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Versatile κ^2,η^2-*C* Ligands Assembled at Iridium via [2+2] Oxidative Cyclization

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The cationic Ir(I) complex [Ir(1,2,5,6-η-C_8H_{12})(NCMe)(PMe_3)]BF_4 has been observed to react with ester-substituted internal alkynes via [2+2] oxidative cyclization to form iridacyclopentene derivatives: [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2R)=C(CO_2R)})($NCMe)_2$(PMe_3)]BF_4 (R = Me, *t*Bu). These compounds contain *fac*-tridentate ligands that coordinate the Ir(III) centers κ^2, through sp^3 and sp^2 carbons, and η^2 through the remaining C=C bond of the former cyclooctadienes. The derivative with R = Me has been subjected to different substitution reactions of its labile acetonitriles, including sequential reactions against monodentate ligands such as CO and PMe_3, bidentate ligands such as 2,2′-bipy, and anions such as phenylacetylide, hydride, acetylacetonate, and cyclopentadienyl. The use of these reagents, individually or in combination, has led to compounds containing the new C-donor ligand in various coordination modes, including κ^3; κ^2,η^3; κ^2,η^2; κ^2; and κ,η^2 (or its κ^3 extreme version). The transformations observed for this ligand include a C−H bond activation reaction at the coordination sphere of a formally Ir(V) complex effected by an external base as weak as chloride.

Introduction

The cycloaddition reactions catalyzed by transition metal complexes constitute a powerful method for the synthesis of ring molecules.[1] The [2+2] version between alkenes and alkynes, applicable to the preparation of cyclobutenes, can be driven by a variety of complexes,[2] under conditions especially mild in the case of electron-poor alkynes.[3] The prevalent mechanistic description of such processes involves two consecutive different C−C bond-forming elementary steps: the so-called oxidative cyclization and a reductive elimination.[4] Among the various evidence supporting this mechanism, the key metallacyclopentene intermediate connecting the two C−C forming steps has been observed in a few instances.[5,6] The present work describes a further example of metallacyclopentene, formed by oxidative cyclization between an alkyne and a cationic Ir(COD) fragment. Selected experiments on this species are presented to highlight that, besides its value and potential usage to ascertain mechanistic details, it holds an uncommon class of polydentate ligand bearing various different C-donor functions. This ligand is especially stable and versatile in the coordination sphere of iridium and is just one reaction away from usual starting complexes of this metal.

Results and Discussion

In a previous work,[7] we described and discussed various reactions between alkynes and the cationic iridium(I) complex [Ir(1,2,5,6-η-C_8H_{12})(NCMe)(PMe_3)]BF_4 (**1**), the outcome of which strongly depended on the alkyne features. Thus, a terminal alkyne such as phenylacetylene was observed to initially undergo C−H oxidative addition to form an unstable Ir(III) hydride-alkynyl species, which subsequently evolved into the iridacyclopentadiene complex [Ir(1,4-κ-CH=C(Ph)CH=CPh)(1,2,5,6-η-C_8H_{12})(NCMe)(PMe_3)]BF_4 (eq 1). In contrast, an internal alkyne such as diphenylacetylene was found to form the Ir(III) alkenyl compound [Ir(1,2,3,5,6-η-C_8H_{11}){*Z*-C(Ph)=CHPh}(NCMe)(PMe_3)]BF_4,[7] after alkyne insertion into the hydride ligand, resulting from a previous allylic C−H activation of the cyclooctadiene.[8] Now we have observed that this latter reaction is also not general for internal alkynes, since those bearing ester substituents undergo fast oxidative cyclization with one of the cyclooctadiene double bonds to afford iridacyclopentene compounds (eq 1). This behavior agrees with a trend previously recognized in ruthenium derivatives,

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(1) (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49–92. (b) *Cycloaddition Reactions in Organic Synthesis*; Kobayashi, S.; Jorgensen, K. A., Eds.; Wiley-VCH: Weinheim, 2001.

(2) For recent reports and leading references: (a) Cockburn, N.; Karimi, E.; Tam, W. *J. Org. Chem.* **2009**, *74*, 5762–5765. (b) Treutwein, J.; Hilt, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 6811–6813.

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(5) Rusell, D.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1749–1752.

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(7) Martín, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406–5417.

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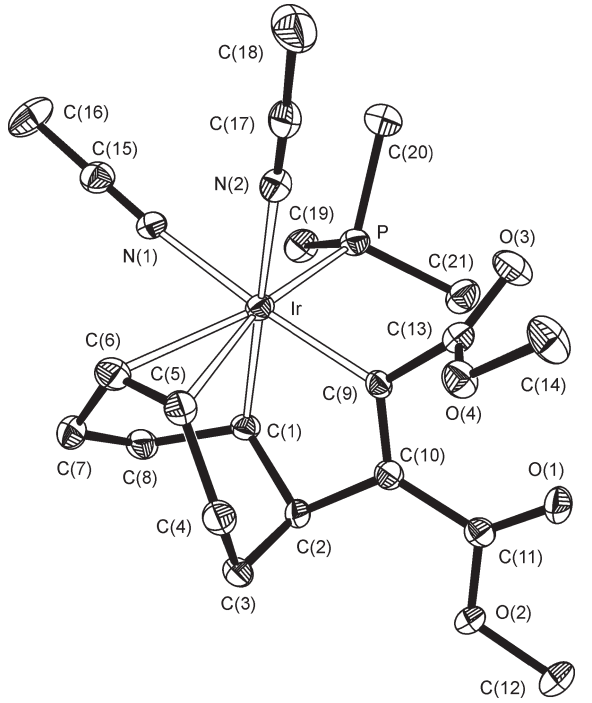
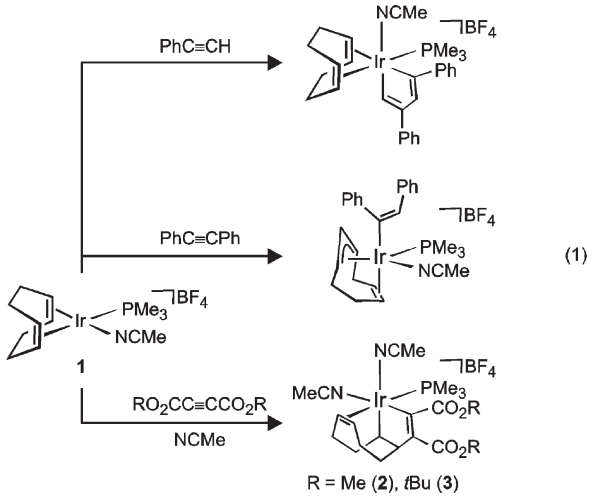


Figure 1. X-ray structure of the cation of complex **2**.

according to which electron-withdrawing substituents at the alkyne favor cycloadditions.[3]

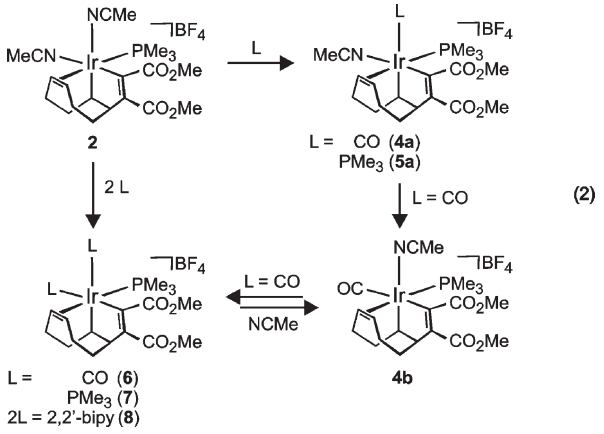


The formation of compounds [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2R)=C(CO_2R)})($NCMe)_2$(PMe_3)]BF_4 (R = Me (**2**) and *t*Bu (**3**), eq 1) from **1** and one equivalent of the corresponding alkyne is selective and almost immediate at 273 K. The structure of **2** determined by X-ray diffraction (Figure 1, Table 1) confirms the occurrence of an oxidative cyclization reaction leading to a *fac*-tridentate ligand. This ligand coordinates κ^2 via sp^3 and sp^2 carbons and η^2 through the remaining intact C=C double bond of the cyclooctadiene. The bond distances within the resulting iridacyclopentene ring are similar to those found in the related species [(Tp)Ir{1,4-κ-$CH_2CH_2C(CO_2Me)$=C(CO_2Me)}(NCMe)][6] and confirm the localization of the double bond between the former alkyne carbons. The metal-bonded carbons of the new ligand produce P-coupled $^{13}C\{^1H\}$ NMR signals at characteristic chemical shifts (at high and low field for the sp^3 and sp^2 κ carbons: 18.69 (2.7 Hz) and 149.96 (11.6 Hz), respectively) and indicative of their coordination trans to phosphine for the η ones (100.91 (10.2 Hz) and 107.47 (11.1 Hz)).

