Stereochemical and Electronic Control of Functionalized Tripodal Phosphines. Reactivity of the Adamantane-Type Ir(tripod)(CO)Cl (tripod = *cis,cis*-1,3,5-$(PPh_2)_3$-1,3,5-$X_3C_6H_6$; X = H, COOMe, CN) Complexes toward H^+, H_2, CO, and C_2H_4[1]

Philipp Stössel, Wolfgang Heins, Hermann A. Mayer,*[,2] Riad Fawzi, and Manfred Steimann

Institut für Anorganische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received January 3, 1996[⊗]

Treatment of the tripodal phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (**2**) with $Ir(PPh_3)_2(CO)Cl$ gives the carbonyl chloro complex Ir(tdppcyme)(CO)Cl (**2a**). NMR spectroscopic investigations prove a dynamic equilibrium between a square-planar (**2a′**) and a trigonal-bipyramidal (**2a**) complex with two and three phosphine groups coordinated to iridium, respectively. This is in contrast to the comparable complexes Ir(tripod)(CO)Cl (**1a, 3a**) [tripod = *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy) (**1**), *cis,cis*-1,3,5-tricyano-*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcycn) (**3**)] which only exist in the trigonal-bipyramidal form. The three compounds Ir(tripod)(CO)Cl (**1a**−**3a**), which only differ in the functionalization of the ligand backbone, display altered basicity and thus different reaction patterns. The carbonyl chloro complexes **1a**−**3a** are readily protonated by the strong acid HBF_4 to give the octahedral cations **1b**−**3b**. The weaker acid NH_4PF_6 is only able to protonate the most basic complex Ir(tdppcy)(CO)Cl (**1a**). While Ir(tdppcycn)(CO)Cl (**3a**) shows no reaction in the presence of NH_4PF_6, **2a** is orthometalated to complex **2f′**. The compounds Ir(tdppcy)(CO)Cl (**1a**) and Ir(tdppcycn)(CO)Cl (**3a**) oxidatively add H_2 with dissociation of Cl^- to yield the octahedral dihydrides $[Ir(tripod)(CO)(H)_2]Cl$ (**1c′, 3c′**). Under the same conditions a phosphine arm dissociates from **2a** to form the dihydride Ir(η^2-tdppcyme)$(CO)(H)_2Cl$ (**2c′**). In a CO atmosphere the Ir(tripod)(CO)Cl (**1a**−**3a**) complexes give the dicarbonyl derivatives $[Ir(tripod)(CO)_2]Cl$ (**1d′**−**3d′**). The dicarbonyls **2d′** and **3d′** are in an equilibrium with their starting materials. Replacement of the Cl^- by BPh_4^- allows the isolation of all three dicarbonyl complexes. Treatment of **1a**−**3a** with ethylene in the presence of $NaBPh_4$ gives the ethylene complexes $[Ir(tripod)(CO)(C_2H_4)]BPh_4$ (**1e**−**3e**). Variable-temperature NMR studies show that there is an exchange process which equilibrates the equatorial with the apical phosphorus nuclei while the CO and ethylene ligands remain rigid. In the cases of **2e** and **3e** a second dynamic process with a low-energy barrier exists. Above 45 and 35 °C, respectively, **1e** and **2e** lose ethylene and are orthometalated to **1f** and **2f**. The cyclometalated products **1f** and **2f** can also be obtained by the direct reaction of **1a** and **2a** with $NaBPh_4$. For the dicarbonyl complex **3a** and the orthometalated product **2f** X-ray structure determinations have been performed.

Introduction

Polyphosphines are popular ligands for chemical control devices because their basicity and stereochemistry can be varied over a wide range.[3] Some remarkable chemical behavior can be developed from specially designed polypodal phosphine ligands which impose unusual coordination geometries on transition metal complexes. A result of this is the important role of polyphosphines in stoichiometric[4] and in catalytic[5] reactions.

In particular the interesting coordination chemistry of branched tripodal phosphine ligands which are based on the neopentyl backbone has attracted researchers for many years.[3a,b,6] In these ligand systems the stereoselective occupation of a triangular face of a coordination

---

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

[1] Dedicated to Prof. Marianne Baudler on the occasion of her 75th birthday.

[2] E-mail address: hermann.mayer@uni-tuebingen.de.

[3] (a) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183. (b) Sacconi, L.; Mani, F. *Transition Met. Chem.* **1982**, *8*, 179. (c) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179. (d) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239.

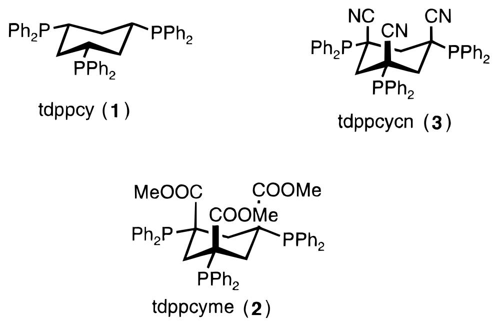
[4] (a) Bianchini, C.; Caulton, K. G.; Folting, K.; Meli, A.; Peruzzini, M.; Polo, A.; Vizza, F. *J. Am. Chem. Soc.* **1992**, *114*, 7290. (b) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505. (c) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010.

[5] (a) Meek, D. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 257. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Coord. Chem. Rev.* **1992**, *120*, 193.

[6] (a) Di Vaira, M.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330. (b) Janssen, B. C.; Sernau, V.; Huttner, G.; Asam, A.; Walter, O.; Büchner, M.; Zsolnai, L. *Chem. Ber.* **1995**, *128*, 63. (c) Heidel, H.; Scherer, J.; Asam, A.; Huttner, G.; Walter, O.; Zsolnai, L. *Chem. Ber.* **1995**, *128*, 293.

S0276-7333(96)00006-4 CCC: $12.00

Chart 1



tdppcy (**1**)

tdppcycn (**3**)

tdppcyme (**2**)

polyhedron allows assembly of the participating ligands exclusively in *cis*-positions.[7] This is a requirement for transformations of substrates in the coordination sphere of a metal center.[8]

The advantage of polypodal phosphine complexes over their monodentate counterparts has been outlined earlier.[3a] Thus the increased thermal stability of metal complexes stabilized by tripodal phosphine ligands has allowed the use of those phosphine complexes in catalytic processes which require drastic reaction conditions.[9]

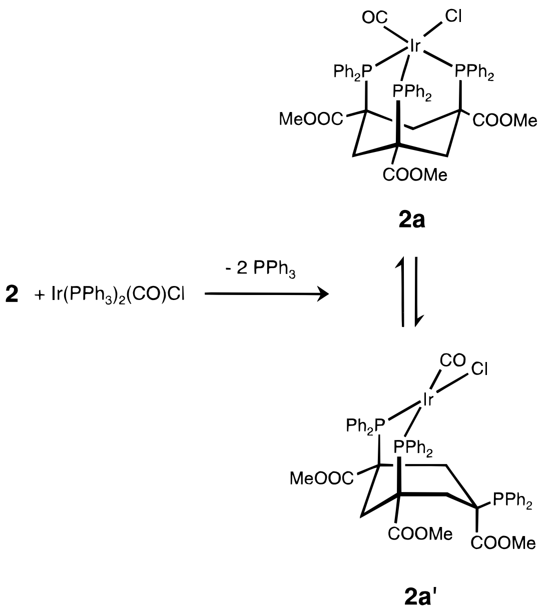
We have recently reported on the preparation of new tripodal phosphine ligands with three diphenylphosphine groups stereospecifically bound *cis,cis* to the 1,3,5 positions of the cyclohexane ring (Chart 1).[10] A consequence of the specific coordination behavior of these ligands is a metal template adamantane-type polyhedron with rigid stereochemistry and stoichiometry control of the resulting metal complexes. The opportunity to add other functional groups at the *ipso* positions of the cyclohexane ring[10b,c] offers the advantages of (i) improvement of the synthesis, (ii) control of the electron density at the metal center, (iii) control of the solubility, and (iv) use of the groups as spacers to support the metal complexes.[10c]

Here we wish to report on the reactivity of the adamantane-type complexes Ir(tripod)(CO)Cl [tripod = *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy) (**1**), *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (**2**), and *cis,cis*-1,3,5-tricyano-*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcycn) (**3**)] (Chart 1) with acids and the small molecules H_2, CO, and C_2H_4.

Results and Discussion

Synthesis and Characterization of Ir(tdppcyme)(CO)Cl (2a,a′). The orange carbonyl chloro complex **2a** is obtained when the potentially tripodal phosphine ligand tdppcyme (**2**) (Chart 1) and Ir(PPh$_3$)$_2$(CO)Cl are heated in toluene (Scheme 1).

