Synthesis and Characterization of Arylamide-Bridged Binuclear Palladium(II) Complexes. Crystal Structure of *anti*-[{Pd(C_6F_5)(*t*-BuNC)(μ-NHPh)}$_2$]

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Binuclear μ-hydroxo–μ-amido palladium(II) complexes of the type [{Pd(C_6F_5)(PPh_3)}$_2$(μ-OH)(μ-NHC_6H_4X-*p*)] (X = H (**1**), MeO (**2**), Cl (**3**), Br (**4**), and NO_2 (**5**)) have been prepared by reaction of [{Pd(C_6F_5)(PPh_3)(μ-OH)}$_2$] with the corresponding aromatic amine in dichloromethane. The ^{19}F and ^{31}P NMR spectroscopic data indicate that the isolated complexes are the *anti* isomers. The reaction of [{Pd(C_5F_5)(*t*-BuNC)(μ-Cl}$_2$] with 20% aqueous [NBu_4]OH and the arylamine (1:2:2 mol ratio) in methanol leads to the formation of *syn* and *anti* isomers of the bis(amido) complexes [{Pd(C_6F_5)(*t*-BuNC)(μ-NHC_6H_4X-*p*)}$_2$] (X = H (**6**), Me (**7**), MeO (**8**), Cl (**9**), and Br (**10**)). Complexes **6–9** are obtained as equimolar mixtures of *syn* and *anti* isomers and complex **10** as the *anti* isomer, but all the *syn–anti* mixtures are readily converted to the *anti* isomers by recrystallization from dichloromethane–hexane. The X-ray structure determination of *anti*-**6** has been established. The geometry at each palladium atom center is distorted square planar, and the Pd_2N_2 is substantially puckered.

Introduction

There has been increasing interest in the potential use of late-transition-metal amide complexes to facilitate the formation of carbon–nitrogen bonds.[1,2] through the insertion of unsaturated organic molecules into the metal–nitrogen bond.[3] Although metal amide complexes are common for the early transition elements in high oxidation states, analogous complexes for the later transition-metal ions are still relatively uncommon.[4–15] Their inherently low metal–nitrogen bond dissociation energies and/or facile decomposition pathways are presumed to lead to the difficulties in their preparation. Metathetical exchange of halide (or other leaving group) with a group 1 amide compound, deprotonation of a primary or secondary amine that is coordinated to a metal cation (taking advantage of the fact that an amine becomes more acidic when it is coordinated to a Lewis acid) or the elimination of HX by the action of the amine on a basic ligand (e.g., X = OH^-, alkyl) are typical routes to the preparation of metal amide complexes.

In the course of our investigations on the chemistry of hydroxo complexes of the group 10 elements[16–19] we have demonstrated that in the reaction of amines with hydroxo-bridged nickel(II), palladium(II), and platinum(II) in the presence of carbon disulfide, C–N bonds are formed to give *N,N*-dialkyldithiocarbamate complexes.[20,21] Possible routes to amido derivatives have now been examined, and here we report the successful synthesis of some (arylamido)palladium(II) complexes of the types [{Pd(C_6F_5)(PPh_3)}$_2$(μ-OH)(μ-NHR)] and [{Pd(C_6F_5)(*t*-BuCN)(μ-NHR)}$_2$] based on the acid–base reaction between a para-substituted aniline and [{Pd(C_6F_5)(PPh_3)(μ-OH)}$_2$] or the formal metathesis of Cl^- by RNH^- on the chloro-bridged complex [{Pd(C_6F_5)(*t*-BuCN)(μ-Cl)}$_2$], respectively. The first crystal structure of a bis(μ-arylamido)palladium(II) complex, [{Pd(C_6F_5)(*t*-BuCN)(μ-NHC_6H_5)}$_2$], is also reported.

Experimental Section

The C, H, and N analyses were performed with a Carlo Erba Model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid samples under nitrogen flow (100

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Table I. Crystal Structure Determination Details

Crystal Data	
formula	$C_{34}H_{30}F_{10}N_4Pd_2$
fw	897.4
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
cell dimensions	
a (Å)	6.178(4)
b (Å)	17.762(4)
c (Å)	16.418(5)
α (deg)	90
β (deg)	95.82(3)
γ (deg)	90
cell vol (Å^3)	1792.2
Z	2
D_{calc} (g cm^{-3})	1.66
$F(000)$	888
monochromated MolKα radiation	
λ (Å)	0.710 69
μ (cm^{-1})	10.7
Data Collection	
cryst size (mm)	0.2 × 0.1 × 0.05
diffractometer	Enraf-Nonius CAD4
no. of reflns for calculating cell; θ_{min}, θ_{max} (deg)	25; 7, 10
scan mode for data collection	0–20
data refln ranges; θ min and max (deg)	h 0 → 7, k 0 → 21, l −19 → 19; 2 → 25
total no. of reflns measd	3571
no. of unique reflns	3270
R_{int}	0.04
no. of significant reflns, $\|F^2\| > 2\sigma(F^2)$[a]	2011
max change in standard reflns (%)	−2.1
decay corr	no
max, min abs corr	1.25, 0.87 (DIFABS)
Structure solution and refinement	
non-H atoms located by	heavy atom methods SHELXS-86
refinement by	full matrix least squares non-H atoms anisotropic Enraf-Nonius MolEN programs
hydrogen atoms	fixed calculated positions $U_{iso} = 1.3U_{eq}$ for parent atom
R[b]	0.0555
R'[b]	0.0590
S	1.2
no. of variables	211
no. of observed reflns	2011
max (Δ/σ)	0.02
max, min (Δ/ρ) (e Å^{-3})	+0.32, −0.31

