Reactivity of $[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Pd or Pt) toward Aromatic Amines and Malononitrile

José Ruiz, Venancio Rodríguez, and Gregorio López*

Departamento de Química Inorgánica, Universidad de Murcia, 30071-Murcia, Spain

Jaume Casabó

Departament de Química, Universitat Autònoma de Barcelona, Campus Universitari de Bellaterra, 08193-Cerdanyola, Barcelona, Spain

Elies Molins and Carles Miravitlles

Institut de Ciència de Materials, CSIC, Campus Universitari de Bellaterra, 08193-Cerdanyola, Barcelona, Spain

Received June 19, 1998

Binuclear μ-hydroxo-μ-arylamido complexes $[Pd_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}NHR)]^{2-}$ (R = C_6H_5, C_6H_4-Cl-*p*, C_6H_4F-*p*) and di-μ-arylamido complexes $[M_2(C_6F_5)_4(\mu\text{-}NHR)_2]^{2-}$ (M = Pd, R = C_6H_5, C_6H_4Cl-*p*, C_6H_4F-*p*, $C_6H_4NO_2$-*p*, C_6F_5; M = Pt, R = $C_6H_4NO_2$-*p*, C_6F_5) have been prepared by reaction of $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ with the corresponding arylamine RNH_2 in 1:1 or 1:2 molar ratio, respectively. The reaction of $[Pd_2(C_6F_5)_4(\mu\text{-}NHPh)_2]^{2-}$ with CS_2 leads to the formation of the mononuclear dithiocarbamate complex $[Pd(C_6F_5)_2(S_2CNHPh)]^-$. Malononitrile and methyl cyanoacetate react with $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ in methanol to give the binuclear complexes $[Pd_2(C_6F_5)_4\{\mu\text{-}CH(CN)CN\}_2]^{2-}$ and $[Pd_2(C_6F_5)_4\{\mu\text{-}CH(CO_2Me)CN\}_2]^{2-}$. However the reaction of $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ with malononitrile in *boiling* methanol gives the mononuclear diiminato complex $[Pd(C_6F_5)_2\{NHC(OMe)CHC(OMe)NH\}]^-$. In wet toluene $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ produces the cyclotrimerization of malononitrile, giving 4,6-diamino-2-cyanomethyl-3,5-pyridinedicarbonitrile. The structures of $[Pd_2(C_6F_5)_4(\mu\text{-}NHC_6F_5)_2]^{2-}$ and $[Pd_2(C_6F_5)_4\{\mu\text{-}CH(CN)CN\}_2]^{2-}$ have been determined by X-ray diffraction.

Introduction

Hydroxo, alkoxo, and amido complexes of late-transition-metal ions are relatively uncommon, and an understanding of their stability and reactivity has not been firmly established. The relatively paucity of these complexes has been attributed to the intrinsic weakness of the M−OH, M−OR, and M−NR_2 bonds owing to the mismatch of a hard, basic ligand (OH^-, OR^-, or NR_2^-) with a soft metal center: π-donation from the basic ligand to the electron-rich metal center is hindered. Despite this general perception, late metal−oxygen and metal−nitrogen bonds are not particularly weak, but the increased electron affinity of the heteroatoms involved and the presence of lone electron pairs give these compounds modes of reactivity not normally open to metal alkyls and hydrides.[1]

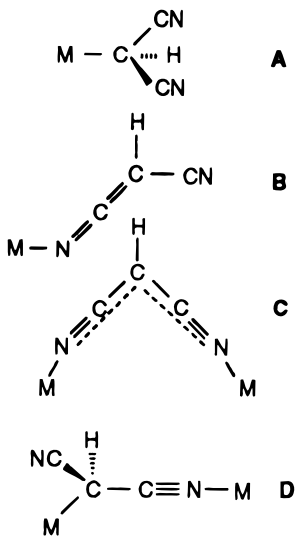
Synthetic routes to reactive late-transition-metal amide complexes have attracted significant attention recently because of their potential use to facilitate the formation of carbon−nitrogen bonds[2] through the insertion of unsaturated organic molecules into the metal−nitrogen bond.[3] The formation of C−N bonds is less common than that forming C−C and C−H bonds. For example, the reported reaction of amines with hydroxo-bridged nickel(II), palladium(II), and platinum(II) complexes in the presence of CS_2 to give *N*,*N*-dialkyldithiocarbamate complexes ($>M(\mu\text{-}OH)_2M< + 2\ RNH_2 + 2\ CS_2 \rightarrow 2\ >MS_2CNHR_2 + 2\ H_2O$) might be the insertion of CS_2 into the M−N bond of an intermediate amido complex.[4,5] Monomeric arylamido and dimeric alkylamido complexes of palladium that produce arylamines through carbon−nitrogen bond-forming reductive elimination have been isolated.[6,7]

Binuclear μ-hydroxo-μ-amido palladium(II) complexes of the type $[\{Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-}NHC_6H_4X\text{-}p)]$ have been prepared by reaction of $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ with the corresponding aromatic amine and the bis(amido) complexes $[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}NHC_6H_4X\text{-}p)\}_2]$ by the reaction of $[\{Pd(C_6F_5)(t\text{-}BuNC)(\mu\text{-}Cl)\}_2]$ with $[NBu_4]OH$ and the arylamine (1:2:2 mol ratio).[8] Mixed amido−acetato-bridged complexes [{Pd(8-quinolylmethyl)}$_2$(μ-NHR)(μ-O_2CMe)] are obtained by reaction of [{Pd(8-quinolylmethyl)}$_2$(μ-OH)(μ-O_2CR)] with arylamines

(1) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.
(2) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963.
(3) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.
(4) López, G.; Sánchez, G.; García, G.; García, J.; Sanmartín, A.; Santana, M. D. *Polyhedron* **1991**, *10*, 2821.
(5) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Rodríguez, V. *J. Organomet. Chem.* **1992**, *436*, 121.
(6) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708.
(7) Louie, J.; Paul F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794.
(8) Ruiz, J.; Martínez, M. T.; Vicente, C.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321. This reference includes the first X-ray structure of a palladium amide.

10.1021/om980508z CCC: $18.00
Publication on Web 03/04/1999

Scheme 1



RNH_2.[9] Very recently, the hydroxo complex [{PdPh(PPh$_3$)(μ-OH)}$_2$] has been used for the isolation of palladium alkylamides by reaction with the corresponding alkylamine.[10] Monomeric anilide complexes *trans*-[Pd(PMe$_3$)$_2$(R)(NR′Ph)] have been prepared by addition of KN(R′)Ph to *trans*-Pd(PMe$_3$)$_2$(R)I; thermolysis of *trans*-[Pd(PMe$_3$)$_2$(Ph)(μ-NHPh)] in the solid state gives the dimeric complex [{Pd(PMe$_3$)(Ph)(μ-NHPh)}$_2$],[11] which, by prolonged heating in solution, reductively eliminates diphenylamine.

