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Reactivity and Regioselectivity of Insertion of Unsaturated Molecules into M−C (M = Ir, Rh) Bonds of Cyclometalated Complexes

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The reactivity of four different cyclometalated iridium and rhodium complexes (**1**, Ir−N−Me; **2**, Rh−N−Me; **3**, Ir−N−Py; **4**, Rh−N−Py) with ancillary ligands with different electronic and steric properties has been investigated by reactions of ethylene (**a**), propylene (**b**), carbon monoxide (**c**), *tert*-butylisocyanide (**d**), acetylene (**e**), and phenylacetylene (**f**). Only coordination products were obtained for the reactions of ethylene and propylene with **1** and **3**, while inserted and rearranged products were achieved for the reactions with **2** and **4**. Insertion of a single equivalent of acetylene was observed for the reactions with **2**, **3**, and **4**, whereas reaction with **1** produces a product in which 4 equiv of acetylene has undergone insertion. The reactions with carbon monoxide showed clean M−C bond insertion products, while *tert*-butylisocyanide formed only terminal adducts. Two equivalents of phenylacetylene were observed to insert for all of the cyclometalated complexes. The regioselectivity was also investigated for each cyclometalated complex by using a series of internal unsymmetrical alkynes, and the results revealed that the regioselectivity was controlled by both steric and electronic factors. The insertion compounds were fully characterized by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, elemental analysis, and X-ray determinations for selected cases.

Introduction

Insertion of unsaturated molecules into transition metal−carbon bonds has been broadly investigated as an important field of organometallic chemistry due to a variety of novel and interesting synthetic applications,[1−4] as well as applications in polymerization and copolymerization catalyzed by transition metals.[5−8] Studies of the fundamental steps of insertion reactions of unsaturated molecules into metal−carbon bonds have revealed very important information about the exact role of the metal during the reactions. Also, cyclometalated complexes with different ancillary ligands have shown different reactivities and different mechanisms depending on the stereoelectronic properties of the unsaturated molecules employed.

Among all the group 10 transition metals, organopalladated complexes have exhibited high reactivity with a wide variety of unsaturated molecules, such as CO,[9] isocyanides,[9b,10] alkenes,[9a,c,e,f,11] alkynes,[9b,11a,f,12] allenes,[13] SO_2,[14] and O_2,[15] showing insertion into the Pd−C (sp^2) and Pd−C (sp^3) bonds of palladacycles. Successive insertions of different

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unsaturated molecules[9a,b,10d,16] and multiple insertions of the same unsaturated molecules[12d,e,g,h,17] have also been observed. Pfeffer and co-workers found that insertion of 2 equiv of diphenylacetylene and dimethylacetylene dicarboxylate (DMAD) into the Pd−C bond of di-μ-chloro-bridged *ortho*-palladated 2-benzylpyridine led to the formation of unexpected spiro-compounds via unobserved 10-membered-ring intermediates.[12h,17c] The Pd center of the intermediates was proposed to interact with the double bond of the benzyl ring, which was responsible for the instability of the intermediates. However, the similar nine-membered-ring product was stabilized by reaction of a di-μ-chloro-bridged cyclopalladated Schiff base dimer with double insertion of diphenylacetylene or hex-3-yne. It also showed that the electron-donating ability of the chelated metallocycle ligand made the insertion more rapid. The related monomeric palladacycles retarded the reaction dramatically,[12g] which implied that the bridging chloride facilitated the coordination of alkyne. The reaction of a 2,2′-bipyridine-coordinated palladacycle in the presence of $AgBF_4$ to remove the halide to form a cationic arylpalladium complex resulted in the insertion of three molecules of DMAD into the Pd−aryl bond, while only one DMAD insertion was observed to insert in the absence of $AgBF_4$.[12e] It was also found that less reactive substrates usually led to monoinserted products, whereas the more reactive ones resulted in further insertion.[12b] Kinetically, it was observed that for the double insertion of alkynes in a di-μ-chloro-bridged cyclopalladated dimer, the insertion of the first alkyne molecule is the rate-determining step, and electron-donating groups on the phenyl ring of the benzyl group increase the reaction rate.[12g] However for the double insertion into the Pd−methyl bond for the palladium chloro methyl complexes, the rate of insertion for the second alkyne is more than 3 orders magnitude slower than the first insertion.[12b]

The regioselectivity for insertion reactions with unsymmetrical alkynes was found to be high for most cases. The Pfeffer group found that in the insertion of 4,4-dimethyl-2-pentyne in palladacycles possessing a chelated sulfur or nitrogen directing group, the major or sole regioisomer was the insertion product in which the *tert*-butyl group was α to the palladium atom. The opposite regiochemistry was observed in the absence of this chelation.[12f] Reactions of the *ortho*-palladated dimethylbenzylamine complexes with unsymmetrical ester-activated alkynes showed that the carboxylate group of the insertion products is preferentially next to the phenyl group of the benzylamine moiety (i.e., β to the metal). The reverse regioselectivity was observed in reactions with electron-deficient palladium centers.[12c] Kinetic and theoretical studies revealed that both electronic and steric factors accounted for the substitution patterns of the products.

For similar insertion reactions with platinum complexes, the insertion reactions with CO,[18] isocyanides,[18b,19] and alkenes[18b,20] have also been observed. It is interesting to notice that CO was selectively inserted into the Pd−O bonds of platinaoxetanes[21] instead of the Pt−C bonds on the basis of both a thermodynamic and kinetic preference, as indicated by DFT calculations.[22] In the complex (dppe)Pt(CH_3)(OCH_3), CO was selectively inserted into the Pt−O bond without further insertion into the available Pt−C bond.[23] However, insertion of CO into both the Pd−C(sp^3) and Pd−C(sp^2) bonds was obtained from the methylplatinum complex ($C_{10}H_{12}OMe$)Pt(PPh_3)(Me).[18c] Insertion of unsaturated molecules into Ni−C bonds is also common.[24] Normally, the regioselectivity for insertion reactions of unsymmetrical alkynes produced the regioisomer that has the bulkier substituents attached to the α-carbon.[24d] The insertion reaction of a nickelacycle with ethyl 2-butynoate, however, resulted in only one regioisomer in which the methyl group is α to the nickel center, the reverse selectivity.[24c] Bothe electronic and steric arguments have been used to explain the regioselectivity observed, but neither could be applied well in all cases.

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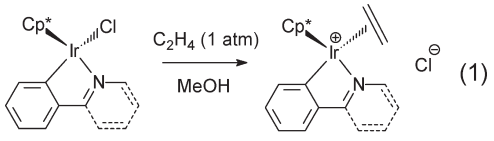
A few examples of insertion reactions of unsaturated molecules into Ru−C bonds have also been documented in the literature.[25] It was found that the Ru−aryl bond was subject to insertion over the Ru−alkyl bond as observed by the reactions with *ortho*-metalated benzyl ruthenium compounds.[25f] However, there have been only limited reports about the insertion reaction with organo-rhodium and organo-iridium complexes.[26−28] In a previous paper, we reported on the mechanism of acetate-assisted electrophilic activation by $[Cp^*RhCl_2]_2$.[29] We also reported an example of the insertion of dimethylacetylene dicarboxylate to produce isoquinolinium salts following oxidative coupling of the insertion products by copper(II) chloride.[29b] Closely related work has been reported recently by Davies et al. on the activation of 4,4-dimethyl-2-oxazolinylbenzene by both $[Cp^*IrCl_2]_2$ and $[(p\text{-cymene})RuCl(MeCN)]^+$ and insertion reactions involving terminal and internal alkynes.[30]

In this paper, we present a detailed study of the insertion reactions of a variety of unsaturated molecules (ethylene, propylene, carbon monoxide, *tert*-butylisocyanide, acetylene, and phenylacetylene) using four five-membered iridium and rhodium cyclometalated complexes. The investigation has been carried out by use of NMR spectroscopic methods as well as X-ray structural determinations for key structures. Mechanistic pathways are also proposed to rationalize the experimental results. The regioselectivity of the insertion reactions with unsymmetrical internal alkynes was also studied with the goal of finding the factors controlling the regioselectivity. The regioisomers were isolated by column chromatography and fully characterized by NMR spectroscopies and X-ray structural analysis for selected cases. Considering that cyclometalated complexes can oftentimes be easily prepared by direct cleavage of a C−H bond adjacent to a donor directing atom (nitrogen for example) under mild conditions, it is important to learn more about factors affecting the insertion chemistry as a guide to the development of synthetic organic methods, especially for heterocycle synthesis.

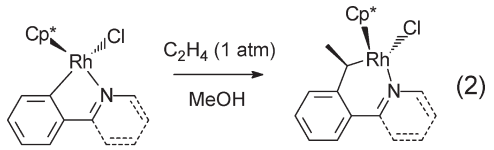
Results and Discussions

1. Reaction with Ethylene. The preparations of metallacycles **1**−**4** have been reported from $[Cp^*IrCl_2]_2$ and $[Cp^*RhCl_2]_2$ and the corresponding imines in the presence of sodium acetate.[29] Each cyclometalated complex was treated with one atmosphere of ethylene (**a**) in methanol at room temperature. The yellow solutions of **1** and **3** turned pale yellow within 5 min, producing **1a** and **3a**, respectively, while the orange solutions of **2** and **4** turned bright red within 5 min, producing **2a** and **4a**, respectively (eqs 1 and 2). The products are readily characterized by ^1H NMR and ^{13}C NMR spectroscopies.



1 Ir-N-Me
3 Ir-N-Py

1a
3a



2 Rh-N-Me
4 Rh-N-Py

2a
4a

From the ^1H NMR spectrum of **1a**, the two doublets at δ 3.16 and 2.96 (δ 3.46 and 3.11 for **3a**) suggest a structure with coordinated freely rotating ethylene rather than an insertion product. The $^{13}C\{^1H\}$ NMR spectrum showed a singlet at δ 88.82 for the bound ethylene in **1a**, also indicating facile rotation. The coodination compounds **1a** and **3a** were unstable and decomposed very quickly to starting material without protection of the ethylene atmosphere. No crystals of the products could be isolated to further confirm the structures. In considering the mechanism of reaction, both **1** and **3** are coordinatively saturated 18-electron complexes, and an open coordination site is required to form a 16-electron intermediate, which could then coordinate ethylene. There are two possible sequences for producing coordinative unsaturation: (1) nitrogen dissociation or (2) chloride dissociation to form a 16-electron iridium cation. On the basis of previous results,[29] the Ir−Cl bond lengths for **1** and **3** are around 2.4 Å, which implies that the bonds are more ionic than covalent and that polar solvents such as methanol could favor ionic species, suggesting that chloride dissociation is the preferred mechanism. By adding an excess of ammonium chloride, the reaction of ethylene with **1** was dramatically retarded, confirming the chloride dissociation mechanism.

^1H NMR confirmed the structures for **2a** and **4a** as shown in eq 2 with an unusual [1,1] ethylene insertion, showing a doublet (J = 7 Hz) for the methyl group and a doublet of quartets (J = 7 Hz) for the methine. The X-ray structures of **2a** and **4a** were also obtained to further confirm the [1,1]-insertion products as shown in Figure 1. After insertion, the Rh−Cl bond is lengthened by 0.02 Å, indicating weaker rhodium chloride bonding. It was noticed that only one of two possible stereoisomers was observed in each case, as a new chiral carbon center was generated after insertion.