Table 1. Bond Distances (Å) and Angles (deg) for Complex 2

Ir−P	2.2848(10)		
Ir−N(1)	2.110(3)	Ir−N(2)	2.135(3)
Ir−C(1)	2.079(3)	Ir−C(9)	2.018(3)
Ir−C(5)	2.394(4)	Ir−C(6)	2.317(4)
C(1)−C(2)	1.550(5)	C(2)−C(10)	1.521(4)
C(9)−C(10)	1.341(5)	C(5)−C(6)	1.346(5)
P−Ir−N(1)	85.32(9)	P−Ir−N(2)	95.06(8)
P−Ir−C(1)	90.60(11)	P−Ir−C(9)	87.48(10)
P−Ir−C(5)	167.35(10)	P−Ir−C(6)	156.58(10)
N(1)−Ir−N(2)	86.70(11)	C(1)−Ir−C(9)	80.62(14)
N(1)−Ir−C(1)	98.02(12)	N(2)−Ir−C(1)	173.93(13)
N(1)−Ir−C(5)	107.02(12)	N(2)−Ir−C(5)	88.57(12)
N(1)−Ir−C(6)	75.69(13)	N(2)−Ir−C(6)	97.36(13)
N(1)−Ir−C(9)	172.66(12)	N(2)−Ir−C(9)	95.36(12)

Although rarely observed, metallacyclopentene skeletons similar to those of **2** and **3**, and related species derived from norbornadiene, norbornene, or other alkenes, are very commonly proposed as intermediates in [2+2] cycloaddition reactions, especially in the chemistry of ruthenium.[9] In spite of this, complexes **2** and **3** have proved to be stable against possible C−C reductive eliminations yielding cyclobutenes, even in the presence of additional ligands (see below). This reluctance to undergo C−C reductive eliminations becomes more significant after observing that **2** contains two weakly coordinating acetonitrile ligands displaying long Ir−N distances, indicative of their easy dissociation.[10] This should contribute to facilitate these reactions since, with regard to a "well-established" mechanistic tenet concerning C−C reductive eliminations,[11,12] they are kinetically much more facile from five-coordinate d^6 metal complexes than from the corresponding six-coordinate compounds. Nevertheless, it should be noted that this conclusion has been extracted from the investigation of tri- and tetramethyl Pt(IV) complexes, in which any coordination vacancy is generated at a position cis to both groups to be coupled.[11] This is not the case of complex **2** and certain Pd(IV) compounds, whose reactivity seems to contradict the above conclusion.[13]



Despite the small difference between the two Ir−N distances of **2**, the acetonitrile ligand with the longest one, that

(9) See for example: Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067–2096.

(10) See for example: (a) Torres, O.; Martín, M.; Sola, E. *Organometallics* **2009**, *28*, 863–870. (b) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534–3546.

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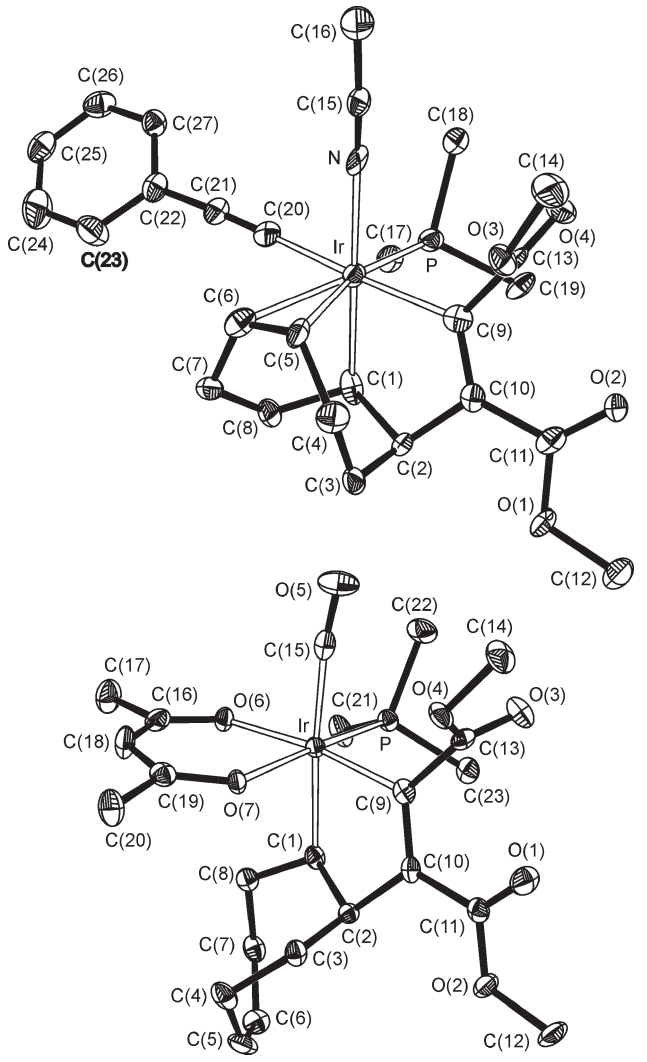


Figure 2. X-ray structures of complexes **9** (above) and **11** (below).

trans to the sp^3carbon, can be selectively substituted in CH_2Cl_2 solution by ligands such as CO and PMe_3. Workup and isolation of these substitution kinetic products, [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(NCMe)(L)(PMe_3)]BF_4 (L = CO (**4a**) and PMe_3 (**5a**), eq 2), has not required provisions other than short reaction times and low CO pressure in the case of **4a** and the careful use of one equivalent of PMe_3 for **5a**. The effects of these ligand substitutions in the NMR spectra are notable in the $^{13}C\{^1H\}$ signal corresponding to the κ CH, which shifts to lower field (from δ 18.69 to 34.49 in **4a** or 30.81 in **5a**) and splits due to an additional J_{CP} coupling constant of 72.5 Hz in the case of **5a**. The transformation of **4a** into its stable isomer **4b** (eq 2) has been monitored by NMR in a sample of isolated **4a** dissolved in CD_2Cl_2. At 323 K, the isomerization was complete in about 20 h. The coordination position of CO in the new isomer **4b** can also be inferred from the $^{13}C\{^1H\}$ NMR signal corresponding to the trans κ carbon, which also shifts downfield, from δ 139.57 (in **4a**) to 158.55. In parallel, that corresponding to the κ CH shifts back to a δ close to that in **2**, 24.30 ppm.

(12) (a) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 9538–9539. (b) Lindner, R.; Wagner, C.; Steinborn, D. *J. Am. Chem. Soc.* **2009**, *131*, 8861–8874. (c) Gosh, R.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 11317–11327.

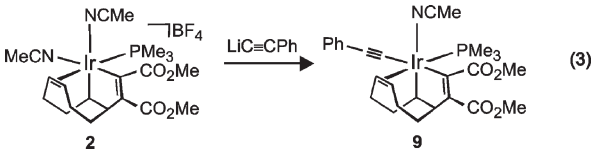
(13) Racowski, J. M.; Dick, A. R.; Sandford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974–10983.

Table 2. Bond Distances (Å) and Angles (deg) for Complexes 9 and 11

	9		11
Ir−P	2.2867(17)		2.2671(12)
Ir−N	2.142(6)	Ir−O(6)	2.126(3)
		Ir−O(7)	2.110(3)
Ir−C(1)	2.063(7)		2.119(4)
Ir−C(5)	2.310(7)		
Ir−C(6)	2.257(7)		
Ir−C(9)	2.059(6)		2.017(4)
Ir−C(20)	2.059(6)	Ir−C(15)	1.913(4)
C(1)−C(2)	1.571(9)		1.545(5)
C(2)−C(10)	1.509(7)		1.507(5)
C(9)−C(10)	1.329(7)		1.341(5)
C(5)−C(6)	1.351(9)		1.323(7)
P−Ir−N	96.32(15)	P−Ir−O(6)	89.97(8)
		P−Ir−O(7)	175.79(8)
P−Ir−C(1)	90.47(16)		88.37(12)
P−Ir−C(5)	165.17(18)		
P−Ir−C(6)	157.26(19)		
P−Ir−C(9)	86.21(18)		91.90(11)
P−Ir−C(20)	85.20(19)	P−Ir−C(15)	91.70(12)
N−Ir−C(1)	171.3(2)	O(6)−Ir−O(7)	88.56(11)
N−Ir−C(5)	87.6(2)	O(6)−Ir−C(1)	92.96(14)
N−Ir−C(6)	96.3(2)	O(6)−Ir−C(9)	171.58(14)
N−Ir−C(9)	94.1(2)	O(6)−Ir−C(15)	93.04(14)
N−Ir−C(20)	89.2(2)	O(7)−Ir−C(1)	87.76(14)
		O(7)−Ir−C(9)	89.00(13)
C(1)−Ir−C(9)	80.9(3)		78.89(17)
C(1)−Ir−C(20)	96.8(3)	C(1)−Ir−C(15)	174.00(17)
C(9)−Ir−C(20)	171.1(2)	C(9)−Ir−C(15)	95.11(17)

After completion of the **4a** to **4b** isomerization, the remaining acetonitrile ligand can also be replaced by CO to give the complex [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})-($CO)_2$(PMe_3)]BF_4 (**6**). This second substitution has proved to be easily reversible, and as a result, the quantitative generation of this product has been possible only in solution under CO excess. By contrast, the other two bis-substituted compounds in eq 1, that with three *fac* PMe_3 ligands (**7**) and the 2,2′-bipyridine derivative (**8**), have been easily isolated and found to be stable against ligand dissociation.

