Preparation of five- and six-coordinate aryl(hydrido) iridium(III) complexes from benzene and functionalized arenes by C–H activation†

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The reaction of the *in situ* generated cyclooctene iridium(I) derivative *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with benzene at 80 °C gave a mixture of the five-coordinate dihydrido and hydrido(phenyl) iridium(III) complexes [IrH_2(Cl)($PiPr_3$)$_2$] **2** and [IrH(C_6H_5)(Cl)($PiPr_3$)$_2$] **3** in the ratio of about 1 : 2. The chloro- and fluoro-substituted arenes C_6H_5X (X = Cl, F), $C_6H_4F_2$ and $C_6H_4F(CH_3)$ reacted also by C–H activation to afford the corresponding aryl(hydrido) iridium(III) derivatives [IrH(C_6H_4X)(Cl)($PiPr_3$)$_2$] **7**, **8**, [IrH($C_6H_3F_2$)(Cl)($PiPr_3$)$_2$] **9–11** and [IrH{$C_6H_3F(CH_3)$}(Cl)($PiPr_3$)$_2$] **12**, **13**, respectively. The formation of isomeric mixtures had been detected by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy. Treatment of **3** and **7–13** with CO gave the octahedral carbonyl iridium(III) complexes [IrH(C_6H_3XX')(Cl)(CO)($PiPr_3$)$_2$] **5**, **14–20** without the elimination of the arene. The reactions of *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with aryl ketones $C_6H_5C(O)R$ (R = Me, Ph), aryl ketoximes $C_6H_5C(NOH)R$ (R = Me, Ph) and benzaloxime $C_6H_5C(NOH)H$ resulted in the formation of six-coordinate aryl(hydrido) iridium(III) compounds **21–25** with the aryl ligand coordinated in a bidentate κ^2-*C*,*O* or κ^2-*C*,*N* fashion. With $C_6H_5C(O)NH_2$ as the substrate, the two isomers [IrH{κ^2-*N*,*O*-$NHC(O)C_6H_5$}(Cl)($PiPr_3$)$_2$] **26** and [IrH{κ^2-*C*,*O*-$C_6H_4C(O)NH_2$}(Cl)($PiPr_3$)$_2$] **27** were prepared stepwise. Treatment of *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] with benzoic acid gave the benzoato(hydrido) complex [IrH{κ^2-*O*,*O*-$O_2CC_6H_5$}(Cl)($PiPr_3$)$_2$] **29** which did not rearrange to the κ^2-*C*,*O* isomer.

Introduction

In the context of our investigations on the chemistry of four- and five-coordinate iridium(I) complexes containing [IrCl($PiPr_3$)$_2$] as a molecular fragment,[1] we found that the labile cyclooctene iridium(I) derivative *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] reacts with vinyl ketones and related Michael systems RCH=C(R′)C(O)X (X = H, OMe, NH_2, NMe_2) at ambient temperature to afford octahedral hydrido(vinyl) iridium(III) compounds with the vinyl ligand coordinated in a bidentate κ^2-*C*,*O* or κ^2-*C*,*N* fashion.[2] With methyl acrylate the corresponding olefin complex *trans*-[IrCl(η^2-CH_2=$CHCO_2Me$)($PiPr_3$)$_2$] could be isolated which was converted at 25 °C or above to the thermodynamically more stable iridium(III) isomer [IrH(Cl){κ^2-*C*,*O*-CH=CH(OMe)=O}($PiPr_3$)$_2$] by intramolecular C–H activation.[2] In contrast, the ethene derivative *trans*-[IrCl(η^2-C_2H_4)($PiPr_3$)$_2$] is thermally rather inert and below its decomposition temperature does not react to give the hydrido(vinyl) complex [IrH(Cl)($CH=CH_2$)($PiPr_3$)$_2$].[3]

Here we report that the *in situ* generated species *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$] can also be used as starting material for the C–H bond activation of benzene and various functionalized arenes. Depending on the substrate, five- or six-coordinate aryl(hydrido) iridium(III) complexes are formed which even in the presence of CO do not react by reductive elimination of the respective arene. A preliminary communication about the very early results of this work had already appeared.[4]

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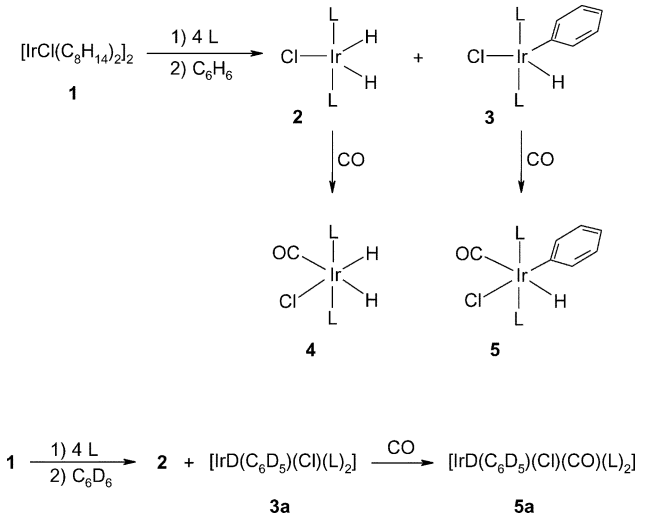
† Dedicated to Professor Ulrich Schubert, with the best of good wishes, on the occasion of his 60th birthday.

Results and discussion

Oxidative addition of benzene, chlorobenzene and fluorobenzenes to an iridium(I) centre

The cyclooctene iridium(I) compound *trans*-[IrCl(C_8H_{14})($PiPr_3$)$_2$], generated *in situ* from **1** and four equivalents of triisopropylphosphine in benzene,[5] reacts at room temperature with HCl and H_2 to give the mono- and dihydrido iridium(III) complexes [IrH$(Cl)_2$($PiPr_3$)$_2$] and [IrH_2(Cl)($PiPr_3$)$_2$] **2**, respectively.[6] Under the same conditions, no reaction occurs with benzene. However, if the benzene solution containing the bis(triisopropylphosphine) cyclooctene derivative is heated for 90 min to 80 °C, a mixture of **2** and **3** is obtained in the ratio of about 1 : 2 (Scheme 1). The separation of the two products can be achieved by repeated crystallization from pentane at −78 °C. The hydrido(phenyl) iridium(III) complex **3** forms orange–red crystals, which are moderately air-sensitive and soluble in most common organic solvents. Regarding the spectroscopic data of **3**, the most typical feature is the Ir–H proton signal at δ −32.23 in the ^{1}H NMR spectrum, the high-field chemical shift appears to be typical for hydrido iridium(III) compounds with a five-coordinate metal centre.[6]

The proposed stereochemistry of **3** has been confirmed by an X-ray crystal structure analysis.[4] The coordination sphere is best described as a distorted trigonal bipyramid with the phosphine ligands in axial positions. The phenyl ring lies exactly in the trigonal plane. The P–Ir–P axis is somewhat bent (angle 168.1(3)°) which is probably a consequence of steric repulsion between the isopropyl groups and the phenyl unit. Particularly noteworthy is the relatively small angle H–Ir–C_{Ph} angle (77.9°)



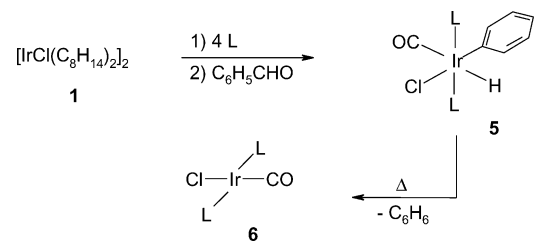
Scheme 1 (L = P*i*Pr$_3$).

in the equatorial plane which according to theoretical work by Jean and Eisenstein[7] is traced to a first-order Jahn–Teller effect and not to an attractive ligand-to-ligand interaction. The so-called "Y structure" (the name reflecting the position of the three ligands in the plane of the bipyramid) seems to be generally favoured when the ligand on the site *trans* to the acute angle of about 70–80° is both a weak σ-donor and a good π-donor such as chloride, amido, methoxide *etc.*[7] Moreover, the calculations suggest that the "squeeze" of the regular 120° angle R–Ir–R′ in the plane of distorted trigonal-bipyramidal iridium(III) complexes of the general composition [IrR(R′)(X)(L)$_2$] is also to be expected for R = R′ = alkyl or aryl and R = R′ = H, which is in agreement with the structural data for [Ir(CH$_2$Ph)$_2${κ^3-*P*,*N*,*P*-N(SiMe$_2$CH$_2$PPh$_2$)$_2$}],[8] [Ir(H)$_2$(OCH$_2$CF$_3$)(PCy$_3$)$_2$],[9] and [Ir(H)$_2$(Cl)(P*t*Bu$_2$Ph)$_2$].[10] The small angle H–Ir–C$_{Ph}$ in compound **3** could also explain the high barrier to rotation about the metal–phenyl bond in solution, as evidenced by the appearance of six signals for the C$_6$H$_5$ carbon atoms in the ^{13}C NMR spectrum of **3** at room temperature. A similar hindered rotation about metal–phenyl bonds had also been reported for complexes such as [Ru(C$_6$H$_4$R)(X)(CO)$_2$(L)$_2$], [Ru(C$_6$H$_4$R)(X)(CO)(L)$_3$] (R = H, Me, Cl, OMe, NMe$_2$; X = Cl, Br, I, OAc; L = PR$_3$, P(OMe)$_3$, AsR$_3$),[11] [(C$_5$Me$_5$)Rh(C$_6$H$_4$R)(X)(PR′$_3$)] (R = H, Me, F, CF$_3$, OMe, NMe$_2$; X = Cl, Br, I; R′ = Me, Ph, *p*-Tol)[12] and *mer*-[IrH(C$_6$H$_5$)(Cl)(PMe$_3$)$_3$],[13] although in all of these cases the metal centre is not five- but six-coordinate and has an 18-electron configuration.

