A Series of Hydrido(vinyl)iridium(III) Complexes That Are Thermodynamically More Stable than Their Olefin Iridium(I) Isomers†

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The reaction of the in situ generated cyclooctene iridium(I) derivative *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with methyl vinyl ketone and other Michael systems RCH=C(R′)C(O)R″ (R = H, Me, Ph, OMe; R′ = H, Me, *i*Pr; R″ = H, Me, OMe, NH_2, NMe_2) resulted in the formation of the octahedral hydrido(vinyl)iridium(III) complexes [IrH(Cl){κ^2(*C*,*O*)-C(R)=C(R′)C(R″)=O}($PiPr_3$)$_2$] (**2**−**13**) with the vinyl ligand coordinated in a bidentate fashion. Treatment of *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with methyl acrylate and either dimethyl fumarate or dimethyl maleate afforded the iridium(I) compounds *trans*-[IrCl(η^2-RCH=CHCO_2Me)($PiPr_3$)$_2$] (**15**, **16**), which thermally or photochemically rearrange to the thermodynamically more stable iridium(III) isomers [IrH(Cl){κ^2(*C*,*O*)-C(R)=CHC(OMe)=O}($PiPr_3$)$_2$] (**17**, **18**) by intramolecular C−H activation. The reaction of *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with PhCH=CHC(O)Ph gave a 1:1 mixture of the isomeric iridium(III) complexes [IrH(Cl){κ^2(*C*,*O*)-C(Ph)=CHC(Ph)=O}($PiPr_3$)$_2$] (**19**) and [IrH(Cl){κ^2(*C*,*O*)-C_6H_4C(CH=CHPh)=O}($PiPr_3$)$_2$] (**20**), which were separated by column chromatography. From *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] and acrylic acid both [IrH(Cl)-{κ^2(*C*,*O*)-CH=CHC(OH)=O}($PiPr_3$)$_2$] (**21**) and [IrH(Cl){κ^2(*O*,*O*)-O_2CCH=CH_2}($PiPr_3$)$_2$] (**22**) were obtained. While the attempted hydrogenation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Me)=O}-($PiPr_3$)$_2$] (**2**) with Pd/C as the catalyst led to the formation of [IrH_2(Cl)($PiPr_3$)$_2$] (**24**) and ethyl methyl ketone, the same starting material reacted with a solution of Cl_2 in chloroform to give the dichloro vinyl complex [$IrCl_2${κ^2(*C*,*O*)-CH=C(Cl)C(Me)=O}($PiPr_3$)$_2$] (**27**) in virtually quantitative yield. The reaction of both **2** and [IrH(I){κ^2(*C*,*O*)-CH=CHC(Me)=O}($PiPr_3$)$_2$] (**29**) with CO afforded the carbonyl compounds [IrH(X){η^1-(*Z*)-CH=CHC(O)Me}(CO)($PiPr_3$)$_2$] (**31**, **32**) by partial opening of the chelate bond. Similarly to the Ir($PiPr_3$)$_2$ counterparts, a series of (olefin)iridium(I) and hydrido(vinyl)iridium(III) compounds with Ir($PMetBu_2$)$_2$ as a molecular unit were also prepared. Most remarkably, treatment of *trans*-[IrCl(η^2-CH_2=CHC(O)H)($PMetBu_2$)$_2$] (**43**) with in situ generated *trans*-[IrCl(C_8H_{14})($PMetBu_2$)$_2$] led to a clean cleavage of coordinated acrolein to CO and ethene and afforded a 1:1 mixture of *trans*-[IrCl(CO)($PMetBu_2$)$_2$] (**44**) and *trans*-[IrCl(C_2H_4)($PMetBu_2$)$_2$] (**45**), respectively.

Introduction

Transition-metal compounds with olefinic ligands belong to the prototypical metal π complexes. Until the mid 1980s it was the general belief that, if a precursor of the general composition [M($L)_n$] (where $(L)_n$ represents the whole set of ligands coordinated to the metal center) reacts with the olefin CH_2=CHR, only an interaction between M and the carbon−carbon double bond would occur. However, in the course of their extensive studies on C−H bond activation,[1] Bergman and co-workers reported that the cyclohexyl hydrido complex [(η^5-C_5Me_5)IrH(C_6H_{11})(PMe_3)] reacts with ethene by elimination of cyclohexane to give both [(η^5-C_5Me_5)-IrH(CH=CH_2)(PMe_3)] and [(η^5-C_5Me_5)Ir(η^2-C_2H_4)(PMe_3)]. The surprising result, later supported by MO calculations,[3] was that the (ethene)iridium(I) compound is the thermodynamically favored product and is *not* an intermediate in the formation of the hydrido vinyl isomer. Moreover, Perutz et al. demonstrated by IR spectroscopic studies that photolysis of [(η^5-C_5H_5)Ir(η^2-C_2H_4)$_2$] in an argon matrix leads to the formation of the iridium-(III) complex [(η^5-C_5H_5)IrH(CH=CH_2)(η^2-C_2H_4)], which isomerizes at 0 °C to regenerate the starting material.[4] Following this pioneering work,[2−4] it was shown by

† Dedicated to Professor Peter Pauson on the occasion of his 80th birthday, with our best wishes and congratulations for his scientific achievements.

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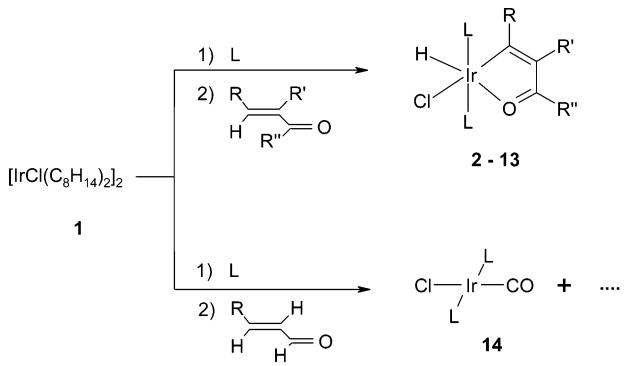
several groups that in general the conversion of the ethene transition-metal compound $[M(\eta^2\text{-}C_2H_4)(L)_n]$ into the hydrido vinyl isomer $[MH(CH{=}CH_2)(L)_n]$ is thermodynamically an uphill process,[5] provided that the labile hydrido vinyl complex is not stabilized either by the presence of *hard* ancillary ligands[6] or by the addition of CO, CH_3CN, etc. to the metal center.[7]

In the present article, we report that the order of thermodynamic stability $[IrH(CH{=}CH_2)(L)_n] < [Ir(\eta^2\text{-}C_2H_4)(L)_n]$ found by Bergman, Perutz, and others can be reversed if instead of ethene the corresponding ethene derivative $CH_2{=}CHR$ containing an aldehyde, ketone, acid, ester, or amido group R is used as the olefinic substrate. In this case, the hydrido(vinyl)-iridium(III) species is stabilized by an additional linkage of the functionality to the metal center and does not rearrange to the (olefin)iridium(I) isomer. Some preliminary results of this work have already been communicated.[8]

Results and Discussion

Preparation of Hydrido(vinyl) Iridium(III) Complexes From Olefins by C−H Activation. The (cyclooctene)iridium(I) derivative *trans*-$[IrCl(C_8H_{14})(P\textit{i}Pr_3)_2]$, generated in situ from **1** and 4 equiv of triisopropylphosphine in benzene,[9] reacts with methyl vinyl ketone even at room temperature. After addition of the substrate, a quick change of color from yellow to red occurred, indicating that the weakly bound cycloolefin is displaced by the unsaturated ketone. The observation of a ν(C=O) band at 1650 cm^{-1} in the IR spectrum of the supposed intermediate *trans*-$[IrCl\{\eta^2\text{-}CH_2{=}CHC(O)Me\}(P\textit{i}Pr_3)_2]$, compared with 1690 cm^{-1} for free $CH_2{=}CHC(O)Me$, supports this assumption. If the solution is subsequently stirred for 30 min, the color changes again, in this case from red to yellow, and after removal of the solvent and chromatographic workup the hydrido(vinyl)iridium(III) complex **2** is isolated as a yellow solid in 85% yield (Scheme 1). The ^1H NMR spectrum of **2** displays in the low-field region two doublets at δ 10.72 and 6.80 ppm, which, in agreement with previous results by Nesmeyanov et al.,[10] are assigned to the vinylic protons in α- and β-positions. For the hydrido ligand, the ^1H NMR spectrum shows a resonance at δ −23.67 ppm, which is split into a triplet due to $^1H{-}^{31}P$ coupling. The appearance of one singlet in the ^{31}P NMR spectrum confirms that the phosphine ligands are trans disposed. The ^{13}C NMR spectrum of **2** displays the signal for the C=O carbon atom at δ 207.1 ppm and the resonances for the vinyl carbon atoms at δ 198.8 and 133.2 ppm, respectively. Due to the cis disposition of the α-C atom and the $P\textit{i}Pr_3$ groups, the signal at δ 198.8 ppm is split into a triplet, while the resonances at δ 207.1 and 133.2 ppm appear as singlets.

Scheme 1[a]



	R	R'	R"
2	H	H	Me
3	OMe	H	Me
4	Me	H	Me
5	Ph	H	Me
6	H	H	H
7	H	Me	H

	R	R'	R"
8	H	*i*Pr	H
9	H	Me	OMe
10	H	H	NH_2
11	H	Me	NMe_2
12	H	Me	NH_2
13	Ph	H	NH_2

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

The most prominent feature in the IR spectrum of **2** is the ν(C=O) stretching mode at 1540 cm^{-1}, which is shifted by ca. 150 cm^{-1} to lower wavenumbers compared with free $CH_2{=}CHC(O)Me$. Since this shift is consistent with a coordination of the carbonyl group to the metal center, an octahedral geometry for compound **2** can be assumed. In this context it should be mentioned that Esteruelas, Oro, et al. reported the preparation of the four-coordinate iridium(I) complex $[Ir(\kappa^2\text{-acac})\{\eta^2\text{-}CH_2{=}CHC(O)Me\}(PCy_3)]$ from $[Ir(\kappa^2\text{-acac})(C_8H_{14})(PCy_3)]$ and methyl vinyl ketone and its thermal rearrangement to a mixture of two six-coordinate hydrido(vinyl)iridium(III) stereoisomers.[11] Regarding the supposed intermediate *trans*-$[IrCl\{\eta^2\text{-}CH_2{=}CHC(O)Me\}(P\textit{i}Pr_3)_2]$, initially formed in the reaction of *trans*-$[IrCl(C_8H_{14})(P\textit{i}Pr_3)_2]$ with methyl vinyl ketone, we note that we had previously isolated the rhodium counterpart *trans*-$[RhCl\{\eta^2\text{-}CH_2{=}CHC(O)Me\}(P\textit{i}Pr_3)_2]$, which slowly rearranges at room temperature to give the C−H activation product $[RhH(Cl)\{\kappa^2(C,O)\text{-}CH{=}CHC(Me){=}O\}(P\textit{i}Pr_3)_2]$ in high yield.[12]

The in situ generated starting material *trans*-$[IrCl(C_8H_{14})(P\textit{i}Pr_3)_2]$ reacts not only with methyl vinyl ketone but also with the related derivatives $RCH{=}CHC(O)Me$ (R = OMe, Me, Ph) to give the corresponding hydrido(vinyl)iridium(III) complexes **3**−**5** in 75−89% yield (Scheme 1). These reactions are considerably slower

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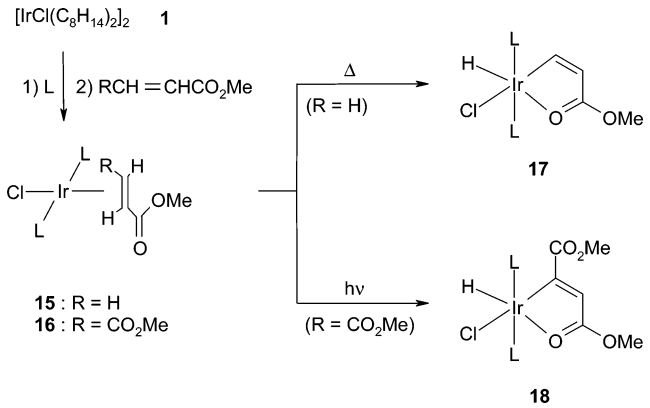
than the reaction leading to **2**, and thus the respective reaction mixture has to be stirred for 2−3 h at 80 °C. In contrast to the conditions employed to obtain **3** and **4**, for the preparation of **5** an excess of PhCH=CHC(O)Me has to be used. If the solution containing the starting material is treated with the ketones at room temperature and stirred for 24 h, in addition to the hydrido vinyl compounds **3**−**5** the dihydrido complex $[IrH_2(Cl)(PiPr_3)_2]$ is formed as a byproduct.[13] Typical spectroscopic features of **3**−**5** are the ^1H NMR resonance for the hydride at δ −23.6 to −24.4 ppm and the ^{13}C NMR signal for the α-carbon atom of the vinylic unit at δ 207.4 to 214.1 ppm, both appearing as triplets. In comparison with **2**, the resonance of the vinylic β-carbon atom of **3** is shifted significantly upfield and that of **5** significantly downfield, thus illustrating the influence of the electron-donating and electron-withdrawing substituents. The ^{31}P NMR spectra of **3**−**5** display only one signal in the region between δ 6.9 to 16.0 ppm, indicating that not only in **2** but also in **3**−**5** the phosphine ligands are trans disposed.

