C−H Activation and C−C Coupling Reactions in 2-Vinylpyridine Cationic Complexes of Iridium

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The complex $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (**1**) reacts with 2-vinylpyridine to form the hydride $[IrH\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**3**) in a reaction that likely involves the observed dihydride $[IrH_2(NC_5H_4\text{-}2\text{-}CH{=}CH_2\text{-}\kappa\text{-}N)(NCCH_3)_2(PiPr_3)]BF_4$ (**2**). Crystallization of the C−H activation product **3** affords the dicationic derivative $[IrH\{\mu\text{-}\eta^2\text{-}NC_5H_4\text{-}2\text{-}(Z\text{-}CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)(PiPr_3)]_2(BF_4)_2$ (**4**). **3** reacts with 2-vinypyridine, $CH_2{=}CH_2$, CH≡CH, PhC≡CH, *t*BuC≡CH, and PhC≡CPh to form the corresponding alkyl or alkenyl insertion products. The structure of $[Ir(NC_5H_4\text{-}2\text{-}(Z\text{-}CH{=}CH)\text{-}\kappa\text{-}N,C)(NC_5H_4\text{-}2\text{-}CH_2CH_2\text{-}\kappa\text{-}N,C)(NCCH_3)(PiPr_3)]BF_4$ (**5**), which contains two chelating ligands derived from 2-vinylpyridine, has been determined by X-ray diffraction. The other insertion products **7**−**11** retain the structure of the precursor **3** even after insertions of different regioselectivity, as evidenced by the 1-alkyne derivatives $[Ir\{C(Ph){=}CH_2\}\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**9**) and $[Ir(E\text{-}CH{=}CHtBu)\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**10**). All obtained insertion products are stable toward the reductive elimination of C−C bonds. However, derivatives **9** and **10** undergo a C−C coupling reaction to form $[Ir\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)CH(R)CH_2\text{-}\kappa\text{-}N,C\}(NCCH_3)(PiPr_3)]BF_4$ (R = Ph, **12**; R = *t*Bu, **13**) after treatment with 2-vinylpyridine excess. These latter products are isostructural, despite the different stereochemistry of the alkenyl ligands in the precursors. Under similar conditions, both the alkyl complex $[Ir(Et)\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**7**) and the diphenylacetylene derivative $[Ir\{Z\text{-}C(Ph){=}CHPh\}\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**11**) form the compound $[Ir\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}_2(NCCH_3)(PiPr_3)]BF_4$ (**15**), after elimination of ethane and *cis*-stilbene, respectively. These latter observations are discussed to conclude that the observed C−C coupling processes comprise the initial generation of an alkene at the coordination sphere of iridium followed by the alkene insertion into an Ir−C bond.

Introduction

The need for sustainable industrial chemical processes has boosted the research on functionalization methods involving C−H activations at metal complexes, since they may lead to catalytic transformations of total atom economy. Among such reactions, those using substrates that can be cyclometalated under C−H oxidative addition have been found to be particularly successful. Actually, the work of Murai and others with aromatic ketones, esters, amines and imines, conjugate enones, acrylic esters, and heteroaromatic-substituted alkenes or dienes has resulted in a widely applicable method for the alkylation, alkenylation, or acylation of such substrates in the presence of alkenes or alkynes and ruthenium or rhodium catalyst precursors.[1]

The mechanistic rationalization of ruthenium-catalyzed alkylations of this type—based on deuterium-labeling experiments, ^{13}C kinetic isotope effects, and reaction rate dependence upon substrate's electronic characteristics—suggests that formation of the new C−C bonds occurs through rate-determining reductive elimination steps, which involve the organic ligand generated by C−H activation and an alkyl group formed after alkene insertion into the metal-hydride moiety.[1a] As a possible alternative to this mechanism, the present study shows that such C−C bonds can also be formed by alkene insertion into the M−C bond generated at the C−H activation step. This is illustrated for a substrate typically involved in the aforementioned functionalizations, the 2-vinylpyridine,[2] and the labile iridium complex $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$,[3] a species that promotes the postulated C−H activation/alkene insertion sequence but fails to give the key C−C reductive coupling.

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(1) For leading references, see: (a) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826−834. (b) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731−1769. (c) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698−1712. (d) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047−1055.

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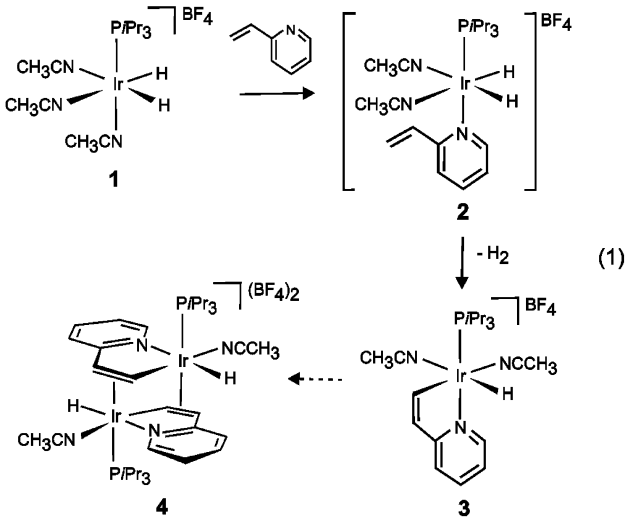
Results and Discussion

2-Vinylpyridine C−H Activation. The reaction of complex $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (**1**) with 1 equiv of 2-vinylpyridine has been found to afford the cationic monohydride complex $[IrH\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (**3**) (eq 1). The ^1H NMR



spectrum of this compound in $CDCl_3$ shows characteristic signals for a hydride ligand, a *Z*-CH=CH moiety, and two different acetonitrile ligands, one of them being broad at room temperature. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ 20.80, which becomes a doublet under off-resonance conditions due to a coupling of 20.1 Hz with the cis hydride ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the two C≡N acetonitrile carbons give rise to a singlet at δ 121.40 and a broad signal at δ 119.47, respectively. At temperatures below 273 K, the latter signal transforms into a singlet, which splits under off-resonance conditions into a doublet due to a J_{CH} coupling constant of 10.0 Hz with the trans-located hydride ligand. This spectrum also shows a doublet at δ 154.26 (J_{CP} = 7.4 Hz) attributable to an alkenyl CH σ-bonded to the iridium atom at a position cis relative to the phosphine. This spectroscopic information leads to the structural proposal for **3** depicted in eq 1.

Our various attempts to obtain crystals of **3** suitable for an X-ray diffraction experiment have systematically afforded yellow crystals which do not contain the compound **3** but the dinuclear species $[IrH\{\mu\text{-}\eta^2\text{-}NC_5H_4\text{-}2\text{-}(Z\text{-}CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)(PiPr_3)]_2(BF_4)_2$ (**4**) (eq 1). Taking into account the lability of one acetonitrile ligand of **3** evidenced by its broad NMR resonances at room temperature, the formation of this dinuclear compound likely involves the reorganization and condensation of two unsaturated fragments generated by acetonitrile dissociation from **3**. The preferred crystallization of

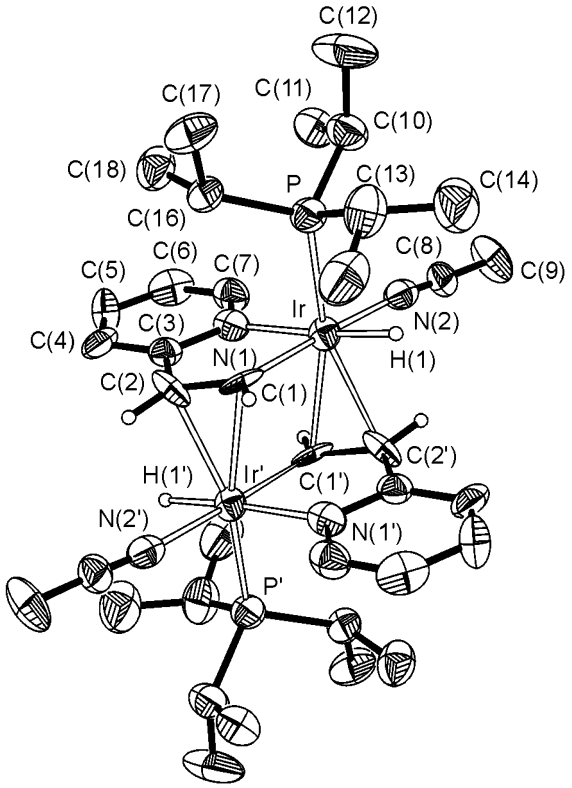


Figure 1. Molecular structure of the cation of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. Primed atoms are related to the unprimed ones by the $-x + 1, -y + 1, -z$ symmetry transformation.

the dicationic compound **4** can be attributed to its insolubility in conventional solvents. Due to the latter, the solution NMR characterization data of the compound could not be obtained. The molecular structure of **4** and its most relevant distances and angles are shown in Figure 1 and Table 1, respectively. The hydride ligands in this structure could not be located, being included at the positions calculated by the HYDEX program.[4]

The structure confirms that reaction between **1** and 2-vinylpyridine involves a cleavage of the alkenylic C−H bond of the organic substrate that leads to the bidentate ligand $NC_5H_4\text{-}2\text{-}(Z\text{-}CH{=}CH)\text{-}\kappa\text{-}N,C$. In **4**, this ligand shows a η^2 additional coordination to the neighboring iridium center, thus stabilizing a centrosymmetric dinuclear compound. Precedents for such a bridging coordination mode have been reported in tri- and hexanuclear clusters of osmium,[5] and several mononuclear 2-vinylpyridine C−H activation products closely related to **3** have been described for Re, Rh, and Ru.[6,7]

The evolution of dihydrogen during the formation of **3** could be confirmed through in situ NMR observations of the reaction in $CDCl_3$ at low temperature. These experiments have also allowed the characterization of

(2) Catalytic alkylations of 2-vinylpyridines: (a) Fujii, N.; Kakiuchi, F.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 939−940. (b) Fujii, N.; Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S. *Chem. Lett.* **1997**, 425−426. (c) Lim, Y.-G.; Kang, J.-B.; Kim, Y. H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 699−707. (d) Lim, Y.-G.; Kang, J.-B.; Koo, B. T. *Tetrahedron Lett.* **1999**, *40*, 7691−7694.

