Organometallics **1997,** *16,* 4077−4088 4077

Alkynes and Diynes as Precursors for Organoiridium Complexes Containing Iridium−Carbon Single and Double Bonds[†,1]

Helmut Werner,* Raimund W. Lass, Olaf Gevert, and Justin Wolf

Institut für Anorganische Chemie der Universität, Am Hubland, D-97074 Würzburg, Germany

Received April 22, 1997[⊗]

The in situ generated species $[IrCl(C_8H_{14})(PiPr_3)_2]$ as well as the dihydrido complex $[IrH_2Cl(PiPr_3)_2]$ (**15**) were found to be quite reactive toward alkynes and diynes with either H or $SiMe_3$ as substituents at the $C{\equiv}C$ and $C{\equiv}CC{\equiv}C$ units. While the thermal or photochemical reaction of $[IrCl(C_8H_{14})(PiPr_3)_2]$ with $Me_3SiC{\equiv}CR$ (R = Ph, Me, *n*Bu, $SiMe_3$, CH_2OH, CMe_2OSiMe_3, CO_2Et) led to *trans*-$[IrCl\{{=}C{=}C(SiMe_3)R\}(PiPr_3)_2]$ (**3**−**9**) for R = CO_2Et via the isolated π-alkyne metal intermediate *trans*-$[IrCl(\eta^2\text{-}Me_3SiC{\equiv}CR)(PiPr_3)_2]$ (**2**), photolysis of **15** in the presence of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ gave *trans*-$[IrCl\{{=}C{=}C(SiMe_3)C{\equiv}CSiMe_3\}(PiPr_3)_2]$ (**19**). Compound **19** was also obtained by thermal or photochemical rearrangement of *trans*-$[IrCl(\eta^2\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(PiPr_3)_2]$ (**18**). The dihydrido complex **15** reacted with $HC{\equiv}CC{\equiv}CH$ at −60 °C to yield $[\{IrHCl(PiPr_3)_2\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)]$ (**16**) and with $HC{\equiv}CC{\equiv}CSiMe_3$ to give $[IrHCl(C{\equiv}CC{\equiv}CSiMe_3)(PiPr_3)_2]$ (**20**), from which the vinylidene isomer *trans*-$[IrCl({=}C{=}CHC{\equiv}CSiMe_3)(PiPr_3)_2]$ (**22**) was generated on heating. The reaction of **15** with propargylic alcohols $HC{\equiv}CCR(R')OH$ led to different types of products, depending on the substituents R and R′. Whereas for R = R′ = *i*Pr the five-coordinate alkynyl hydrido complex $[IrHCl\{C{\equiv}CC(iPr){=}CMe_2\}(PiPr_3)_2]$ (**23**) was formed, the six-coordinate carbonyl hydrido vinyl derivative $[IrHCl\{(E)\text{-}CH{=}CHPh\}(CO)(PiPr_3)_2]$ (**25**) was isolated for R = H and R′ = Ph. Treatment of **15** with $HC{\equiv}CCPh_2OH$ afforded, via $[IrHCl(C{\equiv}CCPh_2OH)(PiPr_3)_2]$ (**27**) or the isomer *trans*-$[IrCl({=}C{=}CHCPh_2OH)(PiPr_3)_2]$ (**28**), the allenylideneiridium(I) compound *trans*-$[IrCl({=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (**29**) in excellent yield. Hydrogenation of **29** gave the allene complex *trans*-$[IrCl(\eta^2\text{-}CH_2{=}C{=}CPh_2)(PiPr_3)_2]$ (**30**), the structure of which was determined by X-ray crystallography. The substituted vinylideneiridium compound *trans*-$[IrCl\{{=}C{=}C(SiMe_3)C{\equiv}CCPh_2OH\}(PiPr_3)_2]$ (**33**) was obtained from $[IrCl(C_8H_{14})(PiPr_3)_2]$ and $Me_3SiC{\equiv}CC{\equiv}CCPh_2OH$ via the isomeric π-alkyne complex **32** as isolated intermediate.

Introduction

We have recently shown that not only terminal alkynes $HC{\equiv}CR$ but also trimethylsilyl-, triphenylsilyl-, and triphenylstannyl-substituted derivatives $XC{\equiv}CR$ (X = $SiMe_3$,[2] $SiPh_3$,[3] $SnPh_3$[4]) can be converted in the coordination sphere of rhodium(I) to the corresponding vinylidenes.[5] The metal-assisted isomerization proceeds either thermally or photochemically and occurs more rapidly for X = $SnPh_3$ than for X = $SiMe_3$ or $SiPh_3$. Since we knew that terminal alkynes $HC{\equiv}CR$ react with both $[RhCl(PiPr_3)_2]_2$ and the related iridium precursor $[IrCl(C_8H_{14})(PiPr_3)_2]$ to give square-planar complexes of the general composition *trans*-$[MCl({=}C{=}CHR)(PiPr_3)_2]$ (M = Rh,[6] Ir[7]), we were interested to find out whether the analogy also exists for the silylated counterparts $Me_3SiC{\equiv}CR$.

In this paper we describe our investigations on the reactivity of the labile cyclooctene derivative $[IrCl(C_8H_{14})(PiPr_3)_2]$ toward trimethylsilyl-substituted alkynes and buta-1,3-diynes, the preparation of iridium alkynyl hydrido, vinylidene, allenylidene, and diyne complexes from $[IrH_2Cl(PiPr_3)_2]$ as the starting material, the isolation of two binuclear iridium(III) compounds with a "naked" C_4 bridge, and the selective hydrogenation of a metal-bonded allenylidene to an allene ligand.

Results and Discussion

Vinylideneiridium(I) Complexes from $SiMe_3$-Substituted Alkynes. The cyclooctene adduct $[IrCl(C_8H_{14})(PiPr_3)_2]$, generated in situ from $[IrCl(C_8H_{14})_2]_2$ (**1**) and $PiPr_3$,[8] reacts with $Me_3SiC{\equiv}CCO_2Et$ in hexane even at 0 °C to give the corresponding square-planar

---

[†] Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) Vinylidene Transition-Metal Complexes. 42. Part 41: see: Wiedemann, R.; Fleischer, R.; Stalke, D.; Werner, H. *Organometallics* **1997**, *16*, 866−870.

(2) (a) Schneider, D.; Werner, H. *Angew. Chem.* **1991**, *103*, 710−712; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700−702. (b) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089−1097.

(3) Baum, M.; Windmüller, B.; Werner, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1994**, *49*, 859−869.

(4) Baum, M.; Mahr, N.; Werner, H. *Chem. Ber.* **1994**, *127*, 1877−1886.

(5) Short reviews: (a) Werner, H. *Nachr. Chem. Tech. Lab.* **1992**, *40*, 435−444. (b) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45−55.

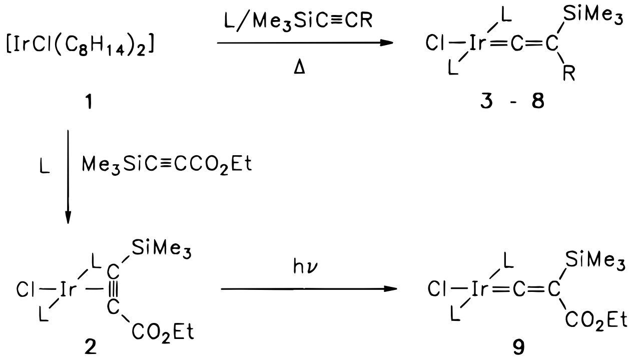
(6) (a) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem.* **1985**, *97*, 401−402; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406−407. (b) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1988**, *43*, 722−726. (c) Werner, H.; Brekau, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1989**, *44*, 1438−1446.

(7) (a) Höhn, A.; Werner, H. *Angew. Chem.* **1986**, *98*, 745−746; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 737−738. (b) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255−272.

(8) Schulz, M. Diploma Thesis, Universität Würzburg, 1988.

S0276-7333(97)00339-7 CCC: $14.00

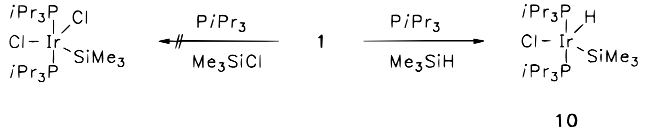
Scheme 1[a]



	R
3	Ph
4	Me
5	*n*Bu
6	$SiMe_3$
7	CH_2OH
8	CMe_2OSiMe_3

[a] L = P*i*Pr$_3$.

Scheme 2



alkyne complex *trans*-[IrCl($Me_3SiC{\equiv}CCO_2Et$)(P*i*Pr$_3$)$_2$] (**2**) in ca. 60% yield. Compound **2** (Scheme 1) is an orange, only moderately air-sensitive solid which is soluble in all common organic solvents and can be stored under argon for weeks without decomposition. The alkyne ligand is strongly electron-withdrawing, which is shown by the decrease of the C≡C stretching frequency from 2150 cm^{-1} in free $Me_3SiC{\equiv}CCO_2Et$ to 1775 cm^{-1} in **2**. The *trans* disposition of the triisopropylphosphine ligands is inferred from the observation of a singlet in the ^{31}P NMR spectrum at δ 17.9 and by the two resonances for the diastereotopic PCHC*H*$_3$ protons in the ^{1}H NMR spectrum, which appear as doublets of virtual triplets.[9] The ^{13}C NMR spectrum of **2** displays (in C_6D_6) two signals at δ 93.5 and 90.1, which show a rather small P–C coupling and are assigned to the carbon atoms of the C≡C unit.

In contrast to $Me_3SiC{\equiv}CCO_2Et$, related alkynes $Me_3SiC{\equiv}CR$ with R = Ph, Me, *n*Bu, SiMe$_3$, CH$_2$OH, CMe$_2$OSiMe$_3$ do not react with **1** in hexane or toluene at 0 °C. When the temperature is raised to 40–60 °C a slow reaction occurs which leads, however, to the formation of the vinylideneiridium(I) complexes **3**–**8** in good yield. They are formed via the corresponding alkyne compounds *trans*-[IrCl($Me_3SiC{\equiv}CR$)(P*i*Pr$_3$)$_2$] as intermediates, since the IR and ^{31}P NMR spectra taken in the course of the reaction display signals which are typical for both isomers. Attempts to separate the isomeric vinylidene- and alkyneiridium compounds by column chromatography failed. In the presence of Al_2O_3, an enhanced isomerization of *trans*-[IrCl($Me_3SiC{\equiv}CR$)(P*i*Pr$_3$)$_2$] to **3**–**8** as well as a subsequent reaction of the Me$_3$Si-substituted vinylidene complexes takes place (see below).

Compound **2**, which at room temperature is quite stable both in the solid state and in solution, rearranges on photolysis in benzene to give the isomer *trans*-[IrCl{=C=C(SiMe$_3$)CO$_2$Et}(P*i*Pr$_3$)$_2$] (**9**) almost quantitatively. The vinylidene complexes **3**–**9** are red or orange-red solids which (with the exception of **7** and **8**) are thermally stable up to at least 100 °C. Typical spectroscopic features of **3**–**9** are the low-field signals in the ^{13}C NMR spectra at δ 240–255 and 80–100, which due to P–C coupling appear as triplets and are assigned to the α-C and β-C vinylidene carbon atoms, respectively. The ^{31}P NMR spectra of **3**–**9** each display a single resonance at δ ca. 29–34 which is shifted 11–26 ppm downfield compared to that of the alkyne complex **2**.

