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Cyclometallation of polydentate ligands containing pyrazole groups, including the synthesis of platinum(IV) complexes with tripodal $[N–C–N]^-$ ligand systems

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Abstract

Dimethylplatinum(II) complexes, $PtR_2(L)$, have been made by reaction of $[PtR_2(\mu\text{-}SEt_2)]_2$ with a range of polydentate nitrogen donor ligands containing one or more pyrazol-1-yl (pz) donor groups, including the new ligand bis(pyrazol-1-yl)(thien-2-yl)methane. The complexes give *cis*-$PtMe_2(py)_2$ when dissolved in pyridine at ambient temperature, except for $PtMe_2(L)$ ($L = (pz)_2CH_2$, $(pz)_2C(H)Ph$, $(pz)_3CH$, or $(pz)_2(mim)CH$ (mim = *N*-methylimidazol-2-yl)), which undergo cyclometallation at a C(5) position of one pyrazol-1-yl ring. The cyclometallated ligands have been examined as 'isoelectronic' analogues of nitrogen donor poly(pyrazol-1-yl)alkane and poly(pyrazol-1-yl)borate ligands. A carbon monoxide derivative, $PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C\}(CO)$ (**1d**) and a series of phosphine complexes have been prepared. The complex $PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C\}(py)$ (**1a**) and polymeric $[PtMe\{(pz)_2(C_3H_2N_2)CH\}]_n$ (**2**) undergo oxidative addition reactions with organohalides to give the platinum(IV) complexes [*fac*-$PtMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C\}(py)]X$ (**7a–d**) and *fac*-$PtXMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C\}$ (**8a,b**), respectively. The new reagent 1-bromo-2-(pyrazol-1-yl)ethane forms [*fac*-$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C\}(pzCH_2CH_2\text{-}N,C)]Br$ (**10**), containing both $[N–C–N]^-$ and $[N–C]^-$ ligands. Reaction of MeI or $PhCH_2Br$ with $PtMe_2\{(pz)_3CH\}$ gives *fac*-$PtXMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C\}$ (**8a,b**) directly, and $PtMe_2\{(pz)_4C\}$ undergoes a similar cyclometallation/oxidative addition in iodomethane to form *fac*-$PtIMe_2\{(pz)_3(C_3H_2N_2)CH\text{-}N,N',C\}$ (**13**).

Introduction

Cyclometallation reactions involving metal–carbon σ-bond formation by donor ligands occur for many reagents containing one donor atom [1–10], usually nitrogen [1–5,7–10], e.g. 2-phenylpyridine (pyPh), 2-benzylpyridine, and α-phenyl-α-(pyridin-2-yl)toluene react readily with palladium(II) acetate to form the palladocycle complexes $[Pd(pyC_6H_4\text{-}N,C)(\mu\text{-}O_2CMe)]_2$ [11,12] and **A** [13,14].

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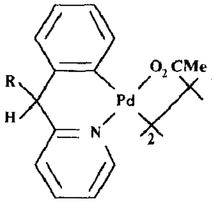
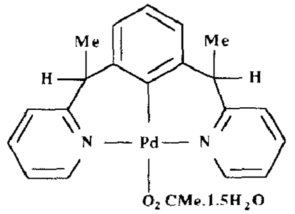
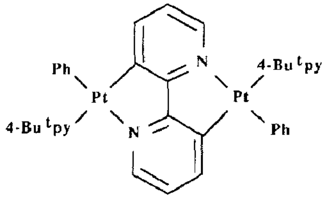
The occurrence of cyclometallation reactions for reagents containing more than one donor group has been reported for two classes of reagent. The most common are those for which polydentate coordination by the donor groups encourages or requires metallation at an addition site(s), e.g. for nitrogen donor ligands palladation of phenyl rings of $\{PhCH_2(Me)NCH_2\}_2CH_2$ and 1,3-bis[1-(pyridin-2-yl)ethyl]benzene results in formation of $PdCl\{PhCH_2(Me)NCH_2CH_2CH_2N(Me)\text{-}CH_2C_6H_4\text{-}N,N',C\}$ [15] and **B** [16], respectively. However, cyclometallation of a heterocyclic ring(s) of a polydentate ligand, rather than simple donor atom chelation by the ring(s), has been reported for only a limited number of reagents, e.g. 2,2′-bipyridyl in $[Ir(C_{10}H_8N_2\text{-}N,N')_2\{C_{10}H_7N(NH)\text{-}N,C\}(H_2O)]^{3+}$ [17] and $\{PtPh(4\text{-}Bu^tpy)\}_2(\mu\text{-}C_{10}H_6N_2\text{-}N,C,N',C')$ (**C**) [18], 2-(2′-thienyl)pyridine $[py(C_4H_3S)]$ in $\{Pd[py(C_4H_2S)\text{-}N,C](\mu\text{-}Cl)\}_2$ [19a], and tris(pyrazol-1-yl)methane $[(pz)_3CH]$ in $PtMe\{(pz)_2(C_3H_2N_2)\text{-}N,C\}(py)$ (**1a**) [20,21]. Complex **1a** is apparently the only reported example of cyclometallation of a potential donor ring in which the rings are linked by a bridging group (CH), rather than linked directly as in



(**A** ; R = H [13], Ph [14])



(**B**)



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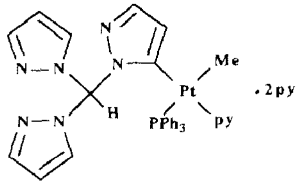

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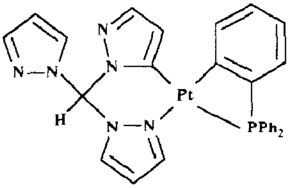

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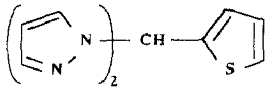
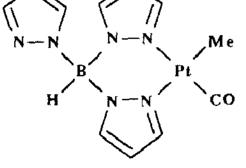


((pz)2(thi)CH)



(F)

2,2′-bipyridyl or 2-(2′-thienyl)pyridine. Reaction of palladium(II) acetate with pyridine groups linked in this manner, e.g. with $(py)_2CH_2$, $(py)_2PhCH$, and $(py)_3CH$, results in isolation of *N*,*N*′-coordination complexes rather than cyclometallation [14]. Complex **1a** is formed when $PtMe_2\{(pz)_3CH\}$ is dissolved in pyridine, and has been characterized by X-ray crystallography, together with the derivative $PtMe\{(pz)_2(C_3H_2N_2)\text{-}C\}(PPh_3)(py).2py$ (**D**), containing the ligand as a unidentate *C*-donor [21]. The derivative $PtMe\{(pz)_2(C_3H_2N_2)\text{-}C\}(PPh_3)_2$ (**6a**) undergoes an additional cyclometallation on melting, to form $Pt\{(pz)_2(C_3H_2N_2)\text{-}N,C\}\{PPh_2(C_6H_4)\text{-}P,C\}$ (**E**). In view of the unusual features exhibited by these complexes we decided to undertake further studies of the tendency of $(pz)_3CH$ and related ligands to undergo platination. The ligands studied include bis(pyrazol-1-yl)alkanes, $(pz)_2C(R)R'$, related ligands containing pyridin-2-yl(py) and *N*-methylimidazol-2-yl)(mim) groups and the new ligand bis(pyrazol-1-yl)(thien-2-yl)methane, $(pz)_2(thi)CH$.

The reactivity of some of the cyclometallated complexes toward phosphine ligands has been studied, together with oxidative addition reactions to give, for example, platinum(IV) complexes with metallated tris(pyrazol-1-yl)methane as a tripodal $[N-C-N]^-$ group formally isoelectronic with tridentate $[(pz)_3BH\text{-}N,N',N'']^-$. This appears to be the first report of tripodal $[N-C-N]^-$ ligands, in contrast to the well established and topical planar $[N-C-N]^-$ [10,16,22–24] and $[N-N-C]^-$ ligands [10,15,23,25,26]; preliminary reports of parts of this work have appeared [27–29].

Results and discussion

The soluble complexes exhibit ^1H NMR spectra with integrations in accord with formulae presented; data for the previously reported complexes **1a** and **6a** are included in Tables 1 and 2, respectively, for comparison. Platinum(II) complexes are shown with square-planar *cis*-PtC_2 geometry in view of the structural results obtained for **1a** and **D**, and of spectroscopic evidence for the *cis*-PtC_2 group for some of the complexes.

