Reactions of the Allenylidenes *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] with Electrophiles: Generation of Butatriene–, Carbene–, and Carbyne–Iridium Complexes

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Dedicated to Professor Max Herberhold on the occasion of his 65th birthday

Abstract: The allenylideneiridium(I) complexes *trans*-[IrX(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (X = Cl: **1**; X = I: **2**) react with excess methyl iodide by C–C coupling and elimination of HI to give the η^2-butatriene compounds *trans*-[IrX(η^2-CH$_2$=*C*=*C*=CPh$_2$)(P*i*Pr$_3$)$_2$] (**3**, **4**), of which **3** (X = Cl) was characterized by X-ray crystallography. Treatment of **1** and **5** (containing C=C=C(Ph)*t*Bu as the allenylidene ligand) with HCl leads to the formation of the six-coordinate hydridoiridium(III) complexes [IrHCl$_2${=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (**6**, **7**) by oxidative addition at the metal center. In contrast, the reactions of **1** and **5** with both CF$_3$CO$_2$H and CF$_3$SO$_3$H afford the four-coordinate vinylcarbene compounds *trans*-[IrCl{=C(X)–CH=C(Ph)R}(P*i*Pr$_3$)$_2$] (**8**–**10**). For X = CF$_3$CO$_2$, in nitromethane a dissociation of the C–X bond occurs and the cationic iridium carbynes *trans*-[IrCl{≡C–CH=C(Ph)R}(P*i*Pr$_3$)$_2$]$^+$ are generated. Upon addition of NaBPh$_4$, the stable carbyne complexes **11b** (R = Ph) and **12b** (R = *t*Bu) with BPh$_4$$^-$ as the counterion were isolated in almost quantitative yields. The X-ray crystal structure analysis of **6** reveals that the chloro ligands are *cis* and the phosphane ligands *trans* disposed.

Keywords: allenylidene complexes · butatriene complexes · carbene complexes · carbyne complexes · iridium

Introduction

After we had shown that the Selegue method for the preparation of transition metal allenylidenes[1] can also be applied to the synthesis of square-planar iridium complexes *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$],[2] we started to investigate the reactivity of these molecules. We found that the chloride cannot only be replaced by other halides but equally by pseudohalides such as OCN$^-$, SCN$^-$, or N$_3$$^-$ and even by hydroxide and similar O-donor ligands. However, in contrast to the vinylidene analogues *trans*-[IrCl{=C=C(Ph)R}(P*i*Pr$_3$)$_2$], which react with organolithium compounds R′Li to give the substitution products *trans*-[Ir(R′){=C=C(Ph)R}(P*i*Pr$_3$)$_2$] in excellent yields,[3] our attempts to obtain the related allenylidene derivatives *trans*-[Ir(R′){=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] failed. For this reason we were unable to carry out C–C coupling reactions, for example with CO, which in the case of the vinylidene complexes *trans*-[Ir(R′){=C=C(Ph)R}(P*i*Pr$_3$)$_2$] led by migratory insertion of the C=C(Ph)R fragment into the Ir–R′ bond to substituted vinyl units.[3]

Therefore, we turned our interest to the reactivity of the compounds *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] towards HCl, CH$_3$I, and other electrophiles with the particular aim to find out whether the electrophilic substrates would preferentially attack the electron-rich metal center or the highly unsaturated IrC$_3$ moiety. Herein we report that both reaction paths are possible and that, depending on the nature of the attacking reagent, the allenylidene unit can be converted into butatriene, carbene, and carbyne ligands. Some preliminary results of this work have already been communicated.[4]

Results and Discussion

Preparation of iridium(I) complexes with an unsymmetrical butatriene ligand: In the context of our studies on the reactivity of rhodium-bonded cumulenylidenes, we recently found that both *trans*-[RhCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] and *trans*-[RhCl(=C=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] react with excess diazomethane in benzene at room temperature within a few minutes to give, via coupling of CH$_2$ with the C$_3$ or C$_5$ unit, the butatriene and hexapentaene complexes *trans*-[RhCl{η^2–CH$_2$=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] and *trans*-[RhCl-

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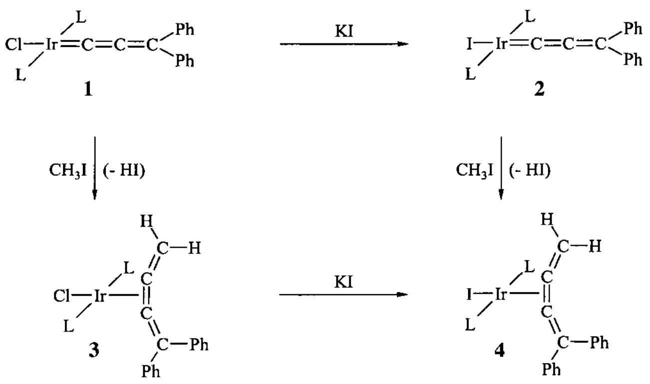
(η^2-CH_2=C=C=C=C=CPh_2)($PiPr_3$)$_2$], respectively.[5, 6] Under the same conditions, the iridium compounds **1** and **2** are completely inert toward CH_2N_2. However, when we attempted to oxidatively add CH_3I to the metal center of the allenylideneiridium(I) complexes **1** and **2** by anticipating that they might react analogously to the Vaska-type compounds *trans*-[IrCl(CO)(PR_3)$_2$] (R = Me, Ph) with methyl iodide, we discovered that CH_3I behaves as a CH_2 source. Treatment of **1** or **2** with excess CH_3I in benzene at room temperature led, although rather slowly, to the formation of the butatriene complexes **3** and **4** (Scheme 1) in high yield without the presence of a base. Since the iodo compound **4** is obtained from **2** and CH_3I together with small amounts of by-products, the more convenient procedure for the preparation of **4** consists of the salt metathesis of **3** and KI. In this case, the yield of **4** is 81%.



Scheme 1. L = P*i*Pr$_3$.

Compounds **3** and **4**, which to the best of our knowledge are the first iridium representatives with a η^2-bonded butatriene ligand, are orange, moderately air-sensitive solids, the composition of which has been confirmed by elemental analysis. The stereochemical inequivalence of the protons of the CH_2 unit of the butatriene is indicated by the ^1H NMR and that of the phenyl groups of the CPh_2 moiety by the ^{13}C NMR spectra. The assignment of the resonances for the H_{endo} and H_{exo} protons follows from the work of Gladysz et al.[7] who assigned the corresponding signals of the CH_2 protons of the allene complex [(η^5-C_5H_5)Re(η^2-CH_2=C=CH_2)(NO)(PPh_3)]BF_4 based on NOE measurements. Owing to the presence of an unsymmetrical butatriene, the ^{13}C NMR spectra of **3** and **4** display four resonances in the region between $\delta = 120$ to 92 for the carbon atoms of the C_4 chain. Two of these signals show a P,C coupling and thus belong to the butatriene C atoms linked to the metal. The IR spectra of **3** and **4** exhibit an intensive band at 1932 and 1928 cm^{-1}, respectively, which is assigned to the stretching mode of the cumulene ligand.

