# Synthesis, Molecular Structure and Reactivity of *cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$, κ$N$)] a Compound displaying an Unusual $\eta^1$ Arene–Palladium Interaction†

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The reaction between *cis*-[Pd$(C_6F_5)_2$(thf)$_2$] (thf = tetrahydrofuran) and benzyldimethylamine rendered *cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$,κ$N$)] **1**, a four-co-ordinate compound containing an unusual $\eta^1$ arene–palladium interaction with the benzyldimethylamine acting as a bidentate chelating ligand. Complex **1** reacts with acetone, acetonitrile, dimethyl sulfoxide or CO (L) to yield *cis*-[Pd$(C_6F_5)_2(NMe_2CH_2C_6H_5)$(L)] **2–5** respectively, which do not have a $\eta^1$ arene–palladium interaction. The reaction of **1** with $Br^-$ or $SPMe_2Ph$ (L′) (molar ratio 1:1) produced the complete displacement of the amine and the formation of [$(F_5C_6)_2Pd(\mu$-L′$)_2Pd(C_6F_5)_2]^{n-}$ ($n$ = 2 or 0), and with $Cl^-$ (molar ratio 1:1) a mixture of complexes is formed. The crystal structures of compounds **1** and **2** have been determined.

Complexes containing arene–metal interactions form an interesting group of organometallic derivatives in which the interaction can be understood as a consequence of the overlap of the ring π and π* orbitals with the appropriate orbitals of the metal centre.[1] In most of these complexes, six carbon atoms of the arene ligand are involved in the interaction with the metal atom ($\eta^6$), although other co-ordination modes of arene ligands ($\eta^4$, $\eta^3$, $\eta^2$ and $\eta^1$) have also been described and structurally characterized.[2–6] Moreover, complexes containing $\eta^1$- or $\eta^2$-arene–metal interactions have been proposed as intermediate species in arene hydrogenation processes catalysed by transition-metal complexes or in oxidative-addition reactions of the C(sp$^2$)–H bond to the metal centre.[5,7–10] Examples of $\eta^1$ arene–metal interactions are very scarce and have been structurally identified in: (*i*) $AgB_{11}C_{12}{\cdot}2C_6H_6$,[11] in which one of the benzene molecules is $\eta^1$ bonded to the silver centre, and in (*ii*) [Li{C(SiMe$_2$Ph)$_3$}(thf)],[12] [Cr{N($C_6H_2Me_3$)B($C_6H_2Me_3$)$_2$}$_2$][13] and [{Li[2,6-($C_6H_2Me_3$)$_2C_6H_3$]}$_2$],[14] which display fairly close M···C interactions with the *ipso* carbons of one of the phenyl or mesityl rings. In the last cases (*ii*), the aryl or mesityl ring which is interacting ($\eta^1$) with the metal centre is part of a ligand which bonds simultaneously to the metal centre through another donor atom. Because of this, the $\eta^1$ arene–metal interaction is assisted by the chelate effect and in all cases a four membered ring is formed (see below). The $\eta^1$ arene–metal interaction seems to be in all cases weak in nature since no perceptible changes in the geometry of the phenyl ring are observed as a consequence of the co-ordination, *i.e.*, planar $C_6$ rings are involved in such interactions with all the C atoms of the ring sp$^2$ hybridized.

In this paper we report the synthesis and structural characterization of *cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$,κ$N$)] **1** an unprecedented palladium compound displaying a $\eta^1$ arene–palladium interaction in the solid state with benzyldimethylamine acting as a chelating ligand. The $\eta^1$-arene interaction is, as in other known cases, weak in nature and can be removed by reaction of **1** with monodentate neutral or anionic ligands. Preliminary results have been reported earlier.[15]

## Results and Discussion

*Synthesis and Characterization of cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$,κ$N$)] **1**.—The reaction of *cis*-[Pd$(C_6F_5)_2$(thf)$_2$] (thf = tetrahydrofuran) with $C_6H_5CH_2NMe_2$ (bdma) in a 1:1 molar ratio in $CHCl_3$ gives *cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$, κ$N$)] **1** in 74% yield, equation (1). As has been established

$$cis\text{-}[Pd(C_6F_5)_2(thf)_2] + C_6H_5CH_2NMe_2 \xrightarrow{CHCl_3} cis\text{-}[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2\text{-}\kappa C^1, \kappa N)] + 2thf \quad (1)$$

by an X-ray diffraction study the amine in complex **1** behaves as a bidentate chelating ligand with an unusual $\eta^1$ arene co-ordination.

The IR spectrum of complex **1** shows two absorptions (785s and 795s cm$^{-1}$) due to the X-sensitive modes of the $C_6F_5$ group, in keeping with its *cis* structure.[16,17] On the other hand, no absorptions due to thf[18] were detected indicating the total substitution of this ligand by the bdma group.

The $^1$H and $^{19}$F NMR data of **1**, which are listed in Tables 1 and 2 respectively, are in accord with its structure. The $^{19}$F NMR spectrum shows two signals due to the *p*-F atoms indicating that the two $C_6F_5$ groups are chemically inequivalent.

