SYNTHESIS AND CHARACTERIZATION OF PALLADIUM COMPLEXES CONTAINING 3,3′-ANNELATED 2,2′-BIPYRIDINES AND 3,3′-ANNELATED 2,2′-BIQUINOLINES

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

The synthesis and characterization of a number of $PdCl_2(N\frown N)$ and $Pd(N\frown N)(fn)$ complexes ($N\frown N$ = 3,3′-annelated 2,2′-bipyridines and 3,3′-annelated 2,2′-biquinolines, fn = fumaronitrile) have been described. Despite the variation in dihedral angle and distance between the nitrogen lone pairs in these series of ligands, they are all capable of forming stable chelates. An investigation was made as to whether the 3,3′-trimethylene-2,2′-biquinoline (3-bq) and 3,3′-tetramethylene-2,2′-biquinoline (4-bq) ligands could serve as C_2-chiral auxiliaries. The ligand 3-bq in Pd(3-bq)(fn) turned out to be conformationally rigid on the NMR time scale, but the diastereomers appeared to be indistinguishable, as could be concluded from the ^{1}H NMR spectra. However, Pd(4-bq)(fn) exists in two diastereomeric forms and their ratio (57 : 43) could be determined from ^{1}H NMR spectra. Assignment of the major and minor isomers was done with a 2D NOESY experiment. Epimerization of the diastereomers occurred on the laboratory time scale which was deduced from a spin saturation transfer experiment and also from the observation that diastereomerically enriched crystalline material of Pd(4-bq)(fn) at low temperature showed a ratio of 80 : 20 which deteriorated to a ratio of 57 : 43. From the spin saturation transfer experiment, the thermodynamic parameters for the inversion could be determined ($\Delta H^{\neq}$ = 29.1 kJ mol^{-1} and $\Delta S^{\neq}$ = –136.3 J K^{-1} mol^{-1}). This large negative entropy of activation favours an epimerization process *via* inversion of the coordinated 4-bq ligand over a mechanism *via* alkene dissociation/recoordination. The structures of the complexes have been studied in solution and in the solid state and the following X-ray crystal structures have been determined: (i) [dichloropalladium(II)](3,3′-trimethylene-2,2′-bipyridine-κ^2N), monoclinic crystals, space group $P2_1/n$, with a =

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8.4230(7) Å, *b* = 16.425(2) Å, *c* = 9.5836(7) Å, β = 106.316(7)°, *Z* = 4, final *R* = 0.033 for 2 309 reflections, (ii) [3,3′-bis(methoxycarbonyl)-2,2′-bipyridine-κ^2N][dichloropalladium(II)], triclinic crystals, space group $P\bar{1}$, with *a* = 7.340(4) Å, *b* = 10.012(3) Å, *c* = 11.954(3) Å, α = 98.10(2)°, β = 104.03(3)°, γ = 107.33(5)°, *Z* = 2, final *R* = 0.039 for 4 273 reflections, (iii) [chloromethylpalladium(II)](4,5-diazafluorene-κ^2N), orthorhombic crystals, space group *Pmcn*, with *a* = 6.713(1) Å, *b* = 10.120(1) Å, *c* = 17.187(3) Å, *Z* = 4, final *R* = 0.048 for 949 reflections.

Key words: Palladium; X-Ray crystallography; Chirality; Annelation; Bipyridine; Biquinoline.

In the past few years we have developed in our laboratory an interest in palladium complexes containing rigid α-diimine ligands, *e.g.* bis(arylimino)acenaphthene (Ar-BIAN) and bis(arylimino)phenanthrene (Ar-BIP) (Fig. 1). These complexes were shown to be versatile catalysts in (i) homogeneous catalyzed hydrogenation of alkenes[1], (ii) the C–C cross coupling reactions of several organic halides with organometallic reagents[2] and (iii) the catalytic synthesis of dienes from alkynes[3]. Moreover, Ar-BIAN appeared to be a useful spectator ligand for mechanistic investigations of the palladium C–C cross coupling reaction and polyketone synthesis[4]. These interesting results prompted us to investigate in more detail the role of the nitrogen ligands with respect to both electronic and steric properties. We have extended our studies on palladium complexes containing rigid bisnitrogen ligands to 3,3′-annelated bipyridines and 3,3′-annelated biquinolines as shown in Fig. 1. The length of the annelating bridge controls both the dihedral angle between the azaaryl groups and the distance between the two nitrogen lone pairs[5–7].

These two interrelated characteristics will undoubtedly influence the coordination properties of these ligands as will be elaborated below. An annelation of sufficient length should lead to the formation of rigid conformational enantiomers with a C_2-symmetry axis. C_2-Chiral auxiliaries are well described in literature[8] and phosphorus[9] as well as nitrogen[10] based ligands are excellent auxiliaries in asymmetric synthesis. Ruthenium complexes[11] containing these azabiaryls ligands[5–7] have been prepared and studied.

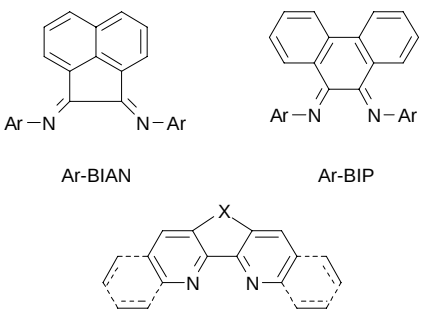


FIG. 1
Selected rigid bisnitrogen ligands

The dihedral angles between the pyridine or quinoline rings of $-(CH_2)_n$-bridged 2,2′-diazabiaryls vary with the number of bridging methylene units (n). The ligands may thus exist as conformational enantiomers if $n > 1$. As the length of the 3,3′-bridge is increased, a point is reached at which the system becomes conformationally rigid[12]. This raises an interesting stereochemical question for zerovalent palladium complexes which contain, besides the C_2-chiral bisnitrogen ligand, an alkene with C_{2h}-symmetry (*e.g.* fumaronitrile (fn)), since in that case the complex should exist as a diastereomeric pair of enantiomers (Fig. 2).