(3) (a) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534−3546. (b) Oro, L. A.; Sola, E.; Navarro, J. In *Perspectives in Organometallic Chemistry*; Screttas, C. G., Steele, B. R., Eds.; Royal Society of Chemistry: Cambridge, UK, 2003; pp 297−305.

(4) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509−2516.

(5) Wong, W. Y.; Wong, W. T. *J. Organomet. Chem.* **1996**, *513*, 27−29 and references therein.

(6) (a) Bruce, M. I.; Goodall, B. L.; Matsuda, I. *Aust. J. Chem.* **1975**, *28*, 1259−1262. (b) Foot, R. J.; Heaton, B. T. *J. Chem Soc., Chem. Commun.* **1973**, 838−839.

(7) Coalter, J. N.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **2000**, *39*, 3749−3756.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 4 and 5

4		5	
Ir−P	2.314(3)	Ir−P	2.2972(10)
Ir−C(1)	1.982(11)	Ir−C(1)	1.988(4)
Ir−C(1′)	2.355(10)	Ir−C(8)	2.082(4)
Ir−C(2′)	2.284(11)	Ir−N(1)	2.150(3)
Ir−N(1)	2.141(9)	Ir−N(2)	2.119(3)
Ir−N(2)	2.069(10)	Ir−N(3)	2.110(3)
C(1)−C(2)	1.388(13)	C(1)−C(2)	1.340(6)
		C(8)−C(9)	1.542(5)
P−Ir−C(1)	90.3(3)	P−Ir−C(1)	91.54(11)
P−Ir−C(1′)	166.4(3)	P−Ir−C(8)	93.30(11)
P−Ir−C(2′)	152.5(3)	P−Ir−N(1)	98.50(8)
P−Ir−N(1)	97.7(2)	P−Ir−N(2)	171.59(10)
P−Ir−N(2)	95.2(3)	P−Ir−N(3)	94.02(9)
C(1)−Ir−C(1′)	76.8(4)	C(1)−Ir−C(8)	94.10(18)
C(1)−Ir−C(2′)	91.5(4)	C(1)−Ir−N(1)	78.08(16)
C(1)−Ir−N(1)	79.3(4)	C(1)−Ir−N(2)	90.70(14)
C(1)−Ir−N(2)	172.8(4)	C(1)−Ir−N(3)	171.02(15)
C(1′)−Ir−N(1)	75.9(3)	C(8)−Ir−N(1)	165.96(14)
C(1′)−Ir−N(2)	97.3(4)	C(8)−Ir−N(2)	78.46(14)
C(2′)−Ir−N(1)	109.6(4)	C(8)−Ir−N(3)	92.63(15)
C(2′)−Ir−N(2)	85.8(4)	N(1)−Ir−N(2)	89.89(12)
N(1)−Ir−N(2)	95.3(3)	N(1)−Ir−N(3)	94.10(12)
		N(2)−Ir−N(3)	84.81(12)
Ir−C(1)−Ir′	103.2(4)	Ir−C(1)−C(2)	117.3(3)
Ir−C(1)−C(2)	115.4(8)	Ir−C(8)−C(9)	106.5(3)
C(1)−C(2)−C(3)	118.0(10)	C(1)−C(2)−C(3)	118.1(4)
		C(8)−C(9)−C(10)	109.6(4)

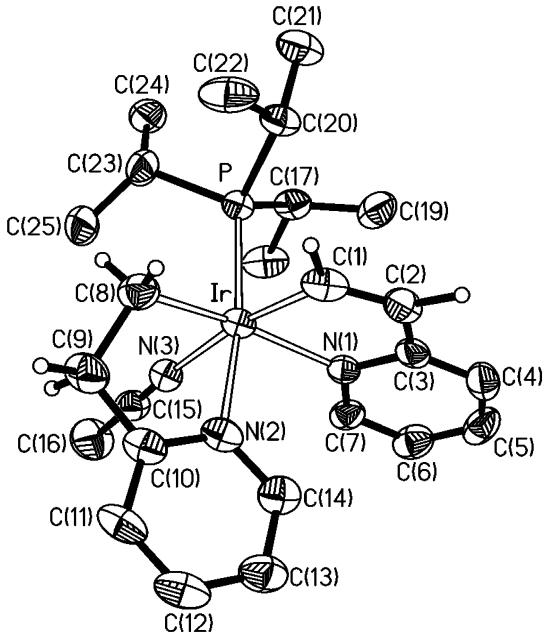
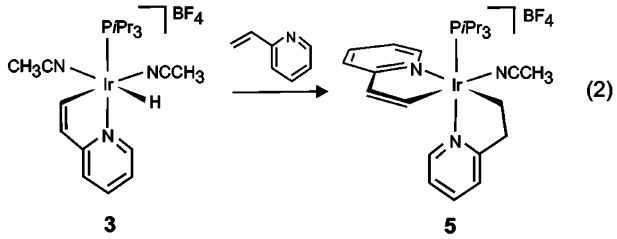


Figure 2. Molecular structure of the cation of complex **5**. Thermal ellipsoids are drawn at the 50% probability level.

the reaction intermediate $[IrH_2(NC_5H_4\text{-}2\text{-}CH{=}CH_2\text{-}\kappa\text{-}N)(NCCH_3)_2(P\textit{i}Pr_3)]BF_4$ (**2**) (eq 1), which was found to be the major species in reaction mixtures maintained below 253 K. In the $^{31}P\{^1H\}$ NMR spectrum at 223 K, this dihydride displays a singlet at δ 29.20 that splits into a triplet (J_{PH} = 20.7 Hz) under off-resonance conditions due to hydride coupling. The ^1H NMR spectrum of this intermediate is consistent with the presence of two equivalent hydrides, two equivalent acetonitrile ligands, and a 2-vinylpyridine ligand. In agreement with the proposed C_s structure, the chemical shifts of the signals corresponding to olefinic protons (δ 7.51, 5.47, and 5.71) strongly suggest that the vinylpyridine ligand only coordinates through the N atom.

The N-coordination of the 2-vinylpyridine at the position trans to phosphine can explain the different behavior of this functionalized alkene when compared to that of simpler olefins such as ethylene and propene, previously observed to undergo rapid insertion into one or both Ir−H bonds of **1**.[3] Such an initial binding of the substrate may well favor the subsequent coordination of the alkenyl moiety after dissociation of a second acetonitrile, although it is also likely to hinder the coplanar disposition of hydride and C=C required for a concerted insertion. This restraint seems to direct the reaction toward an alternative H_2 reductive elimination/C−H activation sequence, as could be inferred from the experiment with $[IrD_2(NCCH_3)_3(P\textit{i}Pr_3)]BF_4$ (**1**-d_2), which selectively produced nondeuterated **3**.

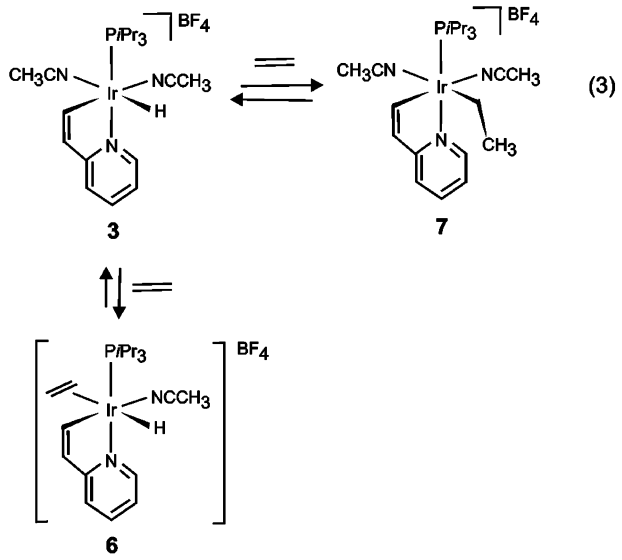
Alkene and Alkyne Insertion. Once the first equivalent of 2-vinylpyridine has blocked the coordination position trans to phosphine, a second equivalent of this substrate can undergo insertion into the Ir−H bond of **3** to give the compound $[Ir(NC_5H_4\text{-}2\text{-}(Z\text{-}CH{=}CH)\text{-}\kappa\text{-}N,C)(NC_5H_4\text{-}2\text{-}CH_2CH_2\text{-}\kappa\text{-}N,C)(NCCH_3)(P\textit{i}Pr_3)]BF_4$ (**5**) (eq 2).



The structure of this insertion product determined by X-ray diffraction is shown in Figure 2. Most relevant distances and angles of this structure are collected in Table 1. The compound contains two chelating ligands derived from the 2-vinylpyridine, one formed by C−H activation and other due to an insertion. Both display the same bite-angle, 78°, and are disposed in an approximately perpendicular fashion. The relatively long Ir−acetonitrile distance, 2.110(3) Å, is consistent with the expected large trans influence due to an alkenyl ligand.[8] Note that this distance is longer than that of **4**, 2.069(10) Å, in which the additional η^2 coordination to a second metal atom is likely to diminish the donor capability of the alkenyl ligand.

This latter structure indicates that formation of **5** is accompanied by a rearrangement affecting the relative position of the NC_5H_4-2-(*Z*-CH=CH)-κ-*N*,*C* and phosphine ligands. Such reorganization could tentatively be associated to restraints due to the presence of two chelating ligands, since the reactions of **3** with other simpler alkenes or alkynes have been observed to afford insertion products retaining the relative positions of these two ligands. This is the case of ethylene, which has been found to react with **3** to give the ethyl complex $[Ir(Et)\{NC_5H_4\text{-}2\text{-}Z\text{-}(CH{=}CH)\text{-}\kappa\text{-}N,C\}(NCCH_3)_2(P\textit{i}Pr_3)]BF_4$ (**7**) (eq 3). The β-elimination reaction in **7** to reform **3** has been spectroscopically observed to be possible but

very slow, being difficult to complete even when heating the $CDCl_3$ solutions of **7** to 333 K under a stream of argon.

