DOI: 10.1002/chem.200701209

Coordination Features of a Hybrid Scorpionate/Phosphane Ligand Exemplified with Iridium

José A. Camerano,[a] Miguel A. Casado,*[a, b] Miguel A. Ciriano,*[a] Cristina Tejel,[a] and Luis A. Oro[a, b]

Abstract: Although the pentacoordinated complex [Ir{(allyl)B(CH_2PPh_2)($pz)_2$}(cod)] (**1**; pz = pyrazolyl, cod = 1,5-cyclooctadiene), isolated from the reaction of [{Ir(μ-Cl)(cod)$\}_2$] with [Li(tmen)][B(allyl)(CH_2PPh_2)($pz)_2$] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine), shows behavior similar to that of the related hydridotris(pyrazolyl)borate complex, the carbonyl derivatives behave in a quite different way. On carbonylation of **1**, the metal–metal-bonded complex [(Ir{(allyl)B(CH_2PPh_2)($pz)_2$}CO$)_2$(μ-CO)] (**2**) that results has a single ketonic carbonyl bridge. This bridging carbonyl is labile such that upon treatment of **2** with PMe_3 the pentacoordinated Ir^I complex [Ir(CO){(pz)B(η^2-$CH_2CH{=}CH_2$)(CH_2PPh_2)(pz)}(PMe_3)] (**3**) was isolated. Complex **3** shows a unique *fac* coordination of the hybrid ligand with the allyl group η^2-bonded to the metal in the equatorial plane of a distorted trigonal bipyramid with one pyrazolate group remaining uncoordinated. This unusual feature can be rationalized on the basis of the electron-rich nature of the metal center. The related complex [Ir(CO){(pz)B(η^2-$CH_2CH{=}CH_2$)(CH_2PPh_2)(pz)}(PPh_3)] (**4**) was found to exist in solution as a temperature-dependent equilibrium between the *cis*-pentacoordinated and *trans* square planar isomers with respect to the phosphorus donor atoms. Protonation of **3** with different acids is selective at the iridium center and gives the cationic hydrides [Ir{(allyl)B(CH_2PPh_2)($pz)_2$}(CO)H(PMe_3)]X (X = BF_4 (**5**), $MeCO_2$ (**6**), and Cl (**7**)). Complex **7** further reacts with HCl to generate the unexpected product [Ir(CO)Cl{(Hpz)B(CH_2PPh_2)(pz)$CH_2CH(Me)$}(PMe_3)]Cl (**9**; Hpz = protonated pyrazolyl group) formed by the insertion of the hydride into the Ir–(η^2-allyl) bond. In contrast, protonation of complex **4** with HCl stops at the hydrido complex [Ir{(allyl)B(CH_2PPh_2)($pz)_2$}(CO)H(PPh_3)]Cl (**8**). X-ray diffraction studies carried out on complexes **2**, **3**, and **9** show the versatility of the hybrid scorpionate ligand in its coordination.

Keywords: iridium · N,P ligands · protonation · scorpionate ligands · tripodal ligands

Introduction

The continuous advances and discoveries in organometallic chemistry are often determined by the synthesis of new types of ligand systems that have been designed to influence the metallic environment and to induce changes in their properties and reactivity. A memorable breakthrough in coordination chemistry occurred in 1966 when Trofimenko introduced the poly(pyrazolyl)borate (Tp) systems, or scorpionates,[1] which have generated wide interest in interdisciplinary fields for a long time.[2] These anionic systems are characterized by their relatively hard nitrogen σ-donor atoms and they exhibit a rich coordination chemistry with virtually all of the metallic centers of the Periodic Table.[3] Additionally, they are extremely versatile as they can adopt both κ^3- and κ^2-coordination modes around the metals,[4] which allows new patterns of reactivity compared with soft π sys-

---

[a] Dr. J. A. Camerano, Dr. M. A. Casado, Prof. M. A. Ciriano,
Dr. C. Tejel, Prof. L. A. Oro
Departamento de Química Inorgánica
Instituto de Ciencias de Materiales de Aragón
CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza
(Spain)
Fax: (+34) 976-761-187
E-mail: mcasado@unizar.es
mciriano@unizar.es

[b] Dr. M. A. Casado, Prof. L. A. Oro
Instituto Universitario de Catálisis Homogénea
Pedro Cerbuna 12, 50009 Zaragoza (Spain)

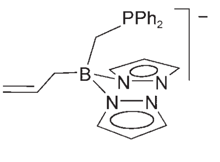
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tems, such as cyclopentadienyl (Cp) ligands. Furthermore, the differences in the electronic nature of the two ligand systems (Cp versus Tp) are largely responsible for the differences in the properties and reactivities observed for analogous complexes.[5]

Related anionic borate ligands with soft phosphorus σ-donor/π-acceptor atoms, such as $[PhB(CH_2PR_2)_3]^-$ (BP_3), have more recently seen their genesis, with new systems being created that have already provided interesting activation processes and different structural situations.[6] A logical consequence of the important catalytic and stoichiometric reactions generated by Tp, and to a lesser extent by BP_3 systems, is the development of the so-called "heteroscorpionate" ligands. However, there are only a few examples, and these are not recent, of boron-based hybrid pyrazolate ligands that contain two pyrazolyl groups and one dimethylamino,[7] arylthio,[8] or alkoxy arm.[9] With the aim of bringing together hard (N) and soft (P) donor atoms in pyrazolylborate systems, we recently reported the synthesis of the novel hybrid pyrazolate/phosphane anionic ligand $[(allyl)B(CH_2PPh_2)(pz)_2]^-$ (BPN_2) (**a**). This modified scorpionate ligand also bears an allyl group directly connected to boron, which has allowed it to be covalently linked to carbosilane dendrimers.[10] We have already anticipated that such a system could lead to new reactivity patterns and open up new possibilities for scorpionate ligands.[11]

In this paper we report the results of a study of a series of iridium complexes produced with this ligand system, paying special attention to the possibilities of coordination through the four arms, and their reactions with protic acids, which reflect the versatility of this hybrid scorpionate when attached to an iridium center.

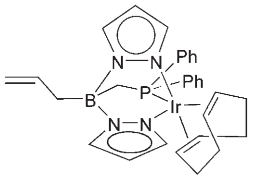


a

Results and Discussion

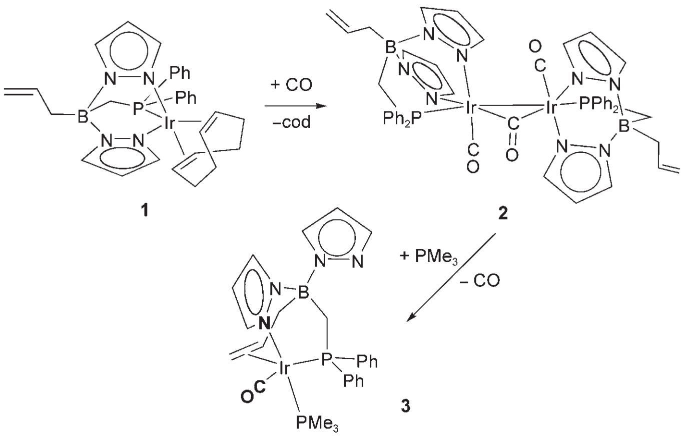
Access to the diolefin complex $[Ir\{(allyl)B(CH_2PPh_2)(pz)_2\}(cod)]$ (**1**; pz = pyrazolyl, cod = 1,5-cyclooctadiene) was easily achieved by treating the lithium salt [Li(tmen)][(allyl)$B(CH_2PPh_2)(pz)_2$] (tmen = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine) with the chlorido-bridged complex $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ in toluene. After removal of LiCl, complex **1** was isolated as a white solid in good yield. Complex **1** is mononuclear and most probably pentacoordinated with a structure similar to that of the analogous rhodium complex $[Rh\{(allyl)B(CH_2PPh_2)(pz)_2\}(cod)]$.[10] In solution, both complexes are fluxional and have a single signal for the olefinic carbon atoms and protons of the cod ligand and the equivalence of the pyrazolyl rings in the $^{13}C\{^1H\}$ and ^1H NMR spectra at room temperature.[10] Although the pyrazolyl rings and the cod carbon atoms are nonequivalent in the solid-state structure of the rhodium complex, the equivalences found in solution can be easily explained on the basis of the lack of stereochemical rigidity associated with pentacoordination or the known turnover mechanism.

In this way, the rhodium and iridium diolefin complexes with the hybrid scorpionate ligand behave in a similar way to the hydridotris(pyrazolyl)borate complexes of iridium.[12]



1

Carbonyl and carbonyl-phosphane complexes: Carbonylation of the complex $[Ir\{(allyl)B(CH_2PPh_2)(pz)_2\}(cod)]$ (**1**) under atmospheric pressure in dichloromethane gave a bright yellow solution from which compound **2** was isolated in excellent yield as a crystalline yellow solid. Replacing cyclooctadiene in the starting material with carbon monoxide results in a dinuclear iridium complex bridged by a single carbonyl ligand characterized as $[(Ir\{(allyl)B(CH_2PPh_2)(pz)_2\}CO)_2(\mu\text{-}CO)]$ (**2**, Scheme 1). The dinuclear nature of **2** was confirmed by X-ray structure determination (Figure 1) and it is best described as consisting of two mononuclear fragments $[Ir\{(allyl)B(CH_2PPh_2)(pz)_2\}(CO)]$ in



Scheme 1. Formation of complexes **2** and **3**.

