Synthesis, Characterization, and Crystal Structures of Monomeric and Dimeric Palladium(II) Amide Complexes

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Received March 7, 1994®

Addition of KN(R)Ph to *trans*-$(PMe_3)_2Pd(R')I$ (R = H, Me; R′ = Ph, Me) results in the formation of the monomeric anilide complexes *trans*-$(PMe_3)_2Pd(R')N(R)Ph$ in good yield. A single-crystal X-ray diffraction study of *trans*-$(PMe_3)_2Pd(Ph)N(H)Ph$ (**1**) reveals that it crystallizes in the space group $P\bar{1}$ with $a = 8.423(3)$ Å, $b = 10.768(4)$ Å, $c = 12.565$ Å, $\alpha = 68.81(3)°$, $\beta = 71.90(3)°$, $\gamma = 87.65(3)°$, $V = 1006.7(7)$ Å^3, and $Z = 2$. There is no evidence for significant interaction between the N lone pair and the metal center, though a shortened N—C distance (1.32(2) Å) may indicate interaction between the N lone pair and the phenyl ring. Thermolysis of **1** at 90 °C in the solid state results in loss of PMe_3 and formation of the dimeric complex $[(PMe_3)Pd(Ph)(\mu\text{-}NHPh)]_2$ (**9**), which was also characterized with a single-crystal X-ray structure study. Compound **9** crystallizes in the space group $P\bar{1}$ with $a = 6.805(1)$ Å, $b = 12.186(2)$ Å, $c = 18.943(3)$ Å, $\alpha = 89.56(1)°$, $\beta = 85.17(1)°$, $\gamma = 87.67(1)°$, $V = 1564.0(4)$ Å^3, and $Z = 2$. The PMe_3 groups are anti with respect to the Pd—Pd vector, while the phenyl groups of the anilides are anti with respect to the $Pd_2N_2P_2C_2$ coordination plane. In solution at 25 °C, **9** undergoes an isomerization equilibrium to form two new isomers. Spectroscopic data suggest that these two new isomers are consistent with syn PMe_3 groups and syn anilide groups. Prolonged heating (110 °C, 12 h) of **9** results in reductive elimination of diphenylamine.

Introduction

During the past several years, the chemistry of late-transition-metal–amide complexes (groups 8–10) has been the subject of extensive research.[1] The main motivation for the study of this group of compounds is their potential to facilitate carbon–nitrogen bond formation through catalytic[2] or stoichiometric[3] reactions. The relatively slow development of the chemistry of late-transition-metal–amide complexes has been attributed to the inability of the electronically saturated, soft metal center to accommodate π-donation from the lone-pair electrons of the hard amide moiety.[4] The absence of this interaction should result in a relatively weak M—N bond, thereby making it reactive with unsaturated organic molecules. Although the synthesis and characterization of amide complexes involving late transition metals is established,[5,6] the factors that influence the stability and reactivity of the M—N bond are still poorly understood. One example of a fundamental transformation that could be of vital importance to the development of metal–amide complexes as catalysts or stoichiometric reagents is reductive elimination from complexes containing the $MR(NR'_2)$ group to generate a product having a C—N bond. This process is well-known when R = H[8d] but appears to be unknown when R = aryl or alkyl.

Recently, our research interests have been directed toward the synthesis of palladium(II) amide complexes.[7] Although amide complexes of the Ni triad are becoming more common in the literature,[8] an understanding of their stability and reactivity has not been firmly established. In this paper, we report the preparation of a variety of monomeric amide complexes of palladium(II) having the general formula *trans*-$(PMe_3)_2Pd(R)(NHR')$

® Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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0276-7333/94/2313-3921$04.50/0

(R = Ph, Me; R′ = Ph). Upon thermolysis, these compounds initially lose PMe_3 and dimerize. The compounds have been characterized by spectroscopy as well as by single-crystal X-ray diffraction techniques. Prolonged heating of the dimers results in C—N bond formation via reductive elimination. The dimerization process becomes less favored relative to reductive elimination when R = *o*-C_6H_4(CNR).

Experimental Section

All procedures were carried out under an atmosphere of argon, using either drybox or Schlenk techniques. Potassium amides were prepared by the reaction between the corresponding aniline and KH in THF. The compound KN(Me)Ph was prepared using modified literature procedures.[9] The compounds *trans*-$(PMe_3)_2Pd(Ph)I$,[10] *trans*-$(PMe_3)_2Pd[CH{=}C(H)C_6H_5]Br$,[11] *trans*-$(PMe_3)_2Pd(CH_3)I$,[12] *cis*-$Pd(PMe_3)_2(CH_3)_2$,[13] and $[(C_6H_4C(H){=}NPh)Pd(PMe_3)_3][BF_4]$[7a] were prepared using literature procedures. Solvents and reagents were dried and deoxygenated by using standard methods prior to use. NMR spectra were obtained on either a General Electric QE-300 or a Varian VXR-300 spectrometer. Proton and carbon chemical shifts were referenced to residual signals in the solvent and are reported relative to TMS. ^{31}P chemical shifts are reported relative to 85% H_3PO_4. All NMR spectral data are found in Tables 1–3. Infrared data were obtained on a Perkin-Elmer 1600 spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., or the analytical services of this department.

Preparation of *trans*-$(PMe_3)_2Pd(Ph)(NHPh)$ (1). A solution of *trans*-$(PMe_3)_2Pd(Ph)I$ (278 mg, 0.60 mmol) in 20 mL of THF was cooled to −78 °C. To this solution was added KNHPh (118 mg, 0.90 mmol) as a solution in THF. Once the anilide solution was added, the reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure, and the remaining residue was extracted with diethyl ether (2 × 15 mL). The orange solution was filtered, concentrated to ca. 10 mL, and cooled to 0 °C. Yellow crystals of **1** were then isolated by filtration at 0 °C (135 mg); yield 52.6%. IR (Nujol): 3327 cm^{-1} (ν_{N-H}). Anal. Calcd for $C_{18}H_{29}NP_2Pd$: C, 50.54; H, 6.79; N, 3.28. Found: C, 49.98; H, 6.90; N, 3.20.

Preparation of *trans*-$(PMe_3)_2Pd(Ph)(^{15}NHPh)$. *trans*-$(PMe_3)_2Pd(Ph)(^{15}NHPh)$ was synthesized by following the same procedure for **1**, using *trans*-$(PME_3)_2Pd(Ph)I$ and $K^{15}NHPh$. ^1H NMR (C_6D_6): δ 1.66 ppm (J_{N-H} = 69 Hz).

Preparation of *trans*-$(PMe_3)_2Pd(Ph)[N(Me)Ph]$ (2). In a procedure identical with that for **1**, *trans*-$(PMe_3)_2Pd(Ph)I$ (450 mg, 1.05 mmol) was allowed to react with KN(Me)Ph (229 mg, 1.58 mmol) in THF at −78 °C. Recrystallization from diethyl ether at 0 °C afforded **2** as yellow crystals (147 mg), yield 31.6%. Anal. Calcd for $C_{19}H_{31}NP_2Pd$: C, 51.65; H, 7.02; N, 3.17. Found: C, 51.71; H, 7.11; N, 3.16.

Preparation of *trans*-$(PMe_3)_2Pd(Ph)(NPh_2)$ (3). In a procedure identical with that for **1**, *trans*-$(PMe_3)_2Pd(Ph)I$ (270 mg, 0.59 mmol) was reacted with $KNPh_2$ (184 mg, 0.89 mmol) in THF at −78 °C. Recrystallization from diethyl ether at 0 °C afforded **3** as yellow crystals (118 mg), yield 39.7%. Anal. Calcd for $C_{24}H_{33}NP_2Pd$: C, 57.21; H, 6.56; N, 2.78. Found: C, 57.11; H, 6.54; N, 2.75.

Preparation of *trans*-$(PMe_3)_2Pd(Ph)(NH\text{-}2,6\text{-}^iPr_2C_6H_3)$ (4). In a procedure identical with that for **1**, *trans*-$(PMe_3)_2Pd(Ph)I$ (316 mg, 0.69 mmol) was allowed to react with $KNH\text{-}2,6\text{-}^iPr_2C_6H_3$ (223 mg, 1.04 mmol) in THF at −78 °C. Recrystallization from diethyl ether at 0 °C afforded **4** as yellow crystals (110 mg), yield 31.2% IR (Nujol): 3385 cm^{-1} (ν_{N-H}). Anal. Calcd for $C_{24}H_{41}NP_2Pd$: C, 56.32; H, 8.02; N, 2.74. Found: C, 56.21; H, 8.08; N, 2.53.

