Rhodium and Iridium Complexes with a New Scorpionate Phosphane Ligand

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Dedicated to Prof. Dr. Antonio Laguna on the occasion of his 65th birthday

Abstract. A straightforward synthesis of a new hybrid scorpionate ligand $[(allyl)_2B(CH_2PPh_2)(Pz)]^-$ ($[A_2BPN]^-$) is reported. Coordination to rhodium resulted in square-planar complexes $[Rh(\kappa^2\text{-}A_2BPN)(L)(L')]$ (L = L'= ½ cod (1,5-cyclooctadiene), CN^tBu, CO (**6**); L = CO, L' = NH_3, pyridine, PPh_3, PMe_3) for which spectroscopic data and the molecular structure of $[Rh(\kappa^2\text{-}A_2BPN)(CO)PPh_3]$ (**11**) indicate the ligand to be $\kappa N,\kappa P$-bound to rhodium with two dangling free allyl groups. Studies in solution point out that the six-membered $\overline{Rh-N-N-B-C-P}$ metallacycle undergoes a fast inversion in all of them. The bis(carbonyl) complex **6** easily loses a CO group to give $[\{Rh(A_2BPN)(CO)\}_2]$, a dinuclear compound in which two mononuclear subunits are brought together by two bridging allyl groups. Coordination to iridium is dominated by a tripodal $\kappa N,\kappa P,\eta^2\text{-}C{=}C$ binding mode in the *TBPY*-5 complexes $[Ir(\kappa^3\text{-}A_2BPN)(L)(L')]$ (L = L' = ½ cod (**3**), CN^tBu (**5**), CO (**7**); L = CO, L' = PPh_3 (**13**), PMe_3 (**14**), $H_2C{=}CH_2$, (**17**), $MeO_2CC{\equiv}CCO_2Me$ (dmad, **18**)), as confirmed by the single-crystal structure determination of complexes **3** and **18**. A fast exchange between the two allyl arms is observed for complexes having L = L' (**3**, **5**, and **7**), while those having CO and L ligands (**14**, **17** and **18**) were found to be non-fluxional species. An exception is complex **13**, which establishes an equilibrium with the *SP*-4 configuration. Protonation reactions on complexes **13** and **14** with HCl yielded the hydride-complex $[Ir(\kappa^2\text{-}A_2BPN)(CO)(Cl)(H)PPh_3]$ (**15**) and the *C*-alkyl compound $[\overline{Ir\{\kappa^3\text{-}(allyl)B(CH_2CHCH_3)(CH_2PPh_2)(Pz)\}}(Cl)(CO)PMe_3]$ (**16**), respectively. The bis(isocyanide) complex **5** reacts with dmad to form $[Ir(\kappa^2\text{-}A_2BPN)(CN^tBu)_2(dmad)]$. On the whole, the electronic density provided to the metal by the $[A_2BPN]^-$ ligand is very sensitive to

the coordination mode. The basicity of the new ligand is similar to that of the Tp^{Me2} ligand in the κ*N*,κ*P* mode, but comparable to Tp if coordinated in the κ*N*,κ*P*,η^2-*C*=*C* mode.

Introduction

Ligand design has become a major concept in organometallic chemistry, a chemical tool developed to tailor the stability and/or chemical reactivity of transition metal complexes. From a certain perspective, the ligand architecture (described by the disposition of the donor atoms) mainly defines the geometry around a transition metal center in a metal complex, while the ligand nature (associated to the donor groups) allows for control over electronic and steric properties. A conjunction of both properties will eventually impact on the reactivity of their complexes. Consequently, an exceptional effort has been dedicated to design ligand scaffolds specifically to stabilize metallic fragments in a pre-defined geometry. In this context, a special mention is required for pincer ligands,[1] in which the meridional coordination results in strong binding to the metal allowing outstanding examples of C−H bond activation.[2]

Unlike the aforementioned pincer ligands, the ubiquitous poly(pyrazolyl)borate (Tp or scorpionate) provides three nitrogen atoms that cap one face of a coordination polyhedron.[3] These versatile ligands have attracted an enormous interest in distinct fields of science for a long time, ranging from bioinorganic chemistry to materials science, and applications in organometallic and coordination chemistry are very well documented.[4] The broad body of work generated by these Tp-based complexes encouraged new adaptations and improvements of the architectures of the scorpionate ligands, mainly by varying alkyl or aryl substituents at the 3 and/or 5 positions of the pyrazolyl rings ('2nd generation'),[5] The structural variations on these ligands allowed tailoring their cone and wedge angles, influencing the metal basicity by changing the nature of the pyrazolyl substituents, giving rise to a new set of late transition metal

complexes able to perform unusual metallorganic transformations.[6] Moreover, structural adjustments by functionalizing the fourth site at boron ('3rd generation')[7] has provided interesting examples of original oligotopic ligands to be used as scaffolds for oligonuclear complexes,[8] and to covalently anchor RhTp-based systems peripherally to carbosilane dendrimers in specific cases.[9]

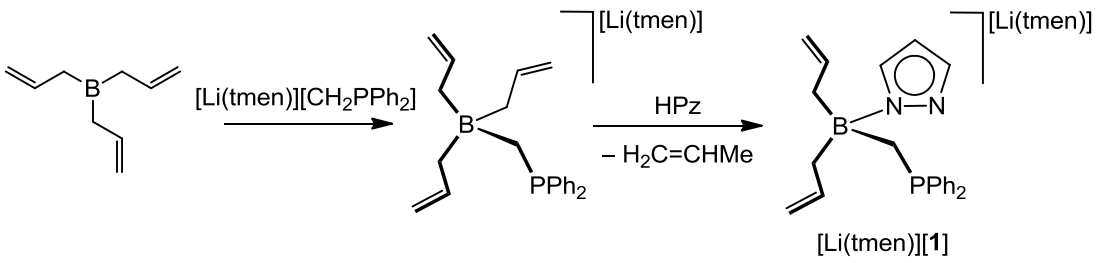
While the catalytic properties of these N-based tripodal systems is being unfolded within the last years,[10] the curiosity of scientists together with the desire for fine-tuning electronic parameters in tripodal assemblies led naturally to the development of non-pyrazolyl, anionic borate-based ligands of the type $[RBD_3]^-$.[11] These new constructs are potentially C_3-symmetric face-capping ligands, which bear donor groups D based on atoms other than N (e.g. P,[12] S,[13] and C[14]) providing different electronic environments to the metals, which has made possible the observation of unusual reactivity patterns.[12d,15]

With the idea of bringing together mixed donor sets 'N_2P', we reported the synthesis[16] of the hybrid, anionic scorpionate-like ligand $[(CH_2{=}CHCH_2)B(CH_2PPh_2)(Pz)_2]^-$ (Pz = pyrazolate), while Peters and co-workers[17] documented the related 'P_2N' hybrid system $[PhB(CH_2P^tBu_2)_2(Pz)]^-$. Aimed by the rich reactivity and coordination chemistry displayed by the iridium complexes stabilized by the 'PN_2' tripodal system, which showed the allyl arm not to be innocent,[18] we decided to take a step further in the design of such hybrid architectures and now we wish to report the synthesis of a new ligand with a flexible scaffold, provided with a set of three different donors based on hard (N) and soft (P, C) atoms of composition $[(allyl)_2B(CH_2PPh_2)(Pz)]^-$ ($[A_2BPN]^-$), as well as the coordination chemistry and reactivity shown by its rhodium and iridium complexes.

Results and Discussion

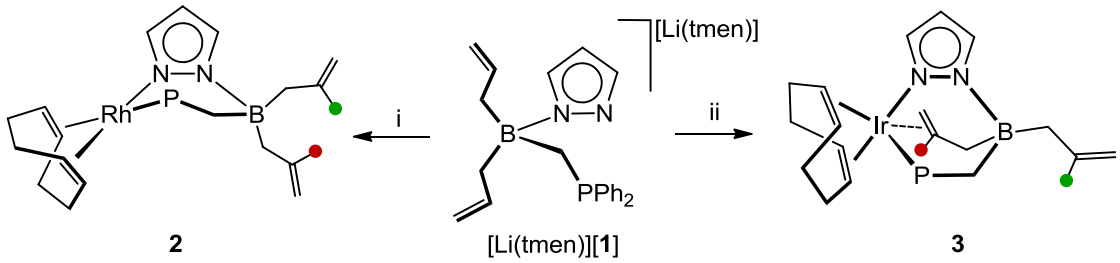
The new ligand $[(allyl)_2B(CH_2PPh_2)(Pz)]^-$ ($[A_2BPN]^-$) features a central boron atom connected to two allyl groups, one pyrazolyl ring and a pendant CH_2PPh_2 moiety. It is a new anionic scorpionate if one considers that the allylic groups may coordinate to metals in a η^2-*C*=*C* fashion.[18] The ligand brings together hard N-donor and soft P- and C-donor groups, which makes the study of its coordination chemistry to transition metals very attractive, since it can accommodate metallic fragments in different ways. The ligand has been synthesized as the [Li(tmen)][A_2BPN] salt ([Li(tmen)][**1**]) in two steps as shown in Scheme 1: i) formation of the intermediate $[(allyl)_3B(CH_2PPh_2)]^-$ by treatment of $B(allyl)_3$ with an equimolar amount of [Li(tmen)][CH_2PPh_2]); ii) protonation of one of the allyl arms with pyrazole. This approach represents a convenient way to this type of system since propene is the only waste in the second step. Tetra-substitution of the boron atom in $[A_2BPN]^-$ was confirmed by the shift of the signal at δ –5.89 ppm, in the $^{11}B\{^1H\}$ NMR spectrum.[19] A broad resonance at δ −13.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum indicated the lithium ion to be coordinated to phosphorous, while the expected resonances for the equivalent allyl arms and the pyrazolyl group were observed in the ^1H NMR spectrum.

Scheme 1. Synthesis of compound [Li(tmen)][**1**].



Coordination of the 'M(cod)' (M = Rh, Ir) fragments to **1** was achieved by reaction of [Li(tmen)][A_2BPN] with the complexes [{M(μ-Cl)(cod)}$_2$], which rendered the compounds [M(A_2BPN)(cod)] (M = Rh, **2**; Ir, **3**; cod = 1,5-cyclooctadiene) as yellow and white solids, respectively, in good yields. Nonetheless, complex **3** was prepared in better yield starting from [Ir(acac)(cod)] (acac = acetylacetonate) (Scheme 2, phenyl groups on the P atom have been omitted for clarity in all schemes and charts).

Scheme 2. Synthesis of complexes **2** and **3**. i = [{Rh(μ-Cl)(cod)}$_2$], ii = [Ir(acac)(cod)].

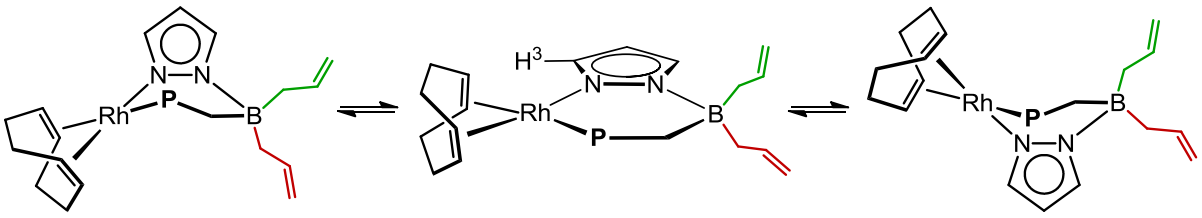


Both complexes were found to be fluxional and the frozen structures, shown in Scheme 2, were observed on cooling. At –80 ºC, both exhibited four resonances for the olefinic-cod protons and inequivalent allyl groups in the ^{1}H NMR spectra, a clear indication of the lack of symmetry of the complexes. Moreover, the =CH protons from the allyl groups (marked with red and green circles in Scheme 2) were found as broad signals at δ 6.81 and 6.05 ppm for the rhodium complex **2**,, i.e., in the typical region for non-coordinated olefins. Therefore, both allyl groups are free in **2** and the ligand binds the rhodium through the P and N ends to produce the puckered structure (Scheme 2) at low temperature. On the contrary, these resonances were found to be at δ 6.45 and 3.60 ppm for the iridium counterpart (**3**). The shift to high-field of one of them (as well as for the corresponding =CH_2 protons, observed at δ 3.92 and 2.10 ppm) agree with the bonding

of one of the allyl groups to iridium, which was confirmed by a single crystal X-ray analysis of complex **3** (see below). Consequently, the frozen structure for complex **3** corresponds to a pentacoordinated compound with the tripodal ligand coordinated in a κN,κP,η^2-C=C fashion.

On raising the temperature, the allyl groups coalesce in both cases, emerging as an unique allyl group above room temperature. For the rhodium complex **2**, the set of signals was found at chemical shifts typical for free allyl ligands, so that an easy inversion of the six-membered metallacycle ($\overline{\text{Rh–N–N–B–C–P}}$) accounts for the experimental data (Scheme 3). This inversion has to occur through the planar C_s-conformation, which presents a steric hindrance between the olefinic-cod protons and the H^3 proton from the pyrazolyl and the phenyl groups on the phosphorus. Consequently, this process should be facilitated by less demanding ligands on the metal centre, as shown below for the bis(carbonyl) and bis(isocyanide) derivatives.

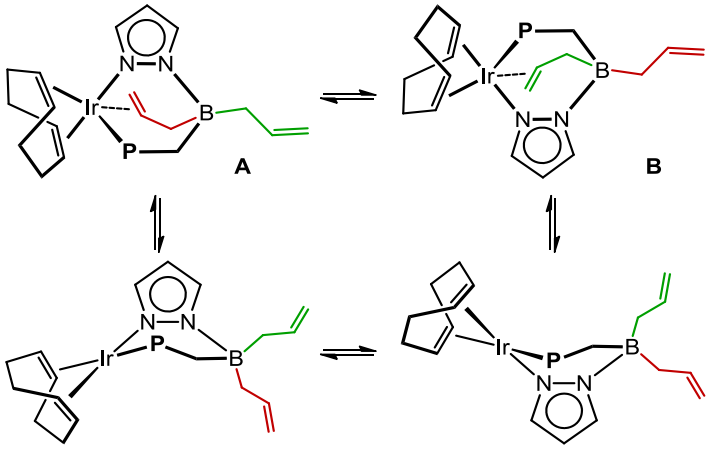
Scheme 3. Fluxional motion undergone by complex **2**.



On the contrary, the allyl groups of the iridium counterpart **3** emerge from the coalescence as a set of signals of the CH_2=CH– moiety still shifted to high field (see Supporting Information). The equivalence of both allyl groups and the modification of chemical shifts can easily be interpreted as an equilibrium between two species, **A** and **B** (Scheme 4), resulting from de-coordination of the allyl group followed by an easy boat-to-boat inversion of the square-planar

species and re-coordination of the other allyl group (Scheme 4). This dynamic process is reminiscent with that generally shown by Tp-complexes,[5d,20] based upon sequential coordination-decoordination steps of the pyrazolyl moieties. However, the dangling groups in the present case are the allylic fragments, while the pyrazolyl and phosphane arms remain coordinated throughout the dynamic process. Accordingly, no appreciable changes in the chemical shifts of the protons of the pyrazolyl group were observed in the VT-^{1}H NMR spectra and the chemical shift of the phosphorus remained almost unaltered in the same range of temperature.

Scheme 4. Proposed motions justifying the fluxional behavior of complex **3**.



The molecular structure of **3** together with the atom labeling scheme used is shown in Figure 1, while Table 1 displays selected bond distances and angles. In the complex, the iridium atom lies at the center of a slightly distorted trigonal bipyramid (*TBPY*-5) coordinated to the scorpionate ligand in a κ*N*,κ*P*,η^2-*C*=*C* fashion and to the C=C bonds of cod in the typical chelating mode.

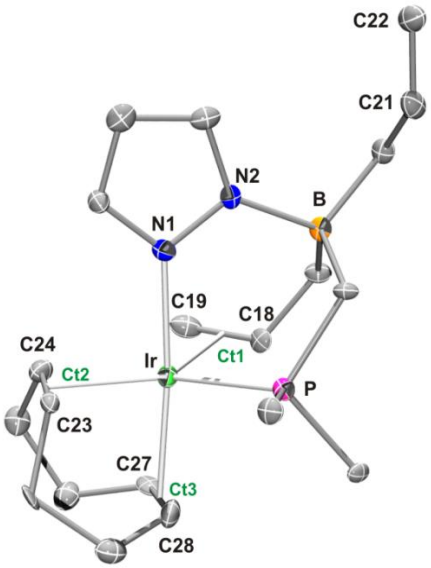


Figure 1. Molecular structure (ORTEP at 50 % level) of complex [Ir(κ^3-A_2BPN)(cod)] (**3**). Hydrogen atoms and solvent of crystallization have been removed and only the ipso carbon atoms of the phenyl groups are shown for clarity.

Table 1. Selected bond distances (Å) and angles (º) for complex **3**.

Ir–P	2.384(2)	N1–Ir–Ct3	174.1(2)
Ir–N1	2.114(5)	Ct1–Ir–Ct2	126.7(2)
Ir–Ct1	2.143(6)	P–Ir–Ct1	101.3(2)
Ir–Ct2	2.034(6)	P–Ir–Ct2	131.4(2)
Ir–Ct3	2.095(6)	N1–Ir–Ct1	86.4(2)
C18–C19	1.385(8)	N1–Ir–Ct2	90.12(2)
C21–C22	1.345(9)	N1–Ir–P	85.1(1)
C23–C24	1.442(9)	P–Ir–Ct3	97.2(2)
C27–C28	1.403(9)		

Ct1, Ct2, and Ct3 represent the middle points of the C18–C19, C23–C24, and C27–C28 bonds, respectively.

