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Reactivity of hydroxo complexes of palladium(II) towards nitriles: formation of carboxamide and imino ether derivatives of palladium(II)

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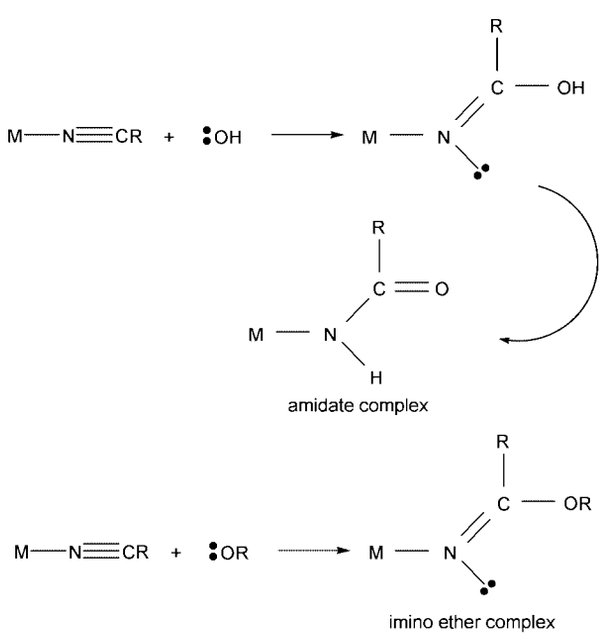
The binuclear hydroxo complexes $[Pd_2(C,N)_2(\mu\text{-}OH)_2]$ [C,N = 2-(dimethylaminomethyl)phenyl (dmba) or 2-(phenylazo)phenyl (az)] have been prepared by addition of 2 equivalents of NBu_4OH to the corresponding di-μ-acetate complexes in acetone. The reactions of both hydroxo complexes with a number of nitriles, RCN, led to the formation of the carboxamide complexes $[Pd_2(C,N)_2(\mu\text{-}NHC(R)O)_2]$ (R = Me, Ph or CH_2=CH) as well as the succinonitrile derivatives [(C,N)Pd{NHC(O)CH_2CH_2C(O)NH}Pd(C,N)]. The complexes $[Pd_2(C,N)_2(\mu\text{-}NHC(Me)O)_2]$ can also be prepared by reaction of $[Pd_2(C,N)_2(\mu\text{-}OH)_2]$ with acetamide. The hydroxo complex $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ reacted with nitriles in methanol or ethanol to give the imino ether complexes $[Pd(C_6F_5)_2\{NH{=}C(OR')R\}_2]$ (R = Ph, R′ = Me or Et; R = Me, R′ = Me or Et) which in acetone solution are present as mixtures of *EE*, *EZ* and *ZZ* isomers. Similar reactions with 2-cyanopyridine and succinonitrile gave $[Pd(C_6F_5)_2\{NC_5H_4C(OR')NH\text{-}2\}]$ and $[Pd(C_6F_5)_2\{NHC(OR')CH_2CH_2NH(OR')\}]$ (R′ = Me or Et) and the reaction with 2-cyanopyridine in acetone yielded $[Pd(C_6F_5)_2\{NC_5H_4C(=O)NH\text{-}2\}]$. The crystal structures of $[Pd_2(dmba)_2(\mu\text{-}NHC(Ph)O)_2]$ and $[Pd(C_6F_5)_2\{NH{=}C(OMe)Me\}_2]$ have been determined by single-crystal X-ray diffraction.

Considerable attention has been focused on reactions involving nucleophilic attack on co-ordinated nitriles in metal complexes and this field of synthetic chemistry is extensively documented.[1] Examples include reactions with hydroxide[2–9] and alkoxide to form amidates and imino ethers,[10–15] respectively (Scheme 1). In particular, the hydrolysis of nitriles in the co-ordination sphere of a transition metal has been known for a long time;[16] the hydrolysis of metal-bound nitriles proceeds fairly easily compared with that of unco-ordinated nitriles, due to the Lewis-acid activation of the metal. Labile complexes serve as catalysts, the main advantage over acids and bases being their selectivity, because in the presence of transition-metal complexes amides are not converted into caboxylic acids.[17] From a biological perspective, the nitrile hydratases are important, little studied metalloenzymes which catalyse the hydration of nitriles *in vivo*[18,19] and recent interest in the chemistry of platinum–imino ether compounds arises from the discovery that some of these compounds have antitumour activity.[20]



Scheme 1 Nucleophilic attack of OH^- and RO^- on co-ordinated nitrile.

Organometallic benzonitrile complexes *cis*-$[MR_2(PhCN)_2]$ (R = C_6F_5, $C_6F_3H_2$ or C_6Cl_5; M = Ni, Pd or Pt) have been used as labile complexes for the synthesis of a variety of compounds. These include mononuclear[21] complexes, R_2ML_2, as well as heterobimetallic complexes, $[R_2Pd(\mu\text{-}X)_2ML_2]$ (M = Ni, Pd or Pt).[22] Interestingly, the metathesis of PhCN by OH^- to synthesize the hydroxo complexes $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ was shown to be metal dependent.[23] When M = Ni or Pd metathesis of PhCN by OH^- takes place, and binuclear hydroxo complexes are obtained, eqn. (1).[24,25] However, for the more kinetically

$$2\ cis\text{-}[M(C_6F_5)_2(NCPh)_2] + 2\ OH^- \longrightarrow [M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-} + 4\ PhCN \quad (1)$$

(M = Ni or Pd)

inert benzonitrileplatinum complex[26] the nucleophilic attack by OH^- is faster than the substitution reaction, and the aqua–η^1-amidate complex is produced, eqn. (2). On heating this

$$cis\text{-}[Pt(C_6F_5)_2(NCPh)_2] + OH^- + H_2O \longrightarrow cis\text{-}[Pt(C_6F_5)_2\{\eta^1(N)\text{-}NHC(=O)Ph\}(H_2O)]^- + PhCN \quad (2)$$

compound the co-ordinated water is lost and the bis(μ-η^2-amidate) complex is formed, eqn. (3). With methanol the

$$2\,[Pt(C_6F_5)_2\{\eta^1(N)\text{-}NHC(=O)Ph\}(H_2O)]^- + \text{heat} \longrightarrow [Pt_2(C_6F_5)_4\{\mu\text{-}\eta^2(N,O)\text{-}NHC(=O)Ph\}_2]^{2-} + 2\,H_2O \quad (3)$$

bis(iminoether) $[Pt(C_6F_5)_2\{NH{=}C(Ph)OMe\}_2]$ is directly obtained.[26]

