Articles

Synthesis and Structural Characterization of Mixed-Sandwich Complexes of Rhodium(III) and Iridium(III) with Cyclopentadienyl and Hydrotris(pyrazolyl)borate Ligands

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MCp*(Tp′)Cl (M = Rh or Ir, Cp* = pentamethylcyclopentadienyl, Tp′ = hydrotris(pyrazolyl)borate (Tp) or hydrotris(3,5-dimethylpyrazolyl)borate (Tp*)) complexes have been synthesized by reaction of the appropriate $[(Cp^*)MCl_2]_2$ with KTp′. Reaction between MCp*(Tp)Cl and $AgNO_3$ in acetonitrile affords ionic $[M(Cp^*)Tp]NO_3$ species, whereas with MCp*(Tp*)Cl B−N bond cleavage within the Tp* ligand occurs. B−N bond scission is also detected during the interaction of $[MCp^*Cl_2]_2$ complexes with KTp′ salts when the reactions are carried out in air for extended periods of time, providing pyrazole derivatives, e.g., $RhCp^*Cl_2(pz^*H)$, (pz*H) = 3,5-dimethylpyrazole) (**8**). Two different compounds have been obtained from the reaction of KBp (Bp = dihydrobis(pyrazolyl)borate) and $[IrCp^*Cl_2]_2$, namely, monomeric $IrCp^*Cl_2(pzH)$ and the binuclear $[IrCp^*Cl]_2(\mu\text{-Cl})(\mu\text{-pz})$ (**10**), which contains bridging chloride and pyrazolate groups. In contrast, the analogous reaction of $[RhCp^*Cl_2]_2$ with KBp produces RhCp*(Bp)Cl. Crystal structure determinations have been performed for some of the complexes. IR data indicate κ^3-Tp binding for $[MCp^*Tp]NO_3$; moreover, the expected correlation between ν(B−H) and the Tp′ hapticity is found for MCp*Tp′ systems.

Introduction

Since the first report of Trofimenko,[1] poly(pyrazolyl)borates, in particular, tris(pyrazolyl)borates (Tp′), have been extensively employed as anionic σ-donor ligands in a wide variety of metal complexes.[2] They form stable complexes in which they often act as tridentate, facial, five-electron donors (covalent formalism for electron counting[3]). Hence they are auxiliary ligands similar to the cyclopentadienyls, and as such, they have been used in many instances.[4] The Tp′ are weak-field, hard ligands. Comparatively, their overall donor properties are weaker than those of the cyclopentadienyls[5,6] (Cp* > Cp; Tp* > Tp). However they are bulkier than the cyclopentadienyls, and moreover, in six-coordinate environments they impose quasi-octahedral coordination at the metal with N−M−N bite angles close to the ideal 90° value.[7] As already noted,[7] this geometry is particularly favorable for low-spin d^6 systems such as Rh(III) and Ir(III).

Rh(III) and Ir(III) complexes of the cyclopentadienyls[8] and tris(pyrazolyl)borate[9] ligands have recently attracted considerable attention because of their ability to activate the aliphatic and aromatic C−H bonds of hydrocarbons and other substrates. It has been shown that the Tp′ ligands may act as more than simple spectators in the course of chemical reactions, having the capability to influence the reactivity of the metal center by means of temporary denticity changes.[10]

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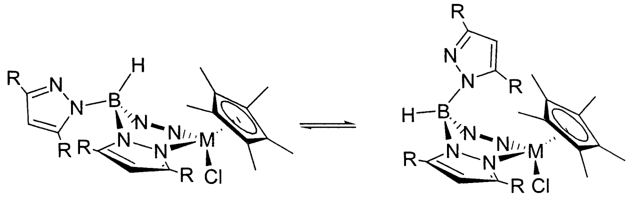
Considering the similarities between the Cp′ and Tp′ ligands and the large number of sandwich and half-sandwich complexes formed by these two families of ligands, the dearth of information that exists on the mixed-sandwich derivatives MCp′Tp′ appears surprising. Following earlier studies,[11−13] a series of $[\mathrm{MCp'Tp'}]^{n+}$ complexes of the first transition elements have been investigated recently.[14] To our knowledge, for the group 9 elements, Rh and Ir, only $[\mathrm{RhCp^*Tp}]\mathrm{PF_6}$ has been structurally characterized;[15] other attempts to obtain stable complexes appear to have been unsuccessful.[16] As an extension of previous work on metal-scorpionates[17] we have undertaken a systematic study of the reactions of the $[\mathrm{MCp^*Cl_2}]_2$ dimers (M = Rh, Ir) with Bp′ and Tp′ salts. Here we report the synthesis and characterization of six new mixed MCp*Tp′ complexes, along with those of a related RhCp*Bp derivative. Some interesting byproducts of the reactions investigated have also been characterized.

Results and Discussion

Synthesis and Characterization of Complexes 1−9. The new compounds MCp*Tp′Cl (M = Rh, Ir; Cp* = $\mathrm{C_5Me_5}$; Tp′ = unsubstituted or 3,5-$\mathrm{Me_2}$-substituted tris(pyrazolyl)borate ligand, Tp and Tp*, respectively; in detail: Rh, Tp, **1**; Ir, Tp, **2**; Rh, Tp*, **3**; Ir, Tp*, **4**) are readily obtained from the reactions of $[\mathrm{MCp^*Cl_2}]_2$ dimers and NaTp′ (or KTp′), in anhydrous toluene, under an atmosphere of $\mathrm{N_2}$. The complexes are air-stable in the solid state but become sensitive to $\mathrm{O_2}$ and $\mathrm{H_2O}$ in solution. However, under an inert atmosphere their solutions are stable indefinitely.

