Organometallics **1995**, *14*, 3659–3668

Bifunctional Phosphines as Ligands and as Substrates: Synthesis of Iridium Hydrido, Carbonyl, Alkynyl, Vinyl, and Vinylidene Complexes from i-$Pr_2PCH_2CH_2X$ ($X =$ OMe, NMe_2), Including the X-ray Crystal Structure of an Unusual Cyclometalated Product[†,1]

Helmut Werner,* Michael Schulz, and Bettina Windmüller

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

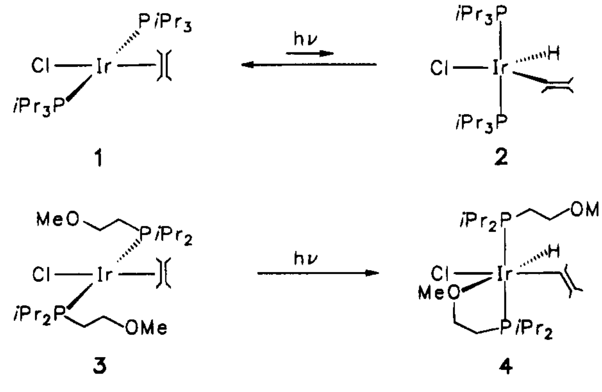
Received February 9, 1995[⊗]

Treatment of $[IrCl(C_8H_{14})_2]_2$ (**5**) with i-$Pr_2PCH_2CH_2OMe$ (**6**) leads to the formation of the octahedral hydridoiridium(III) complex $[IrHCl\{\kappa^2(C,P)\text{-}CH_2OCH_2CH_2P\text{-}i\text{-}Pr_2\}\{\kappa^2(P,O)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}]$ (**8**), which according to the X-ray structure analysis contains both a five- and a six-membered chelate ring. In contrast to **6**, the phosphinoamine i-$Pr_2PCH_2CH_2NMe_2$ (**7**) reacts with **5** to give the expected square-planar iridium(I) compound *trans*-$[IrCl\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}\{\kappa^2(P,N)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}]$ (**9**), which in solution at room temperature is nonfluxional on the NMR time scale. Reaction of **9** with CO yields four-coordinate *trans*-$[IrCl(CO)\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}_2]$ (**10**), while on treatment of **9** with HCl in benzene the six-coordinate $[IrHCl_2\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}\{\kappa^2(P,N)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}]$ (**11**) is obtained. Compound **11** is also one of the products of the reaction of **9** with CH_2Cl_2 which equally gives small quantities of the ionic bis(chelate) complex $[IrCl_2\{\kappa^2(C,P)\text{-}CH_2NMe_2CH_2CH_2P\text{-}i\text{-}Pr_2\}\{\kappa^2(P,N)\text{-}i\text{-}Pr_2PCH_2CH_2NMe_2\}]Cl$ (**12**). The chlorodihydrido and dichlorohydrido complexes $[IrH(Cl)X\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}]$ (**13**, X = H; **14**, X = Cl) are formed at room temperature almost instantaneously from **8** and H_2 or HCl, respectively. At 80 °C, the reaction of **8** (or **13**) with methyl acrylate and methyl vinyl ketone affords the hydrido(vinyl)iridium(III) derivatives $[IrHCl\{\kappa^2(C,O)\text{-}CH{=}CHC(R){=}O\}\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}_2]$ (**15**, R = OMe; **16**, R = Me), whereas with HC≡CR the alkynyl(hydrido) compounds $[IrH(C{\equiv}CR)Cl\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}]$ (**17**, R = Ph; **18**, R = CO_2Me) are obtained. Thermal or photochemical rearrangement of **17** and **18** leads to the formation of the isomeric vinylideneiridium(I) complexes *trans*-$[IrCl({=}C{=}CHR)\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}_2]$ (**20**, **21**) in good yield. The octahedral alkynyl(vinyl) compound $[IrCl(C{\equiv}CCO_2Me)(CH{=}CHCO_2Me)\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}]$ has been prepared from either **8** or **13** and excess $HC{\equiv}CCO_2Me$. Chloride abstraction of **20** and **21** with $AgSbF_6$ affords the SbF_6 salts of the cationic complexes $[Ir({=}C{=}CHR)\{\kappa(P)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)\text{-}i\text{-}Pr_2PCH_2CH_2OMe\}]^+$ (**22**, **23**), in which according to the X-ray structure analysis of **23** the vinylidene ligand and the methoxy unit are *trans* disposed.

Introduction

We have recently shown that in contrast to $P\text{-}i\text{-}Pr_3$ the related but potentially bidentate phosphine i-$Pr_2PCH_2CH_2OMe$, which can form a strong and a weak bond to an electron-rich transition-metal center, behaves as a supporting ligand for the intramolecular conversion of a $Ir(C_2H_4)$ to an isomeric $IrH(CH{=}CH_2)$ unit.[2] Whereas the equilibrium between the ethyleneiridium(I) complex **1** and the five-coordinate hydrido(vinyl)iridium(III) compound **2** lies mainly on the side of the olefin derivative, even in the presence of UV light, photolysis of the analogous starting material **3** in toluene proceeds rapidly and leads to the quantitative formation of the octahedral isomer **4** (Scheme 1).[2] The one-pot synthesis of **3** starts with the dimeric bis(cyclooctene)iridium compound $[IrCl(C_8H_{14})_2]_2$, which reacts stepwise in an ether suspension at −50 °C with i-$Pr_2PCH_2CH_2OMe$ and C_2H_4 to give the square-planar ethylene complex in excellent yield.

Scheme 1



In this paper we report that, on treatment of $[IrCl(C_8H_{14})_2]_2$ with i-$Pr_2PCH_2CH_2OMe$ at room temperature

---

[†] Dedicated to Professor William C. Kaska on the occasion of his 60th birthday.

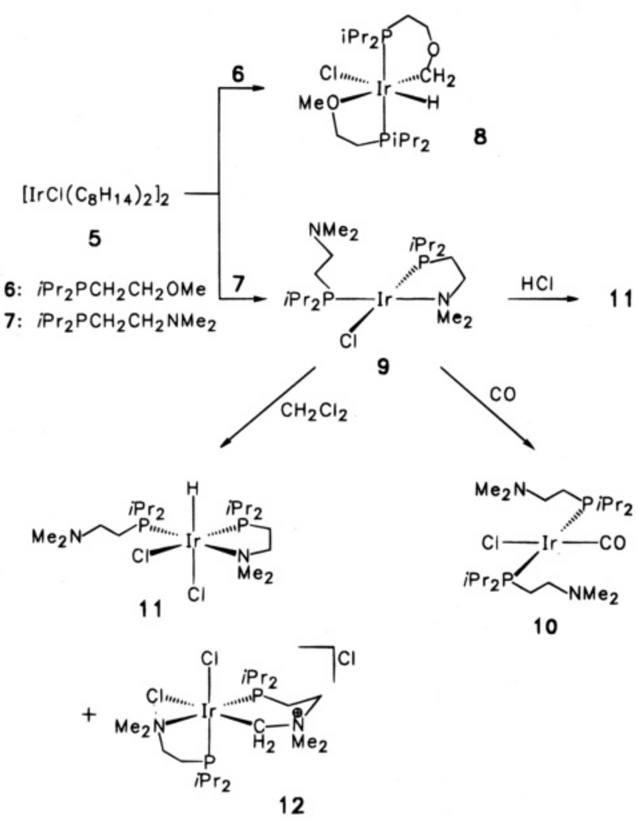
[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1995.

(1) (a) Studies on C–H Activation. 11. Part 10: Wecker, U.; Werner, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1994**, *127*, 1021–1029. (b) This work is part of the Ph.D. Thesis of M. Schulz, University of Würzburg, Würzburg, Germany, 1991.

(2) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2791–2795.

0276-7333/95/2314-3659$09.00/0

Scheme 2



in the absence of ethylene, a different reaction occurs, which leads via intramolecular C−H activation to a novel alkyl(hydrido)iridium(III) derivative. This compound reacts not only with H_2 and HCl but also with terminal alkynes and activated olefins to yield a series of alkynyl(hydrido)-, alkynyl(vinyl)-, vinylidene-, and hydrido(vinyl)iridium complexes. Some preliminary results of this work have already been communicated.[3]

Results and Discussion

Reactions of $[IrCl(C_8H_{14})_2]_2$ (5) with *i*-$Pr_2PCH_2CH_2OMe$ (6) and *i*-$Pr_2PCH_2CH_2NMe_2$ (7). Treatment of a suspension of **5** in benzene with 4 equiv of the bifunctional phosphine **6** at room temperature results in a fairly rapid change of color from red-brown to yellow and, after chromatography on Al_2O_3, yields (88%) a pale yellow solid which is correctly analysed as [IrCl(**6**)$_2$]. However, in contrast to the corresponding rhodium complex [RhCl(**6**)$_2$], which according to the X-ray structure analysis contains one *P*-monodentate and one chelating phosphine ligand,[4] the product from the reaction of **5** and **6** is not an analogous iridium(I) compound. This conclusion is supported not only by the significantly different properties (the rhodium complex [RhCl(**6**)$_2$] is thermally labile and highly air-sensitive, whereas compound **8** (see Scheme 2) can be handled for a short time in air) but more convincingly by the ^{1}H NMR spectrum which displays a high-field signal at δ −22.9 (doublet of doublets), typical for a metal-bonded hydrogen atom. Furthermore, all of the NMR spectra (^{1}H, ^{13}C, ^{31}P) are *not* temperature-dependent, which would be expected if **8** were structurally related to [RhCl(**6**)$_2$].

