# A Series of Carbonyl-, Olefin-, Alkyne-, Hydrido-, and Vinyliridium Complexes Containing Bulky Bifunctional Phosphanes $i$Pr$_2$PCH$_2$X as Ligands☆

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Etheneiridium(I) complexes of the general composition *trans*-[IrCl(C$_2$H$_4$)L$_2$] [L = $i$Pr$_2$PCH$_2$CO$_2$Me (**2a**), $i$Pr$_2$PCH$_2$CO$_2$Et (**2b**), $i$Pr$_2$P(CH$_2$)$_3$NMe$_2$ (**2c**)] have been prepared either from [IrClL$_2$] (**3**) or [IrCl(C$_2$H$_4$)$_2$]$_2$ (**7**) as starting materials. The corresponding carbonyl derivatives *trans*-[IrCl(CO)L$_2$] (**6**, **10**, **11**) are obtained along similar routes. Photolysis of *trans*-[IrCl(C$_2$H$_4$)L$_2$] (L = **2a**, **2b**) leads, by intramolecular C−H activation, to the formation of the octahedral hydrido(vinyl)iridium(III) compounds [IrHCl(CH=CH$_2$)(κ-L)(κ$^2$-L)] (**16**, **17**), which are highly fluctional in solution. Carbonyl(hydrido)(vinyl) complexes are accessible either from **16** or **17** and CO, or from *trans*-[IrCl(C$_2$H$_4$)L$_2$] (L = **2a**) and the propargylic alcohol HC≡CCH(Ph)OH, respectively. Treatment of **3** or the corresponding dihydrido compound [IrH$_2$ClL$_2$] (**4**) with methyl vinyl ketone or methyl acrylate also yields hydrido(vinyl)iridium(III) complexes [IrHCl(CH=CHX)L$_2$] [X = C(=O)Me (**18**), C(=O)OMe (**19**)], in which instead of the C=O function of the phosphanyl ester the carbonyl group of the vinylic moiety is coordinated to the metal. The reaction of **16** (L = **2a**) with terminal alkynes HC≡CR (R = Ph, CO$_2$Me) affords the structurally related alkynyl(hydrido)iridium(III) compounds [IrHCl(C≡CR)(κ-L)(κ$^2$-L)] (**28**, **29**), while from **16** and internal alkynes RC≡CR the iridium(I) complexes *trans*-[IrCl(RC≡CR)L$_2$] (**30**, **31**) are obtained. Stepwise treatment of *trans*-[IrCl(CO)L$_2$] (**6**: L = **2a**) with (i) NaN(SiMe$_3$)$_2$, (ii) H$_2$O, and (iii) HCl leads, in the coordination sphere of the metal center, to a conversion of $i$Pr$_2$PCH$_2$CO$_2$Me to $i$Pr$_2$PCH$_2$CO$_2$H via the isolated phosphanylenolate and phosphanylacetate complexes **32** and **33** as intermediates.

In the continuation of our work on highly reactive, low-valent rhodium complexes with bulky phosphanes as ligands[1], we have recently shown that in contrast to P$i$Pr$_3$, which on treatment with [RhCl(C$_8$H$_{14}$)$_2$]$_2$ forms the labile dimer [RhCl(P$i$Pr$_3$)$_2$]$_2$[2], related bifunctional phosphanes such as $i$Pr$_2$PCH$_2$CH$_2$OMe, $i$Pr$_2$PCH$_2$CH$_2$NMe$_2$, or $i$Pr$_2$PCH$_2$CO$_2$Me react with the same precursor [RhCl(C$_8$H$_{14}$)$_2$]$_2$ to give monomeric species [RhClL$_2$][3]. For L = $i$Pr$_2$PCH$_2$CH$_2$OMe, it has been shown by X-ray crystal structure analysis that one of the phosphane ligands is bonded via P and O in a chelating fashion while the other is coordinated only through the phosphorus atom[3a].

When we attempted to prepare the corresponding iridium derivative [IrCl(κ$^2$-*P*,*O*-$i$Pr$_2$PCH$_2$CH$_2$OMe)(κ-*P*-$i$Pr$_2$PCH$_2$CH$_2$OMe)], we observed that instead of the expected square-planar complex the octahedral C−H activation product [IrHCl(κ$^2$-*P*,*C*-$i$Pr$_2$PCH$_2$CH$_2$OCH$_2$)(κ$^2$-*P*,*O*-$i$Pr$_2$PCH$_2$CH$_2$OMe)] was formed[4]. By using [IrCl(C$_2$H$_4$)$_2$]$_2$ and $i$Pr$_2$PCH$_2$CO$_2$Me as the starting materials, the ethene iridium(I) compound *trans*-[IrCl(C$_2$H$_4$)(κ-*P*-$i$Pr$_2$PCH$_2$CO$_2$Me)$_2$] was obtained[5]. In the present paper we describe the preparation of the ethene-free complex [IrClL$_2$] with L = $i$Pr$_2$PCH$_2$CO$_2$Me, its behaviour towards H$_2$, CO, C$_2$H$_4$, and activated olefins, the reactivity of the so-formed hydrido(vinyl)iridium(III) compounds towards various nucleophiles, and the stepwise conversion of $i$Pr$_2$PCH$_2$CO$_2$Me to $i$Pr$_2$PCH$_2$CO$_2$H in the coordination sphere of the iridium center via phosphanylenolate and phosphanylacetate complexes as intermediates.

## Preparation and Reactivity of the Monomer [IrClL$_2$] (L = $i$Pr$_2$PCH$_2$CO$_2$Me)

In contrast to the reaction of [IrCl(C$_8$H$_{14}$)$_2$]$_2$ (**1**) with $i$Pr$_2$PCH$_2$CH$_2$OMe, which in benzene at room temperature yields the octahedral compound [IrHCl(κ$^2$-*P*,*C*-$i$Pr$_2$PCH$_2$CH$_2$OCH$_2$)(κ$^2$-*P*,*O*-$i$Pr$_2$PCH$_2$CH$_2$OMe)][4], treatment of **1** with $i$Pr$_2$PCH$_2$CO$_2$Me (**2a**) under similar conditions (pentane, 25°C) affords the anticipated product **3** in virtually quantitative yield. The IR spectrum of **3**, which was isolated as a lemon-yellow, air-sensitive solid, reveals that one of the phosphanyl ester ligands possesses a free [ν(C=O) = 1730 cm$^{-1}$] and the other a coordinated [ν(C=O) = 1635 cm$^{-1}$] CO$_2$Me unit. The $^{31}$P-NMR spectrum of **3** in [D$_8$]toluene at −55°C also displays two separate resonances at δ = 32.5 and 15.8, indicating the presence of two inequivalent $i$Pr$_2$P moieties, which is in agreement with the structural proposal shown in Scheme 1.

Similar to the rhodium counterpart [RhClL$_2$] with L = **2a**[3c], compound **3** is highly reactive towards H$_2$, C$_2$H$_4$, and CO at room temperature and quickly generates the dihydridoiridium(III), etheneiridium(I), and carbonyliridium(I) complexes **4**−**6** in good yield. Compound **5** has already been prepared from [IrCl(C$_2$H$_4$)$_2$]$_2$ and **2a** and on treatment with CO is converted to **6**[5]. The dihydrido complex **4**,

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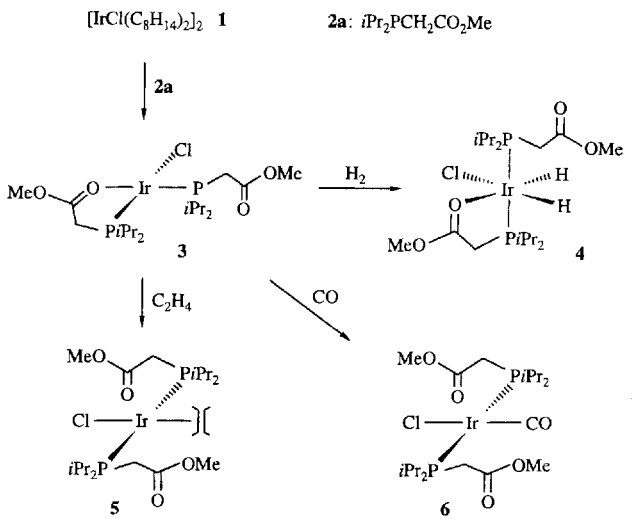
Scheme 1

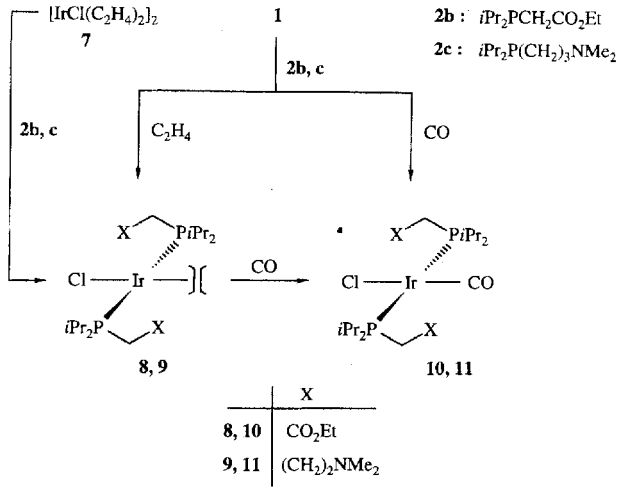



formed from **3** by oxidative addition, is a pale-yellow oil, which due to its pronounced air-sensitivity could not be characterized by elemental analysis. The $^1$H- and $^{31}$P-NMR spectra of **4** display only one signal for the $CO_2CH_3$ protons and the $^{31}$P nuclei at 25°C, while in the $^{31}$P-NMR spectrum in [D$_8$]toluene at −80°C an extremely broad signal appears. Therefore, we assume that compound **4** is highly fluctional at room temperature on the NMR time scale and that the carbonyl-oxygen atoms of the $CO_2Me$ units are only weakly coordinated to the metal center. With $T_c$ < −80°C, $J$(PP') = 360 Hz, and $\Delta\nu$ = 770 Hz, an upper limit for the free enthalpy of activation of 34 kJ/mol can be estimated[6]. The proposal, that in the ground state of **4** one phosphanyl ester ligand is *P*-bonded and the other linked via P and O, is substantiated by the IR spectrum, in which two ν(C=O) bands at 1725 and 1650 cm$^{-1}$ are observed.

### Ligand Substitution Reactions of the Complexes *trans*-[IrCl(C$_2$H$_4$)L$_2$]

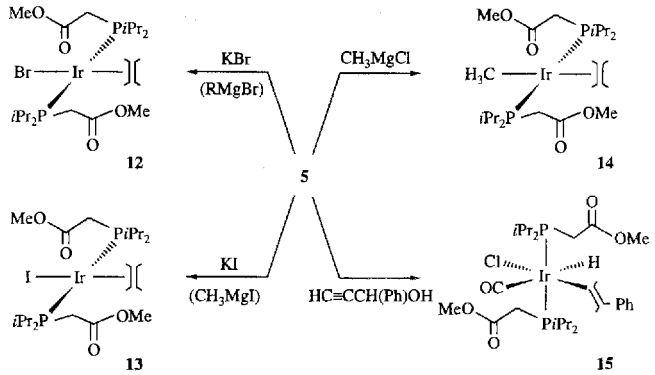
The dimeric compound [IrCl(C$_2$H$_4$)$_2$]$_2$ (**7**) does not only react with **2a** to afford **5**[5] but upon addition of **2b** and **2c** also gives the corresponding ethene complexes **8** and **9** in excellent yield. An alternative (although less effective) route consists in the stepwise reaction of **1** with **2b** or **2c** possibly to generate the species [IrClL$_2$] as an intermediate which on treatment with ethene yields **8** and **9**. The carbonyl derivatives **10** and **11** (Scheme 2) are obtained analogously, i.e., from **1**, **2b,c** and CO as starting materials. The $^{31}$P-NMR spectra of **8**–**11** display only one resonance, which indicates that the phosphorus atoms of the two *i*Pr$_2$PCH$_2$X ligands (X = $CO_2Et$ or $CH_2CH_2NMe_2$) are *trans* disposed. There is also no doubt that in **8** and **10** the $CO_2Me$ unit of the phosphanyl ester groups is not involved in the coordination to the metal, since in the IR spectra only one C=O stretching frequency at ca. 1720 cm$^{-1}$ appears. Like compound **6**, the structurally related carbonyl complexes **10** and **11** can also be prepared from **8** and **9** by displacement of the ethene ligand with CO.

Scheme 2




Attempts to displace the chloro ligand of **5** by an alkyl, vinyl, or aryl group were only partly successful. Treatment of **5** with $CH_2$=$CHMgBr$ or $C_6H_5MgBr$ in ether led instead of the expected vinyl- or phenyliridium complexes to the formation of the bromo derivative **12**, which is more easily prepared from **5** and an excess of KBr in acetone (Scheme 3). Likewise, if $CH_3MgI$ is used as the Grignard reagent, the ethene(iodo)iridium compound **13** is obtained. This complex is also more conveniently prepared from **5** and KI in THF. At room temperature, both **12** and **13** are orange or red air-sensitive oils, the $^1$H-, $^{13}$C-, and $^{31}$P-NMR spectra of which are quite similar to those of **5** and thus deserve no further comments.