IR and NMR data for **1**−**4** point to η^5-Cp* and κ^2-Tp′ coordinations. For instance, a doublet is observed in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of the rhodium derivatives **1** and **3** in the vicinity of δ 96 (J(C−R) ≈ 8 Hz), indicative of η^5-Cp* binding. As solubility properties along with IR data are in accord with chloride binding to the metal (ν(M−Cl) between 260 and 280 $\mathrm{cm^{-1}}$), the most likely coordination of the tris(pyrazolyl)borate must be as the bidentate κ^2-Tp′, and this is confirmed by the observation of an IR absorption at ca. 2450 $\mathrm{cm^{-1}}$ due to ν(B−H).[18] Compound **3** is an exception in this regard because it exhibits two ν(B−H) vibrations at 2490 and 2410 $\mathrm{cm^{-1}}$. X-ray studies (to be discussed below) reveal that this complex crystallizes in two similar conformers (Figure 1) that differ in the position of the noncoordinated pz ring, proximal or distal with respect to the metal. However, assignment of the above bands within these two conformers is not straightforward. At present we cannot offer a reasonable explanation for this observation, which nevertheless finds ample literature precedent.[10a,19]



1: M = Rh, R = H; **2**: M = Ir, R = H
3: M = Rh, R = Me; **4**: M = Ir: R = Me

Figure 1. Two possible conformers for complexes **1**−**4**.

In accord with the proposed structures, two sharp sets of resonances in a 2:1 ratio are recorded for the pz′ protons of compounds **1**−**4** at room temperature in solution. On raising the temperature to 328 K, the spectrum is unchanged, so that exchange between coordinated and uncoordinated pz′ groups must be slow under these conditions. Upon cooling to 218 K the pyrazolyl proton resonances split into two different sets (see Experimental Section), indicating that the equilibrium represented in Figure 1 is in the slow-exchange regime at this temperature. As with other M−Tp complexes, after extended periods of time at 293 K (ca. 48 h), partial degradation of the NMR samples of **1**−**4** occurs.[20,21] As pointed out by Venanzi, it is possible that this degradation, which results from hydrolytic B−N bond cleavage, involves the uncoordinated ring of the κ^2-Tp′ ligand.[22]

Treatment of complexes **1** and **3** with $\mathrm{AgNO_3}$ in $\mathrm{CH_3CN}$ induces precipitation of AgCl with concomitant formation of the new derivatives **5** and **6**. Their IR spectra show ν(B−H) bands at ca. 2490 $\mathrm{cm^{-1}}$, consistent with tridentate Tp-coordination (Figure 2). The IR data also indicate ionic $\mathrm{NO_3^-}$ groups,[23] confirmed by conductivity measurements in both acetonitrile and acetone that give values characteristic of 1:1 electrolytes. The

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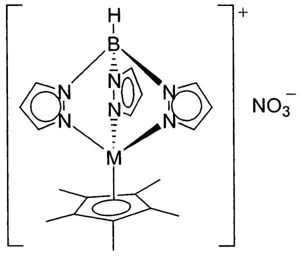
Table 1. Metal Atom Environments

	compound(M)								
	8(Rh)[a]	**3a**(Rh)	**3b**(Rh)	**2**(Ir)	**4**(Ir)	**10**(Ir(1,1′,2,2′))			
				Distances (Å)					
M−C(cp*)	2.1355(7) (2.132(7))	2.155(6)	2.164(5)	2.154(3)	2.140(1)	2.10(1)	2.05(1)	2.06(1)	2.01(1)
(range)	−2.1663(7) (2.159(5))	−2.195(5)	−2.194(5)	−2.175(3)	−2.176(5)	−2.25(1)	−2.23(1)	−2.24(1)	−2.27(1)
⟨M−C(cp*)⟩	2.155(12) (2.144(11))	2.174(16)	2.177(12)	2.164(11)	2.167(15)	2.18(6)	2.14(7)	2.15(7)	2.15(9)
M−C(0)[b]	1.77 (1.76)	1.81	1.80	1.79	1.78	1.88	1.74	1.79	1.77
M−Cl(1)	2.4154(3) (2.413(2))	2.429(1)	2.430(2)	2.416(1)	2.407(3)	2.406(4)		2.409(4)	
M−X	2.4390(2) (2.441(2))	2.135(5)	2.114(4)	2.080(2)	2.083(4)	2.402(3)		2.411(3)	
M−Y	2.1408(7) (2.134(4))	2.108(4)	2.117(4)	(x2)	(x2)	2.07(1)		2.06(1)	
X,Y	Cl(2), N(1)	N(11,21)	N(11,12)	N(11)(x2)	N(11)(x2)	Cl(0), N(1)		Cl(0), N(2)	
				Angles (deg)					
C(0)−M−Cl(1)	126.0 (125.3)	122.3	122.6	124.2	126.8	128.4	130.3	132.8	123.1
C(0)−M−X	124.$_7$ (124.$_3$)	129.$_4$	127.$_0$	129.$_5$	128.$_3$	120.$_5$	125.$_9$	125.$_3$	115.$_5$
C(0)−M−Y	126.$_6$ (128.$_1$)	128.$_4$	131.$_2$	(x2)	(x2)	131.$_9$	124.$_2$	122.$_6$	141.$_1$
Cl(1)−M−X	90.14(1) (92.48(6))	87.9(1)	88.5(1)	87.03(7)	87.0(1)	89.8(1)		88.6(1)	
Cl(1)−M−Y	91.46(2) (86.5(1))	88.2(1)	86.8(1)	(×2)	(×2)	85.0(3)		85.6(3)	
X−M−Y	86.07(2) (86.5(1))	87.4(2)	87.4(2)	85.28(9)	85.2(2)	88.2(3)		88.2(3)	

[a] Values in parentheses are counterpart parameters for the pzH analogue.[20] [b] C(0) is the cp* centroid.



5: M = Rh
6: M = Ir

Figure 2. Structures of complexes **5** and **6**.

NMR data are also in accord with the proposed formulation and need no further comment. We note that the application of the same synthetic procedure to the Tp* derivatives **2** and **4** does not yield the expected complexes analogous to **5** and **6**. These reactions produce only degradation products, presumably in consequence of the high steric demands of the Tp* ligand.

