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The synthesis of tripodal nitrogen donor ligands and their characterization as $Pd^{II}Me_2$ and $Pd^{II}IMe$ derivatives

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Abstract

New tripod ligands containing pyridin-2-yl (py), *N*-methylimidazol-2-yl (mim), and pyrazol-1-yl (pz) groups have been made by addition of 2-bromopyridine to deprotonated (py)(mim)CH_2 or $(mim)_2CH_2$ to form $(py)_2$(mim)CH and (py)$(mim)_2$CH, or by simple condensation reactions of $(pz)_2CO$ with (mim)CHO or (py)CHO to form $(pz)_2$(mim)CH and $(pz)_2$(py)CH. The ligands may have general application in coordination and organometallic chemistry, especially bis(pyrazol-1-yl)(pyridin-2-yl)methane [$(pz)_2$(py)CH], which can be readily synthesized and is an unsymmetrical tripod closely related to $(pz)_3CH$ and $(py)_3CH$. Dimethylpalladium(II) and methyl(iodo)palladium(II) complexes of the ligands have been isolated, and compared with complexes of $(pz)_3CH$, $(py)_3CH$, and $(pz)_4C$.

Introduction

Tripodal nitrogen donor ligands are widely employed in organometallic chemistry, in particular tris(pyrazol-1-yl)methane [$(pz)_3CH$] and the isoelectronic tris(pyrazol-1-yl)borate anion [1]. We report here the synthesis of four ligands related to $(pz)_3CH$ and its pyridine analogue, tris(pyridin-2-yl)methane [$(py)_3CH$], but containing an unsymmetrical donor set, as illustrated. Derivatives of these ligands with $Pd^{II}Me_2$ and $Pd^{II}IMe$ have been obtained, and compared with the complexes of $(pz)_3CH$, $(py)_3CH$, and $(pz)_4C$. The complexes of unsymmetrical ligands exhibit isomerism, and they have played a key role in the development of organopalladium(IV) chemistry, as reported elsewhere [2–4]. Preliminary reports of parts of this work have appeared [2,3,5].

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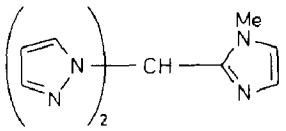
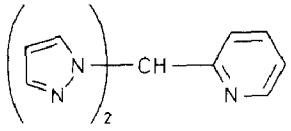


[(pz)$_2$(mim)CH]



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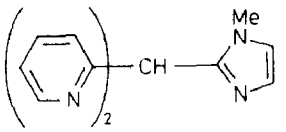

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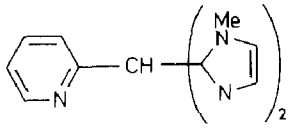


[(py)(mim)$_2$CH]

Results and discussion

The ligands (py)$_2$(mim)CH and (py)(mim)$_2$CH were prepared by deprotonation of (py)(mim)CH$_2$ or (mim)$_2$CH$_2$ with phenyllithium followed by addition of 2-bromopyridine (eq. 1), and both (pz)$_2$(py)CH and (pz)$_2$(mim)CH were obtained by condensation of bis(pyrazol-1-yl)methanone with pyridine-2-carboxaldehyde or *N*-methylimidazole-2-carboxaldehyde, respectively, following the procedure developed by Peterson et al. [6–8] for the synthesis of bis(pyrazol-1-yl)alkanes (eq. 2).

$$(L')(mim)CH_2 \xrightarrow[(ii)\ 2Br\text{-}py]{(i)\ LiPh} (L')(py)(mim)CH\ (L' = py, mim) \quad (1)$$

$$(pz)_2CO \xrightarrow[-CO_2]{(L')CHO} (pz)_2(L')CH\ (L' = py, mim) \quad (2)$$

Although (py)(mim)$_2$CH has proved very useful in the development of organo-palladium(IV) chemistry, giving the first isolable allyl- and ethyl-derivatives [3], the pyrazole ring containing ligands may be of more general interest in view of their close relationship to widely studied (pz)$_3$CH [1] and their ease of synthesis; in particular, (pz)$_2$(py)CH is obtained from commercially available (py)CHO and the readily synthesized (pz)$_2$CO

The Pd^{II}Me$_2$ and Pd^{II}IMe complexes of the new ligands and (pz)$_3$CH, (py)$_3$CH, and (pz)$_4$C were prepared in the same manner as complexes of related bidentate ligands [9]. The new ligands and complexes gave satisfactory microanalyses (C,H,N), and the ^{1}H NMR spectra for the ligands and complexes exhibited the expected integration patterns.

All of the complexes, except PdMe$_2${(py)(mim)$_2$CH}, exhibit ^{1}H NMR spectra that vary with temperature, and the spectra are consistent with fluxional behaviour involving exchange between coordinated and uncoordinated groups, presumably via axial coordination in transition states. Interpretation of the ^{1}H NMR spectra relies mainly on the use of spin correlation spectroscopy (COSY) spectra at both high and low temperatures to allow full assignment of connectivity, and the expected effect of the iodo group on chemical shifts of nearby ligand protons.