It is known that for $-(CH_2)_4$-bridged 2,2′-biquinoline[7], 2,2′-bi[1,8]naphthyridine[13a] and 2,2′-bipyridine[13a], conformational interconversion at room temperature is slow on the NMR time scale but on the real world time scale it is sufficiently rapid to prevent resolution. For the $-(CH_2)_4$-bridged 2,2′-bi[1,8]naphthyridine, a rotational barrier of 73.5 kJ mol^{-1} could be estimated[13a]. Attempts[14] were also made to resolve dibenzo[*a*,*c*]cyclooctatetraene and its diaza analogue, cycloocta[2,1-*b*:3,4-*b*′]bipyridine, but these compounds racemize at ambient temperature. The question can be raised whether the diastereomeric Pd(NN)(fn) complexes reported here will be configurationally stable and the answer is not straightforward. Since coordination of the azabiaryls appears to have a

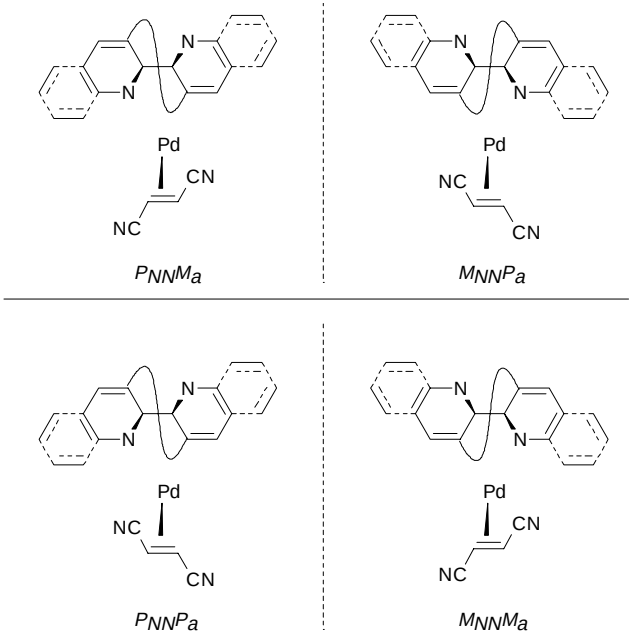


FIG. 2

Diastereomeric pairs of enantiomers for Pd(N⌒N)(fn) complexes with C_2-chiral α-diimine ligands, *i.e.* $-(CH_2)_n$-bridged 2,2′-bipyridine and biquinoline with $n > 1$, Pd–N bonds omitted for clarity, M_{NN}, P_{NN}, M_a and P_a are used here as descriptors for the chiral α-diimine ligand and Pd(alkene) moiety

flattening effect[11b] upon the ligand and the planarity of the annelated diazabiaryls corresponds to the transition-state conformation for racemization of these systems, one might expect a lower barrier for conformational inversion in the coordinated ligand. On the other hand, the five-membered metallacycle portion of the complex represents a second bridge between the two halves of the bipyridine or biquinoline and would thereby impose greater constraints on the conformational mobility of the ligand[5b,11b] so that the ligand is locked into a rigid posture. In order to answer these stereochemical questions, variable temperature ^{1}H NMR experiments were carried out on these complexes.

The aim of this study is to investigate (i) the way in which the bridged azabiaryls coordinate in palladium complexes and (ii) whether they are capable of forming *rigid* chiral templates which in the future can be used in asymmetric synthesis.

EXPERIMENTAL

Material, Methods and Apparatus

All experiments were carried out using standard Schlenk techniques, under an atmosphere of dry nitrogen. The solvents were dried according to standard procedures and distilled before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 NMR spectrometer at 300.13 and 75.48 MHz, respectively. Chemical shift values are in ppm relative to TMS as external standard with high frequency shifts signed positive (protons are numbered according to Fig. 3). ^{1}H NOESY NMR spectra were recorded on a Bruker AMX 300 NMR spectrometer using a standard 2D NOESY pulse sequence with a mixing time of 1 s. The Forsén–Hofmann method[15], which makes use of spin saturation transfer, was used to determine the rates of exchange at different temperatures. For this purpose T_1 values were independently determined through linear interpolation of the values obtained at 233, 273 and 313 K. A straight line is obtained when plotting the natural logarithm of the rate of exchange (ln (k/T)) against the reciprocal temperature $1/T$ with the approximation that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are constant over the employed temperature range (333–213 K). From the Eyring equation[16], $kT^{-1} = k_B h^{-1}\, e^{\Delta S^{\neq}/R}\, e^{-\Delta H^{\neq}/RT}$ with $k_B = 1.3807 \cdot 10^{-23}$ J K^{-1} and $h = 6.63 \cdot 10^{-34}$ J s, the enthalpies ($\Delta H^{\neq}$) and the entropies ($\Delta S^{\neq}$) of activation were calculated. Solid state MAS ^{13}C NMR spectra were recorded on a Bruker AM 500 using a Doty Scientific probe (90° pulse, 50 μs) at the SON National HF-NMR Facility at the University of Nijmegen. IR spectra in KBr pellets were recorded on a Biorad FTS-7 IR spectrometer. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Mass spectra were recorded at the Institute of Mass Spectroscopy of the University of Amsterdam. Fumaronitrile (fn), commercially available, was used without further purification. Dibenzylideneacetone[17] (dba), $Pd(dba)_2$ (ref.[18]), $PdCl_2(MeCN)_2$ (ref.[19]), PdCl(COD)(Me) (ref.[20]), 4,5-diazafluoren-9-one[5,6] (dafo), 4,5-diazafluorene[5,6] (dafe), 5,6-dihydro-1,10-phenanthroline[5] (2-bpy) and 3,3′-bis(methoxycarbonyl)-2,2′-bipyridine[21] (dcm-bpy) were synthesized according to published procedures. The 3,3′-trimethylene-2,2′-bipyridine (3-bpy), 3,3′-trimethylene-2,2′-biquinoline (3-bq) and 3,3′-tetramethylene-2,2′-biquinoline (4-bq) compounds were prepared according to the literature[5,7].

Synthesis of $PdCl_2(N\frown N)$ Complexes **1**–**5**

(4,5-Diazafluoren-9-one-κ^2*N*)[dichloropalladium(II)] (**1**): A mixture of $PdCl_2(MeCN)_2$ (0.1 g, 0.39 mmol), dafo (77 mg, 0.42 mmol) in dichloromethane (40 ml) was stirred at 20 °C. The colour of the suspen-

sion turned in two hours from brown to pale yellow. The solvent was removed under reduced pressure to *ca* 5 ml and the product was precipitated with hexane (30 ml). The suspension was centrifuged and the supernatant was removed. The residue was washed with ether (3 × 20 ml) and hexane (2 × 15 ml). The yellow solid was then dried *in vacuo*, giving 94% of **1**. The other complexes were synthesized in a similar way giving **2** in 89%, **3** in 91%, **4** in 92% and **5** in 94% yield. The characterization of complex **5** has been described previously[21]. Yellow/orange crystals of **4** and **5**, suitable for an X-ray determination, were obtained by slow diffusion of hexane into solutions of the complexes in dichloromethane at 4 °C.