In this paper we report the preparation of a variety of μ-hydroxo-μ-amido and bis(μ-amido) complexes of palladium by activation of the amine N−H bond by the bis(μ-hydroxo) complex [{Pd(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$. Owing to the basic character of the bis(μ-hydroxo) complexes [{M(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$ (M = Ni,[12] Pd,[13] or Pt[14]), these compounds are prone to attack by protic electrophiles HX, and deprotonation, with the concomitant release of water, leads to the formation of >M(μ-OH)(μ-X)M< and >M(μ-X)$_2$M< complexes.[15]

The interaction of [{Pd(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$ with the protic electrophiles malononitrile and methyl cyanoacetate has also been studied. The dicyanomethanide anion, [CH(CN)$_2$]$^-$, resulting from the deprotonation of malononitrile, may coordinate to metal centers by either the nitrogen or the carbon atom, depending on the hard−soft character of the metal ion, and examples of both possibilities (Scheme 1), **A** (dicyanomethyl−metal linkage) and **B** (monocyanoketimine structure), are found in the literature.[16−19] A third coordination mode is a bidentate *N,N*-bonded ligand bridging two metal atoms (**C**).[20] The malononitrilate anion has been suggested to act as a bidentate *C,N*-bonded ligand (**D**), but no full characterization has been reported. Thus structure **D** has been proposed for [Rh(dppe)(CNCHCN)(OOH)]BF$_4$·H$_2$O on the basis of the IR data (ν(CN) at 2220 and 2145 cm^{-1}) and the insolubility of the product,[21] and in the electrochemical study of mixed-valence molecules based on the Ru(II)−Ru(III) couple with malononitrile has also been suggested[22] the formation of [(NH$_3$)$_5$RuNCCH(CN)Ru(NH$_3$)$_5$]$^{4+}$. The crystallographic characterization of a *C,N*-bonded malononitrilate ion is presented here for the first time.

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 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 using Nujol mulls between polyethylene sheets.

Materials. The starting complexes [NBu$_4$]$_2$[(C$_6$F$_5$)$_2$M(μ-OH)$_2$M(C$_6$F$_5$)$_2$] (M = Pd,[13] Pt[14]) were prepared by procedures described elsewhere. Solvents were dried by the usual methods.

Preparation of Complexes [{Pd(C$_6$F$_5$)$_2$}$_2$(μ-OH)(μ-NHR)]$^{2-}$ (R = C$_6$H$_5$ (1), C$_6$H$_4$Cl-*p* (2), C$_6$H$_4$F-*p* (3)). To a solution of [NBu$_4$]$_2$[{Pd(C$_6$F$_5$)$_2$(μ-OH)}$_2$] (80 mg; 0.057 mmol) in CH_2Cl_2 (6 mL) was added the corresponding arylamine RNH_2 (0.085 mmol). The solution was stirred at room temperature for 30 min and then concentrated to dryness under vacuum. The residue was treated with diethyl ether−hexane and the pale yellow solid was collected by filtration and air-dried. Complexes **1**−**3** were recrystallized from dichloromethane−hexane. Complex **1**: Yield: 86%. Anal. Calcd for C$_{62}$H$_{79}$N$_3$F$_{20}$OPd$_2$: C, 49.4; H, 5.3; N, 2.8. Found: C, 49.5; H, 5.4; N, 3.0. Mp: 220 °C dec. Λ_M: 223 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3610 (ν(OH)) 785, 770 (Pd−C$_6$F$_5$). ^{1}H NMR ((CD$_3$)$_2$CO): δ 6.88 (d, 2 H$_o$, J = 7.8), 6.45 (dd, 2 H$_m$, J = 7.8, J' = 7.8), 6.22 (t, 1 H$_p$, J = 7.8), −3.11 (s, 1 H, OH). ^{19}F NMR ((CD$_3$)$_2$CO): δ −113.2 (d, 4 F$_o$, J_{om} = 28.8), −115.2 (br, 4 F$_o$), −166.6 (m, 4 F$_m$ + 2 F$_p$), −168.0 (m, 4 F$_m$ + 2 F$_p$). Complex **2**: Yield: 74%. Anal. Calcd for C$_{62}$H$_{78}$N$_3$ClF$_{20}$OPd$_2$: C, 49.3; H, 5.2; N, 2.8. Found: C, 49.0; H, 5.4; N, 2.9. Mp: 236 °C dec. Λ_M: 234 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3610 (OH str)), 785, 775 (Pd−C$_6$F$_5$ str). ^{1}H NMR ((CD$_3$)$_2$CO): δ 6.87 (d, 2 H$_o$, J = 8.7), 6.46 (d, 2 H$_m$, J = 8.7), −3.07 (s, 1 H, OH). ^{19}F NMR ((CD$_3$)$_2$CO): δ −113.3 (d, 4 F$_o$, J_{om} = 28.2), −115.2 (br, 4 F$_o$), −166.3 (t, 2 F$_p$, J_{mp} = 19.2), −166.6 (m, 4 F$_m$), −167.5 (t, 2 F$_p$, J_{mp} = 18.9), −167.8 (m, 4 F$_m$). Complex **3**: Yield: 85%. Anal. Calcd for C$_{62}$H$_{78}$N$_3$F$_{21}$OPd$_2$: C, 49.9; H, 5.3; N, 2.8. Found: C, 49.6; H, 5.4; N, 2.9. Mp: 213 °C dec. Λ_M: 217 S cm^2 mol^{-1}. IR

(9) Ruiz, J.; Cutillas, N.; Torregrosa, J.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 2353.

(10) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 8, 4206.

(11) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3921.

(12) López, G.; García, G.; Sánchez, G.; García, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518.

(13) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1991**, *30*, 2605.

(14) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53.

(15) Aryloxo palladium and platinum complexes can also be prepared by this general procedure: Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1996**, *15*, 1662.

(16) Badley, W. H.; Choudhury, P. *J. Organomet. Chem.* **1973**, *60*, C74.

(17) (a) Suzuki, K.; Nakamura, S. *Inorg. Chim. Acta* **1977**, *25*, L21, and references therein. (b) Suzuki, K.; Sakurai, M. *Ibid.* **1979**, *32*, L3.

(18) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

(19) (a) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003. (b) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 2886.

(20) In [{Ni(C$_6$F$_5$)$_2$(μ-NCCHCN)}$_2$]$^{2-}$: López, G.; Sánchez, G.; García, G.; Ruiz, J.; García, J.; Martínez-Ripoll, M.; Vegas, A.; Hermoso, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 716.

(21) Morbillo, A.; Bressan, M. *J. Organomet. Chem.* **1987**, *332*, 337.

(22) Krentzien, H.; Taube, H. *Inorg. Chem.* **1982**, *21*, 4001.

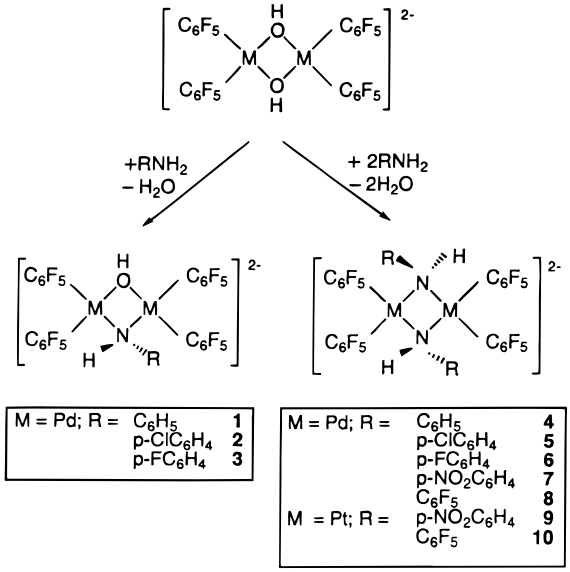
(Nujol, cm^{-1}): 3610 (OH str), 785, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 6.81 (dd, 2 H_o, J = 8.8, J' = 5.1), 6.21 (dd, 2 H_m, J = 8.8, J' = 8.8), −3.08 (s, 1 H, OH). ^{19}F NMR ($(CD_3)_2CO$): δ −113.3 (d, 4 F_o, J_{om} 33.3), −115.2 (br, 4 F_o), −130.1 (m, 1 F_p, *p*-FC_6H_4NH), −166.5 (m, 4 F_m + 2 F_p), −167.8 (m, 4 F_m + 2 F_p).