To substantiate the proposed stereochemistry, an X-ray crystal structure analysis of **3** was carried out (Figure 1), which reveals that the iridium is coordinated in a slightly distorted square-planar fashion with the two phosphane ligands in *trans* disposition. The metal is bound to the central C–C double bond, similarly as found in some rhodium(I) complexes containing symmetrical butatriene ligands.[8] Although the plane of the carbon atoms of the triene lies perpendicular to the plane Cl, Ir, P1, P2 (the dihedral angle being 90.0(3)°), the distances Ir–C2 and Ir–C3 differ by about 0.05 Å. As a consequence, the bond angles Cl-Ir-C2 and Cl-Ir-C3 are unequal and differ by about 12°. The C_4 chain is bent, in agreement with previous findings, possessing C-C-C angles that are similar to those in related butatrienerhodium(I) complexes.[8, 9] The C2–C3 distance (1.384(7) Å) is slightly longer than in other metal butatrienes,[8–10] which could be explained by an increased back-donation from iridium to the π^* orbital of the olefinic C–C double bond. While the Ir–P bond lengths are essentially the same, the P-Ir-P axis is not exactly linear (167.67(4)°), possibly due to the unsymmetric bonding situation of the C_4 unit.

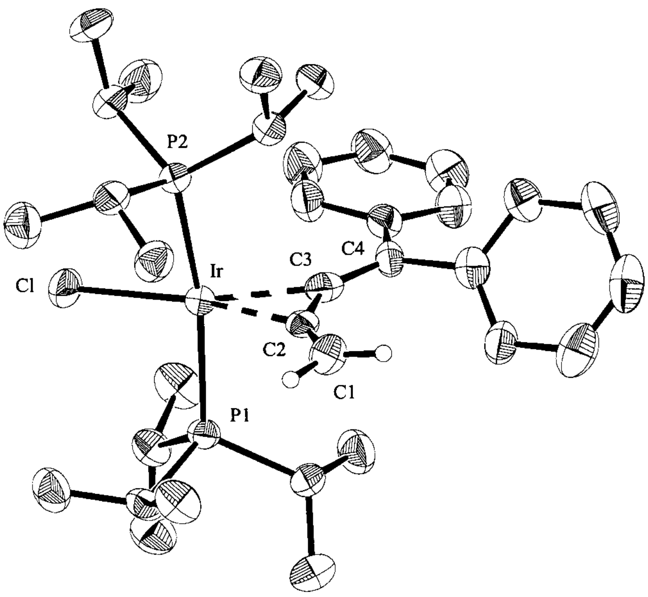
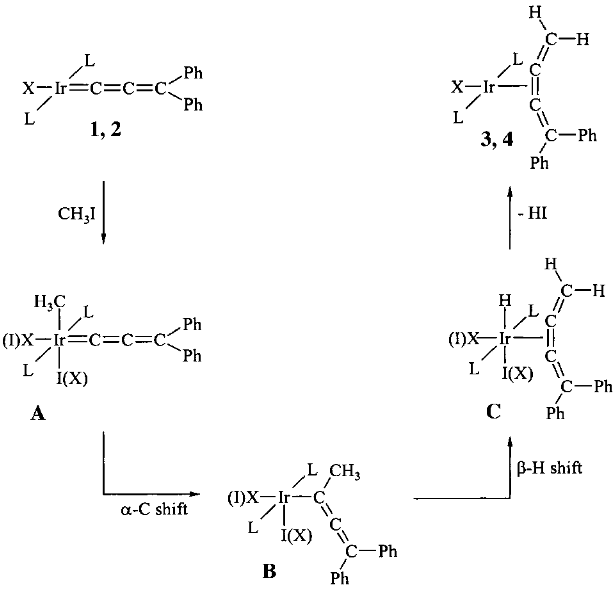


Figure 1. Molecular structure of **3**. Principal bond lengths [Å] and angles [°]: Ir–Cl 2.3700(12), Ir–P1 2.3535(12), Ir–P2 2.3609(12), Ir–C2 2.075(5), Ir–C3 2.031(5), C1–C2 1.303(7), C2–C3 1.384(7), C3–C4 1.358(7); P1-Ir-P2 167.67(4), Cl-Ir-P1 88.06(5), Cl-Ir-P2 87.53(5), Cl-Ir-C2 166.43(12), Cl-Ir-C3 154.18(14), P1-Ir-C2 90.58(13), P1-Ir-C3 93.89(14), P2-Ir-C2 91.01(13), P2-Ir-C3 95.09 (14), C1-C2-C3 146.6(5), C2-C3-C4 142.2(5), C2-Ir-C3 39.38(18).

As far as the mechanism of formation of the butatriene compounds **3** and **4** is concerned, we assume that in the initial step an oxidative addition of CH_3I at the metal center takes place to give intermediate **A** which is followed by the insertion of the allenylidene unit into the Ir–CH_3 bond. The so-formed intermediate **B** (Scheme 2) then reacts by β-H shift to afford the octahedral butatriene(hydrido)iridium(III) species **C**, which reductively eliminates HI to yield the product. We can not exclude, however, that the formation of **C** is preceded by the generation of a thermodynamically less favored isomer in which the terminal C=CH_2 bond of the butatriene is linked to the metal. In the above-mentioned reaction of *trans*-[RhCl{=C=C=C(Ph)R}($PiPr_3$)$_2$] with CH_2N_2, related *trans*-[RhCl{η^2-*CH$_2$=C*=C=C(Ph)R}($PiPr_3$)$_2$] compounds are initially formed, which upon heating in toluene to 80–90°C rearrange to the more stable isomers *trans*-[RhCl{η^2-CH_2=*C=C*=C(Ph)R}($PiPr_3$)$_2$].[5] There is precedence for the first two steps shown in Scheme 2 insofar as both we and

