

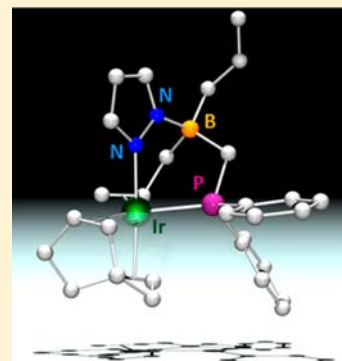
# Rhodium and Iridium Complexes with a New Scorpionate Phosphane Ligand

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## Supporting Information

**ABSTRACT:** A straightforward synthesis of a new hybrid scorpionate ligand  $[(\text{allyl})_2\text{B}(\text{CH}_2\text{PPh}_2)(\text{Pz})]^-$  ( $[\text{A}_2\text{BPN}]^-$ ) is reported. Coordination to rhodium resulted in square-planar complexes  $[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{L})(\text{L}')]$  [ $\text{L} = \text{L}' = \frac{1}{2}\text{cod}$  (1,5-cyclooctadiene),  $\text{CN}^t\text{Bu}$ ,  $\text{CO}$  (**6**);  $\text{L} = \text{CO}$ ,  $\text{L}' = \text{NH}_3$ , pyridine,  $\text{PPh}_3$ ,  $\text{PMe}_3$ ] for which spectroscopic data and the molecular structure of  $[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{CO})\text{PPh}_3]$  (**11**) indicate the ligand to be  $\kappa\text{N},\kappa\text{P}$ -bound to rhodium with two dangling free allyl groups. Studies in solution point out that the six-membered  $\text{Rh-N-N-B-C-P}$  metallacycle undergoes a fast inversion in all of them. The bis(carbonyl) complex **6** easily loses a CO group to give  $[\{\text{Rh}(\text{A}_2\text{BPN})(\text{CO})\}_2]$ , a dinuclear compound in which two mononuclear subunits are brought together by two bridging allyl groups. Coordination to iridium is dominated by a tripodal  $\kappa\text{N},\kappa\text{P},\eta^2\text{-C}\equiv\text{C}$  binding mode in the TBPY-5 complexes  $[\text{Ir}(\kappa^3\text{-A}_2\text{BPN})(\text{L})(\text{L}')]$  [ $\text{L} = \text{L}' = \frac{1}{2}\text{cod}$  (**3**),  $\text{CN}^t\text{Bu}$  (**5**),  $\text{CO}$  (**7**);  $\text{L} = \text{CO}$ ,  $\text{L}' = \text{PPh}_3$  (**13**),  $\text{PMe}_3$  (**14**),  $\text{H}_2\text{C}=\text{CH}_2$ , (**17**),  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  (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  $\text{L} = \text{L}'$  (**3**, **5**, and **7**), while those having CO and L ligands (**14**, **17**, and **18**) were found to be nonfluxional 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  $[\text{Ir}(\kappa^2\text{-A}_2\text{BPN})(\text{CO})(\text{Cl})(\text{H})\text{PPh}_3]$  (**15**) and the C-alkyl compound  $[\text{Ir}\{\kappa^3\text{-}(\text{allyl})\text{B}(\text{CH}_2\text{CHCH}_3)(\text{CH}_2\text{PPh}_2)(\text{Pz})\}(\text{Cl})(\text{CO})\text{PMe}_3]$  (**16**), respectively. The bis(isocyanide) complex **5** reacts with dmad to form  $[\text{Ir}(\kappa^2\text{-A}_2\text{BPN})(\text{CN}^t\text{Bu})_2(\text{dmad})]$ . On the whole, the electronic density provided to the metal by the  $[\text{A}_2\text{BPN}]^-$  ligand is very sensitive to the coordination mode. The basicity of the new ligand is similar to that of the  $\text{Tp}^{\text{Me}_2}$  ligand in the  $\kappa\text{N},\kappa\text{P}$  mode but comparable to Tp if coordinated in the  $\kappa\text{N},\kappa\text{P},\eta^2\text{-C}\equiv\text{C}$  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 with the donor groups) allows for control over electronic and steric properties. A conjunction of both properties will eventually impact the reactivity of their complexes. Consequently, an exceptional effort has been dedicated to design ligand scaffolds specifically to stabilize metallic fragments in a predefined geometry. In this context, a special mention is required for pincer ligands,<sup>1</sup> in which the meridional coordination results in strong binding to the metal, allowing outstanding examples of C–H bond activation.<sup>2</sup>

Unlike the aforementioned pincer ligands, the ubiquitous poly(pyrazolyl)borate (Tp or scorpionate) provides three N atoms that cap one face of a coordination polyhedron.<sup>3</sup> These versatile ligands have attracted enormous interest in distinct fields of science for a long time, ranging from bioinorganic chemistry to materials science, and applications in organometallic and

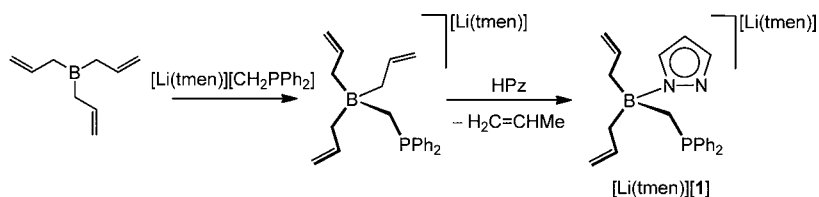
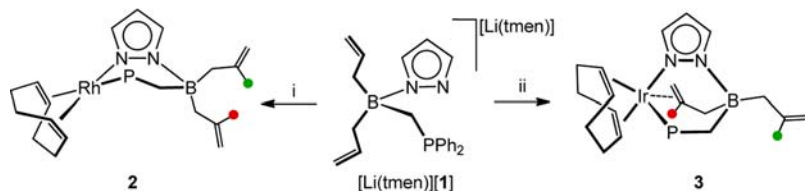
coordination chemistry are very well documented.<sup>4</sup> The broad body of work generated by these Tp-based complexes encouraged new adaptations and improvements of the architectures of the scorpionate ligands, mainly by varying alkyl or aryl substituents at the 3 and/or 5 positions of the pyrazolyl rings (“second generation”).<sup>5</sup> The structural variations on these ligands allowed tailoring of their cone and wedge angles, influencing the metal basicity by changing the nature of the pyrazolyl substituents and giving rise to a new set of late-transition-metal complexes able to perform unusual metallorganic transformations.<sup>6</sup> Moreover, structural adjustments by functionalizing the fourth site at B (“third generation”)<sup>7</sup> have provided interesting examples of original oligotopic ligands to be used as scaffolds for oligonuclear complexes<sup>8</sup> and to covalently anchor RhTp-based systems peripherally to carbosilane dendrimers in specific cases.<sup>9</sup>

While the catalytic properties of these N-based tripodal systems have been unfolding within the last years,<sup>10</sup> the curiosity of scientists together with the desire for fine-tuning electronic parameters in tripodal assemblies led naturally to the development of

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Scheme 1. Synthesis of Compound [Li(tmen)][1]

Scheme 2. Synthesis of Complexes 2 and 3<sup>a</sup>

<sup>a</sup>(i) [ $\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2$ ]; (ii) [ $\text{Ir}(\text{acac})(\text{cod})$ ].

nonpyrazolyl, anionic borate-based ligands of the type  $[\text{RBD}_3]^-$ .<sup>11</sup> 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,<sup>12</sup> S,<sup>13</sup> and C<sup>14</sup>) providing electronic environments different from those of the metals, which has made possible the observation of unusual reactivity patterns.<sup>12d,15</sup>

With the idea of bringing together mixed donor sets “N<sub>2</sub>P”, we reported the synthesis<sup>16</sup> of the hybrid, anionic scorpionate-like ligand  $[(\text{CH}_2=\text{CHCH}_2)\text{B}(\text{CH}_2\text{PPh}_2)(\text{Pz})_2]^-$  (Pz = pyrazolate), while Peters and co-workers<sup>17</sup> documented the related “P<sub>2</sub>N” hybrid system  $[\text{PhB}(\text{CH}_2\text{P}^t\text{Bu}_2)(\text{Pz})]^-$ . Aiming at the rich reactivity and coordination chemistry displayed by the iridium complexes stabilized by the “PN<sub>2</sub>” tripodal system, which showed the allyl arm not to be innocent,<sup>18</sup> we decided to take a step further in the design of such hybrid architectures and now we 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 and C) atoms of composition  $[(\text{allyl})_2\text{B}(\text{CH}_2\text{PPh}_2)(\text{Pz})]^-$  ( $[\text{A}_2\text{BPN}]^-$ ), as well as the coordination chemistry and reactivity shown by its rhodium and iridium complexes.

## RESULTS AND DISCUSSION

The new ligand  $[\text{A}_2\text{BPN}]^-$  features a central B atom connected to two allyl groups, one pyrazolyl ring, and a pendant  $\text{CH}_2\text{PPh}_2$  moiety. It is a new anionic scorpionate if one considers that the allylic groups may coordinate to metals in a  $\eta^2\text{-C}=\text{C}$  fashion.<sup>18</sup> 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 because it can accommodate metallic fragments in different ways. The ligand has been synthesized as the  $[\text{Li}(\text{tmen})][\text{A}_2\text{BPN}]$  salt ( $[\text{Li}(\text{tmen})][1]$ ) in two steps, as shown in Scheme 1: (i) formation of the intermediate  $[(\text{allyl})_3\text{B}(\text{CH}_2\text{PPh}_2)]^-$  by treatment of  $\text{B}(\text{allyl})_3$  with an equimolar amount of  $[\text{Li}(\text{tmen})][\text{CH}_2\text{PPh}_2]$ ; (ii) protonation of one of the allyl arms with pyrazole. This approach represents a convenient way to this type of system because propene is the only waste in the second step. Tetrasubstitution of the B atom in  $[\text{A}_2\text{BPN}]^-$  was confirmed by the shift of the signal at  $\delta -5.89$  ppm, in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum.<sup>19</sup> A broad resonance at  $\delta -13.6$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum indicated the Li ion to be coordinated to P, while the expected resonances for the equivalent allyl arms and the pyrazolyl group were observed in the  $^1\text{H}$  NMR spectrum.

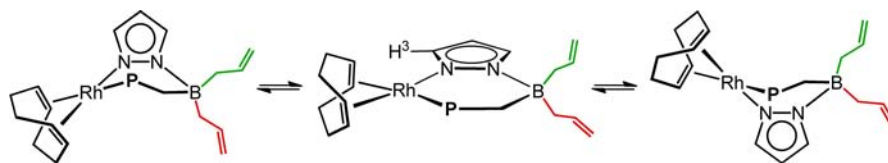
Coordination of the “M(cod)” (M = Rh, Ir) fragments to **1** was achieved by reaction of  $[\text{Li}(\text{tmen})][\text{A}_2\text{BPN}]$  with the complexes  $[\{\text{M}(\mu\text{-Cl})(\text{cod})\}_2]$ , which rendered the compounds  $[\text{M}(\text{A}_2\text{BPN})(\text{cod})]$  (M = Rh, **2**; 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  $[\text{Ir}(\text{acac})(\text{cod})]$  (acac = acetylacetonate; Scheme 2; phenyl groups on the P atom have been omitted for clarity in all schemes and charts).

Both complexes were found to be fluxional, and the frozen structures, shown in Scheme 2, were observed upon cooling. At  $-80$  °C, both exhibited four resonances for the olefinic cod protons and inequivalent allyl groups in the  $^1\text{H}$  NMR spectra, a clear indication of the lack of symmetry of the complexes. Moreover, the  $=\text{CH}$  protons from the allyl groups (marked with red and green circles in Scheme 2) were found as broad signals at  $\delta 6.81$  and  $6.05$  ppm for the rhodium complex **2**, i.e., in the typical region for noncoordinated olefins. Therefore, both allyl groups are free in **2** and the ligand binds the Rh 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  $\delta 6.45$  and  $3.60$  ppm for the iridium counterpart (**3**). The shift to high field of one of them (as well as for the corresponding  $=\text{CH}_2$  protons, observed at  $\delta 3.92$  and  $2.10$  ppm) agrees with the bonding of one of the allyl groups to Ir, 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  $\kappa\text{N},\kappa\text{P},\eta^2\text{-C}=\text{C}$  fashion.

Upon increasing temperature, the allyl groups coalesce in both cases, emerging as a 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 (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<sup>3</sup> proton from the pyrazolyl and the phenyl groups on the P. Consequently, this process should be facilitated by less demanding ligands on the metal center, as shown for the bis(carbonyl) and bis(isocyanide) derivatives.

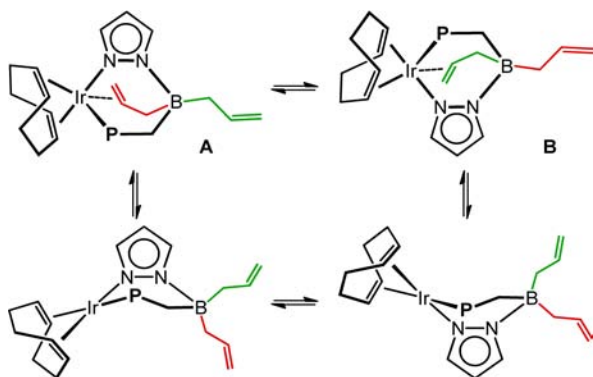
On the contrary, the allyl groups of the iridium counterpart **3** emerge from the coalescence as a set of signals of the  $\text{CH}_2=$

## Scheme 3. Fluxional Motion Undergone by Complex 2



CH- moiety still shifted to high field (see the 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

## Scheme 4. Proposed Motions Justifying the Fluxional Behavior of Complex 3



from decooordination of the allyl group followed by an easy boat-to-boat inversion of the square-planar species and recoordination of the other allyl group (Scheme 4). This dynamic process is reminiscent of that generally shown by Tp complexes,<sup>5d,20</sup> based upon sequential coordination-deoordination 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 variable-temperature (VT) <sup>1</sup>H NMR spectra, and the chemical shift of the phosphorus remained almost unaltered in the same range of temperature.