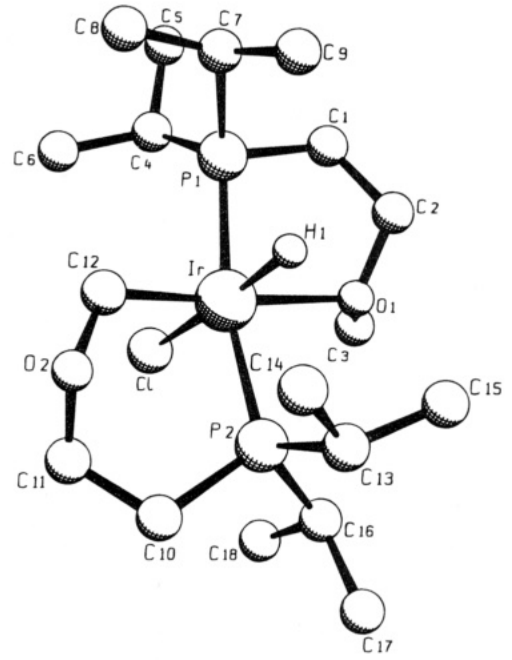


Figure 1. SCHAKAL drawing of complex **8**.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 8

Bond Distances (Å)			
Ir−P1	2.309(1)	Ir−H	1.77
Ir−P2	2.302(1)	O1−C2	1.444(6)
Ir−Cl	2.518(1)	O1−C3	1.430(7)
Ir−O1	2.339(4)	O2−C11	1.424(7)
Ir−C12	2.049(6)	O2−C12	1.425(7)
Bond Angles (deg)			
Cl−Ir−P1	92.07(2)	P2−Ir−O1	91.1(1)
Cl−Ir−P2	98.92(5)	P2−Ir−C12	91.5(2)
Cl−Ir−O1	90.6(1)	O1−Ir−C12	175.7(2)
Cl−Ir−C12	92.3(2)	Ir−O1−C2	106.9(3)
P1−Ir−P2	166.87(5)	Ir−O1−C3	121.5(3)
P1−Ir−O1	81.5(1)	Ir−C12−O2	120.2(4)
P1−Ir−C12	95.2(2)	C11−O2−C12	114.1(5)

The straightforward assumption that compound **8** is an isomer of [IrCl(**6**)$_2$], containing a hydride and a chelating *i*-$Pr_2PCH_2CH_2OCH_2$ ligand instead of an intact *i*-$Pr_2PCH_2CH_2OMe$ unit, has finally been confirmed by an X-ray structural investigation. As the SCHAKAL drawing (Figure 1) reveals, the iridium is coordinated in a somewhat distorted-octahedral fashion with the two phosphorus atoms in *trans* position. The bonding of the P−Ir−P axes (angle 166.87(5)°) points to the direction of the smallest ligand (hydride) and probably originates from steric hindrance between the isopropyl units and the other groups in the basal plane as well as from the ring strain in the five- and six-membered chelate rings. The bond angles Cl−Ir−O1, Cl−Ir−C12, and Cl−Ir−P1 (see Table 1) are near to 90° and are thus in agreement with the octahedral geometry. The position of the metal-bonded hydride was taken from a difference-Fourier synthesis with all non-hydrogen atoms but could not be refined. The observed Ir−H bond length of 1.77 Å is similar to that found in other hydridoiridium(III) complexes.[5]

The distance between the metal and the carbon atom C12 (2.049(6) Å) is almost identical to that in the

---

(3) Schulz, M.; Werner, H. *Abstracts of Papers*, 29th International Conference in Inorganic Chemistry, University of Sussex, Brighton, U.K., 1991; P 74.

(4) Werner, H.; Hampp, A.; Peters, K.; Peters, E.-M.; Walz, L.; von Schnering, H.G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1990**, *45*, 1548−1558.

vinyliridium compounds [$C_5Me_5IrH(CH{=}CH_2)(PMe_3)$] (2.054(4) Å)[6] and [$IrH(CH{=}CH_2)Cl(CO)(Pi\text{-}Pr_3)_2$] (2.059(6) Å)[2] but somewhat longer than in the five-coordinate hydrido(phenyl) complex [$IrH(C_6H_5)Cl(Pi\text{-}Pr_3)_2$] (2.010(5) Å).[7] We note, however, that the bond length Ir−O1 (2.339(4) Å) is relatively long, which probably reflects the rather weak interaction between the CH_3O oxygen and the metal center. The six-membered chelate ring containing the atoms C12 and O2 possesses a typical chair conformation with an Ir−P2 distance (2.302(1) Å) that is significantly shorter than in phosphine iridium complexes with *trans*-$Ir(Pi\text{-}Pr_3)_2$ as a molecular unit.[2,7,8]

Regarding the structure of compound **8** *in solution*, we are convinced that the dominating species is the same as in the crystal. The supporting evidence for the proposed octahedral geometry (in benzene) includes the following: (1) the nonfluxionality of the molecule; (2) the nonequivalence of the two phosphorus atoms illustrated by the doublet-of-doublet splitting of the hydride signal in the ^1H and by the appearance of an AB pattern in the ^{31}P NMR; (3) the large P−P coupling between the two ^{31}P nuclei (349.5 Hz), which is most typical for *trans*-disposed phosphine ligands; and (4) the 2D-(H, C)-COSY spectrum of **8**, which allows correct assignment for the four ^{13}C NMR signals at δ 75.26, 67.66, 62.77, and 31.12 to the CH_2 and CH_3 carbon atoms of the ether-type units. The possibility that the metal center in **8** is five- and not six-coordinated (with the intact $i\text{-}Pr_2PCH_2CH_2OMe$ ligand being only *P*-bonded), as has been proposed by Dombek for the related cyclometalated species [$IrHCl\{\kappa^2(C,P)\text{-}CH_2OCH_2Pt\text{Bu}_2\}\{\kappa(P)\text{-}t\text{Bu}_2PCH_2OMe\}$],[9] can probably be excluded. In contrast to this complex, which is deep red, compound **8** is pale yellow like many other octahedral hydridoiridium(III) derivatives.

The course of the reaction of **5** with the phosphino amine **7** is remarkably different to that of **5** with the phosphino ether **6**. From **5** and 4 equiv of **7** in benzene a yellow air-stable solid is obtained, which is correctly analysed as **9** (see Scheme 2). Since the ^{31}P NMR spectrum displays two well-separated doublets which show only a small P−P coupling of 17.6 Hz, we assume that **9** has a square-planar configuration with the two phosphorus atoms in *cis* position. However, in contrast to the analogous rhodium complex [RhCl(**6**)$_2$] for which this geometry has been confirmed by X-ray analysis,[4] at room temperature compound **9** is nonfluxional on the NMR time scale. This is also substantiated by the appearance of two signals for the NCH_3 protons in the ^1H NMR spectrum, of which only one (at δ 2.62) shows P−H coupling.

While **9** is completely inert toward H_2 and ethylene, it reacts smoothly with CO in benzene at room temperature to give the square-planar monocarbonyl complex **10** in almost quantitative yield. According to the ^1H and ^{31}P NMR data, there is no doubt that the two phosphinoamine ligands are equivalent and that the structure of compound **10** is very similar to that of *trans*-[$IrCl(CO)(Pi\text{-}Pr_3)_2$].[10]

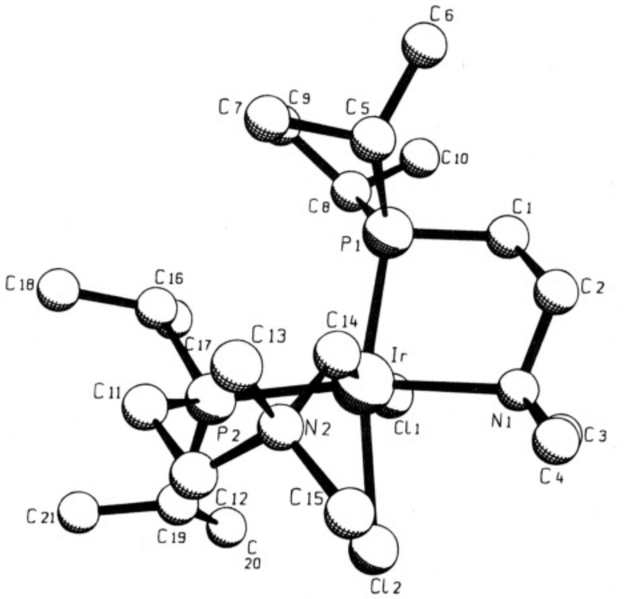


Figure 2. SCHAKAL drawing of complex **12**.

The reaction of **9** with HCl in benzene results in an oxidative addition and the formation of complex **11**. Like the starting material **9**, the dichloro(hydrido)iridium(III) derivative also possesses a rigid structure at room temperature with *cis*-disposed $Pi\text{-}Pr_2$ units. In agreement with this, the ^{31}P NMR spectrum displays two signals at δ 23.45 and −6.8 with a small P−P coupling (13.2 Hz) which, due to additional P−H coupling in off-resonance, appear as a doublet-of-doublets. The hydride signal in the ^1H NMR spectrum is equally a doublet-of-doublets, confirming the inequivalence of the phosphorus atoms.

Surprisingly, the octahedral dichloro(hydrido) complex **11** is also formed on treatment of **9** with dichloromethane. We made this serendipitous discovery in the course of our attempts to grow single crystals of **9** by diffusion of pentane into a saturated solution of the iridium(I) compound in CH_2Cl_2. With this procedure, a mixture of products is formed which contains **11** as the main component. When we stored the reaction mixture of **9** and CH_2Cl_2/pentane for a longer period of time, a small quantity of bright yellow crystals precipitated, which we investigated by X-ray crystallography. As Figure 2 reveals, the cationic complex **12** resembles compound **8** insofar as it also contains a five- and a six-membered chelate ring. In contrast to **8**, however, the two phosphorus atoms in **12** are *cis*-disposed, as are the two chloro ligands. The octahedral geometry around the metal center is considerably distorted, as is illustrated by the bond angles P1−Ir−C12 (165.34(6)°), P2−Ir−N1 (171.6(2)°), Cl1−Ir−Cl4 (173.8(2)°), and P1−Ir−P2 (103.26(7)°). The most remarkable feature, however, is the boat-type conformation of the Ir-containing six-membered ring, which could originate from the direction of the attack of the NMe_2 group of the nonchelated phosphinoamine ligand at the intermediarily formed Ir−CH_2Cl unit from the less hindered side of the molecule.

---

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

(6) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732−5744.

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

(8) Werner, H.; Dirnberger, T.; Schulz, M.; Ertel, T. S.; Hörner, W.; Bertagnolli, H. Submitted for publication.

(9) Dombek, B. D. *J. Organomet. Chem.* **1979**, *169*, 315−325.