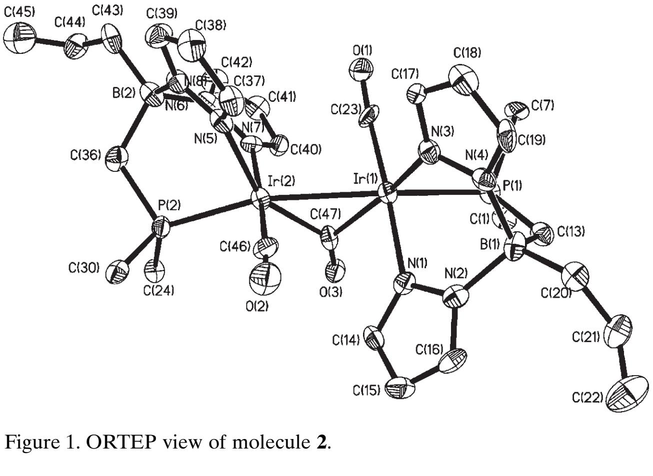


Figure 1. ORTEP view of molecule **2**.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

which the tripod ligand coordinates the iridium atoms in a κ^3 facial fashion, joined together through a bridging carbonyl ligand and a metal–metal bond (see Table 1 for selected bonds and angles). Each iridium center adopts a distorted octahedral geometry with the phosphorus atom *trans* to the metal–metal bond and the perpendicular plane formed by the nitrogen atoms of two pyrazolyl rings and the bridging and terminal carbonyl ligands. The Ir–Ir separation (2.7473(5) Å) is consistent with an Ir–Ir single bond, and it is comparable to those found in related carbonyl-bridged dinuclear iridium systems, such as $[\{Ir(CO)Cp^*\}_2(\mu\text{-}CO)(\mu\text{-}H)]OTf$ (2.831 Å)[13] and $[CH_2\{Ir(CO)(\eta^5\text{-}C_5H_4)\}_2(\mu\text{-}CO)]$ (2.664 Å).[14] If one takes into account the metal–metal bond, the bridging carbonyl should then be considered as divalent, that is, ketonic, to justify the oxidation state of the metal, Ir^{II}, and the diamagnetism of the compound. Indeed, the C47–O3 distance, the IR $\tilde{\nu}$(CO) band at 1715 cm^{-1}, and the chemical shift of the carbon atom ($\delta = 218.3$ ppm) are typical of a C=O double bond.

Table 1. Selected bond lengths [Å] and angles [°] for **2**.

Ir(1)–P(1)	2.335(2)	Ir(2)–P(2)	2.345(2)
Ir(1)–N(1)	2.107(7)	Ir(2)–N(5)	2.148(7)
Ir(1)–N(3)	2.220(7)	Ir(2)–N(7)	2.119(7)
Ir(1)–C(23)	1.855(10)	Ir(2)–C(46)	1.816(11)
Ir(1)–C(47)	2.023(9)	Ir(2)–C(47)	2.027(9)
Ir(1)–Ir(2)	2.7473(5)	C(47)–O(3)	1.216(10)
C(23)-Ir(1)-C(47)	95.8(4)	C(46)-Ir(2)-C(47)	97.5(4)
C(23)-Ir(1)-N(1)	175.3(3)	C(46)-Ir(2)-N(7)	176.8(4)
C(47)-Ir(1)-N(1)	85.5(3)	C(47)-Ir(2)-N(7)	85.7(3)
C(23)-Ir(1)-N(3)	92.3(3)	C(46)-Ir(2)-N(5)	90.2(4)
C(47)-Ir(1)-N(3)	157.4(3)	C(47)-Ir(2)-N(5)	151.3(3)
N(1)-Ir(1)-N(3)	85.7(3)	N(7)-Ir(2)-N(5)	86.9(3)
C(23)-Ir(1)-P(1)	95.8(3)	C(46)-Ir(2)-P(2)	95.8(3)
C(47)-Ir(1)-P(1)	116.5(3)	C(47)-Ir(2)-P(2)	118.2(3)
N(1)-Ir(1)-P(1)	88.3(2)	N(7)-Ir(2)-P(2)	82.75(19)
N(3)-Ir(1)-P(1)	83.42(19)	N(5)-Ir(2)-P(2)	88.2(2)
C(23)-Ir(1)-Ir(2)	79.2(3)	C(46)-Ir(2)-Ir(1)	83.5(3)
C(47)-Ir(1)-Ir(2)	47.3(3)	C(47)-Ir(2)-Ir(1)	47.2(2)
N(1)-Ir(1)-Ir(2)	97.68(19)	N(7)-Ir(2)-Ir(1)	98.65(19)
N(3)-Ir(1)-Ir(2)	114.36(18)	N(5)-Ir(2)-Ir(1)	106.98(19)
P(1)-Ir(1)-Ir(2)	161.53(6)	P(2)-Ir(2)-Ir(1)	164.81(6)

Solution NMR spectroscopy data for **2** are consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR spectrum consists of one singlet because both iridium fragments $[Ir\{(allyl)B(CH_2PPh_2)(pz)_2\}(CO)]$ are in similar environments. The pyrazolyl protons are nonequivalent, which gives six signals in the ^1H NMR spectrum, the CH_2P protons are diastereotopic, and the allyl group attached to the boron atom gives characteristic resonances at $\delta = 6.20$, 5.23, and 2.11 ppm. Furthermore, the dinuclear nature of **2** in solution was confirmed by the peak of the molecular ion at *m*/*z* 1239 in the FAB$^+$ mass spectrum and the medium intensity $\tilde{\nu}$(CO) band of the ketonic carbonyl at 1715 cm^{-1} as well as by the strong absorption at 1999 cm^{-1} of the terminal carbonyl in the IR spectrum.

The yellow color of the solution of **2** disappeared on reaction with trimethylphosphane (2 molequiv) in diethyl ether and gave a white suspension of $[Ir(CO)\{(pz)B(\eta^2\text{-}CH_2CH{=}CH_2)(CH_2PPh_2)(pz)\}(PMe_3)]$ (**3**) in good yield (Scheme 1). This complex is very reactive, solutions of **3** in acetone and in chlorinated solvents decompose within minutes to give mixtures of phosphorus-containing products, as indicated by NMR spectroscopy experiments carried out in situ. Complex **3** proved to be sparingly soluble in aromatic solvents, such as benzene or toluene, which allowed its full characterization in solution.

The absence of signals expected at low field from the allyl-pendant group on the boron is the most striking feature of the ^1H NMR spectrum of **3**. Instead, two signals were observed at $\delta = 2.88$ and 2.22 ppm that could be attributed to the olefinic protons of the allyl group η^2-coordinated to the metal. This shift to high field agrees well with data reported for other η^2-allyl-coordinated iridium complexes such as $[IrCl(dppm)\{\eta^2{:}\eta^2\text{-}(allyl)_2C(CO_2Me)_2\}]$[15] (dppm = bis(diphenylphospino)methane) and $[Ir(cod)\{\eta^2{:}\eta^2\text{-}(allyl)_2NHC\}]BF_4$ ($(allyl)_2NHC$ = 1,3-bis(2-propenyl)benzimidazol-2-ylidene).[16] The η^2 coordination of the allyl group was fully confirmed by an X-ray diffraction study carried out on a colorless monocrystal of **3**. Figure 2 shows a view of this molecule and selected bond lengths and angles are given in Table 2.

Pentacoordinated complex **3** is characterized by a unique $\kappa N,\kappa P,\eta^2$-(allyl) *fac* coordination of the hybrid scorpionate ligand to the iridium(I) center and an uncoordinated pyrazolyl group. The molecule adopts a distorted trigonal bipyra-

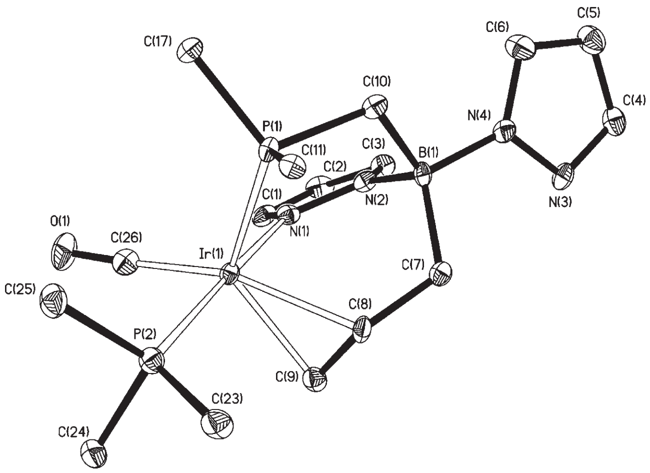


Figure 2. ORTEP view of molecule **3**.