The reactions of the [MCp*Cl$_2$]$_2$ dimers and KBp have also been investigated. For M = Rh the chemistry proceeds as expected to give RhCp*(κ^2-Bp)Cl (**7**), in high yield. Characterization by IR and NMR data is straightforward and merits no further comment. At variance with this, two different compounds, **9** and **10**, are generated during the interaction of [IrCp*Cl$_2$]$_2$ and KBp. Compound **10** is a binuclear species in which a chloride and a pyrazolate bridge the two IrCp*Cl moieties, i.e., {[IrCp*Cl]$_2$(μ-Cl)(μ-pz)}. **9** is a mononuclear derivative that results simply from pz-H coordination to the IrCp*Cl$_2$ unit, e.g., IrCp*Cl$_2$(pzH). The analogous RhCp*Cl$_2$(pz*H) has been isolated following the reaction of [RhCp*Cl$_2$]$_2$ and KTp* in incompletely anhydrous solvents for long periods of time. Interestingly, the ^{1}H NMR spectrum of **9** recorded at room temperature exhibits three signals due to the pyrazolyl C−H protons along with a broad resonance attributable to the N−H group. At 303 K, the 3- and 5-positions of the ring become dynamically averaged by the degenerate site exchange of the metal between the two N atoms,[24] whereas for RhCp*Cl$_2$(pz*H), **8**, the two Me groups are inequivalent at the same temperature. Thus steric hindrance appears to slow this process.

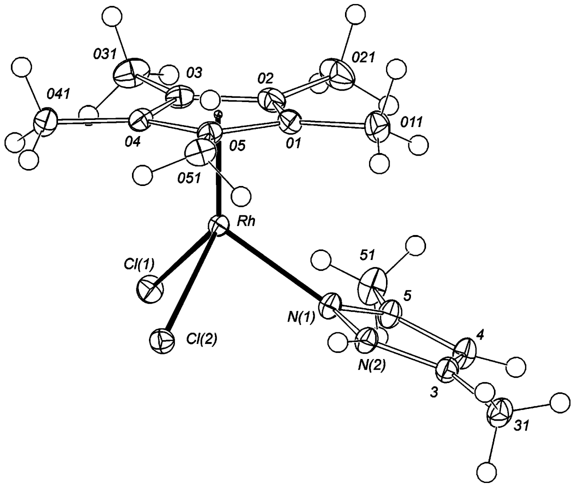


Figure 3. Projection of a single molecule of **8**.

X-ray Diffraction Studies. The results of the single-crystal X-ray studies of **2**, **3**, **4**, and **8** are consistent, in terms of stoichiometry and connectivity, with the formulations proposed above, all species being neutral mononuclear complexes, with **8** of the form RhCp*Cl(pz*-H) (Figure 3) and **2**, **3**, and **4** MCp*(L)Cl, where L is a symmetrically bidentate tris(pyrazolate) ligand. **8** and **3** are devoid of crystallographic symmetry, one molecule comprising the asymmetric unit of each structure, but both **2** and **4** are disposed with the Cp* centroid, the metal atom, the bridge-head atom of the bidentate ligands, and the chloride lying in a crystallographic mirror plane in each case, one-half of the molecule comprising the asymmetric unit of each structure. The metal atom may be regarded as having the familiar "four-coordinate" "piano-stool" coordination environment (Table 1; Figure 3), with three similar, large Cp*(centroid)−M−Cl/N angles, and the other three similar angles close to "octahedral" in their disposition. Bond lengths and angles throughout the four arrays are closely similar regardless of whether the

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central metal atom is rhodium or iridium. The parameters of the structure of **8** are closely comparable with those of the unsubstituted pzH counterpart[25] (Table 1); the rhodium atom lies 0.539(2) Å out of the C_3N_2 plane. The Rh−Cl distances in **8** differ significantly, paralleling a similar difference observed in the pzH complex, despite replacement of H(5) by a methyl group; an asymmetry observed in exocyclic Rh−N(1)−N(2),C(5) (117.71(5)°, 133.83(5)°) also mimics, albeit enlarged, a similar asymmetry seen in the pzH analogue (124.1(4)°, 130.5(4)°). H(2)···Cl(2) is 2.57(2) Å.

A convenient route to a number of first-row MCp*Tp adducts is by way of various chloride precursors, the Tp adopting its familiar tripod mode of coordination to the metal, the chlorine being lost in the process.[14] It is interesting therefore in the present arrays **2**, **3**, and **4** that the Tp ligand chelates as bidentate, yielding species that retain the chloride, the molecule overall approaching or realizing *m*-symmetry. Close similarities and notable differences are found among the three species with their various diverse ligands. As noted above, bond lengths and angles about the metal atoms are similar throughout the various arrays, regardless of metal or Tp′ substitution. As is usual in its η^5-complexes, the methyl substituents of the Cp* lie out of the C_5 plane significantly, to the opposite side of the metal atom, by between 0.09 and 0.21(1) Å in the rhodium pair of structures and between 0.06 and 0.124(7) Å in the iridium, the lesser deviations in those atoms lying over the chlorine. Concomitantly, C(0)(Cp*)−M−Cl are rather larger in **2** and **4** than in **3**.

The most notable difference in these structures (**2**, **3**, **4**) is the disposition of the Tp′ ligand, resulting in distinct isomers. Released of the constraint of a third coordinated pz ring, tripodwise, so that it is now a bidentate chelate, the latter adopts the now familiar mode whereby the four nitrogen atoms of the two rings of the chelate are closely coplanar, with the boron and metal atoms lying at the prows of a six-membered ring; the metal atoms now lie well out of the C_3N_2 ring planes as well by amounts that differ over a considerable range, with a similar wide variation in the interplanar dihedral angles. Fortuitously, compound **3** has crystallized in two forms; the geometries of the two independently defined molecules are very similar, the uncoordinated pyrazolate ring lying at the axial site of the boron prow atom and lying normal to the putative mirror plane as found in **2** and **4**, with the ordered methyl substituent destroying any potential for achievement of that symmetry in this situation. A considerable angular asymmetry is found at the pendant nitrogen atom of the uncoordinated pyrazolate.

