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Synthesis and characterization of heterodinuclear RuPt and IrPt complexes containing pyrazolate bridging ligands. Crystal structure of $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})_3PtMe_3]$ (pz = pyrazolate)

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Abstract

The reaction of the metallo–ligand $[Ru(\eta^6\text{-}p\text{-cymene})(pz)_2(Hpz)]$ with the platinum complex $[\{PtIMe_3\}_4]$ affords mixtures of the heterodinuclear complexes $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_3PtMe_3]$ (**1**) and $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_2(\mu\text{-I})PtMe_3]$ (**2**). The reaction of the iridium derivative $[Ir(\eta^5\text{-}C_5Me_5)(pz)_2(Hpz)]$ with $[\{PtIMe_3\}_4]$ gives $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-I})PtMe_3]$ (**3**). Both $[Ru(\eta^6\text{-}p\text{-cymene})(pz)_2(Hpz)]$ and $[Ir(\eta^5\text{-}C_5Me_5)(pz)_2(Hpz)]$ react with $[\{PtIMe_3\}_4]$ in the presence of NaOH yielding **1** and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})_3PtMe_3]$ (**4**), respectively. While $[Ru(\eta^6\text{-}p\text{-cymene})(pz)_2(Hpz)]$ reacts with $[PtBr_2Me_2S_x]$ to give mixtures of $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_3PtBrMe_2]$ (**5**) and $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_2(\mu\text{-Br})PtBrMe_2]$ (**6**), the reaction of $[Ir(\eta^5\text{-}C_5Me_5)(pz)_2(Hpz)]$ with $[PtBr_2Me_2S_x]$ gives $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-Br})PtBrMe_2]$ (**7**) as the sole product. All species were characterized in solution by ^{1}H-NMR spectroscopy. The crystal structure of complex **4** has been determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iridium; Ruthenium; Platinum; Pyrazolate; Heterodinuclear complexes

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1. Introduction

The coordination chemistry of the poly(pyrazolyl)borate anions, $[RB(pz)3]^-$ (R = pz, H), has been extensively developed by Trofimenko and co-workers [1–4]. These species behave as tridentate ligands of C_{3v} symmetry toward a series of organometallic fragments as, for example, in $[pzB(pz)_3Mn(CO)_3]$ [5], $[HB(pz)_3PtMe_3]$ [6], $[HB(3,5\text{-}Me_2pz)_3PtMe_3]$ [7], $[pzB(pz)_3Ru(\eta^6\text{-}C_6H_6)]PF_6$ [1], and $[HB(pz)_3Rh(\eta^5\text{-}C_5Me_5)]PF_6$ [1]. However, with metals preferring four-coordination, such as Ir(I) or Rh(I), they are bidentate and usually undergo rapid (on the NMR time scale) exchange of the coordinated and uncoordinated pz groups [8,9].

Some years ago, we prepared the dipyrazolate–pyrazole complexes $[Ir(\eta^5\text{-}C_5Me_5)(pz)_2(Hpz)]$ [10], $[Ru(\eta^6\text{-}p\text{-cymene})(pz)_2(Hpz)]$ [11], and $[Ru(\eta^6\text{-mesitylene})(pz)_2(Hpz)]$ [12] comparable, from a coordination point of view, to protonated tris(pyrazolyl)borate. Thus, when deprotonated to give the corresponding monoanionic species $[M(ring)(pz)_3]^-$, are capable of acting as ligands toward a variety of metallic fragments affording heterodinuclear [12,13] or heterotrinuclear [13] compounds. In this context, it has been very recently reported the preparation of the related rhenium pyrazolate–dipyrazole compound [14] $[Re(CO)_3(pz)(Hpz)_2]$ which, in the presence of an appropriate deprotonating agent, reacted with Group 2 metal ions giving rise to trimetallic pyrazolato-bridged ReL_2 (L = Cu^I, Ag^I, Au^I) complexes [15].