Table 2. Selected bond lengths [Å] and angles [°] for **3**.[a]

Ir–P(1)	2.3464(11)	Ir–P(2)	2.2782(11)
Ir–N(1)	2.121(4)	Ir–C(26)	1.874(5)
Ir–C(8)	2.227(4)	Ir–C(9)	2.168(5)
C(8)–C(9)	1.435(6)	C(7)–C(8)	1.517(5)
C(26)-Ir-N(1)	89.11(17)	C(26)-Ir-Du	140.0(2)
N(1)-Ir-Du	85.6(2)	C(26)-Ir-P(2)	86.93(14)
N(1)-Ir-P(2)	172.08(10)	Du-Ir-P(2)	93.0(1)
Du-Ir-P(1)	104.9(1)	C(26)-Ir-P(1)	114.80(14)
N(1)-Ir-P(1)	90.19(10)	P(2)-Ir-P(1)	97.70(4)

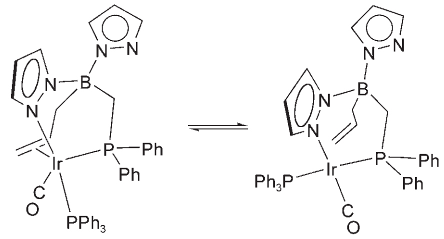
[a] Du is the midpoint between C(8) and C(9).

midal geometry in which the axial positions are occupied by the phosphorus atom of the trimethylphosphane and the nitrogen atom of the sole coordinated pyrazolyl ring. The equatorial positions are occupied by the carbonyl, the η^2-C=C bond of the allyl group, and the phosphorus atom of the phosphane arm of the tripodal ligand, the C=C bond is in the equatorial plane. All three equatorial angles are different from each other and from 120°, the C(26)-Ir-Du angle, in which Du corresponds to the midpoint of the olefinic bond, is the largest (140.0(2)°). The η^2 coordination of the allyl group is characterized by Ir−C(8) and Ir−C(9) bond lengths of 2.227(4) and 2.168(5) Å, respectively, which are similar to the distances found in other η^2-olefin iridium complexes, such as $[IrH(CH{=}CH_2)(C_2H_4)Tpm']PF_6$ (Tpm′ = tris(3,5-dimethylpyrazolyl)methane) (Ir−C, 2.171(10) and 2.142(11) Å)[17] or $[IrCl(cod)(L_{Fe})][PF_6]$ (L_{Fe} = [Fe(η^5-C_5H_5){η^6-1,1-di(2-propenyl)-3-butenyl}benzene] (Ir−C, 2.191(6)–2.319(6) Å).[18] Interestingly, complex **2** is chiral at both the iridium and boron atoms and its synthesis is diastereoselective. Thus, the absolute configuration of the isolated compound was found to be TBPY-5–13*A* (TBPY = trigonal bipyramid) at the iridium center and *R* at the boron atom (*AR*) and its enantiomer was found to have a *CS* configuration. The other possible diastereotopic pair *AS*/*CR* was not detected. In fact, molecular models indicate that the latter pair cannot exist because the chirality at the boron atom determines that at the iridium atom and vice versa.

The structure of **3** in solution deduced from the spectroscopic data corresponds to that observed in the solid state. The methylene protons from both the coordinated allyl group and the phosphane arm are diastereotopic in the ^{1}H NMR spectrum, in accordance with the lack of symmetry elements in the complex. Clearly, the two pyrazolyl rings are nonequivalent. The *cis* disposition of the two phosphane groups is also in accordance with the coupling constant (^2J(P,P) = 12 Hz) observed in the $^{31}P\{^1H\}$ NMR spectrum of **3**. More interesting still is the large shift to higher field observed for the $-CH{=}CH_2$ resonances in the $^{13}C\{^1H\}$ NMR spectrum, which indicates the π coordination of the allyl moiety. In particular, these resonances are observed to be much shielded at $\delta = 45.7$ and 34.3 ppm in **3**, whereas they appear at $\delta = 140.1$ and 114.5 ppm in **1** in which the allyl group remains uncoordinated. Finally, the terminal carbonyl, observed at $\delta = 189.1$ ppm in the $^{13}C\{^1H\}$ NMR spectrum, gives a sole intense band at $\tilde{\nu} = 1925$ cm^{-1} in the IR spectrum, which, in principle, suggests a highly basic iridium center.

The structure of this molecule deserves two further general comments. First, the possible, but not expected, coordination of the allyl group of the modified and hybrid scorpionate ligand reveals that it has four donor arms with which to coordinate metals, although only three of them can be used for this purpose in a mononuclear complex. Three of the arms possess a donor group that is markedly different in nature and properties to the others, which offers the metals the possibility of choosing coordination sites from a set of donors. This is exemplified with **3**, in which the metal prefers to bind to these three different arms rather than to another donor set that includes both pyrazolyl groups, as occurs in a typical poly(pyrazolyl)borate. Moreover, it can be anticipated that the origin of this choice resides in the bonding properties. Inspection of the structure reveals that the π-acceptor ligands, the carbonyl, phosphane, and the C=C bond in the plane occupy the equatorial positions, that is, those sites and dispositions for which back-donation from the metal is strongest. As **3** is coordinatively saturated and the metal is in a relatively low oxidation state, it can be expected that it is an electron-rich center. Therefore, the preference of the metal for η^2-($CH_2{=}CH$) coordination to the allyl and the phosphane rather than the hard nitrogen atom has a dual purpose: The metal not only avoids an increase in the electron density given by the σ-donor, but releases it to the π orbitals of the C=C bond by back-donation.

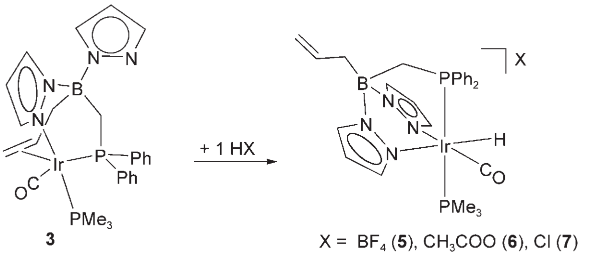
The related triphenylphosphane complex $[Ir(CO)\{(pz)B(\eta^2\text{-}CH_2CH{=}CH_2)(CH_2PPh_2)(pz)\}(PPh_3)]$ (**4**), isolated as a white solid from the reaction of **2** with PPh_3 (2 mol equiv), exists in solution as a mixture of two isomers in a chemical equilibrium (Scheme 2). This equilibrium is slow enough on the NMR timescale to detect both species. At room temperature, the allyl group gives broad resonances in the ^{1}H NMR spectrum at $\delta = 5.60$, 4.60, and 2.13 ppm and very broad signals are also observed in the ^{31}P NMR spectrum. As the temperature is lowered, both species can be clearly detected by ^{31}P NMR spectroscopy. Thus, at −10 °C the pentacoordinated isomer with a *cis* configuration of the two phosphanes is characterized by a coupling constant of ^2J(P,P) = 37 Hz and a $\tilde{\nu}$(CO) band at a very low frequency (1905 cm^{-1}) in the IR spectrum, whereas the square planar complex displays two *trans* phosphane ligands (^2J(P,P) = 308 Hz) and $\tilde{\nu}$(CO) at 2001 cm^{-1}. Furthermore, the relative proportion of the pentacoordinated isomer increases on lowering the temperature and the signals of the allyl-coordinated group begin to appear at a higher field in the ^{1}H NMR spectrum. Finally, the pentacoordinated species is the main isomer observed at −90 °C in solution (see the Supporting Information).



Scheme 2. Equilibrium of complex **4** in solution.

The interconversion between the penta- and tetracoordinated isomers that gives rise to this equilibrium relies on the decoordination of the allyl group from the metal, which leads to a severely distorted tetrahedral intermediate that rapidly rearranges to the square planar configuration characterized by the *trans* phosphanes. Analysis of the variable-temperature ^{31}P NMR spectroscopy data gives values of $\Delta H = 15.0\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = 56.6\,\mathrm{J\,K^{-1}mol^{-1}}$, which show that the dissociation of the allyl group is endothermic and a low-energy process. In addition, it leads to a more disordered system, as indicated by the positive value of the entropy exchange. It must be added that the square planar isomer should be more reactive than the pentacoordinated one as it is an unsaturated 16e$^-$ complex.

