a triflate oxygen and the hydrogen atom of the OH functionality of the ONN′ ligand. The PdMe (2.022(2) Å) and Pd−N2 bond distances (2.212(2) Å) are normal for a NMe_2 group trans to a methyl group.[5a,b,j] The N1−Pd−N2 bond angle (84.54(7)°) is normal for a bidentate bound tmeda ligand.[5a,b,j,6z] The Pd−N4(pyridyl) bond distance (2.047(2) Å) is readily comparable to the Pd−N(γ-picoline) bond distance (2.033(4) Å) trans to bpy in [PdMe(γ-picoline)(bpy)]BF_4.[7] The pyridyl ring of the ONN′ ligand is almost perpendicular to the coordination plane, as indicated by the angle (86.84(9)°) between the mean planes through Pd, N1, N2, N4, and C16, and N4, C10−C14, respectively. The hydrogen bond of the OH group of the ONN′ ligand to the triflate anion has an O1−O3 distance of 2.759(3) Å with an O3−H14 bond distance of 1.93(4) Å and an O1−H14−O3 angle of 173(4)°.

Synthesis and Properties of the Aryl Derivatives. Bis(dibenzylideneacetone)palladium(0), $Pd(dba)_2$, is an excellent starting material for the synthesis of arylpalladium(II) compounds with nitrogen-donor ligands.[5d,e,h,j,6z,15,17,18] For example, the reaction of Pd(dba)$_2$ with aryl iodides in the presence of nitrogen-donor ligands like tmeda or 2,2′-bipyridyl (bpy) gives the PdI(Ar)(N-N) complexes in high yield (eq 2).[5d,e,h,j] In



(2)

(17) Alsters, P. L.; Baesjou, P. J.; Janssen, M. D.; Kooijman, H.; Sicherer-Roetman, A.; Spek, A. L.; van Koten, G. *Organometallics* **1992**, *11*, 4124.
(18) Valk, J. M. Selective Metal-Mediated Oxidation of Naphthalenes. Dutch PhD thesis, Utrecht University, 1993.

Scheme 3

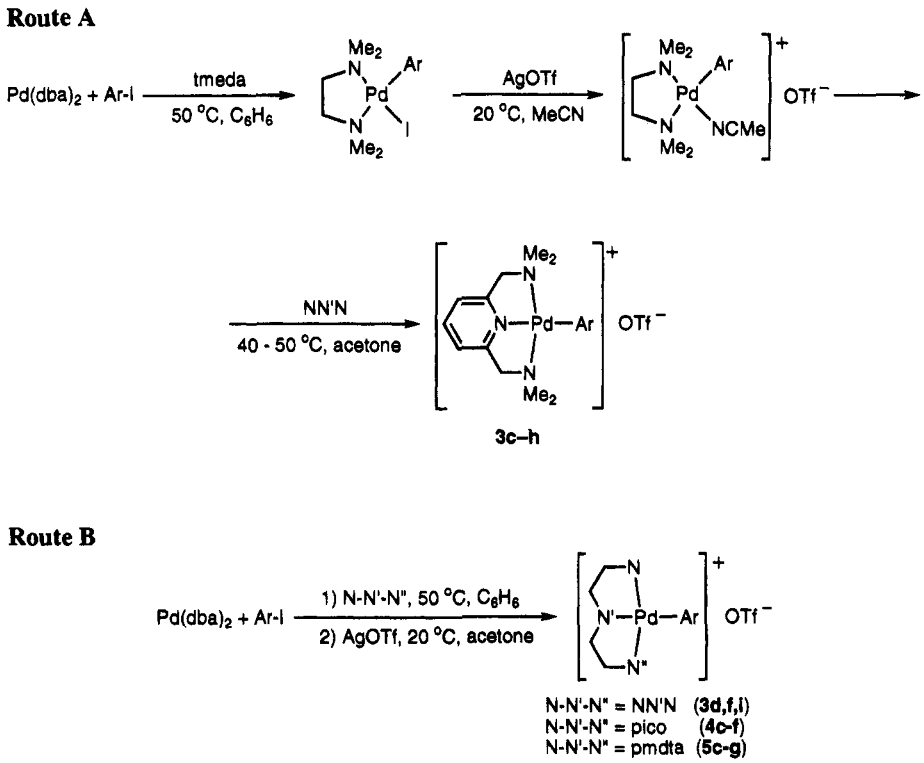


Table 4. Comparison of the Yields of the Aryl Complexes Obtained by Routes A and B (Scheme 3)

complex	group	A (%)	B (%)	complex	group	B (%)
3c	Ph	85		**4c**	Ph	82
3d	2-MePh	72	95	**4d**	4-MeOPh	77
3e	3-MePh	75		**4e**	4-O$_2$NPh	82
3f	4-O$_2$NPh	35	69	**4f**	mesityl	63
3g	2-MeOPh	63				
3h	1-naphthyl	60		**5c**	Ph	84
3i	mesityl		50	**5d**	4-MeOPh	80
				5e	4-O$_2$NPh	60
				5f	mesityl	94
				5g	2-MePh	71

contrast, aryl bromides do not react very smoothly with Pd(dba)$_2$, as was found for the synthesis of PdBrPh(N-N) complexes (N-N = tmeda or bpy; yields <20%).[5j] Exceptions to this are aryl bromides containing a potential donor group.[5h,6z,17,18]

As for the methyl complexes, the tmeda and iodide ligands should be displaceable by a terdentate coordinating N-donor ligand and a noncoordinating triflate anion (route A in Scheme 3). This route[15a] works for the NN'N ligand (Table 4), except for the mesityl derivative, and was also not successful for the pico and pmdeta ligands. As all three tridentate ligands are expected to be able to coordinate also as a bidentate ligand, we devised a more direct and simple route to these aryl derivatives (route B, Scheme 3).[15b] In this route, the intermediacy of the tmeda-coordinated complexes is omitted, resulting not only in a facile synthesis of the mesityl derivative with the NN'N ligand but also in significantly increased yields of other aryl complexes of this ligand (Table 4). An exception to this is the phenyl complex which could not be obtained in this way. This route is satisfactory for the pico and pmdeta ligands, allowing the synthesis of complexes containing aryl groups with electron donating or accepting properties, and strongly sterically hindered aryls. Both routes,

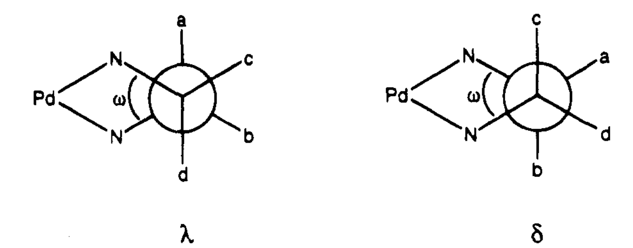


Figure 4. Nomenclature of the conformations of five-membered diamine chelates.

however, do not allow the synthesis of NN'N complexes with the para substituents chloro, acetyl, methoxy, hydroxy, amino, or *N,N*-dimethylamino, on the aryl group and the 2-tolyl complex of the pico ligand.

Conformational Analysis of the NCH$_2$CH$_2$N Fragments. All of the ^{1}H NMR spectra of the pico (**4a–f**) and pmdeta complexes (**5a–g**) show two well resolved td patterns at *ca.* 3.5–4.0 ppm. At higher field, a complex higher order pattern was observed in the case of the pico-ligated complexes, while a (sometimes poorly resolved) ddd pattern was observed for the pmdeta complexes. The td patterns can be readily assigned to the axial protons (Figure 4), as protons in the vicinity of a palladium center are generally strongly deshielded (*cf.* complex **3h** whose naphthyl[8] proton resonates at 9.29 ppm). The high field resonances were assigned to the equatorial protons. The conformation (δ or λ, see Figure 4) of the five-membered chelate rings was analyzed by means of the coupling constant method[19] (Tables 5 and 6). With an (*S*)-configuration of the NMe group of the pico ligand,[20] it is clear from Table 5 that the NCH$_2$CH$_2$N fragments strongly prefer the δ confor-

(19) (a) Sudmeier, J. L.; Blackmer, G. L. *Inorg. Chem.* **1971**, *10*, 2010. (b) Hawkins, C. J.; Peachey, R. M. *Aust. J. Chem.* **1976**, *29*, 33. (c) Hambley, T. W.; Hawkins, C. J.; Martin, J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 2505. (d) Hawkins, C. J.; Palmer, J. A. *Coord. Chem. Rev.* **1982**, *44*, 1.

Table 5. Coupling Constants[a] and Conformational Data of the NCH_2CH_2N Fragments in $[PdR(pico)]^+$ [b]

R		$^2J_{a,b}$	$^3J_{a,c}$	$^3J_{a,d}$	$^3J_{b,c}$	$^3J_{b,d}$	$^2J_{c,d}$	X	Y	ω (deg)	n_δ
Cl	**4a**	−14.00 ± 0.29	3.77 ± 0.29	0.74 ± 0.28	13.90 ± 0.29	3.29 ± 0.29	−13.82 ± 0.29	0.20 ± 0.08	3.69 ± 0.29	53.8 ± 1.2	1.09 ± 0.03
Me	**4b**	−13.36 ± 0.18	3.44 ± 0.18	0.98 ± 0.22	13.90 ± 0.17	3.67 ± 0.23	−13.69 ± 0.38	0.32 ± 0.08	4.04 ± 0.22	55.6 ± 0.7	1.08 ± 0.02
Ph	**4c**	−13.88 ± 0.10	3.57 ± 0.11	1.07 ± 0.14	13.49 ± 0.09	3.28 ± 0.11	−13.82 ± 0.10	0.30 ± 0.04	3.78 ± 0.12	54.6 ± 0.4	1.07 ± 0.01
4-MeOPh	**4d**	−13.72 ± 0.18	3.47 ± 0.18	1.09 ± 0.16	13.53 ± 0.17	3.34 ± 0.18	−13.74 ± 0.18	0.31 ± 0.02	3.90 ± 0.21	55.0 ± 1.1	1.08 ± 0.07
4-NO_2Ph[c]	**4e**										
mesityl	**4f**	−13.92 ± 0.19	3.43 ± 0.19	1.14 ± 0.20	13.63 ± 0.17	3.43 ± 0.19	−13.74 ± 0.19	0.33 ± 0.06	3.97 ± 0.23	55.5 ± 0.7	1.08 ± 0.02

[a] In Hz, values and deviations were determined by spin simulation. [b] The assignments of the protons are shown in Figure 4. [c] The resonances of protons a and d were coincidental with an NMe resonance.