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In the present paper, we report the synthesis and spectroscopic and structural characterization of new heterodinuclear pyrazolato-bridged RuPt and IrPt complexes derived by direct reaction of [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] or [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] with the platinum(IV) derivatives [{$PtIMe_3$}$_4$] [16] and [{$PtBr_2Me_2$}$_n$] [17]. The molecular structure of the IrPt complex [(η^5-C_5Me_5)Ir(μ-pz)$_3$$PtMe_3$]·$CH_2Cl_2$ is also reported.

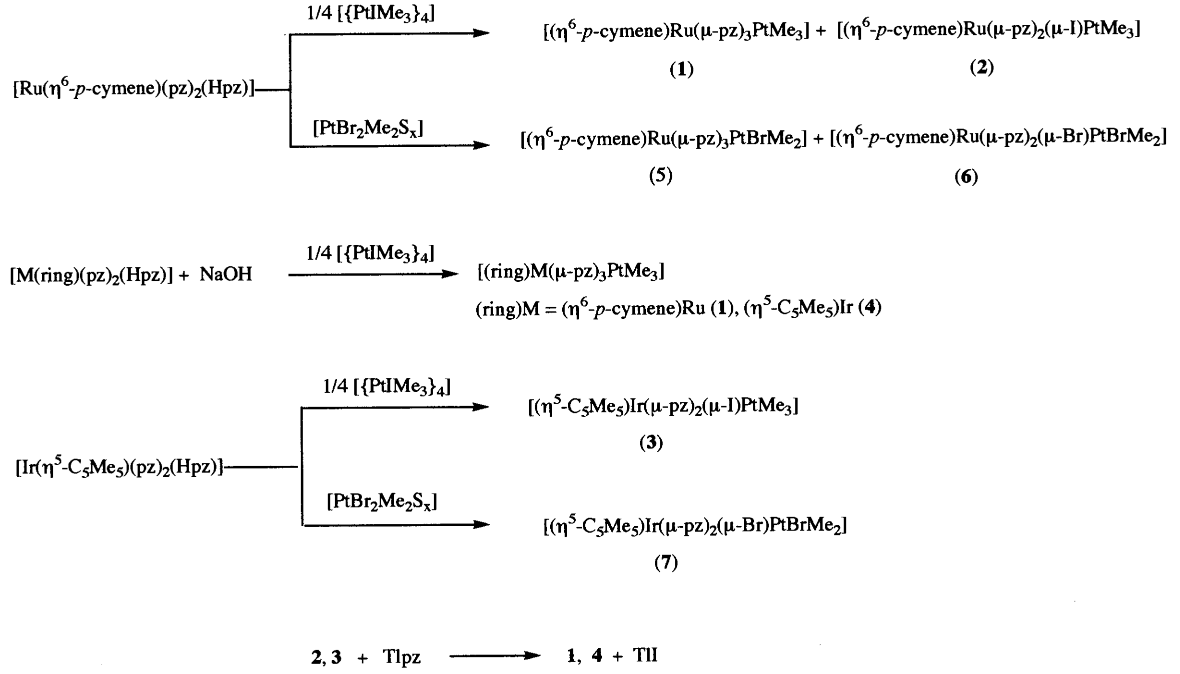
2. Results and discussion

Scheme 1 summarizes all the reactions reported below.

The reaction of the metallo-ligand [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] with the platinum complex [{$PtIMe_3$}$_4$] (4:1 molar ratio), in tetrahydrofuran, afforded mixtures of the heterodinuclear complexes [(η^6-*p*-cymene)Ru(μ-pz)$_3$$PtMe_3$] (**1**, 88%) and [($\eta^6$-*p*-cymene)Ru($\mu$-pz)$_2$($\mu$-I)$PtMe_3$] (**2**, 12%) with three and two pyrazolate bridging ligands, respectively. The major component can be purified by chromatography (basic alumina) and the minor was spectroscopically characterized in the mixture. Formally, compound **1** proceeds from the displacement of one molecule of hydrogen iodide and, therefore, it was obtained as unique product when the aforementioned reaction was carried out in the presence of one equivalent of NaOH.

