Investigation of the C–H Activation Potential of [Hydrotris(1*H*-pyrazolato-κN^1)borato(1–)]iridium ($IrTp^x$) Fragments Featuring Aromatic Substituents *x* at the 3-Position of the Pyrazole Rings

Part 1

The Choice of the Precursor

by **Christian Slugovc***[a]), **Kurt Mereiter**[b]), **Swiatoslaw Trofimenko**[c]), and **Ernesto Carmona***[d])

[a]) Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9/153, A-1060 Vienna (fax: (+43)-1-5880115399; e-mail: slugi@mail.zserv.tuwien.ac.at)

[b]) Institute of Mineralogy, Crystallography and Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/171, A-1060 Vienna

[c]) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716-2522, USA

[d]) Instituto de Investigaciones Químicas, Departamento de Química Inorgánica Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Avda. Américo Vespucio s/n, E-41092 Sevilla (fax: (+34)-954460565; e-mail: guzman@cica.es)

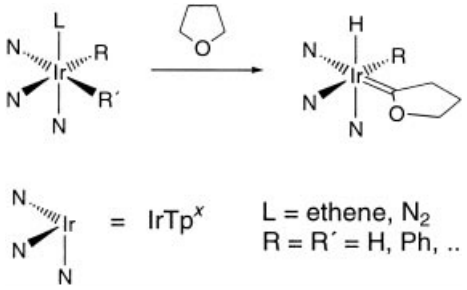
In memory of Professor *Luigi M. Venanzi*

A series of pyrazole-substituted [hydrotris(1*H*-pyrazolato-κN^1)borato(1–)]iridium complexes of the general composition [Ir(Tp^x)(olefin)$_2$] ($Tp^x = Tp^{Ph}$ and Tp^{Th}) and their capability to activate C–H bonds is presented. As a test reaction, the double C–H activation of cyclic-ether substrates leading to the corresponding *Fischer* carbene complexes was chosen. Under the reaction conditions employed, the parent compound [Ir(Tp^{Ph})(ethene)$_2$] was not isolable; instead, (*OC*-6-25)-[Ir($Tp^{Ph}\kappa C^{Ph},\kappa^3 N,N',N''$)(ethyl)($\eta^2$-ethene)] (**1**) was formed diastereoselectively. Upon further heating, **1** could be converted exclusively to (*OC*-6-24)-[Ir($Tp^{Ph}\kappa^2 C^{Ph},C^{Ph},\kappa^3 N,N',N''$)($\eta^2$-ethene)] (**2**). Complex **1**, but not **2**, reacted with THF to give (*OC*-6-35)-[Ir($Tp^{Ph}\kappa^3 N,N',N''$)H(dihydrofuran-2(3*H*)-ylidene)] (**3**), a cyclic *Fischer* carbene formed by double C–H activation of THF. Accordingly, complexes of the general formula [Ir(Tp^x)(butadiene)] (see **4**–**6**; butadiene = buta-1,3-diene, 2-methylbuta-1,3-diene (isoprene), 2,3-dimethylbuta-1,3-diene) reacted with THF to yield **3** or the related derivative **9**. The reaction rate was strongly dependent on the steric demand of the butadiene ligand and the nature of the substituent at the 3-position of the pyrazole rings.

Introduction. – The selective activation of the C–H bonds of organic substrates by transition-metal complexes and the utilization of this reaction for the functionalization of unreactive compounds constitute an important and active area of research [1]. We have recently developed an efficient, straightforward synthetic route to *Fischer*-type carbene iridium complexes by double C–H activation of cyclic-ether substrates (*Scheme 1*). Ir^{III} Species like [Ir(Tp^{Me_2})(H)(CH=CH_2)(H_2C=CH_2)] or [Ir(Tp^{Me_2})(Ph)$_2$(μ-N_2)] (Tp^{Me_2} = [tris(3,5-dimethyl-1*H*-pyrazolato-κN^1)hydroborato(1–)-$\kappa^3 N^2,N^{2'},N^{2''}$]), are able to induce this reaction in five- or six-membered cyclic ethers [2].

The utilization of Tp^{Ph} (Tp^{Ph} = [hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(1–)]) as the coligand has brought about a substantial improvement of this synthetic methodology. [Ir(Tp^{Ph})(isoprene)] is able to activate a variety of ethers and amines to give *Fischer*-type carbenes by means of double C–H bond cleavage reactions [3].

Scheme 1

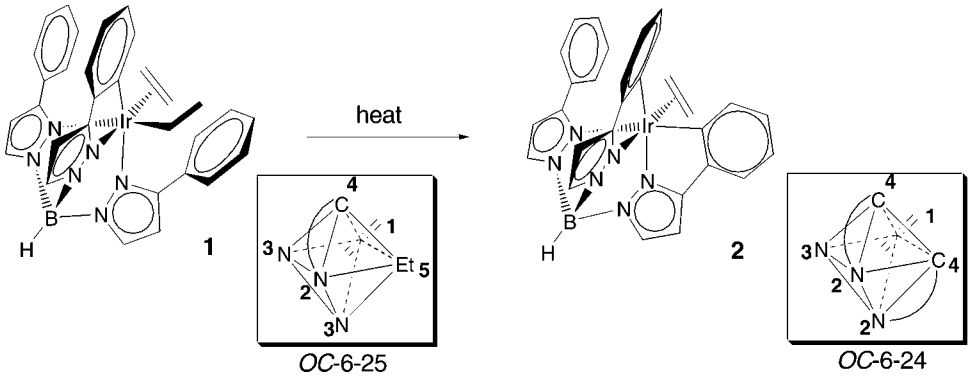


In complexes of Rh^I and Ir^I, with Tp^x ligands, different coordination modes have been demonstrated [4]. $[M(Tp^x)(L)_2]$ Derivatives of d^8-metals adopt either a square-planar geometry with bidentate Tp^x-κ^2, or the trigonal-bipyramidal structure that results from Tp^x-κ^3 coordination. These structures often interconvert. The dynamics of the intramolecular exchange have been extensively studied by *Venanzi* and co-workers [5]. The adoption of one or another structure, or, in other words, the denticity of the Tp^x ligand, depends largely upon the size of the substituent at the 3-position of the pyrazole rings. The Tp^x-κ^3 coordination becomes comparatively disfavored for bulky substituents. Less attention has been paid to the role of the neutral ligands L, but recent studies by *Akita*, *Moro-oka*, and co-workers on compounds of the composition $[Rh(Tp^{iPr_2})(Ph_2P(CH_2)_nPPh_2)]$ have demonstrated an important effect of the chelate size [6] and of the conformation (flat or folded) of the $RhP_2(CH_2)_n$ ring [7] on the Tp^{iPr_2} coordination.

In this line of work, we undertook the preparation and characterization of a series of $[Ir(Tp^x)(olefin)]$ compounds, with $Tp^x = Tp^{Ph}$ and Tp^{Th} (Tp^{Th} = [hydrotris(3-thienyl-1*H*-pyrazolato-κN^1)borato(1−)]; olefin = ethene, buta-1,3-diene, 2-methylbuta-1,3-diene (isoprene), and 2,3-dimethylbuta-1,3-diene) and tested their capacity to achieve the double C−H bond activation of THF, to produce the corresponding *Fischer* carbenes.

Results and Discussion. – *The 'Bis(ethene)' Compound*. The bis(ethene) complex $[Ir(Tp^{Me_2})(\eta^2\text{-ethene})_2]$ (Tp^{Me_2}=[hydrotris(3,5-dimethyl-1*H*-pyrazolato-κN^1)borato(1−)]), readily prepared from $[IrCl(coe)_2]_2$ (coe=cyclooctene) with ethene and $[K(Tp^{Me_2})]$ at low temperatures [8], constitutes a versatile entry to various C−H activation reactions. If $[Tl(Tp^{Ph})]$ is used instead of $[K(Tp^{Me_2})]$, under otherwise similar conditions, a complex with the analytical composition expected for $[Ir(Tp^{Ph})(C_2H_4)_2]$, but of a very different nature, namely the cyclometalated Ir^{III} compound (*OC*-6-25)-[$Ir(Tp^{Ph}$-κC^{Ph},$\kappa^3 N,N',N'')$-(ethyl)(η^2-ethene)] (**1**) is obtained in 86% isolated yield (see *Scheme 2*). Compound **1** is further characterized in the solid-state by X-ray studies (*Fig. 1*). As can be seen, the Ir-center is in a distorted, nonsymmetrical environment that consists of the three N-atoms of the Tp^{Ph} ligand, the C_2H_4 and C_2H_5 groups, and a *C*-metallated phenylpyrazole unit. At variance with structurally characterized $[M(Tp^x$-$\kappa^3)]$ moieties, which exhibit similar N−M−N angles close to 90°, the three N−Ir−N bite angles of **1** amount to 83.3(1), 92.8(2), and 76.1(1)°. The difference between the latter two, 16.7°, is larger than usual differences (<10°) (for a closer discussion of the structure, see [9]).

Scheme 2



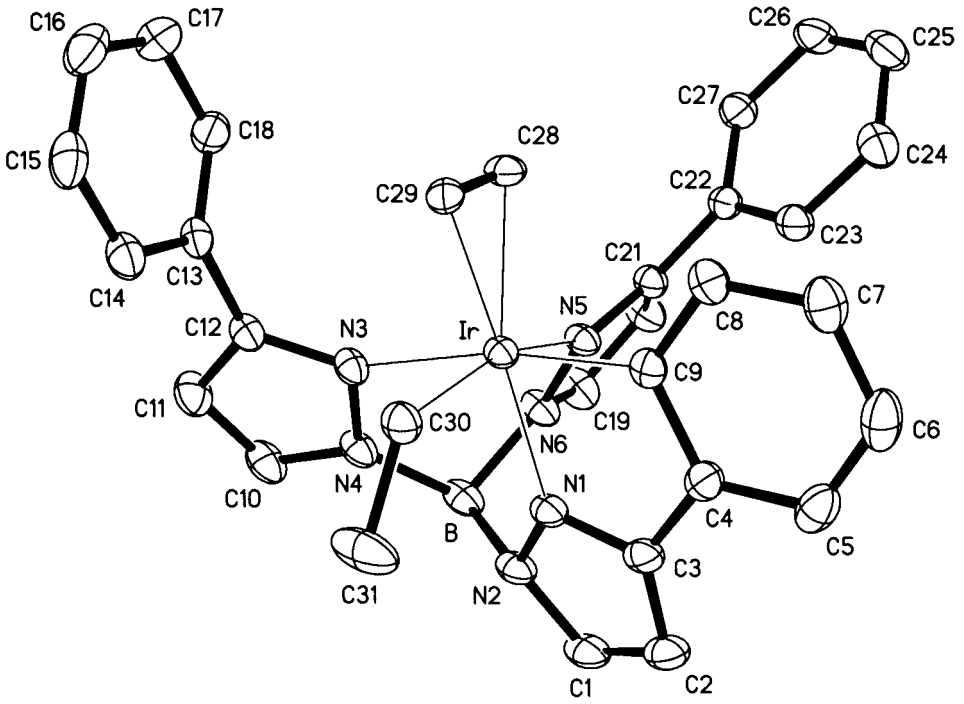


Fig. 1. *ORTEP Plot of* **1**. H-Atoms are omitted for clarity; thermal ellipsoids are at the 20% probability level.

