Interaction of Palladium(II) Acetate with Substituted Pyridines, including a Cyclometallation Reaction and the Structure* of [Pd{*meso*-[(py)PhMeC]$_2$-C$_5$H$_3$N}(O$_2$CMe)][O$_2$CMe]·3H$_2$O

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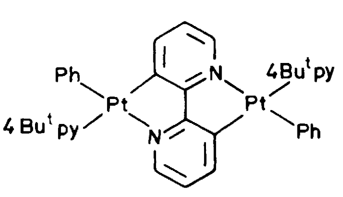
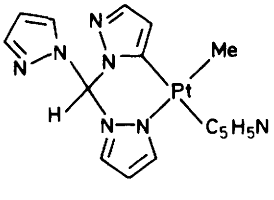
The reactivity of *meso*- and *rac*- diastereoisomers of 2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine {[(py)PhMeC]$_2$C$_5$H$_3$N}, 2,6-bis[1,1-bis(pyridin-2-yl)ethyl]pyridine {[(py)$_2$MeC]$_2$C$_5$H$_3$N}, and the pyridin-2-yl methanes (py)$_n$Ph$_{3-n}$CH (n = 1—3), (py)$_n$CH$_{4-n}$ (n = 2 or 3), and (py)$_3$PhC toward palladium(II) acetate in refluxing glacial acetic acid and at ambient temperature in organic solvents has been investigated. The nitrogen donor ligands form co-ordination derivatives in organic solvents. All except α-phenyl-α-(pyridin-2-yl)toluene[(py)Ph$_2$CH] form identical complexes in glacial acetic acid, with (py)Ph$_2$CH undergoing cyclometallation to form [{Pd[(py)PhHCC$_6$H$_4$](μ-O$_2$CMe)}$_2$]. *meso*-[(py)PhMeC]$_2$C$_5$H$_3$N, which binds as a tripodal tridentate ligand to methylmercury(II), has been shown by a single crystal *X*-ray study to act as a planar tridentate ligand to palladium(II) in [Pd{*meso*-[(py)PhMeC]$_2$C$_5$H$_3$N}(O$_2$CMe)][O$_2$CMe]·3H$_2$O with square-planar co-ordination being completed by a unidentate acetate group [monoclinic, space group $P2_1/c$, a = 11.795(5), b = 23.10(1), c = 12.313(5) Å, β = 95.64(3)°, Z = 4; R = 0.051 for 3 657 'observed' reflections]. Syntheses of the new ligand [(py)$_2$MeC]$_2$C$_5$H$_3$N, with five pyridine donor groups, and α,α,α-tris(pyridin-2-yl)toluene [(py)$_3$PhC] are described.

Cyclometallation reactions involving suitable substrates containing nitrogen-donor groups often proceed readily with palladium(II) compounds,[1-6] *e.g.* reaction of palladium(II) acetate with 2-benzylpyridine, (py)CH$_2$C$_6$H$_5$, gives [{Pd[(py)-CH$_2$C$_6$H$_4$](μ-O$_2$CMe)}$_2$][7] and [PdCl$_4$]$^{2-}$ reacts with 2-phenylpyridine, (py)C$_6$H$_5$, to give [{Pd[(py)C$_6$H$_4$](μ-Cl)}$_2$][8,9] with both reactions involving metallation at the *ortho* position of the phenyl rings and co-ordination through N of pyridine. Closely related polydentate ligands usually give co-ordination compounds rather than metallation products, *e.g.* 2,2′-bipyridyl which has a potential metallation site similar to that of 2-phenylpyridine gives *N,N′*-bidentate co-ordination[10] with [PdCl$_4$]$^{2-}$. However, reactions involving metallation of 2,2′-bipyridyl and other polydentate ligands have been reported, *e.g.* recent reports describe dimetallation of 2,2′-bipyridyl in [PtPh$_2$(N$_2$C$_{10}$H$_8$)] on heating in 4-t-butylpyridine (4Bu^t-py) to form (**A**),[11] and metallation of tris(pyrazol-1-yl)methane in [PtMe$_2${CH(C$_3$H$_3$N$_2$)$_3$}] on heating in pyridine (C$_5$H$_5$N) to form (**B**).[12,13]



(A)



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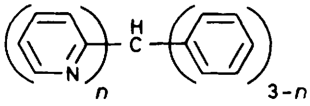
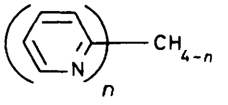
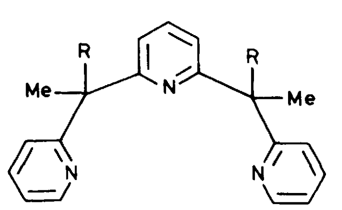


(py)$_n$Ph$_{3-n}$CH (n=1-3)



(py)$_n$CH$_{4-n}$ (n= 2 or 3)



R = Ph: *meso*- and *rac*- [(py)PhMeC]$_2$C$_5$H$_3$N

R = py: [(py)$_2$MeC]$_2$C$_5$H$_3$N

Metallation of tris(pyrazol-1-yl)methane, and earlier reports of metallation of 2-(2-thienyl)pyridine[14] and 2,2′-bipyridyl[15] involving iridium(III), have prompted us to examine the interaction of palladium(II) acetate with a range of 2- and 2,6-substituted pyridines similar to 2-benzylpyridine, but containing additional pyridine and/or phenyl groups: (py)$_n$Ph$_{3-n}$CH (n = 1—3), (py)$_n$CH$_{4-n}$ (n = 2 or 3), (py)$_3$PhC, *meso*- and *rac*-[(py)PhMeC]$_2$C$_5$H$_3$N, and [(py)$_2$MeC]$_2$C$_5$H$_3$N.