Unfortunately, none of the complexes were obtained in a form suitable for X-ray structural studies. The uncoordinated ring in the complexes is assumed to lie in orientation(s) above the square plane, since structural studies of the complexes [AuMe$_2$(L)]$^+$ (L = (pz)$_3$CH, (py)$_3$CH, (py)$_2$(Ph)CH [10], (mim)$_3$COH [11],

$(py)(mim)_2COH$ [12]), $AuMe_2\{(pz)_3BH\}$ [13], $PtMe\{(pz)_3BH\}(CO)$ [14], and $[Pd(L)_2]^{2+}$ [L = $(py)_3CH$, $(pz)_3CH$], $Pd\{(pz)_3BH\}_2$ [15] show square planar geometry with a ring in the axial orientation above the square plane. Molecular models indicate that this is the most likely orientation since there is less steric interaction between the axial ring and the coordinated rings, the equatorial orientation involving weak interaction with hydrogen atoms of coordinated pyridine [H(3)] and pyrazole rings [H(5)], or excessive interaction with the *N*Me groups of coordinated *N*-methylimidazole rings.

In low temperature spectra for the $Pd^{II}Me_2$ complexes of symmetrical ligands, $PdMe_2\{(py)_3CH\}$ and $PdMe_2\{(pz)_3CH\}$, resonances for cooordinated and uncoordinated rings are readily assigned, as they appear in 2/1 integration ratio.

The complex $PdIMe\{(py)_3CH\}$ exhibits broad resonances for an averaged py environment at ambient temperature, environments in the ratio 2/1 at $-60\,^{\circ}C$, and broadening of the resonances of the major environment at lower temperatures. The ring with well resolved resonances at $-60\,^{\circ}C$ and $-90\,^{\circ}C$ appears to be the ring *trans* to PdMe, since this orientation would account for the marked downfield shift for H(6) at 9.16 ppm, owing to its proximity to the iodo group. Similar shifts are observed in complexes of bidentate ligands, e.g. $PdIMe\{(py)_2CH_2\}$ has H(6)

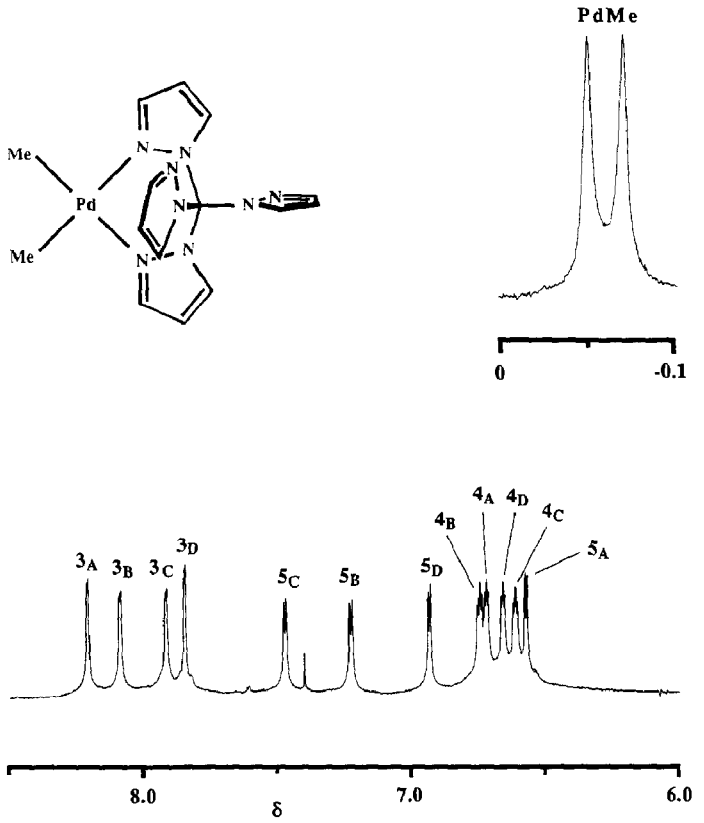


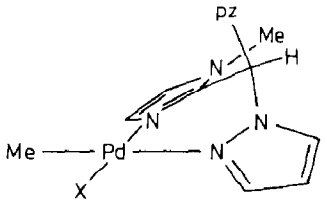
Fig. 1. ^1H NMR spetrum of $PdMe_2\{(pz)_4C\}$ at $-70\,^{\circ}C$ in $(CD_3)_2CO$, showing the pyrazole ring and $PdMe_2$ resonances, with a possible structure based on that reported for $AuMe_2\{(pz)_4B\}$. A definite assignment of coordinated and uncoordinated rings is not attempted, but COSY spectra allow determination of connectivity for the rings A–D.

resonances at 9.12 and 8.61 ppm compared with 8.61 for $PdMe_2\{(py)_2CH_2\}$ [9], and the signal from H(6) proton adjacent to X in PdXMe(bipy) appears at 9.13 (Cl), 9.31 (Br) and 9.53 ppm (I), compared with 8.70–8.73 ppm for the proton adjacent to PdMe [9]. With this assignment the spectra can be accounted for as resulting from two exchange processes, with faster exchange between the uncoordinated py group and the py group *trans* to PdI than between the uncoordinated group and the py group *trans* to PdMe, giving resolution of the resonances for the py group *trans* to PdMe at the higher temperature. The complex $PdIMe\{(pz)_3CH\}$ gives spectra showing similar variable temperature behaviour to that of $PdIMe\{(py)_3CH\}$, with sharp resonances observed for only one ring at low temperature, and with the other two environments partially resolved into six broad resonances.