The problem of how the dihydride **2** is formed from **1**, P*i*Pr$_3$ and benzene has not been finally solved. The hydrido(phenyl) complex **3** is definitely not a precursor of **2** since it is recovered in quantitative yield after heating a benzene solution of **3** for several hours under reflux. The solvent benzene is also not the source of the hydride ligands in **2**, because from **1**, P*i*Pr$_3$ and C$_6$D$_6$ a mixture of **2** (not [Ir(D)$_2$(Cl)(P*i*Pr$_3$)$_2$]) and [IrD(C$_6$D$_5$)(Cl)(P*i*Pr$_3$)$_2$] **3a** is obtained. The most plausible assumption is that cyclooctene coordinated in precursor **1** functions as the H$_2$-transfer reagent which would be in agreement with previous work by Crabtree and others.[14] In this context we note that the reactions of *in situ* generated *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] with RCH=CHCO$_2$Me (R = Me, Ph) proceed, in contrast to those with RCH=CHC(O)Me, not by C–H activation of the olefinic substrate but yield instead the dihydrido compound **2** as the main component.[2]

The mixture of **2** and **3** formed from **1** and P*i*Pr$_3$ in benzene smoothly reacts with CO at room temperature to afford the monocarbonyl complexes **4** and **5** (Scheme 1), which can easily be separated. Even under slightly increased pressure of CO, neither elimination of H$_2$ from **4** nor of C$_6$H$_6$ from **5** to give *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$] takes place. Both **4** and **5** are pale yellow to yellow solids which were characterized by elemental analysis and mass spectroscopy. The dihydrido(carbonyl) compound **4** was previously generated (although not isolated) from *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$] and dihydrogen and studied with regard to its catalytic properties.[15] The ^{1}H NMR spectrum of **4** displays two hydride signals at δ −8.64 and −20.20 which both appear as doublet-of-triplets due to ^{1}H–^{1}H and ^{1}H–^{31}P couplings. In agreement with the data for [IrH$_2$(Cl)(CO)(PMe$_2$Ph)$_2$],[16] we assume that the signal with the lower chemical shift should be assigned to the hydride *trans* to chloride and that with the higher chemical shift to the hydride *trans* to CO. The ^{1}H NMR spectrum of **5** shows the hydride signal at δ −7.29 indicating that in **5**, similarly as in **4**, a *trans* H–Ir–CO arrangement exists. An octahedral iridium(III) complex analogous to **5** with the composition [IrH(C$_6$H$_5$)(Br)(CO)(PEt$_3$)$_2$] was previously prepared by Dahlenburg *et al.* from *trans*-[IrC$_6$H$_5$(CO)(PEt$_3$)$_2$] and HBr but in contrast to **5** has the hydrido and the CO ligands in *cis* disposition.[17] The mixture of **2** and **3a** reacts with CO to give **4** and [IrD(C$_6$D$_5$)(Cl)(CO)(P*i*Pr$_3$)$_2$] **5a**, respectively. The two products were separated due to their different solubility in methanol.

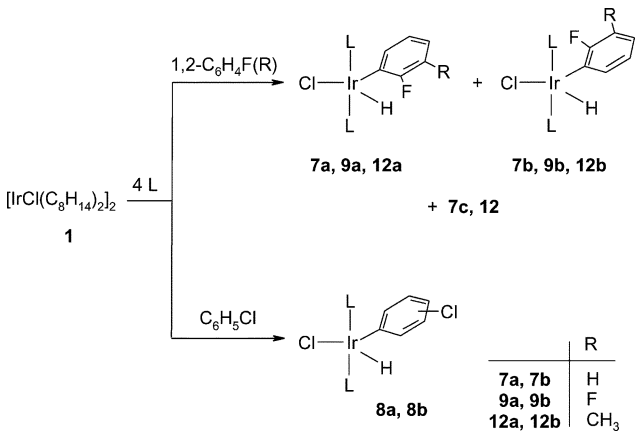
Somewhat unexpectedly, the carbonyl(hydrido)(phenyl) compound **5** was also obtained in excellent yield upon treatment of labile *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] with benzaldehyde (Scheme 2). While the same cyclooctene precursor reacted with acrolein to give almost exclusively six-coordinate [IrH(Cl)(κ^2-*C*,*O*-CH=CHCH=O)(P*i*Pr$_3$)$_2$],[2] in the reaction with benzaldehyde the formation of an analogous κ^2-*C*,*O*-bonded isomer [IrH(Cl)(κ^2-*C*,*O*-C$_6$H$_4$CH=O)(P*i*Pr$_3$)$_2$] could not be observed. We assume that from *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] and C$_6$H$_5$CHO the five-coordinate intermediate [IrH{C(O)C$_6$H$_5$}(Cl)(P*i*Pr$_3$)$_2$] is initially formed which by de-insertion of the CO group from the Ir–C(O)C$_6$H$_5$ unit is transformed to the product. Thermolysis of **5** in refluxing toluene for 6 h affords the Vaska-type complex *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$] **6**; the concomitant formation of [IrH(C$_6$H$_4$Me)(Cl)(CO)(P*i*Pr$_3$)$_2$] does not occur. If the thermal reaction of **5** was carried out in diethylene glycol at 150 °C, besides **6** benzene could be detected by GC.



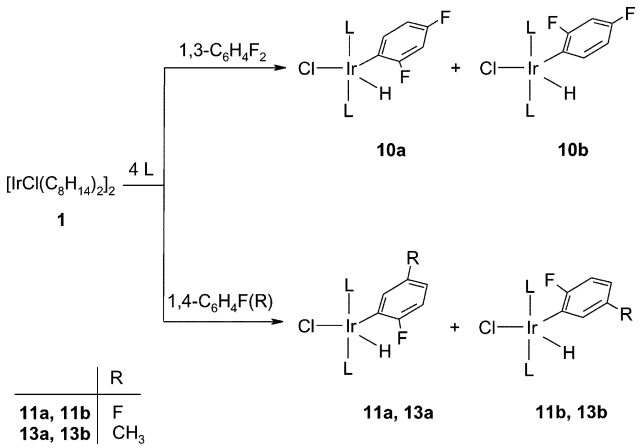
Scheme 2 (L = P*i*Pr$_3$).

Under similar conditions as used for the preparation of **3**, the *in situ* generated starting material *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] also

reacted with mono- and di-substituted arenes C_6H_5X (X = Cl, F), $C_6H_4F_2$ and $C_6H_4F(CH_3)$ in neat arene at 80 °C to afford, apart from the dihydride **2**, the aryl(hydrido) complexes **7–13** in 50–70% yield of isolated product. In all cases a mixture of isomers was formed (see Schemes 3 and 4) which mostly could not be separated by fractional crystallization or column chromatography using deactivated Al_2O_3. Only for **11a/11b** we succeeded in the separation of the two isomers by slow crystallization from pentane at −78 °C, though in low yield. While with chlorobenzene, the 1,2-, 1,3- and 1,4-difluorobenzenes and 1,4-$C_6H_4F(CH_3)$ always two isomers were formed, with C_6H_5F and 1,2-$C_6H_4F(CH_3)$ as the substrates besides the main species **7a/7b** and **12a/12b** a third isomer **7c** and **12c** could be detected by ^{1}H and ^{31}P NMR spectroscopy. Despite the lack of precise data we assume that in contrast to **7a/7b** and **12a/12b** the minor isomers **7c** and **12c** contain the fluoro substituent not in the preferred *ortho* but in *meta* or *para* position of the phenyl ring. Preliminary kinetic data suggest that the rate of the reaction of the precursor *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with the arene increases in the order $C_6H_6 < C_6H_5F < C_6H_4F_2$, which is in agreement with results by Mawby and co-workers.[11] In the same order, the relative amount of the by-product **2** decreases. Attempts to prepare the compounds [IrH(C_6H_4X)(Cl)(P*i*Pr$_3$)$_2$] (X = Br or I) with bromo- or iodo-benzene as the substrate failed; in these cases only the dihydrido complex **2** could be isolated.



Scheme 3 (L = P*i*Pr$_3$).



Scheme 4 (L = P*i*Pr$_3$).

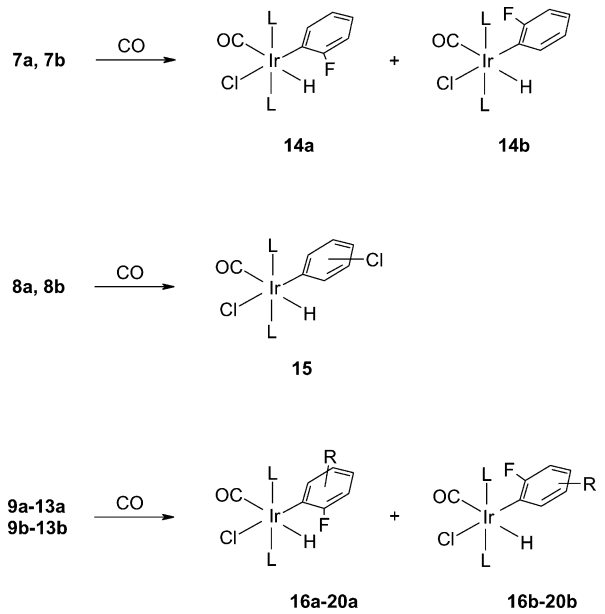
The composition of compounds **7–13** was confirmed by elemental analysis and mass spectra. The ^{1}H NMR spectrum of the chlorophenyl complex **8** shows two hydride signals at δ −35.17 and −34.41 which are split into triplets due to ^2J(P,H) coupling. Based on the small difference in the chemical shift of these signals, we assume that in **8a** the chloro substituent is in the *ortho* and in **8b** either in the *meta* or *para* position of the phenyl ring.

The ^{1}H NMR spectra of **7** and **9–13** also display two hydride resonances which, however, differ more significantly in their chemical shift and appear at around δ −43 to −44 and −35 to −37. The signal at higher field is always split into a doublet-of-triplets indicating that besides the expected ^2J(P,H) coupling with the ^{31}P nuclei of the phosphine ligands an additional ^4J(F,H) coupling with one fluoride takes place. Therefore, we propose that in the respective isomers **7a** and **9a–13a** the fluoro substituent is in the *ortho* position of the phenyl group and *cis* oriented to the Ir–H bond in the trigonal plane of the molecule. A similar through-space F–H coupling of the hydride signal had also been observed in the ^{1}H NMR spectra of [(C_5H_5)($C_5H_4C_6F_5$)MH(C_6F_5)] (M = Mo, W)[18] and [FeH(C_6H_4F)(dmpe)$_2$] (dmpe = 1,2-C_2H_4(PMe$_2$)$_2$).[19] In these cases the ^4J(F,H) coupling constant is 7.4 and 7 Hz and thus nearly the same as for the isomers **7a** and **9a–13a**.

The second hydride signal in the spectra of **7** and **9–13** at around δ −35 to −37 shows no F–H coupling and appears as a triplet. Since the ^2J(P,H) coupling constant is identical to that of the isomers **7a** and **9a–13a**, we assume that also in **7b** and **9b–13b** the fluoro substituent is in the *ortho* position of the phenyl group but in contrast to **7a** and **9a–13a** *trans* oriented to the Ir–H bond. The observed hindered rotation around the metal–phenyl bond in complex **3** supports this proposal.