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

Table 2. Selected Bond Distances and Angles with Esd's for Compound 12

Bond Distances (Å)			
Ir−Cl1	2.488(2)	Ir−C14	2.036(6)
Ir−Cl2	2.420(2)	N1−C2	1.504(9)
Ir−N1	2.264(6)	N2−C12	1.490(9)
Ir−P1	2.310(2)	N2−C14	1.527(9)
Ir−P2	2.305(2)		
Bond Angles (deg)			
Cl1−Ir−Cl2	88.63(6)	P1−Ir−P2	103.26(7)
Cl1−Ir−P1	82.23(6)	P1−Ir−N1	85.2(2)
Cl1−Ir−P2	92.67(6)	P1−Ir−C14	91.6(2)
Cl1−Ir−N1	88.6(2)	P2−Ir−N1	171.6(2)
Cl1−Ir−C14	173.8(2)	P2−Ir−C14	88.2(2)
Cl2−Ir−P1	165.34(6)	N1−Ir−C14	91.4(2)
Cl2−Ir−P2	88.53(6)	Ir−N1−C2	108.8(4)
Cl2−Ir−N1	88.6(2)	Ir−C14−N2	124.7(5)
Cl2−Ir−C14	97.5(2)	C12−N2−C14	113.3(5)

Despite the cationic nature of complex **12**, both the Ir−C and the Ir−P distances (Table 2) are nearly identical to those found in compound **8**. The bond length Ir−N1, however, is significantly shorter (2.264(6) Å) than the corresponding Ir−O1 distance in **8** (2.339(4) Å), which probably reflects the higher donor strength of the NMe_2 compared with the OCH_3 group.

With regard to the mechanism of formation of **11** and **12** from **8** and dichloromethane, we assume that initially oxidative addition of the substrate to the four-coordinate iridium(I) center takes place. There is ample evidence for this type of behavior in other square-planar d^8 systems as well as for the generation of $[L_nMH(Cl)]$ complexes from appropriate precursors $[L_nM]$ and CH_2Cl_2.[11] The formation of the six-membered chelate ring in compound **12** from the supposed intermediate containing a $M-CH_2Cl$ bond is also not without precedent since we have found that the half-sandwich type complex $[C_5H_5RhCH_2I\{\kappa^2(P,P)\text{-}Me_2PCH_2CH_2PMe_2\}]^+$, prepared from $[C_5H_5Rh(dmpe)]$ and CH_2I_2, isomerizes quantitatively in the presence of NEt_3 to give $[C_5H_5RhI\{\kappa^2(C,P)\text{-}CH_2PMe_2CH_2CH_2PMe_2\}]^+$.[12]

Reactions of the Cyclometalated Complex 8 with H_2 and HCl. Although the spectroscopic data of compound **8** provide no hint that in solution it is in equilibrium with the square-planar isomer [IrCl(**6**)$_2$], the octahedral iridium(III) complex nevertheless behaves as if it were a four-coordinate iridium(I) species. It reacts instantaneously with H_2 to yield the dihydrido derivative **13** (Scheme 3), which is obtained as a pale yellow, extremely air-sensitive oil. Since the IR spectrum of **13** shows two bands at 1112 and 1055 cm^{-1} which are assigned to the asymmetric C−O−C stretching frequencies of a free and a coordinated ether functionality,[13] we assume that the iridium is six-coordinate with one monodentate and one bidentate $i\text{-}Pr_2PCH_2CH_2OMe$ ligand. The ^{31}P NMR spectrum, however, displays only one sharp singlet in C_6D_6 (triplet in off-resonance due to P−H coupling), indicating that in solution at room temperature two isomers **A** and **C** exist, which interconvert rapidly (on the NMR time scale) via the five-coordinate species **B**. This proposal is also supported by the ^1H NMR spectrum in which only one signal (δ −28.9, triplet with J(PH) = 15.4 Hz) appears at higher field. The $\Delta G^{\ddagger}$ value for the dynamic process shown in Scheme 3 is probably below 35 kJ/mol since only one very broad signal has been observed in the ^{31}P NMR spectrum (in toluene-d_8) at −80 °C. For the analogous hydrido(vinyl)iridium(III) compound $[IrH(CH{=}CH_2)Cl(\mathbf{6})_2]$, coalescence of the two ^{31}P NMR resonances occurs at −45 °C, which together with the difference in the chemical shift of the two signals results in a $\Delta G^{\ddagger}$ value of approximately 41 kJ/mol.[2]

Treatment of **8** with an equimolar amount of HCl in benzene equally leads to a rapid reaction in which the dichloro(hydrido)iridium(III) complex **14** is formed in excellent yield. Since the spectroscopic data of **13** and **14** resemble each other (IR, $\nu(COC)_{asym}$ 1103 and 1045 cm^{-1}; ^1H NMR at 25 °C, one high-field signal at δ −34.3 as a triplet with J(PH) = 13.2 Hz; ^{31}P NMR at 25 °C, one sharp singlet (doublet in off-resonance) at δ 17.5), we not only assume analogous structures but also similar fluxional behavior (see Scheme 3) of the two compounds in solution.

Preparation of Hydrido(vinyl), Hydrido(alkynyl), and Alkynyl(vinyl) Complexes from 8. In contrast to the formation of **13** and **14**, which is completed at 25 °C in a few minutes, the reactions of **8** with methyl acrylate and methyl vinyl ketone proceed much more slowly but finally yield the hydrido(vinyl)iridium complexes **15** and **16** almost quantitatively. Both compounds are pale yellow air-sensitive oily substances, the composition of which has been confirmed by elemental analysis. In contrast to **13** and **14**, the IR spectra of **15** and **16** display only one asymmetric C−O−C stretch at ca. 1120 cm^{-1}, and thus there is no doubt that the phosphino ether ligands are not involved in chelate-type coordination. On the basis of the appearance of ν(C=O) bands at 1578 (for **15**) and 1539 cm^{-1} (for **16**), which are significantly shifted to shorter wave numbers compared with free $CH_2{=}CHCO_2Me$ and $CH_2{=}CHC({=}O)CH_3$, respectively, we believe that the C=O group of the activated olefins is linked to the metal center and thus completes the octahedral coordination sphere. The structural proposal for **15** and **16** shown in Scheme 4 is fully consistent with the appearance of only one singlet resonance in the ^{31}P NMR spectra which in off-resonance is split into a doublet. It should be noted, however, that the ^1H NMR spectra of **15** and **16** (in contrast to those of **13** and **14**) display a broad multiplet for the $PCHCH_3$ protons of the $Pi\text{-}Pr_2$ units instead of two doublets-of-virtual-triplets. Due to the bonding of four different ligands in the equatorial plane, compounds **15** and **16** contain no mirror plane that passes through the two phosphorus atoms. The two molecules therefore possess four different prochiral centers, which makes all the phosphino CH_3 groups anisochronous and leads to an overlap of four virtually coupled signals.

The octahedral hydrido(vinyl) complexes **15** and **16** are not only accessible from **8** but also on treatment of the dihydridoiridium(III) compound **13** with methyl acrylate or methyl vinyl ketone, respectively. In this case, the yield is 80%−85%. With regard to the mechanism of the reaction, we assume that displacement of the metal-bonded C=O unit by the substituted olefin occurs initially, which is followed by an insertion of the

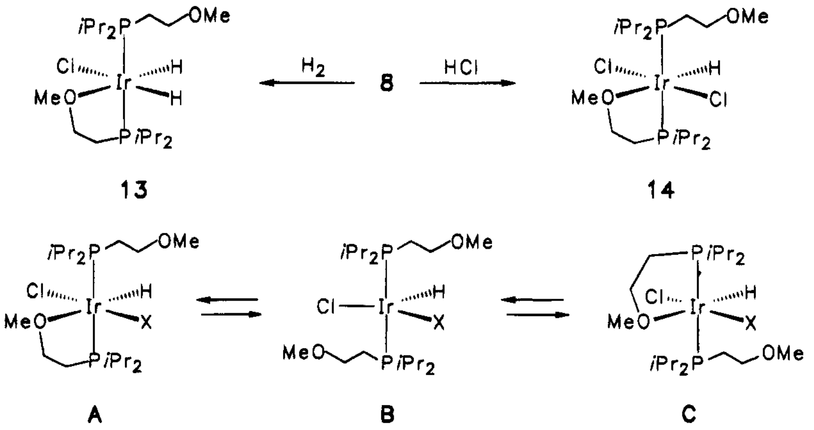
---

[11] (a) Scherer, O. J.; Jungmann, H. *J. Organomet. Chem.* **1981**, *208*, 153−159. (b) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543−1545.

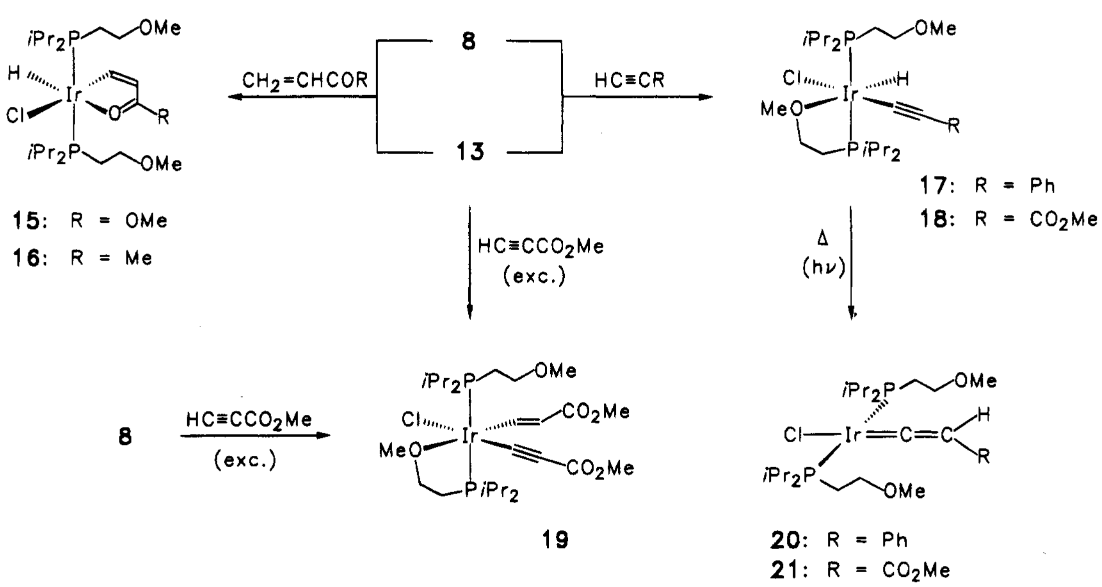
[12] Werner, H.; Hofmann, L.; Paul, W.; Schubert, U. *Organometallics* **1988**, *7*, 1106−1111.