Table 6. Coupling Constants[a] and Conformational Data of the NCH_2CH_2N Fragments in $[PdR(pmdeta)]^+$ [b]

R		$^2J_{a,b}$	$^3J_{a,c}$	$^3J_{a,d}$	$^3J_{b,c}$	$^3J_{b,d}$	$^2J_{c,d}$	X	Y	ω (deg)	n_δ
Cl	**5a**	−13.31 ± 0.29	3.84 ± 0.29	0.89 ± 0.72	13.82 ± 0.23	4.05 ± 0.32	−14.16 ± 0.33	0.23 ± 0.19	3.60 ± 0.28	53.5 ± 1.3	1.08 ± 0.05
Me	**5b**	−13.41 ± 0.31	3.43 ± 0.29	0.78 ± 0.46	13.70 ± 0.31	3.46 ± 0.53	−14.00 ± 0.44	0.23 ± 0.14	3.99 ± 0.35	55.1 ± 1.2	1.10 ± 0.04
Ph	**5c**	−13.33 ± 0.21	3.26 ± 0.21	0.84 ± 0.32	13.30 ± 0.20	3.40 ± 0.32	−14.04 ± 0.29	0.26 ± 0.10	3.26 ± 0.27	52.1 ± 1.2	1.04 ± 0.03
4-MeOPh	**5d**	−13.44 ± 0.12	3.32 ± 0.12	0.83 ± 0.11	13.61 ± 0.12	3.42 ± 0.12	−13.86 ± 0.12	0.28 ± 0.03	3.32 ± 0.15	52.5 ± 0.6	1.04 ± 0.01
4-NO_2Ph	**5e**	−13.42 ± 0.16	3.40 ± 0.16	0.87 ± 0.20	13.64 ± 0.15	3.72 ± 0.20	−14.33 ± 0.34	0.29 ± 0.06	4.01 ± 0.19	55.4 ± 0.6	1.09 ± 0.02
mesityl	**5f**	−13.24 ± 0.32	3.29 ± 0.32	0.97 ± 0.31	13.56 ± 0.31	3.45 ± 0.31	−14.22 ± 0.32	0.29 ± 0.10	4.12 ± 0.41	55.7 ± 1.3	1.10 ± 0.03
2-MePh	**5g**	−13.54 ± 0.17	3.40 ± 0.17	0.97 ± 0.16	13.60 ± 0.17	3.59 ± 0.17	−14.10 ± 0.17	0.29 ± 0.05	4.00 ± 0.21	55.4 ± 0.7	1.09 ± 0.02

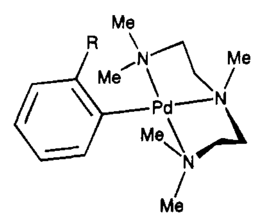
[a] In Hz, values and deviations were determined by spin simulation. [b] The assignments of the protons are shown in Figure 4.

Table 7. Activation and Thermodynamical Parameters of the Aryl Rotational Barriers in [Pd(aryl)(pico)]OTf

complex	aryl	ln A	$E_{act}^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$(298 K),[a] kJ mol^{-1}	$\Delta G^{\ddagger}$(298 K),[b] kJ mol^{-1}
4c	Ph	12 ± 1	23 ± 3	21 ± 3	−154 ± 9	67 ± 4	64[c]
4d	4-MeOPh	23 ± 4	47 ± 3	45 ± 3	−59 ± 12	63 ± 5	63[d]
4e	4-O_2NPh	22.7 ± 0.6	47 ± 2	45 ± 2	−65 ± 5	64 ± 2	63[e]

[a] Determined via line shape analysis. [b] Determined via coalescence. [c] T_c 310 K, $\Delta\delta$ 48.5 Hz. [d] T_c 305 K, $\Delta\delta$ 52.9 Hz. [e] T_c 305 K, $\Delta\delta$ 55.5 Hz.

mation ($n_\delta = 1.0$) upon coordination to palladium. The $\delta\delta$ conformation of the pmdeta ligand is defined here with respect to the view of the complexes as presented for **5a,g**. From Table 6 it is clear that all complexes

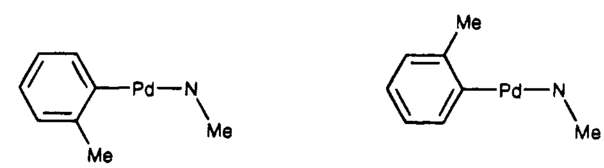


5a: R = H
5g: R = Me

prefer the $\delta\delta$ conformation. The calculated values for n_δ being slightly larger than unity is most probably due to the quality of our analysis and was not further considered. The calculated torsion angles (ω) of the pico and pmdeta complexes range from 52.1 to 55.7°.

NMR Studies of the Aryl Group Rotation. Aryl groups are, in general, oriented perpendicular to the coordination plane in the solid state, as shown by several X-ray studies of related complexes.[5d,e,j,6z] In solution, however, the aryl groups rotate freely except when rotation is sterically hindered by the ligand or the structure of the aryl group.[21]

At ambient temperature, the complexes [PdAr(pico)]-OTf (**4c–e**) show very broad resonances for the aryl group which become sharp on lowering the temperature to *ca.* 263 K. At this temperature the ortho protons have become widely separated ($\Delta\delta \approx$ 48–55 Hz, Table 7), due to the chirality of the NMe group trans to the aryl ring, rendering both the ortho and the meta protons diastereotopic. Raising the temperature above ambient causes further broadening and finally coalescence of the aryl resonances. From these studies we could calculate $\Delta G^{\ddagger}$ for the aryl rotation, including additional activation and thermodynamic parameters which were obtained *via* line shape analysis (Table 7). The mesityl (**4f**) complex shows sharp resonances at ambient temperature which do not broaden below the maximum temperature, *i.e.* the boiling point of acetone (55 °C), showing that aryl rotation is blocked in this complex.



syn anti

Figure 5. Schematic representation of the syn and anti forms of the pmdeta complex **5g**.

Even though the cation of [Pd(2-tolyl)(pmdeta)]OTf (**5g**) contains a mirror plane through the central NMe group, the palladium atom, and the aryl ring, it can exist as two possible rotamers, *i.e. syn*-Me,Me or *anti*-Me,Me (Figure 5), due to the fixed chirality of the central N-donor atom. According to the NMR spectra of **5g** only one of these is present, and thus rotation of the aryl group must be blocked in this complex as in the pico complex **4f**. The complexes [PdAr(pmdeta)]OTf (**5c–e**) show two sharp, separated resonances for the ortho protons at ambient temperature. Aryl rotation is thus also blocked in these complexes and leads to one syn and one anti positioned ortho proton with respect to the central NMe group (*cf.* Figure 5). Raising the temperature to the maximum of 55°C (*vide supra*) only causes broadening of the resonances, indicating that $\Delta G^{\ddagger}$ for

(20) In Figure 1, the enantiomer of the pico complex **4a** is shown with the (*R*)-configuration for the NMe group and with the CH_2CH_2 moiety having the λ conformation. Because the two enantiomers have a reversed preference for the conformation of the CH_2CH_2 moiety, the enantiomer with the (*S*)-configuration will show the δ conformation.

(21) See for example: Terheijden, J.; van Koten, G.; Grove, D. M.; Vrieze, K.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1987**, 1359.

the aryl rotation in these complexes is well above ~67 kJ mol^{-1}. The mesityl (**5f**) complex behaves similarly to **5g** and the pico complex **4f**.

As the NN'N ligand does not cause diastereotopicity of the aryl protons, the rotation of the aryl ring could not be analyzed in the same way as the pico and pmdeta ligands for the complexes containing symmetrical aryl groups. In the case of ortho- and meta-substituted aryl groups, the protons of the CH_2 group of the NN'N ligand will become diastereotopic and show an AB pattern when rotation of the aryl is slow on the NMR time scale. The room temperature ^1H NMR spectra of the 2-tolyl (**3d**), 3-tolyl (**3e**), 2-MeOPh (**3g**), and 1-naphthyl (**3h**) derivatives exhibit an AB pattern for **3d** and **3h** and a singlet for **3e** and **3g**. The ^{13}C NMR spectra show two resonances for the NMe_2 groups of **3d**, **3g**, and **3h**, and a single one for **3e**. These results indicate that aryl rotation is blocked in all these complexes except for **3e**. The observation of the singlet instead of an AB pattern for the CH_2 protons in **3g** is ascribed to the fact that the methoxy group causes only a very small difference in chemical shift between the two protons. This is supported by the smaller $\Delta\delta$ for the two NMe_2 resonances of **3g** (0.19 ppm) compared to **3d** (0.27 ppm) and **3h** (0.67 ppm).

Discussion

Ionic Palladium(II) Complexes with Tridentate Nitrogen-Donor Ligands. Ionic monomethylpalladium(II) complexes with tridentate N-donor ligands are now available *via* the general, high yield synthesis presented in Scheme 2 (route A). The very similar route (B, Scheme 2) allows, however, only the synthesis of the NN'N complex **3b**. Both routes proceed *via* the ionic intermediate [PdMe(MeCN)(tmeda)]OTf (**I**) and differ only in the secondary products formed, *i.e.* silver iodide (route A) or ethane (route B). This may imply that a trace amount of residual AgI or AgOTf assists with the ligand-exchange reaction of tmeda for the pico and pmdeta ligands. Due to the superiority of route A this was not further pursued. Other routes to ionic methylpalladium(II) complexes bearing tridentate nitrogen donor ligands were reported by the groups of Vrieze[10] and Canty.[7] The latter reported the synthesis of [PdMe(terpy)]I (terpy = 2,2':6',2''-terpyridyl) from the reaction of $[PdMe(SMe_2)(\mu\text{-}I)]_2$ and the terpy ligand in 87% yield. Vrieze *et al.* used PdClMe(1,5-cyclooctadiene) to obtain the ionic complexes [PdMe(terpy)]Cl·$2H_2O$ (96%) and [PdMe(*i*Pr-DIP)]OTf (*i*Pr-DIP = 2,6-bis[(*N*-isopropylcarbaldimino)]pyridine) for which no yield was reported.[10] Although both reagents contain ligands which are suitable for ligand-exchange reactions, they are less stable than our starting complex PdIMe(tmeda), which is easily prepared and can be stored at room temperature in air.[5b] Interestingly, the terpy ligand is able to displace both iodide and chloride from the metal, while the ligands NN'N, pico, pmdeta, and *i*Pr-DIP cannot. This is most probably due to the steric problems caused by the greater rigidity of the terpy ligand even though reports have appeared in which terpy coordinates in a bidentate fashion.[22] The isolation of the ionic methyl complexes shows that the palladium–carbon bond is strongly affected by the other groups on the metal center in complexes containing terdentate bound ligands, as attempts to prepare analogous complexes of the anionic aryl-derived NCN and CNN ligands (see Introduction) have failed so far. Why the neutral N-donor ligands are better stabilizing ligands than the NCN and CNN ligands is still a subject of investigation. We can exclude, however, that the anionic character of the NCN and CNN ligands must be held responsible because we recently found that the reaction of PdCl(C'NN) (C'NN = $CH_2C_6H_2(CH_2N(Me)(CH_2CH_2NMe_2)$-2-$Me_2$-3,5)) with methyllithium readily afforded the *cis*-dialkyl complex PdMe(C'NN).[5h] Similarly, the complex PdMePh(tmeda), in which the aryl ring is not contained within an intramolecular coordination system, can also be readily obtained.[5d,j] In this complex the aryl ring is perpendicular to the coordination plane,[5j] while the CNN and NCN ligated complexes the aryl ring is forced into this plane.[5h,14,21] From these results it is clear that not only the nature of the groups (aryl or alkyl) but also, in the case of a mixed aryl–alkyl system, their positioning (cis or trans) and the orientation of the aryl ring, with respect to the coordination plane, are important in the stability of diorganopalladium(II) complexes.