The ^{31}P NMR spectra of the pairs of isomers **7a/7b**, **9a/9b**, **10a/10b**, **11a/11b**, **12a/12b** and **13a/13b** also display two signals, the chemical shift of which differs only by 0.8 to 1.2 ppm. Under off-resonance conditions these signals appear as doublets due to P–H coupling with the Ir–H proton. The ^{19}F NMR spectra of **7a/7b**, **12a/12b** and **13a/13b**, formed from the monofluoroarenes C_6H_5F and $C_6H_4F(CH_3)$, show two resonances while the spectra of compounds **9a/9b**, **10a/10b** and **11a/11b**, formed from the difluoroarenes $C_6H_4F_2$, show four. It is thus obvious that in the latter pairs of isomers the two fluoro substituents are in different environments. Based on reference data,[18,20] we suggest that the respective signals at lower field in the spectra of **9a/9b**, **10a/10b** and **11a/11b** are assigned to the fluoro substituent in *ortho* position and those at higher field to the fluoro substituent in *meta* or *para* position. In agreement with the ^{13}C NMR data of **7a/7b**, **9a/9b**, **11a/11b** and **13a/13b** (for details see Experimental section) we conclude that in the reactions of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with 1,2-C_6H_4F(X) and 1,3-C_6H_4F(X) (X = F, CH_3) the isomers with the fluoro substituent in *ortho* position to the metal-bonded carbon atom of the phenyl ring are preferentially formed. In neither case a C–F activation could be observed.

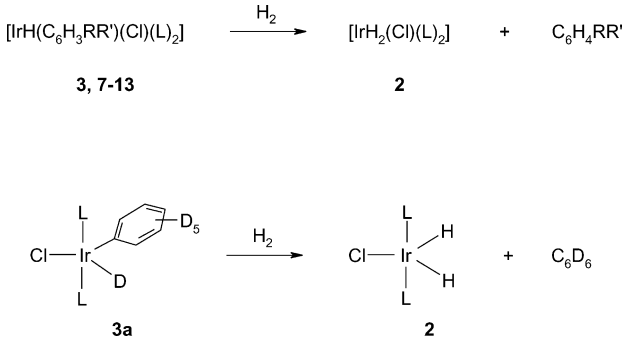
Similarly to the hydrido(phenyl) complex **3**, the structurally related compounds **7–13** also react with CO in benzene at room temperature to give the 1 : 1 adducts **14–20** (Scheme 5). With the exception of **15**, always a mixture of two isomers was formed. In contrast to **16a/16b–20a/20b**, in the case of **14a/14b** they had only been detected by ^{19}F NMR spectroscopy. In the mixtures of products obtained from **7a/7b** and **12a/12b** with CO, the formation of a third isomer had not been observed.



Scheme 5 (L = P*i*Pr$_3$; R = 3-F (**16a**, **16b**), 4-F (**17a**, **17b**), 5-F (**18a**, **18b**), 3-CH$_3$ (**19a**,**19b**), 5-CH$_3$ (**20a**, **20b**); the number indicates the position of R at the phenyl ring).

The ^{1}H NMR spectra of **14a/14b**, **15** and **16a/16b–20a/20b** display the hydride signals at δ −7.1 to −8.5, which is at significantly lower field compared with the five-coordinate compounds **7a/7b–13a/13b**. In contrast, the ^{31}P NMR resonances of **14a/14b**, **15** and **16a/16b–20a/20b** are shifted to higher field compared with **7a/7b–13a/13b**. Since there is only a small difference in the chemical shift of the hydride signal of **5** and **14–20** and also of the phosphorus resonances of these compounds, we assume that the stereochemistry of **14–20** is similar to that of **5**. Moreover, it is conceivable that as in **3** and **7–13** also in **14–20** the rotation around the metal–aryl bond is severely hindered and that the six-membered ring lies in the plane of the IrH(Cl)(CO) moiety.

The aryl(hydrido) complexes **3** and **7–13** react with H_2 in C_6D_6 at room temperature very rapidly to afford the dihydride **2** and the respective arene (Scheme 6). From **3a** and H_2, compound **2** and C_6D_6 are exclusively formed. To rationalize the course of these processes, we assume that from [IrH(C$_6$H$_3$RR′)(Cl)(P*i*Pr$_3$)$_2$] and dihydrogen a 1 : 1 adduct [IrH(C$_6$H$_3$RR′)(Cl)(H$_2$)(P*i*Pr$_3$)$_2$] is initially generated which eliminates the arene and gives the coordinatively unsaturated intermediate [Ir(Cl)(H$_2$)(P*i*Pr$_3$)$_2$]. The latter is finally converted to **2** by intramolecular oxidative addition. In this context

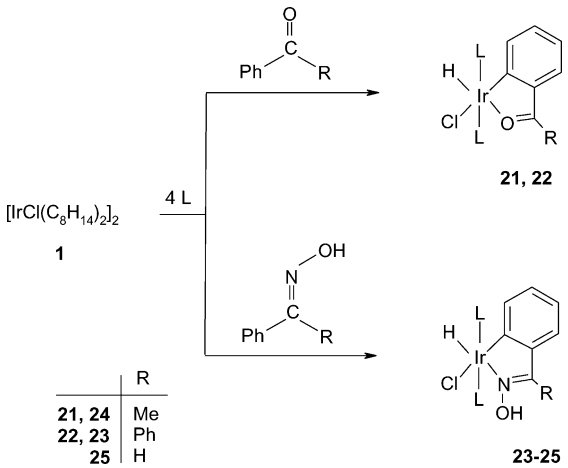


Scheme 6 (L = P*i*Pr$_3$).

we note that both Caulton and co-workers[10] and Jensen and co-workers[21] reported that the monohydrido and the dihydrido compounds [IrH(Cl)$_2$(P*i*Pr$_3$)$_2$] and [IrH$_2$(Cl)(P*i*Pr$_3$)$_2$] react with H_2 to give the corresponding non-classical dihydrogen complexes [IrH(Cl)$_2$(H$_2$)(P*i*Pr$_3$)$_2$] and [IrH$_2$(Cl)(H$_2$)(P*i*Pr$_3$)$_2$], which are stable under a H_2 atmosphere. For [IrH(Cl)$_2$(H$_2$)(P*i*Pr$_3$)$_2$], the structure of the thermodynamically more stable *cis* isomer (H and H$_2$ *cis* to each other) has been confirmed by neutron diffraction.[10] It should also be mentioned that the hydrogenolysis of the metal–aryl bond in cationic aryl(hydrido) iridium(III) chelate complexes probably occurs *via* the formation of Ir(H$_2$) species as intermediates.[22]

Six-coordinate aryl(hydrido) iridium(III) complexes from aryl ketones and oximes

The reaction of *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] with acetophenone proceeds under the same conditions as that with benzene. After removal of the volatiles and chromatographic work-up the aryl(hydrido) complex **21** was isolated as a nearly air-stable solid in 90% yield (Scheme 7). The IR spectrum of **21** displays the ν(C=O) stretching mode at 1580 cm^{-1}, which is shifted by *ca.* 120 cm^{-1} to lower wavenumbers compared with the free ketone. Since this shift is consistent with a coordination of the carbonyl group to the metal centre, an octahedral geometry for compound **21** can be assumed. The ^{1}H NMR spectrum of **21** shows the hydride resonance at δ −25.07 as a triplet. The chemical shift is similar to that of [IrH(Cl){κ^2-*C*,*O*-C(CO$_2$Me)=CHC(OMe)=O}(P*i*Pr$_3$)$_2$] which was prepared from *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] and dimethyl fumarate.[2] For this complex an octahedral coordination sphere with a *trans* disposition of the hydride and the C=O oxygen atom was confirmed by an X-ray crystal structure analysis.[23] We note that the five-membered molecular fragment [M]{κ^2-*C*,*O*-C$_6$H$_4$C(Me)=O} has also been found for [M] = Mn(CO)$_4$ and Re(CO)$_4$[24] as well as for [M] = RuCl(CO)(PPh$_3$)$_2$, respectively.[25]



Scheme 7 (L = P*i*Pr$_3$).

Whereas upon treatment of *trans*-[IrCl(C$_8$H$_{14}$)(P*i*Pr$_3$)$_2$] with acetophenone only minor quantities of the dihydrido compound **2** were formed, the reaction of the same precursor with benzophenone led to a 1 : 1 mixture of **2** and the corresponding aryl(hydrido) complex **22**. Both can be separated by column chromatography. The position of the ν(C=O) band in the IR spectrum and the chemical shift of the hydride and phosphorus resonances in the

^{1}H and ^{31}P NMR spectra of **21** and **22** are quite similar and thus an analogous molecular structure for both complexes is most likely.

In contrast to the ketones RC(O)Ph (R = Me, Ph), the related oximes RC(NOH)Ph react with *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] in toluene even at room temperature. The products **23** and **24**, being yellow microcrystalline solids, were isolated in nearly quantitative yields. The most prominent feature in the IR spectra of **23** and **24** is the ν(OH) stretching mode which appears at 3080 cm^{-1} (for **23**) and 3115 cm^{-1} (for **24**). The ^{1}H NMR spectra of **23** and **24** display the signal for the OH proton at δ 12.19 (for **23**) and δ 11.06 (for **24**) and the hydride signal at δ −16.63 (for **23**) and δ −17.25 (for **24**), respectively.

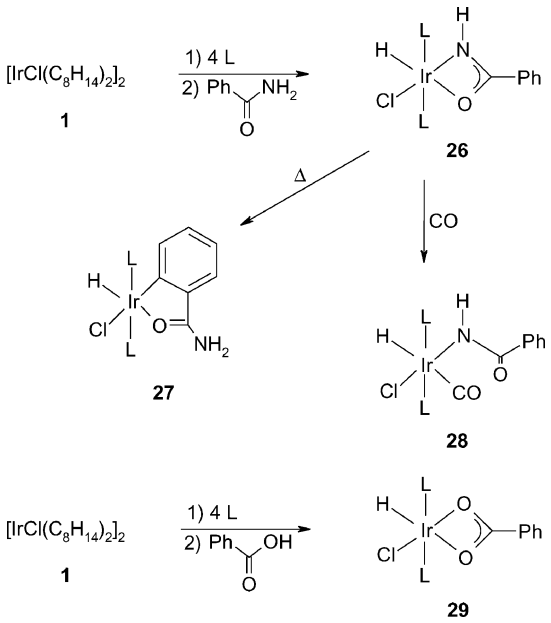
The expected stereochemistry of **23** with the phosphine ligands and the chloride and the metalated carbon atom of the phenyl ring in *trans* disposition was confirmed crystallographically.[26] The bond length Ir–C is comparable 2.026(5) Å to that in [IrH(Cl){κ^2-*C*,*O*-C(CO$_2$Me)=CHC(OMe)=O}(P*i*Pr$_3$)$_2$] (2.005(7) Å).[2] The Ir–N distance is 2.097(4) Å and lies in the region of Ir–N σ-bonds.[27] The P–Ir–P axis (160.4(1)°) is even more bent than in complex **3** and points in the direction of the smallest (hydride) ligand.