In summary, the previous results mentioned above indicate: (i) Ni–NCPh and Pd–NCPh can be metathetically transformed into Ni–OH and Pd–OH by reaction with OH^-; (ii) Pt–NCPh, however, is prone to nucleophilic attack by OH^- (or MeO^-) yielding the amidate complex Pt–NHC(=O)Ph (or the imino ether complex Pt–N=C(OMe)Ph). These different results may easily be interpreted on the basis of the well known inertness of platinum complexes towards substitution reactions. Once the outcome of the reaction palladium nitrile + free OH^- was known the reaction between M–OH and free nitrile following remained unsolved. In binuclear complexes, $\{M(\mu\text{-}OH)_2M\}$, the enhanced nucleophilicity of the OH bridges is manifested by their high-field proton resonances (δ −5.74 (Ni), −2.84 (Pd) and −1.21 (Pt), respectively, for $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$).† Consequently, it was to be expected that the reaction between hydroxo complexes and nitriles should yield, under appropriate conditions, the respective amidate and imino ether complexes, which has been confirmed by the present study. The reactions of the hydroxo complexes $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ and $[Pd_2(C,N)_2(\mu\text{-}OH)_2]$ (C,N = 2-[(dimethylamino)methyl]phenyl-C^1N (dmba) or 2-phenylazophenyl-C^1,N (az)) with a number of nitriles have been studied.

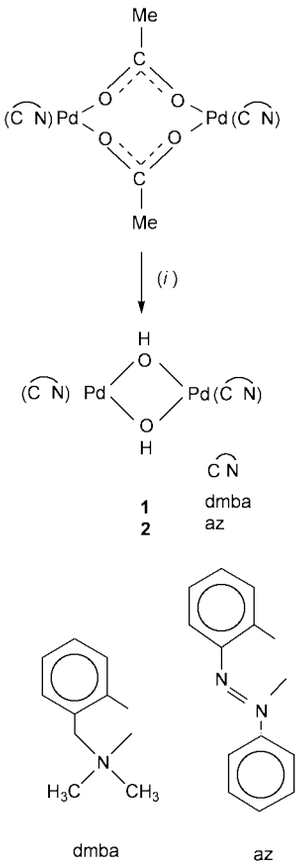
Results and discussion

The anionic complex $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ was prepared as described[25] and the neutral cyclopallated complexes $[Pd_2(C,N)_2(\mu\text{-}OH)_2]$ (C,N = dmba **1** or az **2**) were conveniently prepared by simple metathesis on the corresponding di-μ-acetate complexes[28,29] by addition of 2 equivalents of NBu_4OH (Scheme 2). The reactions take place in acetone at ambient temperature and both complexes are precipitated by addition of water. Although complex **1** was previously prepared,[30] a less convenient route was used, *i.e.* the hydrolysis of a dioxygen-bridged complex, and no spectroscopic data were reported.

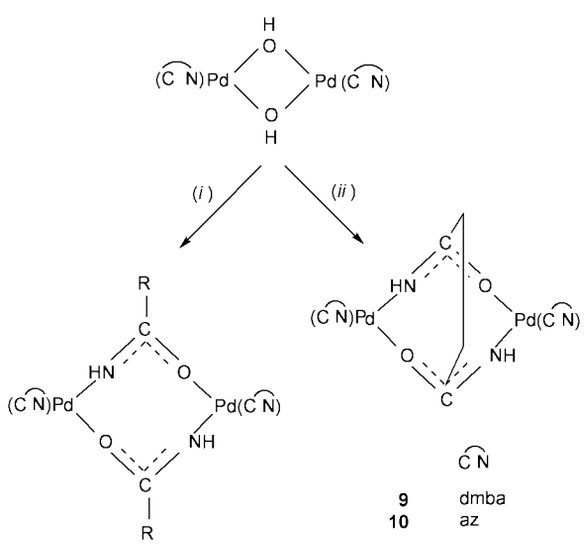
The analytical data are consistent with the proposed formulae as are the IR and ^{1}H NMR data (Table 1) with the presence of hydroxide as bridging ligand,[25,31,32] with an IR band at *ca.* 3560 cm^{-1} due to the O–H stretching vibration and with a high-field ^{1}H resonance at δ −2.40 and −1.13, respectively. Furthermore, the ^{1}H NMR spectrum of complex **1** (Table 1) shows the chemical shift equivalence of the CH_2N and NMe_2 protons of co-ordinated dmba.

The hydroxo-complexes **1** and **2** react with nitriles to give the corresponding di-μ-amidate complexes **3**–**10** shown in Scheme 3. The ^{1}H NMR spectra of **3**, **5**, **7** and **9** (Table 1) show that both the *N*-methyl and the CH_2 groups of the dmba are diastereotopic, two separate signals being observed for the former and an AB quartet for the latter. Therefore there is no plane of symmetry in the palladium co-ordination plane. A folded 'basket' structure related to that observed in acetato-bridged dimers is likely.[33]

Since both $C_6H_4CH_2NMe_2$ and RCONH are unsymmetrical, there are five possible diastereomers for the dimeric complex, two with head-to-head and the other three with head-to-tail



Scheme 2 (*i*) 2 OH^-.



	R	C N
3	Me	dmba
4	Me	az
5	Ph	dmba
6	Ph	az
7	CH_2=CH	dmba
8	CH_2=CH	az

Scheme 3 (*i*) 2 RCN; (*ii*) NCC_2H_4CN.

† In fact these complexes have been used as Brönsted bases in a variety of reactions. For example, the reaction between $[(C_6F_5)_2Ni(\mu\text{-}OH)_2Ni(C_6F_5)_2]^{2-}$ and malononitrile (1:2 ratio) yields the μ-η^2(*N*,*N*)-malonitrilate complex $[(C_6F_5)_2Ni(\mu\text{-}NCCHCN)_2Ni(C_6F_5)_2]^{2-}$, and catalytic cyclotrimerization to 2,4-diamino-6-cyanomethyl-3,5-pyridinedicarbonitrile occurs when an excess of malononitrile is used.[27]

arrangements of the bridging MeCONH ligands, but only one isomer is present in solution at room temperature, perhaps due to the fact that the ligand dmba exerts very different *trans* influences through its C and N atoms.[34] A facile head-to-tail to head-to-head rearrangement has been observed in *cis*-$[M_2(NH_3)_4(\mu\text{-}C_2H_4NO)_2]^{2+}$ (M = Pd or Pt).[35] The observation of a

Table 1 ^{1}H NMR data (δ, J in Hz) for the palladium complexes **1**–**10** (in $CDCl_3$, reference $SiMe_4$)