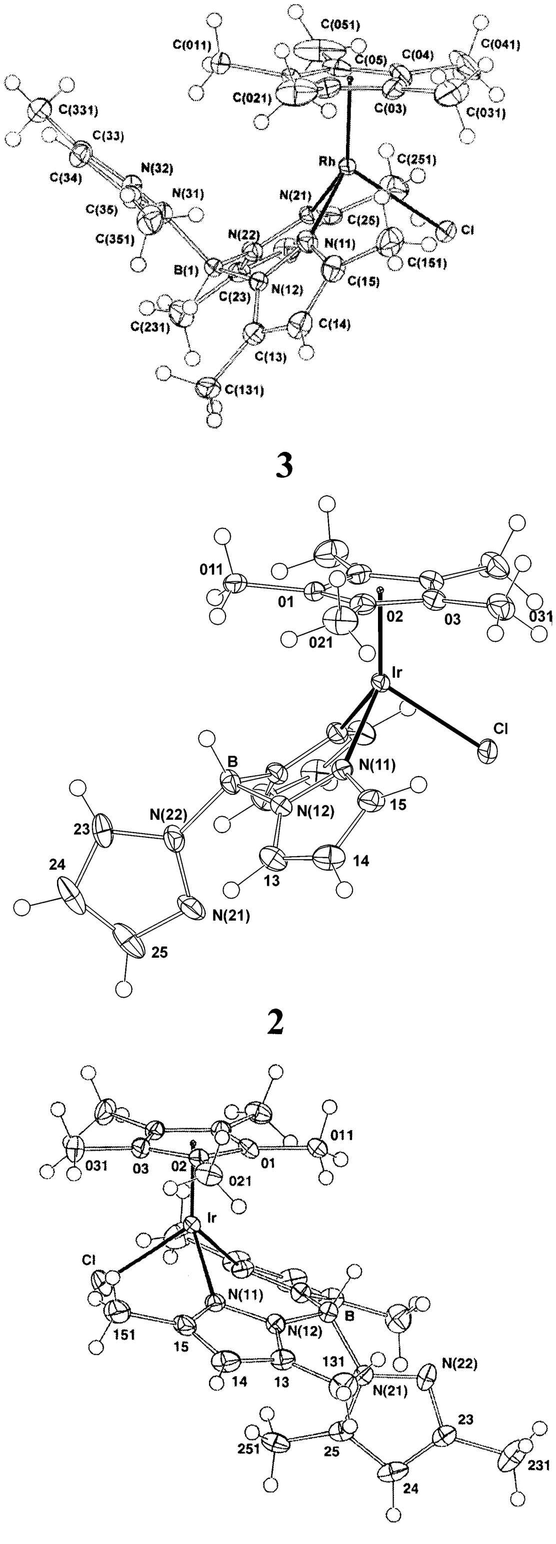

Figure 4. Projections of single molecules of (a) **3a** (**3b** is similar), (b) **2**, and (c) **4**, the latter (**2**, **4**) conforming to crystallographic *m* symmetry.

The latter asymmetry persists, only slightly diminished, in **2**, despite the lack of pyrazolate substituent and despite the uncoordinated ring now lying equatorial in the chelate boat and, also, contained within the molecular mirror plane; the unsubstituted nitrogen of the unchelated ring is unambiguously defined as trans to the boron hydrogen substituent. In **4**, the nitrogen now lies cis; the conformational parameters of the chelate system generally are considerably changed relative to those of **2** and **3**. Although numerous neighborly proximities noted above may account for the minor perturbations noted, this rather major distortion is presumably a consequence of the proximity of methyl 251 (Figure 4) to the chelated pyrazolates (H···N 2.7 Å (est)). Whereas *m* symmetry is rigorously imposed in **2** and **4**, certain pairwise conformational descriptors of the

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Table 2. M(N$_2$)$_2$X Chelate Descriptors in 2, 3, and 4

	3a[a]	**2**	**4**
	(a) Conformational Descriptors (i) Torsion Angles (deg)		
N−M−N−N	−20.1(3), 32.1(3)(−21.4(4), 35.8(4))	−33.8(2)	48.8(5)
M−N−N−B	−17.6(6), −7.4(5)(−17.4(6), −12.4(6))	−3.7(4)	−23(1)
N−N−B−N	52.4(5), −38.2(5)(52.2(6), −35.2(7))	51.9(4)	−20(1)
	(ii) Out-of-Plane Deviations (Å)		
δM(C$_3$N$_2$)	0.411(9), 0.144(8)(0.386(8), 0.215(9))	0.008(5)	0.62(1)
δM(N$_2$)$_2$	0.571(7)(0.608(7))	0.703(4)	0.995(8)
δB(N$_2$)$_2$	0.506(7)(0.488(8))	0.66(2)	0.24(1)
	(iii) Interplanar Dihedral Angles (deg)		
C$_3$N$_2$/C$_3$N$_2$	47.6(2)(48.1(2))	47.9(1)	27.3(3)
C$_3$N$_2$/N$_4$	27.0(2), 21.0(2) (27.2(2), (21.1(2))	24.1(1)	13.7(2)
	(c) Selected Geometries about the Boron Interbond Angles (c = coordinated pz; u = uncoordinated pz)		
N(c)−B−N(c)	111.4(3) (112.1(5))	107.3(3)	112.2(6)
N(c)−B−N(u)	112.5(4), 110.8(4) (113.4(4), 110.8(4))	109.7(2) (×2)	106.7(5) (×2)
B−N(u)−N(u)	116.3(4)(116.1(4))	121.8(2)	117(1)
B−N(u)−C(u)	131.6(5) (132.0(5))	129.6(2)	131(1)

[a] **3b** counterpart values (common chirality) in parentheses.

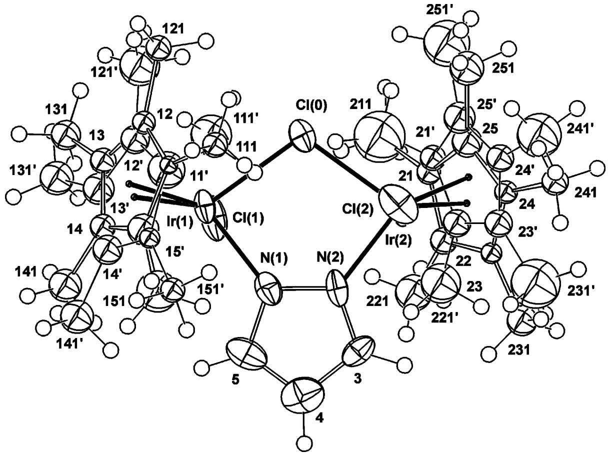

Figure 5. Projection of the dimer of **10**.

chelate ring are surprisingly unsymmetrical, the asymmetry correlating with the asymmetry of the uncoordinated pendant ring in the two phases of **3** (Table 2).

