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Synthesis and structural studies of tripodal and planar [N–C–N]$^-$ intramolecular coordination systems involving pyrazole donor groups, including oxidative addition of an aryl–bromine bond to platinum(II). Crystal structures of [PtClMe$_2${(pz)$_2$CR(CH$_2$)-*N*,*N*′,*C*″}] with R = Me or CH$_2$Cl

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Abstract

The complex [PtMe$_2$(μ-SEt$_2$)]$_2$ undergoes oxidative addition reactions with chloro-2,2-bis(pyrazol-1-yl)propanes and 2,6-(pzCH$_2$)$_2$C$_6$H$_3$Br to form platinum(IV) complexes PtClMe$_2${(pz)$_2$CR(CHX)-*N*,*N*′,*C*″} and PtBrMe$_2${2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*N*′,*C*″[1]}, respectively, with the ligands present as tripodal [N–C–N]$^-$ systems. Structural studies of two of the complexes show distorted octahedral geometry, '*fac*-PtClC$_3$N$_2$', with (pz)$_2$CMeCH$_2^-$ and (pz)$_2$C(CH$_2$Cl)CH$_2^-$ forming NPtN and NPtC angles at platinum ca. 7–12° less than 90°. The reagent 1,3-(pzCH$_2$)$_2$C$_6$H$_4$ undergoes cyclometallation with palladium(II) acetate to form Pd(O$_2$CMe){2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*N*′,*C*″[1]}, which has the ligand present as a planar [N-C-N]$^-$ donor.

Introduction

Tridentate 'M(N–C–N)' [1–5], 'M(N–N–C)' [1,3,6–10], and "M(N–C–N)M′(N′–C′–N)" [11] coordination systems for palladium and platinum are of current interest, and we have recently reported the synthesis of a range of platinum(IV) complexes containing metallated tris(pyrazol-1-yl)methane [(pz)$_3$CH] and closely related (*N*-methylimidazol-2-yl)bis(pyrazol-1-yl)methane, in which the ligands are present as novel tripodal [N–C–N]$^-$ donors [12], e.g. with one pyrazole ring of

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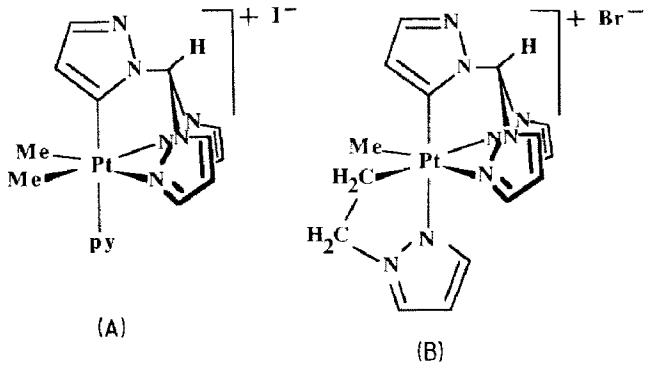


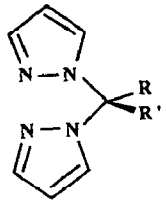
$(pz)_3CH$ metallated at the C(5) position in $[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''^5\}(py)]I$ (**A**). These complexes were formed by oxidative addition reactions of organohalides with organoplatinum(II) substrates, e.g. $PtMe\{(pz)_2(C_3H_2)CH\text{-}N,C'^5\}(py)$ with iodomethane to give **A**.

None of the complexes isolated could be satisfactorily crystallized in a form suitable for X-ray structural studies. However, one of the complexes (**B**) was obtained on oxidative addition of 1-bromo-2-(pyrazol-1-yl)ethane, and this led us to investigate an alternative approach to the synthesis of complexes containing tripodal $[N-C-N]^-$ intramolecular coordination systems in order to find a system amenable to growth of crystals suitable for crystallographic studies. In this approach, four new reagents were synthesized (**1a–1c, 2a**), with each reagent possessing two pyrazole groups and one or more halogen atoms in orientation(s) such that potential oxidative-addition reactions with a platinum(II) substrate would favour formation of tripodal intramolecular $[N-C-N]^-$ coordination in the platinum(IV) product. This approach was successful, giving complexes **3a–3c** and **4**, and was followed by the synthesis of a planar $[N-C-N]^-$ coordination system **6** involving pyrazole *N*-donor groups for comparison, via palladation of the new reagent **2b**. A preliminary report of this work has been published [13]. In a subsequent application of this synthetic strategy, planar and tripodal "Pt(N–N–C)" complexes have been obtained via reactions involving the first examples of oxidative addition of aryl–halogen bonds to platinum(II) [9], and a further such example is reported here.

Results and discussion

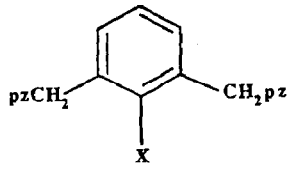
Synthesis and characterization of complexes involving tripodal $[N-C-N]^-$ coordination

The new bis(pyrazol-1-yl)alkanes **1a–1c** were obtained by the cobalt(II) chloride catalysed condensation of bis(pyrazol-1-yl)methanone with the appropriate ketones, e.g. $(pz)_2C{=}O$ with $Me(ClCH_2)C{=}O$ to give **1a**, following the general procedure established by Peterson et al. [14–16] for the synthesis of related reagents; the reagents **2a** and **2b** were obtained by reaction of potassium pyrazolide with 2,6-$(BrCH_2)_2C_6H_3Br$ and 1,3-$(BrCH_2)_2C_6H_4$, respectively, and were characterized by microanalysis and ^1H NMR spectroscopy, and by the formation of platinum(IV) derivatives.



