Hydrotris(pyrazolyl)borato Cycloocta-1,5-diene Complexes of Iridium(I): Synthetic Studies and Equilibria in Solution. X-ray Crystal Structures of a Four- and a Five-Coordinate Iridium(I) Hydrotris(pyrazolyl)borato Complex

Alberto Albinati,[†] Mike Bovens,[‡] Heinz Rüegger,[‡] and Luigi M. Venanzi*[,‡]

Istituto di Chimica Farmaceutica, Università di Milano, I-20131 Milano, Italy, and Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland

Received March 27, 1997[⊗]

The compounds [$Tp^{3R,4R,5R}$Ir(COD)] (COD = cycloocta-1,5-diene; $Tp^{3R,4R,5R}$ = hydrotris(pyrazolyl)borate (**1**), hydrotris(3-methylpyrazolyl)borate (**2**), hydrotris(3-isopropylpyrazolyl)borate (**3**), hydrotris(3,5-dimethylpyrazolyl)-borate, hydrotris(3-(trifluoromethyl)-5-methylpyrazolyl)borate, hydrotris(3-phenyl-5-methylpyrazolyl)borate, hydrotris(3,5-diisopropylpyrazolyl)borate, hydrotris(3,4,5-trimethylpyrazolyl)borate, hydrotris(4-chloro-3,5-dimethylpyrazolyl)borate (**9**), hydrotris(4-bromo-3,5-dimethylpyrazolyl)borate) were prepared and characterized by IR and NMR spectroscopy. The X-ray crystal structure of **9**·2MeOH (triclinic, space group $P\bar{1}$ (No. 2); a = 10.044-(1) Å, b = 11.186(2) Å, c = 15.499(3) Å; α = 77.90(1)°, β = 73.23(1)°, γ = 66.89(1)°; Z = 2; R = 0.0276 for 2469 observed reflections) shows that iridium is four-coordinate with an η^2-hydrotris(pyrazolyl)borate. The X-ray crystal structure of **1** (triclinic, space group $P\bar{1}$ (No. 2); a = 7.345(1) Å, b = 7.645(1) Å, c = 15.893(5) Å; α = 103.17(4)°, β = 90.30(2)°, γ = 93.50(3)°; Z = 2; R = 0.0433 for 2606 observed reflections) shows that iridium is five-coordinate with an η^3-bonded tris(pyrazolyl)borate. Equilibria between corresponding four- (η^2-$Tp^{3R,4R,5R}$) and five-coordinate (η^3-$Tp^{3R,4R,5R}$) species of all the complexes are established in solution. The complex containing the ligand $HB(Pz^{3Me})_3$ (Pz = pyrazolyl group) (**2**) rearranged first to the corresponding complex with $HB(Pz^{3Me})_2(Pz^{5Me})$ and then into that with $HB(Pz^{3Me})(Pz^{5Me})_2$. However, **3**, which contains $HB(Pz^{3iPr})_3$, gave only the complex with coordinated $HB(Pz^{3iPr})_2(Pz^{5iPr})$.

Introduction

In recent years the coordination chemistry of nitrogen donors with the platinum metals has been increasingly studied, as many complexes of these ligands give active catalysts for a wide variety of organic reactions.[1] These studies were recently extended to the complexes formed by the hydrotris(pyrazolyl)-borate anions $[Tp^{3R,4R,5R}]^-$,[2] and the newer developments in this area have been reviewed by Trofimenko.[3]

The hydrotris(pyrazolyl)borato complexes of iridium(I) have received particular attention,[4−16] as some of them, *e.g.*, [$Tp^{CF_3,Me}$-Ir(CO)(C_2H_4)][7] and [$Tp^{Me_2}Ir(C_2H_4)_2$],[14] analogously to some rhodium(I) compounds, *e.g.*, [$Tp^{Me_2}Rh(CO)_2$],[17] easily generate transient species which activate C−H bonds. Additional interest in compounds of the type [$Tp^{3R,4R,5R}ML_2$] (M = Rh, Ir) is connected with the variable denticity of the Tp-type ligands which can show either η^2- or η^3-Tp coordination in the solid state and in solution.[13,18,19]

In general, the reactivity and, therefore, the potential for catalytic applications of complexes of the type "$Tp^{3R,4R,5R}Ir^IL_2$" are likely to depend on the coordination numbers and geometries of the species present in their solutions. Thus, it is desirable to study the influence of the substituents R of the $Tp^{3R,4R,5R}$ anions and the coligands L on the types of products formed, and if more than one species is present in solution, what equilibria are established between such species. As the most readily prepared complexes of the above type are those where L_2 = cycloocta-1,5-diene (COD), extensive structural and solution studies were undertaken of species of the type [$Tp^{3R,4R,5R}$Ir-(COD)].

[†] Università di Milano.
[‡] ETH Zürich.
[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.
(2) The nomenclature used in this publication for the hydrotris(pyrazolyl)-borate ligands and their complexes is that proposed by Trofimenko (see ref 3): (Tp = hydrotris(pyrazolyl)borate, Tp^{Me} = hydrotris(3-methylpyrazolyl)borate, Tp^{iPr} = hydrotris(3-isopropylpyrazolyl)borate, Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borate, $Tp^{CF_3,Me}$ = hydrotris-(3-(trifluoromethyl)-5-methylpyrazolyl)borate, Tp^{iPr_2} = hydrotris(3,5-trimethylpyrazolyl)borate, $Tp^{Me_2,4Cl}$ = hydrotris(3,5-dimethyl-4-chloro-pyrazolyl)borate, $Tp^{Ph,Me}$ = hydrotris(3-phenyl-5-methylpyrazolyl)-borate.
(3) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(4) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726 and **1989**, *111*, 375.
(5) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.
(6) Ball, R. R.; Gosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341.
(7) Gosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480.
(8) Fernandez, M. J.; Rodriguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073.
(9) Pérez, P. J.; Poveda, M. L.; Carmona, E. *J. Chem. Soc., Chem. Commun.* **1992**, 8.
(10) Bovens, M.; Gerfin, T.; Gramlich, V.; Petter, W.; Venanzi, L. M.; Howard, M. T.; Jackson, S. A.; Eisenstein, O. *New J. Chem.* **1992**, *16*, 337.
(11) Fernández, M. J.; Rodríguez, M. J.; Oro, L. A. *J. Organomet. Chem.* **1992**, *438*, 337.
(12) Fernández, M. J.; Modrego, J.; Rodríguez, M. J.; Santamaria, M. C.; Oro, L. A. *J. Organomet. Chem.* **1992**, *441*, 155.
(13) Ciriano, M. A.; Fernandez, M. J.; Modrego, J.; J. Rodriguez, M.; Oro, L. A. *J. Organomet. Chem.* **1993**, *443*, 249.
(14) Boutry, O.; Guitiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.
(15) Guitiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791.
(16) Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519.
(17) (a) Bloyce, P. E.; Mascetti, J.; Rest, A. J. *J. Organomet. Chem.* **1993**, *444*, 223. (b) Purwoko, A. A.; Lees, A. J. *Inorg. Chem.* **1995**, *34*, 424.
(18) Cocivera, M.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J.; Parvez, M.; Ruhl, B. *Organometallics* **1982**, *1*, 1132.
(19) Bucher, U. E.; Currao, A.; Nesper, R.; Rüegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1995**, *34*, 66 and references quoted therein.

S0020-1669(97)00361-3 CCC: $14.00

This paper reports the preparation and characterization of several complexes of composition $[Tp^{3R,4R,5R}Ir(COD)]$ and a study of their behavior in solution. Particular attention is given to (a) their hydrolytic stabilities, (b) their static structures, (c) the equilibria between corresponding four- and five-coordinate species containing η^2- and η^3-bonded Tp-type ligands, respectively, and (d) the 1,2-borotropic rearrangement of pyrazolyl rings in complexes of the type $[Tp^{3R}Ir(COD)]$.

Results

Synthesis. Several complexes of the type $[Tp^{3R,4R,5R}Ir(COD)]$ were prepared by the synthetic route shown in eq 1.

$$[Ir_2(\mu\text{-}Cl_2)(COD)_2] + 2\,M[Tp^{3R,4R,5R}] \xrightarrow{MeCN} 2\,[Tp^{3R,4R,5R}Ir(COD)] + 2\,MCl \quad (1)$$

(M = Na or K)

#	$Tp^{3R,4R,5R}$	^3R	^4R	^5R	#	$Tp^{3R,4R,5R}$	^3R	^4R	^5R
1	Tp	H	H	H	**6**	$Tp^{Ph,Me}$	Ph	H	Me
2	Tp^{Me}	Me	H	H	**7**	Tp^{iPr2}	^{i}Pr	H	^{i}Pr
3	Tp^{iPr}	Pr	H	H	**8**	$Tp^{Me2,4Me}$	Me	Me	Me
4	Tp^{Me2}	Me	H	Me	**9**	$Tp^{Me2,4Cl}$	Me	Cl	Me
5	$Tp^{CF3,Me}$	CF_3	H	Me	**10**	$Tp^{Me2,4Br}$	Me	Br	Me

It is noteworthy that, in almost every case, their formation was accompanied by that of a small amount of a violet byproduct (**11**) which proved to be a dinuclear complex of the type $[Ir_2(\mu\text{-}Pz^{3R,4R,5R})_2(COD)_2]$.[20−22]

Complexes **1** and **4**−**10** are air-stable, yellow to orange solids. However, **2** and **3** are best stored under an argon atmosphere. In solution, most compounds slowly decompose to the corresponding violet products **11**. Their decomposition rates vary with the substitution pattern on the pyrazolyl rings, solvent used, and its moisture content (see Experimental Section).

The infrared spectra of all the compounds, recorded in RbI pellets, show that the ν(B−H) stretching vibrations, which occur in the region 2398−2506 cm^{-1} (see Table 1), are strongly influenced by the nature of the substituents on the Pz rings, the highest value of ν(B−H) being that found for $[Tp^{CF_3,Me}Ir(COD)]$ (**5**), where three strongly electron-attracting CF_3 substituents are present.

