Articles

Stoichiometric C−C Coupling Reactions in the Coordination Sphere of an Iridium(III) Alkyl

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An alkyl hydride η^1-acetone complex of iridium or its α-elimination product undergoes insertion into alkenes to give a carbene dihydride via a proposed pathway that involves C−C bond formation by a rare C(sp^3)−C(sp^3) reductive elimination followed by a double C−H activation. In MeCN solution, reversible α-elimination equilibrates this carbene dihydride insertion product with its MeCN adduct, an iridium alkyl hydride with diastereotopic trans triphenylphosphine ligands ($^2J_{PP}$ = 382 Hz). Alkynes also react, but they give a coupled η^3-allyl complex via a proposed pathway that involves C−C bond formation by C(sp^3)−C(sp^2) reductive elimination. Crystal structures of key products are reported.

1. Introduction

Iridium complexes have been widely used as catalysts, for example, in hydrogenation,[1] dehydrogenation,[2] transfer hydrogenation,[3] and hydrosilation.[4] However, progress in iridium-catalyzed C−C bond-forming reactions lags far behind, and only limited examples exist in iridium-catalyzed allylic alkylation,[5] cycloaddition,[6] acylsilane derivative formation,[7] and alkene insertion into an activated aryl−H bond.[8] This is probably due to the difficulty of C−C reductive elimination from an iridium(III) center, expected to be the last step of the catalytic cycle, since the metal−carbon bond in a third-row transition-metal complex is in general thermodynamically more stable than that in a first- or second-row complex.[9] Probably for this reason, a previously proposed mechanism for an iridium-catalyzed reaction of alkene insertion into an activated aryl−H bond seems to avoid the C−C reductive elimination step.[8] Examples of iridium-mediated stoichiometric C−C bond forming reactions are also rather limited.[10−13] Previously proposed C−C reductive eliminations from Ir(III) usually included at least one sp^2 carbon, and most reports involved vinyl−vinyl or vinyl−acyl reductive elimination to form conjugated systems.[6,10,11] C(sp)−C(sp^2)[10b] and C(sp^2)−C(sp^3)[6a,12] reductive elimination from iridium are already very rare; only a very few examples can be found for the C(sp^3)−C(sp^3) case, and this C−C reductive elimination is oxidatively promoted by single-electron oxidation of the Ir(III) center.[13]

We recently reported the synthesis of *trans*-[(H)Ir(OCMe$_2$)(CH$_2$NMePy)(PPh$_3$)$_2$]BF$_4$ (**1**) and its equilibration with *trans*-[(H)$_2$Ir(=CHNMePy)(PPh$_3$)$_2$]BF$_4$ (**2**) in noncoordinating solvents via a reversible α-elimination (Scheme 1).[14] In a weakly coordinating or noncoordinating solvent, both **1** and **2** can be regarded as direct precursors to coordinatively unsaturated species, due to the presence of the labile acetone ligand in **1** or the possibility of the incoming ligand being accommodated by a retro α-elimination in **2**.

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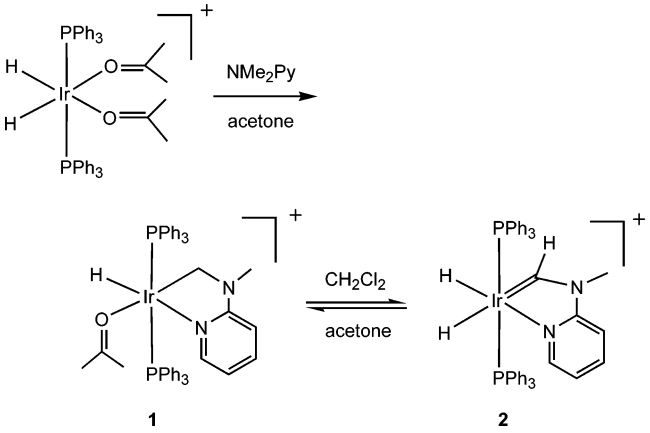
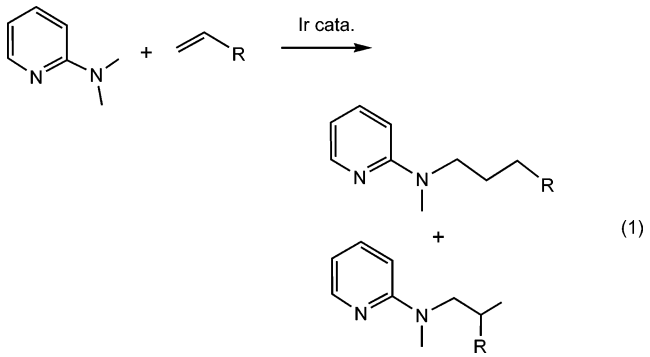
Scheme 1



Both this feature and the rarity of iridium catalysts for C−C coupling led us to attempt an iridium-catalyzed coupling reaction between 2-(dimethylamino)pyridine (NMe_2Py), the ligand precursor for **1** and **2**, and the alkene $RCH{=}CH_2$, a possible incoming ligand for **1** and **2** (eq 1). This reaction is closely related to the well-

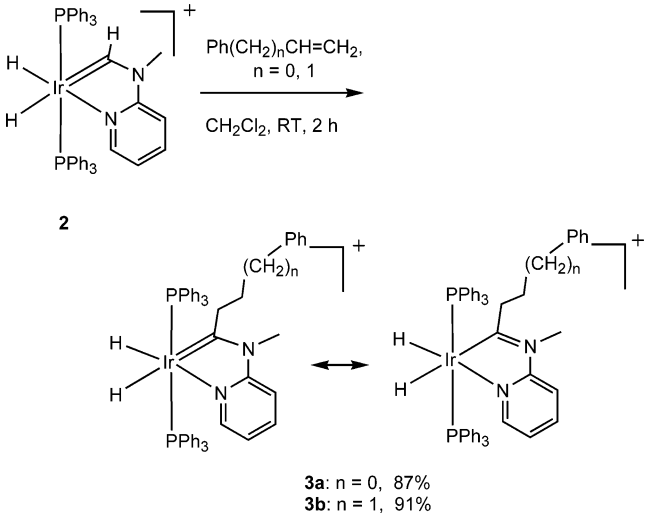


known Murai reaction, where a $C(sp^2)-H$ bond is activated with chelation assistance using a ruthenium catalyst, followed by alkene insertion into the resulting Ru aryl to yield a C−C coupling product.[15] Here, we have studied the insertion of alkenes and alkynes into alkyl **1** or carbene **2** to give stable Ir(III) insertion products. In both cases, C−H activation and C−C reductive elimination are proposed as key steps in the formation of these Ir(III) products. This work casts light on the reasons for the failure of Murai catalysis in the iridium system.

2. Results and Discussion

2.1. Alkene Insertion into 1 or 2. Attempted catalytic coupling reactions between $PyNMe_2$ and styrene, 1-hexene, allylbenzene, and vinyltriethoxysilane all failed in various solvents (acetone, $CHCl_3$, THF, MeCN, and $PhCF_3$) under reflux conditions with 4 mol % loading of **1** or $[Rh(COD)(PPh_3)_2]BF_4$. Stoichiometric reactions were then performed to understand how far the reaction

Scheme 2



proceeded. Indeed, styrene reacts rapidly with **2** in CH_2Cl_2 at room temperature after 2 h to yield **3a** (Scheme 2). The ^1H NMR resonances (CD_2Cl_2) for **3a** at δ −10.45 (td) and −17.52 (td) clearly indicated the presence of two mutually coupled hydrides cis to the PPh_3 ligands. Both ^1H and ^{13}C NMR spectroscopy confirmed that only one styrene unit is incorporated into the iridium system, although excess styrene was present. Importantly, the ^{13}C NMR spectrum (CD_2Cl_2) of **3a** showed a very low field signal at δ 273.5, which is characteristic of a Fischer carbene. The trans orientation of the two PPh_3 ligands is confirmed by the presence of a single peak in the ^{31}P NMR spectrum. The CH_2CH_2 unit in **3a** also shows a second-order AA′BB′ coupling pattern in the ^1H NMR spectrum, as expected for the structure shown in Scheme 2. **3a** was also obtained in comparable yield when **1** and styrene were heated in acetone under reflux, albeit with a much lower reaction rate.