[13] (a) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1971**, *24*, 2533−2540. (b) Lindner, E.; Mayer, H. A.; Wegener, P. *Chem. Ber.* **1986**, *119*, 2616−2630.

Scheme 3



Scheme 4



olefinic ligand into one of the Ir−H bonds. Reductive elimination of $C_2H_5CO_2Me$ or $C_2H_5C(=O)CH_3$ from the alkyl(hydrido)metal derivative would lead to the intermediate $[IrCl(\mathbf{6})_2]$ which, after addition of a second molecule of $CH_2{=}CHX$ (X = CO_2Me, C(=O)Me), gives the olefin complex *trans*-$[IrCl(CH_2{=}CHX)(\mathbf{6})_2]$. Finally, this species intramolecularly rearranges via C−H activation to yield **15** and **16**, respectively. In this context, it should be mentioned that a similar reaction of bis(phosphine)iridium(I) chlorides with $CH_2{=}CHX$ to yield octahedral hydrido(vinyl)iridium(III) compounds has been established for L = Pi-Pr_3[14] and PPh_3[14b,15] and also for some related rhodium complexes.[16]

Terminal alkynes HC≡CR (R = Ph, CO_2Me) react rapidly with equimolar amounts of either **8** or **13** in benzene at room temperature to yield nearly quantitatively the alkynyl(hydrido)iridium(III) derivatives **17** and **18** (Scheme 4). At 25 °C, both compounds are fluxional in solution, which is illustrated by the appearance of one signal in the ^{31}P NMR and one sharp triplet resonance for the metal-bonded hydride ligand in the ^1H NMR spectrum. That the two molecules, however, are not five-coordinate but contain one *P*-monodentate and one chelating phosphino ether unit is indicated by the IR spectra in which *two* asymmetric C−O−C stretching frequencies at 1105 and 1045 cm^{-1} (for **17**) and at 1108 and 1038 cm^{-1} (for **18**) have been observed. On the basis of the spectroscopic data, it cannot be decided whether the alkynyl or the hydride ligand is *trans* to Cl in **17** and **18**.

If compounds **8** and **13** are treated with an excess of methyl propiolate instead of 1 equiv, the alkynyl(vinyl)iridium(III) complex **19** is formed in about 60%−65% yield. Methyl acrylate has been detected as a byproduct in the reaction of **13** with $HC{\equiv}CCO_2Me$. In solution, compound **19** is less fluxional than the corresponding alkynyl(hydrido) derivative **18** and from the coalescence temperature (−3 °C in toluene-d_8) and the difference in the chemical shift of the two signals in the low-temperature ^{31}P NMR spectrum, a $\Delta G^{\ddagger}$ value of approximately 49 kJ/mol can be calculated. Compared with **13**, for which a $\Delta G^{\ddagger}$ value of less than 35 kJ/mol has been estimated, the alkynyl(vinyl)iridium(III) complex is more rigid, which is probably due to a stronger $Ir{-}OCH_3$ bond than in the dihydridometal derivative. The *trans* configuration at the C=C double bond of the vinyl ligand in **19** is confirmed by the H−H coupling of

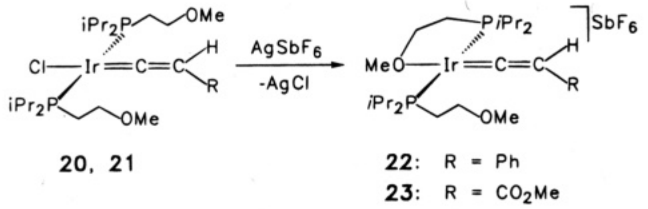
---

(14) (a) Werner, H.; Dirnberger, T.; Schulz, M. *Angew. Chem.* **1988**, *100*, 993−994; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 948−950. (b) Dirnberger, T. Dissertation, University of Würzburg, Würzburg, Germany, 1990.

(15) Papenfuhs, B. Ph.D. Thesis, University of Würzburg, Würzburg, Germany, 1993.

(16) Dirnberger, T.; Werner, H. *Chem. Ber.* **1992**, *125*, 2007−2014.

Scheme 5



15.3 Hz which should be considerably smaller if the substituents were in *cis* position.

Neutral and Cationic Vinylideneiridium Complexes Containing the Phosphino Ether 6 as Ligand. Like several other alkynyl(hydrido)iridium(III) species,[17,18] compounds **17** and **18** rearrange smoothly to give the vinylideneiridium(I) isomers. The rate of rearrangement crucially depends on the substituent R of the alkynyl ligand. While the reaction of **18** already starts at room temperature and is completed after warming a solution of **18** (or **13** and methyl propiolate) in benzene for 5 h at 80 °C, the isomerization of **17** proceeds much more slowly and even after 72 h at 80 °C about 30% of the starting material is still unreacted. The preferred method to prepare the vinylidene complex **20** (see Scheme 4) is the photochemical route, and thus, by using a 125 W UV lamp, the rearrangement of **17** to **20** is complete after 6 h. The spectroscopic data of compounds **20** and **21** resemble those of the corresponding triisopropylphosphine complexes,[17] and therefore both phosphino ether ligands are thought to be coordinated only via the phosphorus atom. As far as the NMR data are concerned, the most characteristic features are the low-field signals of the vinylidene α-carbon atom at δ 263.1 (for **20**) and 254.8 (for **21**) in the ^{13}C NMR and the high-field resonances of the =C*H*R proton at δ −2.5 (for **20**) and −2.1 (for **21**) in the ^{1}H NMR spectrum. We note that in the spectrum of the related rhodium compound *trans*-[RhCl(=C=CHPh){κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$] the signal of the vinylidene proton appears at δ 0.04.[4]

Treatment of **20** and **21** with AgSbF$_6$ leads to the nearly quantitative formation of the first square-planar cationic vinylideneiridium(I) complexes (Scheme 5). In contrast to the neutral compounds **20** and **21**, the SbF$_6$ salts **22** and **23**, which have been isolated as deeply colored solids, are only moderately air-sensitive. Since for both compounds the ^{31}P NMR spectrum in CD$_2$Cl$_2$ at room temperature displays only one sharp signal at δ 40.0 (for **22**) and 35.6 (for **23**), there is no doubt that both cationic species are fluxional in solution on the NMR time scale. Coalescence has been observed (in CD$_2$Cl$_2$) at about −35 °C. In the case of **23**, the ^{31}P NMR spectrum shows at −70 °C again only one singlet instead of the expected AB pattern, which indicates that under these conditions the cation possesses a rigid structure with equivalent P*i*-Pr$_2$ units. A possible explanation is that the low-temperature form of **23** contains a five-coordinate metal center with two chelating phosphino ether ligands thus providing an 18-electron configuration for iridium(I). It should be mentioned that recently square-planar cationic rhodium complexes of the general composition *trans*-[Rh(=C=CHR)(L)(P*i*-Pr$_3$)$_2$]$^+$ (R = H, Me, Ph, *t*Bu; L = NH$_3$, py) have also been prepared either on treatment of η^3-allyl or ethenerhodium(I) precursors with 1-alkynes.[19]

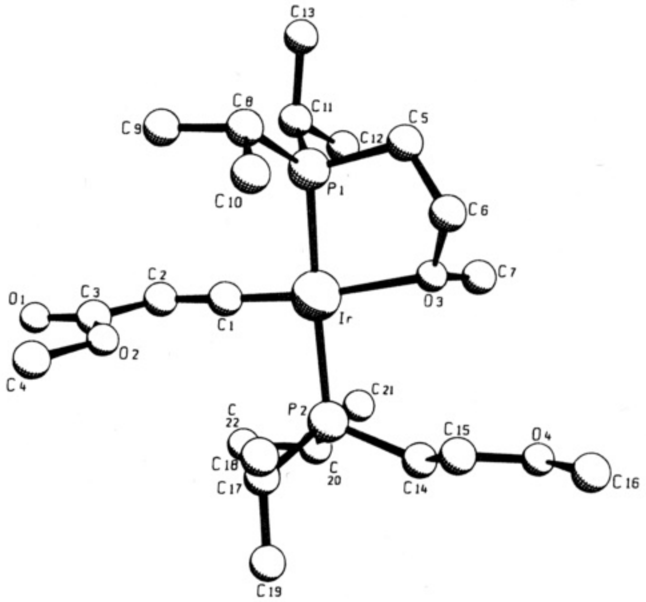


Figure 3. SCHAKAL drawing of complex **23**.

Table 3. Selected Bond Distances and Angles with Esd's for Compound 23

	Bond Distances (Å)		
Ir−P1	2.309(2)	O3−C6	1.46(1)
Ir−P2	2.347(2)	O3−C7	1.43(1)
Ir−C1	1.760(6)	C1−C2	1.33(1)
Ir−O3	2.163(5)	C2−C3	1.43(1)
	Bond Angles (deg)		
P1−Ir−P2	174.56(8)	C1−Ir−O3	172.1(3)
P1−Ir−C1	91.2(3)	Ir−O3−C6	112.2(5)
P1−Ir−O3	82.0(2)	Ir−O3−C7	120.2(5)
P2−Ir−C1	92.2(3)	Ir−C1−C2	175.6(6)
P2−Ir−O3	94.8(2)	C1−C2−C3	124.9(8)

In order to substantiate the exact ligand arrangement for **23**, an X-ray structural investigation has been carried out. The SCHAKAL drawing (Figure 3) reveals that the iridium is coordinated in an almost perfect square-planar fashion with the two phosphorus atoms in *trans* position. The sum of the bond angles in the plane is 360.2°. Compared with Ir−P1, the Ir−P2 distance (see Table 3) is somewhat elongated (by ~0.04 Å), which could be due to steric repulsion between the isopropyl groups at P2 and the CO$_2$Me unit. In agreement with the allene-type stereochemistry of the P$_2$-Ir=C=CHR moiety, the plane of the carbomethoxy substituent is perpendicular to the [Ir, P1, P2, C1, O3] plane, the dihedral angle being 92.4°. The Ir−C1 bond length (1.760(6) Å) is rather short compared with the corresponding distances of carbeneiridium(I) compounds[20] but very similar to the Ir−C bond length of the neutral vinylidene complex *trans*-[IrCl(=C=CHCO$_2$Me)(P*i*-Pr$_3$)$_2$] (1.746(6) Å).[17b] Compared with the Ir−O distance in **8** (2.339(4) Å), the Ir−O3 bond length in **23**

---

(17) (a) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem.* **1985**, *97*, 401−402; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406−408. (b) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852−854. (c) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255−272. (d) Werner, H.; Höhn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777−789.