Protonation reactions at the iridium center of 3: As expected, complex **3** reacts readily with strong and weak acids to undergo selective protonation at the iridium rather than at the nitrogen atom from the pendant pyrazolyl. These reactions confirm the high basicity of the metal in **3**, which resembles the related iridium complex [Ir(CO)$_2$(Tp′)] (Tp′ = HBpz*$_3$ = tris(3,5-dimethylpyrazolido-N)hydridoborato).[19] In this way, the reactions of **3** with equimolar amounts of tetrafluoroboric acid, acetic acid, and dry HCl cleanly afforded the corresponding cationic hydride iridium(III) complexes [Ir{(allyl)B(CH$_2$PPh$_2$)(pz)$_2$}(CO)H(PMe$_3$)]X (X = BF$_4$ (**5**), CH$_3$COO (**6**), and Cl (**7**)), which were isolated as white microcrystalline solids in good yields (Scheme 3). On protonation of the metal, the allyl group becomes uncoordinated and the phosphane ligands adopt a *trans* disposition (^2J(P,P) = 307 Hz). The new hydride ligand is *cis* to the phosphane ligands, as revealed by the doublet of doublets in the ^{1}H NMR spectra of complexes **5** to **7** at around −15.2 ppm as a result of coupling with the two phosphorus nuclei (^2J(H,P) ≈ 16 Hz). Moreover, both pyrazolyl rings become coordinated to the metal. The pyrazolyl protons are observed as six different resonances in the ^{1}H NMR spectra, which indicates the nonequivalence of these groups in the complexes, and the methylenic CH$_2$P protons are diastereotopic owing to the lack of symmetry elements in the molecule. Additionally, complexes **5** and **6** with BF$_4^-$ and acetate counterions behave as 1:1 electrolytes in acetone and exhibit an intense terminal carbonyl band in the IR spectra at around 2055 cm^{-1}, which is in accordance with an Ir^{III} system, and a weak one at around 2180 cm^{-1} assigned to the Ir–H bond. Therefore, the spectroscopic data unambiguously indicate that **5** and **6** are octahedral in solution with the tripod ligand coordinating to the iridium atom in a κ^3 fashion, the phosphanes are mutually *trans*, and the hydride adopts a *cis* disposition relative to the terminal carbonyl and the two phosphane groups (Scheme 3).

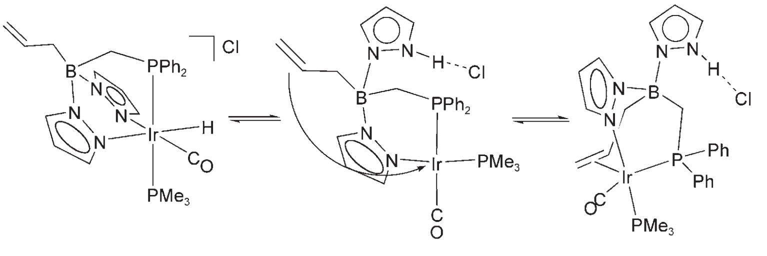


Scheme 3. Formation of the cationic complexes **5** to **7**.

The ^{1}H and ^{31}P{^{1}H } NMR spectra of solutions of **7** are in accordance with the octahedral hydrido iridium complex shown in Scheme 3. However, the signals of a minor species with *cis* phosphane ligands ($\delta = -13.9$, -44.3 ppm; ^2J(P,P) = 22 Hz) were also detected. The phosphorus chemical shifts and coupling constant for this minor species without a hydrido ligand are similar to those of **3**. Moreover, the relative proportion of this minor species increases on cooling the sample to −90 °C and at this point an NH signal can be observed at $\delta = 14.8$ ppm in the ^{1}H NMR spectrum. Therefore, the minor species contains a protonated pyrazolyl arm. Furthermore, the IR spectrum of **7** in the solid state shows two $\tilde{\nu}$(CO) bands at 2052(w) and 1925(s) cm^{-1}, which indicates the presence of two compounds, namely, the octahedral hydridoiridium(III) complex and a pentacoordinated iridium(I) complex. Finally, the molar conductivity values for **7** in acetone lie between those of a nonelectrolyte and a 1:1 electrolyte.

All of these data point to a nonelectrolyte, pentacoordinated Ir^I complex, such as **7′** in Scheme 4, as the minor species in equilibrium with **7** in solution. This equilibrium is slow on the NMR timescale so that both species are observed. A strong H···Cl ionic interaction would be responsible for the behavior of **7′** as a nonelectrolyte (see below), and therefore, the values found for the molar conductivity of the equilibrium mixture are lower than expected for a 1:1 electrolyte. Indeed, there is no evidence for such equilibria for **5** and **6**, which can be attributed to the stabilization of the protonated pyrazolyl complex by association with the chloride anion.

In essence, the interconversion between **7** and **7′** can be viewed as the competition between two basic centers, the iridium and the pyrazolyl nitrogen atom, for a proton, although it might be argued that it encompasses formal changes in the oxidation number of the metal and coordination geometries. A reasonable path for this interconversion



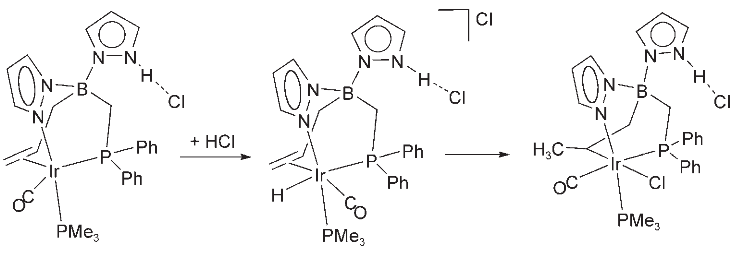
Scheme 4. Equilibrium between octahedral hydrido Ir^{III} complex **7** and pentacoordinated Ir^I complex **7′** found in solution.

would proceed through a prototropism,[20] which involves the migration of the acidic hydride to the nitrogen atom of the *cis* pyrazolyl group. This process would generate square planar Ir^I intermediate **A** in which both phosphane groups adopt either a mutual *trans* or *cis* configuration. We propose that in **7′** there is a pzH⋯Cl ionic interaction, as will be disclosed below. The κ^2 coordination of the scorpionate ligand in **A** makes it very flexible such that coordination of the allyl moiety to the metal would give isomer **7′**, whose trigonal bipyramidal geometry and its stereochemistry are similar to those shown by **3**.

Complex **4** reacts with dry HCl to give the expected cationic hydride $[Ir(CO)\{(CH_2{=}CHCH_2)B(CH_2PPh_2)(pz)_2\}H(PPh_3)]Cl$ (**8**), which was isolated as a white microcrystalline solid in quantitative yield. The spectroscopic data for triphenylphosphane complex **8** in solution are virtually identical to those obtained for **5** and **6**. A hydride signal is observed at $\delta = -14.5$ ppm in its ^1H NMR spectrum, which is in a *cis* disposition with respect to the *trans* phosphanes ($^2J(P,P) = 306$ Hz). Furthermore, the $\tilde{\nu}(CO)$ band at 2067 cm^{-1} is in accordance with an Ir^{III} center, and the molar conductivity values confirm that it is a 1:1 electrolyte in solution.

Although **5**, **6**, and **8** do not react further with HBF_4, CH_3COOH, and HCl, respectively, complex **7** does react with a further molar equivalent of HCl (Scheme 5) to give the unexpected product $[Ir(CO)Cl\{(Hpz)B(CH_2PPh_2)(pz)CH_2CH(CH_3)\}(PMe_3)]Cl$ (**9**), which arises from the protonation of one of the pyrazolyl groups, a formal Markovnikov addition of one proton to the C=C bond with formation of a Ir−C bond, and the coordination of a chloride ligand.

The protonation of a pyrazolyl group is clearly indicated by a broad resonance at low field ($\delta = 16.80$ ppm) in the ^1H NMR spectrum of **9**. Moreover, both phosphane ligands are mutually *cis* in **9**, as shown in the $^{31}P\{^1H\}$ NMR spectrum ($^2J(P,P) = 23$ Hz), and the intense $\tilde{\nu}(CO)$ band at 2052 cm^{-1} in the IR spectrum corresponds to a terminal carbonyl coordinated to an Ir^{III} center. Furthermore, neither a hydrido ligand nor the C=C bond of the former allyl group were detected in the ^1H NMR spectrum, but diastereotopic patterns from the CH_2B and the CH_2P moieties and two new signals in this region. A single-crystal X-ray diffraction study of **9** was therefore undertaken to characterize fully the product of the reaction. Figure 3 shows an ORTEP view of the molecule and selected bond lengths and angles are summarized in Table 3.



7' **B** **9**

Scheme 5. Reaction of complex **7** with HCl.

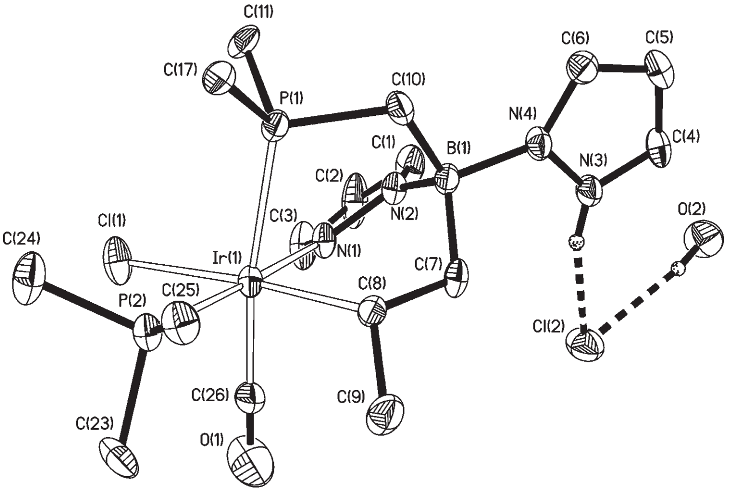


Figure 3. ORTEP view of molecule **9**. Only the *ipso* carbon atoms of the phenyl groups are shown for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for **9**.