The release and substitution of the η^2 ligand moiety has not been observed in any of the reactions summarized in eq 2, even under large ligand excesses. Nevertheless, this process seems to be much easier in the neutral derivatives of **2** described from this point on. A representative example of substitution reaction leading to a neutral complex is shown in eq 3. The reaction between **2** and lithium phenylacetylide has been observed to readily form [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(C≡CPh)(NCMe)(PMe_3)] (**9**), the structure and structural details of which are shown in Figure 2 and Table 2, respectively. The compound meets at the coordination sphere of iridium sp^3, sp^2, and sp κ carbons, together with the η^2 alkene fragment. In spite of such accumulation of reactive groups, the complex has been found to be thermally stable.[14]



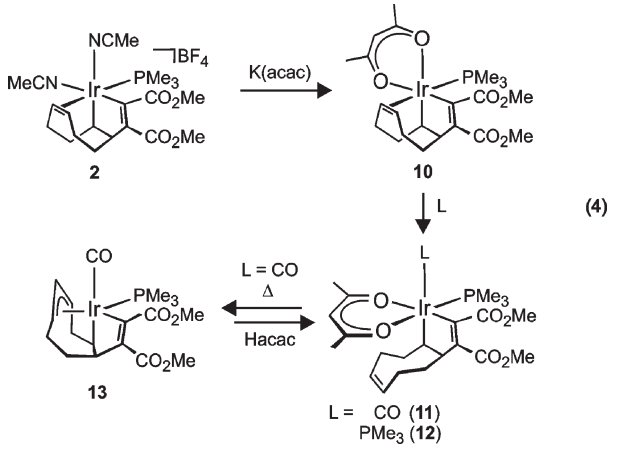
(3)

With regard to the conclusions of eq 2, the structure of **9**, with the incoming acetylide ligand trans to the sp^2 side of the

(14) For related compounds and reactions, see: (a) Chin, C. S.; Kim, M.; Lee, H. *Organometallics* **2002**, *21*, 1679–1683. (b) Chin, C. S.; Lee, H.; Eum, M.-S. *Organometallics* **2005**, *24*, 4849–4852.

iridacyclopentene, is that expected for the thermodynamic substitution isomer. The hypothetic kinetic isomer likely preceding the formation of **9** has not been observed. This might be tentatively attributed to its short life, a possibility that would suggest an enhancement of acetonitrile lability on going from cationic to electron richer neutral complexes. This observation, however, is not fairly supported by the available structural features, which indicate that the Ir−N distances trans to the sp^3 κ carbon are nearly equal in cationic and neutral compounds. Actually, the rest of the structural parameters of **9** are also similar to those of **2**.

Illustration of the coordination versatility of our new tridentate ligand can start in a second example of the neutral derivative, the acetylacetonate complex [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ^2-*O*-acac)(PMe_3)] (**10**), which has been readily prepared from **2** and potassium acetylacetonate. Although **10** has no more acetonitriles available, it has shown itself able to slowly accommodate a CO or PMe_3 additional ligand after release of the η^2-alkene function and reorganization of the acac coordination (eq 4).



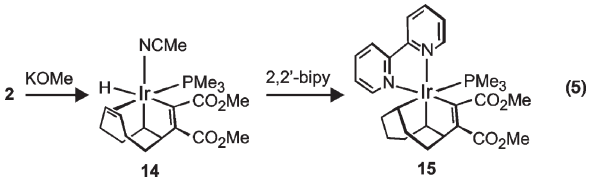
The structure of the carbon monoxide derivative [Ir(1-κ-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ^2-*O*-acac)(CO)(PMe_3)] (**11**) is shown in Figure 2. The relevant bond distances and angles of the structure are collected in Table 2. Comparing this X-ray structure with the previous two indicates that the additional η^2 coordination of the ligand hardly modifies the iridacyclopropene ring geometry. A parameter illustrating some minor structural effects is the Ir−C(9)−C(10)−C(2) torsion angle of the metallacycle double bond, which reaches 15° and 12° in derivatives **2** and **9**, respectively, but relaxes to 2° in complex **11**.

The spectroscopic data of the PMe_3 analogue of **11**, [Ir(1-κ-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ^2-*O*-acac)(PMe_3)$_2$] (**12**), indicate that its structure is indeed analogous. The coordination position of the phosphine ligands is inferred from the $^{13}C\{^1H\}$ NMR signals of the κ carbons: a doublet of doublets at δ 37.85 (J_{CP} = 92.7 and 4.3) and a doublet at δ 146.71 (J_{CP} = 10.3). Additionally, the signals corresponding to the alkene function are now singlets at δ 126.49 and 132.07, chemical shifts typical for noncoordinated olefinic CH carbons.

The bis-phosphine derivative **12** has been found to be thermally stable. In contrast, the heating of a toluene solution of complex **11** under argon at 353 K has been observed to slowly afford the precursor **10**. The same experiment carried out under CO atmosphere to avoid the latter reverse reaction has led to a different evolution, namely, the elimination of acetylacetone and formation of complex [Ir(1-κ-5,6,7-η-C_8H_{11}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(CO)(PMe_3)] (**13**) (eq 4). The NMR spectroscopic observation of this reaction has evidenced that **13** and its precursor **11** are in slow equilibrium. The equilibrium can be shifted to achieve quantitative formation of **13** by heating at 353 K for about 48 h and can be reverted to **11** by addition of acetylacetone excess, always under CO atmosphere to avoid the accumulation of **10**.

The characterization data of **13** are consistent with the structural proposal depicted in eq 4. The $^{13}C\{^1H\}$ NMR APT spectrum reveals the disappearance of one of the four CH_2 characteristic resonances of the ligand to give a new CH signal. The $^1H/^{13}C$ NMR correlation in combination with the ^1H COSY and NOESY spectra indicates that, from the two possible allylic activations, only that leading to the proposed structure has selectively occurred. The $^{13}C\{^1H\}$ NMR signals corresponding to the allyl moiety are two doublets at δ 43.08 (J_{CP} = 21.2 Hz) and 135.80 (J_{CP} = 8.2 Hz) and a singlet at δ 130.72. The magnitude of the two coupling constants is consistent with a η^3 coordination occupying the position trans to phosphine, but the chemical shifts of the latter two signals suggest a κ coordination as a better description. Most likely, this apparent discrepancy just reflects the difficulties of the ligand to reach four of the six octahedral coordination positions.

The attainment of other coordination modes requires the participation of hydrides or protons. The hydride complex [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})H(NCMe)(PMe_3)] (**14**) has been prepared by reaction of **2** with one equivalent of KOH in methanol at low temperature. Following the usual mechanistic proposals, this reaction should involve the initial formation of a methoxo intermediate, which would undergo hydrogen β-elimination to release formaldehyde.[15] Neither this likely methoxo intermediate nor possible isomers of **14** have been observed. Complex **14** displays a characteristic ^1H NMR hydride resonance at δ −11.58 (J_{HP} = 26.7 Hz), which exhibits NOE effects with that of PMe_3, and another two due to =CH and CH_2 hydrogens of the ligand, in agreement with the structure depicted in eq 5.



The treatment of **14** with one equivalent of 2,2′-bipyridine has led to a product of formal insertion of the η^2 alkene fragment into the Ir−H bond: the complex [Ir(1,5-κ-C_8H_{13}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ^2-*N*-bipy)(PMe_3)] (**15**) (eq 5). After this insertion, the ligand becomes formally trianionic and coordinates κ^3 through one sp^2 and two sp^3 carbons. The $^1H/^{13}C$ NMR correlation together with the ^1H COSY and NOESY spectra of **15** confirm that insertion has selectively occurred in the carbon labeled as 6, that is, in the sense expected from the structure of **14**. The $^{13}C\{^1H\}$ NMR signals corresponding to the three κ carbons are a singlet at δ 8.42 and two doublets at δ 16.42 (J_{CP} = 76.6 Hz) and 162.56 (J_{CP} = 11.8 Hz), in agreement with the proposed ligand distribution around iridium.

(15) (a) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343−349. For leading references, see: (b) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 7220–7227.

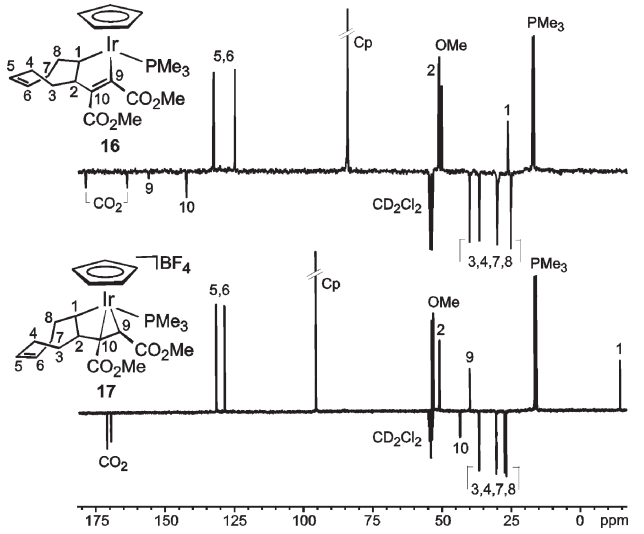
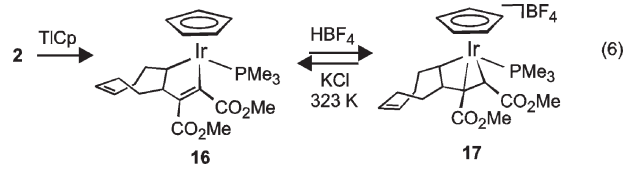


Figure 3. $^{13}C\{^1H\}$ APT NMR spectra of compounds **16** and **17** in CD_2Cl_2.

Complex **2** has also been found able to accommodate a tridentate anionic ligand such as cyclopentadienyl after losing both acetonitrile ligands and releasing the η^2 C=C bond. This substitution reaction has afforded the neutral iridacyclopentene complex $[Ir(\eta^5\text{-}C_5H_5)(1\text{-}\kappa\text{-}C_8H_{12}\text{-}2\text{-}Z\text{-}\{2'\text{-}\kappa\text{-}C(CO_2Me)=C(CO_2Me)\})(PMe_3)]$ (**16**) (eq 6). With regard to our ligand, the spectroscopic features of **16** are similar to those of **11** and **12**, thus indicating the same coordination mode.