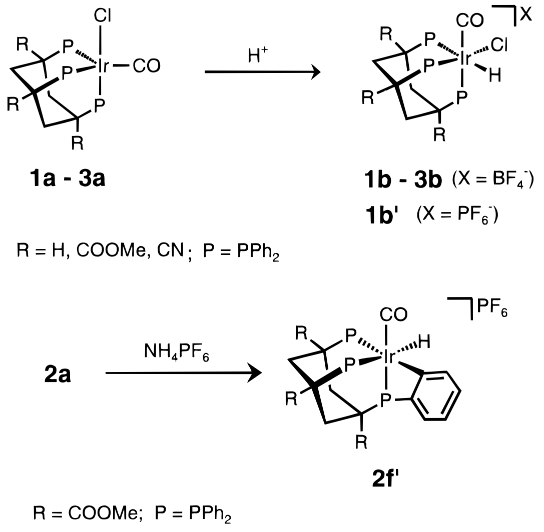
Scheme 1



2a

2a'

Scheme 2



1a - 3a

1b - 3b (X = BF$_4^-$)

1b' (X = PF$_6^-$)

R = H, COOMe, CN; P = PPh$_2$

2a

2f'

R = COOMe; P = PPh$_2$

Compound **2a** is air-sensitive in the solid state and in solution. Like **1a**[10a] (Scheme 2) Ir(tdppcyme)(CO)Cl (**2a**) dissolves in chlorinated solvents and is sensitive to light in these solutions. In contrast to **1a** and Ir(tdppcycn)(CO)Cl[10c] (**3a**) (Scheme 2) two ν(CO) absorptions are observed in the carbonyl region of the IR spectrum of **2a**. In solution (IR/CH$_2$Cl$_2$, $\nu(CO) = 2006$, 1931 cm^{-1}) the relative intensity ratio of 1:15 remains constant while in the solid state (IR/KBr $\nu(CO) = 2008$, 1928 cm^{-1}) altered intensity ratios of 1:1 to 1:10 are found in different batches. A comparison of the observed carbonyl absorption frequencies of **2a** with those of structurally related complexes Ir(tdppcy)(CO)Cl[10a] (**1a**) ($\nu(CO) = 1912$ cm^{-1}), Ir(tdpme)(CO)Cl[11] ($\nu(CO) = 1900$ cm^{-1}), Rh(tdpme)(CO)Cl[11] ($\nu(CO) = 2005$ and 1915 cm^{-1}), and Rh(dppe)(CO)Cl[12] ($\nu(CO) = 2010$ cm^{-1}) (tdpme = 1,1,1-tris[(diphenylphosphino)methyl]ethane, dppe =

---

(7) (a) Johnston, G. G.; Baird, M. C. *Organometallics* **1989**, *8*, 1894. (b) Barbaro, P. L.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227.

(8) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(9) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7505. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370. (c) Bianchini, C.; Jiménez, M. V.; Meli, A.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 2342.

(10) (a) Mayer, H. A.; Otto, H.; Kühbauch, H.; Fawzi, R.; Steimann, M. *J. Organomet. Chem.* **1994**, *472*, 347. (b) Mayer, H. A.; Stössel, P.; Fawzi, R.; Steimann, M. *J. Organomet. Chem.* **1995**, *492*, C1. (c) Mayer, H. A.; Stössel, P.; Fawzi, R.; Steimann, M. *Chem. Ber.* **1995**, *128*, 719.

(11) Siegl, W. O.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158.

(12) Hieber, W.; Kummer, R. *Chem. Ber.* **1967**, *100*, 148.

Table 1. Selected ^{1}H, ^{31}P, and IR Data for Complexes 1a–f, 2a–f, 3a–e, and 2c′

compd	^{1}H (ppm)[a] for hydride/ethylene	^{31}P{^{1}H} (ppm)[a]	ν(IrH)/ν(CO) (cm^{-1}) (KBr)
1a		−14.1	-/1912
2a		5.4	-/2006, 1928 (2008, 1931)[b]
3a		−3.5	-/1928−1951 (1956)[c]
1b	−8.37/-	−34.9, −27.9, −11.8	2144/2081
2b	−9.08/-	−18.2, −11.4, −4.2	2137/2091
3b	−8.53/-	−23.0, −14.4, −7.1	2168/2107
1c	−10.20/-	−23.8, −15.6	2092/2047
2c	−10.25/-	−9.0, −4.1	-/2062
2c′	−10.42, −8.89/-	17.3, 18.0, 28.0	2105, 2049/2007
3c	−8.57/-	−9.8, 7.8	-/2088
1d		−21.8	-/2039, 1961
2d		−5.3	-/2049, 1982
3d		−10.3	-/2064, 1998
1e	-/2.8, 2.0 (N = 4.0 Hz)	−27.6, −32.3[d]	-/2025
2e	-/2.5, 2.1 (N = 7.9 Hz)	−13.8, −18.7[e]	-/2043
3e	-/2.9, 2.4 (N = 7.6 Hz)	−17.3, −25.8[f]	-/2055
1f	−7.81/-	−90.6, −30.5, −25.6	2077/2025
2f	−8.48/-	−81.7, −9.4, −6.2	2086/2048

[a] The multiplicities and coupling constants are given in the Experimental Section. [b] In CH_2Cl_2. [c] In $CHCl_3$. [d] −68 °C, d, t, $^2J_{PP}$ = 32.9 Hz. [e] −26 °C, d, t, $^2J_{PP}$ = 33.5 Hz. [f] −68 °C, d, t, $^2J_{PP}$ = 34.1 Hz.

1,2-bis(diphenylphosphino)ethane) leads to the conclusion that in solution as well as in the solid state two coordination isomers exist (Scheme 1). The carbonyl absorption with lower energy is assigned to isomer **2a**.[10a,c,11] In **2a′** only two phosphine groups are bound to the coordination center while the third remains nonbonded. The steric constraints of the ligand backbone in tdppcyme (**2**) generate a *cis* square-planar environment around iridium with the carbonyl located *trans* to a phosphine group. Consequently the ν(CO) absorption in **2a′** is observed at higher frequencies.[12]

The ^{31}P{^{1}H} NMR spectrum (161.98 MHz) of **2a** and **2a′** at room temperature displays only a broad resonance ($\nu_{1/2}$ = 25 Hz) at δ 5.4. Upon warming of the sample, the peak continues broadening until at 40°C the resonance coalesces into the baseline. When the temperature is lowered to −10 °C the signal becomes sharp ($\nu_{1/2}$ = 5 Hz). Further cooling does not change the line width until below −30 °C the resonance starts to broaden again. At the lowest accessible temperature (−100 °C) the line width of the peak is $\nu_{1/2}$ > 40 Hz. The line broadening above −10 °C is consistent with a fast equilibrium which includes dissociation and association of one phosphine arm from the metal center (Scheme 1). As the temperature is lowered, the equilibrium is shifted toward the isomer **2a**. Such pentacoordinated metal complexes are stereochemically nonrigid.[10a,c,13] A fast exchange process between the different phosphorus sites accounts for the observation of only one sharp singlet in the temperature range of −10 to −30 °C. At lower temperatures the exchange process is slowed down as indicated by line broadening; however, decoalescence is not observed. Solid-state NMR spectroscopy at room temperature does not allow to distinguish between the equilibrium of **2a** $\rightleftarrows$ **2a′** and the high fluxionality of the molecule. One broad singlet and one set of carbon resonances consistent with a C_3 symmetry of the [Ir(tdppcyme)] template in the ^{31}P and ^{13}C CP/MAS NMR spectrum, respectively, are detected.

The increased carbonyl stretching frequencies of the carbonyl chloro complexes **1a-3a** (Table 1) indicate a decrease in the electron-donating ability of the functionalized phosphine ligands tdppcy (**1**) > tdppcyme (**2**) > tdppcycn (**3**). This implies an altered basicity and reactivity of the three complexes which is outlined as follows.

Reactivity of Ir(tripod)(CO)Cl toward Acids. When the chloro carbonyl complexes **1a**−**3a** are treated with an excess of HBF_4 in dichloromethane, they are readily protonated to give the octahedral cationic monohydrides **1b**−**3b** (Scheme 2). If the same reaction is repeated with the weak acid NH_4PF_6, only **1a** is basic enough to be protonated under the formation of the cation **1b′** (Scheme 2). The basicity of the functionalized complexes **2a** and **3a** is too weak to deprotonate the NH_4^+ cation. Although no reaction is observed with Ir(tdppcycn)(CO)Cl (**3a**), replacement of the coordinating anion Cl^- of Ir(tdppcyme)(CO)Cl (**2a**) with the noncoordinating PF_6^- gives intramolecular C−H activation. The final orthometalated product **2f** ′ (Scheme 2) can also be obtained by different methods which are discussed below.