The earlier reported route to the aryl complexes (A, Scheme 3) suffered some limitations with respect to aryls containing electron-withdrawing substituents (4-$O_2NC_6H_4$) or aryls which are strongly sterically demanding (mesityl). The present results show that our new and complementary route (B, Scheme 3) now allows synthesis of the mesityl derivative and significantly increased the yields of at least some of the other complexes (Table 4). Nevertheless, some para-substituted aryl complexes of the NN'N ligand could not be obtained in pure form *via* either route. These substituents include NMe_2, NH_2, OH, OMe, COMe, and Cl. In these cases, the oxidative addition reaction proceeds normally, but upon addition of AgOTf no product could be isolated. No such problems were encountered for the complexes of the other two ligands, except for the 2-tolyl complex of the pico ligand.

Most of the bond distances and angles in the molecular structure of [PdCl(pico)]Cl (**4a**, Figure 1) are readily comparable to the structure of the neutral complex PdI(CNN).[6z] Only the Pd–N bond trans to the phenyl group in PdI(CNN) is much longer (2.193(4) Å) than the same bond trans to the N(pyridyl) in **4a** (2.061(3) Å). This reflects the much greater trans influence of a σ-bound carbon donor compared to a coordinated nitrogen donor. Nevertheless, the Pd–NMe bond distances, *i.e.* 2.065(4) for PdI(CNN) and 2.023(3) Å for **4a**, show only a small difference. The complexes [PdMe(NN'N)]OTf (**3b**) and [PdCl(pico)]Cl (**4a**) both show features comparable to those of the earlier reported terdentate N-donor complexes [PdCl(terpy)]Cl·$2H_2O$,[23a] [Pd(OH)(terpy)]ClO_4·H_2O,[23b] [PdCl{2,6-bis(2-imidazolin-2-yl)pyridine}]Cl·H_2O,[23c] and [PdMe(terpy)]Cl·$2H_2O$.[10a] These features include a short Pd–N(central) bond distance and a small trans N–Pd–N bond angle (see Tables 1

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and 2). These deviations can be due to the terdentate bonding mode of the N-donor ligand whose C–C and C–N bonds within the chelate rings cannot accommodate an ideal square-planar geometry around the palladium center. In contrast, the complex [Pd(C_6H_4-*o*-C_7H_{11})(pmdeta)]OTf (C_7H_{11} = 2-*exo*-norbornyl)[15b] contains at least two longer bond lengths within the chelate framework and has nevertheless a smaller trans N–Pd–N bond angle (164.7(2)°) than **4a**. All three complexes discussed here differ, however, in the positioning of the types of N-donor atoms and in the type of anionic ligand (C or Cl), all of which differ widely in trans influence. Therefore, the observed Pd–N(central) bond distance and trans N–Pd–N bond angle may result from a combination of the ligand trying to accommodate the square-planar geometry and the relative trans influences. The Pd–N1 bond distance (2.009(3) Å) of **4a**, which is relatively short for a Pd–N(pyridyl) trans to a NMe_2 group compared to the one found in **8** (2.087(2) Å), probably also results from the same combination of factors. The Pd–N3 (2.061(3) Å) bond distance in **4a** is, however, normal for Pd–N(sp^3) bonds trans to groups with a low trans influence.[4c] The Pd–Me bond distance in **3b** (2.017(11) Å) is short but is normal for a methyl trans to a N(pyridyl).[5e,j,7,10a,24] The two Pd–N2 and –N3 (NMe_2) bond distances of **3b** are approximately the same, *i.e.* 2.094(7) and 2.099(7) Å, respectively, and are normal for trans-positioned NMe_2 groups (2.075–2.115 Å).[17,21] They are, however, significantly longer than the Pd1–N3 bond distance in **4a**.

As observed in the structure of **8** (Figure 3), the pyridyl group of the ONN′ ligand (**7**) easily displaces the acetonitrile ligand in **I**. A similar course of reaction is expected for the tridentate N-donor ligands. This implies that, after the initial coordination of the N(pyridyl) group, a rearrangement is necessary because the N(pyridyl) donor is trans to the methyl group in the final product. The question which now arises is whether this rearrangement occurs via a five- or three-coordinate intermediate. Several X-ray and NMR studies of palladium and platinum complexes, having a weak interaction of an O- or N-donor ligand as an apical, fifth ligand, have been reported.[6a,g,q,s,t,10b,25] For example, Vrieze *et al.* have prepared five-coordinate complexes containing tridentate N(imine)-donor ligands, *i.e.* Pd(Me)(Cl)(6-RC_5H_3N-2-(H)C=NCH_2CH_2-2-C_5H_4N) with R = H or Me, which were characterized by NMR.[10b] In contrast, when tertiary amine donors are present as a potential fifth ligand, *e.g.* as in Pd($C_6H_4CH_2NMe_2$-2-*C*)(C_6F_5)(1,10-phenanthroline),[26] no interaction with the palladium atom is observed. There are, however, also complexes of imine donors known that are not five-coordinate. For example, in the complexes $PdCl_2$(α-diimine)$_2$ (*e.g.* α-diimine = bis(1,1′-*tert*-butyl)diimine) only two of the four imine donors are connected to the metal center.[27] This is clearly evidenced by the low field shift of one of the imine protons (~9.4–9.9 ppm) which is positioned above the palladium atom when the diimine is monodentate coordinated. The positions in which the Me_2NCH_2 group is expected to coordinate as a fifth ligand are in either the axial position of a square pyramid or an equatorial position of a trigonal bipyramid. Both positions are predicted to be unfavorable, on the basis of the extended Hückel calculations reported by Rossi and Hoffmann,[28] because the N-donor atom cannot act as a π-acceptor but has only σ-donor capacity. It is therefore not surprising that in the molecular structure of **8** the Me_2NCH_2 group is turned away from the metal center even though close examination of the crystal structure shows that there is abundant space in the axial positions on the metal center to allow coordination. This does not mean, however, that a five-coordinate intermediate cannot be formed during the rearrangement.

Conformational Analysis and Aryl Rotation. The conformational analyses of the NCH_2CH_2N moieties in the pico and pmdeta complexes show that these occur only in the δ (pico) or the $\delta\delta$ (pmdeta) conformation. These analyses of the pico and pmdeta complexes agree with the observed δ and $\delta\delta$ conformations in the X-ray molecular structures of the complexes [PdCl(pico)]Cl (**4a**, *vide supra*)[20] and [Pd(C_6H_4-*o*-C_7H_{11})(pmdeta)]OTf (C_7H_{11} = 2-*exo*-norbornyl).[15b] The calculated NCCN torsion angles ((52–56) ± 1°) are within experimental error of the observed angles for the pico (56.7(4)°) and pmdeta complexes (58.0(9) and 58.2(8)°)[15b] and the related complex PdI(CNN) (58.3(5)°).[5h]

Comparison of the ^1H NMR spectra of the aryl complexes shows that the aryl-rotation process is strongly dependent on the ligand and on the presence of ortho substituents. The energy of this process increases in the order NN′N < pico < pmdeta. Dissociation of one arm of the terdentate ligand does not appear to occur as part of the aryl rotation process since this would allow rotation to occur for the 2-tolyl complexes. The trans N–Pd–N bond angles of the NN′N (161.7(3)°) and pmdeta (164.7(2)°) complexes are similar, and thus steric effects on the aryl group rotation presumably arise from the different number (1 or 2) and positioning of the NMe_2 methyl groups. In the NN′N complexes the chelate rings are puckered (Figure 2), causing the two equatorial methyl groups to be in the coordination plane and the two axial methyls to be perpendicular to this plane. However, the NMe_2 methyl groups in the pico and pmdeta complexes are positioned at equal distances from the coordination plane as a consequence of the δ conformation of the NCCN moieties. Effectively, the NN′N and pico complexes have two NMe_2 groups hindering the aryl rotation, while the pmdeta complexes have four such groups. In addition to this, the pico complexes contain a pyridyl group whose H6 atom lies in the coordination plane and is expected to hinder the rotation also. Taking all these features into account, the order in which aryl rotation is expected to be more

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difficult is NN′N < pico < pmdeta. This is in agreement with the observed order.

Examination of the thermochemical data in Table 7 for the aryl rotation in the pico complexes **4c**–**e** reveals two major aspects. Firstly, $\Delta S^{\ddagger}$ has a large negative value in the transition state of the aryl rotation process. Secondly, the parameters for the 4-MeOPh (**4d**) and 4-O_2NPh (**4e**) complexes are similar but differ significantly from the unsubstituted phenyl (**4c**) complex. The negative value for $\Delta S^{\ddagger}$ suggests a more ordered situation in the transition state compared to the starting and final states. This is consistent with the conclusion above that Pd–N bond breakage does not occur during aryl rotation. As the parameters have been determined in acetone, which is a polar and coordinating solvent, it may be that the value of $\Delta S^{\ddagger}$ is partly determined by the interaction of the complexes with the solvent. The observed differences between complexes **4d**,**e** and **4c** may be related to the interaction of the solvent with the polar groups present in the former complexes, and this may be affected by differences in Pd–aryl bonding during rotation.

The blocked rotation observed in the ortho-substituted aryl complexes (**3d**,**g**,**h**,**i** and **5g**) has been noticed before in the related neutral platinum complex Pt(2-tolyl)(NCN).[21] In the case of [Pd(2-tolyl)(pmdeta)]OTf (**5g**), only one of the two possible isomers is observed, which, according to molecular models, is the syn isomer (Figure 5). This is also in agreement with the syn geometry of [Pd(C_6H_4-*o*-C_7H_{11})(pmdeta)]OTf.[15b] The blocked aryl rotation of **5g** is a good example of a type of atropisomerism related to that observed for binaphthyls and homo- or heteroleptic diarylpalladium(II) compounds of the type *cis*-Pd(C-N)$_2$ (C-N = cyclometalated aryl group as, for instance, $C_6H_4CH_2NMe_2$-*C*,*N*).[18]

Conclusions

The ionic compounds [PdR(N-N′-N″)]OTf and [PdCl-[N-N′-N″)]Cl, with the tridentate ligands 2,6-bis[(dimethylamino)methyl]pyridine (NN′N), *N*,*N*,*N*′-trimethyl-*N*′-(2-picolyl)ethylenediamine (pico), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdeta), have been obtained in high yields by convenient routes. Both the methyl derivatives and the first examples of a wide variety of aryl derivatives allow comparative studies of alkyl and aryl complexes, and aryl complexes with different substituents. The ligands presented here have widely differing steric properties accounting for pronounced differences in the aryl rotation process. This process is, to a lesser extent, also influenced by the substituents on the aryl ring except for ortho substitution which results in the occurrence of atropisomerism.

The ionic complexes presented here are not susceptible toward electrophilic attack by water or alcohols in which they are soluble without decomposition.[29] The interesting behavior of the ionic complexes toward nucleophilic reagents, like carbon monoxide[30a] and alkenes,[30b] and during fragmentation in a tandem mass spectrometer[30c] will be reported in future papers.

