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Tris(pyrazol-1-yl)methane-rhodium(I) and -iridium(I) complexes; crystal structure of [Rh(COD)(tpzm)][RhCl$_2$(COD)] · 3CHCl$_3$

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Abstract

Fourteen new rhodium and iridium complexes of the tris(pyrazol-1-yl)methane (tpzm) ligand have been prepared. They are of the three types [MCl(diolefin)(tpzm)], [M(diolefin)(tpzm)]ClO$_4$, and [M(diolefin)(tpzm)] [MCl$_2$(diolefin)], where M is Rh^I or Ir^I and (diolefin) is a cyclic diolefin (1,5-cyclooctadiene, bicyclo-2,2,1-heptadiene, 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphtalene, or 1,3-dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-[9-methyletheno]-naphthalene). Addition of [IrCl(COD)]$_2$ to [RhCl(COD)(tpzm)] gives the complex [Ir(COD)(tpzm)] [RhCl$_2$(COD)] owing to the greater tendency of iridium to form five-coordinated species. The crystal structure of [Rh(COD)(tpzm)] [RhCl$_2$(COD)] has been determined by X-ray diffraction. The space group is $P\bar{1}$ with a 12.4256(21), b 15.4113(25), c 12.0152(16) Å, α 101.48(1), β 105.03(1) and γ 67.21(1)°. The complex exhibits an ionic dinuclear structure and crystallizes with six CHCl$_3$ molecules per unit cell. In the anion, the Rh(2) atom is

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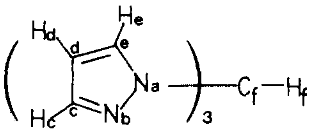
in a square-planar arrangement and in the cation the coordination around Rh(1) is that of a distorted trigonal bipyramid. A careful ^{13}C and ^{1}H NMR study has been carried out, with particular emphasis on the assignment of the pyrazole signals. The shifts induced by complexation (larger in the ^{1}H NMR spectra for iridium than for rhodium), the dynamics aspects, and the COD signals are discussed.

Introduction

Trofimenko has recently reviewed the coordination chemistry of pyrazole-derived ligands [1], and described a fairly large number of metal poly(pyrazol-1-yl)borate complexes. However, the coordination behaviour of the isosteric, but neutral, poly(pyrazol-1-yl)methane complexes has received little attention.

An extensive chemistry of pyrazolate complexes of the platinum metals (especially rhodium) [2–4] has been developed in recent years. In view of our interest in this area, and in continuation of earlier work on rhodium(I) complexes with bis(pyrazol-1-yl)methane ligands [5], we describe here new rhodium(I) and iridium(I) complexes containing the tris(pyrazol-1-yl)methane ligand (tpzm).



	a	b	c	d	e	f
Crystallography	2	1	5	4	3	
	12	11	15	14	13	6
	22	21	25	24	23	
NMR	1	2	3	4	5	1

Metal ions, which normally form square-planar complexes, such as Rh^{I} and Ir^{I}, can extend their environment to five-coordination with suitable tridentate ligands. Thus, four- and five-coordinated precious metal complexes with the tris(pyrazol-1-yl) methane ligand have been reported [6–8], many of which are stereochemically non-rigid. In particular, the X-ray structure of $[AuMe_2(tpzm)]NO_3$ shows a *cis*-square planar coordination, with one pyrazolyl group involved in a weak axial Au...N interaction [8b]. It was of interest to see how Rh and Ir would coordinate with tris(pyrazol-1-yl)methane.

Results and discussion *

The dinuclear complexes $[RhCl(diolefin)]_2$ (diolefin = COD, NBD, or TFB) and $[IrCl(diolefin)]_2$ (diolefin-COD or Me_3TFB) react with tpzm in a 1/2 molar ratio to give the yellow air-stable solids [RhCl(diolefin)(tpzm)] (diolefin = COD, NBD, TFB) or [IrCl(diolefin)(tpzm)] (diolefin = COD, Me_3TFB). The related [IrCl(TFB)(tpzm)] complex can be obtained by addition of tpzm to a suspension of $[IrCl(TFB)_2]$ [9] in acetone in a 1/1 molar ratio. All these compounds are weak electrolytes

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* The following abbreviations are used: COD, 1,5-cyclooctadiene; NBD, 2,5-norbornadiene or bicyclo-2,2,1-heptadiene; TFB, tetrafluorobarrelene or 5,6,7,8-tetraflururo-1,4-dihydro-1,4-ethenonaphtalene; Me_3 TFB, 1,3-dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-[9-methyletheno]naphthalene; tpzm, tris(pyrazol-1-yl)methane.

Table 1

Colours, analytical results, molar conductivities, and yields for isolated complexes