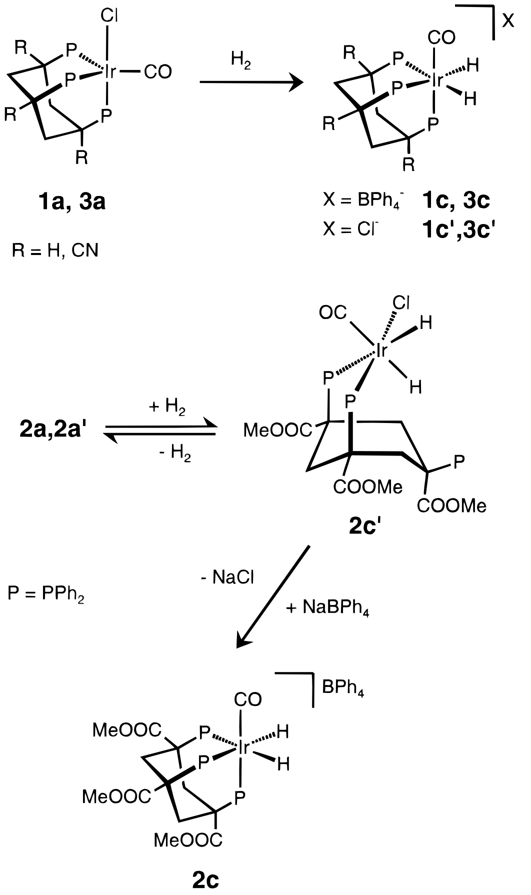
In the ^{31}P{^{1}H} NMR spectra each compound gives rise to three doublets of doublets in the range of −4 to −35 (Table 1). The $^2J_{PP}$ coupling constants between 10.0 to 24.3 Hz are characteristic for the *cis* arrangements of the phosphine groups. The ^{1}H NMR spectra of **1b**−**3b** and **1b′** display multiplet patterns (δ −8.37 to −9.08) which are the result of one large coupling of the hydride resonance to one phosphine group *trans* and smaller splittings by two phosphine groups *cis* to the hydride. The additional interaction ($^4J_{HH}$ = 1.9 Hz) which is observed for the hydride with the C−H proton of the cyclohexane ring in the cases of **1b** and **1b′** is indicative of a rigid ligand backbone.

Reactivity of Ir(tripod)(CO)Cl toward H_2. The carbonyl chloro complexes **1a**−**3a** react with hydrogen in different ways. When Ir(tdppcy)(CO)Cl (**1a**) is treated with H_2 in dichloromethane, the octahedral dihydride complex **1c′** is obtained quantitatively within 24 h. The oxidative addition of H_2 forces the chlorine to dissociate from the metal center irreversibly (Scheme 3). Under the same reaction conditions **3a** forms an equilibrium with **3c′** with the equilibrium lying on the left side. The dihydride complex **3c′** cannot be isolated. Addition of

---

(13) (a) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227. (b) Holmes, R. W. *Prog. Inorg. Chem.* **1984**, *32*, 119. (c) Dahlenburg, L.; Mirzaei, F. *Inorg. Chim. Acta* **1985**, *97*, L1.

Scheme 3

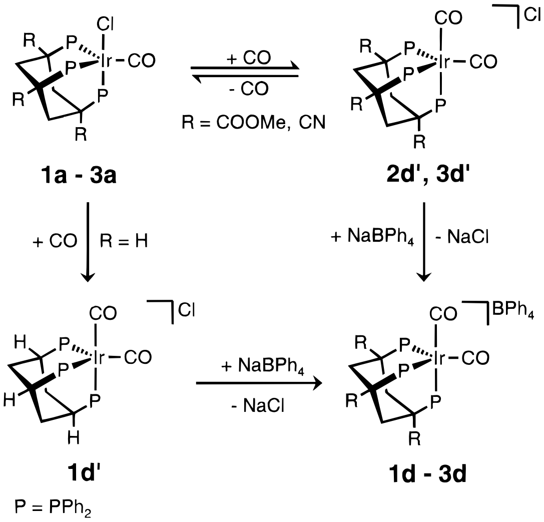


NaBPh$_4$ to the reaction mixture substitutes the Cl$^-$ anion with BPh$_4^-$ and gradually shifts the equilibrium to the right. Because of the weak basicity of Ir(tdppcycn)(CO)Cl (**3a**) the reaction takes 2–3 weeks for completion. In contrast to **1a** and **3a** the reversible oxidative addition to the ester-functionalized complex **2a** is completed within 5–10 min (Scheme 3). The fact that in **2c′** only two phosphine groups are bound to iridium suggests that **2a′** is the actual starting compound (Scheme 1). The stereochemistry of the reaction of H$_2$ with **2a′** to **2c′** is consistent with the kinetic controlled product of the comparable reaction with the *cis*-Ir(dppe)(CO)Cl complex.[14] The reaction of **2a** with H$_2$ in the presence of NaBPh$_4$ leads to the dihydride complex **2c** with all three phosphine groups coordinated to the metal (Scheme 3) which is isostructural to **1c** and **3c**.

In the ^{31}P{^{1}H} NMR spectra of **1c**–**3c** the two phosphine groups *trans* to the hydrogen ligands are observed as doublets at a higher field than the triplets of the phosphine groups coordinated *trans* to CO. This is in agreement with the stronger *trans* influence of the hydride compared to CO. The hydride regions in the ^{1}H NMR spectra of **1c**–**3c** display the AA′ parts of AA′MXX′ spin systems which are typical for two chemically but not magnetically equivalent hydride ligands (Table 1).[4b]

Since the labile dihydride complex **2c′** can only be isolated in pure form under H$_2$ atmosphere, its stereochemical assignment is based on solution NMR and IR spectroscopy under H$_2$ atmosphere and confirms the structure displayed in Scheme 3. The dihydride complex **2c′** contains two different hydride resonances in the ^{1}H NMR spectrum. One resonance (δ −10.42) shows both *cis*- ($^2J_{\mathrm{PH}} = 19.3$ Hz) and *trans*-phosphorus coupling ($^2J_{\mathrm{PH}} = 155.4$ Hz). The chemical shift of the hydride resonance (δ −8.89) which shows only *cis*-phosphorus coupling ($^2J_{\mathrm{PH}} = 17.0$ Hz) is typical for a hydride *trans* to CO. Both hydrides weakly ($^2J_{\mathrm{HH}} < 0.5$ Hz) interact with each other. The three different environments for the phosphorus groups account for three signals in the ^{31}P{^{1}H} NMR spectrum. The resonances of the phosphorus nuclei *trans* to the hydride (δ 17.3) and *trans* to the chlorine (δ 28.0) are split by each other ($^2J_{\mathrm{PP}} = 9.8$ Hz) while the noncoordinated phosphine group gives a singlet at δ 18.0.

Scheme 4



In the IR spectrum of **2c′** the two ν(IrH) absorptions appear at 2105 and 2049 cm^{-1} and are characteristic for hydrogen *trans* to strong *trans* influencing ligands.[15] As expected for octahedral Ir(III) complexes ν(CO) is shifted to higher frequencies (2007 cm^{-1}).

Reaction of the Ir(tripod)(CO)Cl Complexes with CO. The altered basicity of the three functionalized carbonyl chloro complexes is also reflected in the gradation of their affinity toward the π-acid CO (Scheme 4). Thus the dicarbonyl complex **1d′** can be isolated in quantitative yield by treatment of **1a**–**3a** with CO but the corresponding complex [Ir(tdppcyme)(CO)$_2$]Cl (**2d′**) can only be obtained and characterized under a CO atmosphere. The weakest base in this series **3a** hardly reacts with CO to give **3d′**, which is only identified on the basis of its ^{31}P{^{1}H} NMR and IR spectra. Although the formation of **1d′** is irreversible, removal of the CO atmosphere causes the decomposition of **2d′** and **3d′** to the starting materials (Scheme 4). When the reactions of **1a**–**3a** with CO are repeated in the presence of NaBPh$_4$, the cationic dicarbonyl complexes **1d**–**3d** are generated in high yields. Due to the weak electron-donating ability of **3a** the reaction rate is low which leads to a prolonged reaction time of 4 days. In contrast, the conversion of **1a** and **2a** to **1d** and **2d** is complete within 15 h.

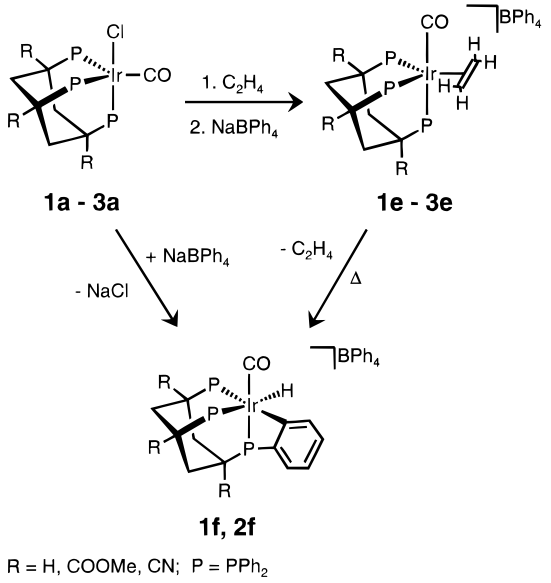
The singlets observed in the ^{31}P{^{1}H} NMR spectra in the region of δ −21.9 to −5.3 (Table 1) are in agreement

---

[14] (a) Fisher, B. J.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 3216. (b) Johnson, C. J.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (c) Johnson, C. R.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148. (d) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764.

[15] Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100.