Results and Discussion

Preparation and Characterization of Complexes.—Several of the ligands are new, and syntheses of these are based on organolithium procedures, with subsequent reactions required in some cases. Thus, α,α,α-tris(pyridin-2-yl)toluene [(py)$_3$PhC] was obtained as a by-product from the reported preparation[16] of (py)$_2$PhCH from lithiated 2-benzylpyridine and 2-bromo-

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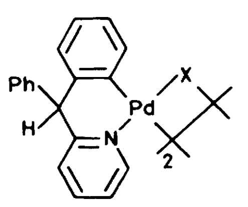
* (Acetato-*O*){*meso*-2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine-*N,N′,N″*}palladium(II) acetate trihydrate.

Supplementary data available (No. SUP 56588, 5 pp.): thermal parameters, H-atom parameters, mean planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical and spectroscopic data

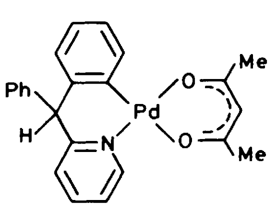
Complex	Form	Analysis (%)[a]			^1H N.m.r.[b]
		C	H	N	
(1) $[\{Pd[(py)PhHCC_6H_4](O_2CMe)\}_2]\cdot\frac{2}{3}CH_2Cl_2$[c]	Pale yellow crystals	54.6 (54.4)	4.2 (3.9)	3.4 (2.9)	*d*
(2) $[\{Pd[(py)PhHCC_6H_4]Cl\}_2]$	Pale yellow powder	55.7 (56.0)	3.6 (3.6)	3.3 (3.6)	*d*
(3) $[Pd\{(py)PhHCC_6H_4\}(acac)]$	Colourless crystals	61.3 (61.4)	5.0 (4.7)	3.1 (3.1)	8.81, **1**, *d*, H(6); 7.7—7.3, *m*, and 7.26, 6.9 *m*, **12**, H(3—5) and Ph; 5.46, **1**, *s*, CH; 5.23, **1**, *s*, CH of acac; 1.99, **3**, *s*, and 1.91, **3**, *s*, CH_3; $J_{(5,6)}$ = 5 Hz
(4) $[Pd\{(py)Ph_2CH\}_2(O_2CMe)_2]$	Pale yellow crystals	67.4 (67.2)	5.3 (5.1)	3.7 (3.9)	9.48, **2**, *br*, H(6); 7.78, **1**, *s*, CH; 7.65—7.0, **26**, *m*, H(3—5) and Ph; 1.30, **6**, *s*, $\frac{1}{2}CH_3$
(5) $[Pd\{(py)_2CH_2\}(O_2CMe)_2]\cdot 0.5CHCl_3$[e]	Yellow crystals	40.4 (40.9)	3.6 (3.7)	6.0 (6.2)	8.63, **2**, *d*, H(6); 7.95—7.65, **2**, *m*, and 7.55—7.15, **4**, *m*, H(3—5); 5.07, **2**, *s*, CH_2; 1.99, **6**, *s*, CH_3
(6) $[Pd\{(py)_2PhCH\}(O_2CMe)_2]\cdot\frac{4}{5}C_6H_6$	Yellow crystals	57.0 (57.0)	5.0 (4.9)	5.2 (5.4)	8.24, **2**, *d*, H(6); 8.0—7.1, **8**, *m*, H(3—5) and Ph; 6.24, **1**, *s*, CH; 1.82, **6**, *s*, CH_3; $J_{(5,6)}$ = 6 Hz
(7) $[Pd\{(py)_3CH\}(O_2CMe)_2]\cdot C_6H_6$[f]	Orange crystals	56.3 (56.8)	4.7 (4.6)	7.6 (7.6)	9.04, **2**, *d*, and 8.64, **1**, *br*, H(6); 8.1—7.0, ~**12**, *m*, H(3—5) and C_6H_6; 5.96, **1**, CH; 2.00, **6**, *s*, CH_3; $J_{(5,6)}$ ~6 Hz
(8) $[Pd\{(py)_3PhC\}(O_2CMe)_2]$	Yellow plates	57.3 (57.0)	4.0 (4.2)	7.5 (7.7)	9.05, **2**, *d*, H(6); 8.65, **1**, *d*, H(6); 7.8—6.6, **14**, *m*, H(3—5) and Ph; 1.80, **6**, *s*, CH_3; $J_{(5,6)}$ = 5.0, 5.8 Hz
(9) $[Pd\{[(py)_2MeC]_2C_5H_3N\}(O_2CMe)][O_2CMe]\cdot 3H_2O$	Pale yellow crystals	54.6 (54.9)	5.0 (5.2)	9.3 (9.7)	8.43, **1**, *t*, H(4); 8.26, **2**, *d*, H(6′); 8.18, **2**, *m*, H(4′); 8.08, **4**, *m*, H(3′,5′); 7.91, **2**, *dd*, H(6″); 7.70, **2**, *m*, H(4″); 7.41, **4**, *m*, H(3″,5″); 6.63, **2**, *d*, H(3,5); 5.03, **6**, *s*, H_2O; 2.40, **6**, *s*, $\frac{1}{2}$Me; 2.01, **6**, *s*, $MeCO_2$; $J_{(3,4)} \equiv J_{(4,5)}$ = 8.0, $J_{(5',6')}$ = 4.3, $J_{(5'',6'')}$ = 5.6, $J_{(4'',6'')}$ = 1.4 Hz
(10) $[Pd\{$*meso*-$[(py)PhMeC]_2C_5H_3N\}(O_2CMe)][O_2CMe]\cdot 3H_2O$	Pale yellow crystals	61.1 (61.4)	5.6 (5.2)	5.4 (6.1)	8.70, **1**, *dd*, H(6); 8.48, **1**, *m*; 8.34—8.22, **2**, *m*; 7.82—7.41, **9**, *m*; 7.18, **2—3**, *m*; 6.97—6.79, **3—4**, *m*; *ca.* 6.5, **2**, *m*; 3.30, **3**, *s*, Me; 2.53, **3**, *s*, Me; 1.93, **3**, *s*, $MeCO_2$; 1.87, **3**, *s*, $MeCO_2$; $J_{(5,6)}$ = 5.27, $J_{(4,6)}$ = 1.17 Hz
(11) $[Pd\{$*rac*-$[(py)PhMeC]_2C_5H_3N\}(O_2CMe)][O_2CMe]\cdot 3H_2O$	Pale yellow crystals	57.2 (57.7)	5.1 (5.4)	6.1 (5.8)	8.70, **1**, *dd*, H(6); 8.50, **1**, *m*; 8.34—8.22, **2**, *m*; 7.8—7.4, **9**, *m*; 7.17, **2—3**, *m*; 6.96—6.79, **3—4**, *m*; *ca.* 6.6, **2**, *m*; 3.31, **3**, *s*, Me; 2.54, **3**, *s*, Me; 1.93 **3**, *s*, $MeCO_2$; 1.87, **3**, *s*, $MeCO_2$; $J_{(5,6)}$ ~ 5.3, $J_{(4,6)}$ = 1.17 Hz