[a] $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, $w = \sigma^{-2}(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized. [b] The opposite absolute structure gave $R = 0.0557$, $R' = 0.0592$.

mL min^{-1}). The NMR spectra were recorded on a Bruker AC 200E (^{1}H) or Varian Unity 300 (^{19}F, ^{31}P) spectrometer, using $SiMe_4$, $CFCl_3$, or H_3PO_4 as the standard, respectively. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods. The starting complexes $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$[19] and $[\{Pd(C_6F_5)(t\text{-}BuCN)(\mu\text{-}Cl)\}_2]$[22] were prepared by procedures described elsewhere.

Complexes $[\{Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-}NHC_6H_4X\text{-}p)]$ (X = H (1), MeO (2), Cl (3), Br (4), NO_2 (5)). To a solution of $[(Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ (100 mg, 0.091 mmol) in CH_2Cl_2 (10 mL) was added the corresponding para-substituted aniline (0.182 mmol). The resulting solution was stirred for 30 min and concentrated under vacuum. The addition of hexane caused the precipitation of a white solid which was collected by filtration and air-dried. However, complexes **3** and **4** gave satisfactory analytical data only when they were recrystallized from dichloromethane–hexane.

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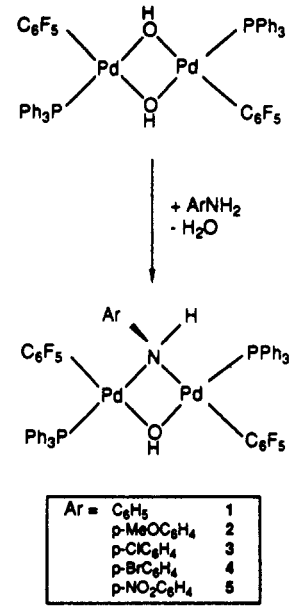
Scheme I



Complex **1**: yield 75%; mp 218 °C dec; IR (Nujol, cm^{-1}) 3600 (ν(OH)), 3300 (ν(NH)), 790 (Pd–C_6F_5). Anal. Calcd for $C_{54}H_{37}NF_{10}OP_2Pd_2$: C, 54.9; H, 3.2; N, 1.2. Found: C, 54.6; H, 3.0; N, 1.4. Complex **2**: yield 72%, mp 218 °C dec; IR (Nujol, cm^{-1}) 3580 (ν(OH)), 3310 (ν(NH)), 795 (Pd–C_6F_5). Anal. Calcd for $C_{55}H_{39}NF_{10}O_2P_2Pd_2$: C, 54.6; H, 3.3; N, 1.2. Found: C, 54.3; H, 3.0; N, 1.4. Complex **3**: yield 60%; mp 207 °C dec; IR (Nujol, cm^{-1}) 3595 (ν(OH)), 3332 (ν(NH)), 790 (Pd–C_6F_5). Anal. Calcd for $C_{54}H_{36}NClF_{10}OP_2Pd_2$: C, 53.4; H, 3.0; N, 1.2. Found: C, 53.4; H, 3.1; N, 1.2. Complex **4**: yield 63%; mp 207 °C dec; IR (Nujol, cm^{-1}) 3590 (ν(OH)), 3320 (ν(NH)), 790 (Pd–C_6F_5). Anal. Calcd for $C_{54}H_{36}NBrF_{10}OP_2Pd_2$: C, 51.5; H, 2.9; N, 1.1. Found: C, 51.4; H, 3.0; N, 1.3. Complex **5**: yield 70%; mp 217 °C dec; IR (Nujol, cm^{-1}) 3570 (ν(OH)), 3330 (ν(NH)), 790 (Pd–C_6F_5). Anal. Calcd for $C_{54}H_{36}N_2F_{10}O_3P_2Pd_2$: C, 52.9; H, 3.0; N, 2.3. Found: C, 52.5; H, 2.6; N, 2.1.