Synthesis of (pz)₂(thi)CH and the N,N′-bidentate complexes

The new ligand $(pz)_2(thi)CH$ was obtained by condensation of thiophene-2-carboxaldehyde with bis(pyrazol-1-yl)methanone according to the procedure developed for the synthesis of related bis(pyrazol-1-yl)alkanes [30–32].

Reaction of the cycloocta-1,5-diene complex, $PtMe_2(cod)$, with $(pz)_3CH$ in refluxing benzene for 30 h gave a moderate yield (ca. 60%) of $PtMe_2\{(pz)_3CH\}$ [21], and improved synthetic routes to this complex were sought prior to studies with other ligands. Reaction in refluxing toluene for ca. 48 h gave a ca. 80% yield, and although this approach was successful and gave similar yields for several other ligands, the most convenient synthetic route involved reaction of $[PtMe_2(\mu\text{-}SEt_2)]_2$ with the ligands under mild conditions (ambient temperature in benzene for ca. 15 min, or heating in acetone) ($L = (pz)_2C(H)Me$, $(pz)_2CMe_2$, $(pz)_2C(H)Ph$, $(pz)_3CH$, $(pz)_2(mim)CH$, $(pz)_2(thi)CH$, $(pz)_4C$). The complexes $PtMe_2(L)$ ($L = (py)(pz)CH_2$ and $(pz)(mim)CH_2$) [33] and $PtPh_2\{(pz)_3CH\}$ were prepared for comparison.

The complexes $PtMe_2(L)$ ($L = (pz)_2CH_2$, $(pz)_3CH$, $(pz)_2CHPh$) are insoluble, but $PtMe_2(L)$ ($L = (pz)_2CHMe$, $(pz)_2CMe$, $(pz)_4C$) and $PtPh_2\{(pz)_3CH\}$ exhibit varia-

Table 1

Selected ^1H NMR data for the cyclometallated complexes [a]

Complex	Metallated group		PtMe	Other
	H(3)	H(4)		
Platinum(II) complexes				
1a			0.92 (86.4)	8.38, CH; 8.54, H(2, 6) (24.6)
1b	7.63 d	6.37 m (24.0)	0.94 (83.6)	8.42 m, CH and H(2, 6)
1c	7.58 m	6.34 t (24.2)	0.88 (86.2)	8.37, CH; 7.02 t, H(4)(mim) (15.2)
1d	7.66 t (9.1)	6.53 t (15.0)	1.21 (87.2)	8.38, CH
Platinum(IV) complexes				
7a	7.43 td (10.7)	6.09 td (14.3)	1.51 t (69.2)	10.45, CH; 8.35 m, H(2, 6)
7b	7.55 td (10.5)	6.39 m (14.2)	1.56 t (69.7)	10.77, CH; 8.41 m, H(2, 6) (22.2); 3.40 td, CH_2 (94.0) and 4.18 td, CH_2 (68), *J*(HH) 9.8 Hz.
7c	7.47 t (8.7)	6.19 t (11.8)	1.51 t (69.6)	10.81, CH; 8.36 m, H(2, 6) (22.0); 5.62 m, =CH; 5.06 m, $=CH_2$; 2.96 dd, $PtCH_2$ (91.5) and 3.77 dd, $PtCH_2$ (88.2), *J*(HH) 9.9 Hz.
7d	7.44 m	6.17 td (13.8)	1.67 t (69.1)	10.88, CH; 8.38 m, H(2, 6); 5.89 tt, =CH (67.1); 4.45 m, $=CH_2$ (45.1)
8a	7.46 td (10.8)	6.12 td (14.0)	1.87 t (74.1)	9.47, CH
8b	7.65 d (9.0)	6.57 d (12.3)	1.80 t (73.8)	9.38, CH; 4.05 d, CH_2 (69.8) and 4.21 d, CH_2 (107.3), *J*(HH) 8.8 Hz
10	7.42 t (10.4)	6.18 t (14.0)	1.42 t (70.4);	10.80, CH
11b	7.42 td (10.4)	6.07 td (14.0)	1.47 t (70.2) 1.36 t (67.0)	8.61, CH; 4.38 NMe
13	7.49 td (9.8)	6.16 td (15.9)	1.76 t (73.9)	

[a] In $CDCl_3$, except for **8b** and **13**, in $(CD_3)_2CO$; $^1H^{195}Pt$ coupling constants in brackets.

ble temperature ^1H NMR spectra similar to related Pd(II) complexes [33–35] and $PtMe_2(L)$ (L = (py)(pz)CH_2, (pz)(mim)CH_2) [33], e.g. for $PtMe_2\{(pz)_2CHMe\}$ one ligand Me resonance at ambient temperature is resolved into two quartets and two doublets at < ca. −20 °C, indicating exchange between two conformers with the Me or H group adjacent to Pt (axial) or away from Pt (equatorial). The spectrum of $PtMe_2\{(pz)_2(thi)CH\}$ has one PtMe and one set of pyrazole group resonances, with the pz resonances shifted downfield by ca. 0.35 ppm from free ligand values and H(3) coupled with platinum (^3J(HPt) 9.3 Hz), and with the thiophene resonances essentially unchanged, consistent with presence of the thiophene ring as the uncoordinated group. The spectrum of $PtMe_2\{(pz)_2(mim)CH\}$ at ambient temperature shows a single *N*-methylimidazole environment, with two pz and two PtMe environments, indicating coordination by the mim and one pz group.

Cyclometallation of pyrazole groups in N,N′-bidentate complexes

Although $PtMe_2\{(pz)_3CH\}$ was initially reported to undergo cyclometallation in hot pyridine [20,21], we have found that the reaction does proceed at ambient temperature during 5–6 h. Gentle warming in 4-methylpyridine (4-mpy) or *N*-methylimidazole (*N*-mim) also resulted in metallation, with the isolation of complexes of these solvents (**1b,c**).

Table 2

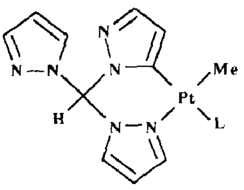
^{31}P and selected ^{1}H NMR data for phosphine complexes of cyclometallated ligands[a]

Complex	^{31}P NMR[b]		^{1}H NMR[c]	
	P *trans* to Me	P *trans* to $C_3H_2N_2$	PtMe	Other[d]
Platinum(II) complexes				
1e		21.8 t (2504)	0.31 td (77.5)	
1f		20.7 t (2599)	0.65 td (83.4)	
3	23.3 td (2215)	19.9 td (1806), *J*(PP) 14 Hz	0.09 tt (64.3)	
4		20.1 t (2560)	0.24 tt (86.9)	
5		25.1 t (2552)	0.58 td (82.5)	
6a	20.5 td (1808)	22.9 td (2239), *J*(PP) 15 Hz	0.11 tt (64.8)	
6b	1.6 td (1718)	2.3 td (2262), *J*(PP) 16 Hz	0.18 tt (62.9)	
6c	−14.3 td (1690)	−15.0 td (2214), *J*(PP) 17 Hz	0.25 tt (65.0)	
6d	11.2 td (1752)	14.1 td (2264), *J*(PP) 16 Hz	0.12 tt (64.3)	
6e	12.8 td (1779)	12.6 td (2281), *J*(PP) 15 Hz	0.26 tt (72.3)	
6f	111.7 td (2863)	106.5 td (3820), *J*(PP) 33 Hz	0.28 tt (67.1)	
6g	−40.0 td (1291)	−43.6 td (1944), *J*(PP) 21 Hz	0.86 tt (70.2)	
6h	40.9 t (1663)	44.0 t (2228)	0.40 tt (67.1)	
Platinum(IV) complexes				
9		−6.9 t (1491)	1.45 td (70.7),	10.60, CH; 6.13 m, H(4)(met)
11a		−11.8 t (1503)	1.38 td (71.0), 1.30 td (68.4), *J*(HP) 7.0 Hz	8.66, CH; 7.38 td, H(3)(met) (9.3); 6.12 m, H(4)(met)

[a] In $CDCl_3$. [b] *J*(PPt) in brackets. [c] *J*(HPt) in brackets. [d] Ligand resonances generally obscured by aryl resonances of phosphine ligands.

