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Synthesis and reactivity of $[Pd(\widehat{C\,N})(C_6F_5)(NCMe)]$ ($\widehat{C\,N}$ = dimethylbenzylamine-C^2,N; 8-quinolylmethyl-C,N). Crystal structure of $(NBu_4)[\{Pd(8\text{-quinolylmethyl-}C,N)(C_6F_5)\}_2(\mu\text{-Cl})]$

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Abstract

The reaction between $[Pd(\widehat{C\,N})(THF)_2]ClO_4$ (THF = tetrahydrofuran; $\widehat{C\,N}$ = dimethylbenzylamine-C^2,N, dmba; 8-quinolylmethyl-C,N, 8-mq) and $(NBu_4)_2[M(C_6F_5)_4]$ (M = Pd, Pt) in the presence of L (L = NCMe, PPh_3, $PPhMe_2$) gave the neutral derivatives $[Pd(\widehat{C\,N})(C_6F_5)L]$, whereas reaction of $[Pd(\widehat{C\,N})(NCMe)_2]ClO_4$ with $(NBu_4)_2[M(C_6F_5)_4]$ (M = Pd, Pt), gave the corresponding species $[Pd(\widehat{C\,N})(C_6F_5)(NCMe)]$ ($\widehat{C\,N}$ = dmba (**1**), 8-mq (**6**)). **1** and **6** reacted with phosphines to yield $[Pd(\widehat{C\,N})(C_6F_5)(PR_3)]$ ($PR_3 = PPh_3$ (**2**, **7**); $PPhMe_2$, $\widehat{C\,N}$ = dmba (**3**)), and with $(NBu_4)Br$ to yield $(NBu_4)[Pd(\widehat{C\,N})(C_6F_5)X]$ (X = Br, $\widehat{C\,N}$ = dmba (**4**), 8-mq (**8**); and **9** (X = Cl, $\widehat{C\,N}$ = 8-mq) was obtained by treatment of **8** with AgCl. The binuclear derivatives with a single bridging halide ligand $(NBu_4)[\{Pd(\widehat{C\,N})(C_6F_5)\}_2(\mu\text{-}X)]$ (X = Br, $\widehat{C\,N}$ = dmba (**5**), 8-mq (**10**); X = Cl, $\widehat{C\,N}$ = 8-mq (**11**)) were obtained by reacting **1** or **6** with **4**, **8** or **9**, respectively.

The molecular structure of **11** was established by a single crystal X-ray study.

Introduction

We have recently reported the synthesis of $[Pd(\widehat{C\,N})S_2]ClO_4$ ($\widehat{C\,N}$ = dimethylbenzylamine-C^2,N, dmba; 8-quinolylmethyl-C,N, 8-mq; S = THF (tetrahydrofuran), $OCMe_2$ or NCMe) and explored their use as intermediates for the synthesis of other $\widehat{C\,N}$-cyclopalladated complexes arising from the lability of the neutral S ligand [1,2].

Since the reactions between $M(C_6F_5)_2S_2$ (S = THF) and $(NBu_4)_2[M'(C_6F_5)_4]$ (M = Pd, Pt; M' = Pd, Pt) yield binuclear homo- or hetero-bimetallic complexes $(NBu_4)_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ [3], the first derivatives containing bridging C_6F_5 groups, we decided to explore the reactions between $[Pd(\widehat{C\,N})S_2]ClO_4$ and

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$(NBu_4)_2[M(C_6F_5)_4]$ (M = Pd, Pt) in an attempt to synthesize new binuclear asymmetric complexes containing bridging C_6F_5 groups. However such reactions did not afford the expected binuclear complexes, since the anionic substrate $(NBu_4)_2[M(C_6F_5)_4]$ acts as an arylating agent and mononuclear neutral complexes of the type $[Pd(\widehat{C\,N})(C_6F_5)(S)]$ are obtained instead. Their reactions are also described below.

Results and discussion

Reaction between $[Pd(\widehat{C\,N})(THF)_2]ClO_4$ *and* $(NBu_4)_2[Pt(C_6F_5)_4]$

The reaction between $[Pd(dmba)(THF)_2]ClO_4$ and $(NBu_4)_2[Pt(C_6F_5)_4]$ (molar ratio 1/1) in $CHCl_3$ at $-30\,^\circ C$ for 15 min yielded a yellow solution, which when evaporated to dryness left only oily residues. The ^{19}F NMR spectrum of a $CH_2Cl_2/CDCl_3$ solution of the oil at $-50\,^\circ C$ in the region of resonances for *o*-F atoms showed no signals corresponding to bridging C_6F_5 groups [3] indicating that only terminal C_6F_5 groups are present in the mixture. However, two of the signals corresponding to *ortho*-fluorenes show platinum satellites while the other does not. This indicates that at least one of the C_6F_5 groups is bonded to palladium and thus the $(NBu_4)_2[Pt(C_6F_5)_4]$ has acted as an arylating agent. When the reaction was carried out with $[Pd(8\text{-}mq)(THF)_2]ClO_4$ as starting material or when $(NBu_4)_2[Pd(C_6F_5)_4]$ was used as a source of C_6F_5 groups only oily residues were obtained. However, the ^{19}F NMR spectra of $CH_2Cl_2/CDCl_3$ solutions of these residues indicate that no bridging C_6F_5 groups are present, pointing to a similar behaviour to that described above.