Table 1 collects the ^{1}H-NMR data for the new complexes. The ^{1}H-NMR spectrum of complex **1** in $CDCl_3$, shows the expected resonances for the protons of the *p*-cymene and pyrazolate bridging ligands, together with a singlet resonance at δ 0.69 ppm assigned to the methyl groups bound to platinum [^2J(PtH) = 66.5 Hz]. The shift of the methyl resonances to higher field, as well as, the decrease of the ^{195}Pt–^{1}H coupling, with respect to the starting complex [{$PtIMe_3$}$_4$] [δ 1.8 ppm, ^2J(PtH) = 78 Hz], are a reflect of the higher *trans* influence of the pyrazolate groups as compared to the iodide ligands. The most relevant feature of the ^{1}H-NMR spectrum of **2** is the presence of two singlets, in a 2:1 ratio, at δ 0.97 and 1.16 ppm, assigned to the two types of methyls bound to platinum. One of the pyrazolate resonances present ^{195}Pt–^{1}H coupling (7.42 ppm, ^3J(PtH) = 5.5 Hz, complex **1**; 7.29 ppm, ^3J(PtH) = 5.4 Hz, complex **2**) and, therefore, it is assigned to the proton nearest to the platinum atom.

On the other hand, the reaction of the iridium derivative [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] with [{$PtIMe_3$}$_4$], under similar conditions (4:1 molar ratio, tetrahydrofuran), proceeded exclusively with displacement of one molecule of pyrazole leading to the heterodinuclear complex [(η^5-C_5Me_5)Ir(μ-pz)$_2$(μ-I)$PtMe_3$] (**3**), in 83% isolated yield. Addition of one equivalent of NaOH to the reaction mixture changed the course of the reaction and produced the formation of the triply pyrazolato-bridged complex [(η^5-C_5Me_5)Ir(μ-pz)$_3$$PtMe_3$] (**4**) by displacement of the HI acid. Complex **4** can be alternatively prepared from [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] and the solvate complex [$PtMe_3S_x$]$^+$, obtained by reaction of [{$PtIMe_3$}$_4$] with $AgPF_6$ in tetrahydrofuran. As expected, the reaction of complexes **2** and **3** with thallium pyrazolate afforded complexes **1** and **4**, respectively.



Scheme 1.

Table 1
^{1}H-NMR [a] chemical shifts (δ, ppm) and coupling constants (Hz) of the heterodinuclear complexes **1**–**7**

Complex	Me	^2J(PtH)	*Trans* atom	Ring	Pyrazolate [b]
1	0.69 (s, 9H)	66.5	N	3.05 (m, 1H, CH, ^{i}Pr)	8.05 (d, H_3, $J(H_4H_3) = 1.7$)
				1.16 (d, 6H, Me (^{i}Pr), $J = 6.2$)	7.42 (d, H_5, $J(H_4H_5) = 2.1$, $J(PtH_5) = 5.5$)
				2.35 (s, Me)	6.19 (pt, H_4)
				5.47, 5.58 (4H, AB system, $J = 6.9$)	
2	0.97 (s, 6H)	68.1	N	3.10 (m, 1H, CH, ^{i}Pr)	7.96 (d, H_3, $J(H_4H_3) = 1.7$)
	1.16 (s, 3H)	74.8	I	1.26 (d, 6H, Me (^{i}Pr), $J = 6.8$)	7.29 (d, H_5, $J(H_4H_5) = 1.6$, $J(PtH_5) = 5.4$)
				2.49 (s, Me)	6.14 (pt, H_4)
				5.38, 5.57 (4H, AB system, $J = 6.1$)	
3	1.13 (s, 6H)	68.7	N	1.86 (s, 15H, C_5Me_5)	7.58 (d, H_3, $J(H_4H_3) = 2.0$)
	1.17 (s, 3H)	75.6	I		7.32 (d, H_5, $J(H_4H_5) = 2.1$)
					6.08 (pt, H_4)
4	0.80 (s, 9H)	66.8	N	1.72 (s, 15H, C_5Me_5)	7.67 (d, H_3, $J(H_4H_3) = 1.7$)
					7.53 (d, H_5, $J(H_4H_5) = 2.1$)
					6.16 (pt, H_4)
5	0.69 (s, 6H)	66.5	N	3.01 (m, 1H, CH, ^{i}Pr)	8.02 (d, H_3, $J(H_4H_3) = 1.9$)
				1.16 (d, 6H, Me (^{i}Pr), $J = 6.8$)	7.43 (d, H_5, $J(H_4H_5) = 2.0$)
				2.35 (s, 3H, Me)	6.24 (pt, H_4)
				5.47, 5.58 (4H, AB system, $J = 6.2$)	
6	1.64 (s, 6H)	67.6	N	3.01 (m, 1H, CH, ^{i}Pr)	7.92 (d, H_3, $J(H_4H_3) = 1.6$)
				1.30 (d, 6H, Me (^{i}Pr), $J = 6.8$)	7.74 (d, H_5, $J(H_4H_5) = 2.2$)
				2.41 (s, Me)	6.21 (pt, H_4)
				5.44, 5.67 (4H, AB system, $J = 6.3$)	
7	1.80 (s, 6H)	68.3	N	1.81 (s, 15H, C_5Me_5)	7.53 (d, H_3, $J(H_4H_3) = 2.0$)
					7.82 (d, H_5, $J(H_4H_5) = 2.1$)
					6.14 (pt, H_4)