Complexes $[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}NHC_6H_4X\text{-}p)\}_2]$ (X = H (6), Me (7), OMe (8), Cl (9), Br (10)). To a suspension of *anti*-$[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}Cl)\}_2]$ (90 mg, 0.115 mmol) in methanol (15 mL) was added $[NBu_4]OH$ (0.230 mmol, ca. 0.30 mL of 20% aqueous solution). The white suspension was stirred for 10 min, and then the amine (0.230 mmol) was added. The resulting suspension was stirred for 1 h, during which time a yellow solution was obtained. The solution was concentrated under vacuum until precipitation of the crude product occurred as a yellowish solid, which was collected by filtration and air-dried. The isolated solids were identified by NMR spectroscopy as equal mixtures of *syn* and *anti* isomers of complexes **6–9**, but **10** was the pure *anti* isomer. Slow recrystallization (over 1 day) from dichloromethane–hexane (2 mL–4 mL) gave yellow crystals of the *anti* isomers.

Complex *anti*-**6**: yield 60%; mp 198 °C dec; IR (Nujol, cm^{-1}) 3300, 3280 (ν(NH)), 2220 (ν(C≡N)), 780 (Pd—C_6F_5). Anal. Calcd for $C_{34}H_{30}N_4F_{10}Pd_2$: C, 45.5; H, 3.4; N, 6.2. Found: C, 45.7; H, 3.4; N, 6.2. Complex *anti*-**7**: yield 50%; mp 197 °C dec; IR (Nujol, cm^{-1}) 3280 (ν(NH)), 2220 (ν(C≡N)), 785 (Pd—C_6F_5). Anal. Calcd for $C_{36}H_{34}N_4F_{10}Pd_2$: C, 46.7; H, 3.7; N, 6.1. Found: C, 46.9; H, 4.1; N, 5.9. Complex *anti*-**8**: yield 47%; mp 193 °C dec; IR (Nujol, cm^{-1}) 3280 (ν(NH)), 2220 (ν(C≡N)), 790 (Pd—C_6F_5). Anal. Calcd for $C_{36}H_{34}N_4F_{10}Pd_2O_2$: C, 45.2; H, 3.6; N, 5.9. Found: C, 44.9; H, 3.6; N, 6.0. Complex *anti*-**9**: yield 65%; mp 203 °C dec; IR (Nujol, cm^{-1}) 3215 (ν(NH)), 2220 (ν(C≡H)), 780 (Pd—C_6F_5). Anal. Calcd for $C_{34}H_{28}N_4F_{10}Pd_2Cl_2$: C, 42.3; H, 2.9; N, 5.8. Found: C, 42.4; H, 2.9; N, 6.0. Complex *anti*-**10**: yield 50%; mp 186 °C dec; IR (Nujol, cm^{-1}) 3220 (ν(NH)), 2215 (ν(C≡N)), 780 (Pd—C_6F_5). Anal. Calcd for $C_{34}H_{28}N_4F_{10}Pd_2Br_2$: C, 38.7; H, 2.7; N, 5.3. Found: C, 38.8; H, 2.8; N, 5.3.

