Synthesis and Structural Study of $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)(\mu\text{-}X)]$ Complexes (R = Me or CF_3; X = Hydroxide, Amide or Thiolate)†

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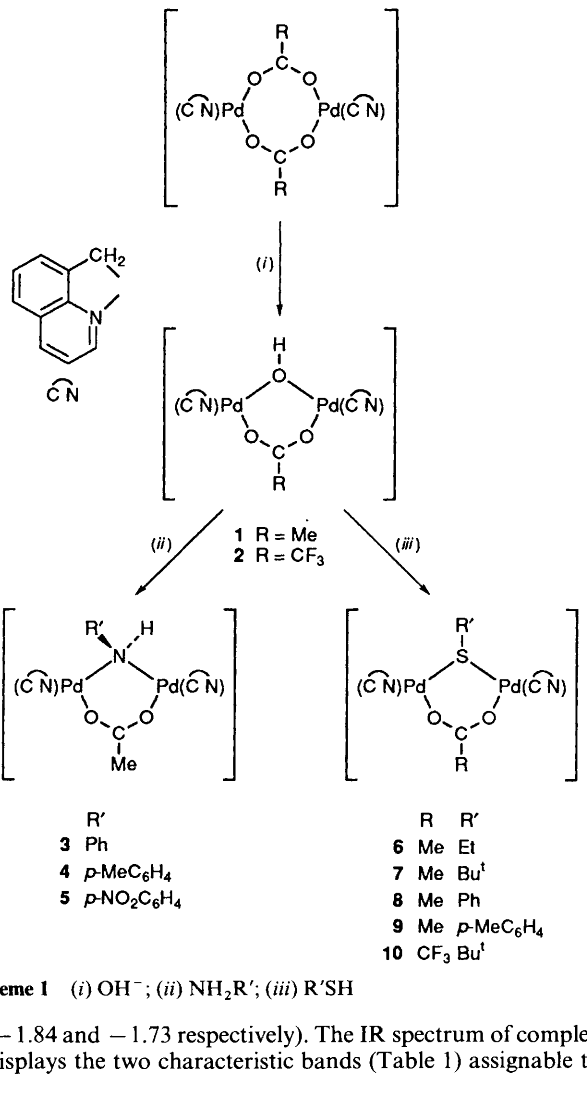
The di-μ-carboxylato complexes $[\{Pd(CH_2C_9H_6N)(\mu\text{-}O_2CR)\}_2]$ ($CH_2C_9H_6N$ = 8-quinolylmethyl, R = Me or CF_3) react in methanol with NaOH(aq) (1 : 1 molar ratio) to give the corresponding mixed hydroxo–carboxylato-bridged complexes $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}OH)(\mu\text{-}O_2CR)]$ (R = Me **1** or CF_3 **2**). The reactions of **1** or **2** with arylamines or thiols (1 : 1 molar ratio) yielded the corresponding amido- or thiolato-carboxylato complexes $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CMe)(\mu\text{-}NHR)]$ (R = Ph **3**, *p*-MeC_6H_4 **4** or *p*-$NO_2C_6H_4$ **5**) or $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)(\mu\text{-}SR')]$ (R = Me, R′ = Et **6**, Bu^t **7**, Ph **8** or *p*-MeC_6H_4 **9**; R = CF_3, R′ = Bu^t **10**). The ^1H NMR data indicate a *cis* arrangement of the $CH_2C_9H_6N$ ligands. The crystal structure of complex **10** has been determined. It confirms the *cis* relationship of the $CH_2C_9H_6N$ ligands. The co-ordination at each palladium atom is approximately square planar and the oxygen atoms of the trifluoroacetate ligands are *trans* to carbon. The $Pd_2(\mu\text{-}OCOCF_3)(\mu\text{-}SBu^t)$ core is quite bent with an angle of 55° between the two palladium co-ordination planes.