Ir(1)−P(1)	2.4018(13)	Ir(1)−P(2)	2.3176(13)
Ir(1)−N(1)	2.101(4)	Ir(1)−Cl(1)	2.5031(13)
Ir(1)−C(8)	2.143(5)	Ir(1)−C(26)	1.899(5)
C(8)−C(9)	1.522(7)	C(7)−C(8)	1.527(6)
Cl(2)−H(N3)	2.16	Cl(2)−H(O(2))	2.22
C(26)-Ir(1)-N(1)	90.0(2)	C(26)-Ir(1)-C(8)	91.0(2)
N(1)-Ir(1)-C(8)	92.24(16)	C(26)-Ir(1)-P(2)	88.82(16)
N(1)-Ir(1)-P(2)	174.95(10)	C(8)-Ir(1)-P(2)	92.69(13)
C(26)-Ir(1)-P(1)	170.74(16)	N(1)-Ir(1)-P(1)	82.16(11)
C(8)-Ir(1)-P(1)	84.33(13)	P(2)-Ir(1)-P(1)	99.39(4)
C(26)-Ir(1)-Cl(1)	84.88(17)	N(1)-Ir(1)-Cl(1)	88.59(10)
C(8)-Ir(1)-Cl(1)	175.84(13)	P(2)-Ir(1)-Cl(1)	86.41(4)
P(1)-Ir(1)-Cl(1)	99.82(5)		

The iridium center lies in the center of a slightly distorted octahedral environment in which the phosphane groups are mutually *cis*. The scorpionate ligand coordinates to iridium as a *fac* tripod system through the phosphorus atom, one pyrazolyl nitrogen atom, and an Ir−C bond from the former allylic fragment, with the other coordination sites occupied by the PMe_3 group, the terminal carbonyl, and a chloride ligand. The noncoordinated pyrazolyl ring is protonated at the nitrogen atom with a strong pair-wise intramolecular hydrogen bond between this proton and the chloride counteranion. The N(3)−H⋯Cl(2) (2.16 Å)separation is smaller than the sum of their van der Waals radii. Additionally, there is an interaction of the chloride anion with a water molecule of crystallization (Cl(2)⋯H−O(2), 2.22 Å). On the other hand, the Ir−C(8) distance of 2.143(5) Å falls into the expected range for a σ-(Ir−C) bond.[21]

The solid-state structure of **9** is thus maintained in solution; the lack of symmetry and the main features can be deduced from the spectroscopic data. Valuable information can be obtained from the conductivity measurements, which, surprisingly, showed that **9** is a nonelectrolyte in acetone, a situation that can be ascribed to a strong ionic interaction between the N−H proton and the chloride counteranion, as reflected in the X-ray molecular structure of **9**. A similar strong pair-wise association is proposed above for **7′**.

The unexpected reaction of **7** with hydrogen chloride can be easily understood on the basis of the equilibrium detected in solutions of this complex (Scheme 4) in which the reactive species is, presumably, isomer **7′** in equilibrium with square planar intermediate **A**. It is precisely this unsaturated intermediate, the one that is protonated stereoselectively at the face closer to the allyl group, that becomes coordinated to the metal to give intermediate **B**. This octahedral cationic Ir^{III} complex, which has coplanar hydrido and π-olefin ligands, will eventually undergo an allylic insertion into the Ir−H bond followed by coordination of the chloride anion *trans* to the new Ir−C bond formed to give **9**. As only **7** undergoes migration of the proton from the metal to the pyrazolyl group to produce the equilibrium with **7′**, related complexes **5**, **6**, and **8** do not react further with protic acids.

Conclusion

In summary, we have reported the coordination chemistry associated with the novel hybrid scorpionate system $[(CH_2{=}CHCH_2)B(CH_2PPh_2)(pz)_2]^-$. We have disclosed how the ligand binds to the metal in Ir^{I} and Ir^{III} complexes with the expected $\kappa^2 N,\kappa P$ facial coordination mode. However, the possible, but not expected, coordination of the allyl group of the scorpionate ligand reveals that it has four donor arms with which to coordinate metals, although only three of them can be used for this purpose. Thus, the metal has the possibility of choosing between different sets of three donors depending on its electronic needs. For example, the $\kappa N,\kappa P,\eta^2$-(C=C) coordination mode is observed in an electron-rich Ir^{I} complex. As expected, the metal in this complex is easily protonated to give hydrido cationic Ir^{III} complexes in which the coordination of the ligand reverts to a $\kappa^2 N,\kappa P$ mode. One of these hydrido complexes, the one with chloride as the counteranion, undergoes a migration of the hydride from the metal to a coordinated pyrazolyl arm, which leads to an equilibrium between the Ir^{III} complex and the pentacoordinated Ir^{I} with the ligand coordinated again in the $\kappa N,\kappa P,\eta^2$-(C=C) mode. It is this equilibrium that is responsible for further reaction with hydrogen chloride, which leads to the addition of the proton to the allyl arm with the concomitant formation of a σ-(Ir−C) bond and the ligand exhibiting the new $\kappa N,\kappa P,\kappa C$ coordination mode.

Experimental Section

All manipulations were performed under a dry argon atmosphere by using Schlenk techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Complex **1** was prepared according to published procedures.[10] All of the other chemicals used in this work were purchased from Aldrich Chemicals and used as received. Carbon and hydrogen analyses were performed by using a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded by using a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode for the metal complexes and in the EI mode. Ions were produced by using a standard Cs$^+$ gun at approximately 30 kV; 3-nitrobenzyl alcohol was used as the matrix. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded by using Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95, 121.42, and 75.47 MHz, 300.13, 121.49, and 75.47 MHz, and 300.08, 121.48, and 75.46 MHz, respectively. Chemical shifts are reported in ppm and referenced to Me_4Si by using the residual signal of the deuteriated solvent in ^{1}H and ^{13}C NMR spectroscopy and with H_3PO_4 as the external reference in the case of ^{31}P NMR spectroscopy.

[(Ir{(allyl)B(CH$_2$PPh$_2$)(pz)$_2$}CO)$_2$(μ-CO)] (2): A solution of complex **1** (0.28 g, 0.41 mmol) in dichloromethane (15 mL) was bubbled with carbon monoxide at atmospheric pressure, which immediately gave a bright yellow solution. Bubbling was continued for 30 min and then hexane (10 mL) was slowly added. The resulting yellow suspension was left to stand for 2 h at −5 °C to afford a microcrystalline yellow solid that was collected by filtration under argon, washed with cold hexane, and then dried under vacuum (0.21 g, 83 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta=8.13$ (m, 8 H; H$_o$ Ph), 8.00 (d, ^{3}J(H,H) = 2.1 Hz, 2 H), 7.84 (d, ^{3}J(H,H) = 2.1 Hz, 2 H), 7.73 (d, ^{3}J(H,H) = 1.8 Hz, 2 H), 7.48 (d, ^{3}J(H,H) = 2.4 Hz, 2 H; pz), 7.21–6.78 (m, 12 H; H$_m$+H$_p$ Ph), 6.20 (m, 2 H; CH allyl), 6.15 (t, ^{3}J(H,H) = 1.8 Hz, 2 H), 5.72 (t, ^{3}J(H,H) = 2.4 Hz, 2 H; pz), 5.24 (d, ^{3}J(H,H) = 17.3 Hz, 2 H; =CH$_2$), 5.21 (d, ^{3}J(H,H) = 10.2 Hz, 2 H; =CH$_2$), 2.11 (d, ^{3}J(H,H) = 6.3 Hz, 4 H; CH$_2$; allyl), 1.65 (m, 2 H), 1.50 ppm (m, 2 H; CH$_2$P); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta=-7.6$ ppm (s); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta=218.3$ (μ-CO), 175.2 (m; CO), 145.5, 142.1 (s; pz), 140.1 (s; CH allyl), 135.0, 133.4 (s; pz), 131.5 (d, ^{2}J(C,P) = 11 Hz; C$_o$ Ph), 129.7 (s; C$_p$ Ph), 128.4 (s; C$_m$ Ph), 114.5 (s; =CH$_2$ allyl), 105.6, 105.3 (s; pz), 29.7 (br s; CH$_2$ allyl), 20.0 ppm (br s; CH$_2$P); IR (toluene): $\tilde{\nu}=1999$ (CO), 1715 cm^{-1} (η^2-CO); MS (FAB$^+$): *m*/*z* (%): 1239 (20) [*M*]$^+$, 1212 (25) [*M*−CO]$^+$, 1183 (15) [*M*−2CO]$^+$; elemental analysis calcd (%) for $C_{47}H_{46}B_2Ir_2N_8O_3P_2$: C 45.56, H 3.74, N 9.04; found: C 46.40, H 3.47, N 8.51.

