Acetimine and 2-Methyl-2-amino-4-iminopentane Complexes of Palladium(II)

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By reaction between the labile complex *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$] and aqueous ammonia-acetone solutions the palladium complexes [Pd(C_6F_5)$_2$$L_2$] [L = NH_3 (**1**), $NHCMe_2$ (**2**) and L_2 = NHC(Me)CH_2C(Me_2)NH_2 (**3**)] are obtained. The reaction product depends on the experimental conditions used. The cationic complexes [Pd(dmba)L_2]ClO_4 [L = NH_3 (**5**), $NHCMe_2$ (**6**) and L_2 = NH C(Me)CH_2C(Me_2)NH_2 (**7**)] with the N,C-chelating 2-(dimethylaminomethyl)phenyl (dmba) ligand have been obtained by treating [(dmba)Pd(μ-Cl)$_2$Pd-(dmba)] with $AgClO_4$ in aqueous ammonia−acetone solution. The mono(acetimine) complex [Pd(dmba)(PPh_3)($NHCMe_2$)]ClO_4 (**8**) is obtained by a similar procedure starting from [Pd-(dmba)(PPh_3)Cl]. The crystal structures of **1**−**3** and **6** and **7** have been determined; there is extensive hydrogen bonding (N−H···F−C or N−H···$OClO_3$) in all the compounds.

Introduction

The addition of ammonia to ketones would be expected to give the corresponding hemiaminal and/or imine. However, these compounds are generally unstable and unsubstituted NH-ketimines spontaneously polymerize, the stable compound being the result of combinations and condensations of one or more molecules of the hemiaminal and/or the imine with each other or with additional molecules of ammonia.[1] In the particular case of acetone, the formation of acetimine (Me_2C═NH) from acetone and ammonia has been reported: low loadings of acetone and ammonia on the medium-pore zeolite HZMS-5 over 250 °C give acetimine, and when the large-pore zeolite HY is used, the ammonia adduct of acetone (2-aminopropan-2-ol) is detected at low temperature;[2] acetimine is also formed by an NH_4Cl-catalyzed reaction between acetone and ammonia at 50 bar and 120 °C.[3] However, the stable product is the result of cyclotrimerization with the loss of one molecule of ammonia.[4] Acetimine is stable at 0 °C for short periods of time and decomposes on storage to give 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine (acetonine).[4]

The instability of both acetimine[5−13] and its amino−imine dimer (2-methyl-2-amino-4-iminopentane)[14−17] could account for the scarcity of metal complexes with these ligands. Furthermore, no systematic method of preparation of these complexes is found in the literature. Chemical or electrochemical oxidation of coordinated isopropylamine,[5] redox-catalyzed condensation of an ammine complex with acetone,[6] oxidative addition of 2-bromo-2-nitrosopropane,[8] oxidative addition of an iminium salt to low-valent metal complexes,[9] reduction of coordinated acetonitrile,[10] controlled-potential electrochemical oxidation of coordinated 2,3-dimethyl-2,3-diaminobutane,[11] the reaction between [LAu(acac)]$^+$-type complexes and NH_4X in acetone,[12] and thermal decomposition of [Si(CMe_3)$_2$(OEt_2){N(CMe_3)$AlCl_3$}][13] are the methods reported in the literature for the synthesis of acetimine complexes.

The work reported in this paper shows that both acetimine and its dimer (2-methyl-2-amino-4-iminopen-

(1) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed.; John Wiley & Sons: New York, 1992; p 896.
(2) Xu, T.; Zhang, J.; Haw, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 3171.
(3) Verardo, G.; Giumanini, A. G.; Strazzolini, P.; Poiana, M. *Synth. Commun.* **1988**, *18*, 1501.
(4) Findeisen, K.; Heitzer, H.; Deehnicke, K. *Synthesis* **1981**, 702.
(5) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336.
(6) Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261.
(7) D. Sellmann, D.; Thallmair, E. *J. Organomet. Chem.* **1979**, *164*, 337.
(8) King, R. B.; Douglas, W. M. *Inorg. Chem.* **1974**, *13*, 1339.
(9) Aresta, M.; Quaranta, E.; Dibenedetto, A.; Giannoccaro, P.; Tommasi, I. *Organometallics* **1997**, *16*, 834.
(10) Yeh, W.-Y.; Ting, C.-S.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 1417.
(11) Wong, K.-Y.; Che, C.-M.; Li, C.-K.; Chiu, W.-H.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 754.
(12) Vicente, J.; Chicote, M. T.; Guerrero, R.; Saura-Llamas, I.-M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **2001**, *7*, 638.
(13) Klingebiel, W.; Noltemeyer, M.; Schmidt, H.-G.; Schmidt-Basë, D. *Chem. Ber./Recl.* **1997**, *130*, 753.
(14) Rose, N. J.; Elder, M. S.; Busch, D. H. *Inorg. Chem.* **1967**, *6*, 1924.
(15) Gould, R. O.; Stephenson, T. A.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1978**, 769.
(16) Alzuet, G.; Ferrer, S.; Casanova, J.; Borrás, J.; Castiñeiras, A. *Inorg. Chim. Acta* **1993**, *205*, 79.
(17) Hanic, F.; Serator, M. *Chem. Zvesti* **1964**, *18*, 572.

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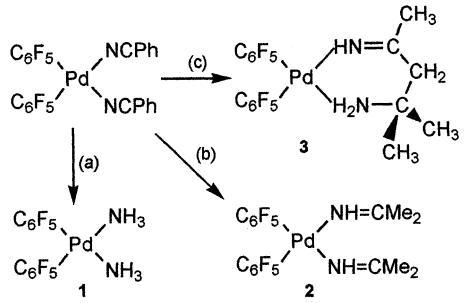
Scheme 1[a]



[a] Conditions: (a) $+2NH_3$(aq), in Me_2CO, room temperature, 10 min. (b) $+20NH_3$(aq), in Me_2CO, room temperature, 4 h. (c) $+2NH_3$(aq), in Me_2CO, room temperature, 2 d.

tane) can be conveniently trapped by Pd^{II} from acetone−ammonia solutions.