Preparation of *trans*-$(PMe_3)_2Pd(C_6H_4C(H){=}NPh)(NHPh)$ (5). A solution of $[C_6H_4C(H){=}NPh)Pd(PMe_3)_3][BF_4]$ (1.00 g, 1.66 mmol) in 30 mL of THF was cooled to −78 °C. To this solution was added KNHPh (240 mg, 1.83 mmol) as a solution in THF (20 mL). Once the anilide solution was added, the reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure, and the remaining residue extracted with diethyl ether (2 × 50 mL). The extract was filtered, concentrated to ca. 30 mL and cooled to 0 °C. Two crops of bright yellow crystals of **5** were isolated (557 mg), yield 63.3%. IR (Nujol): 1615 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{26}H_{36}N_2P_2Pd$: C, 56.56; H, 6.41; N, 5.28. Found: C, 56.31; H, 6.50; N, 5.19.

Preparation of *trans*-$(PMe_3)_2Pd(C_6H_4C(H){=}NPh)(NHC_6H_4\text{-}p\text{-}CH_3)$ (6). A solution of $[(C_6H_4C(H){=}NPh)Pd(PMe_3)_3][BF_4]$ (900 mg, 1.50 mmol) was dissolved in 75 mL of THF and cooled to −78 °C. To this solution was added $KN(H)C_6H_4\text{-}p\text{-}CH_3$ (218 mg, 1.50 mmol) in THF (20 mL). After the mixture was stirred for 12 h, the volatiles were removed under reduced pressure. Extraction of the residue with pentane followed by concentration and cooling to 0 °C gave yellow crystals of **6** (254 mg), yield 31.1%. IR (Nujol): 1605 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{26}H_{36}N_2P_2Pd$: C, 57.31; H, 6.61; N, 5.14. Found: C, 57.06; H, 6.69; N, 5.03.

Preparation of *trans*-$(PMe_3)_2Pd[CH{=}C(H)Ph](NHPh)$ (7). A Schlenk tube charged with *trans*-$(PMe_3)_2Pd[CH{=}C(H)Ph]Br$ (645 mg, 1.47 mmol) and KNHPh (231 mg, 1.76 mmol) was cooled to −60 °C. The solids were dissolved in 20 mL of cold THF, and the reaction mixture was warmed to room temperature. After it was stirred for 2 h at room temperature, the solution became bright orange and a fine white precipitate formed. Removal of solvent under reduced pressure was follwed by extraction with diethyl ether (30 mL). Filtration, concentration, and cooling of the extract to 0 °C afforded **7** as bright yellow crystals (145 mg), yield 28.3%. IR (Nujol): 3342 (ν_{N-H}), 1580 cm^{-1} ($\nu_{C=C}$). Anal. Calcd for $C_{20}H_{31}NP_2Pd$: C, 52.93; N, 6.84; N, 3.09. Found: C, 52.68; H, 6.93; N, 3.01.

Preparation of *trans*-$(PMe_3)_2Pd(CH_3)(NHPh)$ (8). A solution of *trans*-$(PMe_3)Pd(CH_3)I$ (346 mg, 0.86 mmol) in 20 mL of THF was cooled to −60 °C. To this solution was added KNHPh (103 mg, 0.79 mmol) as a solution in THF. Once all the amide was added, the solution color changed to pale yellow, accompanied by the formation of a fine white precipitate. After the mixture was stirred for 3 h at room temperature, the solvent was removed under reduced pressure, and the remaining residue was extracted with 20 mL of diethyl ether. The orange-yellow solution was filtered, concentrated to *ca.* 10 mL, and cooled to 0 °C, affording yellow crystals of **8** (45 mg); yield 15.8%. Due to the tendency of **8** to readily form the dimer **11**, analytical data were consistently low. IR (Nujol): 3340 cm^{-1} (ν_{N-H}). Anal. Calcd for $C_{13}H_{27}NP_2Pd$: C, 42.69; H, 7.39; N, 3.83. Found: C, 41.71; H, 7.26; N, 3.71.

Addition of Aniline to *cis*-$Pd(PMe_3)_2(CH_3)_2$. In the drybox, *cis*-$Pd(PMe_3)_2(CH_3)_2$ (35 mg, 0.12 mmol) was dissolved in 0.5 mL of C_6D_6. To this solution was added 1 equiv of aniline (11 mL). The solution was then syringed into a resealable NMR tube. The sample was placed in a temperature-controlled oil bath, and the progress of the reaction was monitored by NMR spectroscopy.

Preparation of $[(PMe_3)Pd(Ph)(\mu\text{-}NHPh)]_2$ (9). A Schlenk tube charged with **1** (117 mg, 0.27 mmol) was warmed to 90 °C under a pressure of 200 mTorr for 12 h. During this time,

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Table 1. ^{1}H NMR Spectroscopic Data[a,b]

compd	δ, ppm	mult	*J*, Hz	integ	assignt
trans-$(PMe_3)_2Pd(Ph)(NHPh)$ (**1**)	0.74	t	3.0	18	*trans*-PMe_3
	1.66	s		1	−NH
	6.53	t	7.0	1	aromatic
	6.80	d	8.0	2	
	6.97	t	7.0	1	
	7.10	t	7.4	2	
	7.28	t	7.3	2	
	7.37	d	7.4	2	
trans-$(PMe_3)_2Pd(Ph)[N(Me)Ph]$ (**2**)	0.67	t	3.3	18	*trans*-PMe_3
	2.92	s		3	−NMe
	6.57	t	6.3	2	aromatic
	6.94	t	7.4	1	
	7.07	t	7.4	2	
	7.24	d	8.8	1	
	7.32	d	7.7	2	
	7.37	t	7.8	1	
	7.45	t	7.7	1	
trans-$(PMe_3)_2Pd(Ph)(NPh_2)$ (**3**)	0.61	t	3.3	18	*trans*-PMe_3
	6.73	t	7.4	2	aromatic
	6.93	t	7.3	1	
	7.03	t	7.4	2	
	7.29	m		6	
	7.71	d	8.5	4	
trans-$(PMe_3)_2Pd(Ph)(NH\text{-}2,6\text{-}^iPr\text{-}C_6H_3)$ (**4**)	0.71	t	3.0	18	trans-PMe_3
	1.44	d	6.6	12	$-CHCH_3$
	1.83	s		1	−NH
	4.08	m		2	$-CHCH_3$
	6.74	t	6.6	1	aromatic
	6.96	t	7.3	1	
	7.07	t	7.0	2	
	7.18	d	8.1	2	
	7.39	d	7.3	2	
trans-$(PMe_3)_2Pd(C_6H_4C(H)=NPh)(NHPh)$ (**5**)	0.68	s		18	*trans*-PMe_3
	1.53	s		1	−NH
	6.55	t	7.0	1	aromatic
	6.84	d	18.0	2	
	7.04	m		4	
	7.27	t	8.0	2	
	7.34	t	7.0	2	
	7.53	d	7.0	2	
	8.25	d	9.0	1	
	9.30	s		1	−C(*H*)=N
trans-$(PMe_3)_2Pd(C_6H_4C(H)=NPh)(NHC_6H_4\text{-}p\text{-}CH_3)$ (**6**)	0.69	s		18	*trans*-PMe_3
	1.38	s		1	−NH
	2.36	s		3	$-C_6H_4\text{-}p\text{-}CH_3$
	6.78	d	9.2	2	aromatic
	7.05	m		5	
	7.34	t	8.8	2	
	7.52	m	7.4	3	
	8.27	d	7.7	1	
	9.33	s		1	−C(*H*)=N
trans-$(PMe_3)_2Pd[CH=C(H)C_6H_5](NHPh)$ (**7**)	0.87	s		18	*trans*-PMe_3
	1.62	s		1	−NH
	6.51	t	7.0	1	aromatic
	6.64	d	16.9	1	−C=C(*H*)
	6.77	d	8.5	2	aromatic
	7.04	t	7.0	1	
	7.25	m		4	
	7.37	d	8.1	2	
	7.52	dt	17.3	1	Pd−C(*H*)=C
trans-$(PMe_3)_2Pd(CH_3)(NHPh)$ (**8**)	0.05	s		3	$Pd-CH_3$
	0.91	s		18	*trans*-PMe_3
	1.68	s		1	−NH
	6.50	t	7.0	1	aromatic
	6.74	d	8.1	2	
	7.28	t	3.7	2	
$[(PMe_3)Pd(Ph)(\mu\text{-}NHPh)]_2$ (**9**)	0.32	d	9.5	18	PMe_3
	1.28	d	5.1	2	−NH
	6.71	t	7.6	2	aromatic
	7.07	m		18	
$[(PMe_3)Pd(CH_3)(\mu\text{-}NHPh)]_2$ (**11**)	0.10	d	4.4	6	$Pd-CH_3$
	0.51	d	9.2	18	PMe_3
	1.45	d	5.0	2	−NH
	6.67	t	6.2	2	aromatic
	7.10	t	8.1	4	
	7.30	d	8.1	4	

[a] All spectroscopic data were collected at 23 °C in C_6D_6. [b] The multiplicities doublet and triplet are the observed splitting patterns when referring to the PMe_3 protons, and do not necessarily reflect the true coupling constants.