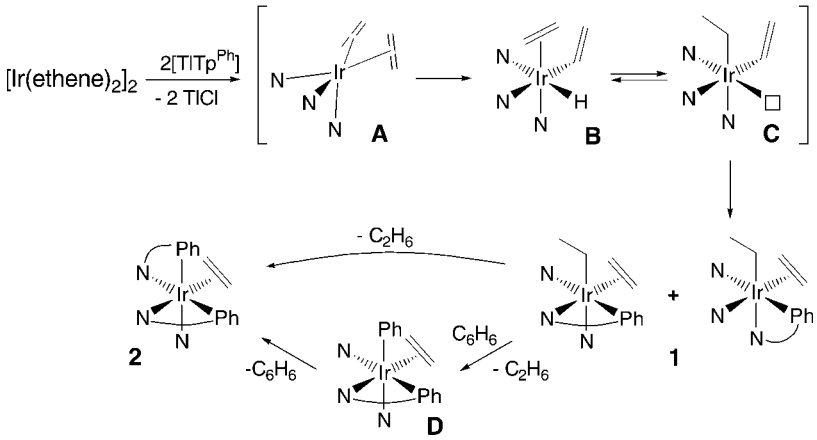
Crude mixtures of **1** contain a by-product (< 4% as established by ^{1}H-NMR spectroscopy; de of **1** > 92%), which cannot be isolated, but, arguably, is the other isomer (*OC*-6-35)-[Ir(Tp^{Ph}-κC^{Ph},$\kappa^3 N,N',N''$)(ethyl)(η^2-ethene)]. Both its η^2-bonded ethene and ethyl ligands are obvious in the ^{1}H-NMR spectrum of the by-product, with the chemical shifts distinctly different from those in **1**.

Heating of **1** in benzene gives the bis-cyclometalated product (*OC*-6-24)-[Ir(Tp^{Ph}-κ^2C^{Ph},C^{Ph},κ^3N,N',N'')(η^2-ethene)] (**2**) as the only isolable product (*Scheme 2*). Accordingly, the second metallation process proceeds diastereoselectively to yield **2**, regardless of whether crude **1** (containing the minor isomer) or pure **1** is used. Nevertheless, some decomposition occurs ($92 \pm 2\%$ isolated yield of **2**), so that it is not clear whether or not the minor isomer contributes to the formation of **2**. The identity of **2** is apparent from three nonequivalent pyrazole rings in the NMR spectra. Note that the other isomer of **2** should have C_{2v} symmetry.

The thermal conversion of **1** into **2** can be monitored by NMR spectroscopy in different solvents. No other species is detected in C_6F_6, $CDCl_3$, or (D_{12})cyclohexane, but, in C_6D_6, an intermediate is observed (*vide infra*), whereas (D_8)THF gives a different reaction product. Generation of the latter on a preparative scale by heating **1** in THF (80°, 16 h) allows its formulation as (*OC*-6-35)-[Ir(Tp^{Ph}-κC^{Ph},κ^3N,N',N'')-H(dihydrofuran-2(3*H*)-ylidene)] (**3**; see below, *Fig. 4*), a cyclic *Fischer* carbene formed by double C–H activation of THF (isolated yield 91%). Again, the transformation is diastereoselective, a by-product present in the raw mixture (< 5%; de of **3** > 90%) is assumed to be the other diastereoisomer based on the NMR-spectroscopic properties. A 2D-NOE experiment with **3** suggests a configuration similar to that of **1**, with the neutral (π-accepting) ligand *trans* to the iridium-bonded N-atom of the *C*-metalated phenylpyrazole unit. A cross-peak of the hydrido ligand with the *ortho*-protons of a nonmetallated phenyl ring is observed.

Proposed Mechanism for the Formation of **1**–**3**. Previous work has shown that the increase of the steric bulk of the Tp^x ligand that accompanies the change from Tp to Tp^{Me_2} facilitates the activation of a coordinated molecule of ethene of [Ir(Tp^x)(C_2H_4)$_2$] compounds [8]. The resulting [Ir(Tp^x)(H)(ethenyl)(η^2-ethene)] species (see, *e.g.*, **B** in *Scheme 3*) react readily with 2-electron donors (*e.g.*, MeCN, PMe_3) to generate [Ir^{III}(ethyl)(ethenyl)] adducts in which the molecule of the *Lewis* base takes up the vacant coordination site of **C** [10]. For the system under investigation, which is based on the bulkier Tp^{Ph} ligand, a combination of steric hindrance and of the close proximity of the Ph rings of the Tp^{Ph} group explains the facile formation of **1** as the direct product of the reaction of [IrCl(coe)$_2$]$_2$ with C_2H_4 and [Tl(Tp^{Ph})]. Clearly, in this case, one of the Ph substituents at the pyrazole moieties promotes the **B** → **C** transformation *via* the formal oxidative addition of an aromatic C–H bond and subsequent hydrido-vinyl reductive coupling, giving rise to **1**. Since intermediates of kind **B** have been shown to add two molecules of C_6H_6 to produce, *e.g.*, [Ir(Tp^{Me_2})(C_6H_5)$_2$(N_2)] [2] through a species like **C**, the mechanism of the formation of **1** may be viewed as readily established. Heating of solutions of **1** allows its conversion into **2**. The reaction may proceed intramolecularly (C_6F_6 as the reaction solvent) or by intervention of a molecule of C_6H_6 when this substance is used as the solvent. In the latter case, an intermediate **D** would be formed, and, while this could not be isolated, it can be assumed to be [Ir(Tp^{Ph}-κC^{Ph},κ^3N,N',N'')(Ph)(η^2-ethene)] on the basis of its characteristic NMR signals (^{1}H-NMR: 3.60 (*m*, 2 H, $H_2C{=}CH_2$); 3.17 (*m*, 2 H, $H_2C{=}CH_2$); $^{13}C\{^1H\}$-NMR: 64.9 (2 C, $H_2C{=}CH_2$)). A related intermediate, [Ir(Tp^{Ph}-κC^{Ph},κ^3N,N',N'')(tetrahydrofuran-2-yl-κC^2)(η^2-ethene)], is proposed for the formation of **3** (for a study of the THF activation see [3]). Finally, evolution of ethane (monitored by NMR spectroscopy) is confirmed.

Scheme 3. *Proposed Mechanism for the Formation of* **1** *and* **2**



The clean activation of THF by **1** to give **3** encouraged us to employ **1** as a precursor for similar activation reactions of ethers, bearing a CH_2 group in α-position. Disappointingly, **1** reacts in neat tetrahydropyran, giving **2** as the major product (82%) and only 18% of the expected (*OC*-6-35)-[Ir(Tp^{Ph}-κC^{Ph},$\kappa^3 N,N',N''$)H(tetrahydro-2*H*-pyran-2-ylidene)] (**8** = 6-membered cyclic ether analogue of **3**). Moreover, the use of 2 equiv. of THF in different solvents (toluene, benzene, cyclohexane) leads to mixtures of **2** and **3**. Finally **2** does not convert to **3** upon heating in neat THF (24 h at 80°). This observation may be seen in connection with the inertness of d^6-transition metal complexes with Tp^x[1]), but is nevertheless somewhat surprising because of the pronounced lability of the ethene ligand in [Ir(Tp^{Me_2})(phenyl-κC^1)$_2$(η^2-ethene)]. This particular compound could not be isolated, instead the related compound [Ir(Tp^x)(phenyl-κC^1)$_2$(N$_2$)] has been formed with the N_2 ligand stemming from the inert gas used [2]. These results clearly show that intramolecular metalation of a phenyl substituent competes favorably with the formation of the *Fischer* carbenes, perhaps as a reflection of the strength of the Ir–Ph bond [12]. On the other hand, **3** does not give **2** upon prolonged heating (72 h toluene, 120°).

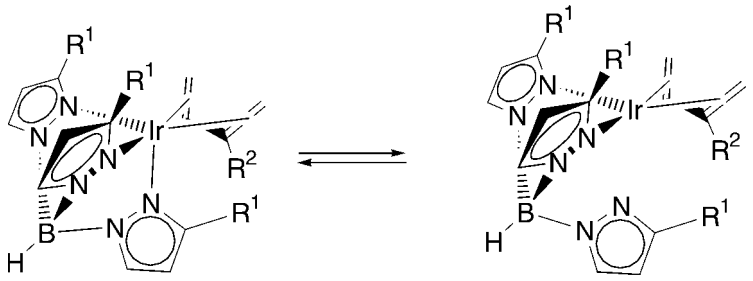
To overcome this problem, we changed our strategy and prepared compounds in which the incoming substrate (*e.g.*, the ether to be activated) can interact with the metal at an early stage of the reaction pathway. Since complexes of the type [Ir(Tp^x)(butadiene)] (Tp^x = Tp, Tp^{Me_2}) are reluctant to form allyl-hydride compounds upon thermal activation [13], but are instead prone to bind an additional ligand, rearranging into the corresponding 'iridacyclobutenediyl' complexes [Ir(Tp^x)(but-2-en-1,4-diyl-$\kappa^2 C^1,C^4$)(L)] (L = aldehydes, CO, phosphines, pyridine) [14], we considered these Ir^I diene derivatives suitable for the above purposes.

The Butadiene Compounds. Reacting [IrCl(coe)$_2$]$_2$ with butadienes (buta-1,3-diene, 2-methylbuta-1,3-diene (= isoprene), and 2,3-dimethylbuta-1,3-diene) and subsequently with [Tl(Tp^{Ph})] or [Tl(TpTh)] in CH_2Cl_2 at room temperature results in the formation

[1]) For instance, the self-exchange reaction of MeCN in [RuTp(MeCN)$_3$]$^+$ has been found to be more than eight orders of magnitude slower than in the corresponding complex [Ru(Cp)(MeCN)$_3$]$^+$ [11].

of compounds of the general formula [Ir(Tp^x)(butadiene)]. A subsequent activation reaction of either the butadiene or the Tp^x ligand is not observed under these conditions, consequently, the iridium core stays formally at oxidation state +1. [Ir(Tp^{Ph})(buta-1,3-diene)] (**4a**), [Ir(TpTh)(buta-1,3-diene)] (**4b**), [Ir(Tp^{Ph})(2-methylbuta-1,3-diene)] (**5a**), and [Ir(TpTh)(2-methylbuta-1,3-diene)] (**5b**) are fluxional in solution (see *Scheme 4*), as deduced from the observation of only one set of signals for the Tp^x ligand in the ^{1}H- and ^{13}C-NMR spectra. It is worth noting that the fluxionality of the C_4H_6 compounds **4a**,**b** is less pronounced than that of the analogous isoprene derivatives **5a**,**b**. For example, the ^{1}H-NMR spectrum of **4a**,**b** becomes sharp at 40°, while the spectrum of **5a**,**b** is already nicely resolved at 20°. From the coalescence temperatures measured (^{1}H-NMR at 300 MHz) for **4a**,**b** and **5a**,**b** of $18 \pm 1°$ and $-24 \pm 1°$, respectively, activation energies $\Delta G^{\neq} = 59 \pm 3$ and $\Delta G^{\neq} = 50 \pm 3$ kJ · mol^{-1} can be computed for the dynamics of the exchange in the compounds.