Unlike **2**, **3a**,**b** failed to react with acetone to form the analogue of **1**, probably due to the lower reactivity of the more stable Fisher carbenes stabilized by the alkyl groups at the α-position. For the same reason, excess styrene failed to further react with **3a**,**b**, and attempts to isolate other iridium(III) alkyl complexes from dissolution of **3a**,**b** in pyridine, 2-(dimethylamino)pyridine, or CH_2Cl_2 solutions of PPh_3 were all unsuccessful. However, when **3b** was dissolved in the more strongly ligating solvent CD_3CN, **4**-d_3 was slowly formed at room temperature. Interestingly, the alkyl complex **4**-d_3 is in equilibrium with carbene complex **3b** under these conditions (eq 2). The [alkyl]/[carbene] ratio at equilibrium was measured at 21−50 °C by ^1H NMR spectroscopy. When ln K_{eq} was plotted against T^{-1}, the thermodynamic data were found to be $\Delta H° = -30.8$ kJ/mol and $\Delta S° = -112$ J/(mol K) for eq 2 ($R^2 = 0.9999$, see Experimental Section). Since the large entropy term causes this equilibrium to shift toward **4** at lower temperature, isolation of **4** was attempted after stirring **3b** and MeCN for 2 days at 0 °C. ^1H NMR spectroscopy showed that the mixture is composed of **3b** and **4** in a ratio of 1:16, where the equilibrium was still not yet established. Fortunately, this ratio allows readily discernible and interpretable ^1H, ^{31}P, and ^{13}C NMR spectra of **4**, even though it cannot be isolated. In the ^1H NMR spectrum, the Ir−C*H* proton appeared as a multiplet

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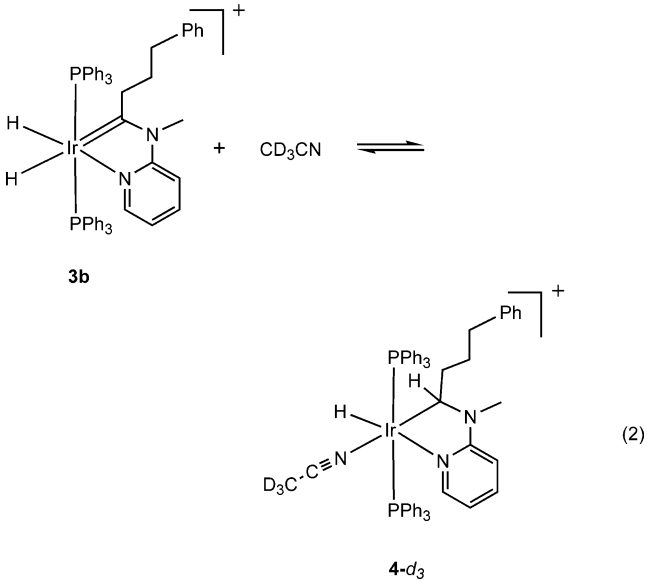
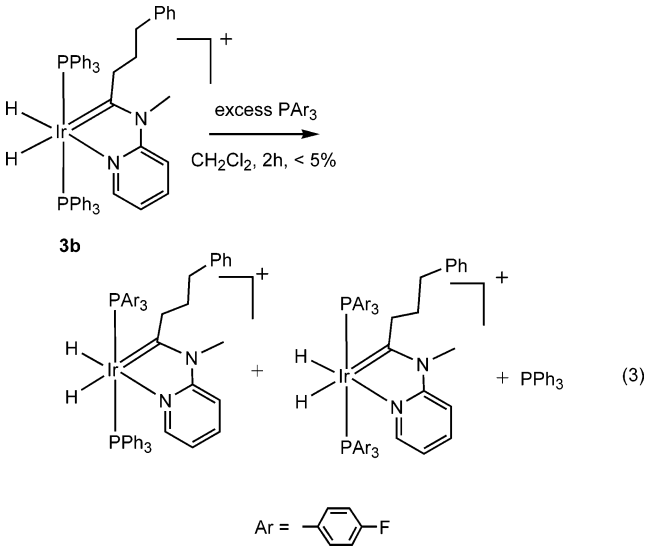


at δ 3.94 and the hydride as a doublet of doublets at δ −16.27 ($^2J_{PH}$ = 16.5 Hz, $^2J_{PH}$ = 13.4 Hz). Upon decoupling of ^{31}P, the Ir−C*H* signal becomes a doublet of doublets ($^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 3.4 Hz) and the hydride signal becomes a singlet. Diasterotopicity was noted for all three CH_2 groups of the $CH_2CH_2CH_2Ph$ chain. The ^{31}P NMR spectrum of **4** showed an AB quartet pattern (δ 17.41 and 9.20, $^2J_{PP}$ = 382.1 Hz). ^{1}H and ^{31}P NMR spectra show that we have a rare case of a pair of inequivalent *trans*-PPh_3 ligands that allows measurement of the trans $^2J_{PP}$; it is the chirality of the alkyl ligand (Ir−*C*) that renders them diastereotopic.

Two pathways are possible for the formation of **3a**,**b** from **2** and alkenes, as shown in Scheme 3. In path a, retro α-elimination of **2** generates an alkyl ligand and a vacant site, which is occupied by the incoming alkene RCH=CH_2, followed by alkene insertion into the hydride to give either a linear or branched Ir(III) alkyl species.[15a,b] Alkene or alkyne insertion is expected to be much more favorable into hydride than into alkyl[16] (Ir−CH_2NMePy) unless hydride and alkene or alkyne are *trans* to each other,[17] unlikely in this case. The disruption of the stable metallacycle during the alkyl insertion that would be required here may make it even less likely. The hydride insertion product is then proposed to undergo a C−C reductive elimination to yield an Ir(I) intermediate, which is expected to be stabilized by the π-acceptor RCH=CH_2. This Ir(I) intermediate then undergoes a double C−H activation (oxidative addition) of N(Me)*C*$H_2$$CH_2$R, as proposed by us[14] and others[18] in similar systems. The alternative N−*C*H_3 double C−H activation product was not observed, probably because it gives a less stable Fischer carbene, although the (Me)N*C*$H_2$$CH_2$R group is sterically more hindered. The fate of the product from the first C−H activation product is of interest. This Ir(III) intermediate is susceptible to β-hydride elimination, but only the α-elimination product is ever observed here, owing to the presence of the α-N atom. A kinetic preference of α- over β-elimination was reported before.[18,19]

In pathway b, one of the PPh_3 ligands dissociates to generate a vacant site, and this five-coordinate species is trapped by an alkene, followed by alkene insertion into one of the Ir−H bonds to give a linear or branched Ir(III) alkyl species (only the linear species is shown in Scheme 3), followed by PPh_3 recoordination to give a carbene alkyl hydride intermediate, with the alkyl cis to the carbene. A migratory insertion[20] of the alkyl into the carbene generates an alkyl hydride, which may also undergo α-elimination to lead to product **3**. In this pathway, no Ir(I) intermediate and no reductive elimination are involved.

We studied phosphine exchange between **3b** and tris(*p*-fluorophenyl)phosphine to probe the possibility of pathway b (eq 3). It is not appropriate to use **2** for this study, because retro α-elimination of **2** accommodates the incoming phosphine ligand to make an iridium(III) tris(phosphine) species, which was directly observed from ^{31}P NMR spectroscopy when PPh_3 was added to the CH_2Cl_2 solution of **2**. No such complication exists for **3b**, which is closely related to **2** in structure. We believe that the rate of PPh_3 dissociation in **3b** would be greater than or similar to that in **2** for both steric



