Closing the Gap between MC$_3$ and MC$_5$ Metallacumulenes: The Chemistry of the First Structurally Characterized Transition-Metal Complex with M=C=C=C=CR$_2$ as the Molecular Unit

Kerstin Ilg and Helmut Werner*[a]

Dedicated to Professor Ulrich Müller-Westerhoff on the occasion of his 65th birthday

Abstract: The reactions of the dihydrido compound [IrH$_2$Cl(P*i*Pr$_3$)$_2$] (**3**) with HC≡CC(O)CHPh$_2$ and HC≡CC(OAc)=CPh$_2$ lead to the formation of alkynyl(hydrido)iridium(III) and vinylideneiridium(I) complexes **4**–**7** which, however, are not suitable precursors for the target molecule *trans*-[IrCl(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**8**). Compound **8** has been prepared in 77% yield from **3** and the vinyl triflate HC≡CC(OTf)=CPh$_2$ in the presence of NEt$_3$. Treatment of **8** with CF$_3$CO$_2$H affords the vinylvinylidene complex *trans*-[IrCl{=C=CHC(O$_2$C-CF$_3$)=CPh$_2$}(P*i*Pr$_3$)$_2$] (**10**) by addition of the electrophile to the C$_\beta$–C$_\gamma$ bond of the MC$_4$ chain. In contrast, the reaction of **8** with HCl yields the five-coordinate butadienyliridium(III) compound [IrCl$_2$-{η^1-(*Z*)-CH=CHC(Cl)=CPh$_2$}(P*i*Pr$_3$)$_2$] (**11**). Salt metathesis of **8** with KI, KOH, and NaN$_3$ leads to the formation of the substitution products *trans*-[IrX(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**12**–**14**) of which the hydroxo derivative **13** reacts with phenol to give *trans*-[Ir(OPh)(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**15**). From **13** and methanol, the octahedral dihydridoiridium(III) complex [IrH$_2$(CH=C=C=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (**16**) is formed by fragmentation of the alcohol. In the presence of CO, both the methyl compound *trans*-[Ir(CH$_3$)(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**17**) (generated from **8** and CH$_3$Li) and the azido complex **14** (X = N$_3$) undergo migratory insertion reactions to yield the four-coordinate iridium(I) carbonyls *trans*-[Ir(C(C≡CCH$_3$)=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (**18**) and *trans*-[Ir(C≡CC(N$_3$)=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (**19**), respectively. Compound **19** rearranges slowly to the thermodynamically more stable isomer *trans*-[Ir(C(N$_3$)=C=C=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (**20**). The molecular structures of **8** and **18** have been determined crystallographically.

Keywords: alkynyl complexes • butatrienylidene complexes • iridium • metallacumulenes • migratory insertion • vinylidene complexes

Introduction

Following the discovery of the first stable transition-metal carbene complex by Fischer and Maasböl in 1964,[1] the stabilization not only of carbenes :CRR′ but also of unsaturated carbenes :C(=C)$_n$RR′ became an area of great interest.[2] While numerous compounds containing vinylidenes :C=CRR′ and allenylidenes :C=C=CRR′ as ligands have been prepared in the last two decades,[2–4] reports about the isolation or at least in situ generation of species of the general composition [L$_x$M(=C=C=C=CRR′)] and [L$_x$M(=C=C=C=C=CRR′)] are quite rare. In 1994, Dixneuf and co-workers disclosed the synthesis of the first cationic complex with Ru=C=C=C=C=CPh$_2$ as the building block,[5] and a few months later we reported the preparation and structural characterization of the first neutral compound with Ir=C=C=C=C=CPh$_2$ as the molecular unit.[6] Since then, some other representatives of the [L$_x$M(=C=C=C=C=CRR′)] series have been described.[7]

Since our activities were mainly concentrated on the chemistry of complexes *trans*-[MX{=C(=C)$_n$RR′}(L)$_2$] with M = Rh, Ir, and L = PR$_3$, anticipating that these molecules with a 16-electron configuration and a square-planar coordination geometry around the metal center are more reactive than their 18-electron (presumably octahedral) analogues, the purpose of this work was to close the gap between the four-coordinate MC$_3$ and MC$_5$ derivatives. Knowing from our studies on the metallahexapentaenes [MCl(=C=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$],[6, 7c] that the corresponding iridium complex is significantly more stable than the rhodium counterpart, we chose as our target compound *trans*-[IrCl(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$]. Herein we report the synthesis and molecular structure of this molecule and illustrate that it is highly

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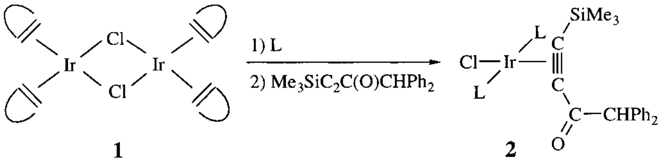
[a] Prof. Dr. H. Werner, K. Ilg
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888 4605
E-mail: anor097@rzbox.uni-wurzburg.de

reactive both towards electrophilic and nucleophilic substrates. Some preliminary results have already been communicated.[8]

Results and Discussion

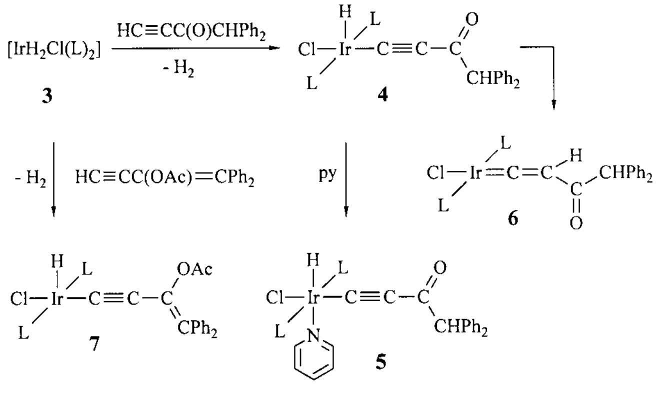
The unsuccessful attempts: Preparation of alkynyl(hydrido)iridium(III) and vinylideneiridium(I) complexes: Taking the structural analogy between the target molecule *trans*-[IrCl(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**8**) and the corresponding iridium allenylidenes *trans*-[IrCl(=C=C=CR$_2$)(P*i*Pr$_3$)$_2$] into consideration, we initially attempted to prepare the IrC$_4$ complex by using the same methodology developed for the IrC$_3$ relatives. Since the C$_3$ ligand of the iridium allenylidenes was formed from propargylic alcohols HC$\equiv$CCR$_2$(OH), for the synthesis of a compound with a homologous C$_4$ unit we had to find a starting material with an additional carbon atom in the C$_n$ chain. The first choice seemed to be the ethynyl ketone Me$_3$SiC$\equiv$CC(O)CHPh$_2$, which is accessible by Friedel–Crafts acylation of bis(trimethylsilyl)acetylene with Ph$_2$CHCOCl[9] and which upon elimination of Me$_3$SiOH in the coordination sphere could generate the wanted ligand :C=C=C=CPh$_2$.

Stepwise reaction of the bis(cyclooctene)iridium(I) derivative **1** with four equivalents of P*i*Pr$_3$ and two equivalents of the ketone Me$_3$SiC$\equiv$CC(O)CHPh$_2$ in hexane at 50 °C affords the alkynyl complex **2** in 85 % yield (Scheme 1). Compound **2** is an orange, only moderately air-sensitive solid that is soluble in most common organic solvents and can be stored under argon for weeks without decomposition. The alkyne ligand is relatively strong electron-withdrawing, which is shown by the decrease of the C$\equiv$C stretching mode from 2158 cm^{-1} in the free alkyne to 1862 cm^{-1} in **2**. The *trans* disposition of the phosphane ligands is inferred both from the observation of a singlet in the ^{31}P NMR spectrum at $\delta = 18.8$ and from the two resonances for the diastereotopic PCHC*H*$_3$ protons in the ^{1}H NMR spectrum appearing as doublets of virtual triplets.[10] The ^{13}C NMR spectrum of **2** displays two signals at $\delta = 109.2$ and 102.0, which are slightly shifted downfield compared with those of the related complex *trans*-[IrCl(η^2-Me$_3$SiC$\equiv$CCO$_2$Et)(P*i*Pr$_3$)$_2$].[11] Attempts to transform **2** either thermally or photochemically to the vinylidene isomer *trans*-[IrCl{=C=C(SiMe$_3$)C(O)CHPh$_2$}(P*i*Pr$_3$)$_2$] (assumed to be a potential precursor for the preparation of **8**) failed.



Scheme 1. L = P*i*Pr$_3$; the olefinic ligands represent cyclooctene.

The next series of experiments was undertaken with the non-silylated alkynylketone HC$\equiv$CC(O)CHPh$_2$ and the corresponding enolacetate HC$\equiv$CC(OAc)=CPh$_2$, both being prepared from HC$\equiv$CCH(OH)CHPh$_2$ as the starting material.[12] Taking into consideration that the synthesis of the IrC$_3$ and IrC$_5$ metallacumulenes started with the dihydrido complex **3** as the precursor, compound **3** was treated first with the ketone HC$\equiv$CC(O)CHPh$_2$ in hexane at low temperature. An evolution of gas (H$_2$) occurred and red crystals of the alkynyl(hydrido)iridium(III) complex **4** precipitated (Scheme 2). The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ exhibits the hydride signal at $\delta = -40.96$, which is at a position similar to that for [IrHCl{C$\equiv$CC(*i*Pr)=CMe$_2$}(P*i*Pr$_3$)$_2$].[11] While this compound is completely inert, **4** rearranges in benzene at room temperature rather quickly to the vinylidene isomer **6**. This reaction can be prevented upon addition of pyridine to a solution of **4** which leads to the formation of the octahedral 1:1 adduct **5**. In contrast to **4**, this is stable in benzene and for a short period of time can even be handled in air. The coordination of pyridine *trans* to hydride is clearly indicated by the chemical shift of the signal for the metal-bonded proton at $\delta = -21.68$ in the ^{1}H NMR spectrum of **5** which appears about 20 ppm downfield compared with that for **4**. The ^{13}C NMR spectrum of **5** displays the triplet resonances for the alkynyl carbon atoms at $\delta = 110.8$ and 105.8 with ^{13}C–^{31}P coupling constants of 4.1 and 2.0 Hz. The vinylidene complex **6** is a red-violet, only slightly air-sensitive solid, the NMR spectroscopic data of which are quite similar to those of *trans*-[IrCl{=C=CHCPh$_2$(OH)}(P*i*Pr$_3$)$_2$].[11] The IR spectrum of **6** shows a strong band at 1654 cm^{-1} assigned to the C=O stretching mode of the ketone functionality.