The axial positions are occupied by the N1 atom of the pyrazolyl ring and one olefinic bond (C27−C28) of cod, while the P atom, the η^2-C=C bond of one allyl group and the other olefinic bond of cod (C23–C24) lay at the equatorial sites. All the equatorial angles are different from each other and from 120°, being the P–Ir−Ct1 angle the smallest (101.3(2)°), probably forced by the rigidity of the coordinate tripodal framework. The C=C bond distance of the cod ligand occupying the equatorial site (1.442(9) Å) is longer than that for the C=C bond at the axial site (1.403(9) Å), as expected from a stronger π-back donation from the metal in the equatorial plane. For the coordinated allyl group, this C=C bond distance was even shorter (1.385(8) Å) and close to that in the free allyl group (1.345(9) Å), suggesting it to be a labile ligand. Noticeably, the η^2-allyl group was found to be bonded to iridium in a very asymmetric way, as reflected by the Ir–C18 and Ir–C19 distances of 2.301(6) and 2.202(6) Å, respectively. On the whole, these distances are similar to those found in other η^2-olefin iridium complexes such as $[Ir(Tpm)(H)(CH=CH_2)(C_2H_4)]PF_6$ (Tpm = tris(3,5-dimethylpyrazolyl)methane) (2.171(10) and 2.142(11) Å),[21] $[IrCl(L_{Fe})(cod)][PF_6]$ (L_{Fe} = [Fe(η^5-C_5H_5){η^6-1,1-di(2-propenyl)-3-butenyl}benzene] (2.191(6) and 2.319(6) Å),[22] and [Ir{(Pz)B(η^2-allyl)(CH_2PPh_2)(Pz)}(CO)PMe_3] (2.227(4) and 2.168(5) Å).[18]

Related isocyanide and carbonyl complexes of formula $[M(A_2BPN)(L)_2]$ (L = CN^{t}Bu, M = Rh, **4**; Ir, **5**; L = CO, M = Rh, **6**; Ir, **7**) were easily prepared by reacting complexes **2** and **3** with CN^{t}Bu in a 1:2 molar ratio, and by bubbling carbon monoxide through solutions of **2** and **3**. The bis(isocyanide) complexes **4** and **5** were stable enough to be isolated as yellow and white solids, respectively. However, the bis(carbonyl) derivatives **6** and **7** were maintained as such only under an atmosphere of carbon monoxide and, consequently, they were characterized *in situ*. In fact, evaporation of the solvent was associated to the loss of one carbonyl ligand from the rhodium

complex (to give the dimer [{Rh(A_2BPN)(CO)}$_2$] (**8**), see below) and a full decomposition for the iridium compound.

Complexes **4**-**7** retain the original stereochemistry of their cod precursors (**2**, **3**), which depends on the metal: while rhodium tends to adopt square-planar geometries, iridium prefers *TBPY*-5 environments facilitated by the η^2-C=C coordination of one allyl group. Accordingly, equivalent free allyl groups were observed in the ^{1}H NMR of the rhodium complexes (**4** and **6**) at room temperature, as commented above for [Rh(κ^2-A_2BPN)(cod)] (**2**) (See Experimental Section). On cooling, no changes in the spectra were observed, which indicates a lower energy barrier for the inversion of the metallacycle than for the cod complexes. This lower barrier can be expected from the lesser steric requirements of the isocyanide and carbonyl ligands relative to cod, which lead to less hindered planar conformations, as observed in related dinuclear puckered structures.[23] In addition, two intense bands at 2159 and 2114 cm^{-1}, assigned to the symmetric and antisymmetric stretches of the isocyanide ligands, were observed in the IR spectrum of **4**. These frequencies compare well with those shown by [Rh(Tp^{Me2})(CNR)$_2$] (R = neopentyl, xylyl, Me), in which a κ^2*N* coordination of the Tp^{Me2} ligand was confirmed both in solution and in the solid state.[24] However, the nature of complex **4** differs drastically from that of the Tp complex [{RhTp}$_2$(μ-CNCy)$_3$], which is stabilized by three isocyanide bridging moieties.[25]

On the other hand, variable temperature NMR spectra of the iridium counterparts (**5** and **7**) indicated both to be penta-coordinated species at low temperature, but undergo a fast allyl-exchange at room temperature. As a way of example, Figure 2 shows the ^{1}H NMR spectra corresponding to the low and fast exchange region for the iridium isocyanide complex **5**.

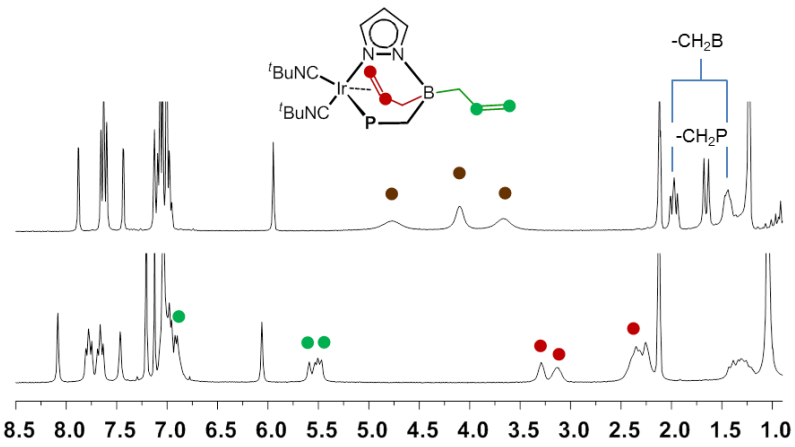


Figure 2. ^{1}H NMR spectra of complex [Ir(κ^{3}-A$_2$BPN)(CN^{t}Bu)$_2$] (**5**) in d$_8$-toluene, showing the two inequivalent allyl groups at −50 ºC (bottom) and their fast exchange a r.t. (top).

The electron density at the metal provided by the new A$_2$BPN ligand can be deduced from the ν(CO) stretchings, which faithfully reflect such event. *SP*-4 [Rh(κ^{2}-A$_2$BPN)(CO)$_2$] (**6**) shows two intense ν(CO) absoptions at 2083 and 2020 cm^{-1} (cyclohexane), similar to that reported for [Rh(κ^{2}-Tp^{Me2})(CO)$_2$] (2080, 2012 cm^{-1} in pentane),[26] while that for *TBPY*-5 [Ir(κ^{3}-A$_2$BPN)(CO)$_2$] (2053, 1982 cm^{-1}, cyclohexane) were found to be closer to that for [Ir(κ^{3}-Tp)(CO)$_2$] (2051, 1971 cm^{-1} in acetonitrile) than for [Ir(κ^{3}-Tp^{Me2})(CO)$_2$] (2035, 1954 cm^{-1} in toluene).[27] Therefore, the electronic density delivered by A$_2$BPN to the metal seems to be similar to that of the Tp^{Me2} ligand in the κ*N*,κ*P* mode, but comparable to Tp if coordinated in the κ*N*,κ*P*,η^{2}-*C*=*C* mode.

As indicated above, attempts to isolate [Rh(κ^{2}-A$_2$BPN)(CO)$_2$] (**6**) led to the loss of one carbonyl ligand with crystallization of the product as the dimer [{Rh(A$_2$BPN)(CO)}$_2$] (**8**). Figure 3 shows the molecular structure of **8** and selected bond lengths and angles are summarized in Table 2. Complex **8** consists of two mononuclear subunits brought together by two bridging allyl

groups coordinated in a μ-η^2-C=C fashion, forming in this way a twelve-membered dimetallacycle. In each metallic subunit, the rhodium atom lies in the center of a slightly distorted square-planar environment with the scorpionate ligand coordinated to the metal through the N and P atoms in a chelating fashion. The CO group is located *trans* to N and the fourth coordination site is occupied by the C=C double bond of the allyl group from the other metallic subunit. In this geometry, the carbonyl and allyl groups having the greatest *trans* influence[28] are mutually *cis*, while the good σ-donor pyrazolyl group is opposite the strongest π acceptor (CO).[29]

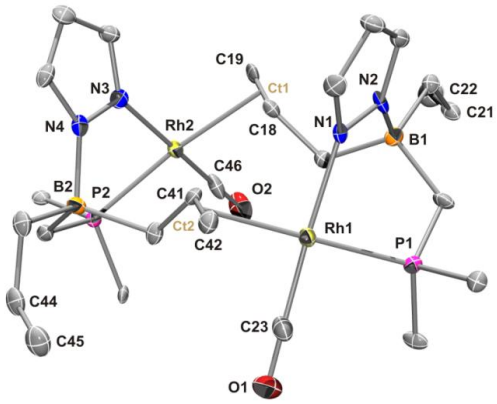


Figure 3. Molecular structure (ORTEP at 50 % level) of complex [{Rh(A$_2$BPN)(CO)}$_2$] (**8**). Hydrogen atoms have been removed and only the ipso carbon atoms of the phenyl groups are shown for clarity.

The Rh–C(olefin) bond distances (2.305 Å in average) were found to be considerably longer than those found for some Rh(I)-ethylene complexes. For comparison, average Rh–C distances of 2.097, 2.125, and 2.206 Å were observed for square-planar complexes of the type [RhX(L)$_2$(C$_2$H$_4$)],[30] [Rh(L$_2$)(C$_2$H$_4$)$_2$],[31] and [Rh(*mer*-L$_3$)(C$_2$H$_4$)]$^{n+}$,[32] respectively. Furthermore, the C18–C19 (1.367(7) Å) and C41–C42 (1.382(7) Å) bond distances are only slightly longer

than those observed for the uncoordinated allyl groups (C21–C22, 1.312(7) Å; C44–C45, 1.326(7) Å), which indicates it to be a labile ligand with weak π-back donation from the metal to the olefin. In good agreement, the signals of the coordinated CH_2=CH– moiety were only slightly shifted upfield (4.91 ppm in average) when compared to the uncoordinated one (5.57 ppm in average) in the ^{1}H NMR spectrum.

Table 2. Selected bond distances (Å) and angles (º) for complex **8**.

Rh1–P1	2.2864(14)	Rh2–P2	2.2905(14)
Rh1–N1	2.098(4)	Rh2–N3	2.108(4)
Rh1–C41	2.291(5)	Rh2–C18	2.349(4)
Rh1–C42	2.286(5)	Rh2–C19	2.294(4)
Rh1–Ct2	2.182(5)	Rh2–Ct1	2.219(4)
Rh1−C23	1.813(6)	Rh2−C46	1.819(6)
C18–C19	1.367(7)	C41–C42	1.382(7)
C21–C22	1.312(7)	C44–C45	1.326(7)
N1–Rh1–C23	176.3(2)	N3–Rh2–C46	175.1(2)
P1–Rh1–Ct2	177.6(2)	P2–Rh2–Ct1	171.4(2)

Ct1 and Ct2 represent the middle point of C18 and C19, and C41 and C42, respectively.

P- and N-donor ligands cleave the dinuclear unit in **8** to generate the square-planar carbonyl complexes [Rh(κ^2-A_2BPN)(CO)L] (L = pyridine (py), **9**; NH_3, **10**; PPh_3, **11**; PMe_3, **12**). Complexes **9**, **11**, and **12** were isolated as yellow solids in good yields, but the formation of the NH_3 compound **10** was found to be reversible; working-up only led to the recovery of the starting material. It was, however, completely characterized in solution, since its synthesis was

quantitative (NMR evidence, See Experimental Section). The κ*N*,κ*P*-coordination of the ligand to rhodium in these complexes was definitively confirmed from an X-ray study on complex **11**, whose molecular structure is shown in Figure 4. Selected bond distances and angles are given in Table 3.

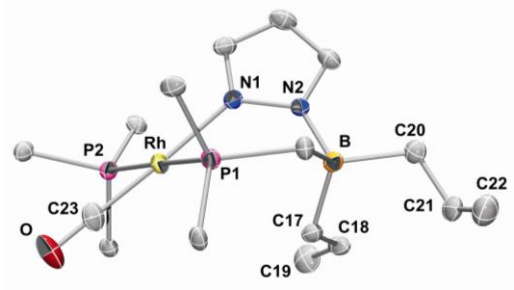


Figure 4. Molecular structure (ORTEP at 50 % level) of complex [Rh(κ^2-A_2BPN)(CO)PPh_3] (**11**). Hydrogen atoms have been removed and only the ipso carbon atoms of the phenyl groups are shown for clarity.

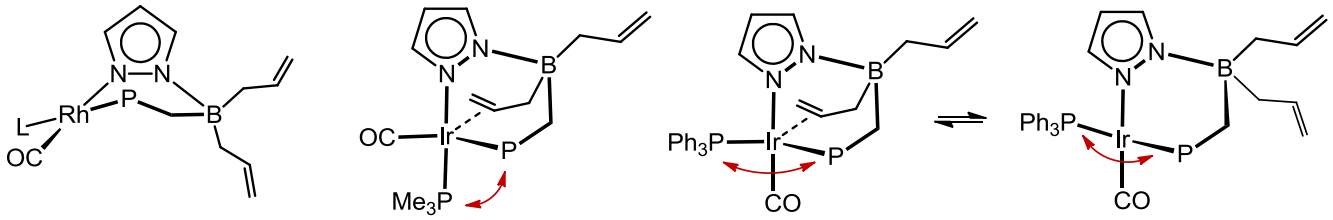
Table 3. Selected bond distances (Å) and angles (º) for complex **11**.

Rh–P1	2.3042(9)	P1–Rh–P2	176.88(3)
Rh–P2	2.3313(9)	N1–Rh–C23	175.42(12)
Rh–N1	2.096(3)	N1–Rh–P1	87.20(7)
Rh–C23	1.811(3)	P2–Rh–C23	87.41(10)
C18–C19	1.313(4)		
C21–C22	1.322(5)		

In the complex, the square-planar rhodium atom is bound to the nitrogen of the pyrazolyl and the phosphorus atoms of the scorpionate ligand, a carbonyl group, and the phosphorus atom from PPh_3. Both phosphane donors are placed mutually *trans*, while the pyrazolyl group remains *trans*

to the strongest π acceptor (CO) as observed for **8**. The six-membered metallacycle ($\overbrace{Rh-N-N-B-C-P}$) shows the expected puckered conformation, which minimizes the steric repulsion between the H^3 proton from the pyrazolyl and the phenyl groups of PPh_3. The terminal CO ligands in **9-12** were located *cis* to the phosphane arm of the ligand ($J_{C,P}$ = 12-17 Hz), while both allyl groups were found to be non-coordinated to rhodium (^{1}H NMR evidence), information that confirms that they are square-planar complexes with the ligand in the bidentate κ*N*,κ*P* coordination mode (Chart 1). Moreover, as found for **11** in the solid state, both phosphane groups in **11** and **12** showed a mutual *trans* disposition as deduced from the large J_{P^A,P^B} values of 297 and 309 Hz, respectively. Furthermore, the ν(CO) stretching (toluene/C_6D_6) of complexes **9-12** (1977, 1972, 1981, and 1977 cm^{-1}, respectively) reflects a weak influence of the basicity of the ligands (pyridine, NH_3, PMe_3, and PPh_3, respectively) on the electronic density of the metal.

Chart 1. Stereochemistry of complexes **9-14**.



The iridium counterparts [Ir(κ^3-A_2BPN)(CO)PR_3] (R = Ph, **13**; Me, **14**) were isolated as white solids in good yields by treating the bis-carbonyl complex **7** with the corresponding phosphanes. Both complexes displayed the typical features for pentacoordinated species (with an allyl bonded to iridium) in their ^{1}H and $^{13}C\{^1H\}$ NMR spectra at low temperature, while they showed a single

ν(CO) band in their solid state IR spectra. However, it was very surprising the divergence in values of this stretching, 2008 cm^{-1} for the PPh_3 complex **13** and 1920 cm^{-1} for the PMe_3 analogue **14**, a difference too large (88 cm^{-1}) to be explained by considering only the basicity of the phosphane ligands. Moreover, the J_{P^A,P^B} coupling constants in the $^{31}P\{^1H\}$ NMR spectra at low temperature (45 Hz for **13** and 12 Hz for **14**) suggest a coupling of the type $^2J_{Peq,Peq}$ for the former while $^2J_{Peq,Pax}$ for the later.[33, 34] Consequently, complexes **13** and **14** differ in their stereochemistry. Thus, the axial location of the CO ligand in **13** accounts for the high ν(CO) stretching, while the low frequency for **14** is consistent with the binding of this ligand in an equatorial position. In fact, theoretical studies on pentacoordinated d^8-complexes[35] predict a strong metal–ligand π-interaction in the equatorial position, so that lower ν(CO) frequencies can be expected for CO(eq) when compared to those for CO(ax) in similar complexes. Moreover, a survey of the reported ν(CO) frequencies in *TBPY*-5 iridium complexes of general formula $[IrR(CO)(olefin)P_2]$[36] and related ones containing *fac*-tripodal ligands of the type $[Ir(\kappa^3\text{-}L_3)(CO)(olefin)]$[37] agree with this consideration. Hence, we propose a *TBPY*-5-34_CO_{ax} configuration for **13** and *TBPY*-5-31_CO_{eq} for **14** (Chart 1) to account for the spectroscopic data.

Further support from this proposal comes from DFT studies carried out on the two possible *TBPY*-5 isomers of **13** and **14**. The *TBPY*-5-34_CO_{ax} configuration for $[Ir(\kappa^3\text{-}A_2BPN)(CO)PPh_3]$ (**13**) was found to be 4.8 kcal mol^{-1} more stable (ΔG) than the *TBPY*-5-31_CO_{eq}, which was found to be samewhat distorted due to the steric hindrance of the close phosphane groups (Figure 5). On the contrary, the configuration with the CO ligand in the equatorial plane was found to be 2.5 kcal mol^{-1} more stable than that with an axial carbonyl in $[Ir(\kappa^3\text{-}A_2BPN)(CO)PMe_3]$ (**14**). Moreover, the observed ν(CO) stretching frequencies fit nicely with the DFT calculated ones for the proposed structures (Table 4).

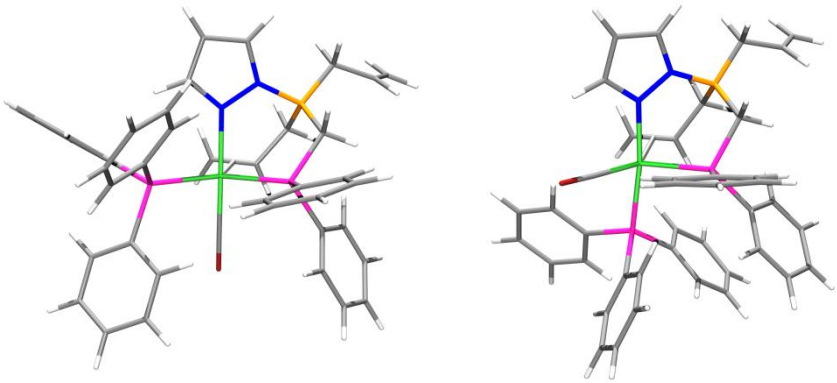


Figure 5. DFT optimized (b3-lyp, TZVP) geometries of [Ir(κ^3-A_2BPN)(CO)PPh_3] (**13**) in different configurations: *TBPY*-5-34_CO_{ax} isomer (left) and *TBPY*-5-31_CO_{eq} (right). Code color: Ir (green), N (blue), P (pink), B (orange) and O (red). P−Ir−P angles (º): 115.7 and 101.6 for *TBPY*-5-34_CO_{ax} and *TBPY*-5-31_CO_{eq}, respectively.