Scheme 4. *Dynamic Behavior of the [Ir(Tp^x)butadiene)] Complexes* **4a**, **4b**, **5a**, *and* **5b**

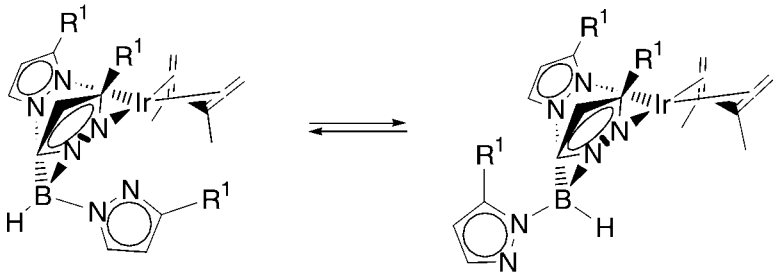


4a R^1 = Ph, R^2 = H
b R^1 = 2–thienyl, R^2 = H
5a R^1 = Ph, R^2 = Me
b R^1 = 2–thienyl, R^2 = Me

The use of the sterically more demanding 2,3-dimethylbuta-1,3-diene introduces unexpected complexity, at least six products (according to TLC and NMR) are formed when Tp^{Ph} is employed as the coligand. The two major products are isolated by column chromatography and identified as four-coordinated [Ir(Tp^{Ph}-κ^2N,N')(η^4-2,3-dimethylbuta-1,3-diene)] (**6a**; *Scheme 5*), and (*OC*-6-43)-[Ir(Tp^{Ph}-κ^2C^{Ph},κ^3N,N',N'')(5-phenyl-1*H*-pyrazole-κN^2)] (**7**; see below, *Fig. 3*), respectively. The reaction giving [Ir(TpTh-κ^2N,N')(η^4-2,3-dimethylbuta-1,3-diene)] (**6b**) proceeds in a cleaner way, and only small amounts of unidentified by-products are formed. The identity of **6a** and **6b** as square-planar 16-electron compounds in solution is established by a combination of NMR and IR spectroscopy (*cf. Table*). Using as first criterion *Venanzi*'s evaluation of ^{13}C-NMR data of olefins and following the suggestion that there is a more pronounced high-field shift for coordinated olefinic C-atoms in a κ^3-compound than in the analogous κ^2-compound due to higher π-back-bonding in the 18-electron system [5], we find that **6a** and **6b**, indeed, fulfill this rule, despite that only the terminal butadiene C-atoms are affected. Further comparison with [Ir(Tp-κ^3)(2,3-dimethylbuta-1,3-diene)] and [Ir(Tp^{Me_2}-κ^3)(2,3-dimethylbuta-1,3-diene)], which exhibit Tp^x-κ^3 coordination [13],

provides additional support. Comparison of the ^1J(C,H) coupling constants of C(1) and C(4) also points in the same direction. *Moro-oka*'s IR criterion [15] confirms the κ^2-formulation of **6a** and **6b**, since both display a distinctly low B–H stretching frequency (55 to 75 cm^{-1} lower than for **4a**,**b** and **5a**,**b**). However, *Jones*' ^{11}B-NMR criterion [16] delivers ambiguous results for our Tp^{Ph} and Tp^{Th} compounds. In our view, the data in the *Table* clearly show that compounds **4a**,**b** and **5a**,**b** are best described as trigonal bipyramidal 18-electron complexes featuring a Tp^x-κ^3 ligand, whereas **6a**,**b** should be considered as square-planar 16-electron compounds with Tp^x-κ^2 coordination. Some brief additional comments should be given for the ^{1}H- and ^{13}C-NMR spectra of **6a** and **6b**. Both compounds exist as a mixture of two diastereoisomers, as deduced from the observation of two different but closely related sets of resonances in a 5:2 ratio. In accord with literature precedents, these two sets of signals can be attributed to the isomers that differ in the axial or equatorial arrangement of the third Ir-uncoordinated pyrazole group [5][17][18] (*Scheme 5*). Due to the absence of NOE-cross peaks, we have been unable to assign the resonances corresponding to each of the isomers.

Scheme 5. *Dynamic Behavior of the [Ir(*Tp^x*)(2,3-dimethylbuta-1,3-diene)] Complexes* **6a** *and* **6b**



6a R^1 = Ph
b R^1 = 2–thienyl

Table. *IR and NMR Data of* **4**–**6** *and of [Ir(Tp)(*C_6H_{10}*)] and [Ir(*Tp^{Me_2}*)(*C_6H_{10}*)]*

	IR ($\tilde{\nu}_{BH}$ [cm^{-1}])	^{11}B-NMR [ppm]	^{13}C-NMR [ppm] [a])	^1J(C,H) [Hz] [b])
4a	2476, 2456	–3.4	8.5	152
b	2461	–3.4	9.4	150
5a	2473, 2457	–3.3	11.1, 7.8	151, 148
b	2482, 2462	–3.3	11.9, 9.5	152, 150
6a	2406	–2.7	35.4, 35.0	158, 160
b	2405	–3.0	36.0, 35.5	160, 162
[IrTp(C_6H_{10})] [c])			14.6	151
[IrTp^{Me_2}(C_6H_{10})] [c])			5.3	150

[a]) ^{13}C-NMR Shifts for C(1) and C(4) of the butadiene ligand. [b]) ^1J(C,H) coupling constant of C(1) and C(4) with their attached H-atoms. [c]) C_6H_{10} = 2,3-dimethylbuta-1,3-diene, IR and ^{11}B-NMR data not comparable.

The solid-state structure of **6b** is established by X-ray diffraction and corresponds to a distorted square-planar geometry, as shown by the angles given in *Fig. 2*. The dangling pyrazole arm is in an equatorial position, the six-membered IR(–N–N–)$_2$B ring adopts a boat conformation, as is usual for [Ir(Tp^x-κ^2] or [Rh(Tp^x-κ^2] compounds

[4]. The 2,3-dimethylbuta-1,3-diene ligand is bonded in such a way that the two Me groups (C(26) and C(27)) point away from the thienyl substituents at the coordinated pyrazole rings. The diene part shows the expected short (C(24)–C(22)) – long (C(22)–C(23)) – short (C(23)–C(25)) binding pattern for the olefinic C-atoms. There is no interaction of the B-bonded hydride with the Ir-atom. Even though the solid-state structure does not often correspond with the solution structure, we believe that both **6a** and **6b** exhibit the same kind of coordination with Tp^{x}-κ^2 in solution and in the solid state, *i.e.*, they are four-coordinate, distorted square-planar complexes. A similar conclusion was reached by *Cano* and co-workers [17a] for the analogous [Rh(Tp^{Ph})(cod)] compound.

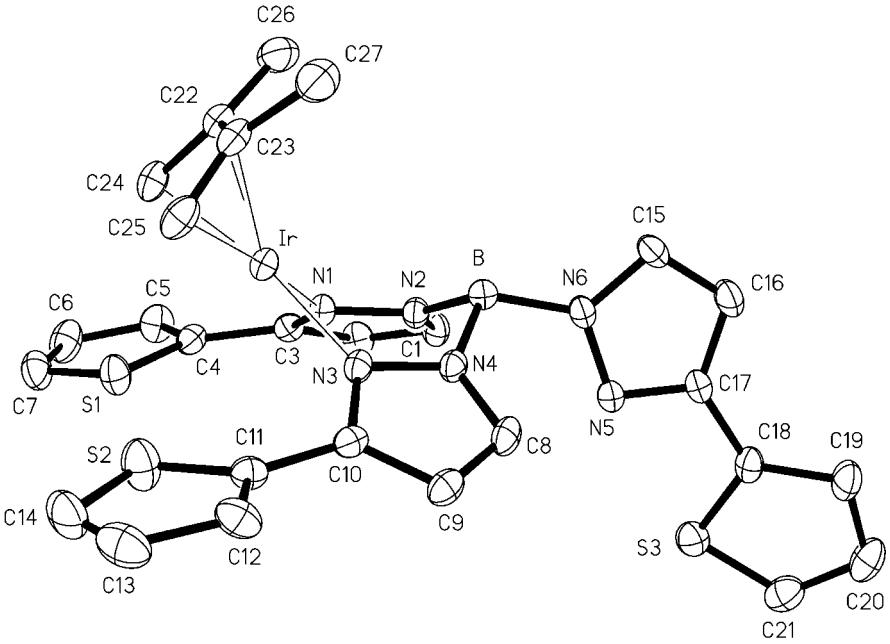


Fig. 2. *ORTEP Plot of* **6b**. H-Atoms are omitted for clarity; thermal ellipsoids are at the 20% probability level. Selected bond lengths [Å] and angles [°]: Ir–N(1) 2.079(8), Ir–N(3) 2.055(7), Ir–C(24) 2.132(10), Ir–C(22) 2.080(9), Ir–C(23) 2.096(10), Ir–C(25) 2.127 (10), C(22)–C(24) 1.399(13), C(22)–C(23) 1.450(14), C(23)–C(25) 1.413(15); N(3)–Ir–N(1) 85.6(3), N(1)–Ir–C(22) 109.6(3), N(3)–Ir–C(23) 113.2(4), C(22)–Ir–C(23) 40.6(4), C(25)–Ir–C(24) 79.2(4), N(3)–Ir–C(25) 97.8(4), N(1)–Ir–C(24) 96.3(3).