Scheme 3




In order to avoid the Cl/Br or Cl/I exchange upon treatment of **5** with RMgBr or RMgI, the reaction of **5** with $CH_3MgCl$ has also been studied. If a solution of **5** in ether is treated at −35°C with an equimolar amount of $CH_3MgCl$, a red extremely air-sensitive oil is formed which according to the spectroscopic data is the desired square-planar ethene(methyl) complex **14**. The most characteristic features are the triplet for the $IrCH_3$ protons at δ = 1.15 in the $^1$H-NMR and the triplet for the corresponding methyl

carbon atom at δ = 5.3 in the $^{13}$C-NMR spectrum. It should be mentioned that recently the preparation of *trans*-[Ir(CH$_3$)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] from *trans*-[IrCl(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] and CH$_3$Li had been described[7].

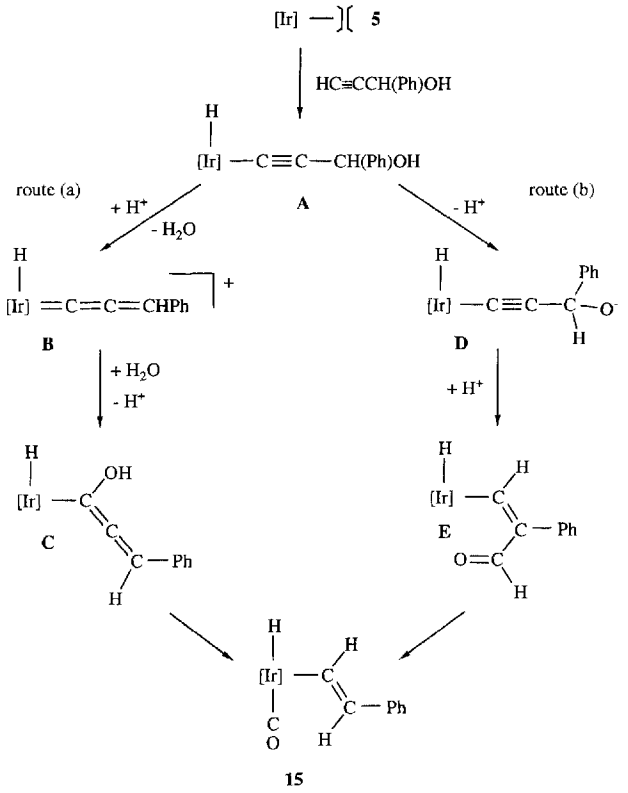
In contrast to HC≡CPh and HC≡CCO$_2$Me, which react with **5** to give first the alkynyl(hydrido) complexes [IrHCl(C≡CR)(κ$^2$-*P*,*O*-*i*Pr$_2$PCH$_2$C(OMe)=O)(κ-*P*-*i*Pr$_2$PCH$_2$CO$_2$Me)] and subsequently the vinylidene isomers *trans*-[IrCl(=C=CHR)(κ-*P*-*i*Pr$_2$PCH$_2$CO$_2$Me)$_2$][5], compound **5** upon treatment with the alkynol HC≡CCH(Ph)OH affords the carbonyl(hydrido)vinyliridium(III) derivative **15** in 72% yield. The strong ν(CO) absorption at 1995 cm$^{-1}$ in the IR spectrum is relevant for the structural proposal shown in Scheme 3 as well as the high-field signal for the hydrido ligand at δ = −8.38 and the two resonances for the vinylic protons at δ = 8.53 and 7.05 (both doublets) in the $^1$H-NMR spectrum. The large H-H coupling constant (18.3 Hz) of the latter confirms the (*E*) configuration at the C=C double bond. The $^{13}$C-NMR spectrum of **15** displays the signals for the carbon atoms of the IrCH=CH unit at δ = 141.0 and 139.1, both of which as triplets due to P-C coupling.

With regard to the mechanism of formation of **15**, we assume that in the initial step the expected alkynyl(hydrido)iridium(III) compound **A** (Scheme 4) is formed as an intermediate. The subsequent conversion to **15** could occur on route (a) via an allenylidene- and a hydroxyallenyliridium intermediate **B** and **C**, as it has similarly been proposed by O'Connor and Hilbner to explain the formation of the carbonyl(vinyl) complex [Ir{κ$^2$-*C*,*C*-C$_4$(CO$_2$Me)$_4$}(PPh$_3$)(CO)(CH=CHR)] (R = H, Me) from [Ir{κ$^2$-*C*,*C*-C$_4$(CO$_2$Me)$_4$}(PPh$_3$)$_2$Cl] and HC≡CCH(R)OH[8]. The alternative route (b) involves as the primary step the deprotonation of the IrC≡CCH(Ph)OH moiety to give an anionic intermediate IrC≡CCH(Ph)O$^-$ (**D**). After attack of a proton, this species could rearrange to **E**, which by CO abstraction and recoordination of CO would generate the Ir(CO)(CH=CHPh) unit. There is precedence for the formation of compounds with an Ir−CH=C(R)−C(R′)=O fragment insofar as the cyclooctene adduct [IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] reacts with α,β-unsaturated aldehydes and ketones to give the octahedral products [IrHCl{κ$^2$-*C*,*O*-CH=C(R)−C(R′)=O}(P*i*Pr$_3$)$_2$] (R = H, Me, *i*Pr; R′ = H, Me) in excellent yield[9]. Moreover, we note that related complexes [IrHCl{κ$^2$-*C*,*O*-CH=C(R)−C(R′)=O}L$_2$] (R = Me, OMe) with L = *i*Pr$_2$PCH$_2$CH$_2$OMe have been prepared from [IrH$_2$Cl(κ$^2$-*P*,*O*-*i*Pr$_2$PCH$_2$CH$_2$OMe)(κ-*P*-*i*Pr$_2$PCH$_2$CH$_2$OMe)] and methyl acrylate or methyl vinyl ketone, respectively[4].

### Hydrido(vinyl)iridium(III) Complexes by C−H Activation

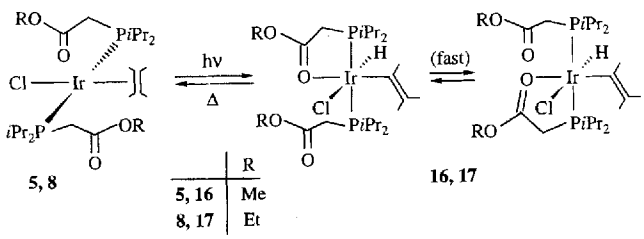
The equilibrium between *trans*-[IrCl(C$_2$H$_4$)L$_2$] and the corresponding isomer [IrHCl(CH=CH$_2$)L$_2$], which for L = P*i*Pr$_3$ lies on the side of the π-ethene compound, can be completely shifted towards the hydrido(vinyl)metal derivative if instead of P*i*Pr$_3$ the phosphanyl ether *i*Pr$_2$PCH$_2$CH$_2$OMe is used as ligand L[10]. We were therefore keen to study also the reactivity of the phosphanyl ester complexes

Scheme 4. Proposed mechanistic routes for the formation of **15** from **5**; [Ir] = IrCl(*i*Pr$_2$PCH$_2$CO$_2$Me)$_2$




**5** and **8**. Both compounds react on irradiation in benzene at 10°C quite rapidly to generate the hydrido(vinyl)iridium(III) isomers **16** and **17** (Scheme 5) in almost quantitative yield. While **16** forms colorless, only moderately air-sensitive crystals, the corresponding species **17** is an oil at room temperature.

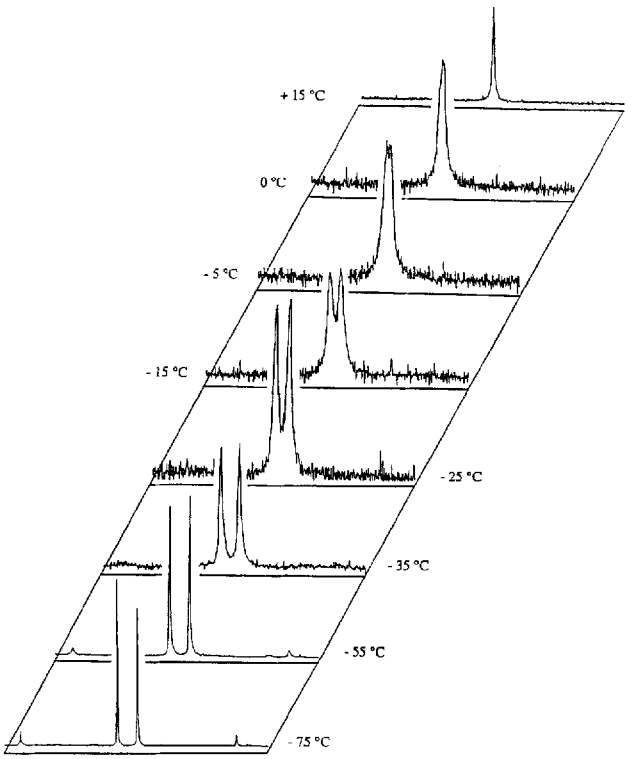
Scheme 5




The NMR spectra of **16** and **17** are strongly temperature-dependent, which indicates that both complexes are fluctional in solution. At 25°C , the $^{31}$P-NMR spectrum of either **16** or **17** displays a slightly broadened singlet which under off-resonance splits into a doublet. Upon cooling, the singlet broadens until at −25°C for **16** and at −10°C for **17** coalescence is observed. Below these temperatures, the pattern of an AB system appears (see Figure 1) which becomes sharp at ca. −75°C, indicating that the molecule now has a rigid structure. The fluctional process most probably consists of a rapid exchange between a κ$^1$- and a κ$^2$-coordination mode of the two hemilabile phosphanyl ester ligands. The presence of both monodentate and bidentate

$i$Pr$_2$PCH$_2$CO$_2$R groups in the ground state is confirmed by two equally strong C=O stretching frequencies in the IR spectrum at 1730 and 1650 cm$^{-1}$ for **16** and at 1725 and 1650 cm$^{-1}$ for **17**, respectively. From the coalescence temperature $T_c$, the difference in chemical shift of the two resonances in the low-temperature $^{31}$P-NMR spectrum $\Delta\nu$ and the respective P-P' coupling constant, $\Delta G^{\neq}$ values of 44 kJ/mol for **16** and 49 kJ/mol for **17** have been calculated[6]. The size of $J$(PP') strongly supports the proposal that in **16** and **17** the two phosphorus atoms are *trans* to each other.

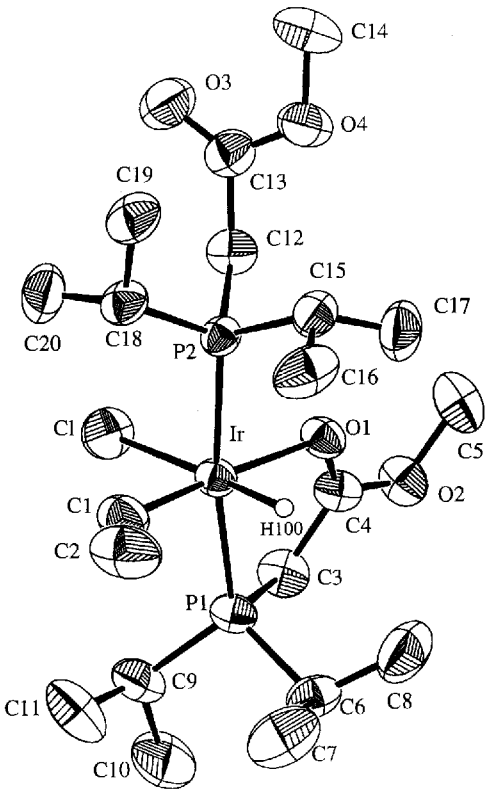
Figure 1. $^{31}$P-NMR spectra of complex **17** in [D$_8$]toluene at different temperature




The $^1$H- and $^{13}$C-NMR spectra of **16** and **17** reveal some similarities to the spectra of the corresponding complex [IrHCl(CH=CH$_2$)L$_2$] with L = $i$Pr$_2$PCH$_2$CH$_2$OMe[10]. The existence of an IrH(CH=CH$_2$) molecular fragment in both products, generated on photolysis of **5** and **8**, is shown by the hydride signal in the $^1$H-NMR spectrum at approximately $\delta$ = −22.5 (for **16** and **17**) and by the triplets at $\delta$ = 120.9 and 118.2 for the vinylic carbon atoms in the $^{13}$C-NMR spectrum of **16**. The assignment of the somewhat less deshielded resonance at $\delta$ = 118.2 to the β-C atom of the IrCH=CH$_2$ moiety is supported by the smaller P-C coupling and the negative amplitude of the signal in the DEPT spectrum. Thermolysis of **16** and **17** in refluxing benzene for 20 h reverses the C−H activation process and regenerates the ethene complexes **5** and **8** almost quantitatively. Due to this observation, there is no doubt that **5** and **8** are the thermodynamically prefered species and that the chelating capability of the phosphanyl esters plays a crucial role for the stabilization of the less stable isomers **16** and **17**.