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to $SiMe_4$ as internal standard. Abbreviations: s, singlet; d, doublet; pt, pseudotriplet; m, multiplet.

[b] H_5 represents the pyrazolate proton nearest to the platinum atom.

The ^{1}H-NMR spectrum of complex **3** exhibits, besides the C_5Me_5 singlet and the pyrazolate signals, the resonances for the platinum methyls in the expected 2:1 ratio, at δ 1.13 ppm [$^2J(PtH) = 68.7$ Hz] and 1.17 ppm [$^2J(PtH) = 75.6$ Hz], assigned to the methyl group protons *trans* to bridging pyrazolate and iodide ligands, respectively. The assignment of the NMR resonances of **4** has been completed on the basis of NOE spectra. Thus, the difference spectrum showed enhancement (6.0%) of the signal due to the H_5 protons of the pyrazolate ligand (closer to the platinum atom) while the methyl protons bound to the platinum were irradiated and irradiation of the C_5Me_5 protons produced NOE enhancement (3%) to the H_3 pyrazolate protons (closer to the iridium atom).

In order to establish unequivocally the structure of complex **4**, and to obtain structural information about heterodinuclear triply pyrazolato-bridged complexes, a crystallographic study was undertaken. Fig. 1 shows the molecular structure of the complex with the atomic numbering scheme. The molecule is dinuclear with the two metallic centers triply bridged by pyrazolate ligands. A pentamethylcyclopentadienyl ring and three methyl groups complete the coordination spheres of the iridium and platinum atoms respectively. The iridium–platinum separation, 3.886(1) Å, excludes any significant intermetallic interaction. The most relevant bond angles and distances are given in Table 2. The geometry around the iridium atom is the usual pseudo-octahedral 'three-legged piano-stool' commonly found for six-coordinated $(C_5Me_5)Ir^{III}$ derivatives and the platinum atom shows a slightly distorted octahedral coordination. The complex has precise (i.e. crystallographically required) C_2 symmetry, the two-fold axis passing through C(7)–Pt–N(2)–N(1)–Ir atoms. As shown in Fig. 1, the atoms in the basic asymmetric unit are labelled

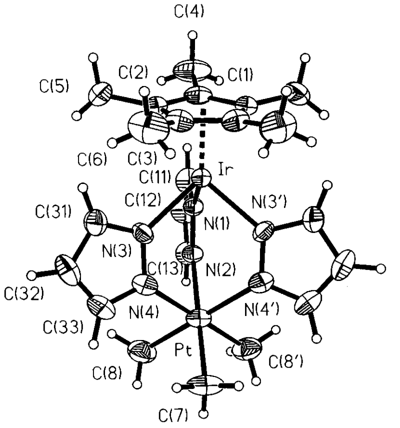


Fig. 1. ORTEP plot of complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3PMe_3]\cdot CH_2Cl_2$ (**4**).