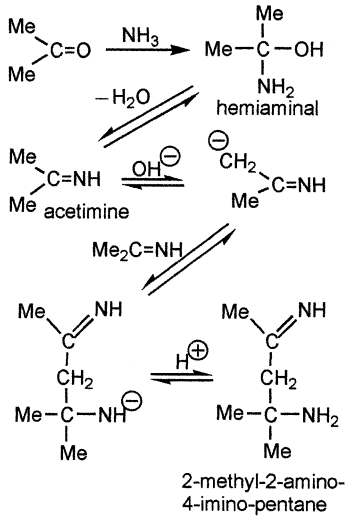
Results and Discussion

Bis(pentafluorophenyl) Complexes. The labile complexes *cis*-$[M(C_6F_5)_2(PhCN)_2]$ (M = Ni, Pd) have been used as starting materials for the preparation of metal complexes.[18,19] When *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$[20] is treated with 20% aqueous ammonia in acetone, complexes **1**−**3** are obtained in high yields, the specific product depending on the experimental conditions given in Scheme 1. Complexes **1**−**3** are all white, air-stable solids that decompose on heating above 190 °C. Their IR spectra show the characteristic absorptions of the C_6F_5 group (1630 m, 1490 vs, 1050 s, and 950 vs cm^{-1})[21] and a split band at ca. 800 cm^{-1} assigned to the *cis*-Pd-$(C_6F_5)_2$ moiety.[22,23] The NH stretching modes are found in the 3300-cm^{-1} region and the C=N vibrations of **2** and **3** at ca. 1660 cm^{-1}.

The ^{19}F NMR spectra of **1** and **2** show the expected three signals for two equivalent C_6F_5 rings with relative intensities of $2F_o$:$1F_p$:$2F_m$. The ^1H NMR spectrum of **2** reveals the inequivalence of the Me groups of the imine ligands, arising from restricted rotation around the C=N bond at room temperature: a singlet at δ 2.38 for the Me group cis to the hydrogen atom of the NH group and a doublet ($^4J_{HH}$ = 1.8 Hz) at δ 2.07 for the *trans*-Me group. The asymmetry of complex **3** due to the presence of the amino−imine ligand is manifested in the ^{19}F NMR spectrum by two sets of signals arising from one C_6F_5 trans to NH_2 and one C_6F_5 trans to NH, respectively. The assignment of the ^1H resonances is straightforward: two broad singlets at δ 9.63 and 3.63 are assigned to the NH and NH_2 groups, respectively, two singlets at δ 2.77 and 1.50 for the CH_2 and the *gem*-Me groups, respectively, and a doublet ($^4J_{HH}$ = 1.45 Hz) at δ 2.20 for the Me group.

Compounds **2** and **3** are the first palladium(II) complexes with these ligands. The synthesis of complexes **1**−**3** can readily be understood on the assumption that in an acetone−ammonia mixture it works the equilibrium shown in Scheme 2. Depending on the experimental conditions used (Scheme 1), the predominant N-donor species (NH_3, $NH{=}CMe_2$ or $NH_2C(Me)_2CH_2C(Me){=}NH$) would be trapped by the *cis*-$Pd(C_6F_2)_2$ fragment with the concomitant displacement of benzonitrile. Since the ammonia complex **1** is formed quickly (within 10 min), compound **2** is more likely derived from **1** by ligand substitution of NH_3 with $NH{=}CMe_2$. So, the unstable acetimine and its dimer are stopped by palladium on the way to the most stable product (acetonine).[4] Furthermore, no acetonine−palladium complex was detected when the reaction was carried out with longer periods of time. However, during the isolation of complex **2** some impurity was detected in the NMR spectra that was attributed to the presence of the mixed complex $[Pd(C_6F_5)_2(NH_3)(NH{=}CMe_2)]$ (**4**). This was confirmed when a 1:1 molar mixture of $[Pd(C_6F_5)_2(NH_3)_2]$ and $[Pd(C_6F_5)_2(NH{=}CMe_2)_2]$ was put into the NMR tube containing $CDCl_3$. After a few minutes the ^1H spectrum showed that there were three palladium species: $[Pd(C_6F_5)_2(NH_3)_2]$, $[Pd(C_6F_5)_2(NH{=}CMe_2)_2]$, and $[Pd(C_6F_5)_2(NH_3)(NH{=}CMe_2)]$ [δ 8.3 (br, 1H, NH), 2.5 (s, 3H, *cis*-Me), 2,1 (d, 6H, *trans*-Me, $^4J_{HH}$ = 1.2 Hz), 1.7 (br, 3H, NH_3)], the integrated intensities being 1:3:5, respectively, because only the diimine complex is completely soluble in $CDCl_3$. The reaction leading to the formation of complex **3** is related to the recently reported palladium-assisted aldol condensation.[24] About the formation of **3**, an alternative mechanism is via deprotonation of a methyl group in **2** under basic conditions, followed by an intramolecular nucleophilic attack. However, when **2** was treated with aqueous $[NBu_4]OH$ in methanol for 24 h the formation of **3** did not take place; the ^1H and ^{19}F NMR spectra showed that the recovered product consisted of unchanged **2** and traces of $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$.

Scheme 2



Crystal Structures of Complexes 1−**3.** The crystal structure of complex **1** is shown in Figure 1. The coordination around Pd is almost square planar. The angle between the two C_6F_5 rings is 85.87(9)° and the

(18) Sánchez, G.; Serrano, J. L.; Momblona, F.; Ruiz, F.; García, J.; Pérez, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Polyhedron* **2001**, *20*, 571.
(19) Sánchez, G.; Momblona, F.; Sánchez, M.; Pérez, J.; López, G.; Casabó, J.; Molins, E.; Miravitlles, C. *Eur. J. Inorg. Chem.* **1998**, 1199.
(20) De Haro, C.; García, G.; Sánchez, G.; López, G. *J. Chem. Res., Synop.* **1986**, 11; *J. Chem. Res., Miniprint* **1986**, 1128.
(21) Long, D. A.; Steel, D. *Spectrochim. Acta* **1963**, *19*, 1955.
(22) Maslowski, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437.
(23) Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777.
(24) Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973.