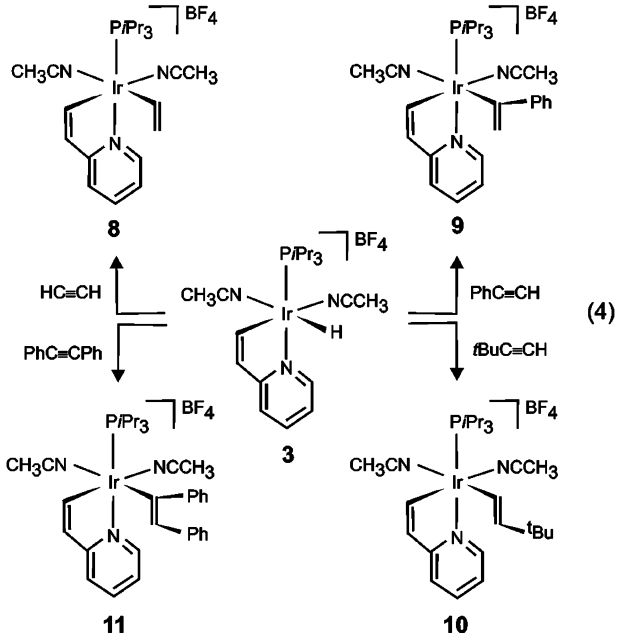


(3)

The NMR investigation of this ethylene insertion, in $CDCl_3$ at low temperature, has also permitted the characterization of the complex [IrH{NC_5H_4-2-*Z*-(CH═CH)-κ-*N*,*C*}(η^2-C_2H_4)($NCCH_3$)(P*i*Pr_3)]BF_4 (**6**), which displays a η^2-ethylene ligand coordinated trans to hydride. This substitution product seems to be that kinetically favored and, given that it cannot undergo insertion, has been found to accumulate in solution in large relative concentration when the reactions are kept below 263 K. The η^2-ethylene ligand of this complex gives rise to a singlet at δ 67.34 in the $^{13}C\{^1H\}$ NMR spectrum, and appears as an AA′BB′ spin system centered at δ 3.27 (J_{AB} = 9.3 Hz, $J_{AA'}$ = 12.9 Hz) in the proton NMR spectrum. These signals are consistent with a coordination position cis to the phosphine, also indicating the fast rotation of the ligand around the Ir−(η^2-C_2H_4) axis in the NMR time scale. The ^1H NMR spectrum also displays a doublet at δ −15.44 (J_{HP} = 19.8 Hz) corresponding to a hydride ligand cis to the phosphine. Compared to those of hydrides trans to acetonitrile, this latter chemical shift is clearly displaced toward lower field, suggesting the ligand in the trans position to be a good π-acceptor such as ethylene. The structural assignment of this six-coordinate compound can be completed after observing a doublet at δ 151.69 (J_{CP} = 7.8 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, attributable to a CH carbon σ-bonded to iridium at a position cis relative to the phosphine.

In agreement with the structure of **7** shown in eq 3, the $^{13}C\{^1H\}$ APT NMR spectrum of this ethyl compound displays two signals attributable to carbons σ-bonded to iridium and cis to the phosphine: a CH_2 at δ −15.66 (J_{CP} = 5.6 Hz) corresponding to the ethyl ligand and a CH at δ 157.48 (J_{CP} = 7.8 Hz) due to the chelating alkenyl. The resonance due to the quaternary carbon of this latter ligand, at δ 166.18, also shows a small but characteristic J_{CP} coupling constant of 1.9 Hz, indicative of a phosphine trans to the pyridinic nitrogen. Both C≡N carbons of the compound give rise to broad singlets, as expected from their coordination trans to labilizing groups such as alkenyl or alkyl.[3] Moreover, the line width of these latter signals at 293 K is not compatible with the relatively large J_{CP} coupling constant (ca. 15 Hz) expected for an alternative coordination of the acetonitrile trans to phosphorus.

Insertion compounds of structures similar to that deduced for **7** are formed by reaction of **3** with alkynes such as HC≡CH, PhC≡CH, *t*BuC≡CH, and PhC≡CPh (eq 4). The structural assignments of complexes **8**−**11**



(4)

based on their NMR data have been corroborated in the case of the diphenylacetylene derivative [Ir{*Z*-C(Ph)═CHPh}{NC_5H_4-2-*Z*-(CH═CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr_3)]BF_4 (**11**) through the X-ray structural determination shown in Figure 3. Most significant bond distances and angles of this structure are collected in Table 2.

Despite the similar coordination environment around the iridium atom shown by all these insertion products, the reactions of PhC≡CH and *t*BuC≡CH have been found to follow different regioselectivities. Thus, the insertion of phenylacetylene selectively takes place in the Markovnikov sense, leading to the product that contains a *gem*-alkenyl ligand (J_{HH} = 2.7 Hz), [Ir{C(Ph)═CH_2}{NC_5H_4-2-*Z*-(CH═CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr_3)]BF_4 (**9**) (eq 4). In contrast, *t*BuC≡CH selectively forms an insertion product with a trans alkenyl ligand (J_{HH} = 16.0 Hz), [Ir(*E*-CH═CH*t*Bu){NC_5H_4-2-*Z*-(CH═CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr_3)]BF_4 (**10**).

C−C Coupling. The insertion products **5** and **7**−**11** have been found to be stable. In particular, thermally induced reactions of C−C reductive elimination have not been observed even under harsh experimental conditions. In this respect, the behavior of these bis-alkenyl and alkenyl-alkyl compounds is similar to that reported for the related bis-phosphine cation [Ir($CH═CH_2$)$_2$($NCCH_3$)$_2$(PPh_3)$_2$]$^+$,[9] although is different from that of the monophosphine analogues [Ir($CH═CHR$)$_2$($NCCH_3$)$_2$(P*i*Pr_3)]$^+$, postulated as intermediates in the formation

(8) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5−80.

(9) Chin, C. S.; Lee, H.; Noh, S.; Park, H.; Kim, M. *Organometallics* **2003**, *22*, 2119−2123.

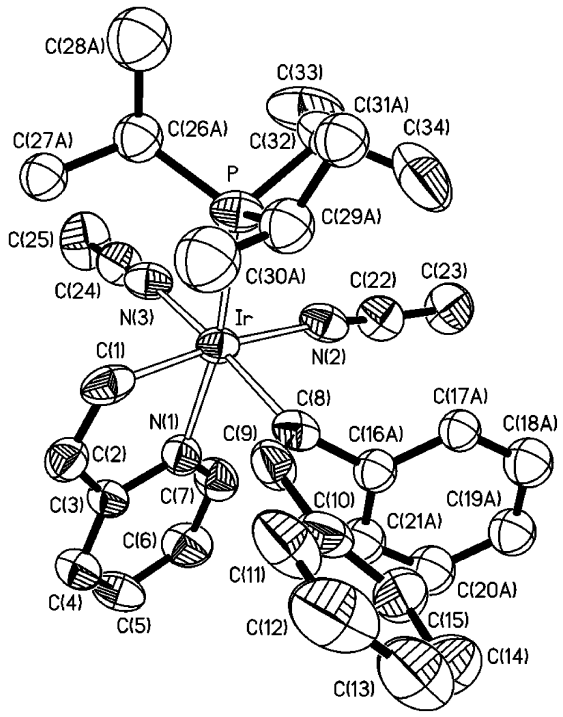
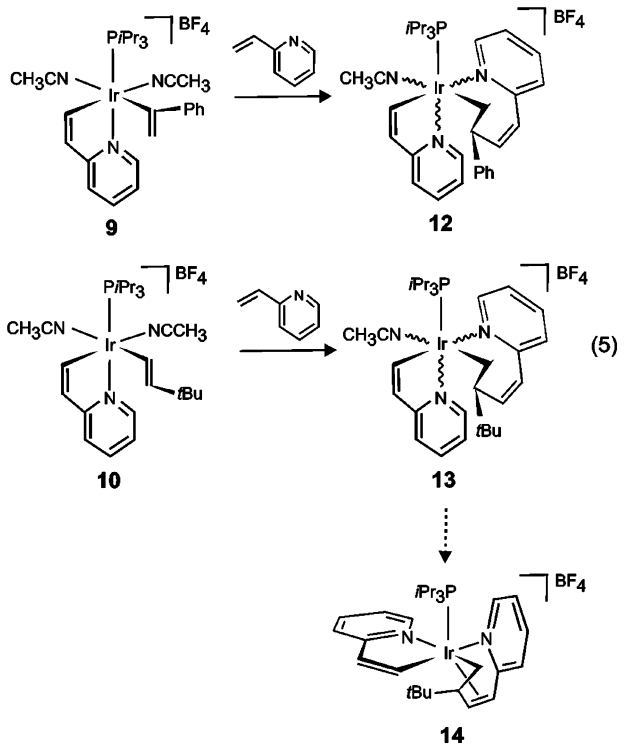


Figure 3. Molecular structure of the cation of complex **11**. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 11 and 14

11		**14**	
Ir−P	2.321(3)	Ir−P	2.3192(18)
Ir−C(1)	1.972(10)	Ir−C(6)	2.300(7)
Ir−C(8)	2.067(9)	Ir−C(7)	2.303(6)
Ir−N(1)	2.106(8)	Ir−C(9)	2.109(9)
Ir−N(2)	2.128(8)	Ir−C(20)	2.012(7)
Ir−N(3)	2.114(7)	Ir−N(1)	2.172(5)
		Ir−N(2)	2.140(6)
		C(6)−C(7)	1.360(10)
		C(7)−C(8)	1.505(11)
		C(8)−C(9)	1.522(10)
		C(19)−C(20)	1.342(13)
P−Ir−C(1)	94.3(3)	P−Ir−C(6)	166.14(19)
P−Ir−C(8)	96.9(2)	P−Ir−C(7)	156.0(2)
P−Ir−N(1)	171.4(2)	P−Ir−C(9)	93.3(2)
P−Ir−N(2)	95.4(2)	P−Ir−C(20)	90.0(2)
P−Ir−N(3)	92.8(2)	P−Ir−N(1)	105.31(16)
C(1)−Ir−C(8)	89.0(3)	P−Ir−N(2)	97.50(15)
C(1)−Ir−N(1)	78.9(3)	C(6)−Ir−N(1)	62.0(2)
C(1)−Ir−N(2)	170.1(3)	C(6)−Ir−N(2)	79.2(2)
C(1)−Ir−N(3)	94.5(3)	C(7)−Ir−N(1)	82.4(2)
C(8)−Ir−N(1)	88.4(3)	C(7)−Ir−N(2)	104.4(3)
C(8)−Ir−N(2)	91.3(3)	C(9)−Ir−N(1)	84.6(3)
C(8)−Ir−N(3)	169.4(3)	C(9)−Ir−N(2)	168.7(3)
N(1)−Ir−N(2)	91.2(3)	C(20)−Ir−N(1)	163.6(3)
N(1)−Ir−N(3)	82.5(3)	C(20)−Ir−N(2)	75.1(3)
N(2)−Ir−N(3)	83.5(3)	N(1)−Ir−N(2)	95.8(2)
C(8)−C(9)−C(10)	131.9(11)	Ir−C(19)−C(20)	116.6(7)
		Ir−C(9)−C(8)	98.7(5)

of Ir(I) butadiene complexes.[10] However, complexes **7**−**11** have been found to readily react with a new equivalent of 2-vinylpyridine. As shown in eq 5, such reaction results in the formation of new C−C bonds for the alkenyl derivatives **9** and **10**.