Scheme 5



with high fluxionality which exchanges the different environments of the phosphorus sites and that of the carbonyl groups. This is confirmed by the $^{13}C\{^1H\}$ NMR spectra of **1d**−**3d**. In the carbonyl region of each dicarbonyl complex a quartet at δ 180.8 (**1d**), 178.2 (**2d**), and 175.6 (**3d**), respectively, with weighted averaged *cis* and *trans* $^2J_{PC}$ coupling constants demonstrate the high flexibility. The increase in deshielding from **3d** < **2d** < **1d** is also consistent with the increased electron density at the metal center and thus with better M−CO back-bonding.[16] This is further supported by the IR spectra of **1d**−**3d**. The two ν(CO) absorptions observed for each compound are shifted to higher frequencies in the order **1d** < **2d** < **3d** (Table 1).

Reaction of the Ir(tripod)(CO)Cl Complexes with Ethylene. Addition of excess ethylene and NaBPh$_4$ to **1a**−**3a** in dichloromethane gives the cationic ethylene complexes **1e**−**3e** in high yields (Scheme 5). Again the different basicity of the starting complexes is mirrored in the extent of the reaction times (6 h for **1e**, 10 h for **2e**, and 10 d for **3e**). The ethylene complexes are stable in the solid state and can be stored in an oxygen free atmosphere. When solutions of [Ir(tripod)(CO)(C$_2$H$_4$)]BPh$_4$ are heated above 45 °C (**1e**), 35 °C (**2e**), and 68 °C (**3e**), respectively, the complexes decompose with loss of ethylene. In the cases of **1e** and **2e** the orthometalated complexes **1f** and **2f** are observed as the major decomposition products (see below) (Scheme 5).

In the ^{1}H NMR spectra of **1e**−**3e** the four ethylene hydrogens give rise to AA′XX′ patterns which are slightly broadened by additional interactions with the phosphorus nuclei (Table 1). The chemical shifts of the ethylene multiplets are basically invariant to changes in temperature from −100 to 45 °C (**1e**), −40 to 35 °C (**2e**), and −70 to 68 °C (**3e**), respectively, and indicate that the two different environments for the hydrogen atoms do not change over this temperature range. Upon coordination of ethylene to the [Ir(tripod)(CO)]$^+$ fragments, the ^{13}C resonances of the ethylene groups are shifted dramatically to higher field [δ 20.1 (**1e**), 25.8 (**2e**), 27.0 (**3e**)]. The observation of two ethylene hydrogen types but a single ethylene carbon chemical shift suggests a C_s symmetry for the ethylene complexes **1e**−**3e** (Scheme 5). This is consistent with the planar equatorial positioning of the ethylene ligand and two of the phosphine groups as shown for **1e**−**3e** in Scheme 5.[17]

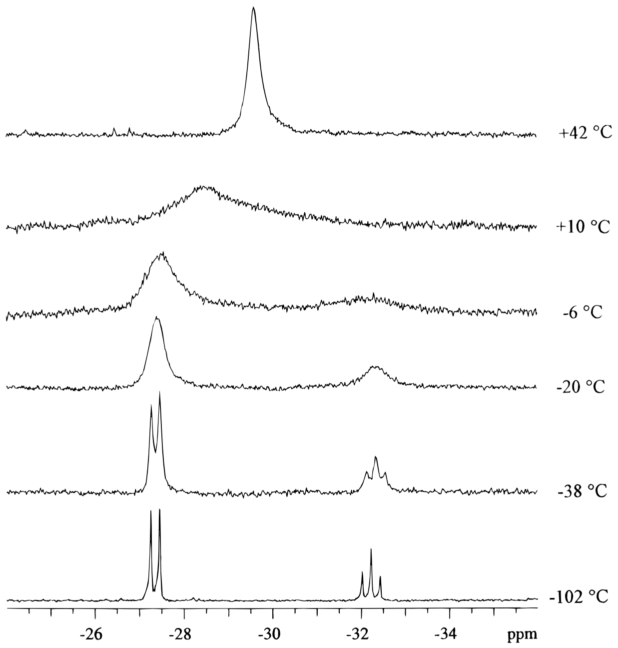


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of [Ir(tdppcy)(CO)(C$_2$H$_4$)]$^+$ (**1e**) (161.98 MHz).

In contrast to the inflexible ethylene ligand the NMR data for the tripodal phosphine backbone are in agreement with high fluxionality of the [Ir(tripod)] fragment. Thus a single set of multiplets (**1e**) and ABX$_2$ (**2e, 3e**) patterns for the six ring methylene protons and unique carbon resonances of the ligand backbone are observed in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra at room temperature, respectively. Further support for a dynamic process which equilibrates the equatorial and apical positions of the ligand backbone in **1e**−**3e** stems from $^{31}P\{^1H\}$ NMR investigations at variable temperatures (Figures 1 and 2). The broad unresolved resonances at δ −27.1 (**1e**), −13.8 (**2e**), and −19.1 (**3e**), which are found at room temperature already indicate that the exchange process is slow. When the temperature is lowered, the coalescence point is reached at 5 °C (**1e**), 10 °C (**2e**), and 2 °C (**3e**), respectively. Further cooling of the samples reveals the separation of two signals (2:1) from the base line until at −68 °C (**1e**), −26 °C (**2e**), and −56 °C (**3e**), respectively, a doublet and a triplet for each compound is fully resolved (Figures 1 and 2; Table 1). The AX$_2$ spin patterns correspond to the trigonal-bipyramidal structures shown in Scheme 5. While in the case of the tdppcy ligand this is the limiting spectrum which is obtained as low as −102 °C, a second dynamic process with a lower energy barrier is found for the complexes **2e** and **3e**. At temperatures below −40 °C in the case of **2e** and −70 °C for the CN-functionalized complex **3e**, the doublets which are due to the two equatorial phosphine groups first broaden and then coalesce [-85 °C (**2e**), −102 °C (**3e**)]. The triplet caused by the phosphorus nuclei *trans* to the

---

[16] Mason, J. *Multinuclear NMR;* Plenum Press: New York, 1987; p 73.

[17] Rossi, A. R.; Hoffmann R. *Inorg. Chem.* **1975**, *14*, 365.

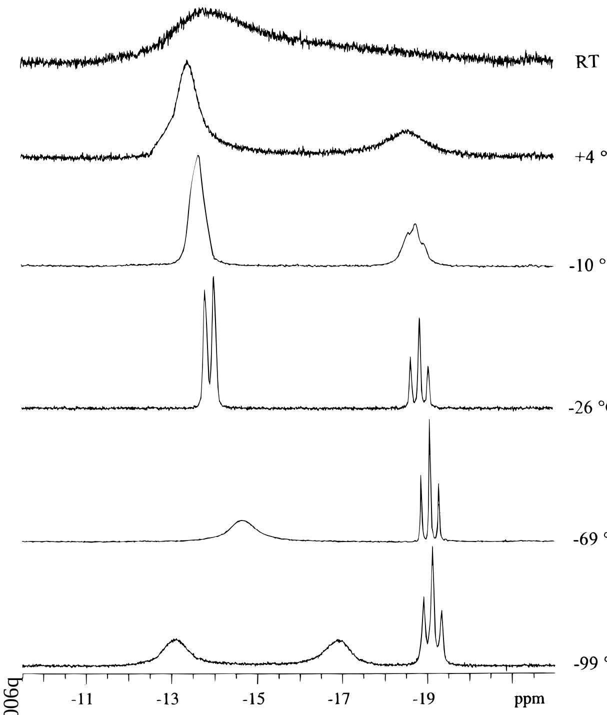


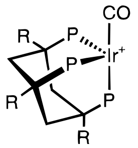
Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[Ir(tdppcyme)(CO)(C_2H_4)]^+$ (**2e**) (161.98 MHz).

carbonyl remains sharp. A completely distorted molecule for **2e** is indicated by two broad unresolved signals at δ −13.1 and −16.8, which are observed besides the triplet resonance due to the phosphorus nucleus *trans* to CO at −99 °C. This second low-barrier process which is only observed for the functionalized ethylene complexes **2e** and **3e** may be attributed to sterical hindrance of the phenyl rings at the phosphine groups and the functional groups at the ligand backbone, although electronic reasons cannot be excluded at this point.

The temperature-dependent $^{13}C\{^1H\}$ NMR spectra follow the same trend. The carbon signals of the ligand backbone first broaden, then coalesce, and finally split into two sets of resonances in a 2:1 intensity ratio at temperatures corresponding to the $^{31}P\{^1H\}$ NMR spectra. Limiting spectra for the lower exchange process in the cases of **2e** and **3e** could not be obtained. In conformation with the ^1H NMR data the singlet of the ethylene carbon resonance remains sharp for **1e**. However, it first broadens and then coalesces into the baseline below −40 °C for $[Ir(tdppcyme)(CO)(C_2H_4)]^+$ (**2e**) and −70 °C for $[Ir(tdppcycn)(CO)(C_2H_4)]^+$ (**3e**), respectively.