The reaction of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with benzaloxime occurs analogously as that with acetophenone and affords the aryl(hydrido) complex **25** in 83% yield of isolated product. Both the chemical properties and the most typical IR and NMR data of **25** are quite similar to those of **23** and deserve no further comment. It is worth mentioning that in contrast to the five-coordinate compounds **3** and **7–13** the six-coordinate iridium(III) complexes **23–25** are inert in the presence of CO and do not react with dihydrogen under normal conditions.

Hydrido iridium(III) complexes from benzoic acidamide and benzoic acid

The reaction of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] and benzoic acidamide in toluene under ultrasound leads to the formation of a yellow crystalline solid which analyzes as **26** and does not result from a C–H activation of the phenyl ring. Instead an N–H activation of the amido group of the acidamide had occurred (Scheme 8). Diagnostic for **26** are the ν(NH) and ν(C=O) stretching modes in the IR spectrum at, respectively, 3325 and 1525 cm^{-1} and the broadened resonance for the NH proton in the ^{1}H NMR spectrum at δ 5.37. The ^{13}C NMR spectrum of **26** displays four signals for the carbon atoms of the aryl group indicating that a C_6H_5 and not a C_6H_4 unit is part of the molecule. In this context we note that Milstein and co-workers have shown that the coordinatively unsaturated iridium(I) species [IrCl(PEt$_3$)$_2$], generated from [IrCl(C_2H_4)(PEt$_3$)$_2$] or [IrCl(PEt$_3$)$_3$] by ligand dissociation, reacts with aniline by N–H activation to afford the corresponding iridium(III) complex with [IrH(NHPh)] as a building block.[28]

If a solution of **26** in benzene is stirred under reflux for 48 h, a rearrangement takes place and the isomer **27** is obtained in excellent yield. It is conceivable that under the thermal conditions a cleavage of the Ir–N bond of **26** occurs and the thermodynamically preferred product **27** is generated by *ortho*-metalation of the six-membered ring. In contrast to **26**, the IR spectrum of **27** shows two ν(NH) stretching modes at 3280 and 3205 cm^{-1} as well as a ν(C=O) band at 1555 cm^{-1}. Compared with **26** the latter is shifted by 30 cm^{-1} to higher frequencies which is in agreement with the data for **21** and **22**, respectively.



Scheme 8 (L = P*i*Pr$_3$).

While compound **27** is inert under an atmosphere of CO, the κ^2-*N*,*O*-bonded isomer **26** reacts rapidly with carbon monoxide at room temperature to give the expected 1 : 1 adduct **28** (see Scheme 8). Typical for the presence of an un-coordinated C=O group is the absorption at 1615 cm^{-1} in the IR spectrum, the position of which being similar to that of free benzoic acidamide.[29] The ^{1}H NMR spectrum of **28** displays the hydride resonance at δ −8.78 and thus at a similar chemical shift as for the non-chelate complexes **14–20**.

The reaction of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with benzoic acid also proceeds at room temperature and affords the chelate compound **29** in nearly quantitative yield. The composition of the benzoato(hydrido) complex, which was isolated as a yellow air-stable solid, was substantiated by elemental analysis and mass spectroscopy. While the same iridium(I) precursor reacts with acrylic acid to give both [IrH(κ^2-*O*,*O*-O$_2$CCH=CH$_2$)(Cl)(P*i*Pr$_3$)$_2$] and [IrH{κ^2-*C*,*O*-CH=CHC(OH)O}(Cl)(P*i*Pr$_3$)$_2$],[2] an analogous product formed by C–H activation was not observed with benzoic acid as the substrate. Attempts to transform **29** either thermally or photochemically to the respective isomer [IrH{κ^2-*C*,*O*-C_6H_4C(=O)O}(Cl)(P*i*Pr$_3$)$_2$] failed.

Conclusion

The present investigation has shown that the *in situ* generated iridium(I) species *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$], containing a labile cyclooctene ligand, reacts thermally with benzene and several substituted benzenes mainly by C–H activation of the arene. Whereas with C_6H_6, C_6H_5Cl, C_6H_5F and the isomers of $C_6H_4F_2$ and $C_6H_4F(CH_3)$ as substrates five-coordinate aryl(hydrido) iridium(III) complexes are formed, with aryl ketones, aryl ketoximes and benzaloxime six-coordinate iridium(III) compounds are obtained. The formation of these products is probably facilitated by the coordination of the C=O oxygen or the C=NOH nitrogen atom to the metal centre, thus generating a five-membered chelate system. The so-formed Ir–O or Ir–N linkage is remarkably stable and remains intact even under a CO atmosphere.

The five-coordinate aryl(hydrido) complexes, in which according to NMR studies and theoretical calculations the rotation around the metal–aryl bond is significantly hindered, react rapidly both with carbon monoxide and dihydrogen at room temperature. While with CO very robust 1 : 1 adducts are formed, which do not rearrange by insertion of CO into the metal–aryl bond, with H_2 elimination of the arene occurs. We assume that also in this case initially an addition of the substrate to the coordinatively unsaturated metal centre takes place thus generating an intermediate with a non-classical Ir(H_2) unit. The reaction of *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] with benzoic acidamide proceeds by N–H activation and affords in the initial step an iridium(III) complex with [IrH{κ^2-*N*,*O*-NHC(Ph)O}] as a molecular fragment. This compound is thermodynamically unstable and smoothly rearranges to the [IrH{κ^2-*C*,*O*-$C_6H_4C(NH_2)O$}] isomer. From *trans*-[IrCl(C_8H_{14})(P*i*Pr$_3$)$_2$] and benzoic acid the corresponding benzoato(hydrido) complex is formed which is inert and cannot be transformed to a ring-metalated isomer.

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**[30] and P*i*Pr$_3$[31] were prepared as described in the literature. NMR spectra were recorded at room temperature (if not otherwise stated) on Jeol FX 90 Q and Bruker AC 200 and AMX 400 instruments. The NMR spectra were referenced to TMS (^{1}H and ^{13}C), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Perkin-Elmer 457 infrared spectrometer, and mass spectra on a Varian MAT CH 7 instrument. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer Du Pont 900. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants *J* and *N* in Hz; $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^2J(P,C) + {}^4J(P,C)$.

Preparations

[IrH(C_6H_5)(Cl)(P*i*Pr$_3$)$_2$] 3. A suspension of **1** (200 mg, 0.22 mmol) in benzene (20 cm^3) was treated under stirring with P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) at room temperature. The yellow solution was warmed at 80 °C for 2 h and then cooled to room temperature. After the solvent and the volatiles were evaporated *in vacuo*, a red oil remained which was repeatedly recrystallized from pentane at −78 °C. The less soluble fraction (being compound **3**) consisted of orange–red crystals which were separated from the mother-liquor, washed with small amounts of pentane (−20 °C) and dried: yield 163 mg (58%); mp 112 °C (decomp.) (Found: C, 46.01; H, 7.75. $C_{24}H_{48}ClIrP_2$ requires C, 46.03; H, 7.73%). MS (70 eV): *m*/*z* 626 (M$^+$). IR (KBr): *ν*(CH_{ar}) 3065, (IrH) 2275 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.30, 6.83 (5 H, both m, C_6H_5), 2.53 (6 H, m, PC*H*CH$_3$), 1.19, 1.06 [18 H each, dvt, $N = 13.3$, $J(H,H) = 6.9$ Hz, PCHC*H*$_3$], −32.23 [1 H, t, $J(P,H) = 12.5$ Hz, IrH]; δ_C (100.6 MHz) 147.2 (s, d in off-resonance, *ipso*-C of C_6H_5), 136.7, 128.9, 124.9, 121.1, 117.7 (all s, d in off-resonance, C_6H_5), 24.3 (vt, $N = 27.8$ Hz, P*C*HCH$_3$), 20.0, 19.6 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 28.2 (s, d in off-resonance). The mother-liquor was slowly concentrated *in vacuo* until yellow crystals of compound **2** precipitated. The crystals were filtered off, washed with small amounts of pentane (−20 °C) and dried. They were characterized by comparing the IR and NMR spectroscopic data with those of an authentic sample:[6] yield 72 mg (29%).

[IrD(C_6D_5)(Cl)(P*i*Pr$_3$)$_2$] 3a. This compound was prepared analogously as described for **3**, from **1** (100 mg, 0.11 mmol) and P*i*Pr$_3$ (0.10 cm^3, 0.50 mmol) in C_6D_6 (2 cm^3). The time of the reaction was 6 h; the by-product **2** was separated as described above. **3a** is an orange–red microcrystalline solid: yield 80 mg (56%). MS (70 eV): *m*/*z* 632 (M$^+$). IR (KBr): *ν*(CD_{ar}) 2190, *ν*(IrD) 1630 cm^{-1}.