Although less precisely secured, because of Cp* disorder as modeled, **10** is definitively established as binuclear {[IrCp*Cl]$_2$(μ-Cl)(μ-pz)} (Table 1, Figure 5); although devoid of crystallographic symmetry, the molecule has quasi-2 symmetry, the putative 2-axis passing through the bridging chlorine, the center of the pz N−N bond, and C(4). Although the disorder may be presumed to impact on the remainder of the structure, concomitant components of the remaining atoms are not resolvable; some caution should be adopted in the use of associated/derivative dimensions.

Conclusions

We have synthesized and characterized (IR, NMR, X-ray) a series of air-stable mixed-sandwich complexes of Cp* and Tp′ with Rh(III) and Ir(III). The successful outcome of the synthesis of these complexes is dependent on the reaction conditions employed, short reaction times, anhydrous solvents, and standard Schlenk techniques being generally required. Some of these compounds are neutral with the formulation MCp*(Tp′)Cl, containing η^5-Cp* and κ^2-Tp′-M linkages, with the overall octahedral coordination environment being achieved by means of coordination of one chloride group. Others are 1:1 electrolytes, [MCp*Tp]X, a distorted octahedral environment arising from κ^3-Tp and an η^5-Cp* ligands, when X is a weakly coordinating anion such as NO$_3^-$, the steric hindrance preventing isolation of mixed κ^3-Tp*/η^5-Cp* complexes. Two different conformers have been found for the MCp*(Tp′)Cl species, but they do not undergo exchange between the coordinated and the free pyrazolyl groups. B−N bond breaking probably due to water attack on the free pyrazolyl of Tp′ ligands occurs when imperfectly anhydrous conditions are employed, Rh(III) and Ir(III) species containing coordinated neutral pyrazoles being readily generated. Another hydrolytic process is operative when Bp is used as chelating ligand, an iridium(III) cyclopentadienyl dimer containing a bridging pyrazolate group being obtained.

Experimental Section

Materials and Methods. All chemicals and reagents were of reagent grade quality and were used as received without further purification. All solvents were distilled prior to use. Toluene and light petroleum (40−60 °C) were dried by refluxing over freshly cut sodium. Methanol was dried over CaO. Dichloromethane was freshly distilled from CaH$_2$. Other solvents were dried and purified by standard procedures. The samples were dried in vacuo to constant weight (20 °C, ∼0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNSO-elemental analyzer. IR spectra from 4000 to 150 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a VXR-300 Varian spectrometer (300 for ^{1}H and 75 MHz for ^{13}C, respectively). Melting points were determined using an IA 8100 Electrothermal instrument.

Syntheses. RhCp*(Tp)Cl (1). A toluene solution/suspension (10 mL) containing [RhCp*Cl$_2$]$_2$ (0.310 g, 0.5 mmol) and KTp (0.250 g, 1.0 mmol) was stirred overnight under N$_2$ at room temperature to give a red-orange precipitate, which was filtered off and washed with 5 mL of toluene. The orange-brown residue obtained was recrystallized from 1:1 CH$_2$Cl$_2$/light petroleum (40−60 °C) and shown to be compound **1** (0.340 g, 0.7 mmol, 70% yield). Mp: 233 °C dec. Anal. Calcd for C$_{19}$H$_{25}$BClN$_6$Rh: C, 46.90; H, 5.18; N, 17.27. Found: C, 46.81; H, 5.35; N, 17.12. IR (Nujol, cm^{-1}): 3150w, 3131w, 3114w, 3099m, 3088m ν(C−H), 2452m ν(B−H), 1557w, 1540w, 1504s, ν(C$\cdots$C, C$\cdots$N), 589w, 542w, 453m, 433m, 399br, 377w, 328w, 314w, 278s ν(Rh−Cl), 264s, 241m, 225m. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.64 (s, 15H, CH_{3Cp*}), 6.27 (pt, 2H, 4-CH_{Tp}, J(H−H) = 1.8 Hz), 6.42 (pt, 1H, 4-CH_{Tp} J(H−H) = 1.8 Hz), 7.06 (pd, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.6 Hz), 7.70 (d, 1H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.72 (d, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.82 (d, 1H, 3- or 5-CH_{Tp}, J(H−H) = 1.8 Hz). ^{1}H NMR (CDCl$_3$, 203 K): δ 1.63 (s, 15H, CH_{3Cp*}), 6.28 (pt, 2H, 4-CH_{Tp}, J(H−H) = 1.8 Hz), 6.39, 6.42 (2 pt, 1H, 4-CH_{Tp} J(H−H) = 1.8 Hz), 7.01 (pd, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.6 Hz), 7.67 (d, 1H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.64, 7.69, 7.75, 7.92 (4d, 2H, 3- or 5-CH_{Tp}, J(H−H) = 1.8 Hz). ^{13}C NMR (CDCl$_3$, 293 K): δ, 9.21 (s, CH$_{3Cp*}$), 95.57 (d, C$_{Cp*}$, J(^{103}Rh−^{13}C): 8.6 Hz), 105.48, 106.59, (s, $C4_{Tp}$), 135.65, 135.81 (s, $C3_{Tp}$ or $C5_{Tp}$) 141.67, 142.70 (s, $C3_{Tp}$ or $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 1.2 Ω^{-1} cm^2 mol^{-1}.