Scheme 2. L = P*i*Pr$_3$.

After attempts to convert **6** into the corresponding enole *trans*-[IrCl{=C=CH–C(OH)=CPh$_2$}(P*i*Pr$_3$)$_2$] (which possibly could generate the target molecule **8** by elimination of water) failed, the enolization was done first and thus the dihydrido compound **3** treated with the enol acetate HC$\equiv$CC(OAc)=CPh$_2$. Similarly to the ketone HC$\equiv$CC(O)=CHPh$_2$, also the enol acetate reacts with **3** in hexane at −78 °C to give the alkynyl(hydrido) complex **7** which, however, in contrast to **4** is surprisingly inert. It does not rearrange to the vinylidene isomer and under various conditions does not eliminate HOAc to give **8**. Compound **7** is a red solid, the composition of which has been confirmed by elemental analysis and mass spectra. Typical spectroscopic features are the hydride signal at $\delta = -42.65$ in the ^{1}H NMR and the resonances for the C=C and C$\equiv$C carbon atoms at, respectively, $\delta = 130.5$, 130.3 and 104.0, 93.4 in the ^{13}C NMR spectrum.

The success: Preparation and molecular structure of the IrC_4 complex: Since the enol acetate turned out not to be the substrate of choice, we decided to bind a better leaving group to the γ-carbon atom of the substituted alkyne and, at the same time, to shift the keto–enol equilibrium to the side of the enol. Attempts to convert the keto function in the coordination sphere of complex **4** to the corresponding enol ester by using $(CF_3SO_2)_2O$ and 4-dimethylaminopyridine led to the decomposition of the iridium precursor. The key to success was the use of the enol triflate $HC{\equiv}CC(OTf){=}CPh_2$ ($Tf = CF_3SO_2$),[9] which reacts with **3** in hexane even at $-100\,^{\circ}C$ in the presence of one equivalent of triethylamine. The reaction is accompanied by evolution of gas (H_2) and a change of color from yellow to olive-green. After separation of the ammonium salt and recrystallization of the crude product from acetone, the IrC_4 complex **8** is isolated as an olive-green, only moderately air-sensitive solid in 77 % yield (Scheme 3). With respect to the color, it should be mentioned that a solution of **8** in benzene appears red.

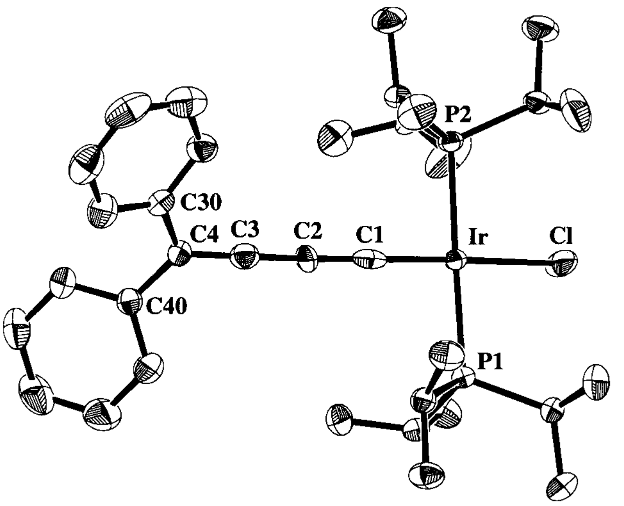
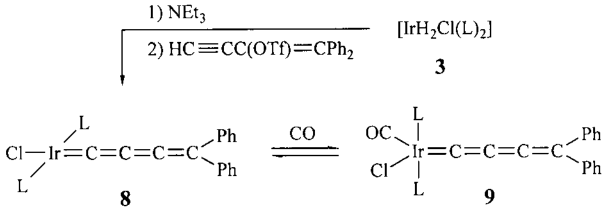


Figure 1. . Molecular structure of **8**. Principal bond lengths [Å] and angles [°]: Ir–Cl 2.3561(15), Ir–P1 2.3501(14), Ir–P2 2.3556(14), Ir–C1 1.816(6), C1–C2 1.283(8), C2–C3 1.275(8), C3–C4 1.339(8); P1-Ir-P2 177.82(5), Cl-Ir-C1 172.88(17), P1-Ir-Cl 90.10(5), P2-Ir-Cl 89.46(5), P1-Ir-C1 90.04(16), P2-Ir-C1 90.67(16), Ir-C1-C2 175.1(5), C1-C2-C3 178.1(6), C2-C3-C4 178.7(7).



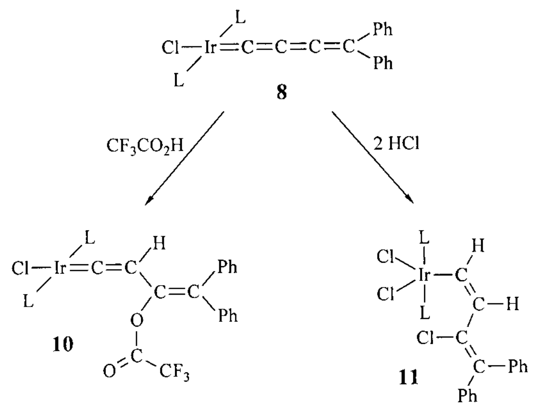
Scheme 3. $L = PiPr_3$.

The presence of the cumulated C_4 chain in **8** is indicated both by the IR spectrum, which shows an absorption for the $\nu(C{=}C{=}C{=}C)$ stretching mode at $1993\,cm^{-1}$, and by the ^1H NMR spectrum, which exhibits a splitting pattern for the signals of the phenyl protons that is typical for a system with a rotational symmetry around the $Ir{-}C_4$ axis. The ^{13}C NMR spectrum of **8** displays four triplet resonances for the carbon atoms of the cumulene moiety, the assignment of which is supported by the size of the $^{13}C-^{31}P$ coupling constants. The proposed structure of **8** was finally confirmed by a single-crystal X-ray structure analysis (Figure 1). The molecular diagram reveals that the iridium atom is coordinated in a slightly distorted square-planar fashion. The two phosphane ligands are *trans* to each other, and the chloride is *trans*-disposed to the metal-bonded carbon atom. The unsaturated C_4 chain is nearly linear and deviates only weakly at C1 from the ideal value of 180°. The bond length Ir–C1 is 1.816(6) Å and thus somewhat shorter than the Ir–C bond lengths in the related complexes *trans*-$[IrCl({=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (1.862(7) Å)[13] and *trans*-$[IrCl({=}C{=}C{=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (1.834(5) Å).[6] The lengths of the two internal carbon–carbon double bonds are almost identical (1.283(8) and 1.275(8) Å), whereas the terminal bond C3–C4 is slightly longer (1.339(8) Å). The Ir–Cl and Ir–P distances are very similar to those of the corresponding IrC_3 and IrC_5 complexes and thus consistent with the related binding properties of the $:C{=}C{=}CPh_2$, $:C{=}C{=}C{=}CPh_2$ and $:C{=}C{=}C{=}C{=}CPh_2$ units.

Addition reactions of complex 8 with CO and Brønsted acids: Similarly to *trans*-$[IrCl({=}C{=}C{=}CPh_2)(PiPr_3)_2]$, the IrC_4 complex also reacts quite rapidly with carbon monoxide. However, in contrast to the reaction of the iridium allenylidene with CO which yields *trans*-$[IrCl(CO)(PiPr_3)_2]$,[11] treatment of **8** with CO gives the 1:1 adduct **9** (Scheme 3). The presence of both the Ir–CO and the intact $Ir{=}C{=}C{=}C{=}CPh_2$ bond in **9** is shown by the appearance of two strong bands in the IR spectrum at 1944 ($\nu(CO)$) and $1987\,cm^{-1}$ ($\nu(C{=}C{=}C{=}C)$), the latter being only slightly shifted to lower wavenumbers compared to that in **8**. The ^{31}P NMR spectrum of **9** displays a single resonance at $\delta = 19.6$ (see **8**: $\delta = 26.7$) which supports the assumption that the two phosphane ligands are *trans*-disposed. Since **9** (like other 18-electron carbonyl iridium(I) compounds)[14] smoothly loses CO in solution as well as in the solid state, a correct elemental analysis could not be obtained.

The reaction of **8** with CF_3CO_2H proceeds analogously to that of the corresponding iridium(I) allenylidene *trans*-$[IrCl({=}C{=}C{=}CPh_2)(PiPr_3)_2]$. The attack of the electrophile is directed to the $C_\beta{-}C_\gamma$ bond of the IrC_4 chain and affords the vinylvinylidene derivative **10** in 87 % yield (Scheme 4). The red-violet solid is relatively air-stable and soluble in most common organic solvents. Typical spectroscopic features are the low-field resonance at $\delta = 255.6$ for the Ir=C atom in the ^{13}C NMR spectrum, the signal at $\delta = -2.81$ for the Ir=C=CH proton in the ^1H NMR spectrum and the asymmetric and symmetric OCO stretching vibrations for the CF_3CO_2 substituent in the IR spectrum. Treatment of **10** with a second equivalent of trifluoracetic acid leads to a mixture of products which could not be separated by fractional crystallization or chromatographic techniques.