As previously established for $[Tp^{Me_2}Ir(COD)]$ (**4**),[10] complexes **1**−**3** and **5**−**10** show equivalent pyrazolyl groups on the NMR time scale, at room temperature. A study of the temperature dependence of the ^{1}H NMR spectra of [TpIr(COD)] (**1**), $[Tp^{Me_2}Ir(COD)]$ (**4**), and $[Tp^{iPr_2}Ir(COD)]$ (**7**) showed that these compounds are still dynamic at 180 K. However, at 173 K, the shape of the ^4H(Pz) signal of $[TpIr^{iPr_2}(COD)]$ (**7**) indicates that this compound may be approaching a "static" structure.

Table 1. ν(B−H) Stretching Frequencies (cm^{-1}) for Complexes of the Types $[Tp^{3R,4R,5R}Ir(COD)]$ (ν(Ir)) and $[Ph_4P][Tp^{3R,4R,5R}RhCl_3]$ (ν(Rh)) and NMR Parameters for Complexes of the Type $[Tp^{3R,4R,5R}Ir(COD)]$

no.	^3R	^4R	^5R	ν(Ir)[a]	ν(Ir)[b]	ν(Rh)[b]	$\delta(^1H(ol))$[c]	$\delta(^{13}C(ol))$[c]
1	H	H	H	2479	2462	2483	3.54	54.1
2A	Me	H	H	2420	2425	2476	4.12[d]	66.6/61.3[e]
2B	Me	H	H	2400	2425	2476	3. 87[d]	63.8
3A	^{i}Pr	H	H	2410	2398	2487	3.91/4.07[f]	64.4
3B	^{i}Pr	H	H	2410	2398	2487	3.75[f]	64.4
4	Me	H	Me	2476	2465	2535	3.87	63.4
5	CF_3	H	Me	2506	2493	2581	3.93	66.7
6	Ph	H	Me	2480	2466	...[g]	3.10	65.6
7	^{i}Pr	H	^{i}Pr	2481	2481	...[g]	3.87	63.6
8	Me	Me	Me	2474	2468	2528	3.83	63.3
9	Me	Cl	Me	2486	2484	2548	3.86	64.6
10	Me	Br	Me	2487	2486	...[g]	3.90	64.9
13	...[h]	H	...[h]				3.74	55.4
14	...[h]	H	...[h]				3.52	52.9
15	...[h]	H	...[h]				3.72	63.2

[a] Recorded in CH_2Cl_2. [b] Recorded in RbI pellets. [c] COD olefinic resonances. [d] Broad signal centered at the given frequency. [e] Signals in a 1:1 ratio. [f] Broad signals, in an approximately 1:1:9 ratio, with maxima at the given frequencies. [g] Not available. [h] See text.

The NMR parameters for the C_{olefin} resonances (see Table 1) show interesting variations: While the ^{13}C δ values of compounds **2**−**7** and **10** fall in the narrow range 63.3−66.7 ppm, that of **1** occurs at 54.1 ppm. A similar pattern is observed for the ^{1}H($C-H_{alkene}$) chemical shifts: those of compounds **2**−**5** and **7**−**10** fall in the range 3.86−4.12 ppm, while that of **1** (3.54 ppm) is outside this range (see Table 1).

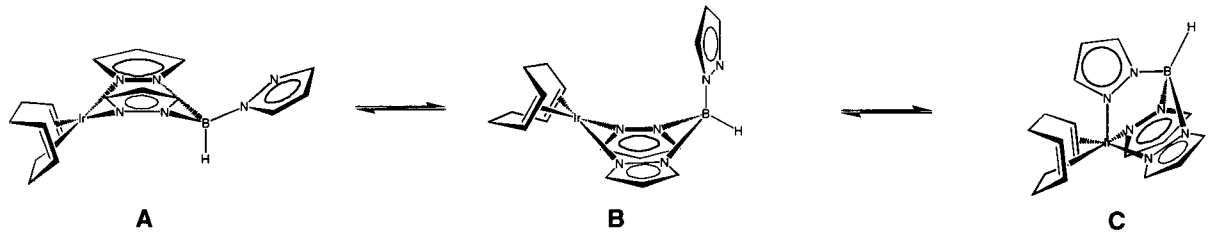
Earlier studies showed that, for complexes of the type $[Tp^{3R,4R,5R}Rh(diolefin)]$, the ^{15}N NMR chemical shifts can be used to assess the position of the fast equilibria between corresponding four-, **B**, and five-coordinate forms, **C** (see Scheme 1).[19] Therefore, these spectra were recorded for some of the above iridium compounds. While the chemical shift of an N^2 atom in an alkali metal salt of a hydrotris(pyrazolyl)-borate salt is ca. −75 ppm, this value changes by ca. −75 ppm upon coordination; *e.g.*, it is −150.5 ppm for $[(\eta^2\text{-}HTp^{Me_2})Ir(COD)](CF_3SO_3)$ (**12**) (HTp^{Me_2} = monoprotonated Tp^{Me_2}), a square planar complex of this bidentate nitrogen ligand.[10,23] Furthermore, the value of this parameter for $[Tp^{Me_2}\text{-}Ir(COD)]$ (**4**), ca. −125 ppm, corresponds to an average value of one free and two coordinated donor atoms in fast exchange on the NMR time scale (note that η^n, is calculated from the value given above using the equation $n = 3(\delta_{obs} - \delta_{free})/(\delta_{coord} - \delta_{free})$).

In order to obtain more information about solution equilibria in these complexes, their infrared spectra were also recorded, as this technique has a time scale which is much faster than that of NMR. It was found that the ν(B−H) values for all the complexes, in CH_2Cl_2 solution, differed only slightly from those in the solid state (see Table 1), and thus, in the former medium, these complexes appear to be, at least predominantly, present in the form characteristic of the solid state. However, these data do not exclude the existence of fast equilibria between conformers of the same isomer.

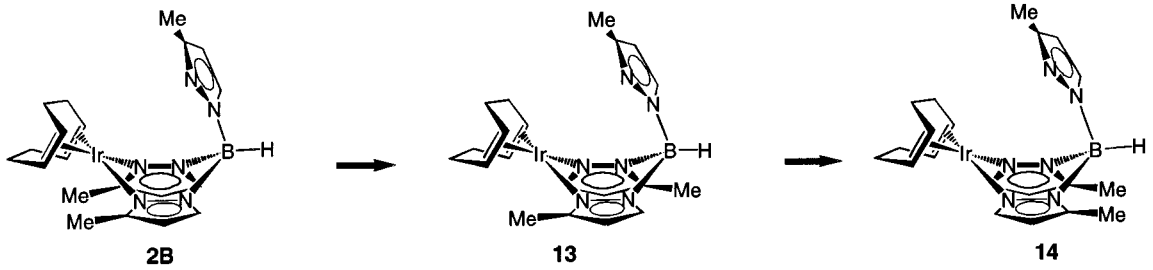
The ^{13}C NMR spectra of solutions of $[\eta^2\text{-}Tp^{Me}Ir(COD)]$ (**2**) show the presence of another form (**2A**) in addition to **2B**, the latter being in equilibrium with a small amount of **2C**.

(20) Bushnell, G. W.; Fjelsted, D. O. K.; Stobart, S. R.; Zaworotko, M. J.; Selby A. R, K.; Macpherson, K. A. *Organometallics* **1985**, *4*, 1107.
(21) Atwood, J. L.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1984**, *23*, 4050.
(22) Rodman, G. S.; Bard, A. J. *Inorg. Chem* **1990**, *29*, 4699.
(23) Albinati, A. Unpublished observations. An ORTEP view of this complex is shown in: Bovens, M. Dissertation, ETH Zürich, 1994; No. 10670.

Scheme 1



Scheme 2



Compound **2A** is a conformational isomer of **2B**, *i.e.*, one with the uncoordinated pyrazolyl ring in a pseudoequatorial position (see Scheme 1). The ratio of **2A**:**2B** is ca. 3:7. This is shown by the ^{15}N NMR spectrum of the solution containing the above mixture, as (a) the chemical shift of the bound nitrogen atoms N^2 in **2A** is −148 ppm and (b) the chemical shift of the equilibrium mixture **2B** ⇌ **2C** is −126 ppm. As a solution of [η^2-Tp^{Me_2}Ir(COD)] (**4**), which contains mainly form **B**, has a δ value of −125 ppm, it follows that also the position of the equilibrium **2B** ⇌ **2C** is shifted toward the former species. At room temperature, forms **2A** and **2B** are in slow exchange with a k value of ca. 10 s^{-1}.

Also solutions of [Tp^{iPr}Ir(COD)] (**3**) show the presence of two conformers, **3A** and **3B**, in the approximate ratio of 2:9, respectively. Their structures and dynamics are analogous to those found in complexes **2A** and **2B**.

The most unusual aspect of this study is a facile intramolecular ligand rearrangement which occurs in complexes of the type [Tp^{3R}Ir(COD)]. NMR studies of the products obtained by reacting [Ir$_2$(μ-Cl)$_2$(COD)$_2$] with Na[Tp^{Me}] at room temperature show that, in addition to the two conformational isomers **2A** and **2B** mentioned earlier, these solutions also contain [{HB(Pz^{3Me})$_2$(Pz^{5Me})}Ir(COD)] (**13**), *i.e.*, the iridium(I) complex of a tris(pyrazolyl)borate in which *one* of the pyrazolyl rings of the original ligand had undergone a 1,2-borotropic rearrangement,[19,24] the methyl substituent in this ring being now in position 5. This mixture, upon warming up to 70 °C for 45 min, gives a single product, [{HB(Pz^{3Me})(Pz^{5Me})$_2$}Ir(COD)] (**14**), in which *two* rings of the original hydrotris(pyrazolyl)borate ligand have rearranged (see Scheme 2). Complex **14** does not undergo further changes with more prolonged heating.