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 Ir atom lies at the center of a slightly distorted trigonal bipyramid (TBPY-5) coordinated to the scorpionate ligand in a  $\kappa N, \kappa P, \eta^2-C=C$  fashion and to the C=C bonds of cod in the typical chelating mode.

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  $\eta^2-C=C$  bond of one allyl group, and the other olefinic bond of cod (C23–C24) lie at the equatorial sites. All of the equatorial angles are different from each other and from 120°, with the P–Ir–Ct1 angle being 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  $\pi$ -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

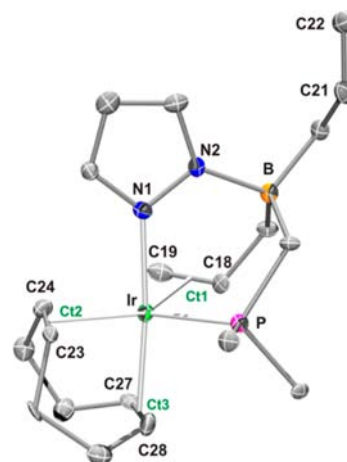


Figure 1. Molecular structure (ORTEP at the 50% level) of complex 3. H atoms and the solvent of crystallization have been removed, and only the *ipso*-C atoms of the phenyl groups are shown for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3<sup>a</sup>

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)		

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

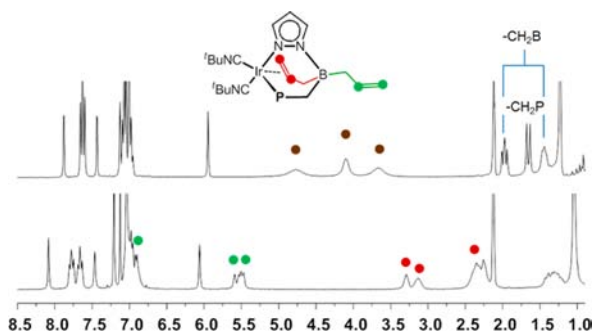
[1.345(9) Å], suggesting it to be a labile ligand. Noticeably, the  $\eta^2$ -allyl group was found to be bonded to Ir in a very asymmetric way, as reflected by the Ir–C18 and Ir–C19 distances of 2.301(6) and 2.202(6) Å, respectively. On the whole, these distances are similar to those found in other  $\eta^2$ -olefin iridium complexes such as [Ir(Tpm)(H)(CH=CH<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>)]PF<sub>6</sub> [Tpm = tris(3,5-dimethylpyrazolyl)methane; 2.171(10) and 2.142(11) Å],<sup>21</sup> [IrCl(L<sub>Fe</sub>)(cod)]PF<sub>6</sub> [L<sub>Fe</sub> = [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]( $\eta^6$ -1,1-di(2-propenyl)-3-butenyl)benzene]; 2.191(6) and 2.319(6) Å],<sup>22</sup> and [Ir{(Pz)B( $\eta^2$ -allyl)(CH<sub>2</sub>PPh<sub>2</sub>)(Pz)}(CO)PMe<sub>3</sub>] [2.227(4) and 2.168(5) Å].<sup>18</sup>

Related isocyanide and carbonyl complexes of the formula [M(A<sub>2</sub>BPN)(L)<sub>2</sub>] (L = CN<sup>t</sup>Bu, M = Rh, 4; Ir, 5; L = CO, M = Rh, 6; Ir, 7) were easily prepared by reacting complexes 2 and 3 with CN<sup>t</sup>Bu in a 1:2 molar ratio and by bubbling carbon monoxide (CO) 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 CO and, consequently, they were characterized in

situ. In fact, evaporation of the solvent was associated with the loss of one carbonyl ligand from the rhodium complex [to give the dimer  $[\text{Rh}(\text{A}_2\text{BPN})(\text{CO})]_2$  (**8**); see below] and a full decomposition for the iridium compound.

Complexes **4**–**7** retain the original stereochemistry of their cod precursors (**2** and **3**), which depends on the metal: while Rh tends to adopt square-planar geometries, Ir prefers TBPY-5 environments facilitated by the  $\eta^2\text{-C}=\text{C}$  coordination of one allyl group. Accordingly, equivalent free allyl groups were observed in the  $^1\text{H}$  NMR spectra of the rhodium complexes (**4** and **6**) at room temperature, as commented on above for  $[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{cod})]$  (**2**; see Experimental Section). Upon cooling, no changes in the spectra were observed, which indicates a lower energy barrier for inversion of the metallacycle than that 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.<sup>23</sup> In addition, two intense bands at 2159 and 2114  $\text{cm}^{-1}$ , assigned to the symmetric and anti-symmetric stretches of the isocyanide ligands, were observed in the IR spectrum of **4**. These frequencies compare well with those shown by  $[\text{Rh}(\text{Tp}^{\text{Me}_2})(\text{CNR})_2]$  (R = neopentyl, xylyl, Me), in which a  $\kappa^2\text{N}$  coordination of the  $\text{Tp}^{\text{Me}_2}$  ligand was confirmed both in solution and in the solid state.<sup>24</sup> However, the nature of complex **4** differs drastically from that of the Tp complex  $[\{\text{RhTp}\}_2(\mu\text{-CNCy})_3]$ , which is stabilized by three isocyanide bridging moieties.<sup>25</sup>

On the other hand, VT-NMR spectra of the iridium counterparts (**5** and **7**) indicated both to be pentacoordinated species at low temperature but to undergo a fast allyl exchange at room temperature. As a way of example, Figure 2 shows the

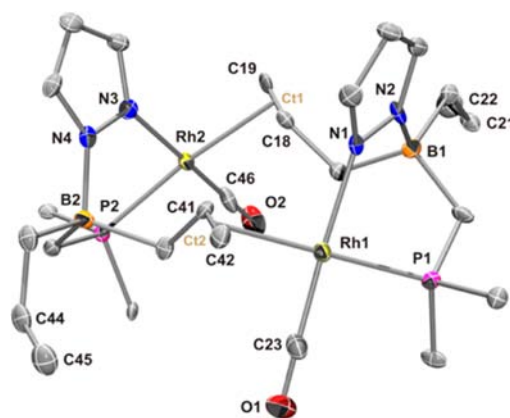


**Figure 2.**  $^1\text{H}$  NMR spectra of complex **5** in toluene- $d_6$ , showing the two inequivalent allyl groups at  $-50\text{ }^\circ\text{C}$  (bottom) and their fast exchange at room temperature (top).

$^1\text{H}$  NMR spectra corresponding to the low- and fast-exchange region for the iridium isocyanide complex **5**.

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

As indicated above, attempts to isolate **6** led to the loss of one carbonyl ligand with crystallization of the product as the dimer **8**. Figure 3 shows the molecular structure of **8**, and selected bond lengths and angles are summarized in Table 2. Complex **8**



**Figure 3.** Molecular structure (ORTEP at the 50% level) of complex **8**. H atoms have been removed, and only the *ipso*-C atoms of the phenyl groups are shown for clarity.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Complex **8**<sup>a</sup>

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)

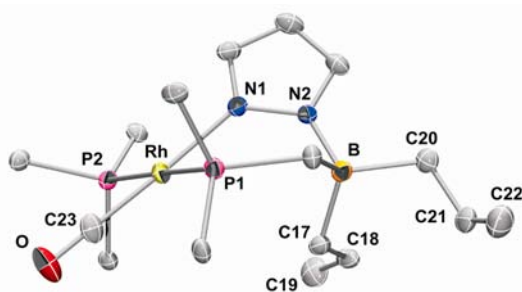
<sup>a</sup>Ct1 and Ct2 represent the middle points of C18 and C19 and of C41 and C42, respectively.

consists of two mononuclear subunits brought together by two bridging allyl groups coordinated in a  $\mu\text{-}\eta^2\text{-C}=\text{C}$  fashion, forming in this way a 12-membered dimetallacycle. In each metallic subunit, the Rh 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  $\text{C}=\text{C}$  double bond of the allyl group from the other metallic subunit. In this geometry, the carbonyl and allyl groups having the greatest trans influence<sup>28</sup> are mutually cis, while the good  $\sigma$ -donor pyrazolyl group is opposite the strongest  $\pi$  acceptor (CO).<sup>29</sup>

The Rh–C(olefin) bond distances (2.305 Å in average) were found to be considerably longer than those found for some rhodium(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  $[\text{RhX}(\text{L})_2(\text{C}_2\text{H}_4)]$ ,<sup>30</sup>  $[\text{Rh}(\text{L}_2)(\text{C}_2\text{H}_4)_2]$ ,<sup>31</sup> and  $[\text{Rh}(\text{mer-L}_3)(\text{C}_2\text{H}_4)]^{\text{m}}$ ,<sup>32</sup> 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  $\pi$ -back-donation from the metal to the olefin.

In good agreement, the signals of the coordinated  $\text{CH}_2=\text{CH}-$  moiety were only slightly shifted upfield (4.91 ppm in average) compared to the uncoordinated one (5.57 ppm in average) in the  $^1\text{H}$  NMR spectrum.

P- and N-donor ligands cleave the dinuclear unit in **8** to generate the square-planar carbonyl complexes  $[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{CO})\text{L}]$  [ $\text{L} = \text{pyridine}$  (**9**);  $\text{NH}_3$ , **10**;  $\text{PPh}_3$ , **11**;  $\text{PMe}_3$ , **12**]. Complexes **9**, **11**, and **12** were isolated as yellow solids in good yield, but formation of the  $\text{NH}_3$  compound **10** was found to be reversible; work-up only led to recovery of the starting material. It was, however, completely characterized in solution because its synthesis was quantitative (NMR evidence; see Experimental Section). The  $\kappa\text{N},\kappa\text{P}$  coordination of the ligand to Rh 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 the 50% level) of complex  $[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{CO})\text{PPh}_3]$  (**11**). H atoms have been removed, and only the *ipso*-C atoms of the phenyl groups are shown for clarity.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) 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 Rh atom is bound to the N atom of the pyrazolyl and the P atoms of the scorpionate ligand, a carbonyl group, and the P atom from  $\text{PPh}_3$ . Both phosphane donors are placed mutually trans, while the pyrazolyl group remains trans to the strongest  $\pi$  acceptor (CO) as observed for **8**. The six-membered metallacycle (Rh–N–N–B–C–P) shows the expected puckered conformation, which minimizes the steric repulsion between the  $\text{H}^3$  proton from the pyrazolyl and the phenyl groups of  $\text{PPh}_3$ . The terminal CO ligands in **9–12** were located cis to the phosphane arm of the ligand ( $J_{\text{C,P}} = 12\text{--}17$  Hz), while both allyl groups were found to be noncoordinated to Rh

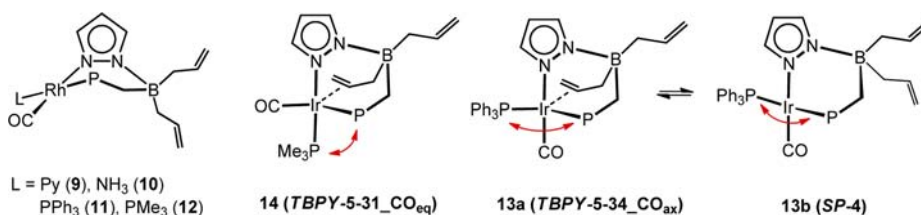
( $^1\text{H}$  NMR evidence), information that confirms that they are square-planar complexes with the ligand in the bidentate  $\kappa\text{N},\kappa\text{P}$  coordination mode (Chart 1). Moreover, as found for **11** in the solid state, both phosphane groups in **11** and **12** showed a mutual trans disposition as deduced from the large  $J_{\text{P}^{\text{A}},\text{P}^{\text{B}}}$  values of 297 and 309 Hz, respectively. Furthermore, the  $\nu(\text{CO})$  stretchings (toluene/ $\text{C}_6\text{D}_6$ ) of complexes **9–12** (1977, 1972, 1981, and  $1977\text{ cm}^{-1}$ , respectively) reflect a weak influence of the basicity of the ligands (pyridine,  $\text{NH}_3$ ,  $\text{PMe}_3$ , and  $\text{PPh}_3$ , respectively) on the electron density of the metal.