[Ir(CO){(pz)B(η^2-CH$_2$CH=CH$_2$)(CH$_2$PPh$_2$)(pz)}(PMe$_3$)] (3): Pure trimethylphosphane (27 μL, 0.020 g, 0.26 mmol) was added to a bright yellow suspension of **2** (0.15 g, 0.12 mmol) in diethyl ether (7 mL) to give a pale brown suspension within 30 min. The mixture was stirred for an additional hour and then slow evaporation of the solvent to around 2 mL under vacuum afforded a white solid that was collected by filtration under argon, washed with cold hexane, and then dried under vacuum (0.14 g, 88 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta=8.15$ (s, 1 H; pz), 8.06 (m, 4 H; H$_o$ Ph), 7.87 (s, 1 H), 7.71 (s, 1 H; pz), 7.33–6.91 (m, 6 H; H$_m$+H$_p$ Ph), 6.55 (s, 1 H), 6.53 (s, 1 H), 5.60 (s, 1 H; pz), 2.88 (m, 1 H, =CH$_2$), 2.75 (m, 1 H; CH$_2$), 2.44 (m, 1 H; CH), 2.22 (m, 1 H; =CH$_2$), 1.66 (m 1 H; CH$_2$, η^2-allyl), 1.41 (m, 1 H), 1.05 (m, 1 H; CH$_2$P), 0.57 ppm (d, ^{2}J(H,P) = 10.5 Hz, 9 H; PMe$_3$); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): $\delta=-2.5$ (d, ^{2}J(P,P) = 12 Hz), −42.4 ppm (d, ^{2}J(P,P) = 12 Hz); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta=189.1$ (m; CO), 143.4, 140.0 (s; pz), 137.2 (d, ^{1}J(C,P) = 35 Hz; C$_{ipso}$ Ph), 133.7 (d, ^{2}J(C,P) = 13 Hz; C$_o$ Ph), 132.4 (d, ^{3}J(C,P) = 3 Hz; C$_m$ Ph), 131.5 (s; pz), 131.0 (d, ^{2}J(C,P) = 10 Hz; C$_o$ Ph), 129.8, 105.8, 104.3 (s; pz), 45.7 (d, ^{2}J(C,P) = 7 Hz; η^2-allyl), 34.3 (d, ^{2}J(C,P) = 21 Hz; η^2-allyl), 25.5 (br s; CH$_2$ η^2-allyl), 21.3 (br s; CH$_2$P), 15.3 ppm (d, ^{1}J(C,P) = 42 Hz; PMe$_3$); IR (toluene): $\tilde{\nu}=1925$ cm^{-1} (CO); MS (FAB$^+$): *m*/*z* (%): 654 (100)[*M*−CO]$^+$; elemental analysis calcd (%) for $C_{26}H_{32}BIrN_4OP_2$: C 45.82, H 4.73, N 8.22; found: C 45.75, H 4.71, N 8.12.

[Ir(CO){(pz)B(η^2-CH$_2$CH=CH$_2$)(CH$_2$PPh$_2$)(pz)}(PPh$_3$)] (4): Solid triphenylphosphane (30 mg, 0.115 mmol) was added to a bright yellow suspension of **2** (71 mg, 0.058 mmol) in diethyl ether (7 mL) to give a white suspension within 30 min. The mixture was stirred for 30 min, filtered off through a cannula, and then dried under vacuum (92 g, 91 %). ^{1}H NMR (300 MHz, [D$_8$]toluene, 293 K): $\delta=7.63$ (m, 4 H; Ph), 7.46 (m, 10 H; Ph+pz), 6.99 (m, 16 H; Ph), 5.79 (br s, 1 H; pz), 5.60 (br m, 1 H; CH allyl), 4,65

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(br m, 1 H), 4.50 (br m, 1 H; =CH allyl), 2.13 (m, 2 H; CH_2 allyl), 1.36 ppm (m, 2 H; CH_2P); ^{1}H NMR (300 MHz, [D$_8$]toluene, 203 K): $\delta = 8.37$ (s, 1 H), 7.82 (s, 1 H; pz), 7.70 (m, 4 H; Ph), 7.51–6.81 (set of m, 21 H; Ph), 6.79 (s, 1 H), 6.64 (s, 1 H), 6.28 (s, 1 H), 5.32 (s, 1 H; pz), 3.71 (m, 1 H; =CH_2), 3.56 (m, 1 H; CH_2), 3.24 (m, 1 H; CH), 2.05 (m, 2 H; CH_2, η^2-allyl), 1.41 (m, 1 H), 1.02 ppm (m, 1 H; CH_2P); ^{31}P{^{1}H} NMR (121 MHz, C_7D_8, 203 K): $\delta = 26.0$ (d, $^2J(P,P) = 308$ Hz), 13.2 (d, $^2J(P,P) = 308$ Hz), 2.3 (d, $^2J(P,P) = 37$ Hz), −13.5 ppm (d, $^2J(P,P) = 37$ Hz); IR (toluene): $\tilde{\nu} = 2001$ (m), 1976 (w), 1905 cm^{-1} (s, CO); MS (FAB$^+$): m/z (%): 868 (100) $[M]^+$; elemental analysis calcd (%) for $C_{41}H_{38}BIrN_4OP_2$: C 56.75, H 4.41, N 6.46; found: C 56.63, H 4.31, N 6.33.

[Ir{(allyl)B(CH_2PPh_2)(pz)$_2$}(CO)H(PMe_3)]BF_4 (5): A solution of **3** (0.13 g, 0.19 mmol) in diethyl ether (15 mL) was treated with a solution of tetrafluoroboric acid in diethyl ether 54 wt % (26 μL, 30.7 mg, 0.19 mmol) to give a white suspension within seconds. The suspension was stirred for 10 min and then allowed to stand. Removal of the liquid phase through a cannula gave a white solid that was subsequently washed with diethyl ether and then dried under vacuum (0.10 g, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.08$ (d, $^3J(H,H) = 2.2$ Hz, 1 H), 7.81 (d, $^3J(H,H) = 1.8$ Hz, 1 H), 7.79 (d, $^3J(H,H) = 2.2$ Hz, 1 H; pz), 7.65 (m, 2 H; Ph), 7.61 (d, $^3J(H,H) = 1.8$ Hz, 1 H; pz), 7.51 (m, 3 H), 7.28 (m, 3 H; Ph), 6.59 (t, $^3J(H,H) = 2.2$ Hz, 1 H), 6.35 (t, $^3J(H,H) = 2.2$ Hz, 1 H; pz), 6.08 (m, 1 H; =CH), 5.21 (d, $^3J(H,H) = 16.9$ Hz, 1 H; =CH_2), 5.11 (d, $^3J(H,H) = 10.2$ Hz, 1 H, =CH_2), 2.23 (d, $^3J(H,H) = 7.1$ Hz, 1 H; CH_2, allyl), 1.64 (dd, $^2J(H,P) = 10.8$, $^4J(H,P) = 2.5$ Hz, 9 H; PMe_3), 1.53 (m, 1 H), 1.21 (m, 1 H; CH_2P), −15.29 ppm (dd, $^2J(H,P) = 15.6$, $^2J(H,P) = 15.9$ Hz, 1 H; Ir–H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): $\delta = -1.3$ (d, $^2J(P,P) = 307$ Hz), −33.7 ppm (d, $^2J(P,P) = 307$ Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 163.7$ (dd, $^2J(C,P) = 8$, $^2J(C,P) = 7$ Hz; CO), 146.6, 144.2 (s; pz), 138.0 (s; =CH allyl), 136.2, 135.4 (s; C_m PPh_2), 133.7 (d, $^1J(C,P) = 54$ Hz; C_{ipso} PPh_2), 133.6 (d, $^2J(C,P) = 12$ Hz; C_o PPh_2), 132.1, 131.0 (s; pz), 129.8 (d, $^2J(C,P) = 10$ Hz), 129.3 (d, $^2J(C,P) = 11$ Hz), 129.0 (d, $^2J(C,P) = 11$ Hz; C_o PPh_2), 128.2 (d, $^1J(C,P) = 54$ Hz; C_{ipso} PPh_2), 116.1 (s; =CH_2 allyl), 108.4, 108.2 (s; pz), 27.4 (br s; CH_2B), 17.2 (br s; CH_2P), 14.7 ppm (d, $^1J(C,P) = 37$ Hz; PMe_3); IR (KBr): $\tilde{\nu} = 2058$ (CO), 2180 cm^{-1} (Ir–H); MS (MALDI-TOF): m/z: 683.2 $[M+H]^+$; elemental analysis calcd (%) for $C_{26}H_{33}B_2F_4IrN_4OP_2$: C 40.59, H 4.32, N 7.28; found: C 40.42, H 4.32, N 7.21; $\Lambda_M = 130\ \Omega^{-1}\,cm^2\,mol^{-1}$ (acetone, 5.0×10^{-4} M).