[IrH$_2$(Cl)(CO)(P*i*Pr$_3$)$_2$] 4 and [IrH(C_6H_5)(Cl)(CO)(P*i*Pr$_3$)$_2$] 5. A slow stream of CO was passed for *ca.* 10 s through a solution of a mixture of **2** and **3**, generated from **1** (200 mg, 0.22 mmol) and P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) in pentane (10 cm^3). A pale yellow solid precipitated, which was filtered off and washed three times with cold methanol (10 cm^3, 0 °C). The filtrate was concentrated *in vacuo* to *ca.* 2 cm^3 and stored for 12 h at −78 °C. Pale yellow, slightly air-sensitive crystals consisting of compound **4** precipitated, which were repeatedly washed with pentane (0° C) and dried. The yellow solid remaining on the fritted disk (being compound **5**) was also washed with pentane (0 °C) and dried. Yield for both **4** and **5** quantitative with respect to the amount of **2** and **3** obtained from **1**. Data for **5**: mp 187 °C (decomp.) (Found: C, 45.71; H, 7.64. $C_{25}H_{48}ClIrOP_2$ requires C, 45.90; H, 7.40%). MS (70 eV): *m*/*z* 654 (M$^+$), 618 (M$^+$ − HCl). IR (KBr): *ν*(CH_{ar}) 3065, *ν*(IrH) 2140, (CO) 1955 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.74, 6.81 (5 H, both m, C_6H_5), 2.30 (6 H, m, PC*H*CH$_3$), 1.20, 1.14 [18 H each, dvt, $N = 13.9$, $J(H,H) = 7.0$ Hz, PCHC*H*$_3$], −7.29 [1 H, t, $J(P,H) = 17.5$ Hz, IrH]; δ_P (36.2 MHz) 13.4 (s, d in off-resonance). Data for **4**: mp 185 °C (decomp.) (Found: C, 39.22; H, 7.85. $C_{19}H_{44}ClIrOP_2$ requires C, 39.47; H, 7.67%). MS (70 eV): *m*/*z* 578 (M$^+$), 576 (M$^+$ − H_2). IR (KBr): (IrH) 2205, 2100, *ν*(CO) 1965 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 3.37 (6 H, m, PC*H*CH$_3$), 1.30, 1.25 [18 H each, dvt, $N = 14.0$, $J(H,H) = 7.1$ Hz, PCHC*H*$_3$], −8.64 [1 H, dt, $J(P,H) = 17.5$, $J(H,H) = 5.5$ Hz, IrH *trans* to CO], −20.20 [1 H, dt, $J(P,H) = 13.2$, $J(H,H) = 5.5$ Hz, IrH *trans* to Cl]; δ_P (36.2 MHz) 32.9 (s, d in off-resonance).

[IrD(C_6D_5)(Cl)(CO)(P*i*Pr$_3$)$_2$] 5a. This compound was prepared analogously as described for **5**, from the mixture of **3a** and **2** and CO (2 cm^3). The by-product **4** was separated as described above. **5a** is a yellow solid. MS (70 eV): *m*/*z* 660 (M$^+$), 623 (M$^+$ − DCl). IR (KBr): (CD_{ar}) 2115, *ν*(CO) 2000, *ν*(IrD) 1530 cm^{-1}.

Alternative method for the preparation of compound 5

A suspension of **1** (150 mg, 0.17 mmol) in toluene (5 cm^3) was treated under stirring stepwise with P*i*Pr$_3$ (0.15 cm^3, 0.75 mmol) and benzaldehyde (0.035 cm^3, 0.34 mmol). After the mixture was stirred for 18 h at room temperature, the solvent and the volatiles were evaporated *in vacuo*. The oily residue was dissolved in hexane–toluene (10 : 1, 3 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, length of column 6 cm). With hexane–toluene (10 : 1) a yellow fraction was eluted which was brought to dryness *in vacuo*. The remaining yellow microcrystalline solid was characterized spectroscopically as compound **5**. Yield 175 mg (80%).

Thermal reaction of compound 5

A suspension of **5** (51 mg, 0.08 mmol) in diethylene glycol (2 cm^3) was stirred for 90 min at 150 °C. After the reaction mixture was cooled to room temperature, the yellow solution was chromatographed on Al_2O_3 (neutral, activity grade I, length of column 5 cm). With diethylene glycol, a nearly colorless fraction was eluted which was analyzed by GC. The presence of benzene could be detected and confirmed by comparing the retention time with that of an pure sample. Continuing elution with chloroform afforded a yellow fraction from which **6** was isolated and characterized by IR and NMR spectroscopy.[32] Yield 42 mg (90%).

General procedure for the preparation of compounds [IrH(C_6H_3RR')(Cl)(P*i*Pr$_3$)$_2$] 7–13

A suspension of **1** (200 mg, 0.22 mmol) in toluene (5 cm^3) was treated under stirring with P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) and 2.5 cm^3 of the corresponding arene. The yellow solution was warmed at 80 °C for 90 min and then cooled to room temperature. After the solvent and the volatiles were evaporated *in vacuo*, the oily residue was dissolved in hexane–toluene (9 : 1, 3 cm^3) and the solution chromatographed on Kieselgel 60. With hexane–benzene (10 : 1) first a pale yellow fraction containing the dihydrido complex **4** was eluted. Continuous elution gave an orange or red fraction which was brought to dryness *in vacuo*. Recrystallization from pentane at −78 °C gave orange–red to red crystals which were washed several times with 2-cm^3 portions of pentane (0 °C) and dried. For **7**, an orange–red oil was obtained.

[IrH(C_6H_4F)(Cl)(P*i*Pr$_3$)$_2$] 7. MS (70 eV): *m*/*z* 644 (M^+), 548 ($M^+ - C_6H_5F$). NMR ($CDCl_3$): δ_H (200 MHz) 7.65, 6.97–6.38 (4 H, br m, C_6H_4), 2.51 (6 H, m, PC*H*CH$_3$), 1.18 (36 H, m, PCHC*H*$_3$), −43.46 [dt, *J*(P,H) = 12.2, *J*(F,H) = 6.7 Hz, IrH for isomer **7a**], −35.92 [t, *J*(P,H) = 12.2 Hz, IrH for isomer **7b**], −35.08 [t, *J*(P,H) = 12.2 Hz, IrH for isomer **7c**]; δ_C (50.3 MHz), data for **7a**: 166.0 [d, *J*(F,C) = 219.1 Hz, C^2F of C_6H_4F], 145.8 [d, *J*(F,C) = 12.0 Hz, C^6 of C_6H_4F], 124.1 (s, C^5 of C_6H_4F), 121.8 [d, *J*(F,C) = 7.9 Hz, C^4 of C_6H_4F], 112.3 [d, *J*(F,C) = 27.2 Hz, C^3 of C_6H_4F], 23.5 (vt, *N* = 27.1 Hz, P*C*HCH$_3$), 19.6, 19.4 (both s, PCH*C*H$_3$), signal for C^1 of C_6H_4F not exactly located; data for **7b**: 166.5 [d, *J*(F,C) = 229.6 Hz, C^6F of C_6H_4F], 137.5 [d, *J*(F,C) = 12.7 Hz, C^2 of C_6H_4F], 122.1 [d, *J*(F,C) = 7.9 Hz, C^4 of C_6H_4F], 120.7 (s, C^3 of C_6H_4F), 113.2 [d, *J*(F,C) = 30.0 Hz, C^5 of C_6H_4F], 24.2 (vt, *N* = 26.2 Hz, P*C*HCH$_3$), 19.5, 19.3 (both s, PCH*C*H$_3$), signal for C^1 of C_6H_4F not exactly located; δ_P (36.2 MHz) 30.6 (s, d in off-resonance, for isomer **7a**), 31.7 (s, d in off-resonance, for isomer **7b**), 29.9 (s, d in off-resonance, for isomer **7c**); δ_F (84.7 MHz) −26.0 (m, for isomer **7a**), −18.9 (m, for isomer **7b**).

[IrH(C_6H_4Cl)(Cl)(P*i*Pr$_3$)$_2$] 8. Yield 146 mg (50%); mp 103 °C (decomp.) (Found: C, 43.19; H, 7.45. $C_{24}H_{47}Cl_2IrP_2$ requires C, 43.63; H, 7.17%). MS (70 eV): *m*/*z* 660 (M^+), 548 ($M^+ - C_6H_5Cl$). NMR ($CDCl_3$): δ_H (90 MHz) 7.39, 6.83 −6.33 (4 H, br m, C_6H_4), 2.64 (6 H, m, PC*H*CH$_3$), 1.29 [36 H, dvt, *N* = 13.5, *J*(H,H) = 6.0 Hz, PCHC*H*$_3$], −35.17 [t, *J*(P,H) = 12.5 Hz, IrH for isomer **8a**], −34.41 [t, *J*(P,H) = 13.0 Hz, IrH for isomer **8b**]; δ_P (36.2 MHz) 30.0 (s, d in off-resonance).

[IrH($C_6H_3F_2$-2,3)(Cl)(P*i*Pr$_3$)$_2$] 9. Yield 204 mg (70%); mp 121 °C (decomp.) (Found: C, 43.70; H, 7.37. $C_{24}H_{46}ClF_2IrP_2$ requires C, 43.52; H, 7.00%). MS (70 eV): *m*/*z* 662 (M^+), 548 ($M^+ - C_6H_4F_2$). NMR ($CDCl_3$): δ_H (200 MHz) 7.50 −6.95, 6.74 −6.33 (3 H, both br m, C_6H_3), 2.61 (6 H, m, PC*H*CH$_3$), 1.22 [36 H, dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], −43.75 [dt, *J*(P,H) = 12.5, *J*(F,H) = 7.0 Hz, IrH for isomer **9a**], −36.58 [t, *J*(P,H) = 12.0 Hz, IrH for isomer **9b**]; δ_C (50.3 MHz), data for **9a**: 140.9 [d, *J*(F,C) = 10.5 Hz, C^6 of $C_6H_3F_2$], 124.2 (br s, C^5 of $C_6H_3F_2$), 108.9 [d, *J*(F,C) = 13.0 Hz, C^4 of $C_6H_3F_2$], 23.8 (vt, *N* = 27.4 Hz, P*C*HCH$_3$), 19.8, 19.5 (both s, PCH*C*H$_3$), signals for C^1, C^2 and C^3 of $C_6H_3F_2$ not exactly located; data for **9b**: 132.4 [d, *J*(F,C) = 11.1 Hz, C^2 of $C_6H_3F_2$], 120.6 [d, *J*(F,C) = 7.1 Hz, C^3 of $C_6H_3F_2$], 109.2 [d, *J*(F,C) = 13.0 Hz, C^4 of $C_6H_3F_2$], 24.5 (vt, *N* = 27.1 Hz, P*C*HCH$_3$), 19.7, 19.2 (both s, PCH*C*H$_3$), signals for C^1, C^5 and C^6 of $C_6H_3F_2$ not exactly located; δ_P (36.2 MHz) 30.8 (s, d in off-resonance, for isomer **9a**), 31.7 (s, d in off-resonance, for isomer **9b**); δ_F (84.7 MHz) −51.8, −44.7 (both m, for isomer **9a**), −51.5, −44.3 (both m, for isomer **9b**).