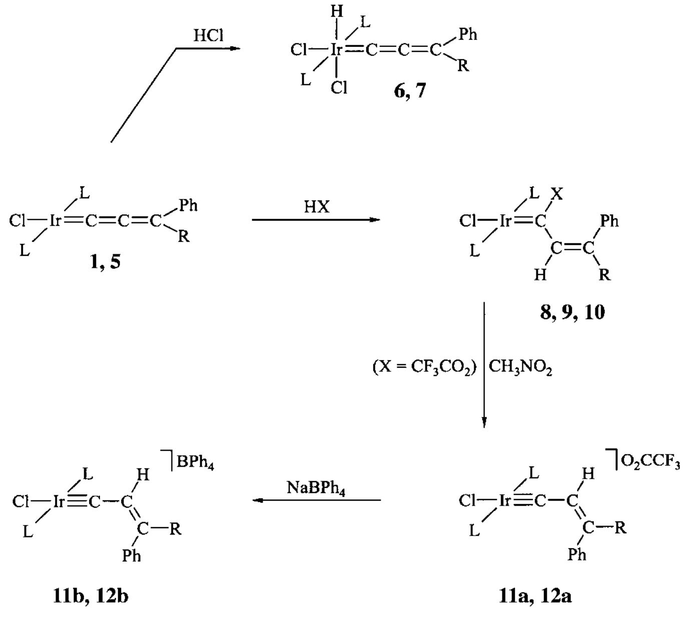


Scheme 2. L = P*i*Pr$_3$.

Fryzuk et al. found that the vinylidene compounds *trans*-[IrCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$] and [Ir(=C=CH$_2$){η^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$}] react with methyl iodide to give the vinyl complexes [IrCl(I){C(CH$_3$)=CH$_2$}(P*i*Pr$_3$)$_2$] and [IrI{C(CH$_3$)=CH$_2$}{η^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$}], respectively.[11, 12] However, in these cases a subsequent β-H shift does not occur.

Reactions of the iridium(I) allenylidenes with Brønsted acids: The reaction of the allenylidene complexes **1** and **5** with HCl proceeds analogously to that of the structurally related carbene derivative *trans*-[IrCl(=CPh$_2$)(P*i*Pr$_3$)$_2$].[13] Treatment of a solution of **1** or **5** in benzene with a solution of HCl in the same solvent affords, after removal of the volatiles and recrystallization of the residue from acetone at −60 °C, the hydridoiridium(III) compounds **6** and **7** (Scheme 3) in almost quantitative yields. The deeply colored solids are thermally quite stable and only slightly air-sensitive. If they are dissolved in CH$_2$Cl$_2$ and the solution is stirred for 3–4 h, a slow reaction to regenerate the starting materials via elimination of HCl can be observed. Typical spectroscopic features of **6** and **7** are the high-field resonance at $\delta = -17.63$ (**6**) and -17.11 (**7**) in the ^{1}H NMR spectra and the intense band at 1834 cm^{-1} (**6**) and 1819 cm^{-1} (**7**), assigned to the C=C=C stretching mode, in the IR spectra. The ^{13}C NMR spectra of **6** and **7** display, in contrast to those of **1** and **5**, the signal for the α-carbon atom of the C$_3$ chain at lower field ($\delta = 267.4$ for **6** and $\delta = 284.4$ for **7**) than that of the β-carbon atom ($\delta = 210.7$ for **6** and $\delta = 217.7$ for **7**), which reflects the different coordination number and oxidation state of the metal in the two types of compounds.

The molecular structure of the diphenylallenylidene(hydrido) complex is shown in Figure 2. The coordination geometry around the metal center corresponds to a slightly distorted octahedron, in which the P-Ir-P axis is somewhat bent (166.91(15)°) towards the hydride ligand. The position of the hydride could be located by a difference Fourier synthesis. The two chloro ligands are *cis* disposed, one being *trans* to hydride and the other *trans* to the allenylidene unit. Like in the starting material **1**,[14] the C1–C2 bond length is about 0.1 Å shorter than the C2–C3 bond length, which suggests that apart from the usual bonding description M=C=C=C for allenylidene transition metal compounds a second zwitterionic resonance structure M–C≡C–C with a positive charge at the a γ-carbon atom and a negative charge at the metal center has to be taken into consideration.[15] The Ir-C-C-C axis of **6** is nearly linear with a marginal bending at C2. The *ipso*-carbon atoms of the phenyl groups lie not exactly in the plane Cl1, Ir,



	R
1, 6, 11a, b	Ph
5, 7, 12a, b	*t*Bu

	X	R
8	O$_2$CCF$_3$	Ph
9	O$_2$CCF$_3$	*t*Bu
10	OSO$_2$CF$_3$	Ph

Scheme 3. L = P*i*Pr$_3$.

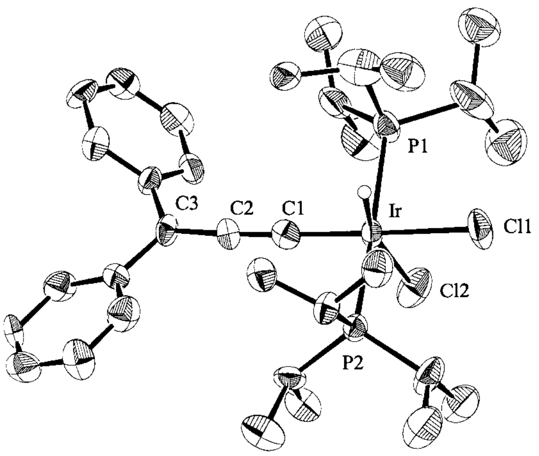


Figure 2. Molecular structure of **6**. Principal bond lengths [Å] and angles [°]: Ir–Cl1 2.407(4), Ir–Cl2 2.478(4), Ir–P1 2.383(4), Ir–P2 2.373(4), Ir–C1 1.877(15), C1–C2 1.249(19), C2–C3 1.349(19); C1-Ir-P1 91.5(4), C1-Ir-P2 91.3(4), C1-Ir-Cl1 176.8(4), C1-Ir-Cl2 94.3(4), Cl1-Ir-P1 88.45(14), Cl1-Ir-P2 88.09(13), Cl1-Ir-Cl2 88.88(16), Cl2-Ir-P1 96.46(15), Cl2-Ir-P2 96.09(14), P1-Ir-P2 166.91(15), Ir-C1-C2 178.7(13), C1-C2-C3 176.0(15).

P1, P2, C1, the dihedral angle between this plane and the plane C10, C3, C20 being 10.9(1)°. Another noteworthy feature is that the Ir–Cl2 distance is about 0.07 Å longer than the Ir–Cl1 distance, which is probably due to the different *trans* influence of the hydrido and the allenylidene ligand.