The preference for six-membered-ring metallacycles over seven-membered-ring metallacycles accounts for the [1,1]-insertion instead of [1,2]-insertion. A proposed mechanism is drawn in Scheme 1. The 16-electron cation is formed first by dissociation of the chloride followed by

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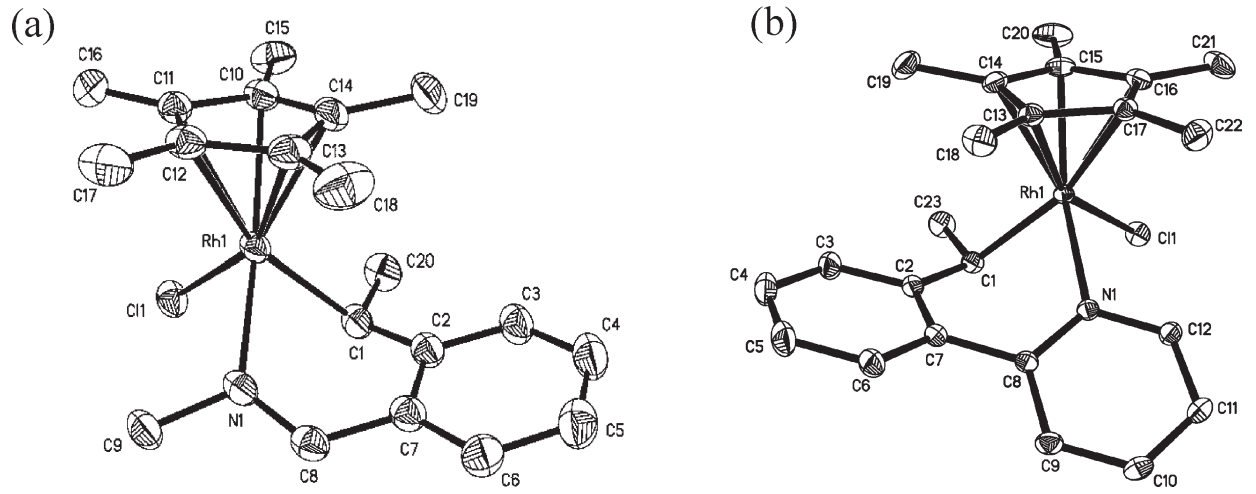
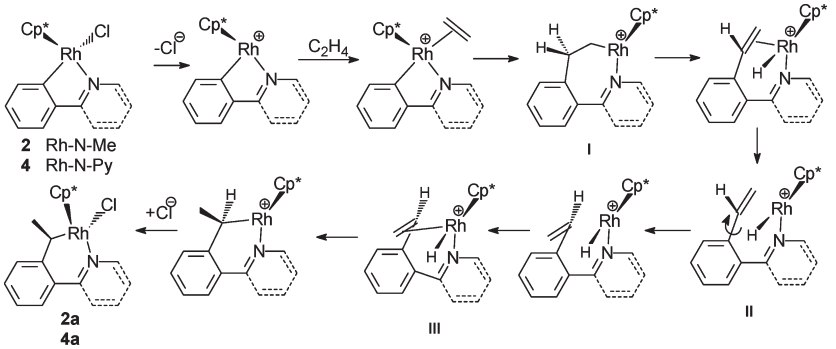


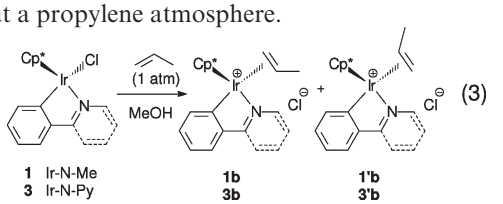
Figure 1. Molecular structures for (a) **2a** and (b) **4a** with 50% displacement ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): (a) Rh(1)−N(1) 2.1003(14), Rh(1)−Cl(1) 2.4282(5), Rh(1)−C(1) 2.1185(16), C(1)−C(2) 1.480(2), C(2)−C(7) 1.410(2), C(7)−C(8) 1.458(2), C(8)−N(1) 1.283(2), N(1)−Rh(1)−Cl(1) 91.55(4), C(1)−Rh(1)−Cl(1) 85.98(5), N(1)−Rh(1)−C(1) 80.55(6), C(2)−C(1)−Rh(1) 108.51(11), C(7)−C(2)−C(1) 119.55(15), C(2)−C(7)−C(8) 120.89(16), N(1)−C(8)−C(7) 124.17(15), C(8)−N(1)−Rh(1) 123.70(11); (b) Rh(1)−N(1) 2.0974(10), Rh(1)−Cl(1) 2.4110(3), Rh(1)−C(1) 2.1112(12), C(1)−C(2) 1.48005(17), C(2)−C(7) 1.4153(17), C(7)−C(8) 1.4793(16), C(8)−N(1) 1.3581(15), N(1)−Rh(1)−Cl(1) 90.73(3), C(1)−Rh(1)−Cl(1) 85.65(3), N(1)−Rh(1)−C(1) 80.86(4), C(2)−C(1)−Rh(1) 106.31(8), C(7)−C(2)−C(1) 120.87(10), C(2)−C(7)−C(8) 121.37(10), N(1)−C(8)−C(7) 119.42(10), C(8)−N(1)−Rh(1) 123.81(8).

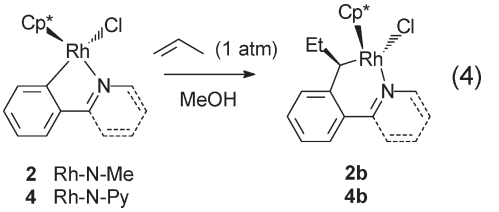
Scheme 1. Proposed Pathway for the Insertion Reaction of Ethylene



ethylene coordination, and the ethylene-coordinated cation undergoes insertion to form the unstable seven-membered metallacycle. β-Hydrogen elimination occurs in intermediate I, leading to an olefin hydride intermediate II. Note that isomerism must occur in species II to give species III by dissociation and recoordination of the olefin in order to achieve the proper facial selectivity for the observed product stereoselectivity at carbon in **2a** and **4a**. The olefin hydride III then proceeds by insertion to produce the six-membered-ring cation complex, which finally coordinates chloride to form the observed product. It also deserves mentioning that no further ethylene insertion was observed in the reactions of ethylene with **2** or **4** under the same reaction conditions, even after a week, which is different from the observation for the reaction of ethylene with cycloruthenated tertiary amines.[25a]

2. Reaction with Propylene. The reactions with propylene (**b**) with **1**−**4** were conducted under the same reaction conditions as with ethylene, and similar results are summarized in eqs 3 and 4, respectively. As propylene is a prochiral olefin, two pale yellow isomers (**1b**/**1′b** or **3b**/**3′b**) were formed in the reactions of propylene with **1** and **3** at room temperature within 5 min (ratios of 1:1.3 and 1:2.0, respectively). The mixture of two rotamers decomposed quickly back to **1** and **3** without a propylene atmosphere.





Bright red [1,1]-insertion products were observed for the reactions of propylene with **2** and **4** at room temperature within 5 min. The product **2b** from reaction with **2** is more reactive, making the reaction not as clean as the reaction with

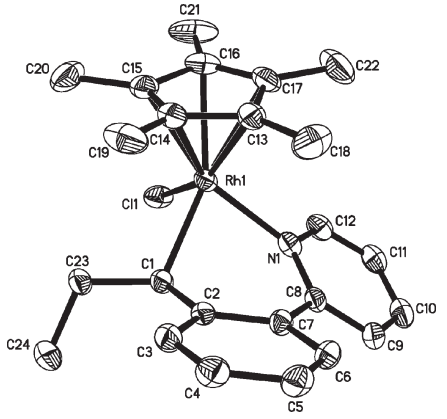
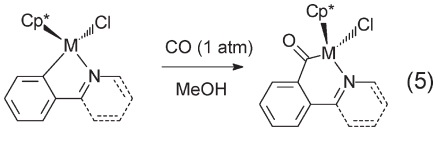


Figure 2. Molecular structure and atom-numbering scheme for **4b** with 50% displacement ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N-(1) 2.1077(17), Rh(1)−Cl(1) 2.4077(5), Rh(1)−C(1) 2.1110(18), C(1)−C(2) 1.482(3), C(2)−C(7) 1.415(2), C(7)−C(8) 1.473(3), C(8)−N(1) 1.350(2), N(1)−Rh(1)−Cl(1) 91.18(4), C(1)−Rh(1)−Cl(1) 86.12(5), N(1)−Rh(1)−C(1) 80.34(7), C(2)−C(1)−Rh(1) 106.00(12), C(7)−C(2)−C(1) 119.70(16), C(2)−C(7)−C(8) 121.51(16), N(1)−C(8)−C(7) 119.52(16), C(8)−N(1)−Rh(1) 123.37(13).

4. One possible reason for this is that the rhodium center with N-methyl substitution is more electron-rich than the center with N-pyridyl substitution, which makes **2** more reactive with electron-rich olefins. The X-ray structure for **4b** was determined to further confirm the [1,1]-insertion product as shown in Figure 2. The X-ray structure confirmed a propyl group instead of an isopropyl group as observed by Pfeffer in the reaction of cycloruthenated tertiary amines.[25a] Only one stereoisomer was observed for **2b** and **4b**, as seen with ethylene.

The varying results with rhodium compounds ([1,1]-insertion) versus iridium compounds (coordination only) could be accounted for by a stronger binding of the olefin to iridium, lowering the energy of this complex relative to the insertion complex. However, since the olefin coordination to iridium is reversible, this is apparently not the reason for the difference in reactivity. Another possibility is that iridium does not undergo olefin insertion because the Ir−aryl bond is stronger than the Rh−aryl bond. There is ample literature precedent for this possibility,[31] which indicates thermodynamics accounts for the difference in reaction products.

3. Reaction with Carbon Monoxide. Light yellow products were observed within 5 min in the reaction of carbon monoxide (**c**) with **1**−**4** under the same reaction conditions as mentioned above (eq 5). However, the insertion products were not very stable and decomposed slowly in either solid state or solution upon exposure to air. The X-ray structure of **2c** was obtained from crystallization of a mixture of **2** and **2c** and is shown in Figure 3.



1 Ir-N-Me
2 Rh-N-Me
3 Ir-N-Py
4 Rh-N-Py

1c
2c
3c
4c

Reaction of **3** and **4** with methyllithium at room temperature overnight in dry dichloromethane produces the analogous compounds with methyl coordination in place of chloride.

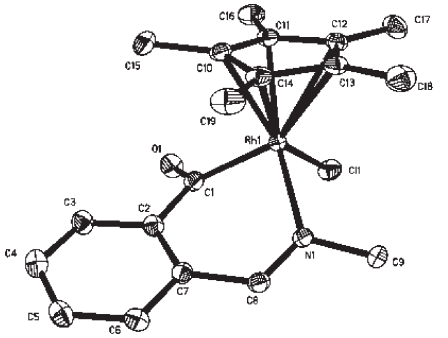
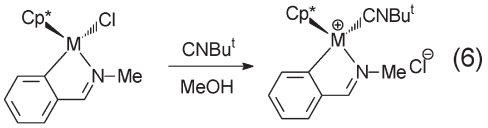


Figure 3. Molecular structure and atom-numbering scheme for **2c** with 50% displacement ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N-(1) 2.0842(16), Rh(1)−Cl(1) 2.4144(5), Rh(1)−C(1) 2.0842(16), C(1)−O(1) 1.215(2), C(1)−C(2) 1.507(3), C(2)−C(7) 1.401(3), C(7)−C(8) 1.463(3), C(8)−N(1) 1.279(2), N(1)−Rh(1)−Cl(1) 91.13(5), C(1)−Rh(1)−Cl(1) 93.12(6), N(1)−Rh(1)−C(1) 88.27(7), C(2)−C(1)−Rh(1) 116.70(13), C(7)−C(2)−CC(1) 123.47(17), C(2)−C(7)−C(8) 123.13(18), N(1)−C(8)−C(7) 124.35(18), C(8)−N(1)−Rh(1) 125.02(14).

The methylated compounds were reacted under 1 atm of carbon monoxide in methanol, and only the metal−methyl insertion products were observed by ^{13}C NMR spectroscopy, in which the chemical shift for carbonyl carbon was above 190 ppm. This observed insertion preference is reversed compared with the analogous ruthenium complexes.[25f] As CO insertions commonly occur by alkyl migration to a coordinated carbon monoxide,[32] the mechanism likely involves nitrogen dissociation in the metallacycle prior to CO binding and insertion. The reactions with methylated compounds took much longer to go to completion, consistent with a slow chelate-opening step. The insertion of CO seen here stands in contrast to the observation of simple CO coordination by Davies et al. in Cp*Ir(4,4-dimethyl-2-oxazolinylphenyl)$(CH_3CN)]^+$.[30]

4. Reaction with *tert*-Butylisocyanide. Isocyanides are isoelectronic with CO and are generally more reactive than alkynes, undergoing facile insertion into metal−carbon bonds.[25b] The same insertion pattern would be expected as seen with CO. However, reaction of **1** and **2** with *tert*-butylisocyanide (**d**) produced yellow, oily products **1d** and **2d**, as shown in eq 6. The products are very stable and undergo no further reaction with excess isocyanide. IR absorptions for the products at 2156 and 2177 cm^{-1}, respectively, suggest the existence of a terminal C≡NR functional group. The X-ray structure for **1d** shown in Figure 4 was determined and confirmed terminal coordination to the metal rather than insertion into the M−C bond. These observations are puzzling considering the established facile insertion of isonitriles relative to carbon monoxide. It is possible that strong metal−aryl bonds are again responsible for the lack of insertion.



1 Ir-N-Me
2 Rh-N-Me

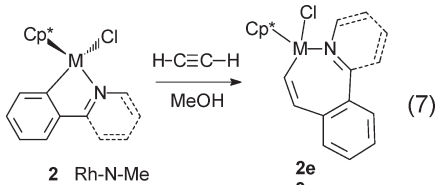
1d
2d

5. Reaction with Acetylene. Similar reactions of **1**−**4** have been examined under 1 atm of acetylene (**e**) in methanol at

(31) Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(32) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.

room temperature. Only 1 equiv of acetylene insertion was observed for **2**, **3**, and **4** within 5 min at room temperature, as shown in eq 7. The aromatic region of the ^{1}H NMR spectrum displayed two proton resonances with large coupling constants, and single-crystal X-ray structures were also obtained for **3e** and **4e**, as shown in Figure 5. The unusual seven-membered metallacycles were obtained without further rearrangement. In the reaction of **1** with acetylene, however, 4 equiv of acetylene was observed to insert. The ^{1}H NMR spectrum revealed eight additional olefinic proton peaks (δ 5.1−2.8). No X-ray structure could be obtained to determine the structure of this species. Compounds **2**, **3**, and **4** also reacted with additional acetylene at long reaction times, but no reliable information could be obtained as to the product identities.