The $^{13}$C NMR spectra of complexes **1–4** in $CDCl_3$ have been recorded at room temperature, the number of signals due to bdma being the same in all cases (Table 3). Three signals at δ *ca.* 130 are assigned to the aromatic (*o*, *m* and *p*) C atoms. No signal corresponding to the *ipso*-C could be detected but the presence of the $C_6F_5$ groups may impede the observation of this signal.

*Structure of cis*-[Pd$(C_6F_5)_2(C_6H_5CH_2NMe_2$-κ$C^1$,κ$N$)] **1**. The structure of complex **1** is depicted in Fig. 1, atomic coordinates are listed in Table 4 and selected bond distances and bond angles are listed in Table 5.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

**Table 1** $^1$H NMR data (δ)[a]

| Complex | $C_6H_5$ | $CH_2$ | $NMe_2$ | L |
|---|---|---|---|---|
| **1** $[Pd(C_6F_5)_2(bdma)]$ | 7.79 (m, 2 H) | 4.04 (s) | 2.61 (s) | |
| | 7.43 (m, 2 H) | | | |
| | 7.18 (m, 1 H) | | | |
| **2** $[Pd(C_6F_5)_2(bdma)(Me_2CO)]$ | 7.89 (m, 2 H) | 3.90 (s) | 2.51 (s) | 2.19 (s, 6 H) |
| | 7.44 (m, 2 H) | | | |
| | 7.27 (m, 1 H) | | | |
| **3** $[Pd(C_6F_5)_2(bdma)(NCMe)]$ | 8.11 (m, 2 H) | 3.69 (s) | 2.38 (s) | 1.96 (s, 3 H) |
| | 7.48 (m, 3 H) | | | |
| **4** $[Pd(C_6F_5)_2(bdma)(dmso)]$ | 8.11 (m, 2 H) | 3.67 (s) | 2.30 (s) | 2.48 (s, 6 H) |
| | 7.45 (m, 3 H) | | | |
| **6** $[\{Pd(C_6F_5)_2(\mu\text{-}SPMe_2Ph)\}_2]$[b] | | | | 8.0–7.4 (m, 5 H) |
| | | | | 2.57 (s, 3 H) |
| | | | | 2.50 (s, 3 H) |

[a] In $CDCl_3$. [b] In $(CD_3)_2CO$.

**Table 2** $^{19}$F NMR data (δ)[a]

| Complex | $F_o$ | $F_m$ | $F_p$ |
|---|---|---|---|
| **1** $[Pd(C_6F_5)_2(bdma)]$ | −117.23 (m) | −163.82 (m) | −160.53 (m) |
| | −118.24 (m) | −164.66 (m) | −161.26 (m) |
| **2** $[Pd(C_6F_5)_2(bdma)(Me_2CO)]$ | −117.25 (m) | −163.84 (m) | −160.57 (t) |
| | −118.24 (m) | −164.62 (m) | −161.23 (t) |
| **3** $[Pd(C_6F_5)_2(bdma)(NCMe)]$ | −116.38 (m) | −163.66 (m) | −160.93 (m) |
| | −117.68 (m) | −164.34 (m) | −161.64 (m) |
| **4** $[Pd(C_6F_5)_2(bdma)(dmso)]$ | −116.16 (d) | −163.60 (m) | −160.44 (m) |
| | −116.80 (d) | −164.03 (m) | −161.47 (m) |
| **6** $[\{Pd(C_6F_5)_2(\mu\text{-}SPMe_2Ph)\}_2]$[b] | −114.83 (d) | −163.47 (m) | −161.15 (t) |

[a] In $CDCl_3$, 20 °C. [b] In $(CD_3)_2CO$.

**Table 3** $^{13}$C-{$^1$H} NMR data (δ)[a]

| Complex | $C_6H_5$ | $CH_2$ | $NMe_2$ | L |
|---|---|---|---|---|
| **1** $[Pd(C_6F_5)_2(bdma)]$ | 133.50 (s) | 67.73 (s) | 50.45 (s) | |
| | 130.64 (s) | | | |
| | 123.23 (s) | | | |
| **2** $[Pd(C_6F_5)_2(bdma)(Me_2CO)]$ | 131.27 (s) | 67.52 (s) | 50.13 (s) | 31.44 (s)[b] |
| | 129.74 (s) | | | |
| | 127.016 (s) | | | |
| **3** $[Pd(C_6F_5)_2(bdma)(NCMe)]$ | 131.91 (s) | 68.41 (s) | 50.70 (s) | 117.89 (s) |
| | 128.74 (s) | | | 2.54 (s) |
| | 128.56 (s) | | | |
| **4** $[Pd(C_6F_5)_2(bdma)(dmso)]$ | 130.93 (s) | 66.60 (s) | 49.61 (s) | 39.1 (s) |
| | 128.62 (s) | | | |
| | 128.61 (s) | | | |

[a] In $CDCl_3$, 20 °C. [b] The signal corresponding to the carbonyl carbon atom is not observed.