In contrast to the reactions of **1** and **5** with HCl, those of the same starting materials with CF_3CO_2H and CF_3SO_3H take a different course. Treating a solution of one equivalent of **1** or **5** in benzene with one equivalent of the corresponding acid at room temperature leads to a rapid change of color from red to brown-yellow or brown and finally to the isolation of crystalline compounds **8**–**10** (see Scheme 3) which, however, are not iridium(III) but iridium(I) complexes. The IR spectra of the products confirm that an allenylidene ligand is no longer present and that, in the case of **8** and **9**, the trifluoroacetate behaves as a substituent linked to the C_3 unit. Therefore, we conclude that both CF_3CO_2H and CF_3SO_3H substrates react like nucleophiles HNu (Nu = OR, SR, NR_2) with **1** and **5** and afford, via addition of the proton to the β-C and of the acid anion to the α-C atom of the allenylidene unit, the carbene derivatives **8**–**10**.[16] The isolated yield of these compounds is 85–90%.

The spectroscopic data of **8**–**10** are in good agreement with the proposed structure shown in Scheme 3. The ^{13}C NMR spectra display one low-field resonance around $\delta = 240-242$ which is split into a triplet due to P,C coupling. The corresponding signal of other Fischer-type carbeneiridium(I) compounds, of which only a few examples are known,[17] lies in a similar region. The C*H*=C(Ph)R vinyl proton of **8**–**10** resonates between $\delta = 2.76$ (for **8**) and 3.77 (for **10**) and, owing to NOE spectra of **9**, there is no doubt that in this case the CH= proton is *cis* disposed to the group R. It should be mentioned that the reactions of **1** and **5** with either HBF_4 or $HBAr^F_4$ ($Ar^F = 2,6-(CF_3)_2C_6H_3$) led to a mixture of products which could not be separated by fractional crystallization or column chromatography. The behavior of the allenylidene complexes is thus different to that of the structurally related iridium carbene *trans*-$[IrCl(=CPh_2)(P\textit{i}Pr_3)_2]$, which reacts with HBF_4 to give the stable five-coordinate cation $[IrHCl(=CPh_2)(P\textit{i}Pr_3)_2]^+$.[13]

While compounds **8** and **9**, if dissolved in benzene, are non-electrolytes, solutions of the same carbene complexes in CH_2Cl_2 and CH_3NO_2 exhibit a significant conductivity. The Λ values in nitromethane are $47\,cm^2\Omega^{-1}mol^{-1}$ for **8** and $51\,cm^2\Omega^{-1}mol^{-1}$ for **9** and this suggests a nearly complete dissoziation of the neutral compounds into the ionic species $[IrCl\{\equiv CCH{=}C(Ph)R\}(P\textit{i}Pr_3)_2]^+$ and $CF_3CO_2^-$. The formation of the carbyneiridium cations is not only indicated by the conductivity measurements but also by the ^1H, ^{13}C, and ^{31}P NMR data (for details see Experimental Section). Since in solution the carbyne–metal cations and the trifluoroacetate anion are in equilibrium with the undissociated carbene complexes, our attempts to isolate saltlike products of the general composition $[IrCl\{\equiv CCH{=}C(Ph)R\}(P\textit{i}Pr_3)_2]CF_3CO_2$ (**11a**,**12a**) failed.

However, the cationic iridium carbynes can be trapped if the starting materials **8** and **9** are dissolved in methanol and one equivalent of $NaBPh_4$ is added. Partial evaporation of the solvent and cooling of the concentrated solution to −60°C leads to the precipitation of brown solids **11b** and **12b**, the composition of which has been substantiated by elemental analyses and conductivity measurements. The ^{13}C NMR spectra of **11b** and **12b** display a triplet resonance for the carbyne carbon atom at $\delta = 238.8$ (**11b**) and 239.6 (**12b**), and the ^1H NMR spectra a signal for the vinyl proton at $\delta = 2.24$ (**11b**) and 2.61 (**12b**). These chemical shifts are quite similar to those of the carbyne(hydrido)osmium(II) complexes $[OsHCl_2(\equiv CCH{=}CMe_2)(PR_3)_2]$ (R = *i*Pr, Cy) which were obtained from six-coordinate hydridoosmium(IV) precursors and terminal alkynes.[18, 19] We note that two relatives of **11b** and **12b** with the general composition *trans*-$[IrCl(\equiv CCH_2R)(P\textit{i}Pr_3)_2]BF_4$ (R=H, Ph) are known and have been prepared by protonation of the iridium vinylidenes *trans*-$[IrCl(=C{=}CHR)(P\textit{i}Pr_3)_2]$ with HBF_4.[20]

In the presence of bases, not only the O-functionalized carbene compounds **8**–**10** but also the carbyne complexes **11b** and **12b** eliminate HX and regenerate the allenylidene-iridium(I) precursors. Although the reaction of **11b** or **12b**, for example with NEt_3, is considerably slower than that of **8**–**10**, both the carbene and the carbyne complexes can only be stored (under argon at 0°C) for days if basic substrates are absent. It seems to be generally true that alkyl and vinyl protons of cations $[M(\equiv CCH_2R)(L)_n]^+$ and $[M(\equiv CCH{=}CR_2)(L)_n]^+$ are highly acidic and easily dissociate upon addition of even weak bases.[17b, 18–21]

Conclusion

The present investigations have shown that the allenylidene ligands of the complexes *trans*-$[IrCl\{=C{=}C{=}C(Ph)R\}(P\textit{i}Pr_3)_2]$ are useful building blocks to generate butatriene, carbene, and even carbyne units in the coordination sphere of the metal center. The different types of reactions, which are summarized in Schemes 1–3, convincingly illustrate that the four-coordinate iridium(I) allenylidenes are good nucleophiles and in some respect behave similarly to the structurally related carbonyl, carbene, and vinylidene derivatives. The remarkable feature, however, is that the attack of the electrophile can be directed either to the metal or the cumulenylidene ligand and it is hard to predict (if, for example, HCl and CF_3CO_2H are compared) which site for attack is preferred.

Two results should become the focus of particular attention. The first is, that methyl iodide behaves as a source of CH_2, even in the absence of a Brønsted base. This is in contrast to the reactivity of the rhodium analogues *trans*-$[RhCl\{=C{=}C{=}C(Ph)R\}(P\textit{i}Pr_3)_2]$, which upon treatment with CH_3I afford corresponding butatriene complexes *only in the presence of* Na_2CO_3.[5] A possible explanation is that due to the higher electronegativity of 5d compared with 4d metals the hydrogen atoms of the Ir–CH_3 fragment are more acidic and thus the deprotonation followed by the elimination of HI is facilitated.