(5)

The spectroscopic characterization of the new complexes [Ir{NC_5H_4-2-*Z*-(CH═CH)-*κ*-*N*,*C*}{NC_5H_4-2-*Z*-(CH═CH)CH(R)CH_2-*κ*-*N*,*C*}($NCCH_3$)(P*i*Pr_3)]BF_4 (R = Ph, **12**; R = *t*Bu, **13**), in particular the ^{1}H-COSY and ^{1}H,^{13}C-HSQC NMR correlation experiments, indicates the presence of a new carbon skeleton comprising a *σ*-bonded CH_2 (cis to phosphine), a CHR group, and a cis olefinic fragment CH═CH connected to a pyridine ring. These NMR spectra also evidence the presence of an acetonitrile cis to the phosphine and an intact NC_5H_4-2-(*Z*-CH═CH)-*κ*-*N*,*C* ligand, the metalated carbon atom of which also binds at a position cis relative to the phosphine. These spectroscopic data do not reveal the coordination positions of the two different pyridinic nitrogens, but lead to the approximate structures shown in eq 5.

The NMR spectroscopic observation of the reactions leading to **12** and **13** in $CDCl_3$ has confirmed that both transformations are quantitative and selective. However, the NMR spectra of the solids obtained after treatment of these solutions with diethyl ether indicate the presence of several minor byproducts, which are likely due to the partial loss of acetonitrile during the precipitation and subsequent workup of the solids. Consistently with this interpretation and with the incorrect elemental analyses obtained for **12** and **13**, the only successful attempt to crystallize these compounds has led, starting from solutions of **13**, to a few crystals of the compound [Ir{NC_5H_4-2-*Z*-(CH═CH)-*κ*-*N*,*C*}{*η*^{2}-NC_5H_4-2-*Z*-(CH═CH)CH(*t*Bu)-CH_2-*κ*-*N*,*C*}(P*i*Pr_3)]BF_4 (**14**) (eq 5). The structure of this compound as determined by X-ray diffraction is shown in Figure 4, and its most relevant bond distances and angles are collected in Table 2. Most likely, the formation of **14** from **13** involves an acetonitrile substitution reaction similar to that previously discussed for the formation of the

(10) Navarro, J.; Sági, M.; Sola, E.; Lahoz, F. J.; Dobrinovitch, I. T.; Kathó, A.; Joó, F.; Oro, L. A. *Adv. Synth. Catal.* **2003**, *345*, 280−288.

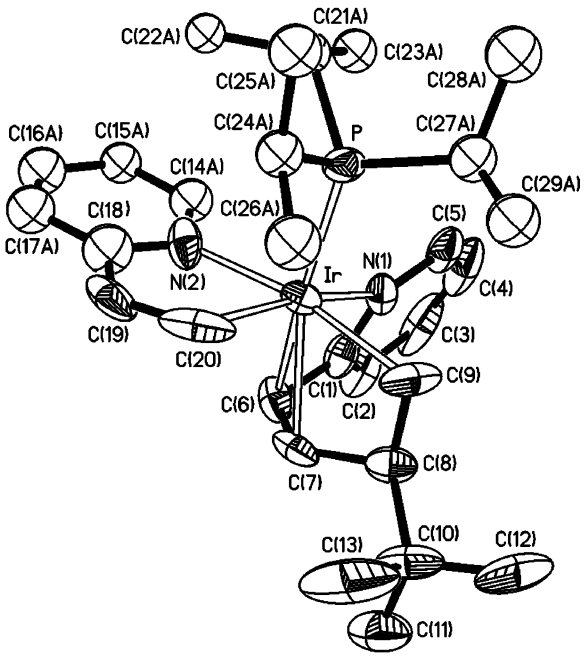
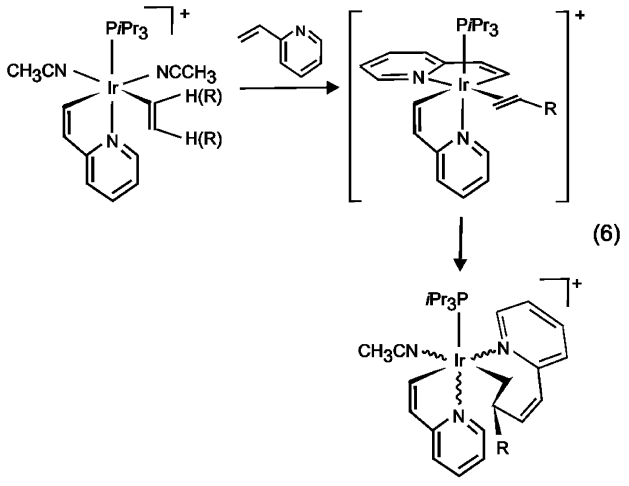


Figure 4. Molecular structure of the cation of complex **14**. Thermal ellipsoids are drawn at the 50% probability level.

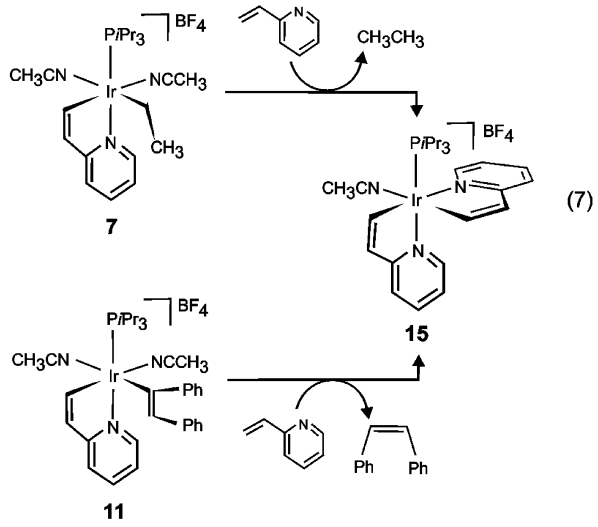
dinuclear complex **4** from **3**. In the case of **14**, the formation of a η^2-alkene complex does not require a dimerization of the postulated unsaturated fragments, since the new seven-membered ring obtained in the C−C coupling reaction offers an intramolecular alternative for the η^2-C=C coordination.

The spectroscopic characterization of **12** and **13** indicates that, irrespective of the gem or trans stereochemistry of the alkenyl ligand in the starting complex, the R group (Ph or *t*Bu, respectively) lies at the β position of the new chelating ligand. This strongly suggests the C−C forming reactions do not involve the alkenyl ligands but the corresponding alkenes. Considering this observation, the mechanism of eq 6 can be



regarded as the most likely for the formation of such C−C coupling products. The mechanism is initiated by a new C−H activation of 2-vinylpyridine that would generate the alkene ligand at the iridium coordination sphere. Such an initial step could consist of either a single-step σ-bond metathesis or a two-step reaction via an Ir(V) intermediate.[11] A subsequent elementary step of alkene insertion into a cis-located Ir−C bond would form the observed seven-membered ring.

The proposed participation of η^2-alkene intermediate complexes can be further supported by the reactions of the alkyl compound **7** and the diphenylacetylene derivative **11** shown in eq 7. Under conditions similar to those



affording **12** and **13**, **7** and **11** have been found to form a complex containing two activated 2-vinylpyridines, [Ir{NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}$_2$($NCCH_3$)(P*i*Pr_3)]BF_4 (**15**), together with ethane or *cis*-stilbene, respectively. Both reactions are consistent with the initial step of the proposed mechanism, also indicating that generation at the metal center of a (bulky) weakly coordinating alkene such as *cis*-stilbene provokes its dissociation, thus precluding any subsequent C−C coupling reaction.

The NMR spectra of **15** are consistent with the structure proposed in eq 7, although they are compatible with either a cis or a trans relative disposition of the two metalated alkenyl carbons. Even though the proposed kinetic intermediates in route to **15** are expected to show mutually trans alkenyl moieties (eq 6), the structural proposal in eq 7 has taken into account that such arrangement of two strong σ-donor ligands is expected to be thermodynamically disfavored with respect to a cis one. Given that formation of **15** from the proposed η^2-alkene (or alkane) intermediate likely involves the participation of a five-coordinate intermediate, an isomerization to the most stable geometry prior to acetonitrile coordination also seems to be likely.

This proposed difference between the structures of the latter kinetic and thermodynamic bis-alkenyl compounds is also in agreement with the observed reactivity of **15**, which fails to react with ethylene, styrene, or *tert*-butylethylene. This fact could be regarded as an additional support for C−C formations involving insertion steps, since in contrast to what is likely in the proposed kinetic alkene intermediates of eq 6, the possible products of acetonitrile substitution by alkene in **15** could hardly develop the planar four-centered transition state required for a concerted insertion. Considering this

(11) For a discussion on this topic and leading references, see: (a) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816−1817. (b) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707−2717.

latter observation and the mild experimental conditions under which these C−C couplings have been observed, it can be concluded that alkene insertions into Ir−C bonds constitute feasible functionalization steps in complexes that favor cis coplanar relationships between the fragments to be coupled. Taking into account the high activation barriers commonly associated with C−C reductive eliminations from transition metal complexes,[12] this conclusion could be significant for the rationalization and further development of Murai-type functionalization processes.