[a] Calculated values are given in parentheses. [b] In $CDCl_3$, chemical shifts are in p.p.m. from $SiMe_4$. Tabulated as chemical shift, **relative intensity**, *multiplicity*, assignment. Measured at 100 MHz, except for (**9**)—(**11**) which were measured as 300 MHz. [c] Mass spectra exhibit an ion with *m/e* 83.9526, calc. for $^{12}C^1H_2{}^{35}Cl_2$ 83.9534. [d] Insufficiently soluble for ^1H n.m.r. determination. [e] Mass spectra exhibit an ion with *m/e* 82.9456, calc. for $^{12}C^1H^{35}Cl_2$ 82.9455. [f] Mass spectra exhibit an ion with *m/e* 78.0456, calc. for $^{12}C_6{}^1H_6$ 78.0469.

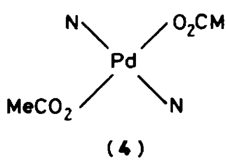


(**1**) X = $MeCO_2^-$

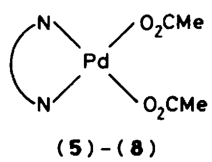
(**2**) X = Cl^-



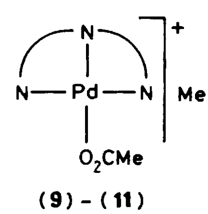
(**3**)



(**4**)



(**5**)-(**8**)



(**9**) - (**11**)

pyridine (2Br-py) [equation (1)]; and 2,6-bis[1,1-bis(pyridin-2-yl)ethyl]pyridine $\{[(py)_2MeC]_2C_5H_3N\}$ was obtained in a stepwise manner from lithiated $(py)_2CH_2$ [equations (2 and 3)].

$$(py)PhCH_2 \xrightarrow[(ii)\ 2Br\text{-}py]{(i)\ LiPh} (py)_2PhCH + (py)_3PhC \tag{1}$$

$$(py)_2CH_2 \xrightarrow[(ii)\ MeI]{(i)\ LiPh} (py)_2MeCH \tag{2}$$

$$2(py)_2MeCH \xrightarrow[(ii)\ 2,6Cl_2\text{-}py]{(i)\ 2LiPh} [(py)_2MeC]_2C_5H_3N \tag{3}$$

The ligands $(py)_3PhC$ and $[(py)_2MeC]_2C_5H_3N$ have satisfactory microanalyses (C,H,N), ^1H n.m.r. and mass spectra, and osmometric molecular weights.

On refluxing solutions of palladium(II) acetate and ligands in glacial acetic acid, under identical conditions to those resulting in metallation of 2-benzylpyridine,[7] only $(py)Ph_2CH$ gave a cyclometallated product, (**1**). For complex (**1**), both chloro (**2**) and acetylacetonato(acac) (**3**) derivatives were obtained to assist with interpretation of ^1H n.m.r. spectra, and the complex $[Pd\{(py)Ph_2CH\}_2(O_2CMe)_2]$ (**4**) was prepared by reaction in benzene for comparison (Table 1). The remaining ligands gave low yields of simple nitrogen-donor palladium(II) acetate complexes (**5**)—(**11**), and these were synthesized more conveniently by reaction in benzene, toluene, or dichloromethane.

