$2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (C^5_{2h}; No. 14), is uniquely defined.

All crystallographic calculations were carried out by using either the UCI-modified version of the UCLA Crystallographic Computing Package[38] or the SHELXTL PLUS program set.[39] The analytical scattering factors for neutral atoms were used throughout the analysis;[40a] the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[24b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma(|F_o|) + 0.0007\ (|F_o|)^2$.

The structures were solved by direct methods (SHELXTL PLUS)[39] and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. There are two independent molecules in the asymmetric unit. Refinement of positional and thermal parameters led to convergence (see Table IV).

Crystals of compounds 2 and 3 were mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[41] using a Nicolet R3m/v diffractometer operating in the ω-scan mode. Data collection was controlled by using the Nicolet P3 program.[42] Empirical absorption corrections were applied to the data using the program PSICOR.[42] Crystal symmetry and space groups were determined by the program XPREP.[39] Further experimental data are given in Table IV.

The structures were solved using the direct-methods program XS,[39] which revealed the positions of most of the heavy atoms. Most but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed-atom contributors in the final cycles; d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Details of the refinement are given in Table IV. Atomic scattering factors and anomalous scattering parameters were as given in ref 40.

Acknowledgment. Financial support of this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Funds for the purchase of the Nicolet R3m/V diffractometer system were made available from the NSF under Grant CHE-85-14495. The Harvard MS Facility is supported by grants from the NSF and NIH. Dr. A. N. Tyler is gratefully acknowledged for assistance with the mass spectroscopic measurements.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for 1–3 (20 pages). Ordering information is given on any current masthead page.

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(40) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; pp 99–101. (b) *Ibid.*, pp 149–150.

(41) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* 1988, 7, 2543.

(42) *P3/R3 Data Collection Manual*; Nicolet Instrument Corp.: Madison, WI, 1988.

C–H Activation of Ethene by Non-Cyclopentadienyl-Containing Iridium Complexes. Supporting Role of *i*Pr$_2$PCH$_2$CH$_2$OMe as Phosphine Ligand[1]

Michael Schulz and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, Germany

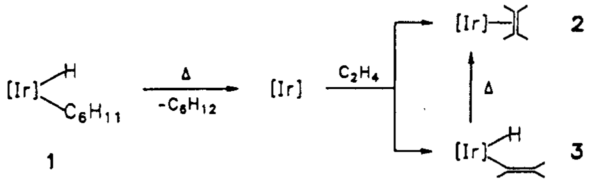
Received January 6, 1992

UV irradiation of *trans*-[IrCl(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (4) in toluene gives only small amounts of the hydrido(vinyl)iridium isomer [IrH(CH=CH$_2$)Cl(P*i*Pr$_3$)$_2$] (5). If, however, the photolysis is carried out in the presence of pyridine, a mixture of two isomers of [IrH(CH=CH$_2$)Cl(py)(P*i*Pr$_3$)$_2$] (6a,b) is formed in 88% yield. Displacement of pyridine by CO gives [IrH(CH=CH$_2$)Cl(CO)(P*i*Pr$_3$)$_2$] (7). Photolysis of *trans*-[IrCl(C$_2$H$_4$)(η^1-*i*Pr$_2$PCH$_2$CH$_2$OMe)$_2$] (8) in toluene proceeds rapidly and leads to the quantitative formation of [IrH(CH=CH$_2$)Cl(η^1-*i*Pr$_2$PCH$_2$CH$_2$OMe)(η^2-*i*Pr$_2$PCH$_2$CH$_2$OMe)] (9). Compound 9, which in solution shows a fluxional behavior (ΔG^* ca. 41 kJ/mol in toluene), also reacts with CO to give [IrH(CH=CH$_2$)Cl(CO)(η^1-*i*Pr$_2$PCH$_2$CH$_2$OMe)$_2$] (10). The thermal reaction of 9 regenerates the π-ethylene complex 8, whereas the carbonyl(hydrido)vinyl derivative 10 reacts in refluxing benzene to form ethylene and the four-coordinate carbonyliridium compound *trans*-[IrCl(CO)(η^1-*i*Pr$_2$PCH$_2$CH$_2$OMe)$_2$] (11). The X-ray crystal structure of 7 has been determined (triclinic space group $P\bar{1}$ (No. 2) with a = 8.848 (3) Å, b = 9.876 (4) Å, c = 16.200 (6) Å, α = 72.38 (2)°, β = 75.10 (2)°, γ = 78.62 (2)°, and Z = 2).

Introduction

Ethylene is certainly one of the most prominent ligands in π-complex chemistry.[2] If a transition-metal compound [ML$_n$] reacts with C$_2$H$_4$, it was until recently the general belief that an interaction between M and C$_2$H$_4$ can only occur via the C=C double bond. However, in 1985 it was shown by Stoutland and Bergman that the reaction of ethylene with a coordinatively unsaturated metal center such as iridium in [(C$_5$Me$_5$)(PMe$_3$)Ir] leads not only to coordination but also to oxidative addition to give a hy-

Scheme I



[Ir] = (C$_5$Me$_5$)(PMe$_3$)Ir

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(1) Studies on C–H Activation. 7. Part 6: Werner, H.; Roder, K. *J. Organomet. Chem.* 1989, *367*, 339–342.