Preparation of Complexes [{Pd(C6F5)2(μ-NHR)}2]2− (R = C6H5 (4), C6H4Cl-*p* (5), C6H4F-*p* (6)). To a solution of $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (80 mg; 0.057 mmol) in methanol (6 mL) was added the corresponding arylamine RNH_2 (0.457 mmol for **4**, 0.228 mmol for **5** and **6**). The solution was stirred at room temperature for 8 h. The solvent was removed under vacuum, and the residue was treated with 2-propanol−hexane. The pale yellow solid was filtered off and air-dried. Complexes **4**−**6** were recrystallized from dichloromethane−hexane. Complex **4**: Yield: 72%. Anal. Calcd for $C_{68}H_{84}N_4F_{20}Pd_2$: C, 52.7; H, 5.5; N, 3.6. Found: C, 52.3; H, 5.7; N, 3.6. Mp: 224 °C dec. Λ_M: 218 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 775, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 6.95 (d, 4 H_o, J = 7.6), 6.55 (dd, 4 H_m, J = 7.6), 6.14 (t, 2 H_p, J = 7.6). ^{19}F NMR ($(CD_3)_2CO$): δ −114.4 (br, 8 F_o), −167.2 (m, 8 F_m), −167.9 (t, 4 F_p, J = 20.0). Complex **5**: Yield: 69%. Anal. Calcd for $C_{68}H_{82}N_4Cl_2F_{20}Pd_2$: C, 50.4; H, 5.1; N, 3.5. Found: C, 50.1; H, 5.4; N, 3.6. Mp: 234 °C dec. Λ_M: 214 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 775, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 6.93 (d, 4 H_o, J = 8.6), 6.55 (d, 4 H_m, J = 8.6). ^{19}F NMR ($(CD_3)_2CO$): δ −114.8 (br, 8 F_o), −167.2 (m, 8 F_o + 4 F_p). Complex **6**: Yield: 67%. Anal. Calcd for $C_{68}H_{82}N_4F_{22}Pd_2$: C, 51.5; H, 5.2; N, 3.5. Found: C, 51.0; H, 5.5; N, 3.3. Mp: 226 °C dec. Λ_M: 220 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 775, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 6.90 (dd, 4 H_o, J = 8.8, J' = 5.0), 6.32 (dd, 4 H_m, J = 8.8, J' = 8.8). ^{19}F NMR ($(CD_3)_2CO$): δ −114.2 (br, 8 F_o), −130.6 (m, 2 F_p, *p*-FC_6H_4NH), −167.3 (m, 8 F_m + 4 F_p).

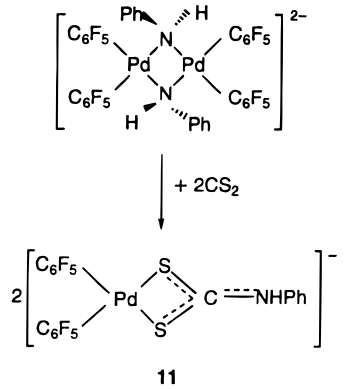
Preparation of Complexes [{Pd(C6F5)2(μ-NHR)}2]2− (R = C6H4NO2-*p* (7), C6F5 (8)). To a solution of $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (80 mg; 0.057 mmol) in dichloromethane (6 mL) was added the corresponding arylamine RNH_2 (0.114 mmol). The resulting solution was stirred at room temperature for 30 min and concentrated under vacuum. The addition of hexane caused the precipitation of an orange or white solid, which was collected by filtration and air-dried. Complexes **7** and **8** were recrystallized from dichloromethane−hexane. Complex **7**: Yield: 93%. Anal. Calcd for $C_{68}H_{82}N_6F_{20}O_4Pd_2$: C, 49.8; H, 5.0; N, 5.1. Found: C, 50.1; H, 5.3; N, 5.0. Mp: 231 °C dec. Λ_M: 217 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3300 (NH str), 775, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 7.60 (d, 4 H_o, J = 8.9), 7.04 (d, 4 H_m, J = 8.9), 2.68 (br, 2 H, NH). ^{19}F NMR ($(CD_3)_2CO$): δ −115.2 (br, 8 F_o), −165.8 (t, 4 F_p, J_{om} 19.8), −166.5 (m, 8 F_m). Complex **8**: Yield: 92%. Anal. Calcd for $C_{68}H_{74}N_4F_{30}Pd_2$: C, 47.2; H, 4.3; N, 3.2. Found: C, 46.9; H, 4.4; N, 3.4. Mp: 246 °C dec. Λ_M: 219 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3310 (NH str), 780, 770 (Pd−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 2.25 (br, 2 H, NH). ^{19}F NMR ($(CD_3)_2CO$): δ −115.1 (d, 8 F_o, J = 27.9), −146.1 (br, 2 F_o, C_6F_5NH), −164.1 (br, 2 F_o, C_6F_5NH), −165.8 (t, 4 F_p, J = 19.8), −166.7 (m, 8 F_m), −169.2 (br, 2 F_m, C_6F_5NH), −171.4 (br, 2 F_m, C_6F_5NH), −178.8 (m, 2 F_p, C_6F_5NH).

Preparation of Complexes [{Pt(C6F5)2(μ-NHR)}2]2− (R = C6H4NO2-*p* (9), C6F5 (10)). To a solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (80 mg; 0.051 mmol) in methanol (6 mL) was added the arylamine RNH_2 (0.102 mmol). The solution was boiled under reflux for 3 h. The solvent was removed under vacuum, and the residue was treated with dichloromethane−hexane. The orange or white solid was filtered off and air-dried. Complexes **9** and **10** were recrystallized from dichloromethane−hexane. Complex **9**: Yield: 90%. Anal. Calcd for $C_{68}H_{82}N_6F_{20}O_4Pt_2$: C, 44.9; H, 4.9; N, 4.4. Found: C, 44.9; H, 5.0; N, 4.4. Mp: 258 °C dec. Λ_M: 232 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 800, 790 (Pt−C_6F_5 str). ^1H NMR ($(CD_3)_2CO$): δ 7.63 (d, 4 H_o, J = 8.9), 7.18 (d, 4 H_m, J = 8.9). ^{19}F NMR ($(CD_3)_2CO$): δ −119.7 (br, 8 F_o), −167.9 (m, 8 F_m + 4 F_p). Complex **10**: Yield 76%. Anal. Calcd for $C_{68}H_{74}N_4F_{30}Pt_2$: C, 42.8; H, 3.9; N, 2.9. Found: C, 42.5; H, 4.2; N, 3.1. Mp: 256 °C dec. Λ_M: 240 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3310 (NH str), 795, 785 (Pt−C_6F_5 str). ^{19}F NMR ($(CD_3)_2CO$): δ −119.4 (d, 8 F_o, J_{om} = 27.1, J_{PtFo} = 495.4), −144.1 (br, 2 F_o, C_6F_5NH), −161.8 (br, 2 F_o, C_6F_5NH), −168.0 (m, 8 F_m + 4 F_p), −168.8 (br, 2 F_m, C_6F_5NH), −170.8 (br, 2 F_m, C_6F_5NH), −175.4 (m, 2 F_p, C_6F_5-NH).

