Synthesis and Migratory Insertion Reactions of (Vinylidene)iridium Complexes *trans*-[IrX(=C=CRR′)(P*i*Pr$_3$)$_2$] Containing Alkyl, Aryl, Alkynyl, and Azide Ligands[†,1]

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The (vinylidene)iridium(I) complexes *trans*-[IrCl(=C=CRR′)(P*i*Pr$_3$)$_2$] (**1**, **4**) react with organolithium compounds R″Li by chloride substitution to afford the organoiridium(I) derivatives *trans*-[IrR″(=C=CRR′)(P*i*Pr$_3$)$_2$] (**5**−**8**) in excellent yields. In contrast, treatment of **1** (R = SiMe$_3$, R′ = Me) with Grignard reagents R″MgX leads to halide metathesis and formation of the bromo- and iodoiridium(I) compounds *trans*-[IrX{=C=C(SiMe$_3$)Me}(P*i*Pr$_3$)$_2$] (X = Br, I), respectively. The alkynyl complexes *trans*-[Ir(C≡CR)(=C=CHPh)(P*i*Pr$_3$)$_2$] (R = Ph, CO$_2$Me) are obtained by an acid−base reaction from *trans*-[Ir(OH)(=C=CHPh)(P*i*Pr$_3$)$_2$] and the free alkyne. Treatment of compounds **5**−**8** and **12** with CO initiates a migratory insertion process which gives the η^1-vinyl complexes *trans*-[Ir{η^1-(*Z*)-C(R″)=CRR′}(CO)(P*i*Pr$_3$)$_2$] (**13**−**17**) in nearly quantitative yields. Acid-induced cleavage of the Ir−C σ-bond of **13**, **14**, and **17** with CH$_3$CO$_2$H or CF$_3$CO$_2$H affords *trans*-[Ir(η^1-O$_2$CR)(CO)(P*i*Pr$_3$)$_2$] and the corresponding olefin. The preparation of the fluoroiridium(I) derivative *trans*-[IrF(=C=CHPh)(P*i*Pr$_3$)$_2$] (**26**) has been achieved either from *trans*-[Ir(OH)(=C=CHPh)(P*i*Pr$_3$)$_2$] and NEt$_3$·3HF or from *trans*-[Ir(η^1-O$_2$CCF$_3$)(=C=CHPh)(P*i*Pr$_3$)$_2$] and [*n*Bu$_4$N]F. The azidoiridium(I) compounds *trans*-[IrN$_3$(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, CO$_2$Me), which are obtained from the related chloro derivatives and excess NaN$_3$, undergo in the presence of CO a migratory insertion reaction to give the cyano-substituted alkyl complexes *trans*-[Ir{CH(CN)R}(CO)(P*i*Pr$_3$)$_2$] (**32**, **33**) and N$_2$. The molecular structure of *trans*-[Ir{η^1-(*Z*)-C(Me)=C(SiMe$_3$)Me}(CO)(P*i*Pr$_3$)$_2$] (**13**) has been determined by X-ray crystallography.

Introduction

Vinylidenes (:C=CRR′) as the thermodynamically less stable isomers of alkynes (RC≡CR′) are among the strongest π-acceptor ligands in organometallic chemistry.[2] However, despite the fact that the parent representative :C=CH$_2$ is isoelectronic with carbon monoxide, only a few examples of migratory insertion reactions of vinylidenes into metal−carbon σ-bonds, well-known for CO, have been reported.[3] In a continuation of our work on (vinylidene)rhodium(I) complexes,[4] we have recently shown that the reaction of *trans*-[Rh(R′)(=C=CHR)(P*i*Pr$_3$)$_2$] (where R′ is an alkyl, aryl, vinyl, or alkynyl ligand) with CO leads to the formation of (η^1-vinyl)rhodium(I) compounds *trans*-[Rh{η^1-(*Z*)-C(R′)=CHR}(P*i*Pr$_3$)$_2$] via C−C coupling of the R′ and C=CHR units.[5] Even in the absence of CO, the methyl and vinyl derivatives *trans*-[Rh(CH$_3$)(=C=CHR)(P*i*Pr$_3$)$_2$] and *trans*-[Rh(CH=CH$_2$)(=C=CHR)(P*i*Pr$_3$)$_2$] rearrange to give the isomeric η^3-allyl and (2−4)η^3-butadienyl complexes, respectively.[5b,6] Acid cleavage of the η^1-vinyl−Rh bond as well as of the η^3-allyl−Rh and (2−4)η^3-butadienyl−Rh bonds yields the respective olefin.

In this paper we describe our investigations on the reactivity of the (vinylidene)iridium(I) complexes *trans*-[IrCl(=C=CRR′)(P*i*Pr$_3$)$_2$] toward both Grignard reagents and organolithium compounds. Moreover, we illustrate not only that the methyl, phenyl, and alkynyl derivatives *trans*-[Ir(R″)(=C=CRR′)(P*i*Pr$_3$)$_2$] undergo in the presence of CO an intramolecular C−C coupling reaction but also that the hydroxo and the azido compounds *trans*-[IrX(=C=CRR′)(P*i*Pr$_3$)$_2$] (X = OH, N$_3$) can be used as starting materials for the preparation of iridium(I) complexes with an Ir−C σ-bond. A few of the results have already been communicated.[7]

[†] Dedicated to Professor William C. Kaska on the occasion of his 65th birthday.

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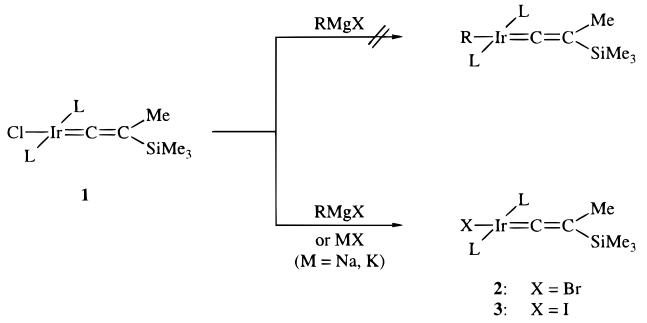
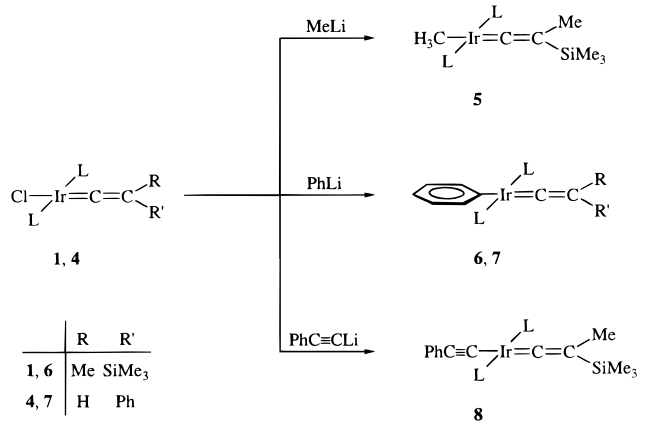
Scheme 1[a]



[a] In this scheme and all those that follow, L = P*i*Pr$_3$.

Scheme 2

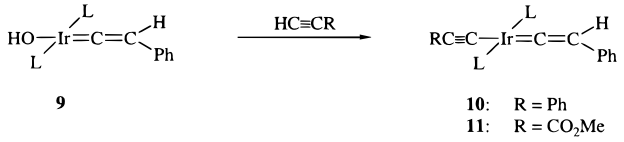


Results and Discussion

Preparation of Iridium(I) Complexes with an Ir−C *σ*-Bond. In contrast to the rhodium(I) compounds *trans*-[RhCl(=C=CRR′)(P*i*Pr$_3$)$_2$], which react with Grignard reagents R″MgX to give the substitution products *trans*-[Rh(R″)(=C=CRR′)(P*i*Pr$_3$)$_2$] in good to excellent yield,[5] treatment of the related iridium(I) complex **1** with CH_3MgI or CH_2=CHMgBr in ether or THF leads to halide exchange and to the formation of the bromo and iodo derivatives **2** and **3** (Scheme 1). These compounds are more conveniently prepared by salt metathesis from **1** and NaBr or KI, respectively. Both **2** and **3** are red-violet, moderately air-sensitive solids which have been characterized by elemental analysis and IR and NMR spectroscopy. The most characteristic features of **2** and **3** are the low-field signals in the ^{13}C NMR spectra at δ 247.5 and 88.5 (for **2**) and δ 242.8 and 88.3 (for **3**), which are assigned to the α-C and β-C vinylidene carbon atoms, respectively.

While the reaction of **1** with Grignard reagents CH_3MgI and CH_2=CHMgBr failed to give the Ir−CH_3 and Ir−CH=CH_2 derivatives, complexes of the general type *trans*-[Ir(R″)(=C=CRR′)(P*i*Pr$_3$)$_2$] were obtained from **1** or **4** and the corresponding organolithium compound in 70−85% isolated yield. In contrast to the starting materials **1** and **4**, the C-substitution products **5**−**8** (Scheme 2) are extremely air-sensitive and stable in solution only for a short period of time. The ^{1}H NMR spectrum of the methyliridium complex **5** displays a triplet resonance for the Ir−CH_3 protons at δ 0.96, which appears at the same chemical shift as for *trans*-[Ir(CH_3)(=C=CHPh)(P*i*Pr$_3$)$_2$].[3b] Despite the lability of **5** in solution, a rearrangement to a η^3-allyl isomer could not be observed.