(4,5-Diazafluoren-9-one-κ²N)[dichloropalladium(II)] (**1**). ^{1}H NMR ($(CD_3)_2SO$, 293 K): 8.83 dd, 2 H, *J*(1,2) = *J*(5,6) = 5.0, *J*(1,3) = *J*(4,6) = 1.6 (H1/H6); 8.13 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.5, *J*(1,3) = *J*(4,6) = 1.5 (H3/H4); 7.54 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.6, *J*(1,2) = *J*(5,6) = 5.0 (H2/H5). ^{13}C NMR ($(CD_3)_2SO$, 293 K): 193.9 s (C=O), 166.9 s, 159.0 d, 135.7 d, 133.3 s, 129.3 d. IR: 1 730.9 s (CO). For $C_{11}H_6Cl_2N_2OPd$ (359.5) calculated: 36.75% C, 1.68% H, 7.79% N; found: 36.88% C, 1.75% H, 7.73% N.

(4,5-Diazafluorene-κ²N)[dichloropalladium(II)] (**2**). ^{1}H NMR ($(CD_3)_2SO$, 293 K): 8.70 d, 2 H, *J*(1,2) = *J*(5,6) = 4.1 (H1/H6); 8.10 d, 2 H, *J*(2,3) = *J*(4,5) = 7.8 (H3/H4); 7.44 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.7, *J*(1,2) = *J*(5,6) = 4.8 (H2/H5); 3.99 s, 2 H (CH_2). ^{13}C NMR (CPMAS): 162.5 s, 144.6 s, 140.6 d, 136.0 d, 126.2 d, 47.3 t. For $C_{11}H_8Cl_2NPd$ (345.5) calculated: 38.24% C, 2.33% H, 8.11% N; found: 38.02% C, 2.28% H, 8.19% N.

[Dichloropalladium(II)](5,6-dihydro-1,10-phenanthroline-κ²N) (**3**). ^{1}H NMR ($(CD_3)_2SO$, 293 K): 8.71 d, 2 H, *J*(1,2) = *J*(5,6) = 5.6 (H1/H6); 8.10 d, 2 H, *J*(2,3) = *J*(4,5) = 7.7 (H3/H4); 7.63 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.5, *J*(1,2) = *J*(5,6) = 5.9 (H2/H5); 3.20 s, 4 H ($[CH_2]_2$). ^{13}C NMR ($(CD_3)_2SO$, 293 K): 157.3 s, 151.0 d, 144.2 d, 141.2 s, 130.9 d, 29.1 t. For $C_{12}H_{10}Cl_2NPd$ (359.5) calculated: 40.09% C, 2.80% H, 7.79% N; found: 39.66% C, 2.95% H, 7.65% N.

[Dichloropalladium(II)](3,3′-trimethylene-2,2′-bipyridine-κ²N) (**4**). ^{1}H NMR ($CDCl_3$, 293 K): 9.40 dd, 2 H, *J*(1,2) = *J*(5,6) = 5.5, *J*(1,3) = *J*(4,6) = 1.1 (H1/H6); 7.92 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.8, *J*(1,3) = *J*(4,6) = 1.1 (H3/H4); 7.48 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.8, *J*(1,2) = *J*(5,6) = 5.6 (H2/H5); 2.90 t, 4 H, *J* = 6.7 ($CH_2CH_2CH_2$); 2.49 quintet, 2 H, *J* = 6.6 ($CH_2CH_2CH_2$). ^{13}C NMR ($(CD_3)_2SO$, 343 K): 160.6 s, 152.2 d, 147.0 d, 144.6 s, 129.6 d, 36.2 t, 34.3 t. Exact mass, *m/z*, found: 336.9748 $[M - Cl]^+$; calculated: 336.9724 $[M - Cl]^+$.

Synthesis of [Chloromethylpalladium(II)](4,5-diazafluorene-κ²*N*) (**6**)

A pale yellow solution of PdCl(Me)(COD) (0.1 g, 0.38 mmol), dafe (70 mg, 0.42 mmol) in dichloromethane (40 ml) was stirred at 20 °C. In two hours a white suspension was formed. The solvent was removed under reduced pressure to *ca* 5 ml and the product was precipitated with hexane (30 ml). The product was then further precipitated by adding an excess of hexane. The suspension was centrifuged and the supernatant was removed. The residue was washed with ether (3 × 20 ml) and hexane (2 × 15 ml). The pale yellow solid was then dried *in vacuo*, giving 91% of **6**. Yellow/orange crystals of **6** suitable for an X-ray determination were obtained by slow diffusion of hexane into a solution of **6** in dichloromethane at 4 °C. ^{1}H NMR ($(CD_3)_2SO$, 293 K): 8.85 d, 2 H, *J*(1,2) = *J*(5,6) = 4.5 (H1/H6); 8.15 d, 2 H, *J*(2,3) = *J*(4,5) = 7.4 (H3/H4); 7.44 dd, 2 H, *J*(2,3) = *J*(4,5) = 7.6, *J*(1,2) = *J*(5,6) = 4.4 (H2/H5); 3.99 s, 2 H (CH_2); 0.92 s, 3 H (CH_3). Exact mass, *m/z*, found: 288.9930 $[M - Cl]^+$, calculated: 289.608 $[M - Cl]^+$.

Synthesis of Pd(N⌒N)(fn) Complexes **7** and **8**

(η^2-Fumaronitrile)(3,3′-trimethylene-2,2′-biquinoline-κ²*N*)[palladium(0)] (**7**): A mixture of $Pd(dba)_2$ (0.1 g, 0.17 mmol), 3-bq (56 mg, 0.19 mmol) and fn (15 mg, 0.19 mmol) in toluene (40 ml) was

stirred at 20 °C. The colour of the suspension turned in two hours from deep purple to bright yellow. The suspension was centrifuged and the supernatant was removed. The solid was dissolved in dichloromethane (50 ml) and this solution was filtered through Celite to remove metallic palladium. The solution was concentrated to *ca* 5 ml and the product was precipitated with hexane (30 ml). The precipitate was filtered off and washed with toluene (2 × 30 ml), ether (2 × 30 ml) and hexane (2 × 30 ml) and dried under vacuum which gave a red brown solid (95%).

(η²-Fumaronitrile)(3,3′-trimethylene-2,2′-biquinoline-κ²N)[palladium(0)] (**7**). ^{1}H NMR ($CDCl_3$, 293 K): 8.64 d, 2 H, *J*(1,2) = *J*(9,10) = 5.6 (H1/H10); 8.31 s, 2 H (H5/H6); 7.94 m, 4 H (H2/H4/H7/H9); 7.76 m, 2 H (H3/H8); –(C**H**$_2$)$_3$–: AA′BB′CC′ (see Figs 8 and 9) 2.92 (1 H, C), 2.94 (1 H, C′), 2.82 (1 H, B), 2.81 (1 H, B′), 2.48 (1 H, A), 2.47 (1 H, A′), *J*(AA′) = 28.9, *J*(A′C) = *J*(AC′) = *J*(AB′) = *J*(A′B) = 4.7, *J*(AC) = *J*(A′C′) = *J*(A′B′) = *J*(AB) = 4.7, *J*(CC′) = *J*(BB′) = –8.5, *J*(BC) = *J*(B′C′) = 32.9, *J*(B′C) = *J*(BC′) = 13.9. ^{13}C NMR ($CDCl_3$, 293 K): 158.6 s, 146.5 s, 138.4 d, 138.3 d, 133.2 s, 131.1 d, 128.9 s, 128.7 d, 126.8 d, 122.7 s (CN), 30.9 t, 30.4 t, 19.3 d. IR: 2 205 w (CN).