The $Pd^{II}$ centre displays a distorted square-planar environment formed by C(1) and C(1′) and the N and C(7) atoms of benzyldimethylamine, which is acting as a chelating ligand. The Pd–C(1), Pd–C(1′) bond distances and the C(1)–Pd–C(1′) bond angle are similar to those observed in *cis*-$[Pd(C_6F_5)_2\{S_2CP(C_6H_{11})_3\}]$.[19]

The co-ordination mode of benzyldimethylamine to the palladium centre deserves some comment. As can be seen from Fig. 1, both the N and C(7) atoms are interacting with the palladium centre so that this typically monodentate ligand is acting as a chelating one. The Pd–C(7) distance [2.335(7) Å] is longer than that of a typical Pd–C σ bond (1.965–2.002 Å),[20] although it is shorter than the Pd–C distances corresponding to the $\eta^2$ arene–palladium interaction in $[Pd\{NC_9H_6\text{-}CH_2C(CF_3)\text{=}C(CF_3)\}\{C(CF_3)\text{=}C(CF_3)(\eta^2\text{-}C_{10}H_6OMe\text{-}8)\}]$[21] [2.571(4) and 2.433(3) Å]. The long Pd–C(8) and Pd–C(12) bond distances [2.706(8) and 2.663(9) Å respectively] exclude an $\eta^3$ phenyl–palladium interaction.[22] Moreover, C(7), which is essentially $sp^2$ hybridized [C(13)–C(7)–C(12) 118.9(7), C(8)–C(7)–C(12) 117.7(8) and C(13)–C(7)–C(8) 123.1(8)°] lies on the best least-squares plane through Pd–N–C(1)–C(1′) (plane A), its mean position being 0.026 Å from this plane[23] and the dihedral angle between the $C_6H_5$ plane and plane A is 92.75(28)°. The Pd–C(7) vector is almost perpendicular to the aryl ring plane [the deviation being only 3.7(3)°]. All these facts indicate that the aryl ring in $C_6H_5CH_2NMe_2$ is $\eta^1$ co-ordinated to the palladium centre, the p(π) orbital of C(7), perpendicular to the aryl ring, being responsible for the interaction with the palladium centre.

It is also noteworthy that in spite of the $\eta^1$ co-ordination to the palladium centre, the phenyl ring is planar and all the C–C bond distances and C–C–C angles are identical within experimental error, *i.e.* no loss of aromaticity is observed as in other $\eta^1$ arene–metal complexes.[11–14]

On the other hand the Pd–N distance [2.314(6) Å] is perceptibly longer, and the N–Pd–C(7) angle [64.4(3)°] is more acute than the corresponding distances (2.10–2.22 Å)[24] and angles (81.6–80.4°)[24] found in complexes containing the $Pd(C_6H_4CH_2NMe_2)$ fragment. Both facts indicate a considerable strain on the four-membered ring formed as a consequence

**Table 4** Atomic coordinates ( × $10^4$) for complex **1**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 0(0) | −183(1) | −2500(0) |
| C(1) | 718(5) | −1861(8) | −2256(5) |
| C(2) | 1174(6) | −2473(11) | −1243(10) |
| C(3) | 1732(6) | −3627(11) | −1058(7) |
| C(4) | 1821(5) | −4150(10) | −1930(8) |
| C(5) | 1434(5) | −3402(11) | −2936(7) |
| C(6) | 896(5) | −2285(9) | −3054(8) |
| F(1) | 983(4) | −2084(9) | −401(5) |
| F(2) | 2071(4) | −3969(9) | −18(6) |
| F(3) | 2432(5) | −5061(8) | −1790(10) |
| F(4) | 1561(5) | −4097(11) | −3740(7) |
| F(5) | 473(5) | −1918(10) | −4140(6) |
| C(1′) | −699(6) | −2020(11) | −2742(10) |
| C(2′) | −899(6) | −2613(9) | −1919(7) |
| C(3′) | −1463(7) | −3570(12) | −2116(9) |
| C(4′) | −1875(5) | −3786(9) | −3170(7) |
| C(5′) | −1679(4) | −3459(9) | −3948(6) |
| C(6′) | −1112(5) | −2555(9) | −3739(6) |
| F(1′) | −538(5) | −1959(9) | −905(6) |
| F(2′) | −1599(5) | −3822(9) | −1250(8) |
| F(3′) | −2383(4) | −4863(8) | −3336(8) |
| F(4′) | −2140(4) | −4112(10) | −4916(7) |
| F(5′) | −1046(5) | −2054(9) | −4599(6) |
| C(7) | −377(5) | 2554(9) | −2629(6) |
| C(8) | −802(4) | 2330(10) | −3686(7) |
| C(9) | −1472(6) | 1699(11) | −4001(7) |
| C(10) | −1720(4) | 1344(10) | −3261(9) |
| C(11) | −1287(5) | 1487(10) | −2131(7) |
| C(12) | −642(5) | 2111(10) | −1841(6) |
| C(13) | 367(5) | 3102(10) | −2240(9) |
| C(14) | 1482(5) | 1755(11) | −1196(8) |
| C(15) | 1090(7) | 2013(11) | −3066(8) |
| N | 845(4) | 1803(7) | −2235(6) |