The NMR data clearly demonstrate that the three carbonyl ethylene complexes **1e**−**3e** belong to the small group of pentacoordinate transition metal complexes where the fluxional process is restricted to the tripodal ligand backbone and does not involve the ethylene ligand.[18] This is in contrast to pentacoordinate carbonyl ethylene complexes in which the ethylene rotation is coupled with a Berry pseudorotation of the carbonyl groups.[19] The fluxionality of the $[Ir(tripod)(CO)(C_2H_4)]^+$ complexes does not occur via a P−M dissociation process, since the activation energy for a phosphorus arm dissociation greatly exceeds that of the fluxionality. This is also consistent with the observation of phosphorus−phosphorus coupling which excludes a dissociation of a phosphine arm from iridium as well.[20] The stereochemical constraints of the backbone of the tripodal phosphine ligands prohibit a Berry pseudorotation so that a turnstile mechanism becomes operative.[13a,b,21]

Chart 2



Orthometalation of the Ir(tripod)(CO)Cl Complexes. The dissociation of Cl^- from the Ir(tripod)(CO)Cl complexes **1a**−**3a** leads to d^8 ML_4 fragments of angular geometry as shown in Chart 2.[22] The steric compression of the tripod ligands **1**−**3** (Chart 1) imposes a facial coordination on the d^8 metal which is highly unstable compared to square-planar d^8 ML_4 complexes.[23] The frontier orbital set of such an angular ML_4 fragment is highly favorable for C−H bond activation.[24] Besides this steric demand a high basicity of the metal fragment is required to donate electron density into the antibonding orbital of the C−H.[22,24] This is nicely demonstrated by the $[Ir(tripod)(CO)]^+$ fragments which are of different basicity. Treatment of the carbonyl chloro complexes **1a** and **2a** with $NaBPh_4$ generates the reactive angular fragments by replacing the chlorine with the noncoordinating anion BPh_4^- and finally gives the orthometalated complexes **1f** and **2f** (Scheme 5). The reactive d^8 ML_4 intermediates can also be obtained by the thermal dissociation of the weakly bound ethylene ligand (Scheme 5). Due to the weak electron-donating ability of tdppcycn (**3**), no orthometalation is observed when either Ir(tdppcycn)(CO)Cl (**3a**) is reacted with $NaBPh_4$ or $[Ir(tdppcycn)(CO)(C_2H_4)]^+$ (**3e**) is heated (see above).

The intramolecular oxidative addition of a phenyl C−H bond to the $[Ir(tripod)(CO)]^+$ fragments results in the formation of four-membered rings which reduce the symmetry of the octahedral complexes **1f** and **2f**. Thus the $^{31}P\{^1H\}$ NMR spectra of **1f** and **2f** display three doublets of doublets (*cis* $^2J_{PP}$ between 16.3 and 27.8 Hz) consistent with three phosphorus atoms in different environments (Table 1). The dramatic high-field shift [δ −90.6 (**1f**), −81.7 (**2f**)] which is observed for one of the signals in each spectrum is typical for phosphorus nuclei incorporated into four-membered rings.[25] The characteristic features in the ^1H NMR spectra of **1f** and

---

(18) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226.

(19) (a) Kruczynski, L.; LiShingMan, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1974**, *69*, 4006. (b) Wilson, T. S.; Coville, N. J.; Shapley, J. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4038. (c) Faller, J. W. *Adv. Organomet. Chem.* **1978**, *16*, 211. (d) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

(20) Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 253.

(21) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288.

(22) Saillard, J.-Y.; Hofmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(23) Yamamoto, A. *Organotransition Metal Chemistry*; John Wiley & Sons: New York, 1986.

(24) Saillard, J.-Y. In *Selective Hydrocarbon Activation Principles and Progress;* Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1990; p 207.

(25) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Pohmer, K. *Inorg. Chem.* **1991**, *30*, 1102. (c) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

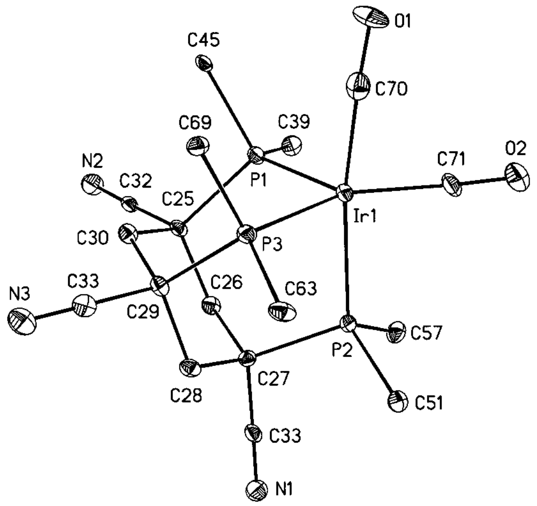


Figure 3. ORTEP drawing and atom-labeling scheme for [Ir(tdppcycn)(CO)$_2$]$^+$ (**3d**). Only the *ipso*-carbon atoms of the phenyl rings are shown for clarity.

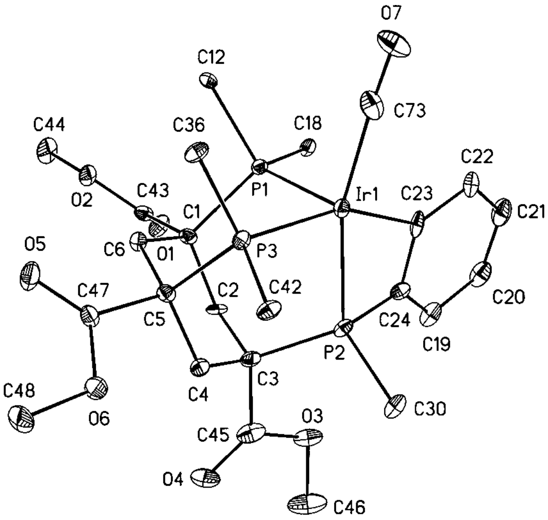


Figure 4. ORTEP drawing and atom-labeling scheme for the orthometalated complex **2f**. Only the *ipso*-carbon atoms of the phenyl rings are shown for clarity.

2f are the hydride resonances at δ −7.81 and −8.48, respectively. Both signals are split by one strong *trans* and two weak *cis* interactions with the phosphorus nuclei. Like in **1b** and **1b′** the hydride peak of **1f** shows an additional splitting due to a C−H proton of the cyclohexane ring. Mass spectra and elemental analysis are also in agreement with an intramolecular oxidative addition of a C−H bond which is thermodynamically favored over the intermolecular metalation.[26]

X-ray Structure Analysis. In order to get a better insight into the constraints of the [Ir(tripod)] template in different coordination geometries, X-ray diffraction studies were undertaken on appropriate crystals of a trigonal-bipyramidal (**3d**) and an orthometalated (**2f**) complex. The perspective views of **3d** and **2f** are presented in Figures 3 and 4, respectively. Selected bond lengths and bond angles are collected in Table 2 for both compounds.

As seen in Figure 3 and 4 the tdppcyme (**2**) and tdppcycn (**3**) ligands are facially coordinated to the metal centers. In the trigonal-bipyramidal complex **3d** the three diphenylphosphine groups take up two equatorial and one apical position. The coordination sphere is completed by the two carbonyl ligands at an equatorial and an apical site, respectively. The angle between the equatorial phosphine groups P(1)−Ir−P(3) (97.2°) strongly deviates from the ideal geometry (120°). This is the largest angle found so far in a series of comparable complexes Ir(tdppcycn)(CO)Cl (**3a**) (95.9°),[10c] Ir(tdpme)(CO)Cl (90.3°),[27] and Rh(tdpme)(CO)Me (90.8°).[28] The P(1)−Ir−C(71) angle (118.3°) remains close to ideal, whereas the reduction of the angle between P(1) and P(3) particularly affects the P(3)−Ir−C(71) angle which opens to 144.7°. The overall sum of 359.9° demonstrates that the equatorial plane is not distorted. The strong *trans* influence of CO causes a weakening of the P_{axial}−metal bond which is expressed in a longer P_{axial}−metal distance than that found in Ir(tdppcycn)(CO)Cl (**3a**). This makes the three Ir−P distances in [Ir(tdppcycn)(CO)$_2$]$^+$ (**3d**) equivalent.

The geometry around Ir in the orthometalated complex **2f** is best described as distorted octahedral (Figure 4). The CO group, the α-carbon atom of the metalated phenyl ring, and the hydride (could not be located from a difference map) occupy the face *trans* to the tdppcyme (**2**) ligand. The P−Ir−P angles fall within the range of 92.56(5)−95.24(5)°. The small angle of 162.7(2)° found for P(2)−Ir−C(73) indicates that the CO group is bent toward the hydride. It is noteworthy that a phenyl ring of the phosphine group *trans* to the CO group is metalated. This supports the assumption of an angular d^8 ML$_4$ fragment (Chart 2) as a reactive intermediate. The formation of the four-membered ring causes only slight deformations of the orthometalated ring. The benzene and the metalaphosphacyclobutane ring show only small deviations from planarity (overall sum of the endocyclic bond angles: 719.9 and 358.0°) with reduced puckering of the four-membered ring which is characteristic for orthometalated complexes.[29]

Conclusion

A characteristic feature of the recently introduced functionalized tripodal phosphine ligands **1**−**3** is their different electron-donating ability to metal complexes which results in an altered basicity of the [Ir(tripod)] template. This is nicely demonstrated by the carbonyl stretching frequencies in the IR spectra of the compounds discussed in this work (Table 1). In all cases ν(CO) increases in the series of the iridium templates [Ir(tdppcy)] < [Ir(tdppcyme)] < [Ir(tdppcycn)] (Table 1). This is consistent with the protonation reactions, the reaction rates with CO, and the formation of the ethylene complexes. However, the reaction pattern cannot be explained in terms of the electronic effect alone. A more complex combination of electronic effects and steric requirements accounts for the dissociation of a phosphine arm from Ir(tdppcyme)(CO)Cl (**2a**), which was not observed for **1a** and **3a**, and for the different dynamic behavior of the ethylene complexes **1e**−**3e**.