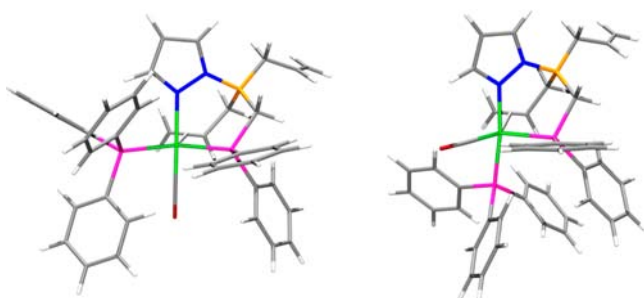
The iridium counterparts  $[\text{Ir}(\kappa^3\text{-A}_2\text{BPN})(\text{CO})\text{PR}_3]$  ( $\text{R} = \text{Ph}$ , **13**;  $\text{Me}$ , **14**) were isolated as white solids in good yield by treating the bis(carbonyl) complex **7** with the corresponding phosphanes. Both complexes displayed the typical features for pentacoordinated species (with an allyl bonded to Ir) in their  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra at low temperature, while they showed a single  $\nu(\text{CO})$  band in their solid-state IR spectra. However, very surprising was the divergence in the values of this stretching,  $2008\text{ cm}^{-1}$  for the  $\text{PPh}_3$  complex **13** and  $1920\text{ cm}^{-1}$  for the  $\text{PMe}_3$  analogue **14**, a difference too large ( $88\text{ cm}^{-1}$ ) to be explained by considering only the basicity of the phosphane ligands. Moreover, the  $J_{\text{P}^{\text{A}},\text{P}^{\text{B}}}$  coupling constants in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra at low temperature (45 Hz for **13** and 12 Hz for **14**) suggest a coupling of the type  $^2J_{\text{P}_{\text{eq}},\text{P}_{\text{eq}}}$  for the former and  $^2J_{\text{P}_{\text{eq}},\text{P}_{\text{ax}}}$  for the latter.<sup>33,34</sup> Consequently, complexes **13** and **14** differ in their stereochemistries. Thus, the axial location of the CO ligand in **13** accounts for the high  $\nu(\text{CO})$  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<sup>35</sup> predict a strong metal–ligand  $\pi$  interaction in the equatorial position, so that lower  $\nu(\text{CO})$  frequencies can be expected for CO(eq) compared to those for CO(ax) in similar complexes. Moreover, a survey of the reported  $\nu(\text{CO})$  frequencies in TBPY-5 iridium complexes of the general formula  $[\text{Ir}(\text{CO})(\text{olefin})\text{P}_2]$ <sup>36</sup> and related ones containing *fac*-tripodal ligands of the type  $[\text{Ir}(\kappa^3\text{-L}_3)(\text{CO})(\text{olefin})]$ <sup>37</sup> agree with this consideration. Hence, we propose a TBPY-5–34\_CO<sub>ax</sub> configuration for **13** and a TBPY-5–31\_CO<sub>eq</sub> for **14** (Chart 1) to account for the spectroscopic data.

Further support from this proposal comes from density functional theory (DFT) studies carried out on the two possible TBPY-5 isomers of **13** and **14**. The TBPY-5–34\_CO<sub>ax</sub> configuration for **13** was found to be  $4.8\text{ kcal mol}^{-1}$  more stable ( $\Delta G$ ) than the TBPY-5–31\_CO<sub>eq</sub>, which was found to be somewhat distorted because of 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  $2.5\text{ kcal mol}^{-1}$  more stable than that with an axial carbonyl in  $[\text{Ir}(\kappa^3\text{-A}_2\text{BPN})(\text{CO})\text{PMe}_3]$  (**14**). Moreover, the observed  $\nu(\text{CO})$  stretching frequencies fit nicely with the DFT-calculated ones for the proposed structures (Table 4).

For the TBPY-5 configurations, the better  $\pi$ -acceptor ligands are expected to be found at the equatorial positions. Complex **14**

**Chart 1.** Stereochemistry of Complexes **9–14**





**Figure 5.** DFT-optimized (b3-lyp, TZVP) geometries of **13** in different configurations: TBPY-5-34\_CO<sub>ax</sub> isomer (left) and TBPY-5-31\_CO<sub>eq</sub> (right). Color code: Ir, green; N, blue; P, pink; B, orange; O, red. P–Ir–P angles (deg): 115.7 and 101.6 for TBPY-5-34\_CO<sub>ax</sub> and TBPY-5-31\_CO<sub>eq</sub>, respectively.

follows this general trend because the CO and C=C groups lie at the equatorial sites. However, steric effects can reverse this trend, as shown for **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) because both P ligands separate from 120 to 180°. 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 an equilibrium can be ascribed to the steric pressure exerted by the bulky PPh<sub>3</sub> ligand, which would facilitate 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**  $\rightleftharpoons$  **13b**:  $\Delta H^\circ = +2.7 \pm 0.1$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = +9.3 \pm 0.5$  cal mol<sup>-1</sup> K<sup>-1</sup>, which results in  $\Delta G^\circ_{293.15\text{ K}} = -0.045$  kcal mol<sup>-1</sup>. In good agreement, values of +3.28 kcal mol<sup>-1</sup> ( $\Delta H^\circ$ ) and -0.20 kcal mol<sup>-1</sup> ( $\Delta G^\circ_{293.15\text{ K}}$ ) were obtained from DFT calculations (see the Supporting Information).

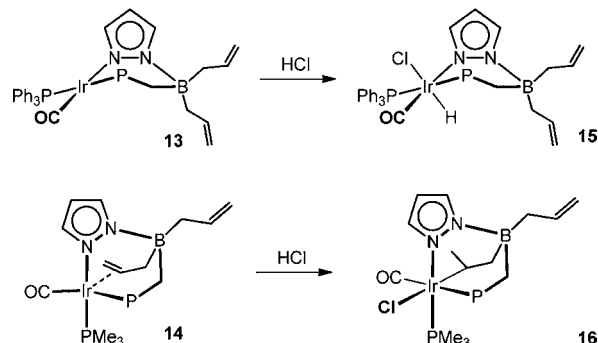
Moreover, both isomers were detected by IR spectroscopy in solution by two broad  $\nu(\text{CO})$  bands at 2000 (m) and 1978 (s) cm<sup>-1</sup>, corresponding to the minor TBPY-5-34\_CO<sub>ax</sub> and the major square-planar isomers, respectively. Again, the frequency of the  $\nu(\text{CO})$  band for the trans square-planar isomer (SP-4) matches satisfactorily with that found by DFT calculations (Table 4).

On the other hand, complex **14** was found to be the sole isomer with a TBPY-5-31\_CO<sub>eq</sub> configuration at room temperature, according to the NMR and IR spectra (see Experimental Section), and hence electronic issues dominate the stereochemistry in this case.

The different structures of the main isomers of **13** and **14** are 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 iridium(III) complexes  $[\text{Ir}(\kappa^2\text{-A}_2\text{BPN})(\text{CO})(\text{Cl})(\text{H})\text{PPh}_3]$  (**15**) and

$[\text{Ir}\{\kappa^3\text{-(allyl)B}(\text{CH}_2\text{CHCH}_3)(\text{CH}_2\text{PPh}_2)(\text{Pz})\}(\text{Cl})(\text{CO})\text{PMe}_3]$  (**16**) respectively, which were isolated as white solids in good yield (Scheme 5).

**Scheme 5.** Protonation Reactions of **13** and **14** Leading to Complexes **15** and **16**



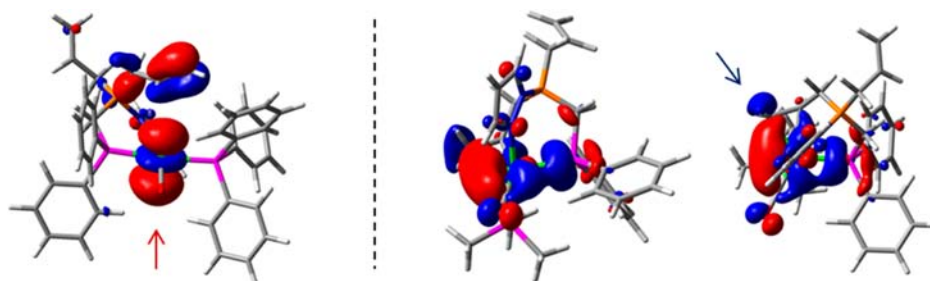
Characterization of complex **15** was achieved by a combination of the usual spectroscopic and analytical methods, which allowed one to detect the phosphane groups mutually trans and the hydrido (at  $\delta = -14.47$  ppm) and CO ligands cis to both P atoms and mutually cis to each other (see the Experimental Section). These data indicated that complex **15** is octahedral, with the scorpionate ligand adopting a  $\kappa\text{P}_2\kappa\text{N}$  coordination mode and the other four sites occupied by PPh<sub>3</sub>, CO, the hydride, and a chloride ligand, a chemical composition confirmed by MALDI spectrometry. Moreover, the shift to higher frequency of the  $\nu(\text{CO})$  band, at 2058 cm<sup>-1</sup>, is in accordance with a decrease of the electron density on the metal or an Ir<sup>III</sup> oxidation state in **15**.

Protonation of the PMe<sub>3</sub> complex **14** with hydrogen chloride followed a different profile and afforded the neutral complex **16**, which did not show hydrido signals in the <sup>1</sup>H NMR spectrum. Instead, there was a new set of resonances that corresponded to a  $\sigma$ -bonded “-CH(Me)CH<sub>2</sub>B” moiety. The spectroscopic data collected for **16** unambiguously pointed out the octahedral structure shown in Scheme 5, which features a new hydrocarbyl arm  $\sigma$ -bonded to Ir (see the Experimental Section for details). The  $\nu(\text{CO})$  band observed at 2061 cm<sup>-1</sup> confirmed the oxidation of the metal to Ir(III) in the reaction. Complex **16** showed a static <sup>1</sup>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 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, which located CO cis to PMe<sub>3</sub> and trans to the phosphane arm because of 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  $[\text{Ir}\{(\text{Hpz})\text{B}(\text{CH}_2\text{CHCH}_3)(\text{CH}_2\text{PPh}_2)(\text{Pz})\}(\text{Cl})(\text{CO})\text{PMe}_3]\text{Cl}$ .<sup>18</sup>

**Table 4.** Experimental and DFT-Calculated  $\nu(\text{CO})$  Stretching Frequencies for **13** and **14**<sup>a</sup>

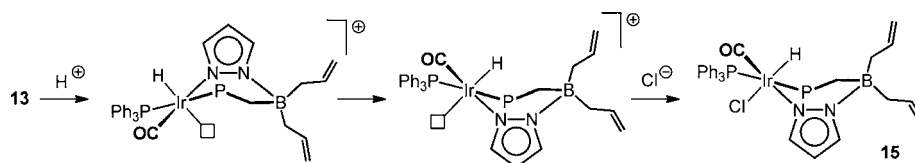
13					14			
solid	toluene	TBPY-5-34	SP-4	TBPY-5-31	solid	toluene	TBPY-5-34	TBPY-5-31
2008	2000, 1978	2004	1971	1938	1920	1928	1992	1935

<sup>a</sup>Calculated DFT frequencies have been corrected by a factor of 0.996.

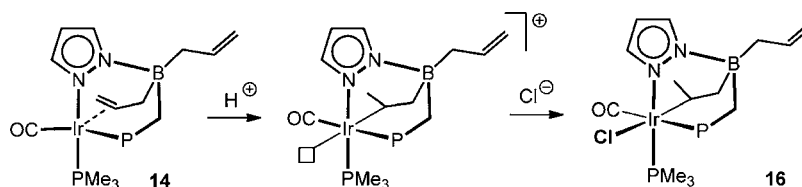


**Figure 6.** HOMO of SP-4 **13** (left) and two views of the HOMO of TBPY-5-31\_CO<sub>eq</sub> **14** (right). The red arrow indicates the external face of the complex, while the blue arrow indicates the C atom in H<sub>2</sub>C= from the coordinated allyl arm.

### Scheme 6. Proposed Mechanism for Protonation of Complex **13**



### Scheme 7. Proposed Mechanism for Protonation of Complex **14**



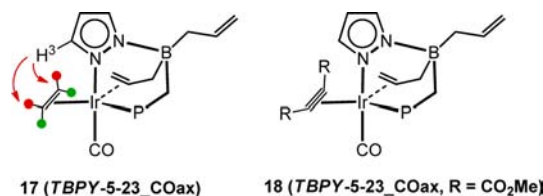
A structural comparison between the iridium(III) complexes **15** and **16** reveals information about the mechanisms following protonation of **13** and **14** with HCl. The square-planar isomer of **13** is favored for a direct protonation at the Ir center (Figure 6, left) from the external face to 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 coordination of the chloride again at the less hindered external face to give the product from a trans oxidative addition of HCl (Scheme 6).<sup>38</sup>

Regarding protonation of the PMe<sub>3</sub> 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 highest occupied molecular orbital (HOMO) mainly formed by the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital of the Ir atom back-donating to both the π\* orbital of the C=C group and the π\* orbital of the C=O ligand (Figure 6).

Consequently, a direct Markovnikov addition of the proton to the C atom in H<sub>2</sub>C= (marked with the blue arrow in Figure 6) seems to be the most probable initial step, although 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).

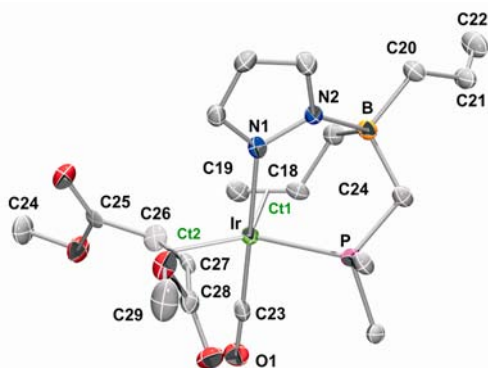
Related complexes of the formula [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(CO)L] [L = H<sub>2</sub>C=CH<sub>2</sub>, **17**; MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me, **18**] were prepared by reacting the bis(carbonyl) compound **7** with ethylene or MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me (dmd), respectively (Chart 2). The ethylene complex **17** was found to be static at room temperature (i.e., no ethylene rotation around the Ir–C<sub>2</sub>H<sub>4</sub> axis takes place on the NMR time scale), which agrees with a η<sup>2</sup>-C=C coordination coplanar with the equatorial plane of a trigonal-bipyramidal

### Chart 2. Stereochemistries of Complexes **17** and **18**



arrangement. As a matter of fact, <sup>1</sup>H–<sup>1</sup>H NOESY experiments corroborated the ethylene ligand to be in the equatorial site of the TBPY-5 geometry because the olefinic protons located upward of the equatorial plane (marked with red circles) gave a strong nuclear Overhauser enhancement effect with the H<sup>3</sup> proton of the pyrazolyl arm (Chart 2). Accordingly, the ν(CO) stretching (C<sub>6</sub>D<sub>6</sub>) at 2013 cm<sup>-1</sup> fits quite well to that expected for a carbonyl ligand at the axial site, as observed for complex **13**.<sup>39</sup> Because steric arguments can be ruled out as a result of the small size of the ethylene ligand, we can conclude that the TBPY-5-23\_CO<sub>ax</sub> configuration represents the most stable isomer on the basis of electronic issues, as observed for related complexes.<sup>39</sup>

Concerning the complex [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(CO)(dmd)] (**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 diffraction study for **18**. Figure 7 shows the ORTEP representation of the molecule, and Table 5 collects selected bond lengths and angles. The Ir 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<sup>2</sup>-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 the 50% level) of complex **18**. H atoms and the solvent of crystallization have been removed, and only the *ipso*-C atoms of the phenyl groups are shown for clarity.