The complex $PdMe_2\{(pz)_4C\}$ exhibits two pz environments in 1/1 ratio at ambient temperature, and on cooling to $-70\,^{\circ}C$ a complex spectrum showing four pz and two PdMe environments is obtained (Fig. 1), with the two PdMe resonances differing by 0.04 ppm. Although COSY spectra allow assignment of protons within rings, assignment of coordinated and uncoordinated rings is not straightforward. Molecular models indicate that the equatorial ring is expected to lie at least close to perpendicular to the coordination plane, as in $AuMe_2\{(pz)_4B\}$ [12], and the axial ring is assumed to favour an orientation resulting in inequivalence of the coordinated rings and PdMe groups, with one possible structure shown in Fig. 1 drawn from the crystal structure analysis of isoelectronic $AuMe_2\{(pz)_4B\}$.

The spectrum of $PdIMe\{(pz)_4C\}$ at $-70\,^{\circ}C$ is consistent with a similar structure, with two orientations (in 2/1 ratio) for the uncoordinated ring since the complex exhibits eight pz environments and two PdMe resonances (separated py 0.08 ppm).

The complex $PdMe_2\{(pz)_2(mim)CH\}$ exhibits sharp mim resonances ca. 0.2–0.7 ppm downfield from the free ligand values at ambient temperature, and four broad (barely visible) resonances for the pz rings, consistent with more rapid exchange of coordinated and uncoordinated pz rings in (I) (X = Me); on cooling resonances for the two pz rings are resolved, one of them showing the expected downfield shifts on coordination for H(3).



(I)

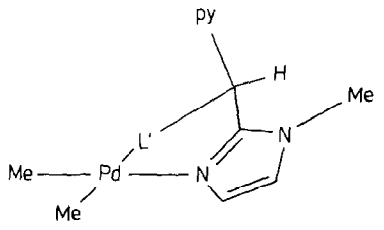
(X = Me, and X = I (major isomers))

The complex $PdIMe\{(pz)_2(mim)CH\}$ exhibits similar variable temperature behaviour, but this is more complex owing to the presence of two isomers in ca. 6/1 ratio. Structures of the isomers are readily assigned, since the signal from PdMe *trans* to a pz donor appears ca. 0.15 ppm downfield from PdMe *trans* to mim in a series of model bidentate complexes [9], giving the major isomer as that with mim *trans* to PdI (I), the minor isomer thus having mim *trans* to PdMe.

Low temperature spectra for $PdMe_2\{(pz)_2(py)CH\}$ indicate isomers **A** and **B** in ca. 3/1 ratio (Fig. 2), with **A** involving two (equivalent) coordinated pz rings and an

uncoordinated py ring, and complex **B** involving py and pz coordination. In addition, the H(5) signal for the uncoordinated pz ring of isomer **B** appears as two very close doublets in 2/3 ratio, consistent with two orientations for the uncoordinated pz ring. The complex $PdIMe\{(pz)_2(py)CH\}$ exhibits similar isomerism, with **A** and **B** in ca. 6/1 ratio, and with the coordinated py ring in **B** *trans* to PdMe.

For $PdMe_2\{(py)_2(mim)CH\}$ the mim resonances are sharp and well resolved at ambient temperature and at $-70\,^\circ C$, but the single py resonances at ambient temperature become resolved into two py environments at $-70\,^\circ C$. The two PdMe resonances are broad at ambient temperature, and at low temperature have shoulders at higher ppm values, and thus it appears that the uncoordinated py ring adopts two conformations (**L′** = py in II).



(II)

(L′ = py in $PdMe_2\{(py)_2(mim)CH\}$ and mim in $PdMe_2\{(py)(mim)_2CH\}$)

The spectrum of $PdIMe\{(py)_2(mim)CH\}$ at $-85\,^\circ C$ is readily interpreted, showing one mim environment and two py environments, with the coordinated py exhibiting H(6) at 9.43 compared with 8.77 ppm for the $Pd^{II}Me_2$ complex, consistent with an orientation adjacent to the iodo group and *trans* to PdMe.

The complex $PdMe_2\{(py)(mim)_2CH\}$ exhibits a simple spectrum, with equivalent mim groups, reflecting the strong donor ability of the mim group, and $PdIMe\{(py)(mim)_2CH\}$ displays two mim environments, presumably with an uncoordinated py ring.