Organometallic binuclear nickel, palladium and platinum complexes of the types $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ (R = C_6F_5, M = Ni,[1] Pd[2] or Pt;[3] R = C_6Cl_5, M = Pd[4] or Pt;[3] R = $C_6H_2F_3$-2,4,6, M = Pd[5]) and $[\{MR(L)(\mu\text{-}OH)\}_2]$ (M = Ni, L = PMe_3, R = Me,[6] $CH_2C_6H_4$-Me-*o*,[7] CH_2SiMe_3, CH_2CMe_2Ph or CH_2Ph;[8] L = PPh_3, R = $CClCCl_2$;[9] M = Pd, L = PPh_3, R = Ph,[10] C_6F_5 or C_6Cl_5[11]) have been described. The basic character of these hydroxo complexes allows the preparation of new binuclear complexes $[(MR_2)_2(\mu\text{-}OH)(\mu\text{-}X)]^{2-}$ and $[\{MR_2(\mu\text{-}X)\}_2]^{2-}$ by reaction with the corresponding protic electrophile (HX = azoles,[1,2,4,12] β-diketones,[2,3,5,13] maleononitrile,[14] methanol[12] or heterocyclic thiones[13]).

Very recently[15] the reaction of $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ with acetic acid was tried in order to obtain the corresponding binuclear μ-hydroxo-μ-carboxylato and di-μ-carboxylato complexes. While the di-μ-acetato complex was formed by adding 2 molar equivalents of acetic acid, attempts to prepare the μ-hydroxo-μ-acetato complexes were unsuccessful, and unresolvable mixtures of hydroxo and acetato complexes were obtained. Since the chemistry of these late transition-metal hydroxides and acetates merits study in its own right, we have now examined the metathesis reaction of the μ-carboxylates $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)_2]$ (R = Me or CF_3; $CH_2C_9H_6N$ = 8-quinolylmethyl) in order to prepare the heterobridged complexes $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)(\mu\text{-}OH)]$. These show the expected chemical reactivity towards arylamines and thiols to yield the corresponding binuclear μ-carboxylato-μ-amido and μ-carboxylato-μ-thiolato palladium complexes.



Scheme 1 (*i*) OH^-; (*ii*) NH_2R'; (*iii*) $R'SH$

Results and Discussion

Addition of 1 equivalent of NaOH to $[\{Pd(CH_2C_9H_6N)(\mu\text{-}O_2CR)\}_2]$ (R = Me or CF_3), in methanol–water solution, results in the formation of complexes **1** and **2** (Scheme 1). The analytical data (Table 1) are in agreement with the proposed formulae and the presence of the μ-OH ligand is demonstrated by an IR band at 3590 cm^{-1} and a high-field ^1H resonance (δ −1.84 and −1.73 respectively). The IR spectrum of complex **1** displays the two characteristic bands (Table 1) assignable to

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

Table 1 Analytical data, yields and physical properties for the palladium complexes

Complex	Yield (%)	M.p.[a] (θ/°C)	Analysis (%)[b] C	H	N	S	Selected IR bands[c] (cm^{-1}) $\nu_{asym}(CO_2^-)$	$\nu_{sym}(CO_2^-)$	Others
1	94	177	45.9 (46.1)	3.3 (3.5)	4.8 (4.9)		1560	1405	
2	70	237	42.2 (42.1)	3.0 (2.7)	4.8 (4.5)		1660		3590 ν(OH)
3	71	228	51.7 (51.9)	3.9 (3.9)	6.4 (6.5)		1555	1410	
4	68	226	52.5 (52.6)	4.3 (4.1)	6.3 (6.3)		1555	1410	3310 ν(NH)
5	77	223	48.3 (48.5)	3.5 (3.5)	8.4 (8.1)		1570	1415	3300 ν(NH)
6	63	194	46.4 (46.7)	3.8 (3.9)	4.5 (4.5)	5.0 (5.2)	1560	1405	
7	67	204	48.6 (48.4)	4.3 (4.4)	4.5 (4.3)	4.8 (5.0)	1565	1410	
8	77	195	50.4 (50.5)	3.7 (3.6)	4.4 (4.2)	4.7 (4.8)	1560	1415	
9	76	199	51.6 (51.3)	4.1 (3.9)	4.4 (4.1)	4.5 (4.8)	1550	1415	
10	75	197	44.5 (44.7)	3.6 (3.6)	4.0 (4.0)	4.3 (4.6)	1670		