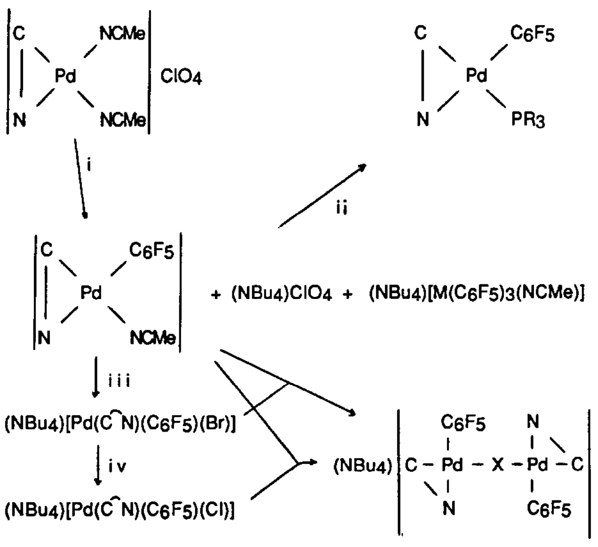
All these reactions probably take place according to eq. 1, the very high solubility of the tetrahydrofuran complexes preventing their isolation.

$$\begin{aligned}\left[Pd(\widehat{C\,N})(THF)_2\right]ClO_4 + (NBu_4)_2\left[M(C_6F_5)_4\right] \rightarrow \\ \left[Pd(\widehat{C\,N})(C_6F_5)(THF)\right] + (NBu_4)\left[M(C_6F_5)_3(THF)\right] \\ + (NBu_4)ClO_4 \qquad (1)\end{aligned}$$

In order to ascertain whether this was a valid assumption we carried out similar reactions but adding a neutral ligand such as NCMe or phosphines at the end of the reactions, since displacement of the THF ligand is to be expected and less soluble products could be formed. All the reactions examined gave a mixture of $[Pd(\widehat{C\,N})(C_6F_5)L]$, $(NBu_4)[Pt(C_6F_5)_3L]$ and $(NBu_4)ClO_4$ ($\widehat{C\,N}$ = dmba, L = NCMe (**1**), PPh_3 (**2**), $PPhMe_2$ (**3**)), in keeping with eq. 1, and these products were readily separated because of their different solubilities. Details of these reactions are given in the Experimental section. Finally it should be mentioned that if $(NBu_4)_2[Pd(C_6F_5)_4]$ is used as arylating agent, slight decomposition to metallic palladium takes place during procedures at room temperature.

Synthesis and reactions of $[Pd(\widehat{C\,N})(C_6F_5)(NCMe)]$

Reactions pertinent to $[Pd(\widehat{C\,N})(C_6F_5)(NCMe)]$ are collected in Scheme 1. As was expected $[Pd(\widehat{C\,N})(C_6F_5)(NCMe)]$ ($\widehat{C\,N}$ = dmba (**1**), 8-mq (**6**)) were also obtained by treating $[Pd(\widehat{C\,N})(NCMe)_2]ClO_4$ with $(NBu_4)_2[Pt(C_6F_5)_4]$ (molar ratio 1/1) in CH_2Cl_2 at room temperature, and the phosphino complexes were readily obtained from **1** or **6** by displacement reactions.



i) (NBu4)2[M(C6F5)4], CH2Cl2 (M= Pd, Pt). ii) PR3= PPh3, PPhMe2
iii) (NBu4)Br iv) AgCl

Scheme 1

Alternatively complexes **1** and **6** can be used as starting materials for the preparation of other mono- or dimeric anionic complexes (Scheme 1). Thus treatment of a CH_2Cl_2 solution of [Pd($\overset{\frown}{\mathrm{C\,N}}$)($C_6F_5$)(NCMe)] with ($NBu_4$)Br results in the displacement of NCMe and formation of the anionic complexes (NBu_4)[Pd($\overset{\frown}{\mathrm{C\,N}}$)($C_6F_5$)Br] ($\overset{\frown}{\mathrm{C\,N}}$ = dmba (**4**), 8-mq (**8**)). Reaction of **8** in CH_2Cl_2 with AgCl for 6 d gave (NBu_4)[Pd($\overset{\frown}{\mathrm{C\,N}}$)($C_6F_5$)Cl] (**9**) (85% yield).

The lability of NCMe in **1** or **6** can be exploited in the synthesis of binuclear palladium complexes bridged only by a single halide, since the reaction between **1** or **6** with (NBu_4)[Pd($\overset{\frown}{\mathrm{C\,N}}$)($C_6F_5$)X] gives ($NBu_4$)[{Pd($\overset{\frown}{\mathrm{C\,N}}$)($C_6F_5$)}$_2$($\mu$-X)] ($\overset{\frown}{\mathrm{C\,N}}$ = dmba, X = Br (**5**); $\overset{\frown}{\mathrm{C\,N}}$ = 8-mq, X = Br (**10**), Cl (**11**)). The proposed structure for **5**, **10** and **11** was confirmed by an X-ray study on complex **11** and is discussed later. Such binuclear complexes possessing a single unsupported halide bridge are rather scarce and the only authenticated examples are $[(N{-}C{-}N)M'(\mu\text{-}X)M(N{-}C{-}N)]^+$ (N–C–N = o,o'-$(Me_2NCH_2)_2C_6H_3$; M, M′ = Pd or Pt; X = halide) [4,5]. The more recently described $[(C_6X_5)_2M(\mu\text{-}X)_2M'(COD)]_n$ (M, M′ = Pd, Pt; X = F, Cl; X′ = Cl, Br, I) [6] displays a very peculiar behaviour since in solution (as indicated by molecular weight determinations) they are binuclear, with a double bridge between both metallic centres, while the X-ray diffraction structure reveals that in solid they are tetranuclear, forming an eight-membered ring with single halide bridges. Analytical data and conductivities are listed in Table 1.

IR spectra

Characteristic absorptions assignable to the C_6F_5 group [7] are observed for all the complexes (1060–1050s, 950–940 vs, 800–750s cm^{-1}).