Table II. NMR Spectroscopic Data[a,b] (J in Hz) for Complexes 1–5

complex	^{1}H	^{19}F	^{31}P
1	7.6–7.1 (m, 30 H, Ph_3P)	−116.3 (m, 2 F_o, J_{FP} 9.0, J'_{FP} 7.6)	30.4 (s)
	6.9–6.7 (m, 5 H, *Ph*NH)	−117.5 (m, 1 F_o, J_{FP} 9.3)	28.0 (s)
	−2.3 (s, 1 H, OH)	−120.2 (m, 1 F_o, J_{FP} 7.6)	
		−161.3 (t, 1 F_p, J_{mp} 19.8)	
		−162.0 (t, 1 F_p, J_{mp} 19.8)	
		−163.4 (m, 1 F_m)	
		−163.8 (m, 1 F_m)	
		−163.9 (m, 1 F_m)	
		−164.8 (m, 1 F_m)	
2	7.6–7.0 (m, 30 H, Ph_3P)	−117.3 (m, 1 F_o, J_{FP} 8.2)	30.3 (s)
	6.7 (d, 2 H, H_o of C_6H_4, *J* 8.4)	−117.4 (m, 1 F_o, J_{FP} 8.5)	27.6 (s)
	6.5 (d, 2 H, H_m of C_6H_4, *J* 8.4)	−118.6 (m, 1 F_o, J_{FP} 9.9)	
	3.7 (s, 3 H, Me)	−121.3 (m, 1 F_o, J_{FP} 8.2)	
	−2.4 (s, 1 H, OH)	−162.6 (t, 1 F_p, J_{mp} 20.6)	
		−163.3 (t, 1 F_p, J_{mp} 19.2)	
		−164.5 (m, 1 F_m)	
		−165.0 (m, 1 F_m)	
		−165.1 (m, 1 F_m)	
		−166.1 (m, 1 F_m)	
3	7.6–7.2 (m, 30 H, Ph_3P)	−116.2 (m, 1 F_o, J_{FP} 6.2)	30.5 (s)
	6.86 (d, 2 H, H_o of C_6H_4, *J* 8.3)	−116.3 (m, 1 F_o, J_{FP} 5.9)	28.3 (s)
	6.72 (d, 2 H, H_m of C_6H_4, *J* 8.3)	−117.3 (m, 1 F_o, J_{FP} 9.0)	
	−2.2 (s, 1 H, OH)	−119.9 (m, 1 F_o, J_{FP} 7.6)	
		−161.0 (t, 1 F_p, J_{mp} 19.8)	
		−161.5 (t, 1 F_p, J_{mp} 20)	
		−163.0 (m, 1 F_m)	
		−163.5 (m, 1 F_m)	
		−163.7 (m, 1 F_m)	
		−164.4 (m, 1 F_m)	
4	7.6–7.2 (m, 30 H, Ph_3P)	−116.2 (m, 1 F_o, J_{FP} 7.6)	30.5 (s)
	6.98 (d, 2 H, H_o of C_6H_4, *J* 8.3)	−116.3 (m, 1 F_o, J_{FP} 9.3)	28.3 (s)
	6.67 (d, 2 H, H_m of C_6H_4, *J* 8.3)	−117.4 (m, 1 F_o, J_{FP} 9.0)	
	−2.2 (s, 1 H, OH)	−119.8 (m, 1 F_o, J_{FP} 9.0)	
		−160.9 (t, 1 F_p, J_{mp} 19.8)	
		−161.5 (t, 1 F_p, J_{mp} 21.4)	
		−163.0 (m, 1 F_m)	
		−163.4 (m, 1 F_m)	
		−163.7 (m, 1 F_m)	
		−164.4 (m, 1 F_m)	
5	7.6–7.2 (m, 32 H, Ph_3P + H_o of C_6H_4)	−117.7 (m, 1 F_o, J_{FP} 8.2)	30.5 (s)
		−118.2 (m, 1 F_o, J_{FP} 8.5)	29.3 (s)
	7.8–7.7 (d, 2 H, H_m of C_6H_4, *J* 8.3)	−118.7 (m, 1 F_o, J_{FP} 8.2)	
	−1.92 (s, 1 H, OH)	−121.5 (m, 1 F_o, J_{FP} 8.5)	
		−161.7 (t, 1 F_p, J_{mp} 20.6)	
		−162.0 (t, 1 F_p, J_{mp} 20.6)	
		−163.9 (m, 1 F_m)	
		−164.2 (m, 1 F_m)	
		−164.8 (m, 1 F_m)	
		−165.1 (m, 1 F_m)	

[a] Chemical shifts in ppm from TMS (^{1}H), from $CFCl_3$ (^{19}F), or from H_3PO_4 (^{31}P). Abbreviations: br, broad: s, singlet; d, doublet; t, triplet: m, multiplet. [b] In $CDCl_3$.

X-ray Structure Determination. A crystal suitable for a diffraction study was grown from dichloromethane–hexane. Details of data collection and refinement are given in Table I.

Results and Discussion

μ-Hydroxo–μ-Arylamido Complexes [{Pd(C_6F_5)(PPh_3)}$_2$(μ-OH)(μ-NHC_6H_4X-*p*)]. The preparation of *anti*-[{Pd(C_6F_5)(PPh_3)(μ-OH)}$_2$] and its reactions with pyrazole have previously been reported.[19] Its reactivity toward protic acids is consistent with the high-field proton resonance (δ −1.6) observed for the OH bridges. This hydroxo complex *anti*-[{Pd(C_6F_5)(PPh_3)(μ-OH)}$_2$] reacts with aniline or para-substituted anilines *p*-$XC_6H_4NH_2$ (X = H, MeO, Cl, Br, or NO_2) in dichloromethane to give the corresponding μ-hydroxo–μ-amido complexes **1–5** (Scheme I) in 60–75% yields. The complexes were obtained as white precipitates by addition of hexane. The assigned structures for **1–5** are based on miroanalytical, IR (Experimental Section), and ^{1}H, ^{19}F, and ^{31}P NMR (Table II) spectroscopic data. The complexes are air-stable solids and thermal analysis shows that in a dynamic N_2 atmosphere they decompose only above 205 °C.