The single-crystal X-ray structure analysis of **16** confirms the structural proposal shown in Scheme 5. There are two independent molecules I and II in the unit cell, the metric parameters of which are very similar. The ORTEP plot of one of the molecules (Figure 2) reveals that the iridium is coordinated in a somewhat distorted octahedral fashion with the two phosphorus atoms in *trans* position. The bending of the P−Ir−P axis [angle 170.84(4)° in I and 167.70(5)° in II] is slightly less than in the triisopropylphosphane derivative [IrHCl(CH=CH$_2$)(CO)($i$PrPr$_3$)$_2$] where the angle P−Ir−P is 164.44(5)°[10]. The bending is directed towards the smallest ligand (hydride) and probably originates from the steric hindrance between the isopropyl groups and the ligands in the basal plane. The plane formed by the atoms Ir, Cl, C1, C2, O1, and H100 is almost perfectly planar, the greatest deviation being found for C2 [0.076(8) Å for I and 0.145(9) Å for II]. The position of the hydride ligand in both molecules could be located by a difference-Fourier synthesis and refined isotropically. The bond angles

Figure 2. Molecular structure (ORTEP) of complex **16**[a]



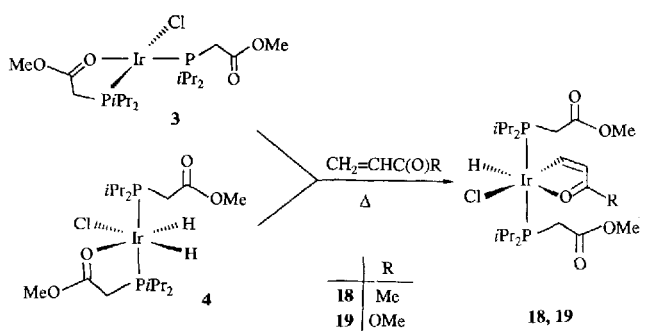

[a] Selected bond lengths [Å] and angles [°] (the numbers in brackets correspond to the second independent molecule in the unit cell):Ir−Cl 2.498(2) [2.499(1)], Ir−P1 2.294(1) [2.285(1)], Ir−P2 2.310(1) [2.300(1)], Ir−O1 2.277(3) [2.261(4)], Ir−C1 1.992(6) [1.995(6)], C1−C2 1.316(8) [1.275(8)], C4−O1 1.227(5) [1.221(6)], Ir−H100 1.58(5) [1.40(5)]; P1−Ir−P2 170.84(5) [167.65(6)], O1−Ir−C1 177.1(2) [173.8(2)], P1−Ir−Cl 88.04(5) [94.13(5)], P1−Ir−O1 80.22(9) [79.49(9)], P1−Ir−C1 96.9(2) [96.1(2)], P2−Ir−Cl 94.69(5) [93.72(5)], P2−Ir−O1 91.22(9) [92.28(9)], P2−Ir−C1 91.6(2) [92.7(2)], O1−Ir−Cl 86.38(9) [81.4(1)], C1−Ir−Cl 93.9(2) [94.6(2)], Ir−C1−C2 133.0(6) [134.5(6)], Ir−O1−C4 117.1(3) [117.1(3)], Ir−P1−C3 104.0(3) [106.8(3)], O1−C4−O2 123.4(5) [122.3(5)], O1−C4−C3 123.4(5) [124.5(5)].

Cl–Ir–Cl and Cl–Ir–O1 are near to 90 ° and thus in agreement with the octahedral geometry.

The distance between the iridium center and the α-carbon atom of the vinyl group [1.992(6) in I and 1.995(6) Å in II] is slightly shorter than in [IrHCl(CH=$CH_2$)(CO)(P-*i*$Pr_3$)$_2$] [2.059(6) Å][10] and [$C_5Me_5$IrH(CH=$CH_2$)($PMe_3$)] [2.059(6) Å][11], but nearly identical to that in [IrH(CH=$CH_2$)(acac)(P*i*$Pr_3$)$_2$] [2.02(1) Å][12]. The bond length Ir–O1 [2.277(3) Å in I and 2.261(4) Å in II] is comparable to that in six-coordinate vinylideneosmium(II) and allenylideneruthenium(II) complexes containing **2a** as ligand. The Ir–Cl and Ir–P distances of **16** correspond to those in related chloro(triisopropylphosphane)iridium derivatives[10][12][13] and deserve no further comments.

The hydrido(vinyl)iridium(III) complexes **18** and **19** in which, instead of the carbonyl function of the phosphanyl ester **2a**, the C=O group of the metalated methyl vinyl ketone or methyl acrylate is coordinated to the metal center, have been prepared from either **3** or **4** and the respective olefin $CH_2$=CHC(O)R (Scheme 6). The reactions were carried out in benzene at 60 °C for 20 h and upon chromatographic workup afforded the compounds **18** and **19** as orange-yellow, slightly air-sensitive oils in 50–60% yield. In contrast to **16** and **17**, the NMR spectra of **18** and **19** are not temperature-dependent, which indicates that both complexes have a rigid structure not only in the solid state but also in solution. Since the IR spectra of **18** and **19** display only one ν(C=O) band for the phosphanyl ester ligands at 1730 $cm^{-1}$, we assume that the carbonyl group of **2a** is not linked to the metal. The coordination of the C=O moiety of the vinylic ligand is confirmed by the appearance of a C=O stretching frequency at 1545 $cm^{-1}$ (for **18**) and 1580 $cm^{-1}$ (for **19**) which is shifted by ca. 150 $cm^{-1}$ to lower wave numbers compared to $CH_2$=CHC(O)$CH_3$ and $CH_2$=$CHCO_2$Me, respectively[14]. Characteristic features of the NMR spectra of **18** and **19** are the single resonance in the $^{31}$P-NMR (confirming the *trans* arrangement of the two phosphorus atoms) and both the signal at high field (δ = −24.36 for **18** and −27.32 for **19**) and rather low field (δ = 10.82 for **18** and 10.34 for **19**) for, respectively, the IrH and IrCH protons in the $^1$H-NMR spectra. The resonances for the vinylic carbon atoms, which for **16** are observed at δ = 120.9 and 118.2, appear in the $^{13}$C-NMR spectrum of **18** at δ = 199.5 and 134.7, and in that of **19** at δ = 184.3 and 120.5, the difference to **16** illustrating the influence of the C(=O)R substituent. On the basis of these data, we conclude that for the bonding in **18** and **19** the participation of a carbene-type resonance form Ir=CH–CH=C(R)O is of minor importance, since otherwise the signal for the IrCH carbon atom should be observed at significantly lower field[15]. It should be mentioned that the formation of hydrido(vinyl)metal complexes containing a *C,O*-bonded vinylic unit from α,β-unsaturated ketones or alkyl acrylates is not without precedence and has been reported in iridium and rhodium[9][16] as well as ruthenium chemistry[17].

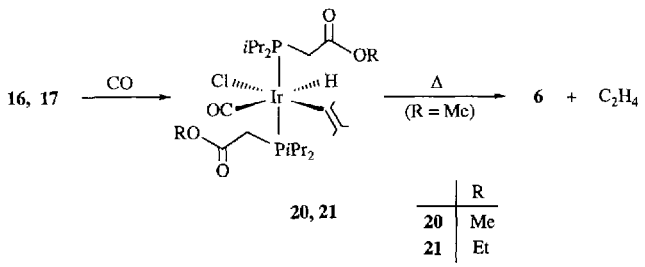
Scheme 6




### Reactions of Octahedral Hydrido(vinyl)iridium(III) Complexes with Nucleophiles

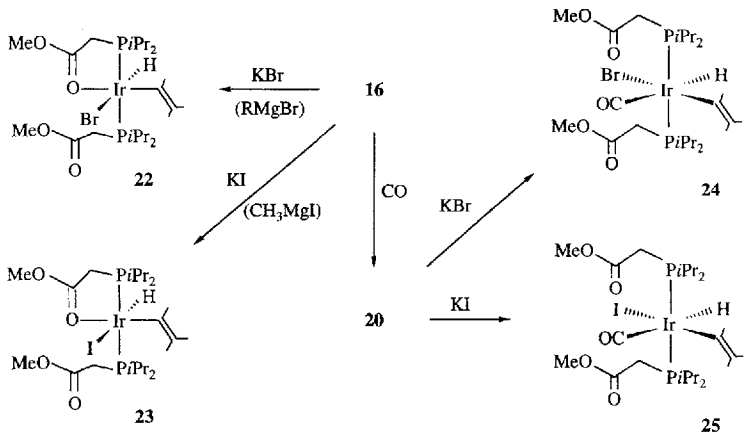
While the Ir–O bond of **18** and **19** is rather strong and therefore these chelate complexes are quite inert towards CO, the related hydrido(vinyl)iridium derivatives **16** and **17** react spontaneously with carbonmonoxide to give the monocarbonyl compounds **20** and **21** in nearly quantitative yield (Scheme 7). In agreement with the structural proposal for the analogous complex [IrHCl(CH=$CH_2$)(CO)(κ-*P*-*i*$Pr_2$P$CH_2CH_2$OMe)$_2$][4], we assume that in the basal plane of the octahedron the CO and the hydride ligand as well as the chloride and the vinyl group are *trans* to each other. The IR spectra of **20** and **21** display only one ν(C=O) stretch at 1730 or 1725 $cm^{-1}$, which is consistent with the monodentate behavior of the phosphanyl ester units. Thermolysis of **20** in refluxing benzene for 40 h leads to the elimination of ethene and to the formation of the carbonyl complex **6**.

Scheme 7

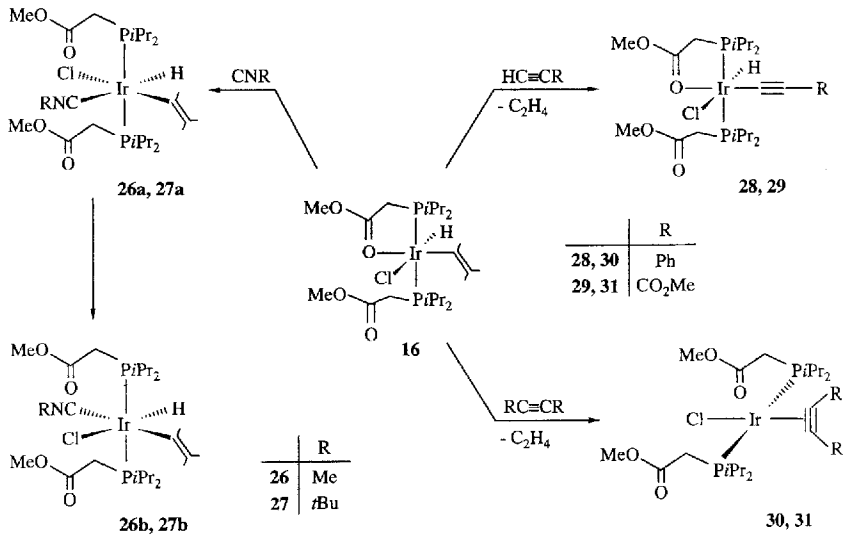



The reactions of the hydrido(vinyl) compounds **16** and **20** with Grignard reagents RMgX, where X is Br or I, take a similar course as those of the π-ethene complex **5** with the same substrates. Instead of the expected aryl(hydrido)vinyl- or alkyl(hydrido)vinyliridium(III) derivatives, the corresponding bromo or iodo compounds **22**, **23** and **24**, **25** (Scheme 8) are formed. Like the counterparts **12** and **13**, they are more conveniently prepared from **16** or **20** and an excess of KBr or KI, respectively. We note that there are only very small differences in the IR and NMR spectroscopic data of the analogous chloro-, bromo-, and iodoiridium derivatives and thus there is no doubt that during the ligand displacement process the configuration at the metal center remains unchanged. In contrast to the reaction of **5** with $CH_3MgCl$, which leads to the formation of the methyliridium complex **14** (Scheme 3), only the starting materials have been re-isolated on treatment of **16** or **20** with $CH_3MgCl$.

Scheme 8



Scheme 9



Compound **16** reacts with isocyanides CNR in a similar fashion as with CO. The remarkable difference, however, is that the initially formed complexes **26a** and **27a** (Scheme 9), which based on their IR and NMR spectra are thought to be structurally related to the carbonyl compounds **20** and **21**, slowly rearrange in solution (benzene, 60°C) to the more stable isomers **26b** and **27b**. The chemical shift of the hydride signal in the $^1$H-NMR spectra, which appears at $\delta \approx -10.5$ for **26a**, **27a** and at $\delta \approx -20.5$ for **26b**, **27b**, is diagnostic for the different coordination sphere around iridium in **26a**, **27a** on one side and **26b**, **27b** on the other. Following the work by Olgemöller and Beck[18], which indicates that the position of the Ir–H stretching frequency in the IR spectra of octahedral hydridoiridium(III) complexes depends critically on the electronegativity of the ligand in *trans* position to the hydride, we conclude that the hydride and the isocyanide in **26a** and **27a** as well as the hydride and the chloride in **26b** and **27b** are *trans* to each other.