(29) The complexes do react, however, with strong electrophiles like dihalogens. For example, the reaction of [PdPh(NN′N)]OTf (**3c**) with I_2 yields iodobenzene and [PdI(NN′N)]OTf quantitatively. The products were identified by GC–MS, NMR, and elemental analysis. The expected palladium(IV) intermediate was not observed. Currently, we are further investigating and extending this chemistry.

Experimental Section

General Procedures. All operations were conducted in an atmosphere of dry nitrogen with the use of established Schlenk-type techniques. Benzene was freshly distilled from sodium benzophenone ketyl. All other solvents were used as received. The solvents acetonitrile (pa), acetone (pa), methanol (pa), and dimethyl sulfoxide and the compounds iodomethane, iodobenzene, 2-iodotoluene, 3-iodotoluene, 2-iodoanisole, 4-iodoanisole, 1-iodo-4-nitrobenzene, 1-iodonaphthalene, 2-bromomesitylene, triethylamine, and iodine were obtained from Janssen Chimica. Dimethylamine was obtained from Fluka. The materials Celite (filter aid), 2,6-bis(hydroxymethyl)pyridine, 2-(hydroxymethyl)pyridine, *N*,*N*,*N*′-trimethylethylenediamine, methyl trifluoromethanesulfonate (MeOTf), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, and silver trifluoromethanesulfonate (AgOTf) were obtained from Aldrich. The reagents 2,6-bis(bromomethyl)pyridine,[31] (2-chloromethyl)-pyridine–hydrochloric acid[32] PdIMe(tmeda),[5a,b] PdMe$_2$(tmeda),[5a,b] and 2-iodomesitylene[33] were prepared following literature procedures. The NMR solvents $CDCl_3$, CD_3OD, and CD_3COCD_3 were obtained from ISOTECinc. ^{1}H (200 or 300 MHz) and ^{13}C (50 or 75 MHz) NMR spectra were recorded on Bruker AC200 or AC300 spectrometers at ambient temperature unless otherwise noted. Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Accurate chemical shifts and coupling constants for conformational analyses were obtained using IvorySoft's geNMR simulation program (version 3.4 for MS-DOS). Elemental analyses were performed by the Institute for Applied Chemistry (TNO), Zeist, The Netherlands, and by Dornis u. Kolbe, Mülheim a. d. Ruhr, Federal Republic of Germany.

2,6-Bis[(dimethylamino)methyl]pyridine (1, NN′N). Dimethylamine (18 g, 400 mmol) was quickly added to 30 mL of precooled (*ca.* 5 °C) benzene after which a solution of 2,6-bis(bromomethyl)pyridine (10.55 g, 40 mmol) in 80 mL of benzene was added dropwise within 30 min. After stirring at room temperature for another 0.5 h the reaction mixture was filtrated over a Büchner funnel. The residue was washed with diethyl ether, and the combined benzene/diethyl ether solutions were evaporated *in vacuo* to give a yellow liquid. After distillation at 47–48 °C and 0.04 mmHg a colorless liquid was obtained. Yield: 7.45 g (97%). ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.23 (s, 12, NMe$_2$), 3.51 (s, 4, CH$_2$), 7.32 (d, ^3J = 7.6 Hz, 2, Py[3,5]), 7.69 (t, ^3J = 7.6 Hz, 1, Py[4]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 45.87 (NMe$_2$), 66.52 (CH$_2$), 121.50 (Py[3,5]), 137.28 (Py[4]), 159.62 (Py[2,6]). Anal. Calcd for $C_{11}H_{19}N_3$: C, 68.35; H, 9.91; N, 21.74. Found: C, 67.73; H, 9.43; N, 21.77.

***N*,*N*,*N*′-Trimethyl-*N*′-(2-picolyl)ethylenediamine (2, pico).** To a solution of 22.7 g (0.14 mol) of (2-chloromethyl)-pyridine–hydrochloric acid in 60 mL of dimethyl sulfoxide was added 60 mL (0.42 mol) of triethylamine upon which a white solid immediately precipitated. After the reaction mixture was stirred for another 5 min, 21 mL (0.16 mol) of *N*,*N*,*N*′-trimethylethylenediamine (trimeda) was added to the mixture, after which stirring was continued for 4 h at 70 °C. The mixture was rendered basic with NaOH (aqueous), and saturated NH$_4$Cl (aqueous) was added for a better separation. The layers were separated, and the water layer was extracted with diethyl ether and chloroform. The combined ether and chloroform layers were washed with NH$_4$Cl (aqueous) and

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dried on magnesium sulfate. After the volatiles were removed *in vacuo*, the resulting brown oil was distilled at 0.05 mmHg and the product collected at 67 °C. Yield: 8.5 g (32%). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 2.15 (s, 6, NMe_2), 2.23 (s, 3, NMe), 2.44 (AA′BB′, 4, CH_2CH_2), 3.62 (s, 2, CH_2), 7.07 (dd, ^3J = 7.3 and 4.7 Hz, 1, Py[5]), 7.36 (d, ^3J = 7.3 Hz, 1, Py[3]), 7.57 (td, 2 × ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1, Py[4]), 8.47 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 1, Py[6]). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 42.80 (NMe); 45.84 (NMe_2); 55.55, 57.41, 64.41 (CH_2); 121.86, 123.08, 136.28, 149.01, 159.36 (Py). Anal. Calcd for $C_{11}H_{19}N_3$: C, 68.35; H, 9.91; N, 21.74. Found: C, 68.44; H, 9.87; N, 21.83.

Chloro{2,6-bis[(dimethylamino)methyl]pyridine}palladium Chloride Monohydrate (3a). Palladium dichloride (177 mg, 1.0 mmol) was dissolved with stirring in acetonitrile (10 mL) for 1 h at 50 °C. To this was added 2,6-bis[(dimethylamino)methyl]pyridine (230 mg, 1.2 mmol). The volatiles were removed *in vacuo*, and the residue was washed with diethyl ether (3 × 5 mL). The residue was dried *in vacuo*, leaving 300 mg (81%) of a yellow crystalline solid. Recrystallization was performed from methanol/diethyl ether. Mp: >200 °C. ^{1}H NMR (300 MHz, CD_3OD, δ): 2.89 (s, 12, NMe_2), 4.50 (s, 4, CH_2), 7.58 (d, ^3J = 8.0 Hz, 2, Py[3,5]), 8.15 (t, 2 × ^3J = 8.0 Hz, 1, Py[4]). ^{13}C NMR (75 MHz, CD_3OD, δ): 53.20 (NMe_2), 74.62 (CH_2), 122.29 (Py[3,5]), 142.65 (Py[4]), 160.11 (Py[2,6]). Anal. Calcd for $C_{11}H_{19}N_3Cl_2Pd{\cdot}H_2O$: C, 34.00; H, 5.45; N, 10.81. Found: C, 34.85; H, 5.40; N, 10.93.[34] Complexes **4a** and **5a** were prepared analogously to the procedure for **3a**.

Chloro{*N,N,N′*-trimethyl-*N′*-(2-picolyl)ethylenediamine}palladium Chloride Monohydrate (4a). Yield: 85%. Mp: >200 °C. ^{1}H NMR (200 MHz, CD_3OD, δ): 2.86 (s, 3, NMe_2), 2.94 (m, ABXY, 1, CH_2CH_2 eq), 2.96 (m, ABXY, 1, CH_2CH_2 eq), 3.04 (s, 3 NMe_2), 3.15 (s, 3, NMe), 3.78 (m, ABXY, 1, CH_2CH_2 ax), 4.15 (m, ABXY, 1, CH_2CH_2 ax), 4.27 (d, AX, ^2J = 15.4 Hz, 1, CH_2), 5.33 (d, AX, ^2J = 15.4 Hz, 1, CH_2), 7.63 (dd, ^3J = 5.6 and 7.8 Hz, 1, Py[5]), 7.77 (d, ^3J = 7.8 Hz, 1, Py[3]), 8.21 (td, 2 × ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1, Py[4]), 8.66 (dd, ^3J = 5.6 Hz, ^4J = 1.2 Hz, 1, Py[6]). ^{13}C NMR (50 MHz, CD_3OD, δ): 46.83 (NMe); 50.50, 53.01 (NMe_2); 61.21, 67.49, 68.84 (CH_2); 124.68, 125.74 (Py[3,5]); 141.96 (Py[4]); 151.70 (Py[2]); 164.47 (Py[6]). Anal. Calcd for $C_{11}H_{19}N_3Cl_2Pd{\cdot}H_2O$: C, 34.00; H, 5.45; N, 10.81. Found: C, 34.12; H, 5.55; N, 10.82.[34]

Chloro{*N,N,N′,N″,N″*-pentamethyldiethylenetriamine}palladium Chloride (5a). Yield: 93%. Mp: 182 °C dec. ^{1}H NMR (200 MHz, CD_3OD, δ): 2.63 (s, 6, NMe_2), 2.68 (m, 2, CH_2CH_2 eq), 2.73 (m, 2, CH_2CH_2 eq), 2.98 (s, 6, NMe_2), 3.05 (s, 3, NMe), 3.54 (m, 2, CH_2CH_2 ax), 3.95 (m, 2, CH_2CH_2 ax). ^{13}C NMR (75 MHz, CD_3OD, δ): 44.65 (NMe); 51.66, 53.23 (NMe_2); 62.00, 67.12 (CH_2). Anal. Calcd for $C_9H_{23}N_3Cl_2Pd$: C, 30.83; H, 6.61; N, 11.98. Found: C, 30.71; H, 6.73; N, 11.91.

General Procedure (Route A) for the Synthesis of the Methyl Complexes 3–5b. A typical procedure is described for the synthesis of [PdMe(NN′N)]OTf (**3b**). To a solution of 0.36 g (0.10 mmol) of PdIMe(tmeda) in 30 mL of acetonitrile was added 0.26 g (0.10 mmol) of silver trifluoromethanesulfonate. The solution was stirred for 2 min, the silver iodide was removed by centrifugation (2400 rpm, 2 min), and the volatiles were removed *in vacuo*. The residue was dissolved in 30 mL of acetone and 0.22 g (0.11 mmol) of 2,6-bis[(dimethylamino)methyl]pyridine (**1**) was added. After the mixture was stirred for 1 h at 40–50 °C, the acetone solution was evaporated *in vacuo*. The residue was recrystallized from methanol/diethyl ether. Yield: 0.42 g (91%) of yellowish needles.

Methyl{2,6-bis[(dimethylamino)methyl]pyridine}palladium Trifluoromethanesulfonate (3b). Yield: 91%. Mp: 131–133 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 0.22 (s, 3, PdMe), 2.88 (s, 12, NMe_2), 4.49 (s, 4, CH_2), 7.62 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.10 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 1.55 (PdMe), 52.44 (NMe_2), 74.19 (CH_2), 121.80 (Py[3,5]), 141.02 (Py[4]), 155.79 (Py[2,6]). Anal. Calcd for $C_{13}H_{22}N_3F_3O_3PdS$: C, 33.67; H, 4.78; N, 9.06. Found: C, 33.52; H, 4.68; N, 9.08.