**Table 5** Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

| | | | |
|---|---|---|---|
| Pd–C(1) | 1.957(8) | Pd–C(7) | 2.335(7) |
| Pd–C(1′) | 2.022(11) | Pd–N | 2.314(6) |
| C(1)–Pd–C(1′) | 88.6(2) | C(12)–C(7)–Pd | 86.2(5) |
| C(1)–Pd–N | 88.0(3) | C(8)–C(7)–Pd | 90.4(5) |
| C(7)–Pd–N | 64.4(3) | C(7)–C(13)–N | 114.1(7) |
| C(13)–C(7)–Pd | 88.9(5) | | |

of the $\eta^1$ arene–metal interaction. As far as this interaction is concerned, **1** is structurally similar to [Li{C(SiMe$_2$Ph)$_3$}(thf)],[12] [Cr{N(C$_6$H$_2$Me$_3$)B(C$_6$H$_2$Me$_3$)$_2$}$_2$][13] and [{Li[2,6-(C$_6$H$_2$Me$_3$)$_2$C$_6$H$_3$]}$_2$][14] (formation of a four-membered ring) and different from AgB$_{11}$C$_{12}$·2C$_6$H$_6$[11] in which the $\eta^1$-arene interaction is not assisted by the chelate effect.

*Reactions of* cis-[Pd(C$_6$F$_5$)$_2$(C$_6$H$_5$CH$_2$NMe$_2$-κ*C*$^1$,κ*N*)] **1** *with Monodentate Ligands* (*L*).—The structural characteristics of this unprecedented $\eta^1$ arene–palladium interaction, in which neither loss of aromaticity of the phenyl ring nor change in the hybridization of the *ipso*-C atom takes place, seem to indicate that this interaction is weak in nature and is assisted by the chelate effect, so that it could be imagined that the treatment of **1** with monodentate ligands L would release the $\eta^1$ interaction. For that reason, we studied the reactions of **1** with different monodentate ligands the results of which depended on the ligand used. Thus, treatment of complex **1** with acetone (Me$_2$CO), acetonitrile, dimethyl sulfoxide (dmso) or carbon monoxide resulted, as expected, in the formation of the four-coordinate complexes **2–5** respectively [equation (2)] in which there is no $\eta^1$ arene–palladium interaction.

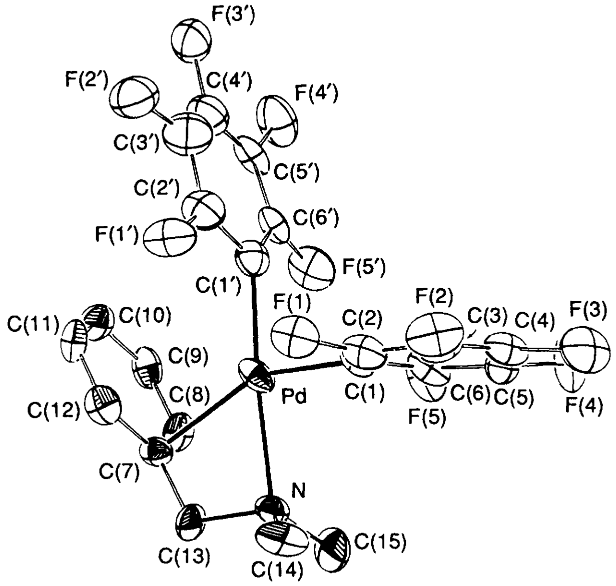

**Fig. 1** Molecular structure of *cis*-[Pd(C$_6$F$_5$)$_2$(C$_6$H$_5$CH$_2$NMe$_2$-κ*C*$^1$,κ*N*)] **1**

$$cis\text{-}[\mathrm{Pd(C_6F_5)_2(C_6H_5CH_2NMe_2}\text{-}\kappa C^1,\kappa N)] + \mathrm{L} \longrightarrow cis\text{-}[\mathrm{Pd(C_6F_5)_2(NMe_2CH_2C_6H_5)L}]\ \mathbf{2\text{–}5} \quad (2)$$

However, the reaction conditions for the preparation of complexes **2–5** are different. Thus, complex **2** is prepared by dissolving **1** in acetone, *i.e.* in the presence of a great excess of acetone, while **3** and **4** have to be prepared by treating chloroform solutions of **1** with L in a 1 : 1 molar ratio, since if **1** is dissolved in MeCN or dmso the total displacement of benzyldimethylamine takes place and *cis*-[Pd(C$_6$F$_5$)$_2$L$_2$] (L = NCMe or dmso) is formed. The carbonyl derivative **5** (L = CO) is obtained by bubbling CO through a dichloromethane solution of **1** at −30 °C. Although it is stable as a solid, it decomposes in CH$_2$Cl$_2$ solution at room temperature and metallic palladium is formed.

Surprisingly, complex **1** does not react under similar conditions with acetylenes (PhC≡CPh or hex-3-yne) or with NBu$_4$ClO$_4$.