[IrH($C_6H_3F_2$-2,4)(Cl)(P*i*Pr$_3$)$_2$] 10. Yield 210 mg (72%); mp 136 °C (decomp.) (Found: C, 43.60; H, 7.40. $C_{24}H_{46}ClF_2IrP_2$ requires C, 43.52; H, 7.00%). MS (70 eV): *m*/*z* 662 (M^+), 548 ($M^+ - C_6H_4F_2$). NMR (C_6D_6): δ_H (90 MHz) 7.22–6.92, 6.63–6.22 (3 H, both br m, C_6H_3), 2.51 (6 H, m, PC*H*CH$_3$), 1.16 (36 H, m, PCHC*H*$_3$), −43.20 [dt, *J*(P,H) = 13.0, *J*(F,H) = 6.7 Hz, IrH for isomer **10a**], −36.03 [t, *J*(P,H) = 13.0 Hz, IrH for isomer **10b**]; δ_P (36.2 MHz) 30.9 (s, d in off-resonance, for isomer **10a**), 30.0 (s, d in off-resonance, for isomer **10b**); δ_F (84.7 MHz) −56.3, −19.6 (both m, for isomer **10a**), −49.8, −19.5 (both m, for isomer **10b**).

[IrH($C_6H_3F_2$-2,5)(Cl)(P*i*Pr$_3$)$_2$] 11. Yield 184 mg (62%); mp 117 °C (decomp.) (Found: C, 43.20; H, 7.31. $C_{24}H_{46}ClF_2IrP_2$ requires C, 43.52; H, 7.00%). MS (70 eV): *m*/*z* 662 (M^+), 548 ($M^+ - C_6H_4F_2$). NMR ($CDCl_3$): δ_H (200 MHz) 7.55–7.23, 6.86–6.33 (3 H, both br m, C_6H_3), 2.59 (6 H, m, PC*H*CH$_3$), 1.23 [36 H, dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], −43.83 [dt, *J*(P,H) = 12.5, *J*(F,H) = 8.0 Hz, IrH for isomer **11a**], −36.92 [t, *J*(P,H) = 12.0 Hz, IrH for isomer **11b**]; δ_C (50.3 MHz), data for **11a**: 162.5 [dd, ^1J(F,C) = 214.2, ^5J(F,C) = 3 Hz, C^2 of $C_6H_3F_2$], 159.0 [dd, ^1J(F,C) = 241.1, ^5J(F,C) = 3 Hz, C^5 of $C_6H_3F_2$], 131.1 [dd, ^2J(F,C) = 20.1, ^3J(F,C) = 12.8 Hz, C^4 of $C_6H_3F_2$], 115.0 [ddt, ^2J(F,C) = 41.2, ^3J(F,C) = 5.5, *J*(P,C) = 7.3 Hz, C^1 of $C_6H_3F_2$], 112.2 [dd, ^2J(F,C) = 30.5, ^3J(F,C) = 9.2 Hz, C^6 of $C_6H_3F_2$], 107.5 [dd, ^2J(F,C) = 24.4, ^3J(F,C) = 9.5 Hz, C^3 of $C_6H_3F_2$], 23.6 (vt, *N* = 26.9 Hz, P*C*HCH$_3$), 19.6, 19.1 (both s, PCH*C*H$_3$); data for **11b**: 163.6 [dd, ^1J(F,C) = 215.0, ^5J(F,C) = 3 Hz, C^6 of $C_6H_3F_2$], 155.8 [dd, ^1J(F,C) = 241.0, ^5J(F,C) = 3 Hz, C^3 of $C_6H_3F_2$], 131.1 [dd, ^2J(F,C) = 20.1, ^3J(F,C) = 12.8 Hz, C^4 of $C_6H_3F_2$], 113.4 [dd, ^2J(F,C) = 33.6, ^3J(F,C) = 9.7 Hz, C^2 of $C_6H_3F_2$], 112 (m, C^1 of $C_6H_3F_2$), 107.9 [dd, ^2J(F,C) = 24.4, ^3J(F,C) = 10.4 Hz, C^5 of $C_6H_3F_2$], 24.3 (vt, *N* = 28.1 Hz, P*C*HCH$_3$), 19.4, 19.0 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 31.7 (s, d in off-resonance, for isomer **11a**), 30.9 (s, d in off-resonance, for isomer **11b**); δ_F (84.7 MHz) −53.4, −33.7 (both m, for isomer **11a**), −51.8, −24.9 (both m, for isomer **11b**).

[IrH(C_6H_3F(CH_3)-2,3)(Cl)(P*i*Pr$_3$)$_2$] 12. Yield 182 mg (63%); mp 115 °C (decomp.). MS (70 eV): *m*/*z* 658 (M^+), 548 ($M^+ - C_7H_7F$). NMR (C_6D_6): δ_H (90 MHz) 7.15–6.58 (3 H, br m, C_6H_3), 2.55 (6 H, m, PC*H*CH$_3$), 2.21 (3 H, s, C_6H_3C*H*$_3$), 1.16 (36 H, m, PCHC*H*$_3$), −42.92 [dt, *J*(P,H) = 13.2, *J*(F,H) = 8.8 Hz, IrH

for isomer **12a**], −35.22 [t, J(P,H) = 13.2 Hz, IrH for isomer **12b**], −33.41 [t, J(P,H) = 13.2 Hz, IrH for isomer **12c**]; δ_P (36.2 MHz) 30.8 (s, d in off-resonance, for isomer **12a**), 29.8 (s, d in off-resonance, for isomer **12b**), 29.3 (s, d in off-resonance, for isomer **12c**); δ_F (84.7 MHz) −49.8 (m, for isomer **12a**), −41.3 (m, for isomer **12b**).

[IrH($C_6H_3F(CH_3)$-2,5)(Cl)(P*i*Pr$_3$)$_2$] 13. Yield 174 mg (60%); mp 118 °C (decomp.) (Found: C, 45.73; H, 7.83. $C_{25}H_{49}ClFIrP_2$ requires C, 45.61; H, 7.50%). MS (70 eV): m/z 658 (M^+), 548 ($M^+ - C_7H_7F$). NMR ($CDCl_3$): δ_H (90 MHz) 7.26–7.06, 6.67–6.57 (3 H, both br m, C_6H_3), 2.50 (6 H, m, PC*H*CH$_3$), 2.18 (3 H, br s, $C_6H_3CH_3$), 1.18 (36 H, m, PCHC*H*$_3$), −43.08 [dt, J(P,H) = 13.0, J(F,H) = 7.5 Hz, IrH for isomer **13a**], −34.92 [t, J(P,H) = 13.0 Hz, IrH for isomer **13b**]; δ_C (50.3 MHz), data for **13a**: 166.5 [d, ^1J(F,C) = 246.5 Hz, C^2 of $C_6H_3F(CH_3)$], 146.8 [d, ^3J(F,C) = 12.2 Hz, C^6 of $C_6H_3F(CH_3)$], 132.6 [s, C^5 of $C_6H_3F(CH_3)$], 122.6 [d, ^3J(F,C) = 8.5 Hz, C^4 of $C_6H_3F(CH_3)$], 112.9 [d, ^2J(F,C) = 23.2 Hz, C^3 of $C_6H_3F(CH_3)$], 107.3 [d, ^2J(F,C) = 33.5 Hz, C^1 of $C_6H_3F(CH_3)$], 23.7 (vt, N = 26.8 Hz, P*C*HCH$_3$), 20.5 [d, ^5J(F,C) = 3.0 Hz, $C_6H_3CH_3$], 19.8, 19.2 (both s, PCH*C*H$_3$); data for **13b**: 165.8 [d, ^1J(F,C) = 234.2 Hz, C^6 of $C_6H_3F(CH_3)$], 137.9 [d, ^3J(F,C) = 12.8 Hz, C^2 of $C_6H_3F(CH_3)$], 129.4 [s, C^3 of $C_6H_3F(CH_3)$], 122.3 [d, ^3J(F,C) = 9.2 Hz, C^4 of $C_6H_3F(CH_3)$], 111.6 [dt, ^2J(F,C) = 31.9, ^2J(P,C) = 7.9 Hz, C^1 of $C_6H_3F(CH_3)$], 111.5 [d, ^2J(F,C) = 20.1 Hz, C^5 of $C_6H_3F(CH_3)$], 24.3 (vt, N = 26.8 Hz, P*C*HCH$_3$), 20.5 [d, ^5J(F,C) = 3.0 Hz, $C_6H_3CH_3$], 19.6, 19.1 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 31.1 (s, d in off-resonance, for isomer **13a**), 29.9 (s, d in off-resonance, for isomer **13b**); δ_F (84.7 MHz) −47.1 (m, for isomer **13a**), −41.4 (m, for isomer **13b**).

General procedure for the preparation of compounds [IrH(C_6H_3RR')(Cl)(CO)(P*i*Pr$_3$)$_2$] 14–20

A slow stream of CO was passed for 10 s through the solution generated from **1** (90 mg, 0.10 mmol), P*i*Pr$_3$ (0.10 cm^3, 0.50 mmol) and 1.2 cm^3 of C_6H_4RR' in toluene (5 cm^3). The yellow solution was warmed at 80 °C for 90 min and then cooled to room temperature. After the reaction mixture was stirred for 5 min, the solvent and the volatiles were evaporated *in vacuo* and methanol (3 cm^3) was added to the residue. A suspension containing a pale yellow solid was obtained. The solid was filtered off, washed three times with small amounts of methanol (0 °C) and dried *in vacuo*. The filtrate contained the dihydrido complex **4** which is readily soluble in methanol.

[IrH(C_6H_4F)(Cl)(CO)(P*i*Pr$_3$)$_2$] 14. Yield 94 mg (70%); mp 177 °C (Found: C, 44.92; H, 7.36. $C_{25}H_{47}ClFIrOP_2$ requires C, 44.67; H, 7.05%). MS (70 eV): m/z 672 (M^+), 636 (M^+ − HCl), 576 ($M^+ - C_6H_5F$). IR (KBr): ν(IrH) 2275, (CO) 1985 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.57, 6.75, 6.64, 6.45 (4 H, all m, C_6H_4), 2.32 (6 H, m, PC*H*CH$_3$), 1.25 (36 H, m, PCHC*H*$_3$), −8.11 [dt, J(P,H) = 17.7, J(F,H) = 2.6 Hz, IrH]; δ_P (36.2 MHz) 13.0 (s, d in off-resonance); δ_F (84.7 MHz) −8.1 (m, for isomer **14a**), −4.1 (m, for isomer **14b**).