Table 4. Experimental and DFT calculated ν(CO) stretching frequencies for **13** and **14**.

[Ir(A_2BPN)(CO)PPh_3] (**13**)					[Ir(κ^3-A_2BPN)(CO)PMe_3] (**14**)			
solid	toluene	*TBPY*-5-34	*SP*-4	*TBPY*-5-31	solid	toluene	*TBPY*-5-34	*TBPY*-5-31
2008	2000, 1978	2004	1971	1938	1920	1928	1992	1935

Calculated DFT-frequencies have been corrected by a factor of 0.996.

For the *TBPY*-5 configurations, the better π-acceptor ligands are expected to be found at the equatorial positions. Complex [Ir(κ^3-A_2BPN)(CO)PMe_3] (**14**) follows this general trend, since the CO and C=C groups lie at equatorial sites. However, steric effects can reverse this trend, as shown for [Ir(κ^3-A_2BPN)(CO)PPh_3] (**13**), in which the CO ligand is located at the axial site to minimize the steric hindrance provided by the bulky phenyl groups. This effect is expected to

reach a maximum in a square-planar configuration (Chart 1), since both P-ligands separate from 120 to 180º. The NMR spectra at room temperature of **13** features equivalent free allyl groups and a coupling constant J_{P^A,P^B} = 194 Hz, close to the expected value for a square-planar *trans* stereochemistry (ca. 300 Hz). Therefore, a fast equilibrium between pentacoordinated (**13a**) and square-planar (**13b**) geometries (Chart 1) accounts for the NMR data at room temperature. Such equilibrium can be ascribed to the steric pressure exerted by the bulky PPh_3 ligand, which would facilitate the dissociation of the allyl arm. The VT-NMR spectroscopic data were analyzed with a Van 't Hoff plot, which provided the following thermodynamic parameters associated with the equilibrium **13a** ⇌ **13b**: $\Delta H° = +2.7 \pm 0.1$ kcal mol^{-1} and $\Delta S° = +9.3 \pm 0.5$ cal mol^{-1} K^{-1}, which results in $\Delta G°_{293.15} = -0.045$ kcal mol^{-1}. In good agreement, values of +3.28 kcal mol^{-1} ($\Delta H°$) and − 0.20 kcal mol^{-1} ($\Delta G°_{293.15}$) were obtained from DFT calculations (see supporting information).

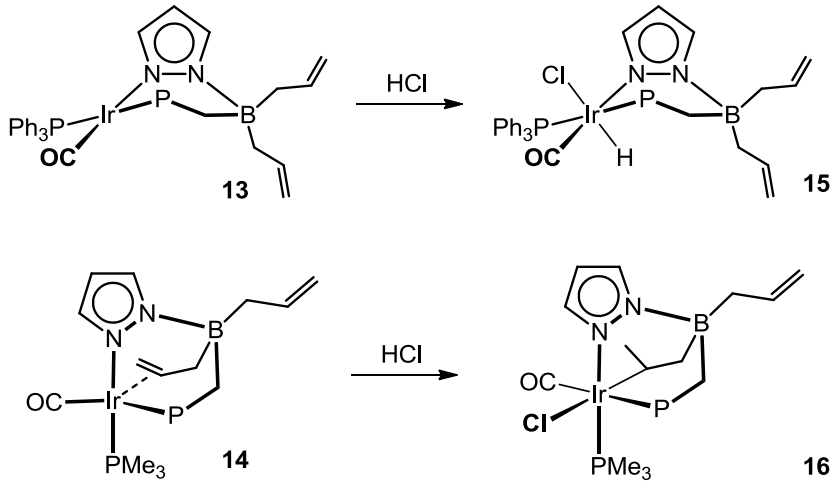
Moreover, both isomers were detected by IR spectroscopy in solution by two broad ν(CO) bands at 2000 (m) and 1978 (s) cm^{-1}, corresponding to the minor *TBPY*-5-34_CO_{ax} and the major square-planar isomers, respectively. Again, the frequency of the ν(CO) band for the *trans* square-planar isomer (*SP*-4) matchs satisfactorily with that found by DFT-calculations (Table 4).

On the other hand, complex [Ir(κ^3-A_2BPN)(CO)PMe_3] (**14**) was found to be the sole isomer with a *TBPY*-5-31_CO_{eq} configuration at room temperature, according to the NMR and IR spectra (see Experimental Section), and hence electronic issues dominates the stereochemistry in this case.

The different structure of the main isomers of **13** and **14** is largely responsible for the reactivity pattern observed in their reactions of protonation. Both complexes reacted readily with dry HCl in a 1:1 molar ratio affording the Ir(III) complexes [Ir(κ^2-A_2BPN)(CO)(Cl)(H)PPh_3] (**15**) and

$[\overline{Ir\{\kappa^3\text{-(allyl)}B(CH_2CHCH_3)(CH_2PPh_2)(Pz)\}}(Cl)(CO)PMe_3]$ (**16**) respectively, which were isolated as white solids in good yields (Scheme 5).

Scheme 5. Protonation reactions of **13** and **14** leading to complexes **15** and **16**.



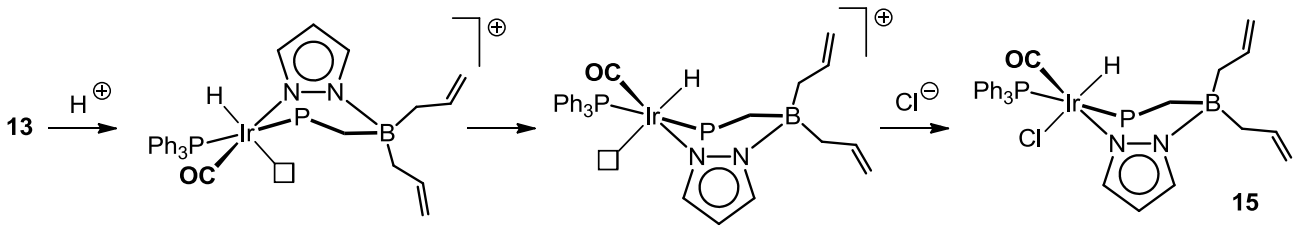
Characterization of complex **15** was achieved by a combination of the usual spectroscopic and analytical methods, which allowed to detect the phosphane groups mutually *trans*, and the hydrido (at $\delta = -14.47$) and CO ligands *cis* to both P atoms and mutually *cis* to each other (See Experimental Section). These data indicated that complex **15** is octahedral with the scorpionate ligand adopting a κ*P*,κ*N* coordination mode and the other four sites occupied by PPh_3, CO, the hydride and a chloride ligand, a chemical composition confirmed by MALDI spectrometry. Moreover, the shift to higher frequency of the ν(CO) band, at 2058 cm^{-1}, is in accordance with a decrease of the electron density on the metal or an Ir(III) oxidation state in **15**.

Protonation of PMe_3 complex **14** with hydrogen chloride followed a different profile and afforded the neutral complex **16**, which did not show hydrido signals in the ^1H NMR spectrum. Instead, there was a new set of resonances that corresponded to a σ-bonded '–CH(Me)CH_2B' moiety. The spectroscopic data collected for **16** unambiguously pointed out to the octahedral

structure shown in Scheme 5, which features a new hydrocarbyl arm σ-bonded to iridium (see Experimental Section for details). The ν(CO) band observed at 2061 cm^{-1} confirmed the oxidation of the metal to Ir(III) in the reaction. Complex **16** showed a static ^{1}H NMR spectrum with several features to be noticed. One of the allyl arms is uncoordinated, while a different set of resonances were deduced to correspond to the new hydrocarbyl fragment arising formally from a Markovnikov addition of the proton to the C=C bond of the other allyl fragment. The low coupling constant J_{P^A,P^B} = 22 Hz indicated a mutual *cis* disposition of both phosphanes. In addition, two well differentiated coupling constants were observed for the terminal CO ($J_{C,P}$ = 132 and 9 Hz) in the $^{13}C\{^{1}H\}$ NMR spectrum, which located CO *cis* to PMe_3 and *trans* to the phosphane arm due to the *fac* imposed coordination of the scorpionate ligand. In this way, NMR data of complex **16** reflect accurately the structure and stereochemistry also found for the closely related compound $[Ir\{(Hpz)B(CH_2CHCH_3)(CH_2PPh_2)(Pz)\}(Cl)(CO)PMe_3]Cl$.[18]

Structural comparison between the Ir(III) complexes **15** and **16** reveals information about the mechanisms following protonation of **13** and **14** with HCl. The square-planar isomer of **13** is favored for a direct protonation at the iridium centre (Figure 6, left) from the external face to give the square pyramidal intermediate with the coordination vacancy *trans* to the hydride ligand. Then, a fast inversion of the metallacycle places the hydride ligand inside the pocket of the complex allowing the coordination of the chloride again at the less hindered external face to give the product from a *trans* oxidative-addition of HCl (Scheme 6).[38]

Scheme 6. Proposed mechanism for the protonation of complex **13**.



Regarding the protonation of the PMe_3 compound **14**, a similar path would require the previous decoordination of the allyl arm, a dynamic process that was not observed by NMR. Nonetheless, complex **14** shows a HOMO mainly formed by the $d_{x^2-y^2}$ orbital of the iridium atom backdonating to both, the π* orbital of rhe C=C group and the π* orbital of the C=O ligand (Figure 6).

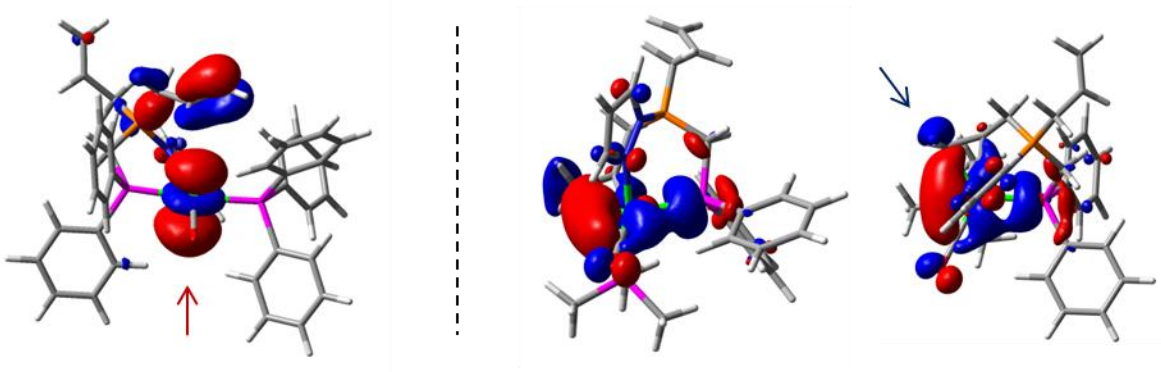
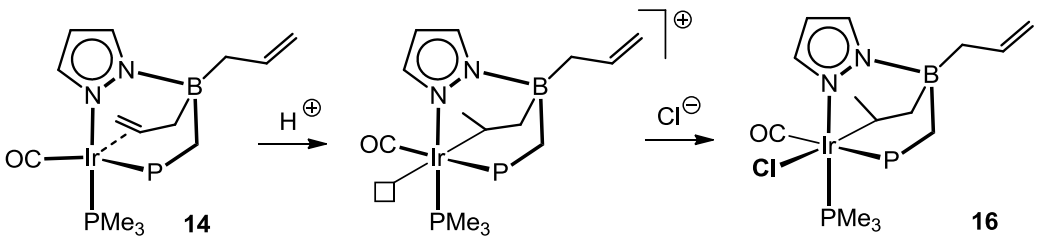


Figure 6. HOMO of *SQ*-4-[Ir(κ^2-A_2BPN)(CO)PPh_3] (**13**, left) and two views of the HOMO of *TBPY*-5-31_CO_{eq} -[Ir(κ^3-A_2BPN)(CO)PMe_3] (**14**). The red arrow indicates the external face of the complex while that in blue indicates the H_2C= carbon from the coordinated allyl arm.

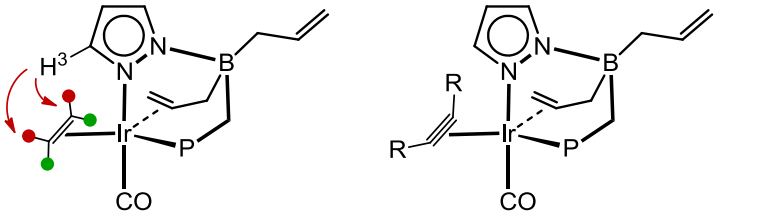
Consequently, a direct Markovnikov addition of the proton to the H_2C= carbon (marked with the blue arrow in Figure 6) seems to be the most probable initial step, although the protonation of the metal followed by insertion of the coplanar olefin into the Ir–H bond cannot be fully excluded. A further binding of the chloride at the coordination vacancy (*trans* to the alkyl group) would give the protonation product **16** (Scheme 7).

Scheme 7. Proposed mechanism for the protonation of complex **14**.



Related complexes of formula [Ir(κ^3-A_2BPN)(CO)L] (L= $H_2C{=}CH_2$, **17**; $MeO_2CC{\equiv}CCO_2Me$, **18**) were prepared by reacting the bis(carbonyl) compound **7** with ethylene or $MeO_2CC{\equiv}CCO_2Me$ (dmad), respectively (Chart 2). The ethylene complex **17** was found to be static at room temperature (*i.e.* no ethylene rotation around the Ir–C_2H_4 axis takes place on the NMR time scale), which agrees with a η^2-(*C*=*C*) coordination coplanar with the equatorial plane of a trigonal bipyramidal arrangement. As a matter of fact, ^{1}H-^{1}H NOESY experiments corroborated the ethylene ligand to be in the equatorial site of the *TBPY*-5 geometry, since the olefinic protons located upwards the equatorial plane (marked with red circles) gave a strong NOE effect with the H^3 proton of the pyrazolyl arm (Chart 2). Accordingly, the *v*(CO) stretching (C_6D_6) at 2013 cm^{-1} fits quite well to that expected for a carbonyl ligand at the axial site, as observed for complex **13**.[39] Since steric arguments can be ruled out because of the small size of the ethylene ligand, we can conclude that the *TBPY*-5-23_CO_{ax} configuration represents the most stable isomer on the basis of electronic issues as observed for related complexes.[39]

Chart 2. Stereochemistry of complexes **17**-**18**.



17 (*TBPY*-5-23_COax) **18 (*TBPY*-5-23_COax, R = CO_2Me)**

Concerning the complex [Ir(κ^3-A_2BPN)(CO)(dmad)] (**18**), in which ethylene is formally replaced by a dimethyl acetylenedicarboxylate ligand in **17**, spectroscopic data indicated both to be similar, as confirmed by a X-ray difraction study for **18**. Figure 7 shows the ORTEP representation of the molecule and Table 5 collects selected bond lengths and angles. The iridium center in **18** has a distorted trigonal bipyramidal environment with the pyrazolyl and the

CO ligands occupying the axial sites, while the equatorial plane is defined by the phosphane arm, the η^2-bonded allyl fragment and the π-bonded acetylene with its initial triple bond asymmetrically bound and lying in the equatorial plane.

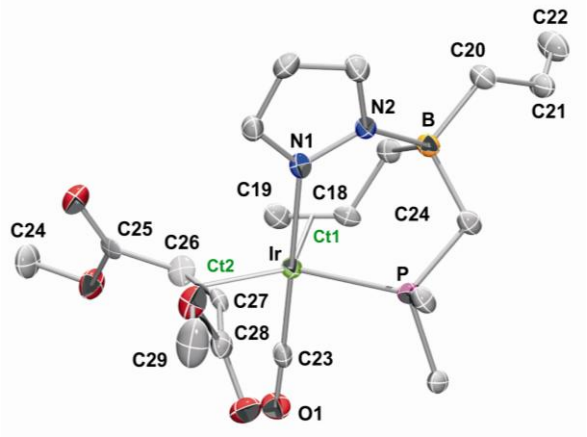


Figure 7. Molecular structure (ORTEP at 50 % level) of complex [Ir(κ^3-A_2BPN)(CO)(dmad)] (**18**). Hydrogen atoms and solvent of crystallization have been removed and only the ipso carbon atoms of the phenyl groups are shown for clarity.

The length of the acetylenic C26−C27 linkage expands from ca. 1.20 to 1.246(9) Å upon coordination, and possesses a *cis*-bent configuration associated with angles at the acetylenic carbons of C25−C26−C27 = 147.3(7)° and C26−C27−C28 = 147.7(7)°, comparable to those found in other dmad iridium complexes such as [Ir($COCH_2CMe_3$)(P(*p*-tolyl)$_3$)(dmad)][39] and [IrMe(CO)(PPh_3)$_2$(dmad)].[40]

Table 5. Selected bond distances (Å) and angles (º) for complex **18**.

Ir–P	2.3543(19)	N1–Ir−C23	179.2(3)
Ir−N1	2.097(6)	Ct1–Ir−Ct2	133.7(3)
Ir–Ct1	2.164(7)	P–Ir−Ct1	102.2 (2)

Ir–Ct2	2.019(7)	P–Ir−Ct2	123.5(2)
Ir–C23	1.856(7)	N1−Ir−Ct1	88.6(2)
C18–C19	1.383(9)	N1−Ir−Ct2	87.5(2)
C21–C22	1.326(10)	N1−Ir−P	86.9(2)
C26−C27	1.246(9)		

Ct1, and Ct2 represent the middle point of C18 and C19, and C27 and C28, respectively.

Spectroscopic data in solution for complex **18** (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR and IR spectra) are consistent with the pentacoordinated structure found in the solid state. In particular, the chemical shifts for the C_{sp} atoms of the coordinated alkyne (δ 91.5 and 86.9 ppm) compare well with those found in the structurally related complex [Ir(Tp^{Me2})(CO)(dmad)] (86.2 ppm),[41] while the quite different coupling constants $J_{C,P}$ of 7 and 40 Hz, respectively, reflect a C27−Ir−P angle (106.3(2)º) more closed than the related C26−Ir−P angle (140.4(2)º). The distinct coupling constants also confirm the lack of rotation of the acetylene around the Ir−C≡C axis, since otherwise similar averaged coupling constants would be observed. The better π-aceptor character of dmad respect to ethylene is clearly observable from blue-shift of the *ν*(CO) stretching in the IR spectra from 2013 (**17**) to 2040 cm^{-1} (**18**).