The reaction of *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$ with acrolein proceeds under the same conditions as that with methyl vinyl ketone and affords nearly quantitatively the expected hydrido vinyl complex **6**. The corresponding α,β-unsaturated aldehydes CH_2=C(R′)C(O)H (R′ = Me, *i*Pr) are less reactive than acrolein and react with the starting material at 80 °C to give the C−H activation products **7** and **8** as orange, only slightly air-sensitive solids in 83−85% yield. Although several transition-metal compounds with acrolein are known,[14] we failed to detect the supposed intermediate *trans*-$[IrCl\{\eta^2\text{-}CH_2{=}CHC(O)H\}(PiPr_3)_2]$ by IR or NMR spectroscopy. The ^1H NMR spectrum of **6** displays the hydride resonance as a doublet of triplets due to $^1H-^1H$ coupling with the aldehyde proton and $^1H-^{31}P$ coupling with the phosphorus nuclei. In the spectra of **7** and **8**, the $^1H-^{31}P$ coupling cannot be observed.

Methyl methacrylate and acid amides such as CH_2=CHC(O)NH_2, CH_2=C(Me)C(O)NH_2, PhCH=CHC(O)NH_2, and CH_2=CHC(O)NMe_2 also react with *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$ by oxidative addition to form the corresponding hydrido vinyl complexes **9**−**13** in good to excellent yields. At room temperature, the acrylic acid amide CH_2=CHC(O)NH_2 is much more reactive than the dimethylamido derivative CH_2=CHC(O)NMe_2, and thus, for the preparation of **11** (see Scheme 1) a long time of reaction is necessary. If the reaction mixture of *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$ and CH_2=CHC(O)NMe_2 is stirred for 3 h at 80 °C (i.e., under the same conditions as employed for the preparation of **9** and **13**), in addition to the hydrido vinyl complex **11** the dihydrido compound **24** (see Scheme 4) is equally formed. Since in the IR spectra of the products obtained from methyl methacrylate and acid amides the C=O stretching mode appears at around 1555−1570 cm^{-1}, there is no doubt that the additional linkage of the vinyl ligand takes place via the C=O and not the OMe or NR_2 functionality.

Scheme 2[a]



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

In contrast to acrolein and CH_2=C(R′)C(O)H (R′ = Me, *i*Pr), the substituted aldehydes RCH=CHC(O)H (R = Me, Ph) react with the in situ generated cyclooctene derivative *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$ to give predominantly the carbonyl iridium(I) complex **14** instead of the expected hydrido(vinyl)iridium(III) compounds $[IrH(Cl)\{\kappa^2(C,O)\text{-}C(R){=}CHCH{=}O\}(PiPr_3)_2]$. In agreement with recent studies by Bianchini et al. on the reactivity of hydridorhodium(I) complexes toward RCH=CHC(O)H (R = Me, Ph),[15] we assume that the formation of **14** proceeds via the five-coordinate acyl hydrido intermediate $[IrH(Cl)\{\eta^1\text{-}C(O)CH{=}CHR\}(PiPr_3)_2]$, which rearranges to the six-coordinate hydrido vinyl species $[IrH(Cl)(\eta^1\text{-}CH{=}CHR)(CO)(PiPr_3)_2]$. In the final step, this species affords the carbonyl complex **14** and the olefin RCH=CH_2 by reductive elimination.

Treatment of a solution of the starting material *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$ in benzene with methyl acrylate led to the formation of the olefin iridium(I) complex **15** (Scheme 2), which is stable at room temperature and, after evaporation of the solvent and recrystallization from pentane, has been isolated as a red solid in 79% yield. In a similar way, by using either dimethyl fumarate or dimethyl maleate as the substrate, compound **16** was formed. On the basis of the observation that in the ^1H NMR spectrum of **16** two signals (doublets of virtual triplets) appear for the diastereotopic methyl protons of the P*i*Pr$_3$ units, we conclude that independent of whether (*Z*)- or (*E*)-RCH=CHR (R = CO_2Me) is used as the reagent, the olefinic ligand of **16** possesses an *E* configuration. The ^{31}P NMR spectrum of **16** displays a single resonance, which supports the proposed structure.

Either on warming at 80 °C (for **15**) or on irradiation in benzene (for **16**), the respective olefin compounds rearrange nearly quantitatively to the hydrido vinyl isomers **17** and **18**. Diagnostic features of **18** are the two resonances for the OCH_3 protons in the ^1H NMR and the two pairs of signals for the C=O and the OCH_3 carbon atoms in the ^{13}C NMR spectrum. The proposed stereochemistry of **18** with the phosphine ligands and the chloride and the α-carbon atom of the vinyl group in trans disposition has been confirmed by an X-ray

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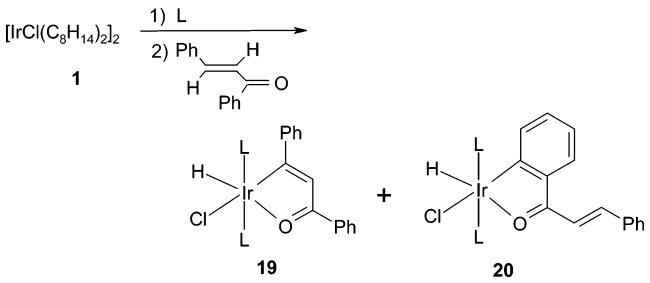
Scheme 3[a]



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

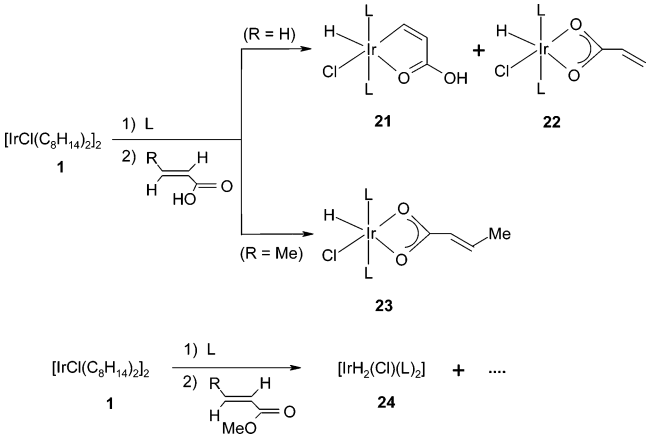
structure analysis.[16] The chelate ring is nearly planar with a maximum deviation of 0.013 and 0.011 Å for the metal-bonded oxygen and carbon atoms out of the plane. The distance between iridium and the vinylic α-carbon atom is 2.005(7) Å and is comparable to that in the hydrido vinyl complex [IrH(CH=CH$_2$)(κ^2-acac)(P*i*Pr$_3$)$_2$] (2.02(1) Å).[7b] The P−Ir−P axis is significantly bent (166.11(6)°) in the direction of the smallest (hydride) ligand, which is probably a consequence of steric repulsion between the isopropyl groups and the substituents at the vinyl moiety. The bending is quite similar to that found for [IrH(CH=CH$_2$)(κ^2-acac)(P*i*Pr$_3$)$_2$] (165.3(1)°).[7b]

Dual Behavior of Other Michael Systems. In contrast to cinnamic aldehyde, PhCH=CHC(O)H, which upon treatment with *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] affords the carbonyl complex **14**, the related phenyl ketone PhCH=CHC(O)Ph reacts with the in situ generated starting material *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] in toluene at 80 °C to give an orange-red product which consists of the two isomers **19** and **20** (Scheme 3). They are formed in a ratio of about 1:1 and can be separated by column chromatography. The NMR data of the "expected" isomer **19** are quite similar to those of compound **5**, which was prepared from *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] and PhCH=CHC(O)Me (see Scheme 1). Typical spectroscopic features of the second isomer **20**, being formed by aromatic and not by olefinic C−H activation, are a triplet resonance for the ipso carbon atom of the C$_6$H$_4$ ring at δ 165.2 ppm and two nearby singlets for the olefinic carbon atoms at δ 118.9 and 118.5 ppm, respectively. In contrast, the vinylic ring carbon atoms of **19** resonate in the ^{13}C NMR spectrum at δ 209.4 and 148.4 ppm. The hydride signal appears in the ^{1}H NMR spectrum of **19** at δ −22.88 ppm and in that of **20** at δ −23.98 ppm. Both signals are split into triplets with the ^{1}H−^{31}P coupling constants being nearly the same.

Similarly to the ketone PhCH=CHC(O)Ph, acrylic acid also reacts with the cyclooctene derivative *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] to afford the two isomeric products **21** and **22** in about equal quantities (Scheme 4). In this case, the reaction took place in toluene at room temperature and the products were separated by fractional crystallization. While the hydrido vinyl complex **21** is a white, only moderately air-sensitive solid, the hydrido carboxylato compound **22** is a yellow oil that has been characterized by IR and NMR spectroscopy. Diagnostic for **21** are the ν(OH) stretching mode in the IR spectrum at 3435 cm^{-1}, the two doublets for the vinyl protons at δ 9.72 and 6.87 ppm in the ^{1}H NMR spectrum, and the singlet resonance at δ 17.0 ppm in the ^{31}P NMR

(16) Schulz, M. Ph.D. Thesis, Universität Würzburg, 1991.

Scheme 4[a]



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

spectrum. Whereas in the ^{1}H NMR spectrum of **21** the triplet for the hydride is observed at δ −25.23 ppm, the corresponding triplet resonance in the ^{1}H NMR spectrum of **22** is significantly shifted upfield and appears at δ −34.80 ppm.

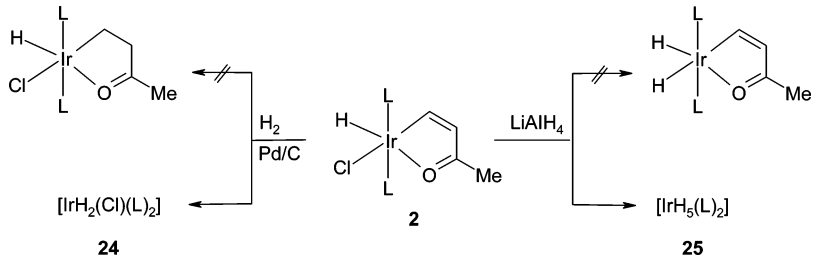
Under conditions similar to those used for the preparation of **21** and **22**, crotonic acid reacts with *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] to give a single product, which according to the analytical and spectroscopic data is the hydrido carboxylato complex **23** (see Scheme 4). The IR spectrum of **23** displays for the asymmetric OCO stretching mode a characteristic absorption at 1520 cm^{-1}, which indicates that the carboxylate unit is coordinated to iridium in a chelating fashion.[17] Note that in the IR spectrum of **21** the asymmetric ν(OCO) band is observed at 1510 cm^{-1}. The reactions of methyl crotonate and methyl cinnamate, RCH=CHCO$_2$Me (R = Me, Ph), with *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] proceed not by C−H activation of the olefinic substrate but yield instead, besides traces of undefined compounds, the dihydrido complex **24** as the main component.

Studies on the Reactivity of the Hydrido(vinyl)iridium(III) Complexes. In contrast to the hydrido(vinyl)ruthenium(II) derivatives [RuH{κ^2(*C*,*O*)-CH=C(Me)C(OR)=O}(PPh$_3$)$_3$] (R = Me, Et, *i*Pr), which react with H$_2$ at room temperature and 1 bar to give [RuH$_2$(H$_2$)(PPh$_3$)$_3$] and the corresponding ester Me$_2$CHCO$_2$R,[18] the hexacoordinate iridium(III) complex **2** is completely inert under a hydrogen atmosphere. Even when the pressure of H$_2$ is increased to 70 bar, no reaction occurs. However, if a solution of **2** in benzene is stirred in the presence of hydrogen and catalytic amounts of Pd on charcoal at 40 °C, the starting material affords the dihydride **24** and the saturated ketone EtC(O)Me by cleavage of the metal−carbon bond (Scheme 5). Although it is conceivable that in the initial step of this reaction a hydrogenation of the vinyl unit takes place, we failed to detect the supposed intermediate [IrH(Cl){κ^2(*C*,*O*)-CH$_2$CH$_2$C(Me)=O}(P*i*Pr$_3$)$_2$] by ^{1}H NMR or IR spectroscopy.

(17) (a) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912−1920. (b) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227−250. (c) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2, pp 435−459.

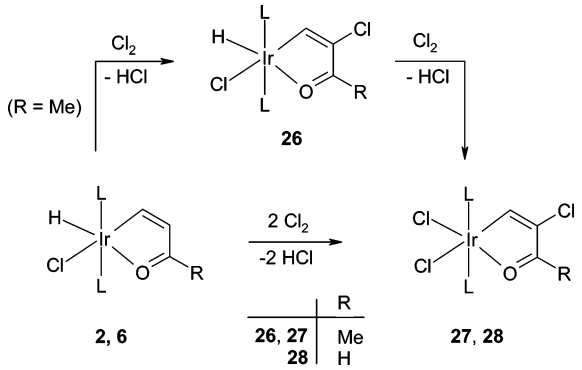
(18) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874−3884.