In the presence of a strong Brønsted acid such as HBF_4, complex **16** has been observed to form the cationic derivative **17** (eq 6). The $^{13}C\{^1H\}$ NMR spectrum of this compound (Figure 3) evidenced that the proton has attacked the former sp^2 κ carbon of the iridacyclopentene instead of the more electron-rich sp^3 one. This choice seems more suitable from a thermodynamic point of view since it leads to a product that remains electronically and coordinatively saturated, conditions more difficult to maintain after the other mentioned alternative. Figure 3 illustrates the marked upfield shifts provoked by the reaction in the $^{13}C\{^1H\}$ NMR signals of the iridacycle atoms, especially large in those of sp^2 carbons (9 and 10 in the figure) but also very notable in that due to the sp^3 one (1). This suggests that these carbons have become much more electron-rich in spite of the protonation. Interestingly, there is also a notable shift of the signal corresponding to the five Cp carbons, but toward downfield. This seems to indicate that, even though the proton has been incorporated into our ligand, the necessary electron density has eventually been supplied by the metal, which, in consequence, demands more from the Cp ligand. Since the transfer of electron density to our ligand must imply an enhanced backdonation to the alkene moiety, it seems more realistic to describe **17** as an Ir(V) metallacyclopropene complex, $[Ir(\eta^5\text{-}C_5H_5)(1\text{-}\kappa\text{-}C_8H_{12}\text{-}2\text{-}Z\text{-}\{1',2'\text{-}\kappa\text{-}C(CO_2Me)=CH(CO_2Me)\})(PMe_3)]BF_4$, rather than as the alternative Ir(III) π-alkene extreme.[16]

(16) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2001; Chapter 3, p 125.

Other spectroscopic details of **17**, such as the very large 13.8 Hz J_{HP} coupling constant found in the ^1H NMR signal of the new CH generated after protonation, also seem rather incompatible with a π-alkene but possible in the iridacyclopropane structure.

Also in agreement with the formulation given to **17**, its reaction with a good potential ligand such as chloride has not led to the replacement of the possible η^2 alkene function. Instead, this very weak base has emerged capable of deprotonating **17** back to **16**. Such an unexpected reaction has been quantitatively achieved after a few minutes heating at 323 K of a CH_2Cl_2 solution of **17** in the presence of a KCl suspension. Complex **17**, or more precisely its Ir(III) π-alkene extreme, resembles a family of Ir(III) cationic compounds with Cp* ligands that has been extensively studied in the context of C−H activation.[17] The numerous mechanistic investigations carried out in these compounds strongly suggest that the activations involve sequences of oxidative addition/reductive elimination elementary steps via Ir(V) intermediates, which are isolable in some cases.[18] However, to the best of our knowledge, external base-induced C−H activations such as that in eq 6 have never been described in either Ir(III) or Ir(V) complexes of this family.[19] Nevertheless, these reactions are known in highly electrophilic complexes of other types.[20]

In summary, we have shown that internal alkynes with ester substituents react with the cationic Ir(I) complex $[Ir(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(NCMe)(PMe_3)]BF_4$ via oxidative cyclizations to afford Ir(III) derivatives having $1\text{-}\kappa\text{-}5,6\text{-}\eta\text{-}C_8H_{12}\text{-}2\text{-}Z\text{-}\{2'\text{-}\kappa\text{-}C(CO_2R)=C(CO_2R)\}$ ligands. In the coordination sphere of Ir(III), this type of ligand has emerged stable against reductive elimination, capable of accommodating its coordination and electronic features as required by different incoming ligands and able to exploit the reversible exchange of hydrides and protons with the metal center, other basic ligands, and external bases. This versatility, together with the ease with which the ligand can be assembled, makes it a candidate to be considered when looking for a simple, stabilizing, and strong-donor polydentate auxiliary in the context of iridium chemistry and catalysis.

Experimental Section

Equipment. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. FAB-MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with a Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. MALDI-TOF-MS were obtained in a Bruker Microflex mass spectrometer using DCTB (1,1-dicyano-4-*tert*-butylphenyl-3-methylbutadiene) as matrix. Infrared spectra were recorded in solution or KBr using a FTIR Perkin-Elmer Spectrum One spectrometer. Molar conductivities (Λ_M) were measured in ca. 5×10^{-4} M solutions using a Philips PW 9501/01 conductimeter. NMR spectra were recorded on Bruker Avance 400 or 300 MHz

(17) (a) Klei, S. R.; Golden, J. T.; Burger, P.; Bergman, R. G. *J. Mol. Catal. A: Chem.* **2002**, *189*, 79−94. See also: (b) Alaimo, P. J.; Arndsten, B. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 2130–2143. (c) Leung, D. H.; Fiedler, D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 963–966.

(18) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707–2717.

(19) For internal base-induced C−H activations in closely related complexes, see: Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210–4211.

(20) Hahn, C. *Organometallics* **2010**, *29*, 1331–1338.

spectrometers. ^{1}H (400.13 or 300.13 MHz) and ^{13}C (100.6 or 75.5 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P NMR (162.0 or 121.5 MHz) chemical shifts were measured relative to H_3PO_4 (85%). Coupling constants, *J*, are given in hertz. In general, NMR spectral assignments were achieved through ^{1}H COSY, ^{1}H NOESY, ^{13}C APT, and ^{1}H/^{13}C-HSQC experiments. Spectroscopic data are given at room temperature unless otherwise indicated.

Synthesis. All manipulations were carried out under argon by standard Schlenk techniques. Solvents were obtained from an Innovative Technology solvent purification system. Deuterated solvents were carefully dried by known procedures and stored under argon prior to use. The starting complex [Ir(1,2,5,6-η-C_8H_{12})(NCMe)(PMe_3)]BF_4 (**1**) was prepared as previously reported.[7] All commercial reagents were used as received without further purification. All new complexes described below are air sensitive in solution.

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})($NCMe)_2$(PMe_3)]BF_4 (2). To a 5 mL CH_2Cl_2 solution of **1** (123 mg, 0.24 mmol) was added dimethylacetylene dicarboxylate (30 μL, 0.24 mmol). The reaction mixture was stirred at 273 K for 10 min, after which it was concentrated under reduced pressure to ca. 0.5 mL. The addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 146 mg (87%). Anal. Calcd (%) for $C_{21}H_{33}BF_4IrN_2O_4P$: C, 36.69; H, 4.84; N, 4.08. Found: C, 36.23; H, 4.47; N, 3.85. MS (FAB+, *m*/*z* (%)): 519 (88) [M^+ − 2 NCMe]. IR (KBr, cm^{-1}): 2322, 2293 ν(N≡C), 1709 ν(OCO), 1059 ν(BF_4). Λ_M (acetone) = 83 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR (CD_2Cl_2): δ 1.63 (d, J_{HP} = 11.2, 9H, PCH_3), 1.68 (m, 3H, CH_2), 2.00 (m, 1H, CH_2), 2.12, 2.28 (both m, 1H each, CH_2), 2.36 (s, 3H, $NCCH_3$), 2.48 (m, 1H, CH_2), 2.49 (m, 1H, IrCH), 2.60 (s, 3H, $NCCH_3$), 2.75 (m, 1H, CH), 3.62, 3.73 (both s, 3H each, OCH_3), 4.98, 5.80 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −25.98 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 2.63, 3.59 (both s, NC*C*H_3), 12.09 (d, J_{CP} = 41.5, PCH_3), 18.69 (d, J_{CP} = 2.7, IrCH), 21.86, 22.16, 25.36 (all s, CH_2), 38.40 (d, J_{CP} = 2.3, CH_2), 47.54 (d, J_{CP} = 1.7, CH), 50.89, 50.93 (both s, OCH_3), 100.91 (d, J_{CP} = 10.2, =CH), 107.47 (d, J_{CP} = 11.1, =CH), 118.91, 122.72 (both s, N*C*CH_3), 139.74 (d, J_{CP} = 4.0, IrC=*C*), 149.96 (d, J_{CP} = 11.6, Ir*C*=C), 163.24 (s, CO), 175.08 (d, J_{CP} = 3.1, CO). The crystals used in the X-ray experiment were obtained from a CH_2Cl_2 solution of **2** layered with hexane, at room temperature.