Scheme 3



The phenyliridium complexes **6** and **7** are significantly more stable than the methyl derivative **5**, and therefore, ^{13}C NMR spectra could be measured in C_6D_6 at room temperature. The typical signals for the α-C and β-C vinylidene carbon atoms appear at δ 266.2 and 98.3 (for **6**) and δ 274.4 and 118.4 (for **7**), each of them being split into a triplet. A triplet pattern is also observed for the *ipso*-C atom of the metal-bonded phenyl group, similar to the situation in [IrH(C_6H_5)Cl(P*i*Pr$_3$)$_2$].[8]

(Vinylidene)iridium(I) complexes containing an additional alkynyl ligand are accessible on two different routes. Besides the substitution reaction of **1** with LiC≡CPh to give **8** (Scheme 2), the related compounds **10** and **11** are formed upon treatment of the hydroxoiridium(I) derivative **9**[3b] with the corresponding alkyne. In this context we note that despite the fact that hydroxometal complexes of d^8−d^{10} systems are still relatively rare,[9,10] work from our laboratory has recently shown that the Rh−OH linkage in mono- and dinuclear bis(phosphine)-rhodium(I) compounds can easily be cleaved by Brønsted acids.[11] The (alkynyl)iridium(I) complexes **10** and **11** are green, air-sensitive solids which are thermally rather labile and smoothly decompose in solution. Both the elemental analysis and the IR and NMR spectroscopic data leave no doubt that the structural proposal for **10** and **11** (see Scheme 3) is correct.

Studies of the Reactivity of Compounds 5−8 and 12. The reactions of the methyl-, phenyl- and (alkynyl)-iridium complexes **5**−**8** and **12**[3b] with carbon monoxide proceed similarly to those of the rhodium counterparts.[5] Passing a slow stream of CO through a solution of **5** or **12** in pentane led even at −78 °C to a quick change of color from violet to yellow and gave after chromatographic workup the four-coordinate iridium(I) complexes **13** and **14** in 77−86% isolated yield. In the same way, using the phenyl and phenylethynyl compounds **6**−**8** as starting materials, the related carbonyl vinyl derivatives **15**−**17** were obtained (Scheme 4). The IR spectra of the insertion products display a strong band at 1920−1930 cm^{-1}, which is assigned to a C≡O stretching frequency. Since in the ^{1}H NMR spectra of **14** and **16** the chemical shift of the signal of the vinylic =CH proton is quite similar to that found for the corresponding rhodium complexes *trans*-[Rh{η^1-(*Z*)-C(R)=CHPh}(CO)(P*i*Pr$_3$)$_2$],[5,12] we assume that the *Z* isomers of **14** and **16**, having the substituents R″ (Me, Ph) and R′ (Ph) in a *trans* orientation at the C=C bond, were exclusively formed. In the case of compound **14** this could be confirmed by measur-

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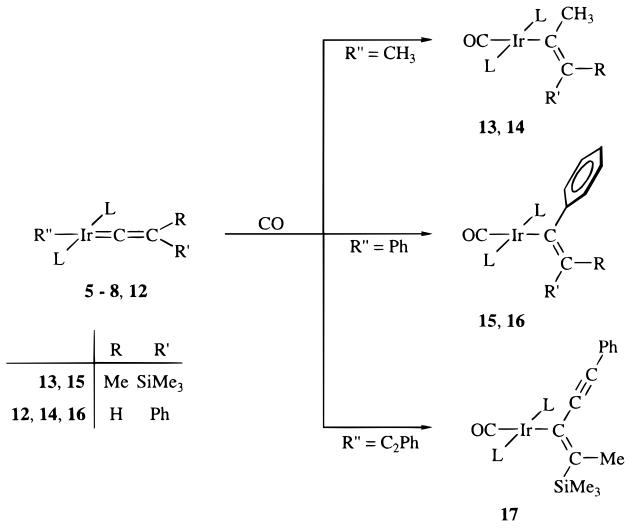
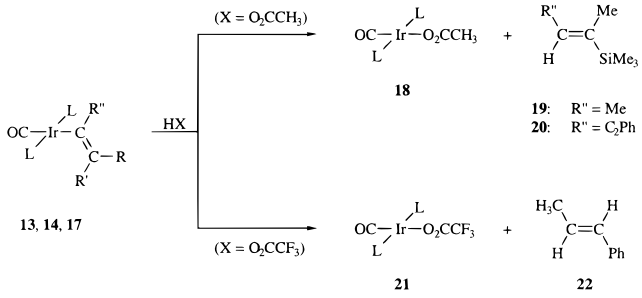
Scheme 4



Scheme 5



ing NOE spectra, which reveal on irradiation at δ 6.27 an NOE effect at δ 1.94 and vice versa. With regard to the mechanism of formation of the vinylic compounds **13**−**17** we assume that the attack of the CO at the metal center of the starting materials is accompanied by a concerted shift of the methyl, phenyl, or alkynyl group to the α-carbon atom of the vinylidene unit. We cannot exclude that a short-lived five-coordinate intermediate with a trigonal-bipyramidal geometry in which the metal center would have an 18-electron configuration is generated. Provided that the bulky phosphines are occupying the apical positions in this intermediate, the group R″ and the vinylidene ligand would approach each other, thus reducing the barrier for the C−C coupling process. The importance of steric factors probably explains why the migration of R″ is directed to that side of the Ir=C=CRR′ moiety which is opposite to phenyl or trimethylsilyl, respectively.

Indirect evidence for the stereochemical arrangement of the vinyl complexes, at least in the case of **13**, **14**, and **17**, is also provided by the acid cleavage reactions of these complexes in benzene (Scheme 5). Under mild conditions (25 °C), the olefins **19**, **20**, and **22**, with the two most bulky substituents in a *trans* disposition at the C=C bond, are formed together with the (acetato)- and (trifluoracetato)iridium(I) derivatives **18** and **21**. While compound **18** was known,[13] the Ir(O_2CCF_3) counterpart was not; it has been identified by IR as well as by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy. It should be mentioned that even after prolonged stirring at room temperature there is no rearrangement of **14** to the corresponding *Z* isomer.

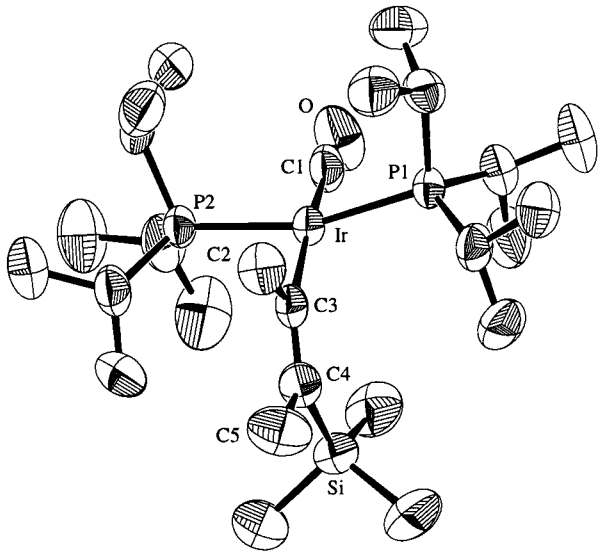
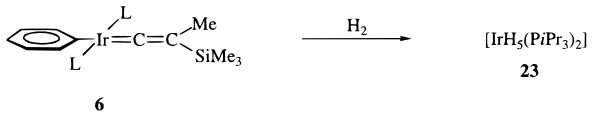


Figure 1. ORTEP diagram of compound **13**. Selected bond distances (Å) and angles (deg): Ir−P1 = 2.337(2), Ir−P2 = 2.331(2), Ir−C1 = 1.834(8), Ir−C3 = 2.115(7), C1−O = 1.168(8), C2−C3 = 1.527(9), C3−C4 = 1.36(1), C4−C5 = 1.55(1); P1−Ir−P2 = 163.07(6), P1−Ir−C1 = 88.4(2), P1−Ir−C3 = 93.5(2), P2−Ir−C1 = 87.8(2), P2−Ir−C3 = 92.6-(2), C1−Ir−C3 = 171.8(3), Ir−C1−O = 173.6(8), Ir−C3−C2 = 113.2(5), Ir−C3−C4 = 130.3(5), C2−C3−C4 = 116.5(6), C3−C4−C5 = 119.5(7), C3−C4−Si = 131.1(6), C5−C4−Si = 109.3(6).