With regard to the mechanism of isomerization of **2** to **9**, we failed to find any evidence for a stepwise rearrangement including the silyliridium(III) compound [IrCl(SiMe$_3$)(C≡CCO$_2$Et)(P*i*Pr$_3$)$_2$] as an intermediate. In contrast to this, the reaction of *trans*-[IrCl(HC≡CR)(P*i*Pr$_3$)$_2$] to give *trans*-[IrCl(=C=CHR)(P*i*Pr$_3$)$_2$] proceeds via the alkynylhydrido complex [IrHCl(C≡CR)(P*i*Pr$_3$)$_2$] as an *isolable* intermediate.[7] In this context it should be noted that we recently described the preparation and structural characterization of the five-coordinate stannylrhodium(III) compound [Rh(SnPh$_3$)(C≡CPh)$_2$(P*i*Pr$_3$)$_2$], which is formed from [Rh(η^2-O$_2$CMe)(P*i*Pr$_3$)$_2$] and 2 equiv of $Ph_3SnC{\equiv}CPh$.[10] This compound does not rearrange to the isomer *trans*-[Rh(C≡CPh){=C=C(SnPh$_3$)R}(P*i*Pr$_3$)$_2$]. Moreover, Milstein et al. reported the reaction of *trans*-[IrCl(C$_2$H$_4$)(PEt$_3$)$_2$] with HSiR$_2$OH, which leads to the hydridosilylmetal derivatives [IrH(SiR$_2$OH)Cl(PEt$_3$)$_2$] in almost quantitative yield.[11] For R = *i*Pr, the X-ray crystal structure analysis revealed a slightly distorted trigonal-bipyramidal geometry around the metal center.

In spite of the above-mentioned unsuccessful attempts to isolate [IrCl(SiMe$_3$)(C≡CCO$_2$Et)(P*i*Pr$_3$)$_2$], related five-coordinate silyliridium(III) complexes are stable, as is evidenced by the synthesis of [IrHCl(SiMe$_3$)(P*i*Pr$_3$)$_2$] (**10**) from [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] and an equimolar amount of HSiMe$_3$. While the Me$_3$Si-substituted alkyne- and vinylideneiridium compounds **2** and **3**–**9** are quite stable and can be handled in air for a short period of time, complex **10** is thermolabile and extremely sensitive to oxygen. An analytically pure sample has been obtained by chromatography on silylated SiO$_2$. The spectroscopic data for **10** (in particular the chemical shift of the hydride signal at δ −20.0) do not allow us to unequivocally assign a square-pyramidal (sqp) or a trigonal-bipyramidal (tbp) structure for the five-coordinate species. Since for the related hydridoiridium(III) compound [IrHCl(C$_6$H$_5$)(P*i*Pr$_3$)$_2$] a tbp configuration has been determined by X-ray crystallography,[12] we favor a similar structure also for **10** (see Scheme 2). With regard to the formation of **10** from **1**, P*i*Pr$_3$, and HSiMe$_3$ it is interesting to note that attempts to prepare the dichloro derivative [IrCl$_2$(SiMe$_3$)(P*i*Pr$_3$)$_2$] in the same

---

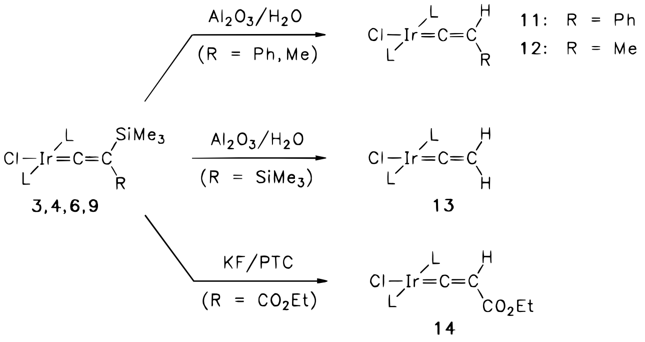
(9) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275–2281.

(10) Werner, H.; Gevert, O.; Haquette, P. *Organometallics* **1997**, *16*, 803–806.

(11) Goikhman, R.; Aizenberg, M.; Kraatz, H.-B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865–5866.

(12) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem.* **1986**, *98*, 1112–1114; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090–1092.

Scheme 3[a]



[a] L = P*i*Pr$_3$.

way (i.e., from **1**, P*i*Pr$_3$, and Me$_3$SiCl) failed. It should also be mentioned that the reaction of the in situ generated species [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] with *2* equiv of HSiMe$_3$ yields the dihydrido complex [IrH$_2$Cl(P*i*Pr$_3$)$_2$].[13]

The C−Si bond of the iridium vinylidenes can easily be cleaved by protic reagents or by fluoride ions. After chromatography of solutions of **3**, **4**, or **6** on deactivated Al$_2$O$_3$ (activity grade V) in hexane, the H derivatives *trans*-[IrCl(=C=CHR)(P*i*Pr$_3$)$_2$] (**11**, **12**) and *trans*-[IrCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$] (**13**)[7b] are eluted instead of the original product. Treatment of **9** with KF in the presence of 18-crown-6 equally leads to cleavage of the C−Si bond and to the formation of the hitherto unknown complex **14** (Scheme 3). We assume that in this case the sources for the proton at the β-C atom of the vinylidene ligand are traces of water either in the solvent or in KF. The properties as well as the spectroscopic data of the red-violet solid **14** are similar to those of *trans*-[IrCl(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$], which has been prepared from [IrH$_2$Cl(P*i*Pr$_3$)$_2$] and HC$\equiv$CCO$_2$Me and characterized by an X-ray crystal structure analysis.[14]

Reactions of Iridium(I) and Iridium(III) Precursors with Buta-1,3-diynes. Following our initial studies on the synthesis of vinylideneiridium(I) complexes from terminal alkynes,[7,14a] we attempted to prepare buta-1,3-diynyl- and buta-1,3-diynediyliridium(III) compounds from the in situ generated [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] or from [IrH$_2$Cl(P*i*Pr$_3$)$_2$] (**15**) as the starting material. If buta-1,3-diyne (which at room temperature is a gas and as a pure substance is not easy to handle due to its high tendency to polymerize) in hexane solution is added dropwise to a solution of [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] in hexane at −78 °C, a rapid change of color from yellow to dark brown occurs. When the mixture is warmed to room temperature, a dark oily material is formed which according to the ^{1}H and ^{13}C NMR spectra consists of a mixture of products. A minor component is the dihydrido complex **15** (probably formed by subsequent reactions of iridium(I)-containing intermediates with cyclooctene),[8] while a major component seems to be the binuclear compound **16** (Scheme 4). This species is obtained without a significant amount of byproducts from **15** and buta-1,3-diyne in hexane at −60 °C and, after chromatographic workup, was isolated as a deep violet, very air-sensitive oil in about 50% yield. We assume that **16** is structurally related to the corresponding binuclear rhodium complex [{RhHCl(P*i*Pr$_3$)$_2$}$_2$(μ-C$\equiv$CC$\equiv$C)], which has been prepared from [RhCl(P*i*Pr$_3$)$_2$]$_2$ and buta-1,3-diyne.[15] The most characteristic spectroscopic features of **16** are the hydride resonance in the ^{1}H NMR spectrum at δ −43.94 (comparable to the chemical shift for the metal-bonded hydrogen of [IrHCl(C$\equiv$CPh)(P*i*Pr$_3$)$_2$] at δ −43.24)[7b] and the two signals in the ^{13}C NMR spectrum at δ 101.0 and 67.8, which are both split into triplets, due to P−C coupling, and assigned to the IrC$\equiv$*C* and Ir*C*$\equiv$C carbon atoms, respectively.

The extremely labile buta-1,3-diynediyl complex **16** (which decomposes, for instance, during chromatography on Al$_2$O$_3$) reacts quite rapidly with pyridine to give the bis(pyridine) adduct **17** in nearly quantitative yield. In contrast to **16**, the corresponding binuclear compound **17** is only moderately air-sensitive and thus could be characterized not only by IR and NMR spectroscopy but also by elemental analysis. Owing to the different coordination spheres around the metal centers in **16** and **17**, in the ^{1}H NMR spectrum of the latter the hydride resonance is observed at δ −22.55, i.e., more than 21 ppm downfield compared to **16**. The ^{13}C NMR spectrum of **17** displays the signals for the IrC$\equiv$*C* and Ir*C*$\equiv$C carbon atoms at δ 88.2 and 57.6, which is 10−13 ppm upfield compared to those for the coordinatively unsaturated complex **16**. A similar upfield shift is found in the ^{31}P NMR spectra, where the signal for the phosphorus nuclei of **16** appears at δ 39.3 and that of **17** at δ 9.5.

Both IrC$_4$Ir derivatives **16** and **17** cannot be converted, either upon heating or upon UV irradiation, to the binuclear compound [{IrCl(P*i*Pr$_3$)$_2$}$_2$(=C=CH-CH=C=)] with a bridging bis(vinylidene) unit. Complex **16** with *two* five-coordinate iridium(III) centers thus behaves differently from the mononuclear compounds [IrHCl(C$\equiv$CR)(P*i*Pr$_3$)$_2$] (R = Me, Ph), which in toluene solution at 110 °C slowly rearrange to the vinylidene isomers *trans*-[IrCl(=C=CHR)(P*i*Pr$_3$)$_2$].[7]

The results concerning the reactivity of the starting materials **1**/P*i*Pr$_3$ and **15** toward Me$_3$SiC$\equiv$CC$\equiv$CSiMe$_3$ are summarized in Scheme 5. The in situ generated species [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] reacts rapidly with the diyne, even at room temperature, to give the orange crystalline compound **18** in ca. 75% yield. The fact that only one of the C$\equiv$C triple bonds of the diyne is coordinated to the metal while the other is not is mainly illustrated by the IR spectrum, in which, besides an absorption at 1774 cm^{-1}, typical for a π-bonded alkyne at iridium(I),[7b] another band at 2114 cm^{-1} assigned to ν(C$\equiv$C) of an uncoordinated alkyne moiety is observed. In agreement with this, there are two signals in the ^{1}H NMR spectrum of **18** for the protons of the two different SiMe$_3$ groups and four signals in the ^{13}C NMR spectrum for the carbon atoms of the coordinated and the uncoordinated triple bonds.

In contrast to [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$], the dihydridoiridium(III) complex **15** is inert toward Me$_3$SiC$\equiv$CC$\equiv$CSiMe$_3$ at room temperature. However, it reacts with the diyne slowly on UV photolysis to afford, by elimination of H$_2$, the vinylideneiridium(I) compound

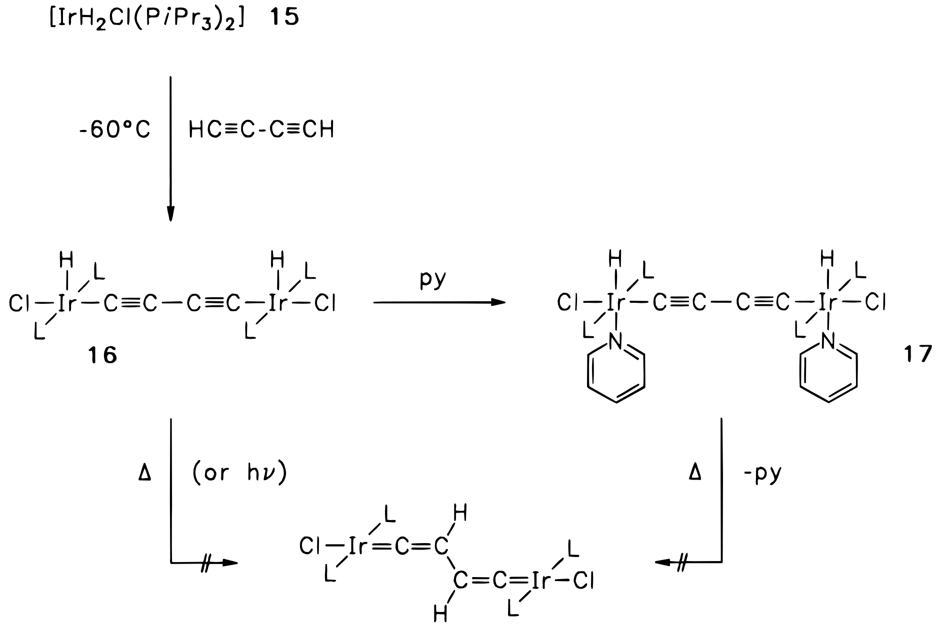
---

[13] (a) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347−357.(b) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407.

[14] (a) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852−854. (b) Werner, H.; Höhn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777-781.

