Carbene Iridium(I) and Iridium(III) Complexes Containing the Metal Center in Different Stereochemical Environments†

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The mixed-ligand complex [IrCl(C_2H_4)(Sb*i*Pr$_3$)(P*i*Pr$_3$)] (**2**), prepared from [IrCl(C_2H_4)-(P*i*Pr$_3$)]$_2$ (**1**) and Sb*i*Pr$_3$, reacts not only with CO, diphenylacetylene, and H_2 by ligand substitution or oxidative addition but also with diaryldiazomethanes R_2CN_2 to give the four-coordinate iridium(I) carbenes [IrCl(=CR_2)(Sb*i*Pr$_3$)(P*i*Pr$_3$)] (**8**−**10**) in 60−70% isolated yield. In contrast, treatment of **2** and of the related cyclooctene derivative *trans*-[IrCl(C_8H_{14})-(Sb*i*Pr$_3$)$_2$] (**12**) with $C_5Cl_4N_2$ affords the diazoalkane complexes *trans*-[IrCl($N_2C_5Cl_4$)(Sb*i*Pr$_3$)-(E*i*Pr$_3$)] (**11**, E = P; **13**, E = Sb) without elimination of N_2. Displacement of the stibine ligand in **8**−**10** by P*i*Pr$_3$ leads to the corresponding bis(phosphine) compounds *trans*-[IrCl(=CR_2)-(P*i*Pr$_3$)$_2$] (**14**−**16**), while the reaction of **8** (R = C_6H_5) with NaC_5H_5 yields the half-sandwich-type complex [(η^5-C_5H_5)Ir(=CPh$_2$)(P*i*Pr$_3$)] (**17**). Protonation of **17** with HCl occurs stepwise to give via the iridium(III) alkyl [(η^5-C_5H_5)IrCl(CHPh$_2$)(P*i*Pr$_3$)] (**20**) the ring-substituted isomer [(η^5-C_5H_4CHPh$_2$)IrHCl(P*i*Pr$_3$)] (**21**); however, if **17** is treated with HBF_4, a cationic complex is formed which probably contains a η^3-coordinated benzylic ligand. The square-planar iridium(I) carbenes **8** and **14** react with HBX_4 (X = F, Ar_F) to afford the ionic products [IrHCl(=CPh$_2$)(P*i*Pr$_3$)(E*i*Pr$_3$)]BX_4 (**23**, **24**, E = P; **25**, E = Sb) and with HCl to give the relatively labile octahedral species [IrHCl_2(=CPh$_2$)(P*i*Pr$_3$)(E*i*Pr$_3$)] (**26**, E = P; **27**, E = Sb). Treatment of **8** and **14** with ethene yields, besides [IrCl(C_2H_4)$_2$(Sb*i*Pr$_3$)$_2$] (**18**) and/or *trans*-[IrCl(C_2H_4)(P*i*Pr$_3$)$_2$] (**28**), a mixture of two isomeric olefinic products CH_2=CHCHPh$_2$ (**29**) and CH_3CH=CPh$_2$ (**30**), the ratio of which is independent of the ligand sphere of the iridium precursor. The molecular structures of **13**, **14**, **17**, and **24** have been determined by X-ray crystallography.

Introduction

In the context of our studies on the chemistry of square-planar complexes of the general composition *trans*-[RhCl{=C(=C)$_n$RR′}(P*i*Pr$_3$)$_2$] (*n* = 1, 2, and 4),[1] we recently reported also a convenient synthetic route to structurally related rhodium carbenes *trans*-[RhCl-(=CRR′)(P*i*Pr$_3$)$_2$].[2] The key to success was to use instead of *trans*-[RhCl(C_2H_4)(P*i*Pr$_3$)$_2$] the more reactive bis(triisopropylstibine) derivative *trans*-[RhCl(C_2H_4)(Sb*i*Pr$_3$)$_2$] as the precursor and, after it had been reacted with R′RCN_2 to give *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$], to subsequently replace the stibine ligands with triisopropylphosphine. Since both *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] and *trans*-[RhCl(=CRR′)(P*i*Pr$_3$)$_2$] provide a rich chemistry including novel C−C coupling reactions,[2,3] we became interested in preparing the corresponding iridium(I) complexes *trans*-[IrCl(=CRR′)(E*i*Pr$_3$)$_2$] (E = Sb, P) in order to find out how similar or how different their reactivity is compared with the rhodium(I) counterparts. However, attempts to obtain the four-coordinate compound *trans*-[IrCl(C_2H_4)(Sb*i*Pr$_3$)$_2$], anticipated to be the best starting material, from [IrCl(C_2H_4)$_2$]$_2$ and excess Sb*i*Pr$_3$ led instead to the formation of the five-coordinate species [IrCl(C_2H_4)$_2$(Sb*i*Pr$_3$)$_2$], which did not react with diazoalkanes R′RCN_2 to give *trans*-[IrCl(=CRR′)-(Sb*i*Pr$_3$)$_2$].[4]

Therefore, we set out to develop another synthetic route to iridium(I) carbenes and found, quite unexpectedly, that the mixed phosphine/stibine complex [IrCl-(C_2H_4)(Sb*i*Pr$_3$)(P*i*Pr$_3$)] is a suitable precursor to prepare the target molecules. Here we describe the preparation of square-planar, octahedral, and half-sandwich-type iridium complexes containing Ir=C(aryl)$_2$ as a molecular unit and discuss in particular their behavior toward Brönsted acids. Some of these results have already been communicated.[5]

† Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday.

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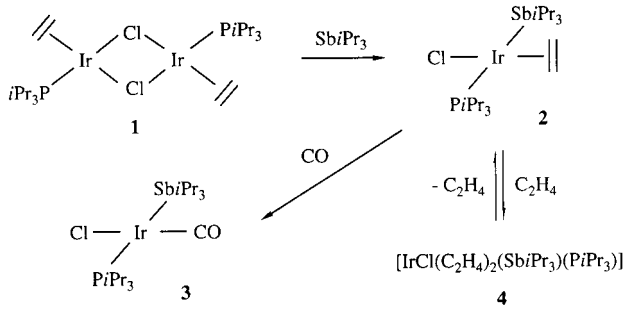
Scheme 1



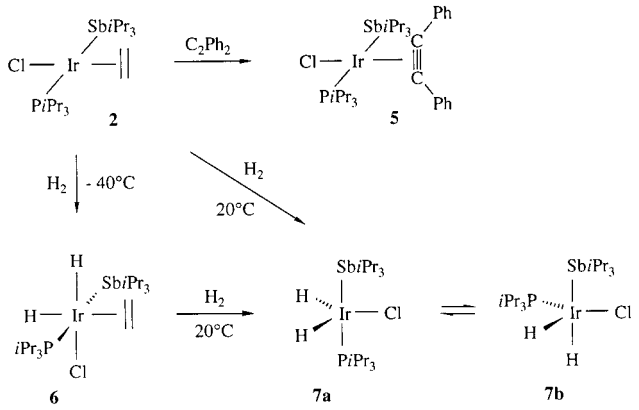
Results and Discussion

1. Preparation, Substitution, and Hydrogenation Reactions of [IrCl(C_2H_4)(Sb*i*Pr$_3$)(P*i*Pr$_3$)]. In contrast to [IrCl(C_8H_{14})(P*i*Pr$_3$)]$_2$,[6] which upon treatment with Sb*i*Pr$_3$ affords a mixture of products, the related ethene-containing dimer **1** reacts with 2 equiv of triisopropylstibine in pentane at room temperature to give the monomeric 16-electron complex **2** in nearly quantitative yield (Scheme 1). The bright orange solid, which can be handled in air for a short period of time and stored under argon at −30 °C for weeks, is relatively unstable in solution and decomposes particularly in dichloromethane quite rapidly. The ^{13}C NMR spectrum of **2** displays not only a doublet at δ 20.2 for the P*C*HCH$_3$ but also one at δ 17.5 for the Sb*C*HCH$_3$ carbon atoms, the latter having a smaller ^{13}C−^{31}P coupling constant of 6.1 Hz.

Passing a slow stream of CO through a solution of **2** in pentane for only ca. 10 s leads to the replacement of the olefinic ligand and the generation of the monocarbonyl derivative **3**, isolated in 80% yield. The IR spectrum of the lemon-yellow, moderately air-sensitive solid shows a strong ν(CO) stretching mode at 1926 cm^{-1}, which is only slightly red-shifted compared with the bis(phosphine) analogue *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$].[7] If treatment of **2** with CO is continued for ca. 1 min, two new compounds are formed, which have been identified by IR and NMR spectroscopy as [IrCl(CO)$_2$(Sb*i*Pr$_3$)$_2$] and *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$].[7,8] We assume that in the course of this reaction a short-lived mixed stibine/phosphine intermediate [IrCl(CO)$_2$(Sb*i*Pr$_3$)(P*i*Pr$_3$)] is generated, which conproportionates to give the thermodynamically more stable Ir(Sb*i*Pr$_3$)$_2$ and Ir(P*i*Pr$_3$)$_2$ products.

The four-coordinate compound **2** also reacts with C_2H_4 to give the bis(ethene) complex **4** (see Scheme 1). In contrast to [IrCl(C_2H_4)$_2$(Sb*i*Pr$_3$)$_2$],[4] the stibine/phosphine derivative **4** is rather labile, and after removing the ethene atmosphere, the starting material **2** is regenerated. The ^{31}P NMR spectrum of **4** shows a singlet resonance at δ −3.4, which appears at significantly higher field compared with **2** (δ 15.5). In C_6D_6 solution, a slow rearrangement of **4** takes place, which finally leads to the formation of the more symmetrical compounds [IrCl(C_2H_4)$_2$(Sb*i*Pr$_3$)$_2$] and *trans*-[IrCl(C_2H_4)(P*i*Pr$_3$)$_2$], respectively.

Scheme 2



The olefinic ligand of **2** can be displaced not only by CO but also by diphenylacetylene and H_2 (Scheme 2). Treatment of **2** with C_2Ph_2 in pentane affords the substitution product **5**, which is the link between the bis(stibine) and bis(phosphine) analogues *trans*-[IrCl(C_2Ph_2)(Sb*i*Pr$_3$)$_2$][4] and *trans*-[IrCl(C_2Ph_2)(P*i*Pr$_3$)$_2$].[6] The hydrogenation of **2** at room temperature leads to the formation of a dihydridoiridium(III) species which is isolated as a mixture of two isomers **7a** and **7b**. If the reaction of **2** with H_2 is carried out at −40 °C in pentane, an oxidative addition occurs to give the octahedral complex **6** as a pale yellow solid in 84% yield. Typical spectroscopic features of **6** are the two high-field ^{1}H NMR resonances for the *cis*-disposed hydrides at δ −10.89 and −28.24 and the two sets of signals for the protons and carbon atoms of the diastereotopic CH$_3$ groups of the Sb*i*Pr$_3$ and P*i*Pr$_3$ ligands in the ^{1}H and ^{13}C NMR spectra. The IR spectrum of **6** displays two bands for the Ir−H stretching modes at 2201 and 2093 cm^{-1}, the positions being nearly identical to those of the related bis(arsine) complex *cis,trans*-[IrH$_2$Cl(C_2H_4)(As*i*Pr$_3$)$_2$].[9]

While in the absence of a dihydrogen atmosphere compound **6** is stable and can be stored under argon for days, in the presence of H_2 it smoothly reacts at room temperature to give **7a/7b** and ethane. After removal of the solvent and recrystallization from acetone at −78 °C a yellow microcrystalline solid was isolated which partly converts to a yellow oil at ca. 20 °C. The ^{1}H and ^{31}P NMR spectra, both taken immediately after the yellow solid is dissolved in C_6D_6, confirm the presence of two isomers **7a** and **7b**, the ratio of which increases from ca. 4:1 to 1:3 upon storing the solution for 3 days. Since the ^{1}H NMR spectrum of the initially dominating isomer **7a** shows only one doublet in the high-field region at δ −25.31, we assume that in **7a** the hydrido ligands are stereochemically equivalent and occupy two basal positions of a trigonal bipyramid. The spectrum of the thermodynamically favored isomer **7b** exhibits two doublet-of-doublet resonances at δ −15.93 and −26.47, thus illustrating the inequivalence of the Ir−H units. Moreover, the similar values of the ^{1}H−^{31}P coupling constants (15.2 and 13.7 Hz) indicate that in **7b** both hydrides are *cis*-disposed to the triisopropylphosphine ligand. We note that even after storing the