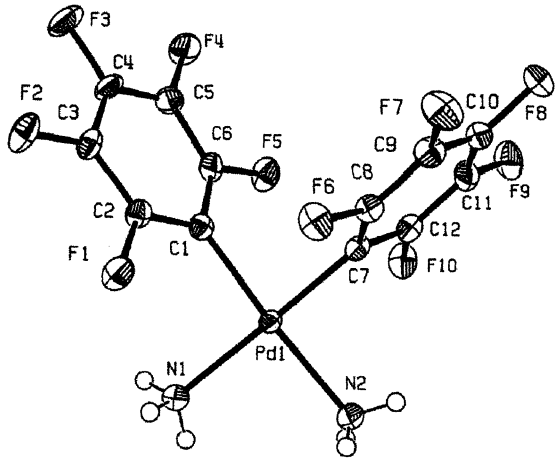


Figure 1. Molecular structure of complex **1**. Selected bond lengths (Å): Pd1−N1 2.132(2), Pd1−N2 2.119(2), Pd1−C1 2.004(2), Pd1−C7 1.997(2). Hydrogen bonds (Å) and angles (deg): N(1)···F(6)#1 3.264(3), H(1A)···F(6)#1 2.53(6), N(1)−H(1A)···F(6)#1 141(4); N(1)···F(4)#2 3.161, H(1B)···F(4)#2 2.38, N(1)−H(1B)···F(4)#2 154(4); N(1)···F(7)#3 3.200(3), H(1C)···F(7)#3 2.49(5), N(1)−H(1C)···F(7)#3 148(4); N(1)···F(10)#4 3.010(3), H(1C)···F(10)#4 2.62(5), N(1)−H(1C)···F(10)#4 112(4); N(2)···F(1)#1 3.029(3), H(2A)···F(1)#1 2.41(5), N(2)−H(2A)···F(1)#1 139(4); N(2)···F(2)#5 3.107(3), H(2B)···F(2)#5 2.62(5), N(2)−H(2B)···F(2)#5 120(4); N(2)···F(3)#5 3.349(3), H(2B)···F(3)#5 2.62(5), N(2)−H(2B)···F(3)#5 148(4); N(2)···F(10)#4 3.065(3), H(2C)···F(10)#4 2.37(6), N(2)−H(2C)···F(10)#4 137 (4) (symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y+1, -z$; #3 $x, -y, z-{}^1/_2$; #4 $-x+{}^1/_2, -y+{}^1/_2, -z$; #5 $x+{}^1/_2, y-1/2, z$).

angle between the two NH_3 ligands is 91.42(9)°. The Pd−N distances (2.119(2) and 2.132(2) Å) are longer than those observed in the ammine palladium complexes *trans*-$[Pd(NH_3)_2(1\text{-MeC})_2](NO_3)_2$ (1-MeC = 1-methylcytosine),[25] $[Pd(CBDA\text{-}O,O')(NH_3)_2]$ (CBDA = cyclobutane-1,1-dicarboxylate),[26] and $[Pd(NH_3)_4]^{2+}$,[27] and slightly shorter than that observed in [Pd(dmpe)Me-(NH_3)] (dmpe = 1,2-bis(dimethylphosphino)ethane) (2.139(5) Å).[28] In the crystal, a rather complex three-dimensional macromolecular network structure is observed built up by extensive hydrogen bonding, which involves the NH groups of the ammine ligands and the *o*- or *m*-fluorine atoms of the pentafluorophenyl rings of five neighboring molecules (see caption of Figure 1), although some of the H···F interactions are within the range reported for the sum of the van der Waals radii of H and F (2.5−2.7 Å)[29] and F···H−N contacts of 2.5 Å and greater are very weak and caution must be exercised in attributing a particular stabilizing significance to interactions of this length and longer.[30] Fluorine, when covalently bound to carbon, does not frequently form hydrogen bonds with conventional hydrogen bond donors such as the O−H and N−H groups,[31] and aryl

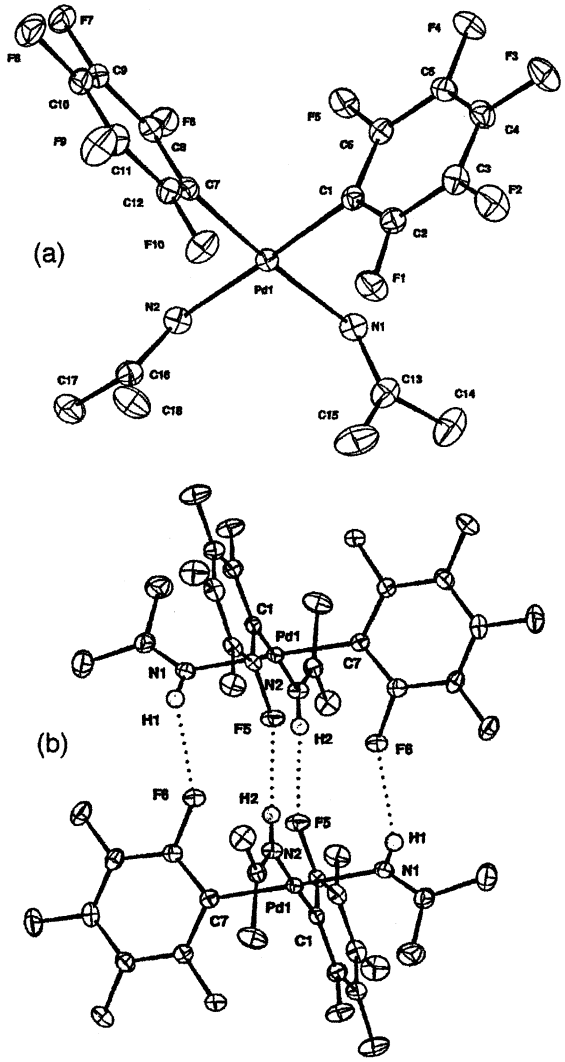


Figure 2. (a) Molecular structure of complex **2**. Selected bond lengths (Å): Pd1−N1 2.082(2), Pd1−N2 2.086(2), Pd1−C1 2.008(3), Pd1−C7 2.005(3), N1−C13 1.259(4), N2−C16 1.268(4). (b) Hydrogen bonds (Å) and angles (deg): N···F 3.089−3.091, N−H···F 151−166.

fluorines are less effective than aliphatic fluorines as hydrogen bond acceptors.[30] Intermolecular hydrogen bonds (O−H···F−C) in $[trans\text{-}Pt\{\mu\text{-}C{\equiv}CC(OH)Ph_2\}(C_6F_5)(PPh_3)]_2{\cdot}CH_2Cl_2$ have been reported.[32] Two of the hydrogen bridges in complex **1**, those involving the H(1C) and H(2B) atoms (caption of Figure 1), are three-center (bifurcated) hydrogen bonds.[33] Three-center hydrogen bonds involving two oxygen atoms are relatively common, whereas those involving two fluorine atoms bound to sp^2- or sp^3-hybridized carbons are rare; three-center CF···HN intramolecular hydrogen bonding in the 2,6-bis(2,6-difluorophenyl)piperidine systems has been observed.[34]