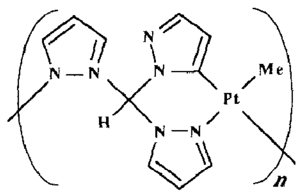
The complex $\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}}N,C\mathrm{\}(py)}$ (**1a**) forms an insoluble white solid (**2**) on refluxing in benzene, with microanalysis and IR spectra consistent with loss of pyridine (e.g. absence for **2** of py ν(CN) at 1602 cm^{-1} observed for **1a**), and addition of pyridine regenerates the pyridine complex **1a**. The complex is thus represented as a polymer $\mathrm{[PtMe\{(pz)_2(C_3H_2N)_2CH\}]_n}$ (**2**) with a structure similar to that proposed [36,37] for the isoelectronic complex $\mathrm{[PtMe\{(pz)_3BH\}]_n}$. The pyridine complex **1a** dissolves at reflux in acetone, and when CO is bubbled into the warm solution the complex $\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}}N,C\mathrm{\}(CO)}$ (**1d**) may be readily precipitated by addition of petroleum ether. The complex is monomeric in chloroform and a Nujol mull has ν(CO) at 2074 cm^{-1}, similar to that for the isoelectronic tris(pyrazol-1-yl)borate complex $\mathrm{PtMe\{(pz)_3BH\text{-}}N,N'\mathrm{\}(CO)}$ (2088 cm^{-1}) [36], which has been shown by X-ray crystallography to have square-planar coordination with bidentate tris(pyrazol-1-yl)borate (**F**) [38].

The complex $\mathrm{PtPh_2\{(pz)_3CH\}}$ dissolves in pyridine without metallation, even on heating, and the ^{1}H NMR spectra in C_5D_5N indicate the presence of free ligand and *cis*-$\mathrm{PtPh_2(py)_2}$. The new dimethylplatinum(II) complexes behaved similarly, giving *cis*-$\mathrm{PtMe_2(py)_2}$, except for the $\mathrm{(pz)_2CH_2}$, $\mathrm{(pz)_2C(H)Ph}$, and $\mathrm{(pz)_2(mim)CH}$ complexes, which underwent cyclometallation at ambient temperature, but the solids isolated from these reactions turned into impure oils. Addition of triphenylphosphine after cyclometallation gave the solid complexes $\mathrm{PtMe\{(pz)(C_3H_2N_2)CH_2\text{-}}C\mathrm{\}(PPh_3)_2}$ (**3**), $\mathrm{PtMe\{(pz)(C_3H_2N_2)C(H)Ph\text{-}}N,C\mathrm{\}(PPh_3)}$ (**4**), and $\mathrm{PtMe\{(pz)(C_3H_2N_2)(mim)CH\text{-}}N,C\mathrm{\}(PPh_3)}$ (**5**). Cyclometallation of $\mathrm{PtMe_2\{(pz)_2}$-



(1a-f)

(1a-c : L = py, 4-mpy, *N*-mim ;
1d : L = CO;
1e,f : L = PPh_2(*o*-tolyl), PPh_2(*o*-$MeOC_6H_4$))



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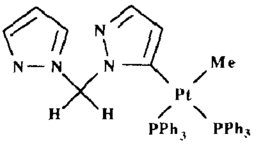

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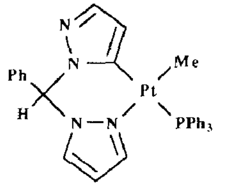

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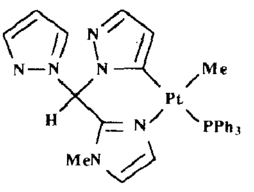

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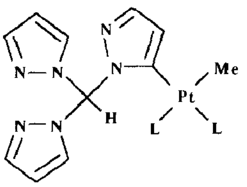


(6a-h)

(6a-f : L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$,
$PPh_2(CH_2Ph)$, $P(OPh)_3$;
6g,h : L_2 = $(PPh_2)_2CH_2$, $(PPh_2CH_2)_2$)

(mim)CH} was particularly rapid, and bubbles of the liberated gas were collected and identified as methane by gas chromatography and mass spectroscopy.

The ^1H and ^{31}P NMR spectra of the complexes may be readily assigned, and exhibit $^3J(^1H^{195}Pt)$ and $^5J(^1H^{195}Pt)$ for the metallated ring, with values of ca. 12–24 and 9 Hz, respectively, and $^2J(^1H^{195}Pt)$ ca. 84–87 Hz for the PtMe group (Tables 1 and 2, Fig. 1).

Since metallation occurs for $PtMe_2\{(pz)_2CH_2\}$ and $PtMe_2\{(pz)_2C(H)Ph\}$, then, at least for these complexes, the mechanism involves an intermediate with the ligand as a unidentate *N*-donor, analogous to the intramolecular roll-over mechanism proposed [18] for metallation of $PtPh_2$(2,2′-bipyridyl) in 4-t-butylpyridine to form **C**. In accord with this interpretation, a donor solvent appears to be necessary for cyclometallation, since the four complexes that do undergo cyclometallation in pyridine are unaffected by reflux (as suspensions) in toluene or xylene, suggesting that donor solvent coordination is necessary to allow unidentate coordination of the ligands.

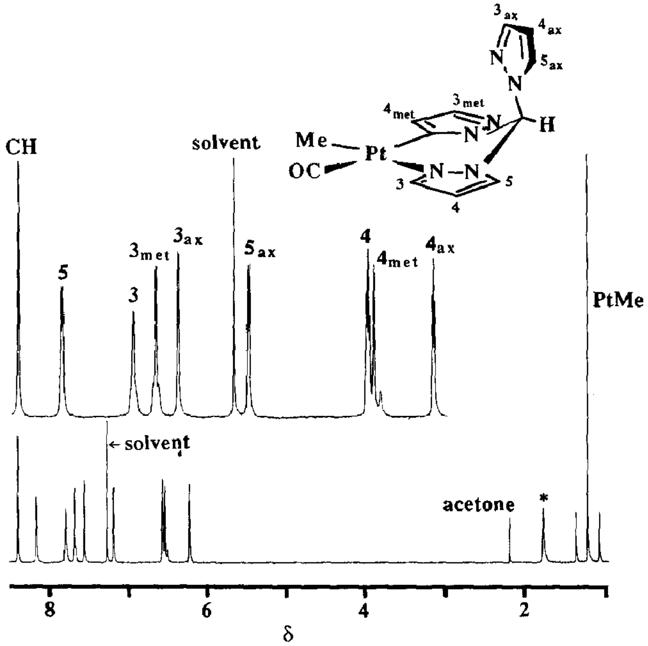


Fig 1. ^{1}H NMR spectrum of PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*N*,*C*′}(CO) (**1d**) in CDCl$_3$, illustrating ^{1}H^{195}Pt coupling for the protons of the metallated ring (^3J(HPt) 15.0, ^5J(HPt) 9.1 Hz) typical for the complexes with cyclometallated ligands, and unresolved ^{1}H^{195}Pt coupling for H(3) of the *N*-coordinated ring. * Indicates an impurity.

Phosphine derivatives of platinum(II) complexes with metallated poly(pyrazol-1-yl)methanes

Phosphine derivatives of the metallated ligand complexes were sought in order to allow further investigation of the formation of [C]$^-$ unidentate systems (as in **D**), and to explore the potential for cyclometallation of phosphines to give complexes related to **E**. The complex PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*N*,*C*}(py) (**1a**) reacts with two molar equivalents of triphenylphosphine in warm benzene to form PtMe{(pz)$_2$(C$_3$-H$_2$N$_2$)CH-*C*}(PPh$_3$)$_2$ (**6a**), and the bidentate ligands bis(diphenylphosphino)-methane and bis(diphenylphosphino)ethane give the expected analogues **6g**, **h**. However, more bulky unidentate phosphines containing one *o*-tolyl or *o*-methoxyphenyl group gave monophosphine complexes (**1e**, **f**), and interaction of **1a** with PR$_3$ (R = *o*-tolyl, mesityl, benzyl) resulted instead in formation of [PtMe{(pz)$_2$(C$_3$-H$_2$N$_2$)CH}]$_n$ (**2**).