Scheme 6



Attempts to hydrogenate the Ir−C double bond of compound **6** led to the cleavage of the phenyl−iridium linkage. When a slow stream of H_2 was passed through a solution of the starting material in pentane at −78 °C, an almost instant change of color from violet to pale yellow occurred, and after removal of the solvent and extraction of the residue with pentane the well-known pentahydrido complex **23** (Scheme 6) was isolated in excellent yield. The behavior of **6** is in contrast to that of the related (allenylidene)iridium(I) derivative *trans*-[IrCl(=C=C=CPh_2)(P*i*Pr_3)$_2$], which reacts with H_2 to afford the allene complex *trans*-[IrCl(η^2-H_2C=*C*=CPh_2)-(P*i*Pr_3)$_2$] without elimination of the hydrocarbon moiety.[14]

Molecular Structure of 13. To substantiate the proposed stereochemistry of the substituted vinyl complex **13**, an X-ray crystal structure analysis was carried out. The ORTEP drawing (Figure 1) reveals that the iridium is coordinated in a slightly distorted square-planar fashion. The two phosphine ligands are *trans* to each other with an eclipsed conformation along the P−Ir−P axis. This axis is not exactly linear, the angle P1−Ir−P2 of 163.07(6)° being similar to that in *trans*-[Rh{η^1-(*Z*)-C(CH=CH_2)=CHPh}(CO)(P*i*Pr_3)$_2$].[5] We assume that this bending is due to steric hindrance

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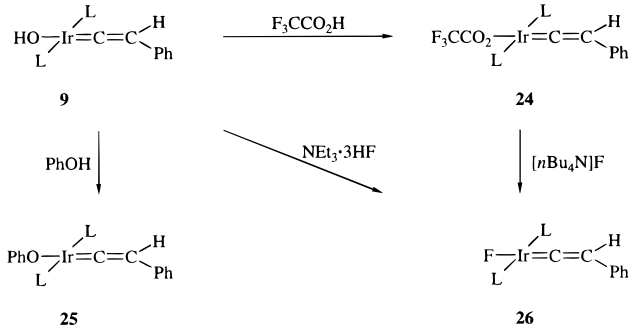
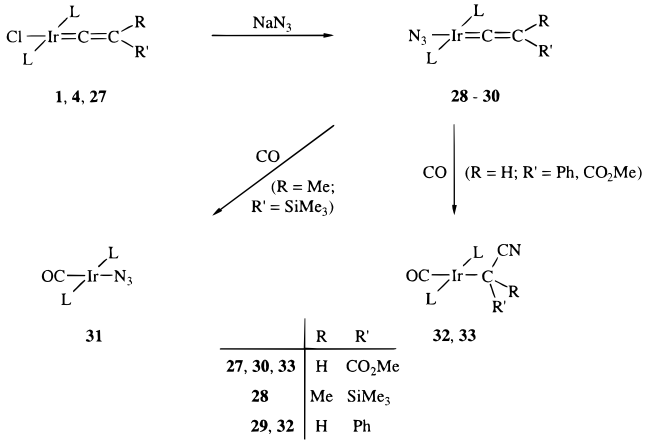
Scheme 7



Scheme 8



between the isopropyl groups and the substituents of the vinyl unit. The Ir−C3 distance of 2.115(7) Å is significantly longer than in the four-coordinate (vinylidene)iridium(I) complex *trans*-[IrCl(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$] (1.764(6) Å)[15] but comparable to the Ir−C bond lengths in [IrH(CH=CH$_2$)Cl(CO)(P*i*Pr$_3$)$_2$] (2.059(6) Å)[16] and [(η^5-C$_5$Me$_5$)IrH(CH=CH$_2$)(PMe$_3$)] (2.054(4) Å).[17]

Novel Fluoro- and Azidoiridium(I) Complexes. The recent discovery that the fluororhodium(I) compounds *trans*-[RhF(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, *t*Bu) are useful starting materials for the synthesis of a variety of organometallic rhodium(I) and rhodium(III) complexes[18] initiated our attempts to produce also an analogous iridium derivative. The fluoro vinylidene complex **26** can be prepared by two different routes (Scheme 7) using either **9** or **24** as the starting material. The hydroxo compound **9** reacts with an equimolar amount of NEt$_3$·3HF[19] in benzene by ligand exchange to afford **26** in 89% isolated yield. Alternatively, complex **9** can be converted with CF$_3$CO$_2$H to the trifluoroacetato derivative **24**, which upon treatment with [*n*Bu$_4$N]F gives **26**. The Ir−OH linkage of **9** is also cleaved by phenol to give the phenolato compound **25** in excellent yield. Both **25** and **26** (the trifluoracetato complex was already prepared using a different method)[13] are red-violet or red air-sensitive solids which are easily soluble in common organic solvents. Typical spectroscopic features of **25** and **26** are the single resonance in the ^{31}P NMR spectra (which in the case of **26** is split into a doublet due to P−F coupling) and the low-field signals in the ^{13}C NMR spectra assigned to the α-C and *β*-C atoms of the vinylidene ligand.

The chloroiridium derivatives **1**, **4**, and **27** react not only with NaBr and KI (see Scheme 1) but also with excess NaN$_3$ in acetone by salt metathesis to give the violet or red-violet azido complexes **28**−**30** in 86−90% yield (Scheme 8). The preparative procedure is quite similar to that used for the related rhodium compounds *trans*-[RhN$_3$(CO)(PR$_3$)$_2$] (R = Ph, Cy)[20] and *trans*-[RhN$_3$(=C=C=CRR′)(P*i*Pr$_3$)$_2$],[21] respectively. The IR spectra of **28**−**30** display a strong band at 2074−2080 cm^{-1}, which is characteristic for a metal-bonded N$_3$ unit.

The reactions of the azidoiridium complexes **28**−**30** with carbon monoxide take a different course. While the Ir=C=C(SiMe$_3$)Me derivative **28** behaves similarly to some chloro(vinylidene)rhodium compounds and affords upon treatment with CO by elimination of the free alkyne MeC≡CSiMe$_3$ the azido carbonyl complex **31** (Scheme 8), the Ir=C=CHR counterparts (R = Ph, CO$_2$Me) react with CO to give N$_2$ and the compounds **32** and **33** in nearly quantitative yields. The most characteristic features of the unexpected products are the triplet resonance for the IrCH proton in the ^{1}H NMR spectrum at *δ* 0.87 (for **32**) and 0.91 (for **33**) and the signal (also a triplet) for the CN carbon atom in the ^{13}C NMR spectra at *δ* 120.9 (for **32**) and 112.6 (for **33**), respectively. The IR spectra of the CN-functionalized alkyl complexes display two strong absorptions at 2279 and 1929 cm^{-1} (for **32**) and 2253 and 1938 cm^{-1} (for **33**), which are assigned to the CN and CO stretching frequencies. With regard to the mechanism of formation of **32** and **33**, we assume that the attack of CO at the iridium center of the starting material leads in the initial step to a migration of the azido ligand to the α-carbon atom of the vinylidene unit which is followed by elimination of N$_2$ and a 1,2-shift of the metal from α-C to *β*-C of the C$_2$ moiety. We note that the conversion of **29** and **30** to **32** and **33** is reminiscent of the formation of the cyano-substituted vinylrhodium(I) compounds *trans*-[Rh{C(CN)=CRR′}(CO)(P*i*Pr$_3$)$_2$], which are obtained upon treatment of the allenylidene complexes *trans*-[Rh(N$_3$)(=C=C=CRR′)(P*i*Pr$_3$)$_2$] with CO.[21]

Conclusions

The present investigations have shown that the substitution of the chloride ligand of the (vinylidene)iridium(I) complexes *trans*-[IrCl(=C=CRR′)(P*i*Pr$_3$)$_2$] by methyl, phenyl, and phenylethynyl can be achieved upon treatment with the corresponding organolithium derivative R″Li. In contrast, the reaction of *trans*-[IrCl{=C=C(SiMe$_3$)Me}(P*i*Pr$_3$)$_2$] with Grignard reagents

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RMgX (X = Br, I) leads only to halide exchange. An alternative procedure for the preparation of the alkynyl compounds *trans*-[Ir(C≡CR)(=C=CHPh)(P*i*Pr$_3$)$_2$] consists of the acid−base reaction of the hydroxo derivative *trans*-[Ir(OH)(=C=CHPh)(P*i*Pr$_3$)$_2$] with the free alkyne HC≡CR. A remarkable feature is that the complexes *trans*-[Ir(R″)(=C=CRR′)(P*i*Pr$_3$)$_2$] with R″ = Me, Ph, C≡CPh undergo in the presence of CO a migratory insertion reaction which leads selectively to the *Z* isomers of the (η^1-vinyl)iridium(I) compounds *trans*-[Ir{η^1-(*Z*)-C(R″)=CRR′)(CO)(P*i*Pr$_3$)$_2$]. Acid-induced cleavage of the Ir−C σ-bond of these compounds gives the respective olefin. Most interestingly, the related azido complexes *trans*-[IrN$_3$(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, CO$_2$Me), which are accessible from the chloro derivatives and NaN$_3$ by salt metathesis, also react with CO by migration of the azide ligand to the α-carbon atom of the vinylidene unit. Subsequent elimination of N$_2$ affords the novel cyano-substituted alkyl complexes *trans*-[Ir{CH(CN)R}(CO)-(P*i*Pr$_3$)$_2$] in excellent yield. This process supplements the recently reported preparation of the vinylrhodium(I) compounds *trans*-[Rh{C(CN)=CRR′}(CO)(P*i*Pr$_3$)$_2$], which are obtained by a migratory insertion reaction from the allenylidene complexes *trans*-[RhN$_3$(=C=C=CRR′)-(P*i*Pr$_3$)$_2$] and CO.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials [IrCl(C$_8$H$_{14}$)$_2$]$_2$,[22] **1**,[14] **4**,[3b] **12**,[3b] and **27**[15b] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 instruments at room temperature if not defined otherwise. IR spectra were recorded on a Bruker IFS 25 FT-IR and mass spectra on a Finnigan MAT 90 (70 eV) or on a Hewlett-Packard G1800 GCD-instrument. Melting points were measured by DTA. The term vt indicates a virtual triplet, and $N = {}^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})$ or ${}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})$.