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for Complex **18**<sup>a</sup>

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)		

<sup>a</sup>Ct1 and Ct2 represent the middle points of C18 and C19 and of C27 and C28, respectively.

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 C atoms 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<sub>2</sub>CMe<sub>3</sub>)(P(*p*-tolyl)<sub>3</sub>)(dmad)]<sup>39</sup> and [IrMe(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmad)].<sup>40</sup>

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

The isoelectronic isocyanide compound **5** reacted with dmad in a different way, keeping the isocyanide ligands to afford the complex [Ir(κ<sup>2</sup>-A<sub>2</sub>BPN)(CN<sup>t</sup>Bu)<sub>2</sub>(dmad)] (**19**) in good yield. Moreover, two inequivalent noncoordinated allylic arms were clearly observable in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **19**. In addition, the coordinated dmad showed coupling constants *J*<sub>C,P</sub> of 6 and 66 Hz, with the latter suggesting an angle C–Ir–P bigger than 140°, which is intermediate between octahedral (OC-6) and TBPY-5 geometries around Ir. Furthermore, the IR stretching

frequencies of the isocyanide ligands in complex **19** are shifted ca. 116 cm<sup>-1</sup> to higher frequencies relative to **5**.

Most probably, the different reactivity involving the addition of dmad to complexes [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(L)<sub>2</sub>] (L = CN<sup>t</sup>Bu, **5**; CO, **7**) could be ascribed to the stronger bonding of the isocyanide to Ir. In fact, complex **18** is even formed in the presence of a CO atmosphere.

## CONCLUSION

In summary, we report the straightforward synthesis of a novel hybrid scorpionate ligand, [(allyl)<sub>2</sub>B(CH<sub>2</sub>PPh<sub>2</sub>)(Pz)]<sup>-</sup>, which is equipped with different donors, including hard N and soft P and C atoms. We have disclosed the coordination behavior 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 rhodium(I) complexes are square-planar, with the ligand coordinated in a bidentate κN,κP fashion, although in a specific example (i.e., the dinuclear carbonyl complex **8**), the ligand adopts the unexpected κN,κP,μ-η<sup>2</sup>-C=C coordination mode. A general behavior observed for these rhodium complexes is the dynamic fast inversion of the six-membered metallacycle (Rh–N–N–B–C–P).

The iridium(I) complexes described herein tend to adopt pentacoordinated TBPY-5 geometries with one allyl arm coordinated; i.e., the ligand adopts a κN,κP,η<sup>2</sup>-C=C coordination mode. The lability of the iridium–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<sup>3</sup>-A<sub>2</sub>BPN)(cod)] (**3**) and [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(L)<sub>2</sub>] (L = CN<sup>t</sup>Bu, **5**; CO, **7**) adopt TBPY-5 structures at low temperature but undergo a fast allyl exchange based on a sequential coordination and decoordination of both allyl groups upon heating. On the contrary, this allyl exchange was not observed for complexes with two different ligands like [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(CO)L] (L = PMe<sub>3</sub>, **14**; CH<sub>2</sub>=CH<sub>2</sub>, **17**; MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me, **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 **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<sup>I</sup>-TBPY-5 complexes having the CO ligand at the axial site led to, at a first glance, counterintuitive high ν(CO) stretching frequencies, 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 the experimental and calculated ν(CO) frequencies.

The phosphane compounds [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(CO)PR<sub>3</sub>] are basic enough to be protonated by HCl, in a reaction driven by the stereochemistry of the starting complexes. Direct protonation of iridium occurs for the square-planar PPh<sub>3</sub> isomer (**13**), but a direct attack of the proton to the C atom of H<sub>2</sub>C= in the TBPY-5 PMe<sub>3</sub> compound (**14**) seems to be the most probable pathway for the synthesis of **15** and **16**, respectively. The stronger bonding to Ir of isocyanides compared to the carbonyl ligands is probably the origin of the different reactivity of complexes [Ir(κ<sup>3</sup>-A<sub>2</sub>BPN)(L)<sub>2</sub>] (L = CN<sup>t</sup>Bu, **5**; CO, **7**) toward dmad, which results in complexes **18** and **19**, respectively.

## EXPERIMENTAL SECTION

**Starting Materials and Physical Methods.** All of 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.<sup>42</sup> Complexes  $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ ,<sup>43</sup>  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ ,<sup>44</sup> and  $[\text{Ir}(\text{acac})(\text{cod})]$ <sup>45</sup> and compounds  $[\text{Li}(\text{tmen})][\text{CH}_2\text{PPh}_2]$ <sup>46</sup> and  $[\text{B}(\text{CH}_2\text{CH}=\text{CH}_2)_3]$ <sup>47</sup> were prepared according to literature procedures. All of 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. Fast-atom-bombardment mass spectra were recorded in a VG Autospec double-focusing mass spectrometer. The ions were produced by the standard  $\text{Cs}^+$  gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as the matrix. Electrospray ionization mass spectra were recorded in methanol on a Bruker MicroTof-Q using sodium formate as the reference. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Microflex mass spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile or dithranol as the matrix. NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers operating at 300.13 and 400.13 MHz, respectively, for  $^1\text{H}$ . Chemical shifts are reported in ppm and referenced to  $\text{SiMe}_4$ , using the internal signal of the deuterated solvent as the reference ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). 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  $\text{cm}^{-1}$ ) equipped with attenuated total reflectance.

**Synthesis of the Compounds.**  $[\text{Li}(\text{tmen})][\text{A}_2\text{BPN}]$  (**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  $[\text{Li}(\text{tmen})][\text{CH}_2\text{PPh}_2]$  (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. The 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 °C for 1 h 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  $\text{C}_{28}\text{H}_{41}\text{BLiN}_4\text{P}$  (482.39): C, 69.71; H, 8.57; N, 11.61. Found: C, 69.62; H, 8.49; N, 11.56.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  8.10 (s, 1H, pz), 7.34 (m, 4H,  $\text{H}^o$  PPh<sub>2</sub>), 7.14 (m, 7H,  $\text{H}^{m+p}$  PPh<sub>2</sub> + pz), 6.41 (s, 1H, pz), 6.32 (m, 2H, =CH), 5.16 (m, 4H, =CH<sub>2</sub>), 1.95 (d,  $J$  = 7.8 Hz, 4H, CH<sub>2</sub>-allyl), 1.80 (s, 12H, CH<sub>3</sub>-tmen), 1.72 (m, 6H, CH<sub>2</sub>-tmen + CH<sub>2</sub>P).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  -13.6 (br s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  144.3 (=CH-allyl), 137.6 (pz), 133.5 (pz), 132.5 (d,  $J_{\text{C,P}}$  = 15 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 128.4–127.3 (PPh<sub>2</sub>), 109.8 (=CH<sub>2</sub>-allyl), 102.7 (pz), 56.6 (CH<sub>2</sub>-tmen), 45.6 (CH<sub>3</sub>-tmen), 33.9 (br s, CH<sub>2</sub>-allyl), 22.7 (br, CH<sub>2</sub>P).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  -5.89 (s). MS (MALDI-TOF<sup>+</sup>):  $m/z$  439.1 (40%,  $[\text{M} - \text{allyl} - \text{H}]^+$ ).

$[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{cod})]$  (**2**). Solid  $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$  (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  $\text{C}_{30}\text{H}_{37}\text{BN}_2\text{PRh}$  (570.33): C, 63.18; H, 6.54; N, 4.91. Found: C, 63.08; H, 6.49; N, 4.87.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.63 (m, 4H,  $\text{H}^o$  PPh<sub>2</sub>), 7.59 (d,  $J$  = 1.7 Hz, 1H, pz), 7.26 (d,  $J$  = 1.8 Hz, 1H, pz), 7.07 (m, 6H,  $\text{H}^{m+p}$  PPh<sub>2</sub>), 6.36 (m, 2H, =CH-allyl), 5.97 (t,  $J$  = 2.1 Hz, 1H, pz), 5.43 (dd,  $J$  = 17.0 and 2.9 Hz, 2H) and 5.28 (dd,  $J$  = 10.1 and 3.0 Hz, 2H) (=CH<sub>2</sub>-allyl), 4.99 (m, 2H) and 3.40 (m, 2H) (=CH-cod), 2.93 (m, 2H, CH<sub>2</sub>-cod), 2.39 (m, 4H, CH<sub>2</sub>-allyl), 2.35 (m, 2H) and 1.79 (m, 4H) (CH<sub>2</sub>-cod), 1.68 (d,  $J_{\text{H,P}}$  = 14.3 Hz, 2H, CH<sub>2</sub>P).  $^1\text{H}$  NMR (400 MHz, toluene- $d_8$ , -80 °C): selected resonances  $\delta$  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 much broader for unequivocal assignment.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  29.1

(d,  $J_{\text{P,Rh}}$  = 144 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  143.3 (=CH-allyl), 138.5 (pz), 135.8 (d,  $J_{\text{C,P}}$  = 39 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 134.9 (pz), 133.0 (d,  $J_{\text{C,P}}$  = 10 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 129.2 (d,  $J_{\text{C,P}}$  = 2 Hz,  $\text{C}^m$  PPh<sub>2</sub>), 127.9 ( $\text{C}^p$  PPh<sub>2</sub>), 110.6 (=CH<sub>2</sub>-allyl), 104.5 (pz), 101.1 (dd,  $J_{\text{C,P}}$  = 13 Hz,  $J_{\text{C,Rh}}$  = 11 Hz) and 72.5 (d,  $J_{\text{C,Rh}}$  = 12 Hz) (=CH-cod), 35.0 (br, CH<sub>2</sub>-allyl), 32.4 and 28.8 (CH<sub>2</sub>-cod), 19.8 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>):  $m/z$  529.2 (100%,  $[\text{M} - \text{allyl}]^+$ ).

$[\text{Ir}(\kappa^2\text{-A}_2\text{BPN})(\text{cod})]$  (**3**). Solid  $[\text{Ir}(\text{acac})(\text{cod})]$  (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  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ : To a white suspension of **1** (0.13 g, 0.28 mmol) in toluene (10 mL) was added solid  $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$  (0.09 g, 0.14 mmol). The mixture was stirred for 1 h and passed through a pad of Celite 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: 0.12 g (68%). Anal. Calcd for  $\text{C}_{30}\text{H}_{37}\text{BIRn}_2\text{P}$  (659.64): C, 54.63; H, 5.65; N, 4.25. Found: C, 54.59; H, 5.59; N, 4.18.  $^1\text{H}$  NMR (400 MHz, toluene- $d_8$ , 100 °C):  $\delta$  7.59 (br s, 1H, pz), 7.41 (m, 4H, PPh<sub>2</sub>), 7.08 (m, 6H, PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 3.4–2.4 (flat, 4H, =CH-cod), 2.12 (m, 4H, CH<sub>2</sub>-cod), 1.72 (br m, 4H, CH<sub>2</sub>-cod), 1.63 (br m, 4H, CH<sub>2</sub>-allyl), 1.15 ( $J_{\text{H,P}}$  = 12.6 Hz, 2H, CH<sub>2</sub>P).  $^1\text{H}$  NMR (400 MHz, toluene- $d_8$ , -80 °C):  $\delta$  7.61 (br, 1H, pz), 7.27 (m, 2H,  $\text{H}^o$  PPh<sub>2</sub>), 7.14 (m, 3H,  $\text{H}^{m+p}$  PPh<sub>2</sub>), 7.08 (m, 2H,  $\text{H}^m$  PPh<sub>2</sub>), 6.99 (m, 1H,  $\text{H}^p$  PPh<sub>2</sub>), 6.95 (m, 2H,  $\text{H}^o$  PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 3.92 (d,  $J$  = 4.9 Hz, 1H, =CH<sub>2</sub>- $\eta^2$ -allyl), 3.70 (s, 1H, =CH-cod), 3.60 (m, 2H, =CH-cod + =CH- $\eta^2$ -allyl), 2.91 (s, 1H, =CH-cod), 2.25 (m, 2H, CH<sub>2</sub>-cod), 2.10 (m, 2H, =CH<sub>2</sub>- $\eta^2$ -allyl + CH<sub>2</sub>- $\eta^2$ -allyl), 1.97 (m, 2H, CH<sub>2</sub>-allyl), 1.88 (m, 1H, CH<sub>2</sub>-cod), 1.72 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl), 1.64 (m, 1H, CH<sub>2</sub>P), 1.60 (m, 2H, CH<sub>2</sub>-cod + =CH-cod), 1.56 (m, 1H, CH<sub>2</sub>-cod), 1.37 (m, 1H), 1.09 (m, 2H, CH<sub>2</sub> cod), 0.73 (m, 1H, CH<sub>2</sub>P).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  1.6.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, toluene- $d_8$ , -80 °C):  $\delta$  143.6 (=CH-allyl), 142.6 (d,  $J_{\text{C,P}}$  = 35 Hz) and 138.8 (d,  $J_{\text{C,P}}$  = 40 Hz) ( $\text{C}^o$  PPh<sub>2</sub>), 134.9 and 133.6 (pz), 133.4 (d,  $J_{\text{C,P}}$  = 8 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 130.8 (d,  $J_{\text{C,P}}$  = 9 Hz,  $\text{C}^m$  PPh<sub>2</sub>), 129.6 ( $\text{C}^p$  PPh<sub>2</sub>), 128.3 (m,  $\text{C}^{o+m+p}$  PPh<sub>2</sub>), 110.9 (=CH<sub>2</sub>-allyl), 104.5 (pz), 75.1, 70.7, and 64.9 (d,  $J_{\text{C,P}}$  = 6 Hz) (=CH-cod), 63.1 (d,  $J_{\text{C,P}}$  = 7 Hz, =CH- $\eta^2$ -allyl), 58.8 (d,  $J_{\text{C,P}}$  = 21 Hz, =CH-cod), 47.3 (d,  $J_{\text{C,P}}$  = 8 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 35.2 (br m, CH<sub>2</sub>-allyl), 34.8 (br m, CH<sub>2</sub>- $\eta^2$ -allyl), 31.9, 31.4, 30.6, and 30.4 (CH<sub>2</sub>-cod), 20.2 (br m, CH<sub>2</sub>P).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  0.55 (br s). MS (MALDI-TOF<sup>+</sup>):  $m/z$  619.1 (100%,  $[\text{M} - \text{allyl}]^+$ ).