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drido(vinyl)metal complex.[3] The main conclusion (which was later supported by MO calculations[4]) was that in the thermal reaction of the precursor compound $[(C_5Me_5)(PMe_3)IrH(C_6H_{11})]$ (**1**) with C_2H_4 the ethylene metal complex $[(C_5Me_5)(PMe_3)Ir(C_2H_4)]$ (**2**) is the thermodynamically favored product and *not* an intermediate in the formation of the corresponding isomer $[(C_5Me_5)(PMe_3)IrH(CH{=}CH_2)]$ (**3**) (see Scheme I). Shortly thereafter, Perutz et al. demonstrated by IR spectroscopic studies that photolysis of $[(C_5H_5)Ir(C_2H_4)_2]$ in an argon matrix gives the hydrido(vinyl)iridium compound $[(C_5H_5)(C_2H_4)IrH(CH{=}CH_2)]$, which isomerizes at 0 °C to regenerate the starting material.[5]

In this publication, we report that although the order of thermodynamic stability $IrH(CH{=}CH_2) < Ir(C_2H_4)$ is maintained if non-Cp-containing, square-planar iridium(I) complexes are used as starting materials, nevertheless the hydrido(vinyl)metal compound is formed via the isomeric π-ethylene complex. Furthermore, it is shown that the equilibrium between the $Ir(C_2H_4)$ and $IrH(CH{=}CH_2)$ isomers is strongly influenced by the type of phosphine ligand coordinated to iridium. As a consequence, a potentially bidentate ("hemilabile")[6,7] phosphine such as $iPr_2PCH_2CH_2OMe$, which contains a strong and a weak donor center, changes the equilibrium significantly and supports the formation of the hydrido(vinyl)metal complex.

Results and Discussion

Photolysis of *trans*-$[IrCl(C_2H_4)(PiPr_3)_2]$ (4). The well-known π-ethylene complex **4**, which is formed from $[IrCl(C_8H_{14})_2]_2$ and triisopropylphosphine in the presence of ethylene,[8] is thermally rather inert and below its decomposition temperature does not react to give the hydrido(vinyl)iridium derivative $[IrH(CH{=}CH_2)Cl(PiPr_3)_2]$ (**5**). If, however, compound **4** is irradiated in toluene-d_8 at −40 °C (i.e., under similar conditions as used for the photolysis of $[(arene)Os(CO)(C_2H_4)]$[9]), the formerly yellow solution slowly turns red. The ^1H NMR spectrum (in toluene-d_8 at −40 °C) shows a triplet in the high-field region at δ −31.6 [$J(PH)$ = 13 Hz], which points to the formation of **5** and is reminiscent of the position of the hydride signal in the ^1H NMR spectrum of the related five-coordinate hydrido(phenyl) complex $[IrH(C_6H_5)Cl(PiPr_3)_2]$ at δ −32.2.[10] In the low-temperature ^{31}P NMR spectrum of the irradiated solution, besides the signal of **4** a sharp singlet appears at δ 33.16, which under off-resonance conditions splits into a doublet and which we therefore attribute to **5**. On warming to room temperature, compound **5** reconverts to the π-ethylene complex **4**.

Scheme II

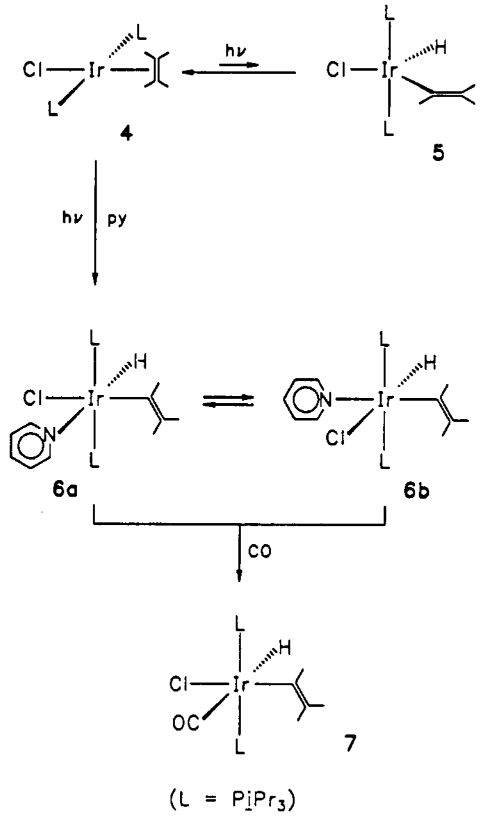

Table I. Selected Bond Distances and Angles with Esd's for 7

		Bond Distances (Å)			
Ir-Cl	2.479 (2)	Ir-C1	2.059 (6)	C1-C2	1.290 (8)
Ir-P1	2.362 (1)	Ir-C3	1.888 (8)	C3-O	1.170 (8)
Ir-P2	2.371 (1)				

	Bond Angles (deg)		
Cl-Ir-P1	90.42 (5)	P1-Ir-C3	98.8 (2)
Cl-Ir-P2	88.71 (5)	P2-Ir-C1	90.3 (2)
Cl-Ir-C1	176.0 (2)	P2-Ir-C3	96.8 (2)
Cl-Ir-C3	92.1 (2)	C1-Ir-C3	91.8 (3)
P1-Ir-P2	164.44 (5)	Ir-C1-C2	129.6 (5)
P1-Ir-C1	89.5 (2)	Ir-C3-O	179.0 (6)

The equilibrium between **4** and the thermodynamically less stable compound **5** can be completely shifted to the side of the hydrido(vinyl) complex if the photochemical reaction is carried out in presence of pyridine. A white, only slightly air-sensitive solid is isolated in 88% yield which according to the elemental analysis is a 1:1 adduct of pyridine and **5**. Whereas the ^1H NMR spectrum at room temperature shows relatively broad resonances, on warming to 60 °C, well-resolved signals are observed which confirm the formation of the octahedral compound $[IrH(CH{=}CH_2)Cl(py)(PiPr_3)_2]$ (**6**) (see Scheme II). According to the NMR measurements, we assume that in solution at room temperature two isomers **6a** and **6b** exist, which at 60 °C rapidly (based on the NMR time scale) interconvert into each other. The ^{31}P NMR spectrum of **6a,b** at 25 °C reveals two broad signals in the approximate ratio of 4:1, which is in agreement with the presence of two isomers.