(18) Werner, H.; Dirnberger, T.; Höhn, A. *Chem. Ber.* **1991**, *124*, 1957−1961.

(19) Nürnberg, O.; Werner, H. *J. Organomet. Chem.* **1993**, *460*, 163−175.

(20) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708−6710 and references cited therein.

is unusually short, which is probably the result of the *trans* arrangement of the strong σ-donating ether and the strong π-accepting vinylidene ligand. This bonding scheme also explains why the cationic compounds [Ir(=C=CHR){κ(*P*)-*i*-$Pr_2PCH_2CH_2OMe$}{κ^2(*P*,*O*)-*i*-$Pr_2PCH_2CH_2OMe$}]$^+$ are quite inert and do not react with HC≡CPh or $HC{\equiv}CCO_2Me$ to give bis(vinylidene)iridium(I) species.

Concluding Remarks

The work presented in this paper has confirmed that bifunctional ("hemilabile")[21] phosphines of the general composition $R_2PCH_2CH_2X$ are not only useful ligands which temporarily are able to protect a free coordination site but can also behave as reacting substrates. Provided that X is OCH_3 and the methoxy oxygen is coordinated to a transition metal that favors oxidative-addition reactions, metalation of the OCH_3 group can occur to generate an alkyl(hydrido)metal derivative. Such an intramolecular C−H activation process involving a phosphino ether like *i*-$Pr_2PCH_2CH_2OMe$ is certainly not limited to iridium since we have recently shown[22] that, in the coordination sphere of osmium, a OCH_3 moiety can even be metalated *twice* to form a metal−carbene M=CHO− unit.

It is most interesting, however, that the substituents R at the phosphorus atom of the phosphino ethers seem to have a pronounced effect on the intramolecular metalation. While $[IrCl(C_8H_{14})_2]_2$ (**5**) reacts with *i*-$Pr_2PCH_2CH_2OMe$ (**6**) at room temperature to give the unexpected octahedral iridium(III) complex **8**, on treatment of $[IrCl(C_8H_{12})]_2$ with $Cy_2PCH_2CH_2OMe$ under nearly the same conditions the square-planar iridium(I) compound [IrCl{κ(*P*)-$Cy_2PCH_2CH_2OMe$}{κ^2(*P*,*O*)-$Cy_2PCH_2CH_2OMe$}] is formed.[23] There is also a difference in the case of C−H activation of OCH_3 and NCH_3 groups, because both **6** and **7** can be transformed with osmium as the metal center to OCH= and NCH= units,[22] whereas with iridium only a metalation of the phosphino ether takes place.

The final and really unusual facet of these studies is that the cyclometalated compound **8**, which is undoubtedly more thermodynamically stable both in the solid state *and* in solution than the hypothetical isomer [IrCl{κ(*P*)-*i*-$Pr_2PCH_2CH_2OMe$}{κ^2(*P*,*O*)-*i*-$Pr_2PCH_2CH_2OMe$}], behaves like the isomeric four-coordinate species in the presence of substrates such as H_2 and HCl (present work) and CO and C_2H_4 (ref 2). These results (and also those obtained with activated olefins and terminal alkynes as substrates) indicate that the C−H activation process which leads to the formation of **8** is reversible, which is in complete analogy with the conversion of [Ru](P*i*-Pr_3) to [Ru]H{κ^2(*C*,*P*)-$CH_2CHMePi$-Pr_2} ([Ru] = $(C_6H_6)Ru$)[24] but in contrast to the formation of $[Ir]H(CH_3)$ from [Ir] and methane ([Ir] = $(C_5Me_5)Ir(CO)$, $(C_5Me_5)Ir(PMe_3)$).[25] We are currently investigating whether a phosphino unit PR_2 and/or a functional group X of a substituted phosphine $R_2P(CH_2)_nX$ can also initiate or facilitate the C−H activation of the $-(CH_2)_n-$ chain, and we will report on this work in due course.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $[IrCl(C_8H_{14})_2]_2$ (**5**),[26] *i*-$Pr_2PCH_2CH_2OMe$ (**6**),[4] and *i*-$Pr_2PCH_2CH_2NMe_2$ (**7**)[4] were prepared as described in the literature. The olefins $CH_2{=}CHC(O)R$ and alkynes HC≡CR were commercial products from Aldrich and Fluka. NMR spectra were recorded on Jeol FX 90 Q, Bruker AC 200, and Bruker AMX 400 instruments, and IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer. Melting points were determined by DTA.

Preparation of [IrClH{κ^2(*C*,*P*)-$CH_2OCH_2CH_2P$*i*-Pr_2}{κ^2(*P*,*O*)-*i*-$Pr_2PCH_2CH_2OMe$}] (8). A solution of **5** (108 mg, 0.12 mmol) in 10 mL of benzene was treated with **6** (90 μL, 0.48 mmol) and stirred for 20 min at room temperature. 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 C_6H_6/CH_2Cl_2 (2:3) a yellow fraction was eluted, from which a pale yellow, only moderately air-sensitive solid was isolated: yield 123 mg (88%); mp 70 °C decomp. Anal. Calcd for $C_{18}H_{42}ClIrO_2P_2$: C, 37.27; H, 7.30. Found: C, 36.98; H, 7.08. IR (C_6H_6): ν(IrH) 2167, $\nu(COC)_{asym}$ 1050 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 5.68 (dd, *J*(PH) = 10.1 Hz, *J*(HH) = 5.8 Hz, 1H of $IrCH_2$), 5.42 (d, br, *J*(HH) = 5.8 Hz, 1H of $IrCH_2$), 3.77, 3.21 (both m, PCH_2CH_2), 3.34 (s, OCH_3), 2.78, 2.00 (both m, $PCHCH_3$), 1.55, 1.41 (both m, PCH_2), 1.49, 1.27, 1.12, 1.00 (all m, $PCHCH_3$), −22.92 (dd, *J*(PH) = 17.2 Hz, *J*(P′H) = 14.2 Hz, Ir*H*). ^{13}C NMR (C_6D_6, 50.2 MHz): δ 75.26 (s, $IrCH_2OCH_2$), 67.66 (s, $PCH_2CH_2OCH_3$), 62.77 (s, OCH_3), 31.12 (s, br, $IrCH_2$), 26.1−20.3 (m, $PCHCH_3$ and $PCH_2CH_2OCH_3$), 20.0−17.7 (m, $PCHCH_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 29.11, 6.72 (both d, *J*(PP) = 349.5 Hz).

Preparation of *cis*-[IrCl{κ^2(*P*,*N*)-*i*-$Pr_2PCH_2CH_2NMe_2$}{κ(*P*)-*i*-$Pr_2PCH_2CH_2NMe_2$}] (9). A solution of **5** (58 mg, 0.065 mmol) in 10 mL of benzene was treated with **7** (55 μL, 0.26 mmol) and stirred for 10 min at room temperature. The solvent was removed, and the residue was recrystallized from pentane to give yellow, only moderately air-sensitive crystals: yield 57 mg (72%); mp 58 °C decomp. Anal. Calcd for $C_{20}H_{48}ClIrN_2P_2$: C, 39.62; H, 7.98; N, 4.62. Found: C, 40.43; H, 7.76; N, 4.33. ^1H NMR (C_6D_6, 90 MHz): δ 2.7 (m, PCH_2CH_2), 2.62 (d, *J*(PH) = 1.8 Hz, NCH_3), 2.11 (s, NCH_3), 2.0−1.8 (m, $PCHCH_3$ and PCH_2), 1.5−0.9 (m, $PCHCH_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.24, 7.21 (both d, *J*(PP) = 17.6 Hz).

Preparation of *trans*-[IrCl(CO){κ(*P*)-*i*-$Pr_2PCH_2CH_2NMe_2$}$_2$] (10). A slow stream of CO was passed through a solution of **9** (43 mg, 0.07 mmol) in 5 mL of benzene at room temperature for 30 s. After the solution was stirred for 5 min, the solvent was removed, 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, almost air-stable solid was isolated: yield 41 mg (91%); mp 98 °C decomp. Anal. Calcd for $C_{21}H_{48}ClIrN_2OP_2$: C, 39.77; H, 7.63; N, 4.42. Found: C, 39.62; H, 7.80; N, 4.59. IR (C_6H_6): ν(IrCO) 1937 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 2.85 (m, PCH_2CH_2), 2.4−

---

[21] Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658−2666.

[22] Werner, H.; Weber, B.; Nürnberg, O.; Wolf, J. *Angew. Chem.* **1992**, *104*, 1079−1081; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1025−1027.

[23] (a) Lindner, E.; Meyer, S. *J. Organomet. Chem.* **1988**, *339*, 193−198. (b) Review: Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27−110.

[24] Werner, H.; Kletzin, H.; Roder, K. *J. Organomet. Chem.* **1988**, *355*, 401−417.

[25] (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190−7191. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121−1122.