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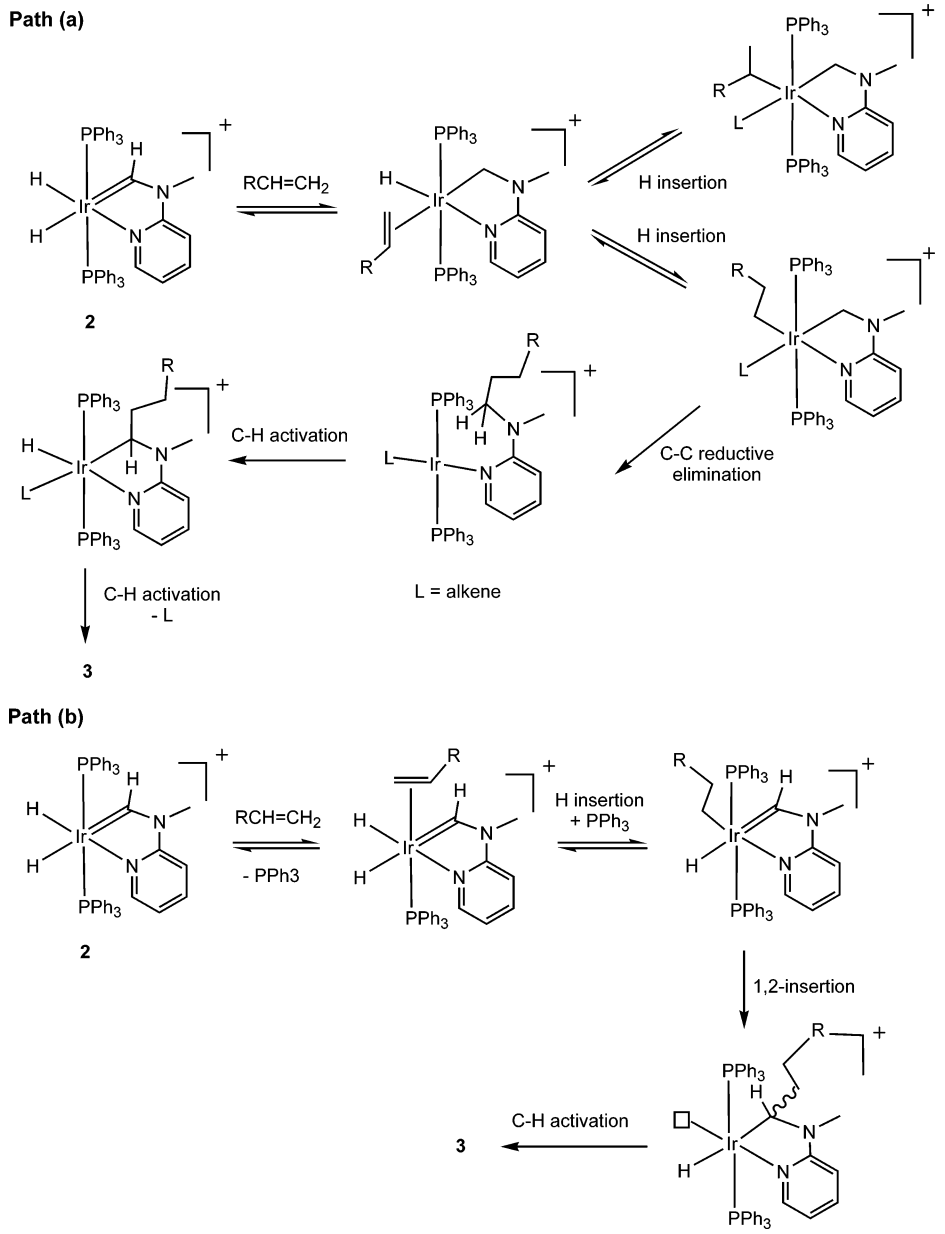
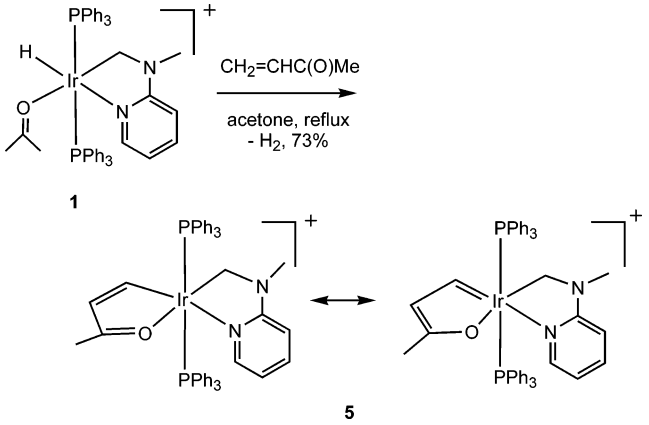
Scheme 3



and electronic reasons. The $CH_2CH_2CH_2Ph$ substituent should promote PPh_3 dissociation sterically, as expected in a dissociative mechanism for d^6 octahedral systems. Electronically, the $-CH_2CH_2CH_2Ph$ group makes the iridium center slightly more electron rich, a factor that should also kinetically favor PPh_3 dissociation. A ^{31}P NMR spectroscopic study (161.91 MHz) of **3b** and 10 equiv of tris(*p*-fluorophenyl)phosphine in CH_2Cl_2 showed that only 4% of **3b** underwent ligand exchange at 21 °C after 2 h to give free PPh_3 and the mono(phosphine) exchange product (AB quartet, δ 16.94, 19.52, $^2J_{PP}$ = 286 Hz). After 12 h, 32% of **3b** underwent ligand exchange and the double phosphine exchange product (δ 16.57) started to be observable. The rate of phosphine exchange between **3b** and tris(*p*-fluorophenyl)phosphine is much lower than that of the reaction between **2** and styrene (75 min, 21 °C, >97% conversion of **2**, see Experimental Section), thus ruling out path b. The phosphine exchange experiment also suggests that dissociation of the chelating pyridine ligand of **3b** is not likely either, because a tris(phosphine) complex would then be expected, instead of a mixed bis(phosphine) species. We therefore prefer path a.

Allylbenzene ($PhCH_2CH{=}CH_2$) also undergoes the same type of insertion into **2** to give **3b** (91%) in CH_2Cl_2 with an excess (8 equiv) of allylbenzene. In the course of the reaction, *trans*-PhCH=CHMe, the isomerization product from allylbenzene, was detected by ^1H NMR spectroscopy. Control experiments showed that the product **3b** failed to catalyze the isomerization of allylbenzene (10 mol % **3b**, 21 °C, CH_2Cl_2, 4 h). The *trans*-PhCH=CHMe product is proposed to arise from the β-hydride elimination of the branched $Ir^{III}-CH(CH_3)CH_2Ph$ intermediate. The C−C reductive elimination pathway of this branched intermediate must be very slow compared with that of the linear Ir(III) alkyl, since no final corresponding Fisher carbene derived from the branched Ir(III) alkyl intermediate was detected in ^1H NMR spectroscopy. This result is in good agreement with mechanistic studies on the ruthenium-catalyzed Murai reaction, where an alkene inserts into a hydride to reversibly lead to both branched and linear Ru(II)

Scheme 4



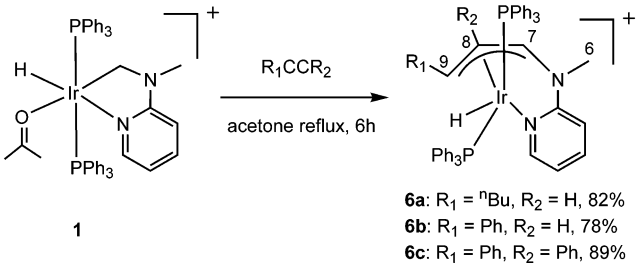
intermediates, but only the linear alkyl ligand is further coupled to the aryl to yield the corresponding product.[15a] Previous reports of C−C reductive elimination from iridium usually involved Ir−C(sp^2) or Ir−C(sp),[6,10−12] and the surprisingly low barrier for the C−C reductive elimination here is probably due to the formation of an Ir(I) intermediate greatly stabilized by excess alkene and possibly by the subsequent formation of stable cyclic Fischer carbenes.

2.2. Reaction between an Enone and 1. Methyl vinyl ketone, significantly different from a terminal alkene electronically, also reacts with **1** or **2** in acetone under reflux conditions. Unlike **3**, product **5** does not come from a formal insertion but from the β-C−H activation of C*H*$_2$=CHC(O)Me with loss of H_2 (Scheme 4). In **5**, the newly formed iridacycle is essentially an iridafuran, owing to the resonance stabilization shown in Scheme 4. For **5**, a very low field doublet signal at δ 10.76 (Ir=C*H*CH) in the ^{1}H NMR spectrum and a triplet at δ 197.3 ($^2J_{PC}$ = 9.0 Hz, Ir=*C*H) in the ^{13}C NMR spectrum are both characteristic of the presence of carbene character in the iridafuran. The Ir−C*H*$_2$ signal appears as a triplet ($^3J_{PH}$ = 12.4 Hz), due to the coupling to two equivalent phosphorus atoms, and the trans orientation of the two PPh_3 ligands also follows from the single peak in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum does not show any hydride resonances. The X-ray crystal analysis confirmed the structure of **5** (Figure 2). Iridafurans are known to be formed through direct C−H activation.[21]

A likely mechanism for the formation of **5** involves the substitution of the acetone ligand in **1** by the β-C−H bond of C*H*$_2$=CHC(O)Me to form an agostic intermediate, followed by a C−H breaking to give a Ir(III) dihydrogen complex. The pendant carbonyl group might substitute the dihydrogen ligand to give **5**. No H_2 acceptor was used in this reaction, since only 1 equiv of CH_2=CHC(O)Me was provided, and molecular hydrogen is proposed to be a coproduct; this is thermodynamically feasible, probably owing to the formation of a stable iridafuran.

2.3. Alkyne Insertion into 1. Terminal alkynes RC≡CH (R = Bu, Ph) react with **1** in acetone or **2** in CH_2Cl for 10 h to afford **6a**,**b** in high yields (Scheme 5).