The second relevant result is the ease of formation of carbyne complexes from allenylidene precursors. Taking the two most recent reviews on the chemistry of transition metal allenylidenes into account,[15d,e] only one example is known describing the conversion of a $M{=}C{=}C{=}CR_2$ into a (cationic)

M≡CC(E)=CR_2 unit.[22] We note that there is ample evidence for the addition of substrates HX to the C_α–C_β bond of a M=C=C=CR_2 chain to form a metal carbene M=C(X)–CH=CR_2 but apparently X must be an excellent leaving group in order to convert the carbene into a carbyne ligand. An easy conversion occurs for the classical Fischer-type carbenes [Cr{=C(X)NEt_2}$(CO)_5$] (X = Cl, Br, I) into the corresponding carbynes [CrX(≡$CNEt_2$)$(CO)_4$] but in this case a CO ligand is eliminated and the stable *trans*-disposed fragment X–Cr≡$CNEt_2$ is formed.[23]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**, **2**, and **5** were prepared as described in the literature.[2, 24] NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a IFS 25 FT-IR infrared spectrometer. Coupling constants *N* and *J* are given in Hertz. Abbreviations used: s: singlet; d: doublet; t: triplet; m: multiplet; v: virtual coupling; br: broadened signal; $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$. Melting points were measured by differential thermal analysis (DTA).

Preparation of *trans*-[IrCl(η^2-H_2C=*C*=*C*=CPh_2)($PiPr_3$)$_2$] (3): A solution of **1** (50 mg, 0.07 mmol) in benzene (10 mL) was treated with an excess of methyl iodide (100 µL, 1.58 mmol) and stirred for 30 h at room temperature. The volatiles were removed in vacuo, the residue was dissolved in acetone (2 mL), and the solution was stored for three days at −78 °C. Orange crystals precipitated, which were separated from the mother liquor, washed with small portions of pentane and dried in vacuo; yield 42 mg (82 %); m.p. 154 °C (decomp); IR (KBr): ν(C=C=C=C) = 1932 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 9.04, 7.82 (both m, 2 H each; *ortho*-H of C_6H_5), 7.37, 7.10 (both m, 6 H; *meta*- and *para*-H of C_6H_5), 5.48 (br s, 1 H; *endo*-H of CH_2), 4.90 (br s, 1 H; *exo*-H of CH_2), 2.58 (m, 6 H; PC*H*CH_3), 1.29 (dvt, *N* = 13.4, *J*(H,H) = 6.7 Hz, 18 H; PCHCH_3), 1.13 (dvt, *N* = 13.1, *J*(H,H) = 6.7 Hz, 18 H; PCHCH_3); ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 142.0, 132.1 (both s; *ipso*-C_6H_5) 128.9, 128.4, 127.5, 126.9, 126.3, 126.2 (all s; C_6H_5), 120.6 (t, *J*(P,C) = 3.1 Hz; Ir–C), 119.5 (br s; =*C*Ph_2), 116.6 (t, *J*(P,C) = 3.6 Hz; Ir–C], 92.4 (br s; =CH_2), 22.3 (vt, *N* = 25.6 Hz; P*C*HCH_3), 20.7, 19.4 (both s; PCH*C*H_3); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 20.4 (s); elemental analysis (%) for $C_{34}H_{54}ClIrP_2$ (752.4): calcd: C 54.27, H 7.23; found: C 53.98, H 7.04.

Preparation of *trans*-[IrI(η^2-H_2C=*C*=*C*=CPh_2)($PiPr_3$)$_2$] (4): A solution of **3** (52 mg, 0.07 mmol) in acetone (10 mL) was treated with an excess of KI (116 mg, 0.70 mmol) and stirred for 14 days at room temperature. The solvent was removed in vacuo, the residue was extracted with pentane (50 mL), and the extract was evaporated to dryness in vacuo. The remaining oily solid was dissolved in acetone (2 mL) and the solution was stored for three days at −78 °C. Orange crystals precipitated, which were separated from the mother liquor, washed with small portions of pentane and dried in vacuo; yield 47 mg (81 %); m.p. 126 °C (decomp); IR (C_6H_6): ν(C=C=C=C) = 1928 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 8.49, 7.71 (both m, 2 H each; *ortho*-H of C_6H_5), 7.28, 6.98 (both m, 6 H; *meta*- and *para*-H of C_6H_5), 5.25 (br s, 1 H; *endo*-H of CH_2), 4.77 (br s, 1 H; *exo*-H of CH_2), 2.84 (m, 6 H; PC*H*CH_3), 1.27 (dvt, *N* = 13.5, *J*(H,H) = 6.9 Hz, 18 H; PCHCH_3), 1.16 (dvt, *N* = 12.8, *J*(H,H) = 6.9 Hz, 18 H; PCHCH_3); ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 141.9, 140.9 (both s; *ipso*-C_6H_5) 133.3, 130.8, 128.8, 128.4, 126.5, 126.4 (all s; C_6H_5), 120.6 (t, *J*(P,C) = 3.7 Hz; Ir–C), 120.0 (br s; =*C*Ph_2), 113.7 (t, *J*(P,C) = 3.8 Hz; Ir–C), 92.4 (br s; =CH_2), 23.1 (vt, *N* = 26.8 Hz, P*C*HCH_3), 20.8, 20.3 (both s; PCH*C*H_3); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 15.6 (s); elemental analysis (%) for $C_{34}H_{54}IIrP_2$ (843.9): calcd: C 48.39, H 6.45; found: C 48.61, H 6.31. Compound **4** was also obtained upon stirring a solution of **2** (62 mg, 0.07 mmol) and CH_3I (100 µL, 1.58 mmol) in benzene (10 mL) for 6 h at room temperature. The ^{1}H and ^{31}P NMR spectra of the reaction mixture showed that apart from some unidentified byproducts, the major component was **4**; yield (by NMR) about 90 %.