The IR spectra of the complexes show the characteristic absorptions of the C_6F_5 group at ca. 1630, 1490, 1450, 1050, 950, and 790 cm^{-1}. The latter absorption derives from the so-called "X-sensitive" mode,[23] and it is observed as a single band, as expected from the presence of only one C_6F_5 group in the coordination sphere of each palladium atom.[24] Two bands at 3600–3570 and 3320–3300 cm^{-1} can be assigned to ν(OH) and ν(NH), respectively. The presence of the hydroxo ligand is also established by the observation of high-field proton resonances (ca −1.9 to −2.4 ppm), but no resonance from the amide NH is detected in the proton spectra. The aromatic protons of the μ-amido ligand in complexes **2–5** appear as an AB pattern. The two resonances observed in the ^{31}P NMR spectra are consistent

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Scheme II

$[(C_6F_5)(t\text{-BuNC})Pd(\mu\text{-Cl})_2Pd(t\text{-BuNC})(C_6F_5)]$

i) + 2 NBu_4OH / MeOH
ii) + 2 $ArNH_2$

$[(C_6F_5)(t\text{-BuNC})Pd(\mu\text{-ArNH})_2Pd(t\text{-BuNC})(C_6F_5)]$

Ar =	C_6H_5	6
	p-MeC_6H_4	7
	p-$MeOC_6H_4$	8
	p-ClC_6H_4	9
	p-BrC_6H_4	10

with the *anti* structure proposed for 1–5 and the ^{19}F spectra also reveal the presence of two different C_6F_5 groups. Each freely rotating pentafluorophenyl ring should give three resonances (in the ratio 2:2:1) for the *o*-, *m*-, and *p*-fluorine atoms, respectively. However, in the *o*- and *m*-F regions four resonances with the intensity ratio of 1:1:1:1 are observed for complexes 1–5, indicating hindered rotation of both C_6F_5 rings around the Pd–C_6F_5 bond. The very small difference between the chemical shifts of the low-field signals in the *o*-F region for complex 1 prevented us from reading two distinct signals, but two different signals are discernible in the corresponding *m*-F region.

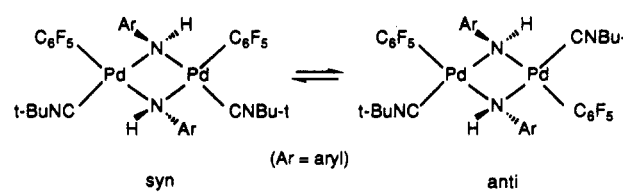
Bis(μ-arylamido) Complexes $[\{Pd(C_6F_5)(t\text{-BuNC})(\mu\text{-}NHC_6H_4X\text{-}p)\}_2]$. Unsuccessful attempts were made to prepare bis(μ-amido) complexes by reacting $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-OH})\}_2]$ with 2 molar equiv of the corresponding aromatic amine. The formation of the μ-amido complex should involve deprotonation of the amine by the OH group, but as expected, there is no correlation between the chemical shift of the bridging OH and its deprotonating ability (δ is −1.6 for the bis(μ-hydroxo) complex whereas δ is in the range −1.9 to −2.4 for the μ-hydroxo–μ-amido complexes), because the chemical shift of a μ-OH group is sensitive to solvent and concentration changes. The real reason for our failure to prepare the bis(amido) complex with triphenylphosphine ligands may be simply kinetic. It should be noted at this point that our recently initiated (unpublished) investigation by us has demonstrated that the dianionic complex $[\{Pd(C_6F_5)_2(\mu\text{-OH})\}_2]^{2-}$ (OH, δ −2.84) reacts with 2 equiv of aniline to give the corresponding bis(μ-anilido) complex. Nevertheless, the bis(μ-amido) complexes **6–10** (Scheme II) have been made from the precursor *anti*-$[\{Pd(C_6F_5)(CN\text{-}t\text{-Bu})(\mu\text{-Cl})\}_2]$ which contains *tert*-butyl isocyanide instead of triphenylphosphine as the neutral ancillary ligand. Attempts were first made to form the corresponding bis(μ-hydroxo) complex by metathesis of μ-Cl by μ-OH in methanol, but inseparable mixtures of hydroxo and methoxo complexes were obtained.[25] Consequently, the strategy was slightly modified: in methanol the bis(μ-chloro) complex was reacted with 20% aqueous $[NBu_4]OH$ (1:2 mol ratio) and, after 10 min of stirring, 2 equiv of the amine were added to give complexes **6–10**. The NMR data for complexes **6–9** showed that they are obtained as a mixture of *anti* and *syn* isomers in approximately equal amounts, small variations depending on the identity of the *p*-X substit-