[Ir{(allyl)B(CH_2PPh_2)(pz)$_2$}(CO)H(PMe_3)]CH_3COO (6): A solution of **3** (31 mg, 0.05 mmol) in diethyl ether (15 mL) was treated with acetic acid (2.8 μL, 3.0 mg, 0.05 mmol) to give a white suspension within seconds. The suspension was stirred for 10 min and then allowed to stand. Removal of the liquid phase through a cannula gave a white solid that was subsequently washed with diethyl ether and then dried under vacuum (29 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.08$ (s, 1 H), 7.95 (s, 1 H), 7.80 (s, 1 H; pz), 7.73 (m, 2 H; Ph), 7.64 (s, 1 H; pz), 7.18–7.51 (m, 6 H), 6.54 (m, 2 H; Ph), 6.58 (s, 1 H), 6.35 (s, 1 H; pz), 6.08 (m, 1 H; =CH), 5.20 (d, $^3J(H,H) = 15.6$ Hz, 1 H; =CH_2), 5.12 (d, $^3J(H,H) = 9.0$ Hz, 1 H; =CH_2), 2.24 (br s, 2 H; CH_2, allyl), 2.13 (s, 3 H, CH_3COO), 1.76 (d, $^2J(H,P) = 10.5$ Hz, 9 H; PMe_3), 1.54 (m, 1 H), 1.26 (m, 1 H; CH_2P), −15.22 ppm (dd, $^2J(H,P) = 16.1$, $^2J(H,P) = 16.0$ Hz, 1 H; Ir–H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): $\delta = -1.3$ (d, $^2J(P,P) = 307$ Hz), −33.4 ppm (d, $^2J(P,P) = 357$ Hz); IR (KBr): $\tilde{\nu} = 2056$ (CO), 2180 cm^{-1} (Ir–H); MS (MALDI-TOF): m/z: 683.2 $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{36}BIrN_4O_3P_2$: C 45.35, H 4.89, N 7.55; found: C 45.29, H 4.78, N 7.45; $\Lambda_M = 113\ \Omega^{-1}\,cm^2\,mol^{-1}$ (acetone, 5.0×10^{-4} M).

[Ir{(allyl)B(CH_2PPh_2)(pz)$_2$}(CO)H(PMe_3)]Cl (7): A solution of complex **3** (0.10 g, 0.15 mmol) in diethyl ether (10 mL) was treated with a solution of hydrogen chloride in diethyl ether (0.22 mL, 0.67 M, 0.15 mmol) to give a white suspension within seconds. The suspension was stirred for 10 min and then allowed to stand. Removal of the liquid phase through a cannula gave a white solid that was subsequently washed with diethyl ether and then dried under vacuum (99 mg, 92 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.05$ (s, 1 H), 7.89 (s, 1 H), 7.76 (s, 1 H; pz), 7.69 (m, 2 H; Ph), 7.61 (s, 1 H; pz), 7.24–7.46 (m, 6 H), 6.54 (m, 2 H; Ph), 6.55 (s, 1 H), 6.31 (s, 1 H; pz), 6.05 (m, 1 H; =CH), 5.17 (d, $^3J(H,H) = 16.8$ Hz, 1 H; =CH_2), 5.07 (d, $^3J(H,H) = 9.6$ Hz, 1 H; =CH_2), 2.20 (br s, 2 H; CH_2, allyl), 1.72 (d, $^2J(H,P) = 10.8$ Hz, 9 H; PMe_3), 1.45 (m, 1 H), 1.17 (m, 1 H; CH_2P), −15.27 ppm (dd, $^2J(H,P) = 15.9$, $^2J(H,P) = 6.0$ Hz, 1 H; Ir–H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): $\delta = -1.3$ (d, $^2J(H,P) = 307$ Hz), −33.2 ppm (d, $^2J(H,P) = 307$ Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 164.1$ (dd, $^2J(C,P) = 8$, $^2J(C,P) = 8$ Hz; CO), 146.7, 144.2 (s; pz), 138.1 (s; =CH allyl), 136.2, 135.6 (s; C_m PPh_2), 133.8 (d, $^1J(C,P) = 54$ Hz; C_{ipso} PPh_2), 133.7 (d, $^2J(C,P) = 11$ Hz; C_o PPh_2), 132.3, 131.1 (s; pz), 129.8 (d, $^2J(C,P) = 10$ Hz), 129.4 (d, $^2J(C,P) = 11$ Hz), 129.0 (d, $^2J(C,P) = 10$ Hz; C_o PPh_2), 116.3 (s; =CH_2 allyl), 108.5, 108.3 (s; pz), 27.7 (br s; CH_2B), 17.1 (br s; CH_2P), 15.1 ppm (d, $^1J(C,P) = 37$ Hz; PMe_3); IR (KBr): $\tilde{\nu} = 1925$ (s), 2052 (w, CO), 2185 cm^{-1} (Ir–H); MS (MALDI-TOF): m/z: 683.2 $[M+H]^+$; elemental analysis calcd (%) for $C_{26}H_{33}BClIrN_4OP_2$: C 43.49, H 4.63, N 7.80; found: C 43.31, H 4.61, N 7.78; $\Lambda_M = 58\ \Omega^{-1}\,cm^2\,mol^{-1}$ (acetone, 5.0×10^{-4} M).

[Ir(CO){(CH_2=$CHCH_2$)B(CH_2PPh_2)(pz)$_2$}H(PPh_3)]Cl (8): A solution of **4** (56 mg, 0.083 mmol) in diethyl ether (10 mL) was treated with a solution of hydrogen chloride in diethyl ether (0.12 mL, 0.67 M, 0.083 mmol) to give a white suspension within seconds. The suspension was stirred for 10 min and then allowed to stand. Removal of the liquid phase through a cannula gave a white solid that was subsequently washed with diethyl ether and then dried under vacuum (71 mg, 95 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.17$ (s, 1 H; pz), 7.78 (m, 2 H; Ph), 7.64 (s, 1 H; pz), 7.43–7.29 (set of m, 16 H), 7.05 (m, 5 H; Ph), 6.80 (s, 1 H; pz), 6.61 (m, 2 H;

Table 4. Selected crystal measurements and refinement data for compounds **2**·1.5C_6H_6, **3**·0.5C_7H_8, and **9**·H_2O.

	2·1.5C_6H_6	**3**·0.5C_7H_8	**9**·H_2O
formula	$C_{56}H_{55}B_2Ir_2N_8O_3P_2$	$C_{29.5}H_{35.5}BIrN_4OP_2$	$C_{26}H_{36}BCl_2IrN_4O_2P_2$
M_r	1356.04	727.07	772.44
color	yellow	colorless	colorless
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	13.5462(8)	8.1746(5)	30.835(2)
b [Å]	13.7830(8)	10.4926(7)	12.8685(8)
c [Å]	15.7155(9)	17.5173(11)	15.5818(10)
α [°]	64.1110(10)	90.0440(10)	90.00
β [°]	82.9060(10)	90.2500(10)	98.689(2)
γ [°]	89.7190(10)	104.3640(10)	90.00
V [Å^3]	2615.6(3)	1455.52(16)	6111.9(7)
Z	2	2	8
$F(000)$	1330	721	3056
ρ_{calcd} [g cm^{-3}]	1.722	1.659	1.679
μ [mm^{-1}]	5.179	4.727	4.679
crystal size [mm]	0.06 × 0.06 × 0.05	0.35 × 0.06 × 0.04	0.15 × 0.12 × 0.08
T [K]	100(2)	100(2)	100(2)
θ limits [°]	1.45–25.06	2.00–27.07	1.72–27.07
collected reflns.	26922	13046	19355
unique reflns. (R_{int})	9230 (0.0845)	6309 (0.0520)	6709 (0.0404)
reflns. [$I > 2\sigma(I)$]	6497	5835	5507
parameters/restraints	641/0	356/0	347/0
R_1 [on F, $I > 2\sigma(I)$]	0.0525	0.0325	0.0378
wR_2 (on F^2, all data)	0.0949	0.0712	0.0901
max/min $\Delta\rho$ [e Å^{-3}]	1.306/−1.295	1.610/−1.612	2.797/−0.729
GOF on F^2	1.014	1.051	1.019

Ph), 6.49 (s, 1H), 6.33 (s, 1H; pz), 6.15 (m, 1H; CH allyl), 5.67 (s, 1H; pz), 5.24 (d, ^{3}J(H,H) = 17.1 Hz, 1H; =CH_2), 5.15 (d, ^{3}J(H,H) = 9.3 Hz, 1H; =CH_2), 2.19 (br m, 2H; CH_2, allyl), 1.60 (m, 1H), 1.39 (m, 1H; CH_2P), −14.48 ppm (dd, ^{2}J(H,P) = 12.0, ^{2}J(H,P) = 13.5 Hz, 1H; Ir−H); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 8.7$ (d, ^{2}J(H,P) = 306 Hz), 0.5 ppm (d, ^{2}J(H,P) = 306 Hz); IR (CH_2Cl_2): $\tilde{\nu} = 2067$ (CO), 2180 cm^{-1} (Ir−H); MS (MALDI-TOF): *m*/*z*: 869 $[M+H]^+$; elemental analysis calcd (%) for $C_{41}H_{38}BClIrN_4OP_2$: C 54.46, H 4.35, N 6.20; found: C 54.31, H 4.21, N 6.18; $\Lambda_M = 128\ \Omega^{-1}\,cm^2\,mol^{-1}$ (acetone, 5.0×10^{-4} M).