Bubbling of CO through a benzene solution of **6a,b** creates a spontaneous reaction, which leads to the quantitative formation of the carbonyl(hydrido)vinyl complex $[IrH(CH{=}CH_2)Cl(CO)(PiPr_3)_2]$ (**7**). As the spectroscopic data confirm, only one isomeric species is obtained. In the ^1H NMR spectrum of **7**, the hydride signal (triplet) appears at δ −7.4, which is at substantially lower field compared with **6a,b** (δ −23.0, at 60 °C). We attribute this significant shift to the strong trans influence of the CO ligand. We have not attempted to prepare compound **7** by irradiating a benzene solution of **4** under a CO atmosphere, because

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(3) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732–5744.

(4) Silvestre, J.; Calhorda, M. J.; Hoffmann, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841–1851.

(5) (a) Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734–1736. (b) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212–9226.

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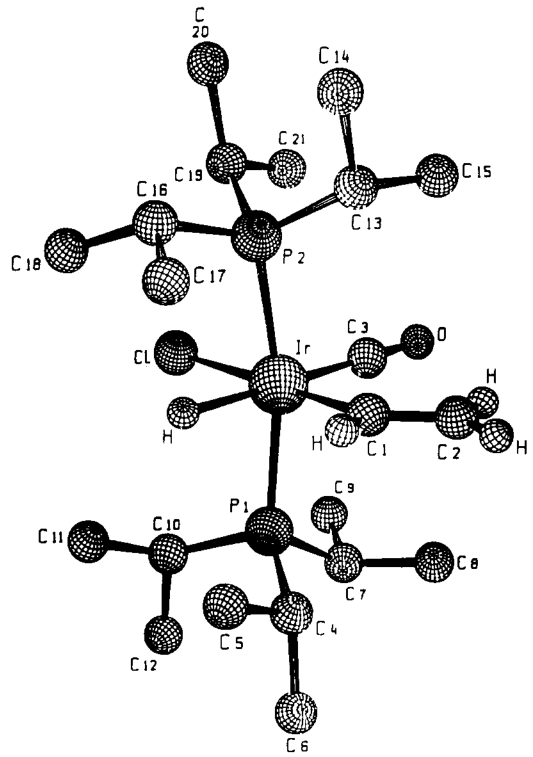


Figure 1. SCHAKAL drawing of complex 7.

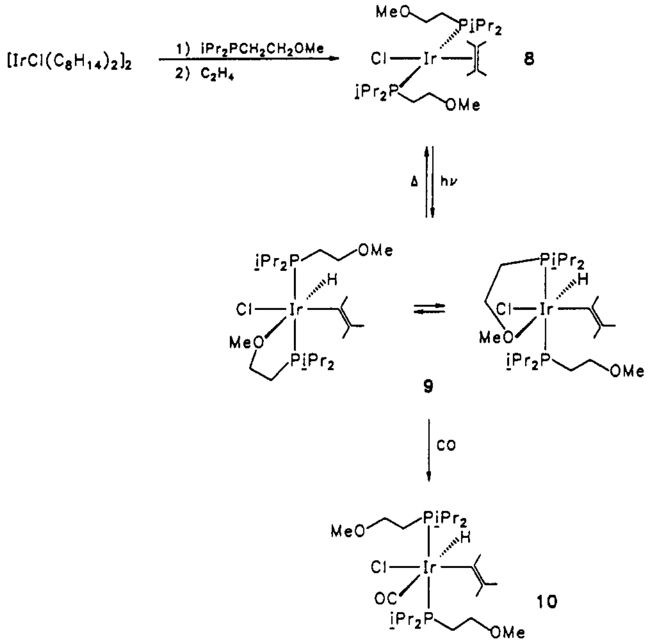
4 smoothly reacts with CO to give *trans*-$[\mathrm{IrCl(CO)(P}i\mathrm{Pr_3)_2}]$.

Molecular Structure of 7. A single-crystal X-ray diffraction study of the hydrido(vinyl) complex 7 confirms the structural proposal shown in Scheme II. The SCHAKAL drawing (Figure 1) reveals that the iridium is coordinated in a somewhat distorted-octahedral fashion with the two phosphine ligands in trans position. The bending of the phosphorus–metal–phosphorus axes (angle 164.44 (5)°) points to the direction of the smallest ligand (hydride) and probably originates from steric hindrance between the bulky phosphines and the other groups in the basal plane. The bond angles Cl–Ir–C3 and C1–Ir–C3 (see Table I) are near to 90° and thus in agreement with the octahedral geometry.

The distance between the iridium and the α-carbon atom of the vinyl group (2.059 (6) Å) is almost identical to that in 3 (2.054 (4) Å),[3] but somewhat longer than in the hydrido(phenyl) complex $[\mathrm{IrH(C_6H_5)Cl(P}i\mathrm{Pr_3)_2}]$ (2.010 (5) Å).[8] The C=C double bond of the vinyl unit is shorter than in ethylene, but the decrease from 1.34 to 1.29 Å again corresponds to that found in 3.[3] The position of the hydride ligand was not determined by X-ray analysis and therefore calculated with the HYDEX program.[11] The value of 1.71 Å is larger than that found in $[\mathrm{IrH(C_6H_5)Cl(P}i\mathrm{Pr_3)_2}]$ (1.44 Å)[8] but similar to that in other hydridoiridium complexes.[12] The distances Ir–Cl and Ir–P correspond to those in related octahedral chloro(phosphine)iridium compounds[13] and deserve no further comment.