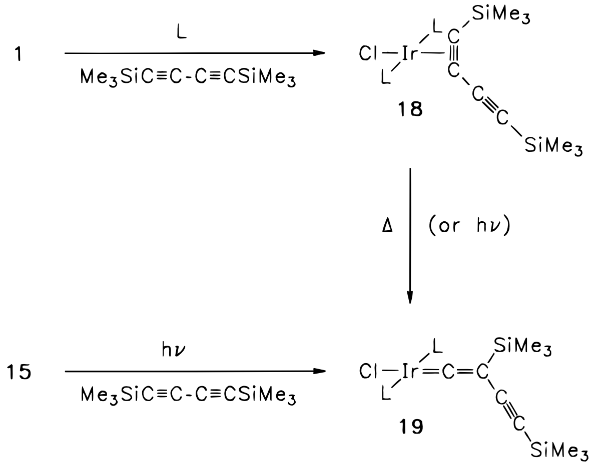
[15] Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359−1364.

Scheme 4[a]



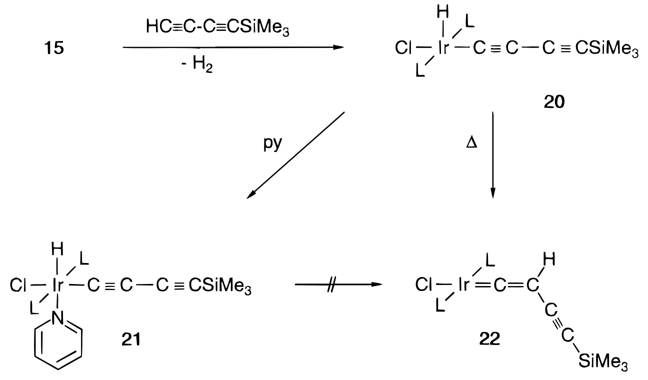
[a] L = P*i*Pr$_3$.

Scheme 5[a]



[a] L = P*i*Pr$_3$.

Scheme 6[a]



[a] L = P*i*Pr$_3$.

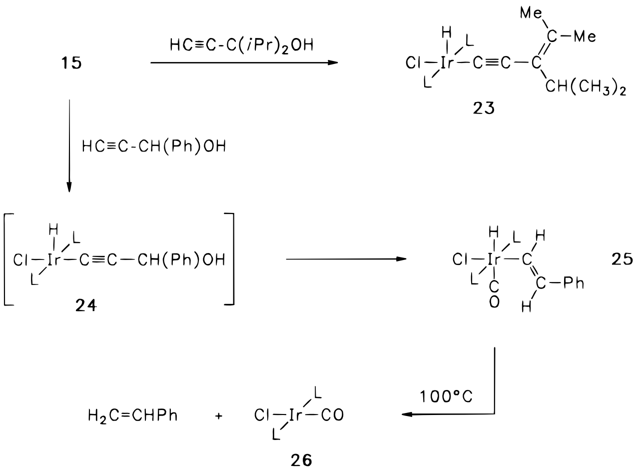
19 in moderate yield. A more efficient method to prepare **19** consists of the thermal or photochemical isomerization of **18**, the photochemical route giving the vinylidene complex nearly quantitatively. The red-violet solid is air-stable (at least for hours) and, in contrast to the related rhodium derivative,[15] exceedingly inert toward hydrolysis. The spectroscopic data for **19**, in particular the ^{13}C NMR spectrum, clearly illustrate the existence of a metal–vinylidene unit and also confirm the different environments of the two SiMe$_3$ groups.

The monosubstituted buta-1,3-diyne HC≡CC≡CSiMe$_3$ reacts with the dihydrido complex **15** similarly to terminal alkynes HC≡CR. If equimolar amounts of **15** and the diyne are used, the diynylhydridoiridium(III) compound **20** (Scheme 6) is formed and isolated as a dark violet oil. Since it is very air-sensitive and smoothly decomposes, even if stored at −20 °C under argon, it has only been characterized by spectroscopic techniques. The structural proposal with a square-pyramidal configuration around the metal center and a free coordination site *trans* to the hydride ligand is mainly supported by the ^{1}H NMR spectrum, in which the hydride signal is observed at δ −42.19, i.e., at a chemical shift similar to that for **16**. Diagnostic for the *trans* disposition of the two phosphine groups are the two doublets of virtual triplets for the PCHCH_3 protons in the ^{1}H NMR and the virtual triplet for the PCHCH$_3$ carbon atoms in the ^{13}C NMR spectrum. The signal for the ^{31}P nuclei appears at δ 39.2 in the ^{31}P NMR spectrum and thus has the same chemical shift as in **16**.

Similar to the binuclear complex **16**, the mononuclear species **20** reacts with pyridine to give the octahedral 1:1 adduct **21** in practically quantitative yield. The spectroscopic data of the off-white crystalline solid are similar to those of **17** and therefore deserve no further comment.

In contrast to **21**, which is rather inert and either on heating in toluene at 80 °C or upon photolysis at room temperature slowly decomposes, the five-coordinate precursor rearranges in toluene at 60 °C to give the alkynyl-substituted vinylideneiridium(I) isomer **22** (Scheme 6). The red-violet, moderately air-stable solid, characterized by elemental analysis and IR and NMR spectroscopy, is an analogue of the rhodium counterpart *trans*-[RhCl(=C=CHC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$], which was not

Scheme 7[a]



[a] L = P*i*Pr$_3$.

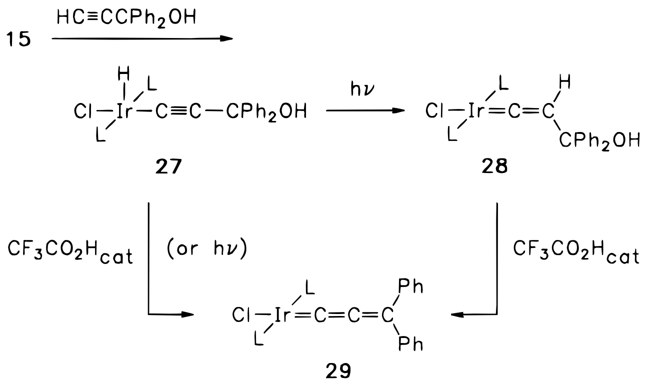
prepared from the (unknown) buta-1,3-diynyl hydrido isomer but from *trans*-[RhCl{=C=C(SiMe$_3$)C≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] upon treatment with small amounts of water in THF.[15]

Reactivity of Propargylic Alcohols toward [IrH$_2$Cl(P*i*Pr$_3$)$_2$]. The dihydridoiridium(III) compound **15** is highly reactive toward propargylic alcohols HC≡CCR(R′)OH but gives different types of products, depending on the substituents R and R′. Dropwise treatment of a solution of **15** in hexane with HC≡CC(*i*Pr)$_2$OH at room temperature leads to a rapid change of color from orange-yellow to red and, after chromatographic workup, yields deep red crystals of the alkynyl hydrido complex **23** (Scheme 7). The coordination of the alkynyl anion is obviously accompanied by the elimination of water, thereby converting a CH(CH$_3$)$_2$ into a =C(CH$_3$)$_2$ unit. The ^{1}H NMR spectrum of **23** displays the hydride signal at δ −44.0, which is at a position similar to that for [IrHCl(C≡CR)(P*i*Pr$_3$)$_2$] (R = H, Me, Ph).[7] The two doublets of virtual triplets for the PCHC*H*$_3$ protons confirm that the two phosphine ligands are *trans*-disposed.

Compound **23** is quite inert and does not rearrange to the vinylidene isomer *trans*-[IrCl{=C=CHC(*i*Pr)=CMe$_2$}(P*i*Pr$_3$)$_2$] either on heating or on UV irradiation. The corresponding rhodium derivative *trans*-[RhCl{=C=CHC(*i*Pr)=CMe$_2$}(P*i*Pr$_3$)$_2$] is known and has been obtained by elimination of water from *trans*-[RhCl{=C=CHC(*i*Pr)$_2$OH}(P*i*Pr$_3$)$_2$] with NH$_4$Cl as a proton source.[16]

The reaction of **15** with HC≡CCH(Ph)OH surprisingly affords the carbonyl hydrido vinyl complex **25** in 84% yield (see Scheme 7). We assume that the expected alkynylhydridoiridium(III) compound **24** is formed as an intermediate, which is indicated by a signal at δ 38.5 in the ^{31}P NMR spectrum of the reaction mixture at low temperature. We note that the chemical shift of the ^{31}P NMR resonance of **23** (δ 38.7) is almost identical. The subsequent conversion of **24** to **25** could occur via an allenylidene- and a (hydroxyallenyl)iridium intermediate. Recently, a similar mechanistic scheme has been proposed by O'Connor and Hilbner for the reaction of [Ir{κ^2(*C*,*C*)-C$_4$(CO$_2$Me)$_4$}(PPh$_3$)$_2$Cl] with HC≡CCH(R)OH (R = H, Me), which gives the carbonylvinylmetal complex [Ir{κ^2(*C*,*C*)-C$_4$(CO$_2$Me)$_4$}(PPh$_3$)(CO)(CH=CHR)] as the final product.[17] Our observation that the deuterated compound [IrD$_2$Cl(P*i*Pr$_3$)$_2$] (**15-d**$_2$) reacts with HC≡CCH(Ph)OH to yield selectively [IrDCl(CH=CHPh)(CO)(P*i*Pr$_3$)$_2$] (**25-*d***) seems to be in agreement with the proposed mechanism.

Scheme 8[a]



[a] L = P*i*Pr$_3$.

However, an alternative route, which involves as an initiating step the deprotonation of the IrC≡CCH(Ph)OH unit by a hydridoiridium compound to give the anionic species IrC≡CCH(Ph)O$^-$, cannot be ruled out. Upon protonation, such a species could rearrange to an intermediate containing an Ir—CH=C(Ph)CHO moiety, which by CO abstraction and recoordination of CO would generate the Ir(CO)(CH=CHPh) unit. There is precedence for the formation of compounds with an Ir—CH=C(R)C(R′)O fragment insofar as the above-mentioned precursor [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] reacts with α,β-unsaturated aldehydes and ketones to give the octahedral products [IrHCl{κ^2(*C*,*O*)-CH=C(R)C(R′)=O}(P*i*Pr$_3$)$_2$] (R = H, Me, *i*Pr; R′ = H, Me) in excellent yield.[18]

The carbonyl hydrido vinyl complex **25** is a colorless solid which is air-stable and soluble in most common organic solvents. Thermolysis of **25** in toluene-*d*$_8$ for 2 h at 100 °C gives styrene and *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$] (**26**) nearly quantitatively. The most typical spectroscopic features of **25** are the strong ν(CO) absorption at 1996 cm^{-1} in the IR spectrum, the high-field signal for the hydride ligand at δ −8.20, and the two resonances for the vinylic protons at δ 8.07 and 6.73 (both doublets of triplets) in the ^{1}H NMR spectrum. The large H−H coupling constant of the latter confirms the *E* configuration at the C=C double bond. With regard to the structural proposal for **25**, as shown in Scheme 7, it should be mentioned that the related complex [IrHCl(CH=CH$_2$)(CO)(P*i*Pr$_3$)$_2$], obtained by photochemical activation of *trans*-[IrCl(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] in the presence of CO, is known and has been characterized by X-ray crystallography.[19]

The reaction of **15** with HC≡CCPh$_2$OH takes a course similar to that for [RhCl(P*i*Pr$_3$)$_2$]$_2$ with the same substrate.[16,20] In pentane at room temperature, the five-coordinate alkynyl hydrido complex **27** (Scheme 8) is formed and isolated as dark red crystals in 80% yield.

---

(16) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721−2727.

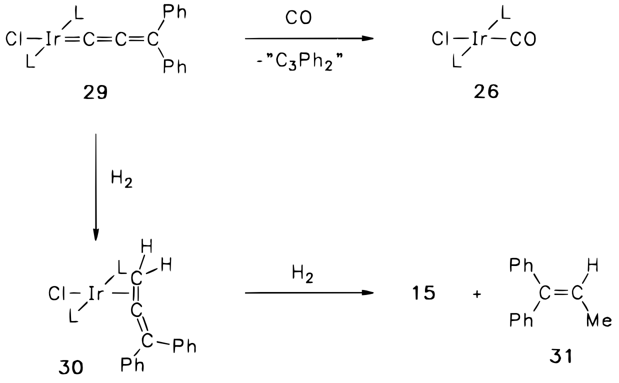
(17) O'Connor, J. M.; Hilbner, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1209−1210.