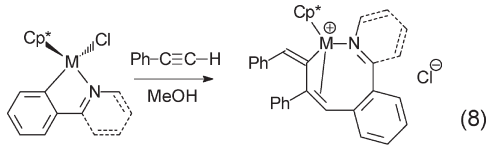


(7)

2 Rh-N-Me
3 Ir-N-Py
4 Rh-N-Py

2e
3e
4e

6. Reaction with Propyne and Phenylacetylene. Terminal alkynes such as propyne and phenylacetylene have been employed in reactions with **1**−**4** in methanol at room temperature. All of the reactions with propyne produced products that were too reactive toward further insertions to yield any useful information about the nature of the products. However, the reactions with phenylacetylene (**f**) showed insertion of 2 equiv of alkyne, as shown in eq 8. The X-ray structure (connectivity only; see Supporting Information) of the product (**1f**) obtained by reaction of phenylacetylene with **1** was determined. The reactions of **2** and **4** with phenylacetylene were not as clean as the reactions of **1** and **3**, and the double-insertion products were formed along with small quantities of byproducts.



(8)

1 Ir-N-Me
2 Rh-N-Me
3 Ir-N-Py
4 Rh-N-Py

1f
2f
3f
4f

A plausible route to **1f** is shown in Scheme 2. Due to the π-overlap of the alkyne with the phenyl group, the alkyne C−C bond is polarized as shown.[33] The chloride of **1** dissociates first to form a 16-electron cation, and then the phenyl acetylene undergoes regioselective insertion to produce the strongest M−C bond (counter to the polarization), forming a seven-membered metallacycle I. Coordination of a second alkyne and rearrangement to its vinylidene isomer allows insertion to give the observed product. Additional evidence for the proposed mechanism is that by adding excess phenylacetylene to the product of **1** with dimethylacetylene dicarboxylate, the analogous phenylacetylene eight-membered-ring cross-insertion product was formed slowly in methanol. However, the reaction did not go to completion at room temperature. A similar double insertion of phenylacetylene

(33) Cox, A. P.; Ewart, I. C.; Stigliani, W. M. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 504.

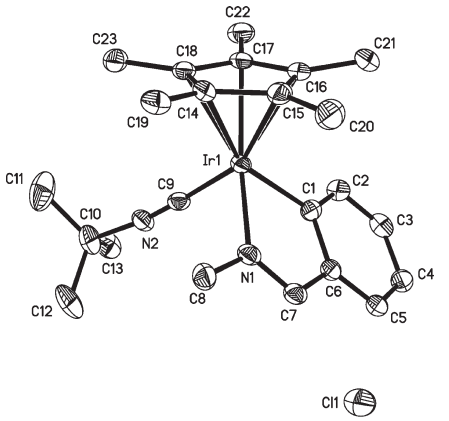
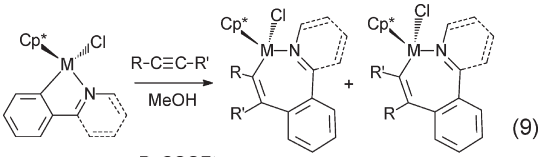


Figure 4. Molecular structure and atom-numbering scheme for **1d** with 50% displacement ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−N(1) 2.076(5), Ir(1)−C(1) 2.060(5), Ir(1)−C(9) 1.924(5), C(1)−C(2) 1.388(8), C(1)−C(6) 1.400(7), C(6)−C(7) 1.438(8), C(8)−N(1) 1.448(7), C(9)−N(2) 1.161(6), Ir(1)−C(9)−N(2) 177.6(5), C(9)−N(2)−C(10) 167.5(6), N(1)−Ir(1)−C(1) 77.8(2), C(2)−C(1)−Ir(1) 128.5(4), C(1)−C(6)−C(7) 114.4(5), C(6)−C(1)−Ir(1) 114.1(4), N(1)−C(7)−C(6) 116.6(5), C(7)−N(1)−Ir(1) 116.8(4).

was seen by Davies et al. in the reaction with Cp*Ir(4,4-dimethyl-2-oxazolinylphenyl)(CH_3CN)]$^+$.[30]

7. Reaction with Unsymmetrical Internal Alkynes. A series of unsymmetrical internal alkynes of the type RC≡CCO_2Et have been employed to investigate the regioselectivity of the insertion reactions. Ethyl 2-butynoate (**g**), ethyl phenylpropiolate (**h**), and ethyl 4,4,4-trifluoro-2-butynoate (**i**) have been reacted with **1**−**4** in methanol at room temperature, and two regioisomers have been obtained for two of the three cases, as shown in eq 9. The regioselectivity results are summarized in Table 1.



(9)

1 Ir-N-Me
2 Rh-N-Me
3 Ir-N-Py
4 Rh-N-Py

R=COOEt
R'=Me, g
Ph, h
CF_3, i

1g-i
see text
3g-i
4g-i

1'g-i

3'g-i
4'g-i

Only one regioisomer was obtained for the reactions with ethyl 2-butynoate, and the bulky but electron-withdrawing carboxylate group of the insertion products is preferentially located adjacent to the metal center, indicating the dominance of electronic effects on the regioselectivity. The ^{1}H NOE spectroscopy for **1g** and X-ray structures for **3g** and **4g** (Figure 6a,b) confirmed the regioselectivity preference. However, the ^{13}C NMR for **2g** showed several doublets with the coupling constants at ~20 Hz, which implied the couplings with the rhodium center. The X-ray determination for **2g** further confirmed the ferrocene-type structure, which is consistent with the ^{1}H NMR and ^{13}C NMR data, as shown in Figure 6h. One new bond was formed between C(1) and C(9), and the bond length of C(1)−C(2) was dramatically lengthened.

However, the reactions of **1**−**4** with ethyl phenylpropiolate and ethyl 4,4,4-trifluoro-2-butynoate yielded two regioisomers. The regioselectivities are not as good as seen in the palladium analogues.[12c,17c] For the reactions with ethyl

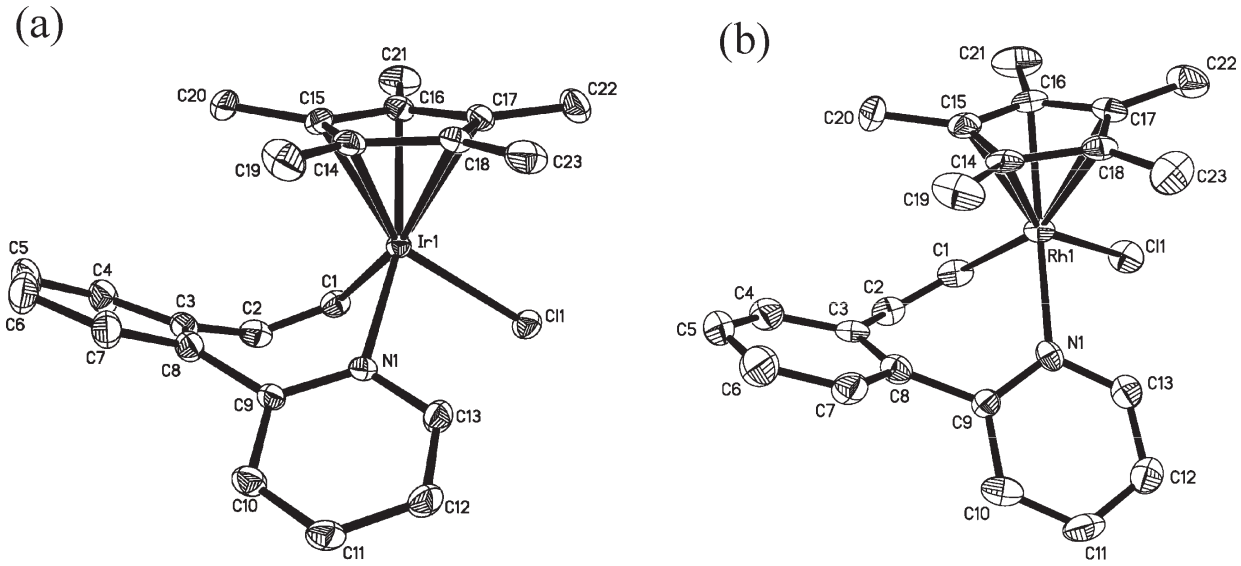
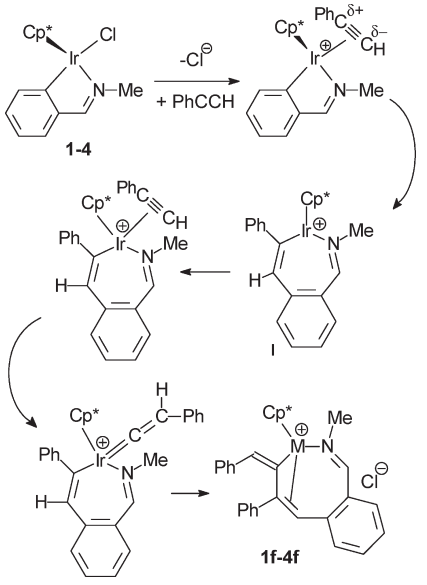


Figure 5. Molecular structure and atom numbering scheme for (a) **3e** and (b) **4e** with 50% displacement ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **3e**: Ir(1)−N(1) 2.112(4), Ir(1)−Cl(1) 2.4230(13), Ir(1)−C(1) 2.041(5), C(1)−C(2) 1.334(8), C(2)−C(3) 1.474(8), C(3)−C(8) 1.399(8), C(8)−C(9) 1.491(7), C(9)−N(1) 1.348(7), N(1)−Ir(1)−Cl(1) 89.16(12), C(1)−Ir(1)−Cl(1) 84.11(15), N(1)−Ir(1)−C(1) 86.5(2), C(2)−C(1)−Ir(1) 128.8(4), C(3)−C(2)−C(1) 124.5(5), C(8)−C(3)−C(2) 124.8(5), C(9)−C(8)−C(3) 125.9(5), N(1)−C(9)−C(8) 123.7(4), C(9)−N(1)−Ir(1) 124.0(3). Selected bond distances (Å) and angles (deg) for **4e**: Rh(1)−N(1) 2.120(5), Rh(1)−Cl(1) 2.4072(17), Rh(1)−C(1) 1.997(7), C(1)−C(2) 1.321(9), C(2)−C(3) 1.461(9), C(3)−C(8) 1.413(9), C(8)−C(9) 1.489(8), C(9)−N(1) 1.363(8), N(1)−Rh(1)−Cl(1) 92.07(14), C(1)−Rh(1)−Cl(1) 85.39(19), N(1)−Rh(1)−C(1) 85.4(2), C(2)−C(1)−Rh(1) 129.2(5), C(3)−C(2)−C(1) 125.1(6), C(8)−C(3)−C(2) 125.2(6), C(9)−C(8)−C(3) 124.7(6), N(1)−C(9)−C(8) 122.7(5), C(9)−N(1)−Rh(1) 125.4(4).

Scheme 2. Proposed Pathway for Double Insertion of Phenylacetylene



phenylpropiolate, the major products were the insertion products with the bulkier phenyl group next to the metal center, which is consistent with both steric and electronic factors affecting the regioselectivity. For the reactions with ethyl 4,4,4-trifluoro-2-butynoate, the major products were the insertion products with the more electron-withdrawing trifluoromethyl group next to the metal center, which also implies that the regioselectivity is determined by electronic factors. Since two electron-withdrawing substituents are present in these alkynes, mixtures of regioisomers are obtained. All the regioisomers, especially the major regioisomers, have been separated by column chromatography and characterized with X-ray structures for selected cases, as shown in Figure 6. The selected bond lengths and bond angles are summarized in Table 2.

Table 1. Regioselectivities in the Reactions with Unsymmetrical Alkynes

R	R′	1:1′	2:2′	3:3′	4:4′
COOEt	Me (**g**)	**1g** only	**2g** only	**3g** only	**4g** only
COOEt	Ph (**h**)	1: 2.4	1:4.0	1:1.7	1:1.2
COOEt	CF_3 (**i**)	1:1.9	1:1.7	1:2.2	1:2.0

Finally, it is interesting to note that the regioselectivity can be changed by the speed of adding the alkynes. For example, when ethyl phenylpropiolate was added dropwise into a solution of **2**, only one regioisomer was observed. Less reactive alkynes were also employed for insertion reactions, such as 4,4-dimethyl-3-pentyne and 2-pentyne, but the reactions were too reactive and multiple products were observed.