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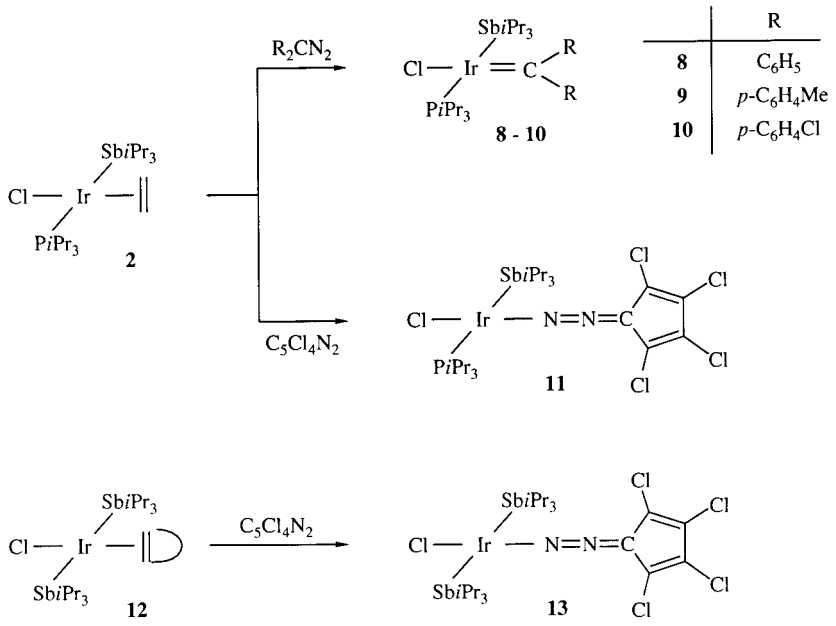
Scheme 3



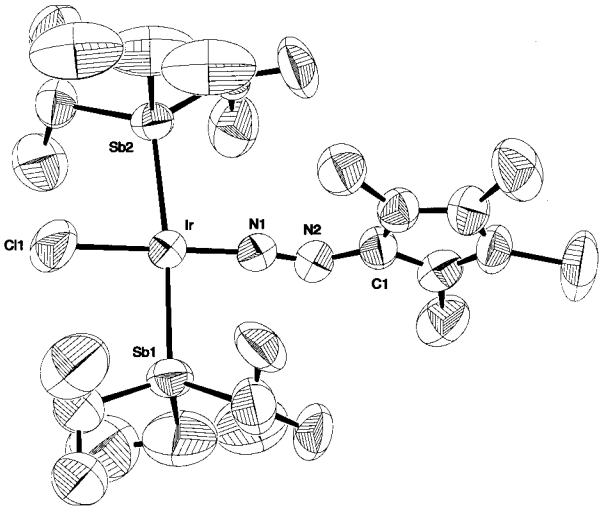


Figure 1. Molecular diagram of compound **13**. Selected bond distances (Å) and angles (deg): Ir−Cl1 2.275(4), Ir−Sb1 2.599(1), Ir−Sb2 2.598(1), Ir−N1 1.79(1), N1−N2 1.18(1), N2−C1 1.36(1); N1−Ir−Cl1 178.7(4), Sb1−Ir−Sb2 174.96(4), Cl1−Ir−Sb1 88.5(1), Cl1−Ir−Sb2 86.6(1), N1−Ir−Sb1 91.2(3), N1−Ir−Sb2 93.8(4), Ir−N1−N2 172(1), N1−N2−C1 136(1).

solution of **7a/7b** in C_6D_6 under a H_2 atmosphere for one week, no conversion to $[IrH_2Cl(PiPr_3)_2]$[10] and $[IrH_2Cl(SbiPr_3)_2]$[4] takes place.

2. Preparation and Molecular Structure of Square-Planar and Half-Sandwich-Type Iridium(I) Carbenes. In contrast to *trans*-$[IrCl(C_2H_4)(PiPr_3)_2]$, which does not cleanly react with Ph_2CN_2 to give *trans*-$[IrCl(=CPh_2)(PiPr_3)_2]$,[11] treatment of the mixed-ligand compound **2** with diphenyldiazomethane as well as with $(p\text{-}C_6H_4Me)_2CN_2$ and $(p\text{-}C_6H_4Cl)_2CN_2$ in benzene at room temperature affords the diarylcarbene complexes **8**−**10** in 60−70% isolated yield. The iridium carbenes **8**−**10** are more air-sensitive and thermally less stable than the bis(stibine)rhodium analogues *trans*-$[RhCl(=CR_2)(SbiPr_3)_2]$.[2,3] However, under argon at −30 °C they can be stored without decomposition for weeks. The most characteristic spectroscopic feature of **8**−**10** is the signal for the carbene carbon atom at, respectively, δ 240.9 (**8**), 244.7 (**9**), and 235.7 (**10**) in the ^{13}C NMR spectra, which in each case is split into a doublet due to $^{13}C-^{31}P$ coupling. With regard to the preparative procedure for **8**−**10** it should be mentioned that the starting materials **2** and R_2CN_2 have to be used in a 1:1 molar ratio since with excess diazoalkane a subsequent reaction of the iridium carbene occurs, leading to a mixture of products which could not be exactly identified.

The ethene-containing precursor **2** also reacts with $C_5Cl_4N_2$, but in this case no evolution of N_2 can be observed. From a pentane solution a green solid precipitates, which after recrystallization from acetone correctly analyzes as $[IrCl(N_2C_5Cl_4)(SbiPr_3)(PiPr_3)]$ (**11**). In contrast to the iridium carbenes **8**−**10**, the diazoalkane derivative **11** is only slightly air-sensitive and less soluble in ether and hexane. The cyclooctene complex **12** behaves similarly to **2** and upon treatment with $C_5Cl_4N_2$ gives the bis(stibine) counterpart of **11** with an analytical composition corresponding to **13** (see Scheme 3). According to the spectroscopic data of **11** and **13**, we assume that the diazoalkane ligand is end-on bonded via the terminal nitrogen atom to the metal center. Diagnostic for this type of coordination[12] is an N−N stretching vibration in the IR spectra at 1830−1840 cm^{-1} as well as a signal in the ^{13}C NMR spectra at δ 63.8 (**11**) and 61.0 (**13**) for the N_2C carbon atom. Attempts to eliminate N_2 from **11** or **13** and to transform these compounds to the corresponding carbene complexes $[IrCl(=CC_4Cl_4)(SbiPr_3)(EiPr_3)]$ (E = P, Sb) remained unsuccessful.

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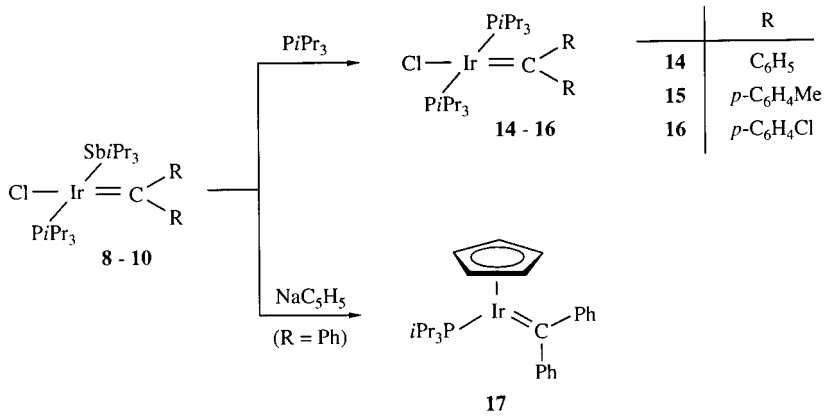
Scheme 4



The result of the X-ray crystal structure analysis of **13** is shown in Figure 1. The coordination sphere around iridium is square-planar with *trans*-disposed stibine ligands and an almost linear Cl−Ir−N1 axis. The $N_2C_5Cl_4$ moiety possesses the "singly bent" geometry, as has also been found for *trans*-[IrCl($N_2C_5Cl_4$)(PPh_3)$_2$].[13] The nitrogen, carbon, and chlorine atoms of the coordinated $N_2C_5Cl_4$ molecule lie in one plane which is not exactly perpendicular to the plane containing Ir, Cl, Sb1, and Sb2. The dihedral angle between the two planes is 77.1(5)°. The distance N1−N2 of 1.18(1) Å is halfway between that of an N−N triple bond (1.098 Å in N_2)[14] and an N−N double bond (1.244 Å in PhN═NPh),[15] being in agreement with the assumption that $N_2C_5Cl_4$ is a moderate π-acceptor ligand. The result that the Ir−Sb distances of **13** (2.599(1) and 2.598(1) Å) are nearly identical to those of [IrHCl(η^3-C_3H_5)(Sb*i*Pr_3)$_2$] (2.5642(5) and 2.5569(7) Å)[8] is noteworthy insofar as in the π-allyl(hydrido) complex the metal is in the oxidation state +III.

In analogy with the rhodium carbenes *trans*-[RhCl(═CRR′)(Sb*i*Pr_3)$_2$],[2,3] the Ir−Sb*i*Pr_3 bond in the iridium compounds **8**−**10** is also readily dissociable. Therefore, treatment of a solution of **8**−**10** in pentane or benzene at room temperature with an equimolar amount of P*i*Pr_3 affords the bis(phosphine) complexes **14**−**16** in good yields (Scheme 4). While **14** and **15** could be isolated, after recrystallization from acetone, as analytically pure brown solids, **16** is much less stable and smoothly decomposes in solution (in toluene even at −20 °C). It has thus been characterized only by spectroscopic techniques. The resonance for the carbene carbon atom appears in the ^{13}C NMR spectra of **14**−**16** at, respectively, δ 234.7 (**14**), 245.5 (**15**), and 237.8 (**16**) and is split into a triplet due to coupling with two ^{31}P nuclei. The ^{1}H NMR spectra of **14**−**16** display for the PCHCH_3 protons a doublet of virtual triplets which is typical for square-planar iridium(I) compounds with the two P*i*Pr_3 ligands in *trans* disposition.[6,16] With regard to the lability of **16** we note that attempts to prepare stable rhodium carbenes with Rh═C(*p*-$C_6H_4Cl)_2$ as a molecular unit remained unsuccessful.[17]

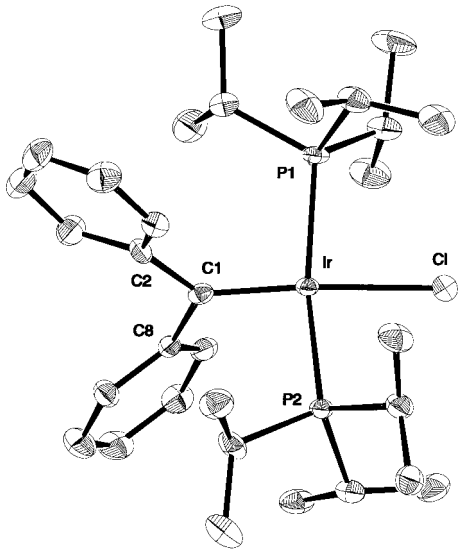


Figure 2. Molecular diagram of compound **14**. Selected bond distances (Å) and angles (deg): Ir−P1 2.344(1), Ir−P2 2.374(1), Ir−Cl 2.434(2), Ir−C1 1.887(5), C1−C2 1.487(7), C1−C8 1.509(7); P1−Ir−P2 162.21(5), P1−Ir−Cl 86.18(6), P1−Ir−C1 96.0(2), P2−Ir−Cl 86.28(6), P2−Ir−C1 95.0(2), Ir−C1−C2 128.9(4), Ir−C1−C8 117.7(3), C2−C1−C8 113.4(4).