Preparation of *trans*-[IrBr{=C=C(SiMe$_3$)Me}(P*i*Pr$_3$)$_2$] (2). (a) A solution of **1** (38 mg, 0.06 mmol) in 10 mL of acetone was treated with NaBr (50 mg, 0.48 mmol), and the mixture was stirred at room temperature for 6 days. A slight change of color from red-violet to violet occurred. The solvent was removed in vacuo, and the residue was extracted with 30 mL of pentane. The extract was brought to dryness in vacuo, the residue was dissolved in 2 mL of methanol, and the solution was stored at −78 °C. Red-violet crystals precipitated: yield 37 mg (91%).

(b) A solution of **1** (58 mg, 0.09 mmol) in 15 mL of THF was treated at −78 °C with a 1.3 M solution of CH$_2$=CHMgBr in THF (0.08 mL, 0.10 mmol). After it was warmed to room temperature, the solution was stirred for 3 h, which led to a change of color from red-violet to violet. The solution was then worked up as described for (a): yield 52 mg (84%); mp 85 °C. Anal. Calcd for C$_{24}$H$_{54}$BrIrP$_2$Si: C, 40.90; H, 7.72. Found: C, 41.11; H, 7.49. IR (hexane): ν(C=C) 1657 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 2.98 (m, 6 H, PC*H*CH$_3$), 2.18 (t, J(PH) = 1.8 Hz, 3 H, =C(CH$_3$)], 1.34 (dvt, N = 13.5, J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), 1.32 (dvt, N = 13.2 Hz, J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), 0.13 (s, 9 H, SiCH$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 247.5 (t, J(PC) = 12.2 Hz, Ir=*C*=C), 88.5 (t, J(PC) = 3.0 Hz, Ir=C=*C*), 23.5 (vt, N = 25.4 Hz, P*C*HCH$_3$), 20.5, 20.4 (both s, PCH*C*H$_3$), −1.1 (s, SiCH$_3$), −7.5 (s (br), =C(*C*H$_3$)). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 29.0 (s). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −26.7 (s).

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Preparation of *trans*-[IrI{=C=C(SiMe$_3$)Me}(P*i*Pr$_3$)$_2$] (3). (a) A solution of **1** (49 mg, 0.07 mmol) in 10 mL of acetone was treated with KI (81 mg, 0.5 mmol), and the mixture was stirred for 5 days at room temperature. A change of color from red-violet to violet occurred. The solution was then worked up as described for **2** to give a red-violet, microcrystalline solid: yield 50 mg (89%).

(b) A solution of **1** (45 mg, 0.07 mmol) in 10 mL of ether was treated at −78 °C with a 0.9 M solution of MeMgI in ether (0.6 mL, 0.08 mmol). After it was warmed to room temperature, the solution was stirred for 3 h, which led to a change of color from red-violet to violet. The solution was then worked up as described for **2**: yield 42 mg (79%); mp 73 °C. Anal. Calcd for C$_{24}$H$_{54}$IIrPSi: C, 38.34; H, 7.23. Found: C; 38.53; H; 7.10. IR (hexane): ν(C=C) 1654 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 3.08 (m, 6 H, PC*H*CH$_3$), 2.19 (t, J(PH) = 2.0 Hz, 3 H, =C(CH$_3$)), 1.33 (dvt, N = 14.2, J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), 1.31 (dvt, N = 13.6, J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), 0.11 (s, 9 H, SiCH$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 242.8 (t, J(PC) = 12.1 Hz, Ir=*C*=C), 88.3 (t, J(PC) = 3.0 Hz, Ir=C=*C*), 24.7 (vt, N = 26.7 Hz, P*C*HCH$_3$), 20.7, 20.6 (both s, PCH*C*H$_3$), −1.2 (s, SiCH$_3$), −7.8 (br s, =C*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 27.0 (s).

Preparation of *trans*-[Ir(CH$_3$){=C=C(SiMe$_3$)Me}-(P*i*Pr$_3$)$_2$] (5). A solution of **1** (82 mg, 0.12 mmol) in 15 mL of hexane was treated at −78 °C with a 0.75 M solution of methyllithium in hexane (0.17 mL, 0.12 mmol). A change of color from red-violet to violet occurred. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. The residue was extracted with 40 mL of pentane, and the solution was concentrated to 1 mL and stored at −78 °C. After 15 h violet crystals precipitated, which were washed twice with small amounts of acetone (1 mL) and dried: yield 56 mg (71%); mp 54 °C dec. Anal. Calcd for C$_{25}$H$_{57}$-IrP$_2$Si: C, 46.92; H, 8.98. Found: C, 47.09; H, 8.77. IR (hexane): ν(C=C) 1606 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 2.74 (m, 6 H, PC*H*CH$_3$), 2.21 (t, J(PH) = 1.8 Hz, 3 H, =C(CH$_3$)), 1.33 (dvt, N = 13.1, J(HH) = 6.6 Hz, 18 H, PCHC*H*$_3$), 1.26 (dvt, N = 13.3 Hz, J(HH) = 6.8 Hz, 18 H, PCHC*H*$_3$), 0.96 (t, J(PH) = 5.8 Hz, 3 H, IrCH$_3$), 0.18 (s, 9 H, SiCH$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 29.7 (s).

Preparation of *trans*-[Ir(C$_6$H$_5$){=C=C(SiMe$_3$)Me}-(P*i*Pr$_3$)$_2$] (6). A solution of **1** (89 mg, 0.13 mmol) in 15 mL of hexane was treated at −78 °C with a solution of phenyllithium in cyclohexane/ether (0.07 mL, 0.13 mmol). A change of color from red-violet to violet occurred. After the solution was warmed to room temperature, the solvent was removed in vacuo and the residue was extracted with 40 mL of pentane. The extract was brought to dryness in vacuo, and the residue was dissolved in 2 mL of hexane. After the solution was stored at −78 °C, a violet solid precipitated, which was separated from the mother liquor and dried in vacuo: yield 72 mg (79%); mp 32 °C dec. Anal. Calcd for C$_{30}$H$_{59}$IrP$_2$Si: C, 51.33; H, 8.47. Found: C, 51.12; H, 8.35. IR (hexane): ν(C=C) 1654 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.53 (m, 2 H, *o*-H of C$_6$H$_5$), 7.26 (m, 2 H, *m*-H of C$_6$H$_5$), 6.88 (m, 1 H, *p*-H of C$_6$H$_5$), 2.48 (m, 6 H, PC*H*CH$_3$), 2.25 (t, J(PH) = 1.9 Hz, 3 H, =C(CH$_3$)), 1.21 (dvt, N = 13.2, J(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$), 0.19 (s, 9 H, SiCH$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 266.2 (t, J(PC) = 12.2 Hz, Ir=*C*=C), 173.5 (t, J(PC) = 11.5 Hz, *i*-C of C$_6$H$_5$), 139.7, 127.3, 121.5 (all s, C$_6$H$_5$), 98.3 (t, J(PC) = 2.9 Hz, Ir=C=*C*), 25.3 (vt, N = 25.7 Hz, P*C*HCH$_3$), 20.4, 20.3 (both s, PCH*C*H$_3$), −0.9 (s, SiCH$_3$), −4.7 (t, J (PC) = 2.3 Hz, =C(*C*H$_3$)). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 24.6 (s).

Preparation of *trans*-[Ir(C$_6$H$_5$)(=C=CHPh)(P*i*Pr$_3$)$_2$] (7). A solution of **4** (60 mg, 0.09 mmol) in 10 mL of hexane was treated at −78 °C with a 2.0 M solution of phenyllithium in cyclohexane/ether (0.05 mL, 0.10 mmol). After the reaction mixture was warmed to room temperature, the solution was stirred for 20 min. Then the solvent was removed in vacuo and the residue was extracted with 40 mL of pentane. The

extract was concentrated to 1 mL and stored at −78 °C. After 15 h dark violet crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried in vacuo: yield 52 mg (83%); mp 56 °C dec. Anal. Calcd for $C_{32}H_{53}IrP_2$: C, 55.55; H, 7.72. Found: C, 55.49; H, 7.46. IR (hexane): ν(C=C) 1594 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.44 (m, 4 H, *o*-H of C_6H_5), 7.26 (m, 4 H, *m*-H of C_6H_5), 7.11 (m, 2 H, *p*-H of C_6H_5), 2.44 (m, 6 H, PC*H*CH$_3$), 1.17 (dvt, N = 13.3, J(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$), −1.19 (t, J(PH) = 3.5 Hz, 1 H, =CHPh). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 274.4 (t, J(PC) = 13.8 Hz, Ir=*C*=C), 174.6 (t, J(PC) = 10.2 Hz, *i*-C of Ir−C_6H_5), 141.7 (s, *i*-C of C_6H_5), 129.0, 128.1, 127.4, 126.5, 125.8, 124.1 (all s, C_6H_5 and Ir−C_6H_5), 118.4 (t, J(PC) = 3.5 Hz, Ir=C=*C*), 25.4 (vt, N = 26.4 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 25.3 (s).