Table III. NMR Spectroscopic Data[a,b] (*J* in Hz) for Complexes 6–10

complex	^1H	^{19}F
anti-**6**	7.00 (d, 4 H, H_o, *J* 7.6)	−117.6 (br, 2 F_o)
	6.81 (dd, 4 H, H_m, *J* 7.6)	−121.9 (br, 2 F_o)
	6.51 (t, 2 H, H_p, *J* 7.6)	−161.6 (t, 2 F_p, J_{mp} 20.6)
	0.91 (s, 18 H, CH_3 of *t*-BuNC)	−164.2 (br, 4 F_m)
syn-**6**	7.41 (m, 4 H)	−119.0 (br, 2 F_o)
	7.15 (m, 4 H)	−119.8 (br, 2 F_o)
	6.70 (m, 2 H)	−160.6 (t, 2 F_p, J_{mp} 19.7)
	1.02 (s, 18 H, CH_3 of *t*-BuNC)	−163.4 (br, 4 F_m)
anti-**7**	6.88 (d, 4 H, H_o, *J* 8.4)	−117.5 (br, 2 F_o)
	6.60 (d, 4 H, H_m, *J* 8.4)	−121.8 (br, 2 F_o)
	2.02 (s, 6 H, CH_3 of *p*-MeC_6H_4)	−162.0 (t, 2 F_p, J_{mp} 19.7)
	0.91 (s, 18 H, CH_3 of *t*-BuNC)	−164.3 (br, 4 F_m)
anti-**8**	6.92 (d, 4 H, H_o, *J* 8.4)	−117.6 (br, 2 F_o)
	6.40 (d, 4 H, H_m, *J* 8.4)	−121.8 (br, 2 F_o)
	3.58 (s, 6 H, CH_3 of *p*-$MeOC_6H_4$)	−161.6 (t, 2 F_p, J_{mp} 21.0)
	0.95 (s, 18 H, CH_3 of *t*-BuCN)	−163.9 (br, 4 F_m)
syn-**8**	7.26 (d, 2 H, H_o, *J* 8.7)	−118.4 (d, 4 F_o, J_{om} 29.0)
	7.04 (d, 2 H, H_m, *J* 8.7)	−160.2 (t, 2 F_p, J_{mp} 19.7)
	6.67 (d, 2 H, H_o, *J* 8.7)	−163.0 (m, 4 F_m)
	6.56 (d, 2 H, H_m, *J* 8.7)	
	3.66 (s, 6 H, CH_3 of *p*-$MeOC_6H_4$)	
	1.07 (s, 18 H, CH_3 of *t*-BuCN)	
anti-**9**	6.95 (d, 4 H, H_o, *J* 8.4)	−117.6 (br, 2 F_o)
	6.80 (d, 4 H, H_m, *J* 8.4)	−122.4 (br, 2 F_o)
	0.97 (s, 18 H, CH_3 of *t*-BuCN)	−160.4 (t, 2 F_p, *J* 19.7)
		−163.5 (br, 4 F_m)
syn-**9**	7.34 (m, 2 H, H_o, *J* 8.4)	−119.7 (br, 4 F_o)
	7.08 (m, 2 H, H_o, *J* 8.4)	−158.6 (t, 2 F_p, J_{mp} 19.7)
	7.00 (m, 2 H, H_m, *J* 8.4)	−162.4 (m, 4 F_m)
	6.50 (m, 2 H, H_m, *J* 8.4)	
	1.04 (s, 18 H, CH_3 of *t*-BuCN)	
anti-**10**	6.96 (d, 4 H, H_o, *J* 9.3)	−117.6 (br, 2 F_o)
	6.90 (d, 4 H, H_m, *J* 8.4)	−122.7 (br, 2 F_o)
	0.97 (s, 18 H, CH_3 of *t*-BuCN)	−160.3 (t, 2 F_p, J_{mp} 21.0)
		−163.3 (br, 4 F_m)

[a] Chemical shifts in ppm from TMS (^1H) or from $CFCl_3$ (^{19}F). Abbreviations: br, broad; s, singlet; d, doublet; t, triplet. [b] In $CDCl_3$.

uent, while **10** is found almost exclusively as the *anti* isomer. Similar 1:1 *syn–anti* mixtures have recently been reported for the complexes $[\{Pt(PMePh_2)(POPh_2)(\mu\text{-}NH_2)\}_2]$[13] and $[\{PtMe(PCy_3)(\mu\text{-}NH_2)\}_2]$.[12] When the benzene solution of the isomeric mixture of the latter compound is allowed to stand for 12 h at ambient temperature, the *syn* isomer precipitates and when an excess of tricyclohexylphosphine is added to the $CDCl_3$ solution of the *syn* isomer, the complex isomerizes to an equimolecular mixture of the *syn* and *anti* isomers.[12] In our case, yellow crystals of pure *anti* isomers could be grown from dichloromethane–hexane. The same result is observed when the *syn–anti* mixture is dissolved in dichloromethane and complete evaporation of the solvent is allowed. All this suggests the existence of an equilibrium between the *syn* and *anti* isomers which is displaced toward the *anti* isomer due to its lower solubility. The isomer-



ization process could not be observed when the equimolecular *syn–anti* mixtures were kept in solution in $CDCl_3$ or C_6D_6 for a prolonged period. Furthermore, when the

(25) In fact μ-methoxo complexes can be obtained by treating μ-hydroxo complexes with methanol; see, for example: López, G.; Ruiz, J.; García, G.; Vicente, C.; Rodríguez, V.; Sánchez, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1681.