Scheme 5[a]



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

Scheme 6[a]



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

Scheme 7[a]

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

Attempts to prepare the dihydrido complex [IrH$_2$-{κ^2(*C*,*O*)-CH=CHC(Me)=O}(P*i*Pr$_3$)$_2$] by treatment of the hydrido chloro compound **2** with LiAlH$_4$, NaBH$_4$, or LiHBEt$_3$ also were unsuccessful. Independent of whether an equimolar amount or an excess of the hydride donor was used, both a substitution of the chloride and a replacement of the vinyl unit occurred. The sole iridium-containing product is the pentahydrido complex **25**, which was first prepared by Clerici et al. from [HP*i*Pr$_3$]-[IrCl$_4$(P*i*Pr$_3$)$_2$] and LiAlH$_4$[19] and later shown by Goldman and Halpern to be an appropriate catalyst for the selective hydrogenation of alkynes to alkenes.[20]

The reaction of compound **2** with a solution of Cl$_2$ in chloroform yields a mixture of two products, of which the dichloroiridium(III) derivative **27** dominates (Scheme 6). The minor component still contains a hydrido ligand, as indicated by the high-field resonance in the ^{1}H NMR spectrum at δ −24.26 ppm. Since this chemical shift differs only slightly from that of the precursor **2**, we assume that the byproduct is the hydrido chloro complex **26**. Treatment of the reaction mixture with an excess of chlorine in CHCl$_3$ leads to the conversion of **26** to **27** and gives this compound as a red air-stable solid in nearly quantitative yield. Both the mass spectrum and the ^{13}C NMR spectrum of **27** confirm that in the course of the chlorination reaction the Ir−C bond is not split and the chelate ring remains intact. A characteristic difference between the intermediate **26** and the final product **27** is observed in the ^{31}P NMR spectrum of the mixture, which shows a singlet for **26** at δ 9.1 ppm and a second singlet for **27** at δ −9.4 ppm. The reaction of the hydrido chloro compound **6** with Cl$_2$ in chloroform gives the dichloro complex **28**, the spectroscopic data of which are quite similar to those of **27**. Regarding the formation of **26** and **27** from **2** and Cl$_2$, we note that owing to previous work by Vrieze et al. the reaction of [IrH(Cl){κ^2(*C*,*N*)-C(Ph)=CHCH=N*i*Pr}(PPh$_3$)$_2$] with chlorine yields only the monochlorinated derivative [IrH-(Cl){κ^2(*C*,*N*)-C(Ph)=C(Cl)CH=N*i*Pr}(PPh$_3$)$_2$], which does not react with excess Cl$_2$ by splitting of the Ir−H bond.[21]

The hydrido iodo complex **29** was prepared in 80% yield by salt metathesis of **2** with an excess of NaI in acetone at room temperature (Scheme 7). Compound **29** is a yellow solid which has been characterized not only by elemental analysis and spectroscopic techniques but also by X-ray crystallography.[16] As expected, the molecular structure of **29** is similar to that of **18** and also has the two phosphines and the halide and the α-carbon atom of the vinyl group trans disposed. The bending of the P−Ir−P axes is 164.2(2)° and is thus slightly less than in **18**. The relatively short Ir−C distance of 1.83-(3) Å indicates that for **29** a second canonical form with an iridium−carbon double bond contributes to the structure for the five-membered ring.

To possibly generate a hydrido(vinyl)iridium(III) complex containing a monodentate vinyl ligand, we also displaced the chloride in compound **2** with acetate. Treatment of a solution of **2** in acetone with an equimolar amount of CH$_3$CO$_2$Ag at room temperature led to the formation of **30**, which, according to the IR and NMR data, is the sole reaction product. In contrast to what we expected, the acetate ligand is probably not coordinated in a bidentate but in a monodentate fashion, as indicated by the position of the corresponding C=O stretching mode in the IR spectrum at 1625 cm^{-1}.[17] In the ^{1}H NMR spectrum of **30**, the IrH and the vinylic protons resonate at about the same chemical shift as those of the hydrido iodo complex **29**, which is in agreement with the proposed structure.

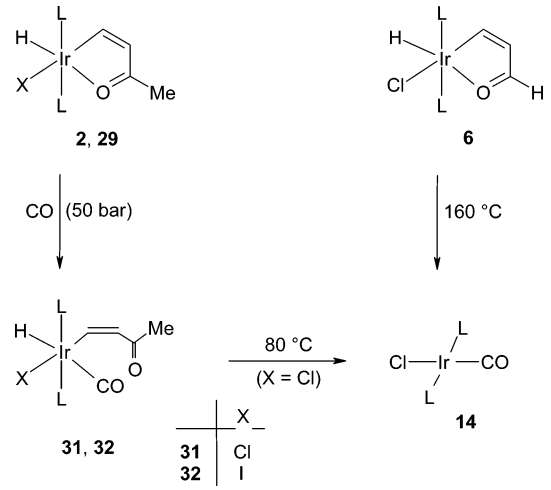
A cleavage of the Ir−O bond of the five-membered chelate ring occurs, if solutions of **2** or **29** in benzene are treated with CO at 50 bar for 48 h at room temperature. After the pressure is released and the solvent evaporated, pale yellow (**31**) or yellow (**32**) air-

(19) Clerici, M. G.; di Gioacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379−388.

(20) Goldman, A. S.; Halpern, J. *J. Organomet. Chem.* **1990**, *382*, 237−253.

(21) van Baar, J. F.; Klerks, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *112*, 95−103.

Scheme 8[a]



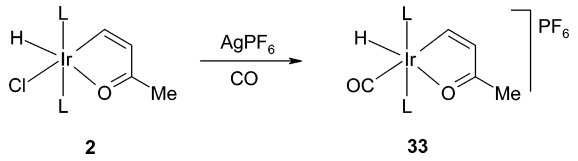
[a] L = P*i*Pr$_3$.

stable microcrystalline solids are isolated in 80−90% yield (Scheme 8). The ^{1}H NMR spectra of **31** and **32** display in the low-field region two signals—one doublet of doublet of triplets at about δ 8.8 ppm and a doublet of triplets at about δ 6.8 ppm—which are assigned to the vinylic protons in α- and β-positions. The ^3J(H,H) coupling constant of ca. 12 Hz indicates that the two protons at the C=C double bond are cis disposed. Due to the different trans influences of oxygen and CO, the hydride resonance appears for **31** at δ −8.14 ppm and for **32** at δ −9.68 ppm and is thus shifted by 15.5 to 14.4 ppm downfield in comparison with the chelate complexes **2** and **29**. A significant difference also exists in the chemical shift of the ^{13}C NMR signal for the IrCH carbon atom, which appears for **2** at δ 198.8 ppm and for **31** at δ 144.7 ppm.

While a solid sample of **31** is thermally rather stable and decomposes at 146 °C, warming a solution of **31** in benzene for 2 h at 80 °C leads to reductive elimination of methyl vinyl ketone and to the formation of **14** as the only detectable iridium-containing product. Quite remarkably, the carbonyl complex **14** is also generated upon stirring a solution of **6** in mesitylene for 3 h at 160 °C. Regarding the mechanism of this reaction, it is conceivable that in the initial step a partial opening of the chelate ring occurs, which is followed by elimination of acrolein. Under the reaction conditions, a fragmentation of acrolein to C_2H_4 and CO probably takes place and the carbon monoxide finally stabilizes the remaining [IrCl(P*i*Pr$_3$)$_2$] fragment to give **14**.

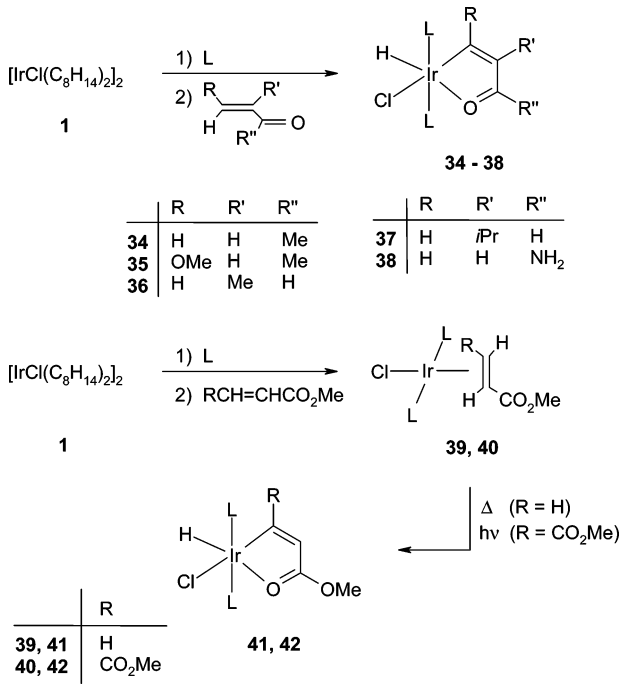
To obtain a coordinatively unsaturated hydrido(vinyl)iridium(III) complex, which could be a useful precursor for addition and/or insertion reactions, we attempted to abstract the chloro ligand from **2** by treatment with a PF_6^- salt. Whereas the starting material **2**, dissolved in acetone or dichloromethane, is relatively inert in the presence of KPF_6, the reaction of **2** with $AgPF_6$ yields, besides AgCl, an ill-defined product that possibly contains the required compound [IrH{κ^2(*C*,*O*)-CH=CHC(Me)=O}(P*i*Pr$_3$)$_2$]PF$_6$. However, if the reaction of **2** with KPF_6 (or $AgPF_6$) was carried out under a CO atmosphere, a quick change of color from yellow to off-white occurred, and after filtration through a column of Al_2O_3, removal of the solvent, and recrystallization from CH_2Cl_2/hexane white air-stable crystals of the cationic

Scheme 9[a]



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

Scheme 10[a]

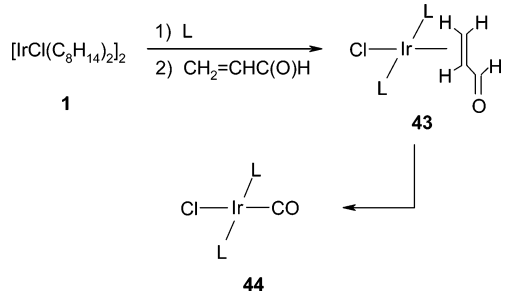


[a] L = PMe*t*Bu$_2$.

carbonyl hydrido complex **33** were obtained (Scheme 9). The molar conductivity Λ in nitromethane of 79.6 Ω^{-1} cm^2 mol^{-1} confirmed the presence of a 1:1 electrolyte. Typical spectroscopic features of **33** are the two ^{1}H NMR resonances for the vinylic protons at δ 10.17 and 7.50 ppm, the hydride signal at δ −20.68 ppm, and the singlet in the ^{31}P NMR spectrum at δ 25.5 ppm, indicating that, similarly to **2**, also in **33** the phosphine ligands are trans disposed. The IR spectrum of **33** shows a strong band for the CO ligand at 2050 cm^{-1} and a medium-to-strong absorption for the ν(C=O) stretching mode at 1565 cm^{-1}. The latter is shifted by 25 cm^{-1} to higher wavenumbers in comparison with **2**.

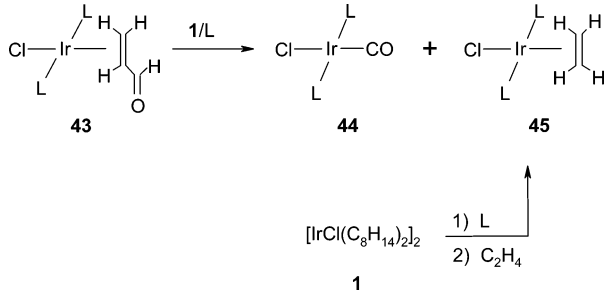
(Olefin)iridium(I) and Hydrido(vinyl)iridium(III) Complexes with [Ir(PMe*t*Bu$_2$)$_2$] as a Molecular Unit. Taking into consideration that occasionally even small changes in the size and symmetry of tertiary phosphines lead to significant differences in the reactivity of the corresponding phosphine−transition-metal complexes, a series of (olefin)iridium(I) and hydrido(vinyl)iridium(III) compounds with Ir(PMe*t*Bu$_2$)$_2$ instead of Ir(P*i*Pr$_3$)$_2$ as a molecular building block were also prepared. The general result is that ketones RCH=CHC(O)Me (R = H, OMe), aldehydes CH$_2$=C(R)C(O)H (R = Me, *i*Pr), and acrylic acid amide react with a mixture of **1** and PMe*t*Bu$_2$ in benzene to give the hexacoordinate hydrido(vinyl) complexes **34**−**38** in excellent yield (Scheme 10). Although we have no convincing evidence that upon addition of a 4−5-fold excess of PMe*t*Bu$_2$ to a solution of **1** the cyclooctene derivative

Scheme 11[a]



[a] L = PMe*t*Bu$_2$.