Preparation of *trans*-[Ir(C≡CPh){=C=C(SiMe$_3$)Me}-(P*i*Pr$_3$)$_2$] (8). A solution of **1** (81 mg, 0.12 mmol) in 15 mL of THF was cooled to −30 °C and treated with PhC≡CLi (70 mg, 0.65 mmol). After the reaction mixture was warmed to 10 °C, the solvent was removed in vacuo, and the residue was extracted with 50 mL of pentane. The extract was concentrated to 2 mL and stored at −78 °C. After 24 h a violet microcrystalline solid precipitated, which was washed twice with small amounts of pentane (0 °C) and dried: yield 77 mg (86%); mp 22 °C dec. Anal. Calcd for $C_{32}H_{59}IrP_2Si$: C; 52.94; H, 8.19. Found: C, 53.09; H, 7.99. IR (hexane): ν(C≡C) 2086, ν(C=C) 1656 cm^{-1}. ^{1}H NMR (d_8-toluene, 400 MHz, 223 K): δ 7.45 (m, 2 H, *o*-H of C_6H_5), 7.12 (m, 2 H, *m*-H of C_6H_5), 6.87 (m, 1 H, *p*-H of C_6H_5), 2.88 (m, 6 H, PC*H*CH$_3$), 2.17 (t, J(PH) = 1.8 Hz, 3 H, =CCH$_3$), 1.34 (dvt, N = 13.8, J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), 1.31 (dvt, N = 14.4, J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), 0.18 (s, 9 H, SiCH$_3$). ^{13}C NMR (d_8-toluene, 100.6 MHz, 223 K): δ 275.5 (t, J(PC) = 12.2 Hz, Ir=*C*=C), 138.1 (s, *i*-C of C_6H_5), 137.5 (s, Ir−C≡*C*Ph), 130.6, 128.9, 128.7 (all s, C_6H_5), 95.5 (br s, Ir=C=*C*), 22.7 (vt, N = 26.4 Hz, P*C*HCH$_3$), 20.6, 20.2 (s each, PCH*C*H$_3$), −1.2 (s, SiCH$_3$), −6.5 (br s, =C*C*H$_3$; the resonance of Ir−*C*≡CPh is probably covered by the solvent. ^{31}P NMR (d_8-toluene, 162.0 MHz, 223 K): δ 30.4 (s).

Preparation of *trans*-[Ir(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] (10). A solution of **9** (50 mg, 0.08 mmol) in 10 mL of pentane was treated at −78 °C with HC≡CPh (4.5 μL, 0.08 mmol). While the reaction mixture was warmed to room temperature, a change of color from orange to green occurred. The solvent was removed in vacuo, and the oily residue was extracted with 40 mL of pentane. The extract was concentrated to 2 mL and stored at −78 °C. Green crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 50 mg (89%); mp 50 °C dec. Anal. Calcd for $C_{34}H_{53}IrP_2$: C, 57.04; H, 7.46. Found: C, 56.88; H, 7.33. IR (benzene) ν(C≡C) 2117, ν(C=C) 1593 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.35, 7.12, 6.88, 6.82 (all m, 10 H, *o*-, *m*-, and *p*-H of C_6H_5), 2.87 (m, 6 H, PC*H*CH$_3$), 1.33 (dvt, N = 13.4, J(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$), −2.63 (t, J(PH) = 3.1 Hz, 1 H, =CHPh). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 31.2 (s).

Preparation of *trans*-[Ir(C≡CCO$_2$Me)(=C=CHPh)-(P*i*Pr$_3$)$_2$] (11). A solution of **9** (66 mg, 0.10 mmol) in 10 mL of pentane was treated at −78 °C with HC≡CCO$_2$Me (6.3 μL, 0.10 mmol) and then warmed to room temperature. A change of color from orange to blue-green occurred. The solvent was removed in vacuo, and the oily residue was extracted with 40 mL of pentane. The extract was concentrated to 1 mL, and the solution was stored at −78 °C. A green microcrystalline solid precipitated, which was separated from the mother liquor and dried: yield 63 mg (87%), mp 38 °C dec. Anal. Calcd for $C_{29}H_{51}IrO_2P_2$: C, 50.78; H, 7.49. Found: C, 50.89; H, 7.34. IR (KBr): ν(C≡C) 2073, ν(OCO)$_{as}$ 1684, ν(C=C) 1623, ν(OCO)$_{sym}$ 1457 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.23 (m, 2 H, *o*-H of C_6H_5), 7.10 (m, 2 H, *m*-H of C_6H_5), 6.81 (m, 1 H, *p*-H of C_6H_5), 3.41 (s, CO_2CH_3), 2.73 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, N = 14.0, J(HH) = 7.0 Hz, PCHC*H*$_3$), −2.54 (t, J(PH) = 3.4 Hz, =C*H*Ph). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 287.9 (t, J(PC) = 13.4 Hz, Ir=*C*=C), 153.1 (s, *C*O$_2$CH$_3$), 134.3 (s, *i*-C of C_6H_5), 129.4, 126.1, 124.9 (all s, C_6H_5), 119.1 (br s, Ir=C=*C*), 117.1 (t, J(PC) = 12.2 Hz, Ir−*C*≡C), 99.8 (br s, = Ir−C≡*C*), 51.1 (s, CO$_2$*C*H$_3$), 25.4 (vt, N = 26.9 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 31.1 (s).

Preparation of *trans*-[Ir{η^1-(*Z*)-C(Me)=C(SiMe$_3$)Me}-(CO)(P*i*Pr$_3$)$_2$] (13). (a) A solution of **5** (55 mg, 0.09 mmol) in 10 mL of pentane was cooled to −78 °C, and a slow stream of CO was passed through for 15 s. A change of color from violet to yellow occurred. The solution was concentrated to 1 mL and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). With pentane a yellow fraction was eluted, which was brought to dryness in vacuo. The residue was dissolved in 2 mL of methanol, and the solution was stored at −78 °C. Yellow crystals precipitated, which were washed twice with methanol (0 °C) and dried: yield 51 mg (86%).

(b) A solution of **1** (78 mg, 0.12 mmol) in 15 mL of hexane was treated with a 0.75 M solution of methyllithium in hexane (0.16 mL, 0.12 mmol), and after removal of the solvent in vacuo the residue was extracted with 50 mL of pentane. The extract was cooled to −78 °C, and a slow stream of CO was passed through for 15 s. A change of color from violet to yellow occurred. The solution was then worked up as described for (a): yield 81 mg (84%); mp 104 °C dec. Anal. Calcd for $C_{26}H_{57}IrOP_2Si$: C, 46.75; H, 8.60. Found: C, 46.82; H, 8.54. MS (70 eV): m/z 668 (M$^+$ for ^{193}Ir). IR (hexane): ν(CO) 1923 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.36 (m, 6 H, PC*H*CH$_3$), 1.87 (br t, J(PH) = 2.9 Hz, 3 H, Ir−C=C(CH$_3$)), 1.84 (br s, 3 H, Ir−C(CH$_3$)=C), 1.25 (dvt, N = 13.5, J(HH) = 6.4 Hz, 18 H, PCHC*H*$_3$), 1.19 (dvt, N = 13.2, J(HH) = 6.2 Hz, 18H, PCHC*H*$_3$), 0.59 (s, 9 H, SiCH$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 188.4 (t, J(PC) = 11.9 Hz, CO), 182.6 (t, J(PC) = 13.7 Hz, Ir-*C*(CH$_3$)=C), 135.7 (t, J(PC) = 4.3 Hz, Ir−C(CH$_3$)=*C*), 26.4 (vt, N = 26.5 Hz, P*C*HCH$_3$), 20.8 (s, CH$_3$), 20.4, 20.1 (both s, PCH*C*H$_3$), 19.7 (s, CH$_3$), 2.3 (s, SiCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 30.7 (s). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −10.3 (s).