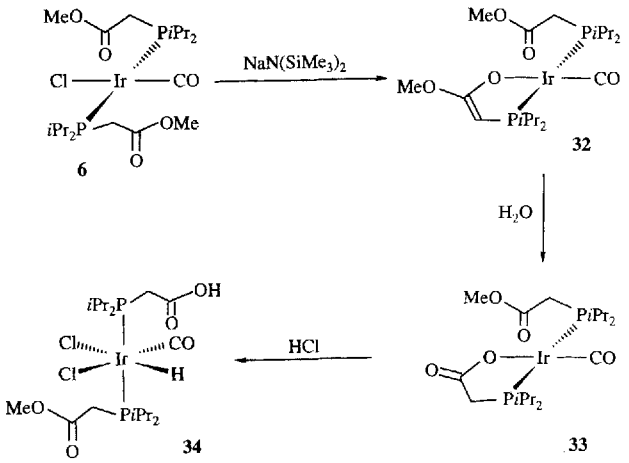
The results concerning the reactivity of **16** towards alkynes are summarized in Scheme 9. The alkynyl(hydrido) compounds **28** and **29**, which are obtained on treatment of **16** with HC≡CPh or HC≡CCO$_2$Me, have already been prepared from **5** and the corresponding 1-alkyne[5]. Regarding the mechanism of formation of **28** and **29**, we assume that in the initial step the Ir–O bond of **16** is split and the alkyne is added to the free coordination site. Subsequent elimination of ethene and intramolecular oxidative addition of HC≡CR would yield the product. The proposal that the initial addition of the alkyne promotes the elimination of ethene is supported by the reaction of **16** with PhC≡CPh and C$_2$(CO$_2$Me)$_2$ which gives the alkyne complexes **30** and **31** in virtually quantitative yield. Both compounds are structurally related to the triisopropylphosphane derivatives *trans*-[IrCl(RC≡CR)(P*i*Pr$_3$)$_2$], the synthesis of which has been described previously[19].

### Stepwise Conversion of *i*Pr$_2$PCH$_2$CO$_2$Me to *i*Pr$_2$CH$_2$CO$_2$H via a Phosphanyl Enolate and a Phosphanylacetate Intermediate

Since it is known that carbonyl(phosphanyl ketone)- and carbonyl(phosphanyl ester)rhodium complexes of the general composition *trans*-[RhCl(CO)L$_2$] (L = *t*Bu$_2$PCH$_2$-

C(O)R with R = *t*Bu, Ph[20]; $i$Pr$_2$PCH$_2$CO$_2$Me[21]) react with strong bases to give the corresponding phosphanyl enolate derivatives [Rh(CO)(κ-*P*,*O*-*t*Bu$_2$PCH=C(O)R)(κ-*P*-*t*Bu$_2$PCH$_2$C(O)R)] and [Rh(CO)(κ-*P*,*O*-$i$Pr$_2$PCH=C(O)-OMe)(κ-*P*-$i$Pr$_2$PCH$_2$CO$_2$Me)], respectively, the reactivity of the related iridium compound **6** has also been investigated[22]. Treatment of a solution of **6** in toluene with an equimolar amount of NaN(SiMe$_3$)$_2$ at 80°C affords the phosphanyl ester enolate complex **32** in ca. 65% yield. The structural proposal (Scheme 10) for the extremely moisture-sensitive substance (which at room temperature is an oil) is mainly supported by the $^1$H-NMR spectrum in which a characteristic signal (pseudo-triplet) for the PCH= proton at δ = 3.43 appears. The $^{31}$P-NMR spectrum displays two resonances (corresponding to an AB spin system) at δ = 46.7 and 44.0, the coupling constant $J$(PP′) = 286.2 Hz indicating that the two phosphorus atoms are *trans* disposed.

Scheme 10




Storing a solution of **32** in benzene, which contains traces of water, for 24 h at room temperature leads to a gradual change of color and upon removal of the solvent affords the phosphanylacetate complex **33** in quantitative yield. Compound **33** has originally been prepared from **6** and deactivated basic $Al_2O_3$ and characterized by X-ray structural analysis[5]. A similar sensitivity of phosphanyl enolate derivatives towards water was also observed by Braunstein et al.[23], who generated the palladium complexes [Pd(κ$^2$-*C*,*N*-*o*-C$_6$H$_4$CH$_2$NMe$_2$)(κ$^2$-*P*,*O*-R$_2$PCH$_2$CO$_2$)] from the corresponding enolates and $H_2O$.

While on treatment of **33** with $CH_3I$ the phosphanylacetate unit is maintained and the octahedral chelate compound [Ir(CH$_3$)I(CO)(κ$^2$-*P*,*O*-$i$Pr$_2$PCH$_2$C(=O)O)(κ-*P*-$i$Pr$_2$PCH$_2$-CO$_2$Me)] formed[5], the reaction of **33** with HCl yields the chloro(dihydrido)iridium(III) complex **34** almost quantitatively. The coordination of two inequivalent $i$Pr$_2$PCH$_2$X ligands in **34** is shown by $^{31}$P-NMR spectrum, in which two signals (AB spin system) at δ = 15.2 and 14.6 are observed. Moreover, the IR spectrum of **34** displays, besides the Ir–H and C≡O stretching frequencies at 2195 and 2010 cm$^{-1}$, two ν(C=O) bands at 1730 and 1700 cm$^{-1}$, which are assigned to the $CO_2Me$ and $CO_2H$ moieties of the phosphane ligands. The $^1$H-NMR spectrum of **34** shows a broadened singlet at δ = 9.38 which on addition of $D_2O$ disappears and therefore corresponds to the OH proton of the $i$Pr$_2$PCH$_2$CO$_2$H unit. The $^1$H-NMR spectrum also confirms that all the $CH_3$ groups of the four isopropyl substituents of the ligands $i$Pr$_2$PCH$_2$CO$_2$Me and $i$Pr$_2$PCH$_2$CO$_2$H are different, indicating that the molecule has no mirror plane. Due to this result, the configuration of the octahedral complex as shown in Scheme 10 can be assumed. Attempts to find out, whether in the initial step of the reaction of **33** with HCl an oxidative addition occurs (thereby maintaining the chelate link of the phosphanylacetate unit) or the Ir–O bond is opened by attack of the acid, failed. Upon addition of one equiv of HCl to a solution of **33** in benzene, one half of the starting material reacted to give **34** and one half remained unchanged.

## Conclusion

The present work, which is an extension of previous studies in our laboratory[3][4][5], has shown that bulky bifunctional phosphanes $i$Pr$_2$PCH$_2$X, in particular those with X = $CO_2Me$ and $CO_2Et$, are useful ligands in organoiridium chemistry. Due to their "hemilabile" binding mode[24], they are not only able to temporarily protect a free coordination site but can also promote C–H activation processes of olefinic substrates. An interesting facet is that in the hydrido(vinyl)iridium(III) complexes formed from substituted olefins such as $CH_2$=CHC(O)Me and $CH_2$=CHCO$_2$Me it is not the C=O function of the phosphanyl ester but the carbonyl group of the vinylic moiety that forms a chelate bond to the metal center.

The second aspect serving special attention is the stepwise conversion of the phosphanyl ester $i$Pr$_2$PCH$_2$CO$_2$Me to the corresponding phosphanylcarboxylic acid $i$Pr$_2$PCH$_2$-CO$_2$H in the coordination sphere of the iridium center. While there is ample precedence for the transformation of coordinated phosphanyl esters to phosphanyl ester enolates[22][23][24] and also for the metal-mediated loss of alkyl groups R′ from R$_2$PCH$_2$CO$_2$R′ to form phosphanylacetates R$_2$PCH$_2$CO$_2^-$[25], to the best of our knowledge it has never been proved that the conversion of R$_2$PCH$_2$CO$_2$R′ to R$_2$PCH$_2$CO$_2$H occurs via phosphanyl ester enolate and phosphanylacetate chelate complexes as intermediates. In the meantime, we found that metal-bonded phosphanyl ester enolates can also rearrange to isomeric $CO_2Me$-substituted phosphanylmethanides[26] and will report on this work in a forthcoming paper.

We acknowledge the support for this work by the *Deutsche Forschungsgemeinschaft* (SFB 347) and the *Fonds der Chemischen Industrie*. Moreover, we are also grateful to Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses and DTA measurements as well as to Mrs. *M. L. Schäfer* and Dr. *W. Buchner* for recording NMR spectra.

## Experimental Section

All operations were carried out under argon with the Schlenk technique. The starting materials **1**[27], **2a**, **2b**[3c], **2c**[3b], **7**[28], and

HC≡CCH(Ph)OH[29] were prepared by published procedures. – IR: Perkin-Elmer 1420. – NMR: Jeol FX 90 Q, Bruker AC 200 and AMX 400; v = virtual coupling.

1. *Preparation of cis-[IrCl(κ²-P,O-iPr₂PCH₂C(OMe)=O)(κ-P-iPr₂PCH₂CO₂Me)]* (**3**): A suspension of 197 mg (0.22 mmol) of **1** in 5 ml of pentane was treated with 173 µl (0.88 mmol) of **2a** and stirred for 30 min at room temp. A lemon-yellow, air-sensitive solid precipitated, which was filtered, repeatedly washed with 2-ml portions of pentane (0°C) and dried; yield 252 mg (94%), m.p. 128°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1730, 1635 cm$^{-1}$ [ν(C=O)]. – $^{31}$P NMR (36.2 MHz, [D$_8$]toluene, −55°C): δ = 32.5, 15.8 [2 d, *J*(PP) = 22.0 Hz]. – $C_{18}H_{38}ClIrO_4P_2$ (608.1): calcd. C 35.55, H 6.30; found C 35.24, H 6.51.

2. *Preparation of [IrH₂Cl(κ²-P,O-iPr₂PCH₂C(OMe)=O)(κ-P-iPr₂PCH₂CO₂Me)]* (**4**): A slow stream of $H_2$ was passed through a solution of 76 mg (0.12 mmol) of **3** in 8 ml of benzene for 30 sec at room temp. After the solution was stirred for 1 h under $H_2$, the solvent was removed and the oily, pale-yellow, extremely air-sensitive residue dried in vacuo; yield 50 mg (64%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2260, 2170 cm$^{-1}$ [ν(IrH)], 1725, 1650 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 3.22 (s, 6 H, $CO_2CH_3$), 3.19 (vt, *N* = 7.3 Hz, 4 H, $PCH_2$), 2.40 (m, 4 H, PC*H*CH$_3$), 1.17, 1.16 [2 dvt, *N* = 14.5, *J*(HH) = 7.0 Hz, 12 H each, PCHC*H*$_3$], −27.60 [t, *J*(PH) = 15.0 Hz, 2 H, IrH]. – $^{31}$P NMR (36.2 MHz, [D$_8$]toluene, 25°C): δ = 41.2 (s; t in off-resonance); at −80°C: δ = 41.2 (br. s).

3. *Reaction of* **3** *with* $C_2H_4$: A slow stream of ethene was passed through a solution of 76 mg (0.12 mmol) of **3** in 10 ml of benzene for 1 min at room temp. A change of color from yellow to orange occurred. After the solution was stirred for 5 min, it was concentrated to ca. 2 ml in vacuo. An orange, air-stable solid precipitated, which was filtered, repeatedly washed with pentane and dried; yield 48 mg (63%). Compound **5** was characterized by $^1$H- and $^{31}$P-NMR spectroscopy[5].

4. *Reaction of* **3** *with CO:* A slow stream of carbon monoxide was passed through a solution of 73 mg (0.12 mmol) of **3** in 10 ml of benzene for 30 sec at room temp. After the solution was stirred for 2 min, the solvent was removed, the bright yellow, air-stable residue was repeatedly washed with pentane and dried; yield 54 mg (71%). Compound **6** was characterized by IR and $^1$H-NMR spectroscopy[5].

5. *Preparation of trans-[IrCl(C₂H₄)(κ-P-iPr₂PCH₂CO₂Et)₂]* (**8**). – a) A suspension of 104 mg (0.12 mmol) of **1** in 5 ml of pentane was treated with 98 µl (0.48 mmol) of **2b** and stirred for 30 min at room temp. A brown-yellow solid precipitated, which was separated from the mother liquor, repeatedly washed with small amounts of pentane (0°C) and dried. The solid was then dissolved in 3 ml of benzene, and a slow stream of ethene was passed through the solution for 1 min at room temp. A change of color from brownish-yellow to orange occurred. The solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, an orange fraction was eluted from which after removal of the solvent an orange, moderately air-stable solid was obtained; yield 57 mg (37%).

b) A suspension of 191 mg (0.34 mmol) of **7** in 5 ml of pentane was treated with 285 µl (1.35 mmol) of **2b** and stirred for 30 min at room temp. An orange precipitate was formed, which was separated from the mother liquor, repeatedly washed with small amounts of pentane (0°C) and dried; yield 427 mg (96%), m. p. 75°C. – IR (KBr): $\tilde{\nu}$ = 1720 cm$^{-1}$ [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 3.84 [q, *J*(HH) = 7.1 Hz, 4 H, C*H*$_2$CH$_3$], 2.89 (m, 4 H, PC*H*CH$_3$), 2.45 (vt, *N* = 5.6 Hz, 4 H, $PCH_2$), 1.62 [t, *J*(PH) = 4.5 Hz, 4 H, $C_2H_4$], 1.41 [dvt, *N* = 15.5, *J*(HH) = 6.9 Hz, 24 H, PCHC*H*$_3$], 0.91 [t, *J*(HH) = 7.1 Hz, 6 H, CH$_2$C*H*$_3$]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 20.25 (s). – $C_{22}H_{46}ClIrO_4P_2$ (664.2): calcd. C 39.78, H 6.98; found C 39.44, H 7.29.