Preparation of [IrHCl_2(=C=C=CPh_2)($PiPr_3$)$_2$] (6): A solution of **1** (45 mg, 0.06 mmol) in benzene (10 mL) was treated dropwise with a 0.1 M solution of HCl in benzene (0.7 mL, 0.07 mmol) and stirred for 5 min at room temperature. A gradual change of color from red to red-brown occurred. The solvent was removed in vacuo, the residue was dissolved in acetone (2 mL), and the solution was stored for 24 h at −60 °C. Dark red crystals precipitated, which were separated from the mother liquor and dried in vacuo; yield 44 mg (94 %); m.p. 124 °C (decomp); IR (CH_2Cl_2): ν(IrH) = 2210, ν(C=C=C) = 1834 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.92 (m, 4 H; *ortho*-H of C_6H_5), 7.86 (m, 2 H; *para*-H of C_6H_5), 7.34 (m, 4 H; *meta*-H of C_6H_5), 2.64 (m, 6 H; PC*H*CH_3), 1.29, 1.24 (both dvt, *N* = 14.4, *J*(H,H) = 6.5 Hz, 18 H each; PCHCH_3), −17.63 (t, *J*(P,H) = 11.6 Hz, 1 H; Ir–H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ = 267.4 (t, *J*(P,C) = 8.7 Hz, Ir=*C*=C=C), 210.7 (br s; Ir=C=*C*=C), 164.1 (s; Ir=C=C=*C*), 149.1 (s; *ipso*-C_6H_5), 130.9, 129.2, 127.5 (all s; C_6H_5), 24.0 (vt, *N* = 24.5 Hz; P*C*HCH_3), 18.2, 18.1 (both s; PCH*C*H_3); ^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ = 11.6 (s); elemental analysis (%) for $C_{31}H_{53}Cl_2IrP_2$ (774.8): calcd: C 51.15, H 6.89; found: C 51.31, H 7.00.

Preparation of [IrHCl_2{=C=C=C(Ph)*t*Bu}($PiPr_3$)$_2$] (7): This compound was prepared as described for **6**, from **5** (60 mg, 0.08 mmol) and a 0.1 M solution of HCl in benzene (0.9 mL, 0.09 mmol). Olive-green solid; yield 60 mg (95 %); m.p. 86 °C (decomp); IR (CH_2Cl_2): ν(IrH) = 2255, ν(C=C=C) = 1819 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.45 (m, 2 H; *ortho*-H of C_6H_5), 7.17 (m, 1 H; *para*-H of C_6H_5), 6.94 (m, 2 H; *meta*-H of C_6H_5), 2.68 (m, 6 H; PC*H*CH_3), 1.32, 1.24 (both dvt, *N* = 13.8, *J*(H,H) = 6.9 Hz, 18 H each; PCHCH_3), 1.18 (s, 9 H; C$(CH_3)_3$), − 17.11 (t, *J*(P,H) = 12.3 Hz; Ir–H); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 284.4 (t, *J*(P,C) = 8.1 Hz; Ir=*C*=C=C), 217.7 (br s; Ir=C=*C*=C), 178.7 (s; Ir=C=C=*C*), 153.3 (s; *ipso*-C_6H_5), 128.5, 125.8, 125.4 (all s, C_6H_5), 52.9 (s; *C*$(CH_3)_3$), 27.9 (s; C$(CH_3)_3$), 24.9 (vt, *N* = 26.4 Hz; P*C*HCH_3), 19.5, 19.4 (both s; PCH*C*H_3); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 9.5 (s); elemental analysis (%) for $C_{31}H_{57}Cl_2IrP_2$ (754.9): calcd: C 49.33, H 7.61; found: C 49.61, H 7.45.

Preparation of *trans*-[IrCl{=C(O_2CCF_3)CH=CPh_2}($PiPr_3$)$_2$] (8): A solution of **1** (127 mg, 0.17 mmol) in benzene (10 mL) was treated with CF_3CO_2H (13 µL, 0.17 mmol) and stirred for 5 min at room temperature. A change of color from red to yellow-brown occurred. The solvent was removed in vacuo, pentane (20 mL) was added, and the mixture was irradiated in an ultrasonic bath for 10 min. A yellow-brown solid was formed, which was separated from the mother liquor and dried in vacuo; yield 128 mg (88 %); m.p. 114 °C (decomp); IR (CH_2Cl_2): ν$(OCO)_{as}$ = 1659, ν$(OCO)_{sym}$ = 1389 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.66, 7.43, 7.35, 7.25, 7.06 (all m, 10 H; C_6H_5), 2.76 (s, 1 H; C*H*=CPh_2), 2.48 (m, 6 H; PC*H*CH_3), 1.12 (dvt, *N* = 14.7, *J*(H,H) = 7.3 Hz, 36 H; PCHCH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 240.5 (t, *J*(P,C) = 9.2 Hz; Ir=C), 195.8 (s, *C*Ph_2), 160.1 (q, *J*(F,C) = 34.6 Hz; *C*O_2CF_3), 138.9, 138.8 (both s; *ipso*-C_6H_5), 132.2, 130.7, 130.2, 129.8, 128.8, 128.4, 128.2 (all s; C_6H_5 and *C*H=CPh_2), 113.4 (q, *J*(F,C) = 286.1 Hz; CO_2*C*F_3), 26.5 (vt, *N* = 27.5 Hz; P*C*HCH_3), 19.8 (s; PCH*C*H_3); ^{19}F NMR (C_6D_6, 376.0 MHz): δ = −75.2 (s); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 50.2 (s); elemental analysis (%) for $C_{35}H_{53}ClF_3IrO_2P_2$ (852.4): calcd.: C 49.32, H 6.27; found: C 49.12, H 6.51.

Preparation of *trans*-[IrCl{=C(O_2CCF_3)CH=C(Ph)*t*Bu}($PiPr_3$)$_2$] (9): This compound was prepared as described for **8**, from **5** (100 mg, 0.14 mmol) and CF_3CO_2H (11 µL, 0.14 mmol) in benzene (10 mL). Pale brown solid; yield 105 mg (91 %); m.p. 114 °C (decomp); IR (CH_2Cl_2): ν$(OCO)_{as}$ = 1658, ν$(OCO)_{sym}$ = 1390 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.26 (m, 3 H; *ortho*- and *para*-H of C_6H_5), 6.98 (m, 2 H; *meta*-H of C_6H_5), 2.65 (s, 1 H; C*H*=C(Ph)*t*Bu), 2.48 (m, 6 H; PC*H*CH_3), 1.11 (dvt, *N* = 15.0, *J*(H,H) = 7.4 Hz, 36 H; PCHCH_3), 0.97 (s, 9 H; C$(CH_3)_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 241.4 (t, *J*(P,C) = 8.1 Hz; Ir=C), 183.1 (s, *C*(Ph)*t*Bu), 160.2 (q, *J*(F,C) = 38.7 Hz; *C*O_2CF_3), 138.4 (s; *ipso*-C_6H_5), 132.2, 130.6, 129.0, 126.3 (all s; C_6H_5 and *C*H=C(Ph)*t*Bu), 116.9 (q, *J*(F,C) = 289.0 Hz; CO_2*C*F_3), 41.3 (s; *C*$(CH_3)_3$), 28.6 (s; C$(CH_3)_3$), 26.6 (vt, *N*=27.5 Hz; P*C*HCH_3), 19.8 (s, PCH*C*H_3); ^{19}F NMR (C_6D_6, 376.0 MHz): δ = −75.3 (s); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 51.7 (s); elemental analysis (%) for $C_{33}H_{57}ClF_3IrO_2P_2$ (832.4): calcd: C 7.62, H 6.90; found: C 47.25, H 6.59.