All the phosphine complexes are monomeric in chloroform and they exhibit ^{1}H NMR characteristics expected for the (pz)$_2$(C$_3$H$_2$N$_2$)CH group (coupling from ^{195}Pt to the protons of the metallated ring, one pz environment for **6a**–**h**, and two pz environments for **6f**, **g**). The bis(phosphine) complexes **6a**–**f** exhibit ^{31}P spectra (Table 2) appropriate for the structures shown, rather than possible structures involving equivalent *trans* phosphines, e.g. the monomeric *cis*-bidentate (PPh$_2$)$_2$CH$_2$ (**6g**) and (PPh$_2$CH$_2$)$_2$ (**6h**) complexes give spectra similar to that of the PPh$_3$ complex (**6a**).

Cyclometallation of phosphines

When the new phosphine complexes **1e**, **f**, **3**, **5**, **6a–h** are heated as solids in a vacuum at their melting points, in the manner described [21] for the synthesis of $Pt\{(pz)_2(C_3H_2N_2)\text{-}N,C\}\{PPh_2(C_6H_4)\text{-}P,C\}$ (**E**) from **1a**, the complexes of PPh_2(*o*-tolyl) (**1f**), $PMePh_2$ (**6b**), and $PEtPh_2$ (**6d**) liberated bubbles of a gas on melting with darkening and decomposition, but the other complexes melted similarly without apparent gas evolution. No products could be isolated from the thermolyses, but the occurrence of cyclometallation, followed by decomposition, was supported by mass spectra and thermogravimetric analyses for several of the complexes. Thus, mass spectra (electron impact) for the complexes containing PPh_3 or other unidentate phosphines exhibit parent ions for the complex and the expected product of cyclometallation, e.g. $Pt\{(pz)_2(C_3H_2N_2)CH\text{-}N,C\}\{PMe_2(C_6H_4)\text{-}P,C\}$ for **6c**. Thermogravimetric analyses (in a vacuum) for the PPh_3 complex **6a** show weight loss appropriate for loss of methane at the melting point, followed by loss of PPh_3 (160–200 °C), but the complexes of other unidentate phosphines, except PMe_2Ph (**6c**) and $P(OPh)_3$ (**6f**), exhibited rapid gas evolution, presumably methane, with occurrence of cyclometallation, immediately followed by nonstoichiometric weight loss as expected for decomposition of the product(s). Thermal analyses for the PMe_2Ph, $P(OPh)_3$, and bidentate ligand complexes are as expected for decomposition, but do not exclude gas evolution at the melting point.

Cyclometallated $(pz)_3CH$ and $(pz)_2(mim)CH$ as tridentate $[N–C–N]^-$ ligands

Metallated $(pz)_3CH$ and $(pz)_2(mim)CH$, if bound to octahedral Pt^{IV}, rather than square-planar Pt(II), would be expected to act as tripodal $[N–C–N]^-$ tridentates,

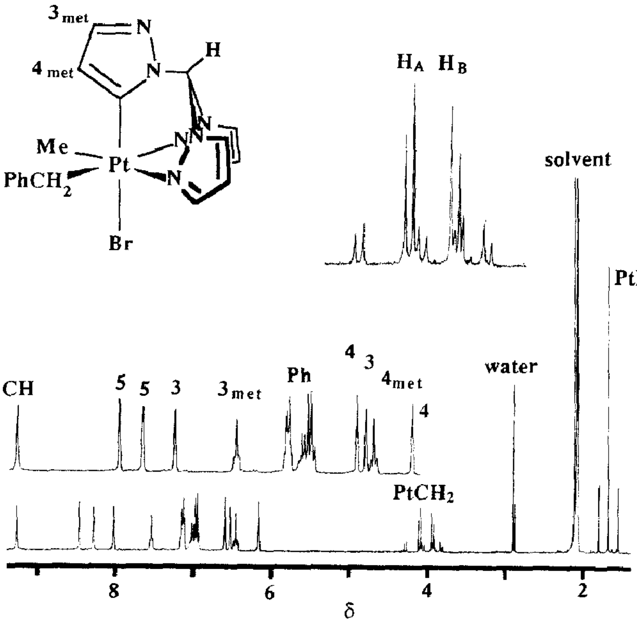
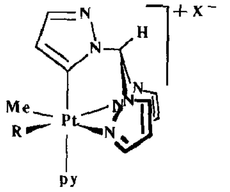


Fig. 2. ^1H NMR spectrum of $PtBrMe(CH_2Ph)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}$ (**8b**) in $(CD_3)_2CO$, illustrating three ring environments, $^1H^{195}Pt$ coupling for the protons of the metallated ring ($H4_{met}$, $^3J(HPt)$ 12.3, $H3_{met}$ $^5J(HPt)$ 9.0 Hz), and inequivalent benzylic protons with $^2J(HPt)$ 107.3 for H_A and 69.8 Hz for H_B with $^2J(HH)$ 8.8 Hz).

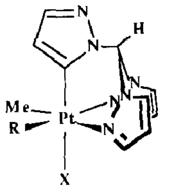
isoelectronic with commonly observed tridentate (pz)$_3$CH and [(pz)$_3$BH]$^-$, e.g. [*fac*-PtMe$_3${(pz)$_3$CH-*N*,*N*′,*N*″}]X (X = PF$_6$ [39], I [28,40]). In view of this, and interesting reports of planar [N–C–N]$^-$ systems, e.g. complex **B** [16] and 2,6-bis[(dimethylamino)methyl]phenyl- in the Pt^{IV} complex *mer*-PtCl$_3${2,6-(Me$_2$CH$_2$)$_2$C$_6$H$_3$-*N*,*N*′,*C*} [41], we sought Pt^{IV} derivatives of the metallated ligands.

Diorganoplatinum(II) complexes with nitrogen donor ligands are known to undergo oxidative addition reactions readily to form triorganoplatinum(IV) complexes, e.g. PtR$_2$(2,2′-bipyridyl) (R = Me, Ph) with iodomethane to form *fac*-PtIMeR$_2$(bipy) [42–45]. We have found that the two Pt^{II} substrates PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*N*,*C*}(py) (**1a**) and [PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH}]$_n$ (**2**) react with MeI in acetone at ambient temperature to form a cationic complex with coordinated pyridine (**7a**) and a neutral complex with coordinated iodide (**8a**), respectively. Addition of pyridine to **8a** readily gives **7a**, and addition of PPh$_3$ to a solution of **1a** prior to addition of MeI gives a PPh$_3$ analogue (**9**). Benzyl bromide reacts in a similar way with **1a** and **2** to form the cationic **7b** and neutral **8b**, and the synthesis of cations has been extended to include allyl (**7c**) and allenyl (**7d**) complexes. The allenyl complex was formed by oxidative addition of propargyl bromide to **1a**, and



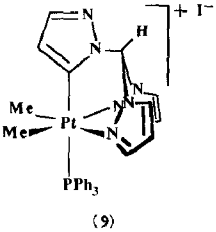
(7a-d)

(**7a** : R = Me, X = I;
7b : R = PhCH$_2$, X = Br;
7c : R = CH$_2$=CH-CH$_2$, X = Br;
7d : R = CH$_2$=CH=CH$_2$, X = Br)

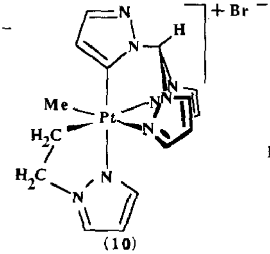


(8a,b)

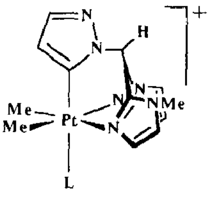
(**8a** : R = Me, X = I;
8b : R = PhCH$_2$, X = Br)



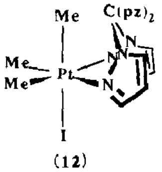
(9)



(10)



(**11a** : L = PPh$_3$;
11b : L = py)



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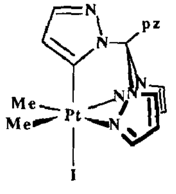

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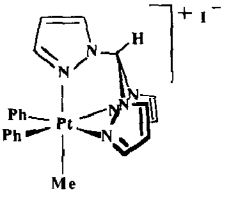

(14)

similar isomerizations of the propargyl group to an allenyl group have been reported [46].