Scheme 2



Scheme 3



Reaction of Complex 4 with Carbon Disulfide. To a solution of **4** (100 mg; 0.064 mmol) in methanol (8 mL) was added CS_2 (1.280 mmol). The solution was stirred at room temperature for 8 h, and the solvent was removed under vacuum. The residue was then treated with diethyl ether−hexane, and a pale yellow solid (complex **11**; Scheme 3) was filtered off and air-dried. Yield: 94%. Anal. Calcd for $C_{34}H_{42}N_2S_2F_{10}Pd$: C, 49.4; H, 4.9; N, 3.3; S, 7.5. Found: C, 49.2; H, 5.0; N, 3.2; S, 7.7. Mp: 116 °C dec. Λ_M: 107 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3230 (NH str), 782, 774 (Pd−C_6F_5 str), 1538 (CN str), 978 (CS str). ^1H NMR ($(CD_3)_2CO$): δ 10.52 (br, 1 H, NH), 7.69 (d, 2H_o, J_{om} = 9.5), 7.36 (dd, 2H_m, J_{mp} = 5.38), 7.18 (t, 1H_p). ^{19}F NMR ($(CD_3)_2CO$): δ −111.7 (d, 4 F_o, J_{om} = 27.4), −165.8 (t, 2 F_p, J_{mp} = 18.1), −166.7 (m, 4 F_m).

Preparation of Complexes 12 and 13. To a solution of $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (0.1 g, 0.0714 mmol) in methanol (6 mL) was added malononitrile or methyl cyano acetate (0.1428 mmol). The resulting solution was stirred at room temperature for 1 h, and the solvent was then partially evaporated under reduced pressure. On addition of water the white complexes **12** and **13** precipitated and were filtered off and air-dried. Complex **12**: yield 89%; mp 169 °C dec; Λ_M =

Table 1. Crystal Structure Determination Details

	8	**12**
formula	$C_{34}H_{37}F_{15}N_2Pd$	$C_{62}H_{74}F_{20}N_6Pd_2$
fw	865.06	1496.07
temperature (K)	293(2)	294(2)
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
cell dimens		
a (Å)	12.567(3)	10.652(4)
b (Å)	17.637(6)	22.162(7)
c (Å)	17.016(4)	30.1090(10)
α (deg)		74.74(3)
β (deg)	97.88(2)	80.27(3)
γ (deg)		89.91(3)
cell vol (Å^3)	3736(2)	6752(3)
Z	4	4
D_{calc} (g cm^{-3})	1.538	1.472
F(000)	1744	3040
monochromated Mo Kα radiation		
λ (Å)	0.71069	0.71069
μ (mm^{-1})	0.598	0.630
cryst size (mm)	0.41 × 0.24 × 0.17	0.72 × 0.30 × 0.16
θ range for data collection (deg)	1.67−24.98	2.21−26.26
index ranges	$-14 \le h \le 14$, $0 \le k \le 20$, $0 \le l \le 20$	$0 \le h \le 13$, $-27 \le k \le 27$, $-36 \le l \le 37$
no. of reflns collected	6793	28771
no. of ind reflns	6558 [R(int) = 0.0364]	27236 [R(int) = 0.0252]
structure solution	MULTAN 11/80	SHELX-86
refinement method	full-matrix least-squares on F^2 SHELXL-93	full-matrix-block least-squares on F^2 SHELXL-93
no. of data/restraints/parameters	6546/−/460	27227/4364/1640
goodness-of-fit on F^2	1.022	1.042
final R indices [$I > 2\sigma(I)$]	R1 = 0.069, wR2 = 0.1990	R1 = 0.0529, wR2 = 0.1362
R indices (all data)	R1 = 0.1982, wR2 = 0.2798	R1 = 0.1663, wR2 = 0.1851
largest diff peak and hole (e Å^{-3})	1.364 and −0.427	0.726 and −0.668

201 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2250, 2200 ν(CN), 790, 775 (Pd−C_6F_5 str). Anal. Calcd for $C_{62}H_{74}N_6F_{20}Pd_2$: C, 49.8; H, 5.0; N, 5.6. Found: C, 49.6; H, 5.1; N, 5.6. ^{1}H NMR ($(CD_3)_2CO$): δ 2.68 (s, 2 H, CH), 2.65 (s, 2 H, CH) and additional peaks from $[NBu_4]^+$. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 127.0 (CN), 119.5 (CN), −6.2 (br, CH) and additional peaks from $[NBu_4]^+$. ^{19}F NMR ($(CD_3)_2CO$): δ −114.1 (m, 12 F_o), −114.9 (m, 4 F_o), −164.3 (t, 2 F_p), −164.35 (t, 2 F_p), −164.8 (t, 4 F_p), −165.6 (m, 8 F_m), −166.1 (m, 4 F_m), −166.7 (m, 4 F_m). Complex **13**: yield 91%; mp 194 °C dec; Λ_M = 203 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2240 ν(CN), 1700 ν(CO), 790, 775 (Pd−C_6F_5 str). Anal. Calcd for $C_{64}H_{80}N_4F_{20}O_2Pd$: C, 49.2; H, 5.2; N, 3.6. Found: C, 49.3; H, 5.2; N, 3.6. ^{1}H NMR ($(CD_3)_2CO$): δ 3.23 (s, CO_2Me), 3.14 (s, CO_2Me), 2.84 (s, CH), 2.79 (s, CH) and additional peaks from $[NBu_4]^+$. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 173.1 (CO_2Me), 129.1 (CN), 50.4 (MeO), 17.6 (br, CH) and additional peaks from $[NBu_4]^+$. ^{19}F NMR ($(CD_3)_2CO$): δ −113.6 (m, 12 F_o), −114.45 (d, 4 F_o), −114.75 (d, 2 F_o), −115 (m, 2 F_o), −115.3 (d, 4 F_o), −165.35 (t, 4 F_p), −165.40 (t, 2 F_p), −166.30 (m, 12 F_m), −166.7 (t, 4 F_p), −166.75 (t, 2 F_p), −167.70 (m, 12 F_m).

Preparation of Complex 14. To a solution of $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (0.1 g, 0.0714 mmol) in methanol (8 mL) was added malononitrile (9.44 mg, 0.1428 mmol). The solution was stirred under reflux for 1.5 h, and the solvent was then partially evaporated under reduced pressure. On addition of water the white complex **14** precipitated and was filtered off and air-dried. Yield: 79%. Mp: 217 °C dec. Λ_M = 105 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3400, 3370 ν(NH), 1605 ν(C═N), 1535 ν(C═C), 790, 780 (Pd−C_6F_5 str). Anal. Calcd for $C_{34}H_{45}NF_{10}OPd$: C, 48.8; H, 5.6; N, 5.2. Found: C, 48.7; H, 5.7; N, 5.1. ^{1}H NMR ($(CD_3)_2CO$): δ 4.81 (br, 2 H, NH), 3.64 (s, CH), 3.53 (s, 6 H, MeO) and additional peaks from $[NBu_4]^+$. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 168.3 (C═N), 60.1 (CH), 53.2 (MeO) and additional peaks from $[NBu_4]^+$. ^{19}F NMR ($(CD_3)_2CO$): δ −113.1 (d, 4 F_o, J_{om} 25.1 Hz), −166.2 (t, 2 F_p, J_{mp} 19.8 Hz), −166.8 (m, 4 F_m).