[a] Decomposition temperatures. [b] Calculated values in parentheses. [c] In Nujol mulls.

the antisymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching modes of the carboxylate group, and the $\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$ value of 155 cm^{-1} is consistent with the presence of bridging bidentate acetate.[16] The $\nu_{asym}(CO_2^-)$ mode for complex **2** is observed at 1660 cm^{-1} but the corresponding $\nu_{sym}(CO_2^-)$ band, expected at *ca.* 1450 cm^{-1},[16] should be masked by the strong absorption from Nujol in this infrared region. The ancillary ligand on each palladium centre is the non-symmetric C,N chelate 8-quinolylmethyl bonded to the metal through a hard-donor nitrogen and a softer σ-bonded carbon atom. Previous studies[17] have demonstrated that complexes of the type [(L–L)Pd(μ-X)(μ-Y)Pd(L–L)] (X = halide, Y = a functional carbanion[18] or a carbonylmetalate anion,[19] L–L = C,N chelate) are characterized by a *cis* structure for the chelate and by a *trans* position for the halide X with respect to the σ-bonded carbon atoms. The observation of only one set of ^{1}H NMR resonances for the $CH_2C_9H_6N$ ligands in complexes **1** and **2** (Table 2) indicates a *cis* arrangement for these groups.

The high-field proton resonance of the μ-OH groups suggests that complexes **1** and **2** should be prone to attack by protic electrophiles [$>Pd(\mu\text{-}OH)(\mu\text{-}O_2CCX_3)Pd< + HY \longrightarrow >Pd(\mu\text{-}Y)(\mu\text{-}O_2CCX_3)Pd< + H_2O$]. In fact arylamines are readily deprotonated by complex **1** yielding the mixed μ-amide-μ-acetate complexes [$\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CMe)(\mu\text{-}NHR)$] (R = Ph **3**, *p*-$MeC_6H_4$ **4** or *p*-$NO_2C_6H_4$ **5**) with the concomitant release of water (Scheme 1). Metal amide complexes of the late transition-metal ions are still relatively uncommon[20–22] and the behaviour of complexes **1** and **2** towards arylamines is similar to that recently observed for [$\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2$], from which [$\{Pd(C_6F_5)(PPh_3)(NHR)(\mu\text{-}OH)\}_2$] (R = aryl) type complexes were obtained as the *anti* isomers.[23] The IR spectra of compounds **3**–**5** exhibit a very weak band at *ca.* 3300 cm^{-1} due to ν(NH) as well as the ν_{asym} and ν_{sym} absorptions corresponding to bridging acetate, but no NH resonance could be observed in the ^{1}H NMR spectra. The ^{1}H NMR data again indicate a *cis* arrangement for the $CH_2C_9H_6N$ ligands and that the aryl group is freely rotating about the C–N bond.

Thiols are similarly deprotonated by complexes **1** and **2** to give the μ-thiolato-μ-carboxylato compounds [$\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}SR')(\mu\text{-}O_2CR)$] (R = Me, R′ = Et **6**, Bu^t **7**, Ph **8** or *p*-MeC_6H_4 **9**; R = CF_3, R′ = Bu^t **10**) (Scheme 1). Some μ-azolato-μ-thiolato and di-μ-thiolato binuclear nickel complexes have been previously obtained by the reaction between [$\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ and a thiol.[24] Binuclear palladium and platinum complexes containing the central M(μ-azolate)(μ-SR)M core are also known,[25,26] and some complexes *cis*-[$\{Pd(L\text{–}L)\}_2(\mu\text{-}O_2CCHClMe)(\mu\text{-}SR)$] (L–L = *ortho*-palladated imine ligand) have been obtained by treating *trans*-[$\{Pd(L\text{–}L)(\mu\text{-}O_2CCHClMe)\}_2$] with HSR.[27] The analytical and spectroscopic data for complexes **6**–**10** are collected in Tables 1 and 2. The ^{19}F NMR spectrum of **10** shows a singlet signal at δ −75.4 and the ^{1}H NMR data for complexes **6**, **8** and **9** are those expected for the presence of the respective R′ groups. The *cis* arrangement of the $CH_2C_9H_6N$ groups is also inferred from the NMR data.