1a-c

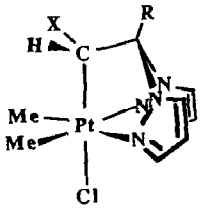
	R	R'
1a :	Me	CH_2Cl
1b :	CH_2Cl	CH_2Cl
1c :	Me	$CHCl_2$



2a,b

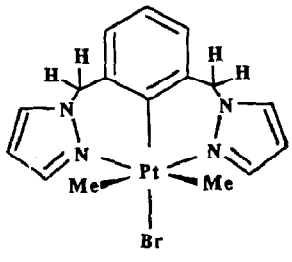
2a : X = Br

2b : X = H



3a-c

	R	X
3a :	Me	H
3b:	CH_2Cl	H
3c :	Me	Cl



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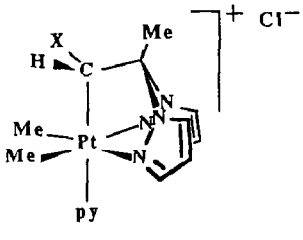

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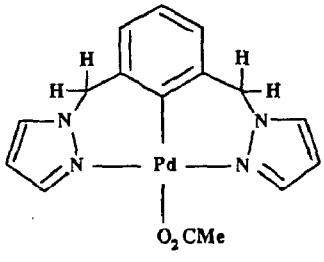

6

The complex $[PtMe_2(\mu\text{-}SEt_2)]_2$ [17,18] was chosen as a substrate for attempted oxidative addition reactions with **1a–1c** and **2a** for several reasons. Dimethylplatinum(II) thioether complexes are known to readily undergo oxidative addition reactions [17,19], e.g. with benzyl bromide [17], and thioether ligands are readily displaced by *N*-donor ligands [12,17,20], e.g. by poly(pyrazol-1-yl)alkanes [12]. If the reagents **1a–1c** and **2a** displace diethylsulphide initially rather than oxidatively add

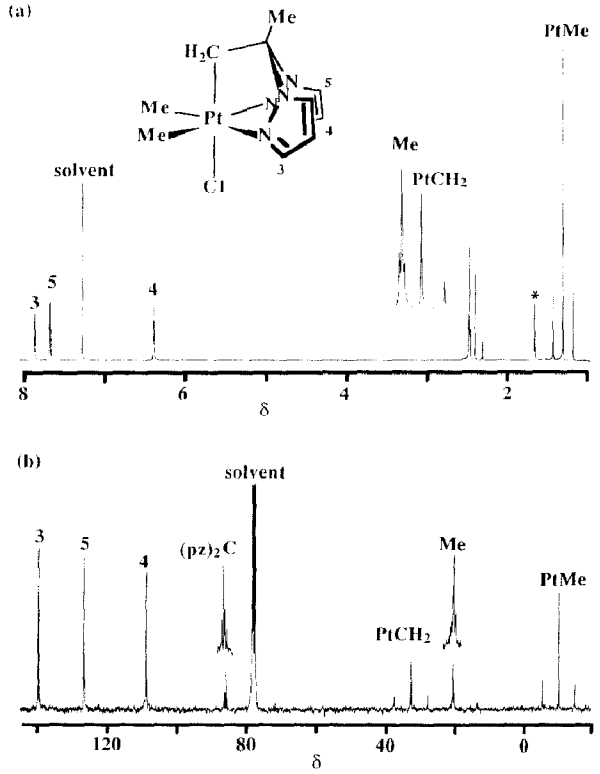

Fig. 1. (a) ^{1}H NMR spectrum of $PtClMe_2\{(pz)_2CMeCH_2\text{-}N,N',C''\}$ (**3a**) illustrating J(HPt) for PtMe (73.7 Hz), J(HPt) for $PtCH_2$ (51.5 Hz), J(HPt) for the apical methyl group (5.8 Hz), and single environments for the PtMe and pyrazole groups. * is an impurity. (b) ^{13}C NMR spectrum of **3a** illustrating J(CPt) for PtMe (693.4 Hz), J(CPt) for $PtCH_2$ (729.4 Hz), J(CPt) for the apical methyl group (51.9 Hz), and J(CPt) for the $(pz)_2C$ carbon (51.9 Hz).

directly, then subsequent oxidative addition may well occur in view of both the proximity of carbon–halogen group(s) and platinum in "$PtMe_2\{(pz)_2CRR'\}$" and the reported facile oxidative addition reactions of dimethylplatinum(II) complexes of *N*-donor ligands with organic chlorides and bromides, e.g. that of the 2,2′-bipyridyl complex with chloromethane [20] and benzyl bromide [17,21]. Initial coordination of the reagents is assumed in view of the recent isolation of related platinum(II) complexes, e.g. $PtMe_2(Me_2NCH_2CH_2N{=}CH\text{-}o\text{-}C_6H_4Br\text{-}N,N')$ prior to oxidative addition to form a platinum(IV) complex [9].

When $[PtMe_2(\mu\text{-}SEt_2)]_2$ was treated with **1a–1c** or **2a** in benzene under nitrogen colourless crystalline complexes **3a–3c** or **4** were formed, and were filtered off from the hot solution, and washed with benzene and diethyl ether, except for the more soluble **3c** for which addition of hexane to the benzene solution followed by cooling was required.

The complexes were characterized by microanalysis, ^{1}H and ^{13}C NMR spectroscopy, osmometric molecular weight determinations in chloroform, and conductance measurements in acetone (non-electrolytes). Only the NMR spectra allow differentiation between formulation of the products as platinum(II) complexes "$PtMe_2\{(pz)_2CRR'\text{-}N,N'\}$" or as the platinum(IV) complexes **3a–3c** and **4**. The ^{1}H NMR spectra exhibit appropriate integration for **3a–3c** and **4**, and **3a–3c** exhibit

coupling of ^{195}Pt with protons of the CHX and R moieties in addition to coupling for the PtMe groups, e.g. as shown in Fig. 1 for **3a**. Complex **3c**, with a chlorine atom of 'PtCHCl' adjacent to one PtMe group, exhibits two PtMe and two pyrazole environments.