6. *Preparation of trans-[IrCl(C₂H₄)(κ-P-iPr₂P(CH₂)₃NMe₂)₂]* (**9**). – a) A suspension of 132 mg (0.15 mmol) of **1** in 5 ml of pentane was treated with 149 µl (0.60 mmol) of **2c** and stirred for 5 min at room temp. A slow stream of ethene was then passed through the reaction mixture for 1 min. A change of color from yellow to orange occurred. The solvent was removed, the residue was dissolved in 3 ml of benzene, and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, an orange fraction was eluted from which, after removal of the solvent, an orange, moderately air-sensitive oil was obtained; yield 82 mg (42%).

b) A suspension of 153 mg (0.27 mmol) of **7** in 5 ml of pentane was treated with 273 µl (1.08 mmol) of **2c** and stirred for 1 h at room temp. A dark oily precipitate was formed, which was separated by filtration. The filtrate was brought to dryness in vacuo, the orange oily residue was repeatedly washed with small amounts of pentane (0°C) and dried; yield 336 mg (94%). – $^1$H NMR (400 MHz, $C_6D_6$): δ = 2.55 (m, 4 H, PC*H*CH$_3$), 2.09 [t, *J*(HH) = 6.7 Hz, 4 H, C*H*$_2$NMe$_2$], 2.06 (s, 12 H, $NCH_3$), 1.83 [t, *J*(PH) = 4.3 Hz, 4 H, $C_2H_4$], 1.60 (m, 8 H, $PCH_2CH_2$), 1.39 [dvt, *N* = 14.3, *J*(HH) = 7.1 Hz, 12 H, PCHC*H*$_3$], 1.14 [dvt, *N* = 13.1, *J*(HH) = 7.0 Hz, 12 H, PCHC*H*$_3$]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 13.5 (s). – $C_{24}H_{56}ClIrN_2P_2$ (662.3): calcd. C 43.52, H 8.52, N 4.23; found C 43.29, H 8.69, N 3.87.

7. *Preparation of trans-[IrCl(CO)(κ-P-iPr₂PCH₂CO₂Et)₂]* (**10**). – a) Analogously as described for **8**, from 126 mg (0.14 mmol) of **1**, 119 µl (0.56 mmol) of **2b** and CO. Yellow air-stable oil; yield 100 mg (53%).

b) A slow stream of CO was passed through a solution of 84 mg (0.13 mmol) of **8** in 5 ml of benzene for 15 sec at room temp. A change of color from orange to bright yellow occurred. The solvent was removed in vacuo and the residue repeatedly washed with pentane (0°C) to give a yellow, air-stable oil; yield 69 mg (83%). – IR ($C_6H_5$): $\tilde{\nu}$ = 1935 cm$^{-1}$ [ν(CO)], 1725 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 3.83 [q, *J*(HH) = 7.1 Hz, 4 H, C*H*$_2$CH$_3$], 3.34 (vt, *N* = 7.6 Hz, 4 H, $PCH_2$), 2.69 (m, 4 H, PC*H*CH$_3$), 1.33 [dvt, *N* = 16.5, *J*(HH) = 7.0 Hz, 12 H, PCHC*H*$_3$], 1.22 [dvt, *N* = 14.6, *J*(HH) = 7.3 Hz, 12 H, PCHC*H*$_3$], 0.92 [t, *J*(HH) = 7.1 Hz, 6 H, CH$_2$C*H*$_3$]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 35.5 (s). – $C_{21}H_{42}ClIrO_5P_2$ (664.2): calcd. C 37.98, H 6.37; found C 37.63, H 5.98.

8. *Preparation of trans-[IrCl(CO)(κ-P-iPr₂P(CH₂)₃NMe₂)₂]* (**11**). – a) Analogously as described for **9**, from 145 mg (0.16 mmol) of **1**, 164 µl (0.64 mmol) of **2c** and CO. Yellow air-stable solid; yield 164 mg (76%).

b) A slow stream of CO was passed through a solution of 73 mg (0.11 mmol) of **9** in 5 ml of benzene for 15 sec at room temp. After the solution was worked up as described for **10**, a yellow air-stable solid was isolated; yield 63 mg (86%); m.p. 81°C. – IR (KBr): $\tilde{\nu}$ = 1930 cm$^{-1}$ [ν(CO)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 2.32 (m, 4 H, PC*H*CH$_3$), 2.77 [t, *J*(HH) = 6.7 Hz, 4 H, C*H*$_2$NMe$_2$], 2.12 (s, 12 H, $NCH_3$), 2.11 (m, 4 H, $PCH_2CH_2$), 1.97 (m, 4 H, $PCH_2CH_2$), 1.32 [dvt, *N* = 14.9, *J*(HH) = 7.2 Hz, 12 H, PCHC*H*$_3$], 1.14 [dvt, *N* = 13.9, *J*(HH) = 7.1 Hz, 12 H, PCHC*H*$_3$]. – $^{13}$C NMR (100.6 MHz, $C_6D_6$): δ = 173.0 [t, *J*(PC) = 11.0 Hz, IrCO], 61.3 (vt, *N* = 14.7 Hz, *C*H$_2$NMe$_2$), 45.6 (s, $NCH_3$), 24.8 (vt, *N* = 31.7 Hz, PCHCH$_3$), 24.5 (s, $PCH_2CH_2$), 19.8 (s, PCH*C*H$_3$), 19.3 (vt, *N* =

28.1 Hz, $PCH_2$), 18.5 (s, $PCHCH_3$). – $^{31}P$ NMR (162.0 MHz, $C_6D_6$): δ = 35.3 (s). – $C_{23}H_{52}ClIrN_2OP_2$ (662.3): calcd. C 41.71, H 7.91, N 4.23; found C 41.64, H 8.24, N 3.86.

9. *Preparation of trans-[IrBr(C$_2$H$_4$)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**12**). – a) A solution of 80 mg (0.13 mmol) of **5** in 8 ml of ether was treated with 0.1 ml of a 1.35 M solution (0.13 mmol) of PhMgBr in ether at −35°C and stirred for 2 h. Upon warming to room temp., the solvent was removed, and the residue was extracted with a mixture of 5 ml of pentane and 2 ml of benzene. The extract was filtered and, after the filtrate was brought to dryness in vacuo, an orange air-sensitive oil was obtained; yield 57 mg (67%).

b) A solution of 161 mg (0.25 mmol) of **5** in 5 ml of acetone was treated with a large excess of KBr (ca. 1 g) and stirred for 6 h at room temp. The solution was filtered, the filtrate was brought to dryness in vacuo, and the residue was extracted with a mixture of 10 ml of pentane and 2 ml of benzene. The extract was worked up as described for a) to give an orange air-sensitive oil; yield 109 mg (63%). – IR (KBr): $\tilde{\nu}$ = 1725 $cm^{-1}$ [ν(C=O)]. – $^1H$ NMR (400 MHz, $C_6D_6$): δ = 3.25 (s, 6 H, $CO_2CH_3$), 2.98 (m, 4 H, $PCHCH_3$), 2.43 (vt, *N* = 5.4 Hz, 4 H, $PCH_2$), 1.63 [t, *J*(PH) = 4.7 Hz, 4 H, $C_2H_4$], 1.37 [dvt, *N* = 15.4, *J*(HH) = 7.1 Hz, 12 H, $PCHCH_3$], 1.19 [dvt, *N* = 13.9, *J*(HH) = 6.9 Hz, 12 H, $PCHCH_3$]. – $^{13}C$ NMR (100.6 MHz, $C_6D_6$): δ = 170.3 (vt, *N* = 4.1 Hz, $CO_2CH_3$), 51.4 (s, $CO_2CH_3$), 24.2 (vt, *N* = 27.1 Hz, $PCHCH_3$), 20.2 (br. s, $C_2H_4$), 19.9 (br. s, $PCHCH_3$), 19.0 (s, $PCHCH_3$), 17.6 (vt, *N* = 11.1 Hz, $PCH_2$). – $^{31}P$ NMR (162.0 MHz, $C_6D_6$): δ = 19.2 (s). – $C_{20}H_{42}BrIrO_4P_2$ (680.6): calcd. C 35.29, H 6.22; found C 35.52, H 6.35.

10. *Preparation of trans-[IrI(C$_2$H$_4$)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**13**). – a) A solution of 155 mg (0.24 mmol) of **5** in 10 ml of ether was treated with 0.27 ml of a 0.9 M solution (0.24 mmol) of $CH_3MgI$ in ether at −35°C and stirred for 2 h. The work-up procedure was the same as that described for **12**, a). Red air-sensitive oil; yield 94 mg (53%).

b) A solution of 168 mg (0.26 mmol) of **5** in 5 ml of THF was treated with a large excess of KI (ca. 1 g) and stirred for 6 h at room temp. The reaction mixture was worked up as described for **12**. Red air-sensitive oil; yield 151 mg (79%). – IR ($C_6H_6$): $\tilde{\nu}$ = 1725 $cm^{-1}$ [ν(C=O)]. – $^1H$ NMR (400 MHz, $C_6D_6$): δ = 3.24 (s, 6 H, $CO_2CH_3$), 3.15 (m, 4 H, $PCHCH_3$), 2.46 (vt, *N* = 5.3 Hz, 4 H, $PCH_2$), 1.76 [t, *J*(PH) = 4.9 Hz, 4 H, $C_2H_4$], 1.38 [dvt, *N* = 15.4, *J*(HH) = 7.9 Hz, 12 H, $PCHCH_3$], 1.18 [dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, 12 H, $PCHCH_3$]. – $^{31}P$ NMR (162.0 MHz, $C_6D_6$): δ = 18.7 (s). – $C_{20}H_{42}IIrO_4P_2$ (727.6): calcd. C 33.01, H 5.81; found C 32.56, H 6.22.

11. *Preparation of trans-[Ir(CH$_3$)(C$_2$H$_4$)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**14**): A solution of 255 mg (0.40 mmol) of **5** in 20 ml of ether was treated with 0.50 ml of a 0.85 M solution (0.42 mmol) of $CH_3MgCl$ in ether at −35°C and stirred for 2 h. By using the same work-up procedure as described for **12**, a red extremely air-sensitive oil was obtained; yield 140 mg (57%). – IR ($C_6H_6$): $\tilde{\nu}$ = 1725 $cm^{-1}$ [ν(C=O)]. – $^1H$ NMR (400 MHz, $C_6D_6$): δ = 3.27 (s, 6 H, $CO_2CH_3$), 2.63 (m, 4 H, $PCHCH_3$), 2.60 (vt, *N* = 4.9 Hz, 4 H, $PCH_2$), 1.68 [t, *J*(PH) = 4.0 Hz, 4 H, $C_2H_4$], 1.25 [dvt, *N* = 14.9, *J*(HH) = 7.2 Hz, 12 H, $PCHCH_3$], 1.22 [dvt, *N* = 13.3, *J*(HH) = 7.0 Hz, 12 H, $PCHCH_3$], 1.15 [br. t, *J*(PH) = 6.0 Hz, 3 H, $IrCH_3$]. – $^{13}C$ NMR (50.3 MHz, $C_6D_6$): δ = 171.1 (br. s, $CO_2CH_3$), 51.2 (s, $CO_2CH_3$), 27.9 (br. s, $C_2H_4$), 23.0 (vt, *N* = 25.9 Hz, $PCHCH_3$), 19.2 (vt, *N* = 4.6 Hz, $PCHCH_3$), 18.4 (s, $PCHCH_3$), 17.4 (br. vt, *N* = 7.4 Hz, $PCH_2$), 5.3 [br. t, *J*(PC) = 8.3 Hz, $IrCH_3$]. – $^{31}P$ NMR (162.0 MHz, $C_6D_6$): δ = 24.1 (s).

12. *Preparation of [IrHCl(E-CH=CHPh)(CO)(κ-P-iPr$_2$PCH$_2$-CO$_2$Me)$_2$]* (**15**): A solution of 88 mg (0.14 mmol) of **5** in 5 ml of benzene was treated with 34 μl (0.28 mmol) of HC≡CCH(Ph)OH and stirred for 40 min at room temp. The solvent was removed, the residue was dissolved in 2 ml of benzene and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, a dark red fraction was eluted from which after removal of the solvent a red-brown, almost air-stable oil was isolated; yield 75 mg (72%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2275 $cm^{-1}$ [ν(IrH)], 1995 [ν(CO)], 1725 [ν(C=O)]. – $^1H$ NMR (400 MHz, $C_6D_6$): δ = 8.53 [d, *J*(HH) = 18.3 Hz, 1 H, IrCH], 7.51 (m, 2 H, $C_6H_5$), 7.23 (m, 2 H, $C_6H_5$), 7.05 [d, *J*(HH) = 18.3 Hz, 1 H, IrCH=C*H*Ph], 7.01 (m, 1 H, $C_6H_5$), 3.67 [dvt, *N* = 9.3, *J*(HH) = 14.8 Hz, 2 H, $PCH_2$], 3.13 (s, 6 H, $CO_2CH_3$), 3.10 [dvt, *N* = 7.8, *J*(HH) = 14.8 Hz, 2 H, $PCH_2$], 2.79, 2.44 (2 m, 2 H each, $PCHCH_3$), 1.22 [dvt, *N* = 16.5, *J*(HH) = 6.9 Hz, 6 H, $PCHCH_3$], 1.18, 1.14, 1.04 [3 dvt, *N* = 14.9, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], −8.38 [t, *J*(PH) = 15.2 Hz, 1 H, IrH]. – $^{13}C$ NMR (50.3 MHz, $C_6D_6$): δ = 169.9 [t, *J*(PC) = 8.3 Hz, IrCO], 169.8 (vt, *N* = 3.7 Hz, $CO_2CH_3$), 142.8 [t, *J*(PC) = 1.9 Hz, *ipso*-C of $C_6H_5$], 141.0 [t, *J*(PC) = 8.1 Hz, IrCH], 139.1 [t, *J*(PC) = 2.8 Hz, IrCH=CHPh], 128.8, 125.4, 125.2 (3 s, $C_6H_5$), 51.4 (s, $CO_2CH_3$), 25.3 (vt, *N* = 29.6 Hz, $PCHCH_3$), 24.8 (vt, *N* = 20.4 Hz, $PCH_2$), 23.3 (vt, *N* = 31.4 Hz, $PCHCH_3$), 18.1, 17.9, 17.5, 17.3 (4 s, $PCHCH_3$). – $^{31}P$ NMR (162.0 MHz, $C_6D_6$): δ = 10.9 (s; d in off-resonance). – $C_{27}H_{46}ClIrO_5P_2$ (740.3): calcd. C 43.81, H 6.26; found C 43.53, H 6.34.