Complex	
1	6.9 (m, 8 H, aromatics)
	3.77 (s, 4 H, NCH_2)
	2.70 (s, 12 H, NMe_2)
	−2.40 (s, 2 H, OH)
2	7.9–7.0 (m, 18 H, aromatics)
	−1.13 (s, 2 H, OH)
3	7.0–6.8 (m, 8 H, aromatics)
	4.9 (s, 2 H, NH)
	3.43 (d, 2 H, NCH_2, J 13.6)
	3.02 (s, 2 H, NCH_2, J 13.6)
	2.63 (s, 6 H, NMe_2)
	2.10 (s, 6 H, NMe_2)
	2.02 (s, 6 H, CH_3CONH)
4	7.6 (d, 2 H, J 7.6)
	7.43 (d, 4 H, J 7.6)
	7.30 (m, 6 H)
	7.04 (dd, 2 H, $J \approx J'$ 7.6)
	6.8 (dd, 2 H, J 7.6)
	6.6 (d, 2 H, J 7.6)
	5.0 (s, 2 H, NH)
	1.94 (s, 6 H, CH_3CONH)
5	7.8–7.3 (m, 10 H, C_6H_5)
	7.0–6.9 (m, 8 H, aromatics dmba)
	5.74 (s, 2 H, NH)
	3.5 (d, 2 H, NCH_2, J 13.6)
	3.1 (d, 2 H, NCH_2, J 13.6)
	2.7 (s, 6 H, NMe_2)
	2.1 (s, 6 H, NMe_2)
6	7.6–6.6 (m, 28 H, aromatics)
	5.91 (s, 2 H, NH)
7	7.0–6.8 (m, 8 H, aromatics)
	6.19 (dd, 2 H, CH=CH_2, J 16.9, J' 10.0)
	5.85 (dd, 2 H, CH=$CH_{2(a)}$, J 16.9, J' 1.7)
	5.25 (dd, 2 H, CH=$CH_{2(b)}$, J 9.7, J' 1.7)
	5.1 (s, 2 H, NH)
8	7.68 (dd, 2 H, J 7.6, J' 1.4)
	7.47 (d, 4 H, J 7.2)
	7.30 (m, 6 H)
	7.06 (ddd, 2 H, $J \approx J'$ 7.4, J'' 1.2)
	6.71 (ddd, 2 H, $J \approx J'$ 7.3, J'' 1.4)
	6.55 (ddd, 2 H, $J \approx J'$ 7.7, J'' 1.3)
	6.21 (dd, 2 H, CH=CH_2, J 16.9, J' 9.7)
	6.02 (dd, 2 H, CH=$CH_{2(a)}$, J 16.9, J' 2.1)
	5.41 (dd, 2 H, CH=$CH_{2(b)}$, J 9.7, J' 2.1)
	5.37 (s, 2 H, NH)
9	7.0–6.8 (m, 8 H, aromatics dmba)
	4.9 (s, 2 H, NH)
	3.50 (d, 2 H, NCH_2, J 13.8)
	3.05 (d, 2 H, NCH_2, J 13.6)
	2.6 (s, 6 H, NMe_2)
	2.5 (m, 4 H, C_2H_4)
	2.06 (s, 6 H, NMe_2)
10	7.69 (d, 2 H, J 7.3)
	7.3 (m, 8 H)
	7.06 (ddd, 2 H, $J \approx J'$ 7.2, J'' 1.7)
	6.70 (m, 4 H)
	5.19 (s, 2 H, NH)
	2.5 (m, 4 H, C_2H_4)

unique resonance for the MeCO and NH protons in the ^{1}H spectrum of complex **3** (Table 1), together with the observed $C_6H_4CH_2NMe_2$ resonances, is consistent with only the head-to-tail structures (Scheme 3) containing the central core Pd-{μ-OC(Me)NH}{μ-NHC(Me)O}Pd. Furthermore, we should expect that the O atom would be *trans* to the carbon atom of the $C_6H_4CH_2NMe_2$ chelate by analogy to the imidate complexes [{Pd(C,N)(μ-$NCOC_2H_4CO$)}$_2$] (C,N = *o*-$C_6H_4CH_2NMe_2$ or *o*-C_6H_4CH=NPh).[36] This point has been confirmed by X-ray determination of the crystal structure of the benzamidato complex **5**.

Suitable crystals of complex **5** were grown from dichloromethane–hexane. The structure of **5** is shown in Fig. 1 and selected bond lengths and angles in Table 2. So far as we are aware this is the first dipalladium species bridged by two benzamidate ligands to be structurally characterized. The two palladium atoms are crystallographically inequivalent, although the bond lengths and angles about each are not markedly different. Co-ordination at palladium is approximately square planar with the two co-ordination planes inclined at 35.50(11)° to each other giving a basket-shaped 8-membered ring. The cyclometallated rings are puckered with the nitrogen atom significantly out of the plane defined by the palladium and carbon atoms, a feature which is quite commonly observed in cyclometallated dmba complexes.

Table 2 Selected distances (Å) and angles (°) for complex **5**

Pd(1)–C(1)	1.916(3)	Pd(2)–C(24)	1.963(3)
Pd(1)–N(1)	2.079(3)	Pd(2)–N(2)	2.017(3)
Pd(1)–Pd(2)	3.0054(5)	Pd(2)–N(4)	2.087(3)
Pd(1)–N(3)	2.013(3)	Pd(2)–O(2)	2.118(3)
Pd(1)–O(1)	2.130(3)		
C(1)–Pd(1)–N(3)	95.45(14)	C(24)–Pd(2)–N(2)	95.78(13)
C(1)–Pd(1)–N(1)	82.76(14)	C(24)–Pd(2)–N(4)	82.37(13)
N(3)–Pd(1)–O(1)	88.49(12)	N(2)–Pd(2)–O(2)	87.50(12)
N(1)–Pd(1)–O(1)	92.74(12)	N(4)–Pd(2)–O(2)	94.10(12)

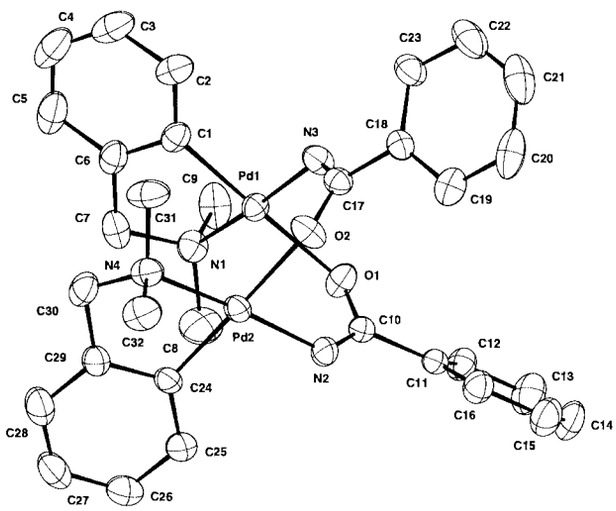
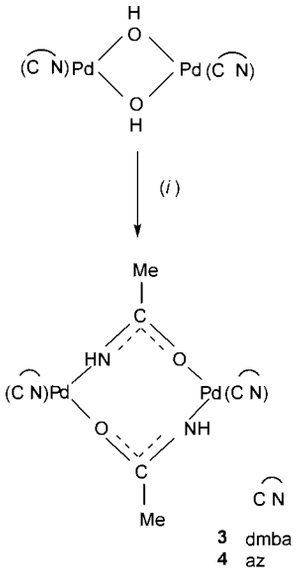


Fig. 1 Perspective view of the molecular structure of complex **5**.