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

Table 4. Crystallographic Data for 8, 12, and 23

formula	$C_{18}H_{42}ClIrO_2P_2$ (**8**)	$C_{21}H_{50}Cl_3IrN_2P_2$ (**12**)	$C_{22}H_{46}F_6IrO_4P_2Sb$ (**23**)
fw	580.15	691.17	864.52
cryst size, mm^3	0.5 × 0.5 × 0.7	0.15 × 0.15 × 0.4	0.3 × 0.45 × 0.5
cryst syst	triclinic	orthorhombic	monoclinic
space group	*P*1 (No. 2)	$Pna2_1$ (No. 33)	$P2_1/n$ (No. 14)
cell dimens determn	24 reflns, 10° < θ < 15°	23 reflns, 10° < θ < 15°	25 reflns, 10° < θ < 16°
a, Å	7.852(1)	9.921(1)	13.167(2)
b, Å	9.529(2)	22.070(4)	16.956(2)
c, Å	15.747(3)	14.162(2)	14.534(2)
α, deg	78.67(2)		
β, deg	79.62(2)		99.32(1)
γ, deg	84.63(2)		
V, $Å^3$	1134.2(4)	3100.8(7)	3201.9(8)
Z	2	4	4
d_{calcd}, g cm^{-3}	1.70	1.48	1.79
diffractometer	Enraf Nonius CAD4		
radiation (graphite monochromator)	Mo Kα (0.709 30 Å)		
temp, °C	−80 ± 1	−50 ± 1	20 ± 1
μ, cm^{-1}	61.3	66.9	51.4
scan method	ω/θ	ω/θ	ω/θ
2θ(max), deg	44	50	44
tot no. of reflns scanned	3026	3107	4296
no. of unique reflns	2776	3107	3714
no. of obsd reflns	2638	2258	3088
no. of params refined	217	288	361
R	0.031	0.028	0.028
R_w	0.039	0.031	0.030
refln:param ratio	12.16	7.84	8.55
resid electron density, e $Å^{-3}$	1.00	1.30	1.14

2.1 (m, PC*H*CH$_3$ and PC*H*$_2$), 2.27 (s, NC*H*$_3$), 1.40, 1.23 (both dvt, *N* = 15.1 Hz, *J*(HH) = 6.8, PCHC*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 32.68 (s).

Preparation of [IrCl$_2$H{κ^2*(P,N)*-*i*-Pr$_2$PCH$_2$CH$_2$NMe$_2$}{κ*(P)*-*i*-Pr$_2$PCH$_2$CH$_2$NMe$_2$}] (11). A solution of **9** (62 mg, 0.102 mmol) in 10 mL of benzene was treated with 0.32 mL of a 0.32 M solution of HCl in benzene (0.102 mmol) and stirred for 15 min at room temperature. The solvent was removed, and the pale yellow residue was washed repeatedly with pentane and dried in vacuo: yield 44 mg (67%); mp 82 °C decomp. Anal. Calcd for $C_{20}H_{49}Cl_2IrN_2P_2$: C, 37.38; H, 7.69; N, 4.10. Found: C, 37.23; H, 7.86; N, 4.36. IR (C$_6$H$_6$): ν(IrH) 2232 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 3.75, 2.81 (both m, PCH$_2$C*H*$_2$), 2.58 (d, *J*(PH) = 2.0 Hz, NC*H*$_3$), 2.4–2.1 (m, PC*H*CH$_3$), 2.06 (s, NC*H*$_3$), 1.93, 1.55 (both m, PC*H*$_2$), 1.62 (dd, *J*(PH) = 16.0 Hz, *J*(HH) = 6.8, PCHC*H*$_3$), 1.51 (dd, *J*(PH) = 15.4 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 1.39 (dd, *J*(PH) = 15.2 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 1.15 (dd, *J*(PH) = 14.0 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 1.06 (dd, *J*(PH) = 11.2 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 1.04 (dd, *J*(PH) = 12.4 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 0.87 (dd, *J*(PH) = 16.0 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), 0.74 (dd, *J*(PH) = 12.0 Hz, *J*(HH) = 6.8, PCHC*H*$_3$), −22.59 (dd, *J*(PH) = 19.8 Hz, *J*(P′H) = 16.0 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 23.45, −6.81 (both d, *J*(PP) = 13.2 Hz).

Reaction of 5 with CH$_2$Cl$_2$. Compound **9** (50 mg, 0.08 mmol) was dissolved in 1 mL of dichloromethane at room temperature, and the solution was layered with 1.5 mL of pentane. After it had been stored for 48 h, a small quantity of bright yellow crystals **12** precipitated, which were separated from the reaction mixture and dried in vacuo: yield ca. 10 mg.

Preparation of [IrClH$_2${κ^2*(P,O)*-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ*(P)*-*i*-Pr$_2$PCH$_2$CH$_2$OMe}] (13). A slow stream of H$_2$ was passed through a solution of **8** (95 mg, 0.164 mmol) in 10 mL of benzene at room temperature for 30 s. After the solution was stirred for 5 min, the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$/CH$_2$Cl$_2$ (1:2) a yellow fraction was eluted, from which a pale yellow, very air-sensitive oil was isolated: yield 70 mg (73%). IR (C$_6$H$_6$): ν(IrH) 2260, $\nu(COC)_{asym}$ 1112 and 1055 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 3.69 (m, PCH$_2$C*H*$_2$), 3.26 (s, OC*H*$_3$), 2.20 (m, PC*H*CH$_3$), 1.82 (m, PC*H*$_2$), 1.16, 1.12 (both dvt, *N* = 14.3 Hz, *J*(HH) = 7.1, PCHC*H*$_3$), −28.87 (t, *J*(PH) = 15.4 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 40.07 (s, t in off-resonance).

Preparation of [IrCl$_2$H{κ^2*(P,O)*-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ*(P)*-*i*-Pr$_2$PCH$_2$-CH$_2$OMe}] (14). A solution of **8** (47 mg, 0.08 mmol) in 5 mL of benzene was treated with 0.25 mL of a 0.32 M solution of HCl in benzene (0.08 mmol) and stirred for 5 min at room temperature. After the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$/CH$_2$Cl$_2$ (2:1) a yellow fraction was eluted from which a pale yellow, moderately air-sensitive solid was isolated: yield 40 mg (80%); mp 96 °C decomp. Anal. Calcd for $C_{18}H_{43}Cl_2IrO_2P_2$: C, 35.06; H, 7.03. Found: C, 35.49; H, 7.18. IR (C$_6$H$_6$): ν(IrH) 2275, $\nu(COC)_{asym}$ 1103 and 1045 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 3.60 (m, PCH$_2$C*H*$_2$), 3.28 (s, OC*H*$_3$), 2.75 (m, PC*H*CH$_3$), 2.05 (m, PC*H*$_2$), 1.30 (dvt, *N* = 14.2 Hz, *J*(HH) = 6.8, PCHC*H*$_3$), 1.22 (dvt, *N* = 13.7 Hz, *J*(HH) = 6.8, PCHC*H*$_3$), −34.31 (t, *J*(PH) = 13.2 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 17.53 (s, d in off-resonance).

Preparation of [IrClH{κ^2*(C,O)*-CH=CHC(O)OMe}{κ*(P)*-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$] (15). (a) A solution of **8** (43 mg, 0.074 mmol) in 5 mL of benzene was treated with methyl acrylate (0.1 mL) and stirred for 20 h at 80 °C. After the solution was cooled to room temperature, the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the resulting solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$/CH$_2$Cl$_2$ (1:2) a yellow fraction was eluted, from which a pale yellow, air-sensitive oil was isolated: yield 43 mg (88%). Anal. Calcd for $C_{22}H_{48}ClIrO_4P_2$: C, 39.66; H, 7.26. Found: C, 40.11; H, 7.49. IR (C$_6$H$_6$): ν(IrH) 2230, ν(C=O) 1578, $\nu(COC)_{asym}$ 1110 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 10.55 (d, *J*(HH) = 7.8 Hz, IrC*H*=CH), 6.62 (d, *J*(HH) = 7.8 Hz, IrCH=C*H*), 3.85 (m, PCH$_2$C*H*$_2$), 3.69 (s, C(O)OC*H*$_3$), 3.22 (s, OC*H*$_3$), 2.38 (m, PC*H*CH$_3$), 2.10 (m, PC*H*$_2$), 1.30–0.95 (m, PCHC*H*$_3$), −26.90 (t, *J*(PH) = 15.4 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 11.95 (s, d in off-resonance). (b) The preparation of **15** from **13** (38 mg, 0.065 mmol) was performed analogously as described in (a): yield 36 mg (82%).

Preparation of [IrClH{κ^2*(C,O)*-CH=CHC(O)Me}{κ*(P)*-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$] (16). (a) A solution of **8** (47 mg, 0.081 mmol) in 5 mL of benzene was treated with methyl vinyl ketone (0.1 mL) and stirred for 20 h at 80 °C. After the solution was cooled to room temperature, the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the resulting solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$/CH$_2$Cl$_2$ (1:2) a yellow fraction was eluted, from which a pale yellow, air-sensitive oil was isolated: yield 44 mg (83%). Anal. Calcd for C$_{22}$H$_{48}$ClIrO$_3$P$_2$: C, 40.64; H, 7.44. Found: C, 40.50; H, 7.76. IR (C$_6$H$_6$): ν(IrH) 2213, ν(C=O) 1539, ν(COC)$_{asym}$ 1125 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 11.00 (d, *J*(HH) = 7.1 Hz, IrC*H*=CH), 6.84 (d, *J*(HH) = 7.1 Hz, IrCH=C*H*), 3.80 (m, PCH$_2$C*H*$_2$), 3.23 (s, OC*H*$_3$), 2.40 (m, PC*H*CH$_3$), 2.14 (s, C(O)C*H*$_3$), 1.93 (m, PC*H*$_2$), 1.29–0.91 (m, PCHC*H*$_3$), −23.80 (t, *J*(PH) = 15.9 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 12.36 (s, d in off-resonance). (b) The preparation of **16** from **13** (41 mg, 0.07 mmol) was performed analogously as described in (a): yield 39 mg (86%).

Preparation of [IrClH(C≡CPh){κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}] (17). (a) A solution of **8** (84 mg, 0.145 mmol) in 10 mL of benzene was treated with phenylacetylene (16 μL, 0.145 mmol) and stirred for 5 min at room temperature. After the solvent was removed, the colorless solid was washed repeatedly with small amounts of pentane and dried in vacuo: yield 89 mg (90%); mp 108 °C decomp. Anal. Calcd for C$_{26}$H$_{48}$ClIrO$_2$P$_2$: C, 45.77; H, 7.09. Found: C, 46.10; H, 7.27. IR (C$_6$H$_6$): ν(IrH) 2280, ν(IrC≡C) 2096, ν(C=C) 1595, ν(COC)$_{asym}$ 1105 and 1045 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 7.27 (m, C$_6$*H*$_5$), 3.64 (m, PCH$_2$C*H*$_2$), 3.27 (s, OC*H*$_3$), 2.78 (m, PC*H*CH$_3$), 2.05 (m, PC*H*$_2$), 1.43–1.08 (m, PCHC*H*$_3$), −31.24 (t, *J*(PH) = 13.5 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 23.06 (s, d in off-resonance). (b) The preparation of **17** from **13** (61 mg, 0.105 mmol) was performed analogously as described in (a): yield 62 mg (87%).