$[\text{Rh}(\kappa^2\text{-A}_2\text{BPN})(\text{CN}^t\text{Bu})_2]$  (**4**). To a yellow solution of **2** (0.12 g, 0.21 mmol) in diethyl ether (10 mL) was added slowly via syringe  $\text{CN}^t\text{Bu}$  (39 mg, 53  $\mu\text{L}$ , 0.47 mmol), 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 a 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  $\text{C}_{32}\text{H}_{43}\text{BN}_4\text{PRh}$  (628.41): C, 61.16; H, 6.90; N, 8.92. Found: C, 61.09; H, 6.80; N, 8.81. IR (toluene,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2159 (s), 2114 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.91 (m, 4H,  $\text{H}^o$  PPh<sub>2</sub> + 1H, pz), 7.80 (d,  $J$  = 1.8 Hz, 1H, pz), 7.09 (m, 6H,  $\text{H}^{m+p}$  PPh<sub>2</sub>), 6.39 (m, 2H, =CH-allyl), 6.14 (t,  $J$  = 2.1 Hz, 1H, pz), 5.22 (dd,  $J$  = 16.8 and 3.3 Hz, 2H) and 5.08 (dd,  $J$  = 12.6 and 3.3 Hz, 2H) (=CH<sub>2</sub>-allyl), 2.86 (m, 2H) and 2.13 (m, 2H) (CH<sub>2</sub>-allyl), 1.58 (d,  $J_{\text{H,P}}$  = 13.2 Hz, 2H, CH<sub>2</sub>P), 1.99 (s, 9H) and 0.86 (s, 9H) ( $\text{CN}^t\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  28.2 (d,  $J_{\text{P,Rh}}$  = 130 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  144.0 (=CH-allyl), 142.5 (pz), 139.9 (d,  $J_{\text{C,P}}$  = 39 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 134.0 (pz), 133.5 (d,  $J_{\text{C,P}}$  = 12 Hz,  $\text{C}^o$  PPh<sub>2</sub>), 128.5 (d,  $J_{\text{C,P}}$  = 2 Hz,  $\text{C}^m$  PPh<sub>2</sub>), 127.7 ( $\text{C}^p$  PPh<sub>2</sub>), 109.5 (=CH<sub>2</sub>-allyl), 103.4 (pz), 55.9 and 55.6 ( $\text{CMe}_3$ ), 35.1 (br, CH<sub>2</sub>-allyl), 30.0 and 29.8 ( $\text{CMe}_3$ ), 20.6 (br s, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>):  $m/z$  586.2 (10%,  $[\text{M} - \text{allyl}]^+$ ).

**[Ir( $\kappa^3$ -A<sub>2</sub>BPN)(CN<sup>t</sup>Bu)<sub>2</sub>] (5).** To a solution of **3** (0.10 g, 0.15 mmol) in diethyl ether (7 mL) was added dropwise via syringe CN<sup>t</sup>Bu (39  $\mu$ L, 0.34 mmol). The color of the solution changed rapidly to orange, and after 20 min, the reaction mixture was evaporated to dryness, affording an orange oily residue. The 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<sub>32</sub>H<sub>43</sub>BrN<sub>4</sub>P (717.72): C, 53.55; H, 6.04; N, 7.81. Found: C, 53.48; H, 5.95; N, 7.67. IR (toluene, cm<sup>-1</sup>):  $\nu$ (CN) 2085 (s), 2043 (s). <sup>1</sup>H NMR (300 MHz, toluene-*d*<sub>8</sub>, -50 °C):  $\delta$  8.05 (s, 1H, pz), 7.74 (m, 2H) and 7.63 (m, 2H) (H<sup>o</sup> PPh<sub>2</sub>), 7.43 (s, 1H, pz), 7.00 (m, 6H, H<sup>m+p</sup> PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 3.26 (m, 1H, =CH<sub>2</sub>), 3.10 (m, 1H, =CH), 1H, =CH<sub>2</sub> + 1H, CH<sub>2</sub>) ( $\eta^2$ -allyl), 2.22 (m, 2H, CH<sub>2</sub>-allyl + 1H, CH<sub>2</sub>P), 1.31 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl + 1H, CH<sub>2</sub>P), 1.01 (s, 9H) and 0.46 (s, 9H) (CN<sup>t</sup>Bu). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene-*d*<sub>8</sub>, 25 °C):  $\delta$  0.0. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, toluene-*d*<sub>8</sub>, -50 °C):  $\delta$  144.6 (=CH-allyl), 142.7 (d, *J*<sub>C,P</sub> = 36 Hz) and 141.6 (d, *J*<sub>C,P</sub> = 25 Hz) (CN<sup>t</sup>Bu), 141.1 (pz), 137.3 (d, *J*<sub>C,P</sub> = 43 Hz) and 137.3 (d, *J*<sub>C,P</sub> = 49 Hz) (C<sup>i</sup> PPh<sub>2</sub>), 133.7 (d, *J*<sub>C,P</sub> = 13 Hz, C<sup>o</sup> PPh<sub>2</sub>), 131.4 (pz), 131.1 (d, *J*<sub>C,P</sub> = 10 Hz, C<sup>o</sup> PPh<sub>2</sub>), 128 (m, C<sup>m+p</sup> PPh<sub>2</sub>), 110.4 (=CH<sub>2</sub>-allyl), 105.0 (pz), 56.1 and 55.9 (CMe<sub>3</sub>), 40.0 (d, *J*<sub>C,P</sub> = 6 Hz, =CH- $\eta^2$ -allyl), 35.2 (br, CH<sub>2</sub>-allyl), 30.9 (d, *J*<sub>C,P</sub> = 25 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 30.2 and 29.9 (CMe<sub>3</sub>), 24.9 (br, CH<sub>2</sub>- $\eta^2$ -allyl), 21.4 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 719.2 (5%, [M - H]<sup>+</sup>), 677.2 (100%, [M - allyl]<sup>+</sup>).

**[Rh( $\kappa^2$ -A<sub>2</sub>BPN)(CO)<sub>2</sub>] (6).** A solution of **2** (0.02 g, 0.03 mmol) in toluene-*d*<sub>8</sub> (0.4 mL) was shaken with CO for 10 min to give a clear yellow solution. NMR monitoring of the sample showed a clean and quantitative conversion to **6**. IR (toluene, cm<sup>-1</sup>):  $\nu$ (CO) 2077 (s), 2018 (s). IR (cyclohexane, cm<sup>-1</sup>):  $\nu$ (CO) 2083 (s), 2020 (s). <sup>1</sup>H NMR (300 MHz, toluene-*d*<sub>8</sub>, -50 °C):  $\delta$  7.38 (dd, *J* = 6.7 and 3.1 Hz, 2H, H<sup>o</sup> PPh<sub>2</sub>), 7.35 (d, *J* = 2.2 Hz, 1H, pz), 7.32 (dd, *J* = 6.2 and 3.1 Hz, 2H, H<sup>o</sup> PPh<sub>2</sub>), 7.14 (br, 1H, pz), 6.90 (m, 6H, H<sup>m+p</sup> PPh<sub>2</sub>), 6.11 (ddd, *J* = 17.3, 14.9, and 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<sub>2</sub>-allyl), 2.28 (dd, *J* = 12.2 and 7.7 Hz, 2H) and 1.78 (dd, *J* = 12.0 and 8.4 Hz, 2H) (CH<sub>2</sub>-allyl), 1.50 (d, *J*<sub>H,P</sub> = 14.9 Hz, 2H, CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene-*d*<sub>8</sub>, 25 °C):  $\delta$  30.9 (d, *J*<sub>P,Rh</sub> = 120 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, toluene-*d*<sub>8</sub>, -50 °C):  $\delta$  189.0 (br) and 185.4 (d, *J*<sub>C,Rh</sub> = 66 Hz) (CO), 142.9 (=CH-allyl), 141.8 (pz), 135.8 (d, *J*<sub>C,P</sub> = 45 Hz, C<sup>i</sup> PPh<sub>2</sub>), 134.7 (pz), 132.4 (d, *J*<sub>C,P</sub> = 11 Hz, C<sup>o</sup> PPh<sub>2</sub>), 130.0 (d, *J*<sub>C,P</sub> = 2 Hz, C<sup>o</sup> PPh<sub>2</sub>), 128.5 (d, *J*<sub>C,P</sub> = 10 Hz, C<sup>m</sup> PPh<sub>2</sub>), 105.3 (=CH<sub>2</sub>-allyl), 104.5 (pz), 34.3 (br, CH<sub>2</sub>-allyl), 19.1 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 517.3 (2%, [M - H]<sup>+</sup>).

**[Ir( $\kappa^3$ -A<sub>2</sub>BPN)(CO)<sub>2</sub>] (7).** **7** was prepared as described for **6** starting from a solution of **3** (0.03 g, 0.05 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.4 mL). IR (diethyl ether, cm<sup>-1</sup>):  $\nu$ (CO) 2053 (s), 1986 (s). IR (cyclohexane, cm<sup>-1</sup>):  $\nu$ (CO) 2053 (s), 1982 (s). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -55 °C):  $\delta$  7.57 (s, 1H, pz), 7.51–7.34 (m, 10H, PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 3.56 (m, 1H, =CH), 3.35 (m, 1H, =CH<sub>2</sub>) and 1.96 (m, 1H, =CH<sub>2</sub>) ( $\eta^2$ -allyl), 1.62 (m, 1H, CH<sub>2</sub>P), 1.60 (m, 1H, CH<sub>2</sub>-allyl), 1.57 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl), 1.44 (m, 1H, CH<sub>2</sub>-allyl), 1.35 (m, 1H, CH<sub>2</sub>P), 0.20 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -0.6. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -55 °C):  $\delta$  184.6 (d, *J*<sub>C,P</sub> = 17 Hz) and 166.8 (d, *J*<sub>C,P</sub> = 5 Hz) (CO), 143.8 (pz), 143.1 (=CH-allyl), 137.6 (d, *J*<sub>C,P</sub> = 43 Hz) and 135.4 (d, *J*<sub>C,P</sub> = 43 Hz) (C<sup>i</sup> PPh<sub>2</sub>), 132.8 (pz), 132.4 (d, *J*<sub>C,P</sub> = 12 Hz) and 130.4 (d, *J*<sub>C,P</sub> = 11 Hz) (C<sup>o</sup> PPh<sub>2</sub>), 128.5 (m, C<sup>m+p</sup> PPh<sub>2</sub>), 110.7 (=CH<sub>2</sub>-allyl), 106.1 (pz), 53.8 (br, =CH- $\eta^2$ -allyl), 36.6 (d, *J*<sub>C,P</sub> = 16 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 33.9 (br, CH<sub>2</sub>-allyl), 24.4 (br, CH<sub>2</sub>- $\eta^2$ -allyl), 16.8 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 607.1 (100%, [M]<sup>+</sup>).