^{1}H NMR spectra exhibit coupling to ^{195}Pt for Me, R, and metallated $(pz)_3CH$ groups (Fig. 2), with values for Me and R consistent with *trans*-nitrogen donors, e.g. $^2J(^1H^{195}Pt)$ for PtMe ca. 67–74 Hz, similar to that reported for [*fac*-$PtMe_3\{(pz)_3CH$-$N,N',N''\}]I$ (72 Hz) [40] and *fac*-$PtIMe_3\{(pz)_2CH_2$-$N,N'\}$ (72.7 Hz) [39].

The oxidative addition approach has been extended to include 1-bromo-2-(pyrazol-1-yl)ethane, $pzCH_2CH_2Br$, in an attempt to synthesise a complex containing two intramolecular coordination systems, $[N–C–N]^-$ and $[N–C]^-$. The new reagent $pzCH_2CH_2Br$ was obtained from 1,2-dibromoethane and pyrazole by a modification of the phase transfer method used for synthesis of $(pz)_2CH_2$ [47], and it was found to react readily with both **1a** or **2** to form the desired complex, $[PtMe_2\{(pz)_2(C_3H_2N_2)CH$-$N,N',C'\}(pzCH_2CH_2$-$N,C)]Br$ (**10**). Examples of metallated $(pz)_2(mim)CH$ as a tripodal $[N–C–N]^-$ ligand (**11a**, **b**) were also obtained by reaction of MeI with **5** and the pyridine analogue.

Cyclometallation under oxidative addition conditions

The iodide salt $[PtMe_3\{(pz)_3CH$-$N,N',N''\}]I$ was previously made directly from iodotrimethylplatinum(IV) species and $(pz)_3CH$ [40], but in an attempted synthesis of this complex by oxidative addition of MeI to $PtMe_2\{(pz)_3CH\}$ in acetone or dichloromethane at ambient temperature we found that the cyclometallated Pt^{IV} complex (**8a**) was formed. A similar result was obtained by addition of benzyl bromide, which gave **8b**, and although $PtMe_2\{(pz)_4C\}$ reacted with MeI in acetone to form $PtIMe_3\{(pz)_4C$-$N,N')\}$ (**12**), it also reacted in neat MeI (with acetone and hexane added later for isolation) to form an analogue of **8a**, $PtIMe_2\{(pz)_3(C_3H_2N_2)$-$CH$-$N,N',C\}$ (**13**).

$$PtMe_2\{(pz)_3CH\} + RX \rightarrow PtXMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C\}\,(\mathbf{8a},\,\mathbf{b})$$

$$(RX = MeI\ (\mathbf{8a}),\ PhCH_2Br\ (\mathbf{8b}))$$

These unexpected reactions may proceed via cyclometallation of $PtMe_2(L)$, e.g. to form $[PtMe\{(pz)_2(C_3H_2N_2)CH\}]_n$ (**2**) (perhaps $n = 1$ with coordinated acetone), prior to rapid oxidative addition, with the solvent systems acetone/RX and CH_2Cl_2/RX encouraging the cyclometallation that does not occur in acetone or CH_2Cl_2 alone. Under these conditions unidentate $(pz)_3CH$ is unlikely as a precursor to metallation, and indeed an analogous reaction does not occur for $PtMe_2\{(pz)_2CH_2\}$, which does undergo cyclometallation in pyridine. If unidentate coordination is precluded, then cyclometallation of the axial uncoordinated ring by the PtC_2N_2 centre presumably occurs, with the reactivity of platinum perhaps activated by the initial stages of oxidative addition or coordination of RX. In contrast to $PtMe_2\{(pz)_3CH\}$, the palladium analogue reacts with methyl iodide to form the palladium(IV) complex $[PdMe_3\{(pz)_3CH$-$N,N',N''\}]I$ [28,40].

In view of these results we treated methyl iodide with $PtPh_2\{(pz)_3CH\}$, but no cyclometallation occurred, the Pt^{IV} product having the formula $[PtPh_2Me\{(pz)_3CH$-$N,N',N''\}]I$ (**14**).

Experimental

The reagents $[PtMe_2(SEt_2)_2]_2$ [42], $[PtPh_2(SEt_2)_2]_2$ [48], $(pz)_3CH$, $(pz)_2$(mim)-CH, $(pz)_2CO$ [34], $PtMe_2(L)$ (L = $(pz)_2CH_2$, (py)(pz)CH_2, (pz)(mim)CH_2) [33], (py)(pz)CH_2 and (pz)(mim)CH_2 [35], $(pz)_2CH_2$ [47], $(pz)_2CHMe$, $(pz)_2CMe_2$ and $(pz)_2CHPh$ [30], and thiophene-2-carboxaldehyde [49] were prepared as previously reported. Hexane was dried over $CaCl_2$, distilled from Na/benzophenone, and stored over Na wire; pyridine was refluxed over KOH, fractionally distilled, and stored over 4 Å molecular sieves; 4-methylpyridine was dried over KOH, decanted, and fractionally distilled; allyl and propargyl bromide were washed with aq. $NaHCO_3$ then with water, dried over $MgSO_4$, and fractionally distilled; benzyl bromide was washed with conc. H_2SO_4, water, 2*M* NaOH and water, dried over $MgSO_4$, fractionally distilled under reduced pressure in the dark and stored over sieves; dichloromethane was predried over $CaCl_2$, filtered, and distilled from P_2O_5; diethyl ether was dried over $CaCl_2$ then passed through a column of sieves, refluxed, and distilled from sodium/benzophenone, and stored over sodium; other reagents and solvents were purified as previously described [14].

Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and the Canadian Microanalytical Service, Vancouver. NMR spectra were recorded with a Bruker AM 300 spectrometer, with ^1H chemical shifts given in ppm relative to Me_4Si and ^{31}P shifts relative to external 85% H_3PO_4. Thermogravimetric measurements were carried out with a Rigaku-Denki Differential Scanning Calorimeter (Thermoflex 8085). Molecular weights were determined with a Knauer vapor pressure osmometer for ca. $1-3 \times 10^{-2}$ *M* solutions in chloroform at 37 °C, and molar conductances were measured with a Philips PW 9504/00 conductivity meter with a Griffin and George conductivity cell for ca. 10^{-3} *M* solutions in acetone at 25 °C. Several complexes were insufficiently soluble for these measurements.

Bis(pyrazol-1-yl)(thien-2-yl)methane, $(pz)_2$(thi)CH

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol), thiophene-2-carboxaldehyde (0.58 g, 6.2 mmol), and a catalytic amount of anhydrous cobalt(II) chloride (0.01 g) were placed in a flask which was being flushed with nitrogen through a side arm. The mixture was warmed for ca. 2 h until evolution of CO_2 had ceased, water (5 ml) was added, and the mixture extracted with dichloromethane (2 × 20 ml). The combined extracts were dried ($MgSO_4$), the dichloromethane was removed under vacuum after filtration, and the product recrystallized from hot hexane (white crystals, m.p. 87 °C). (Found: C, 57.4; H, 4.5; N, 24.3. $C_{11}H_{10}N_4S$ calcd.: C, 57.4; H, 4.4; N, 24.3%). ^1H NMR ($(CD_3)_2CO$): δ 8.17 (1H, s, CH), 7.92 (2H, d, H(5), J_{45} 2.4 Hz), 7.59 (1H, dd, H(5)(thi), J_{45} 5.1 Hz), 7.58 (2H, d, H(3), J_{34} 1.5 Hz), 7.08 (2H, m, H(3) and H(4)(thi)), 6.33 (2H, t, H(4)). MS: *m/e* 320 (*M*, 5%), 214 (8%), 163 (100%), 91 (2%).

1-bromo-2-(pyrazol-1-yl)ethane, $pzCH_2CH_2Br$

A mixture of pyrazole (7 g, 102.9 mmol) and tetrabutylammonium bisulphate (0.4 g) in sodium hydroxide (30 ml of 40% solution) were vigorously stirred under nitrogen as 1,2-dibromoethane (50 ml) was added. The mixture was vigorously refluxed for 1 h then cooled, and the organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 20 ml). The combined organic extracts were dried ($MgSO_4$), taken to low volume by rotary evaporation, the residue distilled under vacuum (64–66 °C at 0.5 mmHg) to give a viscous oil 52% yield. ^1H NMR ($CDCl_3$): δ 7.56 (1H, d, H(3), J_{34} 1.6 Hz), 7.47 (1H, d, H(5), J_{45} 2.1 Hz), 6.26 (1H, t, H(4)), 4.51 (2H, t, CH_2Br) and 3.73 (2H, t, $pzCH_2$, J(HH) 12.7 Hz). MS: *m/e* 175 (*M*, 5%), 174 (60%), 176 (60%), 95 (100%), 68 (100%).