The NMR data for the complexes described give clear evidence for the *cis* arrangement of the $CH_2C_9H_6N$ ligands. For these types of complexes a *trans* position for the σ-bonded carbon atoms with respect to the oxygen atoms of the bridging carboxylate is expected as well as a folded structure of the dimer. Both have been confirmed for complex **10** by a single-crystal X-ray diffraction study. However, an AB NMR pattern is expected for the CH_2 protons of bonded $CH_2C_9H_6N$ but complexes **1**–**6**, **8** and **9** all show a sharp singlet signal for both CH_2 protons, indicating that they are isochronous. Such behaviour suggests that in solution at room temperature a rapid dynamic process occurs on the NMR time-scale which creates an average plane of symmetry for these CH_2 groups. A plausible mechanism[28] involves opening of the carboxylate bridge, rotation about Pd–O (**1** and **2**), Pd–N (**3**–**5**) or Pd–S (**6**, **8** and **9**) bonds in the remaining bridge and remaking of the double bridge. The CH_2 resonances are a broad singlet or a broad doublet for complexes **7** and **10**, respectively, which is in agreement with a slower rotation caused by the bulkier Bu^t group.

The structure of complex **10** (Fig. 1, Tables 3–5) confirms the cisoid arrangement of the cyclometallated ligands, and the arrangement of the bridges so that the oxygen atoms of the trifluoroacetate ligand are *trans* to carbon. The co-ordination at each palladium atom is approximately square planar with a distinct tetrahedral distortion, largely originating in the small bite angle of the quinolylmethyl ligand (≈83.5°). Overall the molecule adopts a folded conformation, with an angle between

Table 2 Proton NMR data for the palladium complexes (solvent $CDCl_3$)

	Chemical shifts (δ, *J* in Hz)					
Complex	H^2	H^4	$H^{3,5,6,7}$	CH_2	$MeCO_2$	Others
1	8.78 (dd)	8.14 (dd)	7.5–7.3 (m)	3.42 (s)	2.21 (s)	−1.84 (s) (OH)
2	8.74 (dd)	8.19 (dd)	7.6–7.3 (m)	3.57 (s)		−1.73 (s) (OH)
3	8.96 (dd)	8.14 (dd)	7.6–7.3 (m)	3.28 (s)	2.33 (s)	7.09 (t, 2 H_o, C_6H_5NH, *J* 7.4) 6.82 (m, 3 H_{m+p}, C_6H_5NH)
4	8.96 (dd)	8.15 (dd)	7.6–7.3 (m)	3.28 (s)	2.32 (s)	7.45 (d, 2 H_o, *p*-MeC_6H_4NH, *J* 8.1) 6.89 (d, 2 H_m, *p*-MeC_6H_4NH, *J* 8.1) 2.17 (s, 3 H, *p*-MeC_6H_4NH)
5	8.96 (dd)	8.19 (dd)	7.6–7.3 (m)	3.29 (s)	2.35 (s)	7.99 (d, 2 H_o, *p*-$NO_2C_6H_4NH$, *J* 8.0) 7.45 (d, 2 H_m, *p*-$NO_2C_6H_4NH$, *J* 8.0)
6	8.87 (dd)	8.16 (dd)	7.6–7.3 (m)	3.28 (s)	2.20 (s)	2.38 (q, 2 H, CH_2S, *J* 7.2) 1.39 (t, 3 H, CH_3CH_2S, *J* 7.2)
7	9.01 (dd)	8.19 (dd)	7.6–7.3 (m)	3.38 (br)	2.23 (s)	1.60 (s, 9 H, Bu^tS)
8	8.88 (dd)	8.24 (dd)	7.6–7.3 (m)	3.46 (s)	1.81 (s)	8.07 (dd, 2 H_o, C_6H_5S, $J_{H_oH_p}$ 2.2, $J_{H_oH_m}$ 7.7) 7.13 (m, 3 H_{m+p})
9	8.88 (dd)	8.19 (dd)	7.6–7.3 (m)	3.44 (s)	2.23 (s)	7.91 (d, 2 H_o, *p*-MeC_6H_4S, *J* 8.1) 6.94 (d, 2 H_m, *p*-MeC_6H_4S, *J* 8.1) 1.85 (s, 3 H, *p*-MeC_6H_4S)
10	8.90 (dd)	8.19 (dd)	7.6–7.4 (m)	3.56 (br) 3.36 (br)		1.56 (s, 9 H, Bu^tS)