The spectral studies support the expected '*fac*-$PtXC_3N_2$' geometry for the complexes, as found for the closely related bis(3,5-dimethylpyrazol-1-yl)methane complex $PtIMe_3\{(Me_2pz)_2CH_2\text{-}N,N'\}$ [22], e.g. similar values of J(HPt) for the inequivalent PtMe groups in **3c** as they are both *trans* to pyrazole donors, and

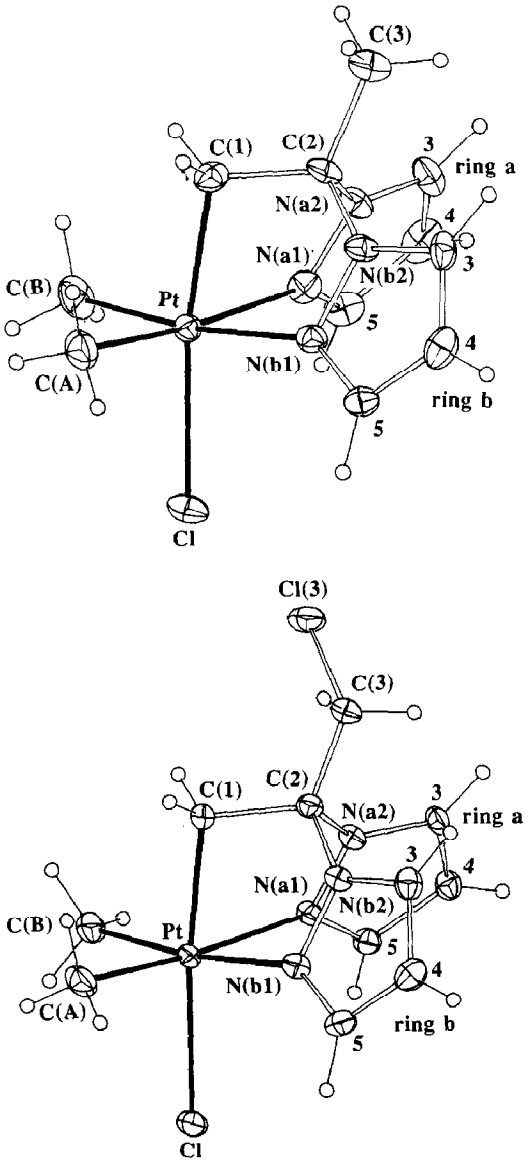

Fig. 2. The molecular structures of $PtClMe_2\{(pz)_2CR(CH_2)\text{-}N,N',C''\}$. (a) R = Me (**3a**), (b) R = CH_2Cl (**3b**). Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, 20% thermal ellipsoids for the non-hydrogen atoms.

Table 1

Coordination and chelate ring geometry for $PtClMe_2\{(pz)_2CRCH_2\text{-}N,N',C''\}$ (**3a**, R = Me; **3b**, R = CH_2Cl)

Coordination geometry	**3a**	**3b**
Pt–C(A,B)	2.05(1), 2.00(1)	2.043(7), 2.035(9)
Pt–C(1)	2.06(1)	2.030(6)
Pt–N(a1,b1)	2.129(8), 2.145(7)	2.166(4), 2.163(6)
Pt–Cl	2.421(3)	2.443(2)
C(A)–Pt–C(B)	89.2(5)	88.1(3)
C(1)–Pt–C(A,B)	93.8(5), 94.7(4)	94.3(3), 93.6(3)
C(1)–Pt–N(a1,b1)	78.7(4), 77.9(3)	78.5(2), 79.1(2)
C(A)–Pt–N(a1,b1)	172.1(4), 93.6(4)	171.9(2), 93.7(2)
C(B)–Pt–N(a1,b1)	93.8(5), 172.1(4)	95.9(2), 172.5(2)
C(A,B)–Pt–Cl	92.8(4), 91.3(3)	90.4(2), 90.8(2)
C(1)–Pt–Cl	171.2(3)	173.6(2)
N(a1)–Pt–N(b1)	82.5(4)	81.4(2)
N(a1,b1)–Pt–Cl	94.5(3), 95.9(2)	96.6(1), 96.4(1)
Chelate ring geometry		
C(1)–C(2)	1.50(1)	1.539(9)
C(2)–N(a2,b2)	1.44(1), 1.46(1)	1.463(8), 1.485(9)
N(a1)–N(a2)	1.38(1)	1.362(6)
N(b1)–N(b2)	1.35(1)	1.371(6)
Pt–C(1)–C(2)	101.4(6)	102.2(4)
Pt–N(a1)–N(a2)	108.8(6)	108.8(9)
Pt–N(a1)–C(a5)	143.4(8)	143.4(4)
Pt–N(b1)–N(b2)	109.1(5)	109.5(4)
Pt–N(b1)–C(b5)	144.3(7)	144.6(5)
C(1)–C(2)–N(a2,b2)	107.2(8), 106.2(8)	106.6(5), 105.9(4)
N(a2)–C(2)–N(b2)	106.7(8)	106.0(5)
C(2)–N(a2)–N(a1)	114.9(7)	115.8(4)
C(2)–N(b2)–N(b1)	115.5(7)	114.1(5)
Deviations (Å) of Pt from the 'C_3N_2' mean planes of the rings [a]		
Ring a	0.059	0.410
Ring b	0.016	0.075

[a] For **3a** the mean planes have χ^2 1.5 and 2.8 for rings a and b, respectively; the dihedral angle between the planes is 75.5°, and the planes form dihedral angles of 58.7 and 59.8° with the 'C_2N_2' coordination plane; similarly, **3b** has χ^2 7.2 and 4.8, and the dihedral angle between the planes is 88.1°, and the planes form dihedral angles of 62.4 and 61.3° with the 'C_2N_2' coordination plane.

equivalent PtMe group environments for **3a**, **3b**, confirmed for **3a** and **3b** by the X-ray structural studies. The $[N–C–N]^-$ group in **4** acts as a tripod ligand, e.g. there are equivalent PtMe groups with J(HPt) as expected for *trans*-pz donors, although the group is able to act as a planar $[N–C–N]^-$ ligand, as in **6**, but this arrangement would give the less favoured '*mer*-PtC_3' unit. The synthesis of **4** represents one of very few examples of oxidative addition of aryl–halogen bonds to platinum(II) [9].