Analytical and spectroscopic data for the complexes are presented in Table 1 with degree of solvation required to account for microanalyses (confirmed by ^1H n.m.r. and/or mass spectra). Although crystallographic studies of (**10**) show it to be a trihydrate (see below), the crystals became opaque on drying over P_2O_5 in a vacuum prior to microanalysis, consistent with

Table 2. Co-ordination geometry for the palladium atom in [Pd{*meso*-[(py)PhMeC]$_2$C$_5$H$_3$N}(O$_2$CMe)][O$_2$CMe]·3H$_2$O; distances in Å, angles in °

Pd-N(a1)	2.020(5)	Pd-N(c1)	2.009(5)
Pd-N(b1)	1.999(5)	Pd-O(1)	2.003(5)
N(a1)-Pd-N(b1)	89.0(2)	Pd-N(a1)-C(a2)	118.5(4)
N(a1)-Pd-N(c1)	177.8(2)	Pd-N(a1)-C(a6)	121.1(4)
N(b1)-Pd-N(c1)	88.7(2)	Pd-N(b1)-C(b2)	117.7(4)
N(a1)-Pd-O(1)	90.8(2)	Pd-N(b1)-C(b6)	120.3(4)
N(b1)-Pd-O(1)	177.9(2)	Pd-N(c1)-C(c2)	121.0(4)
N(c1)-Pd-O(1)	91.4(2)	Pd-N(c1)-C(c6)	117.0(4)
		Pd-O(1)-C	117.2(4)

Deviation of atoms from the 'PdN$_3$O' mean plane:
Pd, −0.001; N(a1), −0.008; N(b1), 0.033; N(c1), −0.006; O(1), 0.037 Å

Deviation of Pd from the 'C$_5$N' mean planes of rings a, b, c:
0.067, 0.388, 0.160 Å

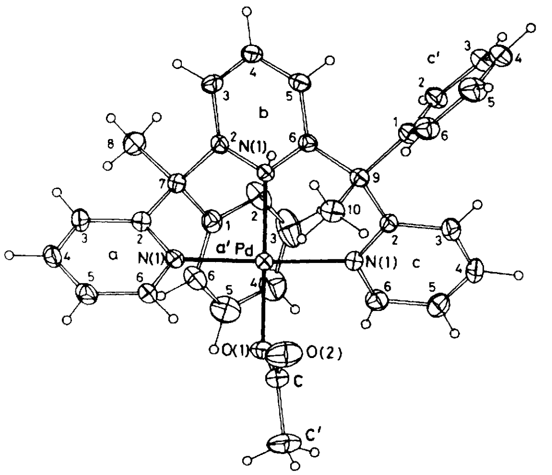


Figure. The cation [Pd{*meso*-[(py)PhMeC]$_2$C$_5$H$_3$N}(O$_2$CMe)]$^+$ projected normal to the 'PdN$_3$O' co-ordination plane. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å

partial dehydration. The acetone soluble ionic complexes (**9**)—(**11**) have molar conductances of 56, 42, and 52 ohm^{-1} cm^2 mol^{-1}, respectively.

The acetates exhibit i.r. absorptions in the region expected for ν(CO$_2^-$), although for most of the complexes extensive overlapping absorptions preclude definite assignment. For (**1**) acetate bands at 1 586m and 1 416m cm^{-1} are consistent with the dimeric structure shown, and are at similar positions to the dimeric palladated complex of 2-benzylpyridine (1 585, 1 420 cm^{-1}).[7]

^{1}H N.m.r. spectra are readily interpretable for most of the complexes, in particular relative intensities, assignment of methylene and methine protons, and assignment of H(6) for pyridine rings. Thus, although (**1**) and (**2**) were insufficiently soluble, the acac derivative (**3**) exhibited resonances for acac protons, including two methyl environments as expected, single resonances for H(6) and the methine protons, and complex multiplets for the phenyl and remaining pyridine resonances. Complexes (**5**) and (**6**), with bidentate (py)$_2$CH$_2$ and (py)$_2$PhCH, respectively, exhibit one pyridine environment; (**7**) and (**8**), with bidentate (py)$_3$CH and (py)$_3$PhC, respectively, exhibit both co-ordinated and unco-ordinated pyridine ring environments in a 2:1 ratio, *e.g.* (**8**) shows H(6) resonances as doublets at 9.05 and 8.65 p.p.m.

The bidentate ligands clearly form complexes of *cis* stereochemistry, *cis*-PtN$_2$O$_2$, in (**5**)—(**8**), but the unidentate ligand (py)Ph$_2$CH presumably forms a *trans*-complex in (**4**) similar to that proposed[17] for [Pd(C$_5$H$_5$N)$_2$(O$_2$CMe)$_2$].

Complex (**9**), involving the ligand [(py)$_2$MeC]$_2$C$_5$H$_3$N, gives ^{1}H n.m.r. spectra indicating the presence of the central pyridine ring [H(3—5)], and two other pyridine ring environments [H(3′—6′) and H(3″—6″)] in a 1:1 ratio (Table 1), consistent with the presence of the ligand as a tridentate with two unco-ordinated rings. Resonances H(3′—6′) are downfield from H(3″—6″) and are assumed to result from the co-ordinated rings. Although only one acetate resonance is observed, a structure with one co-ordinated and one unco-ordinated acetate is assumed, as found for (**10**) and (**11**), which have acetate resonances almost coincident. ^{1}H N.m.r. spectra of (**10**) and (**11**) are further discussed after the presentation of *X*-ray crystallographic results for the trihydrate form of (**10**).