Catalytic Conversion of Malononitrile into Its Trimer, 4,6-Diamino-3,5-dicyano-2-cyanomethylpyridine. $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (0.1 g, 0.0714 mmol) was added to a solution of malononitrile (7.14 mmol) in wet toluene (20 mL toluene; 2.57 μL H_2O), and the mixture was boiled under reflux for 6 h. The toluene was evaporated under vacuum, and the resulting sticky material was treated with ethanol and vigorously stirred to give a beige solid, which was isolated (55% yield), recrystallized from dioxane, dried in the oven at 110 °C, and identified as 4,6-diamino-3,5-dicyano-2-cyanomethylpyridine (trimer I). MS: m/z 198 (M^+, 100%). Anal. Calcd for $C_9H_6N_6$: C, 54.5; H, 3.0; N, 42.4. Found: C, 54.2; H, 2.9; N, 42.1. IR (Nujol, cm^{-1}): 3400−3200 ν(NH), 2210 ν(C═N), 1600, 1560, 1500. Vis−UV (in MeOH) λ_{max} (nm): 313, 245 (sh), 237. ^{1}H NMR ($(CD_3)_2SO$): δ 4.15 (s, 2 H), 7.45 (s, 2 H), 7.65 (s, 2 H).

X-ray Structure Determination of 8 and 12. A crystal suitable for a diffraction study was grown from dichloromethane−hexane (complex **8**) or dichloromethane−diethyl ether (complex **12**). Details of data collection and refinement are given in Table 1.

Results and Discussion

***μ*-Hydroxo-*μ*-arylamido Complexes [{Pd(C_6F_5)$_2$}$_2$(*μ*-OH)(*μ*-NHR)]$^{2-}$.** In dichloromethane solution, $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ reacts readily with 1 equiv of aniline or *p*-substituted aniline RNH_2 (R = C_6H_5, *p*-ClC_6H_4, *p*-FC_6H_4) to give the corresponding pale yellow *μ*-hydroxo-*μ*-amido complexes **1**−**3** (Scheme 2) in 74−86% yield. The amine is deprotonated by the coordinated OH group generating the amide RNH^-, which enters the coordination sphere of palladium with the concomitant release of water. The microanalytical data and molar conductances (217−234 S cm^2 mol^{-1}, in acetone solution) are in agreement with the proposed formulas.[23]

The IR spectra of complexes **1**−**3** show the characteristic absorptions of the C_6F_5 group[24] at 1630, 1490,

(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(24) Long, D. A.; Steel, D. *Spectrochim. Acta* **1963**, *19*, 1955.

1450, 1050, and 950 and a split band at ca. 800 cm^{-1}, derived from the so-called X-sensitive mode in C_6F_5 halogen molecules, which is characteristic of the *cis*-Pd-$(C_6F_5)_2$ fragment[25,26] and behaves like a ν(M−C) band.[27] A band at 3610 cm^{-1} is assigned to ν(OH). The presence of the hydroxo ligand is also established by the observation of a proton resonance at ca. −3.1 ppm; this signal is found at higher field than in the starting hydroxo complex $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (δ −2.84).[13] No resonance from the amide proton is detected in the spectra. The observation of three or two signals for the aromatic protons of the aryl groups indicates that rotation of the R group around the C−N bond is rapid on the NMR time scale.[28] The ^{19}F NMR spectra reveal the presence of two different types of C_6F_5 groups: two *trans* to O and two *trans* to N. Two sets of signals each with an intensity ratio 2:1:2 ($2F_o$:$1F_p$:$2F_m$) should be seen in the ^{19}F NMR spectra, but there is partial overlapping of some of the *m*- and *p*-fluorine signals. One of the *o*-fluorine resonances is observed as a broad signal at higher field than the other one. This broadening may be the result of the magnetic anisotropy derived from restricted rotation of the R group around the carbon−nitrogen bond. Complex **3** gives an additional signal at δ −130 owing to the *p*-FC_6H_4 group; its multiplet structure arises from coupling to the ring protons, which is clearly evidenced on comparing the ^1H NMR data of **2** and **3**.

The reaction of the di-μ-hydroxo palladium complex with *p*-$NO_2C_6H_4NH_2$ or $C_6F_5NH_2$ in 1:1 molar ratio gave a mixture containing, in accord with the ^1H NMR data, the μ-hydroxo-μ-amido (δ −2.75 and −2.71 for the OH group, respectively) and di-μ-amido (see below) complexes together with the starting di-μ-hydroxo complex (δ −2.84 for the OH groups).

Di-μ-arylamido Complexes $[\{M(C_6F_5)_2(\mu\text{-}NHR)\}_2]^{2-}$. In dichloromethane or methanol solution, $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (M = Pd or Pt) reacts with 2 equiv of aniline or *p*-substituted anilines RNH_2 (R = C_6H_5, *p*- ClC_6H_4, *p*- FC_6H_4, *p*-$NO_2C_6H_4$, and C_6F_5) to give the corresponding di-μ-amido complexes **4**−**10** (Scheme 2). The reaction takes place at room temperature for **4**−**8**, but the preparation of complexes **4**−**6** required using an excess of amine. Complexes **9** and **10** were prepared under refluxing conditions. In acetone solution complexes **4**−**10** behave as 2:1 electrolytes.[23]

The IR spectra of **7**, **8**, and **10** exhibit a weak absorption at 3310−3300 cm^{-1}, assigned to ν(NH). The aromatic proton resonances of the μ-amido RNH^- ligand in complexes **4**−**7** and **9** indicate that rotation of the R group around the C−N bond is rapid on the ^1H NMR time scale. However, the observation in the ^{19}F NMR spectra of these complexes of one broad resonance in the *o*-fluorine region suggests that there is restricted rotation of the C_6F_5 groups. In fact, the ^{19}F NMR spectra of complexes **4**−**7** and **9** were temperature dependent; for example, the broad resonance (δ −115.2 br, $8F_o$) observed in the spectrum of **7** at ambient temperature was seen as two doublets (δ −113.8 and −115.8; *J* 33.3 and 34.7 Hz, respectively) with the intensity ratio 1:1 when the spectrum was obtained at −70 °C. Since the spectra, both at ambient and low temperature, showed a single resonance for the *p*-fluorine atoms, a mixture of *syn*−*anti* isomers must be discarded. The ^{19}F NMR spectra of complexes **8** and **10** show three sharp resonances with the intensity ratio $2(F_o)$:$1(F_p)$:$2(F_m)$ for the Pd−C_6F_5 groups, indicating freely rotating pentafluorophenyl rings around the C−Pd bond, but two broad resonances in the *o*-fluorine region of the HN−C_6F_5 groups suggest restricted rotation of these C_6F_5 groups around the C−N bonds (Experimental Section). When the spectrum of **8** was recorded at low temperature (−70 °C), it showed that completely restricted rotation of both types of C_6F_5 groups (Pd−C_6F_5 and HN−C_6F_5) had occurred: δ −114.2 (d, 4 F_o, C_6F_5Pd), −115.9 (d, 4 F_o, C_6F_5Pd), −146.7 (d, 2 F_o, C_6F_5NH), −163.6 (d, 2 F_o, C_6F_5NH), −164.3 (t, 4 F_p, C_6F_5Pd), −165.4 (m, 8 F_m, C_6F_5Pd), −168.2 (d, 2 F_m, C_6F_5NH), −169.6 (d, 2 F_m, C_6F_5NH), and −177.0 (m, 2 F_p, C_6F_5-NH).