(η²-Fumaronitrile)(3,3′-tetramethylene-2,2′-biquinoline-κ²N)[palladium(0)] (**8**) was synthesized in a similar way in a yield of 89%. For determination major (ma) and minor (mi) isomer see Discussion. ^{1}H NMR ($CDCl_3$, 293 K): 8.57 d, *J*(1,2) = *J*(9,10) = 8.8, ma (H1/H10); 8.51 d, *J*(1,2) = *J*(9,10) = 8.6, mi (H1/H10); 8.35 s, ma + mi (H5/H6); 7.91 mp, ma + mi (H2/H4/H7/H9); 7.72 p, ma + mi (H3/H8); 3.31 s, mi (=C**H**); 3.12 s, ma (=C**H**); 3.21 m (ma + mi); 2.35 m (ma + mi); 1.92 m (ma + mi). ^{13}C NMR ($CDCl_3$, 293 K): 158.03 s (ma), 157.8 s (mi), 146.4 s (ma), 145.9 s (mi), 139.9 d (ma + mi), 139.7 d (ma + mi), 136.2 s (ma), 136.0 s (mi), 131.3 d (mi), 131.2 d (ma), 130.8 d (mi), 130.4 d (ma), 123.4 s (ma, CN), 123.2 s (mi, CN), 32.2 t (ma + mi), 29.1 d (ma + mi), 19.4 d (ma), 19.1 d (mi). IR: 2 201 s (CN).

X-Ray Crystal Structure Determination of $PdCl_2$(3-bpy) (**4**), $PdCl_2$(dcm-bpy) (**5**) and PdCl(Me)(dafe) (**6**)

Data collection for the crystals of complexes **4**, **5** and **6** was performed on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation for **4** and **6** and MoKα radiation for **5** and ω – 2θ scan. Two reference reflections were measured hourly and showed no decrease during the course of the data collection for the complexes **4** and **6** and a 6% decrease (corrected) for complex **5**. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 80 < 2θ < 90° for **4**, 40 < 2θ < 42° for **5** and 80 < 2θ < 91° for complex **6**. Corrections for Lorentz and polarization effects were applied. For **6**, the entire molecule is positioned at a special position on the mirror plane at $x = 0.75$ except for two hydrogen atoms (H11 and H121) which are on general positions, so one is on one side of the plane and a symmetry-related one is on the other side of the plane. The structure of the complexes **4** and **5** was solved by the PATTY option of the DIRDIF91 program system[22,23] while the structure of **6** was solved by Direct Methods. The positions of hydrogen atoms were calculated. Full-matrix least-squares refinement on *F*, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to the *R*-values given in Table I. For **6**, the temperature factors of the hydrogen atoms were kept fixed at $U = 0.11$ Å (ref.[23]). An empirical absorption correction, DIFABS, was applied[24]. For **4** and **5**, the secondary isotropic extinction coefficient[25,26] refined to *Ext* = 0.015(2) and 0.04(2), respectively. Scattering factors were taken from Cromer and Mann[27] and *International Tables for X-Ray Crystallography*[28]. The anomalous scattering of Pd and Cl was taken into account. All calculations were performed with XTAL (ref.[29]), unless stated otherwise. Thermal ellipsoid plots were made using the PLATON program[30]. The crystal, collection and refinement data have been compiled in Table I.

TABLE I
Crystallographic data for $PdCl_2$(3-bpy) **4**, $PdCl_2$(dcm-bpy) **5** and PdCl(Me)(dafe) **6**

Data	Complex		
	4	**5**	**6**
	Crystal		
Formula	$C_{13}H_{12}Cl_2N_2Pd$	$C_{14}H_{12}Cl_2N_2O_4Pd$	$C_{12}H_{11}ClN_2Pd$
M.w.	373.3	449.6	325.1
Cryst. system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	*Pmcn*
a, Å	8.4230(7)	7.340(4)	6.713(1)
b, Å	16.425(2)	10.012(3)	10.120(1)
c, Å	9.5836(7)	11.954(3)	17.187(3)
α, °	90	98.10(2)	90
β, °	106.316(7)	104.03(3)	90
γ, °	90	107.33(5)	90
V, $Å^3$	1 272.5(2)	791.7(7)	1 167.6(2)
Z	4	2	4
D_c, g cm^{-3}	1.95	1.89	1.85
μ, cm^{-1}	158.75 (CuKα)	15.2 (MoKα)	150.96 (CuKα)
F(000)	736	444	640
Crystal size, mm	0.05 × 0.10 × 0.60	0.30 × 0.35 × 0.80	0.05 × 0.10 × 0.60
	Collection		
T, K	293	293	293
θ_{min}, θ_{max}, °	5.4–74.7	2.2–29.9	5.1–74.6
Radiation, Å	1.5418 (CuKα)	0.71069 (MoKα)	1.5418 (CuKα)
Scan type	ω/2θ	ω/2θ	ω/2θ
Acq. time, h	32	49	15
Linear decay, %	0	6	0
Ref. reflections	$\bar{1}$ 1 3, $\bar{2}$ 5 1	$\bar{1}$ 0 1, $\bar{1}$ $\bar{2}$ 0	$\bar{1}$ 0 4, $\bar{2}$ 1 1
Data set, *h*, *k*, *l*	–10:10; 0:20; 0:11	–9:0; –14:0; –16:16	–8:0; 0:12; 0:21
Total unique data	2 614	4 572	1 307
Total obs. data	2 309 ($I > 2.5\sigma(I)$)	4 273 ($I > 2.5\sigma(I)$)	949 ($I > 2.5\sigma(I)$)
DIFABS corr. range	0.72 1.64	0.82 1.26	0.75 1.58

TABLE I
(*Continued*)

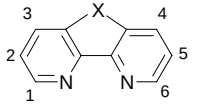
Data	Complex		
	4	**5**	**6**
	Refinement		
Refined parameters	212	257	178
Final R^a	0.033	0.039	0.048
Final $R_w{}^b$	0.036	0.054	0.074
w^{-1}	$6.2 + 85 \cdot 10^{-4} (\sigma F_o)^2 + + 9 \cdot 10^{-5}/\sigma F_o$	$7.0 + F_o + 0.0064F_o^2$	$6.7 + F_o + 0.0073F_o^2$
$(\Delta/\sigma)_{max}$	0.60	0.36	0.07
ρ_{min}, ρ_{max}, e Å^{-3}	–0.8, 1.0	–1.4, 1.4	–0.7, 1.1

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $R_w = [\Sigma[w(||F_o| - |F_c||)^2]/\Sigma[w(F_o^2)]]^{0.5}$.