Conclusions

The insertion reactions of the five-membered iridium and rhodium cyclometalated complexes with varying directing groups have been studied with a wide range of unsaturated molecules (ethylene, propylene, carbon monoxide, *tert*-butylisocyanide, acetylene, and phenylacetylene). The results showed that the reactivity was affected by both electronic and steric factors. Ethylene and propylene insert into the rhodium derivatives in a [1,1] fashion, whereas only coordination is seen with iridium. Carbon monoxide inserts into both rhodium and iridium derivatives, but isonitrile only coordinates without inserting. Acetylene inserts one equivalent with most of the derivatives, yet phenyl acetylene inserts two equivalents, the first in a regiospecific [1,2] fashion and

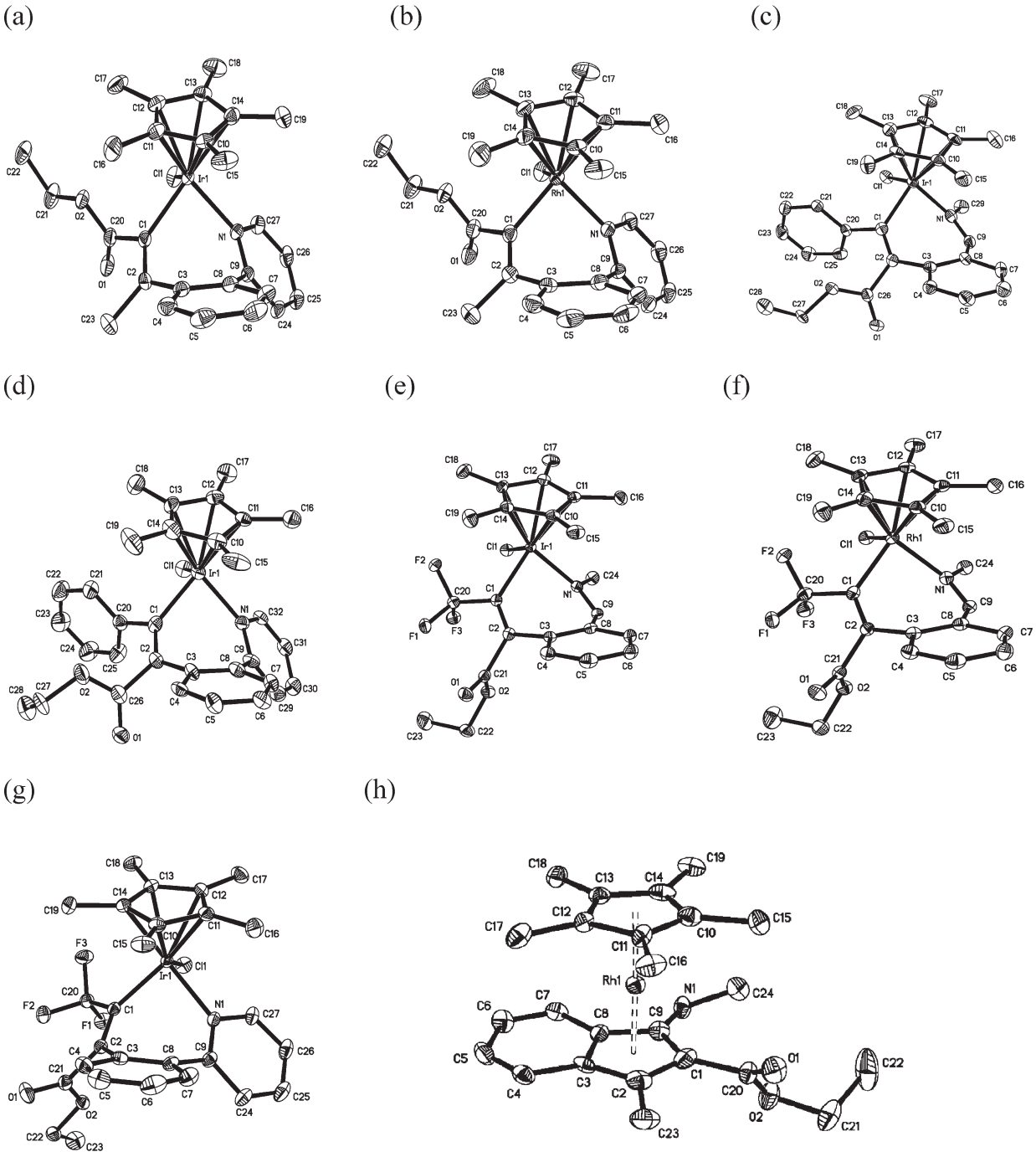


Figure 6. Molecular structure and atom-numbering scheme for (a) **3g**, (b) **4g**, (c) **1′h**, (d) **3′h**, (e) **1′i**, (f) **2′I**, (g) **3′i**, and (h) **2g** (Cl^- not shown) with 50% displacement ellipsoids. H atoms are omitted for clarity. For **2g**, selected bond distances (Å) and angles (deg): Rh(1)−C(1) 2.177(9), Rh(1)−C(2) 2.159(8), Rh(1)−C(3) 2.223(6), Rh(1)−C(8) 2.246(7), Rh(1)−C(9) 2.274 (9), C(1)−C(2) 1.459(12), C(2)−C(3) 1.440(10), C(3)−C(8) 1.440(8), C(8)−C(9) 1.432(13), C(9)−C(1) 1.459(10), C(1)−C(2)−C(3) 106.3(6), C(2)−C(3)−C(8) 108.5(6), C(3)−C(8)−C(9) 109.8(6), C(8)−C(9)−C(1) 105.9(6), C(9)−C(1)−C(2) 109.5(7).

the second in a [1,1] fashion. Ester-substituted internal acetylenes RCCCOOEt give mixtures of single substrate insertion regioisomers for R = Ph or CF_3, but only a single regioisomer for R = Me. These observations with unsymmetrical internal alkynes revealed that the regioselectivity was controlled mainly by electronic factors, favoring products with an electron-withdrawing group on the carbon adjacent to the metal. This preference is in line with the anticipated associated metal−carbon bond strengths when an α-electron-withdrawing group is present.[34]

Experimental Section

General Information. $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 3H_2O$ were purchased from Pressure Chemical Co., and their dimers $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$ were prepared by literature methods.[35] The four cyclometalated complexes were prepared as published.[29] Anhydrous methanol was purchased from Mallinckrodt and used

(34) Evans, M. E.; Li, T.; Vetter, A. J.; Rieth, R. D.; Jones, W. D. *J. Org. Chem.* **2009**, *74*, 6907.

Table 2. Selected Bond Lengths (Å) and Angles (°) for (a) 3g, (b) 4g, (c) 1′h, (d) 3′h, (e) 1i, (f) 2′i, and (g) 3′i[a]

	3g	4g	1′h	3′h	1i	2′i	3′i
M(1)−C(1)	2.071(4)	2.058(3)	2.051(5)	2.054(6)	2.067(2)	2.058(3)	2.070(2)
M(1)−Cl(1)	2.4081(16)	2.4015(8)	2.4133(13)	2.4175(15)	2.4286(7)	2.4274(7)	2.4266(6)
M(1)−N(1)	2.116(3)	2.118(2)	2.076(4)	2.121(5)	2.0991(19)	2.103(2)	2.121(2)
C(1)−C(2)	1.346(6)	1.339(4)	1.352(7)	1.331(8)	1.352(3)	1.346(4)	1.347(3)
C(2)−C(3)	1.486(6)	1.477(4)	1.485(7)	1.485(8)	1.491(3)	1.490(3)	1.496(3)
C(3)−C(8)	1.407(5)	1.404(4)	1.404(7)	1.402(8)	1.395(3)	1.403(4)	1.403(3)
C(8)−C(9)	1.484(5)	1.486(4)	1.466(7)	1.487(8)	1.472(3)	1.468(3)	1.485(3)
C(9)−N(1)	1.353(5)	1.352(4)	1.286(6)	1.352(8)	1.282(3)	1.279(3)	1.352(3)
C(1)−M(1)−N(1)	85.87(13)	86.81(10)	86.20(17)	86.3(2)	87.23(8)	87.93(9)	88.23(8)
C(1)−M(1)−Cl(1)	87.34(12)	88.65(9)	88.96(14)	89.26(16)	89.94(7)	91.36(7)	88.40(6)
N(1)−M(1)−Cl(1)	87.10(9)	88.97(7)	89.42(12)	87.26(14)	87.05(6)	88.44(6)	85.73(6)
M(1)−C(1)−C(2)	126.8(3)	126.2(2)	125.2(4)	125.2(5)	125.54(18)	125.65(19)	126.04(16)
C(1)−C(2)−C(3)	122.1(3)	123.0(3)	126.4(4)	126.4(6)	125.6(2)	125.8(2)	123.6(2)
C(2)−C(3)−C(8)	123.9(4)	124.5(3)	125.0(4)	123.5(5)	124.5(2)	124.7(2)	123.1(2)
C(3)−C(8)−C(9)	125.2(4)	124.9(3)	126.2(5)	124.3(6)	126.0(2)	126.2(2)	126.6(2)
C(8)−C(9)−N(1)	122.1(3)	121.2(2)	126.4(5)	123.2(5)	127.2(2)	127.0(2)	121.3(2)
C(9)−N(1)−M(1)	124.0(2)	125.03(19)	127.3(3)	124.3(4)	126.63(16)	127.15(18)	126.37(16)

[a] M = Ir for **3g**, **1h**, **3h**, **1i,** and **3i**; M = Rh for **4g** and **2i**.

without further drying. Propylene, phenylacetylene, ethyl phenylpropiolate, and ethyl 4,4,4-trifluoro-2-butynoate were purchased from Aldrich, carbon monoxide and acetylene were purchased from Airgas, ethylene was purchased from Air Products, *tert*-butylisocyanide was purchased from Strem, and ethyl 2-butynoate was purchased from Fluka. All reactions described below were carried out under nitrogen. However, once the reactions were completed, the further workups were done without precaution. All NMR spectra were recorded on Bruker AMX400, AVANCE400, or AVANCE500 spectrometers in $CDCl_3$ (δ 7.26). Regioisomers were separated by column chromatography (silica gel, J. T. Baker, 40−140 mesh, and 1−5% $MeOH/CH_2Cl_2$ as the eluent). Elemental analyses were determined using a PerkinElmer 2400 Series II analyzer equipped with a PerkinElmer model AD-6 autobalance by Dr. William W. Brennessel.

1a. A yellow solution of **1** (10.0 mg, 0.021 mmol) in CD_3OD (1.0 mL) in a J-Young tube with 1 atm of ethylene at room temperature turned pale yellow within 5 min. The product **1a** decomposed slowly without ethylene protection. ^{1}H NMR: δ 8.87 (d, 1 H, J = 1.0 Hz, HC=N), 7.77 (dd, 1 H, J = 7.4, 1.4 Hz), 7.48 (d, 1 H, J = 7.8 Hz), 7.22 (td, 1 H, J = 7.5, 1.6 Hz), 7.15 (td, 1 H, J = 7.4, 1.0 Hz), 4.11 (d, 3 H, J = 1.0 Hz, N-Me), 3.16 (d, 2 H, J = 8.6 Hz, C_2H_4), 2.96 (d, 2 H, J = 8.4 Hz, C_2H_4), 1.79 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 180.97 (HC=N), 160.19 (Ir−C), 145.87, 135.15, 131.96, 130.71, 124.71, 99.83 (C_5Me_5), 88.82 (C_2H_4), 51.73 (N-Me), 8.78 (C_5Me_5).

2a. An orange solution of **2** (40.0 mg, 0.10 mmol) in methanol (15.0 mL) was bubbled with ethylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **2a** was obtained (39.6 mg, 92%). Anal. Calcd for $C_{20}H_{27}ClNRh$: C, 57.22; H, 6.48; N, 3.34. Found: C, 56.86; H, 6.35; N, 3.32. ^{1}H NMR: δ 7.98 (dd, 1 H, J = 2.6, 1.4 Hz, HC=N), 7.42 (td, 1 H, J = 7.6, 1.2 Hz), 7.36 (d, 1 H, J = 7.6 Hz), 7.11 (dd, 1 H, J = 7.4, 1.3 Hz), 7.01 (tt, 1 H, J = 7.4, 0.8 Hz), 4.36 (dq, 1 H, J = 6.8, 2.6 Hz, $CHCH_3$), 3.86 (d, 3 H, J = 1.0 Hz, N-Me), 1.61 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 1.30 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 165.01 (HC=N), 151.51, 133.76, 131.95, 130.55, 122.82, 122.66, 93.91 (d, J = 6.6 Hz, C_5Me_5), 52.34 (N-Me), 33.18 (d, J = 6.6 Hz, $CHCH_3$), 18.75 ($CHCH_3$), 8.70 (C_5Me_5).

3a. A yellow solution of **3** (10.0 mg, 0.019 mmol) in CD_3OD (1.0 mL) in a J-Young tube with 1 atm of ethylene at room temperature turned pale yellow within 5 min. The product **3a** decomposed slowly without ethylene protection. ^{1}H NMR: δ 9.32 (d, 1 H, J = 5.8 Hz, HC=N), 7.89 (td, 1 H, J = 8.2, 0.9 Hz), 7.82 (d, 1 H, J = 8.0 Hz), 7.71 (td, J = 8.2, 0.9 Hz, 2 H), 7.58 (dd, 1 H, J = 7.6, 0.8 Hz), 7.29 (td, 1 H, J = 7.4, 1.4 Hz), 7.23 (td, 1 H, J = 7.4, 1.0 Hz), 3.46 (d, 2 H, J = 8.4 Hz, C_2H_4), 3.11 (d, 2 H, J = 8.2 Hz, C_2H_4), 1.72 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 166.14 (HC=N), 155.47 (Ir-C), 152.11, 143.40, 140.09, 136.50, 131.21, 125.44, 125.34, 125.10, 120.00, 99.82 (C_5Me_5), 88.64 (C_2H_4), 8.57 (C_5Me_5).