The second main product from the reaction of [Ir(2,3-dimethylbuta-1,3-diene)Cl]$_2$ with [Tl(Tp^{Ph})] is the doubly cyclometallated complex (*OC*-6-43)-[Ir(Tp^{Ph}-κ^2C^{Ph},C^{Ph},κ^3,*N*,*N*′,*N*″)(5-phenyl-1*H*-pyrazole-κN^2)] (**7**), as characterized by NMR and IR spectroscopy as well as by a X-ray structure determination (*Fig. 3*). This study confirms the structure proposed for **2** on the basis of spectroscopic data. As already discussed, this includes a κ^5-coordination of the Tp^{Ph} ligand, as a result of the cyclometallation by two phenyl substituents located at the pyrazole rings. Compounds **2** and **7** differ only in the nature of the sixth neutral ligand, a molecule of C_2H_4 in **2** and 5-phenyl-1*H*-pyrazole in the case of **7**, the latter stemming from partial decomposition of

the Tp^{Ph} ligand [5][18][19]. The most salient structural feature of **7** is doubtless the considerable distortion of the pentadentate Tp^{Ph} group, manifested, *e.g.*, in the values of the *cisoid* and *transoid* angles around the Ir-atom of 77.7–103.6(1)° and 154.4–172.7(1)°, respectively [7][9].

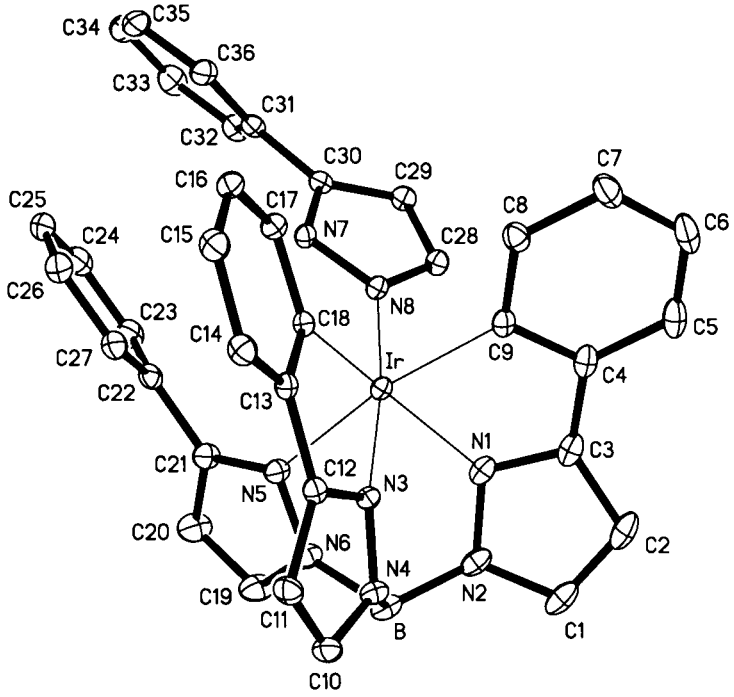


Fig. 3. *ORTEP Plot of* **7**. H-Atoms are omitted for clarity; thermal ellipsoids are at the 20% probability level.

To ascertain the usefulness of the diene complexes **4**–**6** in C–H bond-activation reactions, we tested their capacity to give *Fischer* carbenes derived from tetrahydrofuran by cleavage of two of its α-CH bonds [2]. Compounds **4**–**6** all react with THF to generate complex **3** or the analogous Tp^{Th} derivative (*OC*-6-35)-[Ir(Tp^{Th}-κC^{Th},$\kappa^3 N$,N',N'')H(dihydrofuran-2(3*H*)-ylidene)] (**9**). Exclusive formation of the cyclic carbene **3** or **9** is observed, even when only 1 equiv. of THF is added to a solution of the appropriate complex in toluene. In a series of experiments, whose results are summarized in *Fig. 4*, the diene complexes are allowed to react in neat THF at 70° (bath temperature) to study the dependency of the reaction rate with the nature of both, the diene and Tp^x ligands. Compound **6a** (Tp^{Ph} and 2,3-dimethylbuta-1,3-diene: complete conversion within *ca.* 3 h) and **4b** (Tp^{Th} and buta-1,3-diene: *ca.* 17% conversion within 48 h) are found to exhibit the fastest and the slowest reaction rate, respectively.

As the data in *Fig. 4* show, the Tp^{Ph} derivatives **4a**, **5a**, and **6a** react faster than their Tp^{Th} counterparts **4b**, **5b**, and **6b** (see, *e.g.*, **6a** and **6b**). Since [Ir(Tp^{Me_2})(2,3-

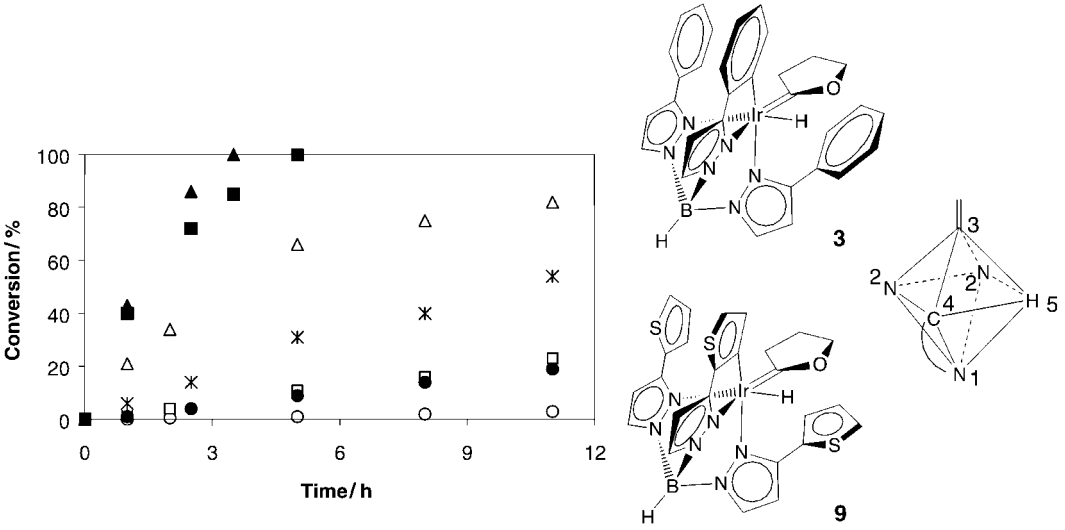


Fig. 4. *Reaction of* **1** (*), **4a** (●), **5a** (■), **6a** (▲), **4b** (○), **5b** (□), *or* **6b** (△) *with THF to give* **3** *or* **9**, *respectively.* Conditions: 20 mg of the corresponding compound in 2 ml of neat THF at 70° bath temp.

dimethylbuta-1,3-diene)] does not react with THF after heating at 70° for 5 days, the conclusion can be reached that a very bulky Tp^x ligand is needed for the [Ir(Tp^x)(diene)] complexes to be able to activate THF at a reasonable reaction rate. Additionally, and in line with previous observations [20], the coordination behavior of Tp^{Th} appears to resemble the less bulky Tp^x ligands, rather than Tp^{Ph}. As for the influence of the diene moiety, the experimental reactivity order, namely buta-1,3-diene < isoprene < 2,3-dimethylbuta-1,3-diene, points, once more, to the importance of steric factors and to the facility with which the 16-electron, four-coordinate [Ir(Tp^x-κ^2)(diene)] structure can be accessed.

Note, however, that as the $\Delta G^{\neq}$ values for the $\kappa^3 \rightarrow \kappa^2$ isomerism within **4a** and **4b** or **5a** and **5b** are the same within experimental error, the generation of the square-planar intermediate is not rate-determining in this reaction sequence. Finally, the high reactivity of **5a** and **6a** (Tp^{Ph}; 2-methyl- and 2,3-dimethylbuta-1,3-diene, resp.) in the double C–H bond activation of cyclic ethers can be exploited to improve the preparation of the tetrahydro-2*H*-pyran-2-ylidene derivative **8** (*vide supra*). This compound can be obtained in *ca.* 75% yield by reacting **5a** with tetrahydro-2*H*-pyran (see *Exper. Part*), whereas the analogous reaction of **1** and the cyclic ether produces yields of **8** lower than 20%.

Experimental Part

General. All preparations and manipulations were carried out under O_2-free N_2 or Ar following conventional *Schlenk* techniques. Solvents were dried rigorously and degassed before use. Light petroleum ether (p.e.), b.p. 40–60°, was used. The complexes $[IrCl(coe)_2]_2$ [21], [Tl(Tp^{Ph})] [22], and [Tl(Tp^{Th})] [20] were prepared according to the literature. The given temp. for heating experiments is always that of the oil bath employed. CC = Column chromatography. IR Spectra: *Bruker Vector-22* spectrometer; in cm^{-1}. NMR Spectra:

Bruker AMX-300, *AMX-400*, and *AMX-500* spectrometers; δ(H) and δ(C) with respect to the solvent as internal standards, but reported with respect to $SiMe_4$, δ(B) referenced to $BF_3 \cdot Et_2O$; most assignments by extensive $^1H,^1H$ decoupling experiments, NOE-DIFF measurements, and homo- and heteronuclear two-dimensional spectra; ^{q} denotes a quaternary C-atom, ^{m} a metallated C-atom or H-atom of the metallated Ph substituent, and *v* a virtual multiplicity. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla).

*(*OC*-6-25)-(η^2-Ethene)(ethyl)[hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(2 −)-κC^2,κN^2,κN$^{2'}$,κN$^{2''}$]iridium* (**1**). Through a suspension of $[(IrCl(coe)_2)_2]$ (433 mg, 0.483 mmol) in CH_2Cl_2 (15 ml), ethene was bubbled at −35° for 5 min to give a colorless soln., whereupon a soln. of $[Tl(Tp^{Ph})]$ (624 mg, 0.966 mmol) in CH_2Cl_2 (15 ml) was added. Stirring the mixture for 4 h and then allowing a gradual warming from −35° to r.t. resulted in the precipitation of TlCl (starting at −20°). The mixture was transferred *via* a cannula to separate part of the precipitate and was then centrifuged. The clear soln. was again evaporated and the residue treated with p.e. (7 ml). Upon cooling at −20°, a pale yellow precipitate was formed, which was collected on a glass frit and washed with p.e. (2 × 2 ml). Drying the residue in *vacuo* gave anal. pure **1** (570 mg, 86%). IR (Nujol): 2473*m* (BH). ^{1}H-NMR (300 MHz, (D_6)benzene, 20°): 7.62 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.51 (*d*, ^3J = 2.5, H−C(5)(pz)); 7.43 (*m*, 1 H, Ph^m); 7.35 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.15–6.90 (*m*, 12 H, Ph); 6.34 (*m*, 1 H, Ph^m); 6.14 (*d*, ^3J = 2.5, H−C(4)(pz)); 5.94 (*d*, ^3J = 2.3, H−C(4)(pz)); 5.92 (*d*, ^3J = 2.3, H−C(4)(pz)); 3.40 (*m*, 2 H, H_2C=CH_2); 2.80 (*m*, 2 H, H_2C=CH_2); 2.05 (br. *q*, ^3J = 7.4, MeCH_2); 0.25 (*t*, ^3J = 7.4, *Me*CH_2). ^{13}C{^{1}H}-NMR (75.5 MHz, (D_6)benzene, 20°): 161.6, 156.6, 156.3 (3 C(3)(pz)); 141.6, 140.3 (2 C, Ph^q); 136.8, 136.2, 135.9 (3 C(5)(pz)); 134.1, 134.0 (2 C, Ph^{q,m}); 130.4 (1 C, Ph^m); 129.8, 129.3, 128.4, 127.9, 127.8, 127.5, 126.2 (11 C, Ph); 122.2, 121.9 (2 C, Ph^m); 108.4, 106.3, 102.1 (3 C(4)(pz)); 60.2 (H_2C=CH_2); 15.9 (*Me*CH_2); −4.7 (Me*C*H_2). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): −2.6. Anal. calc. for $C_{31}H_{30}BIrN_6$ (689.84): C 54.0, H 4.4, N 12.2; found: C 54.0, H 4.5, N 12.3.