**[Rh(A<sub>2</sub>BPN)(CO)<sub>2</sub>] (8).** A solution of **2** (0.15 g, 0.26 mmol) in diethyl ether (20 mL) was bubbled with CO 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 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<sub>46</sub>H<sub>50</sub>B<sub>2</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub> (908.31): C, 56.36; H, 5.14; N, 5.72. Found: C, 56.28; H, 5.02; N, 5.68. IR (toluene, cm<sup>-1</sup>):  $\nu$ (CO) 1995 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.55 (m, 8H, H<sup>o</sup> PPh<sub>2</sub>),

7.32 (d, *J* = 2.3 Hz, 2H, pz), 6.91 (m, 12H, H<sup>m+p</sup> PPh<sub>2</sub>), 6.71 (d, *J* = 1.9 Hz, 2H, pz), 6.33 (dq, *J* = 17.2 and 8.3 Hz, 2H, =CH-allyl), 5.60 (t, *J* = 2.5 Hz, 2H, pz), 5.24 (dd, *J* = 16.9 and 2.9 Hz, 2H) and 5.13 (dd, *J* = 10.0 and 2.8 Hz, 2H) (=CH<sub>2</sub>-allyl), 4.98 (br, 2H, =CH- $\eta^2$ -allyl + 2H, =CH<sub>2</sub>- $\eta^2$ -allyl), 4.77 (d, *J* = 11.0 Hz, 2H, CH<sub>2</sub>- $\eta^2$ -allyl), 4.45 (d, *J* = 5.6 Hz, 2H, =CH<sub>2</sub>- $\eta^2$ -allyl), 2.09 (t, *J* = 10.5 Hz, 2H, CH<sub>2</sub>- $\eta^2$ -allyl), 1.95 (m, 2H) and 1.84 (m, 2H) (CH<sub>2</sub>-allyl), 1.72 (t, *J*<sub>H,P</sub> = 15.2 Hz, 2H) and 1.57 (t, *J*<sub>H,P</sub> = 13.7 Hz, 2H) (CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  30.6 (d, *J*<sub>P-Rh</sub> = 150 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  192.1 (dd, *J*<sub>C,Rh</sub> = 71 Hz, *J*<sub>C,P</sub> = 14 Hz, CO), 142.1 (=CH-allyl), 138.7 (dd, *J*<sub>C,P</sub> = 46, 3 Hz, C<sup>i</sup> PPh<sub>2</sub>), 138.4 (pz), 135.0 (d, *J*<sub>C,P</sub> = 48 Hz, C<sup>i</sup> PPh<sub>2</sub>), 134.8 (pz), 133.5 (d, *J*<sub>C,P</sub> = 11 Hz) and 131.5 (d, *J*<sub>C,P</sub> = 11 Hz) (C<sup>o</sup> PPh<sub>2</sub>), 129.6 (d, *J*<sub>C,P</sub> = 2 Hz) and 129.2 (d, *J*<sub>C,P</sub> = 2 Hz) (C<sup>o</sup> PPh<sub>2</sub>), 128.3 (d, *J*<sub>C,P</sub> = 10 Hz) and 128.1 (d, *J*<sub>C,P</sub> = 10 Hz) (C<sup>m</sup> PPh<sub>2</sub>), 126.7 (dd, *J*<sub>C,Rh</sub> = 18 Hz, *J*<sub>C,P</sub> = 7 Hz, =CH- $\eta^2$ -allyl), 111.4 (=CH<sub>2</sub>-allyl), 105.2 (pz), 79.8 (dd, *J*<sub>C,Rh</sub> = 12 Hz, *J*<sub>C,P</sub> = 6 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 45.7 (br s, CH<sub>2</sub>- $\eta^2$ -allyl), 31.7 (CH<sub>2</sub>-allyl), 21.5 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 840 (M<sup>+</sup> - allyl - CO).

**[Rh( $\kappa^2$ -A<sub>2</sub>BPN)(CO)py] (9).** To a yellow solution of **8** (0.12 g, 0.13 mmol) in diethyl ether (6 mL) was added via syringe pyridine (21 mg, 21  $\mu$ L, 0.26 mmol). After 1 h 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<sub>28</sub>H<sub>30</sub>BN<sub>3</sub>OPRh (569.25): C, 59.08; H, 5.31; N, 7.38. Found: C, 59.13; H, 5.28; N, 7.25. IR (ATR, cm<sup>-1</sup>):  $\nu$ (CO) 1967 (s). IR (toluene, cm<sup>-1</sup>):  $\nu$ (CO) 1977 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  8.36 (s, 1H, py), 7.91 (m, 4H, H<sup>o</sup> PPh<sub>2</sub>), 7.76 (d, *J* = 3.0 Hz, 1H, pz), 7.27 (s, 1H, py), 7.14 (m, 6H, H<sup>m+p</sup> PPh<sub>2</sub> + 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<sub>2</sub>-allyl), 2.85 (m, 2H) and 2.36 (m, 2H) (CH<sub>2</sub>-allyl), 1.95 (d, *J*<sub>H,P</sub> = 15.0 Hz, 2H, CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  41.7 (d, *J*<sub>P,Rh</sub> = 145 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  191.0 (dd, *J*<sub>C,Rh</sub> = 56 Hz, *J*<sub>C,P</sub> = 13 Hz, CO), 151.4 (py), 142.3 (=CH-allyl), 138.0 (pz), 137.4 (d, *J*<sub>C,P</sub> = 36 Hz, C<sup>i</sup> PPh<sub>2</sub>), 135.9 (py), 133.6 (pz), 131.7 (d, *J*<sub>C,P</sub> = 10 Hz, C<sup>o</sup> PPh<sub>2</sub>), 128.1 (py), 126.2–128.5 (C<sup>m+p</sup> PPh<sub>2</sub> + py), 123.4 (py), 109.5 (=CH<sub>2</sub>-allyl), 102.7 (pz), 33.8 (br, CH<sub>2</sub>-allyl), 19.4 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 529.3 (90, [M - allyl]<sup>+</sup>), 491.3 (70%, [M - py]<sup>+</sup>).

**[Rh( $\kappa^2$ -A<sub>2</sub>BPN)(CO)NH<sub>3</sub>] (10).** A solution of **8** (0.02 g, 0.02 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) was shaken with gaseous ammonia, leading to a colorless solution within 5 min. Inspection of the NMR spectra revealed a clean and quantitative conversion to complex **10**. IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 1972 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.81 (m, 4H, H<sup>o</sup> PPh<sub>2</sub>), 7.71 (s, 1H, pz), 7.12 (m, 6H, H<sup>m+p</sup> PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 2.73 (m, 2H) and 2.25 (m, 2H) (CH<sub>2</sub>-allyl), 1.83 (d, *J*<sub>H,P</sub> = 15.0 Hz, 2H, CH<sub>2</sub>P), -0.03 (free and coordinated NH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  42.0 (d, *J*<sub>P,Rh</sub> = 150 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  192.3 (dd, *J*<sub>C,Rh</sub> = 74 Hz, *J*<sub>C,P</sub> = 17 Hz, CO), 143.6 (=CH-allyl), 138.7 (d, *J*<sub>C,P</sub> = 47 Hz, C<sup>i</sup> PPh<sub>2</sub>), 137.9 and 134.6 (pz), 132.7 (d, *J*<sub>C,P</sub> = 11 Hz, C<sup>o</sup> PPh<sub>2</sub>), 129.1 (d, *J*<sub>C,P</sub> = 2 Hz, C<sup>o</sup> PPh<sub>2</sub>), 127.9 (d, *J*<sub>C,P</sub> = 10 Hz, C<sup>m</sup> PPh<sub>2</sub>), 110.1 (=CH<sub>2</sub>-allyl), 104.1 (pz), 34.9 (br, CH<sub>2</sub>-allyl), 20.7 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 478.1 (80%, [M - CO]<sup>+</sup>).

**[Rh( $\kappa^2$ -A<sub>2</sub>BPN)(CO)PPh<sub>3</sub>] (11).** To a solution of **8** (0.15 g, 0.17 mmol) in diethyl ether (7 mL) was added solid triphenylphosphane (0.089 g, 0.34 mmol), and the resulting yellow mixture was stirred for 30 min. Evaporation of the solvent under vacuum to ca. 2 mL and the slow addition of hexanes (7 mL) caused 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<sub>41</sub>H<sub>40</sub>BN<sub>2</sub>OP<sub>2</sub>Rh (752.44): C, 65.45; H, 5.36; N, 3.72. Found: C, 65.15; H, 5.15; N, 3.92. IR (ATR, cm<sup>-1</sup>):  $\nu$ (CO) 1976 (s). IR (toluene, cm<sup>-1</sup>):  $\nu$ (CO) 1981 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.24 (m, 10H, H<sup>o</sup> PPh<sub>2</sub> + PPh<sub>3</sub>), 6.87 (s, 1H, pz), 6.69 (m, 15H, H<sup>m+p</sup> PPh<sub>2</sub> + PPh<sub>3</sub>), 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 and 3.0 Hz, 2H) and 4.86 (dd, *J* = 10.0 and 3.0 Hz, 2H) (=CH<sub>2</sub>-allyl), 2.13 (m, 4H, CH<sub>2</sub>-allyl), 1.58 (d, *J*<sub>H,P</sub> = 11.7 Hz, 2H, CH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): ABX spin system (X = <sup>103</sup>Rh)  $\delta$ <sub>P<sup>a</sup></sub> = 31.6,  $\delta$ <sub>P<sup>b</sup></sub> = 30.0, *J*<sub>P<sup>a</sup>,P<sup>b</sup></sub> = 297 Hz, *J*<sub>P<sup>a</sup>,Rh</sub> = 122 Hz, *J*<sub>P<sup>b</sup>,Rh</sub> = 125 Hz).

$^{13}\text{C}\{^1\text{H}\}$  (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  192.9 (ddd,  $J_{\text{C,Rh}} = 71$  Hz,  $J_{\text{C,P}} = 16$  and 12 Hz, CO), 143.6 (=CH-allyl), 140.9 (pz), 137.2 (dd,  $J_{\text{C,P}} = 40$  and 12 Hz,  $\text{C}^i$  PPh $_3$ ), 135.2 (pz), 134.4 (d,  $J_{\text{C,P}} = 11$  Hz,  $\text{C}^o$  PPh $_2$ ), 133.9 (dd,  $J_{\text{C,P}} = 39$  and 9 Hz,  $\text{C}^i$  PPh $_3$ ), 132.6 (dd,  $J_{\text{C,P}} = 10$  Hz,  $\text{C}^o$  PPh $_2$ ), 130.3 ( $\text{C}^p$  PPh $_3$ ), 129.2 ( $\text{C}^p$  PPh $_2$ ), 128.5 (d,  $J_{\text{C,P}} = 8$  Hz,  $\text{C}^m$  PPh $_3$ ), 127.9 (d,  $J_{\text{C,P}} = 8$  Hz,  $\text{C}^m$  PPh $_2$ ), 110.8 (=CH $_2$ -allyl), 104.1 (pz), 35.5 (br, CH $_2$ -allyl), 19.4 (br, CH $_2$ P). MS (MALDI-TOF $^+$ ):  $m/z$  711.0 (30%, [M - allyl] $^+$ ).

[Rh( $\kappa^2$ -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  $\mu\text{L}$ , 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 the slow addition of hexanes (10 mL) caused precipitation of a yellow solid, which was filtered, washed with cold hexanes, and then vacuum-dried. Yield: 0.10 g (95%). Anal. Calcd for  $\text{C}_{26}\text{H}_{34}\text{BN}_2\text{OP}_2\text{Rh}$  (566.23): C, 55.15; H, 6.05; N, 4.95. Found: C, 55.05; H, 6.10; N, 4.92. IR (ATR,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1970 (s). IR (toluene,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1977 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.71 (m, 4H,  $\text{H}^o$  PPh $_2$  + 1H, pz), 7.10 (m, 6H,  $\text{H}^{m+p}$  PPh $_2$  + 1H, pz), 6.32 (m, 2H, =CH-allyl), 5.93 (t,  $J = 2.1$  Hz, 1H, pz), 5.39 (dd,  $J = 17.1$  and 3.0 Hz, 2H) and 5.24 (dd,  $J = 9.9$  and 3.0 Hz, 2H) (=CH $_2$ -allyl), 2.62 (m, 2H) and 2.30 (m, 2H) (CH $_2$ -allyl), 1.85 (d,  $J_{\text{H,P}} = 13.2$  Hz, 2H, CH $_2$ P), 1.00 (d,  $J_{\text{H,P}} = 10.5$  Hz, 9H, PMe $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  28.8 (dd,  $J_{\text{P,P}} = 309$  Hz,  $J_{\text{P,Rh}} = 116$  Hz), -12.6 (dd,  $J_{\text{P,P}} = 309$  Hz,  $J_{\text{P,Rh}} = 121$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  193.1 (ddd,  $J_{\text{C,Rh}} = 69$  Hz,  $J_{\text{C,P}} = 15$  and 12 Hz, CO), 143.5 (=CH-allyl), 140.0 (pz), 137.1 (d,  $J_{\text{C,P}} = 41$  Hz,  $\text{C}^i$  PPh $_2$ ), 134.7 (pz), 132.4 (d,  $J_{\text{C,P}} = 11$  Hz,  $\text{C}^o$  PPh $_2$ ), 129.1 ( $\text{C}^p$  PPh $_2$ ), 127.9 (d,  $J_{\text{C,P}} = 9$  Hz,  $\text{C}^m$  PPh $_2$ ), 110.1 (=CH $_2$ -allyl), 104.1 (pz), 34.6 (br, CH $_2$ -allyl), 19.8 (br, CH $_2$ P), 17.0 (d,  $J_{\text{C,P}} = 26$  Hz, PMe $_3$ ). MS (MALDI-TOF $^+$ ):  $m/z$  525.2 (85%, [M - allyl] $^+$ ), 539.2 (20%, [M - CO] $^+$ ).