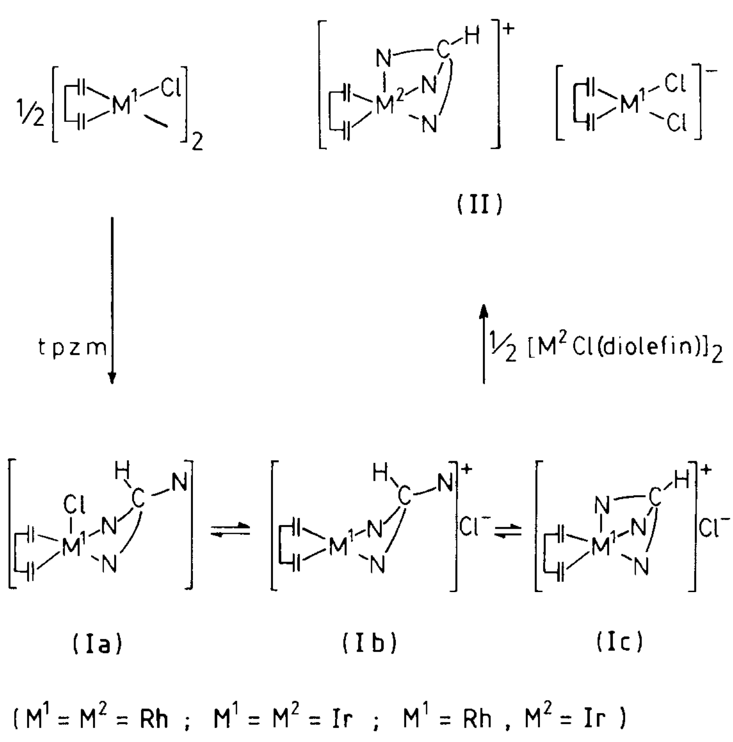
Complex	Colour	Analyses (Found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
		C	H	N		
[RhCl(COD)(tpzm)]	Yellow	47.14	4.77	18.45	67 [a]	89
(1)		(46.92)	(4.81)	(18.24)	(0 [b])	
[Rh(COD)(tpzm)] ClO_4	Yellow	41.33	4.29	16.30	112 [c]	71
(2)		(41.20)	(4.22)	(16.02)		
[Rh(COD)(tpzm)]-	Yellow	44.62	4.72	12.09	20 [c]	63
$[RhCl_2(COD)]$ (3)		(44.15)	(4.84)	(11.88)	(63 [a])	
[RhCl(NBD)(tpzm)]	Yellow	46.74	4.00	18.47	4 [c]	83
(4)		(45.91)	(4.08)	(18.90)	(61 [a])	
[Rh(NBD)(tpzm)]-	Yellow	43.26	4.01	11.77	23 [c]	64
$[RhCl_2(NBD)]$ (5)		(42.69)	(3.78)	(12.44)	(75 [a])	
[RhCl(TFB)(tpzm)]	Yellow	45.24	2.88	14.17	56 [a]	61
(6)		(45.66)	(2.78)	(14.52)		
[Rh(TFB)(tpzm)]-	Yellow	42.66	2.80	8.61	60 [a]	91
$[RhCl_2(TFB)]$ (7)		(43.29)	(2.35)	(8.91)		
[IrCl(COD)(tpzm)]	Yellow	39.40	4.03	15.33	74 [a]	81
(8)		(39.30)	(3.90)	(15.28)		
[Ir(COD)(tpzm)]ClO_4	Yellow	34.97	3.28	13.65	129 [c]	80
(9)		(35.21)	(3.61)	(13.69)		
[Ir(COD)(tpzm)]-	Yellow	35.50	3.87	9.60	30 [c]	72
$[IrCl_2(COD)]$ (10)		(35.25)	(3.87)	(9.49)	(74 [a])	
[Ir(COD)(tpzm)]-	Yellow	39.11	3.86	10.64	72 [a]	48
$[RhCl_2(COD)]$ (11)		(39.20)	(4.30)	(10.55)		
[IrCl(TFB)(tpzm)]	White	39.87	2.47	12.80	13 [c]	67
(12)		(39.55)	(2.41)	(12.58)		
$[IrCl(Me_3TFB)(tpzm)]$	Yellow	42.40	3.24	12.14	–	75
(13)		(42.28)	(3.55)	(11.83)		
$[Ir(Me_3TFB)(tpzm)]$-	Yellow	39.87	2.89	6.82	–	92
$[IrCl_2(Me_3TFB)]$ (14)		(39.83)	(1.84)	(6.97)		

[a] In MeOH. [b] In $CHCl_3$. [c] In $(CH_3)_2CO$.

(Table 1) in acetone or chloroform suggesting that the chloride ion is coordinated to the metal (Ia), but in methanol solution there seems to be significant dissociation to give $[M(diolefin)(tpzm)]^+Cl^-$ species (Ib and Ic).

The NMR spectra (see later) support the existence of the equilibria represented in Scheme 1. Further confirmation of the existence of these equilibria is given by the formation of the mixed $[Ir(COD)(tpzm)][RhCl_2(COD)]$ complex (II) upon addition of $[IrCl(COD)]_2$ to an acetone solution of [RhCl(COD)(tpzm)] in a 1/2 molar ratio. This reaction must involve the initial coordination of the iridium atom to the free pyrazolyl group of Ib. The well-known greater tendency of iridium than of rhodium to form five-coordinated species [10] favours the formation of the $[Ir(COD)(tpzm)]^+$ cation. As expected, the addition of $[RhCl(COD)]_2$ to an acetone suspension to [IrCl(COD)(tpzm)] in a 1/2 molar ratio also leads to the formation of the same mixed $[Ir(COD)(tpzm)][RhCl_2(COD)]$ complex. This suggests that formation of $[Ir(COD)(tpzm)]^+Cl^-$ (Ib or Ic) species is followed by rapid coordination of the Cl^- ion to the $[RhCl(COD)]_2$ dimer.

When the above mentioned reaction between $[RhCl(diolefin)]_2$ or $[IrCl(diolefin)]_2$ and tpzm was carried out in a 1/1 molar ratio the ion-pair complexes



Scheme 1

[Rh(diolefin)(tpzm)][$RhCl_2$(diolefin)] (diolefin = COD, NBD, TFB) or [Ir(diolefin)(tpzm)][$IrCl_2$(diolefin)] (diolefin = COD, Me_3TFB) (II) were obtained. They have relatively low conductivities compared with related ion-pair compounds [11,12], but the X-ray crystal structure of [Rh(COD)(tpzm)][$RhCl_2$(COD)] (**3**) (Fig. 1) confirms the nature of the products, at least in the solid state.

Recently, it has been reported that $[MCl(diolefin)]_2$ (M = Rh, diolefin = COD, NBD; M = Ir, diolefin = COD) complexes react with bidentate N-donor ligands (L–L) in a 1/1 molar ratio to form the corresponding ion-pair compounds of formula [M(diolefin)(L–L)][MCl_2(diolefin)] [11,12]. In this context it is noteworthy that $[Ir(COD)(pic)_2]^+$ and $[IrCl_2(COD)]^-$ species have been postulated as intermediates on the basis of a kinetic study of the reaction between $[IrCl(COD)]_2$ and 2-picoline [13], but not as contributing significantly to the overall reaction.

Crystal structure

The molecular structure of [Rh(COD)(tpzm)][$RhCl_2$(COD)] (**3**) (Fig. 1) is that of a salt formed from two complex ions. The coordination around the rhodium atom of the cation corresponds to a distorted trigonal bipyramid (Fig. 2), as reflected in the different angles around the Rh(1) atom given in Table 2. The N(21) atom and the centroid of the C(31)–C(32) olefinic bond are at apical positions. The distance between the Rh(1) and the apical N(21) atoms is within the range (2.069–2.174 Å) characteristic of twenty structures containing rhodium coordinated with N atoms and COD ligands as found in the Cambridge Structural Data Base (CSDB) [14]. In