Methyl{*N,N,N′*-trimethyl-*N′*-(2-picolyl)ethylenediamine}palladium Trifluoromethanesulfonate (4b). Yield: 80%. Mp: 128 °C. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 0.45 (s, 3, PdMe), 2.64 (s, 3, NMe_2), 2.74 (s, 3, NMe), 2.91 (m, ABXY, 1, CH_2CH_2 eq), 2.93 (m, ABXY, 1, CH_2CH_2 eq), 2.96 (s, 3, NMe_2), 3.68 (m, ABXY, 1, CH_2CH_2 ax), 3.79 (m, ABXY, 1, CH_2CH_2 ax), 4.20 (d, ^2J = 15.1 Hz, 1, CH_2), 4.85 (d, ^2J = 15.1 Hz, 1, CH_2), 7.60 (dd, ^3J = 5.5 and 7.8 Hz, 1, Py[5]), 7.71 (d, ^3J = 7.8 Hz, 1, Py[3]), 8.12 (td, 2 × ^3J = 7.8 Hz, ^4J = 1.1 Hz, 1, Py[4]), 8.35 (dd, ^3J = 5.5 Hz, ^4J = 1.1 Hz, 1, Py[6]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 3.43 (PdMe); 42.88 (NMe); 50.42, 52.41 (NMe_2); 57.02, 65.40, 68.25 (CH_2); 125.47, 125.95 (Py[3,5]); 140.78 (Py[4]); 150.43 (Py[2]); 165.34 (Py[6]). Anal. Calcd for $C_{13}H_{23}N_3F_3O_3PdS$: C, 33.66; H, 4.78; N, 9.06. Found: C, 33.69; H, 4.79; N, 8.97.

Methyl{*N,N,N′,N″,N″*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5b). Yield: 85%. Mp: 126–128 °C. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 0.12 (s, 3, PdMe), 2.59 (s, 6, NMe_2), 2.64 (m, 2, CH_2CH_2 eq), 2.75 (s, 3, NMe), 2.76 (m, 2, CH_2CH_2 eq), 2.85 (s, 6, NMe_2), 3.47 (m, 2, CH_2CH_2 ax), 3.70 (m, 2, CH_2CH_2 ax). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 3.71 (PdMe); 41.14 (NMe); 51.35, 52.58 (NMe_2); 57.48, 67.69 (CH_2). Anal. Calcd for $C_{11}H_{26}N_3F_3O_3PdS$: C, 29.77; H, 5.91; N, 9.47. Found: C, 29.80; H, 6.03; N, 9.38.

Alternative Synthesis (Route B) of [PdMe(NN′N)]OTf (3b). To a vigorously stirred solution of $PdMe_2$(tmeda) (3.04 g, 12 mmol) in acetonitrile (20 mL) was added dropwise methyl trifluoromethanesulfonate (1.98 g, 12 mmol). Stirring was continued for 20 min, and then the volatiles were removed *in vacuo*. The residual oil was taken up in acetone (20 mL), treated with 2,6-bis[(dimethylamino)methyl]pyridine (**1**, 2.76 g, 14.4 mmol) and subsequently stirred for 1 h at 40–50 °C. After the volatiles were removed *in vacuo*, the residue was treated with acetone (20 mL) and the mixture was evaporated to dryness. This procedure was repeated twice. Finally, the residue was washed three times with diethyl ether (3 × 5 mL) and dried *in vacuo*. Yield: 4.42 g (79%).

Methyl{2-(hydroxymethyl)-6-[(dimethylamino)methyl]pyridine}{*N,N,N′,N′*-tetramethylethylenediamine}palladium(II) Trifluoromethanesulfonate (8). ^{1}H NMR (300 MHz, CD_3COCD_3 + 5% C_6D_6, δ): 0.28 (s, 3, PdMe), 2.31 (s, 6, NMe_2), 2.38 (s, 6, NMe_2), 2.74 (s, 6, NMe_2), 2.84 (m, AA′BB′, 4, CH_2CH_2), 4.50 (AB, $^2J \approx$ 15 Hz, 1, $PyCH_2$), 4.54 (AB, $^2J \approx$ 15 Hz, 1, $PyCH_2$), 5.18 (d, AX, ^2J = 15.7 Hz, 1, $PyCH_2$), 5.84 (d, AX, ^2J = 15.7 Hz, 1, $PyCH_2$), 7.77 (d, ^3J = 7.7 Hz, 1, Py[3,5]), 7.83 (d, ^3J = 7.7 Hz, 1, Py[3,5]), 8.03 (t, 2 × ^3J = 7.7 Hz, 1, Py[4]), OH not observed. ^{13}C NMR (75 MHz, CD_3COCD_3 + 5% C_6D_6, δ): −7.80 (PdMe); 40.74, 43.78, 44.00, 45.55 (br), 53.58, 58.29, 61.86, 63.33 (alkyl); 117.80, 119.31, 134.72, 156.09, 158.66 (pyridyl). Anal. Calcd for $C_{17}H_{33}N_4F_3O_4PdS$: C, 36.93; H, 6.02; N, 10.13. Found: C, 37.02; H, 5.88; N, 10.10.

Synthesis of the Aryl Complexes *via* Route A. A typical procedure is described for the synthesis of [Pd(1-naphthyl)(NN′N)]OTf (**3h**). To a solution of $Pd(dba)_2$ (1.15 g, 2 mmol) in benzene (20 mL), under a nitrogen atmosphere, was added 1-iodonaphthalene (0.52 g, 2 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.33 mL, 2.2 mmol). The solution was stirred at 50 °C until the color changed from purple to dark green (2–5 min). After filtration of the solution through filter aid, the filtrate was evaporated to dryness. The brown residue was washed with dry diethyl ether (4 × 60 mL) and was subsequently dissolved in acetonitrile (10 mL). To this solution silver trifluoromethanesulfonate (0.51 g, 2 mmol) was added, whereupon a yellow solid and a brown solution formed. The

(34) The complexes **3a** and **4a** were found to be hygroscopic when left in air. The presence of water was confirmed by IR spectroscopy. The absence of water in the crystal structure of **4a** is due to crystal picking directly from solution with immediate transfer to the diffractometer.

solution was filtered off and the residue washed with acetone. After removing the volatiles *in vacuo*, the resulting red oil was taken up in acetone (20 mL) and 2,6-bis[(dimethylamino)-methyl]pyridine (**1**; 0.45 g, 2.3 mmol) was added. The solution was stirred at 40−50 °C for 2 h, after which the solvent was removed *in vacuo*. The residue was washed with acetone (3 × 50 mL) and the product obtained by trituration with pentane. Recrystallization was performed from methanol/diethyl ether. Yield: 0.69 g (60%). Complexes **3c−h** were prepared according to this procedure.

Synthesis of the Aryl Complexes *via* Route B. A typical procedure is described for the synthesis of [PdPh(pmdeta)]OTf (**5c**). To a solution of 1.15 g (2.0 mmol) of $Pd(dba)_2$ in 20 mL of benzene was added 0.50 g (2.9 mmol) of pmdeta and 0.23 mL (2.1 mmol) of iodobenzene. The solution was heated to 50 °C for 1 h, after which the volatiles were evaporated and the residue extracted with 3 × 50 mL of diethyl ether. The residue was taken up in 30 mL of acetone and 0.51 g (2.0 mmol) of silver trifluoromethanesulfonate was added. After the solution was stirred for 1 h, the black precipitate was filtered off and washed with 30 mL of acetone. The combined acetone layers were evaporated *in vacuo*, and the residue was washed with 3 × 50 mL of Et_2O. After recrystallization from methanol/diethyl ether 0.85 g (84%) of yellow crystals were obtained. Complexes **3d,f,i**, **4c−f** and **5c−g** were prepared according to this procedure.

Phenyl{2,6-bis[(dimethylamino)methyl]pyridine}palladium Trifluoromethanesulfonate (3c). Route A yield: 85%. Mp: 135 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 2.77 (s, 12, NMe_2), 4.58 (s, 4, CH_2), 7.00 (m, 3, Ph[3,4,5]), 7.57 (m, 2, Ph[2,6]), 7.65 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.14 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 52.73 (NMe_2); 74.05 (CH_2); 121.84 (Py[3,5]); 124.49 (Ph[4]); 127.93 (Ph[3,5]); 133.93 (Ph[2,6]); 141.50 (Py[4]); 156.73 (Py[2,6]); 159.91 (Ph[1]). Anal. Calcd for $C_{18}H_{24}N_3F_3O_3PdS$: C, 41.11; H, 4.61; N, 7.99. Found: C, 40.88; H, 4.72; N, 7.94.

(2-Tolyl){2,6-bis[(dimethylamino)methyl]pyridine}-palladium Trifluoromethanesulfonate (3d). Route A yield: 72%. Route B yield: 95%. Mp: 125−128 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 2.75 (s, 6, NMe_2), 2.81 (s, 6, NMe_2), 2.95 (s, 3, tolyl Me), 4.53 (d, AB, ^2J = 16.3 Hz, 2, CH_2), 4.68 (d, AB, ^2J = 16.3 Hz, 2, CH_2), 6.89 (m, 3, Ph), 7.56 (m, 1, Ph), 7.66 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.14 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 24.51 (tolyl Me), 52.84, 53.11 (NMe_2), 74.18 (CH_2), 121.85 (Py[3,5]), 124.47 (Ph-[4]), 125.17 (Ph[5]), 129.00 (Ph[3]), 133.77 (Ph[6]), 141.47 (Py-[4]), 141.60 (Ph[2]), 156.75 (Py[2,6]), 159.04 (Ph[1]). Anal. Calcd for $C_{19}H_{26}N_3F_3O_3PdS$: C, 42.27; H, 4.85; N, 7.78. Found: C, 42.21; H, 4.85; N, 7.83.

(3-Tolyl){2,6-bis[(dimethylamino)methyl]pyridine}-palladium Trifluoromethanesulfonate (3e). Route A yield: 75%. Mp: 148 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.28 (s, 3, tolyl Me), 2.76 (s, 12, NMe_2), 4.56 (s, 4, CH_2), 6.78 (d, ^3J = 7.4 Hz, 1, Ph[4]), 6.93 (t, 2 × ^3J = 7.4 Hz, 1, Ph[5]), 7.34 (d, ^3J = 7.4 Hz, 1, Ph[6]), 7.42 (s, 1, Ph[2]), 7.63 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.12 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 21.71 (tolyl Me), 52.72 (NMe_2), 74.04 (CH_2), 121.82 (Py[3,5]), 125.32 (Ph[4]), 127.56 (Ph[5]), 130.75 (Ph[2]), 134.37 (Ph[6]), 136.74 (Ph[3]), 141.44-(Py[4]), 156.71 (Py[2,6]), 159.82 (Ph[1]). Anal. Calcd for $C_{19}H_{26}N_3F_3O_3PdS$: C, 42.27; H, 4.85; N, 7.78. Found: C, 42.23; H, 4.66; N, 7.83.

(4-Nitro-1-phenyl){2,6-bis[(dimethylamino)methyl]pyridine}palladium Trifluoromethanesulfonate (3f). Route A yield: 35%. Route B yield: 69%. Mp: 179 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 2.80 (s, 12, NMe_2), 4.64 (s, 4, CH_2), 7.69 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 7.97 (AA′BB′, 4, Ph), 8.18 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 52.94 (NMe_2), 74.22 (CH_2), 121.25 (Ph[3,5]), 121.92 (Py[3,5]), 135.32 (Ph[2,6]), 141.84 (Py[4]), 146.53 (Ph[4]), 156.99 (Py-[2,6]), 175.25 (Ph[1]). Anal. Calcd for $C_{18}H_{23}N_4F_3O_5PdS$: C, 37.87; H, 4.06; N, 9.81. Found: C, 37.92; H, 4.12; N, 9.75.