The isoelectronic isocyanide compound [Ir(κ^{3}-A$_2$BPN)(CN^{t}Bu)$_2$] (**5**) reacted with dmad in a different way keeping the isocyanide ligands to afford the complex [Ir(κ^{2}-A$_2$BPN)(CN^{t}Bu)$_2$(dmad)] (**19**) in good yields. Moreover, two inequivalent non-coordinated allylic arms were clearly observable in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **19**. In addition, the coordinated dmad showed coupling constants $J_{C,P}$ of 6 and 66 Hz, the later suggesting an angle C−Ir−P bigger than 140º, which is intermediate between octahedral (*OC*-6) and *TBPY*-5

geometries around iridium. Furthermore, the IR stretching frequencies of the isocyanide ligands in complex **19** are shifted ca. 116 cm^{-1} to higher frequencies relative to **5**.

Most probably, the different reactivity involving the addition of dmad to complexes [Ir(κ^3-A_2BPN)$(L)_2$] (L = CN^{t}Bu, **5**; CO, 7) could be ascribed to the stronger bonding of the isocyanide to iridium. In fact, complex [Ir(κ^3-A_2BPN)(CO)(dmad)] (**18**) is even formed in the presence of a carbon monoxide atmosphere.

Conclusion

Summarizing, we report the straightforward synthesis of a novel hybrid scorpionate ligand $[(allyl)_2B(CH_2PPh_2)(Pz)]^-$, which is equipped with different donors, including hard N and soft P and C atoms. We have disclosed the coordination behaviour of this ligand system, which has proven to be highly versatile in stabilizing rhodium and iridium metallic complexes in a number of different coordination modes. The Rh(I) complexes are square-planar, with the ligand coordinated in a bidentate $\kappa N,\kappa P$ fashion, although in a specific example (*i.e* the dinuclear carbonyl complex [{Rh(A_2BPN)(CO)}$_2$]) the ligand adopts the unexpected $\kappa N,\kappa P,\mu$-η^2-(*C*=*C*) coordination mode. A general behaviour observed for these rhodium complexes is the dynamic fast inversion of the six-membered metallacycle ($\overline{\text{Rh}-\text{N}-\text{N}-\text{B}-\text{C}-\text{P}}$).

The Ir(I) complexes described herein tend to adopt pentacoordinated *TBPY*-5 geometries with one allyl arm coordinated, *i.e.* the ligand adopts a $\kappa N,\kappa P,\eta^2$-(*C*=*C*) coordination mode. The lability of the Ir-allyl interaction and the flexibility of the ligand architecture lead to distinct behavior in solution. Thus, complexes with symmetrical or equivalent ancillary ligands like [Ir(κ^3-A_2BPN)(cod)] (**3**) and [Ir(κ^3-A_2BPN)$(L)_2$] (L = CN^{t}Bu, **5**; CO, **7**) adopt *TBPY*-5 structures at low temperature, but undergo a fast allyl-exchange based on a sequential coordination and de-

coordination of both allyl groups on heating. On the contrary, this allyl-exchange was not observed for complexes with two different ligands like [Ir(κ^3-A_2BPN)(CO)L] (L = PMe_3, **14**; CH_2=CH_2, **17;** $MeO_2CC{\equiv}CCO_2Me$, **18**), indicative of the electronic preference of the more π-accepting ligand for the equatorial position (CO in **14**, and the alkene/alkyne in **17** and **18**). An exception was [Ir(κ^3-A_2BPN)(CO)PPh_3] (**13**) for which steric effects dominate: i) placing the CO at the axial site and ii) producing a fast equilibrium with the less hindered square-planar isomer. The Ir(I)-*TBPY*-5 complexes having the CO ligand at the axial site led to, at a first glance, a '*counterintuitive*' high *ν*(CO) stretching frecuencies, even higher than those expected for square-planar configurations. Nonetheless, the weak π-back retrodonation from the metal to the CO ligand at the axial site accounts for the data, as proven from some DFT-calculations on selected examples, which result in a nice fitting between experimental and calculated *ν*(CO) frequencies.

The phosphane compounds [Ir(κ^3-A_2BPN)(CO)PR_3] are basic enough to be protonated by HCl, in a reaction drived by the stereochemistry of the starting complexes. Direct protonation of iridium occurs for the square-planar PPh_3 isomer (**13**), but a direct attack of the proton to the H_2C= carbon in *TBPY*-5 PMe_3 compound (**14**) seem to be the most probable pathways for the syntesis of [Ir(κ^2-A_2BPN)(CO)(Cl)(H)PPh_3] (**15**) and [Ir{κ^3-(allyl)B(CH_2CHCH_3)(CH_2PPh_2)(Pz)}(Cl)(CO)PMe_3] (**16**), respectively. The stronger bonding to iridium of isocyanides when compared to the carbonyl ligands is probably the origin of the different reactivity of complexes [Ir(κ^3-A_2BPN)$(L)_2$] (L = CN^tBu, **5**; CO, 7) towards dmad, which results in complexes [Ir(κ^2-A_2BPN)(CO)(dmad)] (**18**) and [Ir(κ^2-A_2BPN)$(CN^tBu)_2$(dmad)] (**19**), respectively.

Experimental Section.

Starting Materials and Physical Methods. All the operations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled under argon before use by standard methods.[42] Complexes $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$,[43] $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$[44] and [Ir(acac)(cod)],[45] and compounds $[Li(tmen)][CH_2PPh_2]$[46] and $[B(CH_2CH{=}CH_2)_3]$[47] were prepared according to literature procedures. All the other chemicals used in this work have been purchased from Aldrich Chemicals and used as received. Carbon, hydrogen and nitrogen analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer. FAB mass spectra were recorded in a VG Autospec double-focusing mass spectrometer. The ions were produced by the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. Electrospray mass spectra (ESI-MS) were recorded in methanol on a Bruker MicroTof-Q using sodium formiate as reference. MALDI-Tof mass spectra were obtained on a Bruker Microflex mass spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) or dithranol as matrix. NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers operating at 300.13 and 400.13 MHz, respectively, for ^1H. Chemical shifts are reported in ppm and referenced to $SiMe_4$, using the internal signal of the deuterated solvent as reference (^1H, ^{13}C) and external H_3PO_4 (^{31}P). IR spectra in solution were recorded with a Nicolet 550 spectrophotometer using NaCl cells, while IR spectra of solid samples were recorded with a Perkin-Elmer 100 FT-IR Spectrometer (4000-400 cm^{-1}) equipped with an ATR (Attenuated Total Reflectance).

Synthesis of the compounds: [Li(tmen)][A_2BPN] (1). Tris(allyl)borane (1.31 g, 1.70 mL, 9.80 mmol) was slowly added for 10 min *via* syringe to a bright yellow suspension of $[Li(tmen)][CH_2PPh_2]$ (3.17 g. 9.83 mmol) in toluene (15 mL) at room temperature. The color of

the mixture gradually discharged to form a milky suspension, which was stirred for 40 min. Addition of a solution of pyrazole (0.68 g, 9.80 mmol) in toluene (15 mL) to the reaction mixture *via* cannula resulted in the precipitation of a white solid, which was dissolved upon heating at 50^{o} C for one hour to give a clear colorless solution. The reaction mixture was evaporated to dryness under vacuum leaving a white oily residue that was washed with cold hexanes to afford a white solid, which was vacuum-dried. Yield: 3.07 g (65 %). Anal. Calcd (%) for $C_{28}H_{41}BLiN_4P$ (482.39): C 69.71, H 8.57, N 11.61; found: C 69.62, H 8.49, N 11.56. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 8.10 (s, 1H, pz), 7.34 (m, 4H, H^{o} PPh_2), 7.14 (m, 7H, H^{m+p} PPh_2 + pz), 6.41 (s, 1H, pz), 6.32 (m, 2H, =CH), 5.16 (m, 4H, =CH_2), 1.95 (d, J = 7.8 Hz, 4H, CH_2-allyl), 1.80 (s, 12H, CH_3-tmen), 1.72 (m, 6H, CH_2-tmen + CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): δ −13.6 (br s). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 ºC): δ 144.3 (=CH-allyl), 137.6 (pz), 133.5 (pz), 132.5 (d, $J_{C,P}$ = 15 Hz, C^{o} PPh_2), 128.4−127.3 (PPh_2), 109.8 (=CH_2-allyl), 102.7 (pz), 56.6 (CH_2-tmen), 45.6 (CH_3-tmen), 33.9 (br s, CH_2-allyl), 22.7 (br, CH_2P). ^{11}B{^{1}H} NMR (96 MHz, C_6D_6, 25 ºC): δ −5.89 (s). MS (MALDI-TOF^{+}): *m/z* (%):439.1 (40) [M−allyl−H]$^{+}$.

[Rh(κ^{2}-A$_2$BPN)(cod)] (2). Solid [{Rh(μ-Cl)(cod)}$_2$] (0.37 g, 0.75 mmol) was added to a solution of **1** (0.72 g, 1.49 mmol) in toluene (10 mL). The mixture was stirred for 30 min to give a yellow cloudy suspension, which was filtered *via* cannula through a pad of celite under argon to afford a clean yellow solution. Evaporation of the solvent under vacuum gave an oily material, which was triturated with pentane to yield a yellow solid that was subsequently filtered and then vacuum-dried. Yield: 0.77 g (91 %). Anal. Calcd (%) for $C_{30}H_{37}BN_2PRh$ (570.33): C 63.18, H 6.54, N 4.91; found: C 63.08, H 6.49, N 4.87. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.63 (m, 4H, H^{o} PPh_2), 7.59 (d, J = 1.7 Hz, 1H, pz), 7.26 (d, J = 1.8 Hz, 1H, pz), 7.07 (m, 6H, H^{m+p} PPh_2), 6.36 (m, 2H, =CH-allyl), 5.97 (t, J = 2.1 Hz, 1H, pz), 5.43 (dd, J = 17.0, 2.9 Hz, 2H) and 5.28

(dd, J = 10.1, 3.0 Hz, 2H) (=CH_2-allyl), 4.99 (m, 2H) and 3.40 (m, 2H) (=CH-cod), 2.93 (m, 2H, CH_2-cod), 2.39 (m, 4H, CH_2-allyl), 2.35 (m, 2H) and 1.79 (m, 4H) (CH_2-cod), 1.68 (d, $J_{H,P}$ = 14.3 Hz, 2H, CH_2P). ^{1}H NMR (400 MHz, d^8-toluene, − 80 ºC): *selected resonances* δ 7.44 (br, 1H, pz), 7.03(br s, 1H, pz), 6.81 (br m, 1H) and 6.05 (br m, 1H) (=CH-allyl), 5.88 (br, 1H, pz), 5.58 (br m, 2H) and 5.40 (br d, J = 9.9 Hz, 2H), 4.86 (br, 1H), 4.61 (br, 1H), 3.47 (br, 1H) and 2.80 (br, 1H) (=CH-cod). The remaining signals were found to be too much broad for unequivocal assignment. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 ºC): δ 29.1 (d, $J_{P,Rh}$ = 144 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 ºC): δ 143.3 (=CH-allyl), 138.5 (pz), 135.8 (d, $J_{C,P}$ = 39 Hz, C^i PPh_2), 134.9 (pz), 133.0 (d, $J_{C,P}$ = 10 Hz, C^o PPh_2), 129.2 (d, $J_{C,P}$ = 2 Hz, C^m PPh_2), 127.9 (C^p PPh_2), 110.6 (=CH_2-allyl), 104.5 (pz), 101.1 (dd, $J_{C,P}$ = 13 Hz, $J_{C,Rh}$ = 11 Hz) and 72.5 (d, $J_{C,Rh}$ = 12 Hz) (=CH-cod), 35.0 (br, CH_2-allyl), 32.4 and 28.8 (CH_2-cod), 19.8 (br, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%):529.2 (100) $[M-allyl]^+$.

[Ir(κ^3-A_2BPN)(cod)] (3). Solid [Ir(acac)(cod)] (0.20 g, 0.50 mmol) was added to a white suspension of **1** (0.24 g, 0.50 mmol) in diethyl ether (10 mL). The mixture was stirred for 30 min to form a suspension, which was filtered *via* cannula through a pad of celite under argon to afford a clean pale-orange solution. Evaporation of the solvent under vacuum gave an orange solid, which was recrystallized from dichloromethane-hexane. Yield: 0.27 g (81 %). Starting from [{Ir(μ-Cl)(cod)}$_2$]: To a white suspension of 1 (0.13 g, 0.28 mmol) in toluene (10 mL) solid [{Ir(μ-Cl)(cod)}$_2$ (0.09 g, 0.14 mmol) was added. The mixture was stirred for 1 hour and passed through a pad of cellite to remove the solid. The resulting solution was evaporated to dryness and the resulting orange oil was treated with cold hexanes to afford an orange solid, which was then filtered out and dried by vacuum. Yield: 0.12g (68%). Anal. Calcd (%) for $C_{30}H_{37}BIrN_2P$ (659.64): C 54.63, H 5.65, N 4.25; found: C 54.59, H 5.59, N 4.18. ^{1}H NMR (400 MHz, d_8-

toluene, 100 ºC): δ 7.59 (br s, 1H, pz), 7.41 (m, 4H, PPh_2), 7.08 (m, 6H, PPh_2), 6.70 (br s, 1H) and 5.82 (br s, 1H) (pz), 4.94 (br s, 2H, =CH-allyl), 4.49 (d, J = 9.5 Hz, 2H) and 3.74 (d, J = 14.3 Hz, 2H) (=CH_2-allyl), 3.4-2.4 (flat, 4H, =CH-cod), 2.12 (m, 4H, CH_2-cod), 1.72 (br m, 4H, CH_2-cod), 1.63 (br m, 4H, CH_2-allyl), 1.15 (J = 12.6 Hz, 2H, CH_2P). ^{1}H NMR (400 MHz, d_8-toluene, −80 ºC): δ 7.61 (br, 1H, pz), 7.27 (m, 2H, H^o PPh_2), 7.14 (m, 3H, H^{m+p} PPh_2), 7.08 (m, 2H, H^m PPh_2), 6.99 (m, 1H, H^p PPh_2), 6.95 (m, 2H, H^o PPh_2), 6.61 (br, 1H, pz), 6.45 (m, 1H, =CH-allyl), 5.87 (br, 1H, pz), 5.31 (d, J = 16.9 Hz, 1H) and 5.21 (d, J = 16.9 Hz, 1H) (=CH_2-allyl), 3.92 (d, J = 4.9 Hz, 1H, =CH_2-η^2-allyl), 3.70 (s, 1H, =CH-cod), 3,60 (m, 2H, =CH-cod + =CH-η^2-allyl), 2.91 (s, 1H, =CH-cod), 2.25 (m, 2H, CH_2-cod), 2.10 (m, 2H, =CH_2-η^2-allyl + CH_2-η^2-allyl), 1.97 (m, 2H, CH_2-allyl), 1.88 (m, 1H, CH_2-cod), 1.72 (m, 1H, CH_2-η^2-allyl, 1.64 (m, 1H, CH_2P), 1.60 (m, 2H, CH_2-cod + =CH-cod), 1.56 (m, 1H, CH_2-cod), 1.37 (m, 1H), 1.09 (m, 2H, CH_2 cod), 0.73 (m, 1H, CH_2P). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6, 25 ºC): δ 1.6. ^{13}C{^{1}H} NMR (100 MHz, d_8-toluene, –80 ºC): δ 143.6 (=CH-allyl), 142.6 (d, $J_{P,C}$ = 35 Hz) and 138.8 (d, $J_{P,C}$ = 40 Hz) (C^i PPh_2), 134.9 and 133.6 (pz), 133.4 (d, $J_{P,C}$ = 8 Hz, C^o PPh_2), 130.8 (d, $J_{P,C}$ = 9 Hz, C^m PPh_2), 129.6 (C^p PPh_2), 128.3 (m, C^{o+m+p} PPh_2), 110.9 (=CH_2-allyl), 104.5 (pz), 75.1, 70.7 and 64.9 (d, $J_{P,C}$ = 6 Hz) (=CH-cod), 63.1 (d, $J_{P,C}$ = 7 Hz, =CH-η^2-allyl), 58.8 (d, $J_{P,C}$ = 21 Hz, =CH-cod), 47.3 (d, $J_{P,C}$ = 8 Hz, =CH_2-η^2-allyl), 35.2 (br m, CH_2-allyl), 34.8 (br m, CH_2-η^2-allyl), 31.9, 31.4, 30.6, and 30.4 (CH_2-cod), 20.2 (br m, CH_2P). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$, 25 ºC): δ 0.55 (br s). MS (MALDI-TOF$^+$): *m/z* (%): 619.1 (100) [M−allyl]$^+$.

[Rh(κ^2-A_2BPN)(CN^{t}Bu)$_2$] (4). To a yellow solution of **2** (0.12 g, 0.21 mmol) in diethyl ether (10 mL), CN^{t}Bu (39 mg, 53 µl, 0.47 mmol) was slowly added *via* syringe and the resulting mixture was stirred for 30 min at room temperature. The solution was concentrated under vacuum to ca. 2 mL and a further addition of hexanes gave a light orange oil. This was

redissolved in diethyl ether and further addition of hexanes afforded a yellow powder which was isolated by filtration and then vacuum-dried. Yield: 0.11 g (86 %). Anal. Calcd (%) for $C_{32}H_{43}BN_4PRh$ (628.41): C 61.16, H 6.90, N 8.92; found: C 61.09, H 6.80, N 8.81. IR (toluene): ν(CN)/cm^{-1}: 2159 (s), 2114 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.91 (m, 4H, H^o PPh_2 + 1H ,pz), 7.80 (d, J = 1.8 Hz, 1H, pz), 7.09 (m, 6H, H^{m+p} PPh_2), 6.39 (m, 2H, =CH-allyl), 6.14 (t, J = 2.1 Hz, 1H, pz), 5.22 (dd, J = 16.8, 3.3 Hz, 2H) and 5.08 (dd, J = 12.6, 3.3 Hz, 2H) (=CH_2-allyl), 2.86 (m, 2H) and 2.13 (m, 2H) (CH_2-allyl), 1.58 (d, $J_{H,P}$ = 13.2 Hz, 2H, CH_2P), 1.99 (s, 9H) and 0.86 (s, 9H) (CN^{t}Bu). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): δ 28.2 (d, $J_{P,Rh}$ = 130 Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 ºC): δ 144.0 (=CH-allyl), 142.5 (pz), 139.9 (d, $J_{C,P}$ = 39 Hz, C^i PPh_2), 134.0 (pz), 133.5 (d, $J_{C,P}$ = 12 Hz, C^o PPh_2), 128.5 (d, $J_{C,P}$ = 2 Hz, C^m PPh_2), 127.7 (C^p PPh_2), 109.5 (=CH_2-allyl), 103.4 (pz), 55.9 and 55.6 (*C*Me_3), 35.1 (br, CH_2-allyl), 30.0 and 29.8 (C*Me*$_3$), 20.6 (br s, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%): 586.2 (10) [M−allyl]$^+$.