Scheme 5



The hydride region of **6a** or **6b** in the ^{1}H NMR spectra showed one hydride signal as a doublet of doublets, due to the coupling to two phosphorus atoms in different environments, while the ^{31}P{^{1}H} NMR spectrum showed two peaks with essentially equal intensity. These observations indicate that the two PPh_3 ligands are not equivalent. In the ^{1}H NMR spectrum (CD_2Cl_2) of **6b**, a signal at δ 6.24 (dd, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 4.5 Hz, H-8) is coupled to two different protons: one resonance at δ 5.48 (dd, $^3J_{PH}$ = 9.6 Hz, $^3J_{HH}$ = 4.5 Hz, H-7) and the other at δ 3.84 (dd, $^3J_{HH}$ = 12.2, $^3J_{PH}$ = 7.2 Hz, H-9). These H−H coupling patterns are consistent with the presence of an η^3-allyl ligand: the 4.5 Hz coupling constant between H-7 and H-8 is typical for a syn coupling on an η^3-allyl ligand, while the 12.2 Hz one between H-8 and H-9 is typical for a anti coupling. These $^3J_{HH}$ coupling constants between H-7, H-8, and H-9 were determined from ^{31}P-decoupled ^{1}H NMR spectra, where the H-7 and H-9 signals became doublets and Ir−H became a singlet. Confirmation of the assignments of H-7 and H-9 for **6b** was made by comparison with the ^{1}H NMR spectrum of **6a**, where H-9 (δ 2.84, m) is further coupled to the two proximal diastereotopic protons in C*H*$_2$CH$_2$CH$_2$CH$_3$. ^{13}C and ^{1}H NMR spectra of **6a**,**b** are too complicated to allow secure assignment, and structure elucidation was carried out by an X-ray crystal analysis of **6b** (Figure 3). The internal alkyne diphenylacetylene also reacts with **1** or **2** to give the analogous complex **6c**. **6a**−**c** all failed to react with CO, PPh_3, and excess PhC≡CH, which indicates the difficulty of η^3 to η^1 conversion of the allyl ligand, owing to the tethering effect of the pyridine ligand.

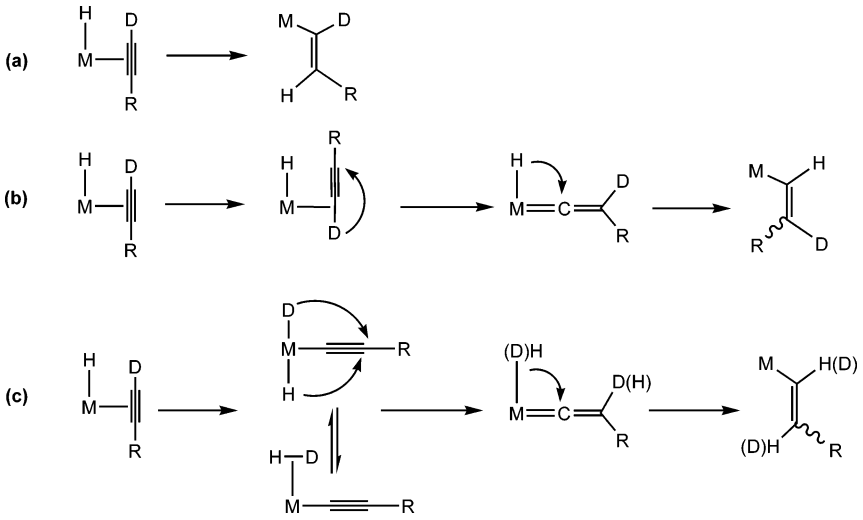
It is well-known that terminal alkynes (RC≡CH) insert into metal hydrides to form vinyl complexes. The mechanism behind this apparent insertion could be much more complicated, however. At least three types of mechanisms were previously proposed (Scheme 6): (a) a direct metal hydride insertion into an alkyne to afford a vinyl ligand,[22] (b) a concerted intraligand 1,2-hydrogen shift in the RC≡CH unit to yield a vinylidene ligand, followed by a hydride insertion, where the hydride behaves as a spectator for this rearrangement,[23] or (c) a RC≡CH oxidative addition to the metal followed by a 1,3-hydrogen shift from the metal to the ligand to

(21) (a) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Rohde, A. M. *Organometallics* **1995**, *14*, 5127. (b) Castarlenas, R.; Esteruelas, M. A.; Martín, M.; Oro, L. A. *J. Organomet. Chem.* **1998**, *564*, 241.

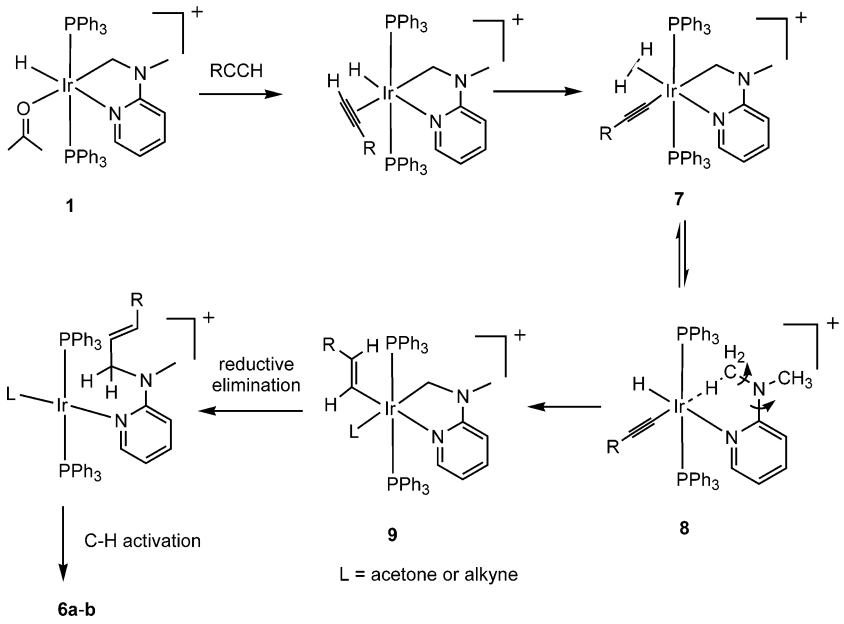
(22) The initially formed metal vinyl complexes are cis with respect to metal and hydrogen, but they can rearrange to the trans isomers probably via η^2-vinyl intermediates.[4a,b]

(23) (a) Li, X.; Incarvito, C. D.; Crabtree, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 3698. (b) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461. (c) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (e) Akita, M.; Ishii, N.; Takabuchi, A.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 258. (f) De Angelis, F.; Sgamellotti, A.; Re, N. *Organometallics* **2002**, *21*, 2715.

Scheme 6



Scheme 7



form a vinylidene, followed by another insertion of this vinylidene into the M−H bond to yield a vinyl ligand, a route in which the hydrides on the metal are not spectators.[24] In paths b and c, the well-known alkyne to vinylidene rearrangement is involved.[25]

The mechanism was better understood by a deuterium labeling experiment involving 1 equiv of PhC≡CD and **1**. Comparison of the ^{1}H NMR spectrum of this product with that of **6b** shows that deuterium scrambles extensively, with 9% present at Ir−H, 14% at H-9, 30% at H-8, 36% at H-6, and 12% at H-7. This result makes paths a and b unlikely, because no deuterium scrambling is expected. In contrast, in path c, the hydride is not a spectator and naturally leads to the scrambling of the deuterium to the H-8 and H-9 positions. Since the deuterium also scrambles to other positions, the mechanism must be more complex, and a plausible sequence is proposed in Scheme 7. C-H oxidative addition of RC≡CH to this electron-rich Ir(III) could afford an Ir(V) or an Ir(III) dihydrogen intermediate **7**.[25,26] At this stage, either the H or D on the Ir can undergo a 1,3-shift to give a vinylidene followed by a hydride/deuteride insertion to form a D-scrambled vinyl ligand.[24a] By analogy with previous reports,[26,28] **7** can also be in a rapid equilibrium with **8**, an agostic Ir(III) intermediate, leading to the deuterium scrambling into both methyl groups (N(CH_3)$_2$). Reductive elimination of the vinyl and the D-scrambled alkyl in **9** could afford an Ir(I) species similar to the Ir(I) intermediate in Scheme 3. A C−H or C−D activation of this Ir(I) could afford a stable Ir(III) allyl compound with deuterium fully scrambled.

(24) (a) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (b) De los Ríos, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (c) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. (d) Garcia Alonso, F. J.; Hoehn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem.* **1985**, *97*, 401.

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(26) Ng, S. M.; Lam, W. H.; Mak, C. C.; Tsang, C. W.; Jia, G.; Lin, Z.; Lau, C. P. *Organometallics* **2003**, *22*, 641.

(27) (a) Gérard, H.; Eisenstein, O.; Lee, D.-H.; Chen, J.; Crabtree, R. H. *New J. Chem.* **2001**, *25*, 1121. (b) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242.