Experimental Section

Equipment. Infrared spectra were recorded in KBr with a Perkin-Elmer Spectrum One spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Bruker Avance 300-MHz spectrometer. ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P (121.48 MHz) chemical shifts were measured relative to H_3PO_4 (85%). Coupling constants (J) are given in hertz. Generally, spectral assignments were achieved by ^{1}H COSY, NOESY, ^{13}C DEPT, and ^{1}H/^{13}C HSQC experiments. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Conductivities were measured in ca. 5×10^{-4} M solutions with a Philips PW 9501/01 conductimeter.

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use.[13] The complex $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (**1**) was prepared as previously reported.[3] Its isotopomer $[IrD_2(NCCH_3)_3(PiPr_3)]BF_4$ (**1**-d_2) was generated in situ by exposing a solution of **1** in $CDCl_3$ to a D_2 atmosphere during 12 h at room temperature, finally removing the D_2 excess with an argon stream. Phenylacetylene (Aldrich) was distilled under argon prior to use. All other reagents were obtained from commercial sources and were used as received. All new compounds described below are air-sensitive in solution.

$[IrH_2(NC_5H_4$-2-CH=CH_2-κ-$N)(NCCH_3)_2(PiPr_3)]BF_4$ (2). A solution of **1** (40 mg, 0.07 mmol) in $CDCl_3$ (0.5 mL) contained in a NMR tube was cooled at 253 K and reacted with 2-vinylpyridine (7 μL, 0.06 mmol). The sample was shaken and rapidly introduced in the NMR spectrometer at 223 K. The spectra revealed the presence of a 1:6 mixture of complexes **1** and **2**, together with detectable amounts of complex **3** (see below). Data for **2**: ^{1}H NMR ($CDCl_3$, 223 K) δ −22.21 (d, J_{HP} = 20.7, 2H, IrH), 1.14 (dd, J_{HP} = 14.0, J_{HH} = 7.2, 18H, PCHCH_3), 2.11 (m, 3H, PCHCH$_3$), 2.33 (s, 6H, NCCH$_3$), 5.47 (d, J_{HH} = 11.3, 1H, CH_2=CHPy), 5.71 (d, J_{HH} = 18.0, 1H, CH_2=CHPy), 7.43 (t, J_{HH} = 8.4, 1H, CH), 7.51 (dd, J_{HH} = 18.0, 11.3, 1H, CH$_2$=CHPy), 7.61 (d, J_{HH} = 8.4, 1H, CH), 7.77 (t, J_{HH} = 7.8, 1H, CH), 9.28 (m, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 223 K) δ 29.20 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K) δ 3.12 (s, NCCH$_3$), 18.72 (s, PCHCH$_3$), 24.06 (d, J_{CP} = 34.56, PCHCH$_3$), 118.69 (s, =CH$_2$), 118.94 (s, NCCH$_3$), 121.88, 124.88, 137.70, 141.87, 154.79 (all s, CH), 158.93 (s, C).

Preparation of $[IrH\{NC_5H_4$-2-Z-(CH=CH)-κ-$N,C\}(NCCH_3)_2(PiPr_3)]BF_4$ (3). A solution of **1** (300 mg, 0.53 mmol) in acetone (8 mL) was reacted with 2-vinylpyridine (69 μL, 0.64 mmol) at 253 K. After 30 min, the reaction was allowed to reach room temperature and stirred for 1 h. The resulting yellow solution was concentrated to ca. 0.5 mL and diethyl ether was slowly added to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 282 mg (85%). Anal. Calcd for $C_{20}H_{34}N_3BF_4IrP$: C, 38.34; H, 5.47; N, 6.71. Found: C, 38.53; H, 5.69; N, 6.70. MS (FAB+, m/z (%)) 499 (20) [M^+ − NCCH$_3$], 456 (100) [M^+ − 2 NCCH$_3$)]. Λ_M(acetone) = 124 Ω^{-1} cm^2 mol^{-1} (1:1). IR (cm^{-1}) 2113 ν(Ir−H). ^{1}H NMR (CD_2Cl_2, 293 K) δ −23.11 (d, J_{HP} = 20.1, 1H, IrH), 1.19, 1.23 (both dd, J_{HP} = 13.8, J_{HH} = 7.2, 9H each, PCHCH_3), 2.17 (br, 3H, NCCH_3), 2.34 (m, 3H, PCHCH$_3$), 2.60 (s, 3H, NCCH_3), 6.80 (d, J_{HH} = 8.1, 1H, IrCH=CH), 7.20 (d, J_{HH} = 6.0, 1H, CH), 7.23 (d, J_{HH} = 7.6, 1H, CH), 7.60 (t, J_{HH} = 7.6, 1H, CH), 8.15 (dd, J_{HH} = 8.1, J_{HP} = 3.9, 1H, IrCH=CH), 8.79 (m, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 20.80 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 2.85, 3.46 (both s, NCCH$_3$), 18.46, 18.62 (both s, PCHCH$_3$), 23.95 (d, J_{CP} = 31.3, PCHCH$_3$), 119.35 (s, CH), 119.47 (br, NCCH$_3$), 120.45 (d, J_{CP} = 2.8, CH), 121.40 (s, NCCH$_3$), 134.10 (d, J_{CP} = 2.3, IrCH=CH), 138.56, 149.07 (both s, CH), 154.26 (d, J_{CP} = 7.4, IrCH=CH), 167.30 (d, J_{CP} = 1.8, C).

Preparation of $[Ir(NC_5H_4$-2-(Z-CH=CH)-κ-$N,C)(NC_5H_4$-2-CH_2CH_2-κ-$N,C)(NCCH_3)(PiPr_3)]BF_4$ (5). A solution of **1** (100 mg, 0.18 mmol) in CH_2Cl_2 (8 mL) was reacted with 2-vinylpyridine (41 μL, 0.38 mmol) during 2 h at 273 K. The resulting yellow solution was concentrated to ca. 0.5 mL and diethyl ether was slowly added to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 110 mg (90%). Anal. Calcd for $C_{25}H_{38}N_3BF_4IrP$: C, 43.48; H, 5.55; N, 6.08. Found: C, 43.06; H, 5.48; N, 6.17. MS (FAB+, m/z (%)) 604 (20) [M^+], 563 (100) [M^+ − NCCH$_3$]. Λ_M(acetone) = 136 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 1.08 (dd, J_{HP} = 13.0, J_{HH} = 6.4, 9H, PCHCH_3), 1.12 (dd, J_{HP} = 13.6, J_{HH} = 6.8, 9H, PCHCH_3), 2.32 (m, 3H, PCHCH$_3$), 2.35 (m, 1H, IrCH_2CH$_2$), 2.45 (s, 3H, NCCH_3), 2.50 (m, 1H, IrCH_2CH$_2$), 3.12 (A part of an ABXY spin system, J_{AB} = 17.1, J_{AX} = J_{AY} = 6.3, 1H, IrCH$_2$CH_2), 3.29 (B part of an ABXY spin system, J_{AB} = 17.1, J_{BX} = J_{BY} = 7.2, 1H, IrCH$_2$CH_2), 6.83 (d, J_{HH} = 8.4, 1H, IrCH=CH), 6.97 (dd, J_{HH} = 7.5, 6.4, 1H, CH), 7.1 (m, 1H, CH), 7.26, 7.33 (both d, J_{HH} = 7.5, 1H each, CH), 7.50, 7.57 (both t, J_{HH} = 7.5, 1H each, CH), 7.70 (t, J_{HH} = 7.2, 1H, CH), 8.48 (d, J_{HH} = 8.4, 1H, IrCH=CH), 9.16 (br d, J_{HH} = 7.2, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ −1.85 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ −5.52 (d, J_{CP} = 6.4, IrCH_2CH$_2$), 3.43 (s, NCCH$_3$), 18.63 (d, J_{CP} = 2.0, PCHCH$_3$), 19.08 (s, PCHCH$_3$), 24.32 (d, J_{CP} = 30.4, PCHCH$_3$), 43.30 (d, J_{CP} = 2.7, IrCH$_2C$H$_2$), 120.66 (s, CH), 121.45 (d, J_{CP} = 1.4, CH), 121.64 (s, NCCH$_3$), 122.14 (s, CH), 123.36 (d, J_{CP} = 2.7, CH), 133.59 (s, IrCH=CH), 137.62, 138.60, 146.33, 151.25 (all s, CH), 159.92 (d, J_{CP} = 8.8, IrCH=CH), 167.27 (s, C), 169.67 (d, J_{CP} = 1.2, C). The crystals used in the X-ray structural determination were obtained by slow diffusion of diethyl ether into a saturated solution of **5** in acetone.

$[IrH\{NC_5H_4$-2-Z-(CH=CH)-κ-$N,C\}(\eta^2$-$C_2H_4)(NCCH_3)(PiPr_3)]BF_4$ (6). Ethylene was bubbled during 5 min through a solution of **3** (30 mg, 0.05 mmol) in $CDCl_3$ (0.5 mL) contained in a NMR tube at 253 K. The spectra of this solution obtained at 253 K indicated the presence of a ca. 3:1 mixture of compounds **3** and **6**, respectively. Data for **6**: ^{1}H NMR ($CDCl_3$, 253 K) δ −15.44 (d, J_{HP} = 19.8, 1H, IrH), 0.98, 1.21 (both dd, J_{HP} = 14.3, J_{HH} = 7.0, 9H each, PCHCH_3), 2.32 (m, 3H, PCHCH$_3$), 2.53 (s, 3H, NCCH_3), 3.27 (AA′BB′ spin system: δ_A 2.89, δ_B 3.66, J_{AB} = $J_{A'B'}$ = 9.3, $J_{AA'}$ = $J_{BB'}$ = 12.9, 4H, η^2-C_2H_4), 6.72 (d, J_{HH} = 8.1, 1H, IrCH=CH), 7.35 (m, 2H, IrCH=CH + CH), 7.75 (t, J_{HH} = 7.8, 1H, CH), 9.17 (m, 2H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 253 K) δ 21.34 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 253 K) δ 3.42 (s, NCCH$_3$), 18.30 (d, J_{CP} = 1.4, PCHCH$_3$), 18.65 (s, PCHCH$_3$), 25.10 (d, J_{CP} = 29.9, PCHCH$_3$), 67.34 (s, η^2-C_2H_4), 119.88 (s, CH), 120.78 (s, NCCH$_3$), 122.50 (d, J_{CP} = 3.2, CH),

(12) See for example: (a) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442−9456. (b) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839−2852.