Scheme 12[a]



[a] L = PMe*t*Bu$_2$.

trans-[IrCl(C_8H_{14})(PMe*t*Bu$_2$)$_2$] is formed, we assume that in analogy to the corresponding reaction of **1** with P*i*Pr$_3$ such an intermediate is generated.[9b] After addition of the Michael system to this intermediate, a stepwise change of color from yellow to red and then from red to yellow occurred, indicating that en route to the thermodynamically preferred iridium(III) complexes **34**−**38** the isomeric iridium(I) compounds *trans*-[IrCl{η^2-RCH=C(R′)C(O)R″}(PMe*t*Bu$_2$)$_2$] were probably formed.

With methyl acrylate and either dimethyl fumarate or dimethyl maleate the expected olefin complexes **39** and **40** were prepared and characterized by elemental analysis and spectroscopic means. The NMR data of **40** are very similar to those of the P*i*Pr$_3$ counterpart, and thus there is no doubt that, independent of whether (*E*)- or (*Z*)-RCH=CHR (R = CO_2Me) is used as the precursor, the (dimethyl fumarate)iridium(I) compound is generated. Either on heating at 80 °C (in the case of **39**) or on irradiation (in the case of **40**), the olefin complexes rearrange to the hydrido(vinyl)iridium(III) isomers **41** and **42**, which are also isolated in excellent yields.

While we failed to detect the supposed intermediate *trans*-[IrCl{η^2-CH_2=CHC(O)H}(P*i*Pr$_3$)$_2$] in the reaction of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with acrolein, we succeeded in isolating the Ir(PMe*t*Bu$_2$)$_2$ counterpart **43** (Scheme 11). For this purpose, the reaction mixture of *trans*-[IrCl(C_8H_{14})(PMe*t*Bu$_2$)$_2$] and CH_2=CHC(O)H was stirred only for a few minutes at room temperature and then quickly worked up as described for **15**. Compound **43** is a red, practically air-stable solid, the composition of which has been confirmed by elemental analysis and spectroscopic techniques. Diagnostic for the coordinated acrolein in **43** are the doublet resonance at δ 9.25 ppm for the aldehyde proton and the two signals at δ 3.40 and 1.54 ppm for the olefinic protons in the ^{1}H NMR spectrum. The ^{31}P nuclei resonate at δ 5.9 ppm, the chemical shift being similar to that of **39**. Attempts to convert the olefin complex **43** to the hydrido vinyl isomer [IrH(Cl){κ^2(*C*,*O*)-CH=CHCH=O}(PMe*t*Bu$_2$)$_2$] resulted in the formation of the iridium(I) carbonyl **44**. We assume that the mechanism of this reaction is similar to that proposed for the formation of **14** from *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] and RCH=CHC(O)H, including an acyl(hydrido)iridium(III) species as an intermediate. In this context we note that the half-sandwich-type compound [(η^5-C_5Me_5)Ir(CH_3)(OTf)(PMe_3)] reacts with acrolein to give the olefin complex [(η^5-C_5Me_5)Ir(CH_3){η^2-CH_2=CHC(O)H}(PMe_3)]OTf, which upon warming afforded the iridium(III) carbonyl derivative [(η^5-C_5Me_5)Ir(CH=CH_2)(CO)(PMe_3)]OTf by elimination of methane.[22]

A surprising result was obtained when the acrolein complex **43** reacted with the in situ generated compound *trans*-[IrCl(C_8H_{14})(PMe*t*Bu$_2$)$_2$]. After the reaction mixture was stirred for 30 min in benzene at room temperature and the solvent evaporated in vacuo, an orange solid was isolated, which according to the ^{1}H and ^{31}P NMR spectra consisted of an 1:1 mixture of the iridium(I) complexes **44** and **45** (Scheme 12). The olefin compound **45** was identified by comparison of the spectroscopic data with that of an authentic sample prepared from *trans*-[IrCl(C_8H_{14})(PMe*t*Bu$_2$)$_2$] and ethene. To explain the formation of the two products, we assume that the labile cyclooctene derivative partly dissociates to generate the coordinatively unsaturated intermediate [IrCl(PMe*t*Bu$_2$)$_2$], which attacks the ligated acrolein possibly at the C=O bond to give both the metal carbonyl **44** and the olefin complex **45**. Alternatively, it is also conceivable that in the initial step the acrolein compound **43** is converted to **44** and ethene, which then reacts with *trans*-[IrCl(C_8H_{14})(PMe*t*Bu$_2$)$_2$] by ligand displacement to afford **45** and cyclooctene.

Conclusions

The present investigation has shown that iridium(I) compounds of the general composition *trans*-[IrCl(C_8H_{14})(PR_3)$_2$] (PR_3 = P*i*Pr$_3$, PMe*t*Bu$_2$) containing a labile cyclooctene ligand react with substituted olefins CH_2=CHR′, where R′ is an aldehyde, ketone, carboxylic acid, carboxylic ester, or carboxylic amide functionality, to give hydrido(vinyl)iridium(III) complexes in high yields. These hydrido(vinyl)iridium(III) complexes are definitely (in the case of **17**, **18**, **41**, and **42**) or probably (in the case of **2**−**13**, **19**−**21**, and **34**−**38**) formed via the olefin iridium(I) intermediates *trans*-[IrCl(η^2-CH_2=CHR′)(PR_3)$_2$], which, however, are thermodynamically less stable than the IrH(CH=CHR′) isomers. The high energy barrier, which had previously been observed for most of the reactions involving a C−H activation of a coordinated olefin, is obviously reduced if the C=C double bond bears an electron-withdrawing substituent such as C(O)H, C(O)R, C(O)OH, C(O)OR, C(O)NH_2, and C(O)NMe_2. The formation of the hydrido(vinyl)iridium(III) complexes is certainly facilitated by the coordination of the C=O oxygen atom to the metal center, thus leading to an unusually stable chelate system. It is noteworthy indeed that the five-membered IrC_3O ring in compounds such as **2** and **6** even remains intact if these starting materials are treated with excess Cl_2. A

(22) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 5269−5270.

partial opening of the chelate bond only occurs if precursors such as **2** and **29** are treated with carbon monoxide under severe conditions, which could be due to the preferred ability of iridium to coordinate a CO ligand.[23]

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials $[IrCl(C_8H_{14})_2]_2$ (**1**),[24] *trans*-$[IrCl(N_2)(PPh_3)_2]$ (**A**),[25] and $PMetBu_2$[26] were prepared as described in the literature. P*i*Pr$_3$ was a commercial product from Strem. NMR spectra were recorded on JEOL FX 90 Q, Bruker AC 200, and Bruker AMX 400 instruments at room temperature, if not otherwise stated. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer and mass spectra on a Varian MAT CH 7 instrument. The molar conductivity Λ_M was determined in nitromethane. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal. The term vt indicates a virtual triplet, with $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(Me)=O}-(P*i*Pr$_3$)$_2$] (2). A suspension of **1** (120 mg, 0.13 mmol) in benzene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (120 μL, 0.60 mmol) and then with methyl vinyl ketone (23 μL, 0.26 mmol) at room temperature. After the reaction mixture was stirred for 30 min, a yellow solution was obtained. The solvent was evaporated in vacuo, the oily residue was dissolved in benzene/hexane (6 mL; 1:2), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 8 cm). With benzene/hexane (1:2) a yellow fraction was eluted, which was concentrated in vacuo until the first crystals precipitated. After hexane (5 mL) was added, the solution was stored at −78 °C for 12 h. A yellow microcrystalline solid was formed, which was separated from the mother liquor, washed twice with small amounts of hexane (0 °C), and dried: yield 141 mg (85%); mp 167 °C. Anal. Calcd for $C_{22}H_{48}ClIrOP_2$: C, 42.74; H, 7.83. Found: C, 42.67; H, 7.72. MS (70 eV): *m/z* (*I*$_r$) 618 (M$^+$, 29), 548 (M$^+$ − CH_2=CHC(O)Me, 44), 458 (M$^+$ − P*i*Pr$_3$, 24), 70 (CH_2=CHC(O)Me$^+$, 100). IR (KBr): ν(IrH) 2230, ν(C=O) 1540 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.72 (d, *J*(H,H) = 7.3 Hz, 1 H, IrCH), 6.80 (d, *J*(H,H) = 7.3 Hz, 1 H, IrCH=C*H*), 2.37 (m, 6 H, PC*H*CH$_3$), 2.24 (br s, 3 H, C(O)CH$_3$), 1.21, 1.04 (both dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −23.67 (t, *J*(P,H) = 15.8 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 207.1 (s, C=O), 198.8 (t, *J*(P,C) = 6.1 Hz, IrCH), 133.2 (s, IrCH=*C*H), 24.9 (s, C(O)*C*H$_3$), 24.4 (vt, *N* = 27.4 Hz, P*C*HCH$_3$), 19.1, 18.1 (both s, PCH*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 18.9 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(OMe)=CHC(Me)=O}(P*i*Pr$_3$)$_2$] (3). This compound was prepared analogously as described for **2**, using **1** (160 mg, 0.17 mmol), P*i*Pr$_3$ (160 μL, 0.80 mmol), and MeOCH=CHC(O)Me (0.35 μL, 0.35 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. A white microcrystalline solid was obtained: yield 197 mg (85%); mp 209 °C. Anal. Calcd for $C_{23}H_{50}ClIrO_2P_2$: C, 42.61; H, 7.77. Found: C, 42.75; H, 7.81. MS (70 eV): *m/z* (*I*$_r$) 648 (M$^+$, 100), 612 (M$^+$ − HCl, 16), 548 (M$^+$ − MeOCH=CHC(O)Me, 35), 488 (M$^+$ − P*i*Pr$_3$, 34), 100 (MeOCH=CHC(O)Me$^+$, 46). IR (KBr): ν(IrH) 2275, ν(C=O) 1525 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.22 (s, 1 H, IrCH=C*H*), 3.65 (s, 3 H, OCH$_3$), 2.50 (m, 6 H, PC*H*CH$_3$), 2.19 (br s, 3 H, C(O)CH$_3$), 1.30, 1.16 (both dvt, *N* = 13.4, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −23.62 (t, *J*(P,H) = 16.0 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 213.7 (t, *J*(P,C) = 6.2 Hz, Ir*C*(OMe)), 203.6 (s, C=O), 107.9 (s, IrCH=*C*H), 56.9 (s, OCH$_3$), 24.7 (s, C(O)*C*H$_3$), 24.2 (vt, *N* = 27.3 Hz, P*C*HCH$_3$), 19.1, 18.9 (both s, PCH*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 16.0 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(Me)=CHC(Me)=O}-(P*i*Pr$_3$)$_2$] (4). This compound was prepared analogously as described for **2**, using **1** (160 mg, 0.17 mmol), P*i*Pr$_3$ (160 μL, 0.80 mmol), and MeCH=CHC(O)Me (0.34 μL, 0.35 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. A yellow microcrystalline solid was obtained: yield 169 mg (75%); mp 183 °C dec. Anal. Calcd for $C_{23}H_{50}ClIrOP_2$: C, 43.69; H, 7.97. Found: C, 43.60; H, 8.21. MS (70 eV): *m/z* (*I*$_r$) 632 (M$^+$, 21), 548 (M$^+$ − MeCH=CHC(O)Me, 57), 84 (MeCH=CHC(O)Me$^+$, 100). IR (KBr): ν(IrH) 2255, ν(C=O) 1550 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.58 (s, 1 H, IrC(Me)=C*H*), 2.44 (s, 3 H, IrCCH$_3$), 2.36 (m, 6 H, PC*H*CH$_3$), 2.12 (t, *J*(P,H) = 1.3 Hz, 3 H, C(O)CH$_3$), 1.18, 0.98 (both dvt, *N* = 13.3, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −24.35 (t, *J*(P,H) = 16.2 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 214.1 (t, *J*(P,C) = 5.3 Hz, IrCH), 205.7 (s, C=O), 133.8 (s, IrCH=*C*H), 37.3 (s, Ir*C*CH$_3$), 24.6 (s, C(O)*C*H$_3$), 24.4 (vt, *N* = 27.4 Hz, P*C*HCH$_3$), 19.8, 18.8 (both s, PCH*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 12.1 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(Ph)=CHC(Me)=O}-(P*i*Pr$_3$)$_2$] (5). This compound was prepared analogously as described for **2**, using **1** (160 mg, 0.17 mmol), P*i*Pr$_3$ (160 μL, 0.80 mmol), and PhCH=CHC(O)Me (149 mg, 1.00 mmol) as starting materials. The reaction mixture was stirred for 3 h at 80 °C. An orange microcrystalline solid was obtained: yield 221 mg (89%); mp 159 °C dec. Anal. Calcd for $C_{28}H_{52}ClIrOP_2$: C, 48.44; H, 7.35. Found: C, 48.18; H, 7.57. MS (70 eV): *m/z* (*I*$_r$) 694 (M$^+$, 3), 548 (M$^+$ − PhCH=CHC(O)Me, 13), 146 (PhCH=CHC(O)Me$^+$, 100). IR (KBr): ν(IrH) 2245, ν(C=O) 1535 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.91, 7.21 (both m, 5 H, C_6H_5), 2.43 (m, 6 H, PC*H*CH$_3$), 2.31 (t, *J*(P,H) = 1.5 Hz, 3 H, C(O)CH$_3$), 1.11, 1.03 (both dvt, *N* = 13.7, *J*(H,H) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −23.75 (t, *J*(P,H) = 16.8 Hz, 1 H, IrH), signal of IrCH=C*H* proton probably covered by signals of the phenyl protons. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 207.4 (t, *J*(P,C) = 5.1 Hz, IrC), 205.9 (s, C=O), 147.7 (s, IrC=*C*H), 131.2, 130.8, 129.5, 127.5 (all s, C_6H_5), 25.0 (vt, *N* = 27.1 Hz, P*C*HCH$_3$), 19.8, 19.3 (both s, PCH*C*H$_3$), signal of C(O)*C*H$_3$ methyl carbon atom probably covered by signal of PCH*C*H$_3$ carbons. ^{31}P NMR (36.3 MHz, C_6D_6): δ 6.9 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHCH=O}(P*i*Pr$_3$)$_2$] (6). This compound was prepared analogously as described for **2**, using **1** (140 mg, 0.15 mmol), P*i*Pr$_3$ (150 μL, 0.75 mmol), and acrolein (0.20 μL, 0.30 mmol) as starting materials. A yellow microcrystalline solid was obtained: yield 155 mg (82%); mp 165 °C dec. Anal. Calcd for $C_{21}H_{46}ClIrOP_2$: C, 41.74; H, 7.67. Found: C, 41.65; H, 7.70. MS (70 eV): *m/z* (*I*$_r$) 604 (M$^+$, 27), 548 (M$^+$ − CH_2=CHC(O)H, 31), 444 (M$^+$ − P*i*Pr$_3$, 10), 56 (CH_2=CHC(O)H$^+$, 100). IR (KBr): ν(IrH) 2250, ν(C=O) 1530 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.26 (dd, *J*(H,H) = 2.0 and 7.3 Hz, 1 H, IrCH), 8.83 (ddt, *J*(H,H) = 2.0 and 2.7, *J*(P,H) = 2.4 Hz, 1 H, C(O)H), 6.99 (d, *J*(H,H) = 7.3 Hz, 1 H, IrCH=C*H*), 2.43 (m, 6 H, PC*H*CH$_3$), 1.26, 1.12 (both dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −23.19 (dt, *J*(H,H) = 2.7, *J*(P,H) = 15.8 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 206.6 (t, *J*(P,C) = 6.1 Hz, IrCH), 197.7 (s, C=O), 133.1 (s, IrCH=*C*H), 24.5 (vt, *N* = 27.5 Hz, P*C*HCH$_3$), 19.1, 18.9 (both s, PCH*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 20.0 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=C(Me)CH=O}-(P*i*Pr$_3$)$_2$] (7). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), P*i*Pr$_3$ (120 μL, 0.60 mmol), and methacrolein (22 μL, 0.26 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C.