Experimental

The reagents $[PdIMe(SMe_2)]_2$ [16], $[PdMe_2(pyridazine)]_n$, *trans*-$PdCl_2(SMe_2)_2$, $(mim)_2CH_2$, and $(py)(mim)CH_2$ [9], $(pz)_4C$ [7], and $(py)_3CH$ [17] from $(py)_2CH_2$ [18] were prepared as previously described. Toluene was dried over $CaCl_2$ and distilled from sodium, and stored over sodium; 2-bromopyridine was predried over NaOH, distilled from CaO, and stored over 4Å molecular sieves; dichloromethane was predried over $CaCl_2$ and distilled from P_2O_5. Phosgene in toluene was used as received (Fluka). Other solvents and reagents were purified as described elsewhere [9]. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and the Canadian Microanalytical Service, Vancouver. ^1H NMR spectra were recorded using a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si in $(CD_3)_2CO$ (acetone at 2.06 ppm).

Synthesis of ligands

Tris(pyrazol-1-yl)methane. The procedure described for the original synthesis of $(pz)_3CH$ [19] has not been successful in our laboratory, and we found a modification

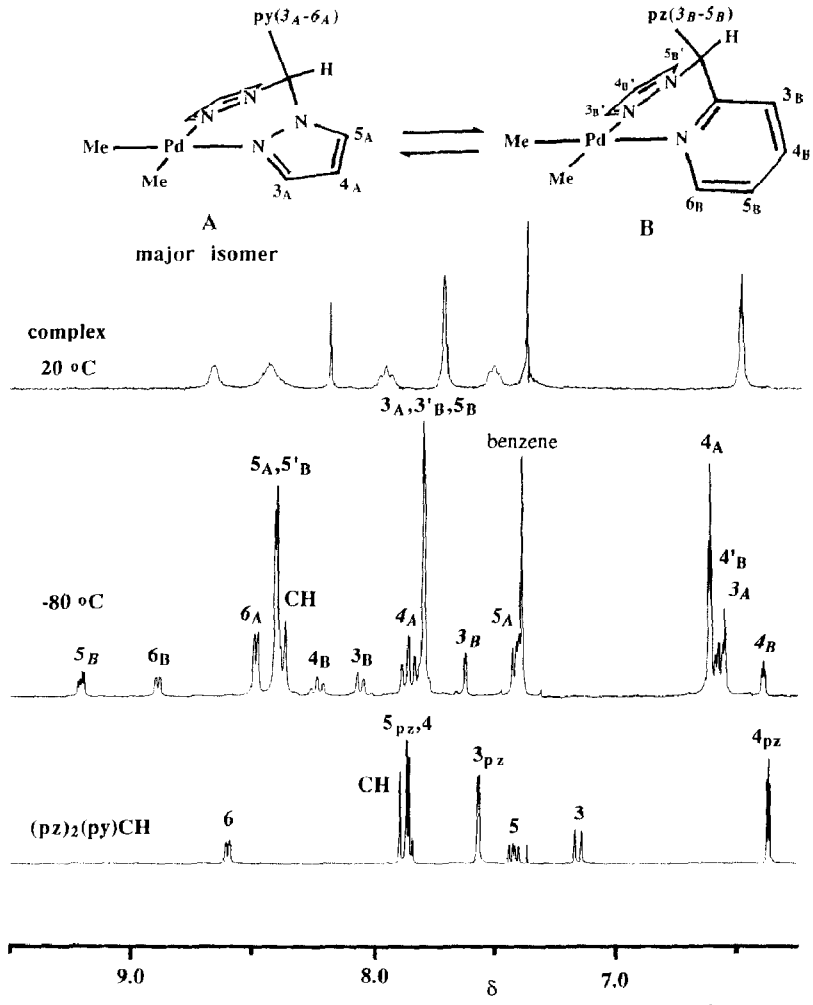


Fig. 2. ^{1}H NMR spectra of the new ligand $(pz)_2(py)CH$ and its $Pd^{II}Me_2$ complex in $(CD_3)_2CO$, illustrating the variable temperature ^{1}H NMR behaviour exhibited by the complexes, and the formation of isomers.

of Trofimenko's method for the synthesis of $(pz)_4C$ [20] to be more reliable. Pyrazole (30 g, 441 mmol) was added to a suspension of potassium (17.24 g, 441 mmol) in tetrahydrofuran (400 ml) under nitrogen, and the mixture was refluxed until the potassium had been consumed (ca. 1.5 h). Chloroform (11.76 ml, 147 mmol) was added in one portion at ambient temperature, and after 30 min stirring the suspension was slowly heated under gentle reflux for 8 h, during which the mixture became tan coloured. The solution was filtered hot, the precipitate of KCl washed with chloroform (3×30 ml), and the combined filtrate and washings reduced to a minimum volume under vacuum. Zone sublimation of the resultant semi-solid residue gave a yellow solid, which was extracted with hot hexane; on reduction of volume and cooling, $(pz)_3CH$ crystallized out and was collected (13.53 g, 43%). ^{1}H NMR: δ 8.74 (3H, s, CH), 7.87 (3H, d, H(5), J_{45} 2.5 Hz), 7.63 (3H, d, H(3), J_{34} 1.5 Hz), 6.41 (3H, dd, H(4), J_{45} 2.6, J_{34} 1.7 Hz).