(13) (a) Shriver, D. F. *The Manipulation of Air-sensitive Compounds*; McGraw-Hill: New York, 1969. (b) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinmann; Oxford, UK, 1996.

133.35 (s, IrCH=*C*H), 138.21, 147.9 (both s, CH), 151.69 (d, J_{CP} = 7.8, Ir*C*H=CH), 165.93 (s, C).

Preparation of [Ir(Et){NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}-($NCCH_3$)$_2$(P*i*Pr$_3$)]BF_4 (7). A solution of **3** (150 mg, 0.24 mmol) in CH_2Cl_2 (8 mL) was stirred under ethylene atmosphere (*P* = 1.1 bar) during 2 h at room temperature. The resulting orange solution was concentrated to ca. 0.5 mL and diethyl ether was slowly added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 118 mg (75%). Anal. Calcd for $C_{22}H_{38}N_3BF_4IrP$: C, 40.37, H, 5.85; N, 6.42. Found: C, 40.19; H, 5.58; N, 6.03. Λ_M(acetone) = 104 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 0.27 (t, J_{HH} = 7.5, 3H, IrCH$_2$C*H*$_3$), 0.62 (dqd, J_{HH} = 10.8, 7.5, J_{HP} = 1.8, 1H, IrC*H*$_2$CH$_3$), 1.27 (dd, J_{HP} = 12.9, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.27 (m, 1H, IrC*H*$_2$CH$_3$), 2.12 (br, 3H, NCC*H*$_3$), 2.55 (m, 3H, PC*H*CH$_3$), 2.60 (br, 3H, NCC*H*$_3$), 6.87 (d, J_{HH} = 8.4, 1H, IrCH=C*H*), 7.21 (m, 2H, CH), 7.64 (t, J_{HH} = 7.5, 1H, CH), 8.70 (dd, J_{HH} = 8.4, J_{HP} = 4.5, 1H, IrC*H*=CH), 8.75 (m, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ −0.04 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ −15.66 (d, J_{CP} = 5.6, Ir*C*H$_2$-CH$_3$), 2.82, 3.73 (both br, NC*C*H$_3$), 15.57 (s, IrCH$_2$*C*H$_3$), 19.07, 19.28 (both s, PCH*C*H$_3$), 23.56 (d, J_{CP} = 29.5, P*C*HCH$_3$), 119.31 (s, CH), 120.41 (d, J_{CP} = 3.2, CH), 121.60, 122.99 (both br, N*C*CH$_3$), 133.24 (d, J_{CP} = 2.7, IrCH=*C*H), 138.56, 148.14 (both s, CH), 157.48 (d, J_{CP} = 7.8, Ir*C*H=CH), 166.18 (d, J_{CP} = 1.9, C).

Preparation of [Ir(CH=CH$_2$){NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr$_3$)]BF_4 (8). A slow acetylene stream was passed during ca. 3 min through a solution of **3** (150 mg, 0.24 mmol) in CH_2Cl_2 (8 mL) at room temperature. The resulting pale orange solution was concentrated to ca. 0.5 mL and diethyl ether was slowly added to give a white solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 124 mg (80%). Anal. Calcd for $C_{22}H_{36}N_3BF_4IrP$: C, 40.49; H, 5.56; N, 6.44. Found: C, 40.83; H, 5.67; N, 6.56. MS (FAB+, *m*/*z* (%)) 484 (100) [M$^+$ − 2 NCCH$_3$)]. Λ_M(acetone) = 119 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 1.25, 1.27 (both dd, J_{HP} = 13.4, J_{HH} = 6.6, 9H each, PCHC*H*$_3$), 2.19 (br, 3H, NCC*H*$_3$), 2.50 (m, 3H, PC*H*CH$_3$), 2.66 (s, 3H, NCC*H*$_3$), 4.69 (dd, J_{HH} = 17.4, 2.1, 1H, IrCH=C*H*$_2$), 5.04 (dd, J_{HH} = 10.2, 2.1, 1H, IrCH=C*H*$_2$), 6.68 (ddd, J_{HH} = 17.4, 10.2, J_{HP} = 3.0, 1H, IrC*H*=CH$_2$), 6.90 (d, J_{HH} = 8.4, 1H, IrCH=C*H*), 7.19 (t, J_{HH} = 6.9, 1H, CH), 7.24 (d, J_{HH} = 7.8, 1H, CH), 7.63 (dd, J_{HH} = 7.8, 1H, CH), 8.59 (dd, J_{HH} = 8.4, J_{HP} = 4.5, 1H, IrC*H*=CH), 8.64 (m, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 1.84 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 3.74 (br, NC*C*H$_3$) 3.93 (s, NC*C*H$_3$), 18.76 (d, J_{CP} = 2.1, PCH*C*H$_3$), 19.30 (s, PCH*C*H$_3$), 23.63 (d, J_{CP} = 30.0, P*C*HCH$_3$), 117.77 (s, N*C*CH$_3$), 117.83 (br, N*C*CH$_3$), 119.66, 120.89 (both s, CH), 121.38 (s, IrCH=*C*H$_2$), 122.35 (d, J_{CP} = 8.0, Ir*C*H=CH$_2$), 134.06 (d, J_{CP} = 3.4, IrCH=*C*H), 138.74, 147.59 (both s, CH), 155.52 (d, J_{CP} = 8.4, Ir*C*H=CH), 165.84 (d, J_{CP} = 1.8, C).

Preparation of [Ir{C(Ph)=CH$_2$}{NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr$_3$)]BF_4 (9). A solution of **3** (150 mg, 0.24 mmol) in CH_2Cl_2 (8 mL) was treated with PhC≡CH (32 μL, 0.29 mmol) and allowed to react for 1 h at room temperature. The resulting red solution was concentrated to ca. 0.5 mL and diethyl ether was added to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 146 mg (84%). Anal. Calcd for $C_{28}H_{40}N_3BF_4IrP$: C, 46.16; H, 5.53; N, 5.77. Found: C, 46.39; H, 5.67; N, 5.53. MS (FAB+, *m*/*z* (%)) 560 (30) [M$^+$ − 2 NCCH$_3$]. Λ_M(acetone) = 109 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 1.32 (dd, J_{HP} = 12.9, J_{HH} = 7.5, 9H, PCHC*H*$_3$), 1.33 (dd, J_{HP} = 13.4, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.21 (s, 6H, NCC*H*$_3$), 2.75 (m, 3H, PC*H*CH$_3$), 4.75, 5.01 (both d, J_{HH} = 2.7, 1H each, IrC(Ph)=C*H*$_2$), 6.51 (dd, J_{HH} = 7.2, 2.2, 2H, CH), 6.88 (d, J_{HH} = 8.1, 1H, IrCH=C*H*), 6.99 (m, 3H, CH), 7.22 (m, 3H, CH), 7.64 (t, J_{HH} = 7.8, 1H, CH), 8.45 (m, 1H, CH), 8.87 (dd, J_{HH} = 8.1, J_{HP} = 4.5 1H, IrC*H*=CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ −3.26 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 3.0 (br, NC*C*H$_3$), 19.38, 19.44 (both s, PCH*C*H$_3$), 24.34 (d, J_{CP} = 29.4, P*C*HCH$_3$), 119.65 (s, CH), 120.41 (d, J_{CP} = 2.8, CH), 122.61 (s, IrC(Ph)=*C*H$_2$), 124.36, 126.60, 127.12 (all s, CH), 133.24 (d, J_{CP} = 7.8, Ir*C*(Ph)=CH$_2$), 133.62, 139.01, 148.15 (all s, CH), 153.34 (s, C), 155.27 (d, J_{CP} = 6.9, Ir*C*H=CH), 166.18 (s, C).

Preparation of [Ir(*E*-CH=CH*t*Bu){NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr$_3$)]BF_4 (10). The procedure described for **9** with use of *t*BuC≡CH (35 μL, 0.29 mmol) as the substrate produced a pale yellow solid: yield 128 mg (75%). Anal. Calcd for $C_{26}H_{44}N_3BF_4IrP$: C, 44.07; H, 6.26; N, 5.93. Found: C, 43.75; H, 5.96; N, 5.73. MS (FAB+, *m*/*z* (%)) 622 (8) [M$^+$]. Λ_M(acetone) = 99 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 0.61 (s, 9H, C(C*H*$_3$)$_3$), 1.23 (dd, J_{HP} = 13.7, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.25 (dd, J_{HP} = 13.2, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.19 (br, 3H, NCC*H*$_3$), 2.57 (m, 3H, PC*H*CH$_3$), 2.67 (s, 3H, NCC*H*$_3$), 4.86 (dd, J_{HH} = 16.0, J_{HP} = 0.5, 1H, IrCH=CH*t*Bu), 5.80 (dd, J_{HH} = 16.0, J_{HP} = 2.7, 1H, IrC*H*=CH*t*Bu), 6.89 (d, J_{HH} = 8.3, 1H, IrCH=C*H*), 7.15 (t, J_{HH} = 6.6, 1H, CH), 7.21 (d, J_{HH} = 7.8, 1H, CH), 7.60 (t, J_{HH} = 7.8, 1H, CH), 8.55 (m, 2H, IrC*H*=CH + CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 1.80 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 3.13 (br, NC*C*H$_3$) 3.92 (s, NC*C*H$_3$), 18.92 (d, J_{CP} = 2.3, PCH*C*H$_3$), 19.50 (s, PCH*C*H$_3$), 23.76 (d, J_{CP} = 30.0, P*C*HCH$_3$), 29.82 (s, C(*C*H$_3$)$_3$), 34.54 (s, *C*(CH$_3$)$_3$), 102.80 (d, J_{CP} = 9.1, Ir*C*H=CH*t*Bu), 119.40 (d, J_{CP} = 2.3, CH), 120.50 (s, CH), 120.55 (s, N*C*CH$_3$), 121.01 (br, N*C*CH$_3$), 133.76 (d, J_{CP} = 3.0, IrCH=*C*H), 138.39 (s, CH), 143.38 (s, IrCH=*C*H*t*Bu), 147.35 (s, CH), 155.69 (d, J_{CP} = 8.3, Ir*C*H=CH), 165.79 (d, J_{CP} = 2.3, C).