Preparation and Reactions of *trans*-$[\mathbf{IrCl(C_2H_4)(\eta^1\text{-}}i\mathbf{Pr_2PCH_2CH_2OMe)_2}]$ (8). The bis(cyclooctene)iridium complex $[\mathrm{IrCl(C_8H_{14})_2}]_2$ reacts at −50 °C in ether suspension with $i\mathrm{Pr_2PCH_2CH_2OMe}$ to give a mixture of products, which besides some as yet unidentified substances probably contains the expected compound *cis*-$[\mathrm{IrCl(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)(\eta^2\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)}]$ as one of the main components.[13] The corresponding rhodium derivative has similarly been prepared and characterized by X-ray analysis.[14] Quite remarkably, on treatment of the reaction mixture at −50 °C with $\mathrm{C_2H_4}$ the π-ethylene complex *trans*-$[\mathrm{IrCl(C_2H_4)(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)_2}]$ (8) is formed in almost quantitative yield. The ^{1}H and ^{31}P NMR spectra of 8 reveal that the two phosphine ligands are equivalent and in trans position to each other (see Scheme III). The appearance of one band in the IR spectrum at 1107 cm^{-1} for the C–O–C stretching frequency furthermore indicates[7,15] that the methoxy groups of the phosphines are not involved in the coordination to the metal.

Scheme III



In contrast to 4, complex 8 reacts on irradiation in toluene quite rapidly to generate the hydrido(vinyl)iridium isomer $[\mathrm{IrH(CH{=}CH_2)Cl(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)(\eta^2\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)}]$ (9). According to various experiments performed at different temperatures, it was found that even at ca. 10 °C (water cooling of the reaction tube) the yield of 9 was better than 90%. Only traces of side products, e.g. $[\mathrm{IrH_2Cl(P}i\mathrm{Pr_3)_2}]$,[16] could be detected. The NMR spectra of 9 are strongly temperature-dependent, and thus there is no doubt that the hydrido(vinyl) complex is fluctional in solution. At 25 °C, the ^{31}P NMR spectrum shows only one sharp singlet which broadens on cooling until at −45 °C coalescence is observed. Below this temperature, the pattern of an AB system appears (see Figure 2) which becomes sharp at ca. −70 °C, indicating that the molecule now has a rigid structure. The size of the P—P coupling strongly favors the proposal that the two phosphorus atoms are trans to each other.

The fluxional process, which is illustrated by the NMR measurements and in similar fashion has also been observed for structurally related rhodium and ruthenium compounds with $i\mathrm{Pr_2PCH_2CH_2OMe}$ as ligand,[14,17] is cer-

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[12] (a) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872–3874. (b) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212–7213.

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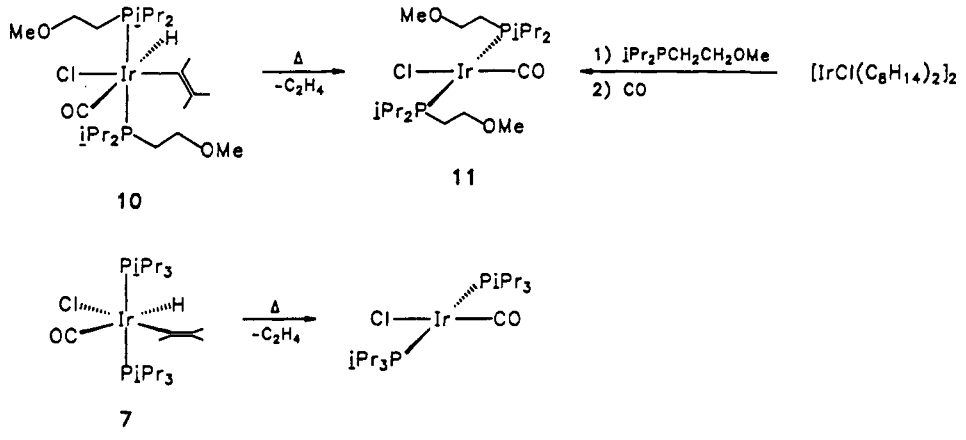
[16] Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395–407.

[17] Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126–1130.

Scheme IV



tainly best explained by a rapid exchange between a η^1 and a η^2 coordination mode of the two hemilabile phosphine ligands. The presence of both η^1- and η^2-bound $i\mathrm{Pr_2PCH_2CH_2OMe}$ groups is proved by two equally strong asymmetric C—O—C stretching frequencies in the IR spectrum of **9** at 1110 and 1055 cm^{-1}, corresponding to the free and the coordinated ether unit. From the coalescence temperature (−45 °C) and the difference in the chemical shift of the two resonances in the low-temperature ^{31}P NMR spectrum, a ΔG^{*} value of approximately 41 kJ/mol for the dynamic process can be calculated. For the comparable alkylnyl(vinyl)iridium complex $[\mathrm{Ir(C{\equiv}CE)(CH{=}CHE)Cl(\eta^1\text{-}\mathit{i}Pr_2PCH_2CH_2OMe)(\eta^2\text{-}\mathit{i}Pr_2PCH_2CH_2OMe)}]$ (E = $\mathrm{CO_2Me}$), a ΔG^{*} value of 49 kJ/mol has been determined.[13] The existence of a $\mathrm{IrH(CH{=}CH_2)}$ molecular fragment in the product formed on photolysis of **8** is shown by the hydride signal in the high-field region of the ^{1}H NMR spectrum at δ −25.12 and by the two triplets at δ 118.93 and 120.52 for the vinylic carbons in the ^{13}C NMR spectrum of **9**. The assignment of the somewhat less deshielded resonance (δ 118.93) to the β-carbon atom of the vinyl ligand is supported by the smaller P—C coupling and the negative amplitude of the signal in the DEPT spectrum.

As the OMe group of the η^2-$i\mathrm{Pr_2PCH_2CH_2OMe}$ ligand in **9** is only weakly coordinated, the compound reacts spontaneously with CO to give the octahedral carbonyl(hydrido)vinyl derivative **10** (see Scheme III). Besides the fact that the phosphines in **7** and **10** are different, the NMR spectroscopic data of both complexes are almost identical. The IR spectrum of **10** shows only one C–O–C band at 1110 cm^{-1}, which is consistent with the monodentate behavior of the two ether–phosphine ligands.