The reaction of **1** with more basic moieties able to act as bridging ligands, such as chloride, bromide or dimethylphenylphosphine sulfide, in a 1 : 1 molar ratio not only releases the weak $\eta^1$ arene–palladium interaction but also displaces the amine and forms the corresponding binuclear complexes. Thus, treatment of a CH$_2$Cl$_2$ or CHCl$_3$ solution of **1** with [N(PPh$_3$)$_2$]Cl (1 : 1 molar ratio) at room temperature renders, after evaporation to dryness and treatment with hexane, a mixture of [N(PPh$_3$)$_2$][Pd(C$_6$F$_5$)$_2$Cl(NMe$_2$CH$_2$C$_6$H$_5$)] and [N(PPh$_3$)$_2$]$_2$[{Pd(C$_6$F$_5$)$_2$(μ-Cl)}$_2$]. When such a mixture is treated with Pr$^i$OH, [N(PPh$_3$)$_2$]$_2$[{Pd(C$_6$F$_5$)$_2$(μ-Cl)}$_2$] can be separated because of its insolubility. However we have not been able to isolate a pure sample of [N(PPh$_3$)$_2$][Pd(C$_6$F$_5$)$_2$Cl(NMe$_2$CH$_2$C$_6$H$_5$)] indicating that the reaction between **1** and [N(PPh$_3$)$_2$]Cl likely results in an equilibrium between the mono- and di-nuclear species [equation (3)].

$$2\,cis\text{-}[\mathrm{Pd(C_6F_5)_2(C_6H_5CH_2NMe_2}\text{-}\kappa C^1,\kappa N)] + 2[\mathrm{N(PPh_3)_2}]\mathrm{Cl} \longrightarrow 2[\mathrm{N(PPh_3)_2}][\mathrm{Pd(C_6F_5)_2Cl(NMe_2CH_2C_6H_5)}] \rightleftharpoons [\mathrm{N(PPh_3)_2}]_2[\{\mathrm{Pd(C_6F_5)_2}(\mu\text{-Cl})\}_2] + 2\mathrm{C_6H_5CH_2NMe_2} \quad (3)$$

The equilibrium constant ($K_{eq}$) of this process can be evaluated (20 °C, CDCl$_3$ solution, $K_{eq}$ 3.32 × $10^{-3}$ mol dm$^{-3}$) from the $^1$H NMR data {free bdma, δ 2.26 (CH$_2$) and 3.45

**Table 6** Atomic coordinates ( × $10^4$) for complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 979(1) | 4296(1) | 2491(1) |
| C(1) | 1374(5) | 2472(5) | 1734(2) |
| C(2) | 2506(5) | 2627(5) | 1194(3) |
| C(3) | 2763(7) | 1449(7) | 625(3) |
| C(4) | 1852(8) | 46(7) | 573(3) |
| C(5) | 689(7) | −162(5) | 1096(3) |
| C(6) | 501(6) | 1019(5) | 1667(3) |
| F(2) | 3431(3) | 4004(3) | 1191(2) |
| F(3) | 3901(5) | 1689(5) | 106(2) |
| F(4) | 2053(5) | −1116(4) | 13(2) |
| F(6) | −634(4) | 712(3) | 2175(2) |
| F(5) | −248(5) | −1542(3) | 1038(2) |
| C(7) | 2197(5) | 3512(5) | 3328(3) |
| C(8) | 3835(5) | 3832(6) | 3469(3) |
| C(9) | 4658(6) | 3310(7) | 4071(3) |
| C(10) | 3848(8) | 2413(7) | 4552(3) |
| C(11) | 2218(7) | 2061(6) | 4442(3) |
| C(12) | 1427(6) | 2627(6) | 3844(3) |
| F(8) | 4699(3) | 4681(4) | 3001(2) |
| F(9) | 6263(4) | 3658(5) | 4182(3) |
| F(10) | 4629(5) | 1875(5) | 5132(2) |
| F(11) | 1426(4) | 1167(4) | 4914(2) |
| F(12) | −179(3) | 2285(4) | 3784(2) |
| O | −385(4) | 4943(3) | 1515(2) |
| C(13) | −1748(6) | 4398(5) | 1244(3) |
| C(14) | −2419(8) | 4861(7) | 501(3) |
| C(15) | −2795(6) | 3268(7) | 1632(3) |
| N | 580(5) | 6334(5) | 3279(2) |
| C(16) | 1475(8) | 6579(6) | 4080(3) |
| C(17) | −1148(7) | 6110(7) | 3409(4) |
| C(18) | 953(6) | 7722(6) | 2890(3) |
| C(19) | 2662(6) | 8054(5) | 2660(3) |
| C(20) | 3044(7) | 7420(6) | 1923(3) |
| C(21) | 4565(8) | 7737(8) | 1691(4) |
| C(22) | 5723(10) | 8687(10) | 2216(6) |
| C(23) | 5370(11) | 9317(10) | 2944(7) |
| C(24) | 3848(9) | 9000(7) | 3178(5) |

($NMe_2$); [$N(PPh_3)_2$][$Pd(C_6F_5)_2Cl(NMe_2CH_2C_6H_5)$], δ 2.32 ($CH_2$) and 4.01 ($NMe_2$); the aromatic proton data are not significant to this study}.

The reaction of complex **1** with $NBu_4Br$ in $CH_2Cl_2$ renders, after evaporating to dryness and washing with hexane, the binuclear complex [$NBu_4$]$_2$[{$Pd(C_6F_5)_2(\mu\text{-}Br)$}$_2$][17] which was identified by its IR spectrum. Similarly, the reaction of **1** with $SPMe_2Ph$ in $CHCl_3$ (1 : 1 molar ratio) produces the neutral binuclear compound [{$Pd(C_6F_5)_2(\mu\text{-}SPMe_2Ph)$}$_2$] **6** by the complete displacement of the amine.