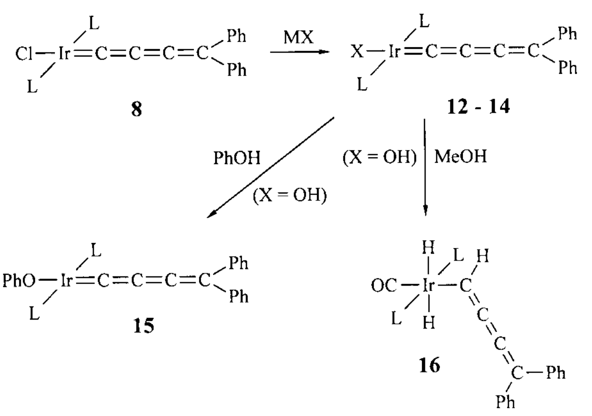
In contrast to the reaction of **8** with CF_3CO_2H, the reaction of **8** with HCl (in benzene) proceeds in the molar ratio of 1:2. Owing to the elemental analysis and the spectroscopic data, the isolated product **11** (a brown, thermally stable solid) is a



Scheme 4. $L = PiPr_3$.

five-coordinate dichloroiridium(III) complex presumably with a trigonal-bipyramidal coordination geometry. Owing to the twofold addition of HCl, the butatrienylidene unit is transformed to a butadienyl ligand which is σ-bonded to the metal center. The ^{13}C NMR spectrum of **11** displays the signal for the α-carbon atom at $\delta = 107.9$, which is split into a triplet and shifted about 118 ppm upfield compared with that for **8**. The new vinyl proton Ir–C*H*=C of **11** resonates at $\delta = 9.63$ and, owing to NOE measurements, it is *cis*-disposed to the =CH proton at the β-carbon atom. With regard to the mechanism of formation of **11**, we assume that in the first step a vinylvinylideneiridium(I) compound *trans*-$[IrCl\{=C=CHC(Cl)=CPh_2\}(PiPr_3)_2]$ is generated, the molecular structure of which being probably analogous to that of **10**. Treating a solution of **8** with one equivalent of Me_3SiCl and a few drops of water led indeed to the formation of a short-lived species which shows two triplet resonances in the ^{13}C NMR spectrum at $\delta = 156.9$ and 111.6 (in $[D_6]$acetone), respectively. The similarity in the chemical shift of these signals to those of **10** supports the assumption that the linear IrC_4 chain of **8** is converted stepwise to the $IrCH=CHC(Cl)=CPh_2$ fragment of **11** via an Ir=C=CHR intermediate.

Ligand displacement and migratory insertion reactions of the IrC_4 complexes: In agreement with previous results,[13] salt metathesis reactions of **8** with KI, KOH, and NaN_3 occur cleanly and give the corresponding substitution products **12**–**14** in excellent yields (Scheme 5). The new IrC_4 complexes are deeply colored, slightly air-sensitive solids which have been characterized by analytical and spectroscopic techniques. The IR spectrum of the azido derivative **14** shows a strong band at 2067 cm^{-1} indicating that for the IrN_3 unit a resonance form with two N–N double bonds dominates.[15]



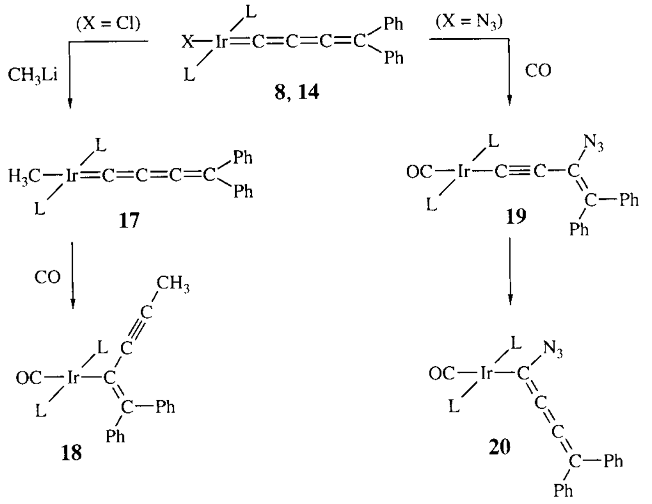
Scheme 5. $L = PiPr_3$.

In benzene, the hydroxo complex **13** reacts smoothly with phenol to give the IrOPh compound **15** in 94% yield. This method of synthesis is more convenient than the salt metathesis of **8** with NaOPh which in the case of the allenylidene derivatives *trans*-$[Ir(OPh)\{=C=C=C(Ph)R\}(PiPr_3)_2]$ (R = *t*Bu, Ph) also provides less favorable results.[13] Apart from the disappearance of the OH stretching mode in the IR spectrum, the spectroscopic data of **15** are similar to those of **13** and thus deserve no further comment.

Attempts to perform substitution reactions of **13** in methanol as solvent led to a surprising result. After dissolving compound **13** in CH_3OH at room temperature, in about one hour a change of color from olive-green to light brown took place and, after evaporation of the solvent and crystallization at −60 °C, the carbonyldihydridoiridium(III) complex **16** containing the novel 4.4-diphenylbutatrienyl ligand was isolated in 82% yield (Scheme 5). The composition of **16** has been confirmed by elemental analysis and mass spectra (FAB). Besides the strong ν(CO) and ν(C=C=C=C) bands at 1931 and 1975 cm^{-1} in the IR spectrum, the most typical spectroscopic features of **16** are both the triplet resonance for the hydride at $\delta = -8.88$ and the signal for the Ir-CH proton at $\delta = 6.82$ in the ^1H NMR spectrum. For the related allenyliridium(III) compound $[IrH_2Cl(CH=C=CPh_2)(PiPr_3)_2]$, the corresponding Ir-CH resonance is observed at $\delta = 6.53$.[13] The signals for the ^{13}C nuclei of the carbon atoms C1–C4 of the IrC_4 chain appear at $\delta = 111.4$, 164.7, 169.2, and 114.9, respectively. Since the NMR spectra of **16** exhibit only one resonance for the IrH protons and only one signal for the phosphorus atoms, there is no doubt that the two hydrides as well as the two $PiPr_3$ ligands are in *trans* disposition.

In contrast to the iridium allenylidenes *trans*-$[IrCl\{=C=C=C(Ph)R\}(PiPr_3)_2]$, which upon treatment with methyl- or phenyllithium afford a mixture of products instead of $IrCH_3$ and IrC_6H_5 derivatives,[16] the reaction of **8** with CH_3Li in pentane at −78 °C gives almost exclusively the methyliridium(I) complex **17** (Scheme 6). After removal of the solvent and separation of the by-product (LiCl) an orange-brown oil remains which is not only extremely air-sensitive but decomposes even under argon at room temperature. It therefore has been characterized by IR and NMR spectroscopy. Diagnostic for the metal-bonded CH_3 group is a triplet at $\delta = 1.56$ in the ^1H NMR spectrum, the position of which is similar to that of the vinylidene counterpart *trans*-$[IrCH_3(=C=CHPh)(PiPr_3)_2]$ ($\delta = 1.06$).[17]

Passing a slow stream of CO through a solution of **17** (generated in situ) in pentane causes a change of color from orange to yellow and gives the carbonyl complex **18** as a yellow solid in 85% yield. However, the assumption that the migratory insertion of the C_4 unit into the Ir–CH_3 bond has led to a product of composition *trans*-$[Ir\{C(CH_3)=C=C=CPh_2\}(CO)(PiPr_3)_2]$ is not in agreement with the ^1H NMR spectrum which instead of a triplet at around $\delta = 1.85$–1.95 for the $IrC(CH_3)$ protons[18] displays a singlet at $\delta = 1.62$.



Scheme 6. L = P*i*Pr$_3$.

Moreover, the ^{13}C NMR spectrum of **18** differs from that of **16** with an IrCH=C=C=CPh$_2$ fragment insofar as only two resonances for the ^{13}C nuclei of the IrC$_4$ chain exhibit a ^{13}C–^{31}P coupling of, respectively, 12.7 and 4.3 Hz.

To substantiate the proposed structure for compound **18**, a single-crystal X-ray structure analysis was carried out. As shown in Figure 2, the coordination geometry around the metal center corresponds to a square plane, the distortion of which is less pronounced than in the related vinyl complex *trans*-[Ir{C(CH$_3$)=C(SiMe$_3$)Me}(CO)(P*i*Pr$_3$)$_2$].[18] 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, however, the bond angle of 167.64(4)° being about 4.5° nearer to the 180° value than in the above-mentioned IrC(CH$_3$)=C(SiMe$_3$)Me derivative. It appears that the bending as well as the enlargement of the bond angles Ir-C4-C5 and C4-C5-C6 to 132.6(3)° and 124.7(3)° is caused by steric hindrance between the isopropyl groups and the substituents of the vinyl unit. The Ir–C4 distance of 2.135(4) Å is significantly larger than the Ir–C bond length in **8** but quite similar to that of *trans*-[Ir{C(CH$_3$)=C(SiMe$_3$)Me}(CO)(P*i*Pr$_3$)$_2$] (2.115(7) Å).[18]

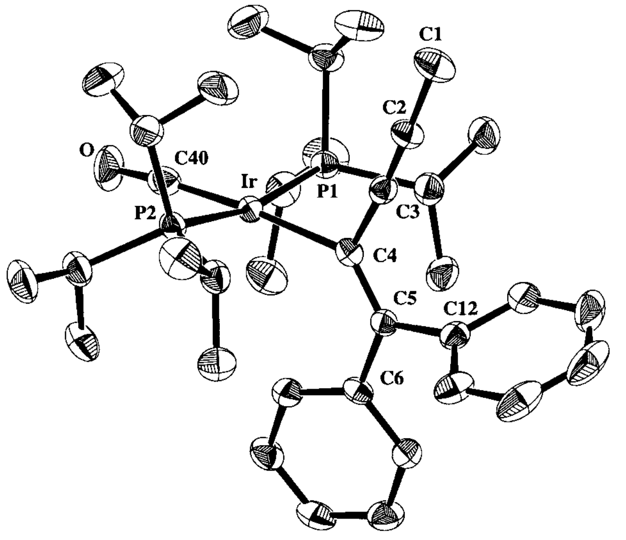


Figure 2. Molecular structure of **18** (the position of the metal-bonded hydrogen atom has been calculated). Principal bond lengths [Å] and angles [°]: Ir–C4 2.135(4), Ir–P1 2.3311(11), Ir–P2 2.3394(11), Ir–C40 1.839(5), C40–O 1.174(6), C2–C3 1.205(6), C3–C4 1.442(6), C4–C5 1.361(6), C5–C6 1.494(5), C5–C12 1.503(5); P1-Ir-P2 167.64(4), C4-Ir-C40 174.89(18), P1-Ir-C4 91.76(10), P2-Ir-C4 92.27(10), P1-Ir-C40 88.62(14), P2-Ir-C40 88.40(13), Ir-C40-O 175.5(4), Ir-C4-C3 108.7(3), Ir-C4-C5 132.6(3), C1-C2-C3 178.1(5), C2-C3-C4 174.5(4), C3-C4-C5 118.6(3), C4-C5-C6 124.7(3), C4-C5-C12 120.4(3).