Selected bond lengths and bond angles for complex **8** are given in Table 2, and Figure 1 shows the structure of the complex anion, which sits on a crystallographic center, so the core group $\{Pd_2N_2\}$ is strictly planar. The

Table 2. Selected Distances (Å) and Bond Angles (deg) for Complex 8

Bond Distances		Bond Angles	
Pd(1)−C(8)	2.005(9)	C(8)−Pd(1)−N(1)#1	179.9(3)
Pd(1)−N(1)	2.007(9)	C(8)−Pd(1)−C(14)	87.9(4)
Pd(1)−C(14)	2.024(9)	N(1)−Pd(1)−C(14)	92.1(4)
Pd(1)−N(1)#1[a]	2.220(9)	C(8)−Pd(1)−N(1)#1	96.1(4)
Pd(1)−Pd(1)#1	3.147(2)	N(1)−Pd(1)−N(1)#1	83.9(4)
N(1)−C(2)	1.367((13)	C(14)−Pd(1)−N(1)#1	175.6(4)
		C(8)−Pd(1)−Pd(1)#1	135.5(3)
		N(1)−Pd(1)-Pd(1)#1	44.5(3)
		C(14)−Pd(1)-Pd(1)#1	136.6(3)
		N(1)#1-Pd(1)−Pd(1)#1	39.3(2)
		Pd(1)−N(1)-Pd(1)#1	96.1(4)

[a] #1: $-x+1, -y, -z+1$.

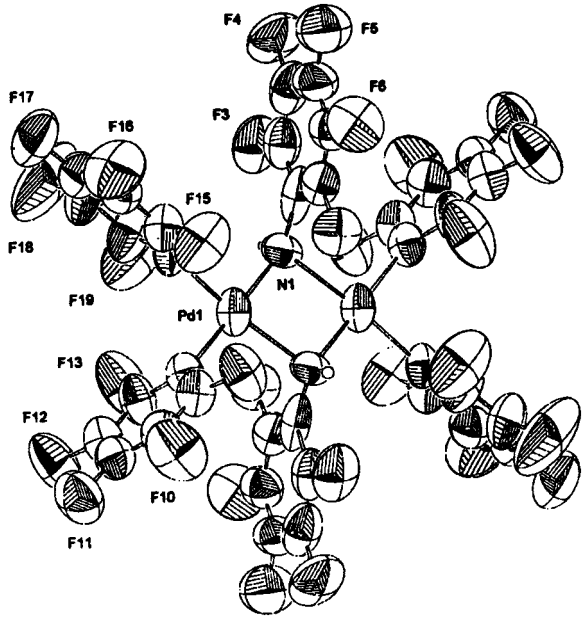
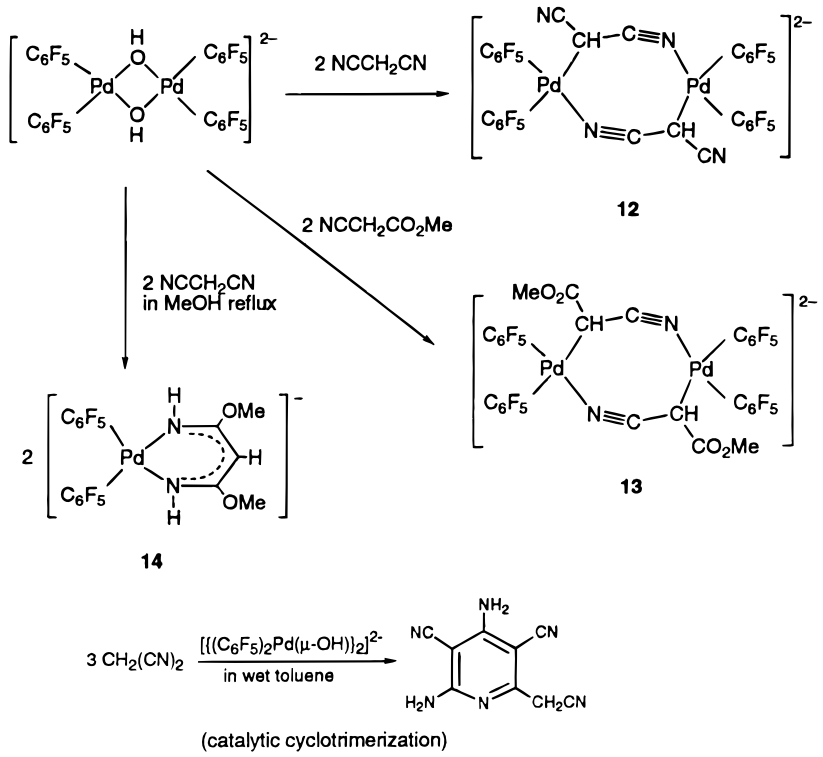


Figure 1. ORTEP diagram of **8**.

(25) López, G.; Ruiz, J.; Vicente, C.; Martí, J. M.; García, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *Organometallics* **1992**, *11*, 4091.
(26) Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777.
(27) Maslowiski, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437.
(28) Martin, G. C.; Palenik., G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027.

Scheme 4



Pd−N distances are 2.007(9) and 2.220(9) Å, and the NPdN and PdNPd angles are 83.9(4)° and 96.1(4)°, respectively. The Pd····Pd distance is 3.147(2) Å, showing no significant metal−metal interaction. Some bridging hydroxo and amido complexes are bent and others are planar. For example, $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ is planar,[13] while $[Pd_2(C_6F_5)_2(CN\text{-}t\text{-}Bu)_2(\mu\text{-}NHPh)_2]$[8] and $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)(\mu\text{-}NH\text{-}t\text{-}Bu)]$,[29] are bent with dihedral angles of 32.7° and 56.91°, respectively. The reasons for the extent of folding in this type of structure is not well understood nor readily predictable, and the driving force for bending of these molecules is modulated by the nature of the metal atom, the terminal ligands, and the bridging atoms; complexes with two or more π-basic or poor σ-donor terminal ligands (e.g., C_6F_5) favor a planar structure.[30]

Reaction of 4 with CS_2. The reaction of complex **4** with carbon disulfide gives the isolable palladium complex $[(C_6F_5)_2Pd(S_2CN(H)Ph)]^-$ (**11**), formed by insertion of CS_2 into the Pd−N bond (Scheme 3). The ^{19}F NMR spectrum shows that both pentafluorophenyl groups are equivalent, and the IR absorption at 978 cm^{-1} supports the bidentate coordination of the dithio ligand.[31,32] The thioureide IR band observed at 1538 cm^{-1} indicates considerable double-bond character in the C≡N bond[33,34] of the coordinated *N*-phenyldithiocarbamate, and the best description of the coordinated carbamate is that presented in Scheme 3. The general synthetic method for the preparation of transition-metal dithiocarbamate complexes[35] involves the reaction of a transition-metal halocomplex with the preformed alkali dithiocarbamate ($CS_2 + RNH_2 + MOH \rightarrow M^+[RHNCS_2]^-$ and $M^+[RHNCS_2]^- + M'Cl \rightarrow M'S_2CNHR + MCl$). However, we have previously shown[5] that palladium and platinum dithiocarbamate complexes can be prepared by a "single-pot reaction" starting from di-μ-hydroxo complexes ($[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-} + 2\ RNH_2 + 2\ CS_2 \rightarrow 2\ [M(C_6F_5)_2(S_2CNHR)]^- + 2\ H_2O$; M = Pd or Pt). The result reported herein shows that most probably after the deprotonation of the amine by the hydroxo complex and subsequent formation of the amide complex there is insertion of CS_2 into the M−N bond.