The crystal structure of complex **2** is shown in Figure 2. The coordination around Pd is almost square planar. The N1, N2, C1, and C7 atoms form a perfect plane with the Pd atom 0.06(1) Å above. The four ligands are plane fragments. The angle between the two C_6F_5 rings is

(25) Krumm, M.; Mutikainen, I.; Lippert, B. *Inorg. Chem.* **1991**, *30*, 884.
(26) Barnham, K. J.; Djuran, M. I.; Frey, U.; Mazid, M. A.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1994**, 65.
(27) Mealli, C.; Pichierri, F.; Randaccio, L.; Zangrando, E.; Krumm, M.; Holtenrich, D.; Lippert, B. *Inorg. Chem.* **1995**, *34*, 3418.
(28) Seligson, A. L.; Togler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.
(29) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1997**, *36*, 4372.
(30) Howard J. A. K.; Hoy, V. J.; O'Hagan D.; Smith, G. T. *Tetrahedron* **1996**, *52*, 12613.
(31) Dunitz, J.; Taylor, R. *Chem. Eur. J.* **1997**, *3*, 89.
(32) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martín, A.; Serrano, B. *J. Chem. Soc., Dalton Trans.* **2001**, 2926.
(33) Steiner T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.
(34) Pham, M.; Gdaniec, M.; Polonski, T. *J. Org. Chem.* **1998**, *63*, 3731.

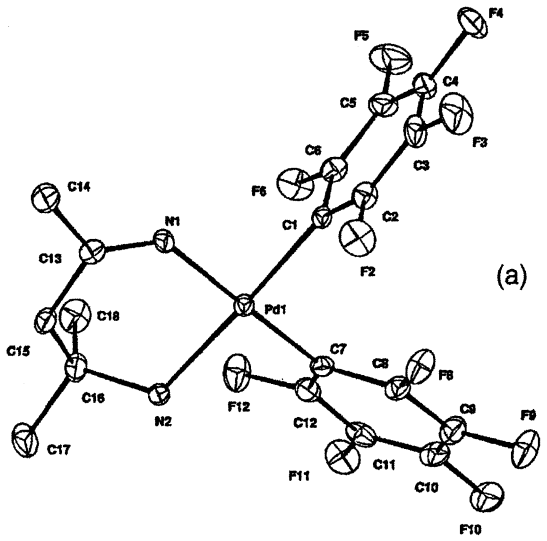
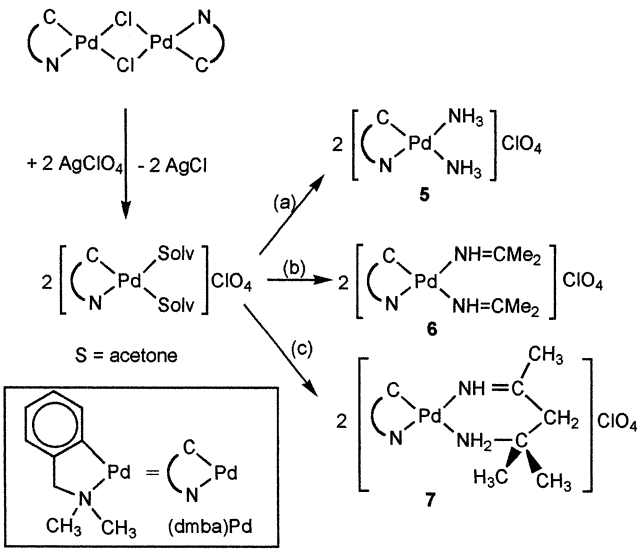


Figure 3. Molecular structure of complex **3**. Selected bond lengths (Å): Pd1−C1 2.009(5), Pd1−C7 2.010(5), Pd1−N1 2.068(4), Pd1−N2 2.100(4).

88.8(1)° and the angle between the two imines is 89.1(1)° with the two CMe_2 groups toward the same side of the coordination plane. The Pd−N distances lie within the range reported in complexes containing the $\{Pd(C_6F_5)_2N_2\}$ moiety (2.064−2.131 Å) such as $[Pd(C_6F_5)_2\{NH{=}C(OMe)Me\}_2]$[35] and $[Pd(C_6F_5)_2(pz\cdots H\cdots pz)]$ (pz = pyrazolate).[36] The acetimino ligands present in complex **2** show C=N bond lengths (1.259(4) and 1.268(4) Å) similar to those observed in $[AlCl_3(NH{=}CMe_2)]$ (1.282(4) Å),[13] $[W(PhC{\equiv}CPh)_3(NH{=}CMe_2)]$ (1.284(7) Å),[10] and $[Au(NH{=}CMe_2)_2]^+$ (1.285(8) and 1.271(7) Å)[12] but somewhat longer than those found in $[Ru(bipy)_2(NH{=}CMe_2)_2]^+$ (1.159 Å).[11] In the crystal, dimeric aggregates are formed through four hydrogen bonds between the NH groups of the acetimine ligands and half the *o*-fluorine atoms of the pentafluorophenyl rings as shown in Figure 2b. The coordination planes of the two fragments are parallel to each other, forming a very symmetrical structure.

The crystal structure of complex **3** is shown in Figure 3. Only three crystal structures of 2-methyl-2-amino-4-iminopentane complexes are available for comparison with that of **3** (Figure 3).[15−17] The amino−imino ligand acts in a bidentate fashion achieving a six-membered ring. The imine C13−N1 bond is 0.23 Å shorter than the amine C16−N2 distance and both are similar to those found in related complexes: $[Ru(PMe_2Ph)_2\{SC(O)Ph\}_2\{NH{=}C(Me)CH_2C(Me_2)NH_2\}]$[15] (1.333(26) and 1.482(26) Å), $[Co(methazolamidate)(NH_3)\{NH{=}C(Me)CH_2C(Me_2)NH_2\}_2](NO_3)_2{\cdot}2H_2O$[16] (1.30(3) and 1.50(2) Å), and $[Cu\{NH{=}C(Me)CH_2C(Me_2)NH_2\}_2]$[17] (1.30 and 1.51 Å). The Pd−N1 bond length is 0.032 Å shorter than the Pd−N2 distance. The three N−H groups, two *p*-fluorines, and one *o*-fluorine are involved in hydrogen bonding; each molecule is surrounded by three other molecules forming two hydrogen bonds with each one and resulting in a sheet parallel to the *ac* plane.