Similarly to the methyliridium compound **17**, the azido complex **14** also reacts with carbon monoxide by migratory insertion. If a slow stream of CO is passed through a solution of **14** in CH$_2$Cl$_2$/pentane at −78 °C, a change of color from olive-green to orange occurs. After warming to room temperature, removal of the solvent and chromatographic workup a yellow solid is isolated, the spectroscopic data of which correspond to the alkynyl(carbonyl)iridium(I) compound **19** (see Scheme 6). Characteristic features are the three strong absorptions in the IR spectrum at, respectively, 2102, 2062 and 1929 cm^{-1}, assigned to the ν(N=N=N), ν(C≡C) and ν(CO) stetching modes, the two triplet resonances for the alkynyl carbon atoms at δ = 139.2 and 120.5 in the ^{13}C NMR spectrum, and the two sets of signals for the C$_6$H$_5$ protons and C$_6$H$_5$ carbon atoms of the terminal =CPh$_2$ unit. Owing to the last observation, there is no doubt that the two phenyl groups are stereochemically different.

When we attempted to further purify compound **19** by recrystallization, we observed that in solution a slow rearrangement of the alkynyl complex takes place. After stirring a solution of **19** in benzene for 36 h at room temperature, the reaction is completed and the isomeric species **20** can be isolated as an orange-yellow, moderately air-sensitive solid in 80 % yield. In contrast to **19**, the IR spectrum of **20** displays an intense ν(C=C=C) band at 1992 cm^{-1}, that is at a similar position as found for **16**. The appearance of four resonances at δ = 165.3, 154.5, 146.2 and 104.7 for the carbon atom of the Ir–C=C=C=C chain, each split into a triplet due to ^{13}C–^{31}P coupling, equally supports the structural proposal shown in Scheme 6. Interestingly, the allenyliridium(I) compound *trans*-[Ir{C(N$_3$)=C=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$], structurally related to **20** and obtained from *trans*-[Ir(N$_3$)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] and CO, is quite labile and rapidly loses dinitrogen to give the vinyl complex *trans*-[Ir{C(CN)=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$].[13] Under the same conditions, the butatrienyl derivative **20** is exceedingly stable and reacts neither under UV irradiation nor in refluxing benzene by elimination of N$_2$.

Conclusion

The work presented herein confirms that, by using the appropriate substrate, metallacumulenes with a linear MC$_4$ unit are not only accessible but can be isolated as stable species in good to excellent yields. After it was shown, first by Fischer et al.[19] and Berke,[20] that transition-metal compounds with M=C=C=CRR′ as the building block exist, various efforts were made to prepare related molecules with four carbon atoms in the chain. Early attempts date back to

Lomprey and Selegue[21] and somewhat later to Bruce and coworkers,[22] both choosing ruthenapentatetraenes as the targets. The Bruce group succeeded, with $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(thf)]PF_6$ and buta-1,3-diyne as starting materials, to generate in situ a cationic complex containing the fragment $Ru{=}C{=}C{=}C{=}CH_2$ and supported the presence of this species in solution by trapping experiments with nucleophiles such as $NHPh_2$, PPh_3, H_2O, and imines. More recently, both Dixneuf et al.[23] and Winter and Hornung[24] reported about the in situ formation of cationic intermediates with an analogous RuC_4 unit and showed that this can be converted to corresponding acylvinylidene, acylalkynyl, butenynyl, and allenylidene ruthenium derivatives. In 1999, Lapinte et al. described the preparation of dinuclear cationic iron compounds with the core fragment $[Fe]{=}C{=}C{=}C{=}CH[Fe']$ ($[Fe] = (\eta^5\text{-}C_5Me_5)Fe('P_2')$; $[Fe'] = (\eta^5\text{-}C_5Me_5)Fe(CO)_2$; $'P_2' = $ 1,2-bis(diphenylphosphanyl)ethane, 1,2-bis(diisopropylphosphanyl)ethane) using the butadiynediyl complex $[Fe]{-}C{\equiv}C{-}C{\equiv}C[Fe']$ as the precursor.[25] Our results now provide firm evidence for the existence of metallapentatetraenes and also illustrate how manifold the chemistry of these molecules is. Among the reactions outlined in Scheme 4, Scheme 5 and Scheme 6, the conversion of the target compound **8** with HCl and methanol into the five-coordinate butadienyl- and the six-coordinate butatrienyliridium(III) complexes deserve particular attention. Moreover, the migratory insertion reactions of the azido and methyl derivatives **14** and **17** with CO reveal that four-coordinate compounds of the general composition *trans*-$[IrX({=}C{=}C{=}C{=}CPh_2)(PiPr_3)_2]$ can be considered as suitable precursors for the generation of ligand systems which are hardly accessible on conventional routes.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[26] **3**,[27] $HC{\equiv}CC(O)CHPh_2$,[12] $Me_3SiC{\equiv}CC(O)CHPh_2$, and $HC{\equiv}CC(OTf){=}CPh_2$[9] were prepared as described in the literature. $HC{\equiv}CC(OAc){=}CPh_2$ was prepared analogously as the triflate derivative. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Bruker IFS 25 FT-IR spectrometer, and mass spectra on a Finnigan MAT 90 instrument (70 eV). Melting points were measured by DTA. Abbreviations used: virt. t = virtual triplet; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^1J(PC) + {}^3J(PC)$.

Preparation of *trans*-$[IrCl\{\eta^2\text{-}Me_3Si\mathit{C}{\equiv}\mathit{C}C(O)CHPh_2\}(PiPr_3)_2]$ (2): A suspension of **1** (60 mg, 0.07 mmol) in hexane (10 mL) was treated dropwise with $PiPr_3$ (51 μL, 0.28 mmol) at room temperature. A yellow solution was formed which after stirring for 10 min was treated with $Me_3SiC{\equiv}CC(O)CHPh_2$ (40 mg, 0.14 mmol). The solution was heated at 50 °C for 2 h, which led to a change of color from yellow to orange. After the mixture had been cooled to room temperature, the solvent was evaporated in vacuo until an orange solid started to precipitate. The precipitation was facilitated by storing the solution at −78 °C for 12 h. An orange microcrystalline solid was formed which was separated from the mother liquor, washed with small amounts of pentane (−20 °C), and dried; yield 93 mg (85 %); m.p. 69 °C (decomp); IR (benzene): $\tilde{\nu} =$ 1862 ($\nu(C{\equiv}C)$), 1618 ($\nu(C{=}O)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.70$ (m, 4H; *ortho*-H of C_6H_5), 7.08 (m, 6H; *meta*- and *para*-H of C_6H_5), 5.86 (s, 1H; C(O)CH), 2.39 (m, 6H; $PCHCH_3$), 1.17 (d virt. t, $N = 13.5$, $J(H,H) = 6.5$ Hz, 18H; $PCHCH_3$), 1.11 (d virt. t, $N = 13.5$, $J(H,H) = 6.5$ Hz, 18H; $PCHCH_3$), 0.50 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 179.7$ (s; C(O)CH), 140.8 (s; *ipso*-C of C_6H_5), 128.7, 128.3, 126.9 (all s; C_6H_5), 109.2, 102.0 (both s, br; $C{\equiv}C$), 64.7 (s; C(O)CH), 21.6 (virt. t, $N = 24.4$ Hz; $PCHCH_3$), 20.1, 19.9 (both s; $PCHCH_3$), 1.4 (s; $Si(CH_3)_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 18.8$ (s); elemental analysis (%) for $C_{35}H_{62}ClIrOP_2Si$ (816.6): calcd: C 51.48, H 7.65; found: C 51.62, H 7.81.

Preparation of $[IrHCl\{C{\equiv}CC(O)CHPh_2\}(PiPr_3)_2]$ (4): A solution of **3** (115 mg, 0.22 mmol) in hexane (10 mL) was cooled to −78 °C and then treated with a solution of $HC{\equiv}CC(O)CHPh_2$ (48 mg, 0.22 mmol) in hexane (10 mL). A quick change of color from yellow to red occurred. After the reaction mixture was warmed to 0 °C, it was worked up as described for **2**. A red microcrystalline solid was obtained; yield 150 mg (90 %); m.p. 96 °C; IR (benzene): $\tilde{\nu} = 2310$ ($\nu(IrH)$), 2062 ($\nu(C{\equiv}C)$), 1683 ($\nu(C{=}O)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.42$ (m, 4H; *ortho*-H of C_6H_5), 7.08 (m, 6H; *meta*- and *para*-H of C_6H_5), 5.34 (s, 1H; C(O)CH), 2.89 (m, 6H; $PCHCH_3$), 1.15 (d virt. t, $N = 14.2$, $J(H,H) = 7.1$ Hz, 18H; $PCHCH_3$), 1.07 (d virt. t, $N = 14.5$, $J(H,H) = 7.3$ Hz, 18H; $PCHCH_3$), −40.96 (t, $J(P,H) = 11.6$ Hz, 1H; IrH); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 39.2$ (s); elemental analysis (%) for $C_{34}H_{54}ClIrOP_2$ (768.4): calcd: C 53.14, H 7.08; found: C 52.97, H 7.23.