Complexes **3a**–**3c**, but not **4**, react with pyridine to form cations, e.g. **5**, which give ^{1}H NMR spectra showing J(HPt) coupling for the *ortho* protons of pyridine.

*Structures of $PtClMe_2\{(pz)_2CR(CH_2)\text{-}N,N',C''\}$ (**3a**, R = Me; **3b**, R = CH_2Cl)*

Molecules of **3a** and **3b** are shown in Figure 2, with details of the coordination and chelate geometry given in Table 1, and other crystallographic data in Tables 2

Table 2

Crystal data and refinement parameters for $PtClMe_2\{(pz)_2CRCH_2\text{-}N,N',C''\}$ (**3a**, R = Me; **3b**, R = CH_2Cl)

	3a	**3b**
Formula	$C_{11}H_{17}ClN_4Pt$	$C_{11}H_{16}Cl_2N_4Pt$
Space group	$P2_12_12_1$	$P2_1/c$
a, Å	14.206(8)	8.407(2)
b, Å	10.888(6)	13.836(6)
c, Å	8.959(5)	13.139(4)
β, deg	90	110.16(2)
V, Å^3	1386(1)	1434.6(8)
Z	4	4
mol wt	435.8	470.3
D_{calcd}, g cm^{-3}	2.09	2.17
Cryst size, mm	0.18×0.16×0.48	0.15×0.40×0.10
μ, cm^{-1}	99	97
$F(000)$	824	888
$2\theta_{max}$, deg	60	60
$A^*_{min,max}$	4.0,6.3	2.3,3.4
N	2248	4213
N_o, with $I > 3\sigma(I)$	1818	2912
R	0.032	0.032
R'	0.029	0.033
	(preferred chirality)	

Table 3

Non-hydrogen atom coordinates for $PtClMe_2\{(pz)_2CRCH_2\text{-}N,N',C''\}$ (**3a**, R = Me; **3b**, R = CH_2Cl)

Atom	**3a**			**3b**		
	x	y	z	x	y	z
Pt	0.62756(3)	0.80350(3)	0.79945(4)	0.16091(3)	0.23098(2)	0.24395(2)
C(A)	0.7695(8)	0.8349(10)	0.8016(15)	0.3584(9)	0.1382(6)	0.3114(7)
C(B)	0.6106(11)	0.9427(11)	0.9432(12)	0.3057(8)	0.2988(6)	0.1695(6)
Cl	0.6369(3)	0.6571(2)	1.0023(3)	0.2684(2)	0.3384(1)	0.4003(1)
Tridentate ligand						
C(1)	0.6053(9)	0.9092(9)	0.6127(11)	0.0457(7)	0.1444(5)	0.1148(5)
C(2)	0.5397(7)	0.8291(9)	0.5247(10)	−0.1402(7)	0.1468(5)	0.1092(5)
C(3)	0.5091(9)	0.8807(12)	0.3714(14)	−0.2639(8)	0.0860(5)	0.0226(5)
N(a1)	0.4804(6)	0.7793(8)	0.7661(10)	−0.0689(6)	0.3113(4)	0.1620(4)
N(a2)	0.4592(5)	0.8042(9)	0.6183(9)	−0.1899(6)	0.2487(3)	0.1018(4)
C(a3)	0.3663(8)	0.7907(10)	0.5984(12)	−0.3443(7)	0.2917(5)	0.0667(5)
C(a4)	0.3263(7)	0.7609(11)	0.7345(16)	−0.3194(8)	0.3849(5)	0.1027(5)
C(a5)	0.4003(8)	0.7542(10)	0.8357(12)	−0.1464(8)	0.3947(5)	0.1612(5)
N(b1)	0.6363(7)	0.6702(6)	0.6237(8)	−0.0106(6)	0.1506(3)	0.3027(4)
N(b2)	0.5886(5)	0.7121(7)	0.5037(9)	−0.1392(6)	0.1129(4)	0.2166(4)
C(b3)	0.5919(7)	0.6292(10)	0.3864(12)	−0.2520(8)	0.0663(5)	0.2506(6)
C(b4)	0.6453(8)	0.5337(10)	0.4392(13)	−0.1947(10)	0.0710(6)	0.3605(6)
C(b5)	0.6697(7)	0.5591(9)	0.5867(12)	−0.0450(9)	0.1262(5)	0.3895(5)
Cl(3)				−0.2606(2)	0.1171(2)	−0.1078(1)

and 3 *. Both complexes have the $[N-C-N]^-$ ligands present as tripods; the methyl groups are *trans* to the pyrazole donors, and the chloro ligands are *trans* to the carbon atom of the tripods, to give '*fac*-$PtClC_3N_2$' coordination. The '*fac*-PtC_3' groups form C–Pt–C angles 89.2(5)–94.7(4)° (**3a**) and 88.1(3)–94.3(3)° (**3b**).