The X-ray crystal structure analysis of **14** confirmed the proposed coordination geometry of the molecule (Figure 2). Both the P1−Ir−P2 and Cl−Ir−C1 axes are somewhat bent, the two bond angles (162.21(5)° and 166.7(2)°) being quite similar to those of the rhodium counterpart *trans*-[RhCl(═CPh_2)(P*i*Pr_3)$_2$] (161.55(3)° and 166.24(9)°).[3b] The repulsive forces between the isopropyl and phenyl groups of the P*i*Pr_3 and CPh_2 ligands are probably responsible for this bending. We assume that steric effects also explain why the dihedral angle between the planes [Ir,Cl,P1,P2] and [C1,C2,C8] is not 0° (as suggested by bonding arguments)[18] but is 67.3(3)°

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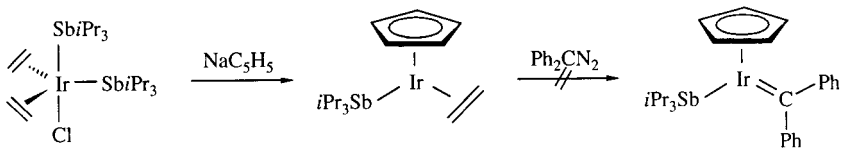
Scheme 5



18 **19**

and thus deviates significantly from the expected value. The Ir−C1 bond length (1.887(5) Å) is longer than in the vinylidene and butatrienylidene iridium analogues, *trans*-[IrCl(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$] (1.764(6) Å)[16b] and *trans*-[IrCl(=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (1.816(6) Å),[19] and is almost the same as in the methylene complex [Ir(=CH$_2$){κ^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$}] (1.868(9) Å).[20]

The reactivity of the structurally related molecules **8** and **14** toward NaC_5H_5 is quite different. While the bis(phosphine) derivative **14** is completely inert toward sodium cyclopentadienide (THF, room temperature), the mixed-ligand compound **8** reacts under the same conditions with NaC_5H_5 to give, after recrystallization from pentane at −78 °C, the half-sandwich-type complex **17** in 70% yield. We note that in one case, when we used a larger amount of the starting material **8** (ca. 0.5 mmol), instead of a dark violet solid an oily substance was isolated which contained besides **17** as the byproduct some free Sb*i*Pr$_3$. It could be separated from **17** via conversion (with CH_3I) to [CH_3Sb*i*Pr$_3$]I. The ^{1}H NMR spectrum of **17** displays a doublet for the C_5H_5 protons at δ 4.92 and the ^{13}C NMR spectrum a doublet for the carbene carbon atom at δ 217.2. The most remarkable spectroscopic feature, however, is the appearance of two sets of signals for the carbon atoms of the phenyl rings indicating that the rotation around the Ir=C bond is considerably hindered. A similar observation was reported by Klein and Bergman for the analogous methylene compound [(η^5-C$_5$Me$_5$)Ir(=CH$_2$)(PMe$_3$)].[21] It is worth mentioning that in contrast to this Ir=CH$_2$ species (generated upon photolysis of the metallacycle [(η^5-C$_5$Me$_5$)Ir(κ-*C*,*O*-CH$_2$CMe$_2$O)(PMe$_3$)] at −60 °C) the diphenylcarbene complex **17** is thermally quite stable and decomposes only at temperatures above 93 °C.

The result of the X-ray crystal structure analysis of **17** is shown in Figure 3. The iridium has a somewhat distorted trigonal coordination sphere if the midpoint of the cyclopentadienyl ring is taken as one coordination site. The Ir−C1 bond length (1.904(5) Å) is practically identical to that in the related rhodium carbene [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(CO)] (1.906(3) Å).[22] The Ir−C$_{cyclopentadienyl}$ distances lie between 2.210(7) and 2.316(6) Å, reflecting the different binding properties of the P*i*Pr$_3$ and CPh$_2$ groups. We note that, to the best of our knowledge, compound **17** is the first structurally characterized iridium complex of the general composition [(η^5-C$_5$H$_5$)Ir(L)(PR$_3$)], where L is a carbene, vinylidene, or allenylidene ligand.[23]

Attempts to prepare the stibine analogue of **17** following the sequence of reactions outlined in Scheme 5 failed. Treatment of **18**[4] with NaC_5H_5 in THF affords the expected half-sandwich-type compound **19**, which, however, does not react even with an excess of Ph_2CN_2 by ligand exchange. The ^{1}H and ^{13}C NMR spectroscopic data of **19** are rather similar to those of the corresponding rhodium complex [(η^5-C$_5$H$_5$)Rh(C$_2$H$_4$)(Sb*i*Pr$_3$)][22] and deserve no further comment.

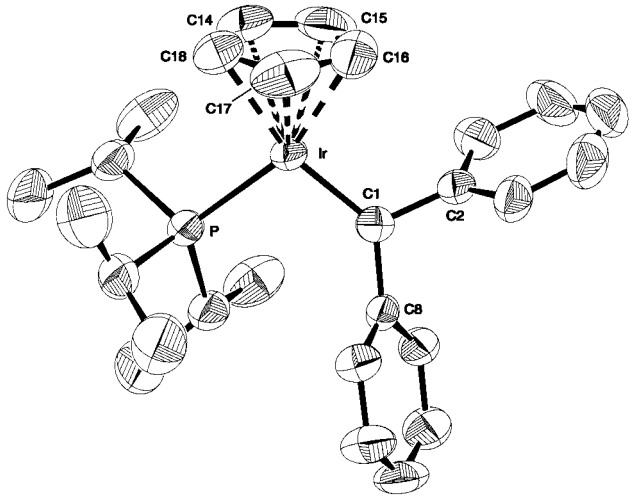


Figure 3. Molecular diagram of compound **17**. Selected bond distances (Å) and angles (deg): Ir−P 2.262(2), Ir−C1 1.904(5), Ir−C14 2.308(7), Ir−C15 2.266(7), Ir−C16 2.210(7), Ir−C17 2.239(7), Ir−C18 2.316(6), C1−C2 1.499(7), C1−C8 1.492(7); P−Ir−C1 99.9(2), Ir−C1−C2 116.2(4), C2−C1−C8 109.2(4).

3. Reactions of the Iridium Carbenes with Brönsted Acids. While investigating the reactivity of diphenylcarbenerhodium(I) compounds of the general composition [(η^5-L)Rh(=CPh$_2$)(Sb*i*Pr$_3$)] and [(η^5-L)Rh(=CPh$_2$)(PR$_3$)] (L = C$_5$H$_5$, C$_5$H$_4$SiMe$_3$, C$_9$H$_7$),[22,24] we recently observed that upon treatment of [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_3$)] with HCl or CF_3CO_2H a migratory insertion of the CPh$_2$ moiety into one of the C−H bonds of the cyclopentadienyl ring occurs.[25] From a labeling study we concluded that initially, via addition of the Brönsted acid to the rhodium−carbene bond, a labile intermediate [(η^5-C$_5$H$_5$)RhX(CHPh$_2$)(P*i*Pr$_3$)] is formed, which quickly rearranges to the isomeric ring-substituted derivative [(η^5-C$_5$H$_4$CHPh$_2$)RhHX(P*i*Pr$_3$)].

The supposed M(CHPh$_2$) species could be isolated for M = Ir. Treatment of a solution of **17** in pentane with

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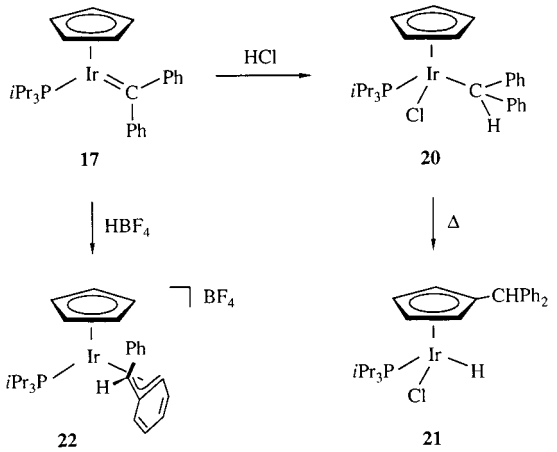
(24) (a) Bleuel, E.; Werner, H. *C. R. Acad. Sci. Paris, Ser. IIc* **1999**, 341−349. (b) Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 3109−3114.
(25) (a) Herber, U.; Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **1998**, *17*, 10−12. (b) Bleuel, E.; Schwab, P.; Laubender, M.; Werner, H. *J. Chem. Soc., Dalton* Trans. **2001**, 266−273.

Scheme 6

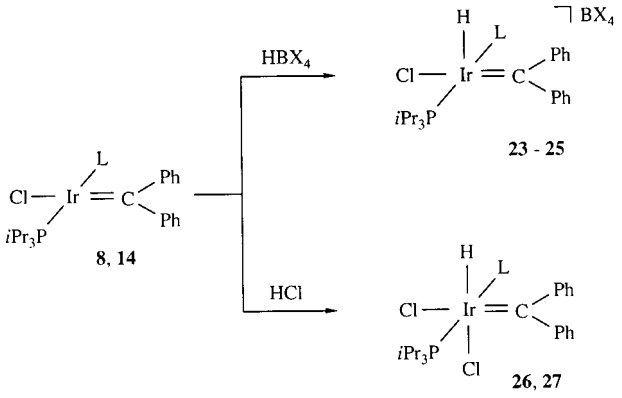


gaseous HCl results in a rapid change of color from violet to orange-yellow and affords the slightly air-sensitive alkyliridium(III) complex **20** in virtually quantitative yield (Scheme 6). Diagnostic for the metal-bonded $CHPh_2$ unit is a resonance in the ^1H NMR spectrum at δ 5.75 for the CH proton and a signal in the ^{13}C NMR spectrum at δ 24.6 for the substituted methyl carbon atom. Due to $^1H-^{31}P$ and $^{13}C-^{31}P$ couplings, these signals are split into doublets. Since **20** contains a chiral center, the CH_3 groups of the phosphine are diasterotopic and thus give rise to two resonances (as doublets of doublets) in the ^1H NMR spectrum.

Warming a solution of **20** in benzene for 2 min to reflux temperature leads to a stepwise change of color from orange-yellow to red and after ca. 10 s from red to yellow. After removal of the solvent and recrystallization from CH_2Cl_2/hexane the chloro(hydrido) complex **21** is isolated as a yellow solid in 95% yield. We assume that in the initial step of the isomerization a migration of the $CHPh_2$ unit from the metal to the five-membered ring takes place to give the cyclopentadieneiridium(I) intermediate [(η^4-$C_5H_5CHPh_2$)IrCl(P*i*Pr$_3$)]. Subsequently, this intermediate could rearrange via an exo-H migration on the upper face of the ring to generate an isomer with both an exo and an endo hydrogen, and final migration of the endo-H from the ring to iridium would lead to **21**. Following the conversion of **20** to **21** in C_6D_6 by ^1H NMR spectroscopy, the formation of a new species can be observed for which the appearance of two doublets at δ 3.42 and 3.19 (with a $^1H-^1H$ coupling of ca. 10 Hz) is characteristic. In agreement with previous findings,[25] we assign these signals to the ring-CH protons of the cyclopentadiene ligand. In this context we note that related rhodium compounds of the general composition [(η^4-diene)RhX(PR$_3$)], being formally isoelectronic to the supposed intermediate [(η^4-$C_5H_5CHPh_2$)-IrCl(P*i*Pr$_3$)], exist and in one case (for X = triflate and PR$_3$ = P*i*Pr$_3$) have been characterized by X-ray crystallography.[26]

The reaction of **17** with HBF_4 in ether leads to the diphenylmethyliridium(III) complex **22**, for which the structure shown in Scheme 6 is proposed. The dark red solid is readily soluble in methanol and dichloromethane but insoluble in benzene and ether, in agreement with

Scheme 7



	L	X
23	P*i*Pr$_3$	F
24	PiPr$_3$	Ar$_F$
25	Sb*i*Pr$_3$	Ar$_F$

	L
26	P*i*Pr$_3$
27	Sb*i*Pr$_3$

(Ar_F = 2.6-$C_6H_3(CF_3)_2$)

the ionic character of the compound. The ^1H NMR spectrum of **22** displays the resonance for the C*H*Ph$_2$ proton at δ 3.32 and thus at higher field (ca. 2.3 ppm) compared to **20**. Since in the ^1H and ^{13}C NMR spectra of **22** the signals for the C_6H_5 protons and the phenyl carbon atoms are relatively broad, we assume that the diphenylmethyl ligand is coordinated as a substituted η^3-benzyl group and exhibits, at room temperature, a fluxional behavior similarly to that of the structurally related ruthenium compound [(η^5-C_5H_5)Ru(η^3-$CHPh_2$)-(PPh_3)].[27,28] Attempts to slow the fluctional process and confirm the η^3-coordination of the $CHPh_2$ moiety by spectroscopic means failed because the BF_4 salt **22** precipitates even in CD_2Cl_2 below 0 °C.