---

[26] (a) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

[27] Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* **1985**, *269*, 229.

[28] Thaler, F. G.; Folding. K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664.

[29] Andreucci, L.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1986**, 803.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complexes 3d and 2f

	3d	2f		3d	2f
Ir−P(1)	2.365(2)	2.3870(14)	P(1)−Ir−P(3)	97.22(7)	95.24(5)
Ir−P(2)	2.360(2)	2.329(2)	P(1)−Ir−P(2)	93.46(7)	92.77(5)
Ir−P(3)	2.362(2)	2.3485(14)	P(3)−Ir−P(2)	89.02(8)	92.56(5)
Ir−C(23)		2.140(5)	P(1)−Ir−C(23)		86.65(14)
Ir−C(71)	1.860(10)		P(1)−Ir−C(73)		93.8(2)
Ir−C(70)	1.901(12)		P(1)−Ir−C(71)	118.0(3)	
Ir−C(73)		1.902(7)	P(1)−Ir−C(70)	96.5(3)	
C(70)−O(1)	1.168(14)		P(2)−Ir−C(73)		162.7(2)
C(71)−O(2)	1.169(13)		P(2)−Ir−C(71)	88.3(3)	
C(73)−O(7)		1.116(7)	P(2)−Ir−C(70)	169.9(3)	
P(1)−C(1)		1.881(5)	C(23)−Ir−C(73)		98.6(3)
P(2)−C(3)		1.835(6)	C(71)−Ir−C(70)	85.4(4)	
P(3)−C(5)		1.917(5)	P(3)−Ir−C(70)	91.5(3)	
P(1)−C(25)	1.888(8)		P(3)−Ir−C(71)	144.7(3)	
P(2)−C(27)	1.884(8)		P(2)−Ir−C(23)		65.9(2)
P(3)−C(29)	1.900(8)		Ir−C(23)−C(24)		106.2(4)
P(2)−C(24)		1.790(6)	C(23)−C(24)−P(2)		98.5(4)
			C(24)−P(2)−Ir		87.4(2)
			C(25)−C(26)−C(27)	117.0(7)	
			C(29)−C(30)−C(25)	118.2(7)	
			C(27)−C(28)−C(29)	115.2(6)	
			C(3)−C(2)−C(1)		117.4(5)
			C(3)−C(4)−C(5)		117.7(4)
			C(5)−C(6)−C(1)		117.4(4)

Further investigations for a better understanding of these effects in order to improve control of reactivity and selectivity in stoichiometric reactions as well as in catalysis are in progress.

Experimental Section

General Comments. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled under Ar; benzene, toluene, diethyl ether, and THF were distilled from Na/Ph_2CO; *n*-pentane and *n*-hexane were distilled from $LiAlH_4$; dichloromethane was distilled from CaH_2; ethanol was distilled from Na; and methanol was distilled from Mg. The gases H_2, CO, and C_2H_4 were of commercial grade and used without further purification. The phosphine ligands **1**,[10a] **2**,[10b] and **3**[10c] and the complexes **1a**,[10a] and **3a**,[10c] and $Ir(PPh_3)_2(CO)Cl$[30] were prepared as described in the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 or a Bruker AMX 400 operating at 250.13 or 400.13, 62.90 or 100.62, and 101.26 or 161.98 MHz, respectively. ^1H chemical shifts were referenced to the residual proton peaks of the solvents versus TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet relative to TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. In addition to the $^{13}C\{^1H\}$ NMR spectrum a ^{13}C-DEPT[31] experiment was routinely performed for each compound. The assignments of the ethylene groups in **1e**−**3e** were supported by $^1H/^{13}C$ 2D HMQC[32] experiments using standard Bruker software. The numbers of hydrides bound to the metal centers in **1b**−**3b**, **1c**−**3c**, **1f**, and **2f** were also confirmed on the basis of the multiplicities of the off-resonance proton-decoupled ^{31}P NMR spectra. ^1H, ^{13}C, and ^{31}P DNMR experiments were carried out on a Bruker AMX 400. The temperature was measured using the Eurotherm temperature control unit and an external thermocouple (Pt 100). ^{13}C and ^{31}P CP/MAS NMR spectra were taken on a Bruker ASX 300 (121 MHz). Infrared spectra were recorded on a Bruker IFS 48. Mass spectra (FD) were detected on a Finnigan MAT 711 A modified by AMD; FAB spectra were detected on a Finnigan MAT TSQ70. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Conductivities were measured on a Model DIGI 610 WTW connected to a LTA/S conducting cell. The conductivity data were obtained at sample concentrations of 1 mmol in dichloromethane solutions at room temperature. Single-crystal X-ray structure determinations of **3d** and **2f** were carried out on a Siemens P4 diffractometer.

Carbonylchloro[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(I) (2a). A suspension of **2** (405.4 mg, 0.5 mmol) and $Ir(PPh_3)_2(CO)Cl$ (390.1 mg, 0.5 mmol) in 20 mL of toluene was heated at 80 °C for 2 h, during which time an orange precipitate was formed. This was collected on a sintered glass frit, washed twice with 10 mL of toluene each and three times with 10 mL of *n*-pentane each, and dried in vacuo. Yield: 469.5 mg (88%). Mp: >174 °C (dec). IR (KBr, cm^{-1}): 2006 m, 1928 st ν(CO), 1722 sst $\nu(COOCH_3)$. IR(CH_2Cl_2, cm^{-1}): 2008 w, 1931 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 5.4$ [s]. ^{31}P CP/MAS NMR: $\delta = -0.4$ [s]. ^1H NMR (CD_2Cl_2): $\delta = 2.42$ [br m, 3 H, CHH_a], 3.27 [br m, 3 H, CHH_e], 3.44 [s, 9 H, $COOCH_3$], 7.10−7.39 [m, 30 H, C_6H_5]. ^{13}C CP/MAS NMR: $\delta = 32.9$ [s, CH_2], 46.3 [s, CP], 50.6 [s, CH_3], 126.6−139.3 [m, C_6H_5], 171.9 [s, $COOCH_3$], 197.9 [s, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 0.6. MS (FAB), *m/z*: 1038.1 [$M^+ - CO$], 1031.2 [$M^+ - Cl^-$]. Anal. Calcd for $C_{49}H_{45}ClIrO_7P_3$ (1066.48): C, 55.19; H, 4.25; Cl, 3.32. Found: C, 54.72; H, 4.19; Cl, 2.93.

Reactions of 1a−3a with HBF_4 and NH_4PF_6. To a solution of **1a**−**3a** in 50 mL of CH_2Cl_2 was added 0.1 mL of an aqueous solution of HBF_4 (8 M) or 1 mL of an aqueous solution of NH_4PF_6 (1 M). The reaction mixture was stirred for 15 h at room temperature. The aqueous phase was removed, the organic phase was concentrated in volume to 3 mL, and 50 mL of *n*-pentane was added. The resulting off-white precipitate was filtered out, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure.

Carbonylchlorohydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Tetrafluoroborate (1b) and **Hexafluorophosphate (1b′)**. In both cases the amount of 178.6 mg (0.20 mmol) of **1a** was used. Yield: 187.0 mg (95%) of **1b** and 200.2 mg (96%) of **1b′**. Mp: >185 °C (dec) (**1b**), >180 °C (dec) (**1b′**). - IR (KBr, cm^{-1}): 2144 w ν(IrH), 2081 st ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -143.0$ [sept, $^1J_{PF} = 713.3$ Hz, PF_6, **1b′**], −34.9 [dd, $^2J_{PP} = 23.3$ Hz, $^2J_{PP} = 10.0$ Hz, P *trans* to H], −27.9 [dd, $^2J_{PP} = 23.3$ Hz, $^2J_{PP} = 23.3$ Hz, P], −11.8 [dd, $^2J_{PP} = 23.3$ Hz, $^2J_{PP} = 10.0$ Hz, P]. ^1H NMR ($CDCl_3$): $\delta = -8.37$ [dddd, $^2J_{PH} = 132.9$ Hz, $^2J_{PH} = 9.4$ Hz, $^2J_{PH} = 9.4$ Hz, $^4J_{HH} = 1.9$ Hz, 1 H, IrH], 2.19−2.44 [m, 2 H, CHH_a], 2.57−2.73 [m, 1

---

[30] Brauer, G. *Handbook of Preparative Inorganic Chemistry;* F. Enke Verlag: Stuttgart, Germany, 1981; Vol. 3, p 2010.