In the final product, **14**, the two rings which have undergone rearrangement, and now have a methyl substituent in position 5, are coordinated, as their ^{15}N chemical shift value is −148.9 ppm. However, the chemical shift of the ring which has not rearranged is −127.5 ppm. This value, taken in conjunction with the "standard" value for a coordinated N atom mentioned earlier, indicates that here the equilibrium **B** ⇌ **C** in **14** is ca. 70% in favor of the five-coordinate form **C**. The presence of two inverted rings in **14** was confirmed by NOE experiments (see figure in Supporting Information).

Shifts of the equilibria toward the five-coordinate forms **C** also occur in **13** and **14**, as suggested by the ^{13}C δ values of the olefinic carbon resonances, 55.4 and 52.9 ppm, respectively, values close to that recorded for **1** (see Table 1).

Ligand rearrangements were also observed in [Tp^{iPr}Ir(COD)] (**3**). Thus, in one case, instead of this complex, an isomeric species **15** was obtained. Its ^{1}H and ^{13}C NMR spectra are consistent with a structure in which iridium is coordinated to a ligand containing two of the original pyrazolyl substituents and one which has undergone a 1,2-borotropic shift, *i.e.*, [{HB(Pz^{3iPr})$_2$(Pz^{5iPr})}Ir(COD)]. Its metal coordination and the ligand conformation are as in **3B**. This formulation is supported by a comparison of the ^{1}H NMR data for **15** (see Table 2), particularly for the ^{5}*H*(Pz) protons, with those for the corresponding compound [{HB(Pz^{3iPr,4Br})$_2$(Pz^{5iPr,4Br})}Rh(COD)], which was more thoroughly studied.[20]

The occurrence of borotropic rearrangements in complexes **2** and **3**, *i.e.*, complexes whose pyrazolyl groups have substituents only in positions 3, raised the question as to whether such rearrangements also take place in compounds containing 3,5-disubstituted pyrazolyl groups. The complex [Tp^{Me_2}Ir(COD)] (**4**) was chosen as a test case. As its NMR data excluded an exchange of this type at room temperature, its possible occurrence at higher temperatures was tested by spin-saturation-transfer experiments. These showed that there was no magnetization transfer from the methyl group in position 3 to that in position 5 even when a $CDCl_2CDCl_2$ solution of **4** was heated to 383 K. Higher temperatures caused decomposition of this complex.

X-ray Crystal Structures. [η^2-Tp^{Me_2,4Cl}Ir(COD)] (9). The crystals contain discrete molecules, separated by normal van der Waals distances. An ORTEP view of this molecule is shown in Figure 1, and a selection of interatomic distances and angles is given in Table 2.

The iridium atom in this complex is four-coordinate and is bonded to two pyrazolyl rings of the tris(pyrazolyl)borate anion and the two double bonds of cyclooctadiene. The coordination geometry is approximately square planar.

As usual for pyrazolylborate complexes, the six-membered chelate ring in **9** has a boat conformation. The uncoordinated pyrazolyl ring occupies an axial position and is placed above the coordination plane. There does not appear to be any significant interaction between the metal center and either of the nitrogen atoms of this ring, as the Ir−N1b and Ir−N2b

(24) Cano, M.; Heras, J. V.; Jones, C. J.; McCleverty, J. A.; Trofimenko, S. *Polyhedron* **1990**, *9*, 619.

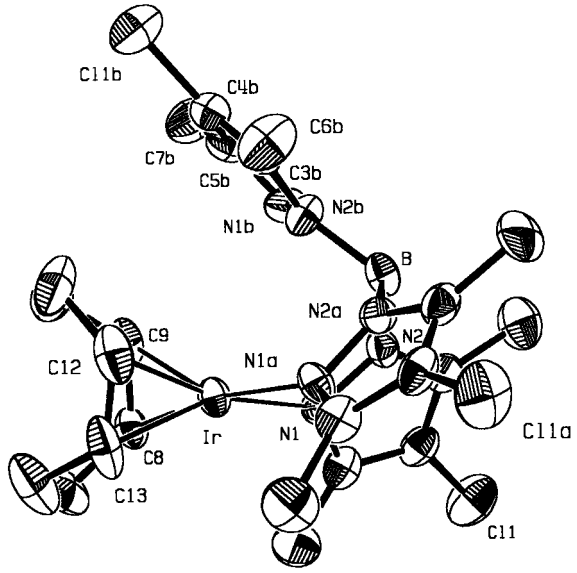


Figure 1. ORTEP view of [η^2-Tp^{Me_2,4Cl}Ir(COD)] (**9**). (*Note that the atom numbering in this structure does not correspond to the chemical numbering used earlier.*)

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [κ^3-Tp^{Me_2,Cl}Ir(COD)] (**9**) and [κ^3-TpIr(COD)] (**1**)

	9	**1**		**9**	**1**
			Distances		
Ir−N1	2.082(5)	2.218(9)	Ir−N2	3.010(5)	3.133(8)
Ir−N1a	2.100(6)	2.242(9)	Ir−N2a	2.974(5)	3.139(8)
Ir−N1b	3.748(7)	2.086(9)	Ir−N2b	3.176(7)	3.050(8)
Ir−C8	2.124(7)	2.13(1)	B−N2	1.53(1)	1.54(1)
Ir−C9	2.11(1)	2.12(1)	B−N2a	1.55(1)	1.51(2)
Ir−C_{m1}[a]	2.00(1)	2.01(1)	B−N2b	1.54(1)	1.55(1)
Ir−C12	2.128(9)	2.06(1)	C8−C9	1.41(1)	1.39(2)
Ir−C13	2.129(6)	2.03(1)	C12−C13	1.38(1)	1.40(2)
Ir−C_{m2}[b]	2.01(1)	1.92(1)	Ir−B	3.196(8)	3.28(1)
			Angles		
N1−Ir−N1a	82.7(2)	80.6(3)	C_{m2}−Ir−N1	173.5(3)	138.2(2)
N1−Ir−N1b	...[c]	83.7(3)	C_{m2}−Ir−N1a	96.4(3)	140.0(2)
N1a−Ir−N1b	...[c]	83.1(3)	C_{m2}−Ir−N1b	...[c]	90.5(2)
C_{m1}−Ir−C_{m2}	86.6(2)	86.6(3)	N2−B−N2a	107.7(8)	109.4(9)
C_{m1}−Ir−N1	95.5(3)	98.1(2)	N2−B−N2b	109.8(7)	108.3(8)
C_{m1}−Ir−N1a	168.5(3)	98.9(3)	N2a−B−N2b	111.3(6)	108.6(9)
C_{m1}−Ir−N1b	...[c]	177.2(2)			

[a] C_{m1} = midpoint between C8 and C9. [b] C_{m2} = midpoint between C12 and C13. [c] Atom N1b is not bonded to Ir.

distances are 3.748(7) and 3.176(7) Å, respectively. Furthermore, the plane of this ring (a) is not parallel to the coordination plane and (b) is tilted sideways (see Figure 1). The angle between these two planes is 47.9(3)°. The other bonding parameters of the pyrazolylborate anion and the cyclooctadiene do not show significant deviations from standard values.

The only structurally characterized, closely related COD-containing complex reported in the literature appears to be [{η^2-Bpz$_4$}Rh(COD)] (**22**).[18] Although this compound has a different metal center, and the η^2-bonded pyrazolyl ligand has two bulky pyrazolyl substituents on the boron atom, the overall features of the coordination polyhedron are quite similar to those of **9** except for the N−M−N angles, which are 82.7(2)° in **9** and 86.6(1)° in **22**.

[η^2-Tp^{Me_2}Ir(COD)] (4). The molecular disorder present in the COD ligand in this compound (see Experimental Section) did not allow a full determination of its structure. However, the data unambiguously showed that the coordination polyhedron in this compound is fully analogous to that of **9**.

[η^3-TpIr(COD)] (1). The crystals contain discrete molecules, separated by normal van der Waals distances. An ORTEP view

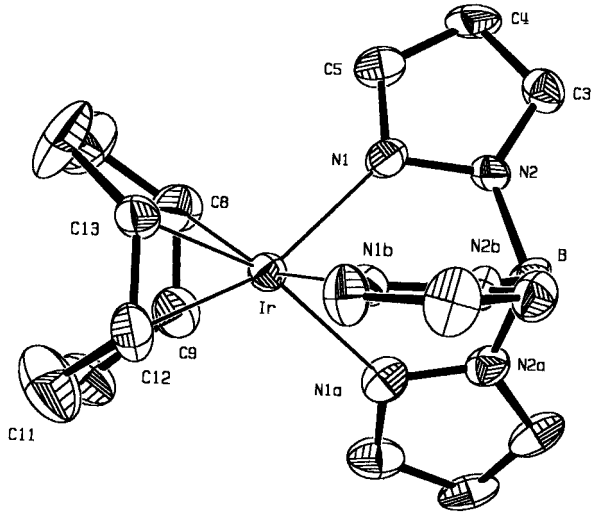


Figure 2. ORTEP view of [η^3-TpIr(COD)] (**1**). (*Note that the atom numbering in this structure does not correspond to the chemical numbering used earlier.*)

of this complex is shown in Figure 2, and a selection of interatomic distances and angles is given in Table 2.

The iridium atom is five-coordinate and is bonded to one of the nitrogen atoms of each of the three pyrazolyl rings and the two double bonds of cyclooctadiene. The coordination geometry is distorted trigonal bipyramidal, the apical positions being occupied by one of the nitrogen atoms and one of the double bonds. The largest deviations from regular geometry are found in the equatorial angles which, instead of 120°, are N1−Ir−N1a = 80.6(3)°, C_{m2}−Ir−N1 = 138.2(2)°, and C_{m2}−Ir−N1a = 140.0(2)° (C_{m2} = midpoint of the C12═C13 double bond). The three Ir−N distances differ significantly, ranging from 2.086(9) Å (Ir−N1b) to 2.242(9) Å (Ir−N1a).