(2-Methoxy-1-phenyl){2,6-bis[(dimethylamino)methyl]-pyridine}palladium Trifluoromethanesulfonate (3g). Route A yield: 63%. Mp: 145 °C dec. ^{1}H NMR (200 Mhz, CD_3COCD_3, δ): 2.78 (s, 12, NMe_2), 3.89 (s, 3, MeO), 4.57 (s, 4, CH_2), 6.65 (dd, ^3J = 7.9 Hz, ^4J = 0.7 Hz, 1, Ph[3]), 6.75 (ddd, ^3J = 6.9 and 7.7 Hz, ^4J = 0.7 Hz, 1, Ph[5]), 7.00 (ddd, ^3J = 7.7 and 7.9 Hz, ^4J = 1.4 Hz, 1, Ph[4]), 7.42 (dd, ^3J = 6.9 Hz and 1.4 Hz, 1, Ph[6]), 7.68 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.17 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 52.90, 53.09 (NMe_2); 55.61 (MeO); 74.15 (CH_2); 109.98 (Ph-[3]); 121.29 (Ph[5]); 121.92 (Py[3.5]); 125.72 (Ph[4]); 135.18 (Ph-[6]); 141.49 (Py[4]); 145.29 (Ph[2]); 156.94 (Py[2,6]); 163.53 (Ph[1]). Anal. Calcd for $C_{19}H_{26}N_3F_3O_4PdS$: C, 41.05; H, 4.71; N, 7.56. Found: C, 41.12; H, 4.73; N, 7.62.

(1-Naphthyl){2,6-bis[(dimethylamino)methyl]pyridine}-palladium Trifluoromethanesulfonate (3h). Route A yield: 60%. Mp: 150 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.64 (s, 6, NMe_2), 2.77 (s, 6, NMe_2), 4.61 (d, AB, ^2J = 16.3 Hz, 2, CH_2), 4.68 (d, AB, ^2J = 16.3 Hz, 2, CH_2), 7.25 (dd, ^3J = 6.9 and 8.3 Hz, 1, naphthyl[3]), 7.41 (ddd, ^3J = 6.7 and 7.5 Hz, ^4J = 1.2 Hz, 1, naphthyl[6]), 7.51 (d, ^3J = 6.9 Hz, 1, naphthyl[4]), 7.53 (ddd, ^3J = 8.4 and 6.7 Hz, ^4J = 1.3 Hz, 1, naphthyl[7]), 7.68 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 7.77 (d, ^3J = 8.3 Hz, 1, naphthyl[2]), 7.77 (dd, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1, naphthyl[5]), 8.17 (t, 2 × ^3J = 7.9 Hz, 1, Py[4]), 9.29 (dd, ^3J = 8.3 Hz, ^4J = 1.2 Hz, 1, naphthyl[8]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 52.74, 53.41 (NMe_2); 74.32 (CH_2); 121.86 (Py[3,5]); 124.27, 125.35, 125.67, 125.87, 129.23, 130.90, 132.49, 134.98, 139.45 (naphthyl); 141.58 (Py[4]); 156.93 (Py[2,6]); 161.64 (naphthyl[1]). Anal. Calcd for $C_{22}H_{26}N_3F_3O_3PdS$: C, 45.88; H, 4.55; N, 7.30. Found: C, 45.76; H, 4.74; N, 7.28.

Mesityl{2,6-bis[(dimethylamino)methyl]pyridine}palladium Trifluoromethanesulfonate (3i). Route B yield: 50%. Mp: 140 °C dec. ^{1}H NMR (300 Mhz, CD_3COCD_3, δ): 2.18 (s, 3, mesityl 4-Me), 2.75 (s, 12, NMe_2), 3.00 (s, 6, mesityl 2,6-Me), 4.58 (s, 4, CH_2), 6.64 (s, 2, mesityl), 7.63 (d, ^3J = 7.9 Hz, 2, Py[3,5]), 8.12 (t, ^3J = 7.9 Hz, 1, Py[4]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 20.96 (mesityl 4-Me), 24.40 (mesityl 2,6-Me) 53.24 (NMe_2), 74.32 (CH_2), 121.93 (Py[3,5]), 127.71 (mesityl[3,5]), 133.64 (mesityl[4]), 141.01 (mesityl[2,6]), 141.43 (Py[4]), 152.20 (mesityl[1]), 156.59 (Py[2,6]). Anal. Calcd for $C_{21}H_{30}N_3F_3O_3PdS$: C, 44.41; H, 5.32; N, 7.40. Found: C, 44.28; H, 5.36; N, 7.43.

Phenyl{*N,N,N′*-trimethyl-*N′*-(2-picolyl)ethylenediamine}palladium Trifluoromethanesulfonate (4c). Route B yield: 82%. Mp: 142 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, 263 K, δ): 2.59 (s, 3, NMe), 2.75 (s, 3, NMe_2), 2.92 (s, 3, NMe), 2.99 (m, ABXY, 1, CH_2CH_2 eq), 3.01 (m, ABXY, 1, CH_2CH_2 eq), 3.78 (m, ABXY, 1, CH_2CH_2 ax), 3.93 (m, ABXY, 1, CH_2CH_2 ax), 4.25 (d, AX, ^2J = 15.2 Hz, 1, CH_2), 5.04 (d, AX, ^2J = 15.2 Hz, 1, CH_2), 7.00 (m, 2, Ph[3,5]), 7.13 (m, 1, Ph[4]), 7.37 (m, 2, Ph[2 or 6] + Py[5]), 7.52 (dd, ^3J = 5.4 Hz, ^4J = 1.3 Hz, 1, Py[6]), 7.63 (d, ^3J = 7.5 Hz, 1, Ph[2 or 6]), 7.73 (d, ^3J = 7.8 Hz, 1, Py[3]), 8.08 (td, 2 × ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, 263 K, δ): 43.23 (NMe); 50.24, 52.92 (NMe_2); 57.05, 65.33, 67.80 (CH_2); 124.89 (Ph[4]); 125.37, 125.82 (Py[3,5]); 128.09, 128.67 (Ph[3,5]); 134.23, 135.15 (Ph[2,6]); 140.98 (Py[4]); 151.89 (Py[2]); 158.94 (Ph[1]); 165.16 (Py[6]). Anal. Calcd for $C_{18}H_{24}N_3F_3O_3PdS$: C, 41.11; H, 4.60; N, 7.99. Found: C, 41.19; H, 4.55; N, 7.94.

(4-Methoxy-1-phenyl){*N,N,N′*-trimethyl-*N′*-(2-picolyl)-ethylenediamine}palladium Trifluoromethanesulfonate (4d). Route B yield: 77%. Mp: 150 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, 263 K, δ): 2.60 (s, 3, NMe), 2.76 (s, 3, NMe_2), 2.91 (s, 3, NMe_2), 2.97 (m, ABXY, 1, CH_2CH_2 eq), 2.98 (m, ABXY, 1, CH_2CH_2 eq), 3.73 (s, 3, OMe), 3.77 (m, ABXY, 1, CH_2-CH_2 ax), 3.92 (m, ABXY, 1, CH_2CH_2 ax), 4.26 (d, AX, ^2J = 15.2 Hz, 1, CH_2), 5.03 (d, AX, ^2J = 15.2 Hz, 1, CH_2), 6.68 (dd, ^3J = 8.3 Hz, ^4J = 2.9 Hz, 1, Ph[3 or 5]), 6.81 (dd, ^3J = 8.3 Hz, ^4J = 2.9 Hz, 1, Ph[3 or 5]), 7.23 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 1, Ph[2 or 6]), 7.41 (dd, ^3J = 5.4 and 7.8 Hz, 1, Py[5]), 7.50 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 1, Ph[2 or 6]), 7.57 (dd, ^3J = 5.4, ^4J

= 1.3 Hz, Py[6]), 7.73 (d, ^3J = 7.8 Hz, Py[3]), 8.10 (td, 2 × ^3J = 7.8, ^4J = 1.3 Hz, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, 263 K, δ): 43.20 (NMe); 50.20, 52.85 (NMe_2); 55.13 (OMe); 57.15, 65.43, 67.82 (CH_2); 113.83, 114.38 (Ph[3,5]); 125.30, 125.83 (Py[3,5]); 134.11, 135.02 (Ph[2,6]); 140.91 (Py[4]); 146.56 (Ph[1]); 152.07 (Py[2]); 158.02 (Ph[4]); 165.14 (Py[6]). Anal. Calcd for $C_{19}H_{26}N_3F_3O_4PdS$: C, 41.05; H, 4.71; N, 7.56. Found: C, 40.96; H, 4.78; N, 7.50.

(4-Nitro-1-phenyl){*N,N,N'*-trimethyl-*N'*-(2-picolyl)ethylenediamine}palladium Trifluoromethanesulfonate (4e). Route B yield: 82%. Mp: 155 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, 263 K, δ): 2.64 (s, 3, NMe), 2.82 (s, 3, NMe_2), 2.96 (s, 3, NMe_2), 3.00 (m, 2, CH_2CH_2 eq), 3.93 (m, 2, CH_2CH_2 ax), 4.30 (d, AX, ^2J = 15.2 Hz, 1, CH_2), 5.15 (d, ^2J = 15.2 Hz, 1, CH_2), 7.41 (dd, ^3J = 5.7 and 7.7 Hz, 1, Py[5]), 7.49 (dd, ^3J = 5.7 Hz, ^4J = 1.4 Hz, Py[6]), 7.77 (d, ^3J = 7.7 Hz, Py[3]), 7.80 (d, ^3J = 8.3 Hz, 1, Ph[2 or 6]), 7.88 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1, Ph[3 or 5]), 8.00 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1, Ph[3 or 5]), 8.07 (d, ^3J = 8.3 Hz, 1, Ph[2 or 6]), 8.12 (td, 2 × ^3J = 7.7 Hz, ^4J = 1.4 Hz, Py[4]). ^{13}C NMR (50 MHz, CD_3COCD_3, 263 K, δ): 43.54 (NMe); 50.54, 53.12 (NMe_2); 57.33, 65.62, 68.04 (CH_2); 121.45, 122.00 (Ph[3,5]); 125.44, 126.08 (Py[3,5]); 135.60, 136.26 (Ph[2,6]); 141.31 (Py[4]); 146.41 (Ph[4]); 152.06 (Py[2]); 165.25 (Py[6]); 173.94 (Ph[1]). Anal. Calcd for $C_{18}H_{23}N_4F_3O_5PdS$: C, 37.87; H, 4.06; N, 9.81. Found: C, 37.74; H, 4.01; N, 9.88.