Table 2
Selected bond distances (Å) and angles (°) for complex **4** [a]

Ir–C(1)	2.227(10)	Pt–N(2)	2.148(8)
Ir–C(2)	2.194(7)	Pt–N(4)	2.137(7)
Ir–C(3)	2.199(8)	Pt–C(7)	2.059(12)
Ir–G [b]	1.841	Pt–C(8)	2.079(9)
Ir–N(1)	2.112(9)	Ir–N(3)	2.130(6)
Ir–Pt	3.886(1)		
N(1)–Ir–N(3)	84.8(2)	C(7)–Pt–N(2)	179.2(4)
N(3)–Ir–N(3′)	93.3(3)	C(7)–Pt–N(4)	92.3(3)
G–Ir–N(1)	131.4	C(7)–Pt–C(8)	87.8(4)
G–Ir–N(3)	124.8	C(8)–Pt–N(4)	91.5(3)
N(2)–Pt–N(4)	88.3(2)	C(8)–Pt–N(2)	91.7(3)
N(4)–Pt–N(4′)	89.1(4)	C(8)–Pt–C(8′)	88.0(6)
C(8)–Pt–N(4′)	179.4(3)		

[a] Primed atoms are related to those unprimed by the transformation: x, $-y+1/2$, z.

[b] G represents the centroid of the C_5Me_5 ring.

normally, while those in the ‘other half’ of compound which is related to the basic unit by the transformation $(x', y', z') = (x, -y+1/2, z)$ are primed.

The methyl substituents of the C_5Me_5 ring are bent away from the iridium atom. The Ir–G (C_5Me_5 cetroid) length (1.841 Å) and the Ir–C_5Me_5 metal–carbon distances [range 2.194(9)–2.223(11) Å] compare well with those found in other pentamethylcyclopentadienyl–iridium complexes [12,18–20]. The Ir–N bond distances [Ir–N(1) = 2.112(9) and Ir–N(3) = 2.130(6) Å] are similar to those found in the two previously described iridium compounds with a triple pyrazolato bridge [(η^5-C_5Me_5)Ir(μ-pz)$_3$Ni{HB(3-^{i}Pr-4-Brpz)$_3$}] [mean 2.109(6) Å] [12] and [(η^5-C_5Me_5)Ir(μ-pz)$_3$Rh(OOH)(dppe)]BF_4 [mean 2.106(5) Å] [21]. The Pt–N bond distances [Pt–N(2) = 2.148(8) and Pt–N(4) = 2.137(7) Å] are slightly shorter than those found in the related pyrazolato platinum complexes [Me_2I_2Pt(pz)$_2$CH(C_4H_3S)] [mean 2.189(6) Å] [22] and [Me_3IPt(pz)$_2$CHMe] [mean 2.155(1) Å] [23]. The Pt–C distances [Pt–C(7) = 2.059(12) and Pt–C(8) = 2.079(9) Å] are in agreement with the Pt–C bond distances found in the above mentioned complexes (mean 2.085(8) [22] and 2.050(1) Å [23], respectively).

Finally, the solvated platinum(IV) complex [$PtBr_2Me_2(THF)_x$] (prepared by dissolving [{$PtBr_2Me_2$}$_n$] in tetrahydrofuran) reacted with [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] affording a mixture of the heterodinuclear compounds [(η^6-*p*-cymene)Ru(μ-pz)$_3$PtBrMe$_2$] (**5**) and [(η^6-*p*-cymene)Ru(μ-pz)$_2$(μ-Br)PtBrMe$_2$] (**6**). Analytically pure **6** was obtained by chromatography on basic alumina and complex **5** was spectroscopically characterized. However, the reaction of the iridium complex [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] with [$PtBr_2Me_2(THF)_x$] afforded the di-μ-pyrazolato-bridged complex [(η^5-C_5Me_5)Ir(μ-pz)$_2$(μ-Br)PtBrMe$_2$] (**7**) as the sole product.