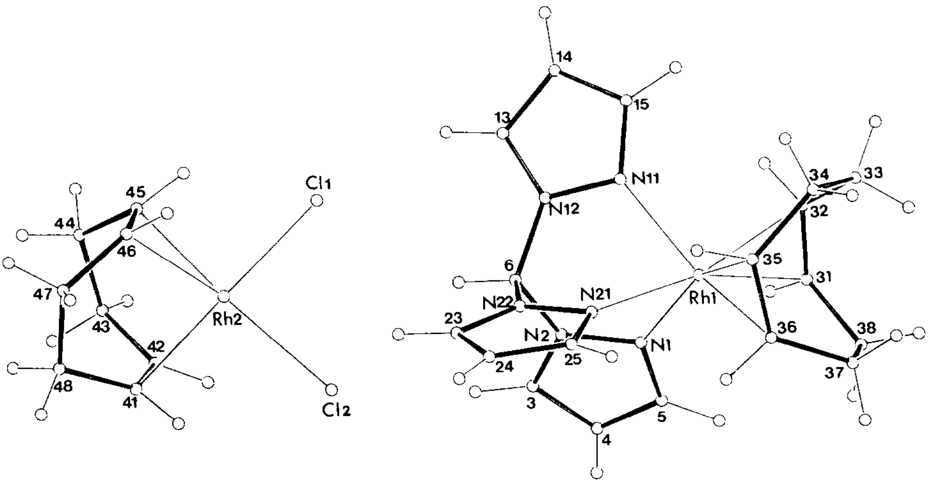


Fig. 1. An ORTEP [40] view of the two complex ions of [Rh(COD)(tpzm)][$RhCl_2$(COD)] (3) showing their relative positions and the numbering scheme.

particular, the Rh(1)–N(21) distance (2.096(9) Å) is in agreement with that observed in the related [Rh(COD){$CH_2(pz)_2$}]$^+$ cation (2.097(7) and 2.111(8) Å) [5] which possesses nitrogen atoms *trans* to olefinic bonds. This Rh–N(apical) distance is significantly shorter than the Rh–N(equatorial) distances; furthermore, the apical olefin exhibits longer Rh–C bonds than the equatorial ones. A similar situation has been found for the five-coordinated trigonal bipyramid [Rh{$B(pz)_4$}(duroquinone)] complex [15]. However, the [Rh{$B(pz)_4$}(COD)] analogue is four-coordinate square-planar in the solid state, but five-coordinate in solution [15,16]. The other two Rh–N (equatorial) distances, 2.293(7) and 2.242(7) Å, are longer than the longest found in the CSD Base [14], perhaps due to COD steric hindrance. The distances between the mid-points of the olefinic bonds of the COD ligand and the rhodium atom are comparable to those found for 1,5-cyclooctadienerhodium complexes (range: 1.897–2.070 Å) [14].

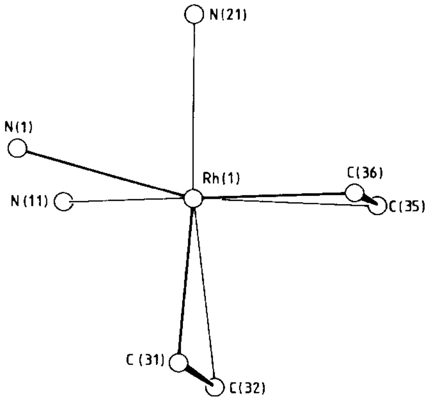


Fig. 2. Details [40] of the coordination around Rh(1) in compound 3.

Table 2

Selected geometrical parameters for complex **3** [a]

(a) Bond distances (Å) and angles (°)

Cation			
Rh(1)–N(1)	2.293(7)	Rh(1)–C(36)	2.080(10)
Rh(1)–N(11)	2.242(7)	Rh(1)–C(312)	2.024(10)
Rh(1)–N(21)	2.096(9)	Rh(1)–C(356)	1.947(7)
Rh(1)–C(31)	2.120(14)	Rh(2)–C(412)	1.986(7)
Rh(1)–C(32)	2.151(14)	Rh(2)–C(456)	1.985(8)
Rh(1)–C(35)	2.071(9)		
N(1)–Rh(1)–N(11)	78.9(3)	N(11)–Rh(1)–C(312)	98.5(3)
N(1)–Rh(1)–N(21)	80.8(3)	N(11)–Rh(1)–C(356)	140.7(3)
N(1)–Rh(1)–C(312)	99.6(4)	N(11)–Rh(1)–N(21)	83.5(3)
N(1)–Rh(1)–C(356)	138.9(3)	N(21)–Rh(1)–C(312)	178.1(3)
C(312)–Rh(1)–C(356)	86.7(3)	N(21)–Rh(1)–C(356)	91.8(3)
Anion			
Rh(2)–Cl(1)	2.384(2)	Rh(2)–C(42)	2.104(9)
Rh(2)–Cl(2)	2.384(2)	Rh(2)–C(45)	2.099(10)
Rh(2)–C(41)	2.105(12)	Rh(2)–C(46)	2.103(13)
Cl(1)–Rh(2)–Cl(2)	89.28(8)	Cl(2)–Rh(2)–C(456)	178.63(20)
Cl(1)–Rh(2)–C(456)	92.07(23)	Cl(2)–Rh(2)–C(412)	91.18(21)
Cl(1)–Rh(2)–C(412)	179.38(24)	C(412)–Rh(2)–C(456)	87.48(30)

(b) Some least-square planes

i: C(31),C(32),C(35),C(36)	ii: C(43),C(44),C(47),C(48)
iii: N(1),N(2),C(3),C(4),C(5)	iv: N(11),N(12),C(13),C(14),C(15)
v: (N(21),N(22),C(23),C(24),C(25)	vi: Rh(1),N(1),N(2),C(6)
vii: Rh(1),N(11),N(12),C(6)	viii: Rh(1),N(21),N(22),C(6)

Planes	Angles (°)	Planes	Angles (°)
i-ii	6.6(4)	vi-vii	62.6(3)
iii-iv	54.4(4)	vi-viii	60.5(3)
iii-v	69.6(4)	vii-viii	56.8(4)
iv-v	56.3(4)		

[a] C(312), C(356), C(412), C(456) are the midpoints of the olefinic bonds in the COD's.

The Rh(1) atom and the N atoms belonging to the pyrazolyl groups together with C(6) form three six-membered rings in boat conformation with C(6) at the most puckered part. The pyrazolyl rings are planar within the experimental uncertainty.

As expected, the Rh(2) atom is square-planar coordinated (see, Table 2). The distances from rhodium to the olefinic carbon atoms are very similar to those reported for the same anion in the complex $[Rh\{PhP(OCH_2CH_2)_2NH\}_2][RhCl_2(COD)]$ (average distance equal to 2.09 Å) [17].