Table 2. $^{13}C\{^1H\}$ NMR Spectroscopic Data[a]

compd	δ, ppm	mult	J, Hz	assignt
trans-$(PMe_3)_2Pd(Ph)(NHPh)$ (**1**)	12.9	t	13.5	*trans*-PMe_3
	108.6	s		aromatic
	115.2	s		
	122.1	s		
	127.2	s		
	129.2	s		
	137.0	t	4.5	
	157.1	t	12.2	Pd—C
	162.0	s		N—C
trans-$(PMe_3)_2Pd(Ph)[N(Me)Ph]$ (**2**)	13.5	t		*trans*-PMe_3
	39.5	s		NCH_3
	108.6	s		aromatic
	108.7	s		
	116.3	s		
	122.3	s		
	127.2	s (br)		
	128.4	s		
	129.9	s		
	136.7	t	3.6	
	137.3	t	3.8	
	156.3	t	10.0	Pd—C
	160.4	s		N—C
trans-$(PMe_3)_2Pd(Ph)(NPh_2)$ (**3**)	13.2	t	14.1	*trans*-PMe_3
	115.2	s		aromatic
	119.3	s		
	122.5	s		
	127.3	s		
	128.8	s		
	137.1	t	4.5	
	155.0	t	9.5	Pd—C
	155.8	s		N—C
trans-$(PMe_3)_2Pd(Ph)(NH\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)$ (**4**)	13.0	t	14.2	*trans*-PMe_3
	24.0	s		$C(H)(CH_3)_2$
	28.7	s		$C(H)(CH_3)_2$
	110.6	s		aromatic
	122.5	s		
	122.7	s		
	127.1	s		
	132.4	s		
	137.7	t	4.2	
	156.5	t	11.0	Pd—C
	157.8	s		N—C
trans-$(PMe_3)_2Pd[CH{=}C(H)C_6H_5]$-(NHPh) (**7**)	12.9	t	13.6	*trans*-PMe_3
	108.7	s		aromatic
	115.1	s		
	124.5	s		
	125.1	s		
	128.6	s		
	129.2	s		
	135.0	s (br)		Pd—C=*C*
	141.1	s		
	147.6	t	11.5	Pd—*C*=C
	162.4	s		N—C
trans-$(PMe_3)_2Pd(CH_3)(NHPh)$ (**8**)	−12.0	s		Pd—CH_3
	13.0	s (br)		*trans*-PMe_3
	108.4	s		aromatic
	115.1	s		
	129.1	s		
	162.7	s		N—C
$[(PMe_3)Pd(CH_3)(\mu\text{-}NHPh)]_2$ (**11**)	−1.0	d	8.2	Pd—CH_3
	13.8	d	29.3	PMe_3
	117.0	s		aromatic
	121.8	s		
	122.6	s		
	128.0	s		

[a] All spectroscopic data were collected at 23 °C in C_6D_6.

the yellow solid was converted to a gray powder. Extraction of the gray powder with diethyl ether gave a colorless solution. Filtration, concentration, and cooling to 0 °C afforded **9** as white microcrystals (64 mg), yield 33.4%. IR (KBR): 3292 cm^{-1} (ν_{N-H}). Anal. Calcd for $C_{30}H_{40}N_2P_2Pd_2$: C, 51.22; H, 5.69; N, 3.98. Found: C, 51.23; H, 5.72; N, 3.95.

Table 3. $^{31}P\{^1H\}$ NMR Spectroscopic Data[a]

compd	δ, ppm	mult
trans-$(PMe_3)_2Pd(Ph)(NHPh)$ (**1**)	−16.79	s
trans-$(PMe_3)_2Pd(Ph)[N(Me)Ph]$ (**2**)	−15.06	s
trans-$(PMe_3)_2Pd(Ph)(NPh_2)$ (**3**)	−17.31	s
trans-$(PMe_3)_2Pd(Ph)(NH\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)$ (**4**)	−18.43	s
trans-$(PMe_3)_2(C_6H_4C(H){=}NPh)(NHPh)$ (**5**)	−16.77	s
trans-$(PMe_3)_2Pd(C_6H_4C(H){=}NPh)(NHC_6H_4\text{-}p\text{-}CH_3)$ (**6**)	−16.63	s
trans-$(PMe_3)_2Pd[CH{=}C(H)C_6H_5](NHPh)$ (**7**)	−16.26	s
trans-$(PMe_3)_2Pd(CH_3)(NHPh)$ (**8**)	−14.15	s
$[(PMe_3)Pd(Ph)(\mu\text{-}NHPh)]_2$ (**9**)[b]	−15.04	s
$[(PMe_3)Pd(CH_3)(\mu\text{-}NHPh)]_2$ (**11**)[b]	−7.58	s
	−8.23	s
	−9.92	s

[a] All spectroscopic data were collected at 23 °C in C_6D_6. [b] Represents all isomers of the dimer.

Preparation of $[(PMe_3)Pd(CH_3)(\mu\text{-}NHPh)]_2$ (11). A Schlenk tube charged with **8** (174 mg, 0.48 mmol) was warmed to 70 °C under reduced pressure (200 mTorr) for 16 h. During this time, the yellow compound **8** was converted to a white powder. A ^1H NMR spectrum of the soluble portion of the solid revealed complete conversion to the dimer **11**. Recrystallization of **11** from diethyl ether at 0 °C afforded **11** as a white crystalline solid (111 mg), yield 80.6%. Anal. Calcd for $C_{20}H_{36}N_2P_2Pd$: C, 41.47; H, 6.22; N, 4.84. Found: C, 41.54; H, 6.29; N, 4.75.

Addition of PMe_3 to Compounds 9 and 11. In the drybox, approximately 20 mg of **9** or **11** was dissolved in 0.5 mL of C_6D_6 in a resealable NMR tube. To this solution was added 3−4 equiv of PMe_3 as a solution in C_6D_6. The conversion of **9** and **11** to **1** and **8**, respectively, was monitored by proton NMR spectroscopy.

X-ray Crystallography. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). A total of 50 reflections with 15.0° ≤ 2θ ≤ 22.0° were used to refine the cell parameters of each crystal. Four reflections were measured every 96 reflections to monitor instrument and crystal stability for each data set (maximum corrections on I were 6, 2.4, and 1% for **1**, **9**, and **10**, respectively). Absorption corrections for **1** and **9** were applied using measured crystal faces and the *SHELXTL plus*[14] software; absorption corrections were not applied to **10**. A summary of data collection parameters is found in Table 4. The fractional coordinates of non-H atoms of compounds **1**, **9**, and **10** are found in Tables 8−10, respectively. The structures were solved by the heavy-atom method in *SHELXTL plus*, from which the locations of the Pd atoms were obtained. The rest of the non-hydrogen atoms were obtained from subsequent Fourier maps. The structures were refined in *SHELXTL plus* using full-matrix least squares. All non-H atoms were refined anisotropically. The positions of all H atoms of **1** were calculated in ideal positions, and their isotropic thermal parameters were fixed. In **9**, the amide protons were located from a difference Fourier map and were refined without constraints, with the exception of the thermal parameter of H′, which was fixed. In **10**, the methyl H atoms, as well as H12, H18, and H18′, were placed in idealized positions and their isotropic thermal parameters were fixed; the rest of the H atoms were refined without constraints. The linear absorption coefficients were calculated from values from ref 15. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[16] with anomalous dispersion corrections

(14) Sheldrick, G. M. *SHELXTL plus*, version 4.21/v; Siemens XRD, Madison, WI, 1990.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 55 (present distributor D. Reidel, Dordrecht, The Netherlands).

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321−324.