[Ir(CO)Cl{(Hpz)B(CH_2PPh_2)(pz)$CH_2CH(CH_3)$}(PMe_3)]Cl (9): A solution of **7** (0.21 g, 0.31 mmol) in diethyl ether (20 mL) was treated with a solution of hydrogen chloride in diethyl ether (0.46 mL, 0.67 M, 0.32 mmol) to give a white suspension within seconds. The suspension was stirred for 10 min and then allowed to stand. Removal of the liquid phase through a cannula gave a white solid that was subsequently washed with diethyl ether and then dried under vacuum (0.22 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 16.80$ (br s, 1H; NH), 8.29 (s, 1H; pz), 8.14 (m, 2H; Ph), 8.01 (s, 1H; pz), 7.36 (m, 2H; Ph), 7.28 (s, 1H; pz), 7.09–7.26 (m, 6H; Ph), 6.13 (s, 2H), 5.84 (s, 1H; pz), 2.74 (m, 1H; CH_2B), 2.63 (m, 1H; CH), 2.04 (m, 1H; CH_2B), 1.65 (d, ^{3}J(H,H) = 5.4 Hz, 3H; CH_3), 1.10 (d, ^{2}J(H,P) = 10.7 Hz, 9H; PMe_3), 0.85 (m, 1H), 0.72 ppm (m, 1H; CH_2P); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -16.4$ (d, ^{2}J(P,P) = 23 Hz), −46.1 ppm (d, ^{2}J(P,P) = 23 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 167.3$ (dd, ^{2}J(C,P) = 132, ^{2}J(C,P) = 9 Hz; CO), 143.8, 136.3 (s; pz), 135.1 (d, ^{2}J(C,P) = 10 Hz; C_o PPh_2), 134.5 (s; pz), 132.9, 132.8, 132.7 (m; Ph), 131.0 (s; pz), 128.9 (d, ^{2}J(C,P) = 10 Hz; C_o PPh_2), 107.1, 106.9 (s; pz), 37.0 (s; CH), 29.8 (br s; CH_2B), 15.3 (br s; CH_2P), 14.0 (d, ^{1}J(C,P) = 42 Hz; PMe_3), 8.5 ppm (s; CH_3); IR (KBr): $\tilde{\nu} = 2052\ cm^{-1}$ (CO); elemental analysis calcd (%) for $C_{26}H_{34}BCl_2IrN_4OP_2$: C 41.39, H 4.54, N 7.43; found: C 41.25, H 4.37, N 7.32.

X-ray diffraction studies of 2, 3, and 9: Complexes **2**·1.5C_6H_6, **3**·0.5C_7H_8, and **9**·H_2O were studied by X-ray diffraction. Intensity measurements were collected by using a Smart Apex diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. A semi-empirical absorption correction was applied to each data set by using multi-scan[22] methods. Selected crystallographic data is given in Table 4. The structures were solved by the Patterson method and refined by full-matrix least-squares by using the SHELX97 program[23] in the WINGX[24] software package.

CCDC 656086, 656087, and 656088 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Generous financial support from MEC/FEDER (Project CTQ2005-06807/BQU) and DGA (Research group E70) is gratefully acknowledged. J.A.C. thanks the Ministerio de Educación y Ciencia for a fellowship. M.A.C. would like to give special thanks to his wife Amada Miravete.

---

[1] S. Trofimenko, *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844.

[2] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**.

[3] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943–980.

[4] Novel κ^1- and κ^0-coordination modes of Tp systems have been reported recently, see: M. Paneque, S. Sirol, M. Trujillo, E. Carmona, E. Gutierrez-Puebla, M. A. Monge, C. Ruiz, F. Malbosc, C. Serra-Le Berre, P. Kalck, M. Etienne, *Chem. Eur. J.* **2001**, *7*, 3868–3879.

[5] a) D. M. Tellers, R. G. Bergman, *J. Am. Chem. Soc.* **2000**, *122*, 954–955; b) D. M. Tellers, R. G. Bergman, *Organometallics* **2001**, *20*, 4819–4832; c) D. M. Tellers, S. J. Skoog, R. G. Bergman, T. B. Gunnoe, W. D. Harman, *Organometallics* **2000**, *19*, 2428–2432; d) N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 419–531; e) J. L. Koch, P. A. Shapley, *Organometallics* **1997**, *16*, 4071–4076; f) E. Gutierrez-Puebla, A. Monge, M. C. Nicasio, P. J. Perez, M. L. Poveda, L. Rey, C. Ruiz, E. Carmona, *Inorg. Chem.* **1998**, *37*, 4538–4546; g) E. Gutierrez-Puebla, A. Monge, M. Paneque, M. L. Poveda, S. Taboada, M. Trujillo, E. Carmona, *J. Am. Chem. Soc.* **1999**, *121*, 346–354.

[6] a) J. D. Feldman, J. C. Peters, T. D. Tilley, *Organometallics* **2002**, *21*, 4050–4064; b) D. Feldman, J. C. Peters, T. D. Tilley, *Organometallics* **2002**, *21*, 4065–4075; c) C. C. Lu, C. T. Saouman, M. W. Day, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 4–5; d) C. M. Thomas, J. C. Peters, *Angew. Chem.* **2006**, *118*, 790–794; *Angew. Chem. Int. Ed.* **2006**, *45*, 776–780; e) S. D. Brown, M. P. Mehn, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 13146–13147; f) L. Turculet, J. D. Feldman, T. D. Tilley, *Organometallics* **2004**, *23*, 2488–2502; g) J. C. Peters, J. D. Feldman, T. D. Tilley, *J. Am. Chem. Soc.* **1999**, *121*, 9871–9872.

[7] K. Niedenzu, S. Trofimenko, *Inorg. Chem.* **1985**, *24*, 4222–4223.

[8] J. S. Thompson, J. L. Zitzmann, T. J. Marks, J. A. Ibers, *Inorg. Chim. Acta* **1980**, *46*, L101–L105.

[9] P. Ghosh, G. Parkin, *Chem. Commun.* **1998**, 413–414.

[10] M. A. Casado, V. Hack, J. A. Camerano, M. A. Ciriano, C. Tejel, L. A. Oro, *Inorg. Chem.* **2005**, *44*, 9122–9124.

[11] a) S. Trofimenko, *Polyhedron* **2004**, *23*, 197–203; b) a boron-based system that has one pyrazoyl arm and two phosphane groups has been reported recently, see: C. M. Thomas, N. P. Mankad, J. C. Peters, *J. Am. Chem. Soc.* **2006**, *128*, 4956–4957.

[12] A. Albinati, M. Bovens, H. Rüegger, L. M. Venanzi, *Inorg. Chem.* **1997**, *36*, 5991–5999.

[13] D. M. Heinekey, D. A. Fine, D. Barnhart, *Organometallics* **1997**, *16*, 2530–2538.

[14] T. E. Bitterwolf, G. Valle, *Organometallics* **1991**, *10*, 1416–1420.

[15] T. Makino, Y. Yamamoto, K. Itoh, *Organometallics* **2004**, *23*, 1730–1737.

[16] F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203–2209.

[17] I. I. Padilla-Martínez, M. L. Poveda, E. Carmona, M. A. Monge, C. Ruiz-Valero, *Organometallics* **2002**, *21*, 93–104.

[18] S. Marcén, M. V. Jiménez, I. T. Dobrinovich, F. J. Lahoz, L. A. Oro, *Organometallics* **2002**, *21*, 326–330.

[19] R. G. Ball, C. K. Ghosh, J. K. Hoyano, A. D. McMaster, W. A. G. Graham, *J. Chem. Soc., Chem. Commun.* **1989**, 341–342.

[20] a) C. Tejel, M. A. Ciriano, M. Millaruelo, J. A. López, F. J. Lahoz, L. A. Oro, *Inorg. Chem.* **2003**, *42*, 4750–4758; b) H. C. Lo, M. A. Iron, J. M. L. Martín, E. Keinan, *Chem. Eur. J.* **2007**, *13*, 2812–2823.

[21] a) J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *119*, 8503–8511; b) M. Paneque, M. L. Poveda, L. L. Santos, E. Carmona, A. Lledós, G. Ujaque, K. Mereiter, *Angew. Chem.* **2004**, *116*, 3794–3797; *Angew. Chem. Int. Ed.* **2004**, *43*, 3708–3711.

[22] G. M. Sheldrick, SADABS, Bruker AXS, Madison, WI (USA), **1997**.

[23] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), **1997**.

[24] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Received: August 2, 2007
Published online: December 6, 2007