Preparation of $[IrHCl(py)\{C{\equiv}CC(O)CHPh_2\}(PiPr_3)_2]$ (5): A solution of **4** (66 mg, 0.07 mmol) in diethyl ether (10 mL) was treated with pyridine (7 μL, 0.07 mmol) and stirred for 5 min at room temperature. A change of color from red to light brown occurred. The solvent was evaporated in vacuo, and the residue dissolved in hot hexane (60 °C). After the solution was cooled to room temperature, it was stored at −78 °C for 12 h. An off-white solid precipitated, which was washed with small amounts of pentane (0 °C) and dried; yield 67 mg (93 %); m.p. 127 °C. IR (KBr): $\tilde{\nu} = 2252$ ($\nu(IrH)$), 2054 ($\nu(C{\equiv}C)$), 1620 ($\nu(C{=}O)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 10.24$, 9.90 (both s, br, 1H each; *ortho*-H of C_5H_5N), 7.49 (m, 4H; *ortho*-H of C_6H_5), 7.05 (m, 6H; *meta*- and *para*-H of C_6H_5), 6.82 (m, 1H; *para*-H of C_5H_5N), 6.56 (m, 2H; *meta*-H of C_5H_5N), 5.43 (s, 1H; C(O)CH), 2.84 (m, 6H; $PCHCH_3$), 1.06 (d virt. t, $N = 14.0$, $J(H,H) = 7.3$ Hz, 18H; $PCHCH_3$), 1.01 (d virt. t, $N = 14.0$, $J(H,H) = 7.3$ Hz, 18H; $PCHCH_3$), −21.68 (t, $J(P,H) = 16.0$ Hz, 1H; IrH); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 182.3$ (s; C(O)CH), 154.9, 152.3, 136.7, 129.7, 129.4, 128.5, 128.3, 126.7 (all s; C_5H_5N and C_6H_5), 140.8 (s; *ipso*-C of C_6H_5), 110.8 (t, $J(P,C) = 4.1$ Hz; $Ir{-}C{\equiv}C$), 105.8 (t, $J(P,C) = 2.0$ Hz; $Ir{-}C{\equiv}C$), 67.1 (s; C(O)CH), 23.8 (virt. t, $N = 26.4$ Hz; $PCHCH_3$), 19.2, 19.1 (both s; $PCHCH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 10.4$ (s); elemental analysis (%) for $C_{39}H_{59}ClIrNOP_2$ (847.5): calcd: C 55.27, H 7.02, N 1.65; found: C 54.91, H 6.92, N 1.51.

Preparation of *trans*-$[IrCl\{{=}C{=}CHC(O)CHPh_2\}(PiPr_3)_2]$ (6): Method a: A solution of **4** (62 mg, 0.08 mmol) in benzene (5 mL) was stirred for 3 h at room temperature. A gradual change of color from red to red-violet occurred. The solvent was evaporated in vacuo and the residue treated with pentane (1 mL). A red-violet solid precipitated, the formation of which was facilitated by storing the solution for 15 h at −78 °C. The solid was separated from the mother liquor, washed with small amounts of pentane (−20 °C) and dried; yield 57 mg (92 %). Method b: A solution of **3** (50 mg, 0.09 mmol) in hexane (10 mL) was cooled to −78 °C and then treated with a solution of $HC{\equiv}CC(O)CHPh_2$ (20 mg, 0.09 mmol) in hexane (10 mL). A quick change of color from yellow to red occurred. After warming the reaction mixture to room temperature, it was stirred for 3 h and then worked up as described for Method a; yield 59 mg (85 %); m.p. 142 °C; MS (70 eV): *m/z*: 768 (M^+ for ^{193}Ir and ^{35}Cl); IR (KBr): $\tilde{\nu} = 1654$ ($\nu(C{=}O)$), 1544 ($\nu(C{=}C)$ cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.30$ (m, 4H; *ortho*-H of C_6H_5), 7.06 (m, 6H; *meta*- and *para*-H of C_6H_5), 4.84 (s, 1H; C(O)CH), 2.78 (m, 6H; $PCHCH_3$), 1.28 (d virt. t, $N = 14.5$, $J(H,H) = 7.3$ Hz, 36H; $PCHCH_3$), −1.45 (t, $J(P,H) = 2.9$ Hz, 1H; $=CHC(O)CHPh_2$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 255.2$ (t, $J(P,C) = 11.6$ Hz; $Ir{=}C{=}C$), 181.3 (s; C(O)CH), 140.9 (s; *ipso*-C of C_6H_5), 129.6, 128.4, 126.9 (all s; C_6H_5), 112.4 (t, $J(P,C) = 9.5$ Hz; $Ir{=}C{=}C$), 64.3 (s; C(O)CH), 23.5 (virt. t, $N = 26.8$ Hz; $PCHCH_3$), 20.1 (s; $PCHCH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 37.1$ (s); elemental analysis (%) for $C_{34}H_{54}ClIrOP_2$ (768.4): calcd: C 53.14, H 7.08; found: C 52.66, H 6.64.

Preparation of $[IrHCl\{C{\equiv}CC(OAc){=}CPh_2\}(PiPr_3)_2]$ (7): A solution of **3** (110 mg, 0.20 mmol) in hexane (10 mL) was cooled to −78 °C and then treated with a solution of $HC{\equiv}CC(OAc){=}CPh_2$ (52 mg, 0.20 mmol) in hexane (5 mL). A quick change of color from yellow to violet occurred. After warming the solution to room temperature, it was concentrated to 2 mL in vacuo and then stored at −78 °C for 16 h. Red crystals precipitated which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried; yield 131 mg (81 %); m.p. 59 °C (decomp); MS (70 eV): *m/z*: 810 (M^+ for ^{193}Ir and ^{35}Cl); IR (KBr): $\tilde{\nu} = 2073$ ($\nu(C{\equiv}C)$), 1752

($\nu(\mathrm{OCO})_{\mathrm{as}}$), 1457 ($\nu(\mathrm{OCO})_{\mathrm{sym}}$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.75$, 7.36 (both m, 2 H each; *ortho*-H of $\mathrm{C_6H_5}$), 7.04 (m, 6 H; *meta*- and *para*-H of $\mathrm{C_6H_5}$), 2.98 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.65 (s, 3 H; $\mathrm{CO_2CH_3}$), 1.23 (d virt. t, $N = 13.1$, $J(\mathrm{H,H}) = 6.0$ Hz, 18 H; $\mathrm{PCHC}H_3$), 1.17 (d virt. t, $N = 12.8$, $J(\mathrm{H,H}) = 6.0$ Hz, 18 H; $\mathrm{PCHC}H_3$), -42.65 (t, $J(\mathrm{P,H}) = 11.6$ Hz, 1 H; IrH); ^{13}C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta = 168.0$ (s; $C\mathrm{O_2CH_3}$), 141.0, 140.4 (both s; *ipso*-C of $\mathrm{C_6H_5}$), 130.5, 130.3 (both s; C = C), 130.9, 130.2, 128.2, 126.8 (all s; $\mathrm{C_6H_5}$), 104.0 (s; $\mathrm{Ir{-}C{\equiv}}C$), 93.4 (t, $J(\mathrm{P,C}) = 12.0$ Hz; $\mathrm{Ir{-}}C\mathrm{{\equiv}C}$), 23.2 (virt. t, $N = 26.8$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 20.5 (s; $\mathrm{CO_2}C\mathrm{H_3}$), 19.9, 19.6 (both s; $\mathrm{PCH}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta = 40.0$ (s); elemental analysis (%) for $\mathrm{C_{36}H_{56}ClIrO_2P_2}$ (810.5): calcd: C 53.35, H 6.96; found: C 52.91, H 6.88.

Preparation of *trans*-$[\mathrm{IrCl({=}C{=}C{=}C{=}CPh_2)(P}i\mathrm{Pr_3)_2}]$ (8): A solution of **3** (116 mg, 0.22 mmol) in hexane (15 mL) was cooled to −100 °C and treated with $\mathrm{NEt_3}$ (24 µL, 0.22 mmol). To the reaction mixture, a cooled solution (−100 °C) of $\mathrm{HC{\equiv}CC(OTf){=}CPh_2}$ (77 mg, 0.22 mmol), freshly prepared from $\mathrm{Me_3SiC{\equiv}CC(OTf){=}CPh_2}$, in hexane (40 mL) was added. A change of color from yellow to olive-green occurred. After the reaction mixture was warmed to −30 °C, the solvent was evaporated in vacuo. The oily residue was extracted with pentane (50 mL), and the extract was concentrated to 4 mL in vacuo. Storing the solution at −78 °C led to the precipitation of an orange microcrystalline solid, which was separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried; yield 123 mg (77 %); m.p. 62 °C (decomp); MS (70 eV): m/z: 750 (M^+ for ^{193}Ir and ^{35}Cl); IR (KBr): $\tilde{\nu} = 1993$ ($\nu(\mathrm{C{=}C{=}C{=}C})$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz): $\delta = 7.50$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 7.21 (m, 4 H; *meta*-H of $\mathrm{C_6H_5}$), 6.82 (m, 2 H; *para*-H of $\mathrm{C_6H_5}$), 2.89 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.28 (d virt. t, $N = 13.8$, $J(\mathrm{H,H}) = 7.0$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, 100.6 MHz): $\delta = 225.7$ (t, $J(\mathrm{P,C}) = 13.7$ Hz; $\mathrm{Ir{=}}C\mathrm{{=}C{=}C{=}C}$), 174.6, 164.1 (both t, $J(\mathrm{P,C}) = 3.6$ Hz; $\mathrm{Ir{=}C{=}}C\mathrm{{=}C{=}C}$ and $\mathrm{Ir{=}C{=}C{=}}C\mathrm{{=}C}$), 132.1 (s; *ipso*-C of $\mathrm{C_6H_5}$), 130.2, 128.5, 127.3 (all s; $\mathrm{C_6H_5}$), 105.9 (t, $J(\mathrm{P,C}) = 2.5$ Hz; $\mathrm{Ir{=}C{=}C{=}C{=}}C$), 23.6 (virt. t, $N = 26.4$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 20.1 (s; $\mathrm{PCH}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{C_6D_6}$, 162.0 MHz): $\delta = 26.7$ (s); elemental analysis (%) for $\mathrm{C_{34}H_{52}ClIrP_2}$ (750.4): calcd: C 54.42, H 6.98; found: C 54.74, H 6.90.