Table 4. Crystallographic Data

	1	9	10
	A. Crystal Data (298 K)		
a, Å	8.423(3)	6.805(1)	9.588(1)
b, Å	10.768(4)	12.186(2)	18.709(3)
c, Å	12.565(4)	18.943(3)	23.444(4)
α, deg	68.81(3)	89.56(1)	
β, deg	71.90(3)	85.17(1)	90.98(2)
γ, deg	87.65(3)	87.67(1)	
V, Å^3	1006.7(7)	1564.0(4)	4205(1)
formula	$C_{18}H_{29}NP_2Pd$	$C_{30}H_{40}N_2P_2Pd_2$	$C_{44}H_{50}N_4P_2Pd_2$
fw	427.76	703.38	909.62
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	2	2	4
cryst size, mm^3	0.06 × 0.15 × 0.32	0.11 × 0.13 × 0.22	0.10 × 0.17 × 0.39
	B. Data Collection (298 K)		
radiation/λ, Å	Mo Kα/0.710 73		
mode	ω scan		
scan range	symmetrically over χ about Kα$_{1,2}$ max (χ = 1.5, 1.2, 1.2° for **1**, **9**, **10**, respectively)		
bkgd	offset 1.0 and −1.0 in ω from Kα$_{1,2}$ max		
scan rate, deg min^{-1}	3−6		
2θ range, deg	3−45	3−45	3−50
range of *hkl*	$0 \le h \le 9, -11 \le k \le 11, -13 \le l \le 13$	$0 \le h \le 7, -13 \le k \le 13, -20 \le l \le 20$	$0 \le h \le 11, 0 \le k \le 22, -27 \le l \le 27$
total no. of rflns measd	2865	4544	8139
no. of unique rflns	2649	4122	7390
abs coeff μ (Mo Kα), mm^{-1}	1.08	11.77	0.97
min/max transmissn	0.845/0.933	0.848/0.911	N/A
	C. Structure Refinement		
S, goodness-of-fit	2.34	1.34	1.15
no. of rflns used	1944 ($I > 3\sigma(I)$)	3224 ($I > 2\sigma(I)$)	4318 ($I > 2\sigma(I)$)
no. of variables	228	371	587
R/R_w,[a] %	6.12/7.52	3.76/4.15	4.94/4.448
R_{int}, %	2.7	1.41	2.31
max shift/esd	0.001	0.001	0.001
min peak in diff Fourier map, e Å^{-3}	−0.66	−0.41	−0.55
max peak in diff Fourier map, e Å^{-3}	1.51	0.78	0.70

[a] Relevant expressions are as follows, where F_o and F_c represent respectively the observed and calculated structure-factor amplitudes. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 1

Pd−P1	2.301(4)	Pd−C11	2.03(2)
Pd−P2	2.300(4)	N−C21	1.32(2)
Pd−N	2.116(13)		
P1−Pd−P2	169.45(13)	P1−Pd−C11	86.8(4)
P1−Pd−N	95.3(3)	N−Pd−C11	176.5(4)
P2−Pd−N	90.5(3)	C21−Pd−N	130.4(9)
P2−Pd−C11	87.9(4)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 9

Pd−P	2.234(2)	Pd−C11	2.004(7)
Pd−N	2.129(6)	N−C21	1.409(9)
Pd−N(i)	2.148(6)		
P−Pd−N	177.8(2)	N(i)−Pd−C11	174.6(2)
P−Pd−N(i)	97.9(2)	C11−Pd−P	86.9(2)
N−Pd−N(i)	83.9(2)	C21−N−Pd	113.9(4)
N−Pd−C11	91.2(2)		

from Cromer and Liberman,[17] while those for hydrogen atoms were from Stewart, Davidson, and Simpson.[18]

Results and Discussion

All monomeric palladium(II) amide complexes reported were prepared by transmetalation reactions. A typical experiment involved addition of a slight excess of the desired anilide salt to a cold solution of the Pd complex in THF. These complexes are all yellow, crystalline solids. Although air and moisture sensitive, the isolated amide complexes are thermally stable at room temperature and can be stored under an inert atmosphere for an indefinite period of time in the solid state.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 10

Pd−P	2.233(2)	Pd′−N1	2.122(7)
Pd−P′	2.232(2)	Pd′−N1′	2.134(7)
Pd−N1	2.148(6)	C1−Pd	2.017(7)
Pd−N1′	2.144(7)	C1′−Pd′	2.021(7)
P−Pd−N1	97.2(2)	P′−Pd′−N1	174.7(2)
P−Pd−N1′	178.3(2)	P′−Pd′−N1′	96.4(2)
N1−Pd−N1′	83.8(3)	N1−Pd′−N1′	84.7(3)
N1−Pd−C1	174.6(3)	N1−Pd′−C1′	90.2(3)
N1′−Pd−C1	90.8(3)	N1′−Pd′−C1′	174.1(3)
C1−Pd−P	88.2(2)	C1′−Pd′−P′	89.0(2)

The nature of the leaving group as well as the counterion of the anilide salt dictates the extent of amide formation. In order to maximize amide formation, the chloride ion must be avoided so that the reaction can proceed to completion. This observation is consistent with the synthesis of platinum(II) amide complexes reported by Trogler.[3a] The highest yields that we have obtained occurred when the iodide ion was employed as the leaving group. The counterion of the anilide also plays an important role in the synthesis of these compounds. Although lithium and sodium anilides have been used to synthesize some late-transition-metal−amide complexes,[3a,b,5b,6a,8a,d] the use of these

(17) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891−1898.
(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175−3187.

Table 8. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å²) for the Non-H Atoms of Compound 1

atom	*x*	*y*	*z*	*U*
Pd	0.17008(11)	0.00422(9)	0.29760(9)	0.0319(4)
P1	0.1071(4)	0.1447(3)	0.1309(3)	0.0395(14)
P2	0.2711(4)	−0.1477(3)	0.4393(3)	0.043(2)
N	0.2110(14)	0.1574(10)	0.3567(9)	0.055(6)
C1	0.086(2)	0.3184(12)	0.1152(13)	0.062(7)
C2	−0.084(2)	0.0978(13)	0.1105(12)	0.056(7)
C3	0.266(2)	0.1550(13)	−0.0077(11)	0.061(7)
C4	0.185(2)	−0.3208(14)	0.5093(14)	0.070(8)
C5	0.271(2)	−0.110(2)	0.5677(12)	0.067(8)
C6	0.4898(15)	−0.163(2)	0.3675(13)	0.066(7)
C11	0.121(2)	−0.1485(12)	0.2512(11)	0.048(6)
C12	0.246(2)	−0.2057(12)	0.1830(11)	0.049(6)
C13	0.213(2)	−0.3191(15)	0.1635(14)	0.069(9)
C14	0.050(3)	−0.3799(14)	0.2128(15)	0.076(10)
C15	−0.074(2)	−0.3241(14)	0.2785(14)	0.064(8)
C16	−0.037(2)	−0.2108(12)	0.2975(12)	0.051(6)
C21	0.336(2)	0.2512(11)	0.3119(11)	0.039(6)
C22	0.469(2)	0.2624(13)	0.2062(12)	0.052(7)
C23	0.597(2)	0.362(2)	0.1591(13)	0.064(8)
C24	0.600(2)	0.4525(14)	0.2120(14)	0.064(7)
C25	0.474(2)	0.4425(13)	0.3144(14)	0.062(8)
C26	0.344(2)	0.3464(12)	0.3645(11)	0.046(6)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

Table 9. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å²) for the Non-H Atoms of Compound 9

atom	*x*	*y*	*z*	*U*
Pd	0.07694(8)	0.45833(4)	0.07292(3)	0.0376(2)
Pd′	−0.05004(7)	0.06965(4)	−0.42936(2)	0.0359(2)
P	0.0361(3)	0.49762(14)	0.18835(9)	0.0438(7)
P′	−0.0467(3)	0.0570(2)	−0.31146(9)	0.0446(7)
N	0.1276(10)	0.4192(5)	−0.0366(3)	0.046(2)
N′	−0.0396(9)	0.0947(5)	−0.5413(3)	0.038(2)
C1	0.069(2)	0.3879(7)	0.2508(4)	0.077(5)
C1′	0.0045(15)	−0.0778(6)	−0.2733(4)	0.070(4)
C2	−0.2062(12)	0.5559(7)	0.2198(4)	0.068(3)
C2′	−0.2709(12)	0.1011(7)	−0.2591(4)	0.066(3)
C3	0.2037(14)	0.6002(7)	0.2132(4)	0.071(4)
C3′	0.1447(13)	0.1371(7)	−0.2781(4)	0.072(4)
C11	0.2812(10)	0.3446(5)	0.0977(3)	0.041(3)
C11′	−0.1264(11)	0.2293(5)	−0.4153(3)	0.044(3)
C12	0.2376(11)	0.2338(5)	0.1052(3)	0.047(3)
C12′	0.0188(12)	0.3073(5)	−0.4223(3)	0.051(3)
C13	0.3808(13)	0.1557(6)	0.1198(4)	0.061(3)
C13′	−0.0328(14)	0.4184(6)	−0.4234(4)	0.063(4)
C14	0.5679(13)	0.1860(7)	0.1280(5)	0.074(4)
C14′	−0.227(2)	0.4538(7)	−0.4186(4)	0.072(4)
C15	0.6155(12)	0.2921(7)	0.1197(5)	0.071(3)
C15′	−0.3709(14)	0.3781(7)	−0.4121(4)	0.070(4)
C16	0.4724(11)	0.3709(6)	0.1048(4)	0.054(3)
C16′	−0.3199(12)	0.2692(6)	−0.4107(4)	0.057(3)
C21	0.1063(11)	0.3075(5)	−0.0517(3)	0.042(3)
C21′	−0.2084(10)	0.1422(5)	−0.5676(3)	0.037(2)
C22	0.2708(14)	0.2373(6)	−0.0734(4)	0.064(4)
C22′	−0.2190(11)	0.2517(6)	−0.5900(4)	0.051(3)
C23	0.243(2)	0.1262(7)	−0.0845(5)	0.086(5)
C23′	−0.3871(13)	0.2948(7)	−0.6192(4)	0.070(4)
C24	0.059(2)	0.0847(8)	−0.0759(5)	0.093(6)
C24′	−0.5449(14)	0.2304(8)	−0.6255(5)	0.077(4)
C25	−0.098(2)	0.1533(7)	−0.0558(4)	0.073(4)
C25′	−0.5371(12)	0.1226(7)	−0.6016(4)	0.065(3)
C26	−0.0744(12)	0.2629(5)	−0.0443(3)	0.053(3)
C26′	−0.3726(10)	0.0797(6)	−0.5728(3)	0.048(3)

[a] See footnote *a* in Table 8.