Table 1

Analyses [a] and conductivities [b]

Complex		C	H	N	Λ_M [c]
[Pd(dmba)(C_6F_5)(NCMe)]	(**1**)	44.9 (45.50)	3.61 (3.37)	5.70 (6.24)	n.c.
[Pd(dmba)(C_6F_5)(PPh_3)]	(**2**)	59.17 (59.16)	4.19 (4.06)	2.13 (2.09)	n.c.
[Pd(dmba)(C_6F_5)($PPhMe_2$)]	(**3**)	50.02 (50.61)	4.64 (4.24)	2.39 (2.56)	n.c.
(NBu_4)[Pd(dmba)(C_6F_5)(Br)]	(**4**)	50.63 (51.00)	6.90 (6.63)	3.80 (3.83)	117
(NBu_4)[{Pd(dmba)(C_6F_5)}$_2$(μ-Br)]	(**5**)	48.94 (48.56)	5.84 (5.32)	3.44 (3.69)	122
[Pd(8-mq)(C_6F_5)(NCMe)]	(**6**)	47.27 (47.34)	2.75 (2.43)	6.04 (6.13)	n.c.
[Pd(8-mq)(C_6F_5)(PPh_3)]	(**7**)	60.28 (60.24)	3.75 (3.42)	1.95 (2.06)	n.c.
(NBu_4)[Pd(8-mq)(C_6F_5)(Br)]	(**8**)	52.56 (52.08)	6.33 (6.00)	4.09 (3.79)	138
(NBu_4)[Pd(8-mq)(C_6F_5)(Cl)]	(**9**)	54.76 (55.42)	6.72 (6.39)	3.97 (4.04)	100
(NBu_4)[{Pd(8-mq)(C_6F_5)}$_2$(μ-Br)]	(**10**)	49.47 (49.97)	4.59 (4.54)	3.64 (3.64)	90
(NBu_4)[{Pd(8-mq)(C_6F_5)}$_2$(μ-Cl)]	(**11**)	51.19 (51.98)	4.95 (4.72)	3.68 (3.78)	97

[a] Calculated values in parentheses. [b] ohm^{-1} cm^2 mol^{-1}; in 5×10^{-4} mol dm^{-3}; acetone solution. [c] n.c. = Non conducting.

The dimethylbenzylamine-*C*^{2},*N* (dmba) derivatives (**1**–**5**) show absorptions at 870–865s, 850–845m and 745–735s cm^{-1}, assignable to this ligand. The 8-quinolylmethyl-*C*,*N* (8-mq) derivatives (**6**–**11**) show characteristic absorptions at 830–815s and 790–780s cm^{-1}. The IR spectra of the anionic derivatives (**4**, **5**, **8**–**11**) show a broad band at 880 cm^{-1} assignable to the NBu_4^+ counter ion.

The IR spectra of complexes **1** and **6** display two absorptions in the ν(C≡N) region, shifted to higher energies than those for the free ligand, MeCN: 2254, 2290 [8]; **1**: 2314m, 2284m; **6**: 2304m, 2280m cm^{-1}, implying the usual N-coordination of acetonitrile [9,10]. Characteristic absorptions assignable to internal vibrations of the respective phosphines were observed in the IR spectra of the following complexes: **2**: 526s, 507s, 490s; **7**: 522s, 505s, 492s (PPh_3); **3**: 485m cm^{-1} ($PPhMe_2$).

Complex **9** shows a single band at 275m cm^{-1} assignable to ν(Pd–Cl); **11** displays two absorptions at 280 and 240 cm^{-1} which may be due to ν(Pd–Cl), but an unequivocal assignment could not be made since the 8-mq ligand gives a band in this region.

NMR spectra

^{1}H NMR data, which are listed in Table 2, are in accord with the proposed stoichiometries. For [Pd(dmba)$(NCMe)_2$]ClO_4 the signals due to aromatic protons of the dmba ligand appear as a complex multiplet in the range 7.3–6.8 ppm, while for complexes **1**–**5**, one signal (6.40–6.33 ppm) stands out from the complex multiplet; this signal can be assigned to the *ortho*-H atom of the σ-C–metal bond,

Table 2

^{1}H NMR data

Complex	δ (ppm); J (Hz) [a]
1	6.40(d), 7.00–6.70(m) (4H, C_6H_4); 3.90(s) (2H, CH_2); 2.76(s) (6H, $N(CH_3)_2$); 2.15(s) (3H, $NCCH_3$)
2	6.44(t), 6.92(m) (4H, C_6H_4); 3.98(s) (2H, CH_2); 2.24(s) (6H, $N(CH_3)_2$); 7.34(m), 7.60(m) (15H, PPh_3)
3	6.44(t), 6.90(m) (4H, C_6H_4); 3.90(s) (2H, CH_2); 2.41(s) (6H, $N(CH_3)_2$); 7.45(m), 7.70(m) (5H, C_6H_5); 1.32(d) (6H, CH_3), ^2J(P–H) = 7.1 Hz
4	6.33(d), 6.68(t), 6.84–6.90(m) (4H, C_6H_4); 3.85(s) (2H, CH_2); 2.81(s) (6H, $N(CH_3)_2$); 0.95(t), 1.39(q), 1.56(m), 3.10(m) (36H, NBu_4)
5	6.35(d), 6.70(t), 6.9)(m) (4H, C_6H_4); 3.84(s) (2H, CH_2); 2.83(s) (6H, $N(CH_3)_2$); 0.95(t), 1.35(q), 1.57(m), 3.07(m) (36H, NBu_4)
6	7.63–7.85(m), 8.65(d) (6H, C_9H_6); 3.19(s) (2H, CH_2); 2.15(s) (6H, $N(CH_3)_2$) [b]
7	6.89(m), 7.97(m), 8.15(d) (6H, C_9H_6); 7.34–7.57(m) (15H, PPh_3); 3.19(d) (2H, CH_2), ^3J(P–H) = 9.1 Hz
8	7.20–7.60(m), 8.15(d) (6H, C_9H_6); 3.13(s) (2H, CH_2); 0.91(t), 1.35(q), 1.60(m), 3.21(m) (36H, NBu_4)
9	7.20–7.60(m), 8.15(d) (6H, C_9H_6), 3.10(s) (2H, CH_2); 0.91(t), 1.35(q), 1.60(m), 3.21(m) (36H, NBu_4)
10	7.30–7.50(m), 8.15(d) (6H, C_9H_6); 3.20(s) (2H, CH_2); 0.81(t), 1.24(q), 1.46(m), 3.00(m) (36H, NBu_4)
11	7.30–7.50(m), 8.04(d) (6H, C_9H_6); 3.20 (2H, CH_2); 0.79(t), 1.23(q), 1.46(m), 3.00(m) (36H, NBu_4)