Generation of $[\mathrm{IrCl({=}C{=}C{=}C{=}CPh_2)(CO)(P}i\mathrm{Pr_3)_2}]$ (9): A slow stream of CO was passed through a solution of **8** (60 mg, 0.08 mmol) in pentane (15 mL) at −78 °C. A change of color from olive-green to orange occurred and a solid started to precipitate. The solution was carefully concentrated to 2 mL in vacuo and then stored at −60 °C under a CO atmosphere. An orange solid precipitated which was separated from the mother liquor and dried in a slow stream of argon. Owing to the spectroscopic data, the solid consisted of a mixture of **8** and **9**. Attempts to separate the mixture by fractional crystallization under CO failed. Data for **9**: IR (KBr): $\tilde{\nu} = 1987$ ($\nu(\mathrm{C{=}C{=}C{=}C})$, 1944 ($\nu(\mathrm{CO})$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.60$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 7.06 (m, 6 H; *meta*- and *para*-H of $\mathrm{C_6H_5}$), 2.77 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.30 (d virt. t, $N = 12.5$, $J(\mathrm{H,H}) = 6.9$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{31}P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta = 19.6$ (s).

Preparation of *trans*-$[\mathrm{IrCl\{{=}C{=}CHC(O_2CCF_3){=}CPh_2\}(P}i\mathrm{Pr_3)_2}]$ (10): A solution of **8** (53 mg, 0.07 mmol) in benzene (5 mL) was treated with $\mathrm{CF_3CO_2H}$ (5.5 µL, 0.07 mmol) at room temperature. A change of color from olive-green to red-violet occurred. The solvent was evaporated in vacuo, the residue was dissolved in pentane (2 mL) and the solution was cooled to −78 °C. A red-violet solid precipitated which was separated from the mother liquor, washed with pentane (2 mL, 0 °C) and dried; yield 52 mg (87 %); m.p. 106 °C (decomp); IR (KBr): $\tilde{\nu} = 1795$ ($\nu(\mathrm{OCO})_{\mathrm{as}}$), 1626 ($\nu(\mathrm{C{=}C})$), 1457 ($\nu(\mathrm{OCO})_{\mathrm{sym}}$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.27$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 6.93 (m, 6 H; *meta*- and *para*-H of $\mathrm{C_6H_5}$), 2.88 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.28 (d virt. t, $N = 13.4$, $J(\mathrm{H,H}) = 6.7$ Hz, 36 H; $\mathrm{PCHC}H_3$), -2.81 (t, $J(\mathrm{P,H}) = 2.1$ Hz, 1 H; $\mathrm{{=}C}H\mathrm{C(O_2CCF_3)}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta = 255.6$ (t, $J(\mathrm{P,C}) = 12.1$ Hz; $\mathrm{Ir{=}}C\mathrm{{=}C}$), 154.6 (q, $J(\mathrm{F,C}) = 43.2$ Hz; $\mathrm{CF_3}C\mathrm{O_2}$), 148.2 (s, br; $C\mathrm{(O_2CCF_3)}$), 140.0, 138.8 (both s; *ipso*-C of $\mathrm{C_6H_5}$), 138.7 (s; $\mathrm{{=}}C\mathrm{Ph_2}$), 130.2, 129.3, 123.3, 120.2 (all s; $\mathrm{C_6H_5}$), 115.3 (q, $J(\mathrm{F,C}) = 286.0$ Hz; $C\mathrm{F_3CO_2}$), 104.9 (t, $J(\mathrm{P,C}) = 3.8$ Hz; $\mathrm{Ir{=}C{=}}C$), 23.4 (virt. t, $N = 26.7$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 20.0 (s; $\mathrm{PCH}C\mathrm{H_3}$); ^{19}F NMR ($\mathrm{C_6D_6}$, 188.0 MHz): $\delta = -74.4$ (s); ^{31}P NMR ($\mathrm{C_6D_6}$, 162.0 MHz): $\delta = 32.3$ (s); elemental analysis (%) for $\mathrm{C_{36}H_{53}ClIrF_3O_2P_2}$ (864.6): calcd: C 50.01, H 6.18; found: C 50.40, H 6.21.

Preparation of $[\mathrm{IrCl_2\{}\eta^1\mathrm{\text{-}(}Z\mathrm{)\text{-}CH({=}CHC(Cl){=}CPh_2\}(P}i\mathrm{Pr_3)_2}]$ (11): A solution of **8** (52 mg, 0.07 mmol) in benzene (5 mL) was treated with an excess of a solution of HCl in benzene at room temperature. A change of color from olive-green to brown occurred. After the mixture was stirred for 5 min, the solvent was evaporated in vacuo. The oily residue was dissolved in pentane and the solution was stored at −78 °C. A brown solid precipitated which was separated from the mother liquor, washed twice with pentane (1 mL each), and dried; yield 51 mg (88 %); m.p. 138 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz): $\delta = 9.63$ (dt, $J(\mathrm{H,H}) = 12.0$ Hz, $J(\mathrm{P,H}) = 1.8$ Hz, 1 H; $\mathrm{Ir{-}C}H\mathrm{{=}CH}$), 7.45, 7.39 (both m, 2 H each; *ortho*-H of $\mathrm{C_6H_5}$), 7.22 (m, 2 H; *meta*-H of $\mathrm{C_6H_5}$), 7.10 (m, 4 H; *meta*- and *para*-H of $\mathrm{C_6H_5}$), 6.59 (dt, $J(\mathrm{H,H}) = 12.0$, $J(\mathrm{P,H}) = 2.0$ Hz, 1 H; $\mathrm{Ir{-}CH{=}C}H$), 3.08 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.17 (d virt. t, $N = 13.5$, $J(\mathrm{H,H}) = 6.9$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, 100.6 MHz): $\delta = 167.5$ (s; $C\mathrm{Cl{=}CPh_2}$), 142.2 (s; $= C\mathrm{Ph_2}$), 133.7, 130.1 (both s; *ipso*-C of $\mathrm{C_6H_5}$), 130.7, 130.6, 129.0, 128.4, 127.4, 126.9 (all s; $\mathrm{C_6H_5}$), 107.9 (t, $J(\mathrm{P,C}) = 8.0$ Hz; $\mathrm{Ir{-}}C\mathrm{H{=}CH}$), 21.9 (virt. t, $N = 24.4$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 19.7 (s; $\mathrm{PCH}C\mathrm{H_3}$), the signal for $\mathrm{Ir{-}CH{=}}C\mathrm{H}$ could not be exactly located; ^{31}P NMR ($\mathrm{C_6D_6}$, 162.0 MHz): $\delta = 7.6$ (s); elemental analysis (%) for $\mathrm{C_{34}H_{54}Cl_3IrP_2}$ (823.3): calcd: C 49.60, H 6.61; found: C 49.81, H 6.90.

Preparation of *trans*-$[\mathrm{IrI({=}C{=}C{=}C{=}CPh_2)(P}i\mathrm{Pr_3)_2}]$ (12): A solution of **8** (50 mg, 0.07 mmol) in acetone (10 mL) was treated with KI (115 mg, 0.70 mmol) and stirred for 1 h at room temperature. A change of color from olive-green to orange occurred. The solvent was evaporated in vacuo, the residue was extracted with pentane (50 mL), and the extract was concentrated to 3 mL in vacuo. After the solution was stored at −78 °C, an orange solid precipitated which was separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried; yield 51 mg (91 %); m.p. 101 C (decomp); IR (KBr): $\tilde{\nu} = 1992$ ($\nu(\mathrm{C{=}C{=}C{=}C})$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.50$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 7.21 (m, 4 H; *meta*-H of $\mathrm{C_6H_5}$), 6.81 (m, 2 H; *para*-H of $\mathrm{C_6H_5}$), 3.14 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.28 (d virt. t, $N = 13.8$, $J(\mathrm{H,H}) = 6.9$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, 100.6 MHz): $\delta = 215.3$ (t, $J(\mathrm{P,C}) = 14.7$ Hz; $\mathrm{Ir{=}}C\mathrm{{=}C{=}C{=}C}$), 179.1 (t, $J(\mathrm{P,C}) = 3.6$ Hz; $\mathrm{Ir{=}C{=}C{=}}C\mathrm{{=}C}$), 164.4 (t, $J(\mathrm{P,C}) = 4.6$ Hz; $\mathrm{Ir{=}C{=}}C\mathrm{{=}C{=}C}$), 132.2 (s; *ipso*-C of $\mathrm{C_6H_5}$), 130.1, 129.0, 127.0 (all s; $\mathrm{C_6H_5}$), 109.1 (t, $J(\mathrm{P,C}) = 3.0$ Hz; $\mathrm{Ir{=}C{=}C{=}C{=}}C$), 25.3 (virt. t, $N = 27.5$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 20.4 (s; $\mathrm{PCH}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta = 21.3$ (s); elemental analysis (%) for $\mathrm{C_{34}H_{52}IIrP_2}$ (841.6): calcd: C 48.52, H 6.23; found: C 48.76, H 6.31.