Like the half-sandwich-type complex **17**, the square-planar iridium(I) compounds **8** and **14** also react smoothly with HBF_4 or Brookhart's acid $HB(Ar_F)_4$[29] to afford the cationic carbene(hydrido)iridium(III) derivatives **23**−**25** in 83−95% yield (Scheme 7). The red (or red-pink) solids are thermally quite stable, are soluble in acetone and dichloromethane, and can be stored under argon at room temperature for days. While it is conceivable that in solution (acetone or CH_2Cl_2) 1:1 adducts with a solvent molecule are generated, the elemental analyses of **23**−

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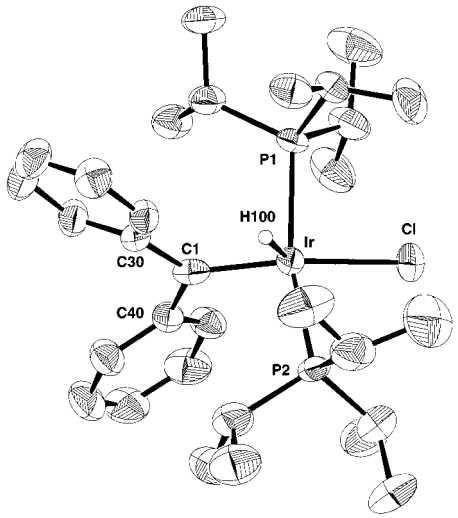

Figure 4. Molecular diagram of compound **24** (the position of the metal-bonded hydrogen atom H100 has been refined isotropically). Selected bond distances (Å) and angles (deg): Ir−Cl 2.378(2), Ir−P1 2.392(2), Ir−P2 2.409(2), Ir−C1 1.921(7), C1−C30 1.474(8), C1−C40 1.481(9); Cl−Ir−P1 86.05(6), Cl−Ir−P2 85.70(7), Cl−Ir−C1 158.66(18), C1−Ir−P1 95.3(2), C1−Ir−P2 98.0(2), P1−Ir−P2 162.37(6), Ir−C1−C30 128.8(5), Ir−C1−C40 115.5(4), C30−C1−C40 115.6(6).

25 reveal that in the solid state unsolvated species are present. The ^{1}H NMR spectra of **23**−**25** show a high-field resonance (triplet) at, respectively, δ −28.84 (**23**), −28.82 (**24**), and −31.20 (**25**) for the hydrido ligand, whereas the ^{13}C NMR spectra display a low-field signal at about δ 266 for the carbene carbon atom. The appearance of this ^{13}C NMR signal at significantly lower field compared to **8** and **14** could be due at least partly to the fact that the carbene(hydrido) complexes are cationic. A pertinent spectroscopic feature is that in both the ^{1}H and ^{13}C NMR spectra of **23**−**25** two sets of signals for the protons and carbon atoms of the C_6H_5 groups are observed, indicating that the two six-membered rings are stereochemically not equivalent.

To elucidate the coordination geometry of the IrH(=CPh_2) derivatives, an X-ray crystal structure analysis of **24** has been carried out. The molecular diagram reveals (see Figure 4) that the two phosphines, the chloride, and the carbene unit are linked in a distorted square-planar fashion to the metal center, forming together with the hydride a square pyramid. Compared with the precursor compound **14**, the Cl−Ir−C1 axis of **24** is somewhat more bent (158.7(2)° vs 166.7(2)°), while the P1−Ir−P2 bond angle of **24** is virtually identical to that of **14**. The Ir−C1 bond length of **24** (1.921(7) Å) is slightly longer than in **14** (1.887(5) Å), which is probably due to the decrease of back-bonding in the cationic species. This aspect is also reflected in the slight elongation of the Ir−P1 and Ir−P2 distances, which are 2.392(2) and 2.409(2) Å in **24** but 2.344(1) and 2.374(1) Å in **14**.

The free coordination site of the carbene(hydrido)-iridium(III) cations is readily occupied by chloride, and thus upon addition of an aqueous solution of NaCl to a solution of **23** in CD_2Cl_2, the neutral compound **26** is formed. However, this molecule is quite labile and in benzene/water eliminates HCl to regenerate **14**. An alternative route to **26** consists of the oxidative addition of gaseous HCl to **14** in benzene. If this reaction is monitored by ^{31}P NMR spectroscopy (in C_6D_6), after 1 min the signal of the starting material at δ 4.2 disappeared and is replaced by a new signal at δ 1.7, which in analogy with the related allenylidene compound [$IrHCl_2$(=C=C=CPh_2)(P*i*Pr_3)$_2$][30] can be assigned to the six-coordinate hydridoiridium(III) complex **26**. The presence of an Ir−H bond is indicated by the high-field resonance in the ^{1}H NMR spectrum at δ −19.23, the chemical shift of which is similar to that of [$IrHCl_2$(=C=C=CPh_2)(P*i*Pr_3)$_2$] (δ −17.63). Attempts to isolate **26** by partial removal of the solvent and addition of pentane led to a green solid, which besides the expected product contains some impurities including **14**. Equally labile appears the mixed-ligand complex **27** (see Scheme 7), which has been prepared from **8** and excess HCl and for which apart from the doublet at δ −18.78 in the ^{1}H NMR spectrum also a deep green color is characteristic. We note in this context that upon treatment of *trans*-[RhCl(=CPh_2)(P*i*Pr_3)$_2$] with HCl, the (red) pentacoordinate alkylrhodium(III) derivative [$RhCl_2$(CHPh_2)(P*i*Pr_3)$_2$] is formed, which seems to be significantly more stable than the carbene(hydrido) isomer.[3a]

4. Reactions of the Square-Planar Iridium Carbenes with Alkenes and Alkynes. The cationic iridium(III) species [IrHCl(=CPh_2)(P*i*Pr_3)(L)]$^+$ (L = P*i*Pr_3, Sb*i*Pr_3), which owing to the 16-electron configuration and the coordination number five of the metal center can be compared with the Grubbs-type catalyst [$RuCl_2$(=CHPh)(PCy_3)$_2$],[31] is completely inert toward olefins such as ethene, 1-hexene, and cyclopentene. Even after stirring a solution of **23**, **24**, or **25** in CD_2Cl_2 with an excess of the respected olefin for 3−4 days, the starting material can be recovered unchanged.

In contrast to the five-coordinate iridium(III) complexes **23**−**25**, the square-planar iridium(I) compounds **8** and **14** react slowly with C_2H_4 to give two new olefins, **29** and **30**, in addition to the ethene derivatives **18** and **28**, respectively (see Scheme 8). Due to the different donor strength of Sb*i*Pr_3 and P*i*Pr_3, it is not unexpected that the reaction of **8** with C_2H_4 is faster than that of **14**. The trisubstituted olefin **30**, which is the product of the catalytic reaction of C_2H_4 and Ph_2CN_2 with rhodium(I) complexes such as [RhCl(P*i*Pr_3)$_2$]$_2$ and [RhCl(C_2H_4)$_2$]$_2$ as catalysts,[32] is formally built up by two carbene fragments, one originating from the CPh_2 ligand of **8** or **14** and the other from ethene. The dominating terminal olefin **29** is obviously generated by insertion of the CPh_2 unit into one of the C−H bonds of ethene. Although any mechanistic scheme for the formation of the two isomers **29** and **30** from **8** or **14** remains highly speculative, the assumption that a carbene(ethene)-iridium complex [IrCl(=CPh_2)(C_2H_4)(L)] or [IrCl(=CPh_2)(C_2H_4)(P*i*Pr_3)(L)] (L = P*i*Pr_3, Sb*i*Pr_3) is involved in the catalytic cycle seems to be reasonable. It is rather surprising that in neither case, with **8** or with **14** and C_2H_4 as starting materials, the formation of a third isomer of composition $C_3H_4Ph_2$, namely, 1,2-diphenyl-

(30) Ilg, K.; Werner, H. *Chem. Eur. J.* **2001**, *7*, 4633−4639.
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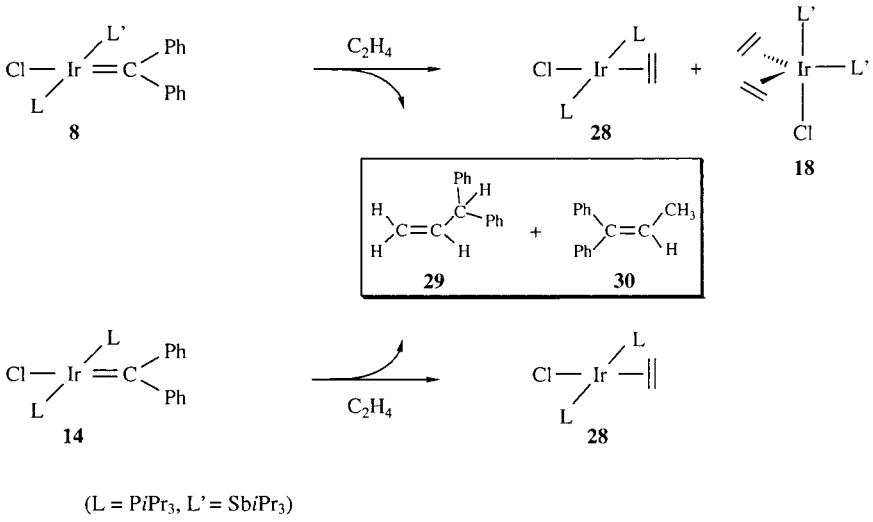
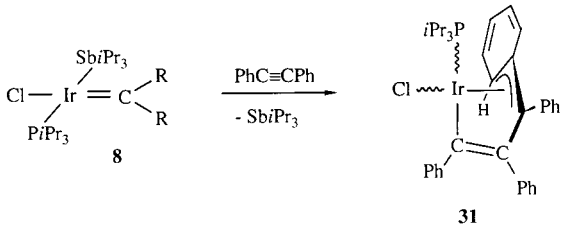
Scheme 8



Scheme 9



cyclopropane, has been observed.[33] Moreover, we note that the ratio of the two olefinic products **29** and **30** is (within the limits of GC analysis) the same, which indicates that a common intermediate—possibly the four-coordinate species $[IrCl(=CPh_2)(C_2H_4)(PiPr_3)]$—is involved. Attempts to detect this species spectroscopically by using the more labile compound **8** as the precursor failed.

The stibine complex **8** also reacts (C_6H_6, 25 °C) with excess cyclopentene. Besides two products containing $Ir(PiPr_3)$ or $Ir(PiPr_3)_2$ as the molecular unit, three organic molecules could be identified by GC/MS of which one undoubtedly is diphenylmethylenecyclopentane. The second compound (equally with *m*/*z* 234) is an isomer of $Ph_2C{=}C_5H_8$, presumably diphenylmethylcyclopentene, while the third (*m*/*z* 232) has two hydrogens less and could also be a cyclopentene derivative. Since none of the etheneiridium(I) complexes **2**, **18**, or **28** behaves as a catalyst for the reaction of Ph_2CN_2 with olefins,[32,34] a detailed analysis of the composition of the organic products has not been carried out.