[Ir( $\kappa^2$ -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 CO to give a bright-yellow solution in 30 min. The addition of triphenylphosphane (0.17 g, 0.66 mmol) to this solution caused a discharge of the color within seconds. After 20 min, evaporation of the solvent under vacuum gave an orange oil, which 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  $\text{C}_{41}\text{H}_{40}\text{B}^+\text{IrN}_2\text{O}_2$  (841.76): C, 58.50; H, 4.79; N, 3.33. Found: C, 58.74; H, 4.93; N, 3.29. IR (ATR,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2008 (s). IR (toluene,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2000 (m), 1978 (s).  $^1\text{H}$  NMR (300 MHz, toluene- $d_8$ , 25 °C):  $\delta$  7.61 (m, 10H,  $\text{H}^o$  PPh $_2$  + PPh $_3$ ), 7.54 (d,  $J = 2.0$  Hz, 1H, pz), 7.06 (m, 15H,  $\text{H}^{m+p}$  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,  $J_{\text{H,P}} = 12.0$  Hz, 2H, CH $_2$ P).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, toluene- $d_8$ , 25 °C): AB spin system  $\delta_{\text{P}^a} = 17.7$ ,  $\delta_{\text{P}^b} = 11.1$ ,  $J_{\text{P}^a\text{P}^b} = 194$  Hz.  $^1\text{H}$  NMR (300 MHz, toluene- $d_8$ , -80 °C):  $\delta$  7.69 (br, 1H, pz), 7.32 (m, 4H,  $\text{H}^o$  PPh $_2$ ), 6.93 (m, 6H,  $\text{H}^{m+p}$  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- $\eta^2$ -allyl), 3.28 (br, 1H, =CH $_2$ - $\eta^2$ -allyl), 2.32 (br, 1H) and 2.22 (br, 1H) (CH $_2$ -allyl), 2.14 (br, 1H, =CH- $\eta^2$ -allyl), 0.98 (m, 1H, CH $_2$ - $\eta^2$ -allyl + 2H, CH $_2$ P), 0.78 (br, 1H, CH $_2$ - $\eta^2$ -allyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz, toluene- $d_8$ , -70 °C): AB spin system  $\delta_{\text{P}^a} = 3.1$ ,  $\delta_{\text{P}^b} = -8.3$ ,  $J_{\text{P}^a\text{P}^b} = 45$  Hz.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  175.7 (t,  $J_{\text{C,P}} = 10$  Hz, CO), 142.5 (pz), 142.4 (d,  $J_{\text{C,P}} = 7$  Hz, =CH-allyl), 138.0 (d,  $J_{\text{C,P}} = 41$  Hz,  $\text{C}^i$  PPh $_3$ ), 134.3 (pz), 134.2 (d,  $J_{\text{C,P}} = 12$  Hz,  $\text{C}^o$  PPh $_3$ ), 133.7 (dd,  $J_{\text{C,P}} = 43$  Hz,  $\text{C}^i$  PPh $_2$ ), 132.2 (d,  $J_{\text{C,P}} = 11$  Hz,  $\text{C}^o$  PPh $_2$ ), 130.0 (d,  $J_{\text{C,P}} = 2$  Hz,  $\text{C}^p$  PPh $_3$ ), 128.9 (d,  $J_{\text{C,P}} = 2$  Hz,  $\text{C}^p$  PPh $_2$ ), 128.2 (d,  $J_{\text{C,P}} = 10$  Hz,  $\text{C}^m$  PPh $_3$ ), 127.7 (d,  $J_{\text{C,P}} = 10$  Hz,  $\text{C}^m$  PPh $_2$ ), 115.0 (=CH $_2$ -allyl), 104.2 (pz), 29.7 (br, CH $_2$ -allyl), 28.0 (br, CH $_2$ P). MS (MALDI-TOF $^+$ ):  $m/z$  801.1 (100%, [M - allyl] $^+$ ).

[Ir( $\kappa^2$ -A $_2$ BPN)(CO)PMe $_3$ ] (14). A solution of 7 (0.33 g, 0.50 mmol) in diethyl ether (20 mL) was bubbled with CO, giving in 30 min a bright-yellow solution. The addition of trimethylphosphane (37 mg, 51  $\mu\text{L}$ , 0.50 mmol) to this solution caused a 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  $\text{C}_{26}\text{H}_{34}\text{B}^+\text{IrN}_2\text{O}_2$  (655.55): C, 47.64; H, 5.23; N, 4.27.

Found: C, 47.35; H, 5.19; N, 4.11. IR (ATR,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1920 (s). IR (toluene,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1928 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.96 (d,  $J = 2.0$  Hz, 1H, pz), 7.93 (m, 2H) and 7.45 (m, 2H) ( $\text{H}^{o+o}$  PPh $_2$ ), 7.43 (d,  $J = 2.1$  Hz, 1H, pz), 7.23 (td,  $J = 6.7$  and 1.1 Hz, 2H,  $\text{H}^m$  PPh $_2$ ), 7.05 (td,  $J = 7.0$  and 1.1 Hz, 1H,  $\text{H}^p$  PPh $_2$ ), 7.00 (m, 3H,  $\text{H}^{m+p}$  PPh $_2$ ), 6.63 (m, 1H, =CH-allyl), 5.89 (t,  $J = 2.1$  Hz, 1H, pz), 5.36 (dd,  $J = 16.8$  and 3.0 Hz, 1H) and 5.28 (dd,  $J = 10.2$  and 3.0 Hz, 1H) (=CH $_2$ -allyl), 2.93 (m, 1H, =CH- $\eta^2$ -allyl), 2.82 (m, 1H) and 2.47 (m, 1H) (=CH $_2$ - $\eta^2$ -allyl), 2.17 (m, 1H, CH $_2$ - $\eta^2$ -allyl), 2.04 (m, 2H, CH $_2$ -allyl + 1H, CH $_2$ P), 1.34 (t,  $J_{\text{H,H}} = J_{\text{H,P}} = 13.6$  Hz, 1H, CH $_2$ P), 1.10 (m, 1H, CH $_2$ - $\eta^2$ -allyl), 0.58 (d,  $J_{\text{H,P}} = 10.5$  Hz, 9H, PMe $_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  3.3 (d,  $J_{\text{P,P}} = 12$  Hz), -42.2 (d,  $J_{\text{P,P}} = 12$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  190.7 (dd,  $J_{\text{C,P}} = 17$  and 14 Hz, CO), 143.7 (=CH-allyl), 143.3 (pz), 138.2 (d,  $J_{\text{C,P}} = 36$  Hz,  $\text{C}^i$  PPh $_2$ ), 133.9 (d,  $J_{\text{C,P}} = 13$  Hz,  $\text{C}^o$  PPh $_2$ ), 131.3 (pz), 131.1 (d,  $J_{\text{C,P}} = 5$  Hz,  $\text{C}^p$  PPh $_2$ ), 128.0 (m,  $\text{C}^m$  PPh $_2$ ), 110.5 (=CH $_2$ -allyl), 105.5 (pz), 49.8 (d,  $J_{\text{C,P}} = 8$  Hz, =CH- $\eta^2$ -allyl), 35.5 (d,  $J_{\text{C,P}} = 20$  Hz, =CH $_2$ - $\eta^2$ -allyl), 34.4 (br, CH $_2$ -allyl), 25.7 (br, CH $_2$ - $\eta^2$ -allyl), 22.7 (br, CH $_2$ P), 15.4 (d,  $J_{\text{C,P}} = 41$  Hz, PMe $_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  -1.15 (br s). MS (MALDI-TOF $^+$ ):  $m/z$  615.1 (40%, [M - allyl] $^+$ ).

[Ir( $\kappa^2$ -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  $\mu\text{L}$ , 0.67 M, 0.12 mmol), which produced the immediate formation of a yellowish precipitate. The solution was stirred for 30 min, and then the solvent was removed to yield a pale-yellow solid, which was filtered out and dried by vacuum. Yield: 0.10 g (98%). Anal. Calcd for  $\text{C}_{41}\text{H}_{41}\text{B}^+\text{ClIrN}_2\text{O}_2$  (878.22): C, 56.07; H, 4.71; N, 3.19. Found: C, 55.51; H, 4.67; N, 3.00. IR ( $\text{CDCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{Ir-H})$  2253 (w),  $\nu(\text{CO})$  2058 (s).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.84 (m, 2H,  $\text{H}^o$  PPh $_2$ ), 7.63 (m, 6H,  $\text{H}^o$  PPh $_3$ ), 7.45 (d,  $J = 1.9$  Hz, 2H, pz), 7.37 (m, 2H,  $\text{H}^o$  PPh $_2$ ), 6.96 (m, 3H,  $\text{H}^{m+p}$  PPh $_2$  + 9H,  $\text{H}^{m+p}$  PPh $_3$ ), 6.86 (m, 3H,  $\text{H}^{m+p}$  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,  $J = 12.6$  and 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,  $J_{\text{H,P}} = 12.0$  Hz, 1H, Ir-H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 25 °C): AB spin system  $\delta_{\text{P}^a} = -1.9$ ,  $\delta_{\text{P}^b} = -6.7$ ,  $J_{\text{P}^a\text{P}^b} = 330$  Hz.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  167.1 (dd,  $J_{\text{C,P}} = 8$  and 7 Hz, CO), 144.1 (pz), 143.0 and 142.7 (=CH-allyl), 137.7 (pz), 137.2 (d,  $J_{\text{C,P}} = 43$  Hz,  $\text{C}^i$  PPh $_2$ ), 135.0 (d,  $J_{\text{C,P}} = 10$  Hz,  $\text{C}^o$  PPh $_3$ ), 133.9 (dd,  $J_{\text{C,P}} = 9.2$  Hz) and 131.9 (d,  $J_{\text{C,P}} = 9$  Hz) ( $\text{C}^o$  PPh $_2$ ), 131.2 (d,  $J_{\text{C,P}} = 2$  Hz,  $\text{C}^p$  PPh $_3$ ), 130.5 and 130.2 (d,  $J_{\text{C,P}} = 2$  Hz) ( $\text{C}^p$  PPh $_2$ ), 130.0 (d,  $J_{\text{C,P}} = 49$  Hz,  $\text{C}^i$  PPh $_3$ ), 128.7 (d,  $J_{\text{C,P}} = 10$  Hz,  $\text{C}^m$  PPh $_3$ ), 127.8 (m,  $\text{C}^m$  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( $\kappa^3$ -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 min 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  $\text{C}_{26}\text{H}_{35}\text{B}^+\text{ClIrN}_2\text{O}_2$  (692.01): C, 45.13; H, 5.10; N, 4.05. Found: C, 44.67; H, 5.23; N, 3.92. IR ( $\text{CDCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2061 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.17 (d,  $J = 2.3$  Hz, 1H, pz), 7.57 (m, 4H,  $\text{H}^{o+o}$  PPh $_2$ ), 7.39 (m, 3H,  $\text{H}^{m+p}$  PPh $_2$ ), 7.33 (m, 1H, pz), 7.15 (m, 3H,  $\text{H}^{m+p}$  PPh $_2$ ), 6.05 (m, 1H, pz), 6.04 (m, 1H, =CH-allyl), 4.83 (dd,  $J = 15.0$  and 3.0 Hz, 1H) and 4.75 (dd,  $J = 9.0$  and 3.0 Hz, 1H) (=CH $_2$ -allyl), 2.75 (m, 1H, Ir-CH(CH $_3$ )CH $_2$ ), 1.69 (d,  $J = 6.0$  Hz, 3H, Ir-CH(CH $_3$ )CH $_2$ ), 1.62 (m, 1H, CH $_2$ P), 1.56 (m, 2H, CH $_2$ -allyl), 1.34 (d,  $J_{\text{H,P}} = 12.0$  Hz, 9H, PMe $_3$ ), 1.03 (m, 1H, CH $_2$ P), 0.60 (m, 1H) and 0.11 (m, 1H) (Ir-CH(CH $_3$ )CH $_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  -12.8 (d,  $J_{\text{P,P}} = 22$  Hz), -46.4 (d,  $J_{\text{P,P}} = 22$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  168.1 (dd,  $J_{\text{C,P}} = 132$  and 9 Hz, CO), 143.3 (=CH-allyl), 142.2 (d,  $J_{\text{C,P}} = 2$  Hz, pz), 135.4 (dd,  $J_{\text{C,P}} = 40$  and 3 Hz,  $\text{C}^i$  PPh $_2$ ), 134.1 (d,  $J_{\text{C,P}} = 9$  Hz,  $\text{C}^o$  PPh $_2$ ), 133.5 (d,  $J_{\text{C,P}} = 4$  Hz, pz), 132.7 (d,  $J_{\text{C,P}} = 9$  Hz,  $\text{C}^o$  PPh $_2$ ), 131.5 (d,  $J_{\text{C,P}} = 55$  Hz,  $\text{C}^i$  PPh $_2$ ),

Table 6. Selected Crystal, Measurement, and Refinement Data for Compounds 3·0.5C<sub>6</sub>H<sub>14</sub>, 8, 11, and 18·0.5C<sub>6</sub>H<sub>14</sub>

	3·0.5C <sub>6</sub> H <sub>14</sub>	8	11	18·0.5C <sub>6</sub> H <sub>14</sub>
formula	C <sub>30</sub> H <sub>37</sub> BiRn <sub>2</sub> P·0.5C <sub>6</sub> H <sub>14</sub>	C <sub>46</sub> H <sub>50</sub> B <sub>2</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> Rh <sub>2</sub>	C <sub>41</sub> H <sub>40</sub> BN <sub>2</sub> OP <sub>2</sub> Rh	C <sub>29</sub> H <sub>31</sub> BiRNO <sub>3</sub> P·0.5C <sub>6</sub> H <sub>14</sub>
fw	702.68	980.28	752.41	764.62
color	pale-yellow	yellow	yellow	colorless
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/c</i>
<i>a</i> [Å]	10.856(5)	11.9199(19)	11.203(2)	18.5058(18)
<i>b</i> [Å]	16.608(7)	16.647(3)	24.429(4)	9.3837(9)
<i>c</i> [Å]	32.292(12)	22.872(4)	13.786(2)	18.6119(18)
$\beta$ [deg]	90	104.359(3)	102.177(3)	90.491(2)
<i>V</i> [Å <sup>3</sup> ]	5822(4)	4396.6(12)	3688.0(10)	3231.9(5)
<i>Z</i>	8	4	4	4
<i>F</i> (000)	2824	2000	1552	1524
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.603	1.481	1.355	1.571
$\mu$ (mm <sup>-1</sup> )	4.667	0.866	0.584	4.222
cryst size [mm]	0.13 × 0.05 × 0.04	0.11 × 0.05 × 0.04	0.14 × 0.11 × 0.07	0.05 × 0.04 × 0.02
temperature [K]	100(2)	100(2)	100(2)	100(2)
$\theta$ limits [deg]	27.27	26.00	26.00	25.20
collected reflns	33914	25837	21901	24471
unique reflns ( <i>R</i> <sub>int</sub> )	6499 (0.0982)	8645 (0.0955)	7220 (0.0546)	5818 (0.0820)
reflns with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	4686	6354	5300	4237
param/restraints	344/0	523/0	433/0	373/27
<i>R</i> 1 [on <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0483	0.0567	0.0407	0.0402
w <i>R</i> 2 (on <i>F</i> <sup>2</sup> , all data)	0.0898	0.1014	0.0939	0.0896
max/min $\Delta\rho$ [e Å <sup>-3</sup> ]	1.129/−1.808	0.730/−0.844	0.710/−0.360	1.030
GOF	1.055	1.070	0.998	1.521/−0.845

130.3 (d, *J*<sub>C,P</sub> = 2 Hz) and 129.8 (d, *J*<sub>C,P</sub> = 2 Hz) (C<sup>o+o+</sup> PPh<sub>2</sub>), 128.5 (d, *J*<sub>C,P</sub> = 9 Hz) and 127.2 (d, *J*<sub>C,P</sub> = 10 Hz) (C<sup>o+o+</sup> PPh<sub>2</sub>), 110.2 (=CH<sub>2</sub>-allyl), 105.3 (pz), 37.2 (Ir-CH(CH<sub>3</sub>)CH<sub>2</sub>), 37.0 (br, Ir-CH(CH<sub>3</sub>)CH<sub>2</sub>), 33.2 (br, CH<sub>2</sub>-allyl), 16.4 (br, CH<sub>2</sub>P), 15.2 (Ir-CH(CH<sub>3</sub>)CH<sub>2</sub>), 14.6 (d, *J*<sub>C,P</sub> = 41 Hz, PMe<sub>3</sub>). MS (MALDI-TOF<sup>+</sup>): *m/z* 614.9 (20%, [M - PMe<sub>3</sub>]<sup>+</sup>), 586.9 (5%, [M - PMe<sub>3</sub> - CO]<sup>+</sup>).