4a. An orange solution of **4** (40.0 mg, 0.094 mmol) in methanol (15.0 mL) was bubbled with ethylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **4a** was obtained (38.9 mg, 91%). Anal. Calcd for $C_{23}H_{27}ClNRh$: C, 60.60; H, 5.97; N, 3.07. Found: C, 60.33; H, 5.76; N, 3.02. ^{1}H NMR: δ 9.28 (d, 1 H, J = 5.8 Hz, HC=N), 7.74 (d, 2 H, J = 4.7 Hz), 7.47 (d, 1 H, J = 7.5 Hz), 7.47 (d, 1 H, J = 7.6 Hz), 7.35 (dd, 1 H, J = 7.6, 1.2 Hz), 7.23 (dd, 1 H, J = 4.5, 1.2 Hz), 7.05 (td, 1 H, J = 7.6, 1.1 Hz), 3.92 (qd, 1 H, J = 7.0, 2.1 Hz, $CHCH_3$), 1.68 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 1.22 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 158.25, 155.48 (HC=N), 150.31, 137.43, 136.76, 129.88, 129.06, 122.88, 122.78, 122.52, 122.00, 94.16 (d, J = 6.8 Hz, C_5Me_5), 33.49 (d, J = 18.3 Hz, $CHCH_3$), 19.07 ($CHCH_3$), 8.48 (C_5Me_5).

1b and 1′b. A yellow solution of **1** (10.0 mg, 0.021 mmol) in CD_3OD (1.0 mL) in a J-Young tube with 1 atm of propylene at room temperature turned pale yellow within 5 min. The obtained products **1b** and **1′b** in a ratio of 1.3:1 decomposed slowly without propylene protection. ^{1}H NMR for **1b**: δ 8.49 (s, 1 H, HC=N), 7.75 (d, 1 H, J = 6.6 Hz), 7.66 (d, 1 H, J = 7.4 Hz), 7.39 (dd, 1 H, J = 8.1, 7.5 Hz), 7.27 (dd, 1 H, J = 7.6, 7.5 Hz), 3.85 (s, 3 H, N-Me), 3.21 (m, 3 H, CH_2=$CHCH_3$), 1.82 (s, 15 H, C_5Me_5), 1.34 (d, 3 H, J = 4.8 Hz, CH_2=$CHCH_3$). ^{13}C NMR for **1b**: δ 179.97 (HC=N), 162.31 (Ir-C), 145.81, 135.16, 131.57, 129.57, 123.80, 99.13 (C_5Me_5), 64.21 (CH_2=$CHCH_3$), 52.45 (N-Me), 49.03 (CH_2=$CHCH_3$), 16.14 (CH_2=$CHCH_3$), 7.30 (C_5Me_5). ^{1}H NMR for **1′b**: δ 8.41 (s, 1 H, HC=N), 7.74 (d, 1 H, J = 5.3 Hz), 7.69 (d, 1 H, J = 7.8 Hz), 7.35 (dd, 1 H, J = 8.2, 7.7 Hz), 7.24 (dd, 1 H, J = 7.5, 7.1 Hz), 3.91 (s, 3 H, N-Me), 3.60 (m, 1 H, CH_2=$CHCH_3$), 3.53 (d, 1 H, J = 8.1 Hz, CH_2=$CHCH_3$), 2.85 (d, 1 H, J = 12.2 Hz, CH_2=$CHCH_3$), 1.80 (s, 15 H, C_5Me_5), 0.95 (d, 3 H, J = 5.4 Hz, CH_2=$CHCH_3$). ^{13}C NMR for **1′b**: δ 179.69 (HC=N), 164.51 (Ir-C), 145.90, 134.13, 131.36, 129.53, 123.84, 99.45 (C_5Me_5), 67.42 (CH_2=$CHCH_3$), 53.34 (N-Me), 49.42 (CH_2=$CHCH_3$), 17.42 (CH_2=$CHCH_3$), 6.99 (C_5Me_5).

2b. An orange solution of **2** (40.0 mg, 0.10 mmol) in methanol (15.0 mL) was bubbled with propylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **2b** was obtained (40.4 mg, 91%). ^{1}H NMR: δ 8.25 (dd, 1 H, J = 3.9, 1.4 Hz, HC=N), 7.66 (d, 1 H, J = 7.5 Hz), 7.14 (t, 2 H, J = 7.5 Hz), 6.84 (d, 1 H, J = 7.4 Hz), 5.20 (m, 1 H, $CHCH_2CH_3$), 3.78 (d, 3 H, J = 1.0 Hz, N-Me), 2.09 (m, 2 H, $CHCH_2CH_3$), 1.66 (s, 15 H,

(35) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

C_5Me_5), 1.28 (t, 3 H, J = 7.2 Hz, $CHCH_2CH_3$). ^{13}C NMR: δ 172.78 (HC=N), 144.93, 144.16, 142.22, 134.89, 130.14, 121.45, 116.66, 96.08 (d, J = 6.2 Hz, C_5Me_5), 49.06 (N-Me), 24.75 ($CHCH_2CH_3$), 9.56 (C_5Me_5), 9.43 ($CHCH_2CH_3$).

3b and 3′b. A yellow solution of **3** (10.0 mg, 0.019 mmol) in CD_3OD (1.0 mL) in a J-Young tube with 1 atm of propylene at room temperature turned pale yellow within 5 min. The obtained products **3b** and **3′b** in a ratio of 2.0:1 decomposed slowly without propylene protection. ^1H NMR for **3b**: δ 8.56 (d, 1 H, J = 5.7 Hz, HC=N), 8.14 (d, 1 H, J = 7.6 Hz), 7.99 (dd, 1 H, J = 7.8 Hz), 7.91 (d, 1 H, J = 7.6 Hz), 7.65 (d, 1 H, J = 7.7 Hz), 7.39 (dd, 2 H, J = 6.7, 6.3 Hz), 7.28 (dd, 1 H, J = 7.4, 5.3 Hz), 3.38 (m, 1 H, CH_2=$CHCH_3$), 3.18 (d, 1 H, J = 6.7 Hz, CH_2=$CHCH_3$), 1.87 (br, 1 H, CH_2=$CHCH_3$), 1.66 (s, 15 H, C_5Me_5), 1.18 (br, 3 H, CH_2=$CHCH_3$). ^{13}C NMR for **3b**: δ 166.74 (Ir-C), 155.96, 153.57 (HC=N), 143.34, 139.76, 135.19, 130.89, 125.20, 124.38, 123.96, 120.14, 99.18 (C_5Me_5), 67.26 (CH_2=$CHCH_3$), 56.09 (CH_2=$CHCH_3$), 16.34 (CH_2=$CHCH_3$), 7.00 (C_5Me_5). ^1H NMR for **3′b**: δ 8.63 (d, 1 H, J = 5.9 Hz, HC=N), 8.12 (d, 1 H, J = 6.7 Hz), 8.01 (m, 1 H), 7.91 (d, 1 H, J = 7.6 Hz), 7.69 (d, 1 H, J = 7.4 Hz), 7.35 (dd, 2 H, J = 7.7, 5.8 Hz), 7.25 (m, 1 H), 3.72 (m, 1 H, CH_2=$CHCH_3$), 2.73 (d, 1 H, J = 12.1 Hz, CH_2=$CHCH_3$), 2.15 (m, 1 H, CH_2=$CHCH_3$), 1.64 (s, 15 H, C_5Me_5), 0.84 (d, 3 H, J = 5.6 Hz, CH_2=$CHCH_3$). ^{13}C NMR for **3′b**: δ 166.70 (Ir-C), 159.95, 153.63 (HC=N), 143.46, 139.71, 136.03, 130.77, 125.46, 124.44, 123.99, 119.86, 99.31 (C_5Me_5), 65.64 (CH_2=$CHCH_3$), 56.53 (CH_2=$CHCH_3$), 16.89 (CH_2=$CHCH_3$), 6.85 (C_5Me_5).

4b. An orange solution of **4** (40.0 mg, 0.094 mmol) in methanol (15.0 mL) was bubbled with propylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **4b** was obtained (39.8 mg, 91%). ^1H NMR: δ 9.28 (d, 1 H, J = 5.6 Hz, HC=N), 7.75 (m, 2 H), 7.49 (d, 1 H, J = 7.8 Hz), 7.41 (td, 1 H, J = 7.4, 6.8 Hz), 7.34 (dd, 1 H, J = 7.6, 1.0 Hz), 7.22 (m, 1 H), 7.02 (t, 1 H, J = 8.4 Hz), 3.74 (dt, 1 H, J = 11.3, 2.8 Hz, $CHCH_2CH_3$), 2.33 (m, 1 H, $CHCH_2CH_3$), 2.18 (m, 1 H, $CHCH_2CH_3$), 1.22 (s, 15 H, C_5Me_5), 0.98 (t, 3 H, J = 7.2 Hz, $CHCH_2CH_3$). ^{13}C NMR: δ 158.50 (HC=N), 155.42, 149.81, 148.29, 137.45, 129.66 (2 C′s), 122.78, 122.53, 122.47, 121.87, 94.11 (d, J = 6.8 Hz, C_5Me_5), 41.89 (d, J = 6.6 Hz, $CHCH_2CH_3$), 25.78 ($CHCH_2CH_3$), 15.19 ($CHCH_2CH_3$), 8.55 (C_5Me_5).

1c. A yellow solution of **1** (40.0 mg, 0.083 mmol) in methanol (15.0 mL) was bubbled with carbon monoxide at room temperature. The solution turned light yellow within 5 min, the solvent was concentrated under vacuum, and the light yellow solid **1c** was obtained (40.2 mg, 95%). ^1H NMR: δ 9.33 (s, 1 H, HC=N), 7.91 (d, 1 H, J = 7.0 Hz), 7.44 (d, 1 H, J = 7.0 Hz), 7.23 (m, 2 H), 4.08 (s, 3 H, N-Me), 1.98 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 183.85 (HC=N), 164.31 (Ir-C), 150.75, 147.73, 135.44, 133.15, 131.68, 126.03, 101.47 (C_5Me_5), 53.24 (N-Me), 9.56 (C_5Me_5).

2c. An orange solution of **2** (40.0 mg, 0.10 mmol) in methanol (15.0 mL) was bubbled with carbon monoxide at room temperature. The solution turned light yellow within 5 min, the solvent was concentrated under vacuum, and the light yellow solid **2c** was obtained (41.3 mg, 96%). ^1H NMR: δ 8.96 (d, 1 H, J = 2.9 Hz, HC=N), 7.77 (dd, 1 H, J = 7.4, 0.9 Hz), 7.38 (d, 1 H, J = 7.6 Hz), 7.26 (td, 1 H, J = 7.5, 1.1 Hz), 7.16 (dd, 1 H, J = 7.3, 7.0 Hz), 3.84 (s, 3 H, N-Me), 1.83 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 184.85 (d, J = 73.8 Hz, Rh-C), 180.01 (HC=N), 169.15 (d, J = 17.1 Hz), 145.89, 135.87, 132.56, 131.69, 126.10, 105.79 (d, J = 4.6 Hz, C_5Me_5), 51.21 (N-Me), 9.92 (C_5Me_5).

3c. A yellow solution of **3** (40.0 mg, 0.077 mmol) in methanol (15.0 mL) was bubbled with carbon monoxide at room temperature. The solution turned light yellow within 5 min, the solvent was concentrated under vacuum, and the light yellow solid **3c** was obtained (40.8 mg, 97%). ^1H NMR: δ 9.00 (d, 1 H, J = 5.7 Hz, HC=N), 8.03 (t, 1 H, J = 7.4 Hz), 7.96 (d, 1 H, J = 7.6 Hz), 7.76 (dd, 1 H, J = 5.5, 3.1 Hz), 7.70 (t, 1 H, J = 6.5 Hz), 7.46 (dd, 1 H, J = 5.8, 3.1 Hz), 7.25 (dd, 1 H, J = 5.6, 3.8 Hz), 1.88 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 166.51 (Ir-C), 165.56 (HC=N), 155.62, 144.96, 143.82, 141.04, 136.49, 132.02, 126.11, 126.08, 125.76, 120.79, 101.61 (C_5Me_5), 9.24 (C_5Me_5).