Preparation of [Ir{*Z*-C(Ph)=CHPh}{NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}($NCCH_3$)$_2$(P*i*Pr$_3$)]BF_4 (11). The procedure described for **9** with PhC≡CPh (51.2 mg, 0.29 mmol) as the substrate produced a yellow solid: yield 164 mg (85%). Anal. Calcd for $C_{34}H_{44}N_3BF_4IrP$: C, 50.75; H, 5.51; N, 5.22. Found: C, 50.49; H, 5.59; N, 5.30. MS (FAB+, *m*/*z* (%)) 636 (55) [M$^+$ − 2 NCCH$_3$]. Λ_M(acetone) = 109 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR ($CDCl_3$, 293 K) δ 1.43, 1.46 (both dd, J_{HP} = 13.5, J_{HH} = 6.9, 9H each, PCHC*H*$_3$), 2.25, 2.29 (both br, 3H each, NCC*H*$_3$), 2.88 (m, 3H, PC*H*CH$_3$), 6.15 (s, 1H, IrC(Ph)=C*H*Ph), 6.47 (dd, J_{HH} = 6.9, 2.2, 2H, CH), 7.00 (d, J_{HH} = 8.1, 1H, IrCH=C*H*), 7.01−7.08 (all m, 9H, CH), 7.23 (t, J_{HH} = 6.6, 1H, CH), 7.26 (d, J_{HH} = 7.4, 1H, CH), 7.69 (t, J_{HH} = 7.7, 1H, CH), 8.42 (m, 1H, CH), 8.99 (dd, J_{HH} = 8.1, J_{HP} = 4.5, 1H, IrC*H*=CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ −3.96 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ 2.99, 3.18 (both br, NC*C*H$_3$), 19.62 (d, J_{CP} = 1.6, PCH*C*H$_3$), 19.66 (d, J_{CP} = 2.0, PCH*C*H$_3$), 24.59 (d, J_{CP} = 29.1, P*C*HCH$_3$), 119.54 (d, J_{CP} = 1.6, CH), 120.56 (d, J_{CP} = 3.2, CH), 121.12, 121.40 (both br, N*C*CH$_3$), 124.42, 124.66, 127.44, 128.01 (all s, CH), 128.42 (d, J_{CP} = 7.4, Ir*C*(Ph)=CHPh), 133.55 (d, J_{CP} = 2.9, IrC(Ph)=*C*HPh), 136.37 (s, IrCH=*C*H), 139.09 (s, CH), 139.90 (s, C), 148.45 (s, CH), 150.11 (br, C), 155.25 (d, J_{CP} = 6.3, Ir*C*H=CH), 166.21 (d, J_{CP} = 1.1 C). The crystals used in the X-ray structural determination were obtained by slow diffusion of diethyl ether into a saturated solution of **11** in CH_2Cl_2 at 253 K.

Preparation of [Ir{NC_5H_4-2-*Z*-(CH=CH)-κ-*N*,*C*}{NC_5H_4-2-*Z*-(CH=CH)CH(Ph)CH$_2$-κ-*N*,*C*}($NCCH_3$)(P*i*Pr$_3$)]BF_4 (12). A solution of **9** (175 mg, 0.24 mmol) in CH_2Cl_2 (8 mL) was treated with 2-vinylpyridine (31 μL, 0.29 mmol) and allowed to react for 1 h at room temperature. The resulting orange solution was concentrated to ca. 0.5 mL and diethyl ether was slowly added to give a white solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 143 mg (75%). MS (FAB+, *m*/*z* (%)) 665 (15) [M$^+$ − NCCH$_3$]. Λ_M(acetone) = 112 Ω^{-1} cm^2 mol^{-1} (1:1). The NMR spectra of the $CDCl_3$ solutions obtained from this solid revealed the presence of compound **12** together with a mixture of various minor additional compounds, the relative proportion of which was different in the various preparations attempted (between 10% and 20%). Data for **12**: ^{1}H NMR ($CDCl_3$, 293 K) δ 1.09, 1.16 (both dd, J_{HP} = 12.9, J_{HH} = 7.2, 9H each, PCHC*H*$_3$), 2.19 (m, 3H, PC*H*CH$_3$), 2.66 (s, 3H, NCC*H*$_3$), 2.71

(m, J_{HH} = 11.4, 10.8, J_{HP} = 3.0, 1H, IrCH_2CH(Ph)CH=CH), 2.75 (m, J_{HH} = 10.8, 3.6, 1H, IrCH_2CH(Ph)CH=CH), 3.04 (ddd, J_{HH} = 11.4, 8.4, 3.6, 1H, IrCH$_2$C*H*(Ph)CH=CH), 6.26 (dd, J_{HH} = 11.1, 8.4, 1H, IrCH$_2$CH(Ph)C*H*=CH), 6.35 (d, 1H, J_{HH} = 11.1, IrCH$_2$CH(Ph)CH=C*H*), 6.46 (d, J_{HH} = 7.8, 1H, IrCH=C*H*), 6.81, 7.00 (both d, J_{HH} = 7.8, 1H each, CH), 7.11 (t, J_{HH} = 7.8, 1H, CH), 7.15−7.35 (m, 10H, CH), 7.42 (t, J_{HH} = 7.5, 1H, CH), 7.50 (t, J_{HH} = 7.8, 1H, CH), 8.79 (d, J_{HH} = 7.8, 1H, CH), 9.13 (m, 2H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −10.69 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 4.18 (s, NC*C*H$_3$), 6.32 (d, J_{CP} = 6.0, IrCH_2CH(Ph)CH=CH), 19.17, 19.36 (both s, PCH*C*H$_3$), 23.94 (d, J_{CP} = 30.4, P*C*HCH$_3$), 48.59 (s, IrCH$_2$*C*H(Ph)CH=CH), 121.97 (s, N*C*CH$_3$), 119.70, 126.09, 137.05, 138.66, 151.88, 153.76, 121.79, 126.86, 128.77 (all s, CH), 122.42 (d, J_{CP} = 1.8, CH), 124.71 (s, IrCH$_2$CH(Ph)CH=*C*H), 127.04 (d, J_{CP} = 2.7, CH), 132.29 (s, IrCH=*C*H), 142.83 (s, IrCH$_2$CH(Ph)C*H*=CH), 148.61 (s, C), 160.44 (d, J_{CP} = 8.3, Ir*C*H=CH), 159.05, 166.45 (both s, C).

Preparation of [Ir{NC$_5$H$_4$-2-*Z*-(CH=CH)-*κ*-*N*,*C*}{NC$_5$H$_4$-2-*Z*-(CH=CH)CH(*t*Bu)CH$_2$-*κ*-*N*,*C*}(NCCH$_3$)(P*i*Pr$_3$)]BF$_4$ (13). The procedure described for **12** but starting from complex **10** (170 mg, 0.24 mmol) gave a white solid: yield 131 mg (70%). MS (FAB+, *m*/*z* (%)) 645 (60) [M$^+$ − NCCH$_3$]. Λ_M(acetone) = 103 Ω^{-1} cm^2 mol^{-1} (1:1). The NMR spectra of the $CDCl_3$ solutions obtained from this solid also revealed the presence of various nonidentified impurities amounting to ca. 10% of the product (from $^{31}P\{^1H\}$ NMR). Data for **13**: ^1H NMR ($CDCl_3$, 293 K) δ 0.83 (s, 9H, C(C*H*$_3$)$_3$), 1.09, 1.15 (both dd, J_{HP} = 13.2, J_{HH} = 7.2, 9H each, PCHC*H*$_3$), 1.52 (dd, J_{HH} = 10.6, 9.0, 1H, IrCH$_2$C*H*(*t*Bu)CH=CH), 1.89 (ddd, J_{HH} = 12.0, 10.6, J_{HP} = 3.5, 1H, IrCH_2CH(*t*Bu)CH=CH), 2.15 (m, 3H, PC*H*CH$_3$), 2.57 (dd, J_{HH} = 12.0, J_{HP} = 3.2, 1H, IrCH_2CH(*t*Bu)-CH=CH), 2.59 (s, 3H, NCCH$_3$), 6.10 (ddd, J_{HH} = 11.1, 9.0, J_{HP} = 1.5, 1H, IrCH$_2$CH(*t*Bu)C*H*=CH), 6.29 (d, J_{HH} = 11.1, 1H, IrCH$_2$CH(*t*Bu)CH=C*H*), 6.40 (d, J_{HH} = 8.0, 1H, IrCH=C*H*), 6.78 (d, J_{HH} = 8.1, 1H, CH), 6.95 (d, J_{HH} = 7.6, 1H, CH), 6.96 (dd, J_{HH} = 6.6, 1H, CH), 7.25 (dd, J_{HH} = 7.2, 1H, CH), 7.39, 7.43 (both t, J_{HH} = 7.6, 1H each, CH), 8.65 (d, J_{HH} = 8.0, 1H, IrC*H*=CH), 8.93 (m, 1H, CH), 9.05 (d, J_{HH} = 5.3, 1H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −10.20 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −2.50 (d, J_{CP} = 6.7, Ir*C*H$_2$CH(*t*Bu)CH=CH), 3.99 (s, NC*C*H$_3$), 19.01, 19.35 (both d, J_{CP} = 2.3, PCH*C*H$_3$), 23.84 (d, J_{CP} = 30.2, P*C*HCH$_3$), 27.34 (s, C(*C*H$_3$)$_3$), 32.68 (s, *C*(CH$_3$)$_3$), 52.21 (d, J_{CP} = 1.3, IrCH$_2$*C*H(*t*Bu)CH=CH), 118.38 (s, N*C*CH$_3$), 119.44, 121.47, 136.45, 138.24, 151.57, 153.11 (all s, CH), 121.60 (d, J_{CP} = 2.3, CH), 124.04 (s, IrCH$_2$CH(*t*Bu)-CH=*C*H), 126.54 (d, J_{CP} = 3.0, CH), 132.16 (s, IrCH=*C*H), 141.30 (s, IrCH$_2$CH(*t*Bu)*C*H=CH), 160.93 (d, J_{CP} = 9.8, Ir*C*H=CH), 159.44, 166.19 (both s, C).