A number of cyclometallated dmba complexes with nitrogen and oxygen ligands have been structurally characterized. In all instances, both with chelating and non-chelating ligands, the nitrogen atoms occupy *trans* sites at the metal with oxygen *trans* to carbon, as indeed is observed for **5**. The Pd–N(sp^3) distances in **5**, 2.079(3) and 2.087(3) Å, are comparable with those in [(dmba)Pd–OC(=O)CHRNHR′][37] (R = CH_2CH_2SMe or CH_2Ph, R′ = protected sugar; 2.079(6), 2.052(6) Å), [Pd(dmba)-($OC_6H_4NMe_2$-2)][38] (2.075(2) Å) and [Pd(dmba){OC_6H_4-CH=NPh-2}][39] (2.090(10) Å). Two related complexes in which the N- and O-ligands are not part of a chelate have also been studied, [Pd(dmba)(bquin)(OH_2)][ClO_4][40] (bquin = benzo[*h*]-quinoline) and the ylid derivative [Pd(dmba)(py){OC(Me)=CHPPh$_3$}][ClO_4]·CH_2Cl_2.[41] The Pd–NMe_2 distances (2.06(1) and 2.074(3) Å) in these species are also comparable with those in **5**. The Pd–C distances in **5** (1.961(3), 1.963(3) Å) also lie within the range normal for palladium dmba complexes.

The formation of complexes **3**–**10** may be explained by initial formation of an intermediate hydroxonitrile complex ([(C,N)-Pd(μ-$OH)_2$Pd(C,N)] + 2 RCN $\rightleftharpoons$ 2 [Pd(C,N)(OH)(NCR)]) and subsequent nucleophilic attack of OH^- on the co-ordinated nitrile and migration of H^+ to the nitrogen atom bound to palladium. The conversion of acetonitrile into acetamide in the co-ordination sphere of *cis*- and *trans*-M^{II}(amine)$_2$ (M = Pd or Pt) has been reported.[36] The reaction of complexes

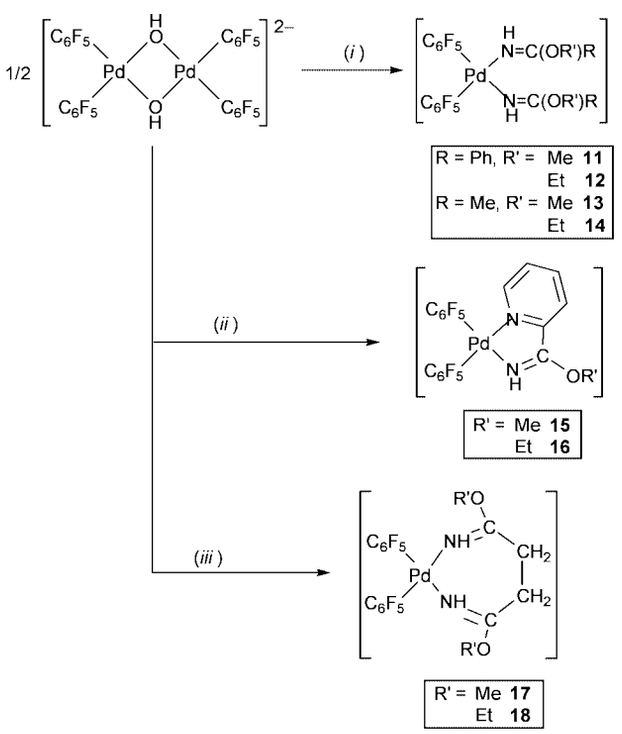
1 or **2** with the fairly weak acid acetamide also yields complex **3** or **4**, respectively (Scheme 4). This is a consequence of the con-



Scheme 4 (*i*) 2 CH_3CONH_2.

siderable basicity of the OH bridges in **1** and **2**, as expected from the high field proton resonances. The basic character of the hydroxo complexes $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ (M = Ni, Pd or Pt) has allowed the preparation of new binuclear or mononuclear complexes by reaction with the corresponding protic electrophile (HX = azoles,[24,25,42,43] β-diketones,[25,26] malononitrile,[27] amines[44] or thiols[45]) with the concomitant release of water.

The hydroxo complex $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ reacts with nitriles in methanol or ethanol to give the corresponding imino ether derivatives **11**–**18** shown in Scheme 5. All these com-



Scheme 5 (*i*) RCN/R′OH; (*ii*) 2-CNpy/R′OH; (*iii*) $NCCH_2CH_2CN$/R′OH.

pounds behave as non-electrolytes in acetone solution and their analytical data are consistent with the proposed formulae. The IR spectra show the characteristic absorptions of the C_6F_5 group[46] at 1630, 1490, 1450, 1050, 950 and a split band at *ca.* 800 cm^{-1} which is derived from the so-called X-sensitive mode in C_6F_5–halogen molecules. This is characteristic of the presence of the *cis*-$Pd(C_6F_5)_2$ fragment[47] and behaves like a ν(M–C) band.[48] The bands at *ca.* 3360 and 1645 cm^{-1} provide evidence for the NH and C=N groups of the imino ether.[49]

The NMR data for the bis(imino ether) complexes **11**–**14** (Table 3) showed that they are present in $(CD_3)_2CO$ solution in three isomeric forms, with *EE*, *EZ* and *ZZ* conformations of the ligands (Chart 1 for complex **11**) in approximately 8:5:1

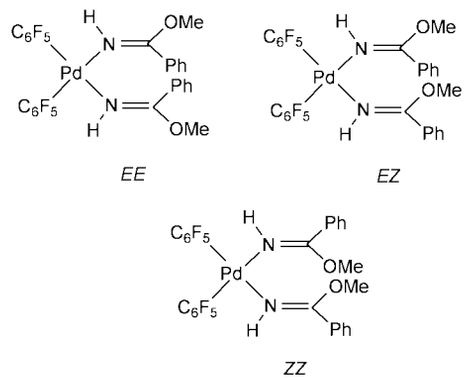


Chart 1

ratio for **11** and **12**, and 12:6:1 for **13** and **14**, respectively. On leaving the mixture of **11** in solution for 1 d no change was observed. The conformation of the imino ether ligands (*E* or *Z*) could be assigned on the basis of the ^1H NMR data.[50] In Chart 1 it is shown for complex **11** how the *ortho* protons of the phenyl, or, alternatively, the methyl protons of the methoxy group, are arranged about the palladium atom depending upon the *E* or *Z* configuration of the imino ether ligand. As a consequence of this a downfield shift is expected for the *ortho* protons of the phenyl group, in the case of the *E* conformation, and for the methyl protons of the methoxy group, in the case of the *Z* conformation. These shifts have been attributed to an induced anisotropic paramagnetic contribution to the molecular susceptibility. The magnitude of the shift is predicted to become greater the closer the protons approach to the metal.[51,52] Furthermore, the *EZ* isomer is expected to show two resonances for the methyl protons of the methoxy groups of equal intensities. As noted in Table 3 the chemical shift separation between the methyl protons of the methoxy group of the *EE* and *ZZ* isomers of complex **11** is more than 1 ppm.