Thermolysis of **9** in refluxing benzene reverses the C–H activation process and regenerates (in 15 min at 80 °C) the π-ethylene complex **8** (see Scheme IV). The carbonyl compound **10** reacts under the same conditions to give ethylene and *trans*-$[\mathrm{IrCl(CO)(\eta^1\text{-}\mathit{i}Pr_2PCH_2CH_2OMe)_2}]$ (**11**). Complex **11** is also prepared in 86% yield on treatment of the reaction mixture, which is obtained from $[\mathrm{IrCl(C_8H_{14})_2}]_2$ and $i\mathrm{Pr_2PCH_2CH_2OMe}$ at −35 °C in ether, with CO. The hydrido(vinyl) derivative **7** behaves quite similarly to **10** and on heating in benzene also eliminates $\mathrm{C_2H_4}$ and forms *trans*-$[\mathrm{IrCl(CO)(P\mathit{i}Pr_3)_2}]$.[18]

Concluding Remarks

The work presented in this paper has shown that the equilibrium between the π-ethylene complex *trans*-$[\mathrm{IrCl(C_2H_4)(PR_3)_2}]$ and the corresponding isomer $[\mathrm{IrH(CH{=}CH_2)Cl(PR_3)_2}]$ can be completely shifted to the side of the hydrido(vinyl)metal derivative if a potential bidentate phosphine ligand such as $i\mathrm{Pr_2PCH_2CH_2OMe}$ is used. The driving force for this C—H activation process probably is the formation of an octahedral coordination sphere at the iridium(III) center through binding of one of the methoxy groups of the ether–phosphine ligands. In the case of the structurally related starting material *trans*-$[\mathrm{IrCl(C_2H_4)(P\mathit{i}Pr_3)_2}]$ (**4**), in which a nonfunctionalized phosphine is coordinated to the metal, the equilibrium between **4** and the isomer $[\mathrm{IrH(CH{=}CH_2)Cl(P\mathit{i}Pr_3)_2}]$ (**5**) can be pushed to the side of the hydrido(vinyl)metal complex by photochemical activation in the presence of pyridine.

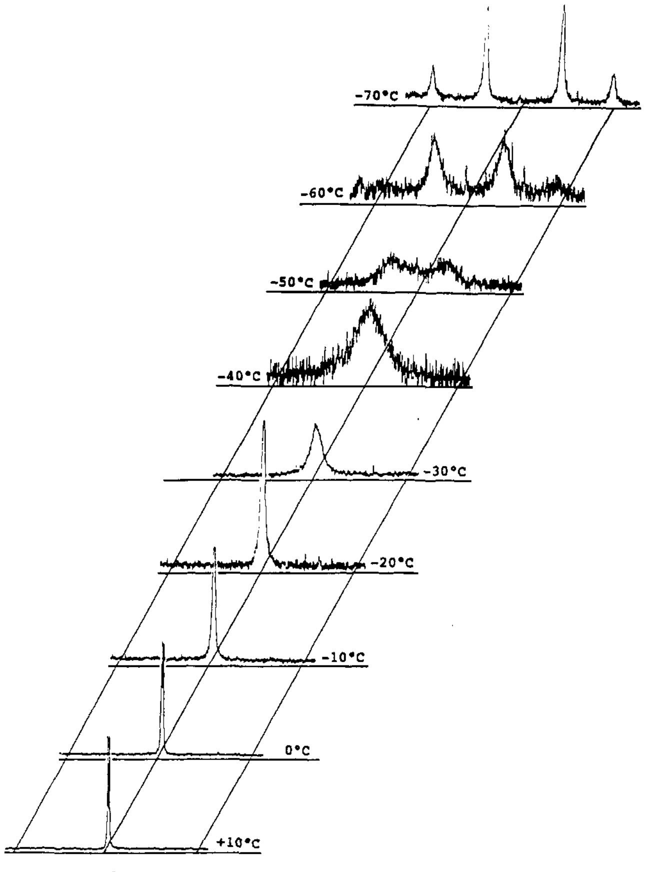


Figure 2. ^{31}P NMR spectra of complex **7** at different temperatures.

As the displacement of the weak donor (the methoxy group in **9** and the pyridine ligand in **6a,b**) by carbon monoxide stabilizes the $\mathrm{IrH(CH{=}CH_2)}$ unit, the prepa-

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[18] (a) Strohmeier, W.; Onada, T. *Z. Naturforsch.* **1968**, *23B*, 1377–1379. (b) Werner, H.; Höhn, A. *Z. Naturforsch.* **1984**, *39B*, 1505–1509.

ration of hydrido(vinyl)iridium(III) compounds of the general type $[\mathrm{IrH(CH{=}CH_2)Cl(CO)(PR_3)_2}]$ is now possible by using easily accessible π-ethylene–metal precursors. Attempts to prepare these compounds from $[\mathrm{IrHCl_2(PR_3)_2}]$ and vinyllithium have failed. It is interesting to note that the equilibrium between an olefin complex $[\mathrm{L}_n\mathrm{M}(\pi\text{-}\mathrm{C_2H_4})]$ and the hydrido(vinyl)metal isomer $[\mathrm{L}_n\mathrm{MH(CH{=}CH_2)}]$ does not only depend on the ligands L but also on the metal M, as has recently been demonstrated by an elegant study by Graham et al.[19]

We are currently exploring the possibility of preparing other octahedral iridium(III) compounds $[\mathrm{IrH(CH{=}CHR)Cl(L)(PR'_3)_2}]$ from olefin precursors, not only with L = CO but also with L = CNR and HC≡CR, with the hope of achieving an insertion of the isocyanide or the alkyne into the Ir—H bond followed by a subsequent coupling of the two σ-bonded organic ligands.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials *trans*-$[\mathrm{IrCl(C_2H_4)(P}i\mathrm{Pr_3)_2}]$ (**4**),[8] $[\mathrm{IrCl(C_8H_{14})_2}]_2$,[20] and $i\mathrm{Pr_2PCH_2CH_2OMe}$[14] were prepared as described previously. NMR spectra were recorded on JEOL FX 90 Q and Bruker AC 200 instruments, and IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer. The assignment of the vinylic protons in the ^{1}H NMR spectra of **6a,b**, **7**, **9**, and **10** is as follows: proton H^1 on α-C, protons H^2 cis and H^3 trans to Ir on β-C.