In contrast to **2**, which upon treatment with diphenylacetylene in pentane at room temperature gives compound **5** by substitution of ethene (see Scheme 2), the related stibine complex **8** reacts with C_2Ph_2 under the same conditions to afford a C−C coupling product **31**, for which the structure shown in Scheme 9 is tentatively assigned. The ^1H NMR spectrum of the brown thermally stable solid displays (in CD_2Cl_2) besides resonances for the $PiPr_3$ protons and for phenyl protons at around δ 6.1−7.3 a broadened singlet at δ 3.78, which owing to the chemical shift probably belongs to the CH unit of a π-allyl system. The signal for the corresponding carbon atom appears in the ^{13}C NMR spectrum at δ 32.1; its assignment is supported by ^{90}DEPT measurements and the $^1H-^{13}C$ coupling constant of 152.6 Hz. The suggested mode of binding of the C_3Ph_4 fragment to iridium in **31** is at least partly reminiscent of that of the $CHPh_2$ unit in **22** (see Scheme 6), where the metal also possesses the oxidation state +III. We note that a similar $\eta^1{:}\eta^3$-coordinated chelating ligand originates through coupling of the $Ir{=}CH_2$ group of the above-mentioned methylene complex $[Ir(=CH_2)\{\kappa^3\text{-}N(SiMe_2CH_2PPh_2)_2\}]$ with butadiene.[35]

Conclusions

The present investigations have shown that in contrast to $[IrCl(C_2H_4)_2(SbiPr_3)_2]$ and *trans*-$[IrCl(C_2H_4)(PiPr_3)_2]$ the mixed-ligand complex $[IrCl(C_2H_4)(SbiPr_3)(PiPr_3)]$ (**2**) is a convenient starting material for the preparation of four-coordinate iridium(I) carbenes **8**−**10**. While **2** reacts with diaryldiazomethanes to give the carbene derivatives, the corresponding reaction of **2** with $C_5Cl_4N_2$ affords the diazoalkane compound **11** without elimination of N_2. Similarly to the rhodium(I) complexes *trans*-$[RhCl(=CR_2)(SbiPr_3)_2]$, which upon treatment with tertiary phosphines yield *trans*-$[RhCl(=CR_2)(PR_3)_2]$,[2,3] the iridium analogues **8**−**10** equally react with $PiPr_3$ by ligand substitution to give the bis(phosphine) counterparts **14**−**16**. The lability of the $Ir-SbiPr_3$ bond in **8** has also been used for the preparation of the half-sandwich-type compound **17**, which is not accessible from **14** and NaC_5H_5.

The square-planar representatives **8** and **14**, containing a metal center with a 16-electron configuration, and the cyclopentadienyl derivative **17**, containing a metal center with an 18-electron configuration, behave differently toward acids HBX_4. While the 16-electron species react with HBX_4 (X = F, Ar_F) via proton attack at iridium(I) to give cationic complexes with $IrH(=CPh_2)$

(33) Rhodium(II) complexes are very efficient catalysts for the cyclopropanation of olefins with diazoalkanes; see: Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669−8680, and references therein.

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as a molecular unit, treatment of **17** with HBF_4 yields a product having a $CHPh_2$ ligand that is probably η^3-coordinated to the metal. The reaction of **17** with HCl also generates an Ir($CHPh_2$) compound, but in this case the diphenylmethyl unit is η^1-bonded. The formation (and structural characterization) of the cationic species $[IrHCl(=CPh_2)(PiPr_3)(EiPr_3)]^+$ deserves particular attention insofar as, to the best of our knowledge, stable carbene(hydrido)iridium complexes with the metal in either the oxidation state +I or +III are quite rare.[36] Various attempts in our laboratory to generate related carbene(hydrido)*rhodium* cations failed.[3c,17] Finally it should be noted that, although the iridium(I) carbenes **8** and **14** react with ethene by C−C coupling, no olefin metathesis occurs and no $Ir=CH_2$ derivatives could be isolated.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**,[6] **12**,[8] and **18**[4] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 instruments at room temperature. IR spectra were recorded on a Bruker IFS 25 FT-IR and mass spectra on a Hewlett-Packard G 1800 GCD instrument. Melting points were measured by DTA. The term vt indicates a virtual triplet, and $N = {}^3J(PH) + {}^5J(PH)$ or ${}^1J(PC) + {}^3J(PC)$.

Preparation of [IrCl(C_2H_4)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (2). A suspension of **1** (105 mg, 0.13 mmol) in pentane (5 mL) was treated under stirring with Sb*i*Pr$_3$ (52 μL, 0.25 mmol) at room temperature. After 5 mL of benzene was added to the reaction mixture, the solvent was evaporated in vacuo as long as a clear orange solution was formed. The solution was stirred for 30 min and then brought to dryness in vacuo. The remaining bright orange solid was washed twice with 1 mL portions of pentane (0 °C) and dried: yield 159 mg (95%); mp 88 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 2.28 (br m, 10 H, SbC*H*CH$_3$, PC*H*CH$_3$, and C_2H_4), 1.42 (d, ^3J(HH) = 7.4 Hz, 18 H, SbCHC*H*$_3$), 1.23 (dd, ^3J(PH) = 12.6 Hz, ^3J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 22.1 (s, SbCH*C*H$_3$), 20.2 (d, ^1J(PC) = 25.4 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$), 17.5 (d, ^3J(PC) = 6.1 Hz, Sb*C*HCH$_3$), 14.0 (s, C_2H_4). ^{31}P NMR (162.0 MHz, C_6D_6): δ 15.5 (s). Anal. Calcd for $C_{20}H_{46}ClIrPSb$: C, 36.02; H, 6.95. Found: C, 35.77; H, 6.70.

Preparation of [IrCl(CO)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (3). A slow stream of CO was passed for 10 s through a solution of **2** (119 mg, 0.18 mmol) in pentane (10 mL) at room temperature. A quick change of color from orange to yellow occurred. The solvent was evaporated in vacuo, the residue was dissolved in pentane (2 mL), and the solution was stored for 12 h at −78 °C. Lemon-yellow crystals precipitated, which were separated from the mother liquor, washed twice with 1 mL portions of pentane (0 °C), and dried: yield 96 mg (80%); mp 146 °C. IR (KBr): ν(CO) 1926 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 2.62 (m, 3 H, PC*H*CH$_3$), 2.35 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.42 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHC*H*$_3$), 1.26 (dd, ^3J(PH) = 13.9 Hz, ^3J(HH) = 7.3 Hz, 19 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 171.9 (d, ^2J(PC) = 10.2 Hz, CO), 24.4 (d, ^1J(PC) = 24.4 Hz, P*C*HCH$_3$), 21.8 (s, SbCH*C*H$_3$), 19.8 (s, PCH*C*H$_3$), 19.0 (d, ^3J(PC) = 4.6 Hz, Sb*C*HCH$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 41.8 (s). Anal. Calcd for $C_{19}H_{42}ClIrOPSb$: C, 34.22; H, 6.35. Found: C, 33.98; H, 6.18.

Generation of [IrCl(C_2H_4)$_2$(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (4). A slow stream of ethene was passed for 15 s through a solution of **2** (23 mg, 0.03 mmol) in C_6D_6 (0.4 mL) at room temperature. The NMR spectra confirmed the formation of **4**. Attempts to isolate the bis(ethene) complex by concentrating the solution at 5 °C in vacuo led to the regeneration of **2**. Data for **4**: ^{1}H NMR (200 MHz, C_6D_6): δ 3.10−3.50 (br m, 6 H, C_2H_4], 2.66 (m, 5 H, C_2H_4 and SbC*H*CH$_3$), 2.29 (m, 3 H, PC*H*CH$_3$), 1.47 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHC*H*$_3$), 0.86 (dd, ^3J(PH) = 12.4, ^3J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ −3.4 (s).

Preparation of [IrCl(PhC≡CPh)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (5). A solution of **2** (86 mg, 0.13 mmol) in pentane (10 mL) was treated with diphenylacetylene (23 mg, 0.13 mmol) and stirred for 3 h at room temperature. A smooth change of color from orange to bright red occurred. The solvent was removed in vacuo, and the residue was dissolved in acetone (1.5 mL). After the solution was stored for 12 h at −78 °C, bright red crystals precipitated, which were separated from the mother liquor, washed with a small amount of acetone (−20 °C), and dried: yield 75 mg (71%); mp 54 °C. IR (KBr): ν(C≡C) 1831 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 8.27 (m, 4 H, *ortho*-H of C_6H_5), 7.21 (m, 4 H, *meta*-H of C_6H_5), 7.06 (m, 2 H, *para*-H of C_6H_5), 2.38 (m, 3 H, PC*H*CH$_3$), 2.05 (sept, ^3J(HH) = 7.6 Hz, 3 H, SbC*H*CH$_3$), 1.26 (d, ^3J(HH) = 7.6 Hz, 18 H, SbCHC*H*$_3$), 0.86 (dd, ^3J(PH) = 13.1, ^3J(HH) = 7.2 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 129.9, 128.3, 126.2 (all s, C_6H_5), 71.8 (d, ^2J(PC) = 2.0 Hz, ≡*C*C$_6$H$_5$), 22.8 (d, ^1J(PC) = 25.4 Hz, P*C*HCH$_3$), 22.1 (s, SbCH*C*H$_3$), 20.3 (s, PCH*C*H$_3$), 18.2 (d, ^3J(PC) = 7.1 Hz, Sb*C*HCH$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 14.9 (s). Anal. Calcd for $C_{32}H_{52}ClIrPSb$: C, 47.04; H, 6.41. Found: C, 46.76; H, 6.13.

Preparation of [IrH$_2$Cl(C_2H_4)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (6). A slow stream of H_2 was passed for 10 s through a solution of **2** (81 mg, 0.12 mmol) in pentane (10 mL) at −40 °C. A change of color from orange to pale yellow occurred. The solution was concentrated at −20 °C in vacuo to ca. 1 mL and then stored at −78 °C for 12 h. Pale yellow crystals precipitated, which were separated from the mother liquor and dried at 0 °C: yield 68 mg (84%); mp 58 °C dec. IR (KBr): ν(Ir−H) 2201, 2093 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 3.18 (s, 4 H, C_2H_4), 2.38 (m, 3 H, PC*H*CH$_3$), 2.25 (sept, ^3J(HH) = 7.2 Hz, 3 H, SbC*H*CH$_3$), 1.33, 1.23 (both d, ^3J(HH) = 7.2 Hz, 9 H each, SbCHC*H*$_3$), 1.20 (m, 9 H, PCHC*H*$_3$), 1.05 (dd, ^3J(PH) = 13.8, ^3J(HH) = 7.1 Hz, 9 H, PCHC*H*$_3$), −10.89 (dd, ^2J(PH) = 16.3, ^2J(HH) = 6.3 Hz, 1 H, IrH), −28.24 (dd, ^2J(PH) = 13.2, ^2J(HH) = 6.3 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 41.7 (s, C_2H_4), 27.6 (d, ^1J(PC) = 27.7 Hz, P*C*HCH$_3$), 21.5, 21.3, 20.1, 19.9 (all s, SbCH*C*H$_3$ and PCH*C*H$_3$), 17.9 (d, ^3J(PC) = 4.6 Hz, Sb*C*HCH$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 26.5 (s). Anal. Calcd for $C_{20}H_{48}ClIrPSb$: C, 35.91; H, 7.23. Found: C, 35.17; H, 6.77.

Preparation of [IrH$_2$Cl(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (7a/7b). A solution of **6** (98 mg, 0.15 mmol) in hexane (20 mL) was stirred under a H_2 atmosphere (1 bar) for 30 min at room temperature. A gradual change of color from pale yellow to yellow occurred. After the solvent was evaporated in vacuo, the oily residue was dissolved in acetone (1 mL), and the solution was stored −78 °C for 12 h. A yellow microcrystalline solid precipitated, which was separated from the mother liquor and dried (at room temperature the solid is partly converted to an oil): yield 39 mg (42%). IR (KBr): ν(Ir−H) 2162, 2110 cm^{-1}. Anal. Calcd for $C_{18}H_{44}ClIrPSb$: C, 33.73; H, 6.92. Found: C, 33.88; H, 6.80. NMR data for **7a**: ^{1}H NMR (400 MHz, C_6D_6): δ 2.41 (m, 3 H, PC*H*CH$_3$), 2.15 (sept, ^3J(HH) = 7.6 Hz, 3 H, SbC*H*CH$_3$), 1.44 (d, ^3J(HH) = 7.6 Hz, 18 H, SbCHC*H*$_3$), 1.21 (dd, ^2J(PH) = 13.7, ^3J(HH) = 7.6 Hz, 18 H, PCHC*H*$_3$), −25.31 (d, ^2J(PH) = 20.2 Hz, 2 H, IrH). ^{31}P NMR (81.0 MHz, C_6D_6): δ 50.9 (s). NMR data for **7b**: ^{1}H NMR (400 MHz, C_6D_6): δ 2.38 (m, 3 H, PC*H*CH$_3$), 2.22 (sept, ^3J(HH) = 7.6 Hz, 3 H, SbC*H*CH$_3$], 1.45

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(d, ^3J(HH) = 7.6 Hz, 9 H, SbCHCH_3), 1.38 (dd, ^2J(PH) = 13.7, ^3J(HH) = 6.8 Hz, 9 H, PCHCH_3), 1.33 (d, ^3J(HH) = 7.6 Hz, 9 H, SbCHCH_3), 1.09 (dd, ^2J(PH) = 13.7, ^3J(HH) = 6.8 Hz, 9 H, PCHCH_3), −15.93 (dd, ^2J(PH) = 15.2, ^2J(HH) = 6.1 Hz, 1 H, IrH), −26.47 (dd, ^2J(PH) = 13.7, ^2J(HH) = 6.1 Hz, 1 H, IrH). ^{31}P NMR (81.0 MHz, C_6D_6): δ 37.0 (s).