Structure of [Pd{*meso*-[(py)PhMeC]$_2$C$_5$H$_3$N}(O$_2$CMe)][O$_2$CMe]·3H$_2$O.—The complex is composed of [Pd{*meso*-[(py)PhMeC]$_2$C$_5$H$_3$N}(O$_2$CMe)]$^+$ cations, acetate ions, and water molecules. Details of the co-ordination geometry are given in Table 2, and a view of the cation is given in the Figure.

The palladium atom has a square-planar co-ordination environment with the nitrogen donor ligand present as a tridentate, with N(b1)-Pd-N(a1,c1) angles 89.0(2) and 88.7(2)°, and a unidentate acetate with O(1)-Pd-N(a1,c1) 90.8(2) and 91.4(2)°. The maximum deviation from the mean plane 'PdN$_3$O' was found for N(c1) (−0.006 Å). The palladium atom lies close to the mean planes of co-ordinated rings a and c, at 0.067 and 0.160 Å, respectively, but is 0.388 Å from the mean plane of the central ring b.

The pyridine and phenyl rings are planar, with the maximum deviation from mean planes C$_5$N or C$_6$ observed for the pyridine ring c (0.028 Å); the co-ordinated and unco-ordinated acetate groups are planar, with the maximum deviation from mean planes 'C$_2$O$_2$' observed for the carboxylate carbon of the unco-ordinated acetate (−0.14 Å).

Neighbouring cations are related by centres of symmetry (space group $P2_1/c$) for which C(7) and C(9) have *S* and *R* chirality, respectively.

Thus, the ligand *meso*-[(py)PhMeC]$_2$C$_5$H$_3$N, whose synthesis is reported in the preceding paper,[18] is able to act as both a tripodal tridentate [with methylmercury(II)][18] and a planar tridentate ligand [with palladium(II)]. This ligand may be regarded as a pyridine analogue of diethylenetriamine, (H$_2$NCH$_2$CH$_2$)$_2$NH, but forming six- rather than five-membered chelate rings.

I.r. and ^{1}H *N.M.R. Spectra for the* meso- *and* rac-*Complexes* (**10**) *and* (**11**).—I.r. spectra of (**10**) and (**11**) are very similar, except for the region containing ν$_{sym}$(CO$_2^-$), which for (**10**) exhibits a very broad absorption at *ca.* 1 382 cm^{-1}, while (**11**) exhibits a strong, sharp band at 1 378 cm^{-1}. ^{1}H N.m.r. spectra of (**10**) and (**11**) are identical, and both exhibit two acetate, methyl, and pyridine H(6) environments. The two acetate environments result from co-ordinated and unco-ordinated acetate groups, and for the *meso*-ligand co-ordination results in two methyl and two pyridine H(6) environments corresponding to methyl orientations near to and far from palladium [C(8) and C(10), respectively, in the Figure]. Similarly, for the *rac*-ligand, two conformations occur, one with both methyl groups near to palladium and one with both methyl groups far from palladium.

Experimental

Palladium(II) acetate,[17] bis(pyridin-2-yl)methane [$(py)_2CH_2$],[19] tris(pyridin-2-yl)methane [$(py)_3CH$],[20] and α,α-bis(pyridin-2-yl)toluene [$(py)_2PhCH$][16] were prepared as described. α-Phenyl-α-(pyridin-2-yl)toluene [$(py)Ph_2CH$] (Aldrich) was used as received, and acetylacetonatothallium(I) was prepared by a method identical to that described for the benzoylacetonato-derivative.[21] Iodomethane was dried over 4 Å molecular sieves; 2-benzylpyridine was distilled under vacuum and stored over sieves; acetic acid was refluxed and distilled from acetic anhydride and potassium permanganate; acetone was refluxed and distilled from magnesium sulphate and stored over sieves; benzene was washed with sulphuric acid, water, potassium hydroxide, then refluxed and distilled from phosphorus pentoxide, and stored over sodium; light petroleum (b.p. 40—60 °C) and chloroform were distilled; other reagents and solvents were purified as described in the preceding paper.[18]

Microanalyses were by the Australian Microanalytical Service, i.r. spectra of Nujol or hexachlorobutadiene mulls were recorded with an Hitachi 270-30 spectrophotometer, ^1H n.m.r. spectra in $CDCl_3$ were measured with JEOL JNM-4H-100 or Bruker AM-300 spectrometers, mass spectra were obtained with a VG MM 70-70F spectrometer, molecular weights were determined in chloroform (37 °C) with a Knauer vapour pressure osmometer, and conductivities in acetone were measured with a Philips PW 9504/00 conductivity meter.