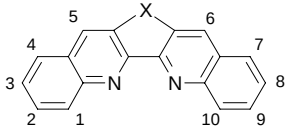
RESULTS AND DISCUSSION

*Synthesis of the $PdCl_2(N\frown N)$ (**1–5**) and $PdCl(Me)(N\frown N)$ (**6**) Complexes*

The complexes **1–5** and **6** of general formula $PdCl_2(N\frown N)$ and $PdCl(Me)(N\frown N)$ could be synthesized in fairly good yields starting from either $PdCl_2(MeCN)_2$ or PdCl(Me)(COD) (*cf.* Fig. 3 and Scheme 1). Establishing the bonding mode of dafo and dafe in the complexes **1**, **2** and **6** is of considerable importance since dafo and dafe may have other than a bidentate chelating coordination mode, *i.e.* (i) dafo can coordinate in a monodentate way in a Pd(0) complex [Pd(4,5-diazafluoren-9-one-κ*N*)$_2$(η^2-tcne)] (tcne = tetracyanoethylene)[31] and (ii) both dafo and dafe can act as bridging ligands in zero[32] and divalent[33] bimetallic palladium complexes.



X = CO (dafo)
= CH_2 (dafe)
= $(CH_2)_2$ (2-bpy)
= $(CH_2)_3$ (3-bpy)
= CO_2Me, CO_2Me (dcm-bpy)

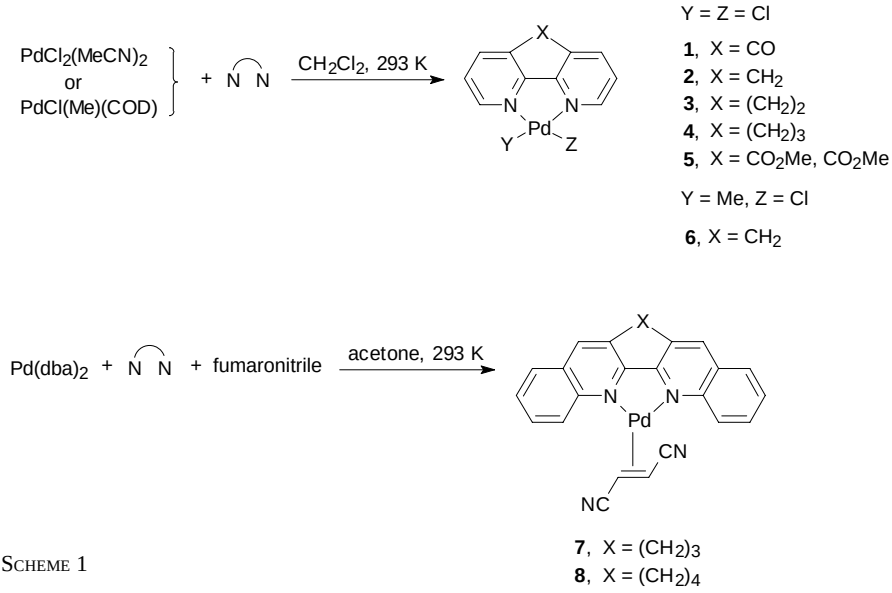


X = $(CH_2)_3$ (3-bq)
X = $(CH_2)_4$ (4-bq)

FIG. 3
α-Diimine ligands and their abbreviations

In the present cases of **1–6**, the analytical data revealed the 1 : 1 ratio of the metal and bisnitrogen ligand and X-ray crystal structure determinations of **4**, **5** and **6** confirmed the monometallic character of these complexes.

In the absence of steric constraints, 2,2′-bipyridine molecules coordinate mainly in a chelating way and are essentially planar[34] although exceptions are known[35]. In one reported structural case, the 2,2′-bipyridine is bridging between two platinum centers in $(PPN)_2[Pt_2(\mu\text{-}2,2'\text{-bpy})(CF_5)_6]$ (ref.[35d]). When methyl substituents are placed in the 3,3′-positions of 2,2′-bipyridine, the molecule can still act as a chelating ligand, but with a concomitant increase in the dihedral angle between the pyridyl rings to 30–35° (ref.[36]). Despite the large methoxycarbonyl substituents at the 3,3′-position in dcm-bpy, this ligand coordinates in $PdCl_2$(NN) (**5**) in a bidentate way. However, recent work in our laboratory showed that this ligand is also capable of bridging between two zerovalent palladium centers forming $Pd_2[\mu^2\text{-(dcm-bpy)}]_2(\eta^2\text{-tcne})_2$ (ref.[37]) with a dihedral angle of 91.5(3)° between the pyridine rings.



SCHEME 1

For 3,3′-annelated 2,2′-bipyridines, the dihedral angle between the pyridine rings is governed by the length of the bridge[5,12,13], and varies between 0 and 65° in going from a $-CH_2-$ to a $-(CH_2)_4-$ bridge (Fig. 4). Two important features control the complexing capabilities of the annelated bipyridyl series (and annelated biquinolines): (i) the nonbonded LP/LP′ distance and (ii) the dihedral LP–N…N′–LP′ angle. Therefore, when the length of the 3,3′-annelation is increased, a point is reached at which the formation of a five-membered metallacycle will be unlikely and monodentate or bridging coordination could result. From the analytical data as well as from the X-ray crystal structure of

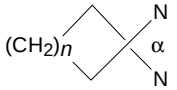
complex **4** it appears that 2- and 3-bpy, containing a $-(CH_2)_2-$ and a $-(CH_2)_3-$ bridge, respectively, still favour bidentate chelation over bridging or monodentate coordination in their palladium dichloride complexes (**3** and **4**). Unfortunately the $-(CH_2)_4$-bridged 2,2′-bipyridine could not be obtained due to synthetic problems. Attempts were made to synthesize the complexes $PdCl_2$(3-bq) and $PdCl_2$(4-bq), however, due to the low solubility and non-crystallinity of these complexes, no characterization has been undertaken.