Table 3 Fractional atomic coordinates (× 10^4) for complex **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	2100.1(3)	1989.1(1)	1196.0(2)	C(9)	−2467(4)	6065(3)	19(3)
Pd(2)	23.1(3)	3681.6(2)	1533.4(2)	C(10)	−1757(4)	3686(2)	881(2)
S	−88(1)	2331(1)	1537(1)	C(11)	2945(3)	3448(2)	2329(2)
F(1)	5169(3)	3933(2)	2381(2)	C(12)	4127(4)	3802(2)	2843(3)
F(2)	4504(4)	3340(2)	3470(2)	C(13)	−487(4)	2000(2)	2649(2)
F(3)	3845(3)	4456(2)	3233(2)	C(14)	626(5)	2221(3)	3294(3)
O(1)	3205(3)	2781(2)	2050(2)	C(15)	−1798(5)	2413(3)	2903(3)
O(2)	1916(2)	3858(1)	2264(2)	C(16)	−649(7)	1116(3)	2615(3)
N(1)	−106(3)	4895(2)	1377(2)	C(17)	5190(4)	1885(2)	949(3)
N(2)	3958(3)	1653(2)	708(2)	C(18)	6369(4)	1662(3)	511(3)
C(1)	711(4)	5445(2)	1680(3)	C(19)	6256(4)	1181(2)	−193(3)
C(2)	535(5)	6247(2)	1481(3)	C(20)	4981(4)	919(2)	−472(2)
C(3)	−480(4)	6469(2)	940(3)	C(21)	3835(4)	1161(2)	10(2)
C(4)	−1380(4)	5899(2)	593(2)	C(22)	2491(4)	919(2)	−206(2)
C(5)	−1179(3)	5110(2)	842(2)	C(23)	2342(4)	461(2)	−931(2)
C(6)	−2034(4)	4502(2)	553(2)	C(24)	3456(5)	236(2)	−1430(2)
C(7)	−3068(4)	4691(3)	−14(3)	C(25)	4740(4)	451(2)	−1208(2)
C(8)	−3269(4)	5488(3)	−285(3)	C(26)	1365(4)	1176(2)	376(3)