[a] Solvent $CDCl_3$. [b] Solvent HDA.

and the upfield shift may be a consequence of the anisotropic effect of the C_6F_5 group, thus indicating that the Pd–C bonds are in *cis* positions. On the other hand the methylenic protons for complexes **6**, **8–11**, appear as a singlet, while for complex

Table 3

^{19}F [a] and ^{31}P{^{1}H} [b] NMR data

Complex	o-F	m-F		p-F	P(PR$_3$)
1	−115.1(d)	−164.8(t)		−163.7(t)	
2	−115.3(d)		−165.0(m)		19.2(s)
3	−114.9(d)	−164.1(t)		−163.2(t)	−13.9(s)
4	−111.8(d)	−166.1(t)		−166.7(t)	
5	−112.6(d)		−166.0(m)		
6	−112.3(d)	−164.3(m)		−163.2(m) [c]	
7	−115.6(d)		−165.8(m)		21.7(s)
8	−112.6(d)		−166.5(m)		
9	−112.7(m)		−166.3(m)		
10	−113.1(d)	−166.1(m)		−165.5(t)	
11	−113.3(m)	−166.2(m)		−165.5(t)	

[a] δ referenced to $CFCl_3$, solvent $CDCl_3$. [b] δ referenced to H_3PO_4, solvent $CDCl_3$. [c] Solvent HDA.

7 the corresponding signal appears as a doublet due to coupling with the P atom of the PPh$_3$ ligand (^3J(P–H) = 9.1 Hz). The value of the coupling constant indicates that the PPh$_3$ ligand is located *trans* to the CH$_2$ groups, i.e. that the Pd–C bonds in **8** are *cis* to each other, since 8-mq derivatives of palladium(II) containing phosphines *cis* to the CH$_2$ group display ^3J(P–H) values in the range 2–4 Hz [11,12,13].

The crystal structure of **11** confirms that the Pd–C bonds are mutually *cis*. From all these data it seems sensible to assume that the arylation of $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\ N}})(\mathrm{L})_2]^+$ with $[\mathrm{M}(\mathrm{C_6F_5})_4]^{2-}$ yields complexes with both aryl groups in *cis*-positions.

Table 3 lists ^{19}F and ^{31}P{^{1}H} NMR data for these complexes. The ^{19}F NMR spectra show three sets of signals (for complexes **2**, **5**, **7**, **8**, **9** signals corresponding to *m*-F and *p*-F are overlapped), in agreement with the presence of one C$_6$F$_5$ group (mononuclear derivatives) or two equivalent C$_6$F$_5$ groups (dinuclear derivatives).

Table 4

Crystal data and experimental details of the crystallographic study of **11**

Formula	$C_{48}H_{52}N_3F_{10}ClPd_2 \cdot 0.38CH_2Cl_2$
M	1109.19
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	12.423(2)
b (Å)	13.843(3)
c (Å)	15.372(3)
α (°)	89.926(17)
β (°)	80.064(14)
γ (°)	69.706(15)
V (Å^3)	2437.33
Diffractometer	Enraf–Nonius CAD 4
T (K)	293 ± 1
Radiation	Mo-K_α
λ (Å)	0.71069
μ (Mo-K_α) (cm^{-1})	9.17 (Absorption correction was not applied)
θ-range (°)	1–22°
Mode	θ–2θ scans
Data measured	7777
Data used	5429 ($F \geq 6\sigma(F)^2$) having excluded 24 low-angle reflections suspected of suffering from secondary extinction.
Solution	Direct methods, ΔF syntheses
Refinement	Full-matrix least squares
Model	All atoms anisotropic. H atoms non resolved. Disordered molecule of CH$_2$Cl$_2$ around a symmetry centre (multiplicity 0.38)
Weighting schemes	$w^{-1} = \sigma^2(F) + 0.005156(F)^2$
R_w	0.0536
R	0.0463
Variables	604
Largest shift/esd, final cycle	0.02
Largest peak, e/Å^3	0.81

Structure of $(NBu_4)[\{Pd(8\text{-}mq)(C_6F_5)\}_2(\mu\text{-}Cl)]$ *(11)*

Details of the crystallographic procedures are given in Table 4. Atomic coordinates are listed in Table 5. The structure of the anion in **11** is depicted in Fig. 1. Bond distances and bond angles are listed in Table 6.

The anionic complex consists of two "$Pd(\overset{\frown}{C\ N})(C_6F_5)$" moieties sharing a single bridging chloride ligand. Both Pd^{II} centres display a distorted square-planar environment formed by one C_6F_5 and one μ-Cl group and the 8-quinolylmethyl-*C,N* ligand. The dihedral angle between the planes Cl(1)–Pd(1)–C(21) and N(1)–Pd(1)–C(1) is 4.1(2)°, and that between the planes Cl(1)–Pd(2)–C(27) and C(11)–Pd(2)–N(2) is 7.6(2)°. The angles formed by the *cis* bonds are listed in Table 6; the small bite angle of the chelating ligands makes the corresponding angles smaller than 90° (C(1)–Pd(1)–N(1) 84.7(3) and C(11)–Pd(2)–N(2) 83.6(2)°).

The Pd–C bonds are *cis* to each other and the Pd–C distances are not significantly different from each other. Similar $Pd{-}C(C_6F_5)$ [14] and Pd–C(quinolyl) [15,16] distances have been reported previously. The structural parameters involving the Pd(8-mq) moieties are similar to those for other complexes containing this fragment [15,16]. The Pd–Cl distances (2.475(1) and 2.468(1) Å) are longer than the corresponding Pd–Cl distances in the binuclear palladium derivative containing a single halide bridge $[(L)Pd(\mu\text{-}Cl)(Pd(L)]BF_4$ [$L = o,o'\text{-}(Me_2NCH_2)_2C_6H_3$ (2.463(1) and 2.458(1) Å) [5], although shorter than the distances in $\{[Pd(8\text{-}mq)]_3(\mu_3\text{-}Mo(CO)_3(Cp)(\mu_3\text{-}Cl)\}BF_4$ (2.520(2), 2.525(2) Å) [16]. The Pd(1)–Cl–Pd(2) angle is 130.0(1)° and the Pd ··· Pd distance is 4.479(1) Å, so any M–M interaction is ruled out.