(18) Dirnberger, T.; Werner, H.; et al., manuscript in preparation. See: Dirnberger, T. Dissertation, Universität Würzburg, 1990.

(19) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790−2795.

(20) Werner, H.; Rappert, T. *Chem. Ber.* **1993**, *126*, 669−678.

Scheme 9[a]



[a] L = P*i*Pr$_3$.

In agreement with the proposed structure, the C≡C stretching vibration is found at 2092 cm^{-1} in the IR spectrum and the signal for the Ir-H proton at δ −43.6 in the ^{1}H NMR spectrum. The single resonance at δ 40.3 for the ^{31}P nuclei appears in the same region as that of the analogous compound **23**.

The alkynyl hydrido complex **27** can be stored for weeks at 25 °C and even when it is warmed in toluene at 70 °C only very slowly rearranges (accompanied by partial decomposition) to the vinylidene isomer **28**. The isomerization is strongly facilitated, however, on UV irradiation in hexane at room temperature, and then **28** is obtained almost quantitatively. The ^{1}H NMR spectrum of the red-violet, only slightly air-sensitive compound displays a triplet at δ −3.29 instead of a resonance at δ ca. −40 (as for **23** and **27**), which is diagnostic for a Ir=C=C*H*R proton.[7] In the ^{31}P NMR spectrum of **28**, the signal for the two phosphine ligands is observed at δ 30.5 and thus shifted 10 ppm upfield if compared to **27**.

On treatment with catalytic amounts of CF_3CO_2H, both isomers, **27** and **28**, are converted to the allenylidene derivative **29** (see Scheme 8). We assume that the acid initiates the elimination of H_2O, thereby generating a cationic $[IrHCl(=C=C=CPh_2)(PiPr_3)_2]^+$ intermediate, which is converted to the final product by dissociation of a proton. Compound **29** is also accessible in excellent yield by photolysis of a solution of **27** in CH_2Cl_2. Under these conditions, it is conceivable that traces of HCl are formed which behave similarly to CF_3CO_2H toward the starting material. The allenylidene complex **29** is a dark red, moderately air-sensitive solid, which is soluble in most organic solvents. As far as the spectroscopic data are concerned, typical features are the strong C=C=C stretching vibration at 1875 cm^{-1} in the IR spectrum and the three low-field resonances for the carbon atoms of the Ir=C=C=C chain at δ 249.7, 199.3, and 138.7 in the ^{13}C NMR spectrum. As in the spectrum of the corresponding rhodium compound *trans*-$[RhCl(=C=C=CPh_2)(PiPr_3)_2]$,[20] the signal of the α-C atom of the allenylidene ligand appears at higher field than that of the β-C atom, which is the opposite to what is found for an Ir=C=C unit.

In contrast to the vinylidene complex **28**, which is quite stable in the presence of carbon monoxide, the allenylidene derivative **29** reacts smoothly with CO in chloroform to give *trans*-$[IrCl(CO)(PiPr_3)_2]$ (**26**). The fate of the C_3Ph_2 fragment is not clear. Attempts to detect the dimer $Ph_2C=C=C=C=C=CPh_2$, which was recently generated in the coordination sphere of rhodium with $[RhH(C\equiv CCPh_2OH)_2(PiPr_3)_2]$ as precursor,[21] remained unsuccessful.

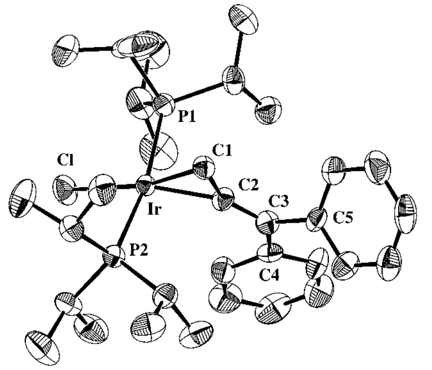


Figure 1. Molecular structure (ORTEP plot) of compound **30**.

An unexpected reaction occurs if a slow stream of hydrogen is passed through a solution of **29** in CH_2Cl_2 (Scheme 9). Since **29**, in a formal sense, is related to **26**, we anticipated that with H_2 either an oxidative addition to yield a six-coordinate dihydridoiridium(III) complex takes place or a five-coordinate allenyl hydrido species is formed. However, the hydrogenation of **29** affords very cleanly the alleneiridium(I) derivative **30**, which is isolated as yellow crystals in 75% yield. The ^{1}H NMR spectrum of **30** displays a signal at δ 1.79 for the CH_2 protons of the allene ligand, which due to P−H coupling is split into a triplet. In the ^{13}C NMR spectrum, the resonances for the carbon atoms of the $H_2C=C=CPh_2$ unit appear at δ 151.6, 117.2, and −4.0; the chemical shift of the last signal seems to be typical for the signal of the CH_2 carbon atom of a substituted ligand.[22]

In order to substantiate the proposed structure of **30**, as shown in Scheme 9, an X-ray crystal structure analysis was carried out. The ORTEP drawing (Figure 1) reveals that the iridium is coordinated in a slightly distorted square-planar fashion. The two phosphine ligands are *trans* to each other, and the chlorine atom is *trans*-disposed to the $C=CH_2$ bond of the allene moiety. The phosphorus−metal−phosphorus axis is not exactly linear, the angle P1−Ir−P2 of 168.3(1)° being comparable to that in *trans*-$[RhCl(\eta^2\text{-}Me_3SiC\equiv CC\equiv CSiMe_3)(PiPr_3)_2]$ [169.6(2)°].[15] The increase in length of the coordinated C=C bond (1.42(1) vs 1.33(1) Å; see Table 1) is similar to that found in other transition-metal allene complexes.[22,23] The elongation of the C1−C2 double bond in **30** is accompanied by a bending of the allene ligand (angle C1−C2−C3 = 141.0(9)°), which is similar to those found in *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CHCO_2Et)(PiPr_3)_2]$ (141.8(5)°),[22b] and $[Pt(\eta^2\text{-}CH_2=C=CH_2)(PPh_3)_2]$ (142(3)°).[24] The bond distances Ir−C1 and Ir−C2 differ by ca. 0.10 Å, which is in the range found for other four-coordinate transition-metal allene derivatives.[22,23]

---

(21) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561-569.

(22) (a) Werner, H.; Schwab, P.; Mahr, N.; Wolf, J. *Chem. Ber.* **1992**, *125*, 2641−2650. (b) Werner, H.; Schneider, D.; Schulz, M. *J. Organomet. Chem.* **1993**, *451*, 175−182.

(23) (a) Shaw, B. L.; Stringer, A. J. *Inorg. Chim. Acta Rev.* **1973**, *7*, 1−10. (b) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245−283.

(24) Kadonaga, M.; Yasuoka, N.; Kasai, N. *J. Chem. Soc. D* **1971**, 1597.

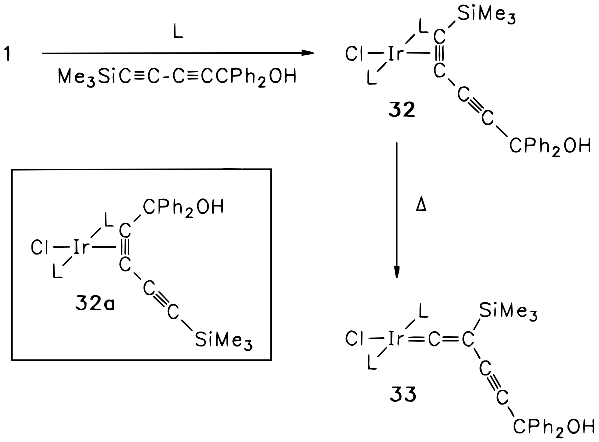
Table 1. Selected Bond Distances and Angles with Esd's for Compound 30

Bond Distances (Å)			
Ir−Cl	2.356(3)	Ir−C2	2.007(9)
Ir−P1	2.341(3)	C1−C2	1.42(1)
Ir−P2	2.362(3)	C2−C3	1.33(1)
Ir−C1	2.112(9)		
Bond Angles (deg)			
P1−Ir−P2	168.3(1)	Cl−Ir−C1	163.0(3)
P1−Ir−Cl	87.5(1)	Cl−Ir−C2	156.9(3)
P1−Ir−C1	91.8(3)	Ir−C1−C2	65.9(5)
P1−Ir−C2	92.9(3)	Ir−C2−C1	74.0(5)
P2−Ir−Cl	88.3(1)	Ir−C2−C3	145.0(7)
P2−Ir−C1	89.0(3)	C1−Ir−C2	40.1(4)
P2−Ir−C2	95.2(3)	C1−C2−C3	141.0(9)

Treatment of a solution of **30** in benzene for 36 h under a H_2 atmosphere leads to the hydrogenation of the allene ligand, giving the olefin $Ph_2C{=}CHCH_3$ (**31**)[25] and the original starting material **15** almost quantitatively. If one takes into consideration that **15** reacts with $HC{\equiv}CCPh_2OH$ to yield **27** (Scheme 8) and that this complex can be converted via **29** to **30**, the hydrogenation of the latter compound to **15** and **31** implies that the respective propargylic alcohol $HC{\equiv}CCPh_2OH$ is transformed into the olefin $Ph_2C{=}CHCH_3$. In this context it seems worth mentioning that **31** is catalytically generated in the coordination sphere of rhodium(I) from C_2H_4 and Ph_2CN_2 as precursors.[5b,26]

The reactivity of the OH-functionalized diyne $Me_3SiC{\equiv}CC{\equiv}CCPh_2OH$, which is a derivative of $HC{\equiv}CCPh_2OH$, toward the labile starting material $[IrCl(C_8H_{14})(P\mathit{i}Pr_3)_2]$ has also been investigated. Originally, these studies were undertaken in order to transform the Me_3Si-substituted diynol into an $Ir{=}C{=}C{=}C{=}C{=}CPh_2$ unit upon coordination, which was finally achieved by using $HC{\equiv}CC{\equiv}CCPh_2OH$ as the substrate.[27] The reaction of $Me_3SiC{\equiv}CC{\equiv}CCPh_2OH$ with $[IrCl(C_8H_{14})(P\mathit{i}Pr_3)_2]$ in ether at room temperature leads to the π-alkyne complex **32**, which is related to the above-mentioned compound **18** (see Scheme 5). Due to similarities in the spectroscopic data for **18** and **32**, we assume that the structural proposal for the diynoliridium(I) complex **32** shown in Scheme 10 is more likely than **32a**. Whereas attempts to convert **32** to the vinylidene derivative **33** by thermolysis or photolysis in benzene failed, the desired isomerization takes place by carefully heating a *solid* sample of **32** to 142 °C, which is the melting point of the diynoliridium precursor. Compound **33** is a red-violet, moderately air-sensitive oil that has been characterized by elemental analysis and IR and NMR spectroscopy. Typical spectroscopic features for the vinylidene ligand are the low-field signals in the ^{13}C NMR spectrum at δ 252.8 and 82.0 (both triplets), which are assigned to the α-C and β-C atoms of the $Ir{=}C{=}C$ chain and which possess chemical shifts almost identical with those of **19**. The substituted vinylidene complex **33** is significantly more labile than **19** and decomposes even upon storing at 0 °C. Treatment of **33** with $(CF_3SO_2)_2O$ in the presence of pyridine does not lead to the formation of the metallacumulene *trans*-$[IrCl({=}C{=}C{=}C{=}C{=}CPh_2)(P\mathit{i}Pr_3)_2]$.[27]

Scheme 10[a]



[a] L = $P\mathit{i}Pr_3$.