Scheme 3[a]



[a] Conditions: (a) +2NH_3(aq), in Me_2CO, room temperature, 5 min. (b) +10NH_3(aq), in Me_2CO, room temperature, 30 min. (c) +10NH_3(aq), in Me_2CO, room temperature, 24 h.

Dmba Complexes. The dmba analogues of complexes **1**−**3** have been prepared from the precursor $[Pd_2(dmba)_2(\mu\text{-}Cl)_2]$. After precipitation of AgCl by addition of $AgClO_4$, the solvento complex $[Pd(dmba)(Me_2CO)_2]ClO_4$ generated in situ reacts with the acetone−ammonia mixture to give complexes **5**−**7** (Scheme 3) in 57−72% yields. As stated above for complexes **1**−**3**, the reaction conditions specified in Scheme 3 are critical for the identity of the isolated complex.

Complexes **5**−**7** are white, air-stable solids that decompose on heating above 170 °C. Their acetone solutions show conductance values corresponding to 1:1 electrolytes (Λ_M in the range 130−145 S cm^2 mol^{-1})[37] and the IR band observed at ca. 1090 cm^{-1} is consistent with the presence of free perchlorate with T_d symmetry. The NH stretching modes for the three complexes are found in the 3300−3150-cm^{-1} range, and a band at 1650 cm^{-1} in the IR spectra of **5** and **6** is assigned to the ν(CN) mode.

The ^1H NMR spectra of complexes **5**−**7** show the presence of the dmba ligand and the observation of the NCH_2 and NMe_2 proton signals as singlets suggests that the inversion of the configuration at the PdCCCN chelate ring is faster than the NMR time scale at room temperature.[35] The assignments given in the Experimental Section for complex **7** were supported by the pertinent heteronuclear ($^1H-^{13}C$) COSY technique. The asymmetry of complexes **5** and **6** derived from the presence of the dmba ligand is manifested in the ^1H NMR spectra and two sets of signals are observed for the L (NH_3 or $NHCMe_2$) ligand: one L trans to C and one L trans to N. On the other hand, the ^1H resonances from the L ligands are found at lower field than in the corresponding complexes **1** and **2** containing the $Pd(C_6F_5)_2$ moiety while a negligible variation is found on comparing the ^1H spectra of **3** and **7**.

The acetimine complex **8** (Scheme 4) was prepared by a similar procedure starting from $[Pd(dmba)(PPh_3)Cl]$ in acetone. After elimination of the chloride ligand

(35) Ruiz, J.; Cutillas, N.; Rodríguez, V.; Sampedro, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1999**, 2939.

(36) López, G.; Ruiz, J.; Vicente, C.; Martí, J. M.; García, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *Organometallics* **1992**, *11*, 1417.

(37) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

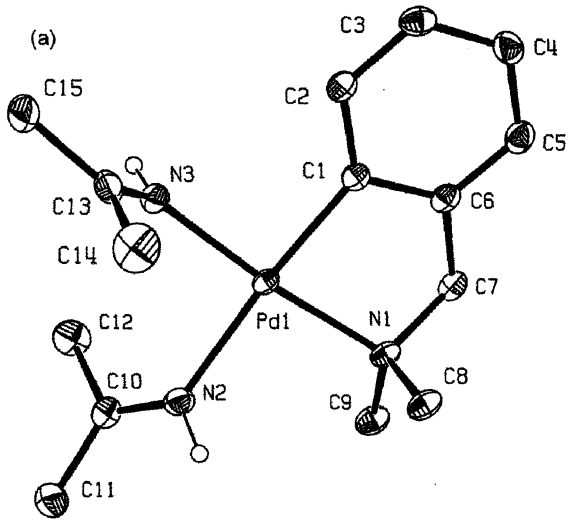
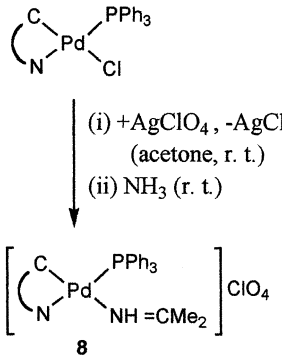


Figure 4. Molecular structure of complex **6**. Selected bond lengths (Å): Pd1−C1 1.989(3), Pd1−N1 2.079(2), Pd1−N2 2.143(2), Pd1−N3 2.018(2).

Scheme 4



8

with $AgClO_4$ followed by addition of 32% aqueous NH_3 (Pd:NH_3 molar ratio = 1:1; 1 h of stirring at room temperature) complex **8** was obtained in 62% yield. The complex behaves as a 1:1 electrolyte (Λ_M = 132 S cm^2 mol^{-1})[37] in acetone and the IR spectrum showed bands at 3250 (ν NH), 1660 (ν CN), and 1060 (ν ClO_4) cm^{-1}. The ^{1}H NMR spectrum is consistent with the proposed structure and the ^{31}P resonance is observed at δ 43.5 as a singlet.

Crystal Structures of Complexes 6 and 7. A drawing of the cationic complex of **6** is shown in Figure 4. The palladium atom is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the cyclometalated dmba ligand and the N atoms of two imino ligands. The cyclometalated ring is puckered with the nitrogen atom significantly out of the plane defined by the palladium and carbon atoms, a feature that is quite commonly observed in cyclometalated dmba complexes. The Pd−C(1) (dmba) and Pd−N(1) (dmba) distances are similar to those found in other Pd(dmba) complexes.[35,38]

The Pd−N(2) (acetimino) distance (2.143 Å) trans to the carbon atom is longer than the Pd−N(3) (acetimino) distance (2.018 Å), due to higher trans influence of the C atom than that of the N atom (dmba, sp^3). Both acetimine ligands show C═N bond lengths (1.271(4) and 1.275(4) Å) similar to those observed in complex **2**. In the crystal, the perchlorate anion is bridging two complex cations through N−H···O bonds (3.260(4) and 2.989(4) Å) forming a lineal chain. Hydrogen bonds between triflate anions and the NH groups of acetimine ligands in $[Au(NHCMe_2)_2](CF_3SO_3)$ have been reported (N···O 2.89−2.91 Å, N···H−O 158−167°).[12]