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An orange microcrystalline solid was obtained: yield 137 mg (83%); mp 167 °C dec. Anal. Calcd for $C_{22}H_{48}ClIrOP_2$: C, 42.74; H, 7.83. Found: C, 42.94; H, 8.01. MS (70 eV): *m/z* (I_r) 618 (M^+, 22), 548 ($M^+ - CH_2{=}C(Me)C(O)H$, 28), 458 ($M^+ - Pi Pr_3$, 12), 70 ($CH_2{=}C(Me)C(O)H^+$, 100). IR (KBr): ν(IrH) 2275, ν(C=O) 1555 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 10.76 (d, *J*(H,H) = 2.0 Hz, 1 H, IrCH), 8.56 (ddt, *J*(H,H) = 2.0 and 2.7, *J*(P,H) = 2.4 Hz, 1 H, C(O)H), 2.43 (m, 6 H, PC*H*CH_3), 1.77 (s, 3 H, IrCH=CC*H*$_3$), 1.18, 1.16 (both dvt, *N* = 13.2, *J*(H,H) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −23.44 (dt, *J*(H,H) = 2.7, *J*(P,H) = 16.0 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 198.5 (s, C=O), 198.3 (t, *J*(P,C) = 6.1 Hz, IrCH), 138.8 (s, IrCH=*C*H), 24.1 (vt, *N* = 27.4 Hz, P*C*HCH$_3$), 19.2, 19.1 (both s, PCH*C*H$_3$), 15.8 (s, =C*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 20.9 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=C(*i*Pr)CH=O}-(P*i*Pr$_3$)$_2$] (8). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), P*i*Pr$_3$ (120 μL, 0.60 mmol), and $CH_2{=}C(iPr)C(O)H$ (26 μL, 0.26 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. An orange microcrystalline solid was obtained: yield 147 mg (85%); mp 170 °C dec. Anal. Calcd for $C_{24}H_{52}ClIrOP_2$: C, 44.60; H, 8.11. Found: C, 44.39; H, 8.41. MS (70 eV): *m/z* (I_r) 646 (M^+, 42), 548 ($M^+ - CH_2{=}C(iPr)C(O)H$, 71), 486 ($M^+ - Pi Pr_3$, 17), 98 ($CH_2{=}C(iPr)C(O)H^+$, 100). IR (KBr): ν(IrH) 2240, ν(C=O) 1550 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 10.85 (d, *J*(H,H) = 2.5 Hz, 1 H, IrCH), 8.68 (ddt, *J*(H,H) = 2.5 and 2.7, *J*(P,H) = 2.4 Hz, 1 H, C(O)H), 2.48 (m, 6 H, PC*H*CH_3), 1.29, 1.12 (both dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), 1.00 (d, *J*(H,H) = 7.0 Hz, 6 H, CCHC*H*$_3$), −23.38 (dt, *J*(H,H) = 2.7, *J*(P,H) = 16.2 Hz, 1 H, IrH), signal of C*H*CH_3 probably covered by signal of PC*H*CH_3 protons. ^{31}P NMR (36.3 MHz, C_6D_6): δ 19.7 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=C(Me)C(OMe)=O}(P*i*Pr$_3$)$_2$] (9). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), P*i*Pr$_3$ (120 μL, 0.60 mmol), and $CH_2{=}C(Me)CO_2Me$ (28 μL, 0.26 mmol) as starting materials. The reaction mixture was stirred for 3 h at 80 °C. A white microcrystalline solid was obtained: yield 149 mg (86%); mp 192 °C dec. Anal. Calcd for $C_{23}H_{50}ClIrO_2P_2$: C, 42.61; H, 7.77. Found: C, 42.20; H, 7.55. MS (70 eV): *m/z* (I_r) 648 (M^+, 17), 548 ($M^+ - CH_2{=}C(Me)CO_2Me$, 47), 488 ($M^+ - Pi Pr_3$, 9), 100 ($CH_2{=}C(Me)CO_2Me^+$, 100). IR (KBr): ν(IrH) 2260, ν(C=O) 1590 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 9.67 (s, 1 H, IrCH), 3.88 (s, 3 H, OCH_3), 2.46 (m, 6 H, PC*H*CH_3), 1.80 (s, 3 H, IrCH=CC*H*$_3$), 1.25, 1.11 (both dvt, *N* = 13.3, *J*(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −26.45 (t, *J*(P,H) = 15.3 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 180.8 (s, C=O), 174.8 (t, *J*(P,C) = 7.7 Hz, IrCH), 123.9 (s, IrCH=*C*), 52.9 (s, OCH_3), 24.1 (vt, *N* = 26.4 Hz, P*C*HCH$_3$), 19.1, 18.8 (both s, PCH*C*H$_3$). ^{31}P NMR (36.3 MHz, C_6D_6): δ 18.8 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(NH$_2$)=O}-(P*i*Pr$_3$)$_2$] (10). A suspension of **1** (150 mg, 0.16 mmol) in benzene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (160 μL, 0.80 mmol) and then with acrylic acid amide (24 mg, 0.32 mmol) at room temperature. After the reaction mixture was irradiated for 1 h in an ultrasonic bath, a colorless solution was obtained. The solution was concentrated in vacuo to ca. 3 mL and stored for 6 h. A white microcrystalline solid precipitated, which was recrystallized from CH_2Cl_2/hexane (1:5, 6 mL): yield 185 mg (89%); mp 235 °C dec. Anal. Calcd for $C_{21}H_{47}ClIrNOP_2$: C, 40.73; H, 7.65; N, 2.26. Found: C, 41.08; H, 7.63; N, 2.35. MS (70 eV): *m/z* (I_r) 619 (M^+, 7), 548 ($M^+ - CH_2{=}CHC(O)NH_2$, 9), 459 ($M^+ - Pi Pr_3$, 9), 71 ($CH_2{=}CHC(O)NH_2^+$, 100). IR (KBr): ν(NH) 3340, 3210, ν(IrH) 2275, ν(C=O) 1555 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 9.87 (d, *J*(H,H) = 7.3 Hz, 1 H, IrCH), 6.22 (d, *J*(H,H) = 7.3 Hz, 1 H, IrCH=C*H*), 2.51 (m, 6 H, PC*H*CH_3), 1.29, 1.17 (both dvt, *N* = 13.2, *J*(H,H) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −25.74 (t, *J*(P,H) = 16.1 Hz, 1 H, IrH), signal of NH_2 protons not exactly located. ^{31}P NMR (36.3 MHz, $CDCl_3$): δ 18.0 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(NMe$_2$)=O}-(P*i*Pr$_3$)$_2$] (11). A suspension of **1** (200 mg, 0.22 mmol) in benzene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (200 μL, 1.00 mmol) and then with $CH_2{=}CHC(O)NMe_2$ (45 μL, 0.44 mmol) at room temperature. After the reaction mixture was stirred for 17 days in the dark, a colorless solution was obtained. The solvent was evaporated in vacuo, and the remaining white microcrystalline solid was washed three times with 5 mL portions of hexane (0 °C) and dried: yield 228 mg (79%); mp 206 °C dec. Anal. Calcd for $C_{23}H_{51}ClIrNOP_2$: C, 42.68; H, 7.94; N, 2.16. Found: C, 42.81; H, 8.14; N, 2.10. MS (70 eV): *m/z* (I_r) 647 (M^+, 18), 548 ($M^+ - CH_2{=}CHC(O)NMe_2$, 20), 487 ($M^+ - Pi Pr_3$, 18), 99 ($CH_2{=}CHC(O)NMe_2^+$, 100). IR (KBr): ν(IrH) 2230, ν(C=O) 1570 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 9.88 (d, *J*(H,H) = 7.9 Hz, 1 H, IrCH), 6.48 (d, *J*(H,H) = 7.9 Hz, 1 H, IrCH=C*H*), 3.10, 3.04 (both s, 3 H each, NCH_3), 2.52 (m, 6 H, PC*H*CH_3), 1.31, 1.13 (both dvt, *N* = 13.4, *J*(H,H) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −25.16 (t, *J*(P,H) = 15.6 Hz, 1 H, IrH]. ^{31}P NMR (36.3 MHz, $CDCl_3$): δ 18.8 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=C(Me)C(NH$_2$)=O}(P*i*Pr$_3$)$_2$] (12). This compound was prepared analogously as described for **10**, using **1** (100 mg, 0.11 mmol), P*i*Pr$_3$ (100 μL, 0.50 mmol), and $CH_2{=}C(Me)C(O)NH_2$ (19 mg, 0.22 mmol) as starting materials. A white microcrystalline solid was obtained: yield 126 mg (89%); mp 174 °C dec. Anal. Calcd for $C_{22}H_{49}ClIrNOP_2$: C, 41.73; H, 7.80; N, 2.21. Found: C, 42.08; H, 8.10; N, 2.13. MS (70 eV): *m/z* (I_r) 633 (M^+, 9), 597 ($M^+ - HCl$, 1), 548 ($M^+ - CH_2{=}C(Me)C(O)NH_2$, 10), 85 ($CH_2{=}C(Me)C(O)NH_2^+$, 100). IR (KBr): ν(NH) 3300, 3195, ν(IrH) 2250, ν(C=O) 1560 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 9.18 (br s, 1 H, IrCH), 2.42 (m, 6 H, PC*H*CH_3), 1.63 (br s, 3 H, =CCH_3), 1.26, 1.15 (both dvt, *N* = 13.2, *J*(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$), −25.46 (t, *J*(P,H) = 15.9 Hz, 1 H, IrH), signal of NH_2 protons not exactly located. ^{31}P NMR (36.3 MHz, $CDCl_3$): δ 17.9 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(Ph)=CHC(NH$_2$)=O}-(P*i*Pr$_3$)$_2$] (13). A suspension of **1** (160 mg, 0.18 mmol) in benzene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (160 μL, 0.80 mmol) and then with cinnamic acid amide (60 mg, 0.36 mmol) at room temperature. After the reaction mixture was stirred for 3 h at 80 °C, a yellow solution was obtained. The solution was concentrated in vacuo to ca. 3 mL and stored for 6 h. A yellow microcrystalline solid precipitated, which was recrystallized from CH_2Cl_2/hexane (1:5, 6 mL): yield 186 mg (75%); mp 201 °C dec. Anal. Calcd for $C_{27}H_{51}ClIrNOP_2$: C, 46.64; H, 7.39; N, 2.01. Found: C, 46.83; H, 7.23; N, 2.21. MS (70 eV): *m/z* (I_r) 695 (M^+, 10), 548 ($M^+ - PhCH{=}CHC(O)NH_2$, 20), 147 ($PhCH{=}CHC(O)NH_2^+$, 100). IR (KBr): ν(NH) 3370, 3190, ν(IrH) 2260, ν(C=O) 1565 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.68, 7.21 (both m, 5 H, C_6H_5), 6.73 (t, *J*(P,H) = 1.3 Hz, 1 H, IrC(Ph)=C*H*), 2.50 (m, 6 H, PC*H*CH_3), 1.17, 1.14 (both dvt, *N* = 13.3, *J*(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$), −26.05 (t, *J*(P,H) = 16.5 Hz, 1 H, IrH), signal of NH_2 protons not exactly located. ^{31}P NMR (36.3 MHz, CD_2Cl_2): δ 6.9 (s, d in off-resonance).