13. *Preparation of [IrHCl(CH=CH$_2$)(κ$^2$-P,O-iPr$_2$PCH$_2$C-(OMe)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)]* (**16**): A solution of 47 mg (0.07 mmol) of **5** in 3 ml of benzene was irradiated with a UV lamp (Osram HBO 500W) for 15 min at 10°C. The solvent was removed, the pale yellow oily residue was repeatedly washed with 1-ml portions of pentane (0°C) and dried. Colorless, only moderately air-sensitive crystals were obtained; yield 43 mg (92%), m.p. 104°C. – IR ($C_6H_6$): $\tilde{\nu}$ = 2195 $cm^{-1}$ [ν(IrH)], 1730, 1650 [ν(C=O)], 1555 [ν(C=C)]. – $^1H$ NMR (400 MHz, [D$_8$]toluene): δ = 8.03 [br. dd, *J*(HH) = 16.9 and 9.2 Hz, 1 H, IrCH], 5.95 [br. dd, *J*(HH) = 9.2 and 2.8 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.09 [br. dd, *J*(HH) = 16.9 and 2.8 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.22 (s, 6 H, $CO_2CH_3$), 3.19 (vt, *N* = 7.7 Hz, 4 H, $PCH_2$), 2.82, 2.27 (2 m, 2 H each, $PCHCH_3$), 1.31 [dvt, *N* = 14.6, *J*(HH) = 7.0 Hz, 6 H, $PCHCH_3$], 1.21 [dvt, *N* = 15.1, *J*(HH) = 6.9 Hz, 6 H, $PCHCH_3$], 1.13 [dvt, *N* = 14.3, *J*(HH) = 7.2 Hz, 6 H, $PCHCH_3$], 1.07 [dvt, *N* = 14.8, *J*(HH) = 6.7 Hz, 6 H, $PCHCH_3$], −22.57 (br. s, 1 H, IrH). – $^{13}C$ NMR (22.5 MHz, $C_6D_6$): δ = 177.5 (s, $CO_2CH_3$), 120.9 [t, *J*(PH) = 3.7 Hz, IrCH=$CH_2$], 118.2 [t, *J*(PC) = 8.8 Hz, IrCH], 52.5 (s, $CO_2CH_3$), 28.8 (vt, *N* = 18.3 Hz, $PCH_2$), 24.1 (vt, *N* = 30.8 Hz, $PCHCH_3$), 22.3 (vt, *N* = 27.8 Hz, $PCHCH_3$), 18.3, 18.1, 18.0, 17.9 (4 s, $PCHCH_3$). – $^{31}P$ NMR (162.0 MHz, [D$_8$]toluene, 25°C): δ = 23.3 (br. s, d in off-resonance); at −70°C: δ = 27.9, 20.8 [AB spin system, *J*(PP) = 371.3 Hz]. – $C_{20}H_{42}ClIrO_4P_2$ (636.2): calcd. C 37.76, H 6.65; found C 37.83, H 6.49.

14. *Preparation of [IrHCl(CH=CH$_2$)(κ$^2$-P,O-iPr$_2$PCH$_2$C-(OEt)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Et)]* (**17**): Analogously as described for **16**, from 87 mg (0.13 mmol) of **8**. Colorless, only moderately air-sensitive oil; yield 62 mg (84%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2190 $cm^{-1}$ [ν(IrH)], 1725, 1650 [ν(C=O)], 1555 [ν(C=C)]. – $^1H$ NMR (400 MHz, $C_6D_6$): δ = 8.18 [br. dd, *J*(HH) = 17.0 and 9.3 Hz, 1 H, IrCH], 6.06 [br. dd, *J*(HH) = 9.3 and 2.6 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.19 [br. dd, *J*(HH) = 17.0 and 2.6 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.79 [q, *J*(HH) = 7.1 Hz, 4 H, $CH_2CH_3$], 3.28 [dvt, *N* = 7.8, *J*(HH) = 15.1 Hz, 2 H, $PCH_2$], 3.21 (m, 2 H, $PCH_2$), 2.89, 2.27 (2 m, 2 H each, $PCHCH_3$), 1.37 [br. d, *J*(HH) = 6.6 Hz, 6 H, $PCHCH_3$], 1.26 [dvt, *N* = 15.0, *J*(HH) = 6.9 Hz, 6

H, PCHC$H_3$], 1.18 [dvt, $N$ = 14.1, $J$(HH) = 7.2 Hz, 6 H, PCHC$H_3$], 1.12 [br. d, $J$(HH) = 5.8 Hz, 6 H, PCHC$H_3$], 0.85 [t, $J$(HH) = 7.1 Hz, 6 H, $CH_2CH_3$], −22.42 (br. s, 1 H, IrH). − $^{31}$P NMR (36.2 MHz, [D$_8$]toluene, 25°C): δ = 23.0 (br.s; d in off-resonance); at −75°C: δ = 27.4, 20.4 [AB spin system, $J$(PP) = 371.5 Hz]. − $C_{22}H_{46}ClIrO_4P_2$ (664.2): calcd. C 39.78, H 6.98; found C 39.56, H 6.73.

15. *Thermolysis of* **16** *and* **17**: A solution of 45 mg (0.07 mmol) of **16** or 58 mg (0.09 mmol) of **17** in 5 ml of benzene was stirred for 20 h (**16**) or 50 h (**17**) at 80°C. In both cases, a change of color from off-white to orange occurred. After the solvent was removed, an orange oily residue remained which was washed with small amounts of pentane (0°C) and dried. The $^1$H- and $^{31}$P-NMR data confirmed that **5** or **8**, respectively, was formed; yield 39 mg (86%) of **5** and 42 mg (72%) of **8**.

16. *Preparation of [IrHCl(κ²-C,O-CH=CHC(Me)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**18**). − a) A solution of 249 mg (0.41 mmol) of **3** in 6 ml of benzene was treated with 100 μl (1.20 mmol) of methylvinylketone at room temp. A rapid change of color from brownish-yellow to deep red occurred. The reaction mixture was stirred for 20 h at 60°C which led again to a change of color to orange-yellow. The solvent was removed, the oily residue was dissolved in 3 ml of benzene, and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, an orange fraction was eluted from which upon removal of the solvent an orange-yellow, slightly air-sensitive oil was isolated; yield 164 mg (59%).

b) A solution of 112 mg (0.18 mmol) of **4** in 4 ml of benzene was treated with 100 μl (0.20 mmol) of methylvinylketone and stirred for 20 h at 60°C. By using the same work-up procedure as for a), an orange-yellow oil was obtained; yield 67 mg (54%). − IR ($C_6H_6$): $\tilde{\nu}$ = 2235 cm$^{-1}$ [ν(IrH)], 1730, 1545 [ν(C=O)]. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 10.82 [d, $J$(HH) = 7.5 Hz, 1 H, IrCH], 6.84 [d, $J$(HH) = 7.5 Hz, 1 H, IrCH=C$H$], 3.24 (s, 6 H, $CO_2CH_3$), 3.08, 2.69 [2 dvt, $N$ = 7.8, $J$(HH) = 14.5 Hz, 2 H each, $PCH_2$], 2.82, 2.49 (2 m, 2 H each, PC$H$CH$_3$), 2.05 [s, 3 H, C(O)CH$_3$], 1.32 [dvt, $N$ = 15.4, $J$(HH) = 7.1 Hz, 6 H, PCHC$H_3$], 1.24 [dvt, $N$ = 14.7, $J$(HH) = 6.9 Hz, 6 H, PCHC$H_3$], 1.10 [dvt, $N$ = 15.8, $J$(HH) = 7.1 Hz, 6 H, PCHC$H_3$], 0.98 [dvt, $N$ = 13.8, $J$(HH) = 7.1 Hz, 6 H, PCHC$H_3$], −24.36 [t, $J$(PH) = 16.5 Hz, 1 H, IrH]. − $^{13}$C NMR (50.3 MHz, $C_6D_6$): δ = 208.3 [s, $C$(O)CH$_3$], 199.5 [t, $J$(PC) = 6.4 Hz, IrCH], 170.6 (vt, $N$ = 5.6 Hz, $CO_2CH_3$), 134.7 (s, IrCH=$C$H), 51.2 (s, $CO_2CH_3$), 25.8 [vt, $N$ = 17.6 Hz, $PCH_2$], 24.6 [s, C(O)$CH_3$], 23.6, 23.0 (2 vt, $N$ = 29.6 Hz, P$C$HCH$_3$), 17.9, 17.3, 17.0, 16.7 (4 s, PCH$CH_3$). − $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 15.2 (s; d in off-resonance). − $C_{22}H_{44}ClIrO_5P_2$ (678.2): calcd. C 38.96, H 6.54; found C 38.72, H 6.18.

17. *Preparation of [IrHCl(κ²-C,O-CH=CHC(OMe)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**19**). − a) Analogously as described for **18**, from 187 mg (0.31 mmol) of **3** and 100 μl (1.10 mmol) of methyl acrylate in 5 ml of benzene. Orange-yellow, moderately air-sensitive oil; yield 131 mg (61%).

b) Analogously as described for **18**, from 93 mg (0.14 mmol) of **4** and 100 μl (1.10 mmol) of methyl acrylate in 4 ml of benzene. Orange-yellow, moderately air-sensitive oil; yield 54 mg (52%). − IR ($C_6H_6$): $\tilde{\nu}$ = 2275 cm$^{-1}$ [ν(IrH)], 1730, 1580 [ν(C=O)]. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 10.34 [d, $J$(HH) = 8.0 Hz, 1 H, IrCH], 6.61 [d, $J$(HH) = 8.0 Hz, 1 H, IrCH=C$H$], 3.51 (s, 3 H, = $CHCO_2CH_3$), 3.23 (s, 6 H, $PCH_2CO_2CH_3$), 3.16, 2.75 [2 dvt, $N$ = 7.8, $J$(HH) = 14.4 Hz, 2 H each, $PCH_2$], 2.90, 2.58 (2 m, 2 H each, PC$H$CH$_3$), 1.34 [dvt, $N$ = 15.8, $J$(HH) = 7.1 Hz, 6 H, PCHC$H_3$], 1.25 [dvt, $N$ = 14.8, $J$(HH) = 7.0 Hz, 6 H, PCHC$H_3$], 1.14 [dvt, $N$ = 15.9, $J$(HH) = 7.0 Hz, 6 H, PCHC$H_3$], 1.00 [dvt, $N$ = 13.5, $J$(HH) = 7.1 Hz, 6 H, PCHC$H_3$], −27.32 [t, $J$(PH) = 15.9 Hz, 1 H, IrH]. − $^{13}$C NMR (50.3 MHz, $C_6D_6$): δ = 184.3 [t, $J$(PC) = 7.1 Hz, IrCH], 182.8 (s, =$CHCO_2CH_3$), 170.7 (vt, $N$ = 4.1 Hz, $PCH_2CO_2CH_3$), 120.5 (s, IrCH=$C$H), 52.6 (s, =$CHCO_2CH_3$), 51.2 (s, $PCH_2CO_2CH_3$), 25.5 (vt, $N$ = 17.3 Hz, $PCH_2$), 23.7, 22.8 (2 vt, $N$ = 29.5 Hz, P$C$HCH$_3$), 18.0, 17.9, 17.3, 16.7 (4 s, PCH$CH_3$). − $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 15.3 (s; d in off-resonance). − $C_{22}H_{44}ClIrO_6P_2$ (694.2): calcd. C 38.06, H 6.39; found C 37.55, H 5.94.

18. *Preparation of [IrHCl(CH=CH$_2$)(CO)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**20**): A slow stream of CO was passed through a solution of 47 mg (0.07 mmol) of **16** in 5 ml of benzene for 15 sec at room temp. Upon removal of the solvent, a pale-yellow, almost air-stable oil was obtained, which was repeatedly washed with pentane (0°C) and dried; yield 44 mg (93%). − IR ($C_6H_6$): $\tilde{\nu}$ = 2095 cm$^{-1}$ [ν(IrH)], 1980 [ν(CO)], 1730 [ν(C=O)], 1560 [ν(C=C)]. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.14 [br. ddd, $J$(HH) = 17.6, 9.9, and 3.6 Hz, 1 H, IrCH], 6.24 [br. dd, $J$(HH) = 9.9 and 1.9 Hz, 1 H, one H of =$CH_2$, *trans* to Ir], 5.37 [br. dd, $J$(HH) = 17.6 and 1.9 Hz, 1 H, one H of =$CH_2$, *cis* to Ir], 3.39, 3.30 [2 dvt, $N$ = 8.6, $J$(HH) = 14.7 Hz, 2 H each, $PCH_2$], 3.23 (s, 6 H, $CO_2CH_3$), 2.82, 2.61 (2 m, 2 H each, PC$H$CH$_3$), 1.25, 1.23 [2 dvt, $N$ = 16.2, $J$(HH) = 7.0 Hz, 6 H each, PCHC$H_3$], 1.16, 1.09 [2 dvt, $N$ = 14.6, $J$(HH) = 7.0 Hz, 6 H each, PCHC$H_3$], −7.82 [dt, $J$(PH) = 17.5, $J$(HH) = 3.6 Hz, 1 H, IrH]. − $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 13.1 (s; d in off-resonance). − $C_{21}H_{42}ClIrO_5P_2$ (664.2): calcd. C 37.98, H 6.37; found C 37.87, H 6.42.