Preparation of *trans*-$[\mathrm{Ir(OH)({=}C{=}C{=}C{=}CPh_2)(P}i\mathrm{Pr_3)_2}]$ (13): A solution of **8** (60 mg, 0.08 mmol) in acetone (10 mL) was treated with KOH (32 mg, 0.80 mmol) and stirred for 10 min at room temperature. A gradual change of color from olive-green to green occurred. The solvent was evaporated in vacuo, the residue was extracted with pentane (50 mL) and the extract was brought to dryness in vacuo. Upon treatment of the oily residue with pentane (2 mL) at −30 °C, a green solid precipitated which was separated from the mother liquor and dried; yield 51 mg (87 %); m.p. 56 °C (decomp); IR (KBr): $\tilde{\nu} = 3460$ ($\nu(\mathrm{OH})$), 1996 ($\nu(\mathrm{C{=}C{=}C{=}C})$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 7.61$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 7.23 (m, 4 H; *meta*-H of $\mathrm{C_6H_5}$), 6.83 (m, 2 H; *para*-H of $\mathrm{C_6H_5}$), 2.99 (s, br, 1 H; OH), 2.60 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.26 (d virt. t, $N = 13.9$, $J(\mathrm{H,H}) = 6.9$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, 50.3 MHz): $\delta = 227.8$ (t, $J(\mathrm{P,C}) = 12.7$ Hz; $\mathrm{Ir{=}}C\mathrm{{=}C{=}C{=}C}$), 173.2 (t, $J(\mathrm{P,C}) = 5.1$ Hz; $\mathrm{Ir{=}C{=}}C\mathrm{{=}C{=}C}$), 164.0 (t, $J(\mathrm{P,C}) = 3.1$ Hz, $\mathrm{Ir{=}C{=}C{=}}C\mathrm{{=}C}$); 138.2 (s; *ipso*-C of $\mathrm{C_6H_5}$), 130.2, 129.7, 126.4 (all s; $\mathrm{C_6H_5}$), 103.4 (t, $J(\mathrm{P,C}) = 2.5$ Hz; $\mathrm{Ir{=}C{=}C{=}C{=}}C$), 22.9 (virt. t, $N = 26.7$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 19.9 (s; $\mathrm{PCH}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{C_6D_6}$, 81.0 MHz): $\delta = 31.1$ (s); elemental analysis (%) for $\mathrm{C_{34}H_{53}IrOP_2}$ (732.0): calcd: C 55.79, H 7.18; found: C 55.92, H 6.99.

Preparation of *trans*-$[\mathrm{IrN_3({=}C{=}C{=}C{=}CPh_2)(P}i\mathrm{Pr_3)_2}]$ (14): A solution of **8** (61 mg, 0.08 mmol) in acetone (10 mL) was treated with $\mathrm{NaN_3}$ (52 mg, 0.80 mmol) and stirred for 30 min at room temperature. The solvent was evaporated in vacuo, the residue was extracted with 50 mL of a mixture of pentane/benzene (2:1) and the extract was brought to dryness in vacuo. Upon treatment of the oily residue with pentane (2 mL) at −30 °C, an olive-green solid precipitated which was separated from the mother liquor and dried; yield 55 mg (91 %); m.p. 95 °C (decomp); IR (KBr): $\tilde{\nu} = 2067$ ($\nu(\mathrm{N{=}N{=}N})$), 1994 ($\nu(\mathrm{C{=}C{=}C{=}C})$) cm^{-1}; ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz): $\delta = 7.50$ (m, 4 H; *ortho*-H of $\mathrm{C_6H_5}$), 7.21 (m, 4 H; *meta*-H of $\mathrm{C_6H_5}$), 6.82 (m, 2 H; *para*-H of $\mathrm{C_6H_5}$), 2.63 (m, 6 H; $\mathrm{PC}H\mathrm{CH_3}$), 1.22 (d virt. t, $N = 13.8$, $J(\mathrm{H,H}) = 7.0$ Hz, 36 H; $\mathrm{PCHC}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, 100.6 MHz): $\delta = 233.8$ (t, $J(\mathrm{P,C}) = 14.2$ Hz; $\mathrm{Ir{=}}C\mathrm{{=}C{=}C{=}C}$), 174.1 (t, $J(\mathrm{P,C}) = 7.6$ Hz; $\mathrm{Ir{=}C{=}}C\mathrm{{=}C{=}C}$), 163.8 (t, $J(\mathrm{P,C}) = 3.6$ Hz; $\mathrm{Ir{=}C{=}C{=}}C\mathrm{{=}C}$), 138.7 (s; *ipso*-C of $\mathrm{C_6H_5}$), 130.8, 128.3, 127.4 (all s; $\mathrm{C_6H_5}$), 105.5 (t, $J(\mathrm{P,C}) = 2.5$ Hz; $\mathrm{Ir{=}C{=}C{=}C{=}}C$), 24.4 (virt. t, $N = 27.5$ Hz; $\mathrm{P}C\mathrm{HCH_3}$), 19.8 (s; $\mathrm{PCH}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{C_6D_6}$, 162.0 MHz): $\delta = 30.4$ (s); elemental analysis (%) for $\mathrm{C_{34}H_{52}IrN_3P_2}$ (757.0): calcd: C 53.95, H 6.92; N 5.55; found: C 54.35, H 6.74, N 5.21.

Preparation of *trans*-$[\mathrm{Ir(OPh)({=}C{=}C{=}C{=}CPh_2)(P}i\mathrm{Pr_3)_2}]$ (15): A solution of **13** (50 mg, 0.07 mmol) in benzene (5 mL) was treated with phenol (7 mg, 0.07 mmol) and stirred for 5 min at room temperature. The solvent was evaporated in vacuo, the residue was suspended in pentane (2 mL) and the suspension was stored at $-60\,^{\circ}C$. An olive-green solid precipitated which was separated from the mother liquor, washed with small amounts of pentane ($0\,^{\circ}C$) and dried; yield 52 mg (94 %); m.p. $97\,^{\circ}C$ (decomp); IR (KBr): $\tilde{\nu} = 1998$ ($\nu(C{=}C{=}C{=}C)$) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.55$ (m, 4 H; *ortho*-H of C_6H_5), 7.23 (m, 4 H; *meta*-H of C_6H_5), 7.20 (m, 2 H; *meta*-H of C_6H_5O), 6.82 (m, 2 H; *para*-H of C_6H_5), 6.67 (m, 1 H; *para*-H of C_6H_5O), 6.51 (m, 2 H; *ortho*-H of C_6H_5O), 2.44 (m, 6 H; $PC\mathit{H}CH_3$), 1.22 (d virt. t, $N = 13.8$, $J(H,H) = 7.0$ Hz, 36 H; $PCHC\mathit{H}_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 229.3$ (t, $J(P,C) = 13.7$ Hz; $Ir{=}\mathit{C}{=}C{=}C{=}C$), 167.8 (s; *ipso*-C of C_6H_5O), 167.7, 164.6 (both t, $J(P,C) = 3.0$ Hz; $Ir{=}C{=}\mathit{C}{=}C{=}C$ and $Ir{=}C{=}C{=}\mathit{C}{=}C$), 130.2 (s; *ipso*-C of C_6H_5), 130.2, 129.7, 128.2, 126.9, 121.1, 116.1 (all s; C_6H_5 and C_6H_5O), 103.7 (t, $J(P,C) = 2.9$ Hz; $Ir{=}C{=}C{=}C{=}\mathit{C}$), 24.2 (virt. t, $N = 25.4$ Hz; $P\mathit{C}HCH_3$), 20.0 (s; $PCH\mathit{C}H_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 31.4$ (s); elemental analysis (%) for $C_{40}H_{57}IrOP_2$ (808.1): calcd: C 59.45; H 7.11; found: C 59.73, H 6.89.

Preparation of $[IrH_2(CH{=}C{=}C{=}CPh_2)(CO)(P\mathit{i}Pr_3)_2]$ (16): A solution of **13** (50 mg, 0.07 mmol) in methanol (10 mL) was stirred for 1 h at room temperature. A change of color from olive-green to light brown occurred. The solution was concentrated to 2 mL in vacuo and then stored at $-60\,^{\circ}C$. An off-white solid precipitated which was separated from the mother liquor, washed twice with pentane (2 mL each), and dried; yield 42 mg (82 %); m.p. $100\,^{\circ}C$ (decomp); IR (KBr): $\tilde{\nu} = 2055$ ($\nu(IrH)$), 1975 ($\nu(C{=}C{=}C{=}C)$), 1931 ($\nu(CO)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.93$, 7.72 (both m, 2 H each; *ortho*-H of C_6H_5), 7.24 (m, 4 H; *meta*-H of C_6H_5), 7.04 (m, 2 H; *para*-H of C_6H_5), 6.82 (m, 1 H; Ir-CH), 2.17 (m, 6 H; $PC\mathit{H}CH_3$), 1.16 (d virt. t, $N = 14.5$, $J(H,H) = 7.3$ Hz, 36 H; $PCHC\mathit{H}_3$), -8.88 (dt, $J(P,H) = 14.5$, $J(H,H) = 4.3$ Hz, 2 H; Ir-H); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 176.9$ (t, $J(P,C) = 8.8$ Hz; Ir-CO), 169.2 (t, $J(P,C) = 4.6$ Hz; $Ir{-}CH{=}C{=}\mathit{C}{=}C$), 164.7 (t, $J(P,C) = 5.1$ Hz; $Ir{-}CH{=}\mathit{C}{=}C{=}C$), 142.2 (t, $J(P,C) = 2.0$ Hz; *ipso*-C of C_6H_5), 130.2, 129.1, 127.4, 126.4, 126.2, 120.2 (all s; C_6H_5), 114.9 (t, $J(P,C) = 3.7$ Hz; $Ir{-}CH{=}C{=}C{=}\mathit{C}$), 111.4 (t, $J(P,C) = 13.9$ Hz; $Ir{-}\mathit{C}H$), 25.0 (virt. t, $N = 29.6$ Hz; $P\mathit{C}HCH_3$), 19.1 (s; $PCH\mathit{C}H_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 33.9$ (s); elemental analysis (%) for $C_{35}H_{55}IrOP_2$ (746.0): calcd: C 56.35, H 7.43; found: C 56.51, H 7.20.