$PtMe_2(L)$ (L = $(pz)_3CH$, $(pz)_2CHPh$)

The ligand (0.32 mmol) was added to a suspension of $[PtMe_2(SEt_2)]_2$ (0.16 mmol) in benzene (20 ml) and the mixture stirred and heated to reflux under nitrogen. Near to the reflux temperature a pale yellow solution was formed, and the product separated out after a further 10 min heating. It was collected, washed with diethyl ether, air dried, and then vacuum dried (60 °C, 2 h). The complexes are insoluble in organic solvents.

$PtMe_2\{(pz)_2CH\}$ and $PtMe_2\{(pz)_3CH\}$, 90% yield, white solids, IR spectra as reported [21].

$PtMe_2\{(pz)_2CHPh\}$, 90% yield, white solid. (Found: C, 39.8; H, 4.3; N, 12.0. $C_{15}H_{18}N_4Pt$ calcd.: C, 40.0; H, 4.2; N, 12.5%).

$PtMe_2(L)$ (L = $(pz)_2CHMe$, $(pz)_2CMe_2$, $(pz)_2(mim)CH$, $(pz)_2(thi)CH$)

The ligand (0.32 mmol) was added to a solution of $[PtMe_2(SEt_2)]_2$ (0.16 mmol) in acetone (20 ml) and the solution stirred and heated under nitrogen. After 10 min the solution was cooled, hexane (5 ml) added, and the volume reduced by rotary evaporation until the product began to separate out. The product was collected, washed with diethyl ether, and air and vacuum dried.

$PtMe_2\{(pz)_2CHMe\}$, 88% yield, white microcrystalline solid. (Found: C, 30.7; H, 4.3; N, 14.2. $C_{10}H_{16}N_4Pt$ calcd.: C, 31.0; H, 4.2; N, 14.5%). ^1H NMR ($(CD_3)_2CO$): δ, ambient, all resonances broad, 8.14 (2H, H(5)), 7.79 (2H, H(3)), 7.22 (1H, CH), 6.43 (2H, H(4)), 2.50 (3H, Me), 0.66 (6H, t, PtMe). At −25 °C, conformers A and B, 6.46 (t, H(4)); conformer A, 8.13 (d, H(5), J_{45} 2.7 Hz), 7.84 (d, H(3), J_{34} 2.1 Hz), 7.27 (q, CH) and 2.60 (d, Me, J(HMe) 6.6 Hz), 0.64 (t, PtMe, J(HPt) 89.2 Hz); conformer B, 8.25 (d, H(5), J_{45} 2.7 Hz), 7.76 (d, H(3), J_{34} 2 Hz), 7.14 (q, CH) and 2.46 (d, Me, J(HMe) 7 Hz), 0.62 (t, PtMe, J(HPt) 88.8 Hz).

$PtMe_2\{(pz)_2CMe_2\}$, 82% yield, a white crystalline solid that is unstable and becomes yellow during several days and so gives a poor microanalysis. (Found: C, 31.2; H, 4.4; N, 13.5. $C_{11}H_{18}N_4Pt$ calcd.: C, 32.9; H, 4.5; N, 14.0%). ^1H NMR ($CDCl_3$): δ, ambient, 7.94 (d with poorly resolved J(HPt) satellites, (H(3)), 7.76 (d, H(5)), 6.35 (t, H(4)), 2.71 (b, Me), 0.84 (t, PtMe). At −20 °C, 7.91 (2H, d, H(3), J_{34} 2.1 Hz), 7.78 (2H, d, H(5), J_{44} 2.8 Hz), 6.36 (2H, t, H(4)), 2.96 (3H, s, Me) and 2.46 (3H, s, Me), 0.82 (6H, t, PtMe, J(HPt) 87.4 Hz).

$PtMe_2\{(pz)_2(mim)CH\}$, 86% yield, white crystalline solid. (Found: C, 33.4; H, 3.6; N, 18.2. $C_{13}H_{18}N_6Pt$ calcd.: C, 34.3; H, 4.4; N, 18.4%). ^1H NMR ($(CD_3)_2CO$): δ 9.45 (1H, d, H(5)(uncoord.), J_{45} 2.6 Hz), 8.36 (1H, d, H(5), J_{45} 2.7 Hz), 8.23 (1H, s, CH), 7.95 (1H, d, H(3), J_{34} 2.1 Hz), 7.49 (1H, d, H(5)(mim)), 7.36 (2H, m, H(4)(mim) + H(3)(uncoord.)), 6.50 (1H, t, H(4)), 6.27 (1H, t, H(4)(uncoord.)), 3.97 (3H, s, NMe), 0.70 (3H, t, PtMe, J(HPt) 90 Hz) and 0.60 (3H, t, PtMe, J(HPt) 87.3 Hz).

$PtMe_2\{(pz)_2(thi)CH\}$, 75% yield, white. (Found: C, 34.5; H, 3.7; N, 12.2. $C_{13}H_{16}N_6SPt$ calcd.: C, 34.3; H, 3.5; N, 12.3%). ^1H NMR ($(CD_3)_2CO$): δ 8.51 (1H, s, CH), 8.30 (2H, d, H(5), J_{45} 2.6 Hz), 7.93 (2H, td, H(3), J(HPt) 9.3 Hz), 7.49 (1H, d, H(5)(thi)), 7.10 (1H, b, H(3)(thi)), 6.95 (1H, t, H(4)(thi)), 6.52 (2H, m, H(4)), 0.61 (6H, t, PtMe, J(HPt) 89.5 Hz).

$PtMe_2\{(pz)_4C\} \cdot \frac{1}{4}((CH_3)_2CO)$, 91% yield, white. (Found: C, 38.6; H, 4.1; N, 21.6. $C_{15.75}H_{20.5}N_8O_{0.25}Pt$ calcd.: C, 37.7; H, 4.1; N, 20.4%). ^1H NMR ($(CD_3)_2CO$): δ 8.12 (2H, dd(b), H(3)), 7.90 (2H, s(b), H(3)), 7.30 (2H, dd(b), H(5)), 6.77 (2H, s(b), H(5)), 6.62 (4H, m, H(4)), 0.49 (6H, t, PtMe). At −40 °C, ring A: 7.81 (1H, d, H(3), J_{34} 1.1 Hz), 6.61 (m, H(4)), 6.94 (1H, d, H(5), J_{45} 2.6 Hz); ring B: 8.25 (1H, d, H(3), J_{34} 1.8 Hz), 7.29 (1H, d, H(5), J_{45} 3.0 Hz), 6.77 (1H, t, H(4)); ring C: 8.08 (1H, t, H(3), J_{34} 1.5 Hz), 7.51 (1H, d, H(5), J_{45} 3.0 Hz), 6.63 (m, H(4)); ring D: 8.19 (1H, d, H(3), J_{34} 1.5 Hz), 6.58 (1H, d, H(5), J_{45} 2.7 Hz), 6.71 (1H, m, H(4)); 0.46 (3H, t, PtMe, J(HPt) 89.5 Hz), 0.42 (3H, t, PtMe, J(HPt) 89.8 Hz).

$PtPh_2\{(pz)_3CH\}$

The ligand (0.46 mmol) was added to a suspension of $[PtPh_2(SEt_2)]_2$ (0.23 mmol) in benzene (20 ml) under nitrogen. After 5–10 min heating the solution turned pale yellow and a white precipitate of $PtPh_2\{(pz)_3CH\}$ formed. The white solid was collected, washed with diethyl ether, and air and vacuum dried (94%). (Found: C, 47.1; H, 3.3; N, 14.9. $C_{22}H_{20}N_6Pt$ calcd.: C, 46.9; H, 3.6; N, 15.0%). ^1H NMR ($(CD_3)_2CO$): δ 9.27 (1H, s, CH), 8.62 (1H, d, H(5)(uncoord.), J_{45} 2.6 Hz), 8.49 (2H, dd, H(5)(coord.), J_{45} 3.0 Hz), 7.69 (1H, d, H(3)(uncoord.), J_{34} 1.7 Hz), 7.35 (6H, m, H(3)(coord.) and Ph(2, 6), J(HPt) 73.0 Hz), 6.79 (4H, m, Ph(3.5)), 6.68 (2H, m, Ph(4)), 6.56 (3H, m, H(4)(coord. and uncoord.)).