The IR spectra of complexes **2**–**6** (see Experimental section) show characteristic absorptions assignable to the $C_6F_5$ or bdma groups. The σ-ketone co-ordination mode of acetone in **2** can be inferred from the strong IR absorption at 1667 $cm^{-1}$ due to the ν(CO).[25] Complex **3** shows two absorptions in the ν(C–N) region (2327 and 2305 $cm^{-1}$) shifted to higher energies than those due to the free MeCN (2290 and 2254 $cm^{-1}$) indicating the usual N-co-ordination of the acetonitrile.[26] The absorption at 992 $cm^{-1}$ in the IR spectrum of **4** can be assigned to ν(S=O) and the shift to lower energies, relative to the unco-ordinated dmso (1055 $cm^{-1}$), indicates the O-co-ordination of this ligand.[27] Complex **5** shows a strong absorption in the ν(C–O) region [2135 (solid) and 2130 $cm^{-1}$ ($CH_2Cl_2$ solution)]. Finally, complex **6** shows a strong absorption at 536 $cm^{-1}$ due to ν(P=S); as expected, the co-ordination of $SPMe_2Ph$ to the palladium centre results in a decrease of the P–S bond order and hence in a decrease of the ν(P=S) relative to the free ligand (583 $cm^{-1}$).

Relevant NMR data for complexes **2**–**6** are collected in Tables 1 and 2.

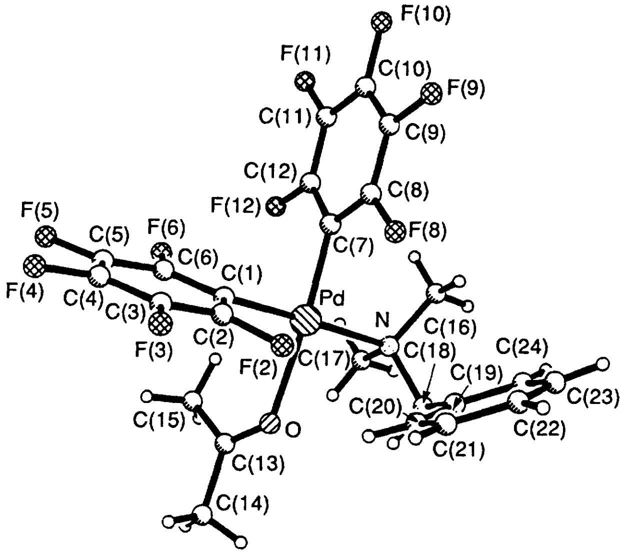

**Fig. 2** Molecular structure of *cis*-[$Pd(C_6F_5)_2(NMe_2CH_2C_6H_5)(Me_2CO)$] **2**

**Table 7** Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

| | | | |
|---|---|---|---|
| Pd–C(1) | 2.011(4) | O–C(13) | 1.221(6) |
| Pd–O | 2.158(3) | C(13)–C(14) | 1.489(8) |
| Pd–C(7) | 1.976(5) | C(13)–C(15) | 1.489(8) |
| Pd–N | 2.184(4) | | |
| C(1)–Pd–C(7) | 86.8(2) | C(14)–C(13)–C(15) | 117.6(4) |
| C(1)–Pd–O | 88.3(1) | Pd–N–C(16) | 114.1(3) |
| C(7)–Pd–N | 94.7(2) | Pd–N–C(17) | 106.7(3) |
| O–Pd–N | 90.3(1) | Pd–N–C(18) | 110.7(3) |
| Pd–O–C(13) | 127.8(3) | C(16)–N–C(17) | 107.2(4) |
| O–C(13)–C(14) | 120.0(5) | C(16)–N–C(18) | 108.1(4) |
| O–C(13)–C(15) | 122.5(5) | N–C(18)–C(19) | 114.8(4) |

*Structure of cis*-[$Pd(C_6F_5)_2(NMe_2CH_2C_6H_5)(Me_2CO)$] **2**.—In order to confirm that in complexes **2**–**5** no $\eta^1$ arene–palladium interaction is present, and with the aim of establishing the structural consequences of the absence of such interaction, a crystal-structure determination was carried out on complex **2**. The structure is presented in Fig. 2, atomic coordinates are given in Table 6 and selected bond distances and angles are presented in Table 7.

The palladium atom displays a slightly distorted square planar environment formed by C(1) and C(7), the N atom of the bdma ligand and the O atom of acetone. The angles between Pd and the *cis* ligands are in the range 86.8–94.7°. As expected the amine acts as a monodentate ligand, and hence the Pd–N distance is perceptibly shorter [2.184(4) Å] than the corresponding one in **1** [2.314(6) Å] where considerable strain is present because of the chelating co-ordination of the amine. Angles around the N atom are as expected for an $sp^3$ hybridized atom and range from 106.7(3) to 114.1(3)°.