Finally the dihedral angle formed by the two virtually equivalent coordination planes on each palladium centres is 69.85(8)° and the two C_6F_5 groups are in a transoidal conformation.

Experimental

C, H and N analyses, infrared spectra, ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra and conductance data were obtained as described previously [2]. Complexes $[Pd_2(\mu\text{-}Cl)_2(dmba)_2]$ [17], $[Pd_2(\mu\text{-}Cl)_2(mq)_2]$ [18] and $(NBu_4)_2[M(C_6F_5)_4]$ (M = Pd, Pt) [19] were prepared as described previously. The synthesis of **1** and **6** requires use of a N_2 atmosphere.

$[Pd(\overset{\frown}{C\ N})(C_6F_5)(NCMe)]$ *(*$\overset{\frown}{C\ N}$ *= dmba (1), 8-mq (6))*

(a) To a solution of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (0.100 g, 0.181 mmol) in THF (20 ml), was added $AgClO_4$ (0.075 g, 0.362 mmol). The mixture was stirred at room temperature for 1 h then the AgCl was filtered off and the filtrate evaporated to dryness. The residue was extracted with $CHCl_3$ (8 ml) and the solution obtained was treated with $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.487 g, 0.362 mmol) to give a deep yellow-orange solution, which was stirred at room temperature for 15 min and then evaporated to dryness. The residue was extracted with NCMe (15 ml), and the extract concentrated to ≈ 1 ml. Addition of Et_2O (30 ml) to the oily residue gave a white solid (a mixture of $(NBu_4)ClO_4$ and $(NBu_4)[(Pt(C_6F_5)_3(NCMe)]$ [20*]). Concentration of the solution to ca. 3 ml gave **1** in 62% yield.

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* Reference number with asterisk indicates a note in the list of references.

Table 5

Atom coordinates for **11**

Atom	*x*	*y*	*z*
Pd1	5050(1)	3768(1)	2851(1)
Pd2	8687(1)	1494(1)	2645(1)
Cl1	6964(1)	2584(1)	2059(1)
N1	5732(4)	4774(3)	3359(3)
N2	7843(4)	575(3)	3323(3)
C1	3477(6)	4803(5)	3433(6)
C2	3748(6)	5586(5)	3972(5)
C3	2901(7)	6349(6)	4533(6)
C4	3190(10)	7078(7)	5041(6)
C5	4332(8)	7056(6)	4925(5)
C6	5199(7)	6284(5)	4384(5)
C7	4896(6)	5559(5)	3901(4)
C8	6843(6)	4690(6)	3264(5)
C9	7212(7)	5388(6)	3714(6)
C10	6398(8)	6183(6)	4241(5)
C11	10109(5)	484(5)	3017(5)
C12	9723(5)	−213(4)	3649(4)
C13	10469(7)	−893(5)	4142(5)
C14	10020(9)	−1497(5)	4743(5)
C15	8912(8)	−1453(6)	4868(5)
C16	8116(7)	−757(5)	4368(5)
C17	8565(6)	−146(4)	3784(4)
C18	6716(6)	696(5)	3403(5)
C19	6239(7)	68(6)	3980(5)
C20	6913(8)	−620(6)	4447(5)
C21	4237(4)	2873(4)	2446(4)
C22	4168(5)	2760(5)	1551(4)
C23	3746(6)	2083(5)	1232(4)
C24	3334(6)	1479(5)	1801(5)
C25	3347(5)	1556(5)	2669(5)
C26	3791(5)	2240(5)	2962(4)
C27	9660(5)	2324(5)	2128(5)
C28	9937(5)	2974(5)	2635(5)
C29	10538(6)	3613(5)	2307(6)
C30	10891(6)	3567(7)	1406(6)
C31	10659(6)	2917(7)	866(5)
C32	10047(5)	2324(5)	1236(4)
F1	4587(3)	3334(3)	961(2)
F2	3751(4)	1988(4)	350(3)
F3	2907(4)	778(4)	1477(4)
F4	2930(4)	976(3)	3220(3)
F5	3782(4)	2274(3)	3854(3)
F6	9602(4)	3067(3)	3526(3)
F7	10775(5)	4250(4)	2836(4)
F8	11483(5)	4186(5)	1071(4)
F9	11004(5)	2909(5)	−15(3)
F10	9823(4)	1710(4)	667(3)
N3	12570(5)	7476(4)	995(3)
C33	12796(6)	6710(5)	222(5)
C34	13141(8)	5600(6)	381(6)
C35	13299(8)	4979(6)	−509(6)
C36	12266(9)	5043(8)	−927(7)

Table 5 (continued)

Atom	*x*	*y*	*z*
C37	13785(7)	7262(6)	1277(5)
C38	13738(10)	8023(8)	1995(7)
C39	15088(10)	7722(8)	2137(8)
C40	15162(10)	8451(10)	2832(9)
C41	12136(6)	8548(5)	660(5)
C42	13005(6)	8843(5)	−2(5)
C43	12371(8)	9856(6)	−381(6)
C44	13243(11)	10203(8)	−1043(8)
C45	11716(7)	7363(7)	1749(6)
C46	10564(7)	7463(8)	1602(6)
C47	9886(10)	7161(9)	2462(7)
C48	8702(10)	7215(12)	2355(9)
C49	445(27)	5146(23)	4885(21)
Cl2	353(12)	4040(8)	5399(9)
Cl3	−1000(9)	5944(9)	5004(10)