α,α,α-Tris(pyridin-2-yl)toluene, $(py)_3PhC$.—A deep red solution was obtained on addition of 2-benzylpyridine (15 cm^3, 93.5 mmol) to a solution of phenyl-lithium [from lithium (1.292 g, 186.2 mmol) and bromobenzene (9.85 cm^3, 93.5 mmol)] in diethyl ether (100 cm^3). After stirring for 20 min, 2-bromopyridine (9.1 cm^3, 93.3 mmol) in diethyl ether (20 cm^3) was added dropwise followed by addition of toluene (200 cm^3). On reflux most of the ether was removed by distillation, and reflux was continued for 12 h to give a dark red-brown solution. On cooling, water (30 cm^3) was added and 5 mol dm^{-3} HCl added until the aqueous phase became acidic to litmus. The aqueous extract was combined with an aqueous wash from the organic phase and made alkaline by addition of a saturated sodium bicarbonate solution. A chloroform (3 × 50 cm^3) extract was dried with magnesium sulphate, filtered, and removal of solvent in a vacuum gave a brown oil containing some crystals. The oil was dissolved in cold ethanol, and the sparingly soluble crystals were collected and recrystallized from hot benzene after treatment with activated charcoal, to give colourless crystals of $(py)_3PhC$ (2.067 g, 6.40 mmol, 7%) (Found: C, 81.1; H, 5.1; N, 13.3. Calc. for $C_{22}H_{17}N_3$: C, 81.7; H, 5.3; N, 13.0%). Mass spectrum: 323 (*M*, 11%), 322(15), 246(50), 245(100), 244(73), 243(33), and 167(50). ^1H N.m.r. (100 MHz, $CDCl_3$): δ 8.84 [d, 3 H, H(6), *J*(5,6) 5 Hz], 7.60—6.90 [m, 14 H, Ph, H(3—5)]. The ethanol solution was reduced to an oil under vacuum, and the oil was extracted with light petroleum (3 × 50 cm^3) with the inclusion of activated charcoal. The filtrate from the extraction gave an initial crop of $(py)_2PhCH$ as almost colourless crystals (1.793 g, 7.29 mmol, 8%) (n.m.r., mass spectral identification).[4] Further crops (totalling 4.80 g) were discoloured by a yellow contaminant. Chromatography on a short silica column with chloroform elution gave $(py)_2PhCH$ (R_f 0.54—0.17, 4.26 g, 18%) after prior elution of the yellow contaminant.

2,6-Bis[1,1-bis(pyridin-2-yl)ethyl]pyridine, $[(py)_2MeC]_2C_5H_3N$.—A deep red solution containing an orange solid was obtained on addition of bis(pyridin-2-yl)methane (9.906 g, 58.3 mmol) in diethyl ether (60 cm^3) to a solution of phenyl-lithium (as above, using 130.4 mmol lithium) in diethyl ether (200 cm^3) at 0 °C. After stirring for 20 min iodomethane (3.65 cm^3, 58.6 mmol) in diethyl ether (20 cm^3) was added to the chilled solution, resulting in rapid discharge of the solution colour. On allowing the solution to warm to ambient temperature, and stirring for a further 1.5 h, water (20 cm^3) was added and 5 mol dm^{-3} HCl added until the aqueous phase became acidic to litmus. The isolated aqueous extract was washed once with dichloromethane (20 cm^3), and made alkaline by addition of a saturated sodium bicarbonate solution. The crude product, $(py)_2MeCH$, was extracted with dichloromethane (3 × 50 cm^3), dried over magnesium sulphate, filtered, and the solvent removed by rotary evaporation to give a red oil. Vacuum distillation, with isolation of the fraction boiling at 84—102 °C (0.15 mmHg) gave $(py)_2MeCH$ as a colourless oil (8.80 g, 47.8 mmol, 82%).

A deep red solution was obtained on addition of $(py)_2MeCH$ (2.987 g, 16.2 mmol) in diethyl ether (30 cm^3) to a chilled solution of phenyl-lithium (as above, using 36.9 mmol lithium) in diethyl ether (100 cm^3). After stirring for 20 min 2,6-dichloropyridine ($2,6Cl_2$-py) (1.205 g, 8.1 mmol) in diethyl ether (30 cm^3) was added rapidly dropwise, partially discharging the solution colour and precipitating an orange solid. Toluene (120 cm^3) was added, diethyl ether removed by distillation, and the resulting suspension refluxed for 12 h. Hydrolysis and extraction (as above) gave a yellow oil that rapidly crystallized. The crude product, $[(py)_2MeC]_2C_5H_3N$, was washed with cold acetone (5 cm^3), and recrystallized from hot acetone after treatment with activated charcoal (1.404 g, 3.17 mmol, 39%) (Found: C, 83.9; H, 6.3; N, 9.4. Calc. for $C_{29}H_{25}N_5$: C, 84.3; H, 6.2; N, 9.5%). Mass spectrum: 443 (*M*, 20%), 429(25), 428(50), 414(43), 366(12), 365(30), 350(37), 280(36), 261(15), 260(39), 245(15), 184(21), 183(100), 182(21), 169(46), and 168(30). ^1H N.m.r. (100 MHz, $CDCl_3$): δ 8.50 [m, 4 H, H(6)], 7.60—6.75 [m, 15 H, H(3—5)], 2.23 (s, 6 H, CH_3).

$[\{Pd[(py)PhHCC_6H_4](O_2CMe)\}_2]\cdot\frac{2}{3}CH_2Cl_2$ (**1**).—Solid $(py)Ph_2CH$ (0.26 g, 1.06 mmol) was added to a warmed solution of palladium(II) acetate (0.248 g, 0.11 mmol) in glacial acetic acid (40 cm^3), and the solution refluxed for 30 min. On cooling, the solvent was removed with warming in a vacuum to give an oil containing crystals and traces of acetic acid. The product was dissolved in dichloromethane (15 cm^3), filtered, and light petroleum added until cloudiness developed. Pale yellow crystals formed on standing, and these were collected and recrystallized from dichloromethane–light petroleum (0.268 g, 0.57 mmol, 54%).

$[\{Pd[(py)PhHCC_6H_4]Cl\}_2]$ (**2**).—Sodium chloride (0.094 g, 1.61 mmol) was added to a stirred suspension of (**1**) (0.166 g, 0.19 mmol) in acetone–water (2:1, 30 cm^3). After stirring for 20 h a pale cream product was collected and washed with water (0.132 g, 0.171 mmol, 90%).