[IrH(C_6H_4Cl)(Cl)(CO)(P*i*Pr$_3$)$_2$] 15. Yield 82 mg (60%); mp 193 °C (Found: C, 43.45; H, 6.80. $C_{25}H_{47}Cl_2IrOP_2$ requires C, 43.60; H, 6.88%). MS (70 eV): m/z 688 (M^+), 652 (M^+ − HCl), 576 ($M^+ - C_6H_5Cl$). IR (KBr): ν(IrH) 2120, ν(CO) 1980 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.65–7.17, 6.87–6.56 (4 H, both br m, C_6H_4), 2.39 (6 H, m, PC*H*CH$_3$), 1.33 [36 H, dvt, N = 22.0, J(H,H) = 6.0 Hz, PCHC*H*$_3$], −7.63 [t, J(P,H) = 17.6 Hz, IrH]; δ_P (36.2 MHz) 13.9 (s, d in off-resonance).

[IrH($C_6H_3F_2$-2,3)(Cl)(CO)(P*i*Pr$_3$)$_2$] 16. Yield 104 mg (75%); mp 230 °C (Found: C, 43.01; H, 7.12. $C_{25}H_{46}ClF_2IrOP_2$ requires C, 43.40; H, 6.71%). MS (70 eV): m/z 690 (M^+), 654 (M^+ − HCl), 576 ($M^+ - C_6H_4F_2$). IR (KBr): ν(IrH) 2140, ν(CO) 2000 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.24–7.03, 6.52–6.21 (3 H, both br m, C_6H_3), 2.34 (6 H, m, PC*H*CH$_3$), 1.32 [36 H, dvt, N = 18.5, J(H,H) = 6.0 Hz, PCHC*H*$_3$], −8.27 [dt, J(P,H) = 18.0, J(F,H) = 2.9 Hz, IrH for isomer **16a**], −7.41 [t, J(P,H) = 17.0 Hz, IrH for isomer **16b**]; δ_P (36.2 MHz) 12.0 (s, d in off-resonance); δ_F (84.7 MHz) −40.1, −3.1 (both m, for isomer **16a**), −36.2, −2.6 (both m, for isomer **16b**).

[IrH($C_6H_3F_2$-2,4)(Cl)(CO)(P*i*Pr$_3$)$_2$] 17. Yield 98 mg (71%); mp 189 °C (Found: C, 44.06; H, 7.04. $C_{25}H_{46}ClF_2IrOP_2$ requires C, 43.40; H, 6.71%). MS (70 eV): m/z 690 (M^+), 654 (M^+ − HCl), 576 ($M^+ - C_6H_4F_2$). IR (KBr): ν(IrH) 2140, (CO) 2000 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.82–7.43, 6.52–6.18 (3 H, both br m, C_6H_3), 2.23 (6 H, m, PC*H*CH$_3$), 1.15 (36 H, m, PCHC*H*$_3$), −8.09 [dt, J(P,H) = 17.6, J(F,H) = 2.9 Hz, IrH for isomer **17a**], −7.48 [t, J(P,H) = 16.1 Hz, IrH for isomer **17b**]; δ_P (36.2 MHz) 11.8 (s, d in off-resonance); δ_F (84.7 MHz) −72.1, −27.3 (both m, for isomer **17a**), −67.7, −22.0 (both m, for isomer **17b**).

[IrH($C_6H_3F_2$-2,5)(Cl)(CO)(P*i*Pr$_3$)$_2$] 18. Yield 110 mg (80%); mp 178 °C (Found: C, 43.48; H, 6.93. $C_{25}H_{46}ClF_2IrOP_2$ requires C, 43.40; H, 6.71%). MS (70 eV): m/z 690 (M^+), 654 (M^+ − HCl), 576 ($M^+ - C_6H_4F_2$). IR (KBr): ν(IrH) 2140, (CO) 2005 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.50–6.95, 6.73–6.27 (3 H, both br m, C_6H_3), 2.37 (6 H, m, PC*H*CH$_3$), 1.28 (36 H, PCHC*H*$_3$), −8.30 [dt, J(P,H) = 17.2, J(F,H) = 2.0 Hz, IrH for isomer **18a**], −7.65 [t, J(P,H) = 16.0 Hz, IrH for isomer **18b**]; δ_P (36.2 MHz) 13.0 (s, d in off-resonance); δ_F (84.7 MHz) −53.9, −33.4 (both m).

[IrH($C_6H_3F(CH_3)$-2,3)(Cl)(CO)(P*i*Pr$_3$)$_2$] 19. Yield 94 mg (69%); mp 187 °C (Found: C, 45.61; H, 7.42. $C_{26}H_{49}ClFIrOP_2$ requires C, 45.50; H, 7.19%). MS (70 eV): m/z 686 (M^+), 650 (M^+ − HCl), 576 ($M^+ - C_7H_7F$). IR (KBr): ν(IrH) 2130, (CO) 2000, 1985 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.65–7.25, 6.70–6.30 (3 H, both br m, C_6H_3), 2.28 (6 H, m, PC*H*CH$_3$), 2.18 (3 H, s, $C_6H_3CH_3$), 1.15 [36 H, dvt, N = 16.1, J(H,H) = 7.3 Hz, PCHC*H*$_3$], −8.22 [t, J(P,H) = 19.1 Hz, IrH for isomer **19a**], −7.35 [t, J(P,H) = 17.6 Hz, IrH for isomer **19b**]; δ_P (36.2 MHz) 12.0 (s, d in off-resonance); δ_F (84.7 MHz) −65.0 (m, for isomer **19a**), −61.3 (m, for isomer **19b**).

[IrH($C_6H_3F(CH_3)$-2,5)(Cl)(CO)(P*i*Pr$_3$)$_2$] 20. Yield 104 mg (75%); mp 188 °C (Found: C, 45.91; H, 7.54. $C_{26}H_{49}ClFIrOP_2$ requires C, 45.50; H, 7.19%). MS (70 eV): m/z 686 (M^+), 650 (M^+ − HCl), 576 ($M^+ - C_7H_7F$). IR (KBr): ν(IrH) 2125, (CO) 2000, 1990 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.45–7.20, 6.95–6.30 (3 H, both br m, C_6H_3), 2.33 (6 H, m, PC*H*CH$_3$), 2.11 (3 H, s, $C_6H_3CH_3$), 1.25, 1.17 [36 H, both dvt, N = 14,7, J(H,H) = 7.3 Hz, PCHC*H*$_3$], −7.96 [dt, J(P,H) = 17.6, J(F,H) = 2.9 Hz, IrH for isomer **20a**], −7.11 [t, J(P,H) = 17.6 Hz, IrH for isomer **20b**]; δ_P (36.2 MHz) 12.1 (s, d in off-resonance, for isomer **20a**), 12.3 (s, d in off-resonance, for isomer **20b**); δ_F (84.7 MHz) −62.4 (m, for isomer **20a**), −58.3 (m, for isomer **20b**).

[IrH{κ²-*C*,*O*-$C_6H_4C(O)Me$}(Cl)(P*i*Pr$_3$)$_2$] 21. This compound was prepared analogously as described for **3**, from **1** (150 mg, 0.17 mmol) and P*i*Pr$_3$ (0.15 cm^3, 0.75 mmol) in acetophenone (3 cm^3, 24.0 mmol). The oily residue, obtained after evaporation of the volatiles, was dissolved in hexane–benzene (15 : 1, 3 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, length of column 6 cm). With hexane–benzene (15 : 1) an orange fraction was eluted which was brought to dryness *in vacuo*. The remaining orange microcrystalline solid was washed several times with 3-cm^3 portions of hexane (0 °C) and dried: yield 201 mg (90%); mp 180 °C (decomp.) (Found: C, 46.26; H, 7.77. $C_{26}H_{50}ClIrOP_2$ requires C, 46.72; H, 7.54%). MS (70 eV): *m*/*z* 668 (M$^+$), 548 (M$^+$ − PhC(O)Me). IR (KBr): *ν*(IrH) 2235, *ν*(C=O) 1580 cm^{-1}. NMR ($CDCl_3$): δ_H (90 MHz) 7.79, 7.26, 6.77 (4 H, all m, C_6H_4), 2.40 (6 H, m, PC*H*CH_3), 2.38 (3 H, s, $C_6H_4CH_3$), 1.23, 0.99 [18 H each, dvt, *N* = 13.2, *J*(H,H) = 7.2 Hz, PCHC*H*$_3$], −25.07 [1 H, t, *J*(P,H) = 16.2 Hz, IrH]; δ_C (50.3 MHz) 211.9 (s, *C*(O)CH_3), 162.8 (t, *J*(P,C) = 6.6 Hz, *ipso*-C of C_6H_4), 145.1, 141.5, 133.5, 130.8, 118.9 (all s, C_6H_4), 24.2 (s, $C_6H_4CH_3$), 23.5 (vt, *N* = 27.1 Hz, P*C*HCH_3), 19.3, 18.6 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 12.0 (s, d in off-resonance).

[IrH{κ²-*C*,*O*-$C_6H_4C(O)Ph$}(Cl)(P*i*Pr$_3$)$_2$] 22. This compound was prepared analogously as described for **3**, from **1** (200 mg, 0.22 mmol), P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) and benzophenone (450 mg, 2.50 mmol) in toluene (3 cm^3). The oily residue, obtained after evaporation of the volatiles, was dissolved in hexane–toluene (10 : 1, 3 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, length of column 6 cm). With hexane–toluene (10 : 1) first a yellow fraction was eluted which contained the dihydride **2** (49 mg, 20%). Continuing elution gave an orange fraction which was brought to dryness *in vacuo*. The remaining orange microcrystalline solid was washed several times with 3-cm^3 portions of hexane (0 °C) and dried: yield 65 mg (20%); mp 211 °C (decomp.) (Found: C, 51.57; H, 7.68. $C_{31}H_{52}ClIrOP_2$ requires C, 50.98; H, 7.18%). MS (70 eV): *m*/*z* 730 (M$^+$), 548 (M$^+$ − PhC(O)Ph). IR (KBr): *ν*(IrH) 2270, *ν*(C=O) 1545 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 7.98–6.59 (9 H, br m, C_6H_4 and C_6H_5), 2.46 (6 H, m, PC*H*CH_3), 1.24, 1.03 [18 H each, dvt, *N* = 13.9, *J*(H,H) = 7.4 Hz, PCHC*H*$_3$], −24.34 [1 H, t, *J*(P,H) = 16.0 Hz, IrH]; δ_P (36.2 MHz) 12.3 (s, d in off-resonance).