(b) $[Pd(dmba)(NCMe)_2]ClO_4$ (0.300 g, 0.710 mmol) was added to a CH_2Cl_2 (15 ml) solution of $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.958 g, 0.710 mmol) and the yellowish solution was stirred at room temperature for 5 h and then evaporated to dryness. The

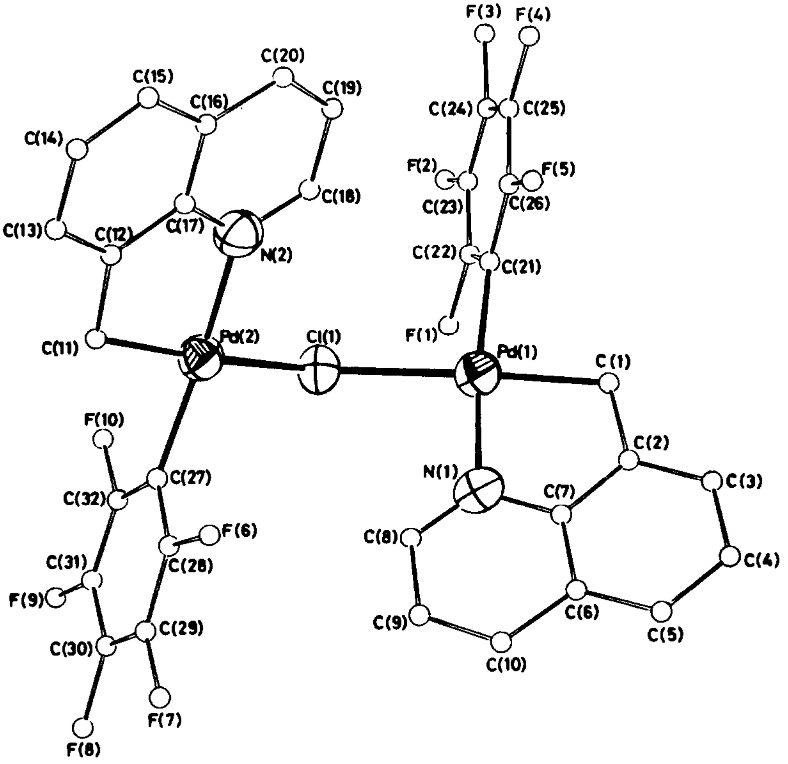

Fig. 1. Structure of $[\{Pd(8\text{-}mq)(C_6F_5)\}_2(\mu\text{-}Cl)]^-$.

Table 6

Bond distances (Å) and bond angles (°) for **11**

Cl1 ··· Pd1	2.475(0.001)	N1 ··· Pd1	2.078(0.006)
C1 ··· Pd1	2.033(0.006)	C21 ··· Pd1	2.007(0.007)
Cl1 ··· Pd2	2.468(0.001)	N2 ··· Pd2	2.086(0.005)
C11 ··· Pd2	2.009(0.006)	C27 ··· Pd2	2.010(0.007)
C7 ··· N1	1.369(0.007)	C8 ··· N1	1.326(0.010)
C17 ··· N2	1.378(0.007)	C18 ··· N2	1.335(0.009)
C2 ··· C1	1.526(0.012)	C3 ··· C2	1.373(0.009)
C7 ··· C2	1.398(0.010)	C4 ··· C3	1.452(0.015)
C5 ··· C4	1.387(0.016)	C6 ··· C5	1.373(0.009)
C7 ··· C6	1.437(0.011)	C10 ··· C6	1.424(0.013)
C9 ··· C8	1.430(0.013)	C10 ··· C9	1.355(0.010)
C12 ··· C11	1.503(0.010)	C13 ··· C12	1.398(0.009)
C17 ··· C12	1.388(0.010)	C14 ··· C13	1.417(0.012)
C15 ··· C14	1.336(0.015)	C16 ··· C15	1.448(0.011)
C17 ··· C16	1.410(0.010)	C20 ··· C16	1.423(0.013)
C19 ··· C18	1.438(0.012)	C20 ··· C19	1.332(0.011)
C22 ··· C21	1.405(0.009)	C26 ··· C21	1.374(0.009)
C23 ··· C22	1.351(0.011)	F1 ··· C22	1.359(0.008)
C24 ··· C23	1.367(0.011)	F2 ··· C23	1.361(0.008)
C25 ··· C24	1.342(0.011)	F3 ··· C24	1.387(0.010)
C26 ··· C25	1.361(0.011)	F4 ··· C25	1.329(0.009)
F5 ··· C26	1.371(0.007)	C28 ··· C27	1.357(0.011)
C32 ··· C27	1.373(0.009)	C29 ··· C28	1.387(0.011)
F6 ··· C28	1.355(0.008)	C30 ··· C29	1.374(0.013)
F7 ··· C29	1.338(0.011)	C31 ··· C30	1.359(0.014)
F8 ··· C30	1.359(0.012)	C32 ··· C31	1.363(0.012)
F9 ··· C31	1.346(0.009)	F10 ··· C32	1.347(0.009)
C33 ··· N3	1.515(0.009)	C37 ··· N3	1.572(0.011)
C41 ··· N3	1.515(0.009)	C45 ··· N3	1.479(0.010)
C34 ··· C33	1.478(0.010)	C35 ··· C34	1.562(0.012)
C36 ··· C35	1.508(0.016)	C38 ··· C37	1.507(0.014)
C39 ··· C38	1.635(0.017)	C40 ··· C39	1.506(0.019)
C42 ··· C41	1.515(0.011)	C43 ··· C42	1.522(0.010)
C44 ··· C43	1.556(0.016)	C46 ··· C45	1.446(0.014)
C47 ··· C46	1.578(0.015)	C48 ··· C47	1.485(0.018)
Cl2 ··· C49	1.751(0.035)	Cl3 ··· C49	1.728(0.029)
N1–Pd1–Cl1	94.6(0.1)	C1–Pd1–Cl1	176.2(0.2)
C1–Pd1–N1	84.7(0.3)	C21–Pd1–Cl1	91.2(0.1)
C21–Pd1–N1	174.1(0.2)	C21–Pd1–C1	89.6(0.3)
N2–Pd2–Cl1	94.9(0.1)	C11–Pd2–Cl1	173.5(0.2)
C11–Pd2–N2	83.6(0.2)	C27–Pd2–Cl1	93.0(0.2)
C27–Pd2–N2	171.3(0.2)	C27–Pd2–C11	89.0(0.3)
Pd2–Cl1–Pd1	130.0(0.1)	C7–N1–Pd1	112.5(0.5)
C8–N1–Pd1	127.8(0.4)	C8–N1–C7	119.6(0.6)
C17–N2–Pd2	111.8(0.4)	C18–N2–Pd2	126.8(0.4)
C18–N2–C17	121.1(0.6)	C2–C1–Pd1	105.8(0.5)
C3–C2–C1	122.8(0.7)	C7–C2–C1	120.3(0.5)
C7–C2–C3	116.9(0.7)	C4–C3–C2	121.3(0.8)
C5–C4–C3	120.1(0.7)	C6–C5–C4	119.5(0.9)
C7–C6–C5	119.3(0.8)	C10–C6–C5	123.5(0.8)
C10–C6–C7	117.1(0.6)	C2–C7–N1	116.0(0.6)
C6–C7–N1	121.3(0.6)	C6–C7–C2	122.7(0.5)
C9–C8–N1	122.4(0.6)	C10–C9–C8	119.0(0.8)