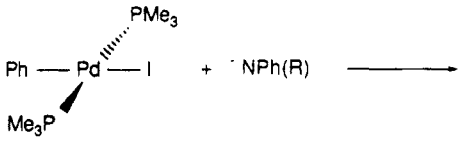
reagents did not successfully generate good yields of monomeric palladium(II) amide complexes. Throughout this work, the potassium salt of the anilide was employed.

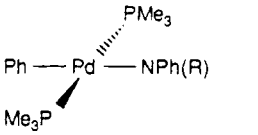
Table 10. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å²) for the Non-H Atoms of Compound 10

atom	*x*	*y*	*z*	*U*
Pd	0.01737(6)	0.58221(3)	0.19086(2)	0.0420(2)
Pd′	0.02161(6)	0.55285(3)	0.32279(2)	0.0397(2)
P	0.0999(2)	0.66380(12)	0.13068(9)	0.0527(9)
P′	−0.1148(2)	0.49775(12)	0.38525(9)	0.0504(8)
N1	0.1393(7)	0.6137(4)	0.2644(3)	0.042(3)
N1′	−0.0682(8)	0.5050(4)	0.2481(3)	0.046(3)
N2	0.1067(8)	0.4012(4)	0.0692(3)	0.063(3)
N2′	0.3676(7)	0.4562(4)	0.4216(3)	0.061(3)
C1	−0.1057(8)	0.5457(4)	0.1266(3)	0.045(3)
C1′	0.1244(8)	0.5998(4)	0.3888(3)	0.043(3)
C2	−0.0697(9)	0.4889(4)	0.0921(3)	0.048(3)
C2′	0.2442(8)	0.5687(4)	0.4133(3)	0.046(3)
C3	−0.1629(11)	0.4643(6)	0.0504(4)	0.068(4)
C3′	0.3198(10)	0.6049(6)	0.4553(4)	0.058(4)
C4	−0.2908(12)	0.4942(7)	0.0417(4)	0.080(5)
C4′	0.2844(12)	0.6709(6)	0.4725(4)	0.066(5)
C5	−0.3291(10)	0.5500(6)	0.0763(4)	0.069(4)
C5′	0.1654(12)	0.7019(5)	0.4495(4)	0.060(4)
C6	−0.2378(9)	0.5753(5)	0.1175(4)	0.058(3)
C6′	0.0866(10)	0.6662(4)	0.4085(3)	0.052(4)
C7	0.0656(9)	0.4527(5)	0.1001(3)	0.055(4)
C7′	0.2863(8)	0.4976(5)	0.3945(4)	0.050(3)
C8	0.2400(10)	0.3704(5)	0.0812(3)	0.057(4)
C8′	0.3938(9)	0.3871(5)	0.3969(5)	0.062(3)
C9	0.2550(13)	0.2987(5)	0.0687(4)	0.076(5)
C9′	0.4257(10)	0.3777(7)	0.3403(5)	0.073(4)
C10	0.384(2)	0.2673(8)	0.0792(5)	0.095(6)
C10′	0.4535(11)	0.3091(8)	0.3204(6)	0.088(5)
C11	0.4923(15)	0.3061(8)	0.0995(6)	0.094(6)
C11′	0.4451(11)	0.2519(7)	0.3579(7)	0.088(4)
C12	0.4794(13)	0.3755(7)	0.1103(5)	0.102(5)
C12′	0.4140(13)	0.2620(8)	0.4130(7)	0.092(5)
C13	0.3511(12)	0.4084(6)	0.1008(5)	0.084(5)
C13′	0.3890(11)	0.3297(7)	0.4323(5)	0.077(5)
C14	0.2877(9)	0.6074(4)	0.2639(3)	0.045(3)
C14′	−0.0392(8)	0.4337(5)	0.2344(3)	0.049(4)
C15	0.3727(10)	0.6572(5)	0.2919(4)	0.060(4)
C15′	−0.1335(11)	0.3890(5)	0.2064(4)	0.061(4)
C16	0.5166(10)	0.6526(6)	0.2896(5)	0.069(4)
C16′	−0.0973(13)	0.3200(5)	0.1900(4)	0.066(5)
C17	0.5769(11)	0.5990(6)	0.2611(5)	0.073(4)
C17′	0.0301(14)	0.2919(6)	0.2057(4)	0.078(5)
C18	0.4971(10)	0.5478(6)	0.2336(4)	0.070(4)
C18′	0.1224(10)	0.3329(5)	0.2361(4)	0.073(4)
C19	0.3511(10)	0.5527(5)	0.2349(3)	0.058(4)
C19′	0.0896(10)	0.4033(5)	0.2508(4)	0.059(4)
C20	0.1732(10)	0.7426(5)	0.1642(4)	0.079(4)
C20′	−0.0280(9)	0.4367(5)	0.4328(4)	0.074(4)
C21	0.2451(9)	0.6309(5)	0.0892(4)	0.078(4)
C21′	−0.2520(9)	0.4439(5)	0.3545(4)	0.080(4)
C22	−0.0163(10)	0.7004(6)	0.0773(4)	0.097(5)
C22′	−0.2106(10)	0.5566(5)	0.4307(4)	0.087(4)

[a] See footnote *a* in Table 8.

Synthesis and Structural Data for *trans*-$(PMe_3)_2$Pd(Ph)(NHPh) (1). The addition of 1.5 equiv of potassium anilide to a cold (−78 °C) solution of *trans*-$(PMe_3)_2$Pd(Ph)I in THF affords the amido complex *trans*-$(PMe_3)_2$Pd(Ph)(NHPh) (**1**; eq 1). The NMR spectral data for compound **1** as well as all other reported compounds can be found in Tables 1−3. The ^{1}H NMR spectrum of **1** in C_6D_6 reveals a broad singlet at 1.66 ppm for the N−H proton, a triplet at 0.74 ppm for the protons of PMe_3, and a well-defined phenyl region. The ^{1}H NMR spectrum of a ^{15}N-enriched sample of **1** reveals a doublet at 1.66 ppm ($^1J_{^{15}N-H}$ = 69 Hz), confirming the above spectral assignment. The presence of a singlet at −16.79 ppm in the ^{31}P{^{1}H} NMR spectrum of **1** as well as a triplet at 157.1 ppm ($^2J_{P-C}$ = 12.2 Hz) in the ^{13}C{^{1}H} NMR spectrum that can be assigned to the ipso





(1)

1 R = H
2 R = Me
3 R = Ph

carbon of the phenyl ring bound to palladium were also consistent with *trans* stereochemistry about the metal center.