Bis(pyrazol-1-yl)(pyridin-2-yl)methane, $(pz)_2(py)CH$. Bis(pyrazol-1-yl)methanone may be prepared by either of Peterson's methods [6,8], with the triethylamine route [8] providing a simple synthesis complete in ca. 30 min. As this is a key reagent for ligand synthesis a simplified procedure was developed. In this pyrazole (5 g, 73.5 mmol), triethylamine (10.25 ml, 73.5 mmol), and diethyl ether (200 ml) were mixed by mechanical stirring under nitrogen, and phosgene (19 ml of a 1.93 *M* solution in toluene) was added in two portions. Stirring was continued for 15 min, the precipitate filtered off (under vacuum), most of the solvent removed from the filtrate by rotary evaporation. Hexane (10 ml) was then added and the solution set aside for crystals of $(pz)_2CO$ to separate (5.65, g, 95%). The product was filtered off, dried under vacuum, and stored under nitrogen. It was generally made as required, and used immediately.

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and pyridine-2-aldehyde (0.60 ml, 6.3 mmol), together with a catalytic amount of anhydrous cobalt(II) chloride (0.01 g) (the reaction also proceeds satisfactorily without addition of the catalyst) were placed in a flask flushed with nitrogen via a side arm. The mixture was gently warmed until evolution of CO_2 was observed, the mixture then cooled and set aside until the reaction had subsided. Water (5 ml) was then added, and the mixture extracted with dichloromethane (2×20 ml). The combined extracts were dried ($MgSO_4$) then filtered, and the solvent was removed under vacuum. The product, $(pz)_2(py)CH$, was recrystallized from hot hexane/charcoal (0.64 g, 45%), m.p. 55 °C. Anal. Found: C, 64.2; H, 4.8; N, 31.4. $C_{12}H_{11}N_5$ calcd.: C, 64.0; H, 4.9; N, 31.1%. ^1H NMR: δ 8.61 (1H, ddd, H(6), J_{56} 4.8, J_{46} 1.8, J_{36} 0.9 Hz), 7.88 (1H, s, CH), ca. 7.85 (3H, m, H(4) (py) and H(5) (pz)), 7.57 (2H, d, H(3)(pz), J_{34} 1.7 Hz), 7.42 (1H, ddd, H(5)(py), J_{45} 7.6, J_{34} 4.8, J_{35} 0.7 Hz), 7.15 (1H, d, H(3)(py), J_{34} 7.9 Hz), 6.36 (2H, dd, H(4), J_{45} 2.4, J_{34} 1.9 Hz). MS: *m/e* 225 (*M*, 15%), 158 (100%), 147 (68%), 131 (35%).

Bis(pyrazol-1-yl)(N-methylimidazol-2-yl)methane, $(pz)_2(mim)CH$. We found the reported preparation of *N*-methylimidazole-2-carbaldehyde [21] to be unreliable, and a modified procedure was developed. Butyllithium (140 ml of 1.2 *M* solution) was added dropwise to a stirred solution of *N*-methylimidazole (13.4 ml, 168 mmol) in diethyl ether (20 ml) at −80 °C under nitrogen. The solution was allowed to warm slowly to 0 °C, recooled to −80 °C, and added dropwise at this temperature to a well stirred mixture of dimethylformamide (25 ml) and diethyl ether (30 ml) at −80 °C. The white suspension was allowed to warm to ambient temperature then stirred for 6 h, and aqueous HCl (100 ml of 5 *M*) added. The organic layer was separated, and washed with small portions of 5 *M* aqueous HCl (2×20 ml). The combined acid extracts were made slightly alkaline with $NaHCO_3$, then extracted twice with chloroform (40 ml), and the combined extracts dried over $MgSO_4$. After filtration, removal of solvent, and vacuum distillation (60–65 °C, 1 mmHg), (mim)CHO was obtained as a clear oil that crystallized on standing (12.8 g, 69%). ^1H NMR ($CDCl_3$): δ 9.82 (1H, s, CHO), 7.28 (1H, s, H(4 or 5)) and 7.12 (1H, s, H(5 or 4)), 4.03 (3H, s, *N*Me).

Reaction of (mim)CHO with $(pz)_2CO$ proceeded similarly to that for the synthesis of $(pz)_2(py)CH$, but neither the $CoCl_2$ catalyst nor the gentle warming was required. On completion of the reaction the tar formed was dissolved in dichloromethane and subjected to column chromatography (silica gel, medium pressure, dichloromethane elution) to give a clear, colourless eluent; all other components

were not eluted or had very low R_f values. Addition of hexane and slow removal of dichloromethane, under a vacuum at ambient temperature, gave $(pz)_2(mim)CH$ as white crystals (1.7 g, 49%), m.p. 104–106 °C. Anal. Found: C, 57.9; H, 5.4; N, 37.0. $C_{11}H_{12}N_6$ calcd.: C, 57.9; H, 5.3; N, 36.8%. ^{1}H NMR: δ 8.00 (1H, s, CH), 7.93 (2H, d, H(5), J_{45} 2.6 Hz), 7.52 (2H, s, H(3)), 7.16 (1H, d, H(4 or 5)) and 6.87 (1H, d, H(5 or 4)(mim), J_{45} 1.1 Hz), 6.33 (2H, dd, H(4), J_{45} 2.5, J_{34} 1.8 Hz), 3.56 (3H, s, *N*Me). MS: *m/e* 228 (*M*, 15), 227 (25), 161 (100), 160 (15), 93 (10%).