Preparation of $[\mathrm{IrH(CH{=}CH_2)Cl(py)(P}i\mathrm{Pr_3)_2}]$ (6a,b). A solution of **4** (33 mg, 0.06 mmol) in a mixture of 0.2 mL of toluene-d_8 and 0.2 mL of pyridine was irradiated at −40 °C for 10 min in a NMR tube with a focused 500-W Hg lamp (Oriel). The color of the solution changed from orange to pale yellow. After warming to room temperature, the solvent was removed in vacuo, and the residue was washed three times with small amounts of pentane (0 °C) to give white, only slightly air-sensitive crystals, yield 33 mg (88%); mp 98 °C dec. Anal. Calcd for $\mathrm{C_{25}H_{51}ClIrNP_2}$: C, 45.82; H, 7.84; N, 2.14. Found: C, 45.19; H, 7.73; N, 2.31. IR ($\mathrm{C_6H_6}$): ν(IrH) 2205 cm^{-1}. ^{1}H NMR (toluene-d_8, 60 °C, 90 MHz): δ 9.5, 7.0 and 6.6 (each m, $\mathrm{NC_5H_5}$), 8.20 (dd, br, J(HH) = 16.1 and 11.0 Hz, H^1), 6.11 (d, br, J(HH) = 11.0 Hz, H^2), 5.47 (d, br, J(HH) = 16.1 Hz, H^3), 2.56 (m, $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 1.23 (dvt, N = 12.7, J(HH) = 6.9 Hz, $\mathrm{PCHC}\mathit{H}_3$), 1.19 (dvt, N = 12.2, J(HH) = 6.3 Hz, $\mathrm{PCHC}\mathit{H}_3$), −23.0 (t, J(PH) = 15.8 Hz, IrH). ^{31}P NMR ($\mathrm{C_6D_6}$, 25 °C, 36.2 MHz): δ 8.48 and −0.32 (both br, d in off-resonance).

Preparation of $[\mathrm{IrH(CH{=}CH_2)Cl(CO)(P}i\mathrm{Pr_3)_2}]$ (7). A slow stream of CO was bubbled for ca. 10 s through a solution of **6a,b** (57 mg, 0.09 mmol) in 10 mL of benzene. The solvent was removed, and the residue was repeatedly washed with small amounts of pentane (0 °C) to give white, virtually air-stable crystals, yield 49 mg (93%); mp 155 °C dec. Anal. Calcd for $\mathrm{C_{21}H_{46}ClIrOP_2}$: C, 41.74; H, 7.67. Found: C, 41.71; H, 7.55. IR ($\mathrm{C_6H_6}$): ν(IrH) 2104, ν(CO) 1965 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C, 90 MHz): δ 7.22 (dddt, J(HH) = 17.7, 10.1, and 3.9, J(PH) = 2.0 Hz, H^1), 6.23 (ddt, J(HH) = 10.1 and 2.3, J(PH) = 1.6 Hz, H^2), 5.49 (ddt, J(HH) = 17.7 and 2.3, J(PH) = 1.5 Hz, H^3), 2.68 (m, $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 1.21 (dvt, N = 14.2, J(HH) = 7.1 Hz, $\mathrm{PCHC}\mathit{H}_3$, diastereotopic shift not resolved), −7.40 (dt, J(PH) = 16.6, J(HH) = 3.9 Hz, IrH). ^{31}P NMR ($\mathrm{C_6D_6}$, 25 °C, 36.2 MHz): δ 18.54 (d in off-resonance).

Preparation of *trans*-$[\mathrm{IrCl(C_2H_4)(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)_2}]$ (8). A suspension of $[\mathrm{IrCl(C_8H_{14})_2}]_2$ (84 mg, 0.09 mmol) in 10 mL of ether was treated at −35 °C with $i\mathrm{Pr_2PCH_2CH_2OMe}$ (70 μL, 66 mg, 0.38 mmol). After stirring for 20 min, a slow stream of ethene was bubbled through the solution for ca. 30 s. The mixture was warmed to room temperature, and then the solvent was removed in vacuo. The residue was dissolved in 3 mL of benzene, and the solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V). With benzene, an orange-yellow fraction was eluted which was brought to dryness in vacuo. The yellow solid was repeatedly washed with pentane and dried, yield 96 mg (84%); mp 85 °C dec. Anal. Calcd for $\mathrm{C_{20}H_{46}ClIrO_2P_2}$: C, 39.50; H, 7.62. Found: C, 39.24; H, 7.70. IR ($\mathrm{C_6H_6}$): $\nu(\mathrm{C{-}O{-}C})_{\mathrm{asym}}$ 1107 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C, 90 MHz): δ 3.57 (m, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.09 (s, $\mathrm{OCH_3}$), 2.30 (m, $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 1.91 (m, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2OCH_3}$), 1.80 (t, J(PH) = 4.4 Hz, $\mathrm{C_2H_4}$), 1.30 (dvt, N = 14.4, J(HH) = 7.2 Hz, $\mathrm{PCHC}\mathit{H}_3$), 1.11 (dvt, N = 13.2, J(HH) = 7.0 Hz, $\mathrm{PCHC}\mathit{H}_3$). ^{31}P NMR ($\mathrm{C_6D_6}$, 25 °C, 36.2 MHz): δ 12.8 (s).