(28) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

Table 1. Crystallographic Data for 3b, 5, and 6b

	3b	5	6b
empirical formula	$C_{52}H_{50}BF_4IrN_2P_2$	$C_{50}H_{50}BF_4IrN_2O_2P_2$	$C_{52}H_{47}BCl_2F_4IrN_2P_2$
mol wt	1043.95	1051.93	1111.83
radiation, λ (Å)	Mo Kα (monochromated), 0.710 69 Å		
T (°C)	−90	−90	−90
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_12_12$ (No. 18)	$P2_1/c$ (No. 14)
a (Å)	23.3215(5)	20.9409(6)	13.6505(3)
b (Å)	16.2968(4)	20.9291(9)	15.9723(4)
c (Å)	24.1017(5)	10.2731(3)	21.6001(6)
β (deg)	90	90	91.028(1)
V (Å^3)	9160.2(2)	4502.4(2)	4708.7(2)
Z	8	4	4
D_{calcd} (g cm^{-3})	1.514	1.552	1.568
μ(Mo Kα) (cm^{-1})	30.47	31.04	30.79
cryst size (mm)	0.05 × 0.05 × 0.14	0.12 × 0.12 × 0.19	0.12 × 0.17 × 0.17
total, unique no. of rflns	49 576, 11 335	13 640, 9603	32 059, 10 730
R_{int}	0.094	0.043	0.052
no. of observns used	4336	4441	6152
no. of params, restrictions	559, 0	560, 0	550, 0
R,[a] R_w[b]	0.027; 0.028	0.038; 0.042	0.032; 0.033
GOF	0.67	1.15	0.92
min, max resid dens (e Å^{-3})	−0.70, 0.64	−0.96, 1.69	−0.80, 0.59

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Lengths and Angles for Complex 3b

Bond Lengths (Å)			
Ir(1)−P(1)	2.300(2)	N(2)−C(1)	1.397(8)
Ir(1)−P(2)	2.317(2)	N(2)−C(6)	1.348(8)
Ir(1)−N(1)	2.140(8)	N(2)−C(16)	1.469(8)
Ir(1)−C(6)	2.020(8)		
Bond Angles (deg)			
P(1)−Ir(1)−P(2)	164.51(5)	Ir(1)−C(6)−N(2)	115.8(4)
N(1)−Ir(1)−C(6)	77.6(2)	Ir(1)−C(6)−C(7)	125.5(6)

Cases where hydride is not a spectator in an alkyne to vinylidene rearrangement are rather rare, and most studies have been theoretical.[23,24]

3. Crystal Structures of 3b, 5, and 6b

Single crystals of **3b**, **5**, and **6b** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into CH_2Cl_2 solutions. X-ray diffraction data for single crystals was measured on a Nonius Kappa CCD diffractometer. Data collection was carried out at −90 °C, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The crystal parameters and other experimental details of the data collection are summarized in Table 1. A complete list of the details of the crystallographic analysis in given in Supporting Information. Metrical data for **3b**, **5,** and **6b** are given in Tables 2−4, respectively.

The structure determination of **3b** was straightforward, and the space group was determined from the systematic absences. The cell for **5** had two similar distances, which suggested the possibility of a tetragonal system; however, R_{int} was ∼0.33 for this system. The ultimate solution of the structure showed that the space group was the fairly unusual $P2_12_12$, which only contains one enantiomer. The correct enantiomer for the crystal chosen was determined by inverting the coordinates, which gave R = 0.057 and R_w = 0.067 versus that for the correct enantiomer of R = 0.038 and R_w = 0.042. The structure for **6b** contained a disordered methylene chloride. A suitable model for the disorder was difficult to obtain, and the program SQUEEZE in the program PLATON[29,30] was used to correct for the residual density from methylene chloride.

Table 3. Selected Bond Lengths and Angles for Complex 5

Bond Lengths (Å)			
Ir(1)−P(1)	2.353(2)	N(2)−C(6)	1.464(11)
Ir(1)−P(2)	2.361(2)	N(2)−C(7)	1.475(11)
Ir(1)−O(1)	2.157(6)	O(1)−C(10)	1.289(12)
Ir(1)−N(1)	2.097(6)	C(8)−C(9)	1.338(13)
Ir(1)−C(6)	2.061(9)	C(9)−C(10)	1.39(1)
Ir(1)−C(8)	2.025(9)	C(10)−C(11)	1.50(2)
N(2)−C(1)	1.323(12)		
Bond Angles (deg)			
P(1)−Ir(1)−P(2)	177.18(9)	Ir(1)−O(1)−C(10)	111.9(6)
N(1)−Ir(1)−C(6)	79.8(3)	C(8)−C(9)−C(10)	115.3(9)
Ir(1)−C(6)−N(2)	109.3(6)	O(1)−C(10)−C(9)	119.3(9)
Ir(1)−C(8)−C(9)	116.7(7)		

Table 4. Selected Bond Lengths and Angles for Complex 6b

Bond Lengths (Å)			
Ir(1)−P(1)	2.362(1)	N(2)−C(1)	1.355(7)
Ir(1)−P(2)	2.297(1)	N(2)−C(6)	1.470(7)
Ir(1)−N(1)	2.181(4)	N(2)−C(7)	1.449(7)
Ir(1)−C(7)	2.184(5)	C(7)−C(8)	1.421(7)
Ir(1)−C(8)	2.183(5)	C(8)−C(9)	1.398(7)
Ir(1)−C(9)	2.345(5)	C(9)−C(10)	1.498(7)
Bond Angles (deg)			
P(1)−Ir(1)−P(2)	107.99(5)	N(1)−Ir(1)−C(7)	76.9(2)

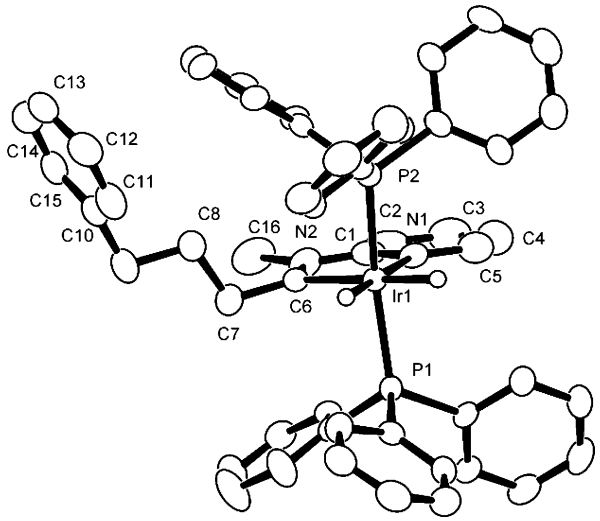

Figure 1. ORTEP diagram of the cation of **3b**, showing 50% probability ellipsoids. The hydrides are shown in calculated positions.

An X-ray single-crystal study of **3b** reveals its octahedral structure (Figure 1): the Ir−C−N−C−N unit defines a plane perpendicular to the P−Ir−P axis. The Ir−C_α distance of 2.020 Å is consistent with predominant single-bond character, while the C_α−N bond distance of 1.348 Å indicates substantial multiple-bond character, as expected from the resonance form generally preferred by Fischer carbenes (Scheme 3). Planar geometry about the carbene carbon and π−π stacking

(29) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
(30) Vandersluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

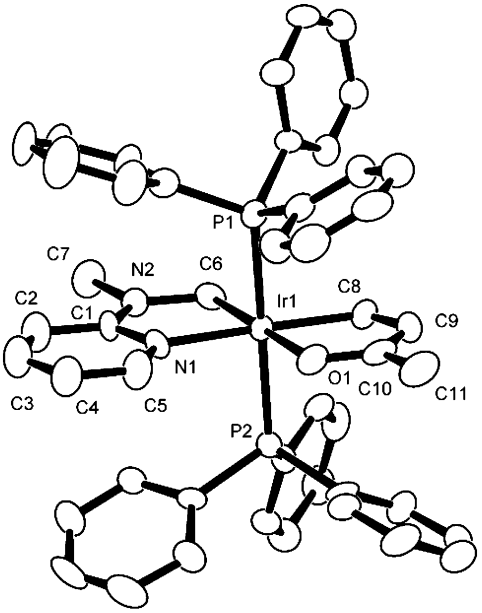

Figure 2. ORTEP diagram of the cation of **5**, showing 50% probability ellipsoids.