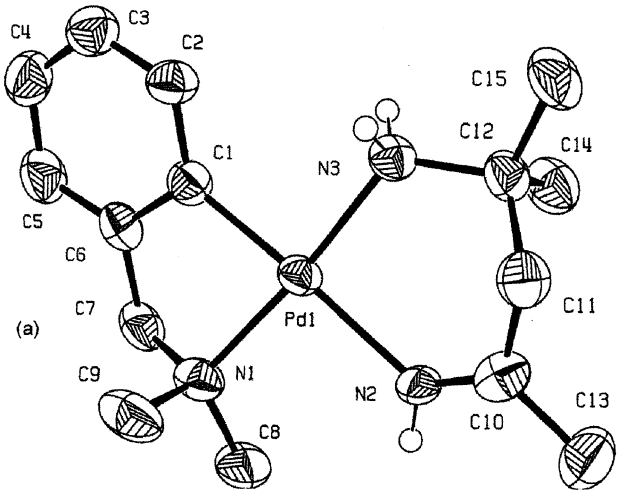


Figure 5. Molecular structure of complex **7**. Selected bond lengths (Å): Pd1−C1 1.975(4), Pd1−N1 2.088(3), Pd1−N2 2.133(3), Pd1−N3 2.058(3).

The crystal structure of complex **7** is shown in Figure 5. The 2-methyl-2-amino-4-iminopentane group acts as a chelate ligand. The coordination around Pd is almost square planar. The structural parameters of the dmba ligand are similar to those found in the diimino complex **6** and other Pd(dmba) complexes.[35,38] The Pd−N(2) (imine) distance (2.133(3) Å) trans to the carbon atom is longer than the Pd−N(3) (amine) (2.058(3) Å) distance due to higher trans influence of the C. As expected, the imine C(10)−N(2) bond (1.236(5) Å) is shorter than the amine C(12)−N(3) distance (1.503(5) Å). In the crystal, the perclorate anion is bridging two complex cations through N−H···O bonds involving the NH_2 groups to give a lineal chain.

Conclusions

The first palladium complexes containing acetimine and its dimer (2-methyl-2-amino-4-iminopentane) have been prepared by using a labile palladium complex and aqueous acetone−ammonia solutions. Acetimine and its dimer are unstable products and the procedure described herein appears to be a systematic approach to the synthesis of these types of complexes. Depending on the experimental conditions used (ammonia concentration and reaction time) the ammine, acetimine, or 2-methyl-2-amino-4-iminopentane complex is isolated. The X-ray diffraction study of the compounds reveals that extensive C−F···H−N or O···H−N interactions are present in the solids.

Experimental Section

Instrumental Measurements. 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 mL min^{-1}). Molar

(38) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1996**, *35*, 3064.

conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Crison 525 conductimeter. The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as the standard, respectively. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer with Nujol mulls between polyethylene sheets. Mass spectra (positive-ion FAB) were recorded on a V.G. AutoSpecE spectrometer and measured with 3-nitrobenzyl alcohol as the dispersing matrix; isotope ^{106}Pd (27.3%) was chosen for peak assignments.

Materials. The starting complexes *cis*-$[Pd(C_6F_5)_2(NCPh)_2]$,[20] $[Pd_2(o\text{-}C_6H_4CH_2NMe_2)_2(\mu\text{-}Cl)_2]$,[39] and $[(o\text{-}C_6H_4CH_2NMe_2)PdCl(PPh_3)]$[40] were prepared as described elsewhere.

Preparation of Complex *cis*-$[Pd(C_6F_5)_2(NH_3)_2]$ (1). To a solution of $[Pd(C_6F_5)_2(NCPh)_2]$ (100 mg, 0.155 mmol) in acetone (15 mL) was added 20% aqueous NH_3 (42.9 μL, 0.464 mmol). The resulting solution was stirred at room temperature for 10 min, and the solvent was then evaporated to dryness. The residue was then treated with 1:3 $CHCl_3$−hexane and the suspension was filtered off to separate the white solid **1**, which was washed with $CHCl_3$ and air-dried. Yield: 60 mg, 81%. Anal. Calcd for $C_{12}H_6N_2F_{10}Pd$: C, 30.37; H, 1.27; N, 5.90. Found: C, 30.77; H, 1.20; N, 5.85. Mp: 189 °C dec. IR (Nujol, cm^{-1}): ν(NH), 3388, 3304; ν(Pd−C_6F_5) 798, 786. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ($SiMe_4$) 1.86 (br, 3H, NH_3). ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$): δ($CFCl_3$) −117.7 (m, $4F_o$), −160.6 (t, $2F_p$, J_{mp} = 19.8 Hz), −163.5 (m, $4F_m$).

Preparation of Complex *cis*-$[Pd(C_6F_5)_2(NHCMe_2)_2]$ (2). To a solution of $(C_6F_5)_2Pd(NCPh)_2$ (100 mg, 0.155 mmol) in acetone (15 mL) was added 20% aqueous NH_3 (286.2 μL, 3.093 mmol). The resulting solution was stirred at room temperature for 4 h, and the solvent was then evaporated to dryness. Addition of 1:5 Et_2O−hexane to the residue, followed by vigorous stirring, rendered a white suspension, from which a white solid was collected by filtration and air-dried. Complex **2** was recrystallized from CH_2Cl_2−toluene−hexane. Yield: 65 mg, 76%. Anal. Calcd for $C_{18}H_{14}N_2F_{10}Pd$: C, 38.97; H, 2.54; N, 5.05. Found: C, 38.56; H, 2.55; N, 5.16. Mp: 196 °C dec. IR (Nujol, cm^{-1}): ν(NH), 3316; ν(C═N), 1668; ν(Pd−C_6F_5), 792, 782. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ($SiMe_4$) 8.40 (br, 2H; NH), 2.38 (s, 6H; *cis*-CH_3), 2.07 (d, 6H, *trans*-CH_3, $4J_{HH}$ = 1.8 Hz). ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$): δ($CFCl_3$) −117.7 (m, $4F_o$), −162.3 (t, $2F_p$, J_{mp} = 19.8 Hz), −164.6 (m, $4F_m$).