In both ions the interatomic distances in the 1,5-cyclooctadiene ligands are the range described in related structures [5,17]. The $C(sp^3)$–$C(sp^3)$ and $C(sp^2)$–$C(sp^3)$ bond lengths are equal to 1.486(15) and 1.506(14) Å for the anion and 1.508(18) and 1.515(10) Å for the cation (averaged values). The two COD ligands are similar in terms of their torsion angles; their relative position in the crystal is given by the pseudo-torsion angle through the C(312)–Rh(1)–Rh(2)–C(412) positions, with a value of 90.9(5)° (see, Table 2).

The Cl(1) and Cl(2) atoms are at the same distance from Rh(2) (2.384(2) Å) and at 3.600(9) and 3.616(9) Å from C(6), respectively. The angle between the lines C(6)...Rh(1) and Rh(2)...CC(4) (CC(4) being the centroid of C(41), C(42), C(45) and C(46)) is 170.6(4)°.

There are close contacts between the chlorine and H atoms: Cl(1)...H(6) 2.83 Å, Cl(2)...H(6) 2.78 Å with angles C(6)–H(6)...Cl(1) 134° and C(6)–H(6)...Cl(2) 141°. The contacts between the H atoms of the $CHCl_3$ and Cl(1) and Cl(2) are: Cl(2)...H(7) (x, $1+y$, z) 2.95 Å and Cl(1)...H(8) ($-x$, $-y$, $1-z$) 2.54 Å with angles C(7)–H(7)...Cl(2) = 124° and C(8)–H(8)...Cl(1) 167°. The $CHCl_3$ groups are arranged in the usual tetrahedral way. The Cl...H distances involving H atoms of the pyrazolyl rings are as follows: Cl(2)...H(3) 2.76 Å, Cl(1)...H(13) 2.80 Å, Cl(1)...H(23) 2.96 Å and Cl(2)...H(23) 2.94 Å; the first and second of these are shorter than the sum of the Van der Waals' radii [18].

NMR Studies. Carbon-13 NMR spectra

The spectra were recorded at 125 MHz with deuteriochloroform solutions (Table 3). The assignments of chemical shifts and coupling constants were made by analogy with those for other pyrazole derivatives [19] and other Rh(COD) complexes [5,20].

The data in Table 3 deserve some comment:

(i) Carbon C(5) of the free ligand and of complex **2** shows a ^3J coupling constant (~ 2 Hz) with H(1) that is characteristic of C(5) [19]. Thus, the problem of assigning C(3) and C(5) in the complexes has been solved without ambiguity.

(ii) The ^1J(C–H) coupling constant for C(5) is larger than that for C(3) both in the free ligand and in the complexes. In contrast the long range C–H coupling constants of C(3) and C(4), respectively, become identical by complexation.

(iii) The three pyrazole residues of tpzm are magnetically equivalent (only one signal for C(3), C(4) and C(5) respectively), i.e. the apical (1) and equatorial (2) pyrazoles exchange their positions very rapidly on the NMR time scale, to yield averaged signals *.

(iv) Contrary to possible expectations, the coordination of N_2 does not modify the chemical shift of C(3) (nor that of C(4)) but shifts the C(5) signal downfield (by ~ 4.8 ppm). This is similar to the shift displacements observed when 1-methylpyrazole (δ(C(3)) 138.7; δ(C(5)) 129.3 ppm) is quaternized at N(2) to give the 1,2-dimethylpyrazolium ion, in which $\delta(C(3)) = \delta(C(5)) = 137.6$ ppm [22]. In both cases, the pyrrole-like N(1) nitrogen, becomes more similar to the pyridine-like N(2) nitrogen. The signal from the methine carbon, C(1), is shifted 8.3 ppm upfield.

(v) The spectra of compounds **3** **, **10**, and, particularly, **1** show broad signals. The broadening mainly involves C(5) and the olefin carbons of COD. On cooling, carbon C(3) of **1** becomes well resolved, whereas the signals due to C(5) and the

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* A ^{13}C NMR spectra of **3** in the solid state (CP/MAS technique, 62.9 MHz) shows two types of pyrazole signals in a 1/2 ratio. The apical pyrazole signals appear at 142.5 (C(3)), 109.7 (C(4)) and 134.9 (C(5)) and those of the equatorial pyrazoles at 145.0 (C(3)), 107.0 (C(4)) and 133.2 (C(5)). The signals from the COD carbons appear at 29.3, 33.0, 73.6, 75.2, 78.0 and 79.8 ppm.

** Compound **3** shows two broad ^{103}Rh signals at 2485.4 and 2572.6 ppm, whereas the signal of the reference $[RhCl(COD)]_2$ appears as a narrow singlet at 2485.0 ppm [21]. The broadening of signals in compound **3** is supplementary evidence for the existence of a dynamic process.

Table 3

^{13}C NMR chemical shifts (δ, ppm) and ^{1}H–^{13}C coupling constants (J, Hz) for tris(pyrazol-1-yl)methane complexes (in $CDCl_3$)