The molecule of acetone is σ bonded to the palladium centre with a Pd–O distance of 2.158(3) Å. The C–O distance [1.221(6) Å] is similar to that found in free acetone [1.222(3) Å][28] or in [$Pt(Me_2CO)Me(PPhMe_2)_2$][29] and is in the range found for other metal–acetone complexes.[25] As usual in metal complexes of this type, the Pd–O–C(13) angle [127.8(3)°] is slightly greater than that expected for an $sp^2$-hybridized oxygen.[25] The molecule of acetone is essentially planar and the angles around C(13) range from 117.6(4)° to 122.5(5)°, in agreement with $sp^2$ hybridization. The palladium co-ordination plane and the plane of the acetone are almost perpendicular, with a dihedral angle

**Table 8** Crystallographic data for complexes **1** and **2**[a]

| | | |
|---|---|---|
| Formula | $C_{21}H_{11}F_{10}NPd$ | $C_{24}H_{17}F_{10}NOPd$ |
| $M$ | 633.8 | 575.8 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $Cc$ | $P\bar{1}$ |
| Systematic absences | $(hkl)$: $h + k \neq 2n$ and $(h0l)$: $l \neq 2n$ | — |
| $a$/Å | 21.084(3) | 8.504(2) |
| $b$/Å | 8.096(1) | 8.934(2) |
| $c$/Å | 13.603(2) | 16.920(3) |
| $\alpha$/° | | 98.08(3) |
| $\beta$/° | 114.69(1) | 93.33(3) |
| $\gamma$/° | | 98.91(2) |
| $U$/Å$^3$ | 2109.65 | 1253.17 |
| $Z$ | 4 | 2 |
| $F(000)$ | 1128 | 628 |
| Crystal size/mm | 0.25 × 0.75 × 0.35 | 0.60 × 0.25 × 0.20 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 9.12 | 8.3 |
| Transmission factors (min., max.) | 0.7211, 0.5471 | — |
| Data collected ($h$, $k$, $l$) | Two sets: $\pm h, k, l$ and $\pm h, -k, -l$ | $\pm h, \pm k, +l$ |
| Orientation reflections: number, 2θ range/° | 24, $26 < 2\theta < 30$ | 24, $23 < 2\theta < 28$ |
| Scan range/° | $4 < 2\theta < 50$ | $4 < 2\theta < 45$ |
| No. of unique data | 3455 | 3274 |
| No. of unique data with $F_o \geqslant n\sigma(F_o)$ | 2660 ($n = 6$) | 2794 ($n = 5$) |
| No. of refined parameters | 296 | 339 |
| $R$[b] | 0.0451 | 0.0300 |
| $R'$[c] | 0.0590 | 0.0413 |
| Weighting parameter $g$[d] | 0.000 246 | 0.0007 |
| Largest shift/e.s.d. final cycle | 0.201 | 0.050 |
| Final Fourier difference max. peak, trough/e Å$^{-3}$ | 0.73 | 0.31 |

[a] Details in common: Siemens/Stoe AED2 diffractometer; graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 73 Å); scan method $\omega$–2θ; temperature 18 ± 1 °C. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] $w^{-1} = [\sigma^2(|F_o|) + g|F_o{}^2|]$.

of 81.64(14)°. Finally the Pd–C ($C_6F_5$) distances are similar to the corresponding ones in **1**.

## Experimental

*General.*—The C, H and N analyses, IR, $^1$H and $^{19}$F NMR spectra were performed as described elsewhere.[30] The compounds *cis*-[Pd($C_6F_5$)$_2$(thf)$_2$][18] and SPMe$_2$Ph[31] were prepared according to the literature methods.

*Synthesis.*—*cis*-[Pd($C_6F_5$)$_2$($C_6H_5CH_2NMe_2$-κ$C^1$,κ$N$)] **1**. To a solution of *cis*-[Pd($C_6F_5$)$_2$(thf)$_2$] (0.30 g, 0.51 mmol) in $CHCl_3$ (20 cm$^3$) at room temperature was added bdma (77 μl, 0.51 mmol), and the mixture stirred at room temperature for 30 min. After evaporation to dryness and addition of hexane (30 cm$^3$), a pale yellow solid, **1**, was isolated in 74% yield (Found: C, 43.65; H, 2.25; N, 2.25. Calc. for $C_{21}H_{11}F_{10}NPd$: C, 43.80; H, 2.25; N, 2.45%); IR $\tilde{\nu}_{max}$/cm$^{-1}$(Nujol): $C_6F_5$ 1628w, 1603w, 1495vs, 1054vs, 955vs, 795s and 785s; bdma 1378s, 1365s, 1355s, 843s, 747vs and 702s.

*cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)($Me_2CO$)] **2**. Complex **1** (0.15 g, 0.26 mmol) was dissolved in acetone (5 cm$^3$), and the solution evaporated almost to dryness. Addition of hexane (20 cm$^3$) rendered **2**, 86% yield (Found: C, 45.20; H, 2.90; N, 2.45. Calc. for $C_{24}H_{17}F_{10}NOPd$: C, 45.50; H, 3.00; N, 2.20%); IR $\tilde{\nu}_{max}$/cm$^{-1}$(Nujol): $C_6F_5$ 1633w, 1608w, 1500vs, 1054vs, 955vs, 797s and 780s; bdma 1376vs, 1365vs, 1350vs, 847s, 742vs and 703s; OCMe$_2$ 1667s.

*cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)(NCMe)] **3**. To a solution of complex **1** (0.20 g, 0.35 mmol) in $CHCl_3$ (10 cm$^3$) was added MeCN (18.2 μl, 0.35 mmol). The resulting solution was stirred for 10 min and taken to dryness. The residue was treated with hexane (30 cm$^3$) and the resulting white solid, **3**, was filtered off and air dried, 87% yield (Found: C, 44.15; H, 2.30; N, 4.40. Calc. for $C_{23}H_{14}F_{10}N_2Pd$: C, 44.80; H, 2.60; N, 4.55%); IR $\tilde{\nu}_{max}$/cm$^{-1}$(Nujol): $C_6F_5$ 1630w, 1603w, 1500vs, 1055vs, 955vs, 794s and 780s; bdma 1374s, 1364s, 1352s, 840s, 740s and 703s; MeCN 2327w and 2305w.

*cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)(dmso)] **4**. This was prepared similarly to **3** in 84% yield using dmso (25 μl, 0.35 mmol) (Found: C, 41.85: H, 2.65; N, 2.05. Calc. for $C_{23}H_{17}F_{10}NOPdS$: C, 42.25; H, 2.95; N, 2.15%); IR $\tilde{\nu}_{max}$/cm$^{-1}$(Nujol): $C_6F_5$ 1632w, 1605w, 1500vs, 1058vs, 957vs, 797s and 783s; bdma 1377s, 1366s, 1352s, 847s, 741s and 671m; dmso 992vs.

*cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)(CO)] **5**. Carbon monoxide was bubbled for 3 min through a solution of **1** (0.19 g, 0.33 mmol) in $CH_2Cl_2$ (2 cm$^3$) at −30 °C and hexane (20 cm$^3$) was added (partial decomposition to Pd metal takes place). After filtration, the colourless solution was stored at −78 °C for 7 h and the resulting white solid, **5**, was filtered off and air dried, 48% yield (Found: C, 43.60; H, 2.35; N, 2.15. Calc. for $C_{22}H_{11}F_{10}NOPd$: C, 43.75; H, 2.15; N, 2.30%); IR $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): $C_6F_5$ 1628w, 1605w, 1500vs, 1058vs, 960vs, 786s and 780s; bdma 1375s, 1365s, 1355s, 836m, 746s and 700s; CO 2135vs (solid) and 2130vs ($CH_2Cl_2$ solution).

[{Pd($C_6F_5$)$_2$(μ-SPMe$_2$Ph)}$_2$] **6**. To a solution of **1** (0.12 g, 0.21 mmol) in $CHCl_3$ (10 cm$^3$) was added SPMe$_2$Ph (0.0355 g, 0.21 mmol). The mixture was stirred at room temperature for 10 min, then the solvent was removed to *ca.* 3 cm$^3$ and hexane (10 cm$^3$) was added; the resulting white solid, **6**, was filtered off and air dried, 91% yield (Found: C, 40.00; H, 1.90. Calc. for $C_{28}H_{12}F_{20}P_2Pd_2S_2$: C, 39.35; H, 1.80%); IR $\tilde{\nu}_{max}$/cm$^{-1}$(Nujol): $C_6F_5$ 1636w, 1609w, 1503vs, 1061vs, 956vs, 793s and 784s; SPMe$_2$Ph 956vs, 908s, 746m, 687m and 536s; $^{31}$P NMR [200 MHz, $(CD_3)_2CO$, internal reference $H_3PO_4$ 85%]: δ 47.39 (s, 2 P).

*X-Ray Crystallography.*—Crystals of *cis*-[Pd($C_6F_5$)$_2$($C_6H_5CH_2NMe_2$-κ$C^1$, κ$N$)] **1** and *cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)($Me_2CO$)] **2** suitable for X-ray diffraction studies were grown by slow diffusion of hexane into dichloromethane solutions of the corresponding complexes at 5 °C and mounted at the end of glass fibres. A summary of crystal data, intensity measurements and structure solution and refinement is given in Table 8. The intensities of the standard reflections were measured every 45 and 120 min for **1** and **2**, respectively, and showed no decay.

*Structure analysis and refinement.* *cis*-[Pd($C_6F_5$)$_2$-($C_6H_5CH_2NMe_2$-κ$C^1$, κ$N$)] **1**. The structure of **1** was solved and developed by direct methods and Fourier techniques. Although the initial location of the Pd and ligated atoms was carried out in space group *C*2/*c*, the remainder of the structure has lower symmetry and the final structural model has space group *Cc*. Because of pseudosymmetry, there was some correlation in the final refinement among the parameters of the two $C_6F_5$ groups. Loose observational restraints were thus applied to the parameters of these groups in the final least-squares cycles.

*cis*-[Pd($C_6F_5$)$_2$($NMe_2CH_2C_6H_5$)($Me_2CO$)] **2**. The structure was solved by the use of Patterson and Fourier methods. All non-hydrogen atoms were refined with anisotropic displacement parameters. One common $U_{iso}$ was refined for each group of methyl hydrogens [$U_{iso}$ = 0.161, 0.103, 0.100 and 0.117 Å$^2$ for hydrogens connected to C(14), C(15), C(16) and C(17) respectively] after positions had been determined from geometrical idealization using difference map information. A common variable $U_{iso}$ was applied to the remaining hydrogen atoms, the positions of which were geometrically detemined ($U_{iso}$ = 0.114 Å$^2$). All the calculations were performed by using the SHELXTL PLUS [32] package on VAX computers.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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