The X-ray crystal structures of three compounds with related five-coordinate structures are known, *i.e.*, [{η^3-BPz$_4$}-Rh(duroquinone)] (**22**),[18] [η^3-Tp^{Me}Rh(NBD)],[19] (**23**), and [η^3-MeTp^{Me}Rh(NBD)] (MeTp^{Me} = MeB(Pz^{Me})$_3$) (**24**).[25] Also in these cases the coordination at the metal center is distorted trigonal bipyramidal with the diene occupying one axial and one equatorial position. The main difference between **1** and compounds **22**−**24** is the N1−M−N1a equatorial angle: this widens from 80.6(3)° in **1** to 87.1(1)° in **22**, 89.6(4)° in **23**, and 90.1(1)° in **24**.

Discussion

Solid State. The X-ray structural investigations described above show that the Tp^{3R,4R,5R} ligand, in complexes of the type [Tp^{3R,4R,5R}Ir(COD)], in the solid state, can be either di- or terdentate. Structures of the former type, found in [Tp^{Me_2}Ir-(COD)] (**4**) and [Tp^{Me_2,4Cl}Ir(COD)] (**9**), correspond to isomer **B** in Scheme 1, while the geometry established for [TpIr(COD)] (**1**) is that assigned to conformer **C** in the same scheme.

Useful structural information is also provided by the values of ν(B−H) stretching vibrations. Previous studies showed that the ν(B−H) values for the square planar rhodium(I) hydrotris-(pyrazolyl)borate complexes of the type [η^2-Tp^{3R,4R,5R}Rh(LL)] (LL = 2 CO, NBD, COD), are 60−90 cm^{-1} higher than those for the corresponding octahedral complexes of the type [η^3-Tp^{3R,4R,5R}RhCl$_3$]$^-$.[26] Similar information should be obtainable by comparing the ν(B−H) values of analogous sets of iridium

(25) Bucher, U. E.; Fässler, T. F.; Hunziker, M.; Nesper, R.; Rüegger, H.; Venanzi, L. M. *Gazz. Chim. Ital.* **1995**, *125*, 181.
(26) (a) Albinati, A.; Bucher, U. E.; Renn. O. Manuscript in preparation. (b) Bucher, U. E. Dissertation, ETH Zürich, 1993; No. 10166.

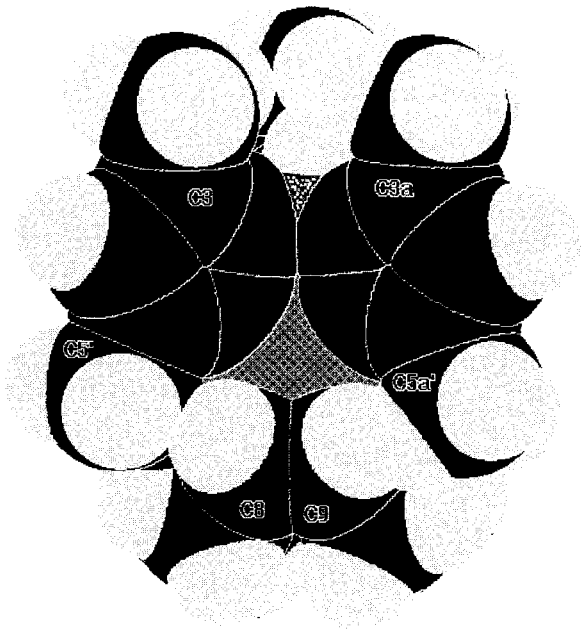


Figure 3. Space-filling model of the hypothetical molecule [η^3-Tp^{Me_2}-Ir(COD)], constructed using the program ALCHEMY and based on the X-ray structural data for [η^3-TpIr(COD)] (**1**).

compounds. However, complexes of the type $[Tp^{3R,4R,5R}IrCl_3]^-$ could not be obtained, and therefore, the ν(B−H) frequencies of the $[Tp^{3R,4R,5R}Ir(COD)]$ species were compared with those of the corresponding $[Tp^{3R,4R,5R}RhCl_3]^-$ anions (see Table 1). As can be seen in Table 1, the $\Delta\nu$(B−H) values for compounds **2**−**10** fall in the range 50−90 cm^{-1}. Typically, this difference is 70 cm^{-1} for solid $[Tp^{Me_2}Ir(COD)]$ (**4**) which, as mentioned earlier, is four-coordinate in this state. On the other hand, [TpIr-(COD)] (**1**) is five-coordinate in the solid state, and therefore, one may associate its low value of $\Delta\nu$(B−H) (21 cm^{-1}) with a five-coordinate structure in the iridium(I) complex. Thus, on this basis, one can deduce that the iridium(I) compounds **2**−**10** have square planar structures in the solid state.

In order to test whether five-coordinate forms of complexes of the type $[\eta^3$-$Tp^{3R,4R,5R}Ir(COD)]$ (R ≠ H) are sterically possible, a space-filling model of $[\eta^3$-$Tp^{Me_2}Ir(COD)]$ (**4**) was constructed using the program ALCHEMY.[27] For this purpose, the X-ray crystal structure of **1** was taken as a starting point and the hydrogen atoms in positions 3 and 5 of each pyrazole ring were replaced by methyl groups in staggered positions. This model structure (see Figure 3) shows that there are several close contacts (ca. 2.7 Å) between the CH groups of COD (C8 and C9) and the methyl groups in position 3 on each ring (those added to C5, C5a, and C5b in the crystal structure of **1**; see Figure 2). The first two are labeled as C5′, C5a′, and C5b′ in Figure 3 while the third, C5b′, is not visible there. Furthermore, the olefinic hydrogens close to C5a′ and C5b′ appear to be in a more crowded region than those close to C5, which occupies an apical position of the trigonal bipyramid. However, the methyl substituents on the boron side, *i.e.*, those bonded to C3, C3a, and C3b in **1**, do not show significant steric crowding, as the nonbonded distances between the C atoms of these methyl groups range from 4.5 to 4.7 Å (see Figure 3).

These model considerations indicate that, when COD is present as a coligand, five-coordinate species are unlikely to be stable if each pyrazole ring carries a methyl or other substituent in position 3, *i.e.*, on the "metal side". However, the transient formation of an isomer of type **C** in a dynamic process **B** ⇌ **C** in solution appears to be still possible.

Solutions. Complexes **1**, **13**, and **14** are probably unique within this class of compounds, being predominantly present as a five-coordinate species of type **C** in solution. In agreement with ν(B−H) and $^{13}C_{olefin}$ δ data, the N^2 δ shift value for [TpIr-(COD)] (**1**), ca. −140 ppm, is indicative of the presence of a considerable amount (ca. 70%) of the five-coordinate form (**C**).

This structure is likely to be be favored relative to a four-coordinate isomer for two reasons: (a) the steric repulsions between the hydrogen substituents in position 3 and the diene would be minimal and (b) the residual positive charge on the metal center in the 16-electron complex [η^2-TpIr(COD)] (**1B**) would be higher than that in the corresponding species [η^2-$Tp^{Me}Ir(COD)$] (**2B**) because of the inductive effect of the three methyl substituents present in the latter compound.[28] Thus, iridium(I) in **1B** would bind the third nitrogen donor of the Tp ligand more readily than in iridium(I) **2B**.

The IR and NMR solution data for the complexes $[Tp^{Me_2}Ir-(COD)]$ (**4**), $[Tp^{CF_3,Me}Ir(COD)]$ (**5**), $[Tp^{Ph,Me}Ir(COD)]$ (**6**), $[Tp^{iPr_2}-Ir(COD)]$ (**7**), $[Tp^{Me_2,4Me}Ir(COD)]$ (**8**),[10] $[Tp^{Me_2,4Cl}Ir(COD)]$ (**9**), and $[Tp^{Me_2,4Br}Ir(COD)]$ (**10**) show that, in each case, isomer **B** predominates and is in fast equilibrium with a small amount of **C**.

As mentioned earlier, the dynamic process of lowest energy in all these cases is likely to be the reversible binding to iridium of the uncoordinated pyrazolyl ring with formation of a five-coordinate intermediate of type **C**. Consequently, given (a) the known fluxionality of such species[29] and (b) the low stability of the five-coordinate complex, the observed equivalence of the pyrazolyl rings on the time scale of this measurement is not unexpected. Furthermore, the observation that in complex **4** only one type of pyrazole ring is detectable by NMR at 180 K indicates that the higher energy interconversion **4A** ⇌ **4B** (see Results) does not occur within the temperature range studied.

Complexes **2**−**10** have one common feature: all pyrazolyl rings have a substituent *on the iridium side* (position 3). Thus, differences between compounds **2** and **3** on one side and **4**−**10** on the other are likely to be due to effects of substituents *on the boron side* of each pyrazolyl ring (position 5).

The failure to detect conformer **A** in compounds of the latter group can also be rationalized by comparing molecular models of two analogous compounds with square planar structure, one with and one without methyl substituents in position 5, *e.g.*, **2** and **4**. Once again, the program ALCHEMY[27] was used for this purpose, and the results are shown in Figure 4. A comparison of Figure 4a and Figure 4b indicates that the presence of methyl groups on the boron side of the molecule is likely to raise (a) the activation energy for the rotation of the uncoordinated pyrazolyl ring around its B−N bond and (b) the inversion of the boat conformation of the chelate ring, required for the transformation of **B** into **A**, as the uncoordinated pyrazolyl ring has to slide past the substituents in positions 3 of the coordinated rings. On this basis then, conformer **A** should be observable only in complexes which have substituents on the "metal side" but not on the "boron side" of each pyrazolyl ring.

The behavior of complexes of the type $[Tp^{3R,4R,5R}Ir(COD)]$ in solution can be summarized as follows:

(a) [TpIr(COD)] (**1**), at equilibrium, is present mainly as the five-coordinate form **C**.

(27) *ALCHEMY III. 3D Molecular Modelling Software*; Tripos Associates Inc.: St. Louis, MO, 1992.

(28) Catalan, J.; Abboud, J. L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987**, *41*, 187.

(29) Burdett, J. K. *Molecular Shapes. Theoretical Models of Inorganic Stereochemistry*; John Wiley & Sons: New York, 1980; pp 204−205.