Compounds	C(1)	C(3)	C(4)	C_5	Olefinic		Aliphatic	
					Cation	Anion	Cation	Anion
tpzm	83.2 ^{1}J 168.9	141.7 ^{1}J 188.4 ^{2}J 5.8 ^{3}J 8.7	107.2 ^{1}J 179.9 ^{2}J 10.6(H(3)) ^{2}J 7.8(H(5))	129.4 ^{1}J 191.7 ^{2}J 9.6 ^{3}J 4.6(H(3)) ^{3}J 2.5 (H(1))	–	–	–	–
[RhCl(COD)(tpzm)] **(1)**	Not observed	141.4 $^{1}J \simeq 188.3$ (slightly broad)	107.2 ^{1}J 182.8 ^{2}J 8.6 ^{2}J 8.6	133.9(br) $^{1}J \simeq 196.6$	74.4(br) $J \simeq 152.6$	–	31.1 ^{1}J 127.9	–
[RhCl(COD)(tpzm)] 253 K **(1)**	74.1 ^{1}J 160.8	141.9 ^{1}J 189.7 ^{2}J 6.8 ^{3}J 6.8	107.8 ^{1}J 183.4 ^{2}J 8.3 ^{2}J 8.3	134.1 ^{1}J 197.2 (slightly broad)	74.6 ^{1}J 153.8 ^{1}J 9.4(^{103}Rh) (slightly broad)	–	31.7 ^{1}J 127.9	–
[Rh(COD)(tpzm)]ClO_4 **(2)**	75.5 ^{1}J 162.7	141.8 ^{1}J 190.9 ^{2}J 7.3 ^{3}J 7.3	107.7 ^{1}J 184.2 ^{2}J 8.6 ^{2}J 8.6	133.6 ^{1}J 197.8 ^{2}J 8.8 ^{3}J 4.8(H(3)) ^{3}J 1.9(H(1))	74.5 ^{1}J 154.6 J 13.8(^{103}Rh)	–	31.0 ^{1}J 129.6	–
[Rh(COD)(tpzm)][$RhCl_2$(COD)] **(3)**	74.6 ^{1}J 162.5	141.3 ^{1}J 189.6 ^{2}J 7.2 ^{3}J 7.2	107.0 ^{1}J 183.2 ^{2}J 8.6 ^{2}J 8.6	134.4(br) ^{1}J 198.0	74.0(br) ^{1}J 155.5	77.8(br) ^{1}J = not measurable (under $CDCl_3$)	31.1 ^{1}J 128.6	31.1 ^{1}J 128.6
[Ir(COD)(tpzm)][$IrCl_2$(COD)] **(10)**	75.0 ^{1}J 163.9	141.1 ^{1}J 191.3 ^{2}J 7.0 ^{3}J 7.0	107.6 ^{1}J 183.9 ^{2}J 8.4 ^{2}J 8.4	134.6 ^{1}J 199.2 (slightly broad)	56.3 ^{1}J 153.1 ^{1}J 13.0(^{103}Rh)	61.0 $^{1}J = 156.6$	32.3 ^{1}J 128.1	32.0 ^{1}J 126.8
[Ir(COD)(tpzm)][$RhCl_2$(COD) **(11)**	75.4 ^{1}J 164.7	141.0 ^{1}J 191.1 ^{2}J 7.2 ^{3}J 7.2	107.4 ^{1}J 184.1 ^{2}J 8.5 ^{2}J 8.5	134.4 ^{1}J 199.6 ^{2}J 8.2 ^{3}J 5.4	56.2 ^{1}J 154.1 ^{1}J 12.5(^{103}Rh)	78.0(br) ^{1}J = not measurable (under $CDCl_3$)	32.2 ^{1}J 127.8	31.1 ^{1}J 127.6

olefinic carbons are still slightly broadened (the ^{1}J coupling constant, $^{13}C-^{103}Rh$, is probably underestimated due to this broadening). The broadening is typical of rhodium derivatives.

(vi) The olefin carbons of COD for the cation and the anion can be distinguished, the position of the signals depending on the nature of the metal (compare compounds **3**, **10**, and **11**).

Proton NMR spectra

All the spectra were recorded at 200 MHz except for those of the free ligand and complexes **1**, **2**, **3**, **10**, and **11**. For these compounds a careful study at 500 MHz (Bruker AM 500) was carried out. The assignment of the protons H(3) and H(5) is based on the fact that there is a characteristic ^{4}J coupling constant between H(1) and H(5) [23]. Furthermore, all compounds obey the rule that in pyrazoles $J_{45} > J_{34}$ [22].

In papers dealing with organometallic derivatives of pyrazole and the problem of assigning H(3) and H(5) three procedures can be found: (i) publication of the data without assignment of the protons [8c,24]; (ii) assignment of the more shifted signal ($\Delta\delta$ between free ligand and complex) to H(3) [26]; (iii) assignment of H(3) to the proton with the lower ^{3}J coupling constant [5,26]. Procedures ii and iii lead to different assignments. In order to solve this problem in the present work, a 2D heteronuclear chemical shift correlation experiment was carried out on compound **3**. This showed that the proton at 7.8 ppm is bonded to the carbon at 141 ppm, and the proton at 8.9 ppm to the carbon at 134 ppm. With the unambiguous assignment of the carbon atoms it follows that H(3) appears at 7.8 ppm and H(5) at 8.9 ppm (Table 4). This leads to the conclusion that criterion iii) ($J_{45} > J_{34}$) should be used when assigning protons H(3) and H(5) in pyrazole organometallic complexes.

The data in Table 4 show the following features:

(i) The effect of complexation on the proton chemical shifts is important only for H(1) and H(5) (Table 5). The effect is always larger for iridium than for rhodium derivatives. All the complexes can be grouped into three families (see Table 5): the largest effect is observed for [MCl(diolefin)(tpzm)] and the smallest for perchlorates (ratio: H(1) $\simeq$ 3.0; H(5) $\simeq$ 1.6). The effect on H(5) is comparable to that caused by quaternization of 1-methylpyrazole ($\Delta\delta$ 1.22 ppm [22]), but the effect of complexation on H(3) is very different from that of quaternization ($\Delta\delta$ 1.08 ppm [22]). This curious behaviour is to be compared with the effect of the lathanide shift reagent, $Eu(fod)_3$. Thus in 1-methylpyrazole, H(3) exhibits a larger lanthanide-induced shift (LIS) than H(5) [27], while the opposite is the case in bis(pyrazolyl)methane [27] and tris(pyrazolyl)methane (tpzm) [28].

(ii) The H(1) signal is more sensitive than the H(5) signal to structural modifications (as it is the signal showing the largest LIS [27,28]). The high shifts for the H(1) signal from [MCl(diolefin)(tpzm)] may be due to the equilibria depicted in Scheme 1. However, the comparison between $[M(diolefin)(tpzm)]^+ ClO_4^-$ and $[M(diolefin)(tpzm)]^+ [MCl_2(diolefin)]^-$ (Table 5) shows that the nature of the anion significantly affects the tpzm signal positions but has little influence on the position of olefin signals (Table 4). The fact that compound **3** shows broad signals (^{1}H, ^{13}C, ^{103}Rh) is indicative of the existence of dynamic equilibria in solution. Depending on the solvent polarity, the $[M(diolefin)(tpzm)][MCl_2(diolefin)]$ compounds can exist as ionic compounds (as in the solid state) or as neutral species.