Crystallization of **1** from diethyl ether at 0 °C afforded a crystal suitable for an X-ray diffraction study. The thermal ellipsoid plot of **1** is found in Figure 1, while selected bond lengths and angles can be found in Table 5. The Pd—N bond distance of 2.116(13) Å is similar to the Pt—N bond distances of previously reported amide complexes.[3a] The expected *trans* square-planar geometry about palladium was observed. The P1—Pd—P2 angle is nearly linear, though bent toward the less sterically demanding phenyl ring. The amide proton could not be located from a difference Fourier map. Its position was calculated by assuming a planar geometry around the N atom. An examination of a set of crystal structures (containing the —NHPh group) obtained from the Cambridge Structural Database[19] revealed that the N atom assumes a planar geometry in all but one example.[20] This could be due to a strong interaction between the lone pair of electrons on the N atom and the π^* orbital of the phenyl ring, as evidenced by the relatively short N—C21 bond distance (1.32(2)Å). To the best of our knowledge, attempts to isolate alkyl- and silylamide complexes of palladium(II) have been unsuccessful.[21]

These findings suggest that substituents that can accommodate π-donation from the electron pair on nitrogen may be required to stabilize monomeric palladium(II) amide complexes. This structural evidence is consistent with previous results that show there are no significant π-interactions between amide ligands and electronically saturated late-transition-metal centers.[1a] The remaining bond lengths and angles fall within expected ranges. Although the structures of several platinum(II)[3a,8a,22] and nickel(II)[8f,23] complexes have been solved, only one other monomeric amide complex of palladium(II) has been characterized structurally by a single-crystal X-ray diffraction study.[8f]

Preparation of Substituted Palladium(II) Amide Complexes. Reaction of *trans*-$(PMe_3)_2Pd(Ph)I$ with KN(Me)Ph affords the *N*-methylanilide complex **2**, as yellow crystals (eq 1). Compound **2** has been characterized with the use of ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ^1H NMR spectrum of **2** displays a singlet at 2.92 ppm for the methyl protons of the anilide moiety. A triplet at 0.67 ppm (J_{P-H} = 3.3 Hz) in the ^1H NMR spectrum assigned to the protons of PMe_3 and a singlet at −15.06 ppm in the $^{31}P\{^1H\}$ NMR spectrum confirm the *trans* stereochemistry about the metal center.

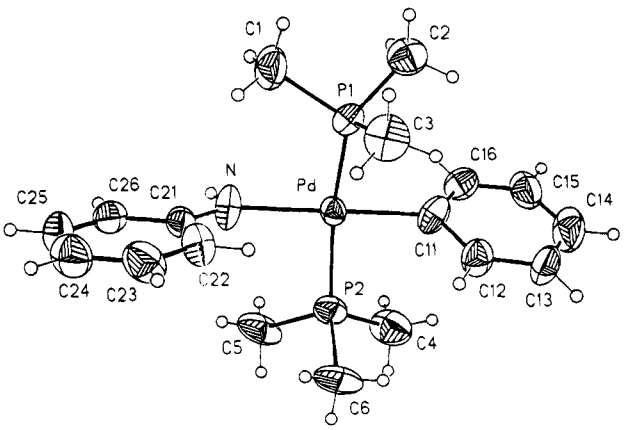


Figure 1. Thermal ellipsoid plot of *trans*-$(PMe_3)_2Pd(PH)(NHPh)$ (**1**).

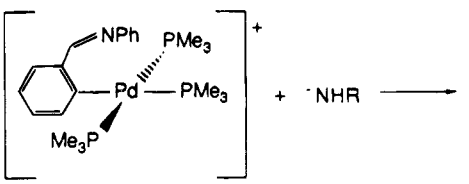
The NMR data for **2** are consistent with hindered rotation of the Pd—C bond as well as the *N*-methylanilide group about the M—N bond. In the $^{13}C\{^1H\}$ NMR spectrum, this hindered rotation gives rise to two triplets from the two ortho carbons of the metal-bound phenyl ring at 136.7 ($^3J_{P-C}$ = 3.6 Hz) and 137.7 ppm ($^3J_{P-C}$ = 3.8 Hz), while the ipso carbon appears as a triplet at 156.3 ppm ($^2J_{P-C}$ = 10.0 Hz). The ^1H NMR spectrum has three triplets in the aryl region that are integrated to one proton each. This result is only possible if at least one of the two phenyl rings in the molecule rotates slowly on the NMR time scale. The larger spectral dispersion of the $^{13}C\{^1H\}$ NMR spectrum allows the observation of 11 peaks in the aromatic region, which indicates that both phenyl rings in this compound experience hindered rotation on the NMR time scale.

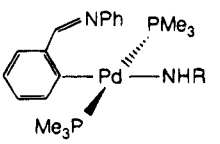
One possible explanation for the observed hindered rotation is that the steric demands of the NMePh group are such that the two PMe_3 ligands prevent free rotation of the anilide group. Furthermore, the increased steric demands of the *N*-methylanilide group also push the PMe_3 ligands closer to the phenyl ring *trans* to the anilide substituent, thereby preventing free rotation of both the Pd-bound phenyl ring and the *N*-methylanilide phenyl ring.

Compound **2** is an example of an amide complex of palladium(II) that possesses β-hydrogen atoms. Although late-transition-metal—amide complexes with β-hydrogen atoms have been isolated,[8a] there is a strong tendency for these complexes to undergo β-hydrogen elimination to generate the corresponding hydride complex.[24] We have not observed β-hydrogen elimination from compound **2** in solution or in the solid state at room temperature. It is likely that compound **2** does not undergo β-H elimination at these low temperatures because dissociation of PMe_3 does not occur very readily at 25 °C.

(19) Cambridge Structural Database; University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, England, 1992.
(20) Dewey, M. A.; Arif, A. M.; Glasdysz, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, *712*.
(21) For the synthesis of monomeric ruthenium(II) and rhodium(I) silyl amide complexes, see: Cetinkaya, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, *843*.
(22) Eadie, D. T.; Pidcock, A.; Stobart, S. R. *Inorg. Chim. Acta* **1982**, *65*, 2111.
(23) (a) Murray, B. D.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 4584. (b) Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 713. (c) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 7563. (d) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M., manuscript in preparation.
(24) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55.

The amide complexes **4**–**7** were prepared in a manner similar to that for compounds **1**–**3**. Spectroscopic characterization of these compounds indicates that they all possess *trans* stereochemistry at the metal center. The synthesis of compounds **5** and **6** (eq 2) shows that



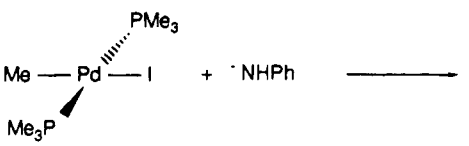


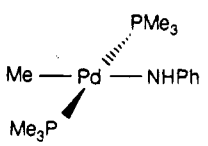
(2)

5 R = Ph
6 R = Ph-p-CH_3

PMe_3 can be used as a leaving group under the proper circumstances, while the preparation of **7** demonstrates that sp^2 carbon atoms other than phenyl groups are compatible with the anilide functionality.

Preparation of *trans*-$(PMe_3)_2Pd(CH_3)(NHPh)$ (8). Addition of KNHPh to a solution of *trans*-$(PMe_3)_2Pd(CH_3)I$ in THF resulted in the formation of *trans*-$(PMe_3)_2Pd(CH_3)(NHPh)$ (**8**; eq 3). The NMR data for **8**



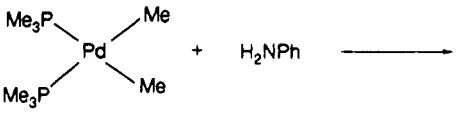


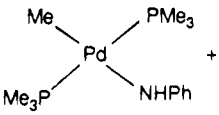
(3)

8

confirm the retention of *trans* stereochemistry. Unlike complexes **1**–**7**, the stoichiometry of the reaction determines the stereochemistry of the product. Compound **8** can only be prepared when slightly less than **1** equiv of KNHPh is added to a solution of *trans*-$(PMe_3)_2Pd(CH_3)I$ in THF. When even a slight excess of amide reagent was used, the *cis* isomer of **8** was isolated. Preliminary experiments indicate that the *trans* to *cis* isomerization of **8** is catalyzed by KNHPh apparently in a fashion similar to the ligand-catalyzed isomerization of square-planar Pt(II) complexes.[25] The nature of the *cis* isomer and its chemistry will be reported separately.

As shown in eq 4, reaction of aniline and *cis*-$Pd(PMe_3)_2(CH_3)_2$ at 70 °C for 22 h also results in the slow formation of **8** (*ca.* 10% conversion), as observed by ^1H NMR spectroscopy. The addition of 1 equiv of aniline to *cis*-$Pd(PMe_3)_2(CH_3)_2$ in C_6D_6 at room temperature does not afford **8**. This lack of reactivity contrasts with the immediate formation of *trans*-$(PMe_3)_2Pd(CH_3)(OPh)$ from the reaction of phenol with *trans*-$Pd(PMe_3)_2(CH_3)_2$





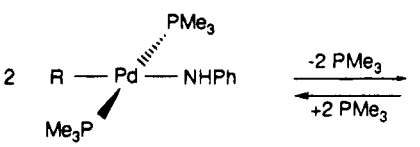
(4)

8

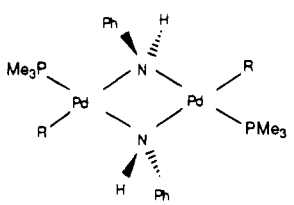
at room temperature.[26] The decrease in acidity as one goes from phenol to aniline is probably responsible for this difference in reactivity.[27]

Increasing the temperature to 80 °C for a further 12 h increases the amount of compound **8** formed but also results in the formation of several new species. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals two singlets assignable to **8** and the starting material, as well as three singlets between −7 and −10 ppm. We assign these three singlets to isomers of the amide-bridged dimer that is formed upon loss of PMe_3 from **8**. Changes in the ^1H NMR spectrum of this product are also consistent with the formation of dimeric species.