[Ir(κ^3-A_2BPN)(CN^{t}Bu)$_2$] (5). To a solution of **3** (0.10 g, 0.15 mmol) in dietyl ether (7 mL), CN^{t}Bu (39 µl, 0.34 mmol) was added dropwise *via* syringe. The colour of the solution changed rapidly to orange and 20 minutes after the reaction mixture was evaporated to dryness affording an orange oily residue. Addition of cold hexanes gave a white solid, which was filtered off and then dried under vacuum. Yield: 0.094 g (87%). Anal. Calcd (%) for $C_{32}H_{43}BIrN_4P$ (717.72): C 53.55, H 6.04, N 7.81; found: C 53.48, H 5.95, N 7.67. IR (toluene): ν(CN)/cm^{-1}: 2085 (s), 2043 (s). ^{1}H NMR (300 MHz, d_8-toluene, −50 ºC): δ 8.05 (s, 1H, pz), 7.74 (m, 2H) and 7.63 (m, 2H) (H^o PPh_2), 7.43 (s, 1H, pz), 7.00 (m, 6H, H^{m+p} PPh_2), 6.88 (m, 1H, =CH-allyl), 6.03 (s, 1H, pz), 5.53 (d, J = 17.0 Hz, 1H) and 5.45 (d, J = 12.0 Hz, 1H) (=CH_2-allyl), 3.26 (m, 1H, =CH_2), 3.10 (m, 1H, =CH) and (m, 1H, =CH_2 + 1H, CH_2) (η^2-allyl), 2.22 (m, 2H, CH_2-allyl + 1H, CH_2P), 1.31 (m, 1H, CH_2-η^2-allyl +1H, CH_2P), 1.01 (s, 9H) and 0.46 (s, 9H) (CN^{t}Bu). ^{31}P{^{1}H} NMR

(121 MHz, d_8-toluene, 25 ºC): δ 0.0. $^{13}C\{^1H\}$ NMR (75 MHz, d_8-toluene, −50 ºC): δ 144.6 (=CH-allyl), 142.7 (d, $J_{P,C}$ = 36 Hz) and 141.6 (d, $J_{C,P}$ = 25 Hz) (*C*N^{t}Bu), 141.1 (pz), 137.3 (d, $J_{C,P}$ = 43 Hz) and 137.3 (d, $J_{C,P}$ = 49 Hz) (C^i PPh_2), 133.7 (d, $J_{C,P}$ = 13 Hz, C^o PPh_2), 131.4 (pz), 131.1 (d, $J_{C,P}$ = 10 Hz, C^o PPh_2), 128 (m, C^{m+p} PPh_2), 110.4 (=CH_2-allyl), 105.0 (pz), 56.1 and 55.9 (*C*Me_3), 40.0 (d, $J_{P,C}$ = 6 Hz, =CH-η^2-allyl), 35.2 (br, CH_2-allyl), 30.9 (d, $J_{P,C}$ = 25 Hz, =CH_2-η^2-allyl) , 30.2 and 29.9 (C*Me*$_3$), 24.9 (br, CH_2-η^2-allyl), 21.4 (br, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%): 719.2 (5) $[M-H]^+$, 677.2 (100) $[M-allyl]^+$.

[Rh(κ^2-A_2BPN)$(CO)_2$] (6). A solution of **2** (0.02 g, 0.03 mmol) in d_8-toluene (0.4 mL) was shaken with carbon monoxide for 10 min to give a clear yellow solution. NMR monitoring of the sample showed a clean and quantitative conversion to **6**. IR (toluene): ν(CO)/cm^{-1}: 2077 (s), 2018 (s); (cyclohexane) ν(CO)/cm^{-1}: 2083 (s), 2020 (s). ^1H NMR (300 MHz, d_8-toluene, −50 ºC): δ 7.38 (dd, J = 6.7, 3.1 Hz, 2H, H^o PPh_2), 7.35 (d, J = 2.2 Hz, 1H, pz), 7.32 (dd, J = 6.2, 3.1 Hz, 2H, H^o PPh_2), 7.14 (br, 1H, pz), 6.90 (m, 6H, H^{m+p} PPh_2), 6.11 (ddd, J = 17.3, 14.9, 7.1 Hz, 2H, =CH-allyl), 5.74 (t, J = 2.2 Hz, 1H, pz), 5.00 (br, 2H) and 4.96 (m, 2H) (=CH_2-allyl), 2.28 (dd, J = 12.2, 7.7 Hz, 2H) and 1.78 (dd, J = 12.0, 8.4 Hz, 2H) (CH_2-allyl), 1.50 (d, $J_{H,P}$ = 14.9 Hz, 2H, CH_2P). $^{31}P\{^1H\}$ NMR (121 MHz, d_8-toluene, 25 ºC): δ 30.9 (d, $J_{P,Rh}$ = 120 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, d_8-toluene, −50 ºC): δ 189.0 (br) and 185.4 (d, $J_{C,Rh}$ = 66 Hz) (CO), 142.9 (=CH-allyl), 141.8 (pz), 135.8 (d, J = 45 Hz, C^i PPh_2), 134.7 (pz), 132.4 (d, J = 11 Hz, C^o PPh_2), 130.0 (d, J = 2 Hz, C^p PPh_2), 128.5 (d, J = 10 Hz, C^m PPh_2), 105.3 (=CH_2-allyl), 104.5 (pz), 34.3 (br, CH_2-allyl), 19.1 (br, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%): 517.3 (2) $[M-H]^+$.

[Ir(κ^3-A_2BPN)$(CO)_2$] (7) was prepared as described for **6** starting from a solution of **3** (0.03 g, 0.05 mmol) in CD_2Cl_2 (0.4 mL). IR (diethyl ether): ν(CO)/cm^{-1}: 2053 (s), 1986 (s); (cyclohexane) ν(CO)/cm^{-1}: 2053 (s), 1982 (s). ^1H NMR (300 MHz, CD_2Cl_2, −55 ºC): δ 7.57 (s,

1H, pz), 7.51-7.34 (m, 10H, PPh_2), 7.22 (s, 1H, pz), 6.04 (m, 1H, =CH-allyl), 5.96 (s, 1H, pz), 4.84 (d, J = 17.4 Hz, 1H) and 4.77 (d, J = 10.0 Hz, 1H) (=CH_2 allyl), 3.56 (m, 1H, =CH), 3.35 (m, 1H, =CH_2) and 1.96 (m, 1H, =CH_2) (η^2-allyl), 1.62 (m, 1H, CH_2P), 1.60 (m, 1H, CH_2-allyl), 1.57 (m, 1H, CH_2-η^2-allyl), 1.44 (m, 1H, CH_2-allyl), 1.35 (m, 1H, CH_2P), 0.20 (m, 1H, CH_2-η^2-allyl). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 ºC): δ −0.6. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −55 ºC): δ 184.6 (d, $J_{C,P}$ = 17 Hz) and 166.8 (d, $J_{C,P}$ = 5 Hz) (CO), 143.8 (pz), 143.1 (=CH-allyl), 137.6 (d, $J_{C,P}$ = 43 Hz) and 135.4 (d, $J_{C,P}$ = 43 Hz) (C^i PPh_2), 132.8 (pz), 132.4 (d, $J_{C,P}$ = 12 Hz) and 130.4 (d, $J_{C,P}$ = 11 Hz) (C^o PPh_2), 128.5 (m, C^{m+p} PPh_2), 110.7 (=CH_2-allyl), 106.1 (pz), 53.8 (br, =CH-η^2-allyl), 36.6 (d, $J_{C,P}$ = 16 Hz, =CH_2-η^2-allyl), 33.9 (br, CH_2-allyl), 24.4 (br, CH_2-η^2-allyl), 16.8 (br, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%): 607.1 (100) $[M]^+$.

[{Rh(A_2BPN)(CO)}$_2$] (8). A solution of **2** (0.15 g, 0.26 mmol) in diethyl ether (20 mL) was bubbled with carbon monoxide for 30 min to give an orange solution. The volume of the reaction mixture was reduced to ca. 5 mL under vacuum and then hexanes were added slowly to facilitate the precipitation of a bright yellow solid, which was filtered, washed with cold hexanes and then dried under vacuum. Yield: 0.11 g (85%). Anal. Calcd (%) for $C_{46}H_{50}B_2N_4O_2P_2Rh_2$ (908.31): C 56.36, H 5.14, N 5.72; found: C 56.28, H 5.02, N 5.68. IR (toluene): ν(CO)/cm^{-1}: 1995 (s). ^1H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.55 (m, 8H, H^o PPh_2), 7.32 (d, J = 2.3 Hz, 2H, pz), 6.91 (m, 12H, H^{m+p} PPh_2), 6.71 (d, J = 1.9 Hz, 2H, pz), 6.33 (dq, J = 17.2, 8.3 Hz, 2H, =CH-allyl), 5.60 (t, J = 2.5 Hz, 2H, pz), 5.24 (dd, J = 16.9, 2.9 Hz, 2H) and 5.13 (dd, J = 10.0, 2.8 Hz, 2H) (=CH_2-allyl), 4.98 (br, 2H, =CH-η^2-allyl + 2H, =CH_2-η^2-allyl), 4.77 (d, J = 11.0 Hz, 2H, CH_2-η^2-allyl), 4.45 (d, J = 5.6 Hz, 2H, =CH_2-η^2-allyl), 2.09 (t, J = 10.5 Hz, 2H, CH_2-η^2-allyl), 1.95 (m, 2H) and 1.84 (m, 2H) (CH_2-allyl), 1.72 (t, J = 15.2 Hz, 2H) and 1.57 (t, J = 13.7 Hz, 2H) (CH_2P). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 ºC): δ 30.6 (d, $J_{P\text{-}Rh}$ = 150 Hz). $^{13}C\{^1H\}$ NMR (75 MHz,

C_6D_6, 25 ºC): δ 192.1 (dd, $J_{C,Rh}$ = 71 Hz, $J_{C,P}$ = 14 Hz, CO), 142.1 (=CH-allyl), 138.7 (dd, $J_{C,P}$ = 46, 3 Hz, C^i PPh_2) 138.4 (pz), 135.0 (d, $J_{C,P}$ = 48 Hz, C^i PPh_2), 134.8 (pz), 133.5 (d, $J_{C,P}$ = 11 Hz) and 131.5 (d, $J_{C,P}$ = 11 Hz) (C^o PPh_2), 129.6 (d, $J_{C,P}$ = 2 Hz) and 129.2 (d, $J_{C,P}$ = 2 Hz) (C^p PPh_2), 128.3 (d, $J_{C,P}$ = 10 Hz) and 128.1 (d, $J_{C,P}$ = 10 Hz) (C^m PPh_2), 126.7 (dd, $J_{C,Rh}$ = 18 Hz, $J_{C,P}$ = 7 Hz, =CH-η^2-allyl), 111.4 (=CH_2-allyl), 105.2 (pz), 79.8 (dd, $J_{C,Rh}$ = 12 Hz, $J_{C,P}$ = 6 Hz, =CH_2-η^2-allyl), 45.7 (br s, CH_2-η^2-allyl), 31.7 (CH_2-allyl), 21.5 (br, CH_2P). MALDI(+): *m/z* 840 (M^+-allyl-CO).

[Rh(κ^2-A_2BPN)(CO)py] (9). To a yellow solution of **8** (0.12 g, 0.13 mmol) in dietyl ether (6 mL), pyridine (21 mg, 21 µL, 0.26 mmol) was added *via* syringe. After 1 hour of stirring a brown solid was formed, which was filtered out, washed with cold hexanes and vacuum-dried. Yield: 0.13 g (88%). Anal. Calcd (%) for $C_{28}H_{30}BN_3OPRh$ (569.25): C 59.08, H 5.31, N 7.38; found: C 59.13, H 5.28, N 7.25. IR (ATR): ν(CO)/cm^{-1}: 1967 (s); IR (toluene): ν(CO)/cm^{-1}: 1977 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 8.36 (s, 1H, py), 7.91 (m, 4H, H^o PPh_2), 7.76 (d, J = 3.0 Hz, 1H, pz), 7.27 (s, 1H, py), 7.14 (m, 6H, H^{m+p} PPh_2 + 1H, py), 6.71 (d, J = 3.0 Hz, 1H, pz), 6.38 (m, 2H, =CH-allyl), 6.35 (s, 1H, py), 6.32 (s, 1H, py), 5.87 (t, J = 3.0 Hz, 1H, pz), 5.36 (d, J = 17.1 Hz, 2H) and 5.25 (d, J = 9.9 Hz, 2H) (=CH_2-allyl), 2.85 (m, 2H) and 2.36 (m, 2H) (CH_2-allyl), 1.95 (d, $J_{H,P}$ = 15.0 Hz, 2H, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): δ 41.7 (d, $J_{P,Rh}$ = 145 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 ºC): δ 191.0 (dd, $J_{C,Rh}$ = 56 Hz, $J_{C,P}$ = 13 Hz, CO), 151.4 (py), 142.3 (=CH-allyl), 138.0 (pz), 137.4 (d, $J_{C,P}$ = 36 Hz, C^i PPh_2), 135.9 (py), 133.6 (pz), 131.7 (d, $J_{C,P}$ = 10 Hz, C^o PPh_2), 128.1 (py), 126.2–128.5 (C^{m+p} PPh_2 + py), 123.4 (py), 109.5 (=CH_2-allyl), 102.7 (pz), 33.8 (br, CH_2-allyl), 19.4 (br, CH_2P). MS (MALDI-TOF^+): *m/z* (%): 529.3 (90) $[M-allyl]^+$, 491.3 (70) $[M-py]^+$.

[Rh(κ^2-A$_2$BPN)(CO)NH$_3$] (10). A solution of **8** (0.02 g, 0.02 mmol) in C_6D_6 (0.5 mL) was shaken with gaseous ammonia leading to a colourless solution within five minutes. Inspection of the NMR spectra revealed a clean and quantitative conversion to complex **10**. IR (C_6D_6): ν(CO)/cm^{-1}: 1972 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.81 (m, 4H, H^o PPh$_2$), 7.71 (s, 1H, pz), 7.12 (m, 6H, H^{m+p} PPh$_2$), 6.81 (s, 1H, pz), 6.31 (m, 2H, =CH-allyl), 5.96 (s, 1H, pz), 5.22 (d, J = 15.6 Hz, 2H) and 5.14 (d, J = 10.2 Hz, 2H) (=CH$_2$-allyl), 2.73 (m, 2H) and 2.25 (m, 2H) (CH$_2$-allyl), 1.83 (d, $J_{H,P}$ = 15.0 Hz, 2H, CH$_2$P), −0.03 (free and coordinated NH$_3$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): δ 42.0 (d, $J_{P,Rh}$ = 150 Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 ºC): δ 192.3 (dd, $J_{C,Rh}$ = 74 Hz, $J_{C,P}$ = 17 Hz, CO), 143.6 (=CH-allyl), 138.7 (d, $J_{C,P}$ = 47 Hz, C^i PPh$_2$), 137.9 and 134.6 (pz), 132.7 (d, $J_{C,P}$ = 11 Hz, C^o PPh$_2$), 129.1 (d, $J_{C,P}$ = 2 Hz, C^p PPh$_2$), 127.9 (d, $J_{C,P}$ = 10 Hz, C^m PPh$_2$), 110.1 (=CH$_2$-allyl), 104.1 (pz), 34.9 (br, CH$_2$-allyl), 20.7 (br, CH$_2$P). MS (MALDI-TOF$^+$): *m/z* (%): 478.1 (80) [M−CO]$^+$.

[Rh(κ^2-A$_2$BPN)(CO)PPh$_3$] (11). To a solution of **8** (0.15 g, 0.17 mmol) in diethyl ether (7 mL), solid triphenylphosphane (0.089 g, 0.34 mmol) was added and the resulting yellow mixture was stirred for 30 min. Evaporation of the solvent under vacuum to ca. 2 ml and slow addition of hexanes (7 ml) caused the precipitation of an orange solid, which was filtered, washed with cold hexanes and then vacuum-dried. Yield: 0.13 g (88%). Anal. Calcd (%) for $C_{41}H_{40}BN_2OP_2Rh$ (752.44): C 65.45, H 5.36, N 3.72; found: C 65.15, H 5.15, N 3.92. IR (ATR): ν(CO)/cm^{-1}: 1976 (s), IR (toluene): ν(CO)/cm^{-1}: 1981 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.24 (m, 10H, H^o PPh$_2$ + PPh$_3$), 6.87 (s, 1H, pz), 6.69 (m, 15H, H^{m+p} PPh$_2$ + PPh$_3$), 6.29 (d, J = 3.0 Hz, 1H, pz), 6.08 (m, 2H, =CH-allyl), 5.17 (t, J = 2.2 Hz, 1H, pz), 5.02 (dd, J = 17.0, 3.0 Hz, 2H) and 4.86 (dd, J = 10.0, 3.0 Hz, 2H) (=CH$_2$-allyl), 2.13 (m, 4H, CH$_2$-allyl), 1.58 (d, $J_{H,P}$ = 11.7 Hz, 2H, CH$_2$P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): ABX spin system (X = ^{103}Rh) δ_{P^A} = 31.6, δ_{P^B} =

30.0, J_{P^A,P^B} = 297 Hz, $J_{P^A,Rh}$ = 122 Hz, $J_{P^B,Rh}$ = 125 Hz). $^{13}C\{^1H\}$ (75 MHz, C_6D_6, 25 ºC): δ 192.9 (ddd, $J_{C,Rh}$ = 71 Hz, $J_{P,C}$ = 16, 12 Hz, CO), 143.6 (=CH-allyl), 140.9 (pz), 137.2 (dd, $J_{C,P}$ = 40, 12 Hz, C^i PPh_3), 135.2 (pz), 134.4 (d, $J_{C,P}$ = 11 Hz, C^o PPh_2), 133.9 (dd, $J_{C,P}$ = 39, 9 Hz, C^i PPh_3), 132.6 (dd, $J_{C,P}$ = 10 Hz, C^o PPh_2), 130.3 (C^p PPh_3), 129.2 (C^p PPh_2), 128.5 (d, $J_{C,P}$ = 8 Hz, C^m PPh_3), 127.9 (d, $J_{C,P}$ = 8 Hz, C^m PPh_2), 110.8 (=CH_2-allyl), 104.1 (pz), 35.5 (br, CH_2-allyl), 19.4 (br, CH_2P). MS (MALDI-TOF$^+$): *m/z* (%): 711.0 (30) $[M-allyl]^+$.