$[Pd\{(py)PhHCC_6H_4\}(acac)]$ (**3**).—Acetylacetonatothallium(I) (0.092 g, 0.303 mmol) was added to a stirred suspension of (**2**) (0.114 g, 0.148 mmol) in dichloromethane (20 cm^3) to give immediate precipitation of TlCl. After stirring for 1 h the precipitate was removed by filtration, and the filtrate reduced in volume under vacuum to give a near colourless gum. The gum was dissolved in benzene (5 cm^3) and light petroleum added until cloudiness developed. A colourless microcrystalline solid formed on standing (0.044 g, 0.098 mmol, 66%).

$[Pd\{(py)Ph_2CH\}_2(O_2CMe)_2]$ (**4**).—A solution of $(py)Ph_2CH$ (0.860 g, 0.35 mmol) in benzene (20 cm^3) was added to a filtered solution of palladium(II) acetate (0.399 g, 0.18 mmol) in benzene (50 cm^3). On standing for 24 h pale yellow crystals of the complex formed and were collected (0.823 g, 0.12 mmol, 66%).

Table 3. Non-hydrogen atom co-ordinates for $[\mathrm{Pd}\{meso\text{-}[(\mathrm{py})\mathrm{PhMeC}]_2\mathrm{C_5H_3N}\}(\mathrm{O_2CMe})][\mathrm{O_2CMe}]\cdot 3\mathrm{H_2O}$

Atom	x	y	z
Pd	0.238 36(4)	0.116 25(2)	0.316 74(4)
Tridentate ligand			
C(7)	0.064 1(6)	0.211 0(3)	0.297 2(5)
C(8)	−0.018 8(5)	0.263 6(3)	0.289 8(6)
C(9)	0.218 0(5)	0.054 4(3)	0.542 2(5)
C(10)	0.194 3(6)	0.004 6(3)	0.459 7(6)
N(a1)	0.111 4(4)	0.126 1(2)	0.195 6(4)
C(a2)	0.041 7(6)	0.172 7(3)	0.198 4(5)
C(a3)	−0.043 0(6)	0.181 1(3)	0.115 1(6)
C(a4)	−0.057 8(6)	0.142 7(4)	0.029 1(6)
C(a5)	0.012 9(6)	0.095 4(4)	0.027 2(6)
C(a6)	0.096 2(6)	0.087 7(3)	0.113 0(5)
C(a′1)	0.184 8(6)	0.238 0(3)	0.303 6(6)
C(a′2)	0.232 6(8)	0.260 9(4)	0.402 0(6)
C(a′3)	0.337 5(9)	0.288 2(4)	0.408 1(7)
C(a′4)	0.397 0(8)	0.291 8(4)	0.319 1(8)
C(a′5)	0.348 4(9)	0.270 8(4)	0.221 8(8)
C(a′6)	0.243 9(7)	0.244 0(4)	0.214 0(6)
N(b1)	0.127 2(4)	0.133 2(2)	0.425 1(4)
C(b2)	0.047 7(6)	0.174 4(3)	0.399 0(5)
C(b3)	−0.043 8(6)	0.179 9(3)	0.460 1(6)
C(b4)	−0.052 4(6)	0.144 7(3)	0.547 5(6)
C(b5)	0.032 1(6)	0.105 6(3)	0.576 2(5)
C(b6)	0.125 2(5)	0.100 2(3)	0.515 6(5)
N(c1)	0.360 0(4)	0.106 5(2)	0.441 4(4)
C(c2)	0.339 3(5)	0.077 7(3)	0.531 6(5)
C(c3)	0.430 4(6)	0.067 1(3)	0.610 1(5)
C(c4)	0.536 1(6)	0.089 3(4)	0.596 7(6)
C(c5)	0.552 9(6)	0.121 1(4)	0.508 6(7)
C(c6)	0.461 9(6)	0.128 8(3)	0.428 9(6)
C(c′1)	0.213 5(6)	0.033 6(3)	0.661 2(5)
C(c′2)	0.228 6(6)	0.072 8(3)	0.745 2(6)
C(c′3)	0.230 4(7)	0.055 6(4)	0.852 1(6)
C(c′4)	0.213 0(7)	−0.001 9(5)	0.876 9(7)
C(c′5)	0.196 8(8)	−0.040 7(4)	0.794 1(8)
C(c′6)	0.196 1(7)	−0.023 4(3)	0.685 8(6)
Co-ordinated acetate			
C	0.377 2(7)	0.049 8(5)	0.189 9(7)
O(1)	0.350 6(4)	0.102 3(2)	0.207 7(4)
O(2)	0.327 1(6)	0.008 5(3)	0.222 5(6)
C′	0.471 9(8)	0.040 9(5)	0.121 6(8)
Unco-ordinated acetate			
C	0.668 1(18)	0.223 3(15)	0.041 8(24)
O(1)	0.712 6(8)	0.237 8(5)	−0.042 7(11)
O(2)	0.713 9(12)	0.254 4(9)	0.103 8(15)
C′	0.623 7(15)	0.169 7(14)	0.052 1(35)
Solvent molecules			
O(1)	0.853 1(6)	0.074 3(3)	0.785 0(5)
O(2)	0.716 8(7)	0.171 1(3)	0.767 2(8)
O(3)	0.692 6(10)	0.178 1(5)	0.306 6(10)