19. *Preparation of [IrHCl(CH=CH$_2$)(CO)(κ-P-iPr$_2$PCH$_2$CO$_2$Et)$_2$]* (**21**): Analogously as described for **20**, from 77 mg (0.12 mmol) of **17** and CO. Pale-yellow, almost air-stable oil; yield 72 mg (90%). − IR ($C_6H_6$): $\tilde{\nu}$ = 2090 cm$^{-1}$ [ν(IrH)], 1975 [ν(CO)], 1725 [ν(C=O)], 1555 [ν(C=C)]. − $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.15 [br. ddd, $J$(HH) = 17.6, 9.9, and 3.7 Hz, 1 H, IrCH], 6.24 [br. dd, $J$(HH) = 9.9 and 1.7 Hz, 1 H, one H of =$CH_2$, *trans* to Ir], 5.37 [br. dd, $J$(HH) = 17.6 and 1.7 Hz, 1 H, one H of =$CH_2$, *cis* to Ir], 3.83 [q, $J$(HH) = 7.1 Hz, 4 H, $CH_2CH_3$], 3.43, 3.32 [2 dvt, $N$ = 9.0, $J$(HH) = 14.7 Hz, 2 H each, $PCH_2$], 2.87, 2.68 (2 m, 2 H each, PC$H$CH$_3$), 1.28, 1.26 [2 dvt, $N$ = 15.9, $J$(HH) = 6.8 Hz, 6 H each, PCHC$H_3$], 1.20, 1.13 [2 dvt, $N$ = 15.2, $J$(HH) = 7.0 Hz, 6 H each, PCHC$H_3$], 0.90 [t, $J$(HH) = 7.1 Hz, 6 H, $CH_2CH_3$], −7.79 [dt, $J$(PH) = 16.4, $J$(HH) = 3.7 Hz, 1 H, IrH]. − $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 13.2 (s; d in off-resonance). − $C_{23}H_{46}ClIrO_5P_2$ (692.2): calcd C 39.91, H 6.70; found C 39.46, H 6.59.

20. *Thermolysis of* **20**: A solution of 42 mg (0.06 mmol) of **20** in 5 ml of benzene was stirred for 40 h at 80°C. After removal of the solvent, the oily residue was dissolved in 2 ml of benzene and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, a yellow fraction was eluted from which a yellow oil was isolated; yield 26 mg (64%). By comparison of the IR and $^1$H NMR spectroscopic data, the product was characterized as **6**.

21. *Preparation of [IrHBr(CH=CH$_2$)(κ²-P,O-iPr$_2$PCH$_2$C(OMe)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)]* (**22**): a) A solution of 68 mg (0.11 mmol) of **16** in 8 ml of ether was treated with 80 μl of a 1.35 M solution (0.11 mmol) of PhMgBr in ether at −35°C. After warming to room temp., the reaction mixture was stirred for 2 h and then the solvent was removed. The residue was worked up as described for **12** to give an off-white oil; yield 61 mg (84%).

b) A solution of 110 mg (0.17 mmol) of **16** in 10 ml of acetone was treated with a large excess of KBr (ca. 1 g) and stirred for 6 h at room temp. After removal of the solvent, the residue was worked up as described for **12** to give an off-white oil; yield 94 mg (80%). − IR ($C_6H_6$): $\tilde{\nu}$ = 2190 cm$^{-1}$ [ν(IrH)], 1730, 1655 [ν(C=O)]. − $^1$H

NMR (400 MHz, $C_6D_6$): δ = 8.25 [br. dd, *J*(HH) = 16.9 and 9.3 Hz, 1 H, IrCH], 5.99 [br. dd, *J*(HH) = 9.3 and 2.9 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.12 [br. dd, *J*(HH) = 16.9 and 2.9 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.25 (m, 4 H, $PCH_2$), 3.13 (s, 6 H, $CO_2CH_3$), 3.00, 2.27 (2 m, 2 H each, $PCHCH_3$), 1.29 [br. d, *J*(HH) = 5.1 Hz, 6 H, $PCHCH_3$], 1.22, 1.16, 1.04 [3 br. d, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], −21.52 (br. s, 1 H, IrH). – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 21.0 (br. s). – $C_{20}H_{42}BrIrO_4P_2$ (680.6): calcd. C 35.29, H 6.22; found C 35.58, H 6.09.

22. *Preparation of [IrHI(CH=CH$_2$)(κ$^2$-P,O-iPr$_2$PCH$_2$C(OMe)=O)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)]* (**23**). – a) A solution of 118 mg (0.16 mmol) of **16** in 8 ml of ether was treated with 0.17 ml of a 0.9 M solution (0.16 mmol) of $CH_3MgI$ in ether at room temp. The work-up procedure was the same as that described for **12**. Colorless, only slightly air-sensitive oil; yield 101 mg (89%).

b) A solution of 115 mg (0.18 mmol) of **16** in 5 ml of THF was treated with a large excess of KI (ca. 1 g) and stirred for 2 h at room temp. After removal of the solvent, the residue was worked up as described for **12** to give a colorless, only slightly air-sensitive oil; yield 73 mg (55%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2190 cm$^{-1}$ [ν(IrH)], 1730, 1650 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 8.35 [br. dd, *J*(HH) = 16.9 and 9.2 Hz, 1 H, IrCH], 5.86 [br. dd, *J*(HH) = 9.2 and 2.7 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.03 [br. dd, *J*(HH) = 16.9 and 2.7 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.29 (m, 4 H, $PCH_2$), 3.14 (s, 6 H, $CO_2CH_3$), 2.30, 2.17 (2 m, 2 H each, $PCHCH_3$), 1.20 (m, 18 H, $PCHCH_3$), 0.99 (m, 6 H, $PCHCH_3$), −19.46 (br. s, 1 H, IrH). – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 17.5 (br. s). – $C_{20}H_{42}IIrO_4P_2$ (727.6): calcd. C 33.01, H 5.81; found C 33.04, H 5.61.

23. *Preparation of [IrHBr(CH=CH$_2$)(CO)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**24**). – a) Analogously as described for **22**, from 122 mg (0.18 mmol) of **20** in 10 ml of ether and 0.14 ml of a 1.35 M solution (0.18 mmol) of PhMgBr in ether. Colorless, almost air-stable oil; yield 41 mg (32%).

b) Analogously as described for **22**, from 113 mg (0.17 mmol) of **20** and ca. 1 g of KBr in acetone. Colorless, almost air-stable oil; yield 64 mg (53%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2100 cm$^{-1}$ [ν(IrH)], 2000 [ν(CO)], 1745 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.20 [br. ddd, *J*(HH) = 17.2, 9.8 and 3.4 Hz, 1 H, IrCH], 6.22 [br. dd, *J*(HH) = 9.8 and 1.3 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.39 [br. dd, *J*(HH) = 17.2 and 1.3 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.39, 3.29 [2 dvt, *N* = 8.6, *J*(HH) = 14.6 Hz, 2 H each, $PCH_2$], 3.22 (s, 6 H, $CO_2CH_3$), 2.90, 2.65 (2 m, 2 H each, $PCHCH_3$), 1.24 [dvt, *N* = 15.6, *J*(HH) = 6.2 Hz, 6 H, $PCHCH_3$], 1.22 [dvt, *N* = 15.1, *J*(HH) = 7.8 Hz, 6 H, $PCHCH_3$], 1.14, 1.07 [2 dvt, *N* = 14.6, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], −8.45 [dt, *J*(PH) = 18.0, *J*(HH) = 3.4 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 9.6 (s; d in off-resonance). – $C_{21}H_{42}BrIrO_5P_2$ (708.6): calcd. C 35.59, H 5.97; found C 35.43, H 6.32.

24. *Preparation of [IrHI(CH=CH$_2$)(CO)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**25**). – a) Analogously as described for **23**, from 74 mg (0.11 mmol) of **20** and 0.12 ml of a 0.9 M solution (0.11 mmol) of $CH_3MgI$ in ether. Colorless, almost air-stable oil; yield 48 mg (57%).

b) Analogously as described for **23**, from 131 mg (0.20 mmol) of **20** and ca. 1 g of KI in THF. Colorless, almost air-stable oil; yield 78 mg (52%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2100 cm$^{-1}$ [ν(IrH)], 1990 [ν(CO)], 1730 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.26 [br. ddd, *J*(HH) = 17.7, 9.7, and 3.9 Hz, 1 H, IrCH], 6.22 [br. dd, *J*(HH) = 9.7 and 1.5 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.42 [br. dd, *J*(HH) = 17.7 and 1.5 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.35, 3.29 [2 dvt, *N* = 8.7, *J*(HH) = 14.6 Hz, 2 H each, $PCH_2$], 3.21 (s, 6 H, $CO_2CH_3$), 3.03, 2.70 (2 m, 2 H each, $PCHCH_3$), 1.26, 1.25 [2 br. d, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], 1.11, 1.05 [2 dvt, *N* = 14.7, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], −9.85 [dt, *J*(PH) = 18.0, *J*(HH) = 3.9 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 4.6 (s; d in off-resonance). – $C_{21}H_{42}IIrO_5P_2$ (755.6): calcd. C 33.38, H 5.60; found C 33.07, H 5.36.

25. *Preparation of [IrHCl(CH=CH$_2$)(CNMe)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**26a**): A solution of 78 mg (0.12 mmol) of **16** in 5 ml of benzene was treated with 6.9 µl (0.12 mmol) of methyl isocyanide and stirred for 2 h at room temp. After the solvent was removed, a colorless, only slightly air-sensitive oil was obtained; yield 68 mg (82%). – IR (KBr): $\tilde{\nu}$ = 2180 cm$^{-1}$ [ν(C≡N)], 1715 [ν(C=O)], 1555 [ν(C=C)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.55 [br. ddd, *J*(HH) = 17.6, 9.9, and 2.6 Hz, 1 H, IrCH], 6.27 [br. dd, *J*(HH) = 9.9 and 3.0 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.32 [br. dd, *J*(HH) = 17.6 and 3.0 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.71, 3.38 [2 dvt, *N* = 8.6, *J*(HH) = 14.6 Hz, 2 H each, $PCH_2$], 3.27 (s, 6 H, $CO_2CH_3$), 2.92, 2.79 (2 m, 2 H each, $PCHCH_3$), 2.28 (s, 3 H, $CNCH_3$), 1.34 (m, 18 H, $PCHCH_3$), 1.19 [dvt, *N* = 14.3, *J*(HH) = 7.1 Hz, 6 H, $PCHCH_3$], −10.48 [dt, *J*(PH) = 18.0, *J*(HH) = 2.6 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 12.0 (s; d in off-resonance). – $C_{22}H_{45}ClIrNO_4P_2$ (677.2): calcd. C 39.02, H 6.70, N 2.07; found C 38.82, H 7.06, N 1.79.

26. *Preparation of [IrHCl(CH=CH$_2$)(CNtBu)(κ-P-iPr$_2$PCH$_2$CO$_2$Me)$_2$]* (**27a**): Analogously as described for **26a**, from 74 mg (0.11 mmol) of **16** and 12 µl (0.11 mmol) of *t*BuNC. Yellow, almost air-stable oil; yield 62 mg (80%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2155 cm$^{-1}$ [ν(C≡N)], 1730 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 7.58 [br. ddd, *J*(HH) = 17.6, 9.9, and 2.4 Hz, 1 H, IrCH], 6.26 [br. dd, *J*(HH) = 9.9 and 3.0 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.36 [br, *J*(HH) = 17.6 and 3.0 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.77, 3.37 [2 dvt, *N* = 8.5, *J*(HH) = 14.7 Hz, 2 H each, $PCH_2$], 3.26 (s, 6 H, $CO_2CH_3$), 2.91, 2.79 (2 m, 2 H each, $PCHCH_3$), 1.38 (m, 18 H, $PCHCH_3$), 1.19 [dvt, *N* = 13.4, *J*(HH) = 7.1 Hz, 6 H, $PCHCH_3$], 1.11 (s, 9 H, $CCH_3$), −10.44 [br. t, *J*(PH) = 18.0 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 12.4 (s; d in off-resonance). – $C_{25}H_{51}ClIrNO_4P_2$ (719.3): calcd. C 41.75, H 7.15, N 1.95; found C 41.44, H 7.38, N 1.76.