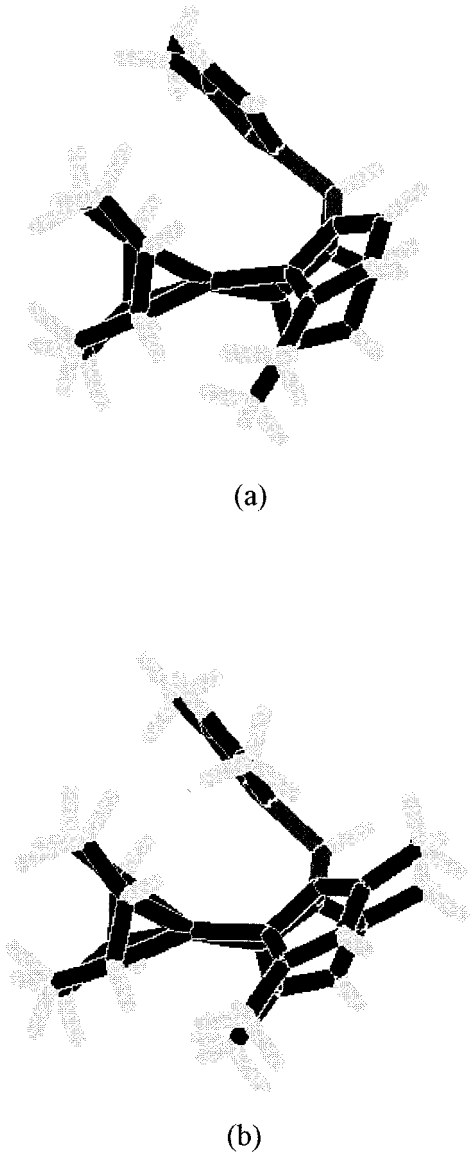


Figure 4. Models of the square planar complexes (a) [η^2-Tp^{3Me}Ir(COD)] (**4**) and (b) [η^2-Tp^{Me_2}Ir(COD)], constructed using the program ALCHEMY and based on the X-ray structural data for [η^2-Tp^{Me_2,4Cl}Ir(COD)] (**1**).

(b) [Tp^{Me}Ir(COD)] (**2**) and [Tp^{iPr}Ir(COD)] (**3**) show a slow **A** ⇌ **B** isomerization as well as a fast **B** ⇌ **C** exchange, with **B** predominating.

(c) Compounds **4**−**10** are present mainly as conformers **B** in fast exchange with small amounts of the corresponding forms **C**. The isomeric forms **A** are not detectable.

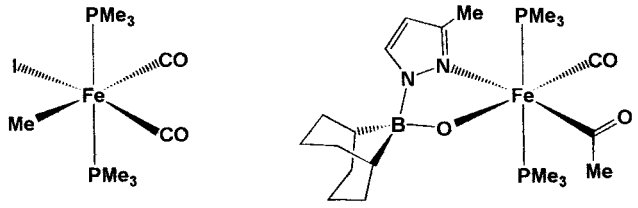
(d) The rearranged rings, in the complex [{HB(Pz^{3Me})(Pz^{5Me})$_2$}Ir(COD)] (**14**), *i.e.*, those with a substituent on the boron side, are always coordinated whereas the third is labile and form **C** predominates over form **B**.

As mentioned earlier, the values of the $^{13}C_{olefin}$ δ of the four- and five-coordinate complexes, **B** and **C**, respectively, differed significantly (see Table 1). These differences can be rationalized as follows: the electron density at the metal center will be higher when the Tp ligand is coordinated to iridium in a η^3 rather than in an η^2 mode. This will, in turn, favor π back-donation from the metal d orbitals to the π^* orbitals of the alkene, and consequently, the bonding within the Ir(C_2H_2) unit will become closer to that of a metallacyclopropane and the ^{13}C δ shifts will show lower values.

One of the more intriguing aspects of this study is the facile 1,2-borotropic rearrangements occurring in the complexes [Tp^{Me}Ir(COD)] (**2**) and [Tp^{iPr}Ir(COD)] (**3**). Such rearrangements have been previously observed in some rhodium Tp^{3R,4R,5R} complexes,[19] in [Co{HB(Pz^{3iPr,4X})$_2$(Pz^{5iPr,4X})}$_2$][30] (X = H, Br), and in [Mo(NO)I(O^{i}Pr){HB(Pz^{iPr,Me})$_3$}].[24] While a more systematic study of these complexes would be required to clearly identify the factors favoring such rearrangements, it is likely that they are mainly driven by the tendency to reduce intramolecular van der Waals-type repulsions.[19,24] This hypothesis is suggested by (a) the failure to observe borotropic shifts in [Tp^{Me_2}Ir(COD)] (**4**) below the decomposition temperatures of its solutions, (b) the positions of the **B**−**C** equilibria in **14** and **15**, and (c) the model studies described above.

Although the structures and properties of violet bimetallic products [Ir$_2$(μ-Pz^{3R,4R,5R})$_2$(COD)$_2$] (**11**) have been amply described in the literature,[20−22] *hydrolytic* cleavage of B−N bonds in complexes of the type [Tp^{3R,4R,5R}Ir(COD)] is worthy of a short comment. Although this cleavage appears to occur in those complexes with η^2 coordination of the Tp-type ligands, the stability of the cationic species [η^2-HTp^{Me_2}Ir(COD)]$^+$ [10] indicates that hydrolysis is not preceded by the addition of a proton to the N^2 atom of an uncoordinated pyrazolyl ring. Therefore, it seems probable that the reaction involves the direct interaction of water with the B and N atoms of *an uncoordinated ring in a Tp-type ligand which is η^2-type bonded*. This hypothesis is based on the observations that (a) [TpIr(COD)] (**1**), which contains a η^3-bonded N-donor, is not moisture sensitive, (b) the complexes with η^2-bonded Tp^{3X,5Me}-type ligands show intermediate sensitivity, and (c) complex **7**, whose pyrazolyl groups contains bulky ^{i}Pr substituents shielding the boron atom, is not moisture-sensitive. This effect does not appear to have been previously observed during the formation of hydrotris(pyrazolyl)borato complexes and may be connected with the slow rates of substitution in iridium(I) compounds.

Occasionally, the rate of B−N bond cleavage becomes comparable with that of complex formation of the resulting "B−OH" fragment. An elegant demonstration of this competition was recently reported by Macchioni *et al.*:[31] the reaction of *cis,trans*-[FeI(Me)(CO)$_2$(PMe$_3$)$_2$] (**30**) with [BBN(Pz^{Me})$_2$]$^-$ (BBN = 9-borabicyclo[3.3.1]nonane) gives a complex, **31**, containing the anion BBN(O$^-$)(Pz^{Me}) acting as a bidentate ligand. In this reaction, the rate of substitution of I$^-$ by an N-donor and that of methyl migration are not sufficiently fast to prevent hydrolytic cleavage of the first but not fast enough to allow hydrolysis of the second B−N bond as the partially hydrolyzed borate is rapidly stabilized by Fe−O bond formation.



30 **31**

Experimental Section

General Procedures. All operations and manipulations were performed under an argon atmosphere on a vacuum line using Schlenk

(30) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.
(31) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Gramlich, V.; Pieroni, F.; Terenzi, S. Proceedings of the XIth FECHEM Conference on Organometallic Chemistry, Parma, Italy, 1995; Tipolitografia Benedettina Editrice: Parma, Italy, 1955; p 101.

techniques. The compounds 3,5-dimethyl-4-bromopyrazole,[32] Na[Tp],[33] K[Tp^{Me}],[34] K[Tp^{Me_2}],[35] K[Tp^{Me_2,4Me}],[35] K[Tp^{CF_3,Me}],[19] K[Tp^{iPr}],[31] K[Tp^{iPr_2}],[36] K[Tp^{Ph,Me}],[37] K[Tp^{Me_2,Cl}],[19] [Ir$_2$Cl$_2$(COD)$_2$],[38] [Tp^{Me_2}Ir(COD)] (**4**),[10] [Tp^{Me_2,4Me}Ir(COD)] (**8**),[10] and [(η^2-HTp^{Me_2})Ir(COD)](CF$_3$SO$_3$) (**12**)[10] were prepared as described in the appropriate reference. Unless otherwise stated, solvents of *puriss.* grade (Fluka AG) were used as supplied. The deuterated solvents CD_3CN, CD_2Cl_2, and acetone-d_6 were purchased from Cambridge Isotope Laboratories, while $CDCl_3$ was obtained from Armar AG, Döttingen.

Bruker AC 200, AC 250, and AMX 500 spectrometers were used to record the ^{1}H, ^{13}C, and ^{15}N NMR spectra. The ^{1}H and ^{13}C chemical shifts (δ, ppm) are given relative to tetramethylsilane. The ^{15}N data were measured indirectly using 2D multiple-quantum spectroscopy and are referenced to CH_3NO_2. The NOESY spectra were recorded using a mixing time of 600 ms.

The infrared spectra (RbI pellets or CH_2Cl_2 solutions) were measured on a Perkin-Elmer 883 spectrophotometer. The elemental analyses were carried out by the Microanalytical Laboratory of the ETH Zürich.