Preparation of *trans*-[Ir{η^1-(*Z*)-C(Me)=CHPh}(CO)-(P*i*Pr$_3$)$_2$] (14). A solution of **12** (40 mg, 0.06 mmol) in 10 mL of pentane was cooled to −78 °C, and a slow stream of CO was passed through for 15 s. A change of color from violet to yellow occurred. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. The residue was then dissolved in 2 mL of acetone and the solution stored at −78 °C for 12 h. Yellow crystals precipitated which were separated from the mother liquor, washed twice with small amounts of acetone (0 °C), and dried: yield 32 mg (77%); mp 138 °C dec. Anal. Calcd for $C_{28}H_{45}IrOP_2$: C; 51.12; H, 7.81. Found: C, 51.21; H, 7.84. IR (hexane): ν(CO) 1930 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.75, 7.52, 7.42, 7.11, 7.00 (all m, 1 H each, *o*-, *m*-, and *p*-H of C_6H_5), 6.27 (m, 1 H, =C*H*Ph), 2.23 (m, 6 H, PC*H*CH$_3$), 1.94 (br d, J(HH) = 6.3 Hz, 3 H, Ir−C(C*H*$_3$)=CHPh), 1.23 (dvt, N = 14.1, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$), 1.11 (dvt, N = 13.3, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (100.6 Hz, C_6D_6): δ 189.3 (t, J(PC) = 10.5 Hz, CO), 174.3 (t, J(PC) = 12.8 Hz, Ir−*C*(CH$_3$)=CHPh), 147.2 (s, *i*-C of C_6H_5), 139.3 (t, J(PC) = 1.9 Hz, Ir−C(CH$_3$)=*C*HPh), 128.3, 125.8, 124.8, 122.4, 118.9 (all s, C_6H_5), 26.3 (vt, N = 26.7 Hz, P*C*HCH$_3$), 20.3, 19.5 (both s, PCH*C*H$_3$), 19.6 (br s, Ir−C(*C*H$_3$)=CHPh). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 33.1 (s).

Preparation of *trans*-[Ir{η^1-(*Z*)-C(Ph)=C(SiMe$_3$)Me}-(CO)(P*i*Pr$_3$)$_2$] (15). This compound was prepared as described in (b) for **13**, starting from **1** (96 mg, 0.15 mmol) and a 2.0 M solution of phenyllithium (0.07 mL, 0.15 mmol) in 15 mL of hexane. After the reaction mixture was worked up by column chromatography on Al_2O_3 (neutral, activity grade V, height of column 5 cm) the product was dissolved in 2 mL of acetone and the solution then stored at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small amounts of methanol, and dried: yield 66 mg (77%); mp 99 °C dec. Anal. Calcd for $C_{31}H_{59}IrOP_2Si$: C,

51.00; H, 8.15. Found: C, 50.56; H, 8.19. IR (hexane): ν(CO) 1927 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.33 (m, 2 H, *o*-H of C_6H_5), 7.18 (m, 2 H, *m*-H of C_6H_5), 6.98 (m, 1 H, *p*-H of C_6H_5), 2.58 (m, 6 H, PC*H*CH$_3$), 2.01 (t, J(PH) = 2.2 Hz, 3 H, =C(CH$_3$)), 1.17 (dvt, N = 12.6, J(HH) = 6.8 Hz, 18 H, PCHC*H*$_3$), 1.15 (dvt, N = 13.0, J(HH) = 6.5 Hz, 18 H, PCHC*H*$_3$), 0.61 (s, 9 H, SiCH$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 187.8 (t, J(PC) = 12.6 Hz, CO), 185.0 (t, J(PC) = 12.6 Hz, Ir−*C*(Ph)=C), 153.0 (s, *i*-C of C_6H_5), 139.1 (t, J(PC) = 4.0 Hz, Ir−C(Ph)=*C*), 131.5, 127.4, 123.7 (all s, C_6H_5), 25.1 (vt, N = 26.3 Hz, P*C*HCH$_3$), 23.2 (s, =C(*C*H$_3$)), 20.2, 20.0 (both s, PCHC*H*$_3$), 2.6 (s, SiCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 24.0 (s). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −8.8 (s).

Preparation of *trans*-[Ir{η^1-(*Z*)-C(Ph)=CHPh}(CO)(P*i*Pr$_3$)$_2$] (16). A solution of **4** (68 mg, 0.10 mmol) in 15 mL of hexane was treated at −78 °C with a 2.0 M solution of phenyllithium in cyclohexane/ether (0.05 mL, 0.10 mmol). The reaction mixture was warmed to room temperature, which led to a change of color from violet to dark violet. The solution was then cooled to −78 °C again, and a slow stream of CO was passed through for 15 s. The color changed from violet to yellow. The solvent was removed in vacuo, and the residue was extracted with 50 mL of pentane. After removal of the solvent, the yellow oily residue was recrystallized from 2 mL of acetone at −78 °C. The yellow crystals were separated from the mother liquor, washed twice with small amounts of acetone, and dried: yield 63 mg (83%); mp 148 °C dec. Anal. Calcd for $C_{33}H_{53}IrOP_2$: C, 55.05; H, 7.42. Found: C, 54.84; H, 7.31. IR (hexane): ν(CO) 1922 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.60 (br s, 2 H, *o*-H of =CH(C_6H_5)), 8.10 (t, J(PH) = 2.9 Hz, 1 H, =C*H*Ph), 7.85 (m, 2 H, *o*-H of C_6H_5), 7.18 (m, 6 H, *m*- and *p*-H of C_6H_5 and =CH(C_6H_5)), 2.40 (m, 6 H, PC*H*CH$_3$), 1.13 (dvt, N = 14.0, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$), 1.08 (dvt, N = 13.3, J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 187.2 (t, J(PC) = 11.7 Hz, CO), 179.9 (t, J(P,C) = 12.9 Hz, Ir−*C*(Ph)=CHPh), 155.6, 144.8 (both s, *i*-C of C_6H_5), 139.1 (t, J(PC) = 4.0 Hz, Ir−C(Ph)=*C*HPh), 131.0, 130.7, 127.2, 126.4, 125.2, 124.9 (all s, C_6H_5), 26.0 (vt, N = 26.7 Hz, P*C*HCH$_3$), 20.4, 20.0 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 28.4 (s).

Preparation of *trans*-[Ir{η^1-(*Z*)-C(C≡CPh)=C(SiMe$_3$)Me}(CO)(P*i*Pr$_3$)$_2$] (17). A solution of **1** (88 mg, 0.13 mmol) in 15 mL of THF was cooled to −30 °C and treated with PhC≡CLi (75 mg, 0.70 mmol). After the reaction mixture was warmed to 10 °C, it was stirred at this temperature for 10 min and then again cooled to −78 °C. A slow stream of CO was passed through for 30 s, which led to a change of color of the dark violet solution to yellow. The solvent was removed in vacuo, and the residue was extracted with 50 mL of pentane. The extract was brought to dryness in vacuo, the residue was dissolved in 1 mL of pentane, and the solution was then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). A yellow fraction was eluted with pentane, from which the solvent was evaporated. The residue was dissolved in 2 mL of acetone, and the solution was stored at −78 °C for 20 h. Yellow crystals precipitated, which were separated from the mother liquor, washed twice with 1 mL of acetone (0 °C), and dried: yield 77 mg (79%); mp 164 °C. Anal. Calcd for $C_{33}H_{59}IrOP_2Si$: C, 52.56; H, 7.89. Found: C, 52.73; H, 7.76. IR (hexane): ν(C≡C) 2152, ν(CO) 1929 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.47 (m, 2 H, *o*-H of C_6H_5), 7.09 (m, 2 H, *m*-H of C_6H_5), 6.95 (m, 1 H, *p*-H of C_6H_5), 2.48 (m, 6 H, PC*H*CH$_3$), 2.44 (t, J(PH) = 1.8 Hz, 3 H, C=C(CH$_3$)), 1.35 (dvt, N = 13.9, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$), 1.20 (dvt, N = 13.2, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$), 0.44 (s, 9 H, SiCH$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 188.2 (t, J(PC) = 10.5 Hz, CO), 166.3 (t, J(PC) = 12.4 Hz, Ir−*C*(C≡CPh)=C), 152.6 (s, Ir−C(C≡CPh)=*C*), 131.2 (s, *i*-C of C_6H_5), 130.5, 127.4, 126.5 (all s, C_6H_5), 100.6, 98.6 (both s, Ir−C(*C*≡CPh) and Ir−C(C≡*C*Ph)), 26.2 (vt, N = 26.8 Hz, P*C*HCH$_3$), 22.7 (s, =C(*C*H$_3$)), 20.6, 19.7 (both s, PCH*C*H$_3$), 0.1 (s, SiCH$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 35.9 (s).

Reaction of Compounds 13 and 17 with Acetic Acid. (a) A solution of **13** (30 mg, 0.04 mmol) in 0.5 mL of C_6D_6 was treated with acetic acid (2.6 μL, 0.05 mmol) at room temperature. After the reaction mixture was stirred for 4 days, both *trans*-[Ir(η^1-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$)$_2$] (**18**)[13] and the olefin (*E*)-CH$_3$-CH=C(SiMe$_3$)Me (**19**)[23] were obtained and identified by comparison of the spectroscopic data with those of an authentic sample. If the reaction was carried out at 50 °C, it was completed after 4 h. Under these conditions, a small amount of decomposition products could be observed in addition to the olefin **19** and the organometallic compound **18**.