Preparation of [IrCl(=CPh$_2$)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (8). A solution of **2** (121 mg, 0.18 mmol) in benzene (10 mL) was treated with Ph_2CN_2 (35 mg, 0.18 mmol) at room temperature. A change of color from orange to dark red, accompanied by an evolution of gas, occurred. After the reaction mixture was stirred at ca. 0.2 bar for 1 h, the solvent was evaporated in vacuo and the residue recrystallized from acetone (2 mL). Storing the solution at −78 °C for 12 h led to the formation of a brown microcrystalline solid, which was washed with a small amount of acetone (−20 °C) and dried: yield 105 mg (72%); mp 42 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 7.87 (m, 4 H, *ortho*-H of C_6H_5), 7.40 (m, 2 H, *para*-H of C_6H_5), 6.96 (m, 4 H, *meta*-H of C_6H_5), 2.39 (m, 3 H, PC*H*CH$_3$), 2.11 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.32 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHCH_3), 1.19 (dd, ^3J(PH) = 13.2, ^3J(HH) = 7.3 Hz, 18 H, PCHCH_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ 240.9 (d, ^2J(PC) = 7.6 Hz, Ir=C), 175.3 (s, *ipso*-C of C_6H_5), 128.5, 127.9, 126.8 (all s, C_6H_5), 24.8 (d, ^1J(PC) = 24.2 Hz, P*C*HCH$_3$), 22.0 (s, SbCH*C*H$_3$), 20.0 (s, PCH*C*H$_3$), 18.9 (d, ^3J(PC) = 5.1 Hz, Sb*C*HCH$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 8.8 (s). Anal. Calcd for $C_{31}H_{52}ClIrPSb$: C, 46.24; H, 6.51. Found: C, 46.49; H, 6.43.

Preparation of [IrCl{=C(*p*-C$_6$H$_4$Me)$_2$}(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (9). This compound was prepared as described for **8** from **2** (112 mg, 0.17 mmol) and (*p*-$C_6H_4Me)_2CN_2$ (38 mg, 0.17 mmol). Dark brown microcrystalline solid: yield 83 mg (59%); mp 24 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 7.91 (m, 4 H, *ortho*-H of C_6H_4), 6.81 (m, 4 H, *meta*-H of C_6H_4), 2.44 (m, 3 H, PC*H*CH$_3$), 2.17 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.73 (s, 6 H, $C_6H_4CH_3$), 1.36 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHCH_3), 1.24 (dd, ^3J(PH) = 13.3, ^3J(HH) = 7.2 Hz, 18 H, PCHCH_3). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 244.7 (d, ^2J(PC) = 7.6 Hz, Ir=C), 171.5 (s, *ipso*-C of C_6H_4), 137.3, 129.3, 128.6 (all s, C_6H_4), 25.0 (d, ^1J(PC) = 25.4 Hz, P*C*HCH$_3$), 22.3 (s, $C_6H_4CH_3$), 22.1 (s, SbCH*C*H$_3$), 20.1 (s, PCH*C*H$_3$), 19.1 (d, ^3J(PC) = 5.1 Hz, Sb*C*HCH$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 9.9 (s). Anal. Calcd for $C_{33}H_{56}ClIrPSb$: C, 47.57; H, 6.77; Ir, 23.07; Sb, 14.61. Found: C, 47.33; H, 6.74; Ir, 22.75; Sb, 14.50.

Preparation of [IrCl{=C(*p*-C$_6$H$_4$Cl)$_2$}(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (10). This compound was prepared as described for **8** from **2** (112 mg, 0.17 mmol) and (*p*-$C_6H_4Cl)_2CN_2$ (38 mg, 0.17 mmol). After recrystallization from pentane at −78 °C a brown microcrystalline solid was obtained: yield 90 mg (61%); mp 39 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 7.57 (m, 4 H, *ortho*-H of C_6H_4), 6.93 (m, 4 H, *meta*-H of C_6H_4), 2.30 (m, 3 H, PC*H*CH$_3$), 2.08 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.24 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHCH_3), 1.12 (dd, ^3J(PH) = 13.5, ^3J(HH) = 7.3 Hz, 18 H, PCHCH_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ 235.7 (d, ^2J(PC) = 7.4 Hz, Ir=C), 173.8 (s, *ipso*-C of C_6H_4), 132.9, 129.0, 128.8 (all s, C_6H_4), 25.0 (d, ^1J(PC) = 25.9 Hz, P*C*HCH$_3$), 21.9 (s, SbCH*C*H$_3$), 19.9 (s, PCH*C*H$_3$), 19.2 (d, ^3J(PC) = 4.6 Hz, Sb*C*HCH$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 8.4 (s). Anal. Calcd for $C_{31}H_{50}Cl_3IrPSb$: C, 42.59; H, 5.77. Found: C, 42.13; H, 5.35.

Preparation of [IrCl(N$_2$C$_5$Cl$_4$)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (11). A solution of **2** (76 mg, 0.11 mmol) in pentane (10 mL) was treated with $C_5Cl_4N_2$ (25 mg, 0.11 mmol), which led to an instantaneous change of color from orange to dark green. After the reaction mixture was stirred for 30 min at room temperature, a dark green solid precipitated, which was separated from the mother liquor, washed with pentane (10 mL), and recrystallized from acetone (4 mL) at −78 °C to give dark green crystals: yield 90 mg (94%); mp 114 °C dec. IR (KBr): ν(N$_2$) 1839 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 2.33 (m, 6 H, SbC*H*CH$_3$ and PC*H*CH$_3$), 1.27 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHCH_3), 1.12 (dd, ^3J(PH) = 14.2, ^3J(HH) = 6.9 Hz, 18 H, PCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 108.7, 99.3 (both s, C_4Cl_4), 63.8 (s, CN_2), 23.7 (d, ^1J(PC) = 25.4 Hz, P*C*HCH$_3$), 21.8 (s, SbCH*C*H$_3$), 19.8 (d, ^3J(PC) = 5.1 Hz, Sb*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 28.9 (s). Anal. Calcd for $C_{23}H_{42}Cl_5IrN_2PSb$: C, 31.80; H, 4.87; N, 3.22. Found: C, 31.82; H, 4.74; N, 3.21.

Preparation of *trans*-[IrCl(N$_2$C$_5$Cl$_4$)(Sb*i*Pr$_3$)$_2$] (13). A solution of **12** (49 mg, 0.06 mmol) in pentane (5 mL) was treated with a solution of $C_5Cl_4N_2$ (13 mg, 0.06 mmol) in ether (3 mL) at room temperature. A rapid change of color from orange to dark green occurred. The reaction mixture was worked up as described for **11** to give a dark green microcrystalline solid: yield 45 mg (82%); mp 93 °C dec. IR (KBr): ν(N$_2$) 1830 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 2.25 (sept, ^3J(HH) = 7.3 Hz, 6 H SbC*H*CH$_3$), 1.25 (d, ^3J(HH) = 7.3 Hz, 36 H, SbCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 108.1, 99.3 (both s, C_4Cl_4), 61.0 (s, CN_2), 21.8 (s, SbCH*C*H$_3$), 20.2 (s, Sb*C*HCH$_3$). Anal. Calcd for $C_{23}H_{42}Cl_5IrN_2Sb_2$: C, 28.79; H, 4.41; N, 2.92. Found: C, 28.76; H, 4.22; N, 2.75.

Preparation of *trans*-[IrCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (14). A solution of **8** (200 mg, 0.28 mmol) in pentane (20 mL) was treated with P*i*Pr$_3$ (55 μL, 0.28 mmol) and stirred for 45 min at room temperature. The solvent was evaporated in vacuo and the residue recrystallized from acetone (2 mL) at −78 °C to give a brown solid: yield 112 mg (56%); mp 83 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 7.87 (br m, 4 H, *ortho*-H of C_6H_5), 7.42 (m, 2 H, *para*-H of C_6H_5), 6.96 (m, 4 H, *meta*-H of C_6H_5), 2.44 (m, 6 H, PC*H*CH$_3$), 1.20 (dvt, N = 13.2, ^3J(HH) = 7.0 Hz, 36 H, PCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 234.7 (t, ^2J(PC) = 8.9 Hz, Ir=C), 175.0 (s, *ipso*-C of C_6H_5), 128.3, 128.2, 127.0 (all s, C_6H_5), 25.2 (vt, N = 25.4 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 4.2 (s). Anal. Calcd for $C_{31}H_{52}ClIrP_2$: C, 52.12; H, 7.34; Ir, 26.91. Found: C, 51.92; H, 7.35; Ir, 27.10.

Preparation of *trans*-[IrCl{=C(*p*-C$_6$H$_4$Me)$_2$}(P*i*Pr$_3$)$_2$] (15). This compound was prepared as described for **14** from **9** (250 mg, 0.30 mmol) and P*i*Pr$_3$ (64 μL, 0.33 mmol). Deep brown microcrystalline solid: yield 136 mg (61%); mp 56 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 7.89 (br m, 4 H, *ortho*-H of C_6H_4), 6.81 (m, 4 H, *meta*-H of C_6H_4), 2.50 (m, 6 H, PC*H*CH$_3$), 1.73 (s, 6 H, $C_6H_4CH_3$), 1.23 (dvt, N = 13.2, ^3J(HH) = 7.0 Hz, 36 H, PCHCH_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ 245.5 (d, ^2J(PC) = 8.9 Hz, Ir=C), 172.2 (d, ^3J(PC) = 3.8 Hz, *ipso*-C of C_6H_4), 136.9, 129.0, 128.8 (all s, C_6H_4), 25.2 (vt, N = 25.4 Hz, P*C*HCH$_3$), 21.9 (s, $C_6H_4CH_3$), 20.4 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 5.7 (s). Anal. Calcd for $C_{33}H_{56}ClIrP_2$: C, 53.39; H, 7.60; Ir, 25.89; P, 8.34. Found: C, 53.32; H, 7.72; Ir, 26.20; P, 8.20.

Preparation of *trans*-[IrCl{=C(*p*-C$_6$H$_4$Cl)$_2$}(P*i*Pr$_3$)$_2$] (16). A solution of **10** (83 mg, 0.10 mmol) in benzene (10 mL) was treated with P*i*Pr$_3$ (19 μL, 0.10 mmol) and stirred for 2 h at room temperature. After evaporation of the solvent in vacuo, an oily brownish residue was obtained, which could not be converted to a crystalline, analytically pure solid. Spectroscopic data: ^{1}H NMR (200 MHz, C_6D_6): δ 7.54 (m, 4 H, *ortho*-H of C_6H_4), 6.92 (m, 4 H, *meta*-H of C_6H_4), 2.35 (m, 6 H, PC*H*CH$_3$), 1.10 (dvt, N = 13.5, ^3J(HH) = 7.3 Hz, 36 H, PCHCH_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ 237.8 (t, ^2J(PC) = 8.9 Hz, Ir=C), 173.6 (s, *ipso*-C of C_6H_4), 133.2, 128.5, 128.3 (all s, C_6H_4), 25.0 (vt, N = 25.4 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 3.5 (s).