Mesityl{*N,N,N'*-trimethyl-*N'*-(2-picolyl)ethylenediamine}palladium Trifluoromethanesulfonate (4f). Route B yield: 63%. Mp: 137 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.21 (s, 3, Me, mesityl), 2.57 (s, 3, Me, mesityl), 2.59 (s, 3, Me, mesityl), 2.83 (s, 3, NMe), 2.92 (s, 3, NMe_2), 2.97 (s, 3, NMe_2), 2.98 (m, ABXY, 1, CH_2CH_2 eq), 3.02 (m, ABXY, 1, CH_2CH_2 eq), 3.82 (m, ABXY, 1, CH_2CH_2 ax), 4.01 (m, ABXY, 1, CH_2CH_2 ax), 4.31 (d, AX, ^2J = 15.3 Hz, 1, CH_2), 5.07 (d, AX, ^2J = 15.3 Hz, 1, CH_2), 6.60 (s, 1, mesityl), 6.72 (s, 1, mesityl), 7.38 (dd, ^3J = 5.5 and 7.7 Hz, 1, Py[5]), 7.49 (dd, ^3J = 5.5 Hz, ^4J = 1.3 Hz, Py[6]), 7.75 (d, ^3J = 7.7 Hz, Py[3]), 8.09 (td, 2 × ^3J = 7.7 Hz, ^4J = 1.3 Hz, Py[4]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 20.73, 24.91, 25.04 (Me, mesityl); 42.79 (NMe); 51.30, 52.94 (NMe_2); 57.25, 65.51, 68.00 (CH_2); 125.39, 126.05 (Py[3,5]); 127.67, 128.14 (Ph[3,5]); 134.24 (Ph[4]); 140.00, 140.60 (Ph[2,6]); 140.86 (Py[4]); 151.63 (Py[2]); 153.53 (Ph[1]); 165.17 (Py[6]). Anal. Calcd for $C_{21}H_{30}N_3F_3O_3PdS$: C, 44.41; H, 5.32; N, 7.40. Found: C, 44.27; H, 5.38; N, 7.45.

Phenyl{*N,N,N',N'',N''*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5c). Route B yield: 84%. Mp: 147 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.38 (s, 6, NMe_2), 2.76 (m, 2, CH_2CH_2 eq), 2.85 (s, 6, NMe_2), 2.87 (m, 2, CH_2CH_2 eq), 2.90 (s, 3, NMe), 3.61 (m, 2, CH_2CH_2 ax), 3.79 (m, 2, CH_2CH_2 ax), 6.97 (m, 3, Ph[3,4,5]), 7.42 (m, 1, Ph[2 or 6]), 7.64 (m, 1, Ph[2 or 6]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 41.33 (NMe); 51.00, 53.24 (NMe_2); 57.74, 67.53 (CH_2); 124.45 (Ph[4]); 127.61, 127.68 (Ph[3,5]); 134.92 (Ph[2,6]); 159.89 (Ph[1]). Anal. Calcd for $C_{16}H_{28}N_3F_3O_3SPd$: C, 37.99; H, 5.58; N, 8.31. Found: C, 37.94; H, 5.49; N, 8.37.

(4-Methoxy-1-phenyl){*N,N,N',N'',N''*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5d). Route B yield: 81%. Mp: 132 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 2.37 (s, 6, NMe_2), 2.73 (m, 2, CH_2CH_2 eq), 2.83 (s, 16, NMe_2), 2.84 (m, 2, CH_2CH_2 eq), 2.88 (s, 3, NMe), 3.59 (m, 2, CH_2CH_2 ax), 3.70 (s, 3, MeO), 3.79 (m, 2, CH_2CH_2 ax), 6.69 (m, 2, Ph[3,5]), 7.29 (m, 2, Ph[2 or 6]), 7.50 (m, 2, Ph[2 or 6]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 41.32 (NMe); 50.98, 53.21 (NMe_2); 55.20 (MeO); 57.72, 67.49 (CH_2); 113.57, 113.79 (Ph[3,5]); 134.66 (Ph[2,6]); 147.66 (Ph[1]); 158.01 (Ph[4]). Anal. Calcd for $C_{17}H_{30}N_3F_3O_4PdS$: C, 38.10; H, 5.64; N, 7.84. Found: C, 37.98; H, 5.70; N, 7.76.

(4-Nitro-1-phenyl){*N,N,N',N'',N''*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5e). Route B yield: 60%. Mp: 171–173 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.41 (s, 6, NMe_2), 2.78 (m, 2, CH_2CH_2 eq), 2.87 (s, 6, NMe_2), 2.90 (m, 1, CH_2CH_2 eq), 2.96 (s, 3, NMe), 3.65 (m, 2, CH_2CH_2 ax); 3.85 (m, 2, CH_2CH_2 ax), 7.86 (m, 3, Ph[3,5 + 2 or 6]), 8.09 (m, 1, Ph[2 or 6]). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 41.63 (NMe); 51.36, 53.47 (NMe_2); 57.96, 67.74 (CH_2); 120.94, 121.10 (Ph[3,5]); 136.04, 136.26 (Ph[2,6]); 146.46 (Ph[4]); 175.34 (Ph[1]). Anal. Calcd for $C_{16}H_{27}N_4F_3O_5PdS$: C, 34.88; H, 4.94; N, 10.17. Found: C, 34.80; H, 5.04; H, 10.12.

Mesityl{*N,N,N',N'',N''*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5f). Yield: 94%. Mp: 130 °C dec. ^{1}H NMR (300 MHz, CD_3COCD_3, δ): 2.15 (s, 3, Me, mesityl), 2.44 (s, 6, NMe_2), 2.76 (s, 6, NMe_2), 2.78 (m, 2, CH_2CH_2 eq), 2.84 (s, 3, Me, mesityl), 2.86 (m, 2, CH_2CH_2 eq), 2.96 (s, 3, NMe), 3.10 (s, 3, Me, mesityl), 3.66 (m, 2, CH_2CH_2 ax), 3.87 (m, 2, CH_2CH_2 ax), 6.61 (s, 2, mesityl). ^{13}C NMR (75 MHz, CD_3COCD_3, δ): 20.63, 24.74, 25.46 (mesityl Me); 40.96 (NMe); 52.82, 53.61 (NMe_2); 57.80, 67.69 (CH_2); 127.91, 128.08 (Ph[3,5]); 133.88 (Ph[4]); 140.29, 141.02 (Ph[2,6]); 151.31 (Ph[1]). Anal. Calcd for $C_{19}H_{34}N_3F_3O_3PdS$: C, 41.65; H, 6.25; N, 7.67. Found: C, 41.39; H, 6.32; N, 7.73.

(2-Tolyl){*N,N,N',N'',N''*-pentamethyldiethylenetriamine}palladium Trifluoromethanesulfonate (5g). Yield: 71%. Mp: 148 °C dec. ^{1}H NMR (200 MHz, CD_3COCD_3, δ): 2.34 (s, 6, NMe_2), 2.73 (m, ABXY, 2, CH_2CH_2 eq), 2.82 (m, ABXY, 2, CH_2CH_2 eq), 2.89 (s, 6, NMe_2), 2.94 (s, 3, NMe), 2.99 (s, 3, Me, tolyl), 3.62 (m, ABXY, 2, CH_2CH_2 ax), 3.78 (m, ABXY, 2, CH_2CH_2 ax), 6.86 (m, 3, Ph[3,4,5]), 7.36 (m, 1, Ph[6]). ^{13}C NMR (50 MHz, CD_3COCD_3, δ): 24.73 (tolyl Me); 40.96 (NMe); 50.84, 53.01 (NMe_2); 57.59, 67.47 (CH_2); 124.56 (Ph[4]); 124.93 (Ph[5]); 128.96 (Ph[3]); 134.83 (Ph[6]); 141.79 (Ph[2]); 156.62 (Ph[1]). Anal. Calcd for $C_{17}H_{30}N_3F_3O_3PdS$: C, 39.27; H, 5.82; N, 8.08. Found: C, 39.06; H, 5.98; N, 7.97.

Conformational Analysis. An NMR simulation of the experimental data gave accurate chemical shifts and coupling constants with their standard deviations, allowing the determination of the conformation (δ or λ) and the NCCN torsion angle (ω) of the five-membered chelate rings using the equations[5h,19]

$$n_\lambda = [X\cos^2\omega - \cos^2(120 - \omega)]/[\alpha\cos^2(120 + \omega) - \cos^2(120 - \omega)] \quad (1)$$

$$n_\lambda = [Y\cos^2\omega - \alpha\cos^2(120 + \omega)]/[\cos^2(120 - \omega) - \alpha\cos^2(120 + \omega)] \quad (2)$$

$$n_\lambda + n_\delta = 1 \quad (3)$$

where n_λ (n_δ) is the mole fraction of the λ (δ) conformation (Figure 3), $X = {}^3J_{a,d}/{}^3J_{a,c}$, and $Y = {}^3J_{b,c}/{}^3J_{a,c}$. A value of 1.208 was previously determined for the ratio of the Karplus constants (α).[19b] The standard deviations in the coupling constants (Tables 5 and 6) were obtained from the NMR simulation, while those of X, Y, n_δ, and ω were obtained from these *via* standard mathematical methods.

NMR Studies of the Aryl Group Rotation. To obtain the kinetic parameters, a set of at least six ^{1}H NMR spectra at different temperatures were obtained. Temperatures were checked internally using a capillary filled with either methanol or ethylene glycol. Rate constants were obtained by comparison to calculated spectra using the geNMR program which also allows exchange processes to be simulated. The deviations of the data stated in Table 7 are obtained from the least squares fit of the data.

Structure Determination and Refinement of [PdMe(NN'N)]OTf (3b) and [PdMe(ONN')(tmeda)]OTf (8). Crystals suitable for X-ray structure determination were mounted on a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-F diffractometer. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range 12.3° < θ < 17.6° and 14.6° < θ < 18.2° for **3b** and **8**, respectively. The unit-cell parameters were checked

Table 8. Crystal Data and Details of the Structure Determination of 4a, 3b, and 8