Conclusions

The work presented in this paper has shown that trimethylsilyl-substituted alkynes $Me_3SiC{\equiv}CR$ can easily be converted not only in the coordination sphere of rhodium(I) but also in that of iridium(I) to the isomeric disubstituted vinylidenes $:C{=}C(SiMe_3)R$. Although the exact mechanism of the rearrangement is unknown, we assume that the 1,2-$SiMe_3$ shift, which for most of the groups R occurs thermally, proceeds in a concerted way possibly via an initial slippage of the alkyne to an η^1 geometry.[28] Such a reaction pathway has been considered as being energetically preferred for the 1,2-H shift in the related compounds $[M(\eta^2\text{-}CH{\equiv}CR)L_n]$, provided that the metal center has an 18-electron configuration.[29] For the square-planar rhodium complexes *trans*-$[RhCl(\eta^2\text{-}HC{\equiv}CR)(PR'_3)_2]$, however, a recent ab initio MO study revealed that the isomerization proceeds via the oxidative addition product $[RhHCl(C{\equiv}CR)(PR'_3)_2]$, followed by a bimolecular hydrogen shift from the metal to the terminal carbon atom of a second five-coordinate molecule.[30] The fact that in some cases the conversion of a Me_3Si-substituted alkyne to the corresponding vinylidene is assisted by UV irradiation is not without precedence and has been observed by us for rhodium as the coordination center[2] as well as by Sakurai in the synthesis of $[C_5H_5Mn(CO)_2\{{=}C{=}C(SiMe_2R)_2\}]$.[31]

From the synthetic point of view, the most remarkable feature of this work is that the dihydridoiridium(III) complex **15** is a versatile starting material not only for the preparation of alkynylhydridoiridium(III) and diynylhydridoiridium(III) but also for that of vinylidene- and allenylideneiridium(I) derivatives. Since we failed to detect an olefin or a diene as a byproduct, we assume that in the initial step of the reaction a 1:1 adduct of the five-coordinate compound **15** and the alkyne or diyne

---

(25) (a) Hernandez, D.; Larson, G. L. *J. Org. Chem.* **1984**, *49*, 4285−4287. (b) Hixson, S. S.; Franke, L. A. *J. Org. Chem.* **1988**, *53*, 2706−2711.

(26) Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem.* **1990**, *102*, 584−586; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 510−512.

(27) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19−23.

(28) For a recent kinetic study on the interconversion between *trans*-$[RhCl(FcC{\equiv}CSiMe_3)(P\mathit{i}Pr_3)_2]$ and *trans*-$[RhCl\{{=}C{=}C(SiMe_3)Fc\}(P\mathit{i}Pr_3)_2]$ (Fc = ferrocenyl) see: Katayama, H.; Onitsuka, K.; Ozawa, F. *Organometallics* **1996**, *15*, 4642−4645.

(29) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461−1506.

(30) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360−366.

(31) Sakurai, H.; Fujii, T.; Sakamoto, K. *Chem. Lett.* **1992**, 339−342.

is formed, followed by the reductive elimination of H_2. As to the formation of the allenylidene complex **29**, we note that most recently a square-planar *cationic* species containing an $Ir{=}C{=}C{=}CPh_2$ unit has been prepared, using $[Ir(OMe)(dien)(PR_3)]$ and $HC{\equiv}CCPh_2OH$ as the precursors.[32] Finally, it should be mentioned that a *cationic* complex related to **17** with a linear $Ir{-}C{\equiv}CC{\equiv}C{-}Ir$ chain also is known, but in contrast to **17** it has been obtained from $[I(Ph)C{\equiv}CC{\equiv}C(Ph)I]X_2$ and not from buta-1,3-diyne as starting material.[33]

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $[IrCl(C_8H_{14})_2]_2$ (**1**),[34] $[IrH_2Cl(PiPr_3)_2]$ (**15**),[13] $HC{\equiv}CC{\equiv}CH$,[35] $HC{\equiv}CC{\equiv}CSiMe_3$,[36] $HC{\equiv}CCH(Ph)OH$,[37] and $Me_3SiC{\equiv}CC{\equiv}CCPh_2OH$[38] were prepared as described in the literature. Due to the high tendency for polymerization, the diynes were stored in dilute solutions at −78 °C. NMR spectra were recorded at room temperature on JEOL FX 90Q, Bruker AC 200, and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, and mass spectra on a Finnigan MAT 90 (70 eV) instrument. Melting points were measured by DTA.

Preparation of *trans*-[IrCl(Me₃SiC≡CCO₂Et)(P*i*Pr₃)₂] (2). A suspension of **1** (79 mg, 0.09 mmol) in 10 mL of hexane was treated, while being continuously stirred, with $PiPr_3$ (72 μL, 0.35 mmol). A yellow solution was formed, which was cooled to 0 °C, and then $Me_3SiC{\equiv}CCO_2Et$ (33 μL, 0.18 mmol) was added dropwise. A change of color from yellow to orange-red occurred. The reaction mixture was slowly warmed to room temperature, the solvent was removed, and the remaining residue was dissolved in 2 mL of hexane. When the solution was stored for 12 h at −78 °C, orange-yellow, only moderately air-sensitive crystals were formed which were separated from the mother liquor and repeatedly washed with small quantities of hexane (−20 °C): yield 72 mg (57%); mp 100 °C. Anal. Calcd for $C_{26}H_{56}ClIrO_2P_2Si$: C, 43.47; H, 7.86. Found: C, 43.72; H, 8.04. IR (hexane): $\nu(C{\equiv}C)$ 1775, $\nu(C{=}O)$ 1695, 1685 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 4.10 (q, J(HH) = 7.1 Hz, 2H, CH_2CH_3), 2.50 (m, 6H, $PCHCH_3$), 1.29 and 1.17 (both dvt, N = 13.4, J(HH) = 7.3 Hz, 18H each, $PCHCH_3$), 1.07 (t, J(HH) = 7.1 Hz, 3H, CH_2CH_3), 0.35 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 22.5 MHz): δ 150.0 (s, CO_2Et), 93.5 (t, J(PC) = 2.6 Hz, $C{\equiv}C$), 90.1 (t, J(PC) = 1.3 Hz, $C{\equiv}C$), 60.0 (s, CH_2CH_3), 21.6 (vt, N = 23.6 Hz, $PCHCH_3$), 18.9 (s, $PCHCH_3$), 14.3 (s, CH_2CH_3), 0.2 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 17.9 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)Ph}(P*i*Pr₃)₂] (3). A suspension of **1** (60 mg, 0.07 mmol) in 10 mL of hexane was treated, while being continuously stirred at room temperature, with $PiPr_3$ (54 μL, 0.27 mmol) and, after a yellow solution was formed, with $Me_3SiC{\equiv}CPh$ (26 μL, 0.13 mmol). The reaction mixture was slowly warmed to 60 °C and then stirred for 2 h. A change of color from yellow to red-violet occurred. When the mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was recrystallized from methanol (−78 °C) to give red-violet crystals: yield 69 mg (71%); mp 131 °C. Anal. Calcd for $C_{29}H_{56}ClIrP_2Si$: C, 48.21; H, 7.81. Found: C, 47.92; H, 7.66. IR (hexane): $\nu(C{=}C)$ 1585 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 7.75, 7.23, 6.87 (all m, 5H, C_6H_5), 2.82 (m, 6H, $PCHCH_3$), 1.34 and 1.24 (both dvt, N = 13.6, J(HH) = 6.6 Hz, 18H each, $PCHCH_3$), 0.41 (s, 9H $SiMe_3$). ^{13}C NMR (C_6D_6, 22.5 MHz): δ 255.9 (t, J(PC) = 11.2 Hz, $Ir{=}C$), 127.5, 124.4, 120.9 (all s, C_6H_5), 101.9 (t, J(PC) = 2.4 Hz, $Ir{=}C{=}C$), 24.2 (vt, N = 26.4 Hz, $PCHCH_3$), 20.7, 20.3 (both s, $PCHCH_3$), 1.0 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 30.7 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)Me}(P*i*Pr₃)₂] (4). This compound was prepared as described for **3**, using **1** (0.07 mmol), $PiPr_3$ (0.27 mmol), and $Me_3SiC{\equiv}CMe$ (0.13 mmol) as starting materials: red-violet microcrystalline solid: yield 53 mg (57%); mp 112 °C dec. Anal. Calcd for $C_{24}H_{54}ClIrP_2Si$: C, 43.65; H, 8.24. Found: C, 43.34; H, 8.40. MS (70 eV): m/z 660 (M^+ for ^{193}Ir, ^{35}Cl). IR (KBr): $\nu(C{=}C)$ 1643 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 2.76 (m, 6H, $PCHCH_3$), 1.99 (s, br, 3H, $\equiv CCH_3$), 1.23 (dvt, N = 13.5, J(HH) = 6.7 Hz, 36H, $PCHCH_3$), −0.97 (s, 9H, $SiMe_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 31.1 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)*n*Bu}(P*i*Pr₃)₂] (5). This compound was prepared as described for **3**, using **1** (0.07 mmol), $PiPr_3$ (0.27 mmol), and $Me_3SiC{\equiv}CnBu$ (0.13 mmol) as starting materials: red-violet microcrystalline solid: yield 64 mg (68%); mp 109 °C. Anal. Calcd for $C_{27}H_{60}ClIrP_2Si$: C, 46.16; H, 8.61. Found: C, 45.86; H, 8.89. IR (hexane): $\nu(C{=}C)$ 1630 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 2.96 (m, $PCHCH_3$), 1.34 (dvt, N = 13.4, J(HH) = 6.2 Hz, $PCHCH_3$), 0.89 (m, 3H, $(CH_2)_3CH_3$), 0.42 (s, 9H, $SiMe_3$); signals of $(CH_2)_3$ protons covered by signals of $PiPr_3$ protons. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 251.9 (t, J(PC) = 10.1 Hz, $Ir{=}C$), 95.1 (t, J(PC) = 3.0 Hz, $Ir{=}C{=}C$), 35.5 (s, $=CHCH_2$), 23.6 (s, CH_2), 23.1 (vt, N = 26.2 Hz, $PCHCH_3$), 20.4 (s, $PCHCH_3$), 14.1 (s, $(CH_2)_3CH_3$), 11.4 (s, CH_2), 0.7 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 29.3 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)₂}(P*i*Pr₃)₂] (6). This compound was prepared as described for **3**, using **1** (0.07 mmol), $PiPr_3$ (0.27 mmol), and $Me_3SiC{\equiv}CSiMe_3$ (0.33 mmol) as starting materials. Upon recrystallization from methanol (−78 °C), orange crystals were obtained: yield 62 mg (64%); mp 141 °C dec. Anal. Calcd for $C_{26}H_{60}ClIrP_2Si_2$: C, 43.46; H, 8.42. Found: C, 43.34; H, 8.18. IR (hexane): $\nu(C{=}C)$ 1608 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 2.89 (m, 6H, $PCHCH_3$), 1.36 (dvt, N = 13.3, J(HH) = 7.1 Hz, 36H, $PCHCH_3$), 0.30 (s, 18H, $SiMe_3$). ^{13}C NMR (C_6D_6, 22.5 MHz): δ 242.5 (t, J(PC) = 10.8 Hz, $Ir{=}C$), 82.3 (s, br, $Ir{=}C{=}C$), 23.9 (vt, N = 25.4 Hz, $PCHCH_3$), 20.6 (s, $PCHCH_3$), 2.6 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 31.5 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)CH₂OH}(P*i*Pr₃)₂] (7). A suspension of **1** (110 mg, 0.11 mmol) in 10 mL of benzene was treated, while being continuously stirred at room temperature, with $PiPr_3$ (95 μL, 0.49 mmol) and, after a yellow solution was formed, with $Me_3SiC{\equiv}CCH_2OH$ (34 μL, 0.23 mmol). The reaction mixture was warmed to 45 °C and stirred for 6 h. When the mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was extracted with 10 mL of methanol. The extract was concentrated to ca. 3 mL and then stored at −78 °C. Red-violet crystals precipitated, which were separated from the mother liquor, washed twice with small quantities of methanol (−20 °C), and dried: yield 109 mg (71%); mp 52 °C dec. Anal. Calcd for $C_{24}H_{54}ClIrOP_2Si$: C, 42.62; H, 8.05. Found: C, 42.45; H, 8.20. IR (KBr): $\nu(OH)$ 3450, $\nu(C{=}C)$ 1625 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 4.66 (s, br, 2H, CH_2OH), 2.90 (m, 6H, $PCHCH_3$), 1.30 (m, 36H, $PCHCH_3$), 0.24 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 251.6 (t, J(PC) = 10.9 Hz, $Ir{=}C$), 97.9 (t, J(PC) = 2.5 Hz, $Ir{=}C{=}C$), 42.4 (s, CH_2OH), 23.0 (vt, N = 26.4 Hz, $PCHCH_3$), 20.4, 20.1 (both s, $PCHCH_3$), 0.3 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 32.1 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe₃)CMe₂OSiMe₃}(P*i*Pr₃)₂] (8). This compound was prepared as described for

---

[32] Esteruelas, M. A.; Oro, L. A.; Schrickel, J. *Organometallics* **1997**, *16*, 796−799.