In $(CD_3)_2CO$ the isomerization about the C=N double bond is fast enough to prevent us from separating species with different conformations of the imino ether ligands (*E* or *Z*). In fact, redissolution in $(CD_3)_2CO$ of white crystals of the *EE* isomer of complex **13** grown from dichloromethane–hexane gives the same ^1H NMR spectrum with the three isomers in the same ratio. The three isomeric forms have also been found in the related bis(imino ether) platinum derivative *cis*-$[PtCl_2\{HN{=}C(OMe)Ph\}_2]$, where the *E* conformation is preferred over *Z*, though the isomerization about the C=N double bond was slow enough in this case to allow separation of species with different conformations of the imino ether ligands. The related complex *cis*-$[Pt(C_6F_5)_2\{HN{=}C(OMe)Ph\}_2]$ was found in solution as a unique form, the *EE* isomer.[26]

The ^{19}F NMR spectra of the imino ether derivative **15** or **16** reveal the presence of two inequivalent C_6F_5 groups (*trans* to NH group and *trans* to N of the pyridine group). The same pattern is observed for the *EZ* isomers of complexes **11** and **12** (the corresponding resonances for the *EZ* isomers of **13** and **14** are overlapped with those of the other isomers).

Nucleophilic attack of alcohols on nitrile complexes of platinum or nickel in the presence of a catalytic amount of base

Table 3 The ^{1}H and ^{19}F NMR data (δ, J in Hz) for the palladium complexes **11**–**19** (in $(CD_3)_2CO$)

Complex	^{1}H ($SiMe_4$)	^{19}F ($CFCl_3$)
11	8.73 (d, H_o, C_6H_5, *EZ*, *J* 7.4)	−115.8 (m, F_o, *EE* and *EZ*)
	8.69 (d, H_o, C_6H_5, *EE*, *J* 7.4)	−116.6 (d, F_o, *ZZ*, *J* 24.6)
	7.73–7.14 (other aromatics)	−116.9 (d, F_o, *EZ*, *J* 24.6)
	6.72 (br, NH)	−163.8 (t, F_p, *EZ*, *J* 19.8)
	5.01 (s, CH_3O, *ZZ*)	−164.0 (t, F_p, *EZ*, *J* 19.8)
	4.87 (s, CH_3O, *EZ*)	−164.2 (t, F_p, *EZ*, *J* 19.8)
	4.00 (s, CH_3O, *EZ*)	−164.4 (t, F_p, *EE*, *J* 19.8)
	3.32 (s, CH_3O, *EE*)	−166.0 (m, F_m, *EE*, *EZ* and *ZZ*)
12	8.76 (d, H_o, C_6H_5, *EZ*, *J* 7.4)	−115.9 (m, F_o, *EE* and *EZ*)
	8.65 (d, H_o, C_6H_5, *EE*, *J* 7.4)	−116.6 (d, F_o, *ZZ*, *J* 24.6)
	7.74–7.13 (other aromatics)	−116.9 (d, F_o, *EZ*, *J* 24.6)
	6.60 (br, NH)	−164.1 (t, F_p, *ZZ*, *J* 19.8)
	5.68 (q, CH_2O, *ZZ*, *J* 7.0)	−164.2 (t, F_p, *EZ*, *J* 19.8)
	5.52 (q, CH_2O, *EZ, J* 7.0)	−164.2 (t, F_p, *EZ*, *J* 19.8)
	4.28 (q, CH_2O, *EZ*, *J* 7.0)	−164.4 (t, F_p, *EE*, *J* 19.8)
	3.41 (q, CH_2O, *EE*, *J* 7.0)	−166.0 (m, F_m, *EE*, *EZ* and *ZZ*)
	1.54 (t, CH_3CH_2O, *ZZ*, *J* 7.0)	
	1.48 (t, CH_3CH_2O, *EZ*, *J* 7.0)	
	1.36 (t, CH_3CH_2O, *EZ*, *J* 7.0)	
	1.16 (t, CH_3CH_2O, *EE*, *J* 7.0)	
13	7.36 (br, NH)	−115.9 (m, F_o)
	4.49 (s, CH_3O, *ZZ*)	−164.4 (m, F_p)
	4.47 (s, CH_3O, *EZ*)	−166.3 (m, F_m)
	3.72 (s, CH_3O, *EZ* and *EE*)	
	2.39 (s, CH_3, *EZ*)	
	2.36 (s, CH_3, *EE*)	
	2.12 (s, CH_3O, *EZ* and *ZZ*)	
14	7.28 (br, NH)	−115.9 (m, F_o)
	5.06 (q, CH_2O, *ZZ*, *J* 7.0)	−164.6 (m, F_p)
	5.00 (q, CH_2O, *EZ*, *J* 7.0)	−166.3 (m, F_m)
	4.02 (q, CH_2O, *EZ* and *EE*, *J* 7.0)	
	2.37 (s, CH_3, *EZ*)	
	2.35 (s, CH_3, *EE*)	
	2.12 (s, CH_3, *EZ*)	
	2.11 (s, CH_3, *ZZ*)	
	1.33 (t, CH_3CH_2O, *ZZ*, *J* 7.0)	
	1.32 (t, CH_3CH_2O, *EZ*, *J* 7.0)	
	1.22 (t, CH_3CH_2O, *EZ* and *EE*, *J* 7.0)	
15	8.34 (m, 1 H, H^5)	−114.7 (d, 4 F_o, J_{om} 26.8)
	8.17 (d, 1 H, H^6, *J* 7.0)	−115.1 (d, 4 F_o, J_{om} 26.8)
	8.09 (d, 1 H, H^3, *J* 5.1)	−162.7 (t, 2 F_p, J_{mp} 19.5)
	7.82 (m, 1 H, H^4)	−163.7 (t, 2 F_p, J_{mp} 19.8)
	4.20 (s, 3 H, CH_3O)	−164.7 (m, 4 F_m)
16	8.97 (br, 2 H, NH)	−115.1 (d, 4 F_o, J_{om} 27.4)
	8.34 (m, 1 H, H^5)	−115.5 (d, 4 F_o, J_{om} 27.4)
	8.19 (d, 1 H, H^6, *J* 7.4)	−163.1 (t, 2 F_p, J_{mp} 19.8)
	8.09 (d, 1 H, H^3, *J* 5.1)	−164.1 (t, 2 F_p, J_{mp} 19.8)
	7.80 (m, 1 H, H^4)	−165.2 (m, 4 F_m)
	4.52 (q, 4 H, CH_2O, *J* 7.0)	
	1.51 (t, 6 H, CH_3CH_2O, *J* 7.0)	
17	7.35 (br, 2 H, NH)	−116.1 (d, 4 F_o, J_{om} 22.9)
	3.75 (s, 6 H, CH_3O)	−164.4 (t, 2 F_p, J_{mp} 19.8)
	3.24 (s, 4 H, CH_2)	−166.2 (m, 4 F_m)
18	7.27 (br, 2 H, NH)	−111.5 (d, 4 F_o, J_{om} 24.3)
	4.04 (q, 4 H, CH_2O, *J* 7.0)	−159.8 (t, 2 F_p, J_{mp} 19.8)
	3.24 (s, 4 H, CH_2)	−161.7 (m, 4 F_m)
	1.24 (t, 6 H, CH_3CH_2O, *J* 7.0)	
19	8.03 (m, 1 H, H^5)	−113.9 (m, 4 F_o)
	7.95 (d, 1 H, H^6, *J* 6.1)	−165.0 (t, 2 F_p, J_{mp} 19.8)
	7.83 (d, 1 H, H^3, *J* 5.1)	−165.7 (t, 2 F_p, J_{mp} 20.0)
	7.44 (m, 1 H, H^4)	−166.9 (m, 4 F_m)
	4.91 (br, 1 H, NH)	
	3.43 (m, 8 H, NCH_2)	
	1.80 (m, 8 H, NCH_2CH_2)	
	1.40 (m, 8 H, CH_2CH_3)	
	0.90 (m, 12 H, CH_3, *J* 7.3)	