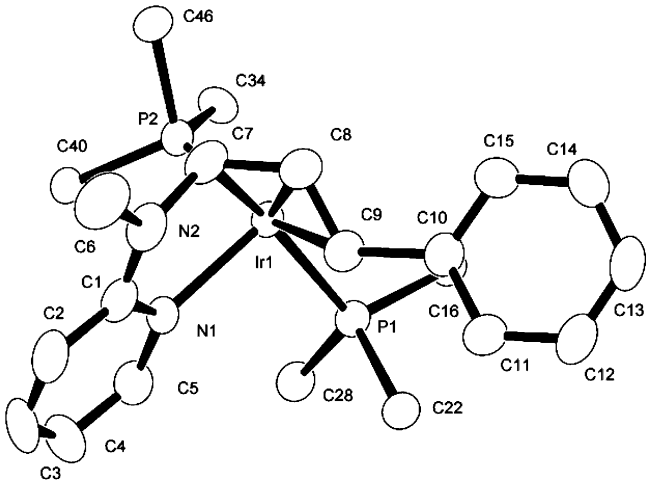

Figure 3. ORTEP diagram of the cation of **6b**, showing 50% probability ellipsoids. Only the ipso carbons on the triphenylphosphines are shown for clarity.

between *Ph*$CH_2CH_2CH_2$− and P*Ph*$_3$ were also observed in **3b**. These results are comparable to those for an analogue of **3b** in our previously published work.[1]

Complex **5** is also octahedral, with the N atom in the pyridine ring trans to the iridafuran carbene/vinyl carbon, a high trans-effect ligand (Figure 2). The electron density in the iridafuran is essentially delocalized, as indicated by the presence of the two similar C−C bond distances (1.34 and 1.39 Å) in the iridafuran. The Ir−C bond (2.025 Å) in the iridafuran is predominantly a single bond, as can be seen by comparison with the Ir−CH_2 single bond (2.061 Å).

Complex **6b** has a distorted-octahedral shape (Figure 3). The trihapticity of the η^3-allyl ligand follows from the bond distances (Ir−C7 = 2.184 Å, Ir−C8 = 2.183 Å, and Ir−C9 = 2.345 Å). It is also clear that H−C8 is anti to H−C9 but syn to H−C7, which is consistent with data from ^{1}H NMR spectroscopy. The PPh_3 ligands are in different environments, and the P−Ir−P angle is 108°, which results in very small coupling ($^2J_{PP}$ = 5.9 Hz) between them. The ipso carbon in each PPh_3 ligand is no longer a virtual triplet, as in the case for **3a**,**b** and **5** (see Experimental Section). The reduced P−Ir−P bond angle results in a small $^2J_{PP}$ and a suppressed virtual coupling, and this is also consistent with a cis triphenylphosphine arrangement in solution.

4. Experimental Section

All reactions were carried out under argon, although most of the products proved to be air stable. Acetone was used without any treatment. PhCH=CH_2, PhC≡CH, ^{n}BuC≡CH, PhC≡CPh, PhC≡CD, methyl vinyl ketone, and PhCH_2CH=CH_2 were purchased from Aldrich without purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 or 500 spectrometers. ^{31}P NMR spectra were recorded on Bruker 400 spectrometers with an external 85% H_3PO_4 standard. Elemental analyses were performed at Atlantic Microlabs.

4.1. *trans*-Dihydridobis(triphenylphosphine)(1-(methyl(2-pyridyl)amino)-3-phenylprop-1-ylidene-*N*,*C*)iridium(III) Tetrafluoroborate (3a). To a Schlenk tube charged with **2** (150 mg, 0.162 mmol) and CH_2Cl_2 (3 mL) was added styrene (102 mg, 0.973 mmol) via syringe. The light yellow solution was stirred for 2 h at 21 °C and was then concentrated to ca. 0.5 mL under reduced pressure, followed by slow addition of diethyl ether (15 mL). A light yellow precipitate appeared and was filtered and washed with diethyl ether (2 × 15 mL). Analytically pure **3a** was obtained by drying under vacuum overnight. Yield: 145 mg (0.141 mmol, 87%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 7.90 (d, $^3J_{HH}$ = 5.4 Hz, 1H, Py), 7.86 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Py), 7.67 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Py), 7.40 (m, 30H, P*Ph*$_3$), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 2H, −CH_2*Ph*), 7.13-(t, $^3J_{HH}$ = 7.5 Hz, 1H, −CH_2*Ph*), 6.69 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Py), 6.64 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2*Ph*), 3.26 (s, 3H, NCH_3), 2.50 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), −10.45 (td, $^2J_{PH}$ = 20.9 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, Ir−H), −17.52 (td, $^2J_{PH}$ = 16.3 Hz, $^3J_{HH}$ = 5.1 Hz, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz, 293 K): δ 273.5 (s, Ir=C), 160.0 (s), 154.8 (s), 141.1 (s), 140.4 (s), 133.8 (virtual t, 5.9 Hz, Ph_3P), 133.6 (virtual t, 28.4 Hz, *ipso*-Ph_3P), 131.4 (s, PPh_3), 129.3 (virtual t, 5.4 Hz, Ph_3P), 129.2 (s), 128.8 (s), 127.0 (s), 123.5 (s), 115.3 (s), 49.6 (s, CH_2), 39.2 (s, CH_2), 37.7 (s, CH_3). ^{31}P{^{1}H} NMR (acetone-d_6, 161.9 MHz, 273 K): δ 19.2 (s). Anal. Calcd for $C_{51}H_{48}BF_4IrN_2P_2$: C, 59.48; H, 4.70; N, 2.72. Found: C, 59.35; H, 4.76; N, 2.72.

NMR Spectroscopic Studies of the Rate of the Formation of 3a. In an NMR tube, **2** (20.0 mg, 0.0216 mmol) and styrene (8 μL, 0.070 mmol) were dissolved in CD_2Cl_2 (0.7 mL). ^{31}P and ^{1}H NMR spectroscopic analysis at 21 °C showed that the conversion of **2** was 47.9%, 72.0%, and >97% after 10, 20, and 75 min, respectively.

4.2. *trans*-Dihydridobis(triphenylphosphine)(1-(methyl(2-pyridyl)amino)-4-phenylbut-1-ylidene-*N*,*C*)iridium(III) Tetrafluoroborate (3b). 3b was synthesized through a method directly analogous to that for **3a** by reacting **2** (137 mg, 0.148 mmol) and allylbenzene (140 mg, 1.19 mmol) in CH_2Cl_2 (3 mL) for 2 h at 21 °C. Yield: 140 mg (0.134 mmol, 91%). The ethereal solutions were combined, and the ether was removed carefully under reduced pressure. A light yellow oily residue (103 mg) was obtained, whose ^{1}H NMR spectrum shows that the oily residue is a mixture of allylbenzene and *trans*-1-phenylpropene in a ratio of 3.5:1. ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 7.90 (d, $^3J_{HH}$ = 4.5 Hz, 1H, Py), 7.87 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Py), 7.61 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Py), 7.20−7.42 (m, 33H, 30 P*Ph*$_3$ + 3 CH_2*Ph*), 6.90 (d, $^3J_{HH}$ = 6.9 Hz, 2H, CH_2*Ph*), 6.70 (t, $^3J_{HH}$ = 6.2 Hz, 1H, Py), 3.15 (s, 3H, NCH_3), 2.32 (t, $^3J_{HH}$ = 7.1 Hz, 2H, C$H_2CH_2CH_2$), 1.79 (m, 2H, CH_2-CH_2CH_2), 1.40 (quint, 7.2 Hz, 2H, $CH_2CH_2CH_2$), −10.49 (td, $^2J_{PH}$ = 20.8 Hz, $^3J_{HH}$ = 5.3 Hz, 1H, Ir−H), −17.75 (td, $^2J_{PH}$ = 15.9 Hz, $^3J_{HH}$ = 5.4 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 293 K): δ 271.6 (s, Ir=C), 159.4 (s), 153.4 (s), 140.9 (s),

140.0 (s), 133.0 (virtual t, 6.0 Hz, Ph_3P), 132.7 (virtual t, 28.1 Hz, *ipso*-Ph_3P), 130.5 (s), 128.4 (virtual t, 5.2 Hz, Ph_3P), 126.0 (s), 122.4 (s), 122.4 (s), 123.5 (s), 115.6 (s), 46.8 (s, CH_2CH_2-CH_2), 36.9 (s, NCH_3), 35.2 (s, $CH_2CH_2CH_2$), 31.1 (s, CH_2CH_2-CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 273 K): δ 19.8 (s). Anal. Calcd for $C_{52}H_{50}BF_4IrN_2P_2$: C, 59.83; H, 4.83; N, 2.68. Found: C, 59.56; H, 4.95; N, 2.92.