[Rh(κ^2-A$_2$BPN)(CO)PMe$_3$] (12). A solution of **8** (0.10 g, 0.11 mmol) in toluene (10 mL) was treated with trimethylphosphane (16 mg, 23 μL, 0.22 mmol) *via* syringe and the resulting yellow mixture was stirred for 15 min. Evaporation of the solvent under vacuum to ca. 5 mL and slow addition of hexanes (10 mL) caused the precipitation of a yellow solid, which was filtered, washed with cold hexanes and then vacuum-dried. Yield: 0.10 g (95%). Anal. Calcd (%) for $C_{26}H_{34}BN_2OP_2Rh$ (566.23): C 55.15, H 6.05, N 4.95; found: C 55.05, H 6.10, N 4.92. IR (ATR): ν(CO)/cm^{-1}: 1970 (s), IR (toluene): ν(CO)/cm^{-1}: 1977 (s). ^1H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.71 (m, 4H, H^o PPh_2 + 1H, pz), 7.10 (m, 6H, H^{m+p} PPh_2 + 1H, pz), 6.32 (m, 2H, =CH-allyl), 5.93 (t, J = 2.1 Hz, 1H, pz), 5.39 (dd, J = 17.1, 3.0 Hz, 2H) and 5.24 (dd, J = 9.9, 3.0 Hz, 2H) (=CH_2-allyl), 2.62 (m, 2H,) and 2.30 (m, 2H) (CH_2-allyl), 1.85 (d, $J_{H,P}$ = 13.2 Hz, 2H, CH_2P), 1.00 (d, $J_{H,P}$ = 10.5 Hz, 9H, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 ºC): δ 28.8 (dd, $J_{P,P}$ = 309 Hz, $J_{P,Rh}$ = 116 Hz), −12.6 (dd, $J_{P,P}$ = 309 Hz, $J_{P,Rh}$ = 121 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 ºC): δ 193.1 (ddd, $J_{C,Rh}$ = 69 Hz, $J_{C,P}$ = 15, 12 Hz, CO), 143.5 (=CH-allyl), 140.0 (pz), 137.1 (d, $J_{C,P}$ = 41 Hz, C^i PPh_2), 134.7 (pz), 132.4 (d, $J_{C,P}$ = 11 Hz, C^o PPh_2), 129.1 (C^p PPh_2), 127.9 (d, $J_{C,P}$ = 9 Hz, C^m PPh_2), 110.1 (=CH_2-allyl), 104.1 (pz), 34.6 (br, CH_2-allyl), 19.8 (br, CH_2P), 17.0 (d, $J_{C,P}$ = 26 Hz, PMe_3). MS (MALDI-TOF$^+$): *m/z* (%): 525.2 (85) $[M-allyl]^+$, 539.2 (20) $[M-CO]^+$.

[Ir(κ^3-A$_2$BPN)(CO)PPh$_3$] (13). A suspension of **3** (0.44 g, 0.66 mmol) in diethyl ether (20 mL) was bubbled with carbon monoxide to give a bright yellow solution in 30 min. The addition of triphenylphosphane (0.17 g, 0.66 mmol) to this solution caused the discharge of the color within seconds. After 20 minutes, evaporation of the solvent under vacuum gave an orange oil, that was washed with cold hexanes to yield a pale yellow solid, which was filtered and then vacuum-dried. Yield: 0.49 g (88%). Anal. Calcd (%) for $C_{41}H_{40}BIrN_2OP_2$ (841.76): C 58.50, H 4.79, N 3.33; found: C 58.74, H 4.93, N 3.29. IR (ATR): ν(CO)/cm^{-1}: 2008 (s), IR (toluene): ν(CO)/cm^{-1}: 2000 (m), 1978 (s). ^{1}H NMR (300 MHz, d$_8$-toluene, 25 ºC): δ 7.61 (m, 10H, H^o PPh_2 + PPh_3), 7.54 (d, J = 2.0 Hz, 1H, pz), 7.06 (m, 15H, H^{m+p} PPh_2 + PPh_3), 6.77 (d, J = 1.8 Hz, 1H, pz), 5.92 (m, 2H, =CH-allyl), 5.53 (d, J = 2.1 Hz, 1H, pz), 4.82 (d, J = 9.9 Hz, 2H) and 4.67 (d, J = 15.9 Hz, 2H) (=CH_2-allyl), 2.31 (m, 2H) and 2.05 (m, 2H) (CH_2-allyl), 2.02 (d, $^2J_{H,P}$ = 12.0 Hz, 2H, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, d$_8$-toluene, 25 ºC): AB spin system δ_{P^A} = 17.7, δ_{P^B} = 11.1, J_{P^A,P^B} = 194 Hz).^{1}H NMR (300 MHz, d$_8$-toluene, −80 ºC): δ 7.69 (br, 1H, pz), 7.32 (m, 4H, H^o PPh_2), 6.93 (m, 6H, H^{m+p} PPh_2 + 15H, PPh_3), 6.78 (m, 1H, =CH-allyl), 6.69 (br, 1H, pz), 5.56 (d, J = 15.9 Hz, 1H) and 5.50 (d, J = 12.5 Hz, 1H) (=CH_2-allyl), 5.52 (s, 1H, pz), 3.79 (br, 1H, =CH-η^2-allyl), 3.28 (br, 1H, =CH_2-η^2-allyl), 2.32 (br, 1H) and 2.22 (br, 1H) (CH_2-allyl), 2.14 (br, 1H, =CH-η^2-allyl), 0,98 (m, 1H, CH_2-η^2-allyl + 2H, CH_2P), 0.78 (br, 1H, CH_2-η^2-allyl). ^{31}P{^{1}H} NMR (121 MHz, d$_8$-toluene, −70 ºC): AB spin system δ_{P^A} = 3.1, δ_{P^B} = −8.3, J_{P^A,P^B} = 45 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC) δ 175.7 (t, $J_{C,P}$ = 10 Hz, CO), 142.5 (pz), 142.4 (d, $J_{C,P}$ = 7 Hz, =CH-allyl), 138.0 (d, $J_{C,P}$ = 41 Hz, C^i PPh_3), 134.3 (pz), 134.2 (d, $J_{C,P}$ = 12 Hz, C^o PPh_3), 133.7 (dd, $J_{C,P}$ = 43 Hz, C^i PPh_2), 132.2 (d, $J_{C,P}$ = 11 Hz, C^o PPh_2), 130.0 (d, $J_{C,P}$ = 2 Hz, C^p PPh_3), 128.9 (d, $J_{C,P}$ = 2 Hz, C^p PPh_2), 128.2 (d, $J_{C,P}$ = 10 Hz, C^m PPh_3), 127.7 (d, $J_{C,P}$ = 10

Hz, C^m PPh_2), 115.0 (=CH_2-allyl), 104.2 (pz), 29.7 (br, CH_2-allyl), 28.0 (br, CH_2P). MS (MALDI-TOF^+): *m/z* (%): 801.1 (100) $[M-allyl]^+$.

[Ir(κ^3-A_2BPN)(CO)PMe_3] (14). A solution of **7** (0.33 g, 0.50 mmol) in diethyl ether (20 mL) was bubbled with carbon monoxide giving in 30 min a bright yellow solution. The addition of trimethylphosphane (37 mg, 51 μL, 0.50 mmol) to this solution caused the discharge of the color to form a white solution within 1 min and then a white solid began to crystallize out after 5 min of stirring. The solid was collected by filtration, washed with cold hexanes and then vacuum-dried. Yield: 0.27 g (98%). Anal. Calcd (%) for $C_{26}H_{34}BIrN_2OP_2$ (655.55): C 47.64, H 5.23, N 4.27; found: C 47.35, H 5.19, N 4.11. IR (ATR): ν(CO)/cm^{-1}: 1920 (s), IR (toluene): ν(CO)/cm^{-1}: 1928 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.96 (d, J = 2.0 Hz, 1H, pz), 7.93 (m, 2H) and 7.45 (m, 2H) ($H^{o+o'}$ PPh_2), 7.43 (d, J = 2.1 Hz, 1H, pz), 7.23 (td, J = 6.7, 1.1 Hz, 2H, H^m PPh_2), 7.05 (td, J = 7.0, 1.1 Hz, 1H, H^p PPh_2), 7.00 (m, 3H, $H^{m'+p'}$ PPh_2), 6.63 (m, 1H, =CH-allyl), 5.89 (t, J = 2.1 Hz, 1H, pz), 5.36 (dd, J = 16.8, 3.0 Hz, 1H) and 5.28 (dd, J = 10.2, 3.0 Hz, 1H) (=CH_2-allyl), 2.93 (m, 1H, =CH-η^2-allyl), 2.82 (m, 1H) and 2.47 (m, 1H) (=CH_2-η^2-allyl), 2.17 (m, 1H, CH_2-η^2-allyl), 2.04 (m, 2H, CH_2-allyl + 1H, CH_2P), 1.34 (t, $J_{H,H}$ = $J_{H,P}$ = 13.6 Hz, 1H, CH_2P), 1.10 (m, 1H, CH_2-η^2-allyl), 0.58 (d, $J_{H,P}$ = 10.5 Hz, 9H, PMe_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 ºC): δ 3.3 (d, $J_{P,P}$ = 12 Hz), −42.2 (d, $J_{P,P}$ = 12 Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 ºC) δ 190.7 (dd, $J_{C,P}$ = 17 Hz, 14 Hz, CO), 143.7 (=CH-allyl), 143.3 (pz), 138.2 (d, $J_{C,P}$ = 36 Hz, C^i PPh_2), 133.9 (d, $J_{C,P}$ = 13 Hz, C^o PPh_2), 131.3 (pz), 131.1 (d, $J_{C,P}$ = 5 Hz, C^p PPh_2), 128.0 (m, C^m PPh_2), 110.5 (=CH_2-allyl), 105.5 (pz), 49.8 (d, $J_{C,P}$ = 8 Hz, =CH-η^2-allyl), 35.5 (d, $J_{C,P}$ = 20 Hz, =CH_2-η^2-allyl), 34.4 (br, CH_2-allyl), 25.7 (br, CH_2-η^2-allyl), 22.7 (br, CH_2P), 15.4 (d, $J_{C,P}$ = 41 Hz, PMe_3). ^{11}B{^{1}H} NMR (96 MHz, C_6D_6, 25 ºC) δ −1.15 (br s). MS (MALDI-TOF^+): *m/z* (%): 615.1 (40) $[M-allyl]^+$.

[Ir(κ^2-A$_2$BPN)(CO)(Cl)(H)PPh$_3$] (15). A suspension of **13** (0.10 g, 0.12 mmol) in diethyl ether (5 mL) was treated with a diethyl ether solution of HCl (176 μL, 0.67 M, 0.12 mmol), that produced the immediate formation of a yellowish precipitate. The solution was stirred for 30 minutes, and then the solvent was removed to yield a pale yellow solid, that was filtered out and dried by vacuum. Yield: 0.10 g (98%). Anal. Calcd (%) for $C_{41}H_{41}BClIrN_2OP_2$ (878.22): C 56.07, H 4.71, N 3.19; found: C 55.51, H 4.67, N 3.00. IR ($CDCl_3$): ν(Ir–H)/cm^{-1}: 2253(w), ν(CO)/cm^{-1}: 2058 (s). ^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ 7.84 (m, 2H, H^o PPh$_2$), 7.63 (m, 6H, H^o PPh$_3$), 7.45 (d, J = 1.9 Hz, 2H, pz), 7.37 (m, 2H, H$^{o'}$ PPh$_2$), 6.96 (m, 3H, H^{m+p} PPh$_2$ + 9H, H^{m+p} PPh$_3$), 6.86 (m, 3H, H$^{m'+p'}$ PPh$_2$), 6.06 (m, 1H) and 5.82 (m, 1H) (=CH-allyl), 5.66 (t, J = 1.8 Hz, 1H, pz), 5.01 (m, 2H) and 4.87 (m, 2H) (=CH$_2$-allyl), 2.52 (m, 1H, CH$_2$-allyl), 2.09 (dd, J = 12.6, 6.7 Hz, 1H, CH$_2$P), 1.94 (m, 2H CH$_2$-allyl + 1H, CH$_2$P), 1.53 (t, J = 9.8 Hz, 1H, CH$_2$-allyl), –14.47 (t, $J_{H,P}$ = 12.0 Hz, 1H, Ir–H). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25ºC): AB spin system δ_{P^A} = –1.9, δ_{P^B} = –6.7, J_{P^A,P^B} = 330 Hz). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ºC): δ 167.1 (dd, $J_{C,P}$ = 8, 7 Hz, CO), 144.1 (pz), 143.0 and 142.7 (=CH-allyl), 137.7 (pz), 137.2 (d, $J_{C,P}$ = 43 Hz, C^i PPh$_2$), 135.0 (d, $J_{C,P}$ = 10 Hz, C^o PPh$_3$), 133.9 (dd, $J_{C,P}$ = 9,2 Hz) and 131.9 (d, $J_{C,P}$ = 9 Hz) (C^o PPh$_2$), 131.2 (d, $J_{C,P}$ = 2 Hz, C^p PPh$_3$), 130.5 and 130.2 (d, $J_{C,P}$ = 2 Hz) (C^p PPh$_2$), 130.0 (d, $J_{C,P}$ = 49 Hz, C^i PPh$_3$), 128.7 (d, $J_{C,P}$ = 10 Hz, C^m PPh$_3$), 127.8 (m, C^m PPh$_2$), 111.1 and 110.3 (=CH$_2$-allyl), 105.3 (pz), 34.9 (br) and 34.3 (br) (CH$_2$-allyl), 14.4 (br, CH$_2$P). MS (MALDI-TOF$^+$): *m/z* (%): 837.2 (60) [M−allyl]$^+$.

[Ir{κ^3-(allyl)B(CH$_2$CHCH$_3$)(CH$_2$PPh$_2$)(Pz)}(Cl)(CO)PMe$_3$] (16). A diethyl ether solution of HCl (0.2 mL, 0.67 M, 0.15 mmol) was added *via* microsyringe to a suspension of **14** (0.10 g, 0.15 mmol) in diethyl ether (5 mL), affording instantly a yellowish precipitate. After 20 minutes of stirring, the supernatant liquid was removed *via cannula* and the solid was washed with cold

diethyl ether (5 mL), and then dried under vacuum. Yield: 0.1 g (94%). Anal. Calcd (%) for $C_{26}H_{35}BClIrN_2OP_2$ (692.01): C 45.13, H 5.10, N 4.05; found: C 44.67, H 5.23, N 3.92. IR ($CDCl_3$): ν(CO)/cm^{-1}: 2061 (s). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 8.17 (d, J = 2.3 Hz, 1H, pz), 7.57 (m, 4H, H$^{o+o'}$ PPh_2), 7.39 (m, 3H, H^{m+p} PPh_2), 7.33 (m, 1H, pz), 7.15 (m, 3H, H$^{m'+p'}$ PPh_2), 6.05 (m, 1H, pz), 6.04 (m, 1H, =CH-allyl), 4.83 (dd, J = 15.0, 3.0 Hz, 1H) and 4.75 (dd, J = 9.0, 3.0 Hz, 1H) (=CH_2-allyl), 2.75 (m, 1H, Ir–C*H*(CH_3)CH_2), 1.69 (d, J = 6.0 Hz, 3H, Ir–CH(C*H*$_3$)CH_2), 1.62 (m, 1H, CH_2P), 1.56 (m, 2H, CH_2-allyl), 1.34 (d, $J_{H,P}$ = 12.0 Hz, 9H, PMe_3), 1.03 (m, 1H, CH_2P), 0.60 (m, 1H) and 0.11 (m, 1H) (Ir–CH(CH_3)CH_2). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ –12.8 (d, $J_{P,P}$ = 22 Hz), – 46.4 (d, $J_{P,P}$ = 22 Hz). ^{13}C{^{1}H} NMR (75 MHz $CDCl_3$, 25 ºC): δ 168.1 (dd, $J_{C\text{-}P}$ = 132, 9 Hz, CO), 143.3 (=CH-allyl), 142.2 (d, $J_{C,P}$ = 2 Hz, pz), 135.4 (dd, $J_{C,P}$ = 40, 3 Hz, C^i PPh_2), 134.1 (d, $J_{C,P}$ = 9 Hz, C^o PPh_2), 133.5 (d, $J_{C,P}$ = 4 Hz, pz), 132.7 (d, $J_{C,P}$ = 9 Hz, C$^{o'}$ PPh_2), 131.5 (d, $J_{C,P}$ = 55 Hz, C$^{i'}$ PPh_2), 130.3 (d, $J_{C,P}$ = 2 Hz) and 129.8 (d, $J_{C,P}$ = 2 Hz) (C$^{p+p'}$ PPh_2), 128.5 (d, $J_{C,P}$ = 9 Hz) and 127.2 (d, $J_{C,P}$ = 10 Hz) (C$^{m+m'}$ PPh_2), 110.2 (=CH_2-allyl), 105.3 (pz), 37.2 (Ir–CH(*C*H_3)CH_2), 37.0 (br, Ir–CH(CH_3)*C*H_2), 33.2 (br, CH_2-allyl), 16.4 (br, CH_2P), 15.2 (Ir–*C*H(CH_3)CH_2), 14.6 (d, $J_{C,P}$ = 41 Hz, PMe_3). MS (MALDI-TOF$^+$): *m/z* (%): 614.9 (20) [M−PMe_3]$^+$, 586.9 (5) [M−PMe_3−CO]$^+$.