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2tBu)=C(CO_2tBu)})($NCMe)_2$(PMe_3)]BF_4 (3). To a 5 mL CH_2Cl_2 solution of **1** (103 mg, 0.20 mmol) was added di-*tert*-butylacetylene dicarboxylate (47 μL, 0.20 mmol). The reaction mixture was stirred at 258 K for 5 min, after which it was concentrated to ca. 0.5 mL. The addition of diethyl ether produced a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 183 mg (81%). Anal. Calcd (%) for $C_{27}H_{45}BF_4IrN_2O_4P$: C, 42.02; H, 5.87; N, 3.63. Found: C, 42.17; H, 5.95; N, 3.90. MS (FAB+, *m*/*z* (%)): 685 (12) [M^+], 644 (32) [M^+ − NCMe], 603 (100) [M^+ − 2NCMe]. IR (KBr, cm^{-1}): 2321, 2290 ν(N≡C), 1698 ν(OCO), 1059 ν(BF_4). ^{1}H NMR (CD_2Cl_2): δ 1.44, 1.51 (both s, 9H each, $C(CH_3)_3$), 1.63 (d, J_{HP} = 11.3, 9H, PCH_3), 1.68 (m, 3H, CH_2), 2.00, 2.12 (both s, 1H each, CH_2), 2.25 (s, 3H, $NCCH_3$), 2.28 (m, 2H, CH_2), 2.48 (m, 1H, CH_2), 2.49 (m, 1H, IrCH), 2.54 (s, 3H, $NCCH_3$), 2.75 (m, 1H, CH), 4.98, 5.80 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −25.69 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 3.01, 3.53 (both s, NC*C*H_3), 12.24 (d, J_{CP} = 41.4, PCH_3), 18.52 (d, J_{CP} = 2.7, IrCH), 21.77, 22.63, 25.43 (all s, CH_2), 28.02, 28.10 (both s, $OC(CH_3)_3$), 38.33 (d, J_{CP} = 2.3, CH_2), 47.90 (d, J_{CP} = 1.4, CH), 79.04, 79.68 (both s, $OC(CH_3)_3$), 100.16 (d, J_{CP} = 10.4, =CH), 105.94 (d, J_{CP} = 11.2, =CH), 118.87, 122.42 (both s, N*C*CH_3), 141.03 (d, J_{CP} = 4.3, IrC=*C*), 147.95 (d, J_{CP} = 12.2, Ir*C*=C), 163.06 (d, J_{CP} = 1.2, CO), 173.80 (d, J_{CP} = 3.0, CO).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(CO)(NCMe)(PMe_3)]BF_4 (4a). A 5 mL CH_2Cl_2 solution of **2** (164 mg, 0.24 mmol) was stirred under CO atmosphere (ca. 1 bar) for 10 min at room temperature. The resulting solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried: yield 148 mg (91%). Anal. Calcd (%) for $C_{20}H_{30}BF_4IrNO_5P$: C, 35.62; H, 4.48; N, 2.08. Found: C, 35.87; H, 4.43; N, 1.92. MS (FAB+, *m*/*z* (%)): 547 (20) [M^+ − NCMe], 519 (60) [M^+ − NCMe − CO]. IR (KBr, cm^{-1}): 2331 ν(N≡C), 2058 ν(C≡O), 1703 ν(OCO), 1059 ν(BF_4). ^{1}H NMR (CD_2Cl_2): δ 1.70 (m, 1H, CH_2), 1.79 (d, J_{HP} = 11.7, 9H, PCH_3), 2.02 (m, 2H, CH_2), 2.20 (m, 1H, CH_2), 2.30, 2.45 (both m, 2H each, CH_2), 2.65 (m, 1H, IrCH), 2.67 (s, 3H, $NCCH_3$), 3.20 (m, 1H, CH), 3.63, 3.75 (both s, 3H each, OCH_3), 5.65, 6.27 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −24.15 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 3.62 (s, NC*C*H_3), 13.94 (d, J_{CP} = 43.8, PCH_3), 21.95, 26.46 (both s, CH_2), 34.49 (d, J_{CP} = 2.7, IrCH), 37.65, 37.68 (both s, CH_2), 46.50 (s, CH), 51.39, 51.62 (both s, OCH_3), 104.56 (d, J_{CP} = 8.3, =CH), 112.36 (d, J_{CP} = 10.1, =CH), 124.45 (s, N*C*CH_3), 139.57 (d, J_{CP} = 11.0, Ir*C*=C), 143.81 (d, J_{CP} = 3.6, IrC=*C*), 163.74 (s, CO), 169.66 (d, J_{CP} = 4.2, IrCO), 174.76 (s, CO).

[Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})-(CO)(NCMe)(PMe_3)]BF_4 (4b). A 0.5 mL CD_2Cl_2 solution of **4a** (65 mg, 0.10 mmol) in a NMR tube was heated at 323 K for 20 h. The NMR monitoring of the resulting solution revealed the quantitative transformation of the precursor complex into its isomer **4b**. MS (FAB, *m*/*z* (%)): 547 (13), [M^+ − NCMe], 519 (100) [M^+ − NCMe − CO]. IR (CD_2Cl_2, cm^{-1}): 2061 ν(C≡O), 1708 ν(OCO). ^{1}H NMR (CD_2Cl_2): δ 1.61 (m, 2H, CH_2), 1.77 (d, 9H, J_{HP} = 11.6, PMe_3), 1.98, 2.06, 2.26, 2.29 (all m, 1H each, CH_2), 2.30 (s, 3H, NCC*H*$_3$), 2.37, 2.63 (m, 1H, IrCH), 2.73 (both m, 1H each, CH_2), 2.78 (m, 1H, CH), 3.58, 3.66 (both s, 3H each, OCH_3), 4.80, 6.25 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −27.78 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 2.88 (s, NC*C*H_3), 14.47 (d, J_{CP} = 43.7, PCH_3), 21.83 (d, J_{CP} = 1.3, CH_2), 22.13 (s, CH_2), 24.30 (d, J_{CP} = 1.6, IrCH), 25.89 (s, CH_2), 43.18 (d, J_{CP} = 1.7, CH_2), 49.08 (d, J_{CP} = 1.5, CH), 51.36, 51.50 (both s, OCH_3), 99.13 (d, J_{CP} = 10.4, =CH), 104.99 (d, J_{CP} = 8.2, =CH), 120.72 (s, N*C*CH_3), 141.59 (d, J_{CP} = 4.6, IrC=*C*), 158.55 (d, J_{CP} = 13.2, Ir*C*=C), 163.23 (d, J_{CP} = 1.4, CO), 172.64 (d, J_{CP} = 8.9, IrCO), 174.18 (d, J_{CP} = 2.9, CO).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(NCMe)($PMe_3)_2$]BF_4 (5a). To a 5 mL CH_2Cl_2 solution of **2** (151 mg, 0.22 mmol) was added trimethylphosphine (28 μL, 0.26 mmol) using a microsyringe. The reaction mixture was stirred at room temperature for 5 min, after which it was concentrated to ca. 0.5 mL. The addition of diethyl ether produced a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 142 mg (81%). Anal. Calcd (%) for $C_{22}H_{39}BF_4IrNO_4P_2$: C, 36.57; H, 5.44; N, 1.94. Found: C, 36.25; H, 5.28; N, 1.91. MS (FAB+, *m*/*z* (%)): 595 (60) [M^+ − NCMe], 519 (78) [M^+ − NCMe − PMe_3]. IR (KBr, cm^{-1}): 2290 ν(N≡C), 1696 ν(OCO), 1060 ν(BF_4). ^{1}H NMR (CD_2Cl_2, 253 K): δ 1.33 (d, J_{HP} = 8.0, 9H, PCH_3), 1.60 (m, 1H, CH_2), 1.61 (d, J_{HP} = 10.8, 9H, PCH_3), 1.89, 2.03, 2.07, 2.18 (all m, 1H each, CH_2), 2.40 (m, 2H, CH_2), 2.45 (m, 1H, CH_2), 2.52 (m, 1H, IrCH), 2.64 (s, 3H, $NCCH_3$), 3.05 (m, 1H, CH), 3.59, 3.68 (both s, 3H each, OCH_3), 5.21, 5.68 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 253 K): δ −53.07, −29.05 (both d, J_{PP} = 5.6). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 3.94 (s, $NCCH_3$), 14.50 (d, J_{CP} = 25.3, PCH_3), 14.74 (dd, J_{CP} = 42.4, 2.5, PCH_3), 21.61, 22.29 (both s, CH_2), 26.71 (d, J_{CP} = 6.5, CH_2), 30.81 (dd, J_{CP} = 72.5, 2.7, IrCH), 37.55 (d, J_{CP} = 2.1, CH_2), 45.90 (d, J_{CP} = 5.0, CH), 51.50, 51.83 (both s, OCH_3), 100.20 (d, J_{CP} = 9.06, =CH), 105.69, (d, J_{CP} = 11.1, =CH), 122.99 (s, $NCCH_3$), 143.09 (dd, J_{CP} = 10.5, 3.9, Ir*C*=C), 145.34 (d, J_{CP} = 13.8, IrC=*C*), 163.73 (d, J_{CP} = 1.1, CO), 177.05 (dd, J_{CP} = 6.3, 3.1, CO).

[Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})($CO)_2$(PMe_3)]BF_4 (6). Method A: CO was bubbled during 1 min through a 0.5 mL CD_2Cl_2 solution of **4b** (45 mg, 0.07 mmol) in a NMR tube. Method B: A 5 mL CH_2Cl_2 solution of **2** (155 mg, 0.22 mmol) was placed under an atmosphere of CO (ca. 1 bar) and heated for 20 h at 323 K. The resulting solution was dried to give a yellow residue. MS (FAB+, *m*/*z* (%)): 547 (65) [$M^+ - CO$], 519 (100) [$M^+ - 2CO$]. IR (KBr, cm^{-1}): 2118, 2084 ν(C≡O), 1695 ν(OCO), 1024 ν(BF_4). ^1H NMR (CD_2Cl_2): δ 1.79 (m, 2H, CH_2), 2.04 (d, 9H, J_{HP} = 11.7, PMe_3), 2.26, 2.31 (both m, 1H each, CH_2), 2.57 (m, 2H, CH_2), 2.72, 2.77 (both m, 1H, CH_2), 2.81 (m, 1H, IrCH), 3.34 (m, 1H, CH), 3.70, 3.80 (both s, 3H each, OCH_3), 5.47, 6.65 (both m, 1H each, =CH). $^{31}P\{^1H\}$ (CD_2Cl_2): δ −25.14 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.13 (d, J_{CP} = 44.7, PCH_3), 19.07, 24.08 (both s, CH_2), 31.52 (s, IrCH), 40.75 (d, J_{CP} = 1.9, CH_2), 46.34 (s, CH), 49.15, 49.38 (both s, OCH_3), 96.89 (d, J_{CP} = 8.0, =CH), 106.86 (d, J_{CP} = 6.0, =CH), 142.97 (d, J_{CP} = 12.0, Ir*C*≡C), 144.48 (d, J_{CP} = 4.2, IrC=*C*), 160.74 (d, J_{CP} = 3.2, IrCO), 161.42 (d, J_{CP} = 0.8, CO), 164.65 (d, J_{CP} = 7.8, IrCO), 171.87 (d, J_{CP} = 2.3, CO).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})($PMe_3)_3$]BF_4 (7). To a 5 mL CH_2Cl_2 solution of **2** (147 mg, 0.22 mmol) was added trimethylphosphine (57 μL, 0.53 mmol) using a microsyringe. The reaction mixture was stirred at room temperature for 5 min, after which it was concentrated to ca. 0.5 mL. The addition of diethyl ether produced a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 146 mg (90%). Anal. Calcd (%) for $C_{23}H_{45}BF_4IrO_4P_3$: C, 36.47; H, 5.99. Found: C, 36.79; H, 6.20. MS (FAB+, *m*/*z* (%)): 595 (56) [$M^+ - PMe_3$]. IR (KBr, cm^{-1}): 1697 ν(OCO), 1060 ν(BF_4). ^1H NMR (CD_2Cl_2): δ 1.33 (d, J_{HP} = 7.6, 9H, PCH_3), 1.73 (d, J_{HP} = 9.6, 9H, PCH_3), 1.92 (d, J_{HP} = 8.0, 9H, PCH_3), 1.5−2.6 (m, CH_2 + IrCH + CH), 3.66, 3.70 (both s, 3H each, OCH_3), 4.33, 5.01 (both m, 1H each, =CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −37.94 (dd, J_{PP} = 26.5, 3.9), −61.87 (dd, J_{PP} = 14.4, 3.9), −62.38 (dd, J_{PP} = 26.5, 14.4).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ²-*N*-bipy)(PMe_3)]BF_4 (8). To a 5 mL CH_2Cl_2 solution of **2** (134 mg, 0.19 mmol) was added 2,2′-bipyridine (30 μL, 0.19 mmol). The reaction mixture was stirred at room temperature for 20 h, after which it was concentrated to ca. 0.5 mL. The addition of diethyl ether produced a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 99 mg (67%). Anal. Calcd (%) for $C_{27}H_{35}BF_4IrN_2O_4P$: C, 42.58; H, 4.63; N, 3.68. Found: C, 42.56; H, 4.73; N, 3.70. MS (MALDI+, *m*/*z*): 675 [M^+]. ^1H NMR (CD_2Cl_2): δ 1.07 (d, J_{HP} = 10.8, 9H, PCH_3), 1.29, 1.48, 1.70, 1.75, 2.08, 2.39, 2.56, 2.62 (all m, 1H each, CH_2), 2.80 (m, 1H, CH), 2.94 (m, 1H, IrCH), 3.71, 3.91 (both s, 3H each, OCH_3), 4.26, 4.43 (both m, 1H each, =CH), 7.66 (dd, J_{HH} = 8.0, 5.2, 1H, CH), 7.86 (dd, J_{HH} = 8.0, 5.6, 1H, CH), 8.23 (dd, J_{HH} = 8.0, 8.0, 1H, CH), 8.35 (dd, J_{HH} = 8.0, 8.0, 1H, CH), 8.52 (d, J_{HH} = 5.6, 1H, CH), 8.57 (d, J_{HH} = 8.0, 1H, CH), 8.68 (d, J_{HH} = 8.0, 1H, CH), 9.17 (d, J_{HH} = 5.2, 1H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2,): δ −28.76 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.93 (d, J_{CP} = 40.5, PCH_3), 16.37 (d, J_{CP} = 3.2, IrCH), 21.73, 22.03, 25.37, 35.93 (all s, CH_2), 49.76 (s, CH), 51.39, 51.64 (both s, OCH_3), 94.31 (d, J_{CP} = 11.0, =CH), 102.78 (d, J_{CP} = 12.8, =CH), 124.78, 125.74, 127.96, 128.26, 139.92, 140.81 (all s, CH), 143.09 (d, J_{CP} = 4.1, IrC=*C*), 147.08 (d, J_{CP} = 13.8, Ir*C*=C), 150.35, 154.09 (both s, CH), 155.82, 156.82 (both s, C), 164.36 (d, J_{CP} = 1.8, CO), 176.21 (d, J_{CP} = 3.7, CO).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(C≡CPh)(NCMe)(PMe_3)] (9). To a 5 mL THF solution of **2** (124 mg, 0.18 mmol) was added lithium phenylacetylide (23 mg, 0.20 mmol). The reaction mixture was stirred at 273 K for 90 min, after which some drops of wet acetone were added to destroy the acetylide excess. The resulting suspension was dried, and the residue was dissolved in CH_2Cl_2, filtered through Celite, and dried again. The residue was treated with a mixture of toluene/hexane at 273 K to form a yellow solid, which was separated by decantation, washed with hexane, and dried: yield 78 mg (66%). Anal. Calcd (%) for $C_{27}H_{35}IrNO_4P$: C, 49.07; H, 5.34; N, 2.11. Found: C, 48.98; H, 5.17; N, 2.01. MS (MALDI+, *m*/*z*): 620 [M^+ − NCMe]. IR (KBr, cm^{-1}): 2218 ν(N≡C), 2099 ν(C≡C), 1690 (ν(OCO). ^1H NMR (CD_2Cl_2, 253 K): δ 1.40 (m, 1H, CH_2), 1.53 (m, 2H, CH_2), 1.65 (d, J_{HP} = 10.9, 9H, PCH_3), 1.89 (m, 1H, CH_2), 2.19 (m, 3H, 2 CH_2 + IrCH), 2.22 (s, 3H, $NCCH_3$), 2.45, 2.53 (both m, 1H each, CH_2), 2.65 (m, 1H, CH), 3.59, 3.71 (both s, 3H each, OCH_3), 3.87, 5.48 (both m, 1H each, =CH), 7.22 (m, 5H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 253 K): δ −30.55 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 253 K): δ 3.39 (s, $NCCH_3$), 13.13 (d, J_{CP} = 41.4, PCH_3), 17.04 (d, J_{CP} = 3.3, IrCH), 21.34, 22.60, 26.94 (all s, CH_2), 40.38 (d, J_{CP} = 2.3, CH_2), 49.47 (s, CH), 50.50, 50.90 (both s, OCH_3), 79.60 (d, J_{CP} = 12.4, =CH), 95.40 (d, J_{CP} = 14.0, =CH), 96.56 (d, J_{CP} = 20.2, Ir*C*≡CPh), 105.56 (d, J_{CP} = 1.7, IrC≡*C*Ph), 114.56 (s, N*C*CH_3), 127.97 (s, CH), 129.88 (s, C), 130.75 (s, CH), 137.37 (d, J_{CP} = 3.2, IrC=*C*), 164.01 (s, CO), 172.76 (d, J_{CP} = 11.9, Ir*C*=C), 178.02 (s, CO). The crystals used in the X-ray experiment were obtained from a CH_2Cl_2 solution of **9** layered with hexane, at room temperature.

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ²-*O*-acac)(PMe_3)] (10). To a 5 mL acetone solution of **2** (309 mg, 0.45 mmol) was added potassium acetylacetonate (62 mg, 0.45 mmol). The reaction mixture was stirred at room temperature for 2 h, after which it was taken to dryness. The residue was dissolved in toluene and filtered through Celite. The resulting solution was concentrated to ca. 0.5 mL and treated with hexane to give a yellow solid. The solid was separated by decantation, washed with hexane, and dried: yield 151 mg (54%). Anal. Calcd (%) for $C_{22}H_{34}IrO_6P$: C, 42.78; H, 5.55. Found: C, 42.56; H, 5.83. MS (FAB+, *m*/*z* (%)): 618 (100) [M^+], 542 (90) [$M^+ - PMe_3$]. IR (KBr, cm^{-1}): 1706, 1677 ν(OCO), 1583, 1517 ν(acac). ^1H NMR ($CDCl_3$): δ 1.20 (m, 1H, CH_2), 1.34 (d, J_{HP} = 11.1, 9H, PCH_3), 1.53, 1.64 (both m, 1H each, CH_2), 1.69, 1.81 (both s, 3H each, CH_3), 2.03 (m, 2H, CH_2), 2.12, 2.18, 2.31 (all m, 1H each, CH_2), 2.61 (m, 1H, IrCH), 2.68 (m, 1H, CH), 3.63, 3.76 (both s, 3H each, OCH_3), 4.64 (m, 1H, =CH), 5.07 (s, 1H, CH), 5.22 (m, 1H, =CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.50 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.65 (d, J_{CP} = 38.8, PCH_3), 13.15 (d, J_{CP} = 3.3, IrCH), 22.38 (d, J_{CP} = 1.4, CH_2), 22.78 (s, CH_2), 25.96 (d, J_{CP} = 0.9, CH_2), 28.11, 28.21 (both s, CH_3), 36.61 (d, J_{CP} = 2.0, CH_2), 48.63 (s, CH), 50.59, 50.81 (both s, OCH_3), 99.26 (d, J_{CP} = 11.5, =CH), 99.47 (s, CH), 108.77 (d, J_{CP} = 13.6, =CH), 137.11 (d, J_{CP} = 2.9, IrC=*C*), 157.32 (d, J_{CP} = 11.2, Ir*C*=C), 163.54 (d, J_{CP} = 1.1, CO), 177.19 (d, J_{CP} = 3.3, CO), 183.72, 187.01 (both s, CO).