Preparation of *trans*-[IrCl{=C(OSO_2CF_3)CH=CPh_2}($PiPr_3$)$_2$] (10): This compound was prepared as described for **8**, from **1** (103 mg, 0.14 mmol) and CF_3SO_3H (12 µL, 0.14 mmol) in benzene (10 mL). Red-brown solid; yield 107 mg (85 %), m.p. 286 °C (decomp); IR (CH_2Cl_2): ν$(S{=}O)_{as}$ = 1389, ν$(S{=}O)_{sym}$ = 1279 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.82, 7.48 (both m, 2 H each; *ortho*-H of C_6H_5), 7.25, 7.21, 7.05 (all m, 2 H each; *meta*- and *para*-H of C_6H_5), 3.77 (s, 1 H; C*H*=CPh_2), 2.50 (m, 6 H; PC*H*CH_3), 1.15 (dvt, *N* = 13.7, *J*(H,H) = 7.6 Hz, 36 H; PCHCH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): δ =

242.3 (t, J(P,C) = 8.9 Hz; Ir=C), 195.7 (s; CPh$_2$), 139.0, 138.2 (both s; *ipso*-C_6H_5), 132.2, 130.8, 130.2, 130.1, 128.5, 128.4 (all s; C_6H_5 and CH=CPh$_2$), 121.9 (q, J(F,C) = 318.6 Hz; CF$_3$), 26.6 (vt, N = 27.5 Hz; PCHCH$_3$), 20.0 (s, PCHCH$_3$); ^{19}F NMR (C_6D_6, 376.0 MHz): $\delta = -77.6$ (s); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 53.4$ (s); elemental analysis (%) for $C_{35}H_{55}ClF_3IrO_3P_2S$ (902.5): calcd: C 45.96, H 6.01, S 3.61; found: C 45.56, H 5.64, S 3.85.

Generation of *trans*-[IrCl(≡CCH=CPh$_2$)(P*i*Pr$_3$)$_2$]O$_2$CCF$_3$ (11a): Compound **8** (43 mg, 0.05 mmol) was dissolved in nitromethane (2 mL) and after stirring for 2 min the molar conductivity was measured. The value $\Lambda = 47\ \mathrm{cm^2\,\Omega^{-1}mol^{-1}}$ indicated that by cleavage of the C−OC(O)CF$_3$ bond most of the starting material was converted to an 1:1 electrolyte. Spectroscopic data for the cation: ^{1}H NMR (CD$_3$NO$_2$, 400 MHz): δ = 7.77, 7.70 (both m, 2H each; *ortho*-H of C_6H_5), 7.64, 7.60, 7.55, 7.50 (all m, 6H; *meta*- and *para*-H of C_6H_5), 2.88 (m, 6H; PCHCH$_3$), 2.63 (s, 1H; CH=CPh$_2$), 1.40 (dvt, N = 15.0, J(H,H) = 7.3 Hz, 36H; PCHCH_3); ^{13}C NMR (CD$_3$NO$_2$, 100.6 MHz): δ = 241.3 (t, J(P,C) = 8.6 Hz; Ir≡C), 197.6 (s; CPh$_2$), 140.1, 139.6 (both s; *ipso*-C_6H_5), 134.4, 134.2, 133.5, 131.7, 130.7, 130.6, 130.4, 129.3 (all s; C_6H_5 and CH=CPh$_2$), 27.4 (vt, N = 28.5 Hz; PCHCH$_3$), 20.1 (s; PCHCH$_3$); ^{31}P NMR (CD$_3$NO$_2$, 162.0 MHz): $\delta = 50.4$ (s).

Preparation of *trans*-[IrCl(≡CCH=CPh$_2$)(P*i*Pr$_3$)$_2$]BPh$_4$ (11b): A solution of **8** (128 mg, 0.15 mmol) in methanol (15 mL) was treated with NaBPh$_4$ (51 mg, 0.15 mmol) and stirred for 2 h at room temperature. The solution was concentrated to 3 mL in vacuo and stored for 16 h at −60 °C. A dark brown solid precipitated, which was separated from the mother liquor, washed with small portions of methanol and dried in vacuo; yield 141 mg (89 %); m.p. 34 °C (decomp); ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.63, 7.49, 7.39 (all m, 10H; C_6H_5), 7.35 (m, 8H; *ortho*-H of BC$_6$H$_5$), 7.05 (m, 8H; *meta*-H of BC$_6$H$_5$), 6.89 (m, 4H; *para*-H of BC$_6$H$_5$), 2.80 (m, 6H; PCHCH$_3$), 2.24 (s, 1H; CH=CPh$_2$), 1.39 (dvt, N = 15.0, J(H,H) = 7.3 Hz, 36H; PCHCH_3); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 238.8 (t, J(P,C) = 9.2 Hz; Ir≡C), 164.4 (q, J(B,C) = 48.8 Hz; *ipso*-BC$_6$H$_5$), 162.0 (s; CPh$_2$), 139.0, 138.5 (both s; *ipso*-C_6H_5), 136.3 (s; *meta*-BC$_6$H$_5$), 134.2, 134.0, 131.0, 130.4, 130.0, 129.6, 128.6 (all s; C_6H_5 and CH=CPh$_2$), 125.9 (q, J(B,C) = 3.0 Hz; *ortho*-BC$_6$H$_5$), 122.0 (s; *para*-BC$_6$H$_5$), 26.8 (vt, N = 27.5 Hz; PCHCH$_3$), 20.1 (s; PCHCH$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 162.0 MHz): $\delta = 50.6$ (s); elemental analysis (%) for $C_{57}H_{73}BClIrP_2$ (1057.8): calcd.: C 64.72, H 6.96; found: C 64.95, H 6.99; $\Lambda = 61\ \mathrm{cm^2\Omega^{-1}mol^{-1}}$ (CH$_3$NO$_2$).