Generation of *trans*-$[Ir(CH_3)({=}C{=}C{=}C{=}CPh_2)(P\mathit{i}Pr_3)_2]$ (17): A solution of **8** (44 mg, 0.06 mmol) in pentane (15 mL) was cooled to $-78\,^{\circ}C$ and treated with a 1.0 M solution of MeLi in hexane (0.06 mL, 0.06 mmol). A change of color from olive-green to orange occurred. After the reaction mixture was warmed to room temperature, it was filtered through cotton and the filtrate was brought to dryness in vacuo. Due to smooth decomposition, the oily residue could not be further purified. Data for **17**: IR (C_6H_6): $\tilde{\nu} = 1997$ ($\nu(C{=}C{=}C{=}C)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.55$ (m, 4 H; *ortho*-H of C_6H_5), 7.19 (m, 4 H; *meta*-H of C_6H_5), 6.85 (m, 2 H; *para*-H of C_6H_5), 2.73 (m, 6 H; $PC\mathit{H}CH_3$), 1.56 (t, $J(P,H) = 6.4$ Hz, 3 H; $Ir\text{-}CH_3$), 1.24 (d virt. t, $N = 13.6$, $J(H,H) = 6.9$ Hz, 36 H; $PCHC\mathit{H}_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 24.2$ (s).

Preparation of *trans*-$[Ir\{C(C{\equiv}CCH_3){=}CPh_2\}(CO)(P\mathit{i}Pr_3)_2]$ (18): A solution of **8** (60 mg, 0.08 mmol) in pentane (15 mL) was cooled to $-78\,^{\circ}C$ and treated with a 1.0 M solution of MeLi in THF (0.08 mL, 0.08 mmol). A change of color from olive-green to orange occurred. After the reaction mixture was warmed to room temperature and stirred for 10 min, it was again cooled to $-78\,^{\circ}C$ and a slow stream of CO was passed through the solution for 15 s. A change of color from orange to yellow occurred. After warming to room temperature, the solution was filtered through cotton and the filtrate was concentrated to 2 mL in vacuo. Storing the solution at $-60\,^{\circ}C$ for 12 h led to the formation of yellow crystals, which were separated from the mother liquor, washed with a small amount of pentane ($0\,^{\circ}C$), and dried; yield 54 mg (85 %); m.p. $162\,^{\circ}C$; MS (70 eV): *m/z*: 758 (M^+ for ^{193}Ir and ^{35}Cl); IR (KBr): $\tilde{\nu} = 1999$ ($\nu(C{\equiv}C)$), 1925 ($\nu(CO)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.42$ (m, 4 H; *ortho*-H of C_6H_5), 7.11 (m, 6 H, *meta*- and *para*-H of C_6H_5), 2.53 (m, 6 H; $PC\mathit{H}CH_3$), 1.62 (s; $\equiv CCH_3$), 1.31 (d virt. t, $N = 13.9$, $J(H,H) = 6.9$ Hz, 18 H; $PCHC\mathit{H}_3$), 1.12 (d virt. t, $N = 12.8$, $J(H,H) = 7.7$ Hz, 18 H; $PCHC\mathit{H}_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 186.7$ (t, $J(P,C) = 11.0$ Hz; Ir−CO), 157.8 (t, $J(P,C) = 12.7$ Hz; $Ir{-}\mathit{C}{=}CPh_2$), 153.5 (t, $J(P,C) = 4.3$ Hz; $Ir{-}C{=}\mathit{C}Ph_2$), 148.5, 145.2 (both s; *ipso*-C of C_6H_5), 130.3, 129.9, 128.4, 127.6, 127.4, 126.8, 126.1, 125.7, 125.6 (all s; C_6H_5), 100.3, 88.7 (both s; $\mathit{C}{\equiv}CCH_3$ and $C{\equiv}\mathit{C}CH_3$), 26.3 (virt. t, $N = 26.8$ Hz; $P\mathit{C}HCH_3$), 24.1 (s; CH_3), 20.5, 19.6 (both s; $PCH\mathit{C}H_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 32.3$ (s); elemental analysis (%) for $C_{36}H_{55}IrOP_2$ (757.9) : calcd: C 57.04, H 7.31; found: C 56.81, H 7.21.

Preparation of *trans*-$[Ir\{C{\equiv}CC(N_3){=}CPh_2\}(CO)(P\mathit{i}Pr_3)_2]$ (19): A slow stream of CO was passed for 15 s through a solution of **14** (60 mg, 0.08 mmol) in 10 mL of a mixture of pentane/dichloromethane (1:1) at $-78\,^{\circ}C$. A change of color from olive-green to orange occurred. The solution was warmed to room temperature which led again to a change of color from orange to yellow. The solvent was evaporated in vacuo, the oily residue was dissolved in benzene (1 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V). With pentane a yellow fraction was eluted, which was dried in vacuo to give a yellow solid. It could not be recrystallized for further purification since in solution it partly rearranged to **20**. Data for **19**: IR (KBr): $\tilde{\nu} = 2102$ ($\nu(N{=}N{=}N)$), 2062 ($\nu(C{\equiv}C)$), 1929 ($\nu(CO)$) cm^{-1}; ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.71$, 7.36 (both m, 2 H each; *ortho*-H of C_6H_5), 7.08 (m, 6 H; *meta*- and *para*-H of C_6H_5), 2.54 (m, 6 H; $PC\mathit{H}CH_3$), 1.21 (d virt. t, $N = 13.9$, $J(H,H) = 6.9$ Hz, 36 H; $PCHC\mathit{H}_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 188.4$ (t, $J(P,C) = 10.5$ Hz; Ir−CO), 143.5 (s; $\mathit{C}(N_3){=}CPh_2$ or $C(N_3){=}\mathit{C}Ph_2$), 141.8, 140.7 (both s; *ipso*-C of C_6H_5), 139.2 (t, $J(P,C) = 17.1$ Hz; $Ir{-}\mathit{C}{\equiv}C$), 131.1, 130.8, 129.0, 128.8, 126.9, 126.8 (all s; C_6H_5), 120.5 (t, $J(P,C) = 2.4$ Hz; $Ir{-}C{\equiv}\mathit{C}$), 112.3 (s; $\mathit{C}(N_3){=}CPh_2$ or $C(N_3){=}\mathit{C}Ph_2$), 26.3 (virt. t, $N = 28.1$ Hz; $P\mathit{C}HCH_3$), 20.2 (s; $PCH\mathit{C}H_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 42.3$ (s).

Preparation of *trans*-$[Ir\{C(N_3){=}C{=}C{=}CPh_2\}(CO)(P\mathit{i}Pr_3)_2]$ (20): A solution of **19** (65 mg, 0.08 mmol) in benzene (3 mL) was stirred for 36 h at room temperature. The solvent was evaporated in vacuo, the oily residue was dissolved in pentane (5 mL) and the solution was stored at $-60\,^{\circ}C$ for 24 h. An orange microcrystalline solid precipitated, which was washed with small amounts of pentane ($0\,^{\circ}C$), and dried; yield 52 mg (80 %); m.p. $108\,^{\circ}C$ (decomp); IR (KBr): $\tilde{\nu} = 2058$ ($\nu(N{=}N{=}N)$), 1992 ($\nu(C{=}C{=}C{=}C)$), 1942 ($\nu(CO)$) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.56$ (m, 4 H; *ortho*-H of C_6H_5), 7.16 (m, 6 H; *meta*- and *para*-H of C_6H_5), 2.48 (m, 6 H; $PC\mathit{H}CH_3$), 1.16 (d virt. t, $N = 14.1$, $J(H,H) = 7.4$ Hz, 36 H; $PCHC\mathit{H}_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 190.0$ (t, $J(P,C) = 10.2$ Hz; Ir−CO), 165.3 (t, $J(P,C) = 16.2$ Hz; $Ir{-}\mathit{C}(N_3){=}C{=}C{=}C$), 154.5 (t, $J(P,C) = 2.0$ Hz; $Ir{-}C(N_3){=}C{=}\mathit{C}{=}C$), 146.2 (t, $J(P,C) = 6.1$ Hz; $Ir{-}C(N_3){=}\mathit{C}{=}C{=}C$), 143.5 (s; *ipso*-C of C_6H_5), 129.0, 128.6, 126.8 (all s; C_6H_5), 104.7 (t, $J(P,C) = 2.0$ Hz; $Ir{-}C(N_3){=}C{=}C{=}\mathit{C}$), 26.1 (virt. t, $N = 27.5$ Hz; $P\mathit{C}HCH_3$), 20.0 (s; $PCH\mathit{C}H_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 41.4$ (s); elemental analysis (%) for $C_{35}H_{52}IrN_3OP_2$ (785.0): calcd: C 53.55, H 6.68, N 5.35; found: C 53.21, H 6.91, N 5.14.

X-ray structural determination of compounds 8 and 18: Single crystals of **8** were grown from a saturated solution in diethyl ether at $5\,^{\circ}C$, and those of **18** from a saturated solution in acetone at room temperature. Crystal data collection parameters are summarized in Table 1. The data were collected on an Enraf-Nonius CAD4 diffractometer (**8**) and a Stoe area-detecting system (**18**) using monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied for **8** (Ψ scan method, minimum transmission 67.21 %) The structures were solved using the Patterson method (SHELXS-97).[28] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least squares on F^2 (SHELXL-97).[29] The positions of all hydrogen atoms were calculated according to ideal geometry (distance C−H = 0.95 Å) and refined by using the riding method; they were used only in structure factor calculation.[30]

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[30] CCDC-138491 (**8**) and CCDC-178705 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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