Table 4

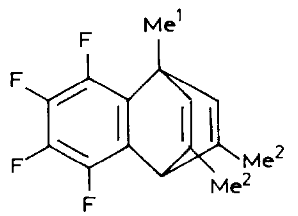
^{1}H NMR chemical shifts and coupling constants for tris(pyrazol-1-yl)methane complexes (in $CDCl_3$)

Compounds	H(1)	H(3)	H(4)	H(5)	J_{34}	J_{45}
tpzm	8.42(d) [a]	7.67(d,d) [b]	6.37(d,d)	7.58(m) [a,b]	1.78	2.59
[RhCl(COD)(tpzm)] (**1**)	11.77(br)	7.82(br)	6.40(d,d)	8.81(br)	1.45	2.40
[RhCl(COD)(tpzm)] (**1**) (253 K)	11.76(s)	7.89(d)	6.43(d,d)	8.73(d)	1.47	2.33
[Rh(COD)(tpzm)] ClO_4 (**2**)	9.51(s)	7.90(d)	6.45(d,d)	8.40(d)	1.83	2.60
[Rh(COD)(tpzm)][$RhCl_2$(COD)] (**3**)	10.96(br)	7.82(br)	6.38(d,d)	8.94(br)	1.56	2.30
[RhCl(NBD)(tpzm)] (**4**)	11.88(br)	7.70(d)	6.32(d,d)	8.69(br)	1.9	2.5
[Rh(NBD)(tpzm)][$RhCl_2$(NBD)] (**5**)	10.50(br)	7.70(d)	6.31(d,d)	8.90(d)	1.9	2.6
[RhCl(TFB)(tpzm)] (**6**)	11.53(br)	7.72(d)	6.38(d,d)	8.72(d)	1.5	2.2
[Rh(TFB)(tpzm)][$RhCl_2$(TFB)] (**7**)	10.85(br)	7.74(d)	6.42(d,d)	8.99(d)	1.5	2.6
[IrCl(COD)(tpzm)] (**8**)	12.28(br)	7.92(d)	6.42(d,d)	8.85(d)	1.6	2.3
[Ir(COD)(tpzm)]ClO_4 (**9**)	9.81(s)	7.96(d)	6.48(d,d)	8.54(d)	1.6	2.5
[Ir(COD)(tpzm)][$IrCl_2$(COD)] (**10**)	10.92(s)	7.91(d)	6.42(d,d)	9.06(d)	1.82	2.41
[Ir(COD)(tpzm)][$RhCl_2$(C0D)] (**11**)	10.97(s)	7.91(d)	6.41(d,d)	9.09(d)	1.75	2.40
[IrCl(TFB)(tpzm)] (**12**)	12.53(s)	7.82(d)	6.45(d,d)	8.92(d)	2.0	2.5
[IrCl(Me_3TFB)(tpzm)] [g] (**13**)	12.82(s)	7.89(d)	6.45(d,d)	8.94(d)	1.7	2.4
[Ir(Me_3TFB)(tpzm)]-[$IrCl_2$(Me_3TFB)] [g] (**14**)	10.88(s)	7.89(d)	6.48(d,d)	9.22(d)	1.8	2.5

Compounds	Olefinic		Aliphatic				Others
	Cation	Anion	Cation		Anion		
tpzm	–	–	–	–	–	–	–
1	4.07(br)	–	2.60(br)	1.94(br)	–	–	–
1 (253 K)	4.04(s)	–	2.63(m)	1.98(m)	–	–	–
2	4.08(m)	–	2.62(m)	1.98(m)	–	–	–
3	4.03(br)	4.30(br)	2.60(br)	1.97(br)	2.50(br)	1.74(br)	–
4	3.40(br)	–	3.80(CH)	1.22(CH_2)	–	–	–
5	3.40(br)	3.77(br)	3.80(CH)	1.22(CH_2)	3.95(CH)	1.15(CH_2)	–
6	3.42(m)	–	5.47(br)	–	–	–	–
7	3.58(br)	3.58(br)	5.55(br)	–	5.55(br)	–	–
8	3.58(m)	–	2.37(m)	1.66(m)	–	–	–
9	3.67(m)	–	2.41(m)	1.79(m)	–	–	–
10	3.64(m) [c]	4.06(m) [d]	2.41(m)	1.75(m) [e]	2.28(m)	1.42(m) [f]	–
11	3.64(m)	4.32(br)	2.41(m)	1.74(m)	2.50(br)	1.74(br)	–
12	2.67(m)	–	5.37(br)	–	–	–	–
13	2.21(m)	–	4.61(br)	–	–	–	2.27(Me(1)), 1.09(Me(2))
14	2.21(m)	2.21(m)	4.61(br)	–	4.89(br)	–	2.27(Me(1)), 1.09, 1.30(Me(2))

[a] J_{15} 0.35 Hz. [b] J_{35} 0.58 Hz. [c] J_{AX} 2.2 Hz. [d] J_{AX} 2.0 Hz. [e] J_{AB} 8.1 Hz. [f] J_{AB} 7.9 Hz.

[g] Me_3TFB =



(iii) Some compounds show broad signals: all are rhodium derivatives. The most striking difference in this respect between rhodium and iridium complexes is between compounds **1** and **8**. The latter gives a well resolved pyrazole pattern and a

Table 5

Coordination induced shifts ($\Delta\delta$ ppm) [a] for Rh^I and Ir^I complexes

	H(1)		H(3)		H(4)		H(5)	
	Rh	Ir	Rh	Ir	Rh	Ir	Rh	Ir
[MCl(diolefin)(tpzm)] (**1, 4, 6, 8, 12, 13**)	3.31	4.12	0.08	0.21	0.00	0.07	1.16	1.32
[M(diolefin)(tpzm)] ClO_4 (**2, 9**)	1.09	1.39	0.23	0.29	0.08	0.11	0.82	0.96
[M(diolefin)(tpzm)][MCl_2(diolefin)] (**3, 5, 7, 10, 11, 14**)	2.35	2.50	0.08	0.23	0.00	0.07	1.36	1.54

[a] $\Delta\delta = \delta_{complex} - \delta_{tpzm}$ (Table 4) (averaged values).

narrow H(1) singlet, whereas the former gives a large H(5) signal and a very large H(1) signal. On cooling (at 500 MHz) the spectrum becomes well resolved, but no splitting of signals is observed. If, as we suggest, the mechanism represented in Scheme 1 is responsible for the broadening, the effect of lowering the temperature is to decrease the rate of interconversion between Ia, Ib and Ic, and at the same time to shift the equilibrium towards one of the forms.