Preparation of [Ir{NC$_5$H$_4$-2-*Z*-(CH=CH)-*κ*-*N*,*C*}$_2$(NCCH$_3$)(P*i*Pr$_3$)]BF$_4$ (15). The procedure described for **12** but starting from complex **11** (193 mg, 0.24 mmol) gave a white solid: yield 132 mg (80%). Anal. Calcd for $C_{25}H_{36}N_3BF_4IrP$: C, 43.61; H, 5.27; N, 6.10. Found: C, 43.41; H, 5.15; N, 6.03. MS (FAB+, *m*/*z* (%)) 561 (100) [M$^+$ − NCCH$_3$]. Λ_M(acetone) = 113 Ω^{-1} cm^2 mol^{-1} (1:1). ^1H NMR ($CDCl_3$, 293 K) δ 0.95 (dd, J_{HP} = 13.4, J_{HH} = 7.4, 9H, PCHC*H*$_3$), 1.13 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.36 (s, 3H, NCC*H*$_3$), 2.45 (m, 3H, PC*H*CH$_3$), 6.67 (dd, J_{HH} = 8.3, 1.0, 1H, IrCH=C*H*), 6.72, 6.78 (both m, 1H, CH), 7.04 (dd, J_{HH} = 8.7, 1.2, 1H, IrCH=C*H*), 7.18 (d, J_{HH} = 8.7, 1H, CH), 7.26 (d, J_{HH} = 7.5, 1H, CH), 7.49 (ddd, J_{HH} = 7.8, 7.5, 1.8, 1H, CH), 7.57 (ddd, J_{HH} = 7.8, 7.2, 1.2, 1H, CH), 7.73 (ddd, J_{HH} = 7.8, 7.5, 1.8, 1H, CH), 7.76 (d, J_{HH} = 8.3, 1H, IrC*H*=CH), 8.92 (dd, J_{HH} = 8.7, J_{HP} = 4.5, 1H, IrC*H*=CH), 9.21 (dd, J_{HH} = 5.7, J_{HP} = 1.0, 1H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 0.96 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 3.53 (s, NC*C*H$_3$), 18.44 (d, J_{HP} = 2.3, PCH*C*H$_3$), 19.20 (s, PCH*C*H$_3$), 23.86 (d, J_{CP} = 30.9, P*C*HCH$_3$), 119.45 (d, J_{CP} = 1.9, CH), 120.65 (d, J_{CP} = 2.7, CH), 122.60 (s, N*C*CH$_3$), 120.73, 122.82, 138.72, 139.15, 145.65 (all s, CH), 133.45 (s, IrCH=*C*H), 134.78 (d, J_{CP} = 3.2, IrCH=*C*H), 151.55 (br, CH), 155.19 (d, J_{CP} = 8.3, Ir*C*H=CH), 156.62 (br, Ir*C*H=CH), 166.22 (s, C), 167.24 (d, J_{CP} = 1.8, C).

Structural Analysis of Complexes 4, 5, 11, and 14. X-ray data were collected for all complexes at low temperature on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), using ω scans (0.3°). Data were collected over the complete sphere by a combination of four sets and corrected for absorption using a multiscan method applied with the SADABS program.[14] The structures were solved by the Patterson or direct methods. Refinement, by full-matrix least squares on F^2 with SHELXL-97,[15] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. Particular details concerning the presence of solvent, static disorder, and hydrogen refinement are listed below.

Crystal Data for 4. $C_{36}H_{62}B_2F_8Ir_2N_4P_2\cdot C_3H_6O$, M = 1228.93; yellow irregular block, 0.08 × 0.07 × 0.05 mm^3; triclinic, $P\bar{1}$; a = 10.7186(13) Å, b = 15.0943(19) Å, c = 15.4843(19) Å, α = 72.521(2)°, β = 83.208(2)°, γ = 78.718(2)°; Z = 2; V = 2338.6-(5) Å^3; D_c = 1.745 g/cm^3; μ = 5.819 mm^{-1}, minimum and maximum transmission factors 0.551 and 0.757; $2\theta_{max}$ = 53°; temperature 173(2) K; 26533 reflections collected, 9642 unique [R(int) = 0.0757]; number of data/restrains/parameters 9642/21/495; final GoF 0.937, R1 = 0.0534 [5222 reflections, $I > 2\sigma(I)$], wR2 = 0.1010 for all data; largest difference peak 2.02 e·Å^{-3}. The BF_4 anions were found disordered and isotropic displacement parameters were eventually used for these atoms. Hydrogen atoms were included in calculated positions and refined riding on carbon atoms, except hydride ligands which were calculated with the program HYDEX,[4] and were refined as free isotropic atoms with displacement parameters 1.2 times those of Ir atoms.

Crystal Data for 5. $C_{25}H_{38}BF_4IrN_3P$, M = 690.56; yellow irregular block, 0.21 × 0.16 × 0.14 mm^3; triclinic, $P\bar{1}$; a = 13.4686(8) Å, b = 14.3097(9) Å, c = 14.8785(9) Å, α = 72.9650-(10)°, β = 88.6210(10)°, γ = 85.8140(10)°; Z = 4; V = 2734.4-(3) Å^3; D_c = 1.677 g/cm^3; μ = 4.987 mm^{-1}, minimum and maximum transmission factors 0.331 and 0.495; $2\theta_{max}$ = 57.5°; temperature 173(2) K; 33990 reflections collected, 12957 unique [R(int) = 0.0376]; number of data/restrains/parameters 12957/0/705; final GoF 0.960, R1 = 0.0310 [10069 reflections, $I > 2\sigma(I)$], wR2 = 0.0575 for all data; largest difference peak 1.40 e·Å^{-3}. Hydrogen atoms were observed or calculated and refined riding on carbon atoms.

Crystal Data for 11. $C_{34}H_{44}BF_4IrN_3P\cdot 1.5CH_2Cl_2$, M = 932.09; pale yellow needle, 0.26 × 0.06 × 0.04 mm^3; monoclinic, $P2(1)/c$; a = 16.319(12) Å, b = 15.033(11) Å, c = 16.734(12) Å, β = 99.540(12)°; Z = 4; V = 4049(5) Å^3; D_c = 1.529 g/cm^3; μ = 3.582 mm^{-1}, minimum and maximum transmission factors 0.456 and 0.870; $2\theta_{max}$ = 57.2°; temperature 100(2) K; 46861 reflections collected, 9639 unique [R(int) = 0.1225]; number of data/restrains/parameters 9639/49/436; final GoF 0.920, R1 = 0.0672 [5010 reflections, $I > 2\sigma(I)$], wR2 = 0.1255 for all data; largest difference peak 1.21 e·Å^{-3}. A phenyl group of the alkenyl ligand and two isopropyl sustituents of the phosphine were observed disordered, and were refined with two moieties for each group with retention of the geometry. Dichloromethane was also observed disordered in two sites over the asymmetric unit. These solvent molecules were refined with fixed occupancy factors and restrained geometry. All disordered atoms were refined with isotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined riding on carbon atoms.

Crystal Data for 14. $C_{29}H_{45}BF_4IrN_2P$, M = 731.65; pale yellow irregular block, 0.14 × 0.12 × 0.08 mm^3; triclinic, $P\bar{1}$;

(14) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. SADABS: Area-detector absorption correction, 1996, Bruker-AXS: Madison, WI.
(15) SHELXTL Package v. 6.10, 2000; Bruker-AXS: Madison, WI. Sheldrick, G. M. SHELXS-86 and SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.

a = 9.6171(13) Å, b = 9.6574(13) Å, c = 16.812(2) Å, α = 84.807(2)°, β = 83.979(2)°, γ = 89.197(2)°; Z = 2; V = 1546.4(4) Å^3; D_c = 1.571 g/cm^3; μ = 4.413 mm^{-1}, minimum and maximum transmission factors 0.577 and 0.719; $2\theta_{max}$ = 56.8°; temperature 173(2) K; 16719 reflections collected, 7016 unique [R(int) = 0.0453]; number of data/restrains/parameters 7016/66/362; final GoF 1.012, R1 = 0.0461 [5604 reflections, $I > 2\sigma(I)$], wR2 = 0.0962 for all data; largest difference peak 1.67 e·Å^{-3}. In the space group $P\bar{1}$, the phosphine ligand, the pyridinic group, and the BF_4 anion were observed disordered about two positions with occupancy factors close to 0.5. This disorder might indicate that the space group designation was incorrect. Several refinements were performed in triclinic $P1$ and $P\bar{1}$ space groups to choose between both. The centrosymmetric description was eventually selected because the $P1$ refinement led to some unacceptable bond lengths which improved when the coordinates were symmetrized, and because the deviations from centrosymmetry were relatively small (the $P\bar{1}$ option was also suggested by an analysis with the Platon program).[16] Two moieties for each disordered group were included. These groups were refined with isotropic parameters and restraints in the geometry and in the thermal parameters. The occupancy factors were estimated from the thermal parameters and fixed (phosphine ligand) or refined (for the rest of the disordered atoms). Hydrogen atoms were included in calculated positions and refined riding on carbon atoms or in observed positions and refined freely.

(16) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

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Supporting Information Available: Details of the X-ray crystallographic study of **4**, **5**, **11**, and **14** and a crystallographic information file (CIF) on the structural analysis of complexes **4**, **5**, **11**, and **14**. T This material is available free of charge via the Internet at http://pubs.acs.org.

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