have been described.[10,11,26,53] The reaction of the previously reported[21a] complex *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ with methanol in the presence of NaOMe (see Experimental section) yields the bis(imino ether) complex **11** with isomers also in the ratio 8 : 5 : 1 (see above). This suggests that, after facile heterolysis of the palladium hydroxo complex $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ in alcoholic solvents when nitrile ligands are present, outer-sphere attack of alcohol on nitrile bound to palladium takes place in the above reactions. The synthesis of the related methoxoplatinum complex $[(C_6F_5)_2Pt(\mu\text{-}OMe)_2Pt(C_6F_5)_2]^{2-}$ by reaction of the corresponding hydroxoplatinum complex with methanol has also been described.[43]

Finally, although the reaction of the labile *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ with NBu_4OH (aq) in acetone solution is a convenient route[25] for the synthesis of the di-μ-hydroxo complex $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$, and the nucleophilic attack of OH^- on

Table 4 Selected distances (Å) and angles (°) for complex **13**

Pd–C(1)	2.001(4)	Pd–N(2)	2.108(4)
Pd–C(7)	2.003(4)	N(2)–C(16)	1.341(7)
Pd–N(1)	2.108(3)		
C(1)–Pd–C(7)	87.4(2)	N(1)–Pd–N(2)	88.68(14)
C(7)–Pd–N(1)	91.4(2)	C(13)–N(1)–Pd	126.2(4)
C(1)–Pd–N(2)	92.6(2)	C(16)–N(2)–Pd	125.8(4)

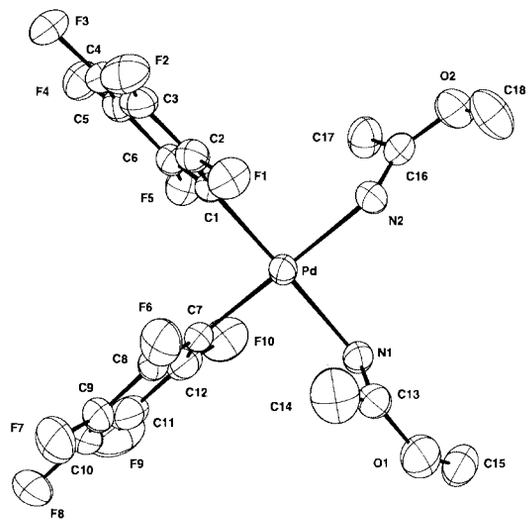
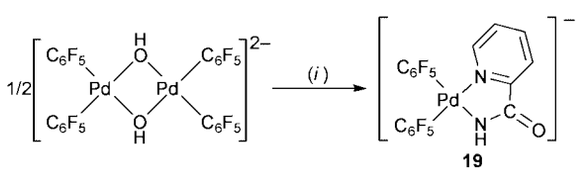


Fig. 2 Perspective view of the molecular structure of complex **13**.

co-ordinated benzonitrile is not detected,‡ the reaction of $[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ with 2-cyanopyridine in acetone yields the carboxamide derivative **19** (Scheme 6). The IR spectrum



Scheme 6 (*i*) 2-CNpy in acetone.

shows ν(NH) and ν(C=O) bands at 3225 and 1630 cm^{-1}, respectively. An alternative iminoenol formulation is excluded by the absence of ν(OH) bands at *ca*. 3500 cm^{-1}. In acetone solution **19** behaves as a 1:1 electrolyte.[54] Again heterolysis of the palladium hydroxo complex in the presence of the good ligand 2-cyanopyridine might take place, and in this case nucleophilic attack of OH^- on co-ordinated 2-cyanopyridine is favourably competitive.

A single isomer of complex **13** (the *EE* isomer), presumably the least soluble one, could be isolated from CH_2Cl_2–hexane as crystals suitable for a diffraction study. The structure is shown in Fig. 2, and selected bond lengths and angles given in Table 4. The co-ordination at palladium is close to square planar, with a small deviation towards tetrahedral, and the C_6F_5 groups are *cis*.

The structures of a small number of $\{(C_6F_5)_2PdN_2\}$ moieties have been previously determined. The Pd–C bond lengths in complex **13**, 2.001(4) and 2.003(4) Å, are quite similar to those in $[Pd(C_6F_5)_2(terpy)]$[55] (2.011(7) and 1.994(7) Å), $[Pd(C_6F_5)_2\{PhP(=O)C_5H_4N\text{-}2\}_2]\cdot 2CHCl_3$ (2.015(4), 2.010(3) Å)[56] and $[NBu_4][Pd(C_6F_5)_2(pz\cdots H\cdots pz)]$.[46] The palladium–nitrogen distances in **13** (2.108(3), 2.108(4) Å) lie within the range reported for Pd–N in these complexes (2.064–2.131 Å), despite the fact that the sp^2 nitrogens involved are of different types. The only palladium iminoether complex which has previously been characterized is *cis*-$[PdCl_2\{NH{=}CCH_2CH_2CH_2O\}(PPh_3)]\cdot 0.5CH_2Cl_2$.[14] This species contains two crystallographic independent molecules with palladium–nitrogen bond lengths 2.026(9) and 2.042(10) Å. The shorter distances here may result from a slightly less crowded molecule, but the authors did note that these bond lengths lay at the extreme of established Pd–N(sp^2) distances. The cyclic nature of the imino ether here makes it difficult to compare bond lengths in the ligand with those in **13**. The C_6F_5 rings in **13** show typical[55] distortions at C1 and C7 with C(2)–C(1)–C(6) 114.4(4) and C(12)–C(7)–C(8) 115.0(4)°.