Preparation of [Ir(1-κ-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ²-*O*-acac)(CO)(PMe_3)] (11). CO was bubbled during 2 min through a 5 mL toluene solution of **10** (105 mg, 0.17 mmol). The reaction was stirred at room temperature for 5 days, after which it was concentrated to ca. 0.5 mL and treated with hexane. The yellow solid formed was separated by decantation, washed with hexane, and dried: yield 68 mg (62%). IR (KBr, cm^{-1}): 2012 ν(C≡O), 1704, 1691 ν(OCO), 1579, 1514 ν(acac). ^1H NMR (CD_2Cl_2): δ 1.35 (m, 1H, CH_2), 1.56 (d, J_{HP} = 11.4, 9H, PCH_3), 1.75 (m, 1H, CH_2), 1.93 (s, 3H, CH_3), 1.95 (m, 1H, CH_2), 1.98 (s, 3H, CH_3), 2.03, 2.10, 2.18, 2.51 (all m, 1H each CH_2), 2.60 (s, 1H, IrCH), 2.66 (m, 1H, CH_2), 3.62, 3.74 (both s, 3H each, OCH_3), 3.94 (s, 1H, CH), 5.39 (s, 1H, CH), 5.48, 5.73 (both m, 1H each, =CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −33.92 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 12.44 (d, J_{CP} = 43.9, PCH_3), 25.73 (s, CH_2), 26.90 (d, J_{CP} = 6.4, CH_3), 27.41 (s, CH_2), 27.53 (s, CH_3), 33.45 (d, J_{CP} = 1.8, CH_2), 33.83 (s, CH_2), 42.01 (d, J_{CP} = 4.4, IrCH), 48.33 (s, CH), 50.62, 50.83 (both s, OCH_3), 100.70 (s, CH), 126.28, 132.20 (both s, =CH), 142.64 (d, J_{CP} = 9.3, Ir*C*=C), 146.60 (s, IrC=*C*), 164.14 (s, CO), 175.19 (d, J_{CP} = 4.8, IrCO), 176.99 (s, CO), 186.00 (d, J_{CP} = 4.0, CO), 186.45 (s, CO). The crystals used in the X-ray experiment were obtained by slow evaporation at room temperature of a solution of **11** in toluene.

Preparation of [Ir(1-κ-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ²-*O*-acac)(PMe_3)₂] (12). To a 5 mL toluene solution of **10** (96 mg, 0.15 mmol) was added trimethylphosphine (16 μL, 0.15 mmol) using a microsyringe. The reaction mixture was stirred at 353 K for 3 h, after which it was concentrated to ca. 0.5 mL and treated with hexane. The yellow solid formed was separated by decantation, washed with hexane, and dried: yield 69 mg (65%). Anal. Calcd (%) for $C_{25}H_{43}IrO_6P_2$: C, 43.28; H, 6.25. Found: C, 43.33; H, 6.31. MS (FAB+, *m*/*z* (%)): 692 (15) [M^+]. IR (KBr, cm^{-1}): 1707, 1680 ν(OCO), 1583, 1517 ν(acac). ^{1}H NMR (toluene-d_8): δ 0.98 (d, J_{HP} = 7.7, 9H, PCH_3), 1.17 (d, J_{HP} = 10.6, 9H, PCH_3), 1.52 (s, 3H, CH_3), 1.58 (m, 1H, CH_2), 1.64 (s, 3H, CH_3), 2.05 (m, 1H, CH_2), 2.45 (m, 3H, CH_2), 2.58, 2.82, 3.00 (all m, 1H each, CH_2), 2.80 (m, 1H, IrCH), 3.44, 3.57 (both s, 3H each, OCH_3), 4.18 (m, 1H, CH), 4.98 (s, 1H, CH), 5.70, 5.90 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (toluene-d_8): δ −38.16, −31.23 (both d, J_{PP} = 4.9). ^{13}C{^{1}H} NMR (toluene-d_8): δ 13.17 (dd, J_{CP} = 41.6, 3.2, PCH_3), 14.27 (d, J_{CP} = 19.7, PCH_3), 26.51 (s, CH_2), 26.81 (d, J_{CP} = 6.2, CH_3), 27.46 (s, CH_3), 28.80 (d, J_{CP} = 2.6, CH_2), 34.23 (d, J_{CP} = 1.9, CH_2), 34.65 (d, J_{CP} = 11.7, CH_2), 37.85 (dd, J_{CP} = 92.7, 4.3, IrCH), 48.02 (d,. J_{CP} = 4.9, CH), 49.92, 50.03 (both s, OCH_3), 100.75 (s, CH), 126.49, 132.07 (both s, =CH), 146.45 (d, J_{CP} = 9.8, IrC=*C*), 146.71 (d, J_{CP} = 10.3, Ir*C*=C), 163.65 (s, CO), 179.12 (d, J_{CP} = 2.3, CO), 182.79, 183.12 (both s, CO).

[Ir(1-κ-5,6,7-η-C_8H_{11}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(CO)(PMe_3)] (13). A 5 mL toluene solution of **11** (35 mg, 0.05 mmol) was placed under an atmosphere of CO (ca. 1 bar) and heated for 48 h. at 353 K. The resulting solution was dried to give a yellow residue, which was studied without further purification. MS (FAB+, *m*/*z* (%)): 546 (92) [M^+], 517 (100) [M^+ − CO]. IR (CH_2Cl_2, cm^{-1}): 1991 ν(C≡O), 1701 ν(OCO). ^{1}H NMR (C_6D_6): δ 1.23 (d, J_{HP} = 9.8, 9H, PCH_3), 2.10, 2.65, 2.72, (all m, 1H each, CH_2), 2.78 (m, 2H, CH_2), 3.05 (m, 1H, IrCH), 3.25 (m, 1H, CH), 3.52 (s, 3H, OCH_3), 3.59 (m, 1H, CH), 3.65 (m, 1H, CH_2), 3.73 (s, 3H, OCH_3), 5.88, 6.10 (both m, 1H each, CH). ^{31}P{^{1}H} NMR (C_6D_6): δ −59.24 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.60 (d, J_{CP} = 30.1, PCH_3), 23.71, 28.20 (both s, CH_2), 29.54 (d, J_{CP} = 3.3, CH_2), 43.08 (d, J_{CP} = 21.2, CH), 45.63 (d, J_{CP} = 6.2, IrCH), 50.08 (s, OCH_3), 50.32 (s, CH), 50.59 (s, OCH_3), 130.72 (s, CH), 135.80 (d, J_{CP} = 8.2, CH), 141.19 (d, J_{CP} = 8.8, IrC=*C*), 149.79 (d, J_{CP} = 14.1, Ir*C*=C), 164.78 (d, J_{CP} = 3.0, CO), 173.07 (d, J_{CP} = 6.5, IrCO), 177.10 (s, CO).

Preparation of [Ir(1-κ-5,6-η-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})H(NCMe)(PMe_3)] (14). To a 5 mL methanol solution of **2** (111 mg, 0.16 mmol) was added 90 μL of another methanol solution of KOH (1.67 M, 0.16 mmol). The reaction mixture was stirred at 248 K for 15 min and dried. The residue was dissolved in CH_2Cl_2, filtered through Celite, and dried again. The new residue was treated with a mixture of toluene/hexane to form a yellow solid, which was separated by decantation, washed with hexane, and dried: yield 85 mg (94%). Anal. Calcd (%) for $C_{19}H_{31}IrNO_4P$: C, 40.70; H, 5.57; N, 2.49. Found: C, 40.21; H, 5.29; N, 2.35. MS (MALDI+, *m*/*z*): 519 [M^+ − NCMe]. IR (KBr, cm^{-1}): 1960 ν(IrH), 1690 ν(OCO). ^{1}H NMR (CD_2Cl_2, 253 K): δ −11.58 (d, J_{HP} = 26.7, 1H, IrH), 1.39, 1.52 (both m, 2H, each, CH_2), 1.56 (d, J_{HP} = 10.4, 9H, PCH_3), 1.69 (m, 1H, IrCH), 2.03 (m, 2H, CH_2), 2.11 (s, 3H, $NCCH_3$), 2.26, 2.55 (both m, 1H each, CH_2), 2.60 (m, 1H, CH), 2.75 (m, 1H, =CH), 3.57, 3.69 (both s, 3H each, OCH_3) 4.75 (m, 1H, =CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 253 K): δ −34.52 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 3.10 (s, $NCCH_3$), 16.32 (d, J_{CP} = 3.7, IrCH), 16.41 (d, J_{CP} = 38.5, PCH_3), 20.90 (d, J_{CP} = 1.9, CH_2), 22.99, 29.63 (both s, CH_2), 42.82 (d, J_{CP} = 2.2, CH_2), 49.44 (s, CH), 50.14, 50.76 (both s, OCH_3), 59.83 (d, J_{CP} = 16.3, =CH), 69.62 (d, J_{CP} = 11.9, =CH), 113.98 (s, $NCCH_3$), 135.19 (d, J_{CP} = 3.4, IrC=*C*), 163.91 (d, J_{CP} = 2.0, CO), 178.58 (d, J_{CP} = 1.5, CO), 181.26 (d, J_{CP} = 12.2, Ir*C*=C).