Preparation of Complex $[Pd(C_6F_5)_2\{NHC(Me)CH_2C(Me_2)NH_2\}]$ (3). To a solution of $(C_6F_5)_2Pd(NCPh)_2$ (100 mg, 0.155 mmol) in acetone (15 mL) was added 20% aqueous NH_3 (286.2 μL, 3.093 mmol). The solution was stirred at room temperature for 2 days, and the solvent was then evaporated to dryness. Addition of 1:5 Et_2O−hexane to the residue, followed by vigorous stirring, rendered a white suspension, from which a white solid was collected by filtration and air-dried. Complex **3** was recrystallized from CH_2Cl_2−hexane. Yield: 62 mg, 72%. Anal. Calcd for $C_{18}H_{14}N_2F_{10}Pd$: C, 38.97; H, 2.54; N, 5.05. Found: C, 38.72; H, 2.66; N, 4.92. Mp: 229 °C dec. IR (Nujol, cm^{-1}): ν(NH), 3342, 3320, 3290; ν(C═N), 1660; ν(Pd−C_6F_5), 792, 782. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ($SiMe_4$) 9.63 (br, 1H; NH), 3.63 (br, 2H, NH_2), 2.77 (s, 2H, CH_2), 2.20 (d, 3H, CH_3, J_{HH} = 1.5 Hz), 1.5 (s, 6H, *gem*-CH_3). ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$): δ($CFCl_3$) −114.4 (m, $2F_o$), −115.0 (m, $2F_o$), −164.1 (t, $1F_p$, J_{mp} = 19.5 Hz), −164.3 (t, $1F_p$, J_{mp} = 19.5 Hz), −165.8 (m, $4F_m$).

Preparation of Complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)(NH_3)_2]ClO_4$ (5). $AgClO_4$ (75.1 mg, 0.362 mmol) was added to an acetone (5 mL) solution of $[(o\text{-}C_6H_4CH_2NMe_2)_2Pd_2(\mu\text{-}Cl)_2]$ (100 mg, 0.181 mmol). After the resulting suspension was stirred at room temperature in the darkness for 30 min, it was filtered through Celite with 2 mL of acetone, and NH_3 (67 μL of 20% $NH_{3(aq)}$; 0.724 mmol) was then added. The solution was stirred at room temperature for 5 min, the solvent was removed under vacuum, and the residue was extracted with diethyl ether and dried in the air. Yield 72%. Anal. Calcd for $C_9H_{18}ClN_3O_4Pd$: C, 28.9; H, 4.9; N, 11.2. Found: C, 29.1; H, 4.9; N, 11.0. Mp: 178 °C dec. Λ_M: 145 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3358, 3288 ν(NH). ^1H NMR at 25 °C (acetone-d_6): δ 7.05−6.89 (m, 4H, C_6H_4), 4.03 (s, 2H, NCH_2), 3.2 (br, 3H, NH_3), 3.0 (s, 6H, NMe_2), 2.59 (br, 3H, NH_3). Positive-ion FAB mass spectrum: *m*/*z* 297 $(M - ClO_4 + 23)^+$, 257 $(M - ClO_4 - NH_3)^+$, 240 $(M - ClO_4 - 2NH_3)^+$.

Preparation of Complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)(NHCMe_2)_2]ClO_4$ (6). $AgClO_4$ (112.7 mg, 0.543 mmol) was added to an acetone (15 mL) solution of $[(o\text{-}C_6H_4CH_2NMe_2)_2Pd_2(\mu\text{-}Cl)_2]$ (150 mg, 0.272 mmol). After the resulting suspension was stirred at room temperature in the darkness for 30 min, it was filtered through Celite with 7 mL of acetone, and NH_3 (338 μL of 32% $NH_{3(aq)}$; 5.6 mmol) was then added. The solution was stirred at room temperature for 30 min, the solvent was removed under vacuum, and the residue was extracted with dichloromethane and filtered. The resulting solution was concentrated under vacuum and water was added to give a white precipitate that was filtered off and air-dried. The solid was crystallized from dichloromethane−toluene. Yield: 57%. Anal. Calcd for $C_{15}H_{26}ClN_3O_4Pd$: C, 39.7; H, 5.8; N, 9.3. Found: C, 39.4; H, 5.9; N, 9.1. Mp: 171 °C dec. Λ_M: 140 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3265 ν(NH), 1660 ν(CN), 1086 (ClO_4^-). ^1H NMR at 25 °C ($CDCl_3$): δ 9.3 (br, 1H, N*H*), 9.07 (br, 1H, N*H*), 7.06−6.85 (m, 3H, C_6H_4), 6.54 (d, 1H, C_6H_4, J_{H-H} = 7.4 Hz), 3.94 (s, 2H, NCH_2), 2.71 (s, 6H, NMe_2), 2.42 (s, 3H, CMe_2), 2.39 (s, 3H, CMe_2), 2.31 (d, 3H, CMe_2, J_{H-H} = 1,2 Hz), 2.25 (s, 3H, CMe_2). Positive-ion FAB mass spectrum: *m*/*z* 354 $(M - ClO_4 - 1)^+$, 297 $(M - ClO_4 - HNCMe_2)^+$, 240 $(M - ClO_4 - 2HNCMe_2)^+$.

Preparation of Complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)\{NHC(Me)CH_2C(Me_2)NH_2\}]ClO_4$ (7). $AgClO_4$ (75.1 mg, 0.362 mmol) was added to an acetone (15 mL) solution of $[(o\text{-}C_6H_4CH_2NMe_2)_2Pd_2(\mu\text{-}Cl)_2]$ (100 mg, 0.181 mmol). After the resulting suspension was stirred at room temperature in the darkness for 30 min, it was filtered through Celite with 2 mL of acetone, and NH_3 (219 μL of 32% aqueous NH_3; 3,62 mmol) was then added. The solution was stirred at room temperature for 24 h, the solvent was removed under vacuum, and the residue was extracted with $CHCl_3$, filtered, and air-dried. Yield: 67%. Anal. Calcd for $C_{15}H_{26}ClN_3O_4Pd$: C, 39.7; H, 5.8; N, 9.3. Found: C, 39.8; H, 5.8; N, 9.4. Mp: 199 °C dec. Λ_M: 130 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3295, 3250, 3164 ν(NH), 1655 ν(CN), 1086 (ClO_4^-). ^1H NMR at 25 °C (DMSO-d_6): δ 9.65 (br s, 1H, N*H*), 7.90 (dd, 1H, C_6H_4, J_{HH} = 6.2 Hz, J_{HH} = 1.6 Hz), 6.97−6.84 (m, 3H, C_6H_4), 3.86 (s, 2H, NCH_2), 3.67 (br s, 2H, NH_2), 2.56 (s, 6H, NMe_2), 2.47 (s, 2H, CCH_2 of amino−imino ligand), 2.23 (s, 3H, CMe), 1.17 (s, 6H, CMe_2). Positive-ion FAB mass spectrum: *m*/*z* 354 $(M - ClO_4 - 1)^+$.