Reaction of the Starting Materials 1 and P*i*Pr$_3$ with RCH=CHC(O)H (R = Me, Ph). A suspension of **1** (80 mg, 0.09 mmol) in toluene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (80 μL, 0.40 mmol) and then with crotonaldehyde (15 μL, 0.18 mmol) or cinnamic aldehyde (23 μL, 0.18 mmol), respectively. Since at room temperature no reaction occurred, the solution was stirred for 2 h at 80 °C. A pale yellow solution was obtained, which, after it was cooled to 20 °C, was evaporated in vacuo. The ^1H and ^{31}P NMR spectra revealed that the residue contained, besides traces of undefined compounds, the carbonyl complex *trans*-[IrCl(CO)-

($PiPr_3$)$_2$] (**14**) as the main component. It was identified by comparison of the NMR data with those of an authentic sample.[27]

Preparation of *trans*-[IrCl(η^2-CH_2=$CHCO_2Me$)($PiPr_3$)$_2$] (15). A suspension of **1** (150 mg, 0.16 mmol) in toluene (5 mL) was treated under continuous stirring first with $PiPr_3$ (160 μL, 0.80 mmol) and then with methyl acrylate (29 μL, 0.32 mmol). After the reaction mixture was stirred for 5 min at room temperature, a red solution was obtained. The solvent was evaporated in vacuo, the residue was dissolved in pentane (3 mL), and the solution was stored for 12 h at −78 °C. A red microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of hexane (0 °C), and dried: yield 168 mg (79%); mp 110 °C dec. Anal. Calcd for $C_{22}H_{48}ClIrO_2P_2$: C, 41.66; H, 7.63. Found: C, 41.57; H, 7.71. MS (70 eV): *m/z* (I_r) 548 ($M^+ - CH_2$=$CHCO_2Me$, 8), 86 (CH_2=$CHCO_2Me^+$, 100). IR (KBr): ν(C=O) 1760 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 3.58 (m, 1 H, =C*H*CO_2Me), 3.42 (s, 3 H, OCH_3), 3.10, 2.44 (both m, 3 H each, PC*H*CH_3), 2.54, 1.77 (both m, 1 H each, =CH_2), 1.29 (m, 36 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 15.8, 13.8 (AB spin system, J(P,P) = 365 Hz).

Preparation of *trans*-[IrCl{η^2-(*E*)-$CHCO_2Me$=$CHCO_2Me$}($PiPr_3$)$_2$] (16). This compound was prepared analogously as described for **15**, using **1** (150 mg, 0.16 mmol), $PiPr_3$ (160 μL, 0.80 mmol), and either dimethyl fumarate (46 mg, 0.32 mmol) or dimethyl maleate (41 μL, 0.32 mmol) as starting material. A red microcrystalline solid was obtained: yield 174 mg (75%); mp 120 °C dec. Anal. Calcd for $C_{24}H_{50}ClIrO_4P_2$: C, 41.64; H, 7.28. Found: C, 41.71; H, 7.99. MS (70 eV): *m/z* (I_r) 548 ($M^+ - CHCO_2Me$=$CHCO_2Me$), 10), 144 ($CHCO_2Me$=$CHCO_2Me^+$, 100). IR (KBr): ν(C=O) 1705 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.82 (t, J(P,H) = 6.3 Hz, 2 H, =CH), 3.45 (s, 6 H, OCH_3), 2.81 (m, 6 H, PC*H*CH_3), 1.33 (dvt, N = 12.8, J(H,H) = 6.6 Hz, 18 H, PCHC*H*$_3$), 1.19 (dvt, N = 13.9, J(H,H) = 7.0 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 174.0 (s, C=O), 51.4 (s, OCH_3), 22.6 (vt, N = 24.2 Hz, P*C*HCH_3), 20.2, 19.6 (both s, PCH*C*H_3), 19.5 (br s, =CH). ^{31}P NMR (36.3 MHz, C_6D_6): δ 9.8 (s).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(OMe)=O}($PiPr_3$)$_2$] (17). A solution of **15** (120 mg, 0.19 mmol) in benzene (5 mL) was stirred either for 21 days at room temperature or for 2 h at 80 °C. A change of color from red to pale yellow occurred. The solvent was evaporated in vacuo, the oily residue was dissolved in benzene/hexane (1:2, 3 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With benzene/hexane (1:2) a nearly colorless fraction was eluted, which was brought to dryness in vacuo. The remaining white microcrystalline solid was washed twice with hexane (3 mL) and dried: yield 108 mg (90%); mp 167 °C dec. Anal. Calcd for $C_{22}H_{48}ClIrO_2P_2$: C, 41.66; H, 7.63. Found: C, 41.43; H, 7.81. MS (70 eV): *m/z* (I_r) 634 (M^+, 75), 548 ($M^+ - CH_2$=$CHCO_2Me$, 100), 474 ($M^+ - PiPr_3$, 86), 86 (CH_2=$CHCO_2Me^+$, 31). IR (KBr): ν(IrH) 2260, ν(C=O) 1575 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.37 [d, J(H,H) = 7.8 Hz, 1 H, IrCH), 6.38 (d, J(H,H) = 7.8 Hz, 1 H, IrCH=C*H*), 3.89 (s, 3 H, OCH_3), 2.53 (m, 6 H, PC*H*CH_3), 1.30, 1.15 (both dvt, N = 13.3, J(H,H) = 6.8 Hz, 18 H each, PCHC*H*$_3$), −26.70 (t, J(P,H) = 15.1 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 183.7 (t, J(P,C) = 7.0 Hz, IrCH), 182.0 (s, C=O), 118.6 (s, IrCH=*C*H), 52.7 (s, OCH_3), 24.1 (vt, N = 26.6 Hz, P*C*HCH_3), 19.1, 19.0 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 18.6 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(CO_2Me)=CHC(OMe)=O}($PiPr_3$)$_2$] (18). A solution of **16** (120 mg, 0.18 mmol) in benzene (5 mL) was irradiated for 12 h with a UV lamp (Hanovia 450 W). After the solution was worked up analogously as described for **17**, a yellow microcrystalline solid was obtained: yield 96 mg (80%); mp 175 °C dec. Anal. Calcd for $C_{24}H_{50}ClIrO_4P_2$: C, 41.64; H, 7.28. Found: C, 41.20; H, 7.20. MS (70 eV): *m/z* (I_r) 692 (M^+, 45), 656 (M^+ − HCl, 3), 548 ($M^+ - CHCO_2Me$=$CHCO_2Me$, 100), 532 ($M^+ - PiPr_3$, 14), 144 ($CHCO_2Me$=$CHCO_2Me^+$, 16). IR (KBr): ν(IrH) 2305, ν(C=O)$_{uncoord}$ 1710, ν(C=O)$_{coord}$ 1590 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.72 (t, J(P,H) = 1.3 Hz, 1 H, IrC=C*H*), 3.82, 3.57 (both s, 3 H each, OCH_3), 2.59 (m, 6 H, PC*H*CH_3), 1.18, 1.03 (both dvt, N = 13.5, J(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −27.86 (t, J(P,H) = 15.1 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 182.1, 176.4 (both s, C=O), 178.9 (t, J(P,C) = 6.8 Hz, IrC), 122.3 (s, IrC=*C*H), 53.0, 51.2 (both s, OCH_3), 24.5 [vt, N = 27.0 Hz, P*C*HCH_3), 19.7, 18.8 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 18.6 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-C(Ph)=CHC(Ph)=O}($PiPr_3$)$_2$] (19) and [IrH(Cl){κ^2(*C,O*)-C_6H_4C(CH=CHPh)=O}($PiPr_3$)$_2$] (20). A suspension of **1** (200 mg, 0.22 mmol) in toluene (5 mL) was treated under continuous stirring first with $PiPr_3$ (200 μL, 1.00 mmol) and then with PhCH=CHC(O)Ph (23 μL, 0.26 mmol). After the reaction mixture was stirred for 2 h at 80 °C, a red solution was obtained. The solution was cooled to room temperature and brought to dryness in vacuo. The oily residue was dissolved in benzene/hexane (6 mL; 1:2), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 8 cm). With benzene/hexane (1:2) an orange fraction was eluted, from which after removal of the solvent compound **19** was obtained. Subsequent elution with benzene/diethyl ether (1:1) afforded a red fraction, from which the solvent was evaporated in vacuo. The red microcrystalline solid analyzed as **20** was washed twice with small amounts of hexane (0 °C) and dried: yield 152 mg (45%) of **19** and 136 mg (40%) of **20**. Data for **19**: mp 181 °C dec. Anal. Calcd for $C_{33}H_{54}ClIrOP_2$: C, 52.40; H, 7.20. Found: C, 52.22; H, 7.32. MS (70 eV): *m/z* (I_r) 756 (M^+, 1), 548 ($M^+ - PhCH$=$CHC(O)Ph$, 6), 208 ($PhCH$=$CHC(O)Ph^+$, 100). IR (KBr): ν(IrH) 2255, ν(C=O) 1545 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.10, 7.36 (both m, 10 H, C_6H_5), 2.48 (m, 6 H, PC*H*CH_3), 1.16, 1.03 (both dvt, N = 13.4, J(H,H) = 6.9 Hz, 18 H each, PCHC*H*$_3$), −22.88 (t, J(P,H) = 16.5 Hz, 1 H, IrH), signal of IrC(Ph)=C*H* proton probably covered by signals of phenyl protons. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.4 (t, J(P,C) = 5.3 Hz, IrCH), 198.1 (s, C=O), 148.4 (s, IrC(Ph)=*C*H), 136.7, 131.4, 130.9, 129.7, 128.5, 127.5, 127.3 (all s, C_6H_5), 25.1 (vt, N = 27.3 Hz, P*C*HCH_3), 19.9, 19.3 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 7.6 (s, d in off-resonance). − Data for **20**: mp 230 °C dec. Anal. Calcd for $C_{33}H_{54}ClIrOP_2$: C, 52.40; H, 7.20. Found: C, 52.68; H, 7.44. IR (KBr): ν(IrH) 2270, ν(C=O) 1515 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07, 7.54 (both br s, 1 H each, =CH), 7.47, 6.81 (both m, 10 H, C_6H_5), 2.25 (m, 6 H, PC*H*CH_3), 1.15, 0.87 (both dvt, N = 13.3, J(H,H) = 6.9 Hz, 18 H each, PCHC*H*$_3$), −23.98 (t, J(P,H) = 16.1 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 201.0 (s, C=O), 165.2 (t, J(P,C) = 6.1 Hz, IrC of C_6H_4), 118.9, 118.5 (both s, =CH), 145.3, 144.7, 142.0, 135.1, 133.5, 130.7, 129.9, 128.9, 128.7 (all s, C_6H_4 and C_6H_5), 23.6 (vt, N = 26.4 Hz, P*C*HCH_3), 19.4, 18.8 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 12.7 (s, d in off-resonance).

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(OH)=O}($PiPr_3$)$_2$] (21) and [IrH(Cl)(κ^2(*O,O*)-O_2CCH=CH_2)($PiPr_3$)$_2$] (22). A suspension of **1** (200 mg, 0.22 mmol) in toluene (5 mL) was treated under continuous stirring first with $PiPr_3$ (200 μL, 1.00 mmol) and then with acrylic acid (30 μL, 0.44 mmol). After the reaction mixture was stirred for 10 min at room temperature, a yellow solution was obtained. The solvent was evaporated in vacuo, the oily residue was dissolved in hexane (3 mL), and the solution was stored for 12 h at −78 °C. White crystals of **21** precipitated, which were separated from the mother liquor, washed twice with small amounts of hexane (0 °C), and dried. The mother liquor was brought to dryness in vacuo to give **22** as a yellow oil, which was characterized by

(27) (a) Strohmeier, W.; Onoda, T. *Z. Naturforsch.*, *B* **1968**, *23*, 1377−1379. (b) Werner, H.; Höhn, A. *Z. Naturforsch.*, *B* **1984**, *39*, 1505−1509.