[33] Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411−4412.

[34] van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92−95.

[35] Niedballa, U. in *Methoden der Organischen Chemie*, 4th ed.; Müller, E., Ed.; Thieme: Stuttgart, Germany, 1977, Vol. 5, Part 2a, p 922.

[36] Zweifel, G.; Rajagopalan, S. *J. Am. Chem. Soc.* **1985**, *107*, 700−701.

[37] Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250−2252.

[38] Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 840−842.

7, using **1** (0.11 mmol), P*i*Pr$_3$ (0.49 mmol), and Me$_3$SiC≡CCMe$_2$OSiMe$_3$ (0.23 mmol) as starting materials: red-violet microcrystalline solid; yield 124 mg (75%); mp 83 °C dec. Anal. Calcd for $C_{29}H_{66}ClIrP_2Si_2$: C, 44.85; H, 8.57. Found: C, 45.29; H, 8.92. IR (hexane): ν(C═C) 1620 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 2.95 (m, 6H, PC*H*CH$_3$), 1.56 (s, 6H, CMe$_2$), 1.36 (m, 36H, PCHC*H*$_3$), 0.46, 0.16 (both s, 9H each, SiMe$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 28.6 (s).

Preparation of *trans*-[IrCl{═C═C(SiMe$_3$)CO$_2$Et}(P*i*Pr$_3$)$_2$] (9). A solution of **2** (60 mg, 0.08 mmol) in 5 mL of benzene was irradiated at room temperature with a 500 W Hg lamp (Osram) for 3 h. The solvent was removed, the residue was extracted with 10 mL of hexane, and the extract was concentrated to ca. 2 mL in vacuo. When the solution was stored at −78 °C for 12 h, red crystals were formed, which were separated from the mother liquor, washed twice with small quantities of hexane (−20 °C), and dried: yield 54 mg (90%); mp 119 °C. Anal. Calcd for $C_{26}H_{56}ClIrO_2P_2Si$: C, 43.47; H, 7.86. Found: C, 43.65; H, 8.11. IR (hexane): ν(C═O) 1678, ν(C═C) 1590 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 4.08 (q, *J*(HH) = 7.2 Hz, 2H, C*H*$_2$CH$_3$), 2.87 (m, 6H, PC*H*CH$_3$), 1.32 (dvt, *N* = 13.7, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 1.05 (t, *J*(HH) = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 0.27 (s, 9H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 254.1 (t, *J*(PC) = 11.2 Hz, Ir═C), 151.2 (s, *C*O$_2$Et), 97.4 (t, *J*(PC) = 2.5 Hz, Ir═C═*C*), 59.4 (s, *C*H$_2$CH$_3$), 25.0 (vt, *N* = 26.2 Hz, P*C*HCH$_3$), 20.4, 20.1 (both s, PCH*C*H$_3$), 14.6 (s, CH$_2$*C*H$_3$), 0.2 (s, SiMe$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 34.0 (s).

Preparation of *trans*-[IrHCl(SiMe$_3$)(P*i*Pr$_3$)$_2$] (10). A suspension of **1** (150 mg, 0.17 mmol) in 10 mL of hexane was treated, while being continuously stirred, with P*i*Pr$_3$ (138 μL, 0.67 mmol) and, upon being cooled to −20 °C, dropwise with HSiMe$_3$ (149 μL of a 2.2 M solution in MeOCH$_2$CH$_2$OMe; 0.33 mmol). A change of color from yellow to orange occurred. After the reaction mixture was warmed to room temperature, it was stirred for 5 min, and then the solvent was removed. The residue was dissolved in 2 mL of hexane, and the solution was chromatographed on silylated SiO$_2$. With hexane, an orange fraction was eluted, from which, after removal of the solvent, an orange-yellow, very air-sensitive oil was isolated: yield 169 mg (84%). Anal. Calcd for $C_{21}H_{31}ClIrP_2Si$: C, 41.96; H, 5.20. Found: C, 42.31; H, 5.55. IR (hexane): ν(IrH) 2200 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 2.60 (m, 6H, PC*H*CH$_3$), 1.21 (dvt, *N* = 13.3, *J*(HH) = 6.4 Hz, 36H, PCHC*H*$_3$), 0.63 (s, 9H, SiMe$_3$), −20.0 (t, *J*(PH) = 13.9 Hz, 1H, IrH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 24.2 (vt, *N* = 25.0 Hz, P*C*HCH$_3$), 21.4, 20.0 (both s, PCH*C*H$_3$), 10.7 (s, SiMe$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 37.6 (s).

Reaction of 3, 4, and 6 with Al$_2$O$_3$/H$_2$O. A solution of **3**, **4**, or **6** (0.10 mmol) in 2 mL of hexane was passed over Al$_2$O$_3$ (neutral, activity grade V, height of column 10 cm). With hexane, a red-violet fraction was eluted, which was concentrated to ca. 2 mL and again passed over Al$_2$O$_3$. This procedure was repeated until no starting material could be detected by ^{1}H NMR spectroscopy. From the final eluted fraction a violet solid was isolated, which was shown by ^{1}H and ^{13}C NMR spectroscopy to be *trans*-[IrCl(═C═CHR)(P*i*Pr$_3$)$_2$] (**11, 12**) or *trans*-[IrCl(═C═CH$_2$)(P*i*Pr$_3$)$_2$] (**13**), respectively; the yields were quantitative.

Preparation of *trans*-[IrCl(═C═CHCO$_2$Et)(P*i*Pr$_3$)$_2$] (14) from 9. A solution of **9** (144 mg, 0.20 mmol) in 10 mL of ether was treated with KF (15 mg, 0.26 mmol) and 18-crown-6 (8 mg, 0.03 mmol) and stirred for 8 h at 0 °C. After the mixture was warmed to room temperature, the solvent was removed in vacuo, the residue was dissolved in 2 mL of toluene, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 5 cm). With toluene a violet fraction was eluted, which was brought to dryness in vacuo. The residue was recrystallized from hexane (−78 °C) to give red-violet crystals, which were separated from the mother liquor, repeatedly washed with small quantities of pentane (−20 °C), and dried: yield 68 mg (52 °C); mp 158 °C. Anal. Calcd for $C_{23}H_{48}ClIrO_2P_2$: C, 42.75; H, 7.45. Found: C, 42.47; H, 7.42. IR (CH$_2$Cl$_2$): ν(C═O) 1686, ν(C═C) 1605 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 4.11 (q, *J*(HH) = 7.1 Hz, 2 H, C*H*$_2$CH$_3$), 2.87 (m, 6H, PC*H*CH$_3$), 1.26 (dvt, *N* = 13.7, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 1.05 (t, *J*(HH) = 7.1 Hz, 3H, CH$_2$C*H*$_3$), −2.27 (t, *J*(PH) = 2.3 Hz, 1H, ═C*H*CO$_2$Et). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 35.5 (s).

Preparation of [{IrHCl(P*i*Pr$_3$)$_2$}$_2$(μ-C≡CC≡C)] (16). A solution of **15** (140 mg, 0.26 mmol) in 10 mL of hexane was treated dropwise (very slowly) at −60 °C with a 0.04 M solution of buta-1,3-diyne in hexane. A change of color from orange-yellow to dark red occurred, and a dark violet oily material precipitated at the wall of the tube. After the reaction mixture was warmed to room temperature, the solution was filtered, the filtrate was brought to dryness in vacuo, and the residue was dissolved in 2 mL of CH$_2$Cl$_2$. The solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 10 cm). With CH$_2$Cl$_2$ a violet fraction was eluted, from which, after removal of the solvent, a deep violet, very air-sensitive oil was isolated: yield 70 mg (48%). The oil was characterized by spectroscopic techniques. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.07 (m, 12 H, PC*H*CH$_3$), 1.29 (m, 72 H, PCHC*H*$_3$; at 60 MHz dvt, *N* = 14.5, *J*(HH) = 6.4 Hz), −43.94 (t, *J*(PH) = 11.5 Hz, 2H, IrH). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 101.0 (t, *J*(PC) = 1.9 Hz, IrC≡*C*), 67.8 (t, *J*(PC) = 13.4 Hz, IrC), 23.0 (vt, *N* = 27.3 Hz, P*C*HCH$_3$), 19.8, 19.6 (both s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ 39.3 (s).

Preparation of [{IrHCl(py)(P*i*Pr$_3$)$_2$}$_2$(μ-C≡CC≡C)] (17). A solution of **16** (30 mg, 0.03 mmol) in 7 mL of CH$_2$Cl$_2$ was treated with an excess of pyridine (1 mL) and stirred for 5 min at room temperature. A quick change of color from deep violet to yellow-green occurred. The solvent was removed, the residue was dissolved in 2 mL of CH$_2$Cl$_2$, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 5 cm). With CH$_2$Cl$_2$ a yellow fraction was eluted, which was brought to dryness in vacuo. The residue was recrystallized twice from CH$_2$Cl$_2$/pentane (1:20) to give a pale yellow microcrystalline solid: yield 34 mg (85%); mp 116 °C dec. Anal. Calcd for $C_{50}H_{96}Cl_2Ir_2N_2P_4$: C, 46.04; H, 7.42; N, 2.15. Found: C, 46.40; H, 7.34; N, 2.22. IR (CHCl$_3$): ν(IrH) 2225, ν(C≡C) 2010 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.11, 7.69, 7.24 (all m, 10H, C$_5$H$_5$N), 2.93 (m, 12H, PC*H*CH$_3$), 1.14 (dvt, *N* = 13.3, *J*(HH) = 6.5 Hz, 72H, PCHC*H*$_3$), −22.55 (t, *J*(PH) = 15.6 Hz, 2H, IrH). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 136.2, 123.6 (both s, C$_5$H$_5$N, third signal of pyridine carbon atoms not observed), 88.2 (s, br, IrC≡*C*), 57.6 (t, *J*(PC) = 11.4 Hz, IrC), 23.4 (vt, *N* = 26.7 Hz, P*C*HCH$_3$), 19.1 (s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ 9.5 (s).

Preparation of *trans*-[IrCl(Me$_3$SiC≡CC≡CSiMe$_3$)(P*i*Pr$_3$)$_2$] (18). A suspension of **1** (159 mg, 0.18 mmol) in 20 mL of hexane was treated with P*i*Pr$_3$ (150 μL, 0.72 mmol), and after it was stirred for 10 min at room temperature, Me$_3$SiC≡CC≡CSiMe$_3$ (69 mg, 0.35 mmol) was added in small portions. The reaction mixture was stirred for 10 min and then filtered, and the filtrate was concentrated to ca. 2−3 mL in vacuo. When this solution was stored for 12 h at −78 °C, orange crystals precipitated, which were separated from the mother liquor, washed twice with small quantities of pentane (−20 °C), and dried: yield 192 mg (73%); mp 79 °C dec. Anal. Calcd for $C_{28}H_{60}ClIrP_2Si_2$: C, 45.29; H, 8.14. Found: C, 45.40; H, 8.34. IR (hexane): ν(C≡C)$_{\mathrm{uncoord}}$ 2114, ν(C≡C)$_{\mathrm{coord}}$ 1774 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.57 (m, 6H, PC*H*CH$_3$), 1.33 and 1.31 (both dvt, *N* = 13.0, *J*(HH) = 6.2 Hz, 18H each, PCHC*H*$_3$), 0.31, 0.19 (both s, 9H each, SiMe$_3$). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 100.4, 94.8 (both s, C≡C$_{\mathrm{uncoord}}$), 80.6 (t, *J*(PC) = 1.3 Hz, *C*≡C$_{\mathrm{coord}}$), 79.7 (t, *J*(PC) = 2.1 Hz, C≡*C*$_{\mathrm{coord}}$), 21.8 (vt, *N* = 24.0 Hz, P*C*HCH$_3$), 20.4, 19.9 (both s, PCH*C*H$_3$), 0.8, −0.4 (both s, SiMe$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ 17.2 (s).