Experimental

The analyses (C, H, N) were performed with a Carlo Erba model EA 1108 microanalyser. Decomposition temperatures were determined on a Mettler TG-50 thermobalance with a heating rate of 5 °C min^{-1} and the solid sample under nitrogen flow. Conductance measurements were made with a Crison 525 conductimeter in acetone solutions ($c \approx 5 \times 10^{-4}$ mol L^{-1}). Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets, the NMR spectra on a Bruker AC 200E or a Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as standards, respectively. The precursors $[\{Pd(C,N)(\mu\text{-}OAc)\}_2]$ (C,N = *o*-$C_6H_4CH_2NMe_2$[28] and *o*-$C_6H_4N{=}NPh$[29]) and $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$[25] were prepared as described. Solvents were dried by the usual methods.

Preparations

Complexes 1 and 2. A 20% solution of NBu_4OH (aq) (1.102 mmol) was added to an acetone (4 cm^3) solution of the corresponding di-μ-acetate complex $[\{Pd(C,N)(\mu\text{-}OAc)\}_2]$ (0.501 mmol). After stirring at room temperature for 10 min a white (**1**) or brown (**2**) solid was collected by filtration, washed with acetone and water, and air dried. Complex **1**: yield 90% (Found: C, 42.0; H, 5.2; N, 5.4. $C_9H_{13}NOPd$ requires C, 42.0; H, 5.1; N, 5.4%), mp 168 °C (decomp.); IR (Nujol, cm^{-1}) 3560 (ν(OH)). Complex **2**: yield 98% (Found: C, 47.0; H, 3.4; N, 9.0. $C_{12}H_{10}N_2OPd$ requires C, 47.3; H, 3.3; N, 9.2%), mp 162 °C (decomp.); IR (Nujol, cm^{-1}) 3575 (ν(OH)).

Complexes 3–8. On addition of the corresponding nitrile (1.164 mmol) to a suspension of complex **1** or **2** (0.116 mmol) in benzene (5 ml) a clear solution resulted. After boiling under reflux for 2 h the solution was concentrated under reduced pressure and the addition of hexane caused the precipitation of a white (**3**, **5**, **7**) or dark green (**4**, **6**, **8**) solid, which was collected by filtration and air dried. Alternatively, **3** and **4** were prepared by addition of $MeCONH_2$ (0.230 mmol) to a solution of **1** or **2** (0.115 mmol) in CH_2Cl_2 (5 cm^3). After stirring at room temperature for 30 min the solution was concentrated under reduced pressure and addition of hexane caused the precipitation of a solid, which was collected by filtration, washed with water and air dried (75–80% yield). Complex **3**: yield 80% (Found: C, 44.5; H, 5.6; N, 9.5. $C_{11}H_{16}N_2OPd$ requires C, 44.3; H, 5.4; N, 9.4%), mp 197 °C (decomp.); IR (Nujol, cm^{-1}) 3340, 3300 (ν(NH)), 1570 (ν(C=O)). Complex **4**: yield 70% (Found: C, 48.2; H, 3.6; N, 11.9. $C_{14}H_{13}N_3OPd$ requires C, 48.6; H, 3.8; N, 12.2%), mp 201 °C (decomp.); IR (Nujol, cm^{-1}) 3380, 3295 (ν(NH)), 1570 (ν(C=O)). Complex **5**: yield 60% (Found: C, 53.1; H, 4.9; N, 8.0. $C_{16}H_{18}N_2OPd$ requires C, 53.3; H, 5.0; N, 7.8%), mp 215 °C (decomp.); IR (Nujol, cm^{-1}) 3390, 3370 (ν(NH)), 1600 (ν(C=O)). Complex **6**: yield 65% (Found: C, 55.2; H, 3.9; N, 10.0. $C_{19}H_{18}N_3OPd$ requires C, 56.0; H, 3.7; N, 10.3%), mp 251 °C (decomp.); IR (Nujol, cm^{-1}) 3340 (ν(NH)), 1570

‡ When a mixture of benzonitrile (0.714 mol) and $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (0.074 mol) was boiled under reflux in benzene (12 ml) for 2 h the solid recovered by precipitation with hexane was identified as unchanged $[NBu_4]_2[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (0.043 mol).

Table 5 Crystal data and structure refinement for complexes **5** and **13**

	5	**13**
Formula	$C_{32}H_{36}N_4O_2Pd_2$	$C_{18}H_{14}F_{10}N_2O_2Pd$
Formula weight	721.5	584.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (non-standard no. 14)
a/Å	15.487(2)	9.243(3)
b/Å	10.811(4)	14.634(6)
c/Å	18.249(3)	15.865(3)
β/°	91.540(10)	94.71(2)
V/Å^3	3054.3(13)	2138.7(12)
Z	4	4
T/K	293	293
Reflections collected	9161	6541
μ/mm^{-1}	1.21	0.97
Independent reflections	8875 [R(int) = 0.0250]	6204 [R(int) = 0.0219]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.040, 0.088	0.047, 0.101
(all data)	0.070, 0.103	0.089, 0.121

(ν(C=O)); ^{1}H NMR ($CDCl_3$) δ 7.6–6.6 (m, 28 H, aromatics) and 5.91 (s, 2 H, NH). Complex **7**: yield 69% (Found: C, 46.3; H, 5.0; N, 9.0. $C_{12}H_{16}N_2OPd$ requires C, 46.4; H, 5.2; N, 9.0%); mp 173 °C (decomp.); IR (Nujol, cm^{-1}) 3360, 3305 (ν(NH)), 1640 (ν(C=C)), 1565 (ν(C=O)). Complex **8**: yield 65% (Found: C, 50.2; H, 3.6; N, 11.6. $C_{15}H_{13}N_3OPd$ requires C, 50.4; H, 3.7; N, 11.7%), mp 194 °C (decomp.); IR (Nujol, cm^{-1}) 3270 (ν(NH)), 1635 (ν(C=C)), 1560 (ν(C=O)).

Complexes 9 and 10. To a suspension of complex **1** or **2** (0.116 mmol) in benzene (5 cm^3) was added succinonitrile (1.164 mmol). The solution was boiled under reflux for 3 h, and then concentrated to dryness under reduced pressure. Addition of acetone–water (**9**) or MeOH (**10**) yielded a white (**9**) or red (**10**) solid which was collected by filtration and air dried. Complex **9**: yield 73% (Found: C, 44.4; H, 4.9; N, 9.5. $C_{13}H_{18}N_3O_2Pd$ requires C, 44.4; H, 5.1; N, 9.4%), mp 275 °C (decomp.); IR (Nujol, cm^{-1}) 3355, 3250 (ν(NH)), 1580 (ν(C=O)). Complex **10**: yield 43% (Found: C, 48.6; H, 3.6; N, 12.3. $C_{16}H_{15}N_4O_2Pd$ requires C, 48.8; H, 3.5; N, 12.2%), mp 275 °C (decomp.); IR (Nujol, cm^{-1}) 3250 (ν(NH)), 1560 (ν(C=O)).