Preparation of [IrClH(C≡CCO$_2$Me){κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}] (18). (a) A solution of **8** (91 mg, 0.157 mmol) in 10 mL of benzene was treated with methyl propiolate (14 μL, 0.157 mmol) and stirred for 5 min at room temperature. After the solvent was removed, the pale red residue was washed repeatedly with small amounts of pentane and dried in vacuo. According to the ^{31}P NMR spectrum, the product contains small amounts of the corresponding vinylidene complex **23**: yield 93 mg (89%). IR (C$_6$H$_6$): ν(IrH) 2254, ν(IrC≡C) 2094, ν(COC)$_{asym}$ 1108 and 1038 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 3.57 (m, PCH$_2$C*H*$_2$), 3.42 (s, C(O)OC*H*$_3$), 3.23 (s, OC*H*$_3$), 2.81 (m, PC*H*CH$_3$), 1.96 (m, PC*H*$_2$), 1.42–1.11 (m, PCHC*H*$_3$), −30.50 (t, *J*(PH) = 15.8 Hz, Ir*H*). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 11.95 (s, d in off-resonance). (b) The preparation of **18** from **13** (69 mg, 0.118 mmol) was performed analogously as described in (a): yield 71 mg (91%).

Preparation of [IrClH(CH=CHCO$_2$Me)(C≡CCO$_2$Me){κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}] (19). (a) A solution of **8** (75 mg, 0.129 mmol) in 10 mL of benzene was treated with methyl propiolate (0.1 mL) and stirred for 15 min at room temperature. After the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the resulting solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$/CH$_2$Cl$_2$ (2:1) a yellow fraction was eluted, from which a pale yellow, air-sensitive oil was isolated: yield 59 mg (61%). Anal Calcd for C$_{26}$H$_{50}$ClIrO$_6$P$_2$: C, 41.73; H, 6.74. Found: C, 42.18; H, 6.82. IR (C$_6$H$_6$): ν(IrC≡C) 2094, ν(C=O) 1675, ν(C=C) 1612, ν(COC)$_{asym}$ 1115 and 1040 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 10.21 (dt, *J*(PH) = 1.8 Hz, *J*(HH) = 15.3 Hz, IrC*H*=CH), 6.86 (dt, *J*(PH) = 1.8 Hz, *J*(HH) = 15.3 Hz, IrCH=C*H*), 3.54 (s, CH=CHC(O)OC*H*$_3$), 3.52 (m, PCH$_2$C*H*$_2$), 3.47 (s, C≡CC(O)OC*H*$_3$), 3.20 (s, OC*H*$_3$), 2.87 (m, PC*H*CH$_3$), 1.89 (m, PC*H*$_2$), 1.40–1.02 (m, PCHC*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 45 °C, 36.2 MHz): δ 3.37 (s). (b) The preparation of **19** from **13** (71 mg, 0.122 mmol) was performed analogously as described in (a): yield 58 mg (64%).

Preparation of *trans*-[IrCl(=C=CHPh){κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$] (20). (a) A solution of **17** (63 mg, 0.092 mmol) in 10 mL of benzene was stirred for 72 h at 80 °C. After the solution was cooled to room temperature, the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the resulting solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$ a red fraction was eluted, from which a deep red air-sensitive oil was isolated: yield 34 mg (54%). Anal. Calcd for C$_{26}$H$_{48}$ClIrO$_2$P$_2$: C, 45.77; H, 7.09. Found: C, 45.35; H, 7.09. IR (C$_6$H$_6$): ν(C=C) 1630, ν(C=C$_{Ph}$) 1592, ν(COC)$_{asym}$ 1108 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 7.16 (m, C$_6$*H*$_5$), 3.76 (m, PCH$_2$C*H*$_2$), 3.06 (s, OC*H*$_3$), 2.48 (m, PC*H*CH$_3$), 2.46 (m, PC*H*$_2$), 1.39 (dvt, *N* = 15.4 Hz, *J*(HH) = 7.1, PCHC*H*$_3$), 1.09 (dvt, *N* = 14.1 Hz, *J*(HH) = 7.0, PCHC*H*$_3$), −2.49 (t, *J*(PH) = 2.9 Hz, =C=C*H*). ^{13}C NMR (C$_6$D$_6$, 50.2 MHz): δ 263.10 (t, *J*(PC) = 13.1 Hz, Ir=*C*=C), 128.31, 128.17, 125.66, 124.84 (all s, *C*$_6$H$_5$), 111.02 (s, Ir=C=*C*), 69.45 (s, PCH$_2$*C*H$_2$OCH$_3$), 57.96 (s, O*C*H$_3$), 24.02 (vt, *N* = 28.7 Hz, P*C*HCH$_3$), 20.88 (vt, *N* = 26.4 Hz, P*C*H$_2$CH$_2$OCH$_3$), 19.94, 18.78 (both s, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 23.02 (s). (b) A solution of **17** (66 mg, 0.097 mmol) in 13 mL of benzene was irradiated with a 125 W mercury vapor UV lamp (Phillips HPK) for 6 h at room temperature. After the solvent was removed, the solution was worked up as described in (a): yield 48 mg (72%).

Preparation of *trans*-[IrCl(=C=CHCO$_2$Me){κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$] (21). A solution of **13** (64 mg, 0.11 mmol) in 10 mL of benzene was treated with methyl propiolate (9.8 μL, 0.11 mmol) and stirred for 5 h at 80 °C. After the solution was cooled to room temperature, the solvent was removed, the oily residue was dissolved in 2 mL of benzene, and the resulting solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V). With C$_6$H$_6$ a red fraction was eluted, which was brought to dryness in vacuo. A deep red air-sensitive solid was isolated, which was recrystallized from pentane at −78 °C: yield 59 mg (81%); mp 92 °C decomp. Anal. Calcd for C$_{22}$H$_{46}$ClIrO$_4$P$_2$: C, 39.78; H, 6.98. Found: C, 40.22; H, 7.14. IR (C$_6$H$_6$): ν(C=O) 1698, ν(C=C) 1637, ν(COC)$_{asym}$ 1108 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 3.76 (m, PCH$_2$C*H*$_2$), 3.53 (s, C(O)OC*H*$_3$), 3.13 (s, OC*H*$_3$), 2.49 (m, PC*H*$_2$), 2.45 (m, PC*H*CH$_3$), 1.27 (dvt, *N* = 15.6 Hz, *J*(HH) = 7.3, PCHC*H*$_3$), 1.10 (dvt, *N* = 14.2 Hz, *J*(HH) = 7.0, PCHC*H*$_3$), −2.09 (t, *J*(PH) = 2.5 Hz, =C=C*H*). ^{13}C NMR (C$_6$D$_6$, 50.2 MHz): δ 254.83 (t, *J*(PC) = 12.8 Hz, Ir=*C*=C), 151.69 (s, *C*(O)OCH$_3$), 103.12 (s, Ir=C=*C*), 69.20 (s, PCH$_2$*C*H$_2$OCH$_3$), 58.08 (s, O*C*H$_3$), 50.29 (s, C(O)O*C*H$_3$), 24.04 (vt, *N* = 30.5 Hz, P*C*HCH$_3$), 20.40 (vt, *N* = 26.7 Hz, P*C*H$_2$CH$_2$OCH$_3$), 19.64, 18.43 (both s, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 26.78 (s).

Preparation of *trans*-[Ir(=C=CHPh){κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}]SbF$_6$ (22). A solution of **20** (54 mg, 0.079 mmol) in 10 mL of dichloromethane was treated with a solution of AgSbF$_6$ (27 mg, 0.079 mmol) in 3 mL of dichloromethane and stirred for 10 min at room temperature. The solution was filtered, and the solvent was removed from the filtrate. An oily residue was obtained, which was dissolved in 2 mL of dichloromethane, and 10 mL of ether was added slowly. A purple-red solid precipitated which was washed with ether and dried in vacuo: yield 61 mg (87%); mp 94 °C decomp. Anal. Calcd for C$_{26}$H$_{48}$F$_6$IrO$_2$P$_2$Sb: C, 35.38; H, 5.48. Found: C, 35.15; H, 5.68. IR (CH$_2$Cl$_2$): ν(C=C) 1667, ν(C=C$_{Ph}$) 1592, ν(COC)$_{asym}$ 1104 and 1054 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 90 MHz): δ 7.12 (m, C$_6$*H*$_5$), 3.86 (m, PCH$_2$C*H*$_2$), 3.48 (s, OC*H*$_3$), 2.48 (m, PC*H*CH$_3$), 2.25 (m, PC*H*$_2$), 1.30, 1.28 (both dvt, *N* = 15.0 Hz, *J*(HH) = 7.2, PCHC*H*$_3$), −1.62 (t, *J*(PH) = 2.6 Hz, =C=C*H*). ^{13}C NMR (CD$_2$Cl$_2$, 50.2 MHz): δ 275.88 (t, *J*(PC) = 13.1 Hz, Ir=*C*=C), 128.65, 126.44, 126.23 (all s, *C*$_6$H$_5$), 111.50 (t, *J*(PC) = 4.4 Hz, Ir=C=*C*), 75.55 (s, PCH$_2$*C*H$_2$OCH$_3$), 62.42 (s, O*C*H$_3$), 25.78 (vt, *N* = 30.7 Hz, P*C*HCH$_3$), 20.40 (vt, *N* = 25.3 Hz, P*C*H$_2$CH$_2$OCH$_3$), 19.57, 18.63 (both s, PCH*C*H$_3$). ^{31}P NMR (CD$_2$Cl$_2$, 36.2 MHz): δ 39.96 (s).