Cyclometallation reactions

$PtMe\{(pz)_2(C_3H_2N_2)CH$-N,C′$\}(py)$ (1a). A suspension of $PtMe_2\{(pz)_3CH\}$ in pyridine (5–10 ml) under nitrogen was kept at ambient temperature until the solid had dissolved. Hexane was added until a cloudiness persisted and the resulting precipitate was collected, washed with diethyl ether, and vacuum dried at 50 °C. Yield 80%, IR and NMR as reported [21].

Complexes with 4-methylpyridine and *N*-methylimidazole were obtained similarly.

$PtMe\{(pz)_2(C_3H_2N_2)CH$-*N*,*C*′$\}$(4-mpy) (**1b**), white crystalline solid, 82%. (Found: C, 40.3; H, 3.8; N, 18.8. $C_{16}H_{17}N_7Pt$ calcd.: C, 39.5; H, 3.7; N, 19.1%).

$PtMe\{(pz)_2(C_3H_2N_2)CH$-*N*,*C*′$\}$(*N*-mim) (**1c**), white crystalline solid, 76%. (Found: C, 35.7; H, 3.6; N, 22.1. $C_{15}H_{18}N_8Pt$ calcd.: C, 35.6; H, 3.6; N, 22.2%).

For complexes **3**–**5** triphenylphosphine was added to the pyridine solution after cyclometallation.

$PtMe\{(pz)(C_3H_2N_2)CH_2$-*C*$\}(PPh_3)_2$ (**3**), white powder, 58%. (Found: C, 59.5; H, 4.4; N, 6.1. $C_{44}H_{40}N_4P_2Pt$ calcd.: C, 59.9; H, 4.6; N, 6.4%).

$PtMe\{(pz)(C_3H_2N_2)CHPh$-*N*,*C*′$\}(PPh_3)$ (**4**), white powder, 63%. (Found: C, 55.2; H, 4.3; N, 7.9. $C_{32}H_{29}N_4PPt$ calcd.: C, 55.2; H, 4.2; N, 8.0%).

$PtMe\{(pz)(mim)(C_3H_2N_2)CH$-*N*,*C*′$\}(PPh_3)$ (**5**), white powder, 79%. (Found: C, 51.4; H, 4.4; N, 12.3. $C_{30}H_{29}N_6PPt$ calcd.: C, 51.5; H, 4.2; N, 12.0%).

Platinum(II) complexes obtained from $PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C'\}(py)$ *(1a)*

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C'\}(CO)$ *(1d).* A suspension of **1a** in acetone was refluxed until a clear solution formed, and carbon monoxide was bubbled through for 10 min at ambient temperature. Hexane was added and the white solid was collected, washed with diethyl ether and vacuum dried, yield 95%. (Found: C, 32.0; H, 2.7; N, 18.5. $C_{12}H_{12}H_6OPt$ calcd.: C, 31.9; H, 2.7; N, 18.6%). ν(CO) 2074 cm^{-1}.

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C'\}\{PPh_2(o\text{-}tolyl)\}$ *(1e).* A suspension of **1a** (0.2 mmol) and PPh_2(*o*-tolyl) (0.4 mmol) in acetone (20 ml) was heated with stirring until the solid dissolved, when the heating was stopped. The solution was allowed to cool to ambient temperature then filtered, and hexane was added until cloudiness persisted and the solution left to allow crystallization. The crystalline product was collected and dried, 70%. (Found: C, 52.5; H, 4.3; N, 12.4; P, 5.0. $C_{30}H_{29}N_6PPt$ calcd.: C, 51.5; H, 4.2; N, 12.0; P, 4.4%).

The following complexes (**1f**, **6a–h**) were prepared by an identical procedure.

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C'\}\{PPh_2(o\text{-}MeOC_6H_4)\}$ (**1f**), white powder, 68%. (Found: C, 51.1; H, 4.1; N, 11.6; P, 3.7. $C_{30}H_{29}N_6OPPt$ calcd.: C, 50.3; H, 4.1; N, 11.7; P, 4.3%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}(PPh_3)_2$ (**6a**), white powder, 68%. IR spectrum as reported [21]. (Found: C, 51.1; H, 4.1; N, 11.6; P, 3.7. $C_{30}H_{29}N_6P_2Pt$ calcd.: C, 50.3; H, 4.1; N, 11.7; P, 4.3%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}(PMePh_2)_2$ (**6b**), white powder, 88%. (Found: C, 53.5; H, 4.9; N, 10.3; P, 7.9. $C_{24}H_{25}N_6P_2Pt$ calcd.: C, 53.9; H, 4.7; H, 10.2; P, 7.5%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}(PMe_2Ph)_2$ (**6c**), white powder, 81%. (Found: C, 46.2; H, 4.9; N, 11.9; P, 9.9. $C_{19}H_{23}N_6P_2Pt$ calcd.: C, 46.3; H, 4.9; N, 12.0; P, 9.9%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}(PEtPh_2)_2$ (**6d**), white powder, 74%. (Found: C, 55.2; H, 5.5; N, 9.6; P, 7.7. $C_{25}H_{27}N_6P_2Pt$ calcd.: C, 55.0; H, 5.0; N, 9.9; P, 7.3%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}\{PPh_2(CH_2Ph)\}_2$ (**6e**), white powder, 76%. (Found: C, 60.5; H, 4.8; N, 8.5; P, 6.8. $C_{30}H_{29}N_6P_2Pt$ calcd.: C, 60.3; H, 4.8; N, 8.6; P, 6.4%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}\{P(OPh)_3\}_2$ (**6f**), white powder, 88%. (Found: C, 53.6; H, 4.1; N, 7.9; P, 6.1. $C_{29}H_{27}N_6O_3P_2Pt$ calcd.: C, 54.1; H, 4.1; N, 8.06; P, 5.9%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}\{(PPh_2)_2CH_2\}$ (**6g**), white powder, 75%. (Found: C, 53.7; H, 4.4; N, 10.5; P, 7.3. $C_{36}H_{34}N_6P_2Pt$ calcd.: C, 53.5; H, 4.2; N, 10.4; P, 7.7%).

$PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}\{(PPh_2CH_2)_2\}$ (**6h**), white powder, 72%. (Found: C, 53.9; H, 4.4; N, 10.2; P, 7.7. $C_{37}H_{36}N_6P_2Pt$ calcd.: C, 54.1; H, 4.4; N, 10.2; P, 7.5%).

$[PtMe\{(pz)_2(C_3H_2N_2)CH\}]_n$ *(2)*

This complex may be obtained either by refluxing a suspension of **1a** in benzene for 30 min or by heating (with stirring) a suspension of **1a** until a clear solution is obtained followed by addition of hexane to the hot solution, yield 96%. (Found: C, 31.8; H, 3.0; N, 20.2. $C_{11}H_{12}N_6Pt$ calcd.: C, 31.2; H, 2.9; N, 19.9%). ν_{max} (Nujol mull) 3100, 1511, 1372, 1286, 1084, 839, 814, 793 cm^{-1}.

Synthesis of $[PtMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}(py)]X$ (7a–d) from 1a

Iodomethane (100 μl, 1.61 mmol) was added to a suspension of **1a** (0.23 mmol) in acetone (10 ml), the flask stoppered, and stirring continued until the solid had dissolved. Addition of hexane and collection and vacuum drying (50 ° C, 2 h) of the precipitate gave **7a** (R = Me, X = I), 95%. (Found: C, 33.0; H, 3.4; N, 14.6. $C_{17}H_{20}N_7IPt$ calcd.: C, 33.3; H, 3.7; N, 14.9%). Ω_M 89 ohm^{-1} cm^2 mol^{-1} in acetone.

The following complexes were prepared similarly.