(b) A solution of **17** (35 mg, 0.05 mmol) in 0.5 mL of C_6D_6 was treated with acetic acid (2.6 μL, 0.05 mmol), and this mixture was stirred for 20 h at 40 °C. A mixture of **18** and the corresponding olefin (*E*)-HC(C≡CPh)=C(SiMe$_3$)Me (**20**) was obtained in addition to a small amount of decomposition products. The solvent was removed in vacuo, the residue was dissolved in 1 mL of pentane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With pentane a colorless fraction was eluted, which was brought to dryness in vacuo. The residue was identified by NMR spectroscopy. Spectroscopic data for **20** are as follows. MS: m/z (I_r) 214 (M^+). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.24, 7.06 (both m, 2 H each, *o*- and *m*-H of C_6H_5), 6.75 (m, 1 H, *p*-H of C_6H_5), 6.29 (m, 1 H, C*H*(C≡CPh)), 1.72 (d, J(HH) = 1.8 Hz, 3 H, CH$_3$), 0.30 (s, 9 H, SiCH$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 137.2 (s, =*C*(SiMe$_3$)Me), 132.9 (s, *i*-C of C_6H_5), 131.8, 129.8, 129.4 (s each, C_6H_5), 107.8 (s, *C*H(C≡CPh)), 102.9, 89.0 (both s, *C*≡CPh and C≡*C*Ph), 22.8 (s, CH$_3$), 2.0 (s, SiCH$_3$).

Reaction of Compound 14 with Trifluoracetic Acid. A solution of **14** (30 mg, 0.05 mmol) in 5 mL of acetone was treated with CF_3CO_2H (4 μL, 0.05 mmol) at room temperature and stirred for 2 h. The solvent was removed in vacuo, and the two products (*E*)-CH$_3$CH=CHPh (**22**)[24] and *trans*-[Ir(η^1-O$_2$CCF$_3$)(CO)(P*i*Pr$_3$)$_2$] (**21**) were identified by spectroscopic techniques. Data for **21** are as follows. IR (C_6H_6): ν(CO) 1945, ν(OCO$_{as}$) 1715, ν(OCO$_{sym}$) 1404 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 2.27 (m, 6 H, PC*H*CH$_3$), 1.20 (dvt, N = 14.3, J(HH) = 7.3 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 174.4 (t, J(PC) = 13.4 Hz, Ir−CO), 159.7 (q, J(FC) = 36.1 Hz, Ir−O$_2$*C*CF$_3$), 117.7 (q, J(FC) = 292.6 Hz, Ir−O$_2$C*C*F$_3$), 24.9 (vt, N = 26.8 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.5 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 47.0 (s).

Reaction of Compound 6 with H_2. A solution of **6** (54 mg, 0.08 mmol) in 15 mL of pentane was stirred for 1 min under an atmosphere of H_2 (1 atm) at room temperature. A change of color from violet to pale yellow occurred. The solvent was removed in vacuo, and the off-white residue was extracted with 30 mL of pentane. The extract was concentrated to 2 mL and stored at −78 °C. Colorless crystals precipitated, which were separated from the mother liquor and washed with small amounts of pentane. By comparison of the ^{1}H NMR, ^{31}P NMR, and IR spectroscopic data they were identified as [IrH$_5$(P*i*Pr$_3$)$_2$] (**23**).[25]

Reaction of Compound 9 with CF_3CO_2H. A solution of **9** (56 mg, 0.08 mmol) in 10 mL of benzene was treated at room temperature with CF_3CO_2H (8 μL, 0.09 mmol). A change of color from orange to violet occurred. The solvent was removed in vacuo, and the residue was recrystallized at −78 °C from 3 mL of pentane. After 15 h violet crystals precipitated, which

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(24) Pouchert, C. J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*: Aldrich: Milwaukee, WI, Vol. 1(2), 24A.
(25) (a) Clerici, M. G.; Di Gioacchino, S.; Maspero, F.; Perroti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379−388. (b) Musco, A.; Naegeli, R.; Venanzi, L. M.; Albinati, A. *J. Organomet. Chem.* **1982**, *228*, C15−C18.

were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried. *trans*-[Ir(O_2CCF_3)(=C=CHPh)(P*i*Pr_3)$_2$] (**24**)[13] was identified by comparison of the spectroscopic data with those of an authentic sample: yield 60 mg (93%).

Preparation of *trans*-[Ir(OPh)(=C=CHPh)(P*i*Pr_3)$_2$] (25). A solution of **9** (55 mg, 0.09 mmol) in 10 mL of pentane was treated with phenol (9 mg, 0.09 mmol), and this mixture was stirred for 5 min. A change of color from orange to violet occurred. The solvent was removed, and the residue was extracted with 40 mL of pentane. The extract was concentrated to 2 mL in vacuo, and the solution was stored at −78 °C. Red-violet crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 53 mg (86%); mp 146 °C dec. Anal. Calcd for $C_{32}H_{53}IrOP_2$: C, 54.29; H, 7.55. Found: C, 53.99; H 7.41. IR (benzene): ν(C=C) 1630 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.27 (m, 2 H, *o*-H of C_6H_5), 7.21 (m, 2 H, *m*-H of C_6H_5), 7.12 (m, 2 H, *m*-H of C_6H_5O), 6.79 (m, 1 H, *p*-H of C_6H_5O), 6.68 (m, 1 H, *p*-H of C_6H_5), 6.61 (m, 2 H, *o*-H of C_6H_5O), 2.43 (m, 6 H, PC*H*CH_3), 1.21 (dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$), −2.15 (t, *J*(PH) = 2.4 Hz, 1 H, =CHPh). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 265.3 (t, *J*(PC) = 12.2 Hz, Ir=*C*=C), 167.9 (s, *i*-C of C_6H_5O), 128.5 (s, *i*-C of C_6H_5), 129.1, 128.1, 125.1, 124.1, 120.9, 115.9 (all s, C_6H_5 and C_6H_5O), 112.4 (t, *J*(PC) = 2.5 Hz, Ir=C=*C*), 23.8 (vt, *N* = 25.4 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 35.1 (s).

Preparation of *trans*-[IrF(=C=CHPh)(P*i*Pr_3)$_2$] (26). (a) A solution of **24** (72 mg, 0.10 mmol) in 15 mL of pentane was treated with [*n*Bu_4N]F (28 mg, 0.10 mmol), and this mixture was stirred for 20 h at room temperature. A change of color from violet to red occurred. The solution was filtered, and the filtrate was concentrated to 2 mL in vacuo and then cooled to −78 °C. After 12 h red crystals precipitated, which were washed twice with 1 mL of pentane and dried: yield 49 mg (78%).

(b) A solution of **9** (39 mg, 0.06 mmol) in 5 mL of benzene was treated with NEt_3·3HF (3.5 μL, 0.06 mmol). A change of color from orange to red occurred. After removal of the solvent in vacuo, the residue was extracted with 30 mL of pentane and concentrated to 2 mL. The solution was stored at −78 °C. Red crystals precipitated, which were separated from the mother liquor and dried: yield 35 mg (89%); mp 70 °C dec. Anal. Calcd for $C_{26}H_{48}FIrP_2$: C, 49.27; H, 7.63. Found: C, 49.41; H, 7.50. IR (hexane): ν(C=C) 1631 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.31 (m, 2 H, *o*-H of C_6H_5), 7.17 (m, 2 H, *m*-H of C_6H_5), 6.77 (m, 1 H, *p*-H of C_6H_5), 2.62 (m, 6 H, PC*H*CH_3), 1.28 (dvt, *N* = 13.6, *J*(HH) = 7.1 Hz, 36 H, PCHC*H*$_3$), −2.18 (dt, *J*(FH) = 9.1 Hz, *J*(PH) = 2.1 Hz, 1 H, =C*H*Ph). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 267.8 (dt, *J*(FC) = 109.8, *J*(PC) = 10.6 Hz, Ir=*C*=C), 131.3 (s, *i*-C of C_6H_5), 128.3, 124.7, 123.7 (all s, C_6H_5), 110.5 (dt, *J*(FC) = 16.3, *J*(PC) = 2.8 Hz, Ir=C=*C*), 23.0 (vt, *N* = 25.7 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 376.6 MHz): δ −201.5 (br t, J(PF) = 22 Hz). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 38.7 (d, *J*(PF) = 22.0 Hz).

Preparation of *trans*-[IrN$_3${=C=C(SiMe$_3$)Me}(P*i*Pr_3)$_2$] (28). A solution of **1** (55 mg, 0.08 mmol) in 10 mL of acetone was treated with NaN_3 (33 mg, 0.50 mmol), and this mixture was stirred for 16 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with 40 mL of pentane. The extract was concentrated to 2 mL and the solution stored at −78 °C. Red-violet crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 50 mg (90%); mp 76 °C. Anal. Calcd for $C_{24}H_{54}IrN_3P_2Si$: C, 43.24; H, 8.16; N, 6.30. Found: C, 42.91; H, 7.98; N, 5.95. IR (CH_2Cl_2) ν(N=N=N) 2080, ν(C=C) 1663 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 2.62 (m, 6 H, PC*H*CH_3), 2.09 (t, *J*(PH) = 1.8 Hz, 3 H, =CCH_3), 1.28 (dvt, *N* = 13.9, *J*(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), 1.21 (dvt, *N* = 13.5 Hz, *J*(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), 0.10 (s, 9 H, $SiCH_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 258.4 (t, *J*(PC) = 11.6 Hz, Ir=*C*=C), 90.5 (t, *J*(PC) = 2.4 Hz, Ir=C=*C*), 23.8 (vt, *N* = 25.6 Hz, P*C*HCH$_3$), 20.2, 20.0 (both s, PCH*C*H$_3$), 16.7 (s, =C*C*H$_3$), −0.9 (s, SiCH$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 34.9 (s).