A by-product (< 4%) was also formed, as seen by integration of the ^{1}H-NMR of the crude mixture. It was not isolated but assumed to be the second diastereoisomer (*OC*-6-35). Observable ^{1}H-NMR data ($CDCl_3$, 20°): 3.50 (*m*, 2 H, H_2C=CH_2); 2.38 (*m*, 2 H, H_2C=CH_2); 0.05 (*t*, ^3J = 7.3, *Me*CH_2).

*(*OC*-6-24)-(η^2-Ethene)[hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(3 −)-κC^2,κC$^{2'}$,κN$^{2'}$,κN$^{2''}$]iridium* (**2**). A soln. of **1** (60 mg, 0.087 mmol) in benzene (4 ml) was heated at 80° for 17 h, or in toluene (4 ml) at 115° for 4 h 30 min. The solvent was evaporated and the crude mixture purified by CC (Al_2O_3, p.e./Et_2O 1:1). The yellow band yielded, after evaporation and drying *in vacuo*, **2** (53 mg, 92%). IR (Nujol): 2482*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 8.15 (*d*, ^3J = 2.5, H−C(5)(pz)); 7.90 (*d*, ^3J = 7.8, 1 H, Ph); 7.79 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.61 (*d*, ^3J = 2.6, H−C(5)(pz)); 7.55 (*dd*, ^3J = 7.3, ^4J = 1.5, 1 H, Ph); 7.47–7.37 (*m*, 3 H, Ph); 7.31–7.23 (*m*, 3 H, Ph); 6.89 (br. *d*, ^3J = 7.2, 2 H, Ph); 6.83 (*d*, ^3J = 7.1, 2 H, Ph); 6.75 (*dd*, ^3J = 7.3, ^4J = 1.5, 1 H, Ph); 6.70 (*d*, ^3J = 2.5, H−C(4)(pz)); 6.42 (*d*, ^3J = 2.6, H−C(4)(pz)); 6.17 (*d*, ^3J = 2.3, H−C(4)(pz)); 3.15 (*m*, 2 H, H_2C=CH_2); 2.74 (*m*, 2 H, H_2C=CH_2). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 164.0, 161.3, 154.8 (3 C(3)(pz)); 144.5 (1 C, Ph^q); 140.5 (C(5)(pz)); 140.1, 139.6 (2 C, Ph^q); 137.8 (1 C, Ph); 136.9, 135.8 (2 C(5)(pz)); 135.4, 132.3 (2 C, Ph^{q,m}); 129.7, 128.74, 128.70, 128.68, 128.65, 128.59, 128.3, 127.0 (8 C, Ph); 123.2, 122.9, 122.7, 122.5 (4 C, Ph^m); 106.3, 105.1, 103.2 (3 C(4)(pz)); 60.6 (H_2C=CH_2). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): −2.4. Anal. calc. for $C_{29}H_{24}BIrN_6$ (659.59): C 52.8, H 3.7, N 12.7; found: C 52.4, H 3.8, N 12.4.

*(*OC*-6-35)-(Dihydrofuran-2(3*H*)-ylidene)hydro[hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(2 −)-κC^2,κN^2,κN$^{2'}$,κN$^{2''}$]iridium* (**3**). A soln. of **1** (92 mg, 0.133 mmol) in THF (4 ml) was heated at 80° for 16 h. The soln. was evaporated, the resulting yellow oil precipitated upon treatment with p.e. (2 ml), and the precipitate collected on a glass frit and dried *in vacuo:* 85 mg (91%) of **3**. Additional purification might be done by CC (neutral aluminium oxide *90* active, Et_2O/p.e. 1:1), sampling the yellow band. IR (Nujol): 2475*m* (BH), 2230*m* (IrH). ^{1}H-NMR (500 MHz, $CDCl_3$, 20°): 7.89 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.82 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.69 (*d*, ^3J = 7.6, 1 H, Ph^m); 7.61 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.58 (*m*, 2 H, Ph); 7.54 (*d*, ^3J = 7.4, 1 H, Ph^m); 7.28–7.10 (*m*, 9 H, Ph); 7.01 (*vt*, ^3J = 7.2, 1 H, Ph^m); 6.51 (*d*, ^3J = 2.3, H−C(4)(pz)); 6.28 (*d*, ^3J = 2.3, H−C(4)(pz)); 6.15 (*d*, ^3J = 2.3, H−C(4)(pz)); 3.92 (*m*, H−C(5)); 3.61 (*m*, H−C(5)); 1.84 (*m*, H−C(3)); 1.36 (*m*, H−C(3)); 0.60–0.51 (*m*, 2 H−C(4)); −20.78 (*s*, H−Ir). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 267.7 (C=Ir); 163.2, 154.6, 153.7 (3 C(3)(pz)); 142.2, 141.4 (2 C, Ph^q); 138.0 (1 C, Ph^m); 137.8, 137.1, 136.1 (3 C(5)(pz)); 134.3, 134.26 (2 C, Ph^q); 129.8, 129.3, 128.02, 128.00, 127.8, 127.7, 126.7 (11 C, Ph); 122.7, 121.5 (2 C, Ph^m); 106.9, 104.8, 103.0 (3 C(4)(pz)); 81.0 (C(5)); 56.4 (C(3)); 21.2 (C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): −3.3. Anal. calc. for $C_{31}H_{28}BIrN_6O$ (703.64): C 52.9, H 4.0, N 11.9; found: C 52.7, H 3.9, N 12.2.

A by-product (< 5%) was also formed, as seen by integration of the ^{1}H-NMR of the crude mixture. It was not isolated but assumed to be the other diastereoisomer (*OC*-6-52)-**3**). Observable ^{1}H-NMR data (500 MHz, 20°): 4.37 (*m*, H–C(5)); 4.15 (*m*, H–C(5)); –18.86 (*s*, H–Ir).

*(η⁴-Buta-1,3-diene)[hydrotris(3-phenyl-1*H*-pyrazolato-κN¹)borato(1–)-κN²,κN²′,κN²″]iridium* (**4a**). Through a suspension of $[(IrCl(coe)_2)_2]$ (175 mg, 0.196 mmol) in CH_2Cl_2 (6 ml), buta-1,3-diene was bubbled at r.t. to give a colorless soln., whereupon a soln. of $[TlTp^{Ph}]$ (253 mg, 0.392 mmol) in CH_2Cl_2 (6 ml) was added. Stirring the mixture for 4 h at r.t. resulted in the precipitation of TlCl. The mixture was transferred *via* a cannula to separate from TlCl and was then centrifuged. The clear soln. was evaporated, the residue treated with p.e. (9 ml), and the white precipitate formed collected on a glass frit and washed with p.e. (2 × 2 ml). Drying the residue *in vacuo* gave anal. pure **4a** (180 mg, 67%). IR (Nujol): 2476*m*, 2456*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 7.75 (br. *s*, 3 H–C(5)(pz)); 7.28 (br. *s*, 15 H, Ph); 6.12 (br. *s*, 3 H–C(4)(pz)); 3.42 (*m*, H–C(2), H–C(3)); 1.43 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.56 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{1}H-NMR ($CDCl_3$, 67°): 7.78 (*d*, ^3J = 2.1, 3 H–C(5)(pz)); 7.29 (br. *s*, 15 H, Ph); 6.14 (*d*, ^3J = 2.1, 3 H–C(4)(pz)); 3.45 (*m*, H–C(2), H–C(3)); 1.48 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.50 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{1}H-NMR ((D$_6$)acetone, –13°): 8.05 (*d*, ^3J = 2.1, H–C(5)(pz)); 7.83 (*d*, ^3J = 2.2, 2 H–C(5)(pz)); 7.40–7.14 (*m*, 15 H, Ph); 6.26 (*d*, ^3J = 2.1, H–C(4)(pz)); 6.07 (*d*, ^3J = 2.2, 2 H–C(4)(pz)); 3.40 (*m*, H–C(2), H–C(3)); 1.34 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.64 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{1}H-NMR ($CDCl_3$, 67°): 7.78 (*d*, ^3J = 2.1, 3 H–C(5)(pz)); 7.29 (br. *s*, 15 H, Ph); 6.14 (*d*, ^3J = 2.1, 3 H–C(4)(pz)); 3.45 (*m*, H–C(2), H–C(3)); 1.48 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.50 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{13}C{^{1}H}-NMR ($CDCl_3$, 20°): 156.5 (3 C(3)(pz)); 135.4 (br. *s*, 3 C(5)(pz)); 135.0 (br. *s*, 3 C_{ipso}); 130.4 (*s*, 6 C_m); 128.4 (br. *s*, 3 C_p); 127.6 (br. *s*, 6 C_o); 107.7 (3 C(4)(pz)); 72.1 (^1J(C,H) = 173, C(2), C(3)); 8.5 (^1J(C,H) = 152, C(1), C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –3.4. Anal. calc. for $C_{31}H_{28}BIrN_6$ (687.64): C 54.2, H 4.1, N 12.2; found: C 54.1, H 4.2, N 12.5.