Bis(N-methylimidazol-2-yl)(pyridin-2-yl)methane, (py)(mim)$_2$CH. Phenyllithium (prepared from 0.35 g Li and 2.63 g PhBr) was added to a stirred suspension of bis(*N*-methylimidazol-1-yl)methane (4.0 g, 23 mmol) in tetrahydrofuran (20 ml) at 0 °C under nitrogen. After ca. 30 min 2-bromopyridine (2.38 ml, 23 mmol) in diethyl ether (10 ml) was added to the clear red solution, and the mixture was stirred at 0 °C for 30 min. Addition of toluene (100 ml) was followed by removal of diethyl ether by distillation. The volume was increased to ca. 200 ml by addition of toluene, and the mixture kept at 110 °C for 12 h. The suspension was treated with the minimum quantity of water required to dissolve the suspended salts, the organic and aqueous phases were separated, and the organic phase was extracted with 4*M* aqueous HCl (5 × 5 ml). The combined aqueous phases were made alkaline with Na_2CO_3, extracted with chloroform (10 × 5 ml), and dried over $MgSO_4$. Filtration and evaporation gave a brown oil, which was dissolved in chloroform. The solution was passed through a short silica column and hexane then added. The product, $(py)(mim)_2CH$ (2.75 g, 48%) separated as cream crystals, m.p. 137–138 °C. Anal. Found: C, 66.2; H, 5.9; N, 27.5. $C_{14}H_{15}N_5$ calcd.: C, 66.4; H, 6.0; N, 27.6%. ^{1}H NMR: δ 8.48 (1H, m, H(6), J_{56} 4.9 Hz), 7.74 (1H, ddd, H(4), $J_{45} \sim J_{34} \sim 7.7$, J_{46} 1.8 Hz), 7.26 (2H, m, H(3,5)), 7.02 (2H, d, H(4 or 5)(mim)) and 6.81 (2H, d, H(5 or 4)(mim), J_{45} 1.2 Hz), 6.02 (1H, s, CH), 3.50 (6H, s, *N*Me). MS: *m/e* 253 (*M*, 100), 252 (15), 175 (20), 172 (15), 161 (40), 158 (80), 96 (60), 95 (20), 78 (15%).

Bis(pyridin-2-yl)(N-methylimidazol-2-yl)methane, (py)$_2$(mim)CH. A similar procedure to that above was used but with (pyridin-2-yl)(*N*-methylimidazol-2-yl)methane as reagent and with heating at 110 °C for 24 h. However, the solution of the oil in chloroform was evaporated and distilled under high vacuum to remove unchanged 2-bromopyridine (20–25 °C, 0.1 mmHg) and $(py)(mim)CH_2$ (105–115 °C, 0.1 mmHg) prior to passage through a short silica column. The product $(py)_2(mim)CH$ (23%) was recrystallized from dichloromethane/hexane to give cream needles, m.p. 79–81 °C. Anal. Found: C, 71.8; H, 5.7; N, 22.3, $C_{15}H_{14}N_2$ calcd.: C 72.0; H, 5.6; N, 22.4%. ^{1}H NMR: δ 8.48 (2H, ddd, H(6), J_{56} 4.8, J_{46} 1.7, J_{36} 0.9 Hz), 7.72 (2H, ddd, H(4), $J_{45} \sim J_{34} \sim 7.7$, J_{46} 1.8 Hz), 7.39 (2H, d, H(3), J_{34} 3.9 Hz), 7.23 (2H, ddd, H(5), J_{45} 7.5, J_{56} 4.9, J_{35} 1.1 Hz), 7.02 (1H, d, H(4 or 5)(mim)) and 6.84 (1H, d, H(5 or 4)(mim), J_{45} 1.1 Hz), 3.60 (3H, s, NMe), 5.95 (1H, s, CH). MS: *m/e* 250 (*M*, 100), 249 (30), 172 (20), 168 (30), 158 (60), 78 (20%).

Synthesis of complexes

The complexes were prepared according to the procedures developed for the synthesis of bidentate ligand complexes [9]. Thus, $PdMe_2(L)$ ($L = (pz)_3CH$, $(pz)_4C$) were prepared by addition of the ligands to solutions obtained by addition of halide free methyllithium to *trans*-$PdCl_2(SMe_2)_2$ at low temperature, and the remaining complexes were obtained from acetone solutions of $[PdMe_2(pyridazine)]_n$ or $[PdIMe(SMe_2)]_2$ and the ligands, except for $PdMe_2(L)$ ($L = (pz)_2(py)CH$, $(pz)_2(mim)CH$,