The tripod ligands form two five-membered PtNNCC rings and one six-membered PtNNCNN ring, with chelate angles at platinum of ca. 7–12° less than 90°, viz. N(a1)–Pt–N(b1) 82.5(4) (**3a**), 81.4(2)° (**3b**), and C(1)–Pt–N(a1, b1) 78.7(4), 77.9(3)° (**3a**) and 78.5(2), 79.1(2)° (**3b**). Angles at C(2), 106.2(8)–115.5(9) (**3a**) and 105.9(4)–116.7(6)° (**3b**), show little deviation from the tetrahedral value, but coordination of the pyrazole groups results in irregular angles at N(1) and N(2) for both complexes, with the chelate ring angles Pt–N(1)–N(2) and C(2)–N(2)–N(1) ca. 16–22 and 35° less than Pt–N(1)–C(5) and C(2)–N(2)–C(3) angles, respectively. The pyrazole rings are planar (maximum deviation from the 'C_3N_2' mean planes is 0.015 Å, for C(b4) in **3a**), and the platinum atoms are 0.016–0.410 Å from these planes (Table 1).

Synthesis and characterization of a complex involving planar $[N-C-N]^-$ coordination

Planar $[N-C-N]^-$ and $[N-N-C]^-$ coordination systems are well established [1–10], but have not been reported previously for pyrazole donor groups. The facile palladation of 1,3-bis[1-(pyridin-2-yl)ethyl]benzene with palladium(II) acetate to form $Pd(O_2CMe)\{2,6\text{-}(pyCHMe)_2C_6H_3\text{-}N,N',C''\}$ has been reported [5], and thus we sought a pyrazole analogue via a similar approach. The new reagent 1,3-bis{(pyrazol-1-yl)methyl}benzene (**2b**) reacted readily with palladium(II) acetate in hot glacial acetic acid (15 min) to give **6**.

Complex **6** has ν_{as} (CO_2) 1588 and $\nu_s(CO_2)$ 1378 cm^{-1}, with a separation of 210 cm^{-1}, similar to that for $Pd(O_2Me)\{2,6\text{-}(pyCHMe)_2C_6H_3\text{-}N,N',C''\}$ (212 cm^{-1}) which has been shown to have unidentate acetate coordination by an X-ray crystallographic study [5]. The ^1H and ^{13}C NMR spectra of **6** are readily interpretable, with the resonances of all protons resolved, e.g. the palladated ring exhibits a triplet for H(4) and a doublet for H(3).

Experimental

Synthesis

The reagents $[PtMe_2(SEt_2)]_2$ [17], $[Pd(O_2CMe)_2]_3$ [23], $(pz)_2CO$ [24], 1,3-$(BrCH_2)_2C_6H_4$ [25], and 2,6-$(BrCH_2)_2C_6H_3Br$ [26] were prepared as described. Glacial acetic acid was refluxed and fractionally distilled from acetic anhydride and $KMnO_4$; monochloroacetone was dissolved in water, shaken with small amounts of diethyl ether, extracted with a large volume of diethyl ether, and distilled under reduced pressure; tetrahydrofuran was predried over KOH then refluxed and distilled from sodium/benzophenone and stored over sodium. Other reagents and solvents were purified as previously described [12].

* Thermal parameters, calculated hydrogen atom positions, least squares planes data, and a list of structure factors are available from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CBZ 1EW (UK). Any request should be accompanied by a full literature citation for this article.

Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and the Canadian Microanalytical Service, Vancouver. NMR spectra were recorded in $CDCl_3$ with a Bruker AM 300 spectrometer and ^1H and ^{13}C chemical shifts are given in ppm relative to Me_4Si. Mass spectra were obtained with a Vacuum General Micromass 7070F spectrometer operating at 70 eV, and molecular weights were determined with a Knauer vapor pressure osmometer for ca. $1-3 \times 10^{-2}$ *M* solutions in chloroform at 37°C.

Synthesis of ligands

2,2-Bis(pyrazol-1-yl)propanes, $(pz)_2CRR'$ (1a–1c)

In a typical synthesis bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and monochloroacetone (1.70 ml, 21.6 mmol), together with a catalytic amount of anhydrous cobalt(II) chloride (0.01 g) were placed in a flask flushed with nitrogen. Gentle warming for 15 min resulted in evolution of bubbles of CO_2. The mixture was allowed to cool to ambient temperature, water (5 ml) added, and the mixture extracted with dichloromethane (2×20 ml). The combined extracts were dried ($MgSO_4$) then filtered, the dichloromethane was removed under vacuum and the product, $(pz)_2CMeCH_2Cl$ (**1a**) was recrystallized from hot hexane/charcoal (3.73 g, 82%), m.p. 60–62°C. (Found: C, 51.5; H, 5.5; N, 26.9. $C_9H_{11}N_4Cl$ calcd.: C, 51.3; H, 5.3; N, 26.6%). ^1H NMR: δ 7.61 (2H, d, H(3), J_{34} 1.6 Hz), 7.36 (2H, d, H(5), J_{45} 2.6 Hz), 6.30 (2H, 't', H(4)), 4.56 (2H, s, CH_2), 2.38 (2H, s, Me). MS: *m/e* 210 (*M*, 20%), 175 (22%), 161 (50%), 143 (100%), 107 (38%).

$(pz)_2C(CH_2Cl)_2$ (**1b**), was prepared similarly, using 1,3-dichloroacetone (1.5 g, 11.8 mmol), with warming for 30 min, gave **1b** in 64% yield, m.p. 127°C. (Found: C, 44.3; H, 4.1; N, 23.1. $C_9H_{10}N_4Cl_2$ calcd.: C, 44.1; H, 4.1; N, 22.9%). ^1H NMR: δ 7.61 (2H, d, H(3), J_{34} 1.7 Hz), 7.52 (2H, d, H(5), J_{45} 2.6 Hz), 6.34 (2H, 't', H(4)), 4.78 (4H, s, CH_2). MS: *m/e* 246 (15%), 245 (*M*, 2%), 244 (24%), 195 (100%), 177 (65%), 176 (60%), 141 (70%), 106 (82%).