Table IV. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U_{iso}/U_{eq}
Pd1	634.5(19)	0	1782.5(7)	32(1)[a]
Pd2	-464.3(20)	1093.3(8)	3109.5(7)	33(1)[a]
F1	-1702(16)	-1602(6)	1269(6)	48(3)
F2	-285(17)	-3001(7)	1540(6)	62(3)
F3	3840(19)	-3287(7)	2240(7)	73(3)
F4	6542(17)	-2111(6)	2674(6)	59(3)
F5	5264(15)	-702(6)	2338(6)	50(3)
F6	-4959(16)	1372(6)	3941(6)	55(3)
F7	-7408(18)	2577(7)	4051(7)	71(3)
F8	-6365(19)	3896(8)	3310(7)	75(3)
F9	-2762(19)	3956(8)	2521(7)	77(4)
F10	-154(16)	2759(6)	2446(6)	53(3)
N1	-287(19)	1154(8)	1859(7)	34(3)
N2	1689(20)	196(7)	2995(7)	35(3)
N3	-1337(23)	-242(8)	15(9)	49(4)
N4	4(23)	973(8)	4979(9)	46(4)
C1	1705(25)	-1060(9)	1823(9)	31(4)
C2	346(25)	-1676(10)	1613(9)	34(4)
C3	1117(28)	-2415(11)	1760(10)	47(5)
C4	3140(29)	-2552(11)	2101(11)	48(5)
C5	4527(29)	-1995(11)	2305(11)	51(5)
C6	3804(26)	-1251(10)	2154(9)	37(4)
C7	-2546(28)	2016(10)	3166(10)	42(4)
C8	-4308(25)	1988(9)	3554(9)	34(4)
C9	-5647(28)	2621(11)	3628(11)	45(5)
C10	-5088(28)	3238(11)	3253(11)	50(5)
C11	-3373(29)	3302(11)	2852(11)	47(5)
C12	-1998(28)	2679(11)	2831(11)	46(5)
C13	-500(27)	-134(11)	666(10)	47(5)
C14	-2482(33)	-405(12)	-808(12)	62(6)
C15	-2019(47)	-1176(20)	-1060(18)	118(10)
C16	-1685(93)	130(42)	-1401(36)	286(29)
C17	-4573(65)	-415(25)	-659(25)	180(17)
C18	-286(25)	1020(10)	4277(9)	38(4)
C19	474(36)	874(13)	5884(13)	74(7)
C20	2964(61)	770(21)	6079(22)	148(13)
C21	-518(57)	114(25)	6046(22)	155(13)
C22	-312(53)	1519(21)	6298(21)	133(12)
C23	-2025(23)	1416(9)	1297(8)	26(4)
C24	-4115(26)	1103(12)	1236(10)	47(4)
C25	-5819(29)	1310(11)	659(11)	53(5)
C26	-5335(34)	1945(13)	145(12)	63(6)
C27	-3343(33)	2288(12)	217(12)	63(6)
C28	-1690(29)	2010(11)	773(11)	45(5)
C29	1764(27)	-410(10)	3572(10)	39(4)
C30	-58(29)	-827(11)	3679(11)	48(5)
C31	21(34)	-1383(13)	4249(12)	65(6)
C32	1937(33)	-1526(12)	4751(12)	60(6)
C33	3755(31)	-1102(12)	4662(11)	56(5)
C34	3770(29)	-542(11)	4090(10)	43(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

anti isomers were redissolved in $CDCl_3$, the ^1H NMR spectra showed no indication of conversion to the *syn* isomers over a period of 3 days. However, when a small amount of *tert*-butyl isocyanide was added to the CD_3Cl solution of a pure sample of *anti*-**9**, a 1:1 mixture of the *syn* and *anti* isomers was formed within 10 min.

The NMR spectroscopic data for the *syn* and *anti* isomers are presented in Table III. Data for the *syn* isomers were obtained from the spectra of the *syn–anti* mixtures. However, in the preparation of **7** the *syn–anti* mixture coexisted with an unidentified species which prevented us from making a reliable assignment for *syn*-**7**. The observation of two or three signals for the aromatic protons of the arylamide groups in the *anti* isomers indicates that rotation of the *p*-XC_6H_4 group about the C–N bond is rapid on the NMR time scale.[4] The *syn* isomers exhibit two different sets of proton resonances,

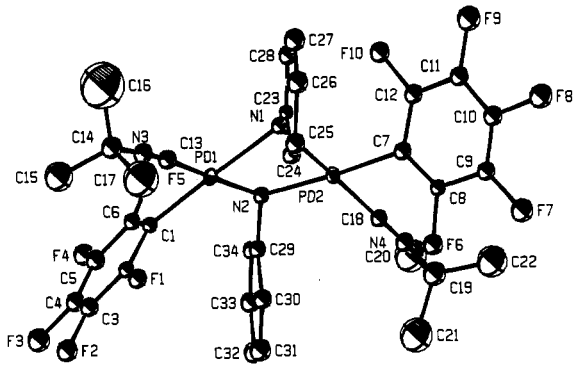


Figure 1. Structure of *anti*-**6**.