4.3. Observation of 4 in the Reaction between 3b and MeCN or CD_3CN. In a Schlenk tube, **3b** (100 mg, 0.096 mmol) was dissolved in acetonitrile (4 mL) to give a light yellow or colorless solution. This solution was stirred at 0 °C for 50 h, followed by removal of acetonitrile under reduced pressure (ca. 0.1 mmHg) at 0 °C. A light yellow powder (102 mg) was obtained, giving ^1H NMR signals consistent with a mixture of **3b** and **4** in a ratio of 1:16. Data for **4** are as follows. ^1H NMR (500 MHz, CD_3CN, 273 K): δ 7.72 (d, $^3J_{HH} = 5.6$ Hz, 1H), 7.20−7.55 (m, H), 7.14 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.88 (d, $^3J_{HH} = 7.2$ Hz, 2H), 6.24 (t, $^3J_{HH} = 5.6$ Hz, 1H), 5.84 (d, $^3J_{HH} = 8.8$ Hz, 1H), 3.94 (m, 1H, Ir−CH), 2.31 (s, 3H, N−CH_3), 1.96 (s, CH_3-CN−Ir), 1.84 (ddd, $^3J_{HH} = 14.0$ Hz, $^3J_{HH} = 10.8$ Hz, $^3J_{HH} = 5.2$ Hz, diastereotopic $CH_2CH_2CH_2Ph$), 1.44−1.58 (m, 3H, CH_2-CH_2CH_2Ph + $CH_2CH_2CH_2Ph$), 1.24 (m, 1H, diastereotopic $CH_2CH_2CH_2Ph$), 1.09 (m, 1H, diastereotopic $CH_2CH_2CH_2Ph$), −16.27 (dd, $^2J_{PH} = 16.5$ Hz, $^2J_{PH} = 13.4$ Hz, 1H, Ir−H). $^1H\{^{31}P\}$ NMR (400 MHz, CD_3CN, 273 K): δ 7.72 (d, $^3J_{HH} = 5.6$ Hz, 1H), 7.20−7.55 (m, H), 7.14 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.88 (d, $^3J_{HH} = 17.2$ Hz, 2H), 6.24 (t, $^3J_{HH} = 5.6$ Hz, 1H), 5.84 (d, $^3J_{HH} = 8.8$ Hz, 1H), 3.94 (dd, $^3J_{HH} = 8.6$ Hz, $^3J_{HH} = 3.4$ Hz, 1H, Ir−CH), 2.31 (s, 3H, N−CH_3), 1.96 (s, CH_3CN−Ir), 1.84 (ddd, $^3J_{HH} = 14.0$ Hz, $^3J_{HH} = 10.8$ Hz, $^3J_{HH} = 5.2$ Hz, diastereotopic $CH_2CH_2CH_2Ph$), 1.44−1.58 (m, 3H, CH_2CH_2-CH_2Ph + $CH_2CH_2CH_2Ph$), 1.24 (m, 1H, diastereotopic CH_2CH_2-CH_2Ph), 1.09 (m, 1H, diastereotopic $CH_2CH_2CH_2Ph$), −16.27 (s, 1H, Ir−H). ^{13}C NMR (125.77 MHz, CD_3CN, 273 K): δ 161.9 (s), 147.4 (s), 143.6 (s), 138.1 (s), 134.9 (dd, 10.0 Hz, 1.0 Hz, PPh_3), 134.4 (dd, 9.5 Hz, 1.1 Hz, PPh_3), 132.2 (dd, 46.3 Hz, 3.3 Hz, *ipso*-PPh_3), 131.4 (d, 2.4 Hz, PPh_3), 131.2 (d, 2.1 Hz, PPh_3), 129.7 (dd, 51.2 Hz, 3.1 Hz, *ipso*-PPh_3), 129.2 (s, PPh_3), 129.1 (s, PPh_3), 129.0 (s), 128.9 (s), 126.4 (s), 119.8 (s, CH_3CN), 112.2 (s), 108.2 (s), 45.6 (dd, 13.7 Hz, 4.3 Hz, $CH_2CH_2CH_2Ph$), 37.2 (t, 5.4 Hz, Ir−C), 36.8 (s, N−CH_3), 35.6 (s), 32.8 (s), 1.83 (s, CH_3CN). ^{31}P NMR (161.9 MHz, CD_3CN, 0 °C): δ 17.41 (d, $^2J_{PP} = 382.1$ Hz), 9.20 (d, $^2J_{PP} = 382.1$).

4.4. Measurement of K_{eq} in Eq 2. In an NMR tube changed with **3b** (20 mg, 0.019 mmol) was quickly added CD_3CN (0.6 mL). ^1H NMR spectra of this sample were taken between 21 and 50 °C. Enough time (1 day at 21 °C and 5 h at 50 °C) was allowed to ensure that equilibrium was reached. Only the hydride region of each spectrum was analyzed for [**4**-d_3]/[**3b**] ratio. The [**4**-d_3]/[**3b**] ratio at equilibrium was found to be 7.94, 5.72, 4.51, 3.73, 3.09, and 2.56 at 21.0, 29.0, 35.0, 40.0, 45.0, and 50.0 °C, respectively, which corresponds to K_{eq} = 0.415, 0.299, 0.236, 0.195, 0.161, and 0.134, respectively ([CD_3CN] = 19.147 mol/L). Plotting ln K_{eq} against T^{-1} gives $\Delta H° = -30.8$ kJ/mol and $\Delta S° = -112$ J/(mol K) with R^2 = 0.9999.

4.5. Bis(triphenylphosphine)(((2-pyridyl)methylamino)methyl-*N,C*)(2-oxobut-3-en-4-yl-*O,C*)iridium(III) Tetrafluoroborate (5). In a Schlenk tube, **1** (165 mg, 0.168 mmol) was dissolved in acetone (6 mL) to give a light yellow solution, to which was added methyl vinyl ketone (12.0 mg, 0.171 mmol) via syringe. The solution was then refluxed for 6 h, during which time it turned orange; this solution was then concentrated to ca. 1 mL. under reduced pressure, followed by addition of diethyl ether (15 mL). A yellow precipitate appeared and was filtered and washed with diethyl ether (2 × 10 mL). Analytically pure **5** was obtained by drying under vacuum overnight. Yield: 121 mg (0.122 mmol, 73%). ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 10.76 (d, 1H, $^3J_{HH} = 8.4$ Hz, Ir−C*H*=CH), 8.45 (d, $^3J_{HH} = 5.7$ Hz, 1H, Py), 7.20 (m, 30H, PPh_3), 6.90 (t, $^3J_{HH} = 8.0$ Hz, 1H, py), 6.46 (d, $^3J_{HH} = 8.4$ Hz, 1H, Ir−CH=C*H*), 6.28 (t, $^3J_{HH} = 7.5$ Hz, 1H, py), 5.19 (d, $^3J_{HH} = 8.8$ Hz, 1H, Py), 4.74 (t, $^3J_{PH} = 12.4$ Hz, 2H, Ir−CH_2), 2.18 (s, 3H, NCH_3), 1.25 (s, 3H, C(O)CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 Hz, 293 K): δ 213.2 (s, *C*(O)Me), 197.3 (t, 9.0 Hz, Ir−*C*H=CH), 160.6 (s), 147.4 (s), 139.3 (s), 138.1 (s), 135.0 (virtual t, 4.9 Hz, PPh_3), 131.5 (s), 128.9 (virtual t, 4.8 Hz, PPh_3), 127.8 (virtual t, 26.5 Hz, *ipso*-PPh_3), 112.3 (s), 108.3 (s), 37.4 (s, NCH_3), 24.8 (s, C(O)*C*H_3), 19.3 (t, 6.7 Hz, Ir−CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.9 MHz, 273 K): δ 7.0 (s). Anal. Calcd for $C_{47}H_{44}BF_4IrN_2OP_2$: C, 56.80; H, 4.46; N, 2.82. Found: C, 56.60; H, 4.66; N, 2.87.

4.6. Hydridobis(triphenylphosphine)(3-butyl-1-((2-pyridyl)methylamino)allyl-*C,C′,C″,N*)iridium(III) Tetrafluoroborate (6a). To a Schlenk tube charged with **1** (215 mg, 0.219 mmol) and acetone (8 mL) was added 1-hexyne (18 mg, 0.219 mmol) via syringe. The colorless solution was then refluxed for 6 h to give a yellow solution, which was then concentrated to ca. 0.5 mL under reduced pressure, followed by addition of diethyl ether (15 mL). A light yellow precipitate appeared and was filtered and washed with diethyl ether (2 × 15 mL). Analytically pure **6a** was obtained by recrystallization using CH_2Cl_2 and diethyl ether. Yield: 182 mg (0.180 mmol, 82%). ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 7.1−7.5 (m, 32H, 30 PPh_3 + 2 Py), 5.92 (d, $^3J_{HH} = 8.7$ Hz, 1H, Py), 5.84 (td, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, Py), 5.51 (dd, $^3J_{HH} = 11.4$ Hz, $^3J_{HH} = 4.5$ Hz, 1H, H-8), 5.27 (q, $^3J_{HH} = 5.4$ Hz, $^3J_{PH} = 5.4$ Hz, 1H, H-7), 2.84 (m, 1H, H-9), 2.75 (s, 3H, N−CH_3), 1.4 (m, 3H, diastereotopic $CH_2CH_2CH_2CH_3$ + CH_2CH_2-CH_2CH_3), 1.0 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.75 (m, 1H, diastereotopic $CH_2CH_2CH_2CH_3$), 0.70 (t, $^3J_{HH} = 7.3$ Hz, CH_2-$CH_2H_2CH_3$), −20.9 (dd, $^2J_{PH} = 20.6$, 14.8 Hz, Ir−H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 293 K): 162.9 (d, 3.4 Hz, Py), 151.6 (d, 2.6 Hz, Py), 139.2 (s, Py), 135.0 (d, 10.4 Hz, PPh_3), 134.5 (d, 54.2 Hz, *ipso*-PPh_3), 134.0 (d, 52.7 Hz, *ipso*-PPh_3), 133.6(d, 10.2 Hz, PPh_3), 132.3 (d, 2.1 Hz, *para*-PPh_3), 131.4 (s, *para*-PPh_3), 130.0 (d, 10.4 Hz, PPh_3), 129.7 (d, 10.7 Hz, PPh_3), 113.6 (s, Py), 108.9 (s, Py), 90.1 (s, C-8), 82.0 (dd, $^2J_{PC} = 30.2$ Hz, $^2J_{PC} = 3.7$ Hz, C-7), 75.8 (d, $^2J_{PC} = 26.3$ Hz, C-9), 39.3 (d, 3.9 Hz, NCH_3), 35.8 (d, 6.1 Hz, C-10), 33.2 (s, C-11), 23.3 (s, C-12), 14.4 (s, C-13). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.9 MHz, 293 K): δ 13.1 (s), 7.9 (s). Anal. Calcd for $C_{49}H_{50}BF_4IrN_2P_2$: C, 58.39; H, 5.00; N, 2.78. Found: C, 58.12; H, 5.04; N, 2.83.