Table 1

Yield and characterization data for the complexes isolated

Complex	Colour	Yield (%)	Analysis (Found(calcd.)(%))			δ(PdMe) [a] (ppm)
			C	H	N	
$PdMe_2(L)$						
$(py)_3CH$	red	25	55.9(56.3)	5.0(5.0)	10.7(11.0)	−0.20
$(pz)_3CH$	white	72	41.4(41.1)	4.8(4.6)	24.0(24.0)	0.09
$(pz)_2(mim)CH$	white	63	43.1(42.8)	5.0(5.0)	22.8(23.0)	0.15(pz),0.03(mim)
$(pz)_2(py)CH$	white	62	46.0(46.5)	4.7(4.7)	19.1(19.4)	−0.03
$(pz)_4C$	white	60	43.0(43.2)	4.3(4.3)	26.9(26.9)	−0.07
$(py)_2(mim)CH$	orange	68	52.7(52.8)	5.2(5.2)	14.4(14.5)	0.02(py), −0.24(mim)
$(py)(mim)_2CH$	buff	75	49.4(49.3)	5.5(5.4)	18.0(18.0)	0.03
PdIMe(L)						
$(py)_3CH$	orange	62	41.2(41.4)	3.3(3.4)	8.5(8.3)	0.35
$(pz)_3CH$	buff	46	29.1(28.6)	3.0(2.8)	17.8(18.2)	0.73
$(pz)_2(mim)CH$ [b]	cream	72	31.1(31.2)	3.4(3.4)	17.2(17.1)	0.81(pz),0.66(mim)
$(pz)_2(py)CH$	yellow	62	33.0(33.0)	3.0(3.0)	14.6(14.8)	0.59
$(pz)_4C$	yellow	49	31.9(31.8)	2.9(2.9)	21.2(21.2)	0.60
$(py)_2(mim)CH$	yellow	67	38.7(38.6)	3.6(3.4)	11.3(11.2)	0.58
$(py)(mim)_2CH$	buff	46	35.6(35.9)	4.0(3.6)	14.6(14.0)	0.61

[a] In $(CD_3)_2CO$ at ambient temperature, with the *trans* group or ^2J(H–Pt) in parentheses. [b] Calculated for PdIMe{$(pz)_2(mim)CH$}·1/4Me_2CO, in view of acetone resonance in the NMR spectrum in $CDCl_3$.

and $(mim)_2(py)CH$)) and PdIMe{$(pz)_4C$}, which were obtained by use of benzene as a solvent, and PdIMe{$(pz)_3CH$} which was obtained by use of diethyl ether as a solvent (Tables 1 and 2).

^1H NMR spectra at ambient temperature

$PdMe_2${$(py)_3CH$}. δ 8.59 (3H, d, H(6)), 7.86 (3H, t, H(4)), 7.61 (3H, s, H(3)), 7.36 (3H, m, H(5)), 6.08 (1H, s, CH), −0.20 (6H, s, PdMe)).

PdIMe{$(py)_3CH$). δ ca. 8.78 (3H, s, H(6)), 7.94 (3H, ddd, H(4)), ca. 7.64 (3H, d(b), H(3)), 7.42 (3H, m, H(5)), 6.24 (1H, s, CH), 0.35 (3H, s, PdMe).

$PdMe_2${$(pz)_3CH$}. δ 9.14 (1H, s, CH), 8.47 (3H, s, H(5)), 7.77 (3H, s, H(3)), 6.50 (3H, s, H(4)), 0.09 (6H, s, PdMe).

PdIMe{$(pz)_3CH$}. δ 9.18 (1H, s, CH), 8.28 (3H, s(b), H(3 or 5)), 7.98 (3H, s(b), H(5 or 3)), 6.60 (3H, t, H(4)), 0.73 (3H, s, PdMe).

$PdMe_2${$(pz)_4C$}. δ (pz) 7.93, 7.25, 6.75, 6.60, all broad, −0.07 (6H, s, PdMe).

PdIMe{$(pz)_4C$}. δ 8.44 (1H, b), 8.06 (1H, b), 8.00 (2H, b), 7.43 (1H, b), 7.36 (b, obscured), 6.87 (2H, b), 6.72 (1H, b), 6.68 (2H, b), 6.60 (1H, b), 0.60 (3H, s, PdMe).

$PdMe_2${$(pz)_2(mim)CH$}. δ(pz) 9.12, 8.27, 7.77, 7.51, 6.37 all broad, mim 7.33 (1H, d, H(4 or 5)) and 7.18 (1H, d, H(5 or 4)), 3.98 (3H, s, *N*Me); 0.15 (3H, s, PdMe *trans* to pz), 0.03 (3H, s, PdMe *trans* to mim).

PdIMe{$(pz)_2(mim)CH$}. δ 8.74, 8.44, 8.37, 7.73, 7.50, 7.23, 6.43, 4.11, 3.98, 0.81, 0.66 all broad.

$PdMe_2${$(pz)_2(py)CH$}. δ(py) 8.66, 8.43, 7.95, 7.50 all broad; (pz) 8.43, 7.71, 6.47 all broad; 8.17 (1H, s, CH), −0.03 (6H, s, PdMe).

PdIMe{$(pz)_2(py)CH$}. δ(py) 8.80 (1H, s, H(6)), 7.97 (m, H(4), obscured), 7.52 (1H, m, H(5)), 7.19 (1H s, H(3)); (pz) 8.39 (2H, d, H(5)), 7.94 (2H, s, H(3)), 6.57 (2H, t, H(4)); 8.31 (1H, s, CH), 0.59 (6H, s, PdMe).