(iv) The broadening of the COD signals in the rhodium derivatives was useful in assigning the spectrum of **11**. The averaged values shown in Table 4 can be presented as follows:

COD							
Olefinic				Aliphatic			
Cation		Anion		Cation		Anion	
Rh	Ir	Rh	Ir	Rh	Ir	Rh	Ir
4.06	3.63	4.31	4.06	2.61	2.40	2.50	2.28
				1.97	1.74	1.74	1.42

Concluding remarks

Tris(pyrazol-1-yl)methane (tpzm) is a useful new ligand, whose rhodium and iridium complexes show interesting structural and dynamic properties that shed new light on the chemistry of other pyrazole ligands, a field already vast and rapidly increasing in importance [1,22,29]. Metallotropy has been shown to be easier for rhodium than for iridium derivatives.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. NMR spectra were recorded with $CDCl_3$ solutions at room temperature on a Varian

XL-200 spectrometer, unless otherwise indicated. IR spectra were recorded on a Perkin–Elmer 783 spectrometer. C, H, N analyses were carried out with a Perkin–Elmer 240-B microanalyzer, and conductivities measured at 20 °C in ca. 5×10^{-4} *M* acetone, methanol or chloroform solutions with a 9501/01 conductometer. The starting materials, tpzm [30], $[RhCl(COD)]_2$ [31], $[RhCl(NBD)]_2$ [32], $[RhCl(TFB)]_2$ [33], $[IrCl(COD)]_2$ (34] $[IrCl(TFB)_2]$ [9] and $[IrCl(Me_3TFB)]_2$ [35] were prepared by published methods.

Preparation of [RhCl(COD)(tpzm)]. A suspension of $[RhCl(COD)]_2$ (212.8 mg, 0.43 mmol) in 20 ml of acetone was treated with tpzm (184.8 mg, 0.86 mmol) and the mixture was stirred for 30 min at room temperature. The yellow precipitate was filtered off, repeatedly washed with acetone, and dried in vacuo; yield 349.2 mg (81%).

Preparation of [RhCl(COD)(tpzm)]ClO$_4$. A suspension of $[RhCl(COD)]_2$ (121.9 mg, 0.25 mmol) in 20 ml of dichloromethane was treated with tpzm (105.8 mg, 0.49 mmol) and $AgClO_4$ (102.4 mg, 0.49 mmol) and the mixture was stirred for 30 min. The precipitated AgCl was removed by filtration through kieselguhr and the yellow filtrate concentrated in vacuo. Addition of diethyl ether gave a yellow precipitate, which was filtered and recrystallized from dichloromethane/ether; yield 184.2 mg (71%).

Preparation of [Rh(COD)(tpzm)][RhCl$_2$(COD)]. The complex was prepared by the procedure described for [RhCl(COD)(tpzm)] from $[RhCl(COD)]_2$ (135.0 mg, 0.27 mmol) and tpzm (58.9 mg, 0.27 mmol). 121.8 mg (63%) of the complex were obtained.

Preparation of [RhCl(NBD)(tpzm)]. The complex was prepared by the procedure described for [RhCl(COD)(tpzm)] from $[RhCl(NBD)]_2$ (105.6 mg, 0.23 mmol) and tpzm (98.2 mg, 0.46 mmol). 168.5 mg (83%) of the complex were obtained.

Preparation of [Rh(NBD)(tpzm)][RhCl$_2$(NBD)]. The complex was prepared by the procedure described for $[Rh(COD)(tpzm)][RhCl_2(COD)]$. From $[RhCl(NBD)]_2$ (110.6 mg, 0.24 mmol) and tpzm (51.2 mg, 0.24 mmol). 103.7 mg (64%) of the complex were obtained.

Preparation of [RhCl(TFB)(tpzm)]. The complex was prepared by the procedure described for [RhCl(COD)(tpzm)] from $[RhCl(TFB)]_2$ (200.9 mg, 0.14 mmol) and tpzm (60.0 mg, 0.28 mmol). 97.7 mg (61%) of the complex were obtained.

Preparation of [Rh(TFB)(tpzm)][RhCl$_2$(TFB)]. The complex was prepared by the procedure described for $[RhCl(COD)(tpzm)][RhCl_2(COD)]$ from $[RhCl(TFB)]_2$ (100.9 mg, 0.14 mmol) and tpzm (29.8 mg, 0.14 mmol). 118.8 mg (91%) of the complex were obtained.

Preparation of [IrCl(COD)(tpzm)]. The complex was prepared by the procedure described for [RhCl(COD)(tpzm)] from $[IrCl(COD)]_2$ (150 mg, 0.22 mmol) and tpzm (95.7 mg, 0.45 mmol). 199 mg (81%) of the complex were obtained.

Preparation of [Ir(COD)(tpzm)]ClO$_4$. The complex was prepared by the procedure described for $[Rh(COD)(tpzm)]ClO_4$ from $[IrCl(COD)]_2$ (200 mg, 0.30 mmol), tpzm (127.6 mg, 0.60 mmol) and $AgClO_4$ (124.4 mg, 0.60 mmol). 292 mg (80%) of the complex were obtained.

Preparation of [Ir(COD)(tpzm)][IrCl$_2$(COD)]. The complex was prepared by the procedure described for $[Rh(COD)(tpzm)][RhCl_2(COD)]$ from $[IrCl(COD)]_2$ (100.0 mg, 0.15 mmol) and tpzm (31.8 mg, 0.15 mmol). 105.4 mg (80%) of the complex were obtained.

Preparation of [Ir(COD)(tpzm)][RhCl$_2$(COD)]. This complex was prepared by two different routes:

(i) A suspension of [IrCl(COD)(tpzm)] (97.6 mg, 0.18 mmol) in 20 ml of acetone was treated with [RhCl(COD)]$_2$ (43.7 mg, 0.09 mmol) and the mixture was stirred

Table 6

Crystal data and data collection parameters

Crystal data	
Formula	Rh(C_8H_{12})Cl_2 Rh(C_8H_{12})(CH($C_3H_3N_2$)$_3$). 3($CHCL_3$)
Crystal habit	Rectangular prism
Crystal size (mm)	0.67×0.50×0.50
Symmetry	Triclinic $P\bar{1}$
Unit cell determination:	Least-squares fit from 89 reflexions [$\theta < 45$]
Unit cell dimensions	12.4256(21), 15.4113(25), 12.0152(16) Å; 101.48(1)°, 105.03(1)°, 67.21(1)°
Packing: V (Å^3), z, D_c(g.cm^{-3}),	2036.1(6), 2, 3.476,
M, F(000)	2130.9, 2120
μ (cm^{-1})	276.06
Experimental data	
Technique	Four circle diffractometer Bisecting geometry Graphite oriented monochromator: Cu-K_α ω-2θ scans, scan width: 1.5° Detector apertures 1.0×1.0 mm
Total measurements	Up to $\theta = 60°$
Speed	4 reflec/min[a]
Number of reflexions:	
Measured	5993
Independent	5993
Observed	5441 (3$\sigma(I)$ criterion)
Standard reflexions:	2 reflexions every 90 minutes Variation: 59% overall decay
Max-min transmission factors:	1.433–0.706 [36]
R values before and after absorption correction:	0.163–0.120
Solution and refinement	
Solution	Patterson function and DIRDIF
Refinement	L.S. on F_{obs} with 2 blocks
Parameters:	
Number of variables	433 (H atoms fixed)
Degrees of freedom	5008
Ratio of freedom	12.6
H atoms	Difference synthesis
Final shift/error	0.08
Max. thermal value	U_{22}(Cl(11)) 0.60(4) Å^2
Final ΔF peaks	1.42 e/Å^{-3} near Rh(2) atom
Extinction correction	no
Final R and R_w	0.078–0.090
Computer and programs	VAX 11/750 XRAY76 SYSTEM [37] DIRDIF [38]
Scattering factors	Int. Tables for X-Ray Crystallography [39]

[a] See Experimental part.

for 8 h at room temperature. The yellow precipitate was filtered off, repeatedly washed with acetone, and dried in vacuo; yield 67.8 mg (48%).