Complexes 11–18. The appropriate nitrile RCN (benzonitrile or acetonitrile, 7.14 mmol; 2-cyanopyridine or succinonitrile, 0.1428 mmol) was added to a solution of $[NBu_4][(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (0.1 g, 0.0714 mmol) in methanol or ethanol (8 mL). The solution was stirred at room temperature for 2 h. After addition of dichloromethane (15 mL) the solution was chromatographed on Florisil and the resulting solution was concentrated under vacuum. On addition of water the white complexes **11**–**18** precipitated, were collected by filtration, and air-dried. Complex **11**: yield 79% (Found: C, 47.7; H, 2.4; N, 4.0. $C_{28}H_{18}F_{10}N_2O_2Pd$ requires C, 47.3; H, 2.6; N, 3.9%), mp 180 °C (decomp.); IR (Nujol, cm^{-1}) 3355 (ν(NH)), 1640 (ν(C=N)), 800, 780 (Pd–C_6F_5). Complex **12**: yield 76% (Found: C, 48.7; H, 2.9; N, 3.8. $C_{30}H_{22}F_{10}N_2O_2Pd$ requires C, 48.8; H, 3.0; N, 3.8%), mp 180 °C (decomp.); IR (Nujol, cm^{-1}) 3360 (ν(NH)), 1630 (ν(C=N)), 795, 780 (Pd–C_6F_5). Complex **13**: yield 75% (Found: C, 37.0; H, 2.3; N, 4.9. $C_{18}H_{14}F_{10}N_2O_2Pd$ requires C, 36.9; H, 2.4; N, 4.8%), mp 168 °C (decomp.); IR (Nujol, cm^{-1}) 3370 (ν(NH)), 1650 (ν(C=N)), 790, 780 (Pd–C_6F_5). Complex **14**: yield 72% (Found: C, 39.3; H, 2.8; N, 4.7. $C_{20}H_{18}F_{10}N_2O_2Pd$ requires C, 39.1; H, 3.0; N, 4.6%), mp 186 °C (decomp.); IR (Nujol, cm^{-1}) 3360 (ν(NH)), 1650 (ν(C=N)), 795, 785 (Pd–C_6F_5). Complex **15**: yield 90% (Found: C, 39.5; H, 1.3; N, 4.8. $C_{19}H_8F_{10}N_2O_2Pd$ requires C, 39.6; H, 1.4; N, 4.9%), mp 252 °C (decomp.); IR (Nujol, cm^{-1}) 3370 (ν(NH)), 1645 (ν(C=N)), 795, 785 (Pd–C_6F_5). Complex **16**: yield 57% (Found: C, 40.9; H, 1.8; N, 4.7. $C_{20}H_{10}F_{10}N_2O_2Pd$ requires C, 40.7; H, 1.7; N, 4.7%), mp 263 °C (decomp.); IR (Nujol, cm^{-1}) 3395 (ν(NH)), 1645 (ν(C=N)), 795, 785 (Pd–C_6F_5). Complex **17**: yield 89% (Found: C, 37.0; H, 1.9; N, 4.7. $C_{18}H_{12}F_{10}N_2O_2Pd$ requires C, 37.0; H, 2.1; N, 4.8%), mp 213 °C (decomp.); IR (Nujol, cm^{-1}) 3365 (ν(NH)), 1665 (ν(C=N)), 795, 780 (Pd–C_6F_5). Complex **18**: yield 73% (Found: C, 39.4; H, 3.0; N, 4.7. $C_{20}H_{16}F_{10}N_2O_2Pd$ requires C, 39.2; H, 2.6; N, 4.6%), mp 208 °C (decomp.); IR (Nujol, cm^{-1}) 3380, 3340 (ν(NH)), 1660 (ν(C=N)), 790, 780 (Pd–C_6F_5).

Reaction of $[Pd(C_6F_5)_2(NCPh)_2]$ with NaOMe. To a solution of $[Pd(C_6F_5)_2(NCPh)_2]$ (100 mg, 0.155 mmol) in MeOH (8 mL) was added Na[OMe] (83.7 mg, 1.55 mmol). The resulting solution was stirred at room temperature for 4 h and concentrated under vacuum. The addition of water caused the precipitation of a white solid which was collected by filtration, washed with water and hexane, air-dried, and characterized as complex **11** (yield 59%).

Complex 19. 2-Cyanopyridine (14.87 mg, 0.1428 mmol) was added to a solution of $[NBu_4][(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (0.1 g, 0.0714 mmol) in acetone (8 mL). The solution was stirred at room temperature. The solution was concentrated under vacuum to dryness. The residue was then treated with diethyl ether (6 mL) and the yellow complex was collected by filtration and air-dried. Yield 94% (Found: C, 50.9; H, 5.0; N, 5.1. $C_{34}H_{41}F_{10}N_2O_2Pd$ requires C, 50.8; H, 5.1; N, 5.2%), mp 267 °C (decomp.); IR (Nujol, cm^{-1}) 3225 (ν(NH)), 1630 (ν(C=O)), 795, 780 (Pd–C_6F_5).

Crystallography

Crystals of complexes **5** and **13** suitable for diffraction studies were grown from dichloromethane–hexane. Single crystals of **5** (approximate dimensions 0.35 × 0.20 × 0.20) and **13** (0.25 × 0.25 × 0.10) were mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator for Mo-Kα radiation. Details of data collection and refinement are given in Table 5.

Accurate cell parameters were determined by least-squares fitting of 25 high-angle reflections. Empirical Ψ scans absorption correction was made for complex **13**. The structures were refined by the full-matrix least-squares technique. For **5** all non-H atoms were refined anisotropically. The H atoms were included in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. For **13** all non-H atoms were refined anisotropically, methyl groups were fixed at idealized geometry but with the torsion angle defining the H atom positions refined and $U_{iso}(H) = 1.2U_{eq}(C)$.

The largest difference peak and hole were 0.41 and −0.96 e Å^{-3} for complex **5**; in the case of **13** they were 0.74 and −0.50 e Å^{-3}.

Programs used were Enraf-Nonius CAD 4 software for data collection,[57] SHELXS 86 for structure solution,[58] SHELXL 93 for structure refinement,[59] and CAMERON for interactive graphics and final drawings.[60]

CCDC reference number 186/1574.

See http://www.rsc.org/suppdata/dt/1999/2939/ for crystallographic files in .cif format.

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