The ^{1}H-NMR spectrum of complex **5** exhibits a singlet at δ 0.69 ppm [^2J(PtH) = 66.5 Hz] assigned to the two methyl groups bound to the platinum metal. Interestingly, the ^{1}H-NMR spectra of complexes **6** and **7** consist of only one set of resonances and they only show a singlet signal [δ 1.64 ppm, ^2J(PtH) = 67.6 Hz (**6**); δ 1.80 ppm, ^2J(PtH) = 68.3 Hz (**7**)] assigned to the methyl platinum groups. Therefore, only one of the two possible isomers (bromide *trans* to nitrogen or *trans* to bromide) is detected and, from the equivalence of the two methyl groups, it is the one in which the terminal and bridging bromide ligands are mutually *trans*.

In conclusion, we report in this paper the capability of the ruthenium and iridium metallo–ligands [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] and [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] to promote the formation of a new type of heterodinuclear Ru(II)-Pt(IV) and Ir(III)–Pt(IV) complexes.

3. Experimental

All reactions were carried out under purified nitrogen using Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complexes [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] [10], [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] [11], [{$PtIMe_3$}$_4$] [16] and [{$PtBr_2Me_2$}$_n$] [17] were prepared by published procedures. Elemental analyses (C, H, N) were made with a Fisons EA 1108 microanalyzer. The ^{1}H-NMR spectra were recorded on a Bruker AC-200P spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ as internal standard.

3.1. Syntheses

3.1.1. [(η^6-*p*-cymene)Ru(μ-pz)$_3$PtMe$_3$] (**1**)

The complex can be prepared by the two alternative methods described below.

(a) Solid [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] (328 mg, 0.54 mmol) was added to a solution of the tetranuclear complex [{$PtIMe_3$}$_4$] (200 mg, 0.135 mmol) in tetrahydrofuran (20 cm^3). The resulting red solution was stirred at r.t. for 3 h and vacuum-evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and chromatographed on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 cm^3) and complex **1** precipitated upon subsequent addition of diethyl ether.

(b) A solution of [{$PtIMe_3$}$_4$] (70 mg, 0.05 mmol), in tetrahydrofuran (20 cm^3), was added to a tetrahydrofuran solution of [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] (83 mg, 0.19 mmol) and NaOH (7.6 mg, 0.19 mmol). After stirring the mixture, at r.t. for 1 h, the solution was evaporated to dryness. The solid residue was dissolved in dichloromethane and chromatographed on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 cm^3) and the complex precipitated by addition of diethyl ether. Yield 91 mg (71%). Anal. Found: C, 38.59; H, 4.65; N, 12.08. Calc. for $C_{22}H_{32}N_6PtRu$: C, 39.04; H, 4.73; N, 12.42%.

3.1.2. [(η^5-C_5Me_5)Ir(μ-pz)$_2$(μ-I)PtMe$_3$] (3)

Solid [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] (238 mg, 0.50 mmol) was added to a solution of [{PtIMe$_3$}$_4$] (200 mg, 0.135 mmol) in tetrahydrofuran (20 cm^3). The resulting orange solution was stirred at r.t. for 3 h and vacuum-evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and chromatographed on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 cm^3) and the complex was crystallized as orange needles by slow addition of diethyl ether. Yield 375 mg (83%). Anal. Found: C, 27.62; H, 3.48; N, 6.39. Calc. for $C_{19}H_{30}IIrN_4Pt$: C, 27.53; H, 3.62; N, 6.76%.

3.1.3. [(η^5-C_5Me_5)Ir(μ-pz)$_3$PtMe$_3$] (4)

A solution of [{PtIMe$_3$}$_4$] (70 mg, 0.05 mmol) in tetrahydrofuran (20 cm^3) was added to a tetrahydrofuran solution of [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] (100 mg, 0.19 mmol) and NaOH (7.6 mg, 0.19 mmol). After stirring the mixture at r.t. for 1 h, the solution was evaporated to dryness. The solid residue was dissolved in dichloromethane and chromatographed on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 cm^3) and the yellow complex precipitated by addition of diethyl ether. Yield 116 mg (63%). Anal. Found: C, 34.24; H, 4.27; N, 10.12. Calc. for $C_{22}H_{33}IrN_6Pt$: C, 34.36; H, 4.29; N, 10.93%.