*(η⁴-Buta-1,3-diene){hydrotris[3-(2-thienyl)-1*H*-pyrazolato-κN¹]borato(1–)-κN²,κN²′,κN²″}iridium* (**4b**). As described for **4a**, from $[(IrCl(coe)_2)_2]$ (177 mg, 0.198 mmol) and $[TlTp^{Th}]$ (262 mg, 0.262 mmol): 165 mg (89%) of **4b**. IR (Nujol): 2461*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 7.75 (br. *s*, 3 H–C(5)(pz)); 7.33 (br. *s*, 3 H, Th); 7.02 (br. *s*, 6 H, Th); 6.23 (br. *s*, 3 H–C(4)(pz)); 3.65 (*m*, H–C(2), H–C(3)); 1.78 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.12 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{1}H-NMR (300 MHz, (D$_6$)acetone, –13°): 8.20 (*d*, ^3J = 2.1, H–C(5)(pz)); 7.95 (*d*, ^3J = 2.1, 2 H–C(5)(pz)); 7.63 (*dd*, ^3J = 5.4, ^4J = 1.1, 2 H–C(5)(Th)); 7.44 (br. *vt*, ^3J = 3.2, H–C(3)(Th)); 7.11–7.05 (*m*, 4 H, Th); 6.92 (br. *d*, ^3J = 3.2, 2 H–C(3)(Th)); 6.45 (*d*, ^3J = 2.1, H–C(4)(pz)); 6.25 (*d*, ^3J = 2.1, 2 H–C(4)(pz)); 3.62 (*m*, H–C(2), H–C(3)); 1.75 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.17 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{1}H-NMR (300 MHz, $CDCl_3$, 67°): 7.77 (*d*, ^3J = 2.0, 3 H–C(5)(pz)); 7.32 (br. *d*, ^3J = 5.4, 3 H–C(5)); 6.99–6.94 (*m*, 6 H, H–C(3), H–C(4)(Th)); 3.70 (*m*, H–C(2), H–C(3)); 1.82 (*m*, H_{trans}–C(1), H_{trans}–C(4)); –1.01 (*m*, H_{cis}–C(1), H_{cis}–C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 148.0 (3 C(3)(pz)); 134.8 (3 C(2)(Th), 3 C(5)(pz)); 129.0 (6 C, Th); 126.2 (3 C, Th); 109.6 (3 C(4)(pz)); 72.4 (^1J(C,H) = 172, C(2), C(3)); 9.4 (^1J(C,H) = 150, C(1), C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –3.4. Anal. calc. for $C_{25}H_{22}BIrN_6S_3$ (705.71): C 42.6, H 3.1, N 11.9; found: C 42.7, H 3.2, N 12.1.

*[Hydrotris(3-phenyl-1*H*-pyrazolato-κN¹)borato(1–)-κN²,κN²′,κN²″](η⁴-2-methylbuta-1,3-diene)iridium* (**5a**). As described for **4a**, with $[(IrCl(coe)_2)_2]$ (177 mg, 0.198 mmol), CH_2Cl_2 (6 ml), 2-methylbuta-1,3-diene (0.3 ml, excess), and $[TlTp^{Ph}]$ (255 mg, 0.395 mmol). Removing the solvent and drying *in vacuo* gave pure **5a** (198 mg, 71%). Additionally, the product (orange powder) can be purified by CC (neutral aluminium oxide *90* active, p.e./Et_2O 15:1 (pale violet band), then 4:1 (yellow band). IR (Nujol): 2473*m*, 2457*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 7.80 (*d*, ^3J = 2.1, 3 H–C(5)(pz)); 7.31 (*m*, 15 H, Ph); 6.14 (*d*, ^3J = 2.1, 3 H–C(4)(pz)); 2.91 (*vt*, ^3J = 6.3, H–C(3)); 2.21 (*d*, ^2J = 3.5, H_{trans}–C(1)); 1.31 (*dd*, ^3J = 6.0, ^2J = 3.3, H_{trans}–C(4)); 0.67 (*s*, Me); –1.34 (*d*, ^2J = 3.5, H_{cis}–C(1)); –1.36 (*dd*, ^3J = 6.6, ^2J = 3.4, H_{cis}–C(4)). ^{1}H-NMR (300 MHz, (D$_6$)acetone, –53°): 8.15 (*d*, ^3J = 2.1, H–C(5)(pz)); 7.95 (*d*, ^3J = 2.2, 3 H–C(5)(pz)); 7.92 (*d*, ^3J = 2.2, H–C(5)(pz)); 7.38–7.10 (*m*, 15 H, Ph); 6.31 (*d*, ^3J = 2.1, H–C(4)(pz)); 6.10 (*d*, ^3J = 2.2, H–C(4)(pz)); 6.02 (*d*, ^3J = 2.2, H–C(4)(pz)); 2.77 (*vt*, ^3J = 6.2, H–C(3)); 2.32 (*d*, ^2J = 3.3, H_{trans}–C(1)); 1.11 (*dd*, ^3J = 6.0, ^2J = 3.3, H_{trans}–C(4)); 0.53 (*s*, Me); –1.36 (*d*, ^2J = 3.2, H_{cis}–C(1)); –1.55 (*dd*, ^3J = 6.3, ^2J = 3.1, H_{cis}–C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 156.5 (3 C(3)(pz)); 135.5 (3 C_{ipso}); 135.1 (3 C(5)(pz)); 130.7 (6 C_o); 128.3 (3 C_p); 127.6 (6 C_m); 108.1 (3 C(4)(pz)); 85.4 (C(2)); 75.3 (^1J(C,H) = 168, C(3)); 18.3 (Me); 11.1 (^1J(C,H) = 151, C(1)); 7.8 (^1J(C,H) = 148, C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –3.3. Anal. calc. for $C_{32}H_{30}BIrN_6$ (701.67): C 54.8, H 4.3, N 12.0; found: C 54.4, H 4.1, N 12.2.

*{Hydrotris[3-(2-thienyl)-1*H*-pyrazolato-κN¹]borato(1–)-κN²,κN²′,κN²″}(η⁴-2-methylbuta-1,3-diene)iridium* (**5b**). As described for **5a**, with $[(IrCl(coe)_2)_2]$ (100 mg, 0.112 mmol), CH_2Cl_2 (6 ml), 2-methylbuta-1,3-diene

(0.3 ml, excess), and [TlTpTh] (149 mg, 0.223 mmol): 136 mg (85%) of **5b**. IR (Nujol): 2482*m*, 2462*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 7.76 (*d*, ^3J = 2.3, 3 H–C(5)(pz)); 7.30 (*dd*, ^3J = 5.1, ^4J = 1.3, 3 H–C(5)(Th)); 7.02 (*dd*, ^3J = 3.5, ^4J = 1.3, 3 H–C(3)(Th)); 6.96 (*dd*, ^3J = 5.1, ^3J = 3.5, 3 H–C(4)(Th)); 6.22 (*d*, ^3J = 2.3, 3 H–C(4)(pz)); 3.11 (*dd*, ^3J = 6.7, ^3J = 6.0, H–C(3)); 2.53 (*d*, ^2J = 3.6, H_{trans}–C(1)); 1.63 (*dd*, ^3J = 6.0, ^2J = 2.8, H_{trans}–C(4)); 0.95 (*s*, Me); –0.93 (*d*, ^2J = 3.6, H_{cis}–C(1)); –0.99 (*dd*, ^3J = 6.7, ^2J = 2.8, H_{cis}–C(4)). ^{1}H-NMR (300 MHz, (D_6)acetone, –53°): 8.18 (*d*, ^3J = 1.7, H–C(5)(pz)); 7.96 (*d*, ^3J = 2.2, H–C(5)(pz)); 7.94 (*d*, ^3J = 2.2, H–C(5)(pz)); 7.60 (br. *d*, ^3J = 4.9, H–C(5)); 7.56 (br. *d*, ^3J = 4.6, H–C(5)(Th)); 7.48 (br. *d*, ^3J = 4.9, H–C(5)(Th)); 7.17–6.96 (*m*, 6 H, H–C(3), H–C(4)(Th)); 6.45 (*d*, ^3J = 2.3, H–C(4)(pz)); 6.24 (*d*, ^3J = 2.2, H–C(4)(pz)); 6.13 (*d*, ^3J = 2.0, H–C(4)(pz)); 2.63 (*vt*, ^3J = 6.4, H–C(3)); H_{trans}–C(1) overlapped by acetone; 1.51 (*dd*, ^3J = 6.3, ^2J = 2.1, H_{trans}–C(4)); 0.84 (*s*, 3 Me); –0.95 (*d*, ^2J = 3.0, H_{cis}–C(1)); –1.16 (*dd*, ^3J = 6.5, ^2J = 2.3, H_{cis}–C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 149.5 (3 C(3)(pz)); 135.6 (3 C(2)(Th), 3 C(5)(pz)); 130.0 (3 C, C(4)(Th)); 126.5 (3 C(3), 3 C(5)(Th)); 110.6 (3 C(4)(pz)); 86.5 (C(2)); 75.3 (^1J(C,H) = 170, C(3)); 18.7 (1 Me); 11.9 (^1J(C,H) = 152, C(1)); 9.5 (^1J(C,H) = 150, C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –3.3. Anal. calc. for $C_{26}H_{24}BIrN_6S_3$ (719.73): C 43.4, H 3.4, N 11.7; found: C 43.6, H 3.7, N 11.6.

*(η^4-2,3-Dimethylbuta-1,3-diene)[hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(1–)-κN^2,κN$^{2'}$]iridium* (**6a**). As described for **5a**, with [(IrCl(coe)$_2$)$_2$] (180 mg, 0.201 mmol), CH_2Cl_2 (6 ml), 2,3-dimethylbuta-1,3-diene (0.3 ml, excess), and [TlTp^{Ph}] (260 mg, 0.403 mmol). The crude product (red oil) was purified by CC (silica gel, p.e./Et_2O 1:1), then 4:1 (red band; R_f (p.e./Et_2O 4:1) 0.48). Evaporation and drying *in vacuo* yielded 90 mg (24%) of **6a** as a diastereoisomer mixture 5:2 as seen by integration of appropriate ^{1}H-NMR signals[2]). IR (Nujol): 2406*w* (BH). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –2.7. Anal. calc. for $C_{33}H_{32}BIrN_6$ (715.69): C 55.4, H 4.5, N 11.7; found: C 55.5, H 4.7, N 11.4.

First (Major) Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): [8.07–8.06 (*m*, 4 H, Ph); 7.98–7.93 (*m*, 5 H, Ph); 7.60 (br. *s*, H–C(5)(pz)); 7.49–7.25 (*m*, 17 H, Ph, H–C(5)(pz))]^2); 6.71 (*d*, ^3J = 2.3, H–C(4)(pz)); 6.45 (*m*, 2 H–C(4)(pz)); 1.80 (*s*, 6 H, Me); 1.70 (br. *s*, H_{trans}–C(1), H_{trans}–C(4)); –0.21 (br. *s*, H_{cis}–C(1), H_{cis}–C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 156.2 (2 C(3)(pz)); 154.6 (C(3)(pz)); 139.4 (C(5)(pz)); [135.6 (2 C(5)(pz)); 135.2, 134.8, 134.7 (3 C, Ph^q); 129.7, 128.8, 128.7, 128.5, 128.3, 128.2, 127.6, 126.2 (15 C, Ph)]^2); 105.4 (2 C(4)(pz)); 102.7 (C(4)(pz)); 85.3 (C(2), C(3)); 35.0 (^1J(C,H) = 160, C(1), C(4)); 19.3 (2 Me).