IrCp*(Tp)Cl (2). Compound **2** (0.425 g, 0.74 mmol, 74% yield) was prepared following a procedure similar to that reported for **1** by using [IrCp*Cl$_2$]$_2$ and NaTp and was recrystallized from CH$_2$Cl$_2$/light petroleum (40−60 °C). Mp: 222 °C. Anal. Calcd for C$_{19}$H$_{25}$BClIrN$_6$: C, 39.62; H, 4.38; N, 14.59. Found: C, 39.46; H, 4.70; N, 14.32. IR (Nujol, cm^{-1}): 3115w, 3100w, 3089w ν(C−H), 2453w ν(B−H), 1560w, 1534w, 1500sh, ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 454w, 445w, 382w, 357w, 277s, 267s ν(Rh−Cl), 226m. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.62 (s, 15H, CH_{3Cp*}), 6.26 (pt, 2H, 4-CH_{Tp}, J(H−H) = 1.8 Hz), 6.42 (pt, 1H, 4-CH_{Tp} J(H−H) = 1.8 Hz), 6.98 (pd, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.6 Hz), 7.62 (pd, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.62 (d, 1H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.82 (d, 1H, 3- or 5-CH_{Tp}, J(H−H) = 1.8 Hz). ^{1}H NMR (CDCl$_3$, 203 K): δ 1.58 (s, 15H, CH_{3Cp*}), 6.23 (pt, 2H, 4-CH_{Tp}, J(H−H) = 1.8 Hz), 6.38, 6.41 (2 pt, 1H, 4-CH_{Tp} J(H−H) = 1.8 Hz), 6.89 (pd, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.6 Hz), 7.58 (d, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.68, 7.73, 7.76, 7.87 (4d br, 2H, 3- or 5-CH_{Tp}). ^{13}C NMR (CDCl$_3$, 293 K): δ 9.06 (s, CH$_{3Cp*}$), 87.36 (d, C$_{Cp*}$), 105.43, 106.47, (s, $C4_{Tp}$), 135.14, 135.91 (s, $C3_{Tp}$ or $C5_{Tp}$) 141.87, 142.31 (s, $C3_{Tp}$ or $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 1.1 Ω^{-1} cm^2 mol^{-1}.

RhCp*(Tp*)Cl (3). Compound **3** (0.456 g, 0.8 mmol, 80% yield) was prepared following a procedure similar to that reported for **1** and was recrystallized from CH$_2$Cl$_2$/light petroleum (40−60 °C). Mp: 202 °C. Anal. Calcd for C$_{25}$H$_{37}$BClN$_6$Rh: C, 52.61; H, 6.53; N, 14.72. Found: C, 52.23; H, 6.36; N, 14.39. IR (Nujol, cm^{-1}): 2489w, 2409w ν(B−H), 1571w, 1551m, 1531m, 1504w, ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 541w, 473w, 454vw, 428vw, 419w, 352w, 326w, 260s ν(Rh−Cl), 247m, 236m, 225m. ^{1}H NMR (CDCl$_3$): δ 1.34 (s, 15H, CH_{3Cp*}), 1.50 (s, 3H, CH_{3Tp*}), 1.63 (s, 3H, CH_{3Tp*}), 2.39 (s, 6H, CH_{3Tp*}), 2.47(s, 6H, CH_{3Tp*}), 5.75 (s, 1H, 4-CH_{Tp*}), 6.04 (s, 2H, 4-CH_{Tp*}). ^{13}C NMR (CDCl$_3$): δ 8.79 (s, CH$_{3Cp*}$), 10.94, 13.87, 14.88, 16.63 (s, CH$_{3Tp*}$), 95.90 (d, C$_{Cp*}$, J(^{103}Rh−^{13}C): 7.95 Hz), 107.31, 109.42 (s, $C4_{Tp}$), 143.01, 148.61, 150.01, 152.68 (s, $C3_{Tp}$ and $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 2.2 Ω^{-1} cm^2 mol^{-1}.

IrCp*(Tp*)Cl (4). Compound **4** (0.429 g, 0.65 mmol, 65% yield) was prepared following a procedure similar to that reported for **1** by using [Ir(Cp*)Cl$_2$]$_2$ and KTp* and was recrystallized from CH$_2$Cl$_2$/light petroleum (40−60 °C). Mp: 129 °C dec. Anal. Calcd for C$_{25}$H$_{37}$BClIrN$_6$: C, 45.49; H, 5.65; N, 12.73. Found: C, 45.77; H, 6.00; N, 12.85. IR (Nujol, cm^{-1}): 3098w ν(CH), 2444m, 2440m ν(B−H), 1540s ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 540w, 495w, 466w, 450m, 424w, 383w, 314s, 285sh, 280s ν(Ir−Cl), 227m. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.36 (s, 15H, CH_{3Cp*}), 1.70 (s, 3H, CH_{3Tp*}), 1.74 (s, 6H, CH_{3Tp*}), 2.18 (s, 3H, CH_{3Tp*}), 2.47(s, 6H, CH_{3Tp*}), 5.59 (s, 1H, 4-CH_{Tp*}), 5.89 (s, 2H, 4-CH_{Tp*}). ^{13}C NMR (CDCl$_3$): δ, 8.59 (s, CH$_{3Cp*}$), 10.68, 12.07, 14.27, 16.95 (s, CH$_{3Tp*}$), 88.06 (s, C$_{Cp*}$), 104.16, 104.86 (s, $C4_{Tp}$), 143.25, 151.70 (s, $C3_{Tp}$ and $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 1.7 Ω^{-1} cm^2 mol^{-1}.

[Rh(Cp*)Tp]NO$_3$ (5). AgNO$_3$ (0.85 g, 0.5 mmol) was added to a CH$_3$CN (7 mL) solution/suspension of **1** (0.243 g, 0.5 mmol) under N$_2$. After 48 h at room temperature a colorless precipitate formed, which was filtered off and shown to be AgCl. The clear orange solution obtained was evaporated under vacuum and the residue washed with light petroleum and shown to be compound **5** (0.135 g, 0.26 mmol, 53%). It was recrystallized from CH$_2$Cl$_2$/light petroleum (40−60 °C). Mp: 240 °C dec. Anal. Calcd for C$_{19}$H$_{25}$BN$_7$O$_3$Rh: C, 44.47; H, 4.91; N, 19.11. Found: C, 44.32; H, 5.22; N, 18.78. IR (Nujol, cm^{-1}): 3149w, 3100w, 3092w ν(C−H), 2490m ν(B−H), 1530w, 1513w, 1502s ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 454w, 358w, 253sh, 246s. ^{1}H NMR (CDCl$_3$): δ 1.99 (s, 15H, CH_{3Cp*}), 6.40 (pt, 3H, 4-CH_{Tp}, J(H−H) = 2.2 Hz), 7.69 (pd, 3H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.98 (pd, 3H, 3- or 5-CH_{Tp}, J(H−H) = 1.8 Hz). ^{13}C NMR (CDCl$_3$, 293 K): δ 9.43 (s, CH$_{3Cp*}$), 97.70 (s, C$_{Cp*}$), 107.23 (s, $C4_{Tp}$), 136.11, (s, $C3_{Tp}$ or $C5_{Tp}$) 140.82 (s, $C3_{Tp}$ or $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 134.2 Ω^{-1} cm^2 mol^{-1}.