4c. An orange solution of **4** (40.0 mg, 0.094 mmol) in methanol (15.0 mL) was bubbled with carbon monoxide at room temperature. The solution turned light yellow within 5 min, the solvent was concentrated under vacuum, and the light yellow solid **4c** was obtained (41.2 mg, 97%). ^1H NMR: δ 9.01 (d, 1 H, J = 5.4 Hz, HC=N), 8.06 (td, 1 H, J = 7.9, 1.1 Hz), 7.99 (d, 2 H, J = 7.1 Hz), 7.80 (dd, 1 H, J = 7.4, 1.8 Hz), 7.73 (td, 1 H, J = 6.6, 1.4 Hz), 7.49 (dd, 1 H, J = 7.3, 1.3 Hz), 7.32 (m, 2 H), 1.89 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 186.65 (d, J = 74.9 Hz, Rh-C), 165.55, 164.76 (d, J = 26.4 Hz), 155.88, 145.40, 141.85, 138.31, 133.30, 127.80, 127.18, 126.88, 122.33, 107.54 (d, J = 4.7 Hz, C_5Me_5), 11.12 (C_5Me_5).

1d. A mixture of **1** (40.0 mg, 0.083 mmol) and *tert*-butylisocyanide (11.0 μL, 0.095 mmol) were stirred at room temperature in 15.0 mL of methanol for 3 h. The product obtained was washed with hexane to remove excess substrate. The light yellow compound **1d** was isolated (43.6 mg, 93%). Anal. Calcd for $C_{23}H_{32}ClN_2Ir\cdot H_2O$ (H_2O found in X-ray structure): C, 47.45; H, 5.89; N, 4.81. Found: C, 47.56; H, 5.81; N, 4.77. ^1H NMR: δ 8.95 (s, 1 H, HC=N), 7.73 (d, 1 H, J = 6.8 Hz), 7.40 (d, 1 H, J = 7.4 Hz), 7.12 (td, 1 H, J = 7.5, 1.3 Hz), 7.07 (td, 1 H, J = 7.5, 1.3 Hz), 3.96 (s, 3 H, N-Me), 1.83 (s, 15 H, C_5Me_5), 1.23 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR: δ 180.54 (HC=N), 179.75 (Ir-C), 156.26, 147.16, 134.67, 132.19, 130.46, 124.26, 96.19 (C_5Me_5), 59.02 ($C(CH_3)_3$), 52.68 (N-Me), 30.95 ($C(CH_3)_3$), 9.45 (C_5Me_5). IR (solid): 2156 cm^{-1}. The analogous phenylpyridyl complex **3d** displays an IR band at 2167 cm^{-1}, but was not otherwise characterized.

2d. The reaction was carried out as for **1d**, using **2** (40.0 mg, 0.10 mmol), *tert*-butylisocyanide (13.0 μL, 0.11 mmol), and 15.0 mL of methanol, RT, 3 h. The light yellow insertion compound **2d** was isolated (46.2 mg, 95%). Anal. Calcd for $C_{23}H_{32}ClN_2Rh\cdot 2H_2O$ (no X-ray structure for **2d**): C, 54.07; H, 7.10; N, 5.48. Found: C, 54.23; H, 7.13; N, 5.45. ^1H NMR: δ 8.81 (dd, 1 H, J = 4.0, 1.3 Hz, HC=N), 7.74 (dd, 1 H, J = 7.4, 1.3 Hz), 7.45 (d, 1 H, J = 7.6 Hz), 7.26 (ddd, 1 H, J = 7.4, 1.3 Hz), 7.17 (td, 1 H, J = 7.4, 0.7 Hz), 3.92 (s, 3 H, N-Me), 1.82 (s, 15 H, C_5Me_5), 1.31 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR: δ 177.01 (HC=N), 174.17 (d, J = 28.5 Hz, Rh-C), 145.34 (2 C's), 135.37, 131.50, 130.17, 124.59, 101.11 (d, J = 4.8 Hz, C_5Me_5), 59.00 ($C(CH_3)_3$), 50.70 (N-Me), 30.45 ($C(CH_3)_3$), 9.65 (C_5Me_5). IR (solid): 2177 cm^{-1}. The analogous phenylpyridyl complex **3d** displays an IR band at 2167 cm^{-1}, but was not otherwise characterized.

1e. A yellow solution of **1** (40.0 mg, 0.083 mmol) in methanol (15.0 mL) was bubbled with acetylene at room temperature. The solution turned light yellow within 5 min, the solvent was concentrated under vacuum, and the bright yellow solid **1e** was obtained (45.4 mg, 93%). ^1H NMR: δ 7.42 (dd, 1 H, J = 6.1, 2.6 Hz, HC=N), 7.17 (m, 2 H), 7.05 (m, 1 H), 6.70 (d, 1 H, J = 12.4 Hz), 5.14 (br, 1 H), 4.77 (dd, 1 H, J = 12.3, 10.2 Hz), 4.59 (dd, 1 H, J = 9.8, 9.0 Hz), 4.23 (d, 1 H, J = 5.4 Hz), 4.19 (d, 1 H, J = 8.8 Hz), 3.57 (s, 3 H, N-Me), 2.77 (d, 3 H, J = 5.0 Hz), 1.84 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 152.06 (HC=N), 145.63 (Ir-C), 142.08, 130.41, 129.14, 128.78, 127.71, 99.74 (2 C's), 96.85 (C_5Me_5), 62.46, 62.39, 57.54, 55.39 (N-Me), 50.08 (2 C's), 44.25, 8.96 (C_5Me_5).

2e. An orange solution of **2** (40.0 mg, 0.10 mmol) in methanol (15.0 mL) was bubbled with acetylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **2e** was obtained (39.8 mg, 93%). The initial product is not stable and undergoes additional reaction during recrystallization. ^1H NMR: δ 8.53 (d, 1 H, J = 2.5 Hz, HC=N), 8.17 (dd, 1 H, J = 9.6, 4.7 Hz), 7.37 (m, 1 H), 7.29 (d, 1 H, J = 9.6 Hz), 7.21 (d, 1 H, J = 7.9 Hz), 7.16 (d, 2 H, J = 4.2 Hz), 3.88 (d, J = 1.3 Hz, N-Me), 1.32 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 171.03 (HC=N), 166.54 (d, J = 29.8 Hz, Rh-C), 140.75, 137.88, 133.20, 131.85, 131.46, 130.84, 124.90, 95.46 (d, J = 6.3 Hz, C_5Me_5), 56.31 (N-Me), 9.06 (C_5Me_5).

3e. A yellow solution of **3** (40.0 mg, 0.077 mmol) in methanol (15.0 mL) was bubbled with acetylene at room temperature. The solution turned bright red within 5 min, the solvent was concentrated under vacuum, and the bright red solid **3e** was obtained (40.7 mg, 97%). Anal. Calcd for $C_{23}H_{25}ClNIr$: C, 50.86; H, 4.64; N, 2.58. Found: C, 50.52; H, 4.51; N, 2.50. ^{1}H NMR: δ 9.36 (dd, 1 H, J = 5.9, 1.5 Hz, HC=N), 8.40 (d, 1 H, J = 10.7 Hz), 7.67 (td, 1 H, J = 7.7, 1.6 Hz), 7.55 (d, 1 H, J = 10.7 Hz), 7.32 (m, 2 H), 7.22 (d, 1 H, J = 7.8 Hz), 7.17 (m, 1 H), 7.10 (m, 2 H), 1.30 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 165.23, 156.15 (Ir-C), 153.16 (HC=N), 144.23, 137.47, 136.47, 133.28, 130.63, 130.43, 128.83, 128.19, 124.49, 123.51, 87.61 (C_5Me_5), 8.88 (C_5Me_5).

4e. An orange solution of **4** (40.0 mg, 0.094 mmol) in methanol (15.0 mL) was bubbled with acetylene at room temperature. The solution turned dark red within 5 min, the solvent was concentrated under vacuum, and the red solid **4e** was obtained (40.3 mg, 95%). Anal. Calcd for $C_{23}H_{25}ClNRh$: C, 60.87; H, 5.55; N, 3.09. Found: C, 60.44; H, 5.56; N, 3.07. ^{1}H NMR: δ 9.48 (dd, 1 H, J = 5.8, 1.4 Hz, HC=N), 8.24 (dd, 1 H, J = 9.4, 4.8 Hz), 7.71 (td, 1 H, J = 7.7, 1.7 Hz), 7.40−7.28 (m, 4 H), 7.19 (m, 3 H), 1.28 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 167.36 (d, J = 29.4 Hz), 164.72, 155.51 (HC=N), 142.17, 137.39, 136.05, 133.39, 130.73, 130.69, 128.89, 128.04, 124.86, 122.81, 95.53 (d, J = 6.5 Hz, C_5Me_5), 9.14 (C_5Me_5).

1f. The reaction was carried out as for **1d**, using **1** (40.0 mg, 0.083 mmol), phenylacetylene (21.0 μL, 0.19 mmol), and 15.0 mL of methanol, RT, 3 h. The bright red insertion compound **1f** was isolated (50.8 mg, 89%). ^{1}H NMR: δ 8.42 (s, 1 H, HC=N), 7.95 (d, 1 H, J = 7.6 Hz), 7.79−7.67 (m, 5 H), 7.46−7.33 (m, 8 H), 6.74 (s, 1 H), 6.01 (s, 1 H), 3.82 (s, 3 H, N-Me), 1.72 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 168.73 (HC=N), 149.36 (Ir-C), 136.12, 134.93, 134.76, 133.33, 131.96, 130.86, 129.63 (2 C's), 129.02 (2 C's), 128.93, 128.71, 128.67, 128.60 (2 C's), 128.19, 127.78, 127.55 (2 C's), 127.45, 121.02, 98.51 (C_5Me_5), 50.10 (N-Me), 8.99 (C_5Me_5).

2f. The reaction was carried out as for **1d**, using **2** (40.0 mg, 0.10 mmol), phenylacetylene (25.0 μL, 0.23 mmol), and 15.0 mL of methanol, RT, 3 h. The dark red insertion compound **2f** was isolated (51.5 mg, 85%). ^{1}H NMR: δ 8.11 (d, 1 H, J = 3.2 Hz, HC=N), 8.01 (d, 1 H, J = 7.6 Hz), 7.76−7.13 (m, 13 H), 6.92 (s, 1 H), 6.08 (s, 1 H), 3.30 (s, 3 H, N-Me), 1.70 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 165.70, 138.93, 136.60, 130.49, 130.19, 130.09, 129.79, 129.56, 128.95, 128.79, 128.66, 128.58, 127.57, 126.59, 103.35 (d, J = 22.3 Hz), 103.12 (d, J = 28.2 Hz), 101.31 (d, J = 30.6 Hz), 94.33 (d, J = 39.1 Hz, C_5Me_5), 86.32 (d, J = 28.4 Hz), 84.31 (d, J = 30.4 Hz), 57.38 (N-Me), 9.60 (C_5Me_5).

3f. The reaction was carried out as for **1d**, using **3** (40.0 mg, 0.077 mmol), phenylacetylene (18.0 μL, 0.16 mmol), and 15.0 mL of methanol, RT, 3 h. The bright red insertion compound **3f** was isolated (52.4 mg, 94%). ^{1}H NMR: δ 9.00 (dd, 1 H, J = 5.9, 1.3 Hz, HC=N), 7.68 (d, 1 H, J = 6.8 Hz), 7.61 (td, 1 H, J = 7.4, 1.1 Hz), 7.48−7.33 (m, 6 H), 7.19−6.99 (m, 8 H), 6.91 (t, 1 H, J = 7.3 Hz), 6.30 (s, 1 H), 4.33 (s, 1 H), 1.67 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 157.83 (HC=N), 156.50 (Ir−C), 154.72, 139.54, 135.62, 135.54, 133.75, 131.81, 130.91, 130.47, 128.78, 128.59, 128.22, 127.40, 127.23, 126.23, 125.94, 124.78, 119.46, 101.91, 98.08, 95.54 (C_5Me_5), 53.60, 51.00, 8.82 (C_5Me_5).

4f. The reaction was carried out as for **1d**, using **4** (40.0 mg, 0.094 mmol), phenylacetylene (22.0 μL, 0.20 mmol), and 15.0 mL of methanol, RT, 3 h. The red insertion compound **4g** was isolated (53.6 mg, 91%). ^{1}H NMR: δ 9.78 (dd, 1 H, J = 5.8, 1.1 Hz, HC=N), 7.79−7.71 (m, 2 H), 7.48−7.35 (m, 5 H), 7.27−7.15 (m, 7 H), 7.10−7.03 (m, 5 H), 1.28 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 175.77 (d, J = 126.2 Hz, Rh-C), 164.17, 155.12 (HC=N), 153.99, 141.93, 137.38, 136.03, 134.76, 133.16, 131.86, 130.48, 130.29, 130.03, 129.08, 128.99, 128.87, 128.04, 127.68, 127.58, 127.19, 126.64, 125.10, 124.56, 122.85, 95.88 (d, J = 26.0 Hz, C_5Me_5), 9.21 (C_5Me_5).