Second (Minor) Isomer: ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): [8.07–8.06 (*m*, 4 H, Ph); 7.98–7.93 (*m*, 5 H, Ph); 7.60 (br. *s*, H–C(5)(pz)); 7.49–7.25 (*m*, 17 H, Ph, H–C(5)(pz)]^2); 6.56 (*m*, 3 H–C(4)(pz)); 1.58 (br. *s*, H_{trans}–C(1), H_{trans}–C(4)); 1.19 (*s*, 2 Me); –0.43 (br. *s*, H_{cis}–C(1), H_{cis}–C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 156.2 (2 C(3)(pz)); 155.8 (C(3)(pz)); 137.4 (C(5)(pz)); [135.6 (2 C(5)(pz)); 135.2, 134.8, 134.7 (3 C, Ph^q); 129.7, 128.8, 128.7, 128.5, 128.3, 128.2, 127.6, 126.2 (15 C, Ph)]^2); 105.1 (2 C(4)(pz)); 102.7 (C(4)(pz)); 85.5 (C(2), C(3)); 35.4 (^1J(C,H) = 158, C(1), C(4)); 18.4 (2 Me).

On further separation by CC (p.e./Et_2O 4:1; R_f (p.e./Et_2O 4:1) 0.20), evaporation, and drying *in vacuo*, 55 mg (19%) of *(*OC*-6-43)[hydrotris(3-phenyl-1*H*-pyrazolato-κN^1)borato(3–)-κC^2,κC$^{2'}$,κN^2,κN$^{2'}$,κN$^{2''}$](5-phenyl-1*H*-pyrazole-κN^2)iridium* (**7**) was obtained. IR (Nujol): 3361*m* (NH), 2474*m* (BH). ^{1}H-NMR (300 MHz, $CDCl_3$, 20°): 9.72 (br. *s*, NH); 8.02 (*d*, ^3J = 2.5, H–C(5)(pz)); 7.81 (*d*, ^3J = 2.3, H–C(5)(pz)); 7.63 (*d*, ^3J = 7.4, 1 H, Ph); 7.52–7.31 (*m*, 7 H, H–C(5)(pz), Ph); 7.17–6.99 (*m*, 9 H, Ph); 6.90 (*vt*, ^3J = 2.3, H–C(3)(neutral pz)); 6.86–6.70 (*m*, 2 H, Ph); 6.59 (*d*, ^3J = 2.5 Hz, H–C(4)(pz)); 6.31 (*d*, ^3J = 2.5, H–C(4)(pz)); 6.23 (*d*, ^3J = 2.3, H–C(4)(pz)); 5.93 (*vt*, ^3J = 2.3, H–C(4)(neutral pz)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 166.0, 163.2, 154.7, 151.3 (4 C(3)(pz)); 143.6 (1 C, Ph^q); 143.5 (C(5)(pz)); 142.8 (1 C, Ph^q); 141.5 (1 C, Ph^q); 140.8 (1 C, Ph^q); 140.4 (C(3)(neutral pz)); 137.1, 137.0, 136.7, 136.3 (6 C, Ph, C(5)(pz)); 133.2 (1 C, Ph^{q,m}); 129.5, 129.40, 129.38 (3 C, Ph); 129.32 (1 C, Ph^{q,m}); 128.34, 128.26, 127.5, 127.4, 125.7 (6 C, Ph); 122.9, 122.5, 122.4, 121.5 (4 C, Ph^m); 106.1, 105.9, 103.6 (3 C(4)(pz)); 103.0 (C(4)(neutral pz)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –2.5. Anal. calc. for $C_{36}H_{28}BIrN_8$ (775.71): C 55.7, H 3.6, N 14.5; found: C 55.8, H 3.8, N 14.6.

*(η^4-2,3-Dimethylbuta-1,3-diene){hydrotris[3-(2-thienyl)-1*H*-pyrazolato-κN^1]borato(1–)-κN^2,κN$^{2'}$}iridium* (**6b**). As described for **5a**, with [(IrCl(coe)$_2$)$_2$] (167 mg, 0.186 mmol), CH_2Cl_2 (6 ml), 2,3-dimethylbuta-1,3-diene (0.75 ml, excess), and [TlTpTh] (248 mg, 0.373 mmol): 210 mg (77%) of **6b** as diastereoisomer mixture 5:2 as seen by integration of appropriate ^{1}H-NMR signals. Red powder. IR (Nujol): 2405*m* (BH). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): –3.0. Anal. calc. for $C_{27}H_{26}BIrN_6S_3$ (733.76): C 44.2, H 3.6, N 11.5; found: C 44.4, H 3.9, N 11.6.

---

[2]) The Ph signals are given in the spectra for both isomers as found; assignment to neither the H- nor to the C-atoms, nor according to isomer was possible.

First (Major) Isomer: ^{1}H-NMR (400 MHz, $CDCl_3$, 20°): 7.84 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.60 (*dd*, ^3J = 3.5, ^4J = 1.1, 2 H−C(3)(Th)); 7.46 (*dd*, ^3J = 5.1, ^4J = 1.1, 2 H−C(5)(Th)); 7.40 (*dd*, ^3J = 3.6, ^4J = 1.1, H−C(3)(Th)); 7.20 (*d*, ^3J = 2.5, 2 H−C(5)(pz)); 7.18 (*dd*, ^3J = 5.1, ^4J = 1.2, H−C(5)(Th)); 7.14 (*dd*, ^3J = 5.1, ^3J = 3.6, 2 H−C(4)(Th)); 7.04 (*dd*, ^3J = 5.1, ^3J = 3.6, H−C(4)(Th)); 6.50 (*d*, ^3J = 2.3, H−C(4)(pz)); 6.22 (*d*, ^3J = 2.5, 2 H−C(4)(pz)); 2.00 (*d*, ^2J = 2.4, H_{trans}−C(1), H_{trans}−C(4)); 1.85 (*s*, 2 Me); 0.07 (*d*, ^2J = 2.4, H_{cis}−C(1), H_{cis}−C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 150.4 (2 C(3)(pz)); 150.2 (C(3)(pz)); 138.7, 137.8 (3 C(2)(Th)); 136.2 (C(5)(pz)); 136.1 (2 C(5)(pz)); 127.9–127.7 (3 C(3), 3 C(4)(Th)); 124.5 (C(4)(Th)); 123.9 (2 C(4)(Th)); 106.2 (2 C(4)(pz)); 103.2 (C(4)(pz)); 86.3 (C(2), C(3)); 35.5 (^1J(C,H) = 162, C(1), C(4)); 19.8 (2 Me).

Second (Minor) Isomer: ^{1}H-NMR (400 MHz, $CDCl_3$, 20°): 7.84 (overlapped by H−C(5)(pz) of the major isomer, H−C(5)(pz)); 7.55 (br. *s*, 2 H−C(5)(pz)); 7.50 (*dd*, ^3J = 3.4, ^4J = 1.1, 2 H−C(3)(Th)); 7.35 (*dd*, ^3J = 5.1, ^4J = 1.1, 2 H−C(5)(Th)); 7.31 (*dd*, ^3J = 3.6, ^4J = 1.2, H−C(3)(Th)); 7.17 (*dd*, ^3J = 5.1, ^4J = 1.2, H−C(5)(Th)); 7.08 (*dd*, ^3J = 5.1, ^3J = 3.6, 2 H−C(4)(Th)); 7.00 (*dd*, ^3J = 5.1, ^3J = 3.6, H−C(4)(Th)); 6.59 (*d*, ^3J = 2.2, 2 H−C(4)(pz)); 6.52 (*d*, ^3J = 2.5, H−C(4)(pz)); 1.88 (*d*, ^2J = 2.4, H_{trans}−C(1), H_{trans}−C(4)); 1.28 (*s*, 2 Me); −0.13 (*d*, ^2J = 2.4, H_{cis}−C(1), H_{trans}−C(4)). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): the Tp^{Th} signals are apart from small deviations, the same as those of the major isomer; 86.6 (C(2), C(3)); 36.0 (^1J(C,H) = 160, C(1), C(4)); 18.8 (2 Me).

*(OC-6-35)-Hydro[hydrotris(3-phenyl-1*H*-pyrazolato-*κN^1*)borato(2−)-*κC^2,κN^2,κN$^{2'}$,κN$^{2''}$*](tetrahydro-2*H*-pyran-2-ylidene)iridium* (**8**). A soln. of **5a** (67 mg, 0.096 mmol) and tetrahydro-2*H*-pyran (100 µl, excess) in toluene (3 ml) was heated at 80° for 5 h. The soln. was evaporated and the crude product (yellow green oil) purified by CC (neutral aluminium oxide *90* active, Et_2O/p.e. 1:1 (yellow band)). Evaporation and drying *in vacuo* yielded 52 mg (76%) of **8**. IR (Nujol): 2474*m* (BH), 2219*m* (IrH). ^{1}H-NMR (300 MHz, (D_6)benzene, 20°): 7.94 (*d*, ^3J = 7.4, 1 H, Ph); 7.69–7.63 (*m*, 2 H, Ph, H−C(5)(pz)); 7.56–7.52 (*m*, 4 H, Ph, H−C(5)(pz)); 7.46 (*d*, ^3J = 2.3, H−C(5)(pz)); 7.41 (*vt*, ^3J = 7.4, 1 H, Ph^m); 7.21 (*vt*, ^3J = 7.4, 1 H, Ph^m); 7.11–6.91 (*m*, 6 H, Ph); 6.31 (*d*, ^3J = 2.4, H−C(4)(pz)); 6.10 (*d*, ^3J = 2.3, H−C(4)(pz)); 6.02 (*d*, ^3J = 2.3, H−C(4)(pz)); 3.30 (*m*, H−C(6)); 3.16 (*m*, H−C(6)); 1.18 (*m*, H−C(3)); 0.93 (*m*, H−C(3)); 0.64 (*m*, H−C(5)); 0.45 (*m*, 2 H−C(4)); 0.16 (*m*, H−C(5)); −20.84 (*s*, H−Ir). ^{13}C{^{1}H}-NMR (75.5 MHz, (D_6)benzene, 20°): 271.7 (C=Ir); 163.2, 154.6, 153.6 (3 C(3)(pz)); 143.6, 141.8 (2 C, Ph^q); 138.3 (1 C, Ph^m); 137.1, 136.3, 135.5 (3 C(5)(pz)); 134.7, 134.6 (2 C, Ph^q); 129.8, 129.3, 128.02, 128.00, 127.8, 127.7, 126.7 (11 C, Ph); 122.9, 121.3 (2 C, Ph^m); 106.8, 104.9, 102.9 (3 C(4)(pz)); 70.7 (C(6)); 49.7 (C(3)); 20.7 (C(5)); 14.8 (C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, (D_6)benzene, 20°): −2.0. Anal. calc. for $C_{32}H_{30}BIrN_6O$ (717.67): C 53.6, H 4.2, N 11.7; found: C 53.9, H 4.5, N 11.6.