(ii) A suspension of [RhCl(COD)(tpzm)] (81.7 mg, 0.18 mmol) in 20 ml of

Table 7. Atomic coordinates

Atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.00679(5)	0.19601(4)	0.28720(5)
N(1)	0.1883(7)	0.1108(5)	0.3906(7)
N(2)	0.2243(6)	0.0162(5)	0.3709(6)
C(3)	0.3242(8)	-0.0260(8)	0.4489(9)
C(4)	0.3519(9)	0.0454(9)	0.5203(10)
C(5)	0.2678(9)	0.1272(8)	0.4815(9)
N(11)	0.0855(6)	0.0882(5)	0.1473(7)
N(12)	0.1431(6)	-0.0023(5)	0.1692(6)
C(13)	0.1812(9)	-0.0602(7)	0.0753(8)
C(14)	0.1475(9)	-0.0032(8)	-0.0110(8)
C(15)	0.0881(8)	0.0875(7)	0.0364(8)
N(21)	-0.0363(6)	0.0865(5)	0.3212(6)
N(22)	0.0398(6)	-0.0051(5)	0.3092(6)
C(23)	-0.0030(10)	-0.0669(7)	0.3342(9)
C(24)	-0.1085(10)	-0.0129(8)	0.3634(10)
C(25)	-0.1274(8)	0.0806(7)	0.3554(8)
C(6)	0.1552(7)	-0.0292(6)	0.2826(7)
C(31)	0.0764(10)	0.3060(7)	0.3146(11)
C(32)	0.0153(12)	0.3033(7)	0.2030(10)
C(33)	-0.1067(14)	0.3776(8)	0.1609(10)
C(34)	-0.2050(12)	0.3462(9)	0.1636(12)
C(35)	-0.1720(9)	0.2803(7)	0.2566(9)
C(36)	-0.1177(10)	0.3001(7)	0.3749(10)
C(37)	-0.0895(12)	0.3890(9)	0.4235(11)
C(38)	0.0344(13)	0.3783(8)	0.4105(11)
Rh(2)	0.27561(6)	-0.37095(4)	0.27645(5)
Cl(1)	0.1554(2)	-0.2583(2)	0.1427(2)
Cl(2)	0.2876(2)	-0.2439(2)	0.4233(2)
C(41)	0.3259(10)	-0.4674(7)	0.3987(9)
C(42)	0.4276(9)	-0.4639(7)	0.3745(9)
C(43)	0.5056(11)	-0.5381(9)	0.3004(11)
C(44)	0.4403(15)	-0.5604(11)	0.1842(14)
C(45)	0.3213(12)	-0.4820(8)	0.1443(9)
C(46)	0.2161(12)	-0.4758(8)	0.1690(10)
C(47)	0.1993(18)	-0.5384(12)	0.2398(15)
C(48)	0.2819(12)	-0.5477(9)	0.3564(11)
C(7)	0.5187(12)	0.6978(12)	0.2436(12)
Cl(3)	0.4841(5)	0.8176(4)	0.2318(4)
Cl(4)	0.6305(7)	0.6654(6)	0.3637(7)
Cl(5)	0.5545(11)	0.6271(7)	0.1208(6)
C(8)	0.1121(16)	0.2813(14)	0.8405(13)
Cl(6)	0.0806(8)	0.2883(7)	0.6957(5)
Cl(7)	0.2317(7)	0.1789(6)	0.8714(9)
Cl(8)	0.13130(7)	0.3792(6)	0.9282(8)
C(9)	0.4644(23)	0.1451(21)	0.1856(19)
Cl(9)	0.3827(11)	0.0932(12)	0.1910(10)
Cl(10)	0.5275(7)	0.1880(4)	0.3242(5)
Cl(11)	0.5549(14)	0.1115(19)	0.1010(12)

acetone was treated with $[IrCl(COD)]_2$ (59.6 mg, 0.09 mmol) and the mixture was stirred for 8 h at room temperature. The yellow precipitate was filtered off, repeatedly washed with acetone, and dried in vacuo; yield 68.2 mg (48%).

Preparation of [IrCl(TFB)(tpzm)] The complex was prepared by the procedure described for [IrCl(COD)(tpzm)] from $[IrCl(TFB)_2]$ (136.0 mg, 0.20 mmol) and tpzm (42.8 mg, 0.20 mmol). 92.2 mg (67%) of the complex were obtained.

Preparation of [IrCl(Me$_3$TFB)(tpzm)] The complex was prepared by the procedure described for [Ir(COD)(tpzm)], from $[IrCl(Me_3TFB)]_2$ (80.0 mg, 0.05 mmol) and tpzm (21.4 mg, 0.10 mmol). 53.5 mg (75%) of the complex were obtained.

Preparation of [Ir(Me$_3$TFB)(tpzm)][IrCl$_2$(Me$_3$TFB)] The complex was prepared by the procedure described for $[Ir(COD)(tpzm)][IrCl_2(COD)]$, from $[IrCl(Me_3TFB)]_2$ (50.0 mg, 0.05 mmol) and tpzm (10.7 mg, 0.05 mmol). 55.8 mg (92%) of the complex were obtained.

X-Ray analysis Crystal data are listed in Table 6. The stability and orientation of the crystal were checked by measuring two standard reflections every 90 min. The hkl reflections were measured at a speed of 4 reflections per minute because of the significant decomposition of the sample detected in the reference reflections during the collection (37% overall decay) in 25 h.

In the final cycle of the refinement weighting schemes were applied as to give no trends in $\langle w\,\Delta^2F\rangle$ vs. $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$. The final positional parameters are showed in Table 7. Tables of hydrogen atom coordinates, thermal parameters and structure factors are available from the authors.

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