During the course of this study, the following known compounds were obtained as byproducts of the syntheses of the corresponding hydrotris(pyrazolyl)borate complexes: [(μ_2-Pz^{Me})$_2$Ir$_2$(COD)$_2$], [(μ_2-Pz^{Me_2})$_2$Ir$_2$(COD)$_2$], [(μ_2-Pz^{CF_3,Me})$_2$Ir$_2$(COD)$_2$], [(μ_2-Pz^{Ph,Me})$_2$Ir$_2$(COD)$_2$], [(μ_2-Pz^{Me_2,4Me})$_2$Ir$_2$(COD)$_2$], and [(μ_2-Pz^{Me_2,4Br})$_2$Ir$_2$(COD)$_2$]. They were characterized by NMR spectroscopy and these data are in agreement with those reported in the literature.[20]

K[Tp^{Me_2,4Br}]. Solid K[BH$_4$] (882 mg, 15.24 mmol) was suspended in kerosene (20 mL) in a 250 mL round-bottom flask, fitted with a reflux condenser and a wet test meter. 4-Bromo-3,5-dimethylpyrazole (9.333 g, 53.34 mmol) was then added, and the stirred mixture was gradually heated to 190 °C and kept at this temperature until 3 equiv of H_2 had evolved (ca. 12 h). After the mixture had cooled to room temperature, the product was filtered off, washed three times with boiling *n*-hexane, and dried *in vacuo*. Additional product was obtained from the filtrate by adding *n*-hexane (100 mL) and leaving the solution at −20 °C overnight. The free pyrazole contained in the crude product was removed by a bulb-to-bulb distillation at 165 °C under high vacuum. Occasionally the product thus obtained contained insoluble byproducts which were removed by extracting the product with CH_2Cl_2 and evaporating the solvent. Yield: 3.920 g. Mp: 257 °C dec (71%). IR (RbI, cm^{-1}): 2457 (ν(B−H), s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.95 (s, 9H, C*H*$_3$(Pz)), 2.17 (s, 9H, C*H*$_3$(Pz)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 11.6 (*C*H$_3$(Pz)), 12.5 (*C*H$_3$(Pz)), 93.3 (*C*Br-(Pz)), 141.2 (*C*CH$_3$(Pz)), 145.8 (*C*CH$_3$(Pz)).

General Synthetic Method for the Preparation of the Complexes [Tp^{3R,4R,5R}Ir(COD)]. To a stirred solution of [Ir$_2$Cl$_2$(COD)$_2$] (0.1 mmol), in degassed MeCN (3 mL), was added portionwise the appropriate M[Tp^{3R,4R,5R}] salt (0.2 mmol). A precipitate formed immediately, its color ranging from pale to dark orange. The darker color of some of the products was due to the presence of very small, variable amounts of a dark violet decomposition product (see below). When the precipitate formed had a pale color, the product was purified as follows: The reaction mixture was stirred for 1 h, the solvent was evaporated under reduced pressure, and the residual solid was washed three times with ice-cold water (2 mL) and once with ice-cold MeCN (1 mL). After drying under high vacuum for a short time, the residue was recrystallized by dissolving it in warm *n*-hexane, leaving the solution at 0 °C overnight, filtering off the precipitate, and drying it under vacuum. Yields ranged from 39 to 89%. The *n*-hexane solution should not be warmed for prolonged periods, or refluxed, as more decomposition product is formed. When appreciable amounts of this decomposition product were present, apparent from the deep orange color of the precipitate, the impurity was removed by column chromatography using a mixture of *n*-hexane and ethyl acetate as eluent. Other purification procedures will be described where appropriate. The following observations were made: (a) compounds **1** and **7** are not moisture-sensitive; (b) the compounds with di-, **4**−**6**, and trisubstituted Pz rings, **8**−**10**, show intermediate sensitivity; and (c) the compounds with monosubstituted Pz rings, **2** and **3**, are particularly moisture-sensitive.

[TpIr(COD)] (1). This compound was prepared as described above using [Ir$_2$Cl$_2$(COD)$_2$] (500 mg, 0.774 mmol) in MeCN (15 mL) and Na[Tp] (351 mg, 1.490 mmol). A pale yellow powder was obtained. Yield: 683 mg (89%). It was recrystallized from hexane but the solution was left overnight at −20 °C. Mp: 180 °C dec. Anal. Found (calcd for $C_{17}H_{22}BIrN_6$): C, 39.44 (39.77); H, 4.35 (4.32); N, 16.36 (16.37). IR (RbI, cm^{-1}): 3158 (ν(C−H)$_{Pz}$, s), 3140 (ν(C−H)$_{Pz}$, s), 3117 (ν(C−H)$_{Pz}$, s), 2462 (ν(B−H), s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.70 (m, 4H, C*H*$_2$(COD)), 2.43 (m, 4H, C*H*$_2$(COD)), 3.54 (m, 4H, C*H*(COD)), 6.20 (d × d, 3H, ^{4}*H*(Pz)), 7.64 (d, 3H, ^{5}*H*(Pz), ^3J(HH) = 1.8 Hz), 7.85 (d, ^3J(HH) = 2.2 Hz, 3H, ^{3}*H*(Pz)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 32.7 (*C*H$_2$(COD)), 54.1 (*C*H(COD)), 105.3 (^{4}*C*(Pz)), 134.7 (^{3}*C*(Pz)), 139.2 (^{5}*C*(Pz)). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −151.6 (^{1}N), −139.6 (^{2}N).

Reaction of [Ir$_2$Cl$_2$(COD)$_2$] with Na[Tp^{Me}]. This was carried out as described above using [Ir$_2$Cl$_2$(COD)$_2$] (715 mg, 1.0 mmol) in MeCN (20 mL) and Na[Tp^{Me}] (592 mg, 2.129 mmol). The solid residue, after recrystallization from MeCN at 0 °C, yielded 899 mg (76%) of a yellow solid. This slowly decomposes to [Ir$_2$(μ_2-Pz^{Me})$_2$(COD)$_2$] in air and must be stored under argon. It also decomposes within a few hours in tetrahydrofuran, acetone, or ethyl acetate solution. Decomposition is also observed on silica gel and Alox plates. Samples thus prepared normally contain only the two conformers of the complexes with the original pyrazolylborate ligand Tp^{Me}, **2A** and **2B**. The complexes with the rearranged Tp ligands, *i.e.*, [{HB(Pz^{3Me})$_2$(Pz^{5Me})}Ir(COD)] (**13**) and [{HB(Pz^{3Me})(Pz^{5Me})$_2$}Ir(COD)] (**14**) can be obtained as described below.

[Tp^{Me}Ir(COD)] (2A and 2B). The NMR spectrum of the solution of some orange crystals, obtained from the above sample by recrystallization from *n*-hexane, showed only the presence of **2A** and **2B**, in dynamic equilibrium. Mp: 120 °C dec. Anal. Found (calcd for $C_{20}H_{28}BIrN_6$): C, 42.24 (43.46); H, 5.05 (5.08); N, 15.10 (15.13). IR (RbI, cm^{-1}): 3148 (ν(C−H)$_{Pz}$, s), 3128 (ν(C−H)$_{Pz}$, s), 3109 (ν(C−H)$_{Pz}$, s), 2425 (ν(B−H), s).

2A. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (m, 4H, C*H*$_2$(COD)), 2.28 (m, 4H, C*H*$_2$(COD)), 2.40 (s, 9H, C*H*$_3$(Pz)), 4.12 (br, 4H, C*H*(COD)), 5.6 (vbr, 1H, B*H*), 5.89 (s, 2H, ^{4}*H*(Pz)), 6.10 (s, 1H, ^{4}*H*(Pz)), 7.14 (s, 2H, ^{5}*H*(Pz)), 7.75 (s, 1H, ^{5}*H*(Pz)). ^{13}C NMR (125.6 MHz, $CDCl_3$, 223 K): δ 14.8 (*C*H$_3$(Pz)), 31.0 (C*H*$_2$(COD)), 61.3, 66.6 (br, C*H*(COD)), 104.1 (1C, ^{4}*C*(Pz)), 105.5 (2C, ^{4}*C*(Pz)), 134.4 (1C, ^{5}*C*(Pz)), 137.9 (2C, ^{5}*C*(Pz)), 149.7 (2C, ^{3}*C*(Pz)), 150.3 (1C, ^{3}*C*(Pz)). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −163.5 (^{1}N), −149.0 (^{2}N), −148.1 (^{2}N$_{coord}$); ^{2}N$_{free}$ is not observed.

2B. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (m, 4H, C*H*$_2$(COD)), 1.93 (m, 4H, C*H*$_2$(COD)), 2.40 (s, 9H, C*H*$_3$(Pz)), 3.87 (br, 4H, C*H*(COD)), 4.3 (vbr, 1H, B*H*), 6.05 (s, 3H, ^{4}*H*(Pz)), 7.50 (s, 3H, ^{5}*H*(Pz)). ^{13}C NMR (125.6 MHz, $CDCl_3$, 223 K): δ 14.8 (*C*H$_3$(Pz)), 30.1 (*C*H$_2$(COD)), 63.8 (*C*H(COD)), 105.7 (^{4}*C*(Pz)), 136.5 (^{5}*C*(Pz)), 150.7 (^{3}*C*(Pz)). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −152.5 (^{1}N), −126.0 (^{2}N).

Reaction of [Ir$_2$Cl$_2$(COD)$_2$] with K[Tp^{iPr}]. A solution of [Ir$_2$Cl$_2$-(COD)$_2$] (501 mg, 0.746 mmol), in MeCN (10 mL), was placed in a 50 mL Schlenk tube and cooled to 0 °C. To this stirred solution was added dropwise a solution of K[Tp^{iPr}] (565 mg, 1.500 mmol) in MeCN (10 mL). The suspension was stirred for 10 min, and the solvent was evaporated under vacuum at 0 °C. Degassed *n*-hexane (20 mL) was added to the residual orange precipitate and the suspension filtered under an argon atmosphere. Evaporation of the solution under vacuum left a dark orange foam. The violet decomposition product present in this sample was removed by column chromatography using *n*-hexane/ethyl acetate (6:1). (R_f(violet product) = 0.71 and R_f(**3A** + **3B**) = 0.33). The fractions containing the product had to be collected at −10 °C and the solvent rapidly evaporated under vacuum to avoid product decomposition. Yield: 786 mg (82%). Mp: 96 °C dec. Anal. Found (calcd for $C_{26}H_{40}BIrN_6$): C, 49.30 (48.82); H, 6.52 (6.30); N, 13.12 (13.14). IR (RbI, cm^{-1}): 3114 (ν(C−H)$_{Pz}$, s), 3112 (ν(C−H)$_{Pz}$, s),

(32) Morgan, G. T.; Ackerman, I. *J. Chem. Soc.* **1923**, *123*, 1308.
(33) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.
(34) Niedenzu, K.; Niedenzu, P. N.; Warner, K. R. *Inorg. Chem.* **1985**, *24*, 1604.
(35) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.
(36) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.
(37) See also: Müller, R.; Pleininger, H. *Chem. Ber.* **1959**, *92*, 3009.
(38) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

2398 (ν(B−H), s). *Slight variations of the above procedure give different isomeric mixtures*. These may contain the two conformers of the complexes with the original pyrazolylborate ligand Tp^{iPr}, **3A** and **3B**, and the complexes, with the rearranged Tp ligands, *e.g.*, [{HB(Pz^{3iPr})$_2$(Pz^{5iPr})}Ir(COD)] (**15**) (see below).