[IrH{κ²-*C*,*N*-$C_6H_4C(NOH)Ph$}(Cl)(P*i*Pr$_3$)$_2$] 23. A suspension of **1** (200 mg, 0.22 mmol) in toluene (5 cm^3) was treated under stirring with P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) at room temperature. An orange solution was formed to which benzophenoneoxime (85 mg, 0.44 mmol) was added. The reaction mixture was stirred for 30 min at room temperature and the volatiles were evaporated *in vacuo*. The oily residue was layered with pentane (1 cm^3) and the solution stored for 6 h. Light yellow crystals precipitated which were separated from the mother-liquor, washed with small amounts of pentane (−20 °C) and dried: yield 296 mg (89%); mp 209 °C (Found: C, 50.20; H, 7.39, N, 1.87. $C_{31}H_{53}ClIrNOP_2$ requires C, 49.95; H, 7.17, N, 1.88%). MS (70 eV): *m*/*z* 745 (M$^+$), 585 (M$^+$ − P*i*Pr$_3$), 548 (M$^+$ − PhC(NOH)Ph). IR (KBr): (OH) 3080, (IrH) 2195 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 12.19 (1 H, s, OH), 7.75–6.71 (9 H, br m, C_6H_4 and C_6H_5), 2.52 (6 H, m, PC*H*CH_3), 1.27, 1.00 [18 H each, dvt, *N* = 13.2, *J*(H,H) = 7.3 Hz, PCHC*H*$_3$], −16.63 [1 H, t, *J*(P,H) = 18.4 Hz, IrH]; δ_P (36.2 MHz) 8.6 (s, d in off-resonance).

[IrH{κ²-*C*,*N*–$C_6H_4C(NOH)Me$}(Cl)(P*i*Pr$_3$)$_2$] 24. This compound was prepared analogously as described for **23**, from **1** (200 mg, 0.22 mmol), P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) and acetophenone oxime (60 mg, 0.44 mmol) in toluene (5 cm^3). A light yellow microcrystalline solid was obtained: yield 274 mg (90%); mp 222 °C (Found: C, 46.08; H, 7.84, N, 2.00. $C_{26}H_{51}ClIrNOP_2$ requires C, 45.70; H, 7.52, N, 2.05%). MS (70 eV): *m*/*z* 683 (M$^+$), 548 (M$^+$ − PhC(NOH)Me), 523 (M$^+$ − P*i*Pr$_3$). IR (KBr): *ν*(OH) 3115, (IrH) 2185 cm^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 11.06 (1 H, s, OH), 7.19, 6.97, 6.72 (4 H, all m, C_6H_4), 2.33 (3 H, t, *J*(P,H) = 1.4 Hz, C(NOH)C*H*$_3$), 2.29(6 H, m, PC*H*CH_3), 1.19, 0.85 [18 H each, dvt, *N* = 13.3, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], −17.25 [1 H, t, *J*(P,H) = 18.0 Hz, IrH]; δ_C (50.3 MHz) 161.6 (s, *C*(NOH)CH_3), 142.4 (t, *J*(P,C) = 6.7 Hz, *ipso*-C of C_6H_4), 142.7, 138.7, 128.6, 124.4, 119.6 (all s, C_6H_4), 23.7 (vt, *N* = 27.2 Hz, P*C*HCH_3), 18.9, 18.6 (both s, PCH*C*H$_3$), 11.4 (s, $C_6H_4CH_3$); δ_P (36.2 MHz) 8.6 (s, d in off-resonance).

[IrH{κ²-*C*,*N*-$C_6H_4C(NOH)H$}(Cl)(P*i*Pr$_3$)$_2$] 25. This compound was prepared analogously as described for **23**, from **1** (200 mg, 0.22 mmol), P*i*Pr$_3$ (0.20 cm^3, 1.00 mmol) and benzaloxime (53 mg, 0.44 mmol) in toluene (5 cm^3). A light yellow microcrystalline solid was obtained: yield 248 mg (83%); mp 167 °C (decomp.) (Found: C, 44.91; H, 7.54, N, 2.39. $C_{25}H_{49}ClIrNOP_2$ requires C, 44.87; H, 7.38, N, 2.10%). MS (70 eV): *m*/*z* 669 (M$^+$), 548 (M$^+$ − PhC(NOH)H), 509 (M$^+$ − P*i*Pr$_3$). IR (KBr): *ν*(OH) 3140, (IrH) 2180 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 11.89 (1 H, s, OH), 7.91 (1 H, br s, C(NOH)*H*), 7.49, 6.90 (4 H, both m, C_6H_4), 2.47 (6 H, m, PC*H*CH_3), 1.24, 0.92 [18 H each, dvt, *N* = 13.2, *J*(H,H) = 7.2 Hz, PCHC*H*$_3$], −17.11 [1 H, t, *J*(P,H) = 18.1 Hz, IrH]; δ_P (36.2 MHz) 8.7 (s, d in off-resonance).

[IrH{κ²-*N*,*O*-NHC(O)Ph}(Cl)(P*i*Pr$_3$)$_2$] 26. A suspension of **1** (180 mg, 0.20 mmol) in toluene (10 cm^3) was treated with P*i*Pr$_3$ (0.18 cm^3, 0.90 mmol) and benzoic acidamide (48 mg, 0.40 mmol) and irradiated in an ultrasonic bath for 30 min at room temperature. A yellow solid precipitated which was separated from the mother-liquor and recrystallized from hexane–CH_2Cl_2 (5 : 1): yield 241 mg (90%); mp 181 °C (decomp.) (Found: C, 44.52; H, 7.75, N, 1.99. $C_{25}H_{49}ClIrNOP_2$ requires C, 44.87; H, 7.38, N, 2.10%). MS (70 eV): *m*/*z* 669 (M$^+$), 548 (M$^+$ − PhC(O)NH$_2$). IR (KBr): *ν*(NH) 3325, (IrH) 2270, (C=O) 1525 cm^{-1}. NMR ($CDCl_3$): δ_H (90 MHz) 7.78–7.51 (5 H, br m, C_6H_5), 5.37 (1 H, br s, NH), 2.87 (6 H, m, PC*H*CH_3), 1.55, 1.51 [18 H each, dvt, *N* = 13.2, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], −31.54 [1 H, t, *J*(P,H) = 13.4 Hz, IrH]; δ_C (50.3 MHz) 176.9 (s, *C*(O)NH), 137.6 (s, *ipso*-C of C_6H_5), 129.6, 128.4, 125.7 (all s, C_6H_5), 22.5 (vt, *N* = 25.8 Hz, P*C*HCH_3), 19.0, 18.8 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 13.6 (s, d in off-resonance).

[IrH{κ²-*C*,*O*-$C_6H_4C(O)NH_2$}(Cl)(P*i*Pr$_3$)$_2$] 27. A suspension of **26** (160 mg, 0.24 mmol) in benzene (5 cm^3) was stirred for 48 h under reflux. After the solution was cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was recrystallized from hexane–CH_2Cl_2 (5 : 1) to give a light yellow microcrystalline solid: yield 136 mg (85%); mp 219 °C (decomp.) (Found: C, 44.94; H, 7.31, N, 2.39. $C_{25}H_{49}ClIrNOP_2$ requires C, 44.87; H, 7.38, N, 2.10%). IR (KBr): (NH) 3280, 3205, *ν*(IrH) 2250, *ν*(C=O)

1555 cm^{-1}. NMR (CD_2Cl_2): δ_H (90 MHz) 7.48–6.76 (4 H, br m, C_6H_4), 2.33 (6 H, m, PC*H*CH_3), 1.59 (1 H, br s, NH), 1.21, 1.01 [18 H each, dvt, $N = 13.2$, J(H,H) = 7.1 Hz, PCHC*H*$_3$], −26.32 [1 H, t, J(P,H) = 16.2 Hz, IrH]; δ_P (36.2 MHz) 11.7 (s, d in off-resonance).

[IrH{κ¹-NHC(O)Ph}(Cl)(CO)(P*i*Pr₃)₂] 28. A slow stream of CO was passed for *ca.* 2 min through a solution of **26** (95 mg, 0.14 mmol) in $CHCl_3$ (5 cm^3) at room temperature. The solvent was evaporated *in vacuo* and the residue recrystallized from hexane–CH_2Cl_2 (5 : 1) to give a white microcrystalline solid: yield 89 mg (94%); mp 190 °C (Found: C, 45.13; H, 6.97, N, 2.29. $C_{26}H_{49}ClIrNO_2P_2$ requires C, 44.78; H, 7.08, N, 2.00%). IR (KBr): ν(NH) 3410, ν(IrH) 2115, ν(CO) 2000, ν(C=O) 1615 cm^{-1}. NMR ($CDCl_3$): δ_H (90 MHz) 7.77–7.47 (5 H, br m, C_6H_5), 4.25 (1 H, br s, NH), 2.72 (6 H, m, PC*H*CH_3), 1.56 [36 H each, br dvt, N = 13.6, J(H,H) = 7.0 Hz, PCHC*H*$_3$], −8.78 [1 H, dt, J(P,H) = 15.4, J(H,H) = 2.0 Hz, IrH]; δ_P (36.2 MHz) 18.6 (s, d in off-resonance).

[IrH{κ²-*O*,*O*-O₂CPh}(Cl)(P*i*Pr₃)₂] 29. A suspension of **1** (210 mg, 0.23 mmol) in toluene (5 cm^3) was treated with P*i*Pr_3 (0.21 cm^3, 1.05 mmol) and benzoic acid (56 mg, 0.46 mmol) and stirred for 30 min at room temperature. The solvent was evaporated *in vacuo* and the oily residue was dissolved in hexane (2 cm^3). After the solution was stored for 12 h at −78 °C, a yellow microcrystalline solid precipitated which was separated from the mother-liquor, washed with small amounts of hexane (−20 °C) and dried: yield 273 mg (87%); mp 132 °C (Found: C, 44.77; H, 7.37. $C_{25}H_{48}ClIrO_2P_2$ requires C, 44.80; H, 7.22%). MS (70 eV): *m*/*z* 670 (M^+), 634 (M^+ − HCl), 548 (M^+ − $PhCO_2H$), 510 (M^+ − P*i*Pr_3). IR (KBr): ν(IrH) 2275, ν(C=O) 1530 cm^{-1}. NMR (CD_2Cl_2): δ_H (90 MHz) 8.37, 7.36 (5 H, both br m, C_6H_5), 2.88 (6 H, m, PC*H*CH_3), 1.63, 1.50 [18 H each, dvt, N = 13.4, J(H,H) = 6.7 Hz, PCHC*H*$_3$], −34.48 [1 H, t, J(P,H) = 12.5 Hz, IrH]; δ_P (36.2 MHz) 20.0 (s, d in off-resonance).

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