$[PtMe(CH_2Ph)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}(py)]Br$ (**7b**), 88%. (Found: C, 41.1; H, 3.6; N, 14.3. $C_{23}H_{24}N_7BrPt$ calcd.: C, 41.0; H, 3.6; N, 14.6%). Ω_M 65 ohm^{-1}cm^2 mol^{-1} in acetone.

$[PtMe(CH_2CH{=}CH_2)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}(py)]Br$ (**7c**), 91%. (Found: C, 36.7; H, 3.6; N, 15.6. $C_{19}H_{22}N_7BrPt$ calcd.: C, 36.6; H, 3.6; N, 15.7%). Ω_M 84 ohm^{-1} cm^2 mol^{-1} in acetone.

$[PtMe(CH{=}C{=}CH_2)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}(py)]Br \cdot \frac{1}{2}(CH_3)_2CO$ (**7d**), 84%, prepared from $HC{\equiv}CCH_2Br$, and recrystallized from acetone. (Found: C, 37.0; H, 3.6; N, 18.0. $C_{20.5}H_{23}N_7BrO_{0.5}Pt$ calcd.: C, 37.8; H, 3.6; N, 15.1%). Ω_M 70 ohm^{-1} cm^2 mol^{-1} in acetone.

Synthesis of $PtXMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}$ (8a, b) from 2

A similar procedure to that above for synthesis of **7a–d** was followed, commencing with **2** and RX and filtration prior to addition of hexane.

$PtIMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\} \cdot \frac{1}{10}((CH_3)_2CO)$ (**8a**), 94%. (Found: C, 29.4; H, 3.4; N, 13.9. $C_{12.3}H_{15.6}N_6O_{0.1}BrPt$ calcd.: C, 28.9; H, 3.4; N, 13.5%).

$PtBrMe(CH_2Ph)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\} \cdot \frac{1}{5}CH_2Cl_2$ (**8b**), 93%. (Found: C, 35.1; H, 3.2; N, 14.3. $C_{18.2}H_{19.4}N_6BrCl_{0.4}Pt$ calcd.: C, 35.1; H, 3.2; N, 13.8%).

Synthesis of $PtXMe(R)\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}$ (8a, b) from $PtMe_2\{(pz)_3CH\}$

Iodomethane or benzyl bromide (1.7 mmol) was added to a suspension of $PtMe_2\{(pz)_3CH\}$ (0.34 mmol) in acetone (10 ml), the flask was stoppered and wrapped with foil, and the suspension stirred for 3 h to give a yellow solution. The excess of MeI was removed by rotary evaporation and hexane added to precipitate a white solid, which was filtered and vacuum dried (60 ° C, 2 h).

$[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}(PPh_3)]I$ (9).

Triphenylphosphine (0.2 mmol) and **1a** (0.2 mmol) were warmed and stirred in acetone (10 ml) under nitrogen until no solid remained (ca. 10 min), then cooled to ambient temperature and methyl iodide (1 mmol) was added and the solution stirred for 30 min. The residual MeI and some acetone were removed by rotary evaporation, and hexane added until precipitation commenced. The precipitate was collected and vacuum dried (50 ° C, 2 h), 92%. (Found: C, 43.8; H, 3.8; N, 10.4; P, 4.0. $C_{30}H_{30}N_6IPPt$ calcd.: C, 43.5: H, 3.7; N, 10.1; P, 3.7%). Ω_M 95 ohm^{-1} cm^2 mol^{-1} in acetone.

$[PtMe(CH_2CH_2pz\text{-}N,C')\{(pz)_2(C_3H_2N_2)CH\text{-}N,N',C''\}]Br \cdot \frac{1}{3}\ CHCl_3$ (10).

A suspension of **1a** (0.2 mmol) and $pzCH_2CH_2Br$ (0.23 mmol) in acetone (20 ml) with some chloroform added to ensure solubility was refluxed for 30 min, then allowed to cool to ambient temperature. The solution volume was reduced by ca. one-half by rotary evaporation and hexane added until cloudiness developed. The solution was set aside overnight and the small crystals of the product were collected; 89% yield. (Found: C, 30.7; H, 3.6; N, 17.4. $C_{16.33}H_{20}N_8BrClPt$ calcd.: C, 30.7; H, 3.1; N, 17.6%).

*[PtMe$_2${(pz)(mim)(C$_3$H$_2$N$_2$)CH-N,N′,C″}(PPh$_3$)]I (**11a**).*

Iodomethane (0.70 mmol) was added to **5** (0.14 mmol) in acetone (10 ml) and the solution stirred for 30 min. The residual MeI was removed by rotary evaporation and hexane added until crystallization commenced, 96% yield. (Found: C, 51.5; H, 4.2; N, 12.0. $C_{31}H_{32}N_6IPPt$ calcd.: C, 51.4; H, 4.4; N, 12.3%). Ω_M 91 ohm^{-1} cm^2 mol^{-1} in acetone.

*[PtMe$_2${(pz)(mim)(C$_3$H$_2$N$_2$)CH-N,N′,C″}(py)]I (**11b**).*

On addition of PtMe$_2${(pz)$_2$(mim)CH} (0.44 mmol) to pyridine (5 ml) under nitrogen the solid dissolved rapidly with evolution of bubbles and formation of a yellow solution. An excess of hexane was added to give a white solid, which was collected and washed with hexane (5 × 5 ml) and diethyl ether (5 × 5 ml). The damp solid was dissolved in acetone (10 ml), MeI (2.2 mmol) added, and the solution stirred for 30 min, then filtered. Addition of hexane gave a precipitate of the product, which was collected and vacuum dried (50 °C, 2 h), 64% yield. (Found: C, 33.3; H, 3.5; N, 14.2. $C_{18}H_{22}N_7IPPt$ calcd.: C, 32.8; H, 3.5; N, 14.4%). Ω_M 78 ohm^{-1} cm^2 mol^{-1} in acetone.

*PtIMe$_3${(pz)$_4$C-N,N′} (**12**)*

An excess of iodomethane was added to PtMe$_2${(pz)$_4$C} in acetone, the mixture stirred for 15 min, the excess of MeI removed by rotary evaporation, hexane added until cloudiness developed, and the white powder collected; 76% yield. (Found: C, 30.2; H, 3.4; N, 17.1. $C_{14}H_{18}N_8IPPt$ calcd.: C, 29.8; H, 2.8; N, 17.4%). ^{1}H NMR ((CD$_3$)$_2$CO): δ 8.36 (2H, d with poorly resolved J(HPt) satellites, H(3), J_{34} 1.8 Hz), 8.06 (1H, d, H(3)(uncoord. A), J_{34} 1.8 Hz), 7.76 (1H, d, H(3)(uncoord. B), J_{34} 1.8 Hz), 7.27 (2H, d, H(5), J_{45} 2.8 Hz), 6.78 (3H, m, H(4) + H(5)(uncoord. B)), 6.67 (1H, m, H(4)(uncoord. A)), 6.61 (1H, m, H(4)(uncoord. B)), 6.52 (1H, d, H(5)(uncoord. A), J_{45} 2.7 Hz), 1.46 (6H, t, PtCH$_3$ *trans* to pz, J(HPt) 73.8 Hz) and 0.26 (3H, t, PtCH$_3$ *trans* to I, J(HPt) 72.5 Hz). Mol. wt. 641 (calcd. 647).

*[PtPh$_2$Me{(pz)$_3$CH-N,N′,N″}]I (**14**)*

A procedure similar to that used for **12** gave **14**. (Found: C, 39.3; H, 3.5; N, 11.7. $C_{23}H_{20}N_6IPPt$ calcd.: C, 39.2; H, 3.5; N, 11.7%). ^{1}H NMR (CDCl$_3$): δ 12.49 (1H, s, CH), 9.20 (3H, m, H(5)), 7.88 (1H, d, H(3), J_{34} 2.2 Hz), 7.79 (2H, d, H(3), J_{34} 2.2 Hz), 7.08 (2H, m, H(4)(Ph)), 7.03 (4H, m, H(3,5)(Ph)), 6.99 (4H, m, H(2,6)(Ph)), 6.58 (3H, m, H(4)), 1.90 (3H, t, PtMe, J(HPt) 72.9 Hz). Ω_M 91 ohm^{-1} cm^2 mol^{-1} in acetone.

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