$(pz)_2CMeCHCl_2$ (**1c**) was prepared in the same way as **1b** but from 1,1-dichloroacetone and warming for 5 h, which gave **1c** in 41% yield, m.p. 83°C. (Found: C, 44.8; H, 4.9; N, 22.3. $C_9H_{10}N_4Cl_2$ calcd.: C, 44.1; H, 4.1; N, 22.9%). ^1H NMR: δ 7.81 (2H, d, H(5), J_{45} 2.6 Hz), 7.60 (2H, d, H(3), J_{34} 1.6 Hz), 7.17 (1H, s, CH), 6.32 (2H, 't', H(4)), 2.61 (3H, s, Me). MS: *m/e* 244 (20%), 245 (*M*, 2%), 244 (35%), 209 (36%), 177 (35%), 161 (100%), 141 (22%), 109 (25%).

2,6-Bis{(pyrazol-1-yl)methyl}bromobenzene (2a) and 1,3-Bis{(pyrazol-1-yl)methyl}benzene (2b)

Pyrazole (0.71 g, 26.2 mmol) was added to a stirred solution of potassium (1.02 g, 26.2 mmol) in tetrahydrofuran (150 ml) under nitrogen. After the initial rapid evolution of hydrogen the mixture was heated at reflux with stirring until beads of molten potassium were no longer evident. The thick white suspension was cooled and 2,6-bis(bromomethyl)bromobenzene (13.1 mmol) added at ambient temperature with stirring. The mixture was refluxed for 8 h then cooled, and filtered, and the solvent removed by rotary evaporation. The residue was recrystallized from hot hexane/charcoal, to give $2,6\text{-}(pzCH_2)_2C_6H_3Br$ (**2a**), in 68% yield, m.p. 95°C. (Found: C, 53.0; H, 4.3; N, 17.6. $C_{14}H_{13}N_4Br$ calcd.: C, 53.0; H, 4.1; N, 17.7%). ^1H NMR: δ 7.58 (2H, d, H(3), J_{34} 1.8 Hz), 7.47 (2H, d, H(5), J_{45} 2.3 Hz), 7.19 (1H, t,

H(4)(Ph), J(HH) 7.7 Hz), 6.76 (2H, d, H(3,5)(Ph), J(HH) 7.7 Hz), 6.31 (2H, 't', H(4)), 5.46 (4H, s, CH_2). MS: m/e 317 (M, 2%), 237 (100%), 169 (50%).

2,6-$(pzCH_2)_2C_6H_4$ (**2b**) was prepared similarly, from 1,3-bis(bromomethyl)benzene, with reflux for 6 h, to give a yield of 82%, m.p. 36 °C. (Found: C, 70.5; H, 5.8; N, 23.6. $C_{14}H_{14}N_4$ calcd.: C, 70.6; H, 5.9; N, 23.5%). ^{1}H NMR: δ 7.54 (2H, d, H(3), J_{34} 1.8 Hz), 7.37 (2H, d, H(5), J_{45} 2.3 Hz), 7.28 (1H, d, H(4)(Ph), J_{45} 7.7 Hz), 7.10 (2H, dd, H(3,5)(Ph), J(HH) 7.7 Hz), 7.04 (1H, b, H(1)), 6.28 (2H, 't', H(4)), 5.29 (4H, s, CH_2). MS: m/e 237 (M, 15%), 170 (100%), 143 (10%), 103 (12%).

Synthesis of $Pt^{IV}Me_2$ complexes 3a–3c and 4

A solution of $[PtMe_2(SEt_2)]_2$ (0.15 g, 0.24 mmol) and **1a** (0.11 g, 0.52 mmol) was stirred and heated in benzene (20 ml) under nitrogen. After 10 min a white microcrystalline precipitate had formed, and was filtered off from the hot solution, washed with warm benzene (2 × 2 ml) and diethyl ether, then recrystallized from a small volume of acetone by diethyl ether vapour diffusion to give $PtClMe_2\{(pz)_2CMeCH_2$-$N,N',C''\}$ (**3a**) in 74% yield. (Found: C, 30.6; H, 3.9; N, 13.0. $C_{11}H_{17}N_4ClPt$ calcd.: C, 30.3; H, 3.9; N, 12.9%). ^{1}H NMR: δ 7.86 (2H, d, H(3), J_{34} 2.0 Hz), 7.65 (2H, d, H(5), J_{45} 2.6 Hz), 6.37 (2H, 't', H(4)), 2.45 (3H, 't', Me, J(HPt) 5.8 Hz), 2.38 (2H, 't', $PtCH_2$, J(HPt) 51.5 Hz), 1.30 (6H, 't', PtMe, J(HPt) 73.7 Hz). ^{13}C NMR: δ 139.7 (s, C(3)), 126.3 (s, C(5)), 108.7 (s, C(4)), 85.7 ('t', $(pz)_2C$, J(CPt) 51.9 Hz), 32.4 ('t', $PtCH_2$, J(CPt) 729.4 Hz), 20.6 ('t', Me, J(CPt) 51.9 Hz), −10.0 ('t', PtMe, J(CPt) 693.4 Hz). Mol. wt. 429 (calcd. 435).