Preparation of [(η^5-C$_5$H$_5$)Ir(=CPh$_2$)(P*i*Pr$_3$)] (17). A solution of **8** (138 mg, 0.19 mmol) in THF (25 mL) was treated with portions of ca. 15 mg of NaC_5H_5 (85.1 mg, 0.97 mmol), and the mixture was stirred for 1 h at room temperature. The solvent was evaporated in vacuo, the residue was dissolved in pentane (20 mL), and the solution was filtered. After the filtrate was brought to dryness in vacuo, the remaining red-brown oil was recrystallized from pentane (2 mL) at −78 °C to give a dark brown microcrystalline solid: yield 77 mg (70%); mp 93 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 7.42 (m, 4 H,

ortho-H of C_6H_5), 7.10 (m, 2 H, *para*-H of C_6H_5), 6.92 (m, 4 H, *meta*-H of C_6H_5), 4.92 (d, ^3J(PH) = 1.1 Hz, 5 H, C_5H_5), 1.54 (dsept, ^3J(PH) = 13.1, ^3J(HH) = 6.9 Hz, 3 H, PC*H*CH_3), 0.98 (dd, ^3J(PH) = 13.1, ^3J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 217.2 (d, ^2J(PC) = 12.7 Hz, Ir=C), 175.8 (s, *ipso*-C of C_6H_5), 170.6 (d, ^3J(PC) = 6.4 Hz, *ipso*-C of C_6H_5), 127.1, 126.6, 125.0, 124.0, 123.4, 123.3 (all s, C_6H_5), 82.3 (d, ^2J(PC) = 3.8 Hz, C_5H_5), 28.0 (d, ^1J(PC) = 28.0 Hz, P*C*HCH$_3$), 20.7 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 27.8 (s). Anal. Calcd for $C_{27}H_{36}$IrP: C, 55.55; H, 6.22. Found: C, 55.34; H, 6.09.

Preparation of [(η^5-C_5H_5)Ir(C_2H_4)(Sb*i*Pr$_3$)] (19). A solution of **18** (200 mg, 0.25 mmol) in THF (20 mL) was treated with NaC_5H_5 (27 mg, 0.30 mmol) at −78 °C and after stirring for 10 min slowly warmed to room temperature. The solvent was evaporated in vacuo and the remaining yellow oil extracted twice with 10 mL portions of pentane. The combined extracts were brought to dryness in vacuo, the residue was dissolved in hexane (2 mL), and the solution was chromatographed on Al_2O_3 (activity grade V, height of column 5 cm). With hexane an off-white fraction was eluted which contained mainly Sb*i*Pr$_3$. Subsequent elution with THF afforded a yellow fraction, which after removal of the solvent gave a yellow oil. Since it still contained small amounts of Sb*i*Pr$_3$, which could not be removed by chromatography or recrystallization, compound **18** was characterized by spectroscopy. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.94 (s, 5 H, C_5H_5), 2.36, 2.00 (both m, 2 H each, C_2H_4), 1.76 (sept, ^3J(HH) = 7.1 Hz, 3 H, SbC*H*CH_3), 1.10 (d, ^3J(HH) = 7.1 Hz, 18 H, SbCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 75.1 (s, C_5H_5), 21.3 (s, SbCH*C*H$_3$), 16.1 (s, Sb*C*HCH$_3$), −3.0 (s, C_2H_4).

Preparation of [(η^5-C_5H_5)IrCl(CHPh_2)(P*i*Pr$_3$)] (20). A slow stream of dry HCl was passed at room temperature through a solution of **17** (163 mg, 0.28 mmol) in pentane (5 mL) until the color of the solution turned to orange-yellow. Storing the solution for 1 h led to the formation of an orange-yellow precipitate, which was separated from the mother liquor, washed twice with 1 mL portions of pentane (0 °C), and dried: yield 172 mg (99%); mp 60 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.30 (m, 2 H, C_6H_5), 7.08 (m, 4 H, C_6H_5), 6.88 (m, 4 H, C_6H_5), 5.75 (d, ^3J(PH) = 2.2 Hz, 1 H, C*H*(C_6H_5)$_2$), 5.09 (d, ^3J(PH) = 1.5 Hz, 5 H, C_5H_5), 2.44 (m, 3 H, PC*H*CH_3), 1.20 (dd, ^3J(PH) = 14.4, ^3J(HH) = 7.1 Hz, 12 H, PCHC*H*$_3$), 0.81 (dd, ^3J(PH) = 12.6, ^3J(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 156.7, 151.0 (both d, ^3J(PC) = 2.8 Hz, *ipso*-C of C_6H_5), 132.2, 127.6, 126.9, 126.8, 124.5, 123.0 (all s, C_6H_5), 83.1 (d, ^2J(PC) = 2.8 Hz, C_5H_5), 24.6 (d, ^2J(PC) = 6.5 Hz, *C*HPh$_2$), 25−22, 21−18 (both br m, P*C*HCH$_3$ and PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 5.5 (s). Anal. Calcd for $C_{27}H_{37}$ClIrP: C, 52.29; H, 6.01. Found: C, 52.54; H, 5.90.

Preparation of [(η^5-C_5H_4CHPh_2)IrHCl(P*i*Pr$_3$)] (21). A solution of **20** (120 mg, 0.19 mmol) in benzene (10 mL) was stirred under reflux for 2 min, which led to a stepwise change of color from orange-yellow to red and then from red to yellow. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuo and the yellow oily residue was dissolved in CH_2Cl_2 (1 mL). Hexane (10 mL) was added and the solution concentrated in vacuo until yellow crystals precipitated. After storing for 12 h at −78 °C, the crystals were separated from the mother liquor, washed with a small amount of pentane (−20 °C), and dried: yield 114 mg (95%); mp 106 °C dec. IR (KBr): ν(Ir−H) 2153 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.46 (m, 4 H, C_6H_5), 7.08 (m, 6 H, C_6H_5), 5.70 (d, ^4J(PH) = 2.2 Hz, 1 H, C*H*(C_6H_5)$_2$), 4.93 (m, 2 H, C_5H_4), 4.49, 4.31 (both m, 1 H each, C_5H_4), 2.13 (m, 3 H, PC*H*CH_3), 0.96 (dd, ^3J(PH) = 13.9, ^3J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), −14.40 (d, ^2J(PH) = 33.4 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 143.4, 143.3 (both s, *ipso*-C of C_6H_5), 130.3, 130.2, 128.6, 128.5, 126.7, 126.6 (all s, C_6H_5), 121.8 (d, ^2J(PC) = 4.6 Hz, *C*CHPh$_2$), 84.0 (s, C_5H_4), 77.1 (d, ^2J(PC) = 9.2 Hz, C_5H_4), 74.8, 67.6 (both s, C_5H_4), 47.9 (s, *C*HPh$_2$), 26.6 (d, ^1J(PC) = 31.4 Hz, P*C*HCH$_3$), 19.8, 19.5 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 37.5 (s). Anal. Calcd for $C_{27}H_{37}$ClIrP: C, 52.29; H, 6.01. Found: C, 51.98; H, 5.78.

Preparation of [(η^5-C_5H_5)Ir(η^3-CHPh_2)(P*i*Pr$_3$)]BF_4 (22). A solution of **17** (73 mg, 0.09 mmol) in ether (20 mL) was treated under stirring dropwise with a 54% solution of HBF_4 in ether (ca. 0.1 mL) at room temperature. A dark red solid precipitated, the formation of which was completed after ca. 30 min. The mother liquor was decanted, and the remaining dark red solid was washed twice with 5 mL portions of ether and dried. Owing to the elemental analysis, the product is the monoetherate of **22**: yield 47 mg (98%); mp 126 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.27 (br m, 10 H, C_6H_5), 4.91 (d, ^3J(PH) = 1.1 Hz, 5 H, C_5H_5), 3.32 (d, ^3J(PH) = 12.1 Hz, C*H*(C_6H_5)$_2$), 2.34 (m, 3 H, PC*H*CH_3), 1.31 (dd, ^3J(HH) = 7.3, ^2J(PH) = 14.5 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 140−124 (br m, C_6H_5), 88.0 (s, C_5H_5), 46.4 (d, ^2J(PC) = 6.4 Hz, *C*H(C_6H_5)$_2$), 27.4 (d, ^1J(PC) = 28.0 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −153.0 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 13.0 (s). Anal. Calcd for $C_{31}H_{47}BF_4$IrOP: C, 49.93; H, 6.35. Found: C, 49.83; H, 5.99.

Preparation of [IrHCl(=CHPh_2)(P*i*Pr$_3$)$_2$]BF_4 (23). A solution of **14** (61 mg, 0.09 mmol) in a 1:1 mixture of pentane/CH_2Cl_2 (10 mL) was treated dropwise with a 50% aqueous solution of HBF_4 until the precipitation of a red solid was finished. The solution was decanted, and the remaining residue was washed with distilled water (5 mL) and then extracted with CH_2Cl_2 (10 mL). The extract was concentrated to ca. 5 mL in vacuo, and pentane (20 mL) was added. After the suspension was stored for 12 h, a dark red solid precipitated, which was separated from the mother liquor, washed with pentane (5 mL), and dried: yield 65 mg (95%); mp 91 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.92, 7.85 (both m, 1 H each, C_6H_5), 7.76, 7.55, 7.49, 7.44 (all m, 2 H each, C_6H_5), 2.30 (m, 6 H, PC*H*CH_3), 1.11 (dvt, N = 15.3, ^3J(HH) = 7.6 Hz, 18 H, PCHC*H*$_3$), 1.03 (dvt, N = 15.3, ^3J(HH) = 7.6 Hz, 18 H, PCHC*H*$_3$), −28.84 (t, ^2J(PH) = 12.2 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 266.5 (s, Ir=C), 157.3, 154.6 (both s, *ipso*-C of C_6H_5), 136.7, 135.0, 133.4, 131.2, 130.9, 125.7 (all s, C_6H_5), 24.9 (vt, N = 28.0 Hz, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 38.2 (s). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −153.6 (s). MS (FAB; *o*-nitrophenyloctyl ether as matrix): *m*/*z* 715 (M^+). Anal. Calcd for $C_{31}H_{53}BClF_4IrP_2$: C, 46.42; H, 6.66. Found: C, 46.79; H, 6.98.

Preparation of [IrHCl(=CHPh_2)(P*i*Pr$_3$)$_2$][B(Ar_F)$_4$] (24). A solution of **14** (74 mg, 0.10 mmol) in pentane (5 mL) was treated with [H(OEt_2)$_2$]B(Ar_F)$_4$ (105 mg, 0.10 mmol) and stirred for 2 h at room temperature. A viscous oily precipitate was formed, which was separated from the mother liquor and then suspended in pentane (5 mL). Irradiating the suspension in an ultrasound bath for 5 min led to the formation of a red-pink solid, which was separated from the solution, washed twice with 2 mL portions of pentane, and dried: yield 136 mg (83%); mp 151 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.83−7.39 (br m, 22 H, C_6H_5 and BC_6H_3), 2.29 (m, 6 H, PC*H*CH_3), 1.10, 1.02 (both dvt, N = 14.5, ^3J(HH) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −28.82 (t, ^2J(PH) = 13.1 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 266.7 (s, Ir=C), 162.4 (q, ^1J(BC) = 49.6 Hz, *ipso*-C of Ar_F), 157.5, 154.7 (both s, *ipso*-C of C_6H_5), 136.6, 135.0, 133.4, 131.2, 130.8, 125.7 (all s, C_6H_5), 135.4 (br s, *ortho*-C of Ar_F), 129.5 (qq, ^2J(FC) = 31.8, ^4J(FC) = 2.4 Hz, *meta*-C of Ar_F), 125.2 (q, ^1J(FC) = 272 Hz, CF_3), 118.1 (br s, *para*-C of Ar_F), 24.9 (vt, N = 28.0 Hz, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 38.3 (s). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −125.2 (s). Anal. Calcd for $C_{63}H_{65}BClF_{24}IrP_2$: C, 47.93; H, 4.15. Found: C, 47.85; H, 4.10.