NMR data. Yield: 127 mg (46%) of **21** and ca. 45% of **22**. Data for **21**: mp 127 °C dec. Anal. Calcd for $C_{21}H_{46}ClIrO_2P_2$: C, 40.67; H, 7.48. Found: C, 41.61; H, 7.53. MS (70 eV): *m/z* (I_r) 548 ($M^+ - CH_2{=}CHCO_2H$, 6), 72 ($CH_2{=}CHCO_2H^+$, 100). IR (KBr): ν(OH) 3435, ν(IrH) 2250 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 9.72 (d, J(H,H) = 7.3 Hz, 1 H, IrCH), 6.87 (d, J(H,H) = 7.3 Hz, 1 H, IrCH=C*H*), 2.75 (m, 6 H, PC*H*CH_3), 1.39 (m, 36 H, PCHC*H*$_3$), −25.23 (t, J(P,H) = 16.1 Hz, 1 H, IrH), signal of OH proton not exactly located. ^{31}P NMR (36.3 MHz, C_6D_6): δ 17.0 (s, d in off-resonance). Data for **22**: IR (KBr): ν(IrH) 2285, ν(OCO) 1510 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 6.12 (dd, J(H,H) = 17.4 and 2.4 Hz, 1 H, one H of $=CH_2$), 5.71 (dd, J(H,H) = 17.4 and 10.0 Hz, 1 H, C*H*$=CH_2$), 5.10 (dd, J(H,H) = 10.0 and 2.4 Hz, 1 H, one H of $=CH_2$), 2.60 (m, 6 H, PC*H*CH_3), 1.33, 1.28 (both dvt, N = 13.2, J(H,H) = 7.2 Hz, 18 H each, PCHC*H*$_3$), −34.80 (t, J(P,H) = 12.2 Hz, 1 H, IrH). ^{31}P NMR (36.3 MHz, C_6D_6): δ 19.6 (s, d in off-resonance).

Preparation of [IrH(Cl)(κ^2(*O,O*)-O_2CCH=CHMe)(P*i*Pr$_3$)$_2$] (23). A suspension of **1** (100 mg, 0.11 mmol) in toluene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (100 μL, 0.50 mmol) and then with crotonic acid (19 μL, 0.22 mmol). After the reaction mixture was stirred for 10 min at room temperature, a yellow solution was obtained. The solvent was evaporated in vacuo, the oily residue was dissolved in hexane (3 mL), and the solution was stored for 12 h at −78 °C. A pale yellow microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of hexane (0 °C), and dried: yield 99 mg (70%); mp 96 °C dec. Anal. Calcd for $C_{22}H_{48}ClIrO_2P_2$: C, 41.66; H, 7.63. Found: C, 41.93; H, 7.59. MS (70 eV): *m/z* (I_r) 634 (M^+, 19), 598 (M^+ − HCl, 3), 548 (M^+ − MeCH=$CHCO_2H$, 90), 474 (M^+ − P*i*Pr$_3$, 27), 86 (MeCH=$CHCO_2H^+$, 100). IR (KBr): ν(IrH) 2260, ν(OCO) 1520 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 6.74 (dq, J(H,H) = 15.5 and 6.9 Hz, 1 H, =C*H*CH_3), 5.56 (dq, J(H,H) = 15.5 and 1.5 Hz, 1 H, C*H*=$CHCH_3$), 2.64 (m, 6 H, PC*H*CH_3), 1.37, 1.33 (both dvt, N = 13.3, J(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −34.46 (t, J(P,H) = 12.4 Hz, 1 H, IrH), signal of =CHC*H*$_3$ protons probably covered by signals of PCHC*H*$_3$ protons. ^{31}P NMR (36.3 MHz, C_6D_6): δ 19.6 (s, d in off-resonance).

Reaction of the Starting Materials 1 and P*i*Pr$_3$ with RCH=$CHCO_2$Me (R = Me, Ph). A suspension of **1** (100 mg, 0.11 mmol) in toluene (5 mL) was treated under continuous stirring first with P*i*Pr$_3$ (100 μL, 0.50 mmol) and then with methyl crotonate (24 μL, 0.22 mmol) or methyl cinnamate (36 mg, 0.22 mmol), respectively. After the reaction mixture was stirred for 24 h at room temperature or irradiated for 2 h with a UV lamp (Hanovia 450 W), a brownish solution was obtained. The solvent was evaporated in vacuo and the yellow-brown residue dried. The ^1H and ^{31}P NMR spectra revealed that, besides traces of undefined compounds the residue contained the dihydrido complex [IrH_2(Cl)(P*i*Pr$_3$)$_2$] (**24**) as the main component. It was identified by comparison of the NMR data with those of an authentic sample.[13,28] The same result was obtained if a 5-fold excess of the corresponding ester was used as the substrate.

Reaction of Compound 2 with Hydrogen and Palladium Catalyst. A solution of **2** (140 mg, 0.22 mmol) in benzene (5 mL) was stirred in the presence of palladium on charcoal under a dihydrogen atmosphere for 45 min at 40 °C. The solution was filtered and the filtrate investigated by ^1H NMR spectroscopy. Both **24** and ethyl methyl ketone were identified by comparison with data reported in the literature.[13,28,29]

Reaction of Compound 2 with Hydride Donors. A solution of **2** (80 mg, 0.13 mmol) in THF (5 mL) was treated with $LiAlH_4$ (25 mg, 0.65 mmol) and stirred for 12 h at room temperature. The solvent was evaporated in vacuo, and the residue was extracted three times with pentane (15 mL each). The combined extracts were brought to dryness in vacuo to give a white microcrystalline solid, which was identified as [IrH_5(P*i*Pr$_3$)$_2$] (**25**) by comparison of the NMR data with those of an authentic sample.[19] The same result was obtained if a solution of **2** in methanol was treated with either $NaBH_4$ or $LiHBEt_3$.

Preparation of [$IrCl_2$(κ^2(*C,O*)-CH=C(Cl)C(Me)=O}-(P*i*Pr$_3$)$_2$] (27). A solution of **2** (95 mg, 0.15 mmol) in chloroform (5 mL) was treated dropwise with a saturated solution of Cl_2 in chloroform (ca. 0.5 mL) at room temperature. A quick change of color from yellow to deep red occurred. After the solution was stirred for 3 min, it was treated with an excess of the solution of Cl_2 in chloroform (1 mL) and continuously stirred for 5 min. The solvent was evaporated in vacuo, and the remaining red microcrystalline solid was washed three times with small amounts of pentane (0 °C) and dried: yield 95 mg (90%); mp 191 °C dec. Anal. Calcd for $C_{22}H_{46}Cl_3IrOP_2$: C, 38.46; H, 6.75. Found: C, 38.90; H, 6.90. MS (70 eV): *m/z* (I_r) 687 (M^+, 10), 651 (M^+ − HCl, 5), 527 (M^+ − P*i*Pr$_3$, 100). IR (KBr): ν(C=O) 1505 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 12.35 (s, 1 H, IrCH), 2.52 (m, 6 H, PC*H*CH_3), 2.47 (t, J(P,H) = 1.6 Hz, 3 H, C(O)CH_3), 1.25, 1.16 (both dvt, N = 13.5, J(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.0 (s, C=O), 198.7 (t, J(P,C) = 5.1 Hz, IrCH), 127.3 (s, IrCH=*C*), 22.7 (s, C(O)*C*H_3), 21.4 (vt, N = 24,5 Hz, P*C*HCH_3), 19.6, 19.5 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, $CDCl_3$): δ −9.4 (s).

Preparation of [$IrCl_2$(κ^2(*C,O*)-CH=C(Cl)CH=O}(P*i*Pr$_3$)$_2$] (28). This compound was prepared analogously as described for **27**, using **6** (80 mg, 0.14 mmol) and a saturated solution of Cl_2 in chloroform as starting materials. A red microcrystalline solid was obtained: yield 78 mg (87%); mp 176 °C dec. Anal. Calcd for $C_{21}H_{44}Cl_3IrOP_2$: C, 37.47; H, 6.59. Found: C, 37.79; H, 6.84. MS (70 eV): *m/z* (I_r) 673 (M^+, 2), 637 (M^+ − HCl, 6), 513 (M^+ − P*i*Pr$_3$, 100). IR (KBr): ν(C=O) 1520 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 12.70 (d, J(H,H) = 3.0 Hz, 1 H, IrCH), 8.14 (dt, J(H,H) = 3.0, J(P,H) = 1.8 Hz, 1 H, C(O)H), 2.57 (m, 6 H, PC*H*CH_3), 1.31, 1.19 (both dvt, N = 13.7, J(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 206.5 (t, J(P,C) = 5.2 Hz, IrCH), 199.2 (s, C=O), 130.4 (s, IrCH=*C*H), 21.5 (vt, N = 24.2 Hz, P*C*HCH_3), 19.8, 19.6 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, $CDCl_3$): δ −10.1 (s).

Preparation of [IrH(I){κ^2(*C,O*)-CH=CHC(Me)=O}-(P*i*Pr$_3$)$_2$] (29). A solution of **2** (130 mg, 0.21 mmol) in acetone (10 mL) was treated with NaI (150 mg, 1.00 mmol) and stirred for 7 days at room temperature. The solvent was evaporated in vacuo, the residue was extracted with benzene (20 mL), and the extract was brought to dryness in vacuo. A yellow microcrystalline solid was obtained, which was washed twice with small amounts of pentane and dried: yield 119 mg (80%); mp 138 °C dec. Anal. Calcd for $C_{22}H_{48}IIrOP_2$: C, 37.23; H, 6.82. Found: C, 37.63; H, 6.75. MS (70 eV): *m/z* (I_r) 710 (M^+, 75), 640 ($M^+ - CH_2{=}CHC(O)Me$, 100), 70 ($CH_2{=}CHC(O)Me^+$, 60). IR (KBr): ν(IrH) 2245, ν(C=O) 1555 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 10.41 (d, J(H,H) = 7.3 Hz, 1 H, IrCH), 6.64 (d, J(H,H) = 7.3 Hz, 1 H, IrCH=C*H*), 2.50 (m, 6 H, PC*H*CH_3), 2.22 (t, J(P,H) = 1.3 Hz, 3 H, C(O)CH_3), 1.21, 1.00 (both dvt, N = 13.5, J(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −24.03 (t, J(P,H) = 15.9 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.7 (s, C=O), 198.9 (t, J(P,C) = 6.7 Hz, IrCH), 133.2 (s, IrCH=*C*H), 26.7 (vt, N = 28.1 Hz, P*C*HCH_3), 25.0 (s, C(O)-*C*H_3), 19.8, 19.3 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 11.0 (s, d in off-resonance).

Preparation of [IrH{κ^1-OC(O)Me}{κ^2(*C,O*)-CH=CHC-(Me)=O}(P*i*Pr$_3$)$_2$] (30). A solution of **2** (105 mg, 0.17 mmol) in acetone (10 mL) was treated with silver acetate (29 mg, 0.17 mmol) and stirred for 1 h at room temperature. The solvent was evaporated in vacuo, the residue was extracted with

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benzene (15 mL), and the extract was brought to dryness in vacuo. A yellow microcrystalline solid was obtained, which was washed twice with small amounts of pentane and dried: yield 93 mg (85%); mp 106 °C. Anal. Calcd for $C_{24}H_{51}IrO_3P_2$: C, 44.84; H, 8.56. Found: C, 45.07; H, 8.52. IR (KBr): ν(IrH) 2265, ν(OCO) 1625, ν(C=O) 1540 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 11.00 (d, J(H,H) = 7.5 Hz, 1 H, IrCH), 6.90 (d, J(H,H) = 7.5 Hz, 1 H, IrCH=C*H*), 2.36 (t, J(P,H) = 1.3 Hz, 3 H, C(O)CH_3), 2.10 (m, 6 H, PC*H*CH_3), 1.89 (s, 3 H, O_2CCH_3), 1.15, 1.09 (both dvt, N = 13.2, J(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −23.64 (t, J(P,H) = 16.4 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 206.8 (s, C=O), 201.7 (t, J(P,C) = 6.2 Hz, IrCH), 176.4 (s, O_2CCH3), 133.3 (s, IrCH=*C*H), 25.3, 24.8 (both s, O_2CCH_3 and C(O)*C*H_3), 24.1 (vt, N = 27.0 Hz, P*C*HCH$_3$), 19.3, 18.9 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 24.4 (s, d in off-resonance).