Table 6 (continued)

C9–C10–C6	120.4(0.9)	C12–C11–Pd2	108.3(0.4)
C13–C12–C11	122.8(0.6)	C17–C12–C11	118.8(0.5)
C17–C12–C13	118.3(0.6)	C14–C13–C12	118.9(0.8)
C15–C14–C13	123.5(0.8)	C16–C15–C14	119.1(0.8)
C17–C16–C15	117.0(0.8)	C20–C16–C15	125.0(0.7)
C20–C16–C17	117.9(0.6)	C12–C17–N2	116.6(0.5)
C16–C17–N2	120.3(0.6)	C16–C17–C12	123.2(0.6)
C19–C18–N2	119.8(0.6)	C20–C19–C18	120.2(0.8)
C19–C20–C16	120.6(0.8)	C22–C21–Pd1	121.6(0.5)
C26–C21–Pd1	125.9(0.5)	C26–C21–C22	112.2(0.6)
C23–C22–C21	123.8(0.6)	F1–C22–C21	118.7(0.6)
F1–C22–C23	117.5(0.6)	C24–C23–C22	119.3(0.7)
F2–C23–C22	120.4(0.7)	F2–C23–C24	120.2(0.8)
C25–C24–C23	120.5(0.8)	F3–C24–C23	119.6(0.7)
F3–C24–C25	119.9(0.7)	C26–C25–C24	118.3(0.7)
F4–C25–C24	120.1(0.7)	F4–C25–C26	121.6(0.6)
C25–C26–C21	125.9(0.6)	F5–C26–C21	119.0(0.6)
F5–C26–C25	115.2(0.6)	C28–C27–Pd2	122.3(0.5)
C32–C27–Pd2	123.1(0.6)	C32–C27–C28	114.5(0.7)
C29–C28–C27	124.6(0.7)	F6–C28–C27	121.3(0.7)
F6–C28–C29	114.1(0.7)	C30–C29–C28	117.1(0.8)
F7–C29–C28	122.2(0.8)	F7–C29–C30	120.7(0.8)
C31–C30–C29	120.9(0.8)	F8–C30–C29	118.1(0.8)
F8–C30–C31	121.0(0.8)	C32–C31–C30	118.6(0.7)
F9–C31–C30	118.9(0.9)	F9–C31–C32	122.5(0.8)
C31–C32–C27	124.3(0.7)	F10–C32–C27	119.8(0.7)
F10–C32–C31	115.9(0.6)	C37–N3–C33	105.9(0.5)
C41–N3–C33	107.4(0.5)	C41–N3–C37	110.1(0.6)
C45–N3–C33	112.7(0.6)	C45–N3–C37	110.2(0.6)
C45–N3–C41	110.5(0.5)	C34–C33–N3	118.8(0.7)
C35–C34–C33	108.9(0.7)	C36–C35–C34	121.2(0.7)
C38–C37–N3	112.9(0.6)	C39–C38–C37	105.1(0.7)
C40–C39–C38	110.3(0.8)	C42–C41–N3	116.5(0.5)
C43–C42–C41	109.2(0.6)	C44–C43–C42	110.7(0.7)
C46–C45–N3	118.4(0.7)	C47–C46–C45	108.4(0.8)
C48–C47–C46	111.8(1.0)	Cl3–C49–Cl2	103.0(1.9)

treatment of the oily residue with Et_2O (50 ml) produced a white solid (a mixture of $(NBu_4)ClO_4$ and $(NBu_4)[Pt(C_6F_5)_3(NCMe)]$) and a colourless solution, and concentration of the latter to ca. 3 ml gave **1** in 47% yield.

A similar reaction between $[Pd(dmba)(NCMe)_2]ClO_4$ and $(NBu_4)_2[Pd(C_6F_5)_4]$ gave **1** in 36% yield.

$[Pd(8\text{-}mq)(C_6F_5)(NCMe)]$ (**6**) was similarly obtained by the reaction of $[Pd(8\text{-}mq)(NCMe)_2]ClO_4$ (0.300 g, 0.697 mmol) with $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.940 g, 0.697 mmol) in CH_2Cl_2 (40 ml) with stirring at room temperature for 5 h. A partial precipitation of **6** took place during the reaction, and reduction of the volume of the suspension to ca. 10 ml gave **6** in 73% total yield.

The reaction between $[Pd(8\text{-}mq)(NCMe)_2]ClO_4$ (0.200 g, 0.465 mmol) and $(NBu_4)_2[Pd(C_6F_5)_4]$ (0.586 g, 0.465 mmol) in CH_2Cl_2 (40 ml) under similar conditions gave a solid, that after recrystallization from CH_2Cl_2 yielded **6** (65% yield).