[Ir( $\kappa^3$ -A<sub>2</sub>BPN)(CO)(H<sub>2</sub>C=CH<sub>2</sub>)] (17). CO was bubbled through an orange solution of 3 (0.10 g, 0.16 mmol) in diethyl ether (12 mL) for 20 min to yield a transparent yellow solution. Then, the solution was exposed to an ethylene atmosphere for 26 h. 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<sub>25</sub>H<sub>29</sub>BiRn<sub>2</sub>OP (607.52): C, 49.43; H, 4.81; N, 4.61. Found: C, 49.52; H, 4.76; N, 4.51. IR (ATR, cm<sup>-1</sup>):  $\nu$ (CO) 2005 (s). IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2013 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.57 (m, 2H, H<sup>o</sup> PPh<sub>2</sub>), 7.47 (d, *J* = 2.0 Hz, 1H, pz), 7.07 (m, 2H, H<sup>m</sup> PPh<sub>2</sub>), 6.94 (1H, H<sup>p</sup> PPh<sub>2</sub> + 5H, H<sup>o+o+o+</sup> PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 4.30 (m, 1H, =CH- $\eta^2$ -allyl), 3.67 (m, 1H, =CH<sub>2</sub>- $\eta^2$ -allyl), 2.73 (m, 2H) and 2.47 (m, 1H) ( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>), 2.33 (dd, *J* = 12.5 and 4.5 Hz, 1H, =CH<sub>2</sub>- $\eta^2$ -allyl), 2.07 (t, *J* = 9 Hz, 1H, CH<sub>2</sub>- $\eta^2$ -allyl), 1.91 (m, 2H, CH<sub>2</sub>-allyl), 1.69 (t, *J*<sub>H,P</sub> = 14.6 Hz, 1H, CH<sub>2</sub>P), 1.33 (m, 1H,  $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>), 1.20 (t, *J*<sub>H,P</sub> = 14.6 Hz, 1H, CH<sub>2</sub>P), 0.86 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -7.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  166.0 (d, *J*<sub>C,P</sub> = 6 Hz, CO), 143.1 (=CH-allyl), 138.4 (d, *J*<sub>C,P</sub> = 44 Hz, C<sup>i</sup> PPh<sub>2</sub>), 138.0 (d, *J*<sub>C,P</sub> = 43 Hz, C<sup>i</sup> PPh<sub>2</sub>), 134.2 (d, *J*<sub>C,P</sub> = 8 Hz, pz), 132.0 (pz), 131.6 (m, C<sup>o+o+</sup> PPh<sub>2</sub>), 129.7 (C<sup>p</sup> PPh<sub>2</sub>), 129.0 (C<sup>o+o+o+</sup> PPh<sub>2</sub>), 111.4 (=CH<sub>2</sub>-allyl), 104.8 (pz), 68.7 (d, *J*<sub>C,P</sub> = 4 Hz, =CH- $\eta^2$ -allyl), 41.2 (d, *J*<sub>C,P</sub> = 9 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 34.6 (br, CH<sub>2</sub>-allyl), 33.8 (d, *J*<sub>C,P</sub> = 6 Hz) and 28.0 ( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>), 25.6 (br, CH<sub>2</sub>- $\eta^2$ -allyl), 18.4 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 539.2 (40%, [M - allyl - CO/C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>).

[Ir( $\kappa^3$ -A<sub>2</sub>BPN)(CO)(*dmad*)] (18). Solid [Ir(acac)(cod)] (0.084 g, 0.21 mmol) was added to a suspension of 1 (0.101 g, 0.21 mmol) in diethyl ether. After 30 min of stirring, the suspension was filtered through a pad of Celite, and then CO was bubbled to give a bright-yellow solution. Then MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me (51  $\mu$ L, 0.42 mmol) was

added via microsyringe. The resulting light-yellow solution was stirred for more than 20 min. Concentration to ca. 0.5 mL and the addition of hexanes yielded an orange solid, which was filtered out and dried under vacuum. Yield: 0.06 g (41%). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>BiRn<sub>2</sub>O<sub>3</sub>P (721.57): C, 48.27; H, 4.33; N, 3.88. Found: C, 48.05; H, 4.11; N, 3.76. IR (ATR, /cm<sup>-1</sup>):  $\nu$ (CO) 2032 (s),  $\nu$ (C=O) 1699 (s). IR (toluene, cm<sup>-1</sup>):  $\nu$ (CO) 2040 (s),  $\nu$ (C=O) 1709 (s). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  7.82 (d, *J* = 2.4 Hz, 1H, pz), 7.74 (m, 2H, H<sup>o</sup> PPh<sub>2</sub>), 7.34 (d, *J* = 2.3 Hz, 1H, pz), 7.10 (m, 2H, H<sup>m</sup> PPh<sub>2</sub>), 7.01 (m, 1H, H<sup>p</sup> PPh<sub>2</sub>), 6.83 (m, 5H, H<sup>o+o+o+</sup> PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 4.36 (m, 1H, =CH- $\eta^2$ -allyl), 4.26 (m, 1H, =CH<sub>2</sub>- $\eta^2$ -allyl), 3.67 (s, 3H) and 3.45 (s, 3H) (OCH<sub>3</sub>), 3.30 (m, 1H, =CH<sub>2</sub>- $\eta^2$ -allyl), 2.06 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl), 1.91 (t, *J*<sub>H,P</sub> = 14.1 Hz, 1H, CH<sub>2</sub>P), 1.70 (m, 2H, CH<sub>2</sub>-allyl), 0.85 (m, 1H, CH<sub>2</sub>P), 0.60 (m, 1H, CH<sub>2</sub>- $\eta^2$ -allyl). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -3.1 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  162.7 (d, *J*<sub>C,P</sub> = 5 Hz, C=O), 162.1 (d, *J*<sub>C,P</sub> = 6 Hz, CO), 162.0 (d, *J*<sub>C,P</sub> = 8 Hz, C=O), 142.6 (=CH-allyl), 138.0 (d, *J*<sub>C,P</sub> = 50 Hz, C<sup>i</sup> PPh<sub>2</sub>), 136.5 and 135.3 (pz), 135.1 (d, *J*<sub>C,P</sub> = 48 Hz, C<sup>i</sup> PPh<sub>2</sub>), 131.7 (d, *J*<sub>C,P</sub> = 11 Hz, C<sup>o+o+</sup> PPh<sub>2</sub>), 130.3 (d, *J*<sub>C,P</sub> = 2 Hz) and 129.7 (d, *J*<sub>C,P</sub> = 2 Hz) (C<sup>p</sup> PPh<sub>2</sub>), 128.8 (d, *J*<sub>C,P</sub> = 10 Hz) and 128.1 (d, hidden behind solvent signal) (C<sup>m</sup> PPh<sub>2</sub>), 111.7 (=CH<sub>2</sub>-allyl), 105.0 (pz), 91.5 (d, *J*<sub>C,P</sub> = 7 Hz) and 86.9 (d, *J*<sub>C,P</sub> = 40 Hz) (C≡C), 82.1 (=CH- $\eta^2$ -allyl), 52.3 and 52.1 (OCH<sub>3</sub>), 48.9 (d, *J*<sub>C,P</sub> = 5 Hz, =CH<sub>2</sub>- $\eta^2$ -allyl), 34.3 (br, CH<sub>2</sub>-allyl), 26.1 (br, CH<sub>2</sub>- $\eta^2$ -allyl), 17.0 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>): *m/z* 663.4 (85%, [M - COOMe]<sup>+</sup>).

[Ir( $\kappa^2$ -A<sub>2</sub>BPN)(CN<sup>t</sup>Bu)<sub>2</sub>(*dmad*)] (19). To a yellow solution of 5 (0.110 g, 0.149 mmol) in tetrahydrofuran (8 mL) was added dropwise via a microsyringe *dmad* (20  $\mu$ L, 0.164 mmol) to give a dark-orange solution. After 1 h 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<sub>38</sub>H<sub>49</sub>BiRn<sub>4</sub>O<sub>4</sub>P (859.83): C, 53.08; H, 5.74; N, 6.52. Found: C, 53.01; H, 5.65; N, 6.45. IR (ATR, cm<sup>-1</sup>):  $\nu$ (CN) 2196 (s), 2164 (s),  $\nu$ (C=O) 1746 (s), 1686 (s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  8.29 (m, 2H, H<sup>o</sup> PPh<sub>2</sub>), 8.17 (d, *J* = 1.2 Hz, 1H, pz), 7.58 (d, *J* = 1.6 Hz, 1H, pz), 7.52 (m, 2H, H<sup>m</sup> PPh<sub>2</sub>), 7.33 (m, 2H, H<sup>p</sup> PPh<sub>2</sub>), 7.11 (m, 1H, H<sup>p</sup> PPh<sub>2</sub>), 7.04 (m, 3H, H<sup>o+o+</sup> PPh<sub>2</sub>), 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<sub>2</sub>-allyl), 4.81 (d,  $J = 10.0$  Hz, 1H) and 4.74 (d,  $J = 17.2$  Hz, 1H) (=CH<sub>2</sub>-allyl), 3.58 (s, 3H) and 3.53 (s, 3H) (OCH<sub>3</sub>), 2.35 (m, 1H, CH<sub>2</sub>P), 2.00 (m, 3H, CH<sub>2</sub>-allyl), 1.76 (m, 1H, CH<sub>2</sub>P), 1.13 (m, 1H, CH<sub>2</sub>-allyl), 0.86 (s, 9H) and 0.69 (s, 9H) (CN<sup>n</sup>Bu). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -6.4 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  166.5 (d,  $J_{C,P} = 12$  Hz), and 163.3 (d,  $J_{C,P} = 10$  Hz) (CN<sup>n</sup>Bu), 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' PPh<sub>2</sub>), 135.4 (d,  $J_{C,P} = 13$  Hz, C<sup>o</sup> PPh<sub>2</sub>), 135.2 (d,  $J_{C,P} = 50$  Hz, C'' PPh<sub>2</sub>), 134.7 (pz), 131.4 (d,  $J_{C,P} = 9$  Hz, C<sup>o'</sup> PPh<sub>2</sub>), 130.3 (d,  $J_{C,P} = 2$  Hz, C<sup>p</sup> PPh<sub>2</sub>), 128.1 (m, PPh<sub>2</sub><sup>m+m'+p'</sup>), 110.6 and 109.2 (=CH<sub>2</sub>-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<sub>3</sub>), 51.8 and 51.7 (OCH<sub>3</sub>), 34.9 and 31.8 (br, CH<sub>2</sub>-allyl), 30.0 and 29.9 (CMe<sub>3</sub>), 17.5 (br, CH<sub>2</sub>P). MS (MALDI-TOF<sup>+</sup>):  $m/z$  677.4 (74%, [M - dmad - allyl]<sup>+</sup>).

**DFT Geometry Optimization.** The computational method used was DFT with the B3LYP exchange-correlation functional<sup>48</sup> using the Gaussian 09<sup>49</sup> program package. The basis sets used for full optimization of the structures and for the frequency calculations were the LanL2TZ(f) effective core potential for the metal atoms and 6-31G(d,p) for the remaining atoms.

**X-ray Diffraction Studies on 3·0.5C<sub>6</sub>H<sub>14</sub>, 8, 11, and 18·0.5C<sub>6</sub>H<sub>14</sub>.** Selected crystallographic data for these complexes can be found in Table 6. Intensity measurements were collected with a SMART APEX diffractometer, with graphite-monochromated Mo K $\alpha$  radiation. A semiempirical absorption correction was applied to each data set, with the multiscan<sup>50</sup> methods. All non-H atoms were refined with anisotropic displacement parameters except one disordered hexane solvent molecule in 18·0.5C<sub>6</sub>H<sub>14</sub>, which was refined with isotropic displacement parameters and with geometrical restraints. The H 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<sup>51</sup> in the WINGX<sup>52</sup> package.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Full ORTEP diagrams, selected spectroscopic data, van't Hoff plotter, atomic coordinates for calculated DFT structures, complete ref 39, and a CIF file giving details of the X-ray crystal structures of 3·0.5C<sub>6</sub>H<sub>14</sub>, 8, 11, and 18·0.5C<sub>6</sub>H<sub>14</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### ■ Notes

The authors declare no competing financial interest.

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## ■ DEDICATION

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

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