Preparation of *trans*-[IrN$_3$(=C=CHPh)(P*i*Pr_3)$_2$] (29). A solution of **4** (63 mg, 0.10 mmol) in 15 mL of acetone was treated with NaN_3 (35 mg, 0.50 mmol), and the reaction mixture was stirred at room temperature for 15 h. The mixture was worked up as described for **28**. A violet microcrystalline solid was isolated: yield 55 mg (86%); mp 86 °C dec. Anal. Calcd for $C_{26}H_{48}IrN_3P_2$: C, 47.54; H, 7.37; N, 6.39. Found: C, 47.56; H, 7.36; N, 6.34. IR (benzene): ν(N=N=N) 2074, ν(C=C) 1633 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.21−7.08 (m, 4 H, *o*- and *m*-H of C_6H_5), 6.77 (m, 1 H, *p*-H of C_6H_5), 2.60 (m, 6 H, PC*H*CH_3), 1.21 (dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$), −2.46 (t, *J*(PC) = 3.0 Hz, 1 H, =C*H*Ph). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 270.4 (t, *J*(PC) = 12.8 Hz, Ir=*C*=C), 131.2 (s, *ipso*-C_6H_5), 125.5, 124.7, 120.0 (all s, C_6H_5), 111.6 (t, *J*(PC) = 6.1 Hz, Ir=C=*C*), 23.9 (vt, *N* = 25.6 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 35.1 (s).

Preparation of *trans*-[IrN$_3$(=C=CHCO$_2$Me)(P*i*Pr_3)$_2$] (30). A solution of **27** (49 mg, 0.08 mmol) in 15 mL of acetone was treated with NaN_3 (35 mg, 0.5 mmol), and the reaction mixture was stirred at room temperature for 6 h. It was worked up as described for **28**. A violet microcrystalline solid was isolated: yield 45 mg (90%); mp 128 °C dec. Anal. Calcd for $C_{22}H_{46}IrN_3O_2P_2$: C, 41.37; H, 7.26; N, 6.58. Found: C, 41.57; H, 7.23; N, 6.39. IR (benzene): ν(N=N=N) 2077, $\nu(OCO)_{as}$ 1693, ν(C=C) 1615, $\nu(OCO)_{sym}$ 1431 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 3.49 (s, 3 H, CO_2CH_3), 2.60 (m, 6 H, PC*H*CH_3), 1.20 (dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$), −1.94 (t, *J*(PC) = 2.1 Hz, 1 H, =C*H*CO$_2$Me). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 262.8 (t, *J*(PC) = 12.2 Hz, Ir=*C*=C), 152.3 (s, *C*O$_2$CH$_3$), 103.5 (br s, Ir=C=*C*), 50.1 (s, CO$_2$*C*H$_3$), 24.9 (vt, *N* = 25.6 Hz, P*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 38.7 (s).

Preparation of *trans*-[IrN$_3$(CO)(P*i*Pr_3)$_2$] (31). A slow stream of CO was passed through a solution of **28** (42 mg, 0.06 mmol) in 10 mL of pentane for 15 s at −78 °C. A change of color from red-violet to yellow occurred. The solution was warmed to room temperature and then concentrated to 1 mL in vacuo. After the solution was stored at −78 °C, a pale yellow solid precipitated, which was separated from the mother liquor, washed with small amounts of pentane, and dried: yield 35 mg (94%); mp 99 °C dec. Anal. Calcd for $C_{19}H_{42}IrN_3OP_2$: C, 39.16; H, 7.26; N, 7.21. Found: C, 38.80; H, 7.20; N, 7.25. IR (benzene): ν(N=N=N) 2076, ν(CO) 1934 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 2.41 (m, 6 H, PC*H*CH_3), 1.20 (dvt, *N* = 13.9, *J*(HH) = 6.9 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 176.4 (t, *J*(PC) = 11.0 Hz, CO), 25.0 (vt, *N* = 26.9 Hz, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 45.4 (s).

Preparation of *trans*-[Ir{CH(CN)Ph}(CO)(P*i*Pr_3)$_2$] (32). A slow stream of CO was passed through a solution of **29** (49 mg, 0.07 mmol) in 10 mL of pentane for 15 s at −78 °C. A change of color from violet to yellow occurred. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. The oily residue was dissolved in 1 mL of acetone, and the solution was stored at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane, and dried: yield 44 mg (90%); mp 84 °C dec. Anal. Calcd for $C_{27}H_{48}IrNOP_2$: C, 49.37; H, 7.37; N, 2.13. Found: C, 49.51; H, 7.31; N, 2.08. IR (benzene): ν(C≡N) 2279, ν(CO) 1929 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.44 (m, 2 H, *o*-H of C_6H_5), 7.10 (m, 2 H, *m*-H of C_6H_5), 6.93 (m, 1 H, *p*-H of C_6H_5), 2.69 (m, 6 H, PC*H*CH_3), 1.32 (dvt, *N* = 13.6, *J*(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$), 0.87 (t, *J*(PH) = 7.1 Hz, 1 H, IrCH). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 188.6 (t, *J*(PC) = 10.2 Hz, CO), 129.2 (t, *J*(PC) = 2.0 Hz, *i*-C_6H_5), 130.6, 128.5, 125.3 (all s, C_6H_5), 120.9 (t, *J*(PC) = 2.0 Hz, IrC(*C*N)), 28.8 (t, *J*(PC) = 6.1 Hz, IrCH), 26.1

(vt, $N = 28.5$ Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 41.8 (s).

Preparation of *trans*-[Ir{C(CN)HCO$_2$Me}(CO)(P*i*Pr$_3$)$_2$] (33). A slow stream of CO was passed through a solution of **30** (40 mg, 0.06 mmol) in 10 mL of pentane for 30 s. A change of color from violet to yellow occurred. After the mixture was stirred at room temperature for 6 h, the solvent was removed in vacuo, the oily residue was dissolved in 1 mL of acetone, and the solution was stored at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane, and dried: yield 37 mg (92%); mp 82 °C dec. Anal. Calcd for $C_{23}H_{46}IrNO_3P_2$: C, 43.25; H, 7.26; N, 2.19. Found: C, 43.12; H, 7.18; N, 2.01. IR (benzene): ν(C≡N) 2253, ν(CO) 1938, $\nu(OCO)_{as}$ 1685, $\nu(OCO)_{sym}$ 1432 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 3.39 (s, 3 H, CO$_2$CH$_3$), 2.61 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, $N = 14.0$, J(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$), 0.91 (t, J(PH) = 7.1 Hz, 1 H, IrCH). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 188.7 (t, J(PC) = 10.4 Hz, IrCO), 154.2 (s, *C*O$_2$CH$_3$), 112.6 (br s, CN), 51.0 (s, CO$_2$*C*H$_3$), 26.2 (vt, $N = 28.5$ Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). The signal for IrCH is probably covered by the signal for P*C*HCH$_3$. ^{31}P NMR (C_6D_6, 81.0 MHz): δ 42.3 (s).

X-ray Structural Analysis of 13. Single crystals were grown from acetone at −60 °C. Crystal data (from 25 reflections, 10° < θ < 15°): monoclinic, space group *C*2/*c* (No. 15), $a = 19.641(4)$ Å, $b = 11.600(4)$ Å, $c = 29.118(5)$ Å, $\beta = 105.812(8)°$, $V = 6383(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.390$ g cm^{-3}, μ(Mo Kα) = 2.01 cm^{-1}, crystal size 0.20 × 0.20 × 0.15 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 16.4), $T = 293(2)$ K, ω/θ scan, maximum $2\theta = 53.92°$, 7138 reflections scanned, 6930 independent reflections, 5175 reflections regarded as observed ($I < 2\sigma(I)$), 6930 reflections used for refinement; intensity data corrected for Lorentz and polarization effects, empirical absorption correction (ψ-scan method, minimum transmission 93.67%) applied; structure solved by direct methods (SHELXS-86);[26] atomic coordinates and anisotropic displacement parameters refined by full-matrix least squares against F_o^2 (SHELXL-93);[27] R1 = 0.0429, wR2 = 0.1033;[28] reflection/parameter ratio 23.33; residual electron density +1.166/−1.541 e Å^{-3}.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) $w^{-1} = [\sigma^2F_o^2 + (0.0407P)^2 + 38.0260P]$, where $P = (F_o^2 + 2F_c^2)/3$.