27. *Thermal Rearrangement of* **26a** *to Isomer* **26b**: A solution of 68 mg (0.10 mmol) of **26a** in 0.5 ml of $C_6D_6$ was kept in an NMR tube for 3 weeks at 60°C. Continuous control by $^{31}$P-NMR spectroscopy confirmed a decrease in concentration of **26a** and an increase in concentration of isomer **26b**. Upon removal of the solvent, a colorless, only slightly air-sensitive oil was isolated; yield 40 mg (59%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2280 cm$^{-1}$ [ν(IrH)], 2160 [ν(C≡N)], 1725 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 8.17 [br. dd, *J*(HH) = 19.1 and 11.8 Hz, 1 H, IrCH], 6.71 [br. dd, *J*(HH) = 11.8 and 4.5 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.70 [br. dd, *J*(HH) = 19.1 and 4.5 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.89, 3.24 [2 dvt, *N* = 8.6, *J*(HH) = 14.6 Hz, 2 H each, $PCH_2$], 3.29 (s, 6 H, $CO_2CH_3$), 3.04, 2.49 (2 m, 2 H each, $PCHCH_3$), 2.25 (s, 3 H, $CNCH_3$), 1.51 [dvt, *N* = 15.4, *J*(HH) = 6.9 Hz, 6 H, $PCHCH_3$], 1.23, 1.16 [2 dvt, *N* = 14.5, *J*(HH) = 6.8 Hz, 6 H each, $PCHCH_3$], 1.04 [dvt, *N* = 13.5, *J*(HH) = 7.1 Hz, 6 H, $PCHCH_3$], −20.50 [t, *J*(PH) = 14.4 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 8.9 (s; d in off-resonance). – $C_{22}H_{45}ClIrNO_4P_2$ (677.2): calcd. C 39.02, H 6.70, N 2.07; found C 38.57, H 6.84, N 1.93.

28. *Thermal Rearrangement of* **27a** *to Isomer* **27b**: Analogously as described for **26b**, from 62 mg (0.07 mmol) of **27a**. After 4 weeks at 60°C, a yellow, almost air-stable oil was isolated; yield 38 mg (61%). – IR ($C_6H_6$): $\tilde{\nu}$ = 2275 cm$^{-1}$ [ν(IrH)], 2135 [ν(C≡N)], 1725

[ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 8.20 [br. dd, *J*(HH) = 19.2 and 11.8 Hz, 1 H, IrCH], 6.72 [br. dd, *J*(HH) = 11.8 and 4.6 Hz, 1 H, one H of $=CH_2$, *trans* to Ir], 5.71 [br. dd, *J*(HH) = 19.2 and 4.6 Hz, 1 H, one H of $=CH_2$, *cis* to Ir], 3.95, 3.26 [2 dvt, *N* = 6.8 Hz, *J*(HH) = 14.4 Hz, 2 H each, $PCH_2$], 3.28 (s, 6 H, $CO_2CH_3$), 3.07, 2.49 (2 m, 2 H each, $PCHCH_3$), 1.52 [dvt, *N* = 15.1, *J*(HH) = 7.0 Hz, 6 H, $PCHCH_3$], 1.28, 1.21 [2 dvt, *N* = 15.4, *J*(HH) = 6.9 Hz, 6 H each, $PCHCH_3$], 1.06 [dvt, *N* = 13.0, *J*(HH) = 7.0 Hz, 6 H, $PCHCH_3$], 0.95 (s, 9 H, $CCH_3$), –20.53 [t, *J*(PH) = 14.0 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 8.4 (s; d in off-resonance). – $C_{25}H_{51}ClIrNO_4P_2$ (719.3): calcd. C 41.75, H 7.15, N 1.95; found C 41.31, H 7.03, N 1.64.

29. *Preparation of [IrHCl(C≡CPh)(κ²-P,O-iPr₂PCH₂C(OMe)=O)(κ-P-iPr₂PCH₂CO₂Me)]* (**28**) from **16**: A solution of 59 mg (0.09 mmol) of **16** in 5 ml of benzene was treated with 10 µl (0.09 mmol) of phenylacetylene and stirred for 2 h at room temp. After the solvent was removed, an orange-yellow oil was obtained which was characterized by $^1$H- and $^{31}$P-NMR spectroscopy as **28**[5]; yield 62 mg (94%).

30. *Preparation of [IrHCl(C≡CCO₂Me)(κ²-P,O-iPr₂PCH₂C(OMe)=O)(κ-P-iPr₂PCH₂CO₂Me)]* (**29**) *from* **16**: Analogously as described for **28**, from 88 mg (0.14 mmol) of **16** and 12 µl (0.14 mmol) of methyl propiolate. The red, only slightly air-sensitive oil was characterized by $^1$H and $^{31}$P NMR spectroscopy as **29**[5]; yield 88 mg (92%).

31. *Preparation of trans-[IrCl(PhC≡CPh)(κ-P-iPr₂PCH₂CO₂Me)₂]* (**30**): A solution of 60 mg (0.09 mmol) of **16** in 5 ml of benzene was treated with 17 mg (0.09 mmol) of diphenylacetylene and stirred for 2 h at 60°C. Upon cooling to room temp., the solvent was removed, the residue was dissolved in 3 ml of benzene, and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade V). With benzene, a yellow fraction was eluted from which, after removal of the solvent, a yellow, moderately air-stable oil was isolated; yield 69 mg (93%). – IR ($C_6H_6$): $\tilde{\nu}$ = 1825 $cm^{-1}$ [ν(C≡C)], 1725 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 8.09 (m, 4 H, *ortho*-H of $C_6H_5$), 7.50 (m, 4 H, *meta*-H of $C_6H_5$), 6.98 (m, 2 H, *para*-H of $C_6H_5$), 2.99 (s, 6 H, $CO_2CH_3$), 2.88 (m, 4 H, $PCHCH_3$), 2.43 (vt, *N* = 6.6 Hz, 4 H, $PCH_2$), 1.52 [dvt, *N* = 15.3, *J*(HH) = 7.2 Hz, 12 H, $PCHCH_3$], 1.07 [dvt, *N* = 14.1, *J*(HH) = 7.1 Hz, 12 H, $PCHCH_3$]. – $^{13}$C NMR (50.3 MHz, $C_6D_6$): δ = 170.2 (vt, *N* = 4.6 Hz, $CO_2CH_3$), 131.9, 129.4, 126.8 (3 s, $C_6H_5$), 90.1 (s, *ipso*-C of $C_6H_5$), 76.1 [t, *J*(PC) = 1.9 Hz, C≡C], 51.1 (s, $CO_2CH_3$), 23.1 (vt, *N* = 25.9 Hz, $PCHCH_3$), 22.0 (vt, *N* = 12.9 Hz, $PCH_2$), 19.8, 18.8 (2 s, $PCHCH_3$). – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 18.2 (s). – $C_{32}H_{48}ClIrO_4P_2$ (790.4): calcd. C 48.88, H 6.15; found C 48.42, H 6.33.

32. *Preparation of trans-[IrCl(MeO₂CC≡CCO₂Me)(κ-P-iPr₂PCH₂CO₂Me)₂]* (**31**): Analogously as described for **30**, from 65 mg (0.10 mmol) of **16** and 15 mg (0.10 mmol) of $C_2(CO_2Me)_2$. Orange, moderately air-stable oil; yield 70 mg (91%). – IR ($C_6H_6$): $\tilde{\nu}$ = 1830 $cm^{-1}$ [ν(C≡C)], 1725 [ν(C=O) of $PCH_2CO_2CH_3$], 1695 [ν(C=O) of $\equiv CCO_2CH_3$]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 3.38 (s, 6 H, $\equiv CCO_2CH_3$), 3.18 (s, 6 H, $PCH_2CO_2CH_3$), 3.01 (m, 4 H, $PCHCH_3$), 2.81 (vt, *N* = 6.8 Hz, 4 H, $PCH_2$), 1.48 [dvt, *N* = 15.5, *J*(HH) = 7.2 Hz, 12 H, $PCHCH_3$], 1.22 [dvt, *N* = 14.3, *J*(HH) = 7.0 Hz, 12 H, $PCHCH_3$]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 19.4 (s). – $C_{24}H_{44}ClIrO_8P_2$ (750.2): calcd. C 38.42, H 5.91; found C 38.40, H 6.24.

33. *Preparation of [Ir(CO)(κ²-P,O-iPr₂PCH=C(OMe)O)(κ-P-iPr₂PCH₂CO₂Me)]* (**32**): A solution of 274 mg (0.43 mmol) of **6** in 5 ml of toluene was treated with 2.5 ml of a 0.17 M solution (0.43 mmol) of $NaN(SiMe_3)_2$ in toluene and stirred for 15 h at 80°C. Upon cooling to room temp., the solvent was removed, and the oily residue was extracted with 20 ml of pentane. The extract was filtered and the filtrate was brought to dryness in vacuo. A yellow, very moisture-sensitive oil was obtained; yield 162 mg (63%). – $^1$H NMR (200 MHz, $C_6D_6$): δ = 3.43 [dd, *J*(PH) = *J*(P'H) = 3.5 Hz, 1 H, PCH=], 3.40 [s, 3 H, $=C(OCH_3)$], 3.20 (s, 3 H, $PCH_2CO_2CH_3$), 3.07 [d, *J*(PH) = 7.6 Hz, 2 H, $PCH_2$], 2.44, 2.05 (2 m, 2 H each, $PCHCH_3$), 1.29, 1.27 [2 dvt, *N* = 13.6, *J*(HH) = 7.0 Hz, 6 H each, $PCHCH_3$], 1.14 (m, 12 H, $PCHCH_3$). – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 46.7, 44.0 [AB system; *J*(PP) = 286.2 Hz].

34. *Preparation of [Ir(CO)(κ²-P,O-iPr₂PCH₂C(=O)O)(κ-P-iPr₂PCH₂CO₂Me)]* (**33**): A solution of 162 mg (0.27 mmol) of **32** in 5 ml of benzene was stored for 24 h at room temp. After the solvent was removed, a yellow microcrystalline solid was obtained. It was identified as **33**[5] by comparison of the $^1$H and $^{31}$P NMR data with those of an authentic sample; yield 153 mg (97%).

35. *Preparation of [IrHCl₂(CO)(κ-P-iPr₂PCH₂CO₂H)(κ-P-iPr₂PCH₂CO₂Me)]* (**34**): A slow stream of HCl gas was passed through a solution of 94 mg (0.16 mmol) of **33** in 5 ml of benzene for 15 sec at room temp. An instantaneous change of color from yellow to off-white occurred. After the solution was stirred for 1 h, the solvent was removed, the residue repeatedly washed with pentane and dried. A colorless, only slightly air-sensitive oil was obtained; yield 91 mg (87%). – IR ($C_6H_6$): $\tilde{\nu}$ = 3120 $cm^{-1}$ [ν(OH)], 2195 [ν(IrH)], 2010 [ν(CO)], 1730, 1700 [ν(C=O)]. – $^1$H NMR (400 MHz, $C_6D_6$): δ = 9.38 (br. s, 1 H, $CO_2H$), 4.00 [br. d, *J*(HH) = 15.3 Hz, 1 H, $PCH_2$], 3.98, 3.68, 3.63 [3 br. d, *J*(HH) = 14.6 Hz, 1 H each, $PCH_2$], 3.20 (s, 3 H, $CO_2CH_3$), 2.71, 2.40 (2 m, 2 H each, $PCHCH_3$), 1.44, 1.41, 1.28, 1.24 [4 br. d, *J*(HH) = 7.0 Hz, 3 H each, $PCHCH_3$], 1.11 [br. d, *J*(HH) = 6.0 Hz, 6 H, $PCHCH_3$], 1.07, 0.97 [2 br. d, *J*(HH) = 7.0 Hz, 3 H each, $PCHCH_3$], –16.04 [dd, *J*(PH) = 12.6, *J*(P'H) = 10.8 Hz, 1 H, IrH]. – $^{31}$P NMR (162.0 MHz, $C_6D_6$): δ = 15.2, 14.6 [AB system; *J*(PP) = 346.2 Hz]. – $C_{18}H_{37}Cl_2IrO_5P_2$ (658.6): calcd. C 32.83, H 5.66; found C 32.57, H 6.03.

36. *Determination of the X-Ray Crystal Structure of* **16**[30]: Single crystals were grown by slow diffusion of hexane into a saturated solution of **16** in benzene. Crystal data (from 23 reflections, 10° < Θ < 12°): triclinic, space group *P*–1 (No. 2); *a* = 8.655(2) Å, *b* = 15.107(3) Å, *c* = 21.594(3) Å, α = 86.83(1)°, β = 88.13(2)°, γ = 80.41(2)°, *V* = 2779(1) Å³, *Z* = 4, $d_{calcd.}$ = 1.52 $gcm^{-3}$, μ(Mo-$K_\alpha$) = 50.2 $cm^{-1}$; crystal size 0.13 × 0.30 × 0.60 mm; Enraf-Nonius CAD4 diffractometer, Mo-$K_\alpha$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.41); *T* = 293 K; ω/Θ scan, max. 2Θ = 44°; 6596 reflections measured, 5492 independent reflections, 4989 reflections with $F_o > 3\sigma(F_o)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (π-scan method) was applied (minimum transmission 55.7%). The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (531 parameters, unit weights, SDP). There are two independent molecules in the unit cell. In both molecules, the hydrogen atom H100 which is directly bonded to the metal could be located by a difference Fourier analysis and was isotropically refined. The positions of the other hydrogen atoms were calculated according to ideal geometry ($d_{C-H}$ = 0.95 Å) and were used only in structure factor calculations. **16** crystallizes with 1/2 molecule of benzene, which is disordered (2:1) in the asymmetric unit. The carbon atoms C100–C600 of this solvent molecule were refined with fixed isotropic thermal parameters. *R* = 0.021 and *wR* = 0.024;

reflection/parameter ratio 9.40; residual electron density +0.43/−0.33 eÅ$^{-3}$.


[*] Dedicated to Professor *Hans Bürger* on the occasion of his 60th birthday.

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[30] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100518. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. +44(0)1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk).


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