Table II. Crystallographic Data for 4

formula	$\mathrm{C_{21}H_{46}ClIrOP2}$
fw	604.22
cryst size, mm	0.10 × 0.15 × 0.20
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
cell dimens determn; θ range, deg	25 reflecns; 10 < θ < 16
a, Å	8.848 (3)
b, Å	9.876 (4)
c, Å	16.200 (6)
α, deg	72.38 (2)
β, deg	75.10 (2)
γ, deg	78.62 (2)
V, Å^3	1293
Z	2
d_{calcd}, g·cm^{-3}	1.55
diffractometer	Enraf-Nonius CAD 4
radiatn (graphite monochrom); λ, Å	Mo Kα; 0.709 30
temp, °C	20 ± 1
μ, cm^{-1}	53.7
scan method	ω/θ
2θ(max), deg	42
total no. of rflns scanned	2995
no. of unique rflns	2531
no. of obsd rflns	2355 ($I > 3\sigma(I)$)
no. of params refined	235
R	0.024
R_{w}	0.028
rfln/param ratio	10.0
residual electron density, e·Å^{-3}	+1.30/−0.57

Preparation of $[\mathrm{IrH(CH{=}CH_2)Cl(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)(\eta^2\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)}]$ (9). A solution of **8** (48 mg, 0.08 mmol) in 0.4 mL of toluene-d_8 was irradiated at 10 °C for 10 min with a focused 500-W Hg lamp (Oriel). The solvent was removed in vacuo, the oily residue was dissolved in 2 mL of benzene, and the solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V). With $\mathrm{C_6H_6/CH_2Cl_2}$ (1:2), a yellow fraction was eluted and concentrated in vacuo to give a pale-yellow air-sensitive oil, yield 44 mg (91%). Anal. Calcd for $\mathrm{C_{20}H_{46}ClIrO_2P_2}$: C, 39.50; H, 7.62. Found: C, 40.10; H, 7.57. IR ($\mathrm{C_6H_6}$): ν(IrH) 2195, $\nu(\mathrm{C{—}O{—}C})_{\mathrm{asym}}$ 1110 and 1055 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C, 200 MHz): δ 8.20 (dddt, J(HH) = 17.1, 9.5, and 1.0, J(PH) = 1.6 Hz, H^1), 5.95 (dddt, J(HH) = 9.5, 2.9, and 1.0, J(PH) = 2.4 Hz, H^2), 5.05 (ddt, J(HH) = 17.1 and 2.9, J(PH) = 2.1 Hz, H^3), 3.49 (m, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.25 (s, $\mathrm{OCH_3}$), 2.77 (m, $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 2.41 (m, $\mathrm{PC}\mathit{H}\mathrm{CH_3}$), 1.87 (m, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2OCH_3}$), 1.18 (m, $\mathrm{PCHC}\mathit{H}_3$), −25.12 (t, J(PH) = 15.4 Hz, IrH, H—H coupling not resolved). ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C, 50.1 MHz): δ 120.52 (t, J(PC) = 9.0 Hz, $\mathrm{Ir}\mathit{C}\mathrm{H{=}CH_2}$), 118.93 (t, J(PC) = 3.4 Hz, $\mathrm{IrCH{=}}\mathit{C}\mathrm{H_2}$), 72.79 (s, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2OCH_3}$), 60.50 (s, $\mathrm{OCH_3}$), 23.16 (vt, N = 31.4 Hz, $\mathrm{P}\mathit{C}\mathrm{HCH_3}$), 22.53 (vt, N = 29.0 Hz, $\mathrm{P}\mathit{C}\mathrm{HCH_3}$), 21.36 (vt, N = 23.0 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2OCH_3}$), 18.73, 18.33, 18.11 (all s, $\mathrm{PCH}\mathit{C}\mathrm{H_3}$). ^{31}P NMR ($\mathrm{C_6D_6}$, 25 °C, 36.2 MHz): δ 20.19 (d in off-resonance).

Preparation of $[\mathrm{IrH(CH{=}CH_2)Cl(CO)(\eta^1\text{-}}i\mathrm{Pr_2PCH_2CH_2OMe)_2}]$ (10). A slow stream of CO was bubbled for ca. 15 s through a solution of **9** (34 mg, 0.06 mmol) in 5 mL of benzene. After the solvent was removed, the oily residue was dissolved in 3 mL of benzene, and the solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V). With $\mathrm{C_6H_6/CH_2Cl_2}$ (1:2), an almost colorless fraction was eluted which was concentrated in vacuo to give a colorless, only slightly air-sensitive oil, yield 32 mg (90%). Anal. Calcd for $\mathrm{C_{21}H_{46}ClIrO_3P_2}$: C, 39.65; H, 7.29. Found: C, 39.83; H, 7.26. IR ($\mathrm{C_6H_6}$): ν(IrH) 2100, ν(CO) 1975, $\nu(\mathrm{C{-}O{-}C})_{\mathrm{asym}}$ 1110 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C, 90 MHz): δ 7.17 (dddt, J(HH) = 17.4, 9.9, and 3.7, J(PH) = 2.1 Hz, H^1), 6.29 (ddt, J(HH) = 9.9 and 2.3, J(PH) = 1.8 Hz, H^2), 5.46 (ddt, J(HH) = 17.4 and 2.3, J(PH) = 1.5 Hz, H^3), 3.71 (m, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.14 (s, $\mathrm{OCH_3}$), 2.35 (m, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2OCH_3}$), 2.28