Generation of *trans*-[IrCl{≡CCH=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$]O$_2$CCF$_3$ (12a): Compound **9** (42 mg, 0.05 mmol) was dissolved in nitromethane (2 mL) and after stirring for 2 min the molar conductivity was measured. The value $\Lambda = 51\ \mathrm{cm^2\Omega^{-1}mol^{-1}}$ indicated that by cleavage of the C−OC(O)CF$_3$ bond most of the starting material was converted to an 1:1 electrolyte. Spectroscopic data for the cation: ^{1}H NMR (CD$_3$NO$_2$, 400 MHz): δ = 7.83 (m, 3H; *ortho*- and *para*-H of C_6H_5), 7.61 (m, 2H; *meta*-H of C_6H_5), 3.32 (s, 1H; CH=C(Ph)*t*Bu), 3.14 (m, 6H; PCHCH$_3$), 1.70 (dvt, N = 15.0, J(H,H) = 7.3 Hz, 36H; PCHCH_3), 1.49 (s, 9H; C(CH$_3$)$_3$); ^{13}C NMR (CD$_3$NO$_2$, 100.6 MHz): δ = 243.6 (t, J(P,C) = 9.2 Hz; Ir≡C), 184.4 (s; C(Ph)*t*Bu), 140.2 (s; *ipso*-C_6H_5), 133.8, 132.2, 130.2, 128.1 (all s; C_6H_5 and CH=C(Ph)*t*Bu), 42.7 (s; C(CH$_3$)$_3$), 29.6 (s; C(CH$_3$)$_3$), 28.1 (vt, N = 28.5 Hz; PCHCH$_3$), 20.9 (s; PCHCH$_3$); ^{31}PNMR (CD$_3$NO$_2$, 162.0 MHz): $\delta = 51.8$ (s).

Preparation of *trans*-[IrCl{≡C−CH=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$]BPh$_4$ (12b): This compound was prepared as described for **11b**, from **9** (90 mg, 0.11 mmol) and NaBPh$_4$ (37 mg, 0.11 mmol) in methanol (20 mL). Brown solid; yield 94 mg (84 %); m.p. 78 °C (decomp) ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.47 (m, 1H; *para*-H of C_6H_5), 7.37 (m, 2H; *meta*-H of C_6H_5), 7.25 (m, 8H; *ortho*-H of BC$_6$H$_5$), 7.04 (m, 2H; *ortho*-H of C_6H_5), 6.96 (m, 8H; *meta*-H of BC$_6$H$_5$), 6.80 (m, 4H; *para*-H of BC$_6$H$_5$), 2.67 (m, 6H; PCHCH$_3$), 2.61 (s, 1H; CH=C(Ph)*t*Bu), 1.39 (dvt, N = 15.2, J(H,H) = 7.4 Hz, 36H; PCHCH_3), 1.07 (s, 9H; C(CH$_3$)$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 239.6 (t, J(P,C) = 8.1 Hz; Ir≡C), 181.6 (s; C(Ph)*t*Bu), 163.6 (q, J(B,C) = 49.8 Hz; *ipso*-BC$_6$H$_5$), 137.5 (s; *ipso*-C_6H_5), 135.5 (s; *meta*-BC$_6$H$_5$), 131.2, 130.4, 128.5, 125.5 (all s; C_6H_5 and CH=C(Ph)*t*Bu), 125.1 (q, J(B,C) = 3.0 Hz; *ortho*-BC$_6$H$_5$), 121.2 (s; *para*-BC$_6$H$_5$), 40.8 (s; C(CH$_3$)$_3$), 28.1 (s; C(CH$_3$)$_3$), 26.0 (vt, N = 27.4 Hz; PCHCH$_3$), 19.3 (s; PCHCH$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 162.0 MHz): $\delta = 52.0$ (s); elemental analysis (%) for $C_{55}H_{77}BClIrP_2$ (1037.9): calcd.: C 63.65, H 7.48; found; C 63.93, H 7.20; $\Lambda = 72\ \mathrm{cm^2\Omega^{-1}mol^{-1}}$ (CH$_3$NO$_2$).

X-ray structure determination of compounds 3 and 6: Single crystals of **3** were grown from a saturated solution in dichloromethane at 5 °C, and those of **6** from a saturated solution in acetone at −60 °C. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied for **6** (ψ-scans). The structures were solved by direct methods (SHELXS-97).[25] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (SHELXL-97).[26] Except for H1a and H1b the positions of all hydrogen atoms of **3** were calculated according to ideal geometry (distance C−H = 0.95 Å) and used only in structure factor calculation. For **6** the hydride ligand was found in a differential fourier synthesis and refined with fixed U_{eq}. The positions of the other hydrogen atoms of **6** were calculated according to ideal geometry and used only in structure factor calculation.[27]

Table 1. Crystal structure data of compounds **3** and **6**.

	3	**6**
formula	$C_{34}H_{54}ClIrP_2$	$C_{33}H_{53}ClP_2Ir$
molecular mass	752.36	774.79
crystal size [mm]	0.20 × 0.18 × 0.14	0.21 × 0.16 × 0.13
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a [Å]	9.0077(13)	12.154(3)
b [Å]	12.329(16)	22.781(2)
c [Å]	15.757(2)	12.410(3)
α [°]	90.468(16)	90.0
β [°]	95.025(17)	91.960
γ [°]	95.843(16)	90.0
V [Å^3]	1706.3(4)	3434.6(10)
Z	2	4
ρ_{calcd} [g cm^{-1}]	1.464	1.498
diffractometer	Stoe IPDS	Enraf-Nonius CAD 4
radiation (graphite-monochromated)	Mo$_{K\alpha}$ (0.71073 Å)	Mo$_{K\alpha}$ (0.71073 Å)
T [K]	173(2)	173(2)
μ [mm^{-1}]	4.105	4.156
transmission min. [%]		88.00
scan method	ϕ scans	ω/θ
2θ (max) [°]	50.00	50.14
total reflections	11626	6542
unique reflections	5660	6034
observed reflections	4895	3677
	$[I > 2\sigma(I)]$	$[I > 2\sigma(I)]$
parameters refined	364	356
R_1	0.0278	0.0697
wR_2	0.0687	0.1725
GOF	1.021	1.010
reflection/parameter ratio	15.54	16.95
residual electron density [eÅ^{-3}]	+1.269/−1.024	+1.484/−2.107

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[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-163326 (**3**) and CCDC-163327 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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