3.1.4. [(η^6-p-cymene)Ru(μ-pz)$_2$(μ-Br)PtBrMe$_2$] (6)

Solid [Ru(η^6-*p*-cymene)(pz)$_2$(Hpz)] (91 mg, 0.21 mmol) was added to a solution of [PtBr$_2$Me$_2$(THF)$_x$] (0.21 mmol) (prepared in situ by treating [{PtBr$_2$Me$_2$}$_n$] (80 mg) with tetrahydrofuran (20 cm^3), and the mixture was stirred for 3 h at r.t. The resulting solution was vacuum-evaporated to dryness, the residue was extracted with dichloromethane, and chromatographed on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 cm^3) and, by addition of diethyl ether, a mixture of complexes **5** and **6** precipitated. Complex **6** was purified by chromatography on aluminium oxide using dichloromethane as eluent. The complex was isolated as orange crystals by addition of diethyl ether to the dichloromethane solution. Yield 41 mg (26%). Anal. Found: C, 28.78; H, 3.53; N, 7.22. Calc. for $C_{18}H_{26}Br_2N_4PtRu$: C, 28.66; H, 3.47; N, 7.43%.

3.1.5. [(η^5-C_5Me_5)Ir(μ-pz)$_2$(μ-Br)PtBrMe$_2$] (7)

Solid [Ir(η^5-C_5Me_5)(pz)$_2$(Hpz)] (137 mg 0.26 mmol) was added to a solution of [PtBr$_2$Me$_2$(THF)$_x$] (0.26 mmol), prepared as above, and the mixture was stirred for 3 h at r.t. The solution was vacuum-evaporated to dryness, and the resulting residue was extracted with dichloromethane and purified by chromatography on basic aluminium oxide using dichloromethane as eluent. The solution was concentrated to a small volume (ca. 2 ml) and the complex was isolated as orange crystals by addition of diethyl ether. Yield 105 mg (48%). Anal. Found: C, 25.67; H, 3.21; N, 6.50. Calc. for $C_{18}H_{27}Br_2N_4Pt$: C, 25.53; H, 3.19; N, 6.62%.

3.2. Crystallography

Suitable crystals for X-ray diffraction determination were obtained by slow diffusion of diethyl ether into a solution of complex **4** in dichloromethane. Intensity data were collected at r.t. on a Siemens R3m/V diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) by the θ–2θ scan method. Semiempirical corrections based on ψ scans were applied for absorption. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares calculations with SHELXL-93 [24]. A riding model was applied to H atoms, placed at calculated positions with

Table 3
Crystallographic data for complex [(η^5-C_5Me_5)Ir(μ-pz)$_3$PtMe$_3$]·CH_2Cl_2 (**4**)

Formula	$C_{23}H_{35}Cl_2IrN_6Pt$
Molecular weight	853.8
Crystal colour, habit	Yellow, prismatic
Crystal size (mm)	0.22 × 0.24 × 0.10
Space system	Monoclinic
Space group	$P2_1/m$
a (Å)	10.818(2)
b (Å)	12.152(3)
c (Å)	10.943(3)
β (°)	112.58(2)
V (Å^3)	1328.3(5)
Z	2
D_{calc} (g cm^{-3})	2.135
F(000)	808
μ (mm^{-1})	10.489
Min and max transmission	0.4205, 0.9030
2θ range (°)	3-56
Number of measured reflections	3542
Number of unique reflections (R_{int})	3375 (0.0167)
Number of observed reflections	2495 [$I > 2\sigma(I)$]
R_1 (observed) [a]	0.0396
R_1 (all data) [a]	0.0601
wR_2 (observed) [a]	0.0973
wR_2 (all data) [a]	0.1039
Goodness-of-fit	1.027
Residual density (e Å^{-3})	1.93–1.38

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\{w(F_o^2)^2\}]^{1/2}$ with $w^{-1} = [\sigma^2(F_o^2) + (0.0595P)^2]$, where $P = [2F_c^2 + \max(F_o^2,0)]/3$.

C–H = 0,96 Å, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of their parent C atoms. Relevant crystal data and refinement parameters are summarized in Table 3.

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre CCDC no. 136184. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-331112, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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