$PtClMe_2\{(pz)_2C(CH_2Cl)CH_2$-$N,N',C''\}$ (**3b**) was obtained similarly, from **1b**, in 78% yield. (Found: C, 28.2; H, 3.2; N, 11.8. $C_{11}H_{16}N_4Cl_2Pt$ calcd.: C, 28.1; H, 3.4; N, 11.9%). ^{1}H NMR: δ 7.89 (2H, d, H(3), J_{34} 2.0 Hz), 7.85 (2H, d, H(5), J_{45} 2.6 Hz), 6.42 (2H, 't', H(4)), 4.65 (2H, 't', CH_2Cl, J(HPt) 2.9 Hz), 2.46 (2H, 't', $PtCH_2$, J(HPt) 54.3 Hz), 1.33 (6H, 't', PtMe, J(HPt) 73.6 Hz). ^{13}C NMR: δ 139.6 (s, C(3)), 127.5 (s, C(5)), 109.2 (s, C(4)), 87.8 ('t', $(pz)_2C$, J(CPt) 51.9 Hz), 42.3 ('t', CH_2Cl, J(CPt) 60.3 Hz), 28.8 ('t', $PtCH_2$, J(CPt) 730.6 Hz), −9.57 ('t, PtMe, J(CPt) 689.3 Hz). Mol. wt. 459 (calcd. 470).

$PtClMe_2\{(pz)_2CMeCHCl$-$N,N',C''\}$ (**3c**) was obtained similarly, from **1c**, but addition of hexane to the benzene solution and cooling were required. The product was recrystallized from acetone with dropwise addition of hexane (78% yield). (Found: C, 28.1; H, 3.5; N, 11.8. $C_{11}H_{16}N_4Cl_2Pt$ calcd.: C, 28.1; H, 3.4; N, 11.9%). ^{1}H NMR: δ 7.92 (1H, d, H(3), J_{34} 2.0 Hz), 7.90 (1H, d, H(3), J_{34} 1.9 Hz), 7.78 (1H, d, H(5), J_{45} 2.7 Hz), 7.73 (1H, d, H(5), J_{45} 2.7 Hz), 6.47 (2H, m, H(4)), 4.53 (1H, 't', PtCH, J(HPt) 34.5 Hz), 2.55 (3H, s, Me), 1.39 (3H, 't', PtMe, J(HPt) 73.8 Hz), 1.36 (3H, 't', PtMe, J(HPt) 75.3 Hz). ^{13}C NMR: δ 139.8 (s, C(3)), 127.5 (s, C(5)), 109.2 (s, C(4)), 87.8 ('t', $(pz)_2C$, J(CPt) 51.9 Hz), 42.3('t', Me, J(CPt) 60.1 Hz), 28.8('t', $PtCH_2$, J(CPt) 730.2 Hz), −9.6 ('t', PtMe, J(CPt) 685.3 Hz). Mol. wt. 464 (calcd. 470).

$PtBrMe_2\{2,6$-$(pzCH_2)_2C_6H_3$-$N,N',C''\}$ (**4**) was obtained similarly to **3a**, from **2a**, as white microcrystals (92% yield). (Found: C, 36.6; H, 3.6; N, 10.0. $C_{14}H_{15}N_4BrPt$ calcd.: C, 35.4; H, 3.5; N, 10.3%, contaminated with a trace of benzene (NMR detection)). ^{1}H NMR: δ 8.37 (2H, d, H(3), J_{34} 1.4 Hz), 7.48 (2H, d, H(5), J_{45} 2.1 Hz), 7.05 (3H, m, Ph), 6.33 (2H, 't', H(4)), 5.85 (2H, d, CH_2) and 4.87 (2H, d, CH_2, J(HH) 14.8 Hz), 1.60 (6H, 't', PtMe, J(HPt) 70.3 Hz). ^{13}C NMR: δ 141.7 (s, H(3)), 137.3 (s, H(4)(Ph)), 133.2 (s, H(1)), 131.8 (s, H(5)), 129.6 ('t',

H(3,5)(Ph), J(CPt) 45.7 Hz), 125.1 (s, H(2,6)), 107.3 (s, H(4)), 59.2 ('t', CH_2, J(CPt) 30.5 Hz), −8.31 ('t', PtMe, J(CPt) 649.9 Hz).

[$PtMe_2${$(pz)_2CMeCH_2$-N,N',C''}(py)]Cl (5)

A solution of complex **3a** (0.05 g) in pyridine (5 ml) in a stoppered flask was set aside for 30 min. Hexane was added until cloudiness developed and crystallization began. The clear microcrystalline product was collected, washed with diethyl ether, air dried, and then vacuum dried at 50 °C for 2 h, yield 92%. (Found: C, 36.1; H, 4.5; N, 13.0. $C_{16}H_{22}N_5ClPt$ calcd.: C, 37.3; H, 4.3; N, 13.6%). ^{1}H NMR: δ 8.79 (2H, d, H(5), J_{45} 2.7 Hz), 8.57 (2H, m, H(6), J(HPt) 18.5 Hz), 8.16 (1H, t, H(4)(py)), 7.73 (2H, 't', H(3,5)(py)), 7.41 (2H, d, H(3), J_{34} 2.0 Hz), 6.46 (2H, 't', H(4)), 2.92 (3H, s, Me), 2.57 (2H, 't', $PtCH_2$, J(HPt) 44.9 Hz), 1.18 (6H, 't', PtMe, J(HPt) 71.0 Hz). ^{13}C NMR: δ 150.2 [s, C(2,6)(py)], 140.5 (s) and 138.4 (s) [C(4)(py) and C(3)(pz)], 131.0 (s) and 128.0 (s) [C(3,5)(py) and C(5)(pz)], 109.3 [C(4)(pz)], 86.9 ('t', $(pz)_2C$, J(CPt) 46.4 Hz), 29.3 ('t', $PtCH_2$, J(CPt) 670.8 Hz), 21.1 ('t', Me, J(CPt) 39.7 Hz), −7.3 ('t', PtMe, J(CPt) 702.4 Hz). Ω_M 72 ohm^{-1} cm^2 mol^{-1}.