Table 2

Selected ^{1}H NMR data for the complexes of tripod ligands at low temperature [a]

Complex	Temp. (°C)	PdMe [b]	Coordinated groups			Uncoordinated groups	
							
			H(b) [c]	H(3) [c]	H(4,5) [c,d]	H(6)	H(3)
$PdMe_2\{(py)_3CH\}$	−70	−0.30	8.66d (Me)			8.35d	
$PdIMe\{(py)_3CH\}$	−60	0.26	9.16m (I) (Me) [e]			[e]	
$PdMe_2\{(pz)_3CH\}$	−70	0.05		7.92			7.64
$PdIMe\{(pz)_3CH\}$	−90	0.62		8.08 (Me?) 8.28d (I?)			7.63
$PdMe_2\{(pz)_2(mim)CH\}$	−20	0.14(pz) 0.01(mim)		7.77d	7.38d,7.17d		7.54d
$PdIMe\{(pz)_2(mim)CH\}$	−50						
Isomer A:		0.76(pz)		8.25d (I)	7.66d,7.29d (Me)		7.71
Isomer B:		0.58(mim)		[f]	7.56d,7.48d		[f]
$PdMe_2\{(pz)_2(py)CH$	−80						
Isomer A:		−0.16(pz)		7.79d		8.48d	
Isomer B:		0.08 0.04	8.90	[f]			7.62d
$PdIMe\{(pz)_2(py)CH\}$	−70						
Isomer A:		0.46(pz)		7.95d (Me) 8.11d (I)		8.56d	
Isomer B:		0.63(py)	9.53d (I)	[f]			[f]
$PdMe_2\{(py)_2(mim)CH\}$	−70	−0.04(py) −0.03(py) −0.16(mim) −0.15(mim)	8.77d		7.30d,6.98d	8.49d	
$PdIMe\{(py)_2(mim)CH\}$	−90	0.44(py)	9.43d (I)		7.48d,7.05d (Me)	8.54d	
$PdIMe\{(py)(mim)_2CH\}$	−20	0.57(mim)			7.37d,7.05d (Me) 7.59d,7.17d (I)	8.58m	

[a] In $(CD_3)_2CO$, and at a temperature giving resolution of coordinated and uncoordinated groups where possible, e.g. solubility limitations on temperature. [b] *Trans* group in parentheses. [c] Adjacent group in the square plane in parentheses: methyl or iodo. [d] Normally not possible to differentiate between H(4) and H(5). [e] Unresolved, broad resonance for uncoord. ⇌ coord. exchange at 8.53 ppm. [f] Obscured.

$PdMe_2\{(py)_2(mim)CH\}$. δ(py) 8.64 (2H, d, H(6)), 7.96 (2H, d, H(3)), 7.81 (2H, ddd, H(4)), 7.30 (2H, m, H(5)); mim 7.16 (1H, d, H(4 or 5)) and 6.99 (1H, d, H(5 or 4)), 3.99 (3H, s, NMe); 6.09 (1H, s, CH), 0.02 (3H, s, PdMe *trans* to py), −0.11 (3H, s, PdMe *trans* to mim).

$PdIMe\{(py)_2(mim)CH\}$. δ(py) 9.02 (2H, d(b), H(6)), 7.88 (2H, ddd, H(4)), 7.71 (2H, d, H(3)), 7.37 (2H, m, H(5)); mim 7.30 (1H, s, H(4 or 5)) and 7.01 (1H, s, H(5 or 4)), 4.13 (3H, s, *N*Me); 6.26 (1H, s, CH), 0.58 (3H, s, PdMe).

$PdMe_2\{(py)(mim)_2CH\}$. At 45 °C, δ (uncoord. py) 8.52 (1H, ddd, H(6), J_{56} 4.9, J_{46} 1.8, J_{36} 0.9Hz), 8.39 (1H, m, H(3), J_{34} ~ 7.8 Hz), 7.73 (1H, ddd, H(4), $J_{34} \sim J_{45}$ ~ 7.6, J_{46} 1.9 Hz), 7.27 (1H, ddd, H(5), J_{56} 4.9, J_{45} 7.6, J_{35} 1.1 Hz); (coord. mim) 7.09 (2H, d, H(4 or 5)) and 7.06 (2H, d, H(5 or 4), J_{45} 1.4 Hz), 3.91 (6H, s, *N*Me); 0.03 (6H, s, PdMe); at ambient: as above, with addition of 6.02 (1H, s, CH).

$PdIMe\{(py)(mim)_2CH\}$. δ(py) 8.56 (1H, ddd, H(6)), 7.99 (1H, d, H(3)), 7.84 (1H, ddd, H(4)), 7.34 (1H, ddd, H(5)); (mim) 7.64 (1H, s), 7.30 (1H, s), 7.10 (1H, s), 7.06 (1H, s), 4.07 (3H, s, *N*Me); 6.14 (1H, s, CH), 0.61 (3H, s, PdMe).

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