[Tp^{iPr}IrCOD] (3A and 3B). NMR studies of samples prepared as described above usually showed the presence of only the two conformers **3A** and **3B** in the approximate ratio 2:9. ^{1}H NMR data are as follows (250 MHz, $CDCl_3$, 223 K). **3A**: δ 1.16−1.30 (m, 18H, CH(CH_3)$_2$), 1.58 (m, 4H, CH_2(COD)), 2.29 (m, 4H, CH_2(COD)), 3.09 (m, 1H, CH(CH$_3$)$_2$), 3.20 (m, 2H, CH(CH$_3$)$_2$), 3.93 (m, 2H, CH(COD)), 4.07 (m, 2H, CH(COD)), 5.94 (d, 2H, ^4H(Pz), ^3J(HH) = 2.3 Hz), 6.15 (d, 1H, ^4H(Pz), ^3J(HH) = 1.9 Hz), 7.12 (d, 2H, ^5H(Pz), ^3J(HH) = 2.3 Hz), 7.80 (d, 1H, ^5H(Pz), ^3J(HH) = 1.9 Hz). **3B**: δ 1.16−1.30 (m, 18H + 4H, CH(CH_3)$_2$ + CH_2(COD)), 2.83 (br, 4H, CH_2(COD)), 3.20 (br, 3H, CH(CH$_3$)$_2$), 3.75 (br, 4H, CH(COD)), 6.11 (s, 3H, ^4H(Pz)), 7.59 (br, 3H, ^5H(Pz)).

[κ^2-Tp^{Me_2}Ir(COD)] (4). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −155.2 (^{1}N), −125.1 (^{2}N).

[Tp^{CF_3,Me}Ir(COD)] (5). This compound was prepared and purified as described above using [$Ir_2Cl_2(COD)_2$] (80 mg, 0.119 mmol), in MeCN (3 mL), and Na[Tp^{CF_3,Me}] (115 mg, 0.238 mmol). The suspension was stirred for 2 h before filtering off the crude product in the form of orange crystals. Yield: 148 mg (82%). Mp: 130 °C dec. Anal. Found (calcd for $C_{23}H_{22}BF_9IrN_6$): C, 36.52 (36.71); H, 2.93 (2.73); N, 11.11 (11.34). IR (RbI, cm^{-1}): 3142 (ν(C−H)$_{Pz}$, w), 2493 (ν(B−H), s), 1251, 1164, 1136 (ν(CF$_3$), vs). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.37 (m, 4H, CH_2(COD)), 1.82 (br, 4H, CH_2(COD)), 2.27 (s, 9H, CH_3(Pz)), 3.93 (br, 4H, CH(COD)), 6.44 (s, 3H, ^4H(Pz)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 13.3 (CH_3(Pz)), 30.1 (CH_2(COD)), 66.7 (CH(COD)), 107.2 (CH(Pz)), 121.3 (q, CF_3, ^1J(CF) = 270.0 Hz), 143.0 (q, ^3C(Pz), ^2J(CF) = 38.1 Hz), 147.2 (^5C(Pz)).

[Tp^{Ph,Me}Ir(COD)] (6). This compound was prepared as described above using [$Ir_2Cl_2(COD)_2$] (500 mg, 0.744 mmol) in MeCN (20 mL) and K[Tp^{Ph,Me}] (778 mg, 1.488 mmol). It was recrystallized from MeCN at 0 °C. Yield: 656 mg (56%). Mp: 236 °C dec. Anal. Found (calcd for $C_{38}H_{40}BN_6Ir$): C, 58.50 (58.23); H, 5.14 (5.14); N, 10.75 (10.72). IR (RbI, cm^{-1}): 2466 (ν(B−H), s). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91 (m, 4H, CH_2(COD)), 1.47 (m, 4H, CH_2(COD)), 2.38 (s, 9H, CH_3(Pz)), 3.09 (br, 4H, CH(COD)), 6.35 (s, 3H, CH(Pz)), 7.35−7.52 (m, 9H, *m*- and *p*-*H*(phenyl)), 8.02 (d, 3H, *o*-*H*(phenyl), ^3J(HH) = 6.2 Hz). ^{13}C NMR (62.7 MHz, $CDCl_3$): δ 13.3 (CH_3(Pz)), 30.5 (CH_2(COD)), 66.1 (CH(COD)), 106.8 (^4C(Pz)), 127.9 (*o*-*C*(phenyl)), 128.1, 128.4 (*p*- and *m*-*C*(phenyl)), 135.1 (*ipso*-*C*(phenyl)), 146.0 (^5C(Pz)), 153.1 (^3C(Pz)).

Tp^{iPr_2}Ir(COD)] (7). This compound was prepared as described above using [$Ir_2Cl_2(COD)_2$] (80 mg, 0.119 mmol), in MeCN (2 mL), and K[Tp^{iPr_2}] (120 mg, 0.238 mmol) at 0 °C. The suspension was stirred for 4 h. Recrystallization from hot MeOH or MeCN afforded orange crystals. Yield: 147 mg (80%). Mp: 172 °C dec. Anal. Found (calcd for $C_{35}H_8BIrN_6$): C, 55.16 (54.89); H, 7.66 (7.63); N, 10.93 (10.97). IR (RbI, cm^{-1}): 2481 (ν(B−H), s). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.14 (d, 18H, CH_3(^{i}Pr), ^3J(HH) = 6.9 Hz), 1.24 (d, 18H, CH_3(^{i}Pr), ^3J(HH) = 6.9 Hz), 1.30 (m, 4H, CH_2(COD)), 1.87 (m, 4H, CH_2(COD)), 3.07 (sept, 3H, CH(^{i}Pr)), 3.19 (sept, 3H, CH(^{i}Pr)), 3.87 (br, 4H, CH(COD)), 5.89 (s, 3H, CH(Pz)). ^{13}C NMR (62.7 MHz, $CDCl_3$): δ 23.3 (CH_3(^{i}Pr)), 23.8 (CH_3(^{i}Pr)), 26.3 (CH(^{i}Pr)), 28.1 (CH(^{i}Pr)), 30.6 (CH_2(COD)), 63.6 (CH(COD)), 98.7 (^4C(Pz)), 156.4 (^5C(Pz)), 159.5 (^3C(Pz)).

[Tp^{Me_2,Cl}Ir(COD)] (9). This compound was prepared as described above using [$Ir_2Cl_2(COD)_2$] (100 mg, 0.149 mmol), in MeCN (2 mL), and K[Tp^{Me_2,Cl}] (126 mg, 0.298 mmol) at −10 °C. The suspension was stirred for 45 min at this temperature. The precipitate was filtered off and extracted with hot methanol to remove the dark purple byproduct [Ir_2(μ_2-4-chloro-3,5-dimethylpyrazolyl)$_2$(COD)$_2$] (**11A**). Yield: 4.5 mg (3.5%). The residue, after recrystallization from MeCN at 0 °C, gave the desired product as a yellow solid. Yield: 81 mg (39%). Mp: 151 °C dec. Anal. Found (calcd for $C_{23}H_{31}BCl_3IrN_6$): C, 39.28 (39.41); H, 4.51 (4.46); N, 11.94 (11.99). IR (RbI, cm^{-1}): 2484 (ν(B−H), s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39 (m, 4H, CH_2(COD)), 1.88 (m, 4H, CH_2(COD)), 2.14 (s, 9H, CH_3(Pz)), 2.34 (s, 9H, CH_3(Pz)), 3.86 (br, 4H, CH(COD)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 11.0 (CH_3-(Pz)), 12.6 (CH_3(Pz)), 30.3 (CH_2(COD)), 64.7 (CH(COD)), 109.7 (^4C(Pz)), 141.9 (CCH_3(Pz)), 146.7 (^3C(Pz)).

[Tp^{Me_2,Br}Ir(COD)] (10). This was prepared as described above using [$Ir_2Cl_2(COD)_2$] (150 mg, 0.223 mmol), in MeCN (2 mL), and K[Tp^{Me_2,Br}] (256 mg, 0.448 mmol) at 0 °C. The dark purple byproduct was isolated by recrystallizing the crude product from hot MeOH as fine orange crystals. Yield: 88 mg (58%). Mp: 191 °C dec. Anal. Found (calcd for $C_{23}H_{31}BBr_3IrN_6$): C, 33.21 (33.11); H, 3.86 (3.75); N, 9.9 (10.07). IR (RbI, cm^{-1}): 2486 (ν(B−H), s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.45 (m, 4H, CH_2(COD)), 1.91 (m, 4H, CH_2(COD)), 2.20 (s, 9H, CH_3(Pz)), 2.39 (s, 9H, CH_3(Pz)), 3.90 (br, 4H, CH(COD)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 12.1 (CH_3(Pz)), 13.7 (CH_3(Pz)), 30.3 (CH_2(COD)), 64.9 (CH(COD)), 96.7 (^4C(Pz)), 143.8 (^5C(Pz)), 148.2 (^3C(Pz)).