Synthesis of the Palladium Complexes Pd(N⌒N)(fn) **7** *and* **8**

Attempts were made to synthesize zerovalent Pd(N⌒N)(fn) complexes with the ligands 3-bpy and dcm-bpy in order to see whether these ligands would give rise to the formation of diastereomeric complexes. Certainly in the latter case this diastereomerism would be expected, since upon coordination the bulky methoxycarbonyl groups of the dcm-bpy will prevent the ligand to racemize. Unfortunately isolable complexes could not be obtained. It is known that zerovalent palladium complexes with 2,2′-bipyridine derivatives are not easily accessible[31,32,38] especially when the electron accepting properties of the alkene are not sufficient to stabilize the metal complex. By using 3-bq and 4-bq as bisnitrogen ligands (Scheme 1), however, zerovalent palladium complexes **7** and **8** with the general formula Pd(N⌒N)(fn) were accessible. The analytical data confirmed the 1 : 1 : 1 ratio of the metal : NN : alkene. These complexes are well soluble and stable in polar solvents such as chloroform, dichloromethane and tetrahydrofuran. Yellow needle-shaped crystals, unsuitable for an X-ray crystal structure determination, were obtained by slow diffusion of hexane into a solution of **8** in dichloromethane at 4 °C.

*X-Ray Structural Analysis of $PdCl_2$(3-bpy) (***4***), $PdCl_2$(dcm-bpy) (***5***) and PdCl(Me)(dafe) (***6***)*

The molecular structure and the adopted numbering scheme are presented in Figs 5–7. Selected bond distances and angles for **4**, **5** and **6** are shown in Tables II and III,



n	2,2'-bipyridine α, °	2,2'-biquinoline α, °
1	0	0
2	19.0	20
3	48.4	50
4	62.7	65

FIG. 4
Calculated dihedral angles between the azaaryl groups in 3,3′-annelated diazabiaryls

respectively. In the complexes **4**, **5** and **6**, the divalent palladium center is coordinated to two nitrogen atoms of 3-bpy, dcm-bpy or dafe. In addition, the palladium in complexes **4** and **5** is bonded to two chlorine atoms and in complex **6**, the palladium atom is bonded to one chlorine and one carbon atom. The complexes can be regarded as square planar, albeit that in cases **4** and **5** there is a distortion of square planarity due to skewing of the pyridyl rings reflected by the dihedral angles mentioned in Table III. The torsion angle N1–C5–C10–N2 in complex **4** is 9.10°, whereas an MM2-V4 calculation on the free ligand[12] estimated the angle between the least-square planes of the two pyridine rings as 49°. Thus it appears that substantial flattening of the ligand has occurred as a result of coordination, similar to observations made for 4-bpy in a Ru(II)-complex[11b].

These three complexes have a N–Pd–N angle of 78.63(15)° for **4**, 79.64(11)° for **5** and 82.6(5)° for **6**. In order to understand the slightly larger N–Pd–N angle in **6** as compared to **4** and **5**, it should be recalled, that there are two ways in which the 3,3′-bridge in 3,3′-annelated 2,2′-bipyridines and 2,2′-biquinolines can affect the geometry of these compounds. Relieve of the eclipsing interaction or torsional strain in the 3,3′-bridge can be achieved by a rotation around the 2,2′-bond causing the pyridine rings to be noncoplanar which is the case for 2-bpy, 3-bpy, 3-bq and 4-bq. The dihedral angles between these rings are therefore governed by the length of the bridge. Whereas systems with a bridge containing more than one carbon atom can relieve strain by twisting about the 2,2′-bond, systems with one bridging carbon (dafo and dafe) remain coplanar and thus a distortion of the trigonal bond angles centered at C2 and C2′ (denoted as C6 and C11 in **6**, Fig. 7) must occur in the latter cases.

TABLE II
Selected bond distances (Å) for the complexes **4**, **5** and **6** (e.s.d.'s in parentheses)

$PdCl_2$(3-bpy) (**4**)		$PdCl_2$(dcm-bpy) (**5**)		PdCl(Me)(dafe) (**6**)	
Atoms	Distances	Atoms	Distances	Atoms	Distances
Pd–N1	2.000(3)	Pd–N1	2.030(3)	Pd–N1	2.080(11)
Pd–N2	2.008(4)	Pd–N2	2.031(2)	Pd–N2	2.222(10)
Pd–Cl1	2.3031(13)	Pd–Cl1	2.2778(10)	Pd–C1	2.051(14)
Pd–Cl2	2.2930(14)	Pd–Cl2	2.2915(11)	Pd–Cl	2.289(4)
N1–C5	1.360(6)	N1–C5	1.360(4)	N1–C6	1.327(19)
N2–C10	1.366(6)	N2–C10	1.356(4)	N2–C11	1.318(16)
C5–C10	1.494(7)	C5–C10	1.487(4)	C6–C11	1.446(18)

This type of in-plane distortion significantly increases the distance between the pyridyl nitrogen lone pairs. As a consequence of the increased nitrogen lone-pair distance, the N–Pd–N angle in the five-membered metallacycle in complex **6** concomitantly increases. Due to the increased nitrogen lone-pair distance, the bisnitrogen ligands

TABLE III
Selected bond and torsion angles (°) for the complexes **4**, **5** and **6** (e.s.d.'s in parentheses)

$PdCl_2$(3-bpy) (**4**)		$PdCl_2$(dcm-bpy) (**5**)		PdCl(Me)(dafe) (**6**)	
Atoms	Angles	Atoms	Angles	Atoms	Angles
N1–Pd–N2	78.63(15)	N1–Pd–N2	79.64(11)	N1–Pd–N2	82.6(5)
Cl1–Pd–Cl2	88.12(5)	Cl1–Pd–Cl2	89.57(4)	Cl–Pd–C1	89.9(5)
Cl1–Pd–N1	96.97(11)	Cl1–Pd–N1	95.40(7)	N1–Pd–C1	93.8(6)
Cl2–Pd–N2	96.32(11)	Cl2–Pd–N2	95.58(9)	Cl–Pd–N2	93.7(3)
Pd–N1–C5	118.6(3)	Pd–N1–C5	114.9(2)	Pd–N1–C6	108.8(9)
Pd–N2–C10	117.4(3)	Pd–N2–C10	114.1(2)	Pd–N2–C11	104.9(8)
N1–C5–C10	111.7(4)	N1–C5–C10	113.4(3)	N1–C6–C11	121.9(11)
N2–C10–C5	113.0(4)	N2–C10–C5	112.4(3)	N2–C11–C6	121.8(11)
C4–C5–C10	127.8(4)	C4–C5–C10	127.3(3)	C5–C6–C11	109.0(12)
C5–C10–C9	127.6(4)	C5–C10–C9	128.0(3)	C6–C11–C10	111.2(12)
N1–C5–C10–N2	9.10	N1–C5–C10–N2	25.08	N1–C6–C11–N2	0.00
C4–C5–C10–C9	12.80	C4–C5–C10–C9	29.24	C5–C6–C11–C10	0.00

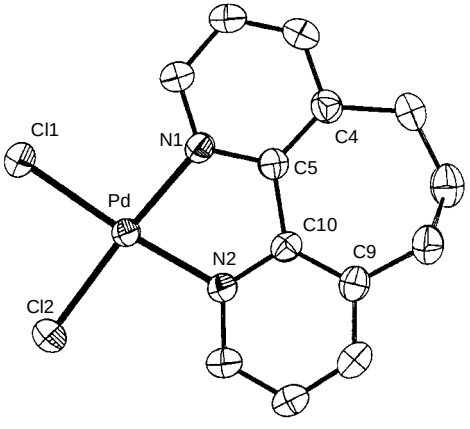


FIG. 5
Ortep drawing (30% probability level) of $PdCl_2$(3-bpy) (**4**)

dafo and dafe have the possibility not only to coordinate in a bidentate way but also in a monodentate way[31] or to occupy a bridging position between two metal centers[32,33].