Table V. Selected Intramolecular Distances (Å) and Angles (deg) for *anti*-6, with Estimated Standard Deviations in Parentheses

	(a) Bonds		
Pd1–N1	2.135(15)	Pd1–N2	2.060(12)
Pd1–C1	1.994(16)	Pd1–C13	1.909(16)
Pd2–N1	2.069(11)	Pd2–N2	2.097(13)
Pd2–C7	2.092(18)	Pd2–C18	1.914(15)
	(b) Angles		
N1–Pd1–N2	80.9(5)	N1–Pd1–C1	173.8(5)
N1–Pd1–C13	95.9(6)	N2–Pd1–C1	93.2(5)
N2–Pd1–C13	176.1(7)	C1–Pd1–C13	90.1(7)
N1–Pd2–N2	81.5(5)	N1–Pd2–C7	95.6(6)
N1–Pd2–C18	173.6(6)	N2–Pd2–C7	176.7(6)
N2–Pd2–C18	93.8(6)	C7–Pd2–C18	89.0(7)
Pd1–N1–Pd2	92.9(5)	Pd1–N2–Pd2	94.2(5)
C13–N3–C14	177.2(2)	C18–N4–C19	177.2(2)

which is in agreement with the presence of two different amide groups. As with the μ-hydroxo–μ-amido complexes, no signal for the NH protons is observed. The ^{19}F NMR spectra of the *syn* and *anti* isomers show one sharp triplet for the *p*-F atoms, indicating the equivalence of both C_6F_5 groups, but one or two broad resonances observed in the *o*-F region show restricted rotation of the perfluorophenyl rings. The IR spectra of the *anti* isomers show one or two weak absorptions at ca. 3280 cm^{-1} assigned to ν(NH), one absorption for ν(C≡N) at 2220 cm^{-1}, and the characteristic bands of the C_6F_5 ring.

Structure of *anti*-[{Pd(C_6F_5)(*t*-BuNC)(μ-NHPh)}₂]. Fractional atom coordinates for *anti*-**6** are given in Table IV, and selected bond lengths and angles, in Table V. The molecular structure and atom numbering scheme are shown in Figure 1. The geometry about each palladium atom is approximately square planar, but the {Pd_2N_2} ring is far from planar. The angle between the planes defined by Pd1, N1, and N2 and Pd2N1 and N2 is 32.7°. There are few literature data which provide a direct comparison, and both bent and planar structures are known. Thus the complexes $[Pd_2(N_3)_6]^{2-}$,[26] $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]CO_3\cdot 2H_2O$,[27] $[Pt_2(\mu\text{-}OH)_2(dmso)_4](ClO_4)_2$,[28] $(Pt_2(\mu\text{-}OH)_2$(tetrahydrothiophene-S oxide)$_4](NO_3)_2$,[29] $[NBu_4]_2[Pd_2(C_6F_4)_4(\mu\text{-}OH)_2]$,[16] and $[Pt_2(\mu\text{-}OH)_2(dppf)][BF_4]_2$[30] all have planar M_2X_2 cores. Although these are all charged species, the presence of charge does not automatically indicate planarity. Thus $[Pd_2(\mu\text{-}OH)_2(dppe)]X_2$ has an angle between

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the $\{PdO_2\}$ planes of 33.8(8)°,[31] and the angle between the $\{PtN_2\}$ planes in $[Pt_2(\mu\text{-}NH_2)_2(PMe_2Ph)_4][BF_4]_2$ is 32°.[32] A folded conformation does seem to be general for phosphine derivatives whether charged or not; the angle between the $\{Pt_2O\}$ planes in $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4][BF_4]_2$ was similar, at 36.4°,[33] and the related angles in $[Pt_2(\mu\text{-}NH_2)(PMePh_2)_2(Ph_2PO)_2]$,[34] $[Pt_2Cl_2(\mu\text{-}NH_2)_2(PPh_3)_2]$,[11] and $[Pt_2Me_2(\mu\text{-}NH_2)_2(PPh_3)_2]$[12] were respectively 44, 45, and 45°. The reasons for the extent of folding in this type of structure is not well understood nor readily predictable. However, in related platinum chemistry there is a distinct preference for folded structures in μ-NH_2 diplatinum derivatives. Both the aryl groups are on the same side of the puckered ring.

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Supplementary Material Available: Tables of intramolecular distances and angles, hydrogen atom coordinates, anisotropic temperature factors (Pd1, Pd2), and least squares planes for **6** (6 pages). Ordering information is given on any current masthead page.

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