Synthesis and Crystal Structure Analyses of Dimeric Palladium(II) Amide Complexes. The tendency of late-transition-metal–amide complexes to dimerize is well-known and is due to the ability of the nitrogen atom of the amide to act as a ligand and coordinate to another metal center.[1] Although compound **1** is thermally stable at room temperature as a monomer, thermolysis of **1** under a dynamic vacuum results in the loss of PMe_3, generating **9** in moderate yield (eq 5).



1 R = Ph
8 R = Me



(5)

9 R = Ph
11 R = Me

The ^1H NMR spectrum of **9** in C_6D_6 reveals a doublet at 0.32 ppm (J_{P-H} = 9.5 Hz) that is assigned to the protons of PMe_3 and a doublet at 1.28 ppm ($^3J_{P-H}$ = 5.1 Hz) due to the anilide proton. The doublet for the amide proton is consistent with a structure that has only one PMe_3 *trans* to the NHPh group. A singlet at −11.12 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also consistent with the formation of **9**.

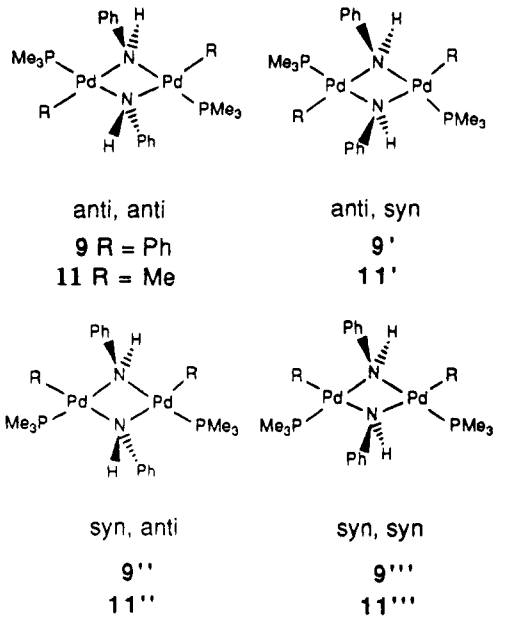
Upon dissolution, compound **9** slowly rearranges to a mixture of isomers. After 1 h at 25 °C, the ^1H NMR

(25) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

(26) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

(27) The pK_a values of phenol and aniline are 10 and 27, respectively.

Chart 1



spectrum of **9** reveals the original signals as well as the presence of a new doublet at 1.22 ppm (J_{P-H} = 6.6 Hz) and a singlet at 1.46 ppm. The presence of two new singlets at −12.22 and −15.04 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the mixture is consistent with the formation of two new isomers of **9**. There are four possible isomers of **9**, as shown in Chart 1.

The doublet at 1.22 ppm suggests that isomer **9'** is present, with the PMe_3 ligands and the phenyl rings of the anilide moieties in the *anti,syn* configuration, respectively. This isomer should give rise to equivalent amide protons that are doublets due to coupling with *trans* phosphines. The second new isomer is probably one which has the PMe_3 ligands *syn* to each other (**9''** or **9'''**). The ^1H NMR spectrum of either of these isomers should have a singlet and triplet for the two inequivalent amide protons. Although only a singlet at 1.46 ppm was observed in the ^1H NMR spectrum, the spectrum is complicated enough so that the other proton could be obscured by overlapping resonances. Isomerization about the anilide substituent has been previously reported for binuclear palladium(II) complexes containing anilide bridging ligands.[28] The potential of bridging amide species involving late transition metals to isomerize about the metal center has also been reported.[8c] The mixture of isomers is rapidly converted to **1** in the presence of excess PMe_3.

Crystallization of **9** from diethyl ether at 0 °C afforded white crystals suitable for X-ray diffraction studies. A thermal ellipsoid plot of **9** is found in Figure 2, with selected bond lengths in Table 6. The crystal structure confirms the stereochemistry of **9** and consists of two crystallographically independent half-dimers, each located at a center of inversion. No significant differences were observed between the dimers. The amide protons were located from a difference Fourier map. The PMe_3 ligands and the phenyl rings of the anilide moieties are in the *anti,anti* configuration, respectively. The geometry about each metal center is square planar, with observed N—Pd—N1 and N'—Pd'—N'1 bond angles at

(28) Okeya, S.; Yoshimatsu, H.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 483.

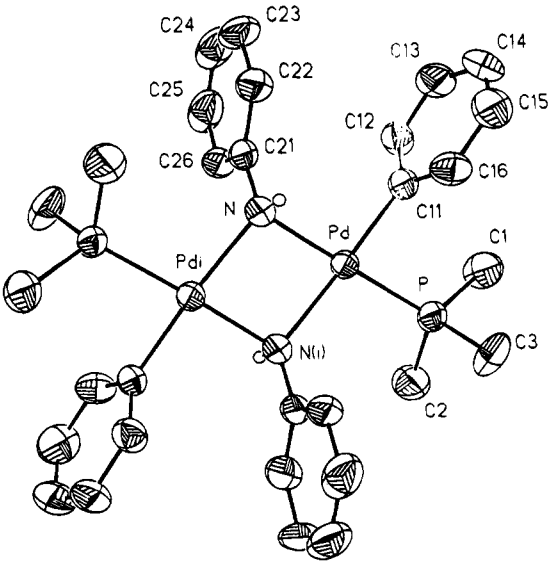
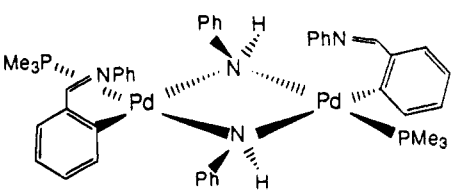


Figure 2. Thermal ellipsoid plot of $[(PMe_3)Pd(Ph)(\mu\text{-}NHPh)]_{10}$ (**9**).

84.4(2) and 83.9(2)°, respectively. The Pd—N distances vary between 2.13 and 2.16 Å. The symmetrical Pd—N—Pd bond distances as well as Pd—Pd distances of 3.181 and 3.190 Å for the two crystallographically independent dimers are similar to those of the platinum(II) bridging amide reported by Roundhill.[8c]

The symmetrical bridging of the anilide groups in **9** is in contrast with the structure of *anti*-$[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}NHPh)\}_2]$, in which the anilide groups form unsymmetrical bridges with Pd—N distances that differ by 0.06 Å.[8g] It is likely that the difference between these two structures reflects the difference in the magnitude of the *trans* influence of ligand *trans* to the anilide groups in the two structures. Thus, PMe_3 and Ph have more similar *trans* influences than C_6F_5 and *t*-BuNC.

After several recrystallizations of a single batch of **5**, small amounts of crystals suitable for X-ray diffraction studies can be obtained from the mother liquors. However, the crystal structure analysis of these crystals revealed that the dimeric amido complex **10** was isolated