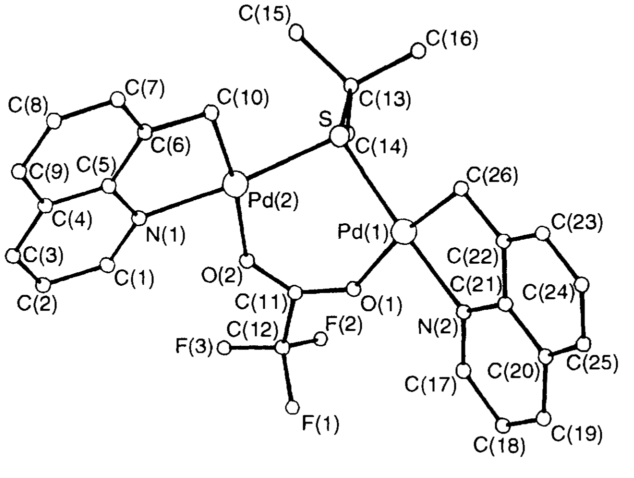

Fig. 1 Structure of complex **10**

the palladium co-ordination planes of 55°. There is some widening of the O–C–O angle of the bridging trifluoroacetate to 131° to accommodate this. The quinolylmethyl ligands are approximately planar and are tilted to a small extent (8–10°) out of the co-ordination planes of the palladium atoms. Whilst the two palladium atoms are crystallographically distinct, the bond lengths and angles in the two halves of the molecule are not, in general, significantly different. The palladium–carbon bond lengths are similar to those noted for $[Pd(CH_2C_9H_6N)\{Ph_2PC(CO_2Et)(CO_2H)\}]$[2.05(2) Å],[18] $[Pd(CH_2C_9H_6N)\{C_{10}H_6(OMe)\text{-}1\}]$ [1.986(4) Å][32] and $[\{Pd(CH_2C_9H_6N)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}Ph_2PCHCO_2Et)][PF_6]$ [2.01(1)–2.06(1) Å][17] in which the carbon is *trans* to an oxygen ligand. To the best of our knowledge this is the first report of the structure of a complex in which the nitrogen of the $CH_2C_9H_6N$ ligand is *trans* to sulfur. The Pd–N bond [average 2.066(3) Å] is shorter than in $[Pd(CH_2C_9H_6N)\{C_{10}H_6(OMe)\text{-}1\}]$ [2.127(6) Å] in which nitrogen is *trans* to carbon[32] or $[Pd(CH_2C_9H_6N)(PMe_2Ph)\text{-}\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ [2.150(7) Å] in which it is *trans* to phosphorus,[33] but in $[Pd(CH_2C_9H_6N)\{Ph_2PC(CO_2Et)\text{-}(CO_2H)\}]$ the Pd–N bond *trans* to phosphorus is only 2.07(2) Å long. This suggests that any attempt to correlate bond length with *trans* influence would require many more examples before useful conclusions could be drawn.

Experimental

The C, H, N and S analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures

Table 4 Selected bond lengths (Å) and angles (°) for complex **10**

Pd(1)–S	2.285(1)	Pd(2)–S	2.293(1)
Pd(1)–N(2)	2.056(3)	Pd(2)–N(1)	2.076(3)
Pd(1)–O(1)	2.166(3)	Pd(2)–O(2)	2.183(2)
Pd(1)–C(26)	2.003(4)	Pd(2)–C(10)	2.006(4)
S–Pd(1)–O(1)	99.56(7)	S–Pd(2)–O(2)	100.12(7)
S–Pd(1)–C(26)	89.3(1)	S–Pd(2)–C(10)	87.9(1)
O(1)–Pd(1)–C(26)	170.9(1)	O(2)–Pd(2)–C(10)	171.8(1)
S–Pd(1)–N(2)	171.52(8)	S–Pd(2)–N(1)	171.02(8)
O(1)–Pd(1)–N(2)	87.5(1)	O(2)–Pd(2)–N(1)	88.6(1)
N(2)–Pd(1)–C(26)	83.7(1)	N(1)–Pd(2)–C(10)	83.5(1)
Pd(1)–S–Pd(2)	102.03(3)	Pd(2)–O(2)–C(11)	131.1(2)
O(1)–C(11)–O(2)	131.3(3)	Pd(1)–O(1)–C(11)	132.5(2)

Table 5 Crystal structure determination details for complex **10**

Formula	$C_{26}H_{25}F_3N_2O_2Pd_2S$
M	699.29
Symmetry	Monoclinic
Space group	$P2_1/n$ (non-standard no. 14)
a/Å	9.790(2)
b/Å	16.958(2)
c/Å	15.476(3)
β/°	90.51(2)
U/Å^3, Z	2569.1(9), 4
D_c/g cm^{-3}, F(000)	1.81, 1384
T/K	295
Monochromated Mo-Kα radiation	
λ/Å	0.710 69
μ/cm^{-1}	15.07
Crystal size/mm	0.25 × 0.28 × 0.23
Diffractometer	Enraf–Nonius CAD4
Reflections for calculating cell: number, θ_{min}, θ_{max}/°	25, 8, 9
Scan mode for data collection	θ–2θ
Data reflection ranges; θ range	h 0–11, k 0–20, l −18 to 18; 2–25
Total reflections measured	4977
Unique reflections	4703
R_{int}	0.016
Significant reflections, $\|F^2\| > 2\sigma(F^2)$	3706
Maximum change in standard reflections (%)	−11.5
Decay correction	Yes
Absorption correction: maximum, minimum	DIFABS[29]: 1.123, 0.903
Non-H atoms:	Located by heavy-atom methods, SHELXS 86[30]
Refinement:	Full-matrix least squares using Enraf–Nonius SDP programs,[31] non-H atoms anisotropic
Hydrogen atoms	Fixed calculated positions, $U_{iso} = 1.3U_{eq}$ for parent atom
R	0.027
R'	0.039
S	1.2
No. variables	325
$(\Delta/\sigma)_{max}$	0.02
$(\Delta\rho)_{max,min}$/e Å^{-3}	0.63, −0.13