Preparation of *trans*-[Ir(=C=CHCO$_2$Me){κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}]SbF$_6$ (23). This compound was prepared analogously as described for **22**, using **21** (58 mg, 0.087 mmol) and AgSbF$_6$ (30 mg, 0.089 mmol) as starting materials: yield 65 mg (84%); mp 130 °C decomp. Anal. Calcd for C$_{22}$H$_{46}$F$_6$IrO$_4$P$_2$Sb: C, 30.57; H, 5.36. Found:

Table 5. Positional Parameters and Their Esd's for 8

atom	x/a	y/b	z/c	B_{eq}
Ir	0.20688(4)	0.03441(4)	0.25186(2)	1.567(7)
Cl	−0.0782(3)	0.0333(2)	0.3551(2)	2.58(5)
P1	0.3280(3)	−0.1485(2)	0.3463(2)	1.76(5)
P2	0.1498(3)	0.2340(2)	0.1498(2)	1.88(5)
O1	0.3207(7)	0.1742(6)	0.3323(4)	2.0(1)
O2	0.0618(9)	−0.0394(7)	0.1015(4)	3.0(1)
C1	0.445(1)	−0.052(1)	0.4071(6)	2.5(2)
C2	0.479(1)	0.0997(9)	0.3553(6)	2.2(2)
C3	0.217(1)	0.226(1)	0.4053(6)	2.9(2)
C4	0.187(1)	−0.2571(9)	0.4378(6)	2.2(2)
C5	0.286(1)	−0.363(1)	0.5008(6)	3.2(2)
C6	0.048(1)	−0.329(1)	0.4074(7)	3.0(2)
C7	0.500(1)	−0.2773(9)	0.3057(6)	2.4(2)
C8	0.435(1)	−0.390(1)	0.2647(7)	3.5(2)
C9	0.645(1)	−0.198(1)	0.2410(7)	3.3(2)
C10	−0.014(1)	0.213(1)	0.0843(6)	2.8(2)
C11	−0.081(1)	0.064(1)	0.1104(7)	3.0(2)
C12	0.124(1)	−0.098(1)	0.1816(6)	2.6(2)
C13	0.339(1)	0.289(1)	0.0647(6)	2.5(2)
C14	0.409(1)	0.171(1)	0.0129(7)	3.7(3)
C15	0.482(1)	0.337(1)	0.1048(7)	3.6(3)
C16	0.077(1)	0.402(1)	0.1913(6)	2.6(2)
C17	0.077(1)	0.537(1)	0.1203(7)	3.5(2)
C18	−0.103(1)	0.390(1)	0.2490(7)	3.7(3)

Table 6. Positional Parameters and Their Esd's for 12

atom	x/a	y/b	z/c	B_{eq}
Ir	0.03375(3)	0.07053(2)	0.000	1.654(5)
Cl1	0.0035(3)	0.0215(1)	−0.1568(2)	2.63(5)
Cl2	−0.1350(3)	0.1443(1)	−0.0447(2)	2.80(5)
Cl3	0.5201(4)	0.1586(2)	0.2289(2)	3.71(7)
Cl4	0.3189(6)	0.1650(2)	0.5237(6)	12.0(2)
Cl5	0.0259(5)	0.2463(2)	0.5001(7)	8.7(1)
P1	0.1529(3)	−0.0172(1)	0.0307(2)	1.82(5)
P2	0.1965(3)	0.1357(1)	−0.0564(2)	2.02(5)
N1	−0.1474(9)	0.0180(5)	0.0526(7)	2.6(2)
N2	0.0598(9)	0.1694(4)	0.1607(7)	2.3(2)
C1	0.012(1)	−0.0688(6)	0.0427(9)	2.9(2)
C2	−0.099(1)	−0.0387(5)	0.1005(9)	2.6(2)
C3	−0.241(1)	−0.0001(6)	−0.0240(9)	3.4(3)
C4	−0.232(1)	0.0505(6)	0.123(1)	3.7(3)
C5	0.238(1)	−0.0232(5)	0.1466(8)	2.4(2)
C6	0.270(1)	−0.0887(6)	0.1786(9)	3.6(3)
C7	0.365(1)	0.0173(6)	0.157(1)	3.4(3)
C8	0.259(1)	−0.0541(5)	−0.0608(9)	2.7(2)
C9	0.412(1)	−0.0539(6)	−0.046(1)	3.5(3)
C10	0.219(2)	−0.1192(7)	−0.083(1)	4.8(3)
C11	0.238(1)	0.1893(5)	0.0390(8)	2.4(2)
C12	0.113(1)	0.2122(5)	0.0883(8)	2.6(2)
C13	0.139(1)	0.1799(6)	0.2508(8)	3.4(3)
C14	0.072(1)	0.1030(5)	0.1319(7)	2.0(2)
C15	−0.083(1)	0.1872(6)	0.183(1)	3.1(3)
C16	0.362(1)	0.1039(6)	−0.0887(9)	2.8(2)
C17	0.360(1)	0.0777(6)	−0.1914(9)	3.3(3)
C18	0.486(1)	0.1434(7)	−0.073(1)	4.1(3)
C19	0.142(1)	0.1890(5)	−0.1494(8)	2.5(2)
C20	0.071(1)	0.1629(6)	−0.2346(9)	3.6(3)
C21	0.253(1)	0.2333(5)	−0.185(1)	3.4(3)

C, 30.76; H, 5.21. IR (CH_2Cl_2): ν(C=O) 1705, ν(C=C) 1638, $\nu(COC)_{asym}$ 1106 and 1040 cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 3.85 (m, PCH_2CH_2), 3.63 (s, C(O)OCH_3), 3.46 (s, OCH_3), 2.58 (m, PC*H*CH_3), 2.34 (m, PCH_2), 1.32 (dvt, *N* = 15.6 Hz, *J*(HH) = 7.1, PCHCH_3), −1.60 (t, *J*(PH) = 2.5 Hz, =C=C*H*). ^{13}C NMR (CD_2Cl_2, 50.2 MHz): δ 267.40 (t, *J*(PC) = 11.3 Hz, Ir=*C*=C), 211.26 (s, *C*(O)OCH_3), 104.08 (s, Ir=C=*C*), 74.59 (s, PCH_2CH_2-OCH_3), 62.07 (s, OCH_3), 51.47 (s, C(O)OCH_3), 25.74 (vt, *N* = 31.4 Hz, P$CHCH_3$), 20.35 (vt, *N* = 26.6 Hz, P$CH_2CH_2OCH_3$), 19.41, 18.54 (both s, PCHCH_3). ^{31}P NMR (CD_2Cl_2, 36.2 MHz): δ 35.59 (s).

Table 7. Positional Parameters and Their Esd's for 23

atom	x/a	y/b	z/c	B_{eq}
Ir	0.20897(2)	0.72791(2)	0.36084(2)	3.299(6)
Sb	0.26778(5)	0.52018(4)	0.84829(5)	5.65(2)
P1	0.0593(2)	0.7197(1)	0.4239(2)	4.33(5)
P2	0.3662(2)	0.7456(1)	0.3071(2)	3.95(5)
F1	0.2040(6)	0.4481(5)	0.9148(5)	11.0(2)
F2	0.3312(7)	0.5913(5)	0.7827(5)	12.3(2)
F3	0.325(1)	0.5588(9)	0.9588(8)	14.0(4)
F4	0.219(1)	0.480(1)	0.735(1)	14.3(5)
F5	0.156(1)	0.581(1)	0.843(2)	17.4(7)
F6	0.381(1)	0.462(1)	0.850(1)	19.8(7)
O1	0.3023(7)	0.4310(4)	0.4453(5)	8.0(2)
O2	0.3469(5)	0.5485(4)	0.5096(5)	6.3(2)
O3	0.1651(4)	0.8508(3)	0.3475(4)	5.2(1)
O4	0.3907(6)	0.9808(4)	0.3233(5)	7.0(2)
C1	0.2265(5)	0.6251(5)	0.3697(5)	3.6(2)
C2	0.2344(7)	0.5470(5)	0.3705(6)	4.6(2)
C3	0.2941(7)	0.5020(5)	0.4428(7)	5.4(2)
C4	0.407(1)	0.5108(7)	0.5884(8)	9.2(4)
C5	0.0207(7)	0.8234(5)	0.4300(7)	5.7(2)
C6	0.1110(8)	0.8766(5)	0.4221(7)	6.6(3)
C7	0.1257(8)	0.8830(6)	0.2583(8)	7.6(3)
C8	0.0676(8)	0.6842(6)	0.5442(7)	6.5(3)
C9	0.073(1)	0.5938(7)	0.5496(8)	10.0(4)
C10	0.1594(9)	0.7216(8)	0.6068(8)	9.2(4)
C11	−0.0491(7)	0.6706(6)	0.3517(7)	6.2(3)
C12	−0.0633(8)	0.7008(7)	0.2526(7)	7.3(3)
C13	−0.1505(7)	0.6769(8)	0.3922(9)	10.4(4)
C14	0.3992(7)	0.8482(5)	0.2834(6)	5.0(2)
C15	0.4088(7)	0.9059(5)	0.3639(7)	5.2(2)
C16	0.4165(9)	1.0428(6)	0.3859(8)	7.6(3)
C17	0.4736(6)	0.7058(5)	0.3909(7)	5.2(2)
C18	0.4714(8)	0.7332(6)	0.4895(7)	6.6(3)
C19	0.5792(7)	0.7164(7)	0.3624(9)	8.2(3)
C20	0.3746(7)	0.7012(5)	0.1936(7)	5.5(2)
C21	0.2840(8)	0.7268(6)	0.1205(7)	6.9(3)
C22	0.3828(8)	0.6105(6)	0.1948(7)	6.9(3)

X-ray Structural Analyses of 8, 12, and 23. Single crystals were grown from toluene/pentane (**8**), dichloromethane/pentane (**12**), and dichloromethane (**29**). Crystal data collection parameters are summarized in Table 4. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmissions were 77.2% (for **8**), 95.3% (for **12**), and 70.3% (for **23**). The structures were solved by direct methods (SHELXS-86) for **8** and **23** and by the Patterson method (SHELXS-86, DIRDIF) for **12**. In the case of **12**, there is one molecule of CH_2Cl_2 in the asymmetric unit. The SbF_6 anion of compound **23** reveals disorder in the octahedral plane with the disordered positions rotated by ca. 45° in the plane; a weighting factor of 0.4 was used for the refinement. The position of the metal-bonded hydrogen atom of **8** was taken from a difference-Fourier synthesis. The positions of all other hydrogen atoms were calculated according to ideal geometry (distance of C−H set at 0.95 Å) and were refined by the riding method. Atomic coordinates (see Tables 5−7) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. For other details see Table 4.

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

Supporting Information Available: Drawings showing the atom-numbering schemes, and tables of crystal data, bond distances, bond angles, positional parameters, and general displacement parameter expressions of compounds **8**, **12**, and **23** (25 pages). Ordering information is given on any current masthead page.

OM950109T