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

Table III. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Ir	0.14839 (3)	0.31998 (3)	0.26103 (2)	2.272 (6)
Cl	0.3298 (2)	0.5048 (2)	0.1949 (1)	4.11 (5)
P1	0.3497 (2)	0.1455 (2)	0.2152 (1)	2.79 (5)
P2	−0.0654 (2)	0.5063 (2)	0.2680 (1)	2.65 (5)
O	0.2055 (8)	0.2766 (7)	0.4460 (4)	6.0 (2)
C1	−0.0066 (8)	0.1700 (8)	0.3075 (5)	3.1 (2)
C2	−0.045 (1)	0.0867 (9)	0.3859 (6)	4.7 (2)
C3	0.1829 (9)	0.2921 (8)	0.3755 (6)	3.9 (2)
C4	0.2713 (9)	0.0034 (7)	0.1914 (5)	3.6 (2)
C5	0.175 (1)	0.0575 (9)	0.1197 (6)	5.4 (2)
C6	0.396 (1)	−0.1230 (9)	0.1711 (7)	6.5 (3)
C7	0.468 (1)	0.0440 (9)	0.2982 (5)	4.2 (2)
C8	0.374 (1)	−0.051 (1)	0.3808 (6)	5.3 (3)
C9	0.5554 (9)	0.142 (1)	0.3210 (6)	5.5 (3)
C10	0.499 (1)	0.2260 (9)	0.1185 (5)	4.1 (2)
C11	0.431 (1)	0.304 (1)	0.0360 (6)	5.7 (3)
C12	0.653 (1)	0.131 (1)	0.0941 (7)	6.6 (3)
C13	−0.2433 (9)	0.4478 (8)	0.3516 (5)	3.5 (2)
C14	−0.4024 (9)	0.543 (1)	0.3419 (6)	5.0 (3)
C15	−0.222 (1)	0.412 (1)	0.4466 (5)	5.3 (3)
C16	−0.1365 (9)	0.5748 (9)	0.1635 (5)	3.8 (2)
C17	−0.198 (1)	0.4587 (9)	0.1416 (5)	4.9 (2)
C18	−0.012 (1)	0.643 (1)	0.0849 (6)	5.5 (3)
C19	−0.0130 (9)	0.6700 (8)	0.2824 (5)	3.5 (2)
C20	−0.149 (1)	0.7943 (9)	0.2835 (7)	6.2 (3)
C21	0.064 (1)	0.6429 (9)	0.3611 (5)	4.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3 \times [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

(m, PC*H*CH$_3$), 1.13 (m, PCHC*H*$_3$), −7.57 (dt, *J*(PH) = 17.2, *J*(HH) = 3.7 Hz, IrH). ^{31}P NMR (C$_6$D$_6$, 25 °C, 36.2 MHz): δ 9.98 (d in off-resonance).

Preparation of *trans*-[IrCl(CO)(η^1-*i*Pr$_2$PCH$_2$CH$_2$OMe)$_2$] (11). A suspension of [IrCl(C$_8$H$_{14}$)$_2$]$_2$ (69 mg, 0.08 mmol) in 10 mL of ether was treated at −35 °C with *i*Pr$_2$PCH$_2$CH$_2$OMe (57.5 μL, 54.3 mg, 0.31 mmol). After stirring for 20 min, a slow stream of CO was bubbled through the solution for ca. 30 s. The reaction mixture was worked-up as described for 5. Yellow, rather air-stable crystals were obtained, yield 81 mg (86%); mp 103 °C. Anal. Calcd for $C_{19}H_{42}ClIrO_3P_2$: C, 37.52; H, 6.96. Found: C, 37.59; H, 7.12. IR (C$_6$H$_6$): ν(CO) 1936, ν(C–O–C)$_{asym}$ 1109 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 25 °C, 90 MHz): δ 3.84 (m, PCH$_2$C*H*$_2$OCH$_3$), 3.14 (s, OCH$_3$), 2.42 (m, PC*H*$_2$CH$_2$OCH$_3$), 2.30 (m, PC*H*CH$_3$), 1.27 (dvt, *N* = 15.0, *J*(HH) = 7.1 Hz, PCHC*H*$_3$), 1.11 (dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, PCHC*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 25 °C, 36.2 MHz): δ 32.59 (s).

Thermolysis of Complex 7. A solution of 7 (43 mg, 0.07 mmol) in 5 mL of benzene was heated at 80 °C for 6 h. After the solution was cooled to room temperature, the solvent was removed and the residue washed with pentane. It was shown by IR and ^{1}H NMR spectroscopy that the yellow solid was *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$],[18] yield 36 mg (88%). If the reaction was carried out in a sealed NMR tube, the ^{1}H NMR spectrum showed the formation of ethene.

Thermolysis of complex 10 was carried out in a NMR tube as described for 7. The ^{1}H NMR spectrum of the reaction mixture which was obtained after 6 h at 80 °C showed the formation of 11 and free ethene, yield virtually quantitative.

X-ray Structural Analysis of 7. Single crystals were grown from CH$_2$Cl$_2$/pentane. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (Ψ-scan method) was applied; the minimal transmission was 78.8%. The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates (see Table III) and anisotropic thermal parameters of the non-hydrogen atoms were refined using the scattering factors for neutral atoms[21] by full-matrix least squares with unit weights. Anomalous dispersion effects were included in the refinement (values for Δ*f*′ and Δ*f*″ from ref 22). The position of the hydride ligand was calculated with the program HYDEX[11] but could not be refined. The positions of the other hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å) and refined by the riding method. ESD's of bond lengths and angles were derived by analysis of the full covariance matrix. All calculations were performed on a Micro-VAX computer using the program system SDP (Enraf-Nonius). For other details see Table II.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the Fonds in particular for a Doktorandenstipendium for M.S. We also gratefully acknowledge support by Mrs. A. Burger (experimental assistance), Dr. W. Burschka (X-ray analysis), M. Schäfer and Mrs. M.-L. Schäfer (NMR spectra), U. Neumann and C. P. Kneis (elemental analyses), and DEGUSSA AG (chemicals).

Registry No. 4, 115680-99-4; 5, 142189-08-0; 6a, 142189-09-1; 6b, 142189-07-9; 7, 142189-10-4; 8, 142189-11-5; 9, 142189-12-6; 10, 142189-13-7; 11, 142189-14-8; [IrCl(C$_8$H$_{14}$)$_2$]$_2$, 67605-99-6; *i*Pr$_2$PCH$_2$CH$_2$OMe, 132280-90-1; *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$], 49548-57-4.

Supplementary Material Available: Drawing of complex 4 showing the atom-numbering scheme and tables of crystal data, bond distances, bond angles, positional parameters, and general displacement parameter expressions (8 pages). Ordering information is given on any current masthead page.

OM920007S

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(21) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2.3.

(22) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.