Reaction of $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ with Malononitrile. The reactions of the di-μ-hydroxo complex $[NBu_4]_2[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]$ with malononitrile and methyl cyanoacetate (1:2 molar ratio), in methanol, lead to the formation of complexes **12** and **13** shown in Scheme 4. Both **12** and **13** gave satisfactory elemental analyses, and in acetone solution they behave as 2:1 electrolytes.[23] The ^{13}C NMR data of the bound malononitrilate in complex **12** indicate the presence of a D-type structure with bridging *N*,*C*-malononitrilate: three different carbon atoms at δ 127.0 (−CN−Pd), 119.5 (−CN) and −6.2 (−CH−). Furthermore, the presence in the ^1H NMR spectrum of **12** of two singlets of the same intensity for the CH protons (at δ 2.68 and 2.66) suggests that **12** exists in solution as a 1:1 mixture of *syn* and *anti* isomers. Similarly, the observation in the ^1H NMR spectrum of **13** of two different sets of signals for the CO_2Me (at δ 3.23 and 3.14) and CH (at δ 2.84 and 2.79) protons also suggests the existence in solution of a mixture of two isomers (*anti*−*syn*) in a 2:1 molar ratio. The ^{13}C NMR spectrum of **13** shows the expected

(29) Driver, M. S.; Hartwig, J. F. *Organometallics* **1997**, *16*, 5706.
(30) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S.; Alemany, P. *Inorg. Chem.* **1998**, *37*, 804.
(31) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1967**, *10*, 257.
(32) Kellner, R.; Nikolov, G. St.; Trendafilova, N. *Inorg. Chim. Acta* **1984**, *84*, 233.
(33) Catheline, D.; Román, E.; Astruc, D. *Inorg. Chem.* **1984**, *23*, 4508.
(34) Fabetti, A. C.; Forghieri, F.; Giusti, A.; Petri, C.; Tosi, G. *Spectrochim. Acta* **1984**, *40A*, 343.
(35) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23.

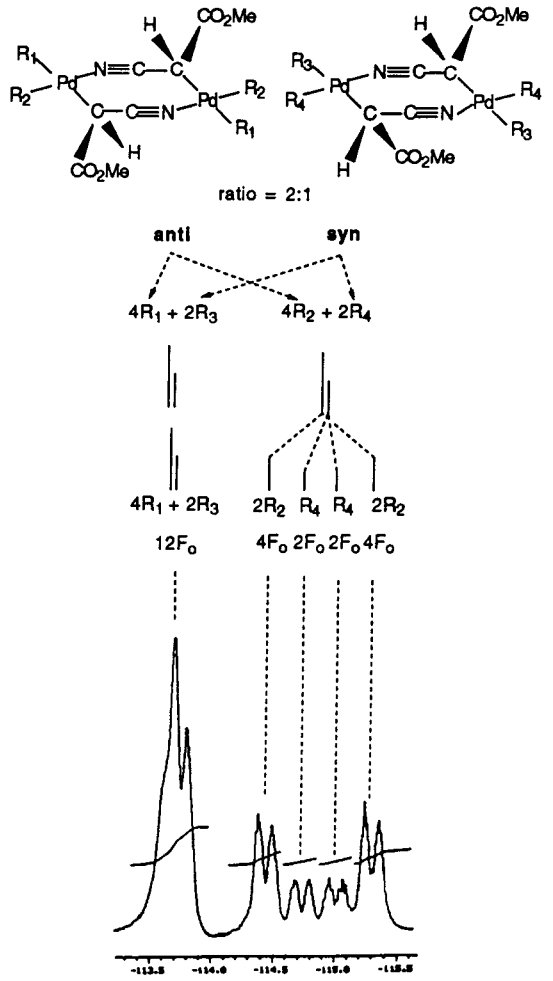


Figure 2. ^{19}F NMR spectrum of complex **13** in the *o*-fluorine region.

four signals for the $CH(CO_2Me)CN$ group (at δ 17.6, 173.1, 50.4, and 129.1, respectively).

The IR spectrum of **12** exhibits two strong bands in the ν(CN) region at 2250 (CN−Pd) and 2200 cm^{-1} (free CN). $[(C_6F_5)_2Ni(NCCHCN)_2Ni(C_6F_5)_2]^{2-}$ gives two bands at 2215 and 2160 cm^{-1},[20] and in platinum complexes containing the $(NCCHCOOMe)^-$ ligand, the presence of a band at 2200 cm^{-1} was attributed to a Pt−CH(CN)-COOMe linkage, whereas a band at 2150−2120 cm^{-1} was attributed[36] to the *N*-bonded structure Pt−N=C=CHCOOMe. The IR spectrum of **13** shows a strong absorption at 2240 cm^{-1} assigned to ν(CN) and a ν(CO) band at 1700 cm^{-1}. The presence of the *cis*-$(C_6F_5)_2Pd$ fragment in **12** and **13** is supported[15] by a split IR band at ca. 800 cm^{-1}.

The ^{19}F NMR spectrum of complex **13** shows four triplets for the *p*-fluorine atoms with relative intensities of 2:1:2:1 indicating the presence of two different types of C_6F_5 rings (two rings *trans* to N and two rings *trans* to C) as well as the existence of *anti* and *syn* isomers in 2:1 molar ratio (Figure 2). The chemical shifts of the corresponding *p*-fluorine atoms of different isomers are nearly coincident, and the 2:1 triplets are seen in the spectrum as two overlapped triplets. The NMR pattern observed in the *o*-fluorine region is more complex, there being five signals with relative intensities of $12F_o$:$4F_o$:$2F_o$:$2F_o$:$4F_o$; the doublet structure of the signals is originated by coupling to the *m*-fluorine. Figure 2 shows our interpretation. Hindered rotation of the C_6F_5 rings adjacent to the >C(H)(CO_2Me) groups renders the *o*-fluorine atoms of R_2 and R_4 inequivalent, but the nonadjacent R_1 and R_3 rings are not affected by the presence of the >C(H)(CO_2Me) group, and the corresponding resonance signal ($12F_o$) is seen as a multiplet comprising the signals from each isomer ($8F_o + 4F_o$). The *m*-fluorine atoms give the expected two signals (1:1) for one C_6F_5 ring *trans* to N and one C_6F_5 ring *trans* to C. The ^{19}F NMR spectrum of complex **12** (see Experimental Section) can be similarly understood from a 1:1 mixture of *anti* and *syn* isomers.

(36) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

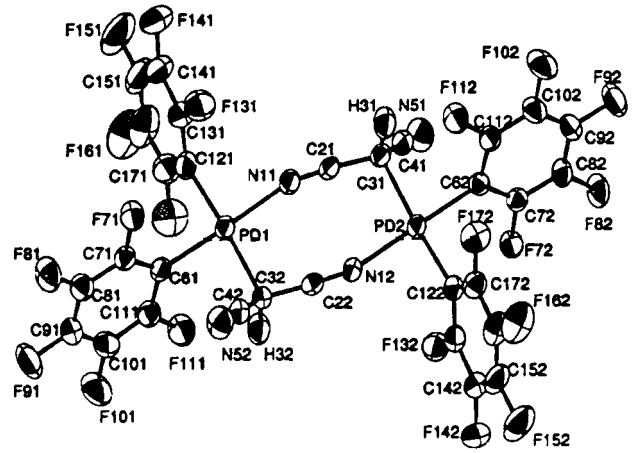


Figure 3. ORTEP diagram of **12**. Selected distances (Å): Pd−N, 2.072(5); Pd−C, 2.191(7); C−N(nonbonded), 1.136(7); C−N(bonded), 1.138(8). Selected angle (deg): Pd−N−C, 165(5).