$[Pd(\widehat{C\,N})(C_6F_5)(PR_3)]$ ($\widehat{C\,N}$ = dmba, $PR_3 = PPh_3$ (2), $PPhMe_2$ (3); $\widehat{C\,N}$ = 8-mq, $PR_3 = PPh_3$ (7))

(a) To a solution of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (0.100 g, 0.181 mmol) in 20 ml of THF was added $AgClO_4$ (0.075 g, 0.362 mmol). The mixture was stirred at room temperature for 30 min and then filtered and the filtrate evaporated to dryness. To the oily residue 8 ml of $CHCl_3$ and $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.488 g, 0.362 mmol) were added, and the solution was stirred at room temperature for 10 min and then PPh_3 (0.171 g, 0.652 mmol) was added. The mixture was stirred at room temperature for 3 h and then evaporated to dryness. The residue was treated with ^iPrOH (60 ml) to yield **2** as a white solid, which was recrystallized from CH_2Cl_2/Et_2O. Yield 46%.

Complex **3** was similarly obtained by using $[Pd(dmba)(\mu\text{-}Cl)]_2$ (0.100 g, 0.181 mmol), $AgClO_4$ (0.075 g, 0.362 mmol); $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.488 g, 0.362 mmol), and $PPhMe_2$ (98 μl, 0.730 mmol). **3** was recrystallized from $CH_2Cl_2/^iPrOH$ (2 ml/8 ml). Yield 42%.

(b) To a solution of $[Pd(8\text{-}mq)(C_6F_5)(NCMe)]$ (0.100 g, 0.218 mmol) in 15 ml of acetone was added PPh_3 (0.057 g, 0.218 mmol). The solution was stirred at room temperature for 10 min and then evaporated to dryness. Addition of Et_2O/n-hexane (5 ml/2 ml) gave **7** in 65% yield.

$(NBu_4)[Pd(\widehat{C\,N})(C_6F_5)Br]$ ($\widehat{C\,N}$ = dmba (4), 8-mq (8))

To a solution of $(NBu_4)Br$ (0.170 g, 0.528 mmol) in CH_2Cl_2 (25 ml) was added $[Pd(dmba)(C_6F_5)(NCMe)]$ (0.237 g, 0.528 mmol). The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The oily residue was treated with Et_2O (ca. 4 ml) to yielding **4**, 70% yield.

Complex **8** was obtained similarly from $(NBu_4)Br$ (0.105 g, 0.328 mmol) and $[Pd(8\text{-}mq)(C_6F_5)(NCMe)]$ (0.150 g, 0.328 mmol) in CH_2Cl_2 (10 ml). Yield 92%.

$(NBu_4)[Pd(C_6F_5)(8\text{-}mq)Cl]$ (9)

Silver chloride (0.037 g, 0.231 mmol) was added to a CH_2Cl_2 (20 ml) solution of $(NBu_4)[Pd(8\text{-}mq)(C_6F_5)Br]$ (**8**) (0.142 g, 0.193 mmol) and the mixture was stirred, protected from light, at room temperature for 6 d. The AgBr was filtered off and the resulting yellow solution evaporated to ca. 2 ml. Addition of Et_2O (25 ml) gave **9** as a yellow solid in 85% yield.

$(NBu_4)[\{Pd(\widehat{C\,N})(C_6F_5)\}_2(\mu\text{-}X)]$ ($\widehat{C\,N}$ = dmba, X = Br (5), $\widehat{C\,N}$ = 8-mq, X = Br (10), X = Cl (11))

To a solution of $(NBu_4)[Pd(dmba)(C_6F_5)Br]$ (*4*) (0.066 g, 0.090 mmol) in 10 ml of CH_2Cl_2 was added $[Pd(dmba)(C_6F_5)(NCMe)]$ (**1**) (0.040 g, 0.090 mmol). The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The oily residue was treated three times with 20 ml of a 1/1 mixture of Et_2O/n-hexane. The solution was cooled at −30 °C for 10 h to give crystals of **4** in 54% yield.

Complexes **10** and **11** were obtained similarly:

10 was made from $(NBu_4)[Pd(8\text{-}mq)(C_6F_5)Br]$ (0.170 g, 0.230 mmol) and $[Pd(8\text{-}mq)(C_6F_5)(NCMe)]$ (0.105 g, 0.230 mmol) in CH_2Cl_2 (20 ml). The oily residue was washed with Et_2O. Yield 87%.

11 was made from $(NBu_4)[Pd(8\text{-}mq)(C_6F_5)Cl]$ (0.100 g, 0.144 mmol) and $[Pd(8\text{-}mq)(C_6F_5)(NCMe)]$ (0.066 g, 0.144 mmol) in CH_2Cl_2 (25 ml). The oily residue was washed with Et_2O. Yield 94%.

Suitable crystals of **11** for the X-ray study were obtained as follows. On a $CHCl_3$ (2 ml) solution of **11** (0.015 g) was carefully layered 1 ml of CH_2Cl_2 and 5 ml of n-hexane. Slow diffusion at 5 ° C during a week gave satisfactory crystals.

Crystal structure analyses. A crystal of **11** was mounted on a glass fibre and covered with epoxy resin adhesive. The lattice dimensions and Laue group of the crystal were based on 25 reflections. Relevant crystal and experimental parameters are given in Table 4. The structure was solved by Direct Methods (Pd1, Pd2 and Cl1), and additional non-H atoms located by subsequent Fourier difference maps. The computer programs SHELX-76 [21], SHELX-86 [22] and CADABS [23] were used for the crystallographic work. Geometrical calculations were carried out with the program PARST [24].

In the final refinement, 604 parameters were fitted to 5429 data with a data to parameter ratio of 8.9. The least-squares residuals are indicated in Table 4. Lists of thermal parameters and structure factors are available from the authors.

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