Preparation of [IrHCl(=CHPh_2)(P*i*Pr$_3$)(Sb*i*Pr$_3$)][B(Ar_F)$_4$] (25). This compound was prepared as described for **24** from **8** (104 mg, 0.13 mmol) and [H(OEt_2)$_2$]B(Ar_F)$_4$ (130 mg, 0.13 mmol). Red-pink solid: yield 183 mg (85%); mp 146 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.90−7.38 (br m, 22 H, C_6H_5

Table 1. Crystallographic Data for 13, 14, 17, and 24

	13	14	17	24
formula	$C_{23}H_{42}Cl_5IrN_2Sb_2$	$C_{31}H_{52}ClIrP_2$	$C_{27}H_{36}IrP$	$C_{63}H_{65}BClF_{24}IrP_2$
M	959.54	714.32	583.73	1578.55
cryst size, mm	0.40 × 0.20 × 0.10	0.20 × 0.15 × 0.11	0.22 × 0.16 × 0.13	0.18 × 0.16 × 0.15
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	14.474(3)	10.353(5)	11.017(2)	12.6422(10)
b, Å	8.64(2)	12.153(4)	14.709(2)	15.2941(10)
c, Å	28.061(6)	13.909(5)	15.374(3)	35.961(3)
α, deg	90	94.04(2)	90	90
β, deg	101.64(1)	93.62(2)	96.006(9)	92.732(10)
γ, deg	90	114.16(2)	90	90
V, Å^3	3439(8)	1585(1)	2477.7(7)	6945.1(9)
Z	4	2	4	4
d_{calcd}, g cm^{-3}	1.853	1.497	1.565	1.510
T, K	293(2)	173(2)	293(2)	173(2)
μ, mm^{-1}	1.998	4.416	0.138	2.108
scan method	*ω*/*θ*	*ω*/*θ*	*ω*/*θ*	*ϕ*
2*θ*(max), deg	48	52.04	49.90	50.04
total no. of rflns	4775	6479	4496	34995
no. of unique rflns	4556 [*R*(int) = 0.2752]	6208 [*R*(int) = 0.0324]	4328 [*R*(int) = 0.0206]	1223 [*R*(int) = 0.0591]
no. of obsd rflns ($I > 2\sigma(I)$)	2892	5555	3565	8581
no. of rflns used for refinement	4556	6208	4328	12 231
no. of params refined	399	328	269	986
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0494, wR2 = 0.0841	R1 = 0.0319, wR2 = 0.0699	R1 = 0.0287, wR2 = 0.0612	R1 = 0.0471, wR2 = 0.1259
R indices (all data)[a]	R1 = 0.0967, wR2 = 0.1174	R1 = 0.0393, wR2 = 0.0758	R1 = 0.0407, wR2 = 0.0696	R1 = 0.0701, wR2 = 0.1259
resid electron density, e Å^{-3}	1.122/−1.029	1.737/−1.275	0.697/−0.568	2.233/−1.598

[a] $w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 38.8077P]$ (**13**), $w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 7.0221P]$ (**14**), $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 4.9566P]$ (**17**), $w = 1/[\sigma^2(F_o^2) + (0.0833P)^2 + 0.0000P]$ (**24**), where $P = [F_o^2 + 2F_c^2]/3$.

and BC_6H_3), 2.35 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 2.29 (m, 3 H, PC*H*CH$_3$), 1.25, 1.20 (both d, ^3J(HH) = 7.3 Hz, 9 H each, SbCHC*H*$_3$), 1.10, 1.05 (both dd, ^3J(PH) = 14.9, ^3J(HH) = 7.3 Hz, 9 H each, PCHC*H*$_3$), −31.20 (d, ^2J(PH) = 11.4 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): *δ* 267.7 (s, Ir=C), 162.4 (q, ^1J(BC) = 49.7 Hz, *ipso*-C of Ar$_F$), 157.0, 153.3 (both s, *ipso*-C of C_6H_5), 136.4, 134.7, 132.8, 131.8, 131.0, 122.7 [all s, C_6H_5], 135.4 (br s, *ortho*-C of Ar$_F$), 129.5 (qq, ^2J(FC) = 31.7, ^4J(FC) = 2.4 Hz, *meta*-C of Ar$_F$), 125.2 (q, ^1J(FC) = 272 Hz, CF_3), 118.1 (br s, *para*-C of Ar$_F$), 25.3 (d, ^1J(PC) = 26.7 Hz, P*C*HCH$_3$), 22.7, 22.6 (both s, SbCH*C*H$_3$), 22.0, 21.8 (both s, PCH*C*H$_3$), 19.6 (s, Sb*C*HCH$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): *δ* 39.9 (s). ^{19}F NMR (188.3 MHz, CD_2Cl_2): *δ* −125.2 (s). Anal. Calcd for $C_{63}H_{65}BClF_{24}IrPSb$: C, 45.33; H, 3.92. Found: C, 44.88; H, 3.86.

Generation of [IrHCl$_2$(=CPh$_2$)(P*i*Pr$_3$)$_2$] (26). A slow stream of dry HCl was passed for 1 min through a solution of **14** (45 mg, 0.06 mmol) in C_6D_6 (0.6 mL) at room temperature. A quick change of color from dark red to green occurred. The composition of the product was determined spectroscopically. ^{1}H NMR (200 MHz, CD_2Cl_2): *δ* 8.82 (m, 2 H, C_6H_5), 7.51 (m, 2 H, C_6H_5), 7.01 (m, 6 H, C_6H_5), 2.61 (m, 6 H, PC*H*CH$_3$), 1.27, 1.19 (both dvt, *N* = 14.5, ^3J(HH) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −19.23 (br s, 1 H, IrH). ^{31}P NMR (81.0 MHz, CD_2Cl_2): *δ* 1.7 (s).

Generation of [IrHCl$_2$(=CPh$_2$)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (27). This compound was generated as described for **26** from **8** (32 mg, (0.04 mmol) and HCl. ^{1}H NMR (200 MHz, C_6D_6): *δ* 7.65 (br m, 2 H, C_6H_5), 7.10, 6.87 (both m, 4 H each, C_6H_5), 2.50 (m, 3 H, PC*H*CH$_3$), 2.27 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.42, 1.34 (both d, ^3J(HH) = 7.3 Hz, 9 H each, SbCHC*H*$_3$), 1.24, 1.19 (both dd, ^3J(PH) = 14.0, ^3J(HH) = 7.3 Hz, 9 H each, PCHC*H*$_3$), −18.78 (d, ^2J(PH) = 13.1 Hz, 1 H, IrH). ^{31}P NMR (81.0 MHz, C_6D_6): *δ* 4.3 (s).

Reaction of *trans*-[IrCl(=CPh$_2$)(P*i*Pr$_3$)(Sb*i*Pr$_3$)] (8) with Ethene. A slow stream of ethene was passed for ca. 1 min into a solution of **8** (30 mg, 0.04 mmol) in C_6D_6 (0.5 mL) at room temperature. After the NMR tube was closed, the reaction mixture was stored for 3 h under an ethene atmosphere, which led to a change of color from dark red to yellow. The ^{31}P NMR spectrum shows the quantitative conversion of **8** to a mixture of **18** and *trans*-[IrCl(C_2H_4)(P*i*Pr$_3$)$_2$] (**28**).[6] The ^{1}H NMR spectrum indicates the formation of a mixture of 3,3-diphenyl-1-propene (**29**) and 1,1-diphenyl-1-propene (**30**) in the ratio of 1.85:1 (65%:35%).[37] After the solution was filtered with Al_2O_3 (neutral, activity grade I), the filtrate was investigated by GC/MS. Under these conditions, the ratio of **29** to **30** was 2.3:1. It was proved by independent studies that neither thermally or in the presence of Al_2O_3 does an isomerization of **29** to **30** occur.

Reaction of *trans*-[IrCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (14) with Ethene. This experiment was carried out analogously as described for **8** using **14** (42 mg, (0.06 mmol) and ethene as starting materials. Since after 3 h at room temperature no reaction occurred, the solvent (C_6D_6) was removed in vacuo. The residue was dissolved in toluene-d_6 (0.5 mL), the argon atmosphere was replaced by ethene, and the reaction mixture was warmed for 2 h at 90 °C. Both the ^{31}P and ^{1}H NMR spectra confirmed the quantitative conversion of **14** to **28** and the formation of a mixture of **29** and **30** in the ratio of 1.80:1 (65%:35%).[37] After the solution was filtered with Al_2O_3 (neutral, activity grade I), the filtrate was investigated by GC/MS to reveal a ratio of **29** to **30** = 2.2:1.

Preparation of [IrCl(*η*^{1}:*η*^{3}-CPh=CPhCPh$_2$)(P*i*Pr$_3$)] (31). A solution of **8** (134 mg, 0.17 mmol) in pentane (15 mL) was treated with diphenylacetylene (29 mg, 0.16 mmol) and stirred for 3 h at room temperature. The initially clear dark red solution became dulled, and a brown finely divided solid started to precipitate. The formation of the solid was facilitated by storing the suspension at −78 °C for 12 h. The mother liquor

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was decanted, and the residue was washed twice with 5 mL portions of pentane (−20 °C) and dried: yield 91 mg (76%); mp 124 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.32, 6.98 (both m, 16 H, C_6H_5), 6.57 (m, 2 H, C_6H_5), 6.08 (m, 1 H, C_6H_5), 3.78 (br s, 1 H, CH of π-bonded C_6H_5), 2.31 (m, 3 H, PC*H*CH$_3$), 1.22, 1.03 (both m, 9 H each, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 145.0 (d, J(PC) = 4.9 Hz, *ipso*-C of C_6H_5), 143.8 (br), 140.4, 136.6 (both s, *ipso*-C of C_6H_5), 132.2 (br), 133.9, 131.3, 128.0, 127.7, 127.3, 127.0, 126.2, 123.1, 122.6 (all s, C_6H_5), 128.5, 114.3 (both s, *C*C_6H_5), 120.0, 109.7 (both br), 32.1 (s, CH of π-bonded C_6H_5), 26.9 (d, ^1J(PC) = 29.4 Hz, P*C*HCH$_3$), 20.7, 19.7 (both s, PCH*C*H$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2), selected data: δ 32.1 (d, ^1J(HC) = 152.6 Hz, CH of π-bonded C_6H_5], 26.9 (dd, ^1J(HC) = 128.4, ^1J(PC) = 29.4 Hz, P*C*HCH$_3$), 20.7, 19.7 (both q, ^1J(HC) = 127.2, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 26.1 (s). Anal. Calcd for $C_{36}H_{41}ClIrP$: C, 59.04; H, 5.64. Found: C, 59.31; H, 6.18.

X-ray Structural Analysis of 13, 14, 17, and 24. Single crystals of **13** and **14** were grown from acetone at −30 °C, those of **17** from pentane at room temperature, and those of **24** from ether/pentane at room temperature. The data were collected on an Enraf-Nonius CAD4 diffractometer (**13**, **14**, **17**) or from a shock-cooled crystal protected by an oil drop on a Stoe IPDS diffractometer (**24**) using monochromated Mo Kα radiation (λ = 0.71 073 Å). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected by Lorentz and polarization effects, and *Lp* and empirical absorption corrections were applied for **13** (Ψ-scan method, minimum transmission 89.46%), for **14** (Ψ-scan method, minimum transmission 88.41%), and for **17** (Ψ-scan method, minimum transmission 83.92%). The structure of **13** was solved by the Patterson method (SHELXS-86), and the structures of **14**, **17**, and **24** were solved by direct methods (SHELXS-86 for **17,** SHELXS-97 for **14**, and **24**).[38] Atomic coordinates and anisotropic displacement parameters were refined by full matrix least-squares against F_o^2 (SHELXL-93 for **13** and **17**, SHELXL-97 for **14** and **24**).[39] One of the stibane ligands of **13** was found to be rotationally disordered over two independent positions and refined anisotropically with restraints on interatomic distances (DFIX) and on $U(ij)$ (DELU, SIMU) with an occupancy factor of 62:38; also one of the isopropyl groups of the second stibane was found to be disordered and refined in the same way with an occupancy factor of 79:21. The two highest electron densities of **13** are less than 0.8 Å away from Cl1 and Sb1. The four highest electron densities of **14** are all near that of the iridium atom (<1.0 Å). The atoms of the cyclopentadienyl ring in **17** were refined with restraints on $U(ij)$ (DELU), and the extinction coefficient was refined to 0.0037(2). Five of the CF_3 groups of the BAr_F anion in **24** were found rotationally disordered and refined anisotropically with restraints on $U(ij)$ (DELU, SIMU) with the following occupancy factors: 86:14 (F1−F3), 55:45 (F4−F6), 58:42 (F10−F12), 51:49 (F13−F15), 74:26 (F19−F21). The metal-bonded hydrogen atom H100 of **24** was found in a differential Fourier synthesis and refined isotropically with a fixed U_{eq}. The positions of all other hydrogen atoms were calculated according to ideal geometry and were refined by using the riding method, except for H100 of **24**.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **13**, **14**, **17**, and **24**; data for these compounds are also given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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