The Pd–N distances in the complexes **4**, **5** and **6** (2.000(3)–2.222(10) Å) are in the range of those observed for other Pd(II)-diimine complexes[39,40]. The slightly longer Pd–N2 bond as compared to Pd–N1 in complex **6** is in agreement with the larger *trans* influence of the methyl group as compared to a chlorine atom and the Pd–C1 distance (2.051(14) Å) is comparable to values reported in literature[39]. Other bond distances and angles are as expected and show no anomalies.

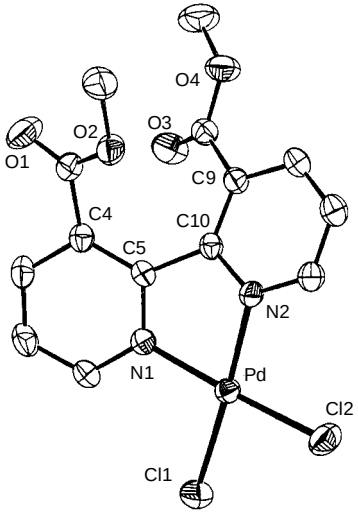


FIG. 6
Ortep drawing (30% probability level) of $PdCl_2$(dcm-bpy) (**5**)

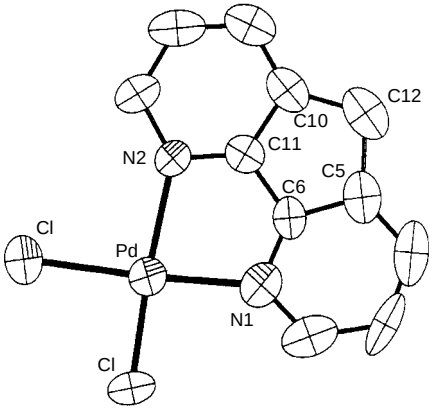


FIG. 7
Ortep drawing (30% probability level) of PdCl(Me)(dafe) (**6**)

Stereochemistry Monitored by ^1H NMR Spectroscopy

At 293 K the ^1H NMR spectra of **2** and **6** show a singlet for the $–CH_2–$ bridge protons as would be expected on the basis of the symmetry of the structure. At 293 K the ^1H NMR spectrum of **3** shows also a singlet for the $–(CH_2)_2–$ bridge protons since the ligand undergoes a rapid conformational inversion by twisting about the 2,2′-bond which causes the geminal methylene protons to become equivalent. This conformational inversion persisted even when the temperature was lowered to 213 K at 300.13 MHz.

Free and coordinated 3-bpy (in **4**) are both conformationally mobile on the NMR time scale down to 213 K at 300.13 MHz as indicated by the multiplicity of the trimethylene protons (A_2B_4). In contrast, free 3-bq is conformationally mobile down to 213 K (A_2B_4 spin system for $–(CH_2)_3–$), but becomes conformationally rigid upon coordination in **7**, as is reflected in the multiplicity of the trimethylene protons which appear as an AA′BB′CC′-spin system (*cf.* Figs 8 and 9). Ring inversion remains in the slow exchange regime up to 330 K (in $CDCl_3$), as is apparent from the unchanged spin multiplicity at this temperature. The limit of fast exchange could not be reached since decomposition of the complex took place above 355 K (in $(CD_3)_2SO$). Apparently the

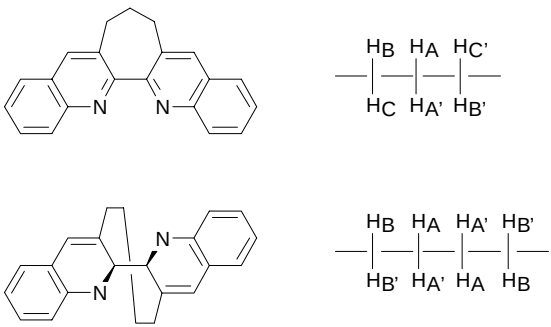


FIG. 8
Spin multiplicity in the ^1H NMR of the $–(CH_2)_n–$ bridge of *n*-bq in **7** and **8** (Pd(fn) part omitted)

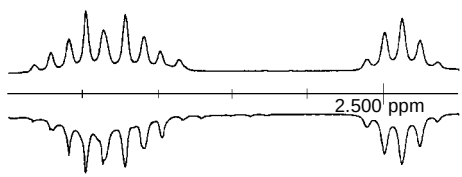


FIG. 9
^1H NMR ($CDCl_3$, 293 K); $–(CH_2)_3–$ fragment of **7**; above: experimental, below: simulated

five-membered metallacyclic portion of the complex [Pd(3-bq-κ^2N)] (**7**), representing *de facto* a second annelation between the quinoline moieties, restricts the conformational mobility of the ligand upon complexation causing it to be locked in a rigid posture on the NMR time scale. Since two chiral conformers of coordinated 3-bq are present (based on the spin multiplicity), together with the C_{2h}-symmetrical alkene (fn), the complex ought to exist as two diastereomeric pairs of enantiomers. These appear to be indistinguishable by ^{1}H NMR, as only one set of signals was observed. As it is unlikely that coordination occurred in a stereoselective manner, there are two alternative explanations for the observed ^{1}H NMR of **7**: (i) two diastereomeric pairs of enantiomers are present, but due to an anticipated relatively small dihedral angle between both quinoline moieties, based on the angle in $PdCl_2$(3-bpy) (**4**), the shift difference between the diastereomeric pairs is negligible and as a consequence they have identical chemical shifts or (ii) rapid diastereomeric interconversion *via* an alkene dissociation/recoordination, *viz*. if this process of alkene dissociation/recoordination is sufficiently fast on the NMR time scale it leads to the observed ^{1}H NMR spectrum.