Preparation of [Ir(1,5-κ-C_8H_{13}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(κ²-*N*-bipy)(PMe_3)] (15). To a 5 mL methanol solution of **2** (211 mg, 0.31 mmol) was added 180 μL of another methanol solution of KOH (1.67 M, 0.31 mmol). The reaction mixture was stirred at 248 K for 15 min and dried. The residue was dissolved in CH_2Cl_2, filtered through Celite, and treated with 2,2′-bipyridine (48 mg, 0.31 mmol). The reaction mixture was stirred for 10 min at room temperature, after which it was concentrated to ca. 0.5 mL and treated with hexane to give a dark red solid. The solid was separated by decantation, washed with hexane, and dried: yield 128 mg (62%). Anal. Calcd (%) for $C_{27}H_{36}IrN_2O_4P$: C, 47.99; H, 5.37; N, 4.15. Found: C, 47.75; H, 5.15; N, 3.93. MS (MALDI+, *m*/*z*): 675 [M^+ − H]. IR (KBr, cm^{-1}): 1700, 1670 ν(OCO). ^{1}H NMR ($CDCl_3$): δ 0.82 (d, J_{HP} = 7.7, 9H, PCH_3), 0.81 (m, 1H, CH_2), 0.94 (m, 1H, IrCH), 1.44 (m, 1H, CH_2), 1.53, 1.69 (m, 2H each, CH_2), 2.02 (m, 1H, CH_2), 2.24 (m, 2H, CH_2), 2.34 (m, 1H, CH_2), 3.04 (m, 1H, CH), 3.25 (m, 1H, IrCH), 3.65, 3.86 (both s, 3H each, OCH_3), 7.32, 7.38, 7.82, 7.89 (all m, 1H each, CH), 8.08 (d, J_{HH} = 3.7, 1H, CH), 8.11 (d, J_{HH} = 3.4, 1H, CH), 9.00 (d, J_{HH} = 5.5, 1H, CH), 9.33 (d, J_{HH} = 5.7, 1H, CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −45.48 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.42 (s, IrCH), 11.87 (d, J_{CP} = 23.3, PCH_3), 16.42 (d, J_{CP} = 76.6, IrCH), 26.14, 28.38 (both s, CH_2), 28.52 (d, J_{CP} = 1.9, CH_2), 33.01 (d, J_{CP} = 2.9, CH_2), 33.14 (d, J_{CP} = 3.2, CH_2), 50.51, 51.61 (both s, OCH_3), 54.33, 121.92, 122.35, 124.80, 125.62, 134.21, 135.12 (all s, CH), 138.51 (d, J_{CP} = 5.2, IrC=*C*), 150.89 (s, CH), 152.88 (d, J_{CP} = 0.8, CH), 156.37 (s, C), 157.16 (d, J_{CP} = 1.4, C), 162.56 (d, J_{CP} = 11.8, Ir*C*=C), 165.42 (d, J_{CP} = 2.7, CO), 180.95 (d, J_{CP} = 2.5, CO).

Preparation of [Ir(η⁵-C_5H_5)(1-κ-C_8H_{12}-2-*Z*-{2′-κ-C(CO_2Me)=C(CO_2Me)})(PMe_3)] (16). To a 5 mL acetone solution of **2** (131 mg, 0.19 mmol) was added cyclopentadienyl thallium (53 mg, 0.19 mmol). The reaction mixture was stirred at room temperature for 3 h, after which the resulting suspension was filtered through Celite and concentrated to ca. 0.5 mL. The addition of hexane gave a yellow solid, which was separated by decantation, washed with hexane, and dried: yield 67 mg (59%). Anal. Calcd (%) for $C_{22}H_{32}IrO_4P$: C, 45.27; H, 5.52. Found: C, 45.06; H, 5.22. MS (FAB+, *m*/*z* (%)): 584 (53) [M^+]. IR (KBr, cm^{-1}): 1699, 1688 ν(OCO). ^{1}H NMR (C_6D_6): δ 1.28 (d, J_{HP} = 10.6, 9H, PCH_3), 1.73, 1.93, 2.16, 2.22, 2.27, 2.64 (all m, 1H each, CH_2), 2.80 (m, 1H, IrCH), 2.85, 3.12 (both m, 1H each, CH_2), 3.53, 3.73 (both s, 3H each, OCH_3), 3.88 (m, 1H, CH), 4.96 (d, 5H, J_{HP} = 1.1, CH), 5.83, 5.94 (both m, 1H each, =CH). ^{31}P{^{1}H} NMR (C_6D_6): δ −31.33 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 16.93 (d, J_{CP} = 39.6, PCH_3), 25.80 (s, CH_2), 26.30 (d, J_{CP} = 5.9, IrCH), 30.53 (d, J_{CP} = 1.9, CH_2), 36.54, 40.82 (both s, CH_2), 50.19, 50.28 (both s, OCH_3), 51.26 (s, CH), 84.04 (d, J_{CP} = 3.2, CH), 125.77, 131.82 (both s, =CH), 143.95 (s, IrC=*C*), 151.72 (d, J_{CP} = 12.8, Ir*C*=C), 163.49 (d, J_{CP} = 1.4, CO), 177.85 (d, J_{CP} = 2.4, CO).

Preparation of [Ir(η⁵-C_5H_5)(1-κ-C_8H_{12}-2-*Z*-{1′,2′-η-C(CO_2Me)=CH(CO_2Me)})(PMe_3)]BF_4 (17). To a 5 mL CH_2Cl_2 solution of **16** (149 mg, 0.25 mmol) was added 35 μL of a diethyl ether solution of HBF_4 (54%, 0.25 mmol). The reaction mixture was stirred at room temperature for 10 min, after which it was concentrated to ca. 0.5 mL. The addition of diethyl ether gave a yellow solid, which was separated by decantation, washed with diethyl ether, and dried: yield 127 mg (75%). Anal. Calcd (%) for $C_{22}H_{33}BF_4IrO_4P$: C, 39.35; H, 4.95. Found: C, 39.24; H, 5.00. MS (FAB+, *m*/*z* (%)): 585 (55) [M^+]. ^{1}H NMR (CD_2Cl_2): δ 1.01 (m, 1H, IrCH), 1.46 (m, 1H, CH_2), 1.87 (d, J_{HP} = 10.8, 9H, PCH_3), 2.02, 2.16, 2.33, 2.35 (all m, 1H each, CH_2), 2.35 (m, 1H, CH), 2.43, 2.64, 2.68 (all m, 1H each, CH_2), 3.09 (d, J_{HP} = 13.8, 1H, C=C*H*(CO_2CH_3)), 3.71, 3.81 (both s, 3H each, OCH_3), 5.50, 5.74 (both m, 1H each, =CH), 5.80 (s, 5H, CH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −28.05 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ −14.25 (d, J_{CP} = 4.3, IrCH), 16.14 (d, J_{CP} = 43.1, PCH_3), 26.85, 27.40, 30.48, 36.66 (all s, CH_2), 39.98 (d, J_{CP} = 3.1, C=*C*H(CO_2CH_3)), 43.47 (d, J_{CP} = 4.1, *C*=CH(CO_2CH_3)), 50.78 (s, CH), 52.91, 53.49 (both s, OCH_3), 95.25 (d, J_{CP} = 1.4, CH), 128.18, 131.16 (both s, =CH), 169.05, 170.65 (both s, CO).

X-ray Crystallography. X-ray data were collected at 100.0(2) K on a Bruker SMART APEX CCD with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected

over the complete sphere by a combination of four sets. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[21] The structures were solved by the Patterson method and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL program package,[22] including isotropic and subsequently anisotropic displacement parameters. Weighted R factors (R_w) and goodness of fit (S) are based on F^2, and conventional R factors are based on F. Hydrogen atoms were calculated using a restricted riding model on their respective carbon atoms with the thermal parameter related to the bonded atom. All the highest electronic residuals were observed in close proximity to the Ir centers and make no chemical sense.

Crystal data for 2: $C_{21}H_{33}BF_4IrN_2O_4P\cdot CH_2Cl_2$, M = 709.35; colorless irregular block, 0.24 × 0.20 × 0.16 mm^3; monoclinic, $P2_1/c$; a = 18.5507(19) Å, b = 8.8012(9) Å, c = 17.5506(18) Å, β = 97.040(2)°; Z = 4; V = 2843.9(5) Å^3; D_c = 1.804 g cm^{-3}; μ = 4.996 mm^{-1}, minimum and maximum transmission factors 0.3802 and 0.5020; $2\theta_{max}$ = 57.74; 34 371 reflections collected, 6996 unique [R(int) = 0.0381]; number of data/restraints/parameters 6996/0/355; final GoF 0.942, R_1 = 0.0281 [5375 reflections $I > 2\sigma(I)$], wR_2 = 0.0584 for all data; largest difference peak 2.29 e Å^{-3}.

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(22) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *SHELXS-86 and SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

Crystal data for 9: $C_{27}H_{35}IrNO_4P\cdot CH_2Cl_2$, M = 745.66; colorless needle, 0.16 × 0.02 × 0.02 mm^3; monoclinic, $P2_1/c$; a = 11.4457(11) Å, b = 12.3481(12) Å, c = 20.3787(19) Å, β = 95.733(2)°; Z = 4; V = 2865.8(5) Å^3; D_c = 1.728 g cm^{-3}; μ = 4.936 mm^{-1}, minimum and maximum transmission factors 0.5056 and 0.9077; $2\theta_{max}$ = 58.02; 24 502 reflections collected, 6917 unique [R(int) = 0.0961]; number of data/restraints/parameters 6917/4/354; final GoF 0.630, R_1 = 0.0406 [3772 reflections $I > 2\sigma(I)$], wR_2 = 0.0640 for all data; largest difference peak 1.530 e Å^{-3}.

Crystal data for 11: $C_{23}H_{34}IrO_7P$, M = 645.67; colorless laminar prism, 0.18 × 0.10 × 0.06 mm^3; monoclinic, $P2_1/c$; a = 8.839(3) Å, b = 34.989(11) Å, c = 8.603(3) Å, β = 114.591(6)°; Z = 4; V = 2.419.3(13) Å^3; D_c = 1.773 g cm^{-3}; μ = 5.625 mm^{-1}, minimum and maximum transmission factors 0.4308 and 0.7289; $2\theta_{max}$ = 57.82°; 16 285 reflections collected, 5837 unique [R(int) = 0.0393]; number of data/restraints/parameters 5837/0/311; final GoF 0.817, R_1 = 0.0297 [4365 reflections $I > 2\sigma(I)$], wR_2 = 0.0430 for all data; largest difference peak 1.56 e Å^{-3}.

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Supporting Information Available: X-ray crystallographic file for complexes **2**, **9**, and **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.