1g. The reaction was carried out as for **1d**, using **1** (40.0 mg, 0.083 mmol), ethyl 2-butynoate (12.0 μL, 0.10 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compound **1g** was isolated (46.5 mg, 94%). Anal. Calcd for $C_{24}H_{31}ClNO_2Ir$: C, 48.60; H, 5.27; N, 2.36. Found: C, 48.46; H, 5.28; N, 2.34. ^{1}H NMR: δ 8.56 (s, 1 H, HC=N), 7.49 (d, 1 H, J = 7.8 Hz), 7.42 (t, 1 H, J = 7.5 Hz), 7.21 (t, 1 H, J = 7.4 Hz), 7.10 (d, 1 H, J = 7.6 Hz), 4.23 (m, 2 H, CH_2CH_3), 3.90 (s, 3 H, N-Me), 2.34 (s, 3 H, Me), 1.33 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.30 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 176.90 (C=O), 170.50 (HC=N), 146.59 (Ir-C), 142.03, 132.63 (2 C's), 131.85, 130.69, 130.59, 125.40, 88.30 (C_5Me_5), 58.79 (CH_2CH_3), 56.63 (N-Me), 23.38 (Me), 15.16 (CH_2CH_3), 8.50 (C_5Me_5).

2g. The reaction was carried out as for **1d**, using **2** (40.0 mg, 0.10 mmol), ethyl 2-butynoate (15.0 μL, 0.13 mmol), and 15.0 mL of methanol, RT, 3 h. The red insertion compound **2g** was isolated (49.8 mg, 97%). ^{1}H NMR: δ 7.85 (m, 1 H, HC=N), 7.42 (m, 2 H), 7.22 (m, 1 H), 7.01 (m, 1 H), 4.44 (dq, 2 H, J = 7.1, 3.3 Hz, CH_2CH_3), 3.25 (d, 3 H, J = 5.4 Hz, N-Me), 2.31 (s, 3 H, Me), 1.57 (s, 15 H, C_5Me_5), 1.43 (t, 3 H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR: δ 166.51 (C=O), 129.21, 128.21, 126.03 (d, J = 3.1 Hz), 122.21, 120.16, 98.65 (d, J = 7.1 Hz), 98.27 (d, J = 7.7 Hz, C_5Me_5), 94.28 (br), 89.05 (d, J = 5.6 Hz), 85.81 (d, J = 8.7 Hz), 72.29 (d, J = 8.7 Hz, N-Me), 62.53 (CH_2CH_3), 32.84 (Me), 14.68 (CH_2CH_3), 8.51 (C_5Me_5).

3g. The reaction was carried out as for **1d**, using **3** (40.0 mg, 0.077 mmol), ethyl 2-butynoate (12.0 μL, 0.10 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compound **3g** was isolated (47.2 mg, 97%). Anal. Calcd for $C_{27}H_{31}ClNO_2Ir$: C, 51.54; H, 4.97; N, 2.23. Found: C, 51.10; H, 4.96; N, 2.24. ^{1}H NMR: δ 9.46 (dd, 1 H, J = 6.0, 1.6 Hz, HC=N), 7.71 (td, 1 H, J = 7.7, 1.7 Hz), 7.53 (dd, 1 H, J = 8.0, 1.2 Hz), 7.42 (m, 2 H), 7.21 (td, 1 H, J = 7.5, 1.1 Hz), 7.15 (td, 1 H, J = 7.5, 1.1 Hz), 7.06 (dd, 1 H, J = 7.8, 1.3 Hz), 4.18 (q, 2 H, J = 7.2 Hz, CH_2CH_3), 2.34 (s, 3 H, Me), 1.28 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.25 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 176.97 (C=O), 164.49 (Ir−C), 155.22 (HC=N), 147.37, 142.63, 137.95, 137.90, 133.63, 133.00, 129.68, 128.99, 127.35, 125.25, 123.70, 88.15 (C_5Me_5), 58.63 (CH_2CH_3), 22.99 (Me), 15.09 (CH_2CH_3), 8.53 (C_5Me_5).

4g. The reaction was carried out as for **1d**, using **4** (40.0 mg, 0.094 mmol), ethyl 2-butynoate (12.0 μL, 0.10 mmol), and 15.0 mL of methanol, RT, 3 h. The red insertion compound **4g** was isolated (49.5 mg, 98%). Anal. Calcd for $C_{27}H_{31}ClNO_2Rh$: C, 60.06; H, 5.79; Cl, 6.57; N, 2.59. Found: C, 59.69; H, 5.86; N, 2.55. ^{1}H NMR: δ 9.55 (dd, 1 H, J = 5.9, 1.3 Hz, HC=N), 7.73 (td, 1 H, J = 7.6, 1.6 Hz), 7.58 (dd, 1 H, J = 7.8, 0.8 Hz), 7.44 (td, 1 H, J = 7.5, 1.2 Hz), 7.40 (d, 1 H, J = 7.6 Hz), 7.21 (m, 2 H), 7.14 (dd, 1 H, J = 7.6, 1.0 Hz), 4.18 (m, 2 H, CH_2CH_3), 2.25 (s, 3 H, Me), 1.28 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.24 (s, 15 H, C_5Me_5). ^{13}C NMR: δ 175.10 (C=O), 163.91 (Ir-C), 154.87 (HC=N), 154.03 (d, J = 34.5 Hz, Rh-C), 145.75, 137.73, 137.33, 133.66, 132.32, 129.78, 129.01, 127.20, 125.49, 123.05, 95.91 (d, J = 6.7 Hz, C_5Me_5), 58.84 (CH_2CH_3), 23.53 (Me), 14.94 (CH_2CH_3), 8.74 (C_5Me_5).

1h and 1′h. The reaction was carried out as for **1d**, using **1** (40.0 mg, 0.083 mmol), ethyl phenylpropiolate (17.0 μL, 0.10 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compounds **1h** and **1′h** with a ratio of 1:2.4 were obtained (51.2 mg, 94%). The two regioisomers were separated by column chromatography using 2% MeOH/CH_2Cl_2 as the eluent. Anal. Calcd for $C_{27}H_{31}ClNO_2Rh$: C, 53.16; H, 5.08; N, 2.14. Found: C, 53.09; H, 5.18; N, 2.16. The ^{1}H NMR for the major regioisomer **1′h**: δ 8.71 (d, 1 H, J = 1.4 Hz, HC=N), 7.39 (m, 2 H), 7.29 (m, 1 H), 7.23 (d, 1 H, J = 8.0 Hz), 7.16 (br, 2 H), 6.95 (m, 1 H), 6.84 (br, 2 H), 3.89 (d, 3 H, J = 1.2 Hz, N-Me), 3.77 (m, 1 H, CH_2CH_3), 3.64 (m, 1 H, CH_2CH_3), 1.34 (s, 15 H, C_5Me_5), 0.77 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **1′h**: δ 171.96 (C=O), 170.61 (HC=N), 166.58 (Ir−C), 153.29, 141.57, 135.46, 132.90, 132.46, 131.06, 130.89, 130.59, 126.06, 125.81, 124.28, 88.51 (C_5Me_5), 60.09 (CH_2CH_3), 56.48 (N-Me), 13.65 (CH_2CH_3), 8.65 (C_5Me_5).

2h and 2′h. The reaction was carried out as for **1d**, using **2** (40.0 mg, 0.10 mmol), ethyl phenylpropiolate (20.0 μL, 0.12 mmol),

and 15.0 mL of methanol, RT, 3 h. The red insertion compounds **2h** and **2′h** with a ratio of 1:4.0 were obtained (54.8 mg, 95%). The two regioisomers were separated by column chromatography using 2% MeOH/CH_2Cl_2 as the eluent. ^{1}H NMR for the major regioisomer **2′h**: δ 8.65 (s, 1 H, HC═N), 7.42 (br, 1 H), 7.25−7.20 (m, 8 H), 3.95 (m, 1 H, CH_2CH_3), 3.91 (s, 3 H, N-Me), 3.68 (m, 1 H, CH_2CH_3), 1.37 (s, 15 H, C_5Me_5), 0.61 (m, 3 H, CH_2CH_3). ^{13}C NMR for **2′h**: δ 172.85 (C═O), 170.60 (HC═N), 159.63 (d, J = 35.0 Hz, Rh-C), 140.18, 134.20, 132.01, 130.46, 129.25, 128.73, 128.63, 127.89, 126.62, 125.85, 124.22, 96.23 (d, J = 6.5 Hz, C_5Me_5), 69.22 (CH_2CH_3), 56.33 (N-Me), 14.25 (CH_2CH_3), 8.78 (C_5Me_5).

3h and 3′h. The reaction was carried out as for **1d**, using **3** (40.0 mg, 0.077 mmol), ethyl phenylpropiolate (16.0 μL, 0.095 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compounds **3h** and **3′h** with a ratio of 1:1.7 were obtained (51.8 mg, 97%). The two regioisomers were separated by column chromatography using 0.5% MeOH/CH_2Cl_2 as the eluent. ^{1}H NMR for the major regioisomer **3′h**: δ 9.60 (dd, 1 H, J = 6.0, 1.2 Hz, HC═N), 7.78 (td, 1 H, J = 7.6, 1.5 Hz), 7.56 (dd, 1 H, J = 7.8, 1.0 Hz), 7.43 (m, 3 H), 7.29 (d, 1 H, J = 7.8 Hz), 7.18 (m, 3 H), 7.02 (br, 2 H), 6.90 (t, 1 H, J = 7.3 Hz), 3.74 (m, 1 H, CH_2CH_3), 3.62 (m, 1 H, CH_2CH_3), 1.28 (s, 15 H, C_5Me_5), 0.74 (t, 3 H, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR for **3′h**: δ 171.89 (C═O), 167.98 (Ir-C), 164.32, 155.23 (HC═N), 154.13, 142.62, 138.88, 137.92, 135.47, 133.68, 130.54, 129.34, 127.69, 127.55, 126.08, 125.93, 124.17, 123.74, 88.69 (C_5Me_5), 60.06 (CH_2CH_3), 13.83 (CH_2CH_3), 8.95 (C_5Me_5). ^{1}H NMR for the minor regioisomer **3h**: δ 9.40 (dd, 1 H, J = 5.8, 1.0 Hz, HC═N), 7.76 (td, 1 H, J = 7.6, 1.2 Hz), 7.45 (d, 1 H, J = 7.8 Hz), 7.23 (dd, 1 H, J = 7.6, 1.2 Hz), 7.18 (td, 1 H, J = 7.6, 1.2 Hz), 7.16−7.02 (m, 8 H), 3.87 (m, 1 H, CH_2CH_3), 3.63 (m, 1 H, CH_2CH_3), 1.32 (s, 15 H, C_5Me_5), 0.54 (br, 3 H, CH_2CH_3). ^{13}C NMR for **3h**: δ 177.01 (C═O), 164.37 (Ir-C), 155.44 (HC═N), 147.91, 146.43, 145.93, 138.39, 138.31, 133.57, 132.94, 130.08, 128.77, 127.79 (2 C's), 127.35, 125.87, 125.57, 124.10, 88.48 (C_5Me_5), 58.07 (CH_2CH_3), 13.99 (CH_2CH_3), 8.55 (C_5Me_5). For **3h** and **3′h**, Anal. Calcd for $C_{32}H_{33}ClIrNO_2$: C, 55.60; H, 4.81; N, 2.03. Found: C, 55.85; H, 4.95; N, 1.97.

4h and 4′h. The reaction was carried out as for **1d**, using **4** (40.0 mg, 0.094 mmol), ethyl phenylpropiolate (20.0 μL, 0.12 mmol), and 15.0 mL of methanol, RT, 3 h. The red insertion compounds **4h** and **4′h** with a ratio of 1:1.2 were obtained (53.4 mg, 95%). The two regioisomers were separated by column chromatography using 1% MeOH/CH_2Cl_2 as the eluent. ^{1}H NMR for the major regioisomer **4′h**: δ 9.52 (d, 1 H, J = 5.8 Hz, HC═N), 7.78 (td, 1 H, J = 7.6, 1.2 Hz), 7.46 (d, 1 H, J = 7.6 Hz), 7.26 (m, 1 H), 7.21−7.05 (m, 9 H), 3.91 (m, 1 H, CH_2CH_3), 3.61 (m, 1 H, CH_2CH_3), 1.32 (s, 15 H, C_5Me_5), 0.53 (m, 3 H, CH_2CH_3). ^{13}C NMR for **4′h**: δ 175.13 (C═O), 163.84, 160.18 (d, J = 34.7 Hz, Rh-C), 155.01 (HC═N), 145.82, 144.45, 140.25, 138.20, 137.79, 133.59, 133.08, 129.63, 128.75, 127.80, 127.21, 125.92, 125.79, 123.48, 96.19 (d, J = 6.7 Hz, C_5Me_5), 58.31 (CH_2CH_3), 13.97 (CH_2CH_3), 8.79 (C_5Me_5). For **4h** and **4′h**, Anal. Calcd for $C_{32}H_{33}ClNO_2Rh$: C, 63.85; H, 5.53; N, 2.33. Found: C, 64.22; H, 5.32; N, 2.23.