[Ir(Cp*)Tp]NO$_3$ (6). Compound **6** (0.198 g, 0.33 mmol, 66% yield) was prepared following a procedure similar to that reported for **5** by using **2**, being recrystallized from CH$_2$Cl$_2$/light petroleum (40−60 °C). Mp: 168 °C dec. Anal. Calcd for C$_{19}$H$_{25}$BIrN$_7$O$_3$: C, 37.88; H, 4.18; N, 16.27. Found: C, 37.95; H, 4.32; N, 16.54. IR (Nujol, cm^{-1}): 3165w, 3100w, 3090w ν(C−H), 2496w ν(B−H), 1557w, ν(C$\cdots$C, C$\cdots$N), 453w, 371w. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.91 (s, 15H, CH_{3Cp*}), 6.40 (pt, 3H, 4-CH_{Tp}, J(H−H) = 2.2 Hz), 7.77 (pd, 3H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.90 (pd, 3H, 3- or 5-CH_{Tp}, J(H−H) = 1.8 Hz). ^{13}C NMR (CDCl$_3$, 293 K): δ 9.86 (s, CH$_{3Cp*}$), 89.9 (s, C$_{Cp*}$), 107.75 (s, $C4_{Tp}$), 135.87, (s, $C3_{Tp}$ or $C5_{Tp}$) 141.07 (s, $C3_{Tp}$ or $C5_{Tp}$). Λ_m (CH$_3$CN, 10^{-3} M): 129 Ω^{-1} cm^2 mol^{-1}.

RhCp*BpCl (7). A toluene solution/suspension (10 mL) containing [RhCp*Cl$_2$]$_2$ (0.310 g, 0.5 mmol) and KBp (0.186 g, 1.0 mmol) was stirred overnight under N$_2$ at room temperature. A red-orange precipitate formed. The suspension was then evaporated and the residue extracted with light petroleum (40−60 °C). From the frozen light petroleum solution a red crystalline precipitate was obtained, which was identified as **7** (0.310 g, 0.74 mmol, 74% yield). Mp: 170−172 °C dec. Anal. Calcd for C$_{16}$H$_{23}$BClN$_4$Rh: C, 45.70; H, 5.51; N, 13.32. Found: C, 45.85; H, 5.60; N, 13.33. IR (Nujol, cm^{-1}): 3150w, 3114w, 3099m, ν(C−H), 2453w, 2406m, 2389m, 2373sh, 2349m, 2279m ν(B−H), 1567w, 1537w, 1531w, 1504s, ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 537w, 542w, 453m, 433m, 330w, 314w, 279s ν(Rh−Cl), 264s, 246m, 230br, 213m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 1.62 (s, 15H, CH_{3Cp*}), 6.26 (pt, 2H, 4-CH_{Tp}, J(H−H) = 1.8 Hz), 7.59 (d, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz), 7.63 (d, 2H, 3- or 5-CH_{Tp}, J(H−H) = 2.2 Hz). ^{13}C NMR (CDCl$_3$): δ 9.19 (s, CH$_{3Cp*}$), 95.2 (s, C$_{Cp*}$), 106.00 (s, $C4_{Tp}$), 136.83, (s, $C3_{Tp}$ or $C5_{Tp}$) 141.90 (s, $C3_{Tp}$ or $C5_{Tp}$).

RhCp*Cl$_2$(pz*H) (8). To a solution of [RhCp*Cl$_2$]$_2$ (0.155 g, 0.25 mmol) in CH$_2$Cl$_2$ (6 mL) was added dropwise a solution of KTp* (0.125 g, 0.5 mmol) in CH$_2$Cl$_2$ (6 mL). The reaction mixture was stirred for 48 h at room temperature. A colorless precipitate formed, which was filtered off. The red-orange solution was then evaporated under vacuum; the residue, washed with light petroleum (40−60° C), has been identified as **8**. Mp: 180 °C dec. Anal. Calcd for C$_{15}$H$_{23}$Cl$_2$N$_2$Rh: C, 44.47; H, 5.72; N, 6.91. Found: C, 44.41; H, 5.84; N, 7.21. IR (Nujol, cm^{-1}): 3240br ν(N−H), 1566s, 1540m ν(C$\overset{\cdot\cdot}{-}$C, C$\overset{\cdot\cdot}{-}$N), 587w, 540w, 455w, 445w, 436w, 397w, 313w, 303w, 272s, ν(Rh−Cl) 253m, 248m. ^{1}H NMR (CDCl$_3$, 293 K): δ, 1.65 (s, 15H, CH_{3Cp*}), 2.27 (s, 3H, 3-CH_{3pz}), 2.46 (s, 3H, 5-CH_{3pz}), 5.96 (s, 1H, 4-CH_{pz}), 11.1 (br, 1H, NH_{pz}). ^{13}C NMR (CDCl$_3$, 293 K): δ 9.42 (s, CH$_{3Cp*}$), 14.3 (br, CH$_{3pz}$), 94.42 (d, C_{Cp*}, J(^{103}Rh−^{13}C): 8.9 Hz) 108.12 (s, $C4_{pz}$).