		Crystal Data	
formula	$C_{11}H_{19}N_3Cl_2Pd$ (**4a**)	$C_{12}H_{22}N_3Pd{\cdot}CF_3O_3S$ (**3b**)	$C_{16}H_{33}N_4OPd{\cdot}CF_3O_3S$ (**8**)
mol wt	370.62	463.81	552.95
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)
a, b, c, Å	15.0760(7), 7.4468(8), 13.553(2)	7.738(1), 21.280(2), 11.399(1)	9.7902(14), 10.0555(15), 12.362(2)
α, β, γ, deg	90, 115.653(6), 90	90, 92.05(1), 90	75.828(12), 81.234(12), 84.836(11)
V, Å^3	1371.6(3)	1875.8(3)	1164.4(3)
D_{calc}, g cm^{-3}	1.795	1.642	1.577
Z	4	4	2
$F(000)$	744	936	568
μ, cm^{-1}	17.1	11.3	9.2
cryst size, mm	0.05 × 0.20 × 0.40	0.25 × 0.25 × 1.0	0.4 × 0.5 × 0.8
		Data Collection	
temp, K	150	293	100
θ_{min}, θ_{max}, deg	1.5, 27.5	0.96, 30.3	1.72, 27.5
wavelength (Mo Kα, Zr-filtered), Å	0.710 73	0.710 73	0.710 73
$\Delta\omega$, deg	$0.80 + 0.35 \tan\theta$	$1.40 + 0.35 \tan\theta$	$0.99 + 0.35 \tan\theta$
hor, ver aperture, mm	3.28, 4.00	4.00, 4.00	2.97, 5.00
X-ray exposure time, h	13	90	112
linear decay, %	2	<1	12
ref reflns	232; $42\bar{2}$; $2\bar{3}2$	$\bar{2}10$, $\bar{2}0\bar{2}$, 031	$\bar{2}3\bar{3}$, 421, 152
data set (hkl)	−19 to +17; −9 to 0; −13 to +17	−10 to 0; 0 to 30; −15 to +16	−12 to +12, −13 to +13, −16 to +16
total no. of data	5032	5707	8931
total no. of unique data	3137	5553	5325
no. of observed data	2637 [$F_o > 4\sigma(F_o)$]	2457 [$I > 3\sigma(I)$]	5099 [$I > 2.5\sigma(I)$]
DIFABS corr range	0.80, 1.20	0.46, 1.48	0.90, 1.16
		Refinement	
no. of refined params	157	232	305
final R^a	0.032	0.066	0.032
final $wR2^b$	0.066		
final $R_w{}^c$		0.065	0.040
goodness of fit	1.03	2.77	0.79
weighting scheme	$1/\sigma^2[(F_o^2) + (0.0239P)^2 + 1.37P]^d$	$1/\sigma^2(F)$	$1/\sigma^2(F)$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.002, 0.000	0.0088, 0.11	0.014, 0.66
min and max residual density, e Å^{-3}	−0.91, 0.82	−0.76, 0.93	−1.34, 1.07 (near Pd)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $R_w = [\sum[w(||F_o| - |F_c||)^2]/\sum[w(F_o^2)]]^{1/2}$. [d] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

for the presence of higher lattice symmetry.[35] Crystal data and details of data collection and refinement are collected in Table 8. Data were corrected for Lp effects. Standard deviations of the intensities, as obtained by counting statistics, were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (pI)^2$ with $p = 0.012$ and 0.07 for **3b** and **8**, respectively.[36] An empirical absorption/extinction correction was applied (DIFABS[37]). Both structures were solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86[38]). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76[39]). The ethylene bridge of tmeda in complex **8** is disordered over two positions; the site occupation factor of the major component refined to a value of 0.836(7). Hydrogen atoms were included in the refinement in calculated positions (C−H = 0.98 Å), riding on their carrier atoms, except for the hydroxyl hydrogen atom (H14) of **8**, which was located on a difference Fourier map and subsequently included in the refinement. The methyl groups were refined as rigid groups. All non-hydrogen atoms, apart from those of the minor disorder component of **8**, were refined with anisotropic thermal parameters. The hydrogen atoms of **3b** were refined with overall isotropic thermal parameters with values of 0.076(19), 0.13(2), and 0.084(9) Å^2 for the aromatic, ethylene, and methyl hydrogen atoms, respectively. The overall isotropic thermal parameter for the hydrogen atoms of **8** refined to a value of 0.0363(15) Å^2. Weights were introduced in the final refinement cycles. Positional parameters for **3b** and **8** are listed in Tables 9 and 10, respectively. Neutral atom scattering factors were taken from Cromer and Mann,[40] and anomalous dispersion corrections from Cromer and Liberman.[41] Geometrical

Table 9. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for 3b

atom	x	y	z	$U_{eq}{}^a$
Pd	0.19983(10)	0.14349(4)	0.27721(6)	0.0489(3)
N1	−0.0248(10)	0.0973(4)	0.2680(7)	0.052(3)
N2	0.1748(11)	0.1323(4)	0.0949(6)	0.055(3)
N3	0.1528(11)	0.1376(5)	0.4571(6)	0.057(3)
C1	−0.1165(14)	0.0938(5)	0.3657(7)	0.052(4)
C2	−0.2699(14)	0.0640(6)	0.3631(9)	0.065(5)
C3	−0.3354(15)	0.0386(5)	0.2560(10)	0.073(5)
C4	−0.2391(14)	0.0443(5)	0.1573(8)	0.058(4)
C5	−0.0838(13)	0.0723(5)	0.1688(8)	0.050(4)
C6	0.0553(14)	0.0772(5)	0.0732(7)	0.063(4)
C7	0.0928(17)	0.1893(6)	0.0465(9)	0.091(6)
C8	0.3296(16)	0.1177(7)	0.0322(11)	0.099(7)
C9	−0.0384(15)	0.1331(6)	0.4644(10)	0.079(5)
C10	0.2383(18)	0.0808(6)	0.5043(10)	0.090(6)
C11	0.2028(18)	0.1918(6)	0.5318(10)	0.088(6)
C12	0.4206(14)	0.1939(6)	0.2853(9)	0.083(5)
S	0.7437(4)	0.08002(14)	0.7646(2)	0.0591(11)
F1	0.4933(13)	0.1590(5)	0.7689(7)	0.163(6)
F2	0.7198(17)	0.1924(4)	0.6913(10)	0.223(7)
F3	0.7046(13)	0.1822(4)	0.8759(9)	0.155(5)
O1	0.9272(10)	0.0883(5)	0.7682(7)	0.102(4)
O2	0.6771(11)	0.0602(4)	0.6525(6)	0.100(4)
O3	0.6781(11)	0.0486(4)	0.8632(5)	0.088(4)
C13	0.664(2)	0.1575(7)	0.7739(12)	0.097(7)

[a] U_{eq} = one-third of the trace of the orthogonalized U.

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Table 10. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of the Non-Hydrogen Atoms for 8

atom	x	y	z	U_{eq}[a]
Pd	0.81648(1)	0.68672(1)	0.17379(1)	0.0154(1)
O1	1.2358(2)	0.5382(2)	0.2596(3)	0.0575(8)
N1	0.73428(18)	0.88914(18)	0.14535(15)	0.0197(5)
N2	0.7575(2)	0.6865(2)	0.35382(15)	0.0232(5)
N3	0.59211(19)	0.30187(19)	0.18875(16)	0.0223(5)
N4	0.89608(18)	0.48780(19)	0.20577(15)	0.0194(5)
C1	0.8420(2)	0.9885(3)	0.0966(2)	0.0295(7)
C2	0.6270(3)	0.9188(3)	0.0679(2)	0.0331(7)
C5	0.6339(3)	0.6114(3)	0.4007(2)	0.0397(8)
C6	0.8655(3)	0.6334(3)	0.4266(2)	0.0373(8)
C7	0.4963(3)	0.3201(3)	0.1059(2)	0.0297(7)
C8	0.5150(2)	0.2804(3)	0.30190(19)	0.0286(6)
C9	0.6788(2)	0.4190(2)	0.16524(18)	0.0230(6)
C10	0.8151(2)	0.3832(2)	0.21187(17)	0.0204(5)
C11	0.8610(2)	0.2483(2)	0.25233(19)	0.0240(6)
C12	0.9930(2)	0.2195(2)	0.28229(19)	0.0254(6)
C13	1.0779(2)	0.3260(2)	0.26839(19)	0.0246(6)
C14	1.0269(2)	0.4591(2)	0.22932(18)	0.0224(6)
C15	1.1174(2)	0.5788(3)	0.2053(2)	0.0300(7)
C16	0.8695(3)	0.6969(3)	0.00747(19)	0.0317(7)
C31[b]	0.6591(3)	0.9081(3)	0.2546(2)	0.0227(8)
C32[b]	0.7242(16)	0.9214(12)	0.2630(9)	0.013(3)
C41[b]	0.7400(3)	0.8371(3)	0.3497(2)	0.0241(7)
C42[b]	0.6515(11)	0.8074(11)	0.3485(9)	0.010(3)
S	0.24712(5)	0.90008(5)	0.27648(4)	0.0218(2)
F1	0.2127(3)	0.7496(2)	0.48185(16)	0.0616(7)
F2	0.3754(2)	0.8917(2)	0.44890(16)	0.0568(7)
F3	0.1618(2)	0.9654(2)	0.46904(15)	0.0498(6)
O2	0.29956(19)	1.03378(18)	0.23086(16)	0.0323(5)
O3	0.33965(17)	0.78740(18)	0.25062(16)	0.0306(5)
O4	0.10424(18)	0.88757(19)	0.26788(18)	0.0341(5)
C17	0.2485(3)	0.8757(3)	0.4273(2)	0.0369(8)

[a] U_{eq} = one-third of the trace of the orthogonalized **U**. [b] Disordered atoms (see text).

calculations and illustrations were performed with PLATON;[42] all calculations were performed on a DECstation 5000/125.

Structure Determination and Refinement of [PdCl(pico)]Cl (4a). A yellow crystal (0.05 × 0.20 × 0.40 mm) was mounted on top of a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer with a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range $11.2° < \theta < 14.0°$. The unit-cell parameters were checked for the presence of higher lattice symmetry.[35] Crystal data and details of data collection and refinement are collected in Table 8. Data were corrected for *Lp* effects. An empirical absorption/extinction correction was applied (DIFABS[37] as implemented in PLATON[42]). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[43]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-92[44]); no observance criterium was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions (C−H = 0.98 Å), riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl and ethyl hydrogen atoms and the other hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. Positional parameters for **4a** are listed in Table 11. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 45. Geometrical calculations and illustrations were performed with PLATON;[42] all calculations were performed on a DECstation 5000/125.

Table 11. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of the Non-Hydrogen Atoms for 4a

atom	x	y	z	U_{eq}[a]
Pd1	0.22371(2)	0.26987(3)	0.22263(2)	0.0154(1)
Cl1	0.16610(6)	0.51025(11)	0.10707(6)	0.0228(2)
N1	0.0932(2)	0.1437(4)	0.1656(2)	0.0181(8)
N2	0.2671(2)	0.0479(4)	0.3178(2)	0.0167(7)
N3	0.3695(2)	0.3461(4)	0.2899(2)	0.0190(8)
C1	0.0031(2)	0.2150(5)	0.1102(3)	0.0228(11)
C2	−0.0808(2)	0.1130(5)	0.0757(3)	0.0250(12)
C3	−0.0722(3)	−0.0680(5)	0.0985(3)	0.0290(12)
C4	0.0205(3)	−0.1427(5)	0.1565(3)	0.0255(12)
C5	0.1019(2)	−0.0340(4)	0.1887(3)	0.0195(11)
C6	0.2066(2)	−0.0996(4)	0.2470(3)	0.0210(12)
C7	0.2492(3)	0.0606(5)	0.4173(3)	0.0248(12)
C8	0.3745(2)	0.0313(5)	0.3472(3)	0.0229(12)
C9	0.4207(2)	0.2143(5)	0.3806(3)	0.0237(11)
C10	0.4072(2)	0.3287(5)	0.2056(3)	0.0247(12)
C11	0.3901(2)	0.5312(5)	0.3349(3)	0.0247(12)
Cl(2)	0.33626(6)	0.89500(14)	0.06775(7)	0.0317(3)

[a] U_{eq} = one-third of the trace of the orthogonalized **U**.

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Supplementary Material Available: Further details of the structure determinations, including tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **3b**, **4a**, and **8** (18 pages). Ordering information is given on any current masthead page.

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