1i and 1′i. The reaction was carried out as for **1d**, using **1** (40.0 mg, 0.83 mmol), ethyl 4,4,4-trifluoro-2-butynoate (16.0 μL, 0.11 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compounds **1i** and **1′i** with a ratio of 1:1.9 were obtained (52.3 mg, 97%). The two regioisomers were separated by column chromatography using 1% MeOH/CH_2Cl_2 as the eluent. Anal. Calcd for $C_{24}H_{28}ClF_3NO_2Ir$: C, 44.54; H, 4.36; N, 2.16. Found: C, 44.50; H, 4.29; N, 2.11. ^{1}H NMR for the major regioisomer **1′i**: δ 8.70 (d, 1 H, J = 1.1 Hz, HC═N), 8.18 (d, 1 H, J = 7.7 Hz), 7.47 (td, 1 H, J = 7.7, 1.2 Hz), 7.37 (td, 1 H, J = 7.5, 1.2 Hz), 7.18 (dd, 1 H, J = 7.7, 1.1 Hz), 4.24 (m, 1 H, CH_2CH_3), 4.03 (m, 1 H, CH_2CH_3), 3.94 (d, 3 H, J = 1.4 Hz, N-Me), 1.28 (s, 15 H, C_5Me_5), 1.24 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **1′i**: δ 171.17 (C═O), 170.72 (HC═N), 145.58 (q, J = 27.9 Hz, Ir-C), 139.90 (q, J = 27.9 Hz), 138.07, 132.69, 131.88, 131.43, 130.86, 128.18 (q, J = 279 Hz, CF_3), 127.42, 89.10 (C_5Me_5), 61.50 (CH_2CH_3), 57.13 (N-Me), 14.10 (CH_2CH_3), 8.47 (C_5Me_5). ^{1}H NMR for the minor regioisomer **1i**: δ 8.63 (s, 1 H, HC═N), 7.68 (d, 1 H, J = 8.0 Hz), 7.50 (td, 1 H, J = 7.7, 1.3 Hz), 7.36 (td, 1 H, J = 7.5, 0.8 Hz), 7.22 (d, 1 H, J = 7.8 Hz), 4.26 (q, 2 H, J = 7.1 Hz, CH_2CH_3), 3.89 (d, 3 H, J = 1.3 Hz, N-Me), 1.32 (t, 3 H, J = 7.1 Hz, CH_2CH_3), 1.29 (s, 15 H, C_5Me_5). ^{13}C NMR for **1i**: δ 174.46 (q, J = 6.0 Hz, Ir-C), 170.65 (HC═N), 160.21 (C═O), 137.82, 134.74, 131.90, 131.61 (q, J = 2.6 Hz), 130.64, 127.16 (q), 126.98, 123.88 (q, J = 280.8 Hz, CF_3), 89.40 (C_5Me_5), 59.10 (CH_2CH_3), 56.49 (N-Me), 14.86 (CH_2CH_3), 8.28 (C_5Me_5).

2i and 2′i. The reaction was carried out as for **1d**, using **2** (40.0 mg, 0.10 mmol), ethyl 4,4,4-trifluoro-2-butynoate (18.0 μL, 0.12 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compounds **2i** and **2′i** with a ratio of 1:1.7 were obtained (54.2 mg, 95%). The two regioisomers were separated by column chromatography using 1% MeOH/CH_2Cl_2 as the eluent. Anal. Calcd for $C_{24}H_{28}ClF_3NO_2Rh$: C, 51.67; H, 5.06; N, 2.51. Found: C, 51.70; H, 5.12; N, 2.49. ^{1}H NMR for the major regioisomer **2′i**: δ 8.65 (d, 1 H, J = 1.7 Hz, HC═N), 8.21 (d, 1 H, J = 8.0 Hz), 7.46 (td, 1 H, J = 7.6, 1.4 Hz), 7.38 (td, 1 H, J = 7.6, 1.2 Hz), 7.26 (d, 1 H, J = 7.4 Hz), 4.20 (m, 1 H, CH_2CH_3), 4.00 (m, 1 H, CH_2CH_3), 3.88 (s, 3 H, N-Me), 1.24 (s, 15 H, C_5Me_5), 1.21 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **2′i**: δ170.72 (HC═N), 170.01 (C═O), 158.05 (m, Rh-C), 138.94 (q, J = 7.4 Hz), 136.79, 132.02, 131.97, 131.31, 130.79, 127.57, 126.69 (q, J = 276.4 Hz, CF_3), 96.69 (d, J = 6.0 Hz, C_5Me_5), 61.58 (CH_2CH_3), 56.65 (N-Me), 14.06 (CH_2CH_3), 8.73 (C_5Me_5). ^{1}H NMR for the minor regioisomer **2i**: δ 8.59 (d, 1 H, J = 1.6 Hz, HC═N), 7.74 (d, 1 H, J = 8.0 Hz), 7.50 (td, 1 H, J = 7.6, 1.4 Hz), 7.38 (td, 1 H, J = 7.6, 1.0 Hz), 7.29 (dd, 1 H, J = 7.7, 1.0 Hz), 4.22 (m, 2 H, CH_2CH_3), 3.82 (d, 3 H, J = 1.2 Hz, N-Me), 1.30 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.26 (s, 15 H, C_5Me_5). ^{13}C NMR for **2i**: δ 173.85 (d, J = 33.6 Hz, Rh-C), 173.08 (C═O), 170.37 (HC═N), 136.37, 134.22, 132.01, 131.51 (q, J = 3.0 Hz), 130.52, 127.16, 125.41 (q, J = 26.4 Hz), 122.25 (q, J = 280.8 Hz, CF_3), 96.93 (d, J = 6.5 Hz, C_5Me_5), 59.34 (CH_2CH_3), 55.93 (N-Me), 14.71 (CH_2CH_3), 8.56 (C_5Me_5).

3i and 3′i. The reaction was carried out as for **1d**, using **3** (40.0 mg, 0.077 mmol), ethyl 4,4,4-trifluoro-2-butynoate (14.0 μL, 0.095 mmol), and 15.0 mL of methanol, RT, 3 h. The bright yellow insertion compounds **3i** and **3′i** with a ratio of 1:2.2 were obtained (52.0 mg, 98%). The two regioisomers were separated by column chromatography using 0.5% MeOH/CH_2Cl_2 as the eluent. Anal. Calcd for $C_{27}H_{28}ClF_3NO_2Ir$: C, 47.47; H, 4.13; N, 2.05. Found: C, 47.33; H, 4.03; N, 2.06. ^{1}H NMR for the major regioisomer **3′i**: δ 9.59 (dd, 1 H, J = 6.0, 1.2 Hz, HC═N), 8.24 (d, 1 H, J = 8.0 Hz), 7.75 (td, 1 H, J = 7.7, 1.5 Hz), 7.44 (m, 2 H), 7.33 (td, 1 H, J = 7.6, 1.1 Hz), 7.20 (td, 1 H, J = 6.8, 1.5 Hz), 7.07 (dd, 1 H, J = 7.7, 1.0 Hz), 4.18 (m, 1 H, CH_2CH_3), 3.96 (m, 1 H, CH_2CH_3), 1.22 (s, 15 H, C_5Me_5), 1.16 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **3′i**: δ 171.29 (C═O), 163.53 (HC═N), 155.27, 147.06 (q, J = 28.3 Hz, Ir-C), 140.12 (q, J = 6.0 Hz), 139.19, 138.45, 138.17, 133.36, 130.86, 129.03, 128.16 (q, J = 279.8 Hz, CF_3), 127.20 (2 C's overlap), 124.05, 88.95 (C_5Me_5), 61.35 (CH_2CH_3), 14.06 (CH_2CH_3), 8.52 (C_5Me_5). ^{1}H NMR for the minor regioisomer **3i**: δ 9.41 (dd, 1 H, J = 6.0, 1.3 Hz, HC═N), 7.77 (td, 1 H, J = 7.7, 1.6 Hz), 7.69 (d, 1 H, J = 8.0 Hz), 7.47 (m, 2 H), 7.32 (td, 1 H, J = 7.6, 1.0 Hz), 7.18 (td, 1 H, J = 6.8, 1.4 Hz), 7.10 (dd, 1 H, J = 7.7, 1.2 Hz), 4.18 (m, 2 H, CH_2CH_3), 1.24 (s, 15 H, C_5Me_5), 1.23 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **3i**: δ 174.47 (m Ir-C), 163.56 (HC═N), 160.51 (C═O), 154.95, 139.97, 138.32 (2 C's overlap), 133.82, 130.84 (m), 128.73, 126.91, 126.85, 126.70, 123.93, 123.47 (q, J = 280.8 Hz, CF_3), 89.05 (C_5Me_5), 58.78 (CH_2CH_3), 14.55 (CH_2CH_3), 8.18 (C_5Me_5).

4i and 4′i. The reaction was carried out as for **1d**, using **4** (40.0 mg, 0.094 mmol), ethyl 4,4,4-trifluoro-2-butynoate (16.0 μL, 0.11 mmol), and 15.0 mL of methanol, RT, 3 h. The red insertion

compounds **4i** and **4′i** with a ratio of 1:2.0 were obtained (54.6 mg, 98%). The two regioisomers were separated by column chromatography using 1% $MeOH/CH_2Cl_2$ as the eluent. Anal. Calcd for $C_{27}H_{28}ClF_3NO_2Rh$: C, 54.61; H, 4.75; N, 2.36. Found: C, 54.76; H, 4.78; N, 2.33. ^{1}H NMR for the major regioisomer **4′i**: δ 9.69 (d, 1 H, J = 4.7 Hz, HC═N), 8.27 (dd, 1 H, J = 8.0, 0.8 Hz), 7.78 (td, 1 H, J = 7.6, 1.6 Hz), 7.47 (td, 1 H, J = 7.7, 1.3 Hz), 7.42 (d, 1 H, J = 7.9 Hz), 7.35 (td, 1 H, J = 7.6, 1.2 Hz), 7.25 (td, 1 H, J = 6.8, 1.1 Hz), 7.14 (dd, 1 H, J = 7.7, 1.1 Hz), 4.17 (m, 1 H, CH_2CH_3), 3.94 (m, 1 H, CH_2CH_3), 1.21 (s, 15 H, C_5Me_5), 1.17 (t, 3 H, J = 7.2 Hz, CH_2CH_3). ^{13}C NMR for **4′i**: δ 170.14 (C═O), 163.10 (HC═N), 159.48 (dq, J = 40.4, 28.3 Rh-C), 155.09, 139.39 (q, J = 8.3 Hz), 138.29, 137.85, 137.72, 133.38, 130.91, 129.02, 127.45, 127.11, 126.87 (q, J = 278.8 Hz, CF_3), 123.50, 96.63 (d, J = 6.9 Hz, C_5Me_5), 61.43 (CH_2CH_3), 14.03 (CH_2CH_3), 8.82 (C_5Me_5). ^{1}H NMR for the minor regioisomer **4i**: δ 9.49 (d, 1 H, J = 4.7 Hz, HC═N), 7.78 (td, 1 H, J = 7.7, 1.6 Hz), 7.74 (d, 1 H, J = 8.0 Hz), 7.49 (td, 1 H, J = 7.7, 1.4 Hz), 7.44 (d, 1 H, J = 7.8 Hz), 7.34 (td, 1 H, J = 7.6, 1.0 Hz), 7.22 (td, 1 H, J = 6.6, 1.4 Hz), 7.18 (dd, 1 H, J = 7.8, 1.2 Hz), 4.17 (m, 2 H, CH_2CH_3), 1.24 (s, 15 H, C_5Me_5), 1.22 (m, 3 H, CH_2CH_3). ^{13}C NMR for **4i**: δ 174.18 (d, J = 70.6 Hz, Rh-C), 173.26 (C═O), 163.16, 154.92 (HC═N), 139.82, 138.36, 136.96, 134.05, 131.08, 128.89, 127.21, 126.94, 125.86 (q, J = 26.3 Hz), 123.57, 122.22 (q, J = 277 Hz, CF_3), 96.86 (d, J = 6.6 Hz, C_5Me_5), 59.19 (CH_2CH_3), 14.64 (CH_2CH_3), 8.65 (C_5Me_5).

X-ray Crystal Structure Determinations. Data were collected on a Bruker SMART APEX II CCD Platform diffractometer at 100.0(1) K. The data collection was carried out using Mo Kα radiation. The intensity data were corrected for absorption. The structures were solved using SIR 97[36] and refined using SHELXL-97.[37] All non-hydrogen atoms were refined with anistropic displacement parameters. All hydrogen atoms were found from the difference Fourier map and refined independently from the carbon atoms with individual isotropic displacement parameters. See Supporting Information for details.

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Supporting Information Available: Full structure descriptions of compounds **2a**, **4a**, **4b**, **2c**, **1d**, **3e**, **4e**, **1f**, **2g**, **3g**, **4g**, **1′h**, **3′h**, **1′i**, **2′i**, and **3′i**, cif files, and ^{1}H and ^{13}C NMR spectra for the compounds. This material is available free of charge via the Internet at http://pubs.acs.org. The cif files have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 786368−786383.

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