Pd(O_2CMe){2,6-$(pzCH_2)_2C_6H_3$-N,N',C'''} (6)

A stirred mixture of palladium(II) acetate (0.24 g, 1.1 mmol) and **2b** (0.26 g, 1.1 mmol) in glacial acetic acid (25 ml) was heated under nitrogen, the suspension clarified during the heating to give a golden yellow solution, which darkened to a purple colour as the reflux temperature of acetic acid was approached. After 20 min under reflux the solution had lightened to golden yellow. Acetic acid was removed under vacuum at 70 °C and the yellow oil recrystallized from dichloromethane/hexane to give **6** as a white crystalline solid (92% yield). (Found: C, 47.5; H, 3.9; N, 13.9. $C_{16}H_{16}N_4O_2Pd$ calcd.: C, 47.7; H, 4.0; N, 14.0%). ^{1}H NMR: δ 7.90 (2H, d, H(3), J_{34} 1.8 Hz), 7.64 (2H, d, H(5), J_{45} 2.2 Hz), 6.99 (3H, m, Ph), 6.32 (2H, 't', H(4)), 5.30 (4H, s, CH_2), 1.94 (3H, b, O_2CMe). ^{13}C NMR: δ 179.0 (s, O_2CMe), 142.4 (s, C(3)), 139.9 (s, C(1)), 136.3 (s, C(2,6)), 130.9 (s, C(5), 125.9 (s, C(3,5)(Ph)), 124.5 (s, C(4)(Ph)), 106.6 (s, C(4)), 58.4 (s, CH_2), 25.0 (s, b, O_2CMe).

Crystallography

For each complex a unique data set was measured at 295 K using a Syntex $P\bar{1}$ four-circle diffractometer in conventional 2θ–θ scan mode with monochromatic Mo-K_α radiation (λ 0.71069 Å), yielding N independent reflections, N_o with $I > 3\sigma(I)$ considered 'observed' and used in the full matrix least-squares refinement after absorption correction, and solution of the structures by the heavy atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms and (x, y, z, U_{iso}) for hydrogen atoms were included at estimated values and constrained. Neutral complex scattering factors were used [27]; computation with the XTAL 83 program system was implemented [28] by S.R. Hall on a Perkin Elmer 3240 computer.

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References and notes

1 G.R. Newkome, W.E. Puckett, V.K. Gupta, and G.E. Kiefer, Chem. Rev., 86 (1986) 451.
2 K. Hiraki, Y. Fuchita, and Y. Matsumoto, Chem. Lett., (1984) 1947.
3 G.R. Newkome, W.E. Puckett, G.E. Kiefer, V.K. Gupta, F.R. Fronczek, D.C. Pantaleo, G.L. McClure, J.B. Simpson, and W.A. Deutsch, Inorg. Chem., 24 (1985) 811.
4 G. van Koten, Pure Appl. Chem., 61 (1989) 1681.
5 A.J. Canty, N.J. Minchin, B.W. Skelton, and A.H. White, J. Chem. Soc., Dalton Trans., (1987) 1477.
6 M.G. Clerici, B.L. Shaw, and B. Weeks, J. Chem. Soc., Chem. Commun., (1973) 516.
7 M. Nonoyama and C. Sugiura, Polyhedron, 1 (1982) 179.
8 G. Minghetti, M.A. Cinellu, G. Chelucci, S. Gladiali, F. Demartin, and M. Manassero, J. Organomet. Chem., 307 (1986) 107.
9 C.M. Anderson, R.J. Puddephatt, G. Ferguson, and A.J. Lough, J. Chem. Soc., Chem. Commun., (1989) 1297.
10 A.J. Blake, C.O. Dietrich-Buchecker, T.I. Hyde, J.-P. Sauvage, and M. Schroder, J. Chem. Soc., Chem. Commun., (1989) 1663.
11 A.J. Canty, N.J. Minchin, L.M. Engelhardt, B.W. Skelton, and A.H. White, Aust. J. Chem., 41 (1988) 651.
12 A.J. Canty and R.T. Honeyman, J. Organomet. Chem., 387 (1990) 247.
13 A.J. Canty, R.T. Honeyman, B.W. Skelton, and A.H. White, Inorg. Chim. Acta, 114 (1986) L39.
14 K.I. The and L.K. Peterson, Can. J. Chem., 51 (1973) 422.
15 K.I. The, L.K. Peterson, and E. Kiehlmann, Can. J. Chem., 51 (1973) 2448.
16 L.K. Peterson, E. Kiehlmann, A.R. Sanger, and K.I. The, Can. J. Chem., 52 (1974) 2367.
17 J. Kuyper, R. van der Laan, F. Jeanneaus, and K. Vrieze, Trans. Metal Chem., 1 (1976) 199.
18 D.P. Bancroft, F.A. Cotton, L.R. Falvello, and W. Schwotzer, Inorg. Chem., 25 (1986) 763.
19 M. Lashanizadeghan, M. Rashidi, J.E. Hux, R.J. Puddephatt, and S.S.M. Ling, J. Organomet. Chem., 269 (1984) 317.
20 J. Kuyper, Inorg. Chem., 16 (1977) 2171.
21 M. Crespo and R.J. Puddephatt, Organometallics, 6 (1987) 2548; K.-T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott, and A.A. Watson, ibid., 8 (1989) 1518.
22 H.C. Clark, G. Ferguson, V.K. Jain, and M. Parvez, J. Organomet. Chem., 270 (1984) 365.
23 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, and G. Wilkinson, J. Chem. Soc., (1965) 3632.
24 P.K. Byers, A.J. Canty, and R.T. Honeyman, J. Organomet. Chem., 385 (1990) 417.
25 W. Wenner, J. Org. Chem., 17 (1952) 523.
26 F. Vogtle, Chem. Ber., 102 (1969) 1784.
27 J.A. Ibers and W.C. Hamilton (Eds.), International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.
28 J.M. Stewart and S.R. Hall (Eds.), The XTAL System, Technical Report TR-1364, Computer Science Center, University of Maryland, 1983.