[Ir(κ^3-A_2BPN)(CO)(H_2C=CH_2)] (17). Carbon monoxide was bubled through an orange solution of **3** (0.10 g, 0.16 mmol) in diethyl ether (12 mL) for 20 minutes to yield a transparent yellow solution. Then, the solution was exposed to an ethylene atmosphere for 26 hours. The solvent was then evaporated and the oily residue was washed with hexanes to yield a pale yellow solid. It was filtered out and dried under vacuum. Yield: 0.070 g (69%). Anal. Calcd (%) for $C_{25}H_{29}BIrN_2OP$ (607.52): C 49.43, H 4.81, N 4.61; found: C 49.52, H 4.76, N 4.51. IR (ATR): ν(CO)/cm^{-1}: 2005 (s). IR (C_6D_6): ν(CO)/cm^{-1}: 2013 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ

7.57 (m, 2H, H^{o} PPh_2), 7.47 (d, J = 2.0 Hz, 1H, pz), 7.07 (m, 2H, H^{m} PPh_2), 6.94 (1H, H^{p} PPh_2 + 5H, $H^{o'+m'+p'}$ PPh_2), 6.40 (m, 1H, =CH-allyl), 6.28 (d, J = 2.0 Hz, 1H, pz), 5.69 (t, J = 2.0 Hz, 1H, pz), 5.24 (d, J = 13.8 Hz, 1H) and 5.16 (d, J = 10.2 Hz, 1H) (=CH_2-allyl), 4.30 (m, 1H, =CH-η^2-allyl), 3.67 (m, 1H, =CH_2-η^2-allyl), 2.73 (m, 2H) and 2.47 (m, 1H) (η^2-H_2C=CH_2), 2.33 (dd, J = 12.5, 4.5 Hz, 1H, =CH_2-η^2-allyl), 2.07 (t, $J_{H,H}$ = 9 Hz, 1H, CH_2-η^2-allyl), 1.91 (m, 2H, CH_2-allyl), 1.69 (t, $J_{H,P}$ = 14.6 Hz, 1H, CH_2P), 1.33 (m, 1H, η^2-H_2C=CH_2), 1.20 (t, $J_{H,P}$ = 14.6 Hz, 1H, CH_2P), 0.86 (m, 1H, CH_2-η^2-allyl). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 ºC): δ – 7.0 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 ºC): δ 166.0 (d, $J_{C,P}$ = 6 Hz, CO), 143.1 (=CH-allyl), 138.4 (d, $J_{C,P}$ = 44 Hz, C^{i} PPh_2), 138.0 (d, $J_{C,P}$ = 43 Hz, $C^{i'}$ PPh_2), 134.2 (d, $J_{C,P}$ = 8 Hz, pz), 132.0 (pz), 131.6 (m, $C^{o+o'}$ PPh_2), 129.7 (C^{p} PPh_2), 129.0 ($C^{m+m'+p'}$ PPh_2), 111.4 (=CH_2-allyl), 104.8 (pz), 68.7 (d, $J_{C,P}$ = 4 Hz, =CH-η^2-allyl), 41.2 (d, $J_{C,P}$ = 9 Hz, =CH_2-η^2-allyl), 34.6 (br, CH_2-allyl), 33.8 (d, $J_{C,P}$ = 6 Hz) and 28.0 (η^2-H_2C=CH_2), 25.6 (br, CH_2-η^2-allyl), 18.4 (br, CH_2P). MS (MALDI-TOF^+): *m/z* (%): 539.2 (40) $[M–allyl–CO/C_2H_4]^+$.

[Ir(κ^3-A_2BPN)(CO)(dmad)] (18). Solid [Ir(acac)(cod)] (0.084 g, 0.21 mmol) was added to a suspensión of **1** (0.101 g, 0.21 mmol) in diethyl ether. After 30 minutes of stirring, the suspension was filtered through a pad of celite, and then carbon monoxide was bubbled to give a bright yellow solution. Then $MeO_2CC{\equiv}CCO_2Me$ (51 μl, 0.42 mmol) was added *via* microsyringe. The resulting light yellow solution was stirred for 20 more minutes. Concentration to ca. 0.5 mL and addition of hexanes yielded an orange solid, which was filtered out and dried under vacuum. Yield: 0.06 g (41%). Anal. Calcd (%) for $C_{29}H_{31}BIrN_2O_5P$ (721.57): C 48.27, H 4.33, N 3.88; found: C 48.05, H 4.11, N 3.76. IR (ATR): ν(CO)/cm^{-1}: 2032 (s), ν(C=O)/cm^{-1}: 1699 (s). IR (toluene): ν(CO)/cm^{-1}: 2040 (s), ν(C=O)/cm^{-1}: 1709 (s). ^1H NMR (300 MHz, C_6D_6, 25 ºC): δ 7.82 (d, J = 2.4 Hz, 1H, pz), 7.74 (m, 2H, H^{o} PPh_2), 7.34 (d, J = 2.3 Hz, 1H, pz), 7.10

(m, 2H, H^m PPh_2), 7.01 (m, 1H, H^p PPh_2), 6.83 (m, 5H, $H^{o'+m'+p'}$ PPh_2), 6.24 (m, 1H, =CH-allyl), 5.85 (t, J = 2.4 Hz, 1H, pz), 5.12 (m, 1H) and 5.08 (m, 1H) (=CH_2-allyl), 4.36 (m, 1H, =CH-η^2-allyl), 4.26 (m, 1H, =CH_2-η^2-allyl), 3.67 (s, 3H) and 3.45 (s, 3H) (OCH_3), 3.30 (m, 1H, =CH_2-η^2-allyl), 2.06 (m, 1H, CH_2-η^2-allyl), 1.91 (t, $J_{H,P}$ = 14.1 Hz, 1H, CH_2P), 1.70 (m, 2H, CH_2-allyl), 0.85 (m, 1H, CH_2P), 0.60 (m, 1H, CH_2-η^2-allyl). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 25 ºC): δ – 3.1 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 ºC): δ 162.7 (d, $J_{C,P}$ = 5 Hz, C=O), 162.1 (d, $J_{C,P}$ = 6 Hz, CO), 162.0 (d, $J_{C,P}$ = 8 Hz, C=O), 142.6 (=CH-allyl), 138.0 (d, $J_{C,P}$ = 50 Hz,C^i PPh_2), 136.5 and 135.3 (pz), 135.1 (d, J_{C-P} = 48 Hz, C^i PPh_2), 131.7 (d, J_{C-P} = 11 Hz, $C^{o+o'}$ PPh_2), 130.3 (d, J_{C-P} = 2 Hz) and 129.7 (d, J_{C-P} = 2 Hz) (C^p PPh_2), 128.8 (d, J_{C-P} = 10 Hz) and 128.1 (d, hidden behind solvent signal) (C^m PPh_2), 111.7 (=CH_2-allyl), 105.0 (pz), 91.5 (d, $J_{C,P}$ = 7 Hz) and 86.9 (d, $J_{C,P}$ = 40 Hz) (C≡C), 82.1 (=CH-η^2-allyl), 52.3 and 52.1 (OCH_3), 48.9 (d, J_{C-P} = 5 Hz, =CH_2-η^2-allyl), 34.3 (br, CH_2-allyl), 26.1 (br, CH_2-η^2-allyl), 17.0 (br, CH_2P). MS (MALDI-TOF^+): *m/z* (%): 663.4 (85) $[M–COOMe]^+$.

[Ir(κ^2-A_2BPN)(CN^{t}Bu)$_2$(dmad)] (19). To a yellow solution of **5** (0.110 g, 0.149 mmol) in THF (8 mL), dmad (20 μl, 0.164 mmol) was added dropwise *via* microsyringe, to give a dark orange solution. After one hour of stirring the solvent was evaporated to give an orange residue, which after treatment with hexanes yielded a creamy white solid, which was filtered out and dried under vacuum. Yield 0.11 g (86%). %). Anal. Calcd (%) for $C_{38}H_{49}BIrN_4O_4P$ (859.83): 53.08, H 5.74, N 6.52; found C 53.01, H 5.65, N 6.45 IR (ATR): ν(CN)/cm^{-1}: 2196 (s), 2164 (s), ν(C=O)/cm^{-1}: 1746 (s), 1686 (s). ^1H NMR (400 MHz, C_6D_6, 25 ºC): δ 8.29 (m, 2H, H^o PPh_2), 8.17 (d, J = 1.2 Hz, 1H, pz), 7.58 (d, J = 1.6 Hz, 1H, pz), 7.52 (m, 2H, $H^{o'}$ PPh_2), 7.33 (m, 2H, H^m PPh_2), 7.11 (m, 1H, H^p PPh_2) 7.04 (m, 3H, $H^{m'+p'}$ PPh_2), 6.34 (m, 1H, =CH-allyl), 5.99 (t, J = 2 Hz, 1H, pz), 5.68 (m, 1H, =CH-allyl), 5.21 (d, J = 14.4 Hz, 1H) and 5.12 (d, J = 10.0 Hz, 1H)

(=CH_2-allyl), 4.81 (d, J = 10.0 Hz, 1H) and 4.74 (d, J = 17.2 Hz, 1H) (=CH_2-allyl), 3.58 (s, 3H) and 3.53 (s, 3H) (OCH_3), 2.35 (m, 1H, CH_2P), 2.00 (m, 3H, CH_2-allyl), 1.76 (m, 1H, CH_2P), 1.13 (m, 1H, CH_2-allyl), 0.86 (s, 9H) and 0.69 (s, 9H) (CN^tBu). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 25 ºC): δ – 6.4 (s). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 ºC): δ 166.5 (d, $J_{C,P}$ = 12 Hz,) and 163.3 (d, $J_{C,P}$ = 10 Hz) (CN^tBu), 152.0 and 151.9 (C=O), 146.0 (pz), 144.3 and 144.1 (=CH-allyl), 143.5 (d, $J_{C,P}$ = 42 Hz, C^i PPh_2), 135.4 (d, $J_{C,P}$ = 13 Hz, C^o PPh_2), 135.2 (d, $J_{C,P}$ = 50 Hz, $C^{i'}$ PPh_2), 134.7 (pz), 131.4 (d, $J_{C,P}$ = 9 Hz, $C^{o'}$ PPh_2), 130.3 (d, $J_{C,P}$ = 2 Hz, C^p PPh_2), 128.1 (m, $PPh_2^{m+m'+p'}$), 110.6 and 109.2 (=CH_2-allyl), 105.3 (d, $J_{C,P}$ = 6 Hz, C≡C), 105.0 (pz), 101.6 (d, $J_{C,P}$ = 66 Hz, C≡C), 57.9 and 57.2 (CMe_3), 51.8 and 51.7 (OCH_3), 34.9 and 31.8 (br, CH_2-allyl), 30.0 and 29.9 (CMe_3), 17.5 (br, CH_2P). MS (MALDI-TOF^+): *m/z* (%): 677.4 (74) $[M–dmad–allyl]^+$.

DFT geometry optimizations. The computational method used was density functional theory (DFT) with the B3LYP exchange-correlation functional,[48] using the Gaussian 09[49] program package. The basis sets used for the full optimization of the structures and for the frequency calculations were LanL2TZ(f) effective core potential for the metal atoms, and 6-31G(d,p) for the remaining atoms.

X-ray diffraction studies on **3**•0.5(C_6H_{14}), **8**, **11**, and·**18**•0.5(C_6H_{14})**.** Selected crystallographic data for these complexes can be found in Table 6. Intensity measurements were collected with a Smart Apex diffractometer, with graphite-monochromated MoK_α radiation. A semi-empirical absorption correction was applied to each data set, with the multi-scan[50] methods. All non-hydrogen atoms were refined with anisotropic displacement parameters except one disordered hexane solvent molecule in **18**·0.5(C_6H_{14}) which was refined with isotropic displacement parameters and with geometrical restraints. The hydrogen atoms were placed at calculated positions and were refined isotropically in riding mode. The structures were solved by direct

methods and refined by full-matrix least-squares with the program SHELX97[51] in the WINGX[52] package.

Table 6. Selected Crystal, Measurement, and Refinement Data for Compounds **3**•0.5(C_6H_{14}), **8**, **11**, and·**18**•0.5(C_6H_{14}).

	3·0.5(C_6H_{14})	**8**	**11**	**18**·0.5(C_6H_{14})
Formula	$C_{30}H_{37}BIrN_2P$·0.5(C_6H_{14})	$C_{46}H_{50}B_2N_4O_2P_2Rh_2$	$C_{41}H_{40}BN_2OP_2Rh$	$C_{29}H_{31}BIrNO_5P$·0.5(C_6H_{14})
formula weight	702.68	980.28	752.41	764.62
Colour	pale-yellow	yellow	yellow	colourless
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	Pbca	P2(1)/n	P2(1)/n	P2(1)/c
a[Å]	10.856(5)	11.9199(19)	11.203(2)	18.5058(18)
b[Å]	16.608(7)	16.647(3)	24.429(4)	9.3837(9)
c[Å]	32.292(12)	22.872(4)	13.786(2)	18.6119(18)
β[º]	90	104.359(3)	102.177(3)	90.491(2)
V[Å^3]	5822(4)	4396.6(12)	3688.0(10)	3231.9(5)
Z	8	4	4	4
F(000)	2824	2000	1552	1524
ρ_{calcd}[g cm^{-3}]	1.603	1.481	1.355	1.571
μ (mm^{-1})	4.667	0.866	0.584	4.222
crystal size[mm]	0.13 × 0.05 × 0.04	0.11 x 0.05 x 0.04	0.14x0.11x0.07	0.05 x 0.04 x 0.02
temperature [K]	100(2)	100(2)	100(2)	100(2)
θ limits [º]	27.27	26.00	26.00	25.20
collected reflns.	33914	25837	21901	24471
unique reflns. (Rint)	6499 (0.0982)	8645 (0.0955)	7220 (0.0546)	5818 (0.0820)
reflns. with $I>2\sigma(I)$	4686	6354	5300	4237
parameters/restraints	344 / 0	523 / 0	433 / 0	373 / 27
R_1 (on F, I>2σ(I))	0.0483	0.0567	0.0407	0.0402
wR_2 (on F^2, all data)	0.0898	0.1014	0.0939	0.0896
max./min. Δρ [e Å^{-3}]	1.129 / −1.808	0.730 / −0.844	0.710 / −0.360	1.030
goodness of fit	1.055	1.070	0.998	1.521 / −0.845

Supporting Information. Full ORTEP diagrams, selected spectroscopic data, Van't Hoff plotter, atomic coordinates for calculated DFT structures, complete reference 39, and a CIF file

giving details of the X-ray crystal structures of **3**•0.5(C_6H_{14}), **8**, **11**, and·**18**•0.5(C_6H_{14}). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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References

(1) Morales-Morales, D.; Jensen, C. M. *The Chemistry of Pincer Compounds*; Elsevier: Amsterdam, 2007.

(2) *See for example* (a) Schneider, S.; Meiners, J.; Askevold, B. *Eur. J. Inorg. Chem.* **2012**, 412–429. (b) Choi, J.; MacArthur, A. M. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761–1779. (c) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048–2076. (d) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553–556. (e) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080–1082.

(3) Pettinari, C. *Scorpionates II: Chelating Borate Ligands*; Imperial College Press: London, 2008.

(4) (a) Trofimenko, S. *Scorpionates - The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *J. Chem. Ed.* **2005**, *82*, 1715–1720.

(5) (a) Valpuesta, J. E. C.; Álvarez, E.; López-Serrano, J.; Maya, C.; Carmona, E. *Chem. Eur. J.* **2012**, *18*, 13149–13159. (b) Conejero, S.; Esqueda, A. C.; Valpuesta, J. E. V.; Álvarez, E.; Maya, C. *Inorg. Chim. Acta* **2011**, *369*, 165–172. (c) Pettinari, R.; Pettinari, C.; Marchetti, F.; Gobetto, R.; Nervi, C.; Chierotti, M. R.; Chan, E. J.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2010**, *49*, 11205−11215. (d) Adams, C. J.; Anderson, K. M.; Charmant, J. P. H.; Connelly, N. G.; Field, B. A.; Hallett, A. J.; Horne, M. *Dalton Trans.* **2008**, 2680–2692. (e) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507−1514.

(6) *See for example*: (a) Choi, G.; Morris, J.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2012**, *134*, 9276−9284. (b) Frauhiger, B. E.; Ondisco, M. T.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2012**, *134*, 8902−8910. (c - , E.; Alvarado-Rodríguez, J. G.; Paneque, M.; Poveda, M. L. *Organometallics* **2012**, *31*, 3185−3198. (d - , E.; Paneque, M.; Poveda, M. L. *Organometallics* **2012**, *31*, 716−721. (e) Conejero, S.; López-Serrano, J.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Vattier, F.; Álvarez, E.; Carmona, E. *Chem. Eur. J.* **2012**, *18*, 4644–4664. (f) Castro-Rodrigo , E. *Organometallics* **2012**, *31*, 1991−2000. (g) Conejero, S.; Maya, C.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Vattier, F.; Alvarez, E.; Carmona, E.; Laguna, A.; Crespo, O. *Dalton Trans.* **2012**, *41*, 14126−14136. (h) Paneque, M.; Poveda, M. L.; Rendón, N. *Eur. J. Inorg. Chem.* **2011**, 19−33. (i) Bajo, S.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2011**, *30*, 5710−5715. (j) Evans, M. E.; Jones, W. D. *Organometallics* **2011**, *30*, 3371−3377. (k) Hernández, Y. A.;

López-Serrano, J.; Paneque, M.; Poveda, M. L.; Vattier, F.; Salazar, V.; Álvarez, E.; Carmona, E. *Chem. Eur. J.* **2011**, *17*, 9302–9305. (l) Tanabe, T.; Evans, M. E.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2011**, *30*, 834–843. (m) Cristobal, C.; García-Rubin, S.; Hernández, Y. A.; López-Serrano, J.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Alvarez, E. *Organometallics* **2010**, *29*, 5744−5747. (n) Evans, M. E.; Li, T.; Jones, W. D. *J. Am. Chem. Soc.* **2010**, *132*, 16278−16284. (o) Engelman, K. L.; White, P. S.; Templeton, J. L. *Organometallics* **2010**, *29*, 4943−4949. (p) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2010**, 29, 4071−4079. (q) Conejero, S.; Paneque, M.; Poveda, M. L.; Santos, L. L.; Carmona, E. *Acc. Chem. Res.* **2010**, *43*, 572−580. (r) Álvarez, E.; Hernández, Y. A.; López-Serrano, J.; Maya, C.; Paneque,M.; Petronilho, A.; Poveda, M. L.; Salazar, V.; Vattier, F.; Carmona, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 3496−3499. (s) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; López, F.; Mascareñas, J. L.; Oliván, M.; Oñate, E.; Saya, L.; Villarino, L. *J. Am. Chem. Soc.* **2010**, *132*, 454–455.