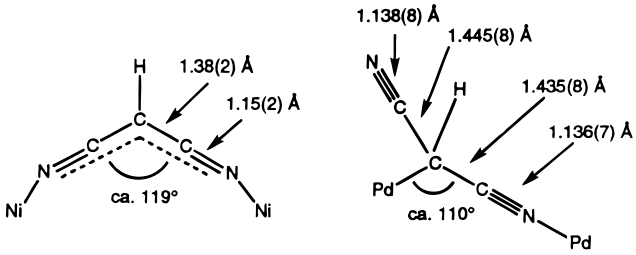


Figure 4. Relevant structural parameters for *N,N*- and *C,N*-bonded dicyanomethanide.

The stability of complex **12** allowed us to characterize it crystallographically (Figure 3). The most relevant structural points are the near coincidence of the C−N lengths of the noncoordinated and coordinated CN groups (1.138(8) and 1.136(7) Å, respectively) and the angle at the central carbon atom of malononitrilate (110°) indicating sp^3-hybridization of carbon. When *N,N*- and *C,N*-bonded malononitrilates are compared (Figure 4; data for the *N,N*-bonded ligand taken from ref 20), the main differences are (i) the C−N and C−C bond lengths are longer and shorter, respectively, in −NC-CHCN− than in −CH(CN)CN− and (ii) the angles at the CH carbon atoms (119° and 110°) indicate that there is sp^2 and sp^3 hybridization, respectively. Thus the *C,N*-bonded malononitrilate may be described as a *dicyanomethanide* ligand further interacting via the nitrogen atom of one of its nitrile groups. By constrast, the electron delocalization over the NCCCN skeleton in *N,N*-bonded malononitrilate resembles that found in an

acetylacetonate-type ligand. The IR data are consistent with the observed shortening of the CN bond in the Pd complex.

The synthesis of diiminato palladium and platinum complexes containing the [M(PPh$_3$)Me] moiety has been previously reported,[37] and we have also described the synthesis of imido-ester[38c] and β-iminoenolate derivatives[39] of palladium and platinum.The reaction between the di-μ-hydroxo palladium complex and malononitrile, in *boiling* methanol, gives the diiminate palladium complex **14** (Scheme 4). In acetone solution **14** behaves as a 1:1 electrolyte.[23] The IR spectrum shows two absorptions at 3400 and 3370 cm^{-1} assigned to ν(NH) and the ^{1}H NMR spectrum exhibits two singlets at δ 3.53 (MeO) and 3.64 (CH), respectively. The ^{19}F NMR spectrum shows the expected set of three resonances with relative intensities of 2:1:2 for the *o*-, *p*-, and *m*-fluorine atoms of four equivalent C_6F_5 rings freely rotating around the Pd−C_6F_5 bond.

In the course of our research into the chemistry of [NBu$_4$]$_2$[(C$_6$F$_5$)$_2$M(μ-OH)$_2$M(C$_6$F$_5$)$_2$]-type complexes (M = Ni, Pd, Pt),[38] we found that the nickel complex can be used as an efficient catalyst for the cyclotrimerization of malononitrile.[20] Similarly, catalytic amounts of the hydroxo palladium complex in wet toluene also effect the cyclotrimerization of malononitrile, leading to 4,6-diamino-2-cyanomethyl-3,5-pyridinedicarbonitrile (Scheme 4), the so-called trimer I of malononitrile.[39] From a 1:100 molar mixture of [{Pd(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$−malononitrile in boiling, wet toluene the cyclic trimer is isolated in 55% yield. The relevant data are listed in the Experimental Section and are identical with those previously reported.[20,40]

Conclusions

The work described herein shows that the hydroxo complexes of the nickel group elements are excellent precursors for the synthesis of amido complexes via the acid−base reactions

$$[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-} + RNH_2 \rightarrow [\{M(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}NHR)]^{2-} + H_2O$$

$$[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-} + RNH_2 \rightarrow [\{M(C_6F_5)_2(\mu\text{-}NHR)\}_2]^{2-} + H_2O$$

and carbon−nitrogen bonds can be formed to give carbamate complexes by insertion of carbon disulfide into the metal−nitrogen bond.

The experimental strategy used to prepare the malononitrilate complex **12** has been decisive for the coordination mode of [CH(CN)$_2$]$^-$. On deprotonation of malononitrile by the hydroxo palladium complex,

$$[R_2Pd(\mu\text{-}OH)_2PdR_2]^{2-} + 2\ CH_2(CN)_2 \rightarrow 2\ [R_2Pd\{CH(CN)_2\}(H_2O)]^-$$

the lability of the aqua ligand in the presumed intermediate aqua complex determines the existence of a quasi-vacant coordination site and the nitrogen atom of a cyano group of the carbon-bonded malononitrilate completes the coordination sphere of palladium:

$$2\ [R_2Pd\{CH(CN)_2\}(OH_2)]^- \rightarrow [R_2Pd\{\mu\text{-}CH(CN)(CN)\}_2PdR_2]^{2-} + 2\ H_2O$$

The preparation of **13** is based on the same concept. This type of complexes belong to the group of the so-called hemilabile compounds,[41] which are potential catalysts because they can readily offer a vacant coordination site: R$_2${(NC)$_2$HC}Pd(vacant). Studies of the equilibrium between [L$_2$Pd(R)(OH)] and [L$_2$Pd$_2$(R)$_2$(μ-OH)$_2$] have been reported very recently.[42]

The two other experiments, the formation of the diiminate complex **14** and the catalytic cyclotrimerization of malononitrile, may be considered the logical outcome of varying the experimental conditions: (i) compounds **12** and **13** are formed in MeOH at room temperature; (ii) in boiling methanol the nucleophilic attack of MeO$^-$ on the C≡N groups (C$^+$=N$^-$) is competitive and the diimine is formed, with the subsequent coordination as diiminate; (iii) in the absence of an external nucleophile (in wet toluene), the nucleophile (CN)$_2$CH$^-$ acts on malononitrile and the cyclic trimer is the reaction product. We have not been able to isolate an aqua palladium complex, but the acid−base equilibrium Pd−OH ⇌ Pd−OH$_2$ may work as the key step of the catalytic process.

Acknowledgment. Financial support of this work by the DGICYT (project PB97-1036), Spain, is acknowledged. V.R. thanks CajaMurcia, Spain, for a research grant.

Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and equivalent isotropic displacement parameters, complete bond distances and angles, and ORTEP views for compounds **8** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980508Z

(37) Yamamoto, H.; Suzuki, K. *J. Organomet. Chem.* **1974**, *71*, C38.
(38) (a) López, G.; García, G.; Ruiz, J.; Sánchez, G.; García, J.; Vicente, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1045. (b) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1991**, *30*, 2605. (c) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53. (d) López, G.; García, G.; Sánchez, G.; García, J.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518.
(39) Fatiadi, A. J. *Synthesis* **1978**, 165.
(40) Inoue, H.; Hara, K.; Osugi, J. *Rev. Phys. Chem. Jpn.* **1976**, *46*, 64.
(41) See, for example: Basato, M.; Grassi, A.; Valle, G. *Organometallics* **1995**, *14*, 4439.
(42) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242.