4.7. Hydridobis(triphenylphosphine)(3-phenyl-1-((2-pyridyl)methylamino)allyl-*C,C′,C″,N*)iridium(III) Tetrafluoroborate (6b). 6b was synthesized as a light yellow powder in 78% yield by a method analogous to that for **6a** using **1** and 1 equiv of phenylacetylene. ^1H NMR (acetone-d_6, 500 MHz, 293 K): δ 7.54 (d, $^3J_{HH} = 5.0$ Hz, 1H), 7.34−7.49 (m, 10H), 7.15−7.30 (m, 15 H), 7.08 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ph), 7.00−7.04 (m, 6H), 6.94 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.82 (t, $^3J_{HH} = 7.5$ Hz, 2H, Ph), 6.59 (dd, $^3J_{HH} = 12.2$ Hz, $^3J_{HH} = 4.5$ Hz, 1H, H-8), 6.17 (d, $^3J_{HH} = 8.7$ Hz, 1H), 5.99 (t, $^3J_{HH} = 6.4$ Hz, 1H), 5.71 (dd, $^3J_{PH} = 9.6$ Hz, $^3J_{HH} = 4.4$ Hz, 1H, H-7), 4.08 (dd, $^3J_{HH} = 12.1$ Hz, $^3J_{PH} = 7.8$ Hz, 1H, H-9), 2.93 (s, 3H, N−CH_3), −20.41 (dd, $^2J_{PH} = 21.0$ Hz, $^2J_{PH} = 15.0$ Hz, 1H, Ir−H). $^1H\{^{31}P\}$ NMR (acetone-d_6, 400 MHz, 293 K): δ 7.54 (d, $^3J_{HH} = 5.0$ Hz, 1H), 7.15−7.50 (m, 25 H), 7.08 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ph), 7.0−7.04 (m, 6H), 6.94 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.82 (t, $^3J_{HH} = 7.5$ Hz, 2H, Ph), 6.59 (dd, $^3J_{HH} = 10.9$ Hz, $^3J_{HH} = 4.5$ Hz, 1H, H-8), 6.17 (d, $^3J_{HH} = 8.7$ Hz, 1H), 5.99 (t, $^3J_{HH} = 6.4$ Hz, 1H), 5.71 (d, $^3J_{HH} = 4.4$ Hz, 1H, H-7), 4.08 (d, $^3J_{HH} = 12.2$ Hz, 1H, H-9), 2.93 (s, 3H, N−CH_3), −20.41 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 125.8 MHz, 293 K): δ 163.0 (d, 1.0 Hz, Py), 151.8 (d, 2.8 Hz, Py), 139.4 (s, Py), 137.7 (d, 3.1 Hz, *ipso*-Ph), 134.6 (d, 10.6 Hz, PPh_3), 134.2 (d, 55.4 Hz, *ipso*-PPh_3), 133.7 (d, 10.3 Hz, PPh_3), 133.2 (d, 50.7 Hz, *ipso*-PPh_3), 132.1 (s, *para*-PPh_3), 131.5 (s, *para*-PPh_3), 129.8 (d, 10.4 Hz, PPh_3), 129.4 (s, Ph), 128.1 (s, Ph), 126.9 (s, Ph), 113.7 (s, Py), 109.0 (s, Py), 87.2 (s, C-8), 79.8 (d, 31.9 Hz, C-7), 76.2 (d, 25.4 Hz, C-9), 39.4 (d, 2.94 Hz, N−CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 293 K): δ 15.8 (d, 5.9 Hz), 9.7 (d, 5.9 Hz). Anal.

Calcd for $C_{51}H_{46}BF_4IrN_2P_2$: C, 59.59; H, 4.51; N, 2.73. Found: C, 59.98; H, 4.88; N, 2.66.

4.8. Hydridobis(triphenylphosphine)(2,3-diphenyl-1-((2-pyridyl)methylamino)allyl-*C,C′,C″,N*)iridium(III) Hexafluoroantimonate (6c). 6c was synthesized as an off-white powder in 89% yield by a method analogous to that for **6a** using the SbF_6^- analogue of **1** and 1 equiv of diphenylacetylene. ^{1}H NMR (CD_2Cl_2, 400 MHz, 293 K): δ 7.59 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, Ph), 7.13−7.46 (m, 23H), 7.08 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 2.2 Hz, 6H, *meta*-PPh_3), 6.99 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 11.1 Hz, 6H, *ortho*-PPh_3), 6.79 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *para*-Ph), 6.55 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *meta*-Ph), 6.49 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *ortho*-Ph), 6.32 (d, $^3J_{HH}$ = 9.3 Hz, 1H, Py), 5.97 (t, $^3J_{HH}$ = 6.5 Hz, 1H, Py), 4.87 (t, $^3J_{PH}$ = 4.7 Hz, 1H, allyl), 4.16 (d, $^3J_{PH}$ = 7.0 Hz, 1H, allyl), 3.01 (s, 3H, NCH_3), −19.84 (dd, $^2J_{PH}$ = 21.3 Hz, $^2J_{PH}$ = 15.4 Hz, 1H, Ir−H). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 100.6 MHz, 393 K): δ 161.1 (d, 3.8 Hz), 151.4 (d, 3.1 Hz), 139.1 (s), 136.6 (s), 134.7 (d, 3.1 Hz), 133.8 (d, 10.6 Hz, PPh_3), 133.1 (d, 10.0 Hz, PPh_3), 132.0 (d, 54.0 Hz, *ipso*-PPh_3), 131.6 (s), 131.5 (d, 50.0 Hz, *ipso*-PPh_3), 131.2 (d, 2.4 Hz), 130.8 (d, 2.3 Hz), 130.3 (d, 2.4 Hz), 128.9 (d, 10.0 Hz), 128.8 (s), 128.7 (s), 128.5 (d, 10.0 Hz), 127.8 (s), 126.3 (s), 113.0 (s), 112.0 (s, allyl C-8), 107.8 (s), 82.3 (dd, 31.7 Hz, 3.8 Hz, allyl), 76.1 (dd, 24.4 Hz, 2.4 Hz), 39.2 (s, CH_3). ^{31}P NMR (CD_2Cl_2, 161.9 MHz, 393 K): δ 10.90 (d, $^2J_{PP}$ = 6.7 Hz), 10.04 (d, $^2J_{PP}$ = 6.7 Hz). Anal. Calcd for $C_{57}H_{50}F_6IrN_2P_2Sb$: C, 54.64; H, 4.02; N, 2.24. Found: C, 54.43; H, 4.01; N, 2.23.

5. Conclusions

The carbene dihydride complex **2** undergoes insertion with alkenes to give the carbene dihydrides **3a**,**b**. CH_3CN can promote a reversible retro-α-elimination to give the alkyl hydride **4**. Methyl vinyl ketone is an exception, in that its reaction with **1** gives the cyclometalated iridafuran derivative **5**. The proposed pathway for **3a**,**b** involves C−C bond formation by a rare C(sp^3)−C(sp^3) reductive elimination. Alkynes also react with **1** or **2** but give tethered η^3-allyl complexes **6a**,**b** via a proposed pathway that involves C−C bond formation by a C(sp^3)−C(sp^2) reductive elimination. The stabilities of **3** and **6** are evidently too high to permit Murai-type catalysis under the conditions we have examined. Crystal structures of **3b**, **5**, and **6b** are reported.

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Supporting Information Available: Tables providing atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions for **3b**, **5**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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