Unfortunately, cooling down a sample of **7** to 213 K (in $CDCl_3$, 300.13 MHz) does not lead to any broadening of the signals, hence we cannot corroborate this conjecture. From an alkene exchange experiment (ratio **7**/fumaronitrile = 1 : 1 in $CDCl_3$, 300.13 MHz) it was observed that the free alkene is in exchange with the coordinated alkene. The free energy of activation for this alkene exchange process $\Delta G^{\neq} = 2.303RT_c\,(10.319 - \log k' + \log T_c)$ (where T_c is coalescence temperature and $k' = \pi\Delta\nu/2^{1/2}$; $\Delta\nu$ is the frequency separation of the coalescing peaks and the equation is strictly valid only for coalescence of two singlets) could be determined[41]. $\Delta G^{\neq}$(323 K) = 48 kJ mol^{-1}, *i.e*. a barrier for which signals with a (site) separation of 3 Hz in slow exchange should decoalesce at 213 K, which was not observed. Based on

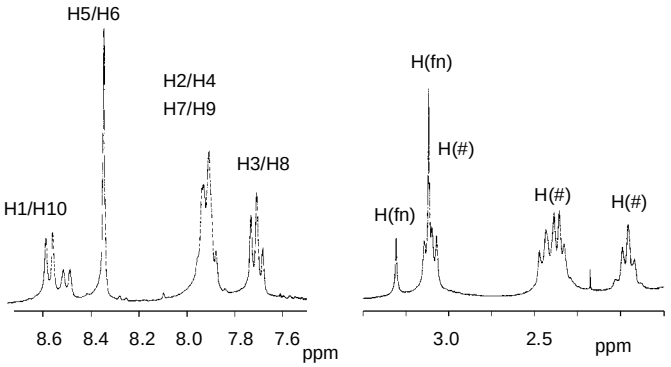


FIG. 10

^{1}H NMR spectrum of **8** ($CDCl_3$, 293 K, 300.13 MHz): numbering as in Fig. 3, H(#): –$(CH_2)_4$– bridge protons, only H1/H10 and H(fn) appear to be different for both diastereomers

theseobservations we have a preference for the first explanation, *i.e.* a coincidental degeneracy of the chemical shifts.

The tetramethylene bridge of both the non-coordinated and coordinated 4-bq is observed as four signals of which two overlap. The nature of this $(AA'BB')_2$ system (*cf.* Figs 8 and 10) can be understood after careful examination of a molecular model. One of the benzylic methylene protons lies nearly in the plane of the adjacent aromatic ring and is thus substantially deshielded. On the other hand, the other benzylic methylene proton is oriented toward the shielding region of the nonadjacent quinoline moiety and thus shows a signal at lower frequency. Complex **8** consists in two diastereomers forms due to the combination of a C_{2h}-symmetrical alkene (fn) and a C_2-symmetrical ligand (4-bq) as is reflected in the protons H1, H10 and the vinyl protons of the coordinated fumaronitrile (H(fn)) (Fig. 10). The other protons (H2–H9 and bridging protons $-(CH_2)_4-$) have identical chemical shifts for both diastereomeric pairs of enantiomers. From the two signals (H1, H10 and H(fn)) the ratio of diastereomers (57 : 43) can be established, apparently there is only a slight preference for one of both adducts.

A 2D NOESY spectrum of **8** revealed a strong NOE interaction between H(fn) and H1, H10 for the major isomer. For the minor isomer only a very weak cross peak could be observed. Based on this observation we are able to distinguish between the major and minor isomer. The major isomer is the enantiomeric pair denoted here as $M_{NN}M_a$ and $P_{NN}P_a$ (see Fig. 2). These are the structures one would expect since in these conformations the alkene experiences the least steric hindrance from the NN ligand in comparison to the other two conformers ($M_{NN}P_a$ and $P_{NN}M_a$, Fig. 2).

At elevated temperature (330 K, 300.13 MHz), no exchange between the diastereomers is observed and the process is still in the slow exchange region, *i.e.* no broadening of H1, H10 and H(fn) was observed. Based on this observation a minimum energy of activation can be estimated according to ref.[41]; $\Delta G^{\neq} > 68$ kJ mol^{-1}. In such cases the Forsén–Hofmann method[15], which makes use of spin saturation transfer, offers the possibility to determine the rates of inversion in the slow exchange region. Subsequently, the thermodynamic parameters of activation could be determined by using the Eyring equation[16]. The difference in chemical shift between H(fn) in the two diastereomers is large enough to irradiate one of them and observe a decrease in magnetization on the other. This procedure gives for **8** values for $\Delta H^{\neq} = 29.1$ kJ mol^{-1} and $\Delta S^{\neq} = -136.3$ J K^{-1} mol^{-1}. Based on these values the energy of activation can be calculated at 330 K; $\Delta G^{\neq}(330\ \text{K}) = 73$ kJ mol^{-1}. The large negative entropy of activation found for the epimerization favours a process *via* inversion of the coordinated 4-bq ligand over a mechanism *via* alkene dissociation/recoordination.

Diastereomeric interconversion was invoked not only from these spin saturation transfer experiments but also from the observation that upon dissolving crystals of **8** at 213 K initially a diastereomeric ratio of 80 : 20 was observed by ^{1}H NMR but after allowing the sample to warm up to 293 K the ratio slowly decreased and finally the

thermodynamic equilibrium of 57 : 43 was reached, which was the same as for the amorphous sample. As was stated for **7** (*vide supra*) diastereomeric interconversion can take place either by inversion of the coordinated C_2-chiral 4-bq ligand, or the alkene can dissociate from the palladium center and recoordinate after rotating 180° around the C=C double bond. From an alkene exchange experiment (ratio **8**/fumaronitrile = 1 : 1 in $CDCl_3$, 300.13 MHz) it was observed that the free alkene exchanges with the coordinated alkene. For this experiment the free energy of activation could not be determined since adding free fumaronitrile to complex **8** gave an unresolvable three site problem, *i.e.* exchange of free ligand with both H(fn) (Fig. 10).

CONCLUSION

The complexes synthesized in this study, using 3,3′-annelated diazabiaryls with the number of bridging groups ranging from one to four, are all monometallic complexes. The ligands 4,5-diazafluoren-9-one and 4,5-diazafluorene show an in-plane distortion around C2 and C2′ which causes the lone pair distance to be enlarged in comparison with 2,2′-bipyridine and 1,10-phenanthroline, however, this distortion is not an obstacle to form stable chelates in these cases. The ligand 3,3′-tetramethylene-2,2′-biquinoline with, at first glance, discouraging geometrical properties, turned out to be a good ligand to form a stable chelate.

Furthermore, it has been shown that it is unlikely that 3,3′-trimethylene-2,2′-biquinoline and 3,3′-tetramethylene-2,2′-biquinoline are good candidates for the utilization in enantioselective synthesis, although the Pd(3-bq) moiety in complex **7** appears to be rigid on the NMR time scale and in complex **8** there is a slight preference for the formation of one diastereomer. However, coordinated 4-bq in complex **8** does not form a *rigid* C_2-template on the laboratory time scale.

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