[Ir$_2$(μ_2-4-chloro-3,5-dimethylpyrazolyl)$_2$(COD)$_2$] (11A). Anal. Found (calcd for $C_{26}H_{36}Cl_2Ir_2N_4$): C, 36.59 (36.31); H, 4.37 (4.22); N, 6.44 (6.52). UV (CH_2Cl_2), nm (ϵ): 524 (10 250), 386 (2068), 238 (25 800). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.86 (m, 8H, CH_2(COD)), 2.29 (s, 12H, CH_3(Pz)), 2.40 (m, 4H, CH_2(COD)), 2.55 (m, 4H, CH_2-(COD)), 3.81 (m, 4H, CH(COD)), 4.19 (m, 4H, CH(COD)).

[(κ^2-HTp^{Me_2})Ir(COD)](CF$_3$SO$_3$) (12). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −165.7 (^{2}N), −166.3 (^{1}N), −150.2 (2N), −186.3 (1 NH).

[{HB(Pz^{3Me})$_2$(Pz^{5Me})}Ir(COD)] (13). One attempt to prepare a mixture of **2A** and **2B** as described above gave mainly this compound. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.54 (m, 4H, CH_2(COD)), 2.27 (m, 4H, CH(COD)), 2.33 (s, 3H, ^{5}Me(Pz)), 2.62 (s, 6H, ^{3}Me(Pz)), 3.74 (br, 4H, CH(COD)), 5.91 (s, 1H, ^4H(Pz)), 6.07 (s, 2H, ^4H(Pz)), 7.19 (s, 1H, ^3H(Pz)), 7.50 (s, 2H, ^5H(Pz)). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 13.2 (2C, ^{3}Me(Pz)), 15.7 (1C, ^{5}Me(Pz)), 32.1 (br, CH_2(COD)), 55.4 (br, CH_2(COD)), 105.6 (1C, ^4C(Pz)), 106.5 (2C, ^4C(Pz)), 135.8 (br, 3C, 2 × ^5C(Pz), 1 × ^3C(Pz)), 144.3 (1C, ^5C(Pz)), 151.7 (br, 2C, ^3C(Pz)).

As the ^{15}N NMR spectrum of compound **13**, in which only one pyrazolyl ring has undergone a borotropic shift, could not be detected, an estimate of the amount of the five-coordinate form **C** present in solution was obtained on the basis of its ^{13}C δ value for the olefinic carbons (see Table 2) using a "carbon scale" which had been "calibrated" with the data obtained for compounds **1**, **2**, and **14**. This method indicates that ca. 50% of isomer **C** was present.

[{HB(Pz^{3Me})(Pz^{5Me})$_2$}Ir(COD)] (14). The NMR spectrum of the sample containing only **2A** and **2B,** described earlier, after storage for 45 min at 70 °C, showed that the signals due to **2A** and **2B** had disappeared. The following new sharp signals due to **14** were observed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (m, 4H, CH_2(COD)), 2.35 (s, 6H, ^{5}Me(Pz)), 2.39 (m, 4H, CH_2(COD)), 2.64 (s, 3H, ^{3}Me(Pz)), 3.52 (br, 4H, CH(COD)), 5.93 (s, 2H, ^4H(Pz)), 6.03 (s, 1H, ^4H(Pz)), 7.53 (s, 1H, ^5H(Pz)), 7.57 (s, 2H, ^3H(Pz)). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 12.8 (2C, ^{5}Me(Pz)), 15.4 (1C, ^{3}Me(Pz)), 32.6 (CH_2(COD)), 52.9 (CH-(COD)), 105.4 (2C, ^4C(Pz)), 106.0 (1C, ^4C(Pz)), 135.9 (1C, ^5C(Pz)), 137.2 (2C, ^5C(Pz)), 151.4 (2C, ^5C(Pz)), 155.7 (1C, ^3C(Pz)). ^{15}N NMR (50.7 MHz, $CDCl_3$): δ −154.4 (3N, ^{1}N), −148.9 (2N), −127.5 (1N, ^{2}N).

[HB(Pz^{3iPr})$_2$(Pz^{5iPr})Ir(COD)] (15). Another attempt to prepare the original complex **3** (see above) led to the isolation of an isomeric species which was also characterized. Anal. Found (calcd for $C_{26}H_{40}BIrN_6$): C, 49.34 (48.82); H, 6.52 (6.48); N, 13.21 (13.14). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.20 (d, 6H, CH(CH_3), ^3J(HH) = 6.9 Hz), 1.27 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.9 Hz), 1.30 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.9 Hz), 1.39 (m, 4H, CH_2(COD)), 2.00 (m, 4H, CH_2(COD)), 3.37 (m, 3H, CH(CH$_3$)$_2$), 3.72 (br, 4H, CH(COD)), 6.08 (d, 1H, ^4H(Pz), ^3J(HH) = 2.2 Hz), 6.11 (d, 2H, ^4H(Pz), ^3J(HH) = 2.3 Hz), 7.30 (d, 1H, ^3H(Pz), ^3J(HH) = 2.2 Hz), 7.37 (d, 2H, ^5H(Pz), ^3J(HH) = 2.3 Hz). ^{13}C NMR (62.7 MHz, $CDCl_3$): δ 22.9, 23.6, 24.7, 26.4, 28.3, 31.5 (C(^{i}Pr)), 31.1 (CH_2(COD)), 63.2 (CH(COD)), 101.7 (2C, ^4C(Pz)), 102.5 (1C, ^4C(Pz)), 136.2 (2C, ^3C(Pz)), 138.1 (1C, ^5C(Pz)), 157.0 (2C, ^5C(Pz)), 162.1 (1C, ^3C(Pz)).

Crystallography. Crystals suitable for X-ray diffraction were obtained as follows: **9**, by recrystallization from hot methanol; **1**, by recrystallization from *n*-hexane at −20 °C; **4**, by recrystallization from hot *n*-hexane.

All crystals were mounted on glass fibers, in random orientations, and placed on an automatic diffractometer (see Supporting Information)

Table 3. Experimental Data for the X-ray Diffraction Study of Compounds **9**·2MeOH and **1**

	9·2MeOH	**1**
empirical formula	$C_{25}H_{38}BCl_3IrO_2N_6$	$C_{17}H_{22}BIrN_6$
mol wt	763.9	513.42
data collecn *T*, °C	23	23
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.044(1)	7.345(1)
b, Å	11.186(2)	7.645(1)
c, Å	15.499(3)	15.893(1)
α, deg	77.90(1)	103.17(4)
β, deg	73.23(1)	90.30(2)
γ, deg	66.89(1)	93.50(3)
V, Å^3	1524.3(4)	865.9(8)
Z	2	2
ρ(calcd), g cm^{-3}	1.664	1.969
μ, cm^{-1}	46.599	76.909
radiation	Mo Kα (graphite monochromated)	
θ range, deg	$2.5 < \theta < 22.0$	$2.5 < \theta < 27.0$
no. of obs reflns (n_o)	2469 ($F_o^2 > 3.0\sigma(F^2)$)	2606 ($F_o^2 > 3.5\sigma(F^2)$)
transm coeff	0.8686−0.9951	0.4603−0.9972
R^a	0.0276	0.0433
$R_w{}^b$	0.0351	0.0530
GOF^c	1.124	1.297

$^a R = \sum(|F_o| - (1/k)F_c|)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - (1/k)|F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} GOF $= [\sum w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

for the unit cell and space group determinations and for the data collections. Unit cell dimensions were obtained by least-squares fits of the 2*θ* values of 25 high-order reflections. Selected crystallographic and other relevant data are listed in Table 3 and in the Supporting Information. Data were measured with variable scan speeds to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystals and of the experimental conditions and were measured every hour. The collected intensities were corrected for Lorentz and polarization factors.[39] For compound **9**·2MeOH, a decay correction was necessary. An empirical adsorption correction[40] was applied to all data sets by using azimuthal (*ψ*) scans of "high-*χ*" ($\chi > 82°$) angle reflections. The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as shown in Table 3. The structures were solved by a combination of Patterson and Fourier methods and refined by full-matrix least-squares procedures[39] (the function minimized being $\sum[w(F_o - (1/k)F_c)^2]$). No extinction correction was deemed necessary for all compounds. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[41] The contribution of the hydrogen atoms in calculated positions (C−H = 0.95 Å, $B(H) = 1.3 \times B(C_{bonded})$ (Å^2)) was taken into account but not refined. Except for the case of **9**, upon convergence (see Supporting Information) no significant features were found in the Fourier difference maps of the three compounds. Final agreement factors and other relevant data for the refinement are given in Table 3. All calculations were carried out using the Enraf-Nonius MOLEN package.[39]

Structural Study of 9·2MeOH. A set of 3233 data were collected, of which 2469 were considered as observed and used for the refinement. A Fourier difference map revealed the presence of two clathrated methanol molecules that were included in the refinement. The final full-matrix least-squares refinement was carried out using anisotropic displacement parameters for all atoms.

Structural Study of 1. A total of 3756 independent reflections were collected, and 2606 were considered as observed. The structure was refined as described above, using anisotropic displacement parameters for all atoms.

Structural Study of 4. Direct and Fourier methods were used to solve this structure. After refinement by full-matrix least-squares procedures, while the tris(pyrazolyl)borate−iridium moiety gave an acceptable geometry, the COD moiety was found to be completely disordered and it did not prove possible to construct a meaningful model. However, the positions of the donor atoms in the Tp^{Me_2} moiety unambiguously show that the bonding of this ligand is fully analogous to that in **9**, and therefore, in the solid state, the iridium center in **4** is four-coordinate square planar.

Acknowledgment. M.B. carried out this work during the tenure of a studentship from the Swiss National Research Council. The authors are indebted to Dr. U. E. Bucher for providing several of the pyrazolylborate salts used in this study.

Supporting Information Available: Listings of complete X-ray experimental details for **9**·2MeOH, **1**, and **4** and tables of positional parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, bond distances, angles, and torsion angles for **1** and **9**·2MeOH, as well as a figure showing contour plots of sections of the ^{1}H 2D NOESY spectrum (500 MHz, room temperature) of [{HB(Pz^{3Me})(Pz^{5Me})$_2$}Ir(COD)] (**14**) (17 pages). See any current masthead page for ordering information.

IC970361O

(39) *MolEN: Molecular Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.
(40) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.
(41) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.