Preparation of [IrH(Cl){η^1-(*Z*)-CH=CHC(O)Me}(CO)-(P*i*Pr$_3$)$_2$] (31). A solution of **2** (95 mg, 0.15 mmol) in benzene (5 mL) was stirred in a 50 mL autoclave under a CO pressure of 50 bar for 2 days at room temperature. After the pressure was reduced and the CO atmosphere replaced by argon, the solvent was evaporated in vacuo. The remaining yellow microcrystalline solid was washed twice with small amounts of hexane and dried: yield 89 mg (90%); mp 146 °C. Anal. Calcd for $C_{23}H_{48}ClIrO_2P_2$: C, 42.75; H, 7.49. Found: C, 43.18; H, 7.83. MS (70 eV): m/z (I_r) 646 (M^+, 1), 618 (M^+ − CO, 62), 576 (M^+ − CH_2=CHC(O)Me, 100), 548 (M^+ − CO−CH_2=CHC(O)Me, 52), 70 (CH_2=CHC(O)Me^+, 62). IR (KBr): ν(IrH) 2115, ν(CO) 2000, ν(C=O) 1665 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 8.70 (ddt, J(H,H) = 12.0 and 4.7, J(P,H) = 2.9 Hz, 1 H, IrCH), 6.74 (dt, J(H,H) = 12.0, J(P,H) = 1.4 Hz, 1 H, IrCH=C*H*), 2.41 (m, 6 H, PC*H*CH_3), 1.83 (s, 3 H, C(O)CH_3), 1.16 (dvt, N = 14.2, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$), −8.14 (dt, J(H,H) = 4.7, J(P,H) = 15.8 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 199.2 (s, C=O), 178.9 (s, IrCO), 144.7 (t, J(P,C) = 7.8 Hz, IrCH), 176.4 (s, O_2CCH_3), 129.6 (s, IrCH=*C*H), 32.1 (s, C(O)-*C*H_3), 23.8 (vt, N = 29.3 Hz, P*C*HCH$_3$), 18.6, 18.4 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 18.0 (s, d in off-resonance).

Preparation of [IrH(I){η^1-(*Z*)-CH=CHC(O)Me}(CO)-(P*i*Pr$_3$)$_2$] (32). This compound was prepared analogously as described for **31**, using **29** (110 mg, 0.15 mmol) and CO (50 bar) as starting materials. A light yellow microcrystalline solid was obtained: yield 103 mg (90%); mp 145 °C. Anal. Calcd for $C_{23}H_{48}IIrO_2P_2$: C, 37.39; H, 6.55. Found: C, 37.16; H, 6.72. IR (KBr): ν(IrH) 2150, ν(CO) 2000, ν(C=O) 1670 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 8.90 (ddt, J(H,H) = 11.8 and 4.7, J(P,H) = 2.2 Hz, 1 H, IrCH), 6.83 (dt, J(H,H) = 11.8, J(P,H) = 1.5 Hz, 1 H, IrCH=C*H*), 2.68 (m, 6 H, PC*H*CH_3), 1.91 (s, 3 H, C(O)CH_3), 1.21, 115 (both dvt, N = 14.2, J(H,H) = 7.0 Hz, 18 H each, PCHC*H*$_3$), −9.68 (dt, J(H,H) = 4.7, J(P,H) = 16.4 Hz, 1 H, IrH). ^{31}P NMR (36.3 MHz, C_6D_6): δ 10.4 (s, d in off-resonance).

Formation of Compound 14 by Reductive Elimination from 31. A solution of **31** (70 mg, 0.11 mmol) in C_6D_6 (0.5 mL) was stirred for 2 h at 80 °C. After the solution was cooled to room temperature, the ^1H and ^{31}P NMR spectra revealed that the starting material was converted to the carbonyl complex **14** and methyl vinyl ketone. The yield was virtually quantitative.

Formation of Compound 14 by Thermolysis from 6. A solution of **6** (100 mg, 0.17 mmol) in mesitylene (5 mL) was stirred for 3 h at 160 °C. After the solution was cooled to room temperature, the volatiles were evaporated in vacuo. The IR and ^1H NMR spectra revealed that the carbonyl complex **14** was exclusively formed.

Preparation of [IrH(CO){κ^2(*C*,*O*)-CH=CHC(Me)=O}-(P*i*Pr$_3$)$_2$]PF$_6$ (33). A solution of **2** (170 mg, 0.27 mmol) in dichloromethane (10 mL) was treated with KPF_6 (184 mg, 1.00 mmol) and stirred for 30 min under a CO atmosphere at room temperature. After CO was replaced by argon, the reaction mixture was filtered through a column (length 3 cm) of Al_2O_3 (neutral, activity grade V). The aluminum oxide was washed three times with 2 mL portions of CH_2Cl_2, and the filtrate was brought to dryness in vacuo. The residue was recrystallized from CH_2Cl_2/hexane (1:10) to give white, air-stable crystals: yield 195 mg (89%); mp 203 °C dec. Anal. Calcd for $C_{23}H_{48}F_6IrO_2P_3$: C, 36.55; H, 6.40. Found: C, 36.45; H, 6.33. Λ_M: 79.6 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(IrH) 2295, ν(CO) 2050, ν(C=O) 1565 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 10.17 (br dd, J(H,H) = 9.2 and 1.0 Hz, 1 H, IrCH), 7.50 (dt, J(H,H) = 9.2, J(P,H) = 1.9 Hz, 1 H, IrCH=C*H*), 2.56 (t, J(P,H) = 1.8 Hz, 3 H, C(O)CH_3), 2.39 (m, 6 H, PC*H*CH_3), 1.33, 1.18 (both dvt, N = 14.9, J(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$), −20.68 (dt, J(H,H) = 1.0, J(P,H) = 12.7 Hz, 1 H, IrH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 216.7 (s, C=O), 203.5 (t, J(P,C) = 9.2 Hz, IrCH), 175.9 (t, J(P,C) = 8.1 Hz, IrCO), 139.8 (t, J(P,C) = 2.4 Hz, IrCH=*C*H), 26.5 (s, C(O)*C*H_3), 25.7 (vt, N = 29.3 Hz, P*C*HCH$_3$), 18.9, 18.1 (both s, PCH*C*H_3). ^{31}P NMR (36.3 MHz, CD_2Cl_2): δ 25.5 (s, d in off-resonance), −144.5 (sept, J(P,F) = 710.1 Hz, PF_6^-).

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Me)=O}-(PMe*t*Bu$_2$)$_2$] (34). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), PMe*t*Bu_2 (120 μL, 0.60 mmol), and methyl vinyl ketone (23 μL, 0.26 mmol) as starting materials. A yellow microcrystalline solid was obtained: yield 141 mg (85%); mp 127 °C.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(OMe)=CHC(Me)=O}(PMe*t*Bu$_2$)$_2$] (35). This compound was prepared analogously as described for **2**, using **1** (160 mg, 0.17 mmol), PMe*t*Bu_2 (160 μL, 0.80 mmol), and MeOCH=CHC(O)Me (0.35 μL, 0.35 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. A white microcrystalline solid was obtained: yield 201 mg (87%); mp 182 °C dec.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=C(Me)CH=O}-(PMe*t*Bu$_2$)$_2$] (36). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), PMe*t*Bu_2 (120 μL, 0.60 mmol), and methacrolein (22 μL, 0.26 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. An orange microcrystalline solid was obtained: yield 131 mg (79%); mp 149 °C dec.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=C(*i*Pr)CH=O}-(PMe*t*Bu$_2$)$_2$] (37). This compound was prepared analogously as described for **2**, using **1** (120 mg, 0.13 mmol), PMe*t*Bu_2 (120 μL, 0.60 mmol), and CH_2=C(*i*Pr)C(O)H (26 μL, 0.26 mmol) as starting materials. The reaction mixture was stirred for 2 h at 80 °C. An orange microcrystalline solid was obtained: yield 133 mg (77%); mp 142 °C dec.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(NH$_2$)=O}-(PMe*t*Bu$_2$)$_2$] (38). This compound was prepared analogously as described for **10**, using **1** (150 mg, 0.16 mmol), PMe*t*Bu_2 (160 μL, 0.80 mmol), and acrylic acid amide (24 mg, 0.32 mmol) as starting materials. A white microcrystalline solid was obtained: yield 178 mg (86%); mp 216 °C dec.

Preparation of *trans*-[IrCl(η^2-CH$_2$=CHCO$_2$Me)-(PMe*t*Bu$_2$)$_2$] (39). This compound was prepared analogously as described for **15**, using **1** (150 mg, 0.16 mmol), PMe*t*Bu_2 (160 μL, 0.80 mmol), and methyl acrylate (29 μL, 0.32 mmol) as starting materials. A red microcrystalline solid was obtained: yield 166 mg (78%); mp 90 °C dec.

Preparation of *trans*-[IrCl{η^2-(*E*)-CHCO$_2$Me=CHCO$_2$Me}(PMe*t*Bu$_2$)$_2$] (40). Method a. A suspension of **1** (150 mg, 0.16 mmol) in toluene (5 mL) was treated under continuous stirring first with PMe*t*Bu_2 (160 μL, 0.80 mmol) and then with dimethyl fumarate (46 mg, 0.32 mmol). After the reaction mixture was stirred for 5 min at room temperature, a red solution was formed. The solvent was evaporated in vacuo, the residue was dissolved in pentane (3 mL), and the solution was stored for 12 h at −78 °C. A red microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of hexane (0 °C), and dried: yield 178 mg (77%).

Method b. The procedure was the same as that described for method a, but instead of dimethyl fumarate the isomeric dimethyl maleate (41 μL, 0.32 mmol) was used as the substrate. Yield: 180 mg (78%); mp 83 °C.

Preparation of [IrH(Cl){κ^2(*C,O*)-CH=CHC(OMe)=O}-(PMe*t*Bu$_2$)$_2$] (41). This compound was prepared analogously as described for **17**, using **39** (120 mg, 0.19 mmol) as starting material. A white microcrystalline solid was obtained: yield 108 mg (90%); mp 145 °C dec.

Preparation of [IrH(Cl){κ^2(*C,O*)-C(CO$_2$Me)=CHC(OMe)=O}(PMe*t*Bu$_2$)$_2$] (42). This compound was prepared analogously as described for **18**, using **40** (120 mg, 0.18 mmol) as starting material. A yellow microcrystalline solid was obtained: yield 100 mg (83%); mp 179 °C dec.

Preparation of *trans*-[IrCl{η^2-CH$_2$=CHC(O)H}-(PMe*t*Bu$_2$)$_2$] (43). This compound was prepared analogously as described for **15**, using **1** (140 mg, 0.15 mmol), PMe*t*Bu$_2$ (150 μL, 0.75 mmol), and acrolein (20 μL, 0.30 mmol) as starting materials. A red microcrystalline solid was obtained: yield 123 mg (65%); mp 92 °C dec.

Generation of *trans*-[IrCl(CO)(PMe*t*Bu$_2$)$_2$] (44). A solution of **43** (50 mg, 0.08 mmol) in benzene (5 mL) was stirred for 30 min at room temperature. A change of color from red to yellow occurred. After the solvent was evaporated in vacuo, a yellow microcrystalline solid was obtained. It was washed three times with small quantities of pentane and identified as *trans*-[IrCl(CO)(PMe*t*Bu$_2$)$_2$] (**44**) by comparison of the IR and NMR data with those of an authentic sample.[30] The same product resulted if a solution of **43** in toluene was stirred for 5 days at −30 °C.

Preparation of *trans*-[IrCl(η^2-C$_2$H$_4$)(PMe*t*Bu$_2$)$_2$] (45). A slow stream of ethene was passed for 30 s through a solution formed from **1** (100 mg, 0.11 mmol) and PMe*t*Bu$_2$ (100 μL, 0.50 mmol) in benzene (5 mL). After the solution was stirred for 10 min at room temperature, the solvent was evaporated in vacuo. The oily residue was dissolved in benzene/hexane (1:1, 3 mL), and the solution was chromatographed on Al_2O_3 (neutral, acctivity grade V, length of column 5 cm). With benzene/hexane (1:1) an orange fraction was eluted, which was brought to dryness in vacuo. An orange microcrystalline solid was obtained, which was washed twice with small quantities of pentane (0 °C) and dried: yield 116 mg (90%); mp 130 °C dec. Anal. Calcd for $C_{20}H_{46}ClIrP_2$: C, 41.69; H, 8.05. Found: C, 41.30; H, 8.10. MS (70 eV): *m/z* (I_r) 576 (M^+, 7), 548 ($M^+ - C_2H_4$, 14), 28 ($C_2H_4^+$, 100). ^{1}H NMR (90 MHz, C_6D_6): δ 1.49 (t, J(P,H) = 4.4 Hz, 4 H, C_2H_4), 1.40 (vt, N = 12.4 Hz, 36 H, PCCH_3), 0.52 (vt, N = 4.6 Hz, 6 H, PCH_3). ^{31}P NMR (36.3 MHz, C_6D_6): δ 9.8 (s).

Generation of 44 and 45 from Compound 43. A suspension of **1** (80 mg, 0.09 mmol) in benzene (5 mL) was treated under continuous stirring first with PMe*t*Bu$_2$ (80 μL, 0.40 mmol) and then with **43** (130 mg, 0.22 mmol). After the reaction mixture was stirred for 30 min at room temperature, an orange solution was formed. The solvent was evaporated in vacuo and the remaining orange solid identified as a 1:1 mixture of **44** and **45** by IR and ^{1}H and ^{31}P NMR spectroscopy.

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Supporting Information Available: Complete list of analytical and spectroscopic data for complexes **34**−**43**. This material is available free of charge via the Internet at http://pubs.acs.org.

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