*(OC-6-35)-(Dihydrofuran-2(3*H*)-ylidene)hydro[hydrotris[3-(2-thienyl)-1*H*-pyrazolato-*κN^1*]borato(2−)-*κC^2,κN^2,κN^2,κN$^{2'}$,κN$^{2''}$*]iridium* (**9**). A soln. of **5b** (50 mg, 0.063 mmol) and THF (2 ml) was heated at 80° for 8 h. Workup as described for **8** yielded 30 mg (66%) of **9**. IR (Nujol): 2488*m* (BH), 2193*m* (IrH). ^{1}H-NMR (400 MHz, $CDCl_3$, 20°): 7.87 (*d*, ^3J = 2.4, H−C(5)(pz)); 7.76 (*d*, ^3J = 2.6, H−C(5)(pz)); 7.55 (*d*, ^3J = 2.4, H−C(5)(pz)); 7.46 (*d*, ^3J = 4.8, H−C(5)(Th)); 7.45 (*dd*, ^3J = 3.5, ^4J = 1.3, H−C(3)Th)); 7.41 (*d*, ^3J = 4.8, H−C(4)(Th^m)); 7.19 (*dd*, ^3J = 5.1, ^4J = 1.1, H−C(5)(Th)); 7.10 (*dd*, ^3J = 5.0, ^4J = 1.2, H−C(5)(Th)); 6.90 (*m*, H−C(3), H−C(4)(Th)); 6.83 (*dd*, ^3J = 5.0, ^3J = 3.5, H−C(4)(Th)); 6.35 (*d*, ^3J = 2.6, H−C(4)(pz)); 6.33 (*d*, ^3J = 2.5, H−C(4)(pz)); 6.11 (*d*, ^3J = 2.4, H−C(4)(pz)); 4.17 (*m*, H−C(5)); 3.97 (*m*, H−C(5)); 1.76 (*m*, H−C(3)); 1.53 (*m*, H−C(3)); 1.05 (*m*, H−C(4)); 0.86 (*m*, H−C(4)); −20.5 (*s*, H−Ir). ^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$, 20°): 267.8 (C=Ir); 159.8, 149.0, 147.1 (3 C(3)(pz)); 141.3 (C(2)(Th)); 139.2, 137.6, 136.5 (3 C(4)(pz)); 136.1 (C(2)(Th)); 136.0 (C(5)(Th^m)); 135.6 (C(2)(Th)); 129.7 (1 C, Th^{q,m}); 128.7 (C(3)(Th)); 127.9, 127.7, 127.5 (C(3), 2 C(4)(Th)); 126.6 (C(5)(Th)); 125.9 (C(5)(Th)); 124.6 (C(5)(Th^m)); 108.2, 106.3, 102.7 (3 C(4)(pz)); 81.8 (C(5)); 57.1 (C(3)); 22.1 (C(4)). ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 20°): −2.3. Anal. calc. for $C_{25}H_{22}BIrN_6OS_3$ (721.70): C 41.6, H 3.1, N 11.6; found: C 41.8, H 3.2, N 11.5.

X-Ray Structure Determination for **6b**. X-Ray crystal data for $C_{27}H_{26}BIrN_6S_3$: monoclinic, space group $P2(1)/n$ (No. 14), ρ_{calc} 1.714 g cm^{-3}, Z = 4, a = 12.906(4) Å, b = 13.436(4) Å, c = 16.423(4) Å, β = 93.390(10)°, V = 2842.8(14) Å^3; MoK_α radiation, λ 0.71073 Å, θ_{max} = 27°, completeness to θ = 99.5%, index ranges $-16 \le h \le 16$, $-17 \le k \le 17$, $-20 \le l \le 20$, 6169 unique reflections, T 297(2) K. Crystals of **6b** were obtained by slow evaporation of a p.e.-layered CH_2Cl_2 soln. of **6b**. X-Ray data were collected with a *Siemens Smart-CCD* area detector diffractometer (graphite-monochromated MoK_α radiation, λ 0.71073 Å, nominal crystal-to-detector distance 4.45 cm, 0.3° ω-scan frames). Corrections for *Lorentz* and polarization effects, for crystal decay, and for absorption were applied (multiscan method, program SADABS [23]). The structure was solved by direct methods with SHELXS97 [24]. Structure refinement on F^2 was carried out with SHELXL97 [25]. Final $R(F)$ = 0.0320, $wR/(F^2)$ = 0.0693 for 364 parameters and 4112 reflections with $I > 2\sigma(I)$. All non-H-atoms were refined anisotropically. H-Atoms were inserted in idealized positions and were refined riding with the atoms to

which they were bonded. Crystallographic data for compound **6b** have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 157587. Copies of the data can be obtained, free of charge, from: The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

This work was supported by the *Fonds zur Förderung der wissenschaftlichen Forschung* with a *Schrödinger Stipendium* for *C.S.* (J1756-CHE), the Spanish Ministry of Education (DGES, Project PB97-0733), and the Junta de Andalucía.

REFERENCES

[1] R. H. Crabtree, *Chem. Rev.* **1985**, *85*, 245; B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. A. Peterson, *Acc. Chem. Res.* **1995**, *28*, 154; A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; T. Junk, W. J. Catallo, *Chem. Soc. Rev.* **1997**, *26*, 401; S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem., Int. Ed.* **1998**, *37*, 2180; S. Niu, M. B. Hall, *Chem. Rev.* **2000**, *2*, 353.

[2] E. Gutiérrez-Puebla, Á. Monge, M. C. Nicasio, P. J. Pérez, M. L. Poveda, E. Carmona, *Chem.–Eur. J.* **1998**, *4*, 2225; E. Gutiérrez, Á. Monge, M. C. Nicasio, M. L. Poveda, E. Carmona, *J. Am. Chem. Soc.* **1994**, *116*, 791.

[3] C. Slugovc, K. Mereiter, S. Trofimenko, E. Carmona, *Angew. Chem.* **2000**, *112*, 2242; *Angew. Chem., Int. Ed.* **2000**, *39*, 2158.

[4] C. Slugovc, I. Padilla-Martínez, S. Sirol, E. Carmona, *Coord. Chem. Rev.* **2001**, *213*, 129; F. Malbosy, P. Kalck, J.-C. Daran, M. Etienne, *J. Chem. Soc., Dalton Trans.* **1999**, 271; M. Paneque, S. Sirol, M. Trujillo, E. Gutiérrez-Puebla, M. A. Monge, E. Carmona, *Angew. Chem., Int. Ed.* **2000**, *39*, 218.

[5] U. E. Bucher, A. Currao, R. Nesper, H. Rüegger, L. M. Venanzi, E. Younger, *Inorg. Chem.* **1995**, *34*, 66.

[6] K. Ohta, M. Hashimoto, Y. Takahashi, S. Hikichi, M. Akita, Y. Moro-oka, *Organometallics* **1999**, *18*, 3234.

[7] M. Akita, M. Hashimoto, S. Hikichi, Y. Moro-oka, *Organometallics* **2000**, *19*, 3744.

[8] Y. Alvarado, O. Boutry, E. Gutiérrez, Á. Monge, M. C. Nicasio, M. L. Poveda, P. J. Pérez, C. Ruíz, C. Bianchini, E. Carmona, *Chem.–Eur. J.* **1997**, *3*, 860.

[9] C. Slugovc, K. Mereiter, S. Trofimenko, E. Carmona, *Chem. Commun.* **2000**, 121.

[10] Y. Alvarado, P. J. Daff, P. J. Pérez, M. L. Poveda, R. Sánchez-Delgado, E. Carmona, *Organometallics* **1996**, *15*, 2192.

[11] E. Rüba, W. Simanko, K. Mereiter, R. Schmid, K. Kirchner, *Inorg. Chem.* **2000**, *39*, 382.

[12] S. P. Nolan, C. D. Hoff, P. O. Stoutland, L. J. Newman, J. M. Buchanan, R. G. Bergman, G. K. Yang, K. S. Peters, *J. Am. Chem. Soc.* **1987**, *109*, 3149; J. A. Martinho Simões, J. L. Beauchamp, *Chem. Rev.* **1990**, *90*, 629.

[13] O. Boutry, M. L. Poveda, E. Carmona, *J. Organomet. Chem.* **1997**, *528*, 143.

[14] E. Gutiérrez-Puebla, Á. Monge, M. Paneque, M. L. Poveda, V. Salazar, E. Carmona, *J. Am. Chem. Soc.* **1999**, *121*, 248; M. Paneque, M. L. Poveda, V. Salazar, E. Gutiérrez-Puebla, Á. Monge, *Organometallics* **2000**, *19*, 3120.

[15] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-oka, *Organometallics* **1997**, *16*, 4121.

[16] T. O. Nurthcutt, R. J. Lachicotte, W. D. Jones, *Organometallics* **1998**, *17*, 5148.

[17] a) D. Sanz, M. D. Santa Mária, R. M. Claramunt, M. Cano, J. V. Heras, J. A. Campo, F. A. Ruíz, E. Pinilla, Á. Monge, *J. Organomet. Chem.* **1996**, *526*, 341; b) A. L. Reingold, R. L. Ostrander, B. S. Haggerty, S. Trofimenko, *Inorg. Chem.* **1994**, *33*, 3666.

[18] A. Albinati, M. Bovens, H. Rüegger, L. M. Venanzi, *Inorg. Chem.* **1997**, *36*, 5991.

[19] G. W. Bushnell, D. O. K. Fjelsted, S. R. Stobart, M. J. Zaworotko, A. R. K. Selby, K. A. Macpherson, *Organometallics* **1985**, *4*, 1107; J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, M. J. Zaworotko, *Inorg. Chem.* **1984**, *23*, 4050; G. S. Rodman, A. J. Bard, *Inorg. Chem.* **1990**, *29*, 4699.

[20] J. C. Calabrese, P. J. Domaille, S. Trofimenko, G. J. Long, *Inorg. Chem.* **1991**, *30*, 2975.

[21] J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.* **1970**, *12*, 99.

[22] S. Trofimenko, J. C. Calabrese, J. S. Thompson, *Inorg. Chem.* **1987**, *26*, 1508.

[23] G. M. Sheldrick, 'SADABS: Program for Absorption Correction', University of Göttingen, Germany, 1996.

[24] G. M. Sheldrick, 'SHELXS97: Program for the Solution of Crystal Structures', University of Göttingen, Germany, 1996.
[25] G. M. Sheldrick, 'SHELXL97: Program for Crystal Structure Refinement', University of Göttingen, Germany 1996.

Received March 16, 2001