(7) (a) Morawitz, T.; Zhang, F.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Wagner, M. *Organometallics* **2008**, *27*, 5067–5074. (b) Reger, D. L.; Watson, R. P.; Gardinier, J. R.; Smith, M. D.; Pellechia, P. J. *Inorg. Chem.* **2006**, *45*, 10088–10097. (c) Ilkhechi, A. H.; Mercero, J. M.; Silanes, I.; Bolte, M.; Scheibitz, M.; Lerner, H.-W.; Ugalde, J. M.; Wagner, M. *J. Am. Chem. Soc.* **2005**, *127*, 10656–10666.

(8) Reger, D. L.; Gardinier, J. R.; Gemmill, W. R.; Smith, M. D.; Shahin, A. M.; Long, G. J.; Rebbouh, L.; Grandjean, F. *J. Am. Chem. Soc.* **2005**, *127*, 2303–2316.

(9) Camerano, J. A.; Casado, M. A.; Ciriano, M. A.; Oro, L. A. *Dalton Trans.* **2006**, 5287–5293

(10) *See for recent examples*: (a) Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. *Organometallics* **2012**, *31*, 6851−6860. (b) Lo, Y. -H.; Wang, T. -H.; Lee, C. -Y.; Feng, Y. -H. *Organometallics* **2012**, *31*, 6887−6899. (c) Hu, T. C; Hsiao, P. I.; Wang, T. H. Yang, Y. W. Chang, C. Y.; Wu, Y. H. Sun, W. C.; Yu, M. S.; Lee, C. Y.; Lo, Y. H. *Dalton Trans.* **2011**, *40*, 12663−12666. (d) Pettinari, C.; Marchetti, F.; Cerquetella, A.; Pettinari, R.; Monari, M.; Mac Leod, T. C. O.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Organometallics*, **2011**, *30*, 1616−1626. (e) Cheung, H. W.; So, C. M.; Pun, K. H.; Zhou, Z. Y.; Lau, C. P. *Adv. Synth. Cat.* **2011**, *353*, 411−425. (f) Lee, T. Y.; Dang, L.; Zhou, Z. Y.; Yeung, C. H.; Lin, Z. Y.; Lau, C. P. *Eur. J. Inorg. Chem.* **2010**, 5675−5684. (g) Foley, N. A.; Lee, J. P.; Ke, Z.; Gunnoe, T. B.; Cundari, T. R. *Acc. Chem. Res.* **2009**, *42*, 585-597. (h) Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379–3394.

(11) Smith, J. M. *Comments Inorg. Chem.* **2008**, *29*, 189–233.

(12) (a) Saouma, C. T.; Lu, C. C.; Peters, J. C. *Inorg. Chem.* **2012**, *51*, 10043–10054. (b) Fuentes, M. A.; Álvarez, E.; Caballero, A.; Pérez, P. J. *Organometallics* **2012,** *31,* 959–965. (c , J. A.; Ciriano, M. A. *Organometallics* **2012**, *31*, 2895−2906. (d) Tejel, C.; Ciriano, M. A; Passarelli, V. *Chem. Eur. J.* **2011**, *17*, 91–95. (e) Saouma, C. T.; Moore, C. E.; Rheingold, A. R.; Peters, J. C. *Inorg. Chem.* **2011**, *50*, 11285–11287. (f) Lipke, M. C.; Tilley, T. D. *J. Am. Chem. Soc.* **2011**, *133*, 16374–16377. (g) Stradiotto, M.; Hesp, K. D.; Lundgren, R. J. *Angew. Chem. Int. Ed.* **2010**, *49*, 494–512 (h) Mehn, M. P.; Peters, J. C. *J. Inorg. Biochem.* **2006**, *100*, 634–643. (i) Jenkins, D. M.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, 127, 7148–7165. (j) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, *23*, 2488–2502. (k) Betley, A. T.; Peters, J. C. *Inorg. Chem.* **2003**, *42*,

5074–5084. (l) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 4627–4629. (m) Barney, A. A.; Heyduk, A. F.; Nocera, D. G. *Chem. Commun.* **1999**, 2379–2380.

(13) (a) Riordan, C. G. *Coord. Chem. Rev.* **2010**, *254*, 1815–1825. (b) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2010**, *29*, 326–336. (c) Mock, M. T.; Kieber-Emmons, M. T.; Popescu, C. V.; Gasda, P.; Yap, G. P. A.; Riordan, C. G. *Inorg. Chim. Acta* **2009**, *362*, 4553–4562. (d) Popescu, C. V.; Mock, M. T.; Stoian, S. A.; Dougherty, W. G.; Yap, G. P. A.; Riordan, C. G. *Inorg. Chem.* **2009**, *48*, 8317–8324. (e) Spicer, M. D.; Reglinski, J. *Eur. J. Inorg. Chem.* **2009**, 1553–1574. (f) Mock, M. T.; Popescu, C. V.; Yap, G. P. A.; Dougherty, W. G.; Riordan, C. G. *Inorg. Chem.* **2008**, *47*, 1889–1891. (g) DuPont, J. A.; Yap, G. P. A.; Riordan, C. G. *Inorg. Chem.* **2008**, *47*, 10700–10707. (h) Ge, P.; Haggerty, B. S.; Rheingold, A. L.; Riordan, C. G *J. Am. Chem. Soc.* **1994**, *116*, 8406–8407.

(14) (a) Chen, F.; Wang, G. -F.; Li, Y. -Z.; Chen, X. -T.; Xue, Z. -L. *Inorg. Chem. Commun.* **2012**, *21*, 88–91. (b) Muñoz, S. B.; Foster, W. K.; Lin, H. –J.; Margarit, C. G.; Dickie, D. A. *Inorg. Chem.* **2012**, *51*, 12660–12668. (c) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841–859.

(15) (a) Smith, J. M.; Mayberry, D. E.; Margarit, C. G.; Sutter, J.; Wang, H.; Meyer, K.; Bontchev, R. P. *J. Am. Chem. Soc.* **2012**, *134*, 6516–6519. (b) Kinney, R. A.; Saouma, C. T.; Peters, J. C.; Hoffman, B. M. *J. Am. Chem. Soc.* **2012**, *134*, 12637–12647. (c) Owen, G. R. *Chem. Soc. Rev.* **2012**, *41*, 3535–3546. (d) Saouma, C. T.; Peters, J. C. *Coord. Chem. Rev.* **2011**, *255*, 920–937. (e) Scepaniak, J. J.; Vogel, C. S.; Khusniyarov, M. M.; Heinemann, F. W.; Meyer, K.; Smith, J. M. *Science* **2011**, *331*, 1049–1052. (f) Saouma, C. T.; Kinney, R. A.; Hoffman, B. M.; Peters, J. C. *Angew. Chem. Int. Ed.* **2011**, *50*, 3446–3449. (g) Scepaniak, J. J.; Bontchev, R.

P.; Johnson, D. L.; Smith, J. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 6630–6633. (h) Jiménez, S.; López, J. A.; Ciriano, M. A.; Tejel, C.; Martínez, A.; Sánchez-Delgado, R. *Organometallics* **2009,** *28,* 3193–3202 (i) Tejel, C.; Ciriano, M. A.; Jiménez, S.; Passarelli, V.; López, J. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 2093–2096.

(16) Casado, M. A.; Hack, V.; Camerano, J. A.; Ciriano, M. A.; Tejel, C.; Oro, L. A. *Inorg. Chem.* **2005**, *44*, 9122–9124.

(17) Thomas, C. M.; Mankad, N. P.; Peters, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 4956–4957.

(18) Camerano, J. A.; Casado, M. A.; Ciriano, M. A.; Tejel, C.; Oro, L. A. *Chem. Eur. J.* **2008**, *14*, 1897–1905.

(19) Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148−5152.

(20) (a) Ruman, T.; Ciunik, Z.; Trzeciak, A. M.; Ziółkowski, J. J. *Organometallics* **2003**, *22*, 1072−1080. (b) Moszner, M.; Wołowiec, S.; Trösch, A.; Vahrenkamp, H. *J. Organomet. Chem.* **2000**, *595*, 178−185. (c) Bucher, U. E.; Currao, A.; Nesper, R.; Rüegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1995**, *34*, 66−74. (d) Cocivera, M.; Desmond, T. J.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O´Sullivan, D. J. *Organometallics* **1982**, *1*, 1125−1132. (e) Cocivera, M.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O´Sullivan, D. J.; Parvez, M.; Ruhl, B. *Organometallics* **1982**, *1*, 1132−1139.

(21) Padilla-Martínez, I. I.; Poveda, M. L.; Carmona, E.; Monje, M. A.; Ruiz-Valero, C.; *Organometallics* **2002**, *21*, 93−104.

(22) Marcén, S.; Jiménez, M. V.; Dobrinovich, I. T.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2002**, *21*, 326−330

(23) Tejel, C.; Villoro, J. M.; Ciriano, M. A.; López, J. A.; Eguizábal, E.; Lahoz, F. J.; Bakhmutov, V. I.; Oro, L. A. Organometallics **1996,** *15,* 2967−2978.

(24) Jones, W. D.; Hessell, E. T. *Inorg. Chem.* **1991**, *30*, 778−783.

(25) Nicasio, M. C.; Paneque, M.; Pérez, P. J.; Pizzano, A.; Poveda, M. L.; Rey, L.; Sirol, S.; Taboada, S.; Trujillo, M.; Monge, A.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **2000**, *39*, 180−188

(26) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341– 342.

(27) Elliott, P. I. P.; Haslam, C. E.; Spey, S. E.; Haynes, A. *Inorg. Chem.* **2006**, *45*, 6269– 6275.

(28) Hartwig, J. *Organotransition metal chemistry;* University Science Books: Sausalito, California, 2010.

(29) Mitoraj, M.; Michalak, A. *Organometallics* **2007**, *26*, 6576–6580.

(30) (a) Böttcher, H.-C.; Graf, M.; Karaghiosoff, K.; Mayer, P. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2374–2379 (X = Cl, L = $^{t}Bu_2PH$, 2.104(3) Å). (b) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1437–1444 (X = F, L = $^{i}Pr_3P$, 2.099(5) Å in av.). (c) Selent, D.; Scharfenberg-Pfeiffer, D.; Reck, G.; Taube, R. *J. Organomet. Chem.* **1991**, *415*, 417–423 (X = Cl, L = $C_5H_{10}NH$, 2.065 Å in av.). (d) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828–1834 (X = Cl, L = $^{i}Pr_3P$, 2.122(2) Å in av.).

(31) (a) Willems, S. T. H.; Russcher,J. C.; Budzelaar, P. H. M.; de Bruin, B.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Chem. Commun.* **2002**, 148–149 (L_2 = bisoxazolinate, 2.127(9) Å in av.). (b) Bühl, M.; Håkansson, M.; Mahmoudkhani, A. H.; Öhrström, L. *Organometallics* **2000**, *19*, 5589−5596 (L_2 = 2,4-pentanedionato, 2.127(5) Å; 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato, 2.121(3) Å). (c) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753–769 (L_2 = β-diiminate, 2.145(4) Å in av.). (d) Baena, M. J.; Reyes, M. L.; Rey, L.; Carmona, E.; Nicasio, M. C.; Pérez, P. J.; Gutierréz, E.; Monge, A. *Inorg. Chim. Acta* **1998**, *273*, 244–254 (L_2 = $H_2B(3,5\text{-}Me_2Pz)_2$, 2.122(5) Å in av.).

(32) (a) Rubio, M.; Suárez, A.; Vega, E.; Álvarez, E.; Díez, J.; Gamasa, M. P.; Pizzano, A. *Eur. J. Inorg. Chem.* **2012**, 655–633 (n = 1, 2.221(6) Å in av.). (b) Rubio, M.; Suárez, A.; del Río, D.; Galindo, A.; Álvarez, E.; Pizzano, A. *Organometallics* **2009**, *28*, 547–560 (n = 0, 2.229(3) Å in av.). (c) Rubio, M.; Suárez, A.; del Río, D.; Galindo, A.; Álvarez, E.; Pizzano, A. *Dalton Trans.* **2007**, 407– 409 (n = 0, 2.227(1) Å in av.). (d) Hahn, C.; Sieler, J.; Taube, R. *Chem. Ber.* **1997**, *130*, 939–945 (n = 1, 2.149 Å in av.).

(33) Angular dependence for the $^2J_{P,P}$ coupling constants and the P–M–P angle can be considered from the well-known strong difference between $^2J_{P,P}$(trans) (around 180º) and $^2J_{P,P}$(cis) (around 90º): (a) Kühl, O. *Phosphoros-31NMR spectroscopy*, Springer-Verlag Berlin Heidelberg, 2008 (p. 22). (b) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W. Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 11817–11825. (c) Gull A. M.; Fanwick P. E.; Kubiak C. P. *Organometallics*, **1993**, *12*, 2121–2125.

(34) Selected examples for complexes of the type [IrR(olefin)$(PMe_3)_3$]: (a) Bleeke J. R.; Thananatthanachon T.; Rath N. P. *Organometallics*, **2007**, *26*, 3904–3907 ($^2J_{P,P}$ = 45.8, 25.6,

22.8 Hz). (b) Bleeke J. R.; Ortwerth M. F.; Chiang M. Y. *Organometallics*, **1992**, *11*, 2740–2743 ($^2J_{P,P}$ = 42.3, 17.6, 16.0 Hz). (c) Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, Jr. T. W.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391–2398 ($^2J_{P,P}$ = 41.8, 18.3 Hz). (d) Merola J. S.; Kacmarcik R. T. *Organometallics*, **1989**, *8*, 778–784 ($^2J_{P,P}$ = 52.0, 12.9, 10.5 Hz). [IrR(CO)(olefin)(PPh_3)$_2$], (e) Ionkin A. S.; Marshall W. J. *Inorg. Chem.* **2005**, 44, 6244–6247 ($^2J_{Peq,Peq}$ = 55.3 Hz). (f) Nishihara Y.; Yoda C.; Osakada K. *Organometallics*, **2001**, *20*, 2124–2126 ($^2J_{Peq,Peq}$ = 43.4 Hz).

(35) (a) Goldberg, S. Z.; Eisenberg, R. *Inorg. Chem.* **1976**, *15*, 58–63. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.

(36) *See for example*: (a) Kirchmann, M.; Fleischhauer, S.; Wesemann, L. *Organometallics* **2008**, *27*, 2803–2808 ([Me_4N][Ir($SnB_{11}H_{11}$)(CO)(C_2H_4)(PPh_3)$_2$], ν(CO)eq = 1942 cm^{-1}). (b) Itazaki, M.; Yoda, C.; Nishihara, Y.; Osakada, K. *Organometallics* **2004**, *23*, 5402–5409 ([Ir(η^1:η^2-$CH_2C(CH_2CH_2Ph)_2CH$=CH2)(CO)(PPh_3)$_2$], ν(CO)eq =1941 cm^{-1}). (c) Brian P. Cleary, B. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1995**, *117*, 3510–3521; ibid *Organometallics* **1992**, *11*, 2336–2337 ([Ir($CH_2C_6H_3Me_2$)(CO)(C_2H_4)(dppe)], ν(CO)eq =1955 cm^{-1}). (d) Li, R. T.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 10032–10040 ([Ir(Cl)(η^2-3,3-diphenylcyclopropene)(CO)(PR_3)$_2$], ν(CO)ax = 1986 (PMe_3), 1993 (PMe_2Ph), 2001 ($PMePh_2$), 1979 (PEt_3) cm^{-1}). (e) Balch, A. L.; Catalano; V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980–3981 ([Ir(Cl)(η^2-C_{60})(CO)(PPh_3)$_2$], ν(CO)ax = 2014 cm^{-1}). (f) Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714–721 ([Ir(σ-C_2H_5)(C_2H_4)(CO)(dppe)], ν(CO)eq =1938, 1893 cm^{-1}). (g) Baddley, W.H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661–3663 ([Ir(σ-CH_2CH_2CN) (CNCH=CHCN)(CO)(PPh_3)$_2$], ν(CO)ax =2035 cm^{-1}).

(37) *See for example*: (a) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538-4546 ([Ir(κ^3-3,5-Me_2Tp)(C_2H_4)(CO)], ν(CO)ax = 1990 cm^{-1}). (b) Stössel, P.; Heins, W.; Mayer, H. A.; Fawzi, R.; Steimann, M. *Organometallics* **1996**, *15*, 3393–3403 ([Ir(κ^3-P_3)(C_2H_4)(CO)]$^+$, ν(CO)ax = 2025 (tdppcy), 2055 (tdppcycn), 2043 (tdppcyme) cm^{-1}). (c) Jenkins, H. A.; Loeb, S. J. *Organometallics* **1994**, *13*, 1840–1850 ([Ir(κ^3-S_3)(C_8H_{14})(CO)]$^+$, ν(CO)ax = 2073 cm^{-1}. (d) Ciriano, M. A., Férnandez, M. J.; Modrego, J.; Rodriguez, M. J.; Oro, L. A. *J. Organomet. Chem.* **1993**, *443*, 249–252 ([Ir(κ^3-Tp)(C_2H_4)(CO)], ν(CO)ax = 2000 cm^{-1}). (e) Perera, S. D.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1995**, 865–866 ([Ir(κ^3-P_2N)(C_2H_4)(CO)], ν(CO)ax = 2015 cm^{-1}).

(38) Tejel, C.; Ciriano, M. A.; Millaruelo, M.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2003**, *42,* 4750–4758.

(39) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 5145–5149.

(40) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *319*, 411–422.

(41) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Organometallics* **2007**, *26*, 3120–3129.

(42) Perrin, D. D. W.; Armarego, L. F. Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Exeter, UK 1988.

(43) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88−90.

(44) Crabtree, R. H., Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395−403.

(45) Ir(acac)(cod) Robinson, S. R.; Shaw, B. L. *J. Chem.* Soc. **1965**, 4997−5001.

(46) Fraenkel, G.; Winchester, W. R.; Williard, P. G. *Organometallics* **1989**, *8*, 2308−2311.

(47) Wagner, C. E.; Kim, J.−S.; Shea, K. J. *J. Am. Chem. Soc.* **2003**, *125*, 12179−12195.

(48) (a) Becke, A. D. *Phys. Rev. A*, **1988**, *38*, 3098–3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, *37*, 785–789. (c) Becke, A. D. J. *Chem. Phys.* **1993**, *98*, 5648–5652.

(49) Gaussian 09, Revision A.02, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C. Iyengar, S. S. Tomasi, J. Cossi, M. Rega, Millam, N. J., Klene, M. Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J., Gian, Inc., Wallingford CT, 2009.

(50) Sheldrick, G. M. SADABS, Bruker AXS, Madison, WI (USA), 1997.

(51) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

(52) Farrugia, L. F. J. *Appl. Crystallogr.* **1999**, *32*, 837–838.

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