Preparation of *trans*-[IrCl{═C═C(SiMe$_3$)C≡CSiMe$_3$}(P*i*Pr$_3$)$_2$] (19). (a) A solution of **18** (120 mg, 0.16 mmol) in 10 mL of hexane was heated for 15 h under reflux. After the mixture was cooled to room temperature, the solvent was removed, and the residue was dissolved in 2 mL of hexane. The solution was stored for 12 h at −78 °C to give red-violet crystals which were filtered, washed twice with small quantities of pentane (−20 °C), and dried: yield 80 mg (67%).

(b) A solution of **18** (80 mg, 0.11 mmol) in 5 mL of benzene was irradiated at room temperature with a 500 W Hg lamp (Osram) for 4 h. The solution was then worked up as described for (a): yield 66 mg (82%).

(c) A solution of **15** (160 mg, 0.29 mmol) and $Me_3SiC\equiv CC\equiv CSiMe_3$ (56 mg, 0.28 mmol) in 10 mL of hexane was irradiated at room temperature with a 500 W Hg lamp (Osram) for 40 h. After the irradiation was stopped, the solution was concentrated in vacuo to ca. 2 mL, and the concentrate was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 7 cm). With benzene a red fraction was eluted, from which red-violet crystals were isolated: yield 50 mg (23%); mp 114 °C dec. Anal. Calcd for $C_{28}H_{60}ClIrP_2Si_2$: C, 45.29; H, 8.14. Found: C, 45.60; H, 8.30. IR (hexane): $\nu(C\equiv C)$ 2106, $\nu(C{=}C)$ 1593 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 2.88 (m, 6H, $PCHCH_3$), 1.37 and 1.31 (both dvt, $N = 13.7$, $J(HH) = 6.8$ Hz, 18H each, $PCHCH_3$), 0.29, 0.23 (both s, 9H each, $SiMe_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 253.7 (t, $J(PC) = 11.8$ Hz, $Ir{=}C$), 96.7 (s, $C\equiv C$), 83.1 (t, $J(PC) = 2.4$ Hz, $C\equiv C$), 77.2 (t, $J(PC) = 2.7$ Hz, $Ir{=}C{=}C$), 23.3 (vt, $N = 26.4$ Hz, $PCHCH_3$), 20.4, 20.3 (both s, $PCHCH_3$), 0.9, −0.85 (both s, $SiMe_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 32.8 (s).

Preparation of [IrHCl(C≡CC≡CSiMe₃)(P*i*Pr₃)₂] (20). A solution of **15** (96 mg, 0.17 mmol) in 10 mL of pentane was treated dropwise at 0 °C with a 0.03 M solution of $HC\equiv CC\equiv CSiMe_3$ (5.7 mL, 0.17 mmol) in ether. A quick change of color from yellow to red occurred. The solvent was removed and the dark violet oily residue, which is very air-sensitive and rapidly decomposes in methanol solution, was characterized by spectroscopic techniques. IR (C_6H_6): $\nu(C\equiv C)$ 2180, 2110 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.96 (m, 6H, $PCHCH_3$), 1.16 and 1.14 (both dvt, $N = 14.0$, $J(HH) = 6.8$ Hz, 18H each, $PCHCH_3$), 0.11 (s, 9H, $SiMe_3$), −42.19 (t, $J(PH) = 11.9$ Hz, 1H, IrH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 94.4, 92.5 (both s, $IrC\equiv C$ and $C\equiv C$), 80.0 (t, $J(PC) = 11.2$ Hz, IrC), 75.5 (s, $C\equiv C$), 23.3 (vt, $N = 27.8$ Hz, $PCHCH_3$), 19.8, 19.5 (both s, $PCHCH_3$), 0.70 (s, $SiMe_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 39.2 (s).

Preparation of [IrHCl(C≡CC≡CSiMe₃)(py)(PiPr₃)₂] (21). To a solution of **20**, which was generated in situ from **15** (66 mg, 0.12 mmol) in 5 mL of benzene and a 0.03 M solution of $HC\equiv CC\equiv CSiMe_3$ (4.0 mL, 0.12 mmol) in ether, was added an excess of pyridine (ca. 0.2 mL). A quick change of color from dark violet to yellow-brown occurred. After the solution was stirred for 2−3 min at room temperature, it was concentrated to ca. 1−2 mL in vacuo and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With benzene, a pale yellow fraction was eluted, which was evaporated in vacuo. The residue was dissolved in 2 mL of boiling hexane, and when the solution was cooled to −78 °C almost white crystals precipitated: yield 81 mg (90%); mp 92 °C dec. Anal. Calcd for $C_{30}H_{57}ClIrNP_2Si$: C, 48.08; H, 7.67; N, 1.87. Found: C, 48.55; H, 7.99; N, 1.66. IR (KBr): $\nu(IrH)$ 2290, $\nu(C\equiv C)$ 2180, 2115 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 10.10, 6.83, 6.47 (all m, 5H, C_5H_5N), 2.91 (m, 6H, $PCHCH_3$), 1.08 and 1.05 (both dvt, $N = 13.5$, $J(HH) = 6.5$ Hz, 18H each, $PCHCH_3$) 0.14 (s, 9H, $SiMe_3$), −20.13 (t, $J(PH) = 15.3$ Hz, 1H, IrH). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 152.3, 136.6, 123.8 (all s, C_5H_5N), 95.6 (s, $IrC\equiv C$), 85.1 (t, $J(PC) = 11.4$ Hz, IrC), 85.0, 71.4 (both s, $C\equiv C$), 23.8 (vt, $N = 26.8$ Hz, $PCHCH_3$), 19.3, 19.3 (both s, $PCHCH_3$), 0.8 (s, $SiMe_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 9.8 (s).

Preparation of *trans*-[IrCl(=C=CHC≡CSiMe₃)(P*i*Pr₃)₂] (22). A solution of **20**, which was generated in situ from **15** (77 mg, 0.14 mmol) in 10 mL of toluene and a 0.03 M solution of $HC\equiv CC\equiv CSiMe_3$ (4.7 mL, 0.14 mmol) in ether, was stirred for 15 h at 60 °C. After the reaction mixture was cooled to room temperature, the solvent was removed, the residue was dissolved in 2 mL of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). With hexane, a red-violet fraction was eluted, which was brought to dryness in vacuo. The residue was dissolved in 2 mL of boiling pentane, and after this solution was cooled and stored at −78 °C, red-violet crystals were obtained: yield 53 mg (56%); mp 87 °C dec. Anal. Calcd for $C_{25}H_{52}ClIrP_2Si$: C, 44.79; H, 7.82. Found: C, 44.98; H, 8.04. IR (KBr): $\nu(C\equiv C)$ 2108, $\nu(C{=}C)$ 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.93 (m, 6H, $PCHCH_3$), 1.33 (dvt, $N = 13.8$, $J(HH) = 6.7$ Hz, 36H, $PCHCH_3$), 0.09 (s, 9H, $SiMe_3$), −3.31 (t, $J(PH) = 2.5$ Hz, 1H, $=CH$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 32.8 (s).

Preparation of [IrHCl{C≡CC(*i*Pr)=CMe₂}(P*i*Pr₃)₂] (23). A solution of **15** (160 mg, 0.29 mmol) in 10 mL of hexane was treated dropwise, while being continuously stirred, with $HC\equiv CC(iPr)_2OH$ (41 mg, 0.29 mmol) at room temperature. A quick change of color from orange-yellow to red occurred. The solution was concentrated to ca. 2 mL in vacuo and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a red fraction was eluted which was brought to dryness in vacuo. The residue was dissolved in 2 mL of acetone, and when this solution was stored for 12 h at −78 °C, deep red crystals were isolated: yield 142 mg (72%); mp 71 °C dec. Anal. Calcd for $C_{27}H_{56}ClIrP_2$: C, 48.38; H, 8.42. Found: C, 48.69; H, 8.63. IR (KBr): $\nu(C\equiv C)$ 2070 cm^{-1}. ^1H NMR (CD_2Cl_2, 400 MHz): δ 3.14 (m, 6H, $PCHCH_3$), 2.67 (sept, $J(HH) = 6.1$ Hz, 1H, $CH(CH_3)_2$), 1.86, 1.70 (both s, 3H each, $=C(CH_3)_2$), 1.32 and 1.31 (both dvt, $N = 13.8$, $J(HH) = 6.4$ Hz, 18H each, $PCHCH_3$), 0.96 (d, $J(HH) = 6.1$ Hz, 6H, $CH(CH_3)_2$), −43.98 (t, $J(PH) = 12.0$ Hz, 1H, IrH). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 128.9, 128.5 (both s, $C{=}C$), 107.7 (t, $J(PC) = 1.1$ Hz, $IrC\equiv C$), 80.8 (t, $J(PC) = 11.2$ Hz, IrC), 34.2 (s, $CH(CH_3)_2$), 23.7 (s, $CH(CH_3)_2$), 23.5 (vt, $N = 26.8$ Hz, $PCHCH_3$), 22.5 (s, $CH(CH_3)_2$), 20.1, 19.8 (both s, $PCHCH_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 38.7 (s).

Preparation of [IrHCl((*E*)-CH=CHPh)(CO)(P*i*Pr₃)₂] (25). A solution of **15** (100 mg, 0.18 mmol) in 5 mL of hexane was treated dropwise, while being continuously stirred, at room temperature with $HC\equiv CCH(Ph)OH$ (24 mg, 0.18 mmol), which led to a rapid change of color from orange-yellow to red. After the solution was concentrated in vacuo to ca. 1 mL, a white solid precipitated, which was filtered and recrystallized from pentane. Upon storage for 12 h at −78 °C white crystals were isolated: yield 101 mg (84%); mp 141 °C dec. Anal. Calcd for $C_{26}H_{50}ClIrOP_2$: C, 46.73; H, 7.54. Found: C, 47.01; H, 7.46. IR (KBr): $\nu(CO)$ 1996 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.07 (dt, $J(HH) = 18.1$, $J(PH) = 2.2$ Hz, 1H, IrCH), 7.29, 7.22, 7.02 (all m, 5H, C_6H_5), 6.73 (dt, $J(HH) = 18.1$, $J(PH) = 1.4$ Hz, 1H, $CH{=}CHPh$), 2.71 (m, 6H, $PCHCH_3$), 1.28 and 1.20 (both dvt, $N = 14.0$, $J(HH) = 7.0$ Hz, 18H each, $PCHCH_3$), −8.20 (t, $J(PH) = 14.8$, 1H, IrH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 167.8 (t, $J(PC) = 8.0$ Hz, CO), 144.9 (t, $J(PC) = 8.0$ Hz, IrCH), 142.7 (t, $J(PC) = 1.6$ Hz, ipso C of C_6H_5), 138.7 (t, $J(PC) = 2.6$ Hz, $CH{=}CHPh$), 128.0, 124.5, 124.1 (all s, C_6H_5), 24.3 (vt, $N = 28.6$ Hz, $PCHCH_3$), 19.2, 18.9 (both s, $PCHCH_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 16.3 (s).

Thermolysis of 25. A solution of **25** (45 mg, 0.07 mmol) in 0.5 mL of toluene-d_8 was heated in an NMR tube for 2 h at 100 °C. After the solution was cooled to room temperature, it was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With toluene, first a colorless fraction containing styrene (GC/MS) and then a yellow fraction containing *trans*-[IrCl(CO)(P*i*Pr₃)₂] (**26**) were eluted. Compound **26** was identified by IR and ^1H NMR data.[39]

Preparation of [IrHCl(C≡CCPh₂OH)(P*i*Pr₃)₂] (27). A solution of **15** (140 mg, 0.26 mmol) in 5 mL of pentane was treated with a solution of $HC\equiv CCPh_2OH$ (54 mg, 0.26 mmol)

---

(39) (a) Strohmeier, W.; Onada, T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1968**, *23*, 1377−1379. (b) Werner, H.; Höhn, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 1505−1509.

in 5 mL of pentane at room temperature. A rapid change of color from orange-yellow to red occurred, and a red solid precipitated. When the solution was stored at −78 °C, dark red crystals were formed, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried: yield 154 mg (80%); mp 122 °C dec. Anal. Calcd for $C_{33}H_{54}ClIrOP_2$: C, 52.40; H, 7.20. Found: C, 52.69; H, 8.13. IR (KBr): ν(OH) 3400, ν(IrH) 2310, ν(C≡C) 2090 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 7.79, 7.17, 7.06 (all m, 10H, C_6H_5), 3.00 (m, 6H, PC*H*CH_3), 1.16 and 1.15 (both dvt, *N* = 13.8, *J*(HH) = 7.0 Hz, 18H each, PCHC*H*$_3$), −34.61 (t, *J*(PH) = 11.8 Hz, 1H, IrH). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 40.3 (s).