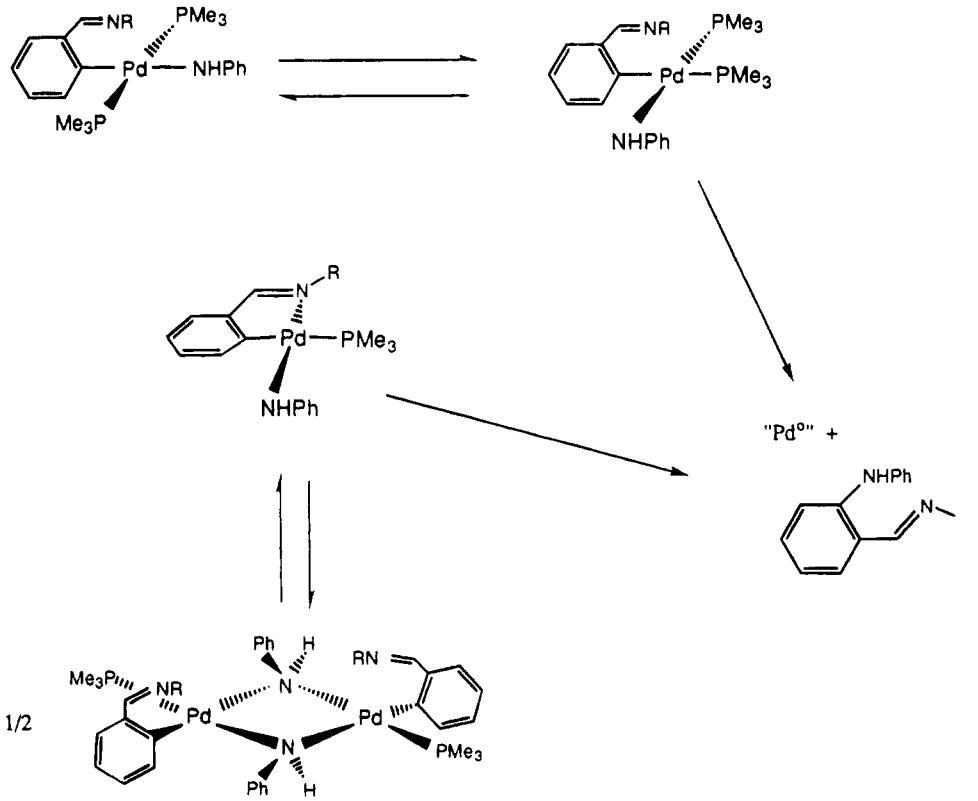


10

rather than the monomeric complex **5**. The thermal ellipsoid drawing of **10** can be found in Figure 3, while selected bond lengths and angles are found in Table 7. The dimers have 2-fold rotational pseudosymmetry with the axis of rotation perpendicular to the Pd···Pd coordination plane. It is interesting to note that all ligands extend to the same side of the coordination plane, giving compound **10** an *anti,syn* disposition of the phosphine and anilide ligands. The Pd—Pd' distance of 3.141 Å as well as the four Pd—N distances are similar to those found in **9**. All other bond lengths and angles of **10** fall within expected ranges.

Attempts to synthesize **10** in a manner similar to that for **9** met with little success. Varying the reaction

Scheme 1



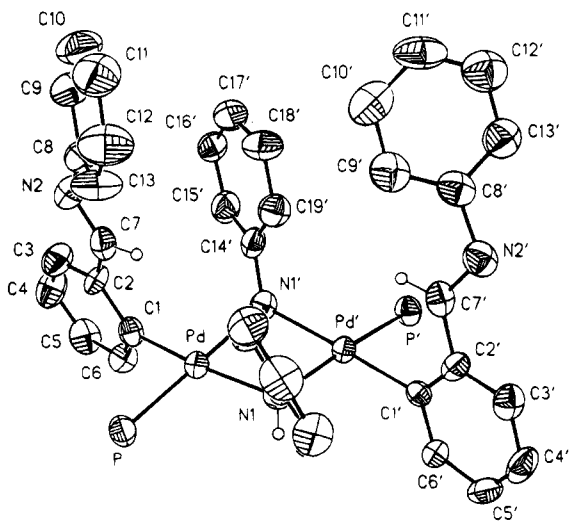


Figure 3. Thermal ellipsoid plot of $[(PMe_3)Pd(C_6H_4C(H)=NPh)(\mu\text{-}NHPh)]_2$ (**10**). The methyl groups have been removed from the PMe_3 ligands for clarity.

conditions such as temperature and pressure led to incomplete conversion from monomer to dimer or reductive elimination. Evidently, repeated recrystallization of **5** at room temperature or below results in the loss of small amounts of phosphine when the solution is concentrated under vacuum. In this fashion, the formation of a small amount of the dimer **10** can occur without reductive elimination. Eventually, after enough recrystallizations (three to four), compound **10** can be isolated in low yield as single crystals.

Although we were unable to isolate significant amounts of pure **10**, NMR data obtained from the thermolysis of **5** show the presence of at least six isomers of **10**, as determined by the six new singlets between 8.8 and 10.3 ppm that are assigned to the protons of the imine functionalites. A series of doublets and singlets between 1.0 and 1.4 ppm for the anilide protons suggests that the anilide moieties are *trans* and *cis* to the PMe_3 ligands. The $^{31}P\{^1H\}$ NMR spectrum of **10** is also consistent with the presence of six or seven isomers of **10** at room temperature. The imine functionality is responsible for the increase in number of observed isomers of **10**, since the steric bulk provided by the *o*-imine substitution gives rise to the possibility of four more isomers due to *syn* and *anti* imine groups (assuming that there is hindered rotation of the phenyl groups).[29]

During the preparation of compound **8**, a small amount of another compound was detected. To confirm that this material was the methyl analog of dimer **9**, we investigated the preparation of this dimeric amide complex. When compound **8** was warmed to 70 °C under reduced pressure (200 mTorr) for 16 h, the yellow solid turned white. The ^1H NMR spectrum of this powder revealed complete conversion of **8** to the dimeric species **11** (eq 5). The NMR data for **11** were similar to those for **9**. A doublet at 1.50 ppm (J = 5.5 Hz) for the N—H resonance and doublets at 0.54 and 0.16 ppm for the protons of the PMe_3 and CH_3 groups confirm dimer formation as the *anti,anti* isomer (Chart 1). Like compound **9**, **11** readily isomerizes in solution at 25 °C. After *ca.* 3 h at room temperature, an NMR sample of **11** displays three new singlets at −7.57, −8.23, and −9.92 ppm in the $^{31}P\{^1H\}$ NMR spectrum as well as

(29) (a) The observation of hindered rotation about the M—C bond in ortho-substituted aryl derivatives of square-planar d^8 metal complexes is well documented.[29b-d] In the specific example of compound **10**, hindered rotation about the M—C bond will give rise to a total of eight possible isomers due to *syn* and *anti* orientations of the anilide, PMe_3, and imine groups. (b) Wada, M.; Kusabe, K.; Oguro, K. *Inorg. Chem.* **1977**, *16*, 446. (c) Wada, M.; Sameshima, K. *J. Chem. Soc., Dalton Trans.* **1981**, *240*. (d) Wada, M.; Kumazoe, M. *J. Organomet. Chem.* **1983**, *259*, 245.

three sets of doublets at 0.5 and 0.2 ppm that are assignable to the PMe_3 and CH_3 groups. This suggests that three new isomers are present in solution. We believe these isomers are the same as those of **9** (Chart 1). Like compound **9**, the three isomers of **11** are rapidly converted to **8** in the presence of PMe_3 at 25 °C.

Although **11** is similar in many aspects to **9**, there is one noticeable difference between the two. The synthesis of **11** requires significantly lower temperatures (70 vs 90 °C). Indeed, when compound **8** was recrystallized from diethyl ether at 0 °C, small amounts of **11** could be detected by NMR spectroscopy. The group *trans* to the anilide moiety appears to be responsible for this difference in reaction temperature. It is unclear whether this is due to a *cis* effect of the CH_3 group or an increase in the basicity of the anilide lone pair.

Compounds **1** and **8** are remarkably resistant to direct reductive elimination of the alkyl and amide groups to form the amine. ^1H NMR studies of the thermolysis of these compounds show no evidence for reductive elimination at 80 °C. Only clean conversion to the dimer was observed. Further heating to 110 °C (24 h) results in slow conversion of the dimer to the amine (Ph_2NH or Ph(Me)NH). Evidently, dimer formation is more favorable than the *trans* to *cis* isomerization that must occur prior to reductive elimination.[30] This shows that the presence of the anilide lone pair opens an alternative reaction path (dimerization) even when reductive elimination of the R and NR_2 groups is feasible.

Compound **5** behaves differently from **1** and **8** when it is thermalized. The product of reductive elimination is observed at temperatures as low at 60 °C, before **5** has been completely converted to **10**. Furthermore, prolonged heating at 80 °C gives a good yield (>90%) of the reductive-elimination product. Identical results were obtained when *trans*-$(PMe_3)_2Pd(C_6H_4C(H)$=N-*i*-Pr)(NHPh)[7] was thermalized. Obviously, the presence of an imine functionality ortho to the metal center facilitates the reductive-elimination process. We have not yet been able to determine whether reductive elimination occurs from the monomer, the dimer, or both. In either case, the imine lone pair has the potential to compete with the anilide lone pair to facilitate the formation of an isomer with *cis* amide and R groups that can undergo reductive elimination, as shown in Scheme 1.

The results of the thermolysis studies clearly demonstrate the importance of the amide lone pair in determining the chemistry of these complexes. When there is no other lone pair in the molecule that can interfere with the amide lone pair, dimerization is preferred. In the case of the imine complexes, the presence of a potential donor facilitates reductive elimination at the expense of dimerization. The basicity of the amide lone pair also plays a strong role in the reactions of these molecules with unsaturated substrates, since only the most electrophilic substrates are observed to react with these[3c] and other amide complexes.[2,3] Thus, the analogy that has often been drawn between a metal alkyl and a metal amide is clearly valid only in the broadest sense and does not extend to the reaction chemistry of the two groups.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and bond distances and angles for **1**, **9**, and **10** (13 pages). Ordering information is given on any current masthead page.

OM940171A

(30) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933 and references therein.