IrCp*Cl$_2$(pzH) (9). To a solution of [IrCp*Cl$_2$]$_2$ (0.200 g, 0.25 mmol) in toluene at room temperature was added KBp (0.093 g, 0.5 mmol). The solution was stirred overnight under N$_2$. A colorless precipitate formed (KCl), which was filtered off. The solution was then evaporated and the residue extracted with light petroleum (20 mL). A red precipitate formed, which was filtered off and washed with 10 mL of light petroleum and identified as compound **9**. Mp: 265 °C dec. Anal. Calcd for C$_{13}$H$_{19}$Cl$_2$IrN$_2$: C, 33.48; H, 6.01; N, 4.11. Found: C, 33.72; H, 6.12; N, 4.18. IR (Nujol, cm^{-1}): 3251br

Table 3. Crystal/Refinement Data

	2 IrCp*(T_p)Cl	**3**(≡**3**a)[a] RhCp*(T_p*)Cl	**3**b(≡**3**·H_2O)[b] RhCp*(T_p*)Cl·H_2O	**4**[c] IrCp*(T_p*)Cl	**8** RhCp*Cl_2(pz*H)	**10**[d] {[IrCp*Cl]$_2$(μ-Cl)(μ-pz)}
formula	$C_{19}H_{25}BClIrN_6$	$C_{25}H_{37}BClN_6Rh$	$C_{25}H_{39}BClN_6ORh$	$C_{25}H_{37}BClN_6Ir$	$C_{15}H_{23}Cl_2N_2Rh$	$C_{23}H_{33}Cl_3Ir_2N_2$
M_r	575.9	576.8	588.8	660.1	405.2	828.3
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/m$(#11)	$P2_1$(#4)	$P2_1/c$(#14)	$Cmc2_1$(#36)	$P\bar{1}$ (#2)	$P2_1/c$(#14)
a/Å	7.1427(8)	9.160(1)	10.987(3)	10.9192(9)	7.0809(5)	10.6875(9)
b/Å	12.085(1)	13.725(2)	14.043(4)	23.088(2)	8.8564(7)	16.980(2)
c/Å	12.077(1)	11.216(1)	17.428(5)	10.4204(9)	14.041(1)	13.871(1)
α/deg					73.309(2)	
β/deg	97.596(2)	113.480(3)	94.991(5)		81.709(2)	92.353(3)
γ/deg					74.761(2)	
V/Å^3	1033	1293	2678	2627	811.5	2515
D_c/g cm^{-3}	1.851	1.465	1.460	1.669	1.658	2.187
Z	2	2	4	4	2	4
μ_{Mo}/mm^{-1}	6.6	0.79	0.77	5.2	1.4	10.9
specimen (mm^3)	0.4 × 0.14 × 0.03	0.32 × 0.20 × 0.01	0.19 × 0.16 × 0.13	0.18 × 0.07 × 0.05	0.28 × 0.15 × 0.13	0.20 × 0.15 × 0.13
$T_{min./max.}$	0.74	0.77	0.81	0.68	0.84	0.53
$2\theta_{max}$/deg	75	70	50	65	75	55
N_t	21323	26505	20925	20685	16590	51402
$N(R_{int})$	5564(0.035)	5737(0.042)	4696(0.063)	2581(0.042)	8298(0.015)	5773(0.070)
N_o	4755	4958	3204	2266	7945	5023
R	0.035	0.043	0.044	0.023	0.017	0.059
R_w	0.036	0.053	0.046	0.025	0.023	0.14

[a] With "Friedel" data preserved distinct, refinement of x_{abs} was indeterminate of chirality; accordingly data were merged in the final least squares cycles. [b] A difference map residue was modeled as a water molecule oxygen atom (associated hydrogens not located). [c] Preferred chirality ($x_{abs} = 0.01(1)$). [d] With data measured on "difficult" material, the structure, as modeled, exhibits disorder in the two Cp* units, with each ring somewhat rotated about a slightly displaced centroid. Site occupancies of each component were set at 0.5 after trial refinement, Cp* units being treated as rigid bodies.

ν(NH), 3122w, 1557w, 1519m, 588m, 537w, 465w, 455w, 282s, 261s, 247m, 226m. ^{1}H NMR ($CDCl_3$, 293 K): δ, 1.60 (s, 30H, CH_{3Cp*}), 6.45 (pt, 1H, 4-CH_{Tp}, J(H−H) = 2.4 Hz), 7.59 (pd, 1H, 3- or 5-CH_{Tp}, J(H−H) = 2.1 Hz), 7.62 (pd, 1H, 3- or 5-CH_{Tp}, J(H−H) = 2.1 Hz). ^{1}H NMR ($CDCl_3$, 303 K): δ 1.62 (s, 30H, CH_{3Cp*}), 6.45 (br, 1H, 4-CH_{Tp}), 7.61 (br, 2H, 3- or 5-CH_{Tp}). ^{13}C NMR ($CDCl_3$, 295 K): 9.24 (s, CH$_{3Cp*}$), 86.18 (s, C_{Cp*}), 108.0 (s, $C4_{pz}$), 129.92 (s, $C3_{pz}$ or $C5_{pz}$), 140.60 (s, $C3_{pz}$ or $C5_{pz}$).

{[IrCp*Cl]$_2$(μ-Cl)(μ-pz)} (10). Compound **10** was obtained as red crystals in 40% yield from the frozen light petroleum solution of the reaction above-described between [IrCp*Cl_2]$_2$ and KBp. Mp: 140 °C dec. Anal. Found: C, 36.55; H, 4.62; N, 3.56. Calcd for $C_{23}H_{33}ClIr_2N_2$: C, 36.47; H, 4.39; N, 3.70. IR (Nujol, cm^{-1}): 3111w, 1540w, 1506m, 440w, 275m, 260m, 220m. ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 30H, CH_{3Cp*}), 6.27 (pt, 1H, 4-CH_{Tp}, J(H−H) = 2.4 Hz), 7.65 (pd, 2H, 3- and 5-CH_{Tp}, J(H−H) = 2.1 Hz).

Crystal Structure Determinations. Full spheres of "low-temperature" CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, T ca. 153 K; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å), yielding $N_{(total)}$ reflections, these merging to N unique (R_{int} quoted) after multiscan/"empirical" absorption correction (proprietary software); N_o with $F > 4\sigma(F)$ were used in the full matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates unless otherwise noted. Conventional residuals R, R_w (weights: $((\sigma^2(F) + 0.0004F^2)^{-1})$ on $|F|$ are cited at convergence; neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[26] Pertinent results are given below and in the tables and figures, the latter showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Crystal and refinement data are reported in Table 3.

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Supporting Information Available: Details of the structure determinations for complexes **2**, **3**, **4**, **8**, and **10**, including tables of crystal and intensity collection data, positional and anisotropic thermal parameters, and all of the bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020930M

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(26) Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds. *The Xtal 3.7 System*; University of Western Australia, 2001.