Preparation of Complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)(NHCMe_2)(PPh_3)]ClO_4$ (8). $AgClO_4$ (38.5 mg, 0.186 mmol) was added to an acetone (10 mL) solution of $[(o\text{-}C_6H_4CH_2NMe_2)PdCl(PPh_3)]$ (100 mg, 0.186 mmol). After the resulting suspension was stirred at room temperature in the darkness for 30 min, it was filtered through Celite with 2 mL of acetone, and NH_3 (172 μL of 32% aqueous NH_3; 0.186 mmol) was then added. The solution was stirred at room temperature for 1 h, the solvent was removed under vacuum, and the residue was extracted with diethyl ether, filtered off, and air-dried. Yield: 62%. Anal. Calcd for $C_{30}H_{34}ClN_2O_4PPd$: C, 54.6; H, 5.2; N, 4.3. Found: C, 54.3; H, 5.4; N, 4.2. Mp: 197.3 °C dec. Λ_M: 132 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν (NH), 3250; ν(CN), 1660; (ClO_4^-), 1096. ^1H NMR at 25 °C ($CDCl_3$): δ 9.40 (br s, 1H, NH), 7.73−7.41 (m, 15 H, PPh_3), 7.03 (d, 1H, C_6H_4, J_{HH} = 7.8 Hz), 6.86 (t false, 1 H, C_6H_4, J_{HH} = 6.8), 6.4 (m, 2 H, C_6H_4), 4.13 (s, 2 H, NCH_2), 2.76 (s, 6H, NMe_2), 2.01 (s, 3H, CMe_2),

(39) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(40) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.

Table 1. Crystal Structure Determination Details

	1	2	3	6	7
formula	$C_{12}H_6F_{10}N_2Pd$	$C_{18}H_{14}F_{10}N_2Pd$	$C_{18}H_{14}F_{10}N_2Pd$	$C_{15}H_{26}ClN_3O_4Pd$	$C_{15}H_{26}ClN_3O_4Pd$
fw	474.59	554.71	554.71	454.24	454.24
temp (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst, space group	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
cell dimens					
a (Å)	17.3430(10)	9.0910(10)	9.6620(10)	9.0790(10)	8.7427(4)
b (Å)	10.4530(10)	9.4170(10)	16.7360(10)	9.5500(10)	20.7105(11)
c (Å)	17.1640(10)	12.9790(10)	12.5130(10)	12.5460(10)	10.4411(6)
α (deg)	90	110.800(10)	90	81.11	90
β (deg)	104.12	101.970(10)	106.27(1)	73.440(10)	92.641(4)
γ (deg)	90	95.440(10)	90	66.150(10)	90
cell vol (Å^3)	3017.6(4)	998.74(17)	1942.4(3)	952.68(16)	1888.52(17)
Z	8	2	4	2	4
D_{calc} (g cm^{-3})	2.089	1.845	1.897	1.583	1.598
F (000)	1824	544	1088	464	928
μ (mm^{-1})	1.340	1.027	1.056	1.137	1.147
cryst size (mm^3)	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.20	0.50 × 0.20 × 0.10	0.40 × 0.20 × 0.20	0.50 × 0.40 × 0.10
θ range for data collection (deg)	3.13 to 25.00	3.25 to 25.00	3.13 to 24.99	3.38 to 25.00	3.05 to 25.00
index ranges	$-20 \le h \le 20$, $-12 \le k \le 12$, $-20 \le l \le 0$	$-10 \le h \le 2$, $-10 \le k \le 10$, $-15 \le l \le 15$	$-11 \le h \le 0$, $-19 \le k \le 3$, $-14 \le l \le 14$	$-9 \le h \le 10$, $-10 \le k \le 11$, $-14 \le l \le 14$	$-10 \le h \le 10$, $-24 \le k \le 3$, $0 \le l \le 12$
no. of reflns collected	5334	4254	4404	6597	4023
ind reflns	2655 [*R*(int) = 0.0202]	3425 [*R*(int) = 0.0109]	3408 [*R*(int) = 0.0241]	3345 [*R*(int) = 0.0163]	3328 [*R*(int) = 0.0296]
no. of data/restraints/params	2655/0/250	3425/0/288	3408/0/280	3345/0/217	3328/0/217
goodness-of-fit on F^2	1.046	1.118	1.122	1.061	1.038
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0196$, $wR2 = 0.0483$	$R1 = 0.0228$, $wR2 = 0.0593$	$R1 = 0.0436$, $wR2 = 0.0882$	$R1 = 0.0259$, $wR2 = 0.0658$	$R1 = 0.0357$, $wR2 = 0.0953$
R indices (all data)	$R1 = 0.0244$, $wR2 = 0.0494$	$R1 = 0.0253$, $wR2 = 0.0625$	$R1 = 0.0507$, $wR2 = 0.0904$	$R1 = 0.0301$, $wR2 = 0.0677$	$R1 = 0.0454$, $wR2 = 0.1000$
largest diff. peak and hole (e Å^{-3})	0.313 and −0.639	0.626 and −0.667	0.894 and −0.602	0.968 and −0.638	0.739 and −0.680

1.65 (s, 3H, C*Me*$_2$). ^{31}P NMR: δ 43.5 (s). Positive-ion FAB mass spectrum: *m*/*z* 559 (M − ClO_4)$^+$, 502 (M − ClO_4 − HN=CMe_2)$^+$.

X-ray Structure Determination of 1, 2, 3, 6, and 7. Crystals suitable for a diffraction study were grown from CH_2Cl_2−hexane (**1**), CH_2Cl_2−toluene−hexane (**2** and **6**), CH_2Cl_2−hexane (**3**), or acetone−water (**7**). Mo Kα radiation was used (λ = 0.71073 Å) and the structures were solved by the SHELXS-97[41] program and refined anisotropically on F^2 (program SHELXL-97[41]). Other details of data collection and refinement are given in Table 1.

(41) Sheldrick, G. M. *SHELX-97*, Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen: Göttingen, Germany, 1998.

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Supporting Information Available: Tables of crystal data and refinements details, atomic coordinates and equivalent isotropic displacement parameters, complete bond distances and angles, and ORTEP views for compounds **1**, **2**, **3**, **6**, and **7**, as well as X-ray crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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