$[\mathrm{Pd}\{(\mathrm{py})_2\mathrm{CH_2}\}(\mathrm{O_2CMe})_2]\cdot 0.5\mathrm{CHCl_3}$ (**5**).—Under anhydrous conditions a filtered benzene (30 cm^3) solution of $(\mathrm{py})_2\mathrm{CH_2}$ (0.152 g, 0.89 mmol) was added to a filtered benzene (50 cm^3) solution of palladium(II) acetate (0.197 g, 0.88 mmol). On standing the solution became orange-red, and after 2 d an orange solid had collected on the flask walls with some discharge of solution colour. The solvent was removed by decantation, the product dissolved in chloroform (10 cm^3), filtered to remove some reddish gum, and dry light petroleum added until cloudiness developed. On standing for 3 h fine yellow crystals of the complex formed (0.282 g, 0.55 mmol, 62%).

$[\mathrm{Pd}\{(\mathrm{py})_2\mathrm{PhCH}\}(\mathrm{O_2CMe})_2]\cdot\frac{4}{5}\mathrm{C_6H_6}$ (**6**).—On standing for a few minutes a benzene solution, obtained in a similar manner to that above, became deep red, and over a period of 12 h the colour discharged to pale yellow with formation of fine yellow crystals. The crystals were collected under nitrogen, washed with benzene (2 × 20 cm^3), and dried under a stream of nitrogen (0.220 g, 0.41 mmol, 60%).

$[\mathrm{Pd}\{(\mathrm{py})_3\mathrm{CH}\}(\mathrm{O_2CMe})_2]\cdot\mathrm{C_6H_6}$ (**7**).—On standing for 10 min a yellow benzene solution, obtained in a similar manner to that above, became deep red, and over a period of 3 d the colour discharged to pale orange with formation of orange crystals. The crystals were collected and treated as above (0.081 g, 46%).

$[\mathrm{Pd}\{(\mathrm{py})_3\mathrm{PhC}\}(\mathrm{O_2CMe})_2]$ (**8**).—On standing for a few minutes a yellow toluene solution, obtained in a similar manner to the benzene solutions above, became slightly opaque and after 24 h a fine yellow precipitate was evident. Large yellow plates formed over 4 d, and these were collected, washed with toluene (2 × 20 cm^3), and dried in a stream of nitrogen (0.110 g, 0.20 mmol, 63%).

$[\mathrm{Pd}\{[(\mathrm{py})_2\mathrm{MeC}]_2\mathrm{C_5H_3N}\}(\mathrm{O_2CMe})][\mathrm{O_2CMe}]\cdot 3\mathrm{H_2O}$ (**9**).—A dichloromethane (10 cm^3) solution of the ligand (0.476 g, 1.07 mmol) and palladium(II) acetate (0.243 g, 1.08 mmol) gave an orange oil on evaporation in a draught. The oil was dissolved in acetone (5 cm^3), filtered, and diethyl ether added until cloudiness developed. On standing, the product formed as yellow microcrystals (0.460 g, 59%).

$[\mathrm{Pd}\{meso\text{-}[(\mathrm{py})\mathrm{PhMeC}]_2\mathrm{C_5H_3N}\}(\mathrm{O_2CMe})][\mathrm{O_2CMe}]\cdot 3\mathrm{H_2O}$ (**10**).—Pale yellow crystals were obtained following a similar procedure to that above (85% yield).

$[\mathrm{Pd}\{rac\text{-}[(\mathrm{py})\mathrm{PhMeC}]_2\mathrm{C_5H_3N}\}(\mathrm{O_2CMe})][\mathrm{O_2CMe}]\cdot 3\mathrm{H_2O}$ (**11**).—This complex is more soluble in acetone than (**10**), and tends to form an oil. Pale yellow crystals were obtained from an acetone solution kept in a sealed chamber with slow dissolution of ether vapour (66%).

Crystallography.—Crystals of $[\mathrm{Pd}\{meso\text{-}[(\mathrm{py})\mathrm{PhMeC}]_2\mathrm{C_5H_3N}\}(\mathrm{O_2CMe})][\mathrm{O_2CMe}]\cdot 3\mathrm{H_2O}$ were obtained, on standing at ambient temperature, from an acetone solution of the complex exposed to diethyl ether vapour in a closed chamber.

Crystal data. $\mathrm{C_{35}H_{39}N_3O_7Pd}$, $M = 720.1$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 11.795(5)$, $b = 23.10(1)$, $c = 12.313(5)$ Å, $\beta = 95.64(3)°$, $U = 3\,339(3)$ Å^3, D_c ($Z = 4$) $= 1.43$ g cm^{-3}, $F(000) = 1\,488$, monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 5.7$ cm^{-1}. Specimen: 0.34 × 0.24 × 0.28 mm. Minimum and maximum transmission factors = 1.12, 1.20. $T \sim 295$ K.

Structure determination. A unique data set was measured to $2\theta_{\mathrm{max.}} = 50°$ using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode, yielding 5 914 independent reflections, 3 657 with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block diagonal least-squares refinement after analytical absorption correction, and solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso}) for hydrogen atoms were included at estimated values. Residuals R,R' (statistical weights) quoted on $|F|$ are 0.051, 0.052 respectively. Neutral complex scattering factors were used;[22] computation used the XTAL 83 program system implemented[23] by S. R. Hall on a Perkin-Elmer 3240 computer. The rather high residual appears to be a consequence of very high anion thermal motion. Atomic co-ordinates are given in Table 3.

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