Preparation of [IrCl(=C=CHCPh$_2$OH)(P*i*Pr$_3$)$_2$] (28). A solution of **27** (80 mg, 0.11 mmol) in 10 mL of hexane was irradiated for 5 h at room temperature with a 500 W Hg lamp (Osram). The solution was concentrated to ca. 1 mL in vacuo and then stored for 12 h at −78 °C. Red-violet crystals precipitated, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried: yield 74 mg (92%); mp 116 °C dec. Anal. Calcd for $C_{33}H_{54}ClIrOP_2$: C, 52.40; H, 7.20. Found: C, 52.48; H, 7.35. IR (CH_2Cl_2): ν(OH) 3390, ν(C=C) 1663 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 7.49, 7.10, 6.99 (all m, 10H, C_6H_5), 2.85 (m, 6H, PC*H*CH_3), 1.23 (dvt, *N* = 13.6, *J*(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), −3.29 (t, *J*(PH) = 2.8 Hz, 1H, =CH). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 30.5 (s).

Preparation of *trans*-[IrCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (29). (a) A solution of **28** (50 mg, 0.07 mmol) in 5 mL of ether was treated with 1 drop of CF_3CO_2H (ca. 2 μL) and stirred for 15 min at room temperature. A quick change of color from violet to dark red occurred. The solvent was removed, the residue was dissolved in 2 mL of toluene/hexane (1:5), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With toluene/hexane (1:5) a dark red fraction was eluted, which was brought to dryness in vacuo. The residue was dissolved in 3 mL of pentane (50 °C), and after the solution was cooled to room temperature and then stored for 12 h at −78 °C dark red crystals precipitated: yield 43 mg (83%).

(b) A solution of **27** (95 mg, 0.13 mmol) in 10 mL of ether was treated with 1 drop of CF_3CO_2H (ca. 2 μL) and stirred for 36 h at room temperature. The solution was then worked up as described for (a): yield 69 mg (72%).

(c) A solution of **27** (40 mg, 0.05 mmol) in 0.5 mL of CH_2Cl_2 was irradiated in an NMR tube for 1 h with a 500 W Hg lamp (Osram). After the irradiation was stopped, the solution was worked up as described for (a): yield 26 mg (91%); mp 122 °C dec. Anal. Calcd for $C_{33}H_{52}ClIrP_2$: C, 53.68; H, 7.10. Found: C, 53.73; H, 6.89. MS (70 eV): *m/z* 738 (M^+ for ^{193}Ir and ^{35}Cl). IR (CH_2Cl_2): ν(C=C=C) 1875 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.90, 7.81, 6.95 (all m, 10H, C_6H_5), 2.91 (m, 6H, PC*H*CH_3), 1.26 (dvt, *N* = 13.5, *J*(HH) = 6.4 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 249.7 (t, *J*(PC) = 3.9 Hz, Ir=C=*C*=C), 199.3 (t, *J*(PC) = 13.4 Hz, Ir=C=), 161.7 (s, ipso-C of C_6H_5), 138.7 (t, *J*(PC) = 2.5 Hz, Ir=C=C=*C*), 129.6, 126.3, 121.1 (all s, C_6H_5), 22.9 (vt, *N* = 26.9 Hz, P*C*HCH_3), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 18.8 (s).

Reaction of 29 with CO. A slow stream of CO was passed through a solution of **29** (50 mg, 0.07 mmol) in 0.5 mL of $CDCl_3$ in an NMR tube. While after 10 s no reaction could be observed, after 10 min an almost quantitative formation of *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$] (**26**) took place. Compound **26** was characterized by ^1H and ^{31}P NMR spectroscopy.[39]

Preparation of *trans*-[IrCl(η^2-H$_2$*C*=*C*=CPh$_2$)(P*i*Pr$_3$)$_2$] (30). A solution of **29** (72 mg, 0.10 mmol) in 5 mL of CH_2Cl_2 was stirred under a H_2 atmosphere for 5 min at room temperature. A smooth change of color from dark red to yellow occurred. The solvent was removed, the residue was dissolved in 3 mL of ether (35 °C), and the solution was stored for 12 h at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried: yield 56 mg (75%); mp 115 °C dec. Anal. Calcd for $C_{33}H_{54}ClIrP_2$: C, 53.68; H, 7.35. Found: C, 53.89; H, 7.36. IR (KBr): ν(C=C) 1670 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.60, 7.20 (both m, 10H, C_6H_5), 2.48 (m, 6H, PC*H*CH_3), 1.79 (t, br, *J*(PH) = 4.9 Hz, 2H, C=CH_2), 1.29 and 1.16 (both dvt, *N* = 13.4, *J*(HH) = 6.5 Hz, 18H each, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 151.6 (t, *J*(PC) = 4.2 Hz, =C=), 144.6, 141.5, 128.3, 128.2, 127.8, 127.3, 125.4, 124.9 (all s, C_6H_5), 117.2 (t, *J*(PC) = 1.8 Hz, *C*Ph$_2$), 21.2 (vt, *N* = 25.0 Hz, P*C*HCH_3), 20.5, 19.3 (both s, PCH*C*H$_3$), −4.0 (s, CH_2). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 21.0 (s).

Reaction of 30 with H$_2$. A solution of **30** (50 mg, 0.07 mmol) in 5 mL of benzene was stirred under a H_2 atmosphere (1 atm) for 36 h at room temperature. No change of color could be observed. The ^1H NMR spectrum of the solution reveals that both **15** and Ph_2C=$CHCH_3$ (**31**) were formed almost quantitatively.

Preparation of *trans*-[IrCl(Me$_3$SiC≡CC≡CCPh$_2$OH)(P*i*Pr$_3$)$_2$] (32). A suspension of **1** (140 mg, 0.16 mmol) in 10 mL of ether was treated with P*i*Pr$_3$ (130 μL, 0.64 mmol) and stirred for 5 min at room temperature. To the yellow solution was added dropwise a solution of Me_3SiC≡CC≡$CCPh_2OH$ (101 mg, 0.33 mmol) in 5 mL of ether, which led to a change of color to orange. The reaction mixture was stirred for 10 min and then concentrated to ca. 2 mL in vacuo. After 10 mL of methanol was added and the solution was stirred for 12 h at −78 °C, orange crystals were formed, which were separated from the mother liquor, washed with small quantities of methanol (0 °C), and dried: yield 210 mg (77%); mp 142 °C. Anal. Calcd for $C_{38}H_{62}ClIrOP_2Si$: C, 53.53; H, 7.33. Found: C, 53.07; H, 6.97. IR (hexane): ν(OH) 3400, $\nu(C{\equiv}C)_{uncoord}$ 2105, $\nu(C{\equiv}C)_{coord}$ 1835 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.81, 7.20, 7.07 (all m, 5H, C_6H_5), 2.25 (m, 6H, PC*H*CH_3), 1.23 and 1.03 (both dvt, *N* = 13.1, *J*(HH) = 6.5 Hz, 18H each, PCHC*H*$_3$), 0.28 (s, 9H, SiMe$_3$); signal of O*H* not observed. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 147.2, 127.5, 126.3, 125.2 (all s, C_6H_5), 100.4 (s, $\mathit{C}{\equiv}C_{uncoord}$), 92.9 (t, *J*(PC) = 1.1 Hz, $\mathit{C}{\equiv}C_{coord}$), 86.1 (t, *J*(PC) = 2.8 Hz, $C{\equiv}\mathit{C}_{coord}$), 71.3, 65.8 (both s, $C{\equiv}\mathit{C}_{uncoord}$ and *C*Ph$_2$OH), 22.0 (vt, *N* = 23.6 Hz, P*C*HCH_3), 20.0, 19.6 (both s, PCH*C*H$_3$), −0.4 (s, SiMe$_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 16.0 (s).

Preparation of *trans*-[IrCl{=C=C(SiMe$_3$)C≡CCPh$_2$OH)}(P*i*Pr$_3$)$_2$] (33). A sample of **32** (120 mg, 0.14 mmol) was heated slowly in an NMR tube in vacuo (10^{-2} Torr) until the crystals started to melt. We carefully controlled the temperature of the oil bath so that it did not exceed 142 °C. After 10 min the melting process was finished and a red-violet oil was formed. The oil was dissolved in 1 mL of toluene; the solution was cooled to −78 °C and then filtered with Al_2O_3. The filtrate was brought to dryness in vacuo to give a red-violet oil that did not crystallize even if it was stored at −78 °C: yield 83 mg (69%). Anal. Calcd for $C_{38}H_{62}ClIrOP_2Si$: C, 53.53; H, 7.33. Found: C, 53.98; H, 6.86. IR (hexane): ν(OH) 3600, ν(C≡C) 2185, ν(C=C) 1595 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.55, 7.24 (both m, 5H, C_6H_5), 2.86 (m, 6H, PC*H*CH_3), 1.33 (dvt, *N* = 13.9, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$), 0.09 (s, 9H, SiMe$_3$); signal of O*H* not observed. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 252.8 (t, *J*(PC) = 11.6 Hz, Ir=C), 147.4, 128.1, 127.3, 126.8 (all s, C_6H_5), 96.0 (t, *J*(PC) = 1.1 Hz, C≡*C*), 82.0 (t, *J*(PC) = 2.4 Hz, Ir=C=*C*), 75.1 (s, *C*Ph$_2$OH), 57.5 (t, *J*(PC) = 2.5 Hz, *C*≡C), 23.4 (vt, *N* = 26.6 Hz, P*C*HCH_3), 20.3 (s, PCH*C*H$_3$), −0.6 (s, SiMe$_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 32.9 (s).

X-ray Structural Analysis of 30. Single crystals were grown from $CDCl_3$ at room temperature. Crystal data (from 25 reflections, 10° < θ < 12°): orthorhombic, space group *Pbca* (No. 61), *a* = 11.934(6) Å, *b* = 24.777(9) Å, *c* = 25.84(2) Å, *V* = 7639(6) Å^3, *Z* = 8, D_{calcd} = 1.495 g cm^{-3}, μ(Mo Kα) = 4.26 cm^{-1}, crystal size 0.50 × 0.35 × 0.30 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 15.4), *T* = 293(2) K, ω/θ scan, maximum 2θ = 45.8°, 5894 reflections measured, 5293 independent reflections, 4083 reflections regarded as being observed ($I > 2\sigma(I)$), 5292 used for refinement; intensity data corrected for Lorentz and polarization effects, linear decay correction (loss of gain 7.1%) and empirical absorption correction (ψ-scan method, minimum transmission 50%) applied; structure solved by Patterson method (SHELXS-86); atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares against F_o^2 (SHELXL-93); one molecule of probably disordered $CDCl_3$ present in the asymmetric unit; only one position of the chloro atoms Cl1−Cl3 could be located and refined anisotropically; positions of the hydrogen atoms calculated according to ideal geometry and used only in structure factor calculation; $R1 = 0.0438$, $wR2 = 0.1018$;[40] reflection/parameter ratio 14.3; residual electron density +1.459/−1.387 e Å^{-3}.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant No. SFB 347) and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. R. Schedl and Mr. C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer and Dr. W. Buchner (NMR spectra), Mrs. Dr. G. Lange and Mr. F. Dadrich (mass spectra), and Degussa AG for various gifts of chemicals. R.W.L. is particularly grateful for a NATO travel grant.

Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **30** (6 pages). Ordering information is given on any current masthead page.

OM9703393

---

(40) $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ (for $F_o > 4\sigma(F_o)$); $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}1/2$, with $w^{-1} = \sigma^2(F_o)^2 + 0.0405P^2 + 86.5\,P$, where $P = (F_o^2 + 2F_c^2)/3$.