$\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$, $w = \sigma^{-2}(F)$, minimizing $\Sigma w(|F_o| - |F_c|)^2$.

were determined with a Mettler TG-50 thermobalance. The NMR spectra were recorded on a Bruker AC 200E (^{1}H) or Varian Unity 300 (^{19}F) spectrometer, using SiMe$_4$ and CFCl$_3$ as standards respectively, infrared spectra on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets.

The starting complex [{Pd(CH$_2$C$_9$H$_6$N)(μ-O$_2$CMe)}$_2$] was prepared as described elsewhere.[28] Its ^{1}H NMR data are in agreement with those reported but the relative intensities indicated that in CDCl$_3$ solution there is a 2.5 : 1 mixture of *trans* and *cis* isomers, respectively. A 4 : 1 mixture is reported in ref. 28 but this discrepancy may be attributed to both the different concentrations and temperatures used to record the spectra.

The bis-(μ-trifluoroacetate) analogue was prepared in 70% yield by reaction of the orange di-μ-acetate complex (0.24 mmol) with trifluoroacetic acid (0.48 mmol) in methanol (5 cm^3). The red crystals formed gave satisfactory C, H and N analysis, an IR band at 1650 cm^{-1} for the antisymmetric stretching mode of the CO$_2^-$ group and the ^{19}F NMR spectrum (solvent CDCl$_3$) displayed a signal at δ −74.5, assigned to the *trans* isomer, and two additional 1 : 1 signals at δ −73.8 and −75.0, assigned to the *cis* isomer (the relative intensities indicated that it was a 3 : 1 mixture of *trans* and *cis* isomers respectively). The ^{1}H NMR spectrum (solvent CDCl$_3$) showed two broad signals at δ 3.7 (*trans* isomer) and 2.8 (*cis* isomer) owing to the CH$_2$ protons of CH$_2$C$_9$H$_6$N.

Preparations.—Complexes **1** *and* **2**. To a solution of [{Pd(CH$_2$C$_9$H$_6$N)(μ-O$_2$CR)}$_2$] (R = Me or CF$_3$) (0.135 mmol) in methanol (3 cm^3) was added NaOH (aq) (0.135 mmol). The resulting solution was stirred for 10 min, during which time the yellow complexes **1** and **2** precipitated spontaneously. They were filtered off and air-dried.

Complexes **3**–**5**. The appropriate amine NH$_2$R′ (0.122 mmol) was added to a solution of [{Pd(CH$_2$C$_9$H$_6$N)}$_2$(μ-OH)(μ-O$_2$CMe)] (0.122 mmol) in dichloromethane (3 cm^3). The solution was stirred at room temperature for 10 min. On addition of hexane the yellow or orange complexes **3**–**5** precipitated and were filtered off and air-dried.

Complexes **6**–**10**. The appropriate thiol R′SH (0.174 mmol) was added to a solution of [{Pd(CH$_2$C$_9$H$_6$N)}$_2$(μ-OH)(μ-O$_2$CR)] (R = Me or CF$_3$) (0.174 mmol) in dichloromethane (4 cm^3) and the solution was stirred at room temperature for 10 min. On addition of diethyl ether–hexane the yellow or orange complexes **6**–**10** precipitated and were filtered off and air-dried.

Crystal Structure Determination of Complex **10**.—Details of the crystal structure determination are given in Table 5.

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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