[31] Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

[32] Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.

H, CH*H*$_a$], 2.88−3.33 [m, 3 H, CH*H*$_e$], 3.39−3.57 [m, 3 H, HCP], 6.83−7.72 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.5, 22.4, and 22.9 [d, $^1J_{PC}$ = 33.4, 9.6, and 16.0 Hz, CP], 26.4, 26.7, and 27.8 [s, CH_2], 125.6−134.1 [m, C_6H_5], 167.3 [ddd, $^2J_{PC}$ = 114.8 Hz, $^2J_{PC}$ = 6.1 Hz, $^2J_{PC}$ = 6.1 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, cm^2 Ω^{-1} mol^{-1}): 27.1 (**1b**), 25.8 (**1b′**). MS (FAB), *m*/*z*: 893.5 [$M^+ - BF_4^-$] (**1b**), 893.1 [$M^+ - PF_6^-$] (**1b′**). Anal. Calcd for $C_{43}H_{40}BClF_4IrOP_3$ (**1b**) (980.2): C, 52.69; H, 4.11; Cl, 3.62; F, 7.75. Found: C, 52.11; H, 3.99; Cl, 3.93; F, 8.13. Calcd for $C_{43}H_{40}ClF_6IrOP_4$ (**1b′**) (1038.3): C, 49.74; H, 3.88; Cl, 3.42; F, 10.98. Found: C, 49.22; H, 3.76; Cl, 3.64; F, 11.41.

Carbonylchlorohydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(III) Tetrafluoroborate (2b). The amount of 213.4 mg (0.20 mmol) of **2a** was used. Yield: 205.5 mg (89%). Mp: >157 °C (dec). IR (KBr, cm^{-1}): 2137 w ν(IrH), 2091 st ν(CO), 1745 st, 1731 st, 1723 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −18.2 [dd, $^2J_{PP}$ = 23.3 Hz, $^2J_{PP}$ = 10.9 Hz, P *trans* to H], −11.4 [dd, $^2J_{PP}$ = 23.3 Hz, $^2J_{PP}$ = 23.3 Hz, P], −4.2 [dd, $^2J_{PP}$ = 23.3 Hz, $^2J_{PP}$ = 10.9 Hz, P]. ^1H NMR (CD_2Cl_2): δ = −9.08 [ddd, $^2J_{PH}$ = 143.9 Hz, $^2J_{PH}$ = 11.0 Hz, $^2J_{PH}$ = 11.0 Hz, 1 H, IrH], 2.69−3.44 [m, 6 H, CH_2], 3.55, 3.59, 3.63 [s, 9 H, $COOCH_3$], 7.11−7.68 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 33.5−33.6 [m, CH_2], 44.9, 45.7, 46.3 [d, $^1J_{PC}$ = 14.5, 20.8, 22.6 Hz, CP], 53.5, 53.7, 53.7 [s, CH_3], 124.4−136.8 [m, C_6H_5], 165.2 [ddd, $^2J_{PC}$ = 119.5, $^2J_{PC}$ = 5.4, $^2J_{PC}$ = 5.4 Hz, CO], 171.3, 171.7, 171.9 [d, $^2J_{PC}$ = 5.8, 6.1, 6.4 Hz, *C*OCH_3]. Λ_M (CH_2Cl_2, 25 °C, cm^2 Ω^{-1} mol^{-1}): 46.1. MS (FAB), *m*/*z*: 1067.2 [$M^+ - BF_4^-$]. Calcd for $C_{49}H_{46}BClF_4IrO_7P_3$ (1154.30): C, 50.99; H, 4.02; Cl, 3.07; F, 6.58. Found: C, 50.61; H, 4.22; Cl, 2.98; F, 6.52.

The reaction of **2a** with NH_4PF_6 resulted in orthometalation (see text).

Carbonylchlorohydrido[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Tetrafluoroborate (**3b**). The amount of 193.5 mg (0.20 mmol) of **3a** was used. Yield: 196.3 mg (93%). Mp: >196 °C (dec). IR (KBr, cm^{-1}): 2230 w ν(CN), 2168 w ν(IrH), 2107 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −23.0 [dd, $^2J_{PP}$ = 21.6 Hz, $^2J_{PP}$ = 10.5 Hz, P *trans* to H], −14.4 [dd, $^2J_{PP}$ = 24.3 Hz, $^2J_{PP}$ = 21.6 Hz, P], −7.1 [dd, $^2J_{PP}$ = 24.3 Hz, $^2J_{PP}$ = 10.5 Hz, P]. ^1H NMR (CD_2Cl_2): δ = −8.53 [ddd, $^2J_{PH}$ = 145.60 Hz, $^2J_{PH}$ = 10.74 Hz, $^2J_{PH}$ = 10.74 Hz, 1 H, IrH], 3.08−4.30 [m, 6 H, CH_2], 6.95−7.98 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 30.0, 30.6, 31.4 [d, $^1J_{PC}$ = 23.9, 17.61, 26.4 Hz, CP], 33.6 [br s, CH_2], 33.9−34.1, 34.7−34.9 [m, CH_2], 118.3, 121.6, 123.9 [d, $^2J_{PC}$ = 47.2, 56.6, 50.3, CN], 125.8−136.9 [m, C_6H_5], 163.7 [ddd, $^2J_{PC}$ = 125.8, $^2J_{PC}$ = 6.2, $^2J_{PC}$ = 6.2 Hz, CO]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 39.9. MS (FAB), *m*/*z*: 968.5 [$M^+ - BF_4^-$]. Calcd for $C_{46}H_{37}BClF_4IrN_3OP_3$ (1055.22): C, 52.36; H, 3.53; Cl, 3.36; F, 7.20; N, 3.98. Found: C, 52.32; H, 3.84; Cl, 3.06; F, 6.93; N, 3.92.

The treatment of **3a** with NH_4PF_6 did not lead to any reaction.

General Procedure for the Reactions of 1a−3a with H_2, CO, and C_2H_4. A solution of **1a**−**3a** in 50 mL of CH_2Cl_2 was degassed by using the freeze−pump−thaw technique. To the frozen solution was added $NaBPh_4$ and one of the gases (1.3 bar) H_2, CO, and C_2H_4, respectively. After the reaction mixture had been allowed to warm to room temperature it was stirred for 15 h. The reaction mixture was separated from NaCl and residual $NaBPh_4$, the solvent was concentrated in volume to 3 mL, and 50 mL of *n*-pentane was added. The resulting off-white precipitate was filtered out, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure.

Carbonyldihydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Tetraphenylborate (**1c**). The amounts of 178.6 mg (0.20 mmol) of **1a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ were used. Yield: 230.4 mg (98%). Mp: >150 °C (dec). IR (KBr, cm^{-1}): 2092 m-w ν(IrH), 2047 st ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −23.8 [d, $^2J_{PP}$ = 23.1 Hz, P *trans* to H], −15.6 [t, $^2J_{PP}$ = 23.1 Hz, P *cis* to H], ^1H NMR ($CDCl_3$): δ = −10.20 [m,[33] 2 H, IrH], 1.61−1.79 [m, 3 H, CH*H*$_a$], 1.90−2.37 [m, 3 H, CH*H*$_e$], 2.67−2.85 [m, 3 H, HCP], 6.90−7.42 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.6, 21.0 [d, $^1J_{PC}$ = 33.0, 31.5 Hz, CP], 25.8, 26.0 [s, CH_2], 122.3−136.8 [m, C_6H_5], 164.3 [q, $^1J_{CB}$ = 49.3 Hz, *ipso*-$B(C_6H_5)_4^-$], 170.9 [dt, $^2J_{PC}$ = 95.9 Hz, $^2J_{PC}$ = 6.9 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, cm^2 Ω^{-1} mol^{-1}): 31.9 MS (FAB), *m*/*z*: 859.2 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{67}H_{61}BIrOP_3$ (1178.2): C, 68.30; H, 5.22. Found: C, 67.95; H, 5.52.

Carbonyldihydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Chloride (1c′). To a degassed solution of 178.6 mg (0.20 mmol) of **1a** in 50 mL of CH_2Cl_2 was added H_2, and the solution was stirred for 24 h. After evaporation of the solvent, **2c′** was obtained quantitatively. The spectroscopic data are comparable to those of **1c**.

Carbonyldihydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(III) Tetraphenylborate (2c). The amount of 213.4 mg (0.20 mmol) of **2a** was used. Yield: 227.2 mg (84%). Mp: >169 °C (dec). IR (KBr, cm^{-1}): 2062 st ν(CO), 1727 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.0 [d, $^2J_{PP}$ = 23.9 Hz, P *trans* to H], −4.1 [t, $^2J_{PP}$ = 23.9 Hz, P *cis* to H]. ^1H NMR (CD_2Cl_2): δ = −10.25 [m,[31] 2 H, IrH], 2.36−2.86 [m, 3 H, CH*H*$_a$], 3.11−3.51 [m, 3 H, CH*H*$_e$], 3.53, 3.58 [s, 9 H, $COOCH_3$], 6.85−7.18 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 33.7−33.8, 34.3−34.5 [m, CH_2], 45.7−46.2 [m, CP], 53.4, 53.5 [s, CH_3], 122.0−136.2 [m, C_6H_5], 164.4 [q, $^1J_{CB}$ = 49.4 Hz, *ipso*-$B(C_6H_5)_4^-$], 169.0 [dt, $^2J_{PC}$ = 101.3, $^2J_{PC}$ = 6.7 Hz, CO], 172.0−172.1 [m, *C*$OOCH_3$]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 39.8. MS (FD), *m*/*z*: 1033.3 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{73}H_{67}BIrO_7P_3$ (1352.28): C, 64.84; H, 4.99. Found: C, 64.30; H, 5.17.

Carbonylchlorodihydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(III) (2c′). Hydrogen was passed through an orange solution of **2a** (1−3 mM) in dichloromethane until the color turned to pale yellow (5−10 min). Evaporation of the solvent in a fast stream of hydrogen gave **2c′** in quantitative yield. - IR (KBr, cm^{-1}): 2105 m, 2049 w ν(IrH), 2007 m ν(CO), 1725 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 17.3 [d, $^2J_{PP}$ = 9.8 Hz, P *trans* to H], 18.0 [s, P *uncoord*], 28.0 [d, $^2J_{PP}$ = 9.8 Hz, P *cis* to H]. ^1H NMR (CD_2Cl_2): δ = −10.42 [ddd, $^2J_{PH}$ = 155.4 Hz, $^2J_{PH}$ = 19.0 Hz, $^2J_{HH}$ < 0.5 Hz, 1 H, IrH], −8.89 [ddd, $^2J_{PH}$ = 17.0 Hz, $^2J_{PH}$ = 17.0 Hz, $^2J_{HH}$ < 0.5 Hz, 1 H, IrH], 1.87−2.53 [m, 3 H, CH*H*$_a$], 3.0−3.6 [m, 3 H, CH*H*$_e$], 3.17, 3.44, 3.49 [s, 9 H, $COOCH_3$], 7.1−7.9 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 34.0−34.2, 37.3−38.3 [m, CH_2], 43.2−47.5 [m, CP], 51.7, 52.4, 52.6 [s, CH_3], 127.1−138.9 [m, C_6H_5], 173.20−173.84 [m, *C*$OOCH_3$], 186.08−186.22 [m, CO]. Λ_M (CH_2Cl_2, 25 °C, cm^2 Ω^{-1} mol^{-1}): 0.6.

Carbonyldihydrido[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Tetraphenylborate (3c). The amounts of 193.5 mg (0.20 mmol) of **3a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ in 50 mL of THF were used. Reaction time: 360 h. Since **3c** reacts with dichloromethane, the workup was changed. The THF was removed under reduced pressure, the remaining yellow solid was extracted with 25 mL of ice cold CH_2Cl_2, and NaCl and residual $NaBPh_4$ were separated by filtration. The solution was concentrated to 3 mL in volume at 0 °C, 50 mL of ice cold *n*-pentane was added, and the resultant yellow precipitate was filtered off, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure. Yield: 215.6 mg (86%). Mp: >148 °C (dec). IR (KBr, cm^{-1}): 2231 w ν(CN), 2088 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.8 [d, $^2J_{PP}$ = 9.1 Hz, P *trans* to H], 7.8 [t, $^2J_{PP}$ = 9.1 Hz, P *cis* to H]. ^1H NMR (CD_2Cl_2): δ = −8.57 [m,[31] 2 H, IrH], 2.80−3.39 [m, 6 H, CH_2], 6.77−7.78 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.5,

---

[33] AA′ part of an AA′MXX′ multiplet.

30.7 [d, $^1J_{PC}$ = 5.7, 5.7 Hz, CP], 35.8 [br. s, CH_2], 36.7 [t, $^2J_{PC}$ = 7.6 Hz, CH_2], 120.1−121.1 [m, CN], 122.2−136.5 [m, C_6H_5], 164.4 [q, $^1J_{CB}$ = 49.4 Hz, *ipso*- $B(C_6H_5)_4^-$]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 37.4. MS (FD), *m/z*: 933.4 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{70}H_{58}BIrON_3P_3$ (1253.20): C, 67.09; H, 4.66; N, 3.35. Found: C, 66.76; H, 4.82; N, 3.27.

Carbonyldihydrido[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Chloride (3c′). IR (CH_2Cl_2, cm^{-1}): 2083 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −9.8 [d, $^2J_{PP}$ = 9.1 Hz, P *trans* to H], 7.7 [t, $^2J_{PP}$ = 9.1 Hz, P *cis* to H].

Dicarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Tetraphenylborate (**1d**). As starting materials, the amounts of 178.6 mg (0.20 mmol) of **1a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ were used. Yield: 228.2 mg (95%). Mp: >145 °C (dec). IR (KBr, cm^{-1}): 2039 st, 1961 st ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.8 [s]. ^1H NMR ($CDCl_3$): δ = 1.79−1.97 [m, 3 H, CHH_a], 2.07−2.38 [m, 3 H, CHH_e], 2.69−2.82 [m, 3 H, HCP], 6.90−7.42 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.3 [d, $^1J_{PC}$ = 32.5 Hz, CP], 26.6 [s, CH_2], 121.8−136.3 [m, C_6H_5], 164.4 [q, $^1J_{CB}$ = 49.2 Hz, *ipso*-$B(C_6H_5)_4^-$], 180.8 [q, $^2J_{PC}$ = 22.1 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 31.2. MS (FAB), *m/z*: 885.2 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{68}H_{59}BIrO_2P_3$ (1204.2): C, 67.83; H, 4.94. Found: C, 67.38; H, 5.10.

Dicarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Chloride (**1d′**). After a solution of **1a** (178.6 mg, 0.20 mmol) in 50 mL of CH_2Cl_2 had been degassed by using the freeze−pump−thaw technique, CO (1.3 bar) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The solution was concentrated to 3 mL in volume, and 50 mL of *n*-pentane was added. The resulting off-white precipitate was filtered out, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure. Yield: 183.5 mg (99%). Mp: >180 °C (dec). IR (KBr, cm^{-1}): 2047 st, 1944 st ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.9 [s]. ^1H NMR ($CDCl_3$): δ = 2.15−2.35 [m, 3 H, CHH_a], 3.20−3.65 [m, 6 H, CHH_e, HCP], 6.95−7.34 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.8 [d, $^1J_{PC}$ = 32.3 Hz, CP], 26.7 [s, CH_2], 128.7−131.8 [m, C_6H_5], 173.0 [q, $^2J_{PC}$ = 32.3 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 29.1. MS (FAB), *m/z*: 884.9 [$M^+ - Cl^-$]. Calcd for $C_{44}H_{39}ClIrO_2P_3$ (920.4): C, 57.42; H, 4.27; Cl, 3.85. Found: C, 56.98; H, 4.39; Cl, 3.54.

Dicarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(I) Tetraphenylborate (**2d**). The amount of 213.4 mg (0.20 mmol) of **2a** was used as starting material. Yield: 245.3 mg (89%). Mp: >177 °C (dec). IR (KBr, cm^{-1}): 2049 st, 1982 st ν(CO), 1727 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −5.3 [s]. ^1H NMR (CD_2Cl_2): δ = 2.58−2.92 [m, 3 H, CHH_a], 3.32−3.48 [m, 3 H, CHH_e], 3.51 [s, 9 H, $COOCH_3$], 6.84−7.44 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 35.1 [br m, CH_2], 45.9−46.8 [m, CP], 53.6 [s, CH_3], 122.0−136.3 [m, C_6H_5], 164.4 [q, $^1J_{CB}$ = 49.4 Hz, *ipso*-$B(C_6H_5)_4^-$], 171.7 [s, $COOCH_3$], 178.2 [q, $^2J_{PC}$ = 23.6 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 43.9. MS (FD), *m/z*: 1059.1 [$M^+ - B(C_6H_5)_4^-$], 1031.2 [$M^+ - B(C_6H_5)_4^- - CO$]. Calcd for $C_{74}H_{65}BIrO_8P_3$ (1378.27): C, 64.49; H, 4.75. Found: C. 63.92; H, 5.10.

Dicarbonyl[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(I) Chloride (2d′). Carbon monoxide was passed through an orange solution of **2a** (1−3 mM) in dichloromethane until the color turned to pale yellow. Evaporation of the solvent in a fast stream of carbon monoxide gave **2d′** in quantitative yield. IR (KBr, cm^{-1}): 2043 st, 1971 st ν(CO), 1727 st ν($COOCH_3$). IR (CH_2Cl_2, cm^{-1}): 1991 st, 1973 m ν(CO), 1728 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −5.3 [s]. ^1H NMR (CD_2Cl_2): δ = 2.72−3.04 [m, 3 H, CHH_a], 3.24−3.47 [m, 3 H,CHH_e], 3.54 [s, 9 H, $COOCH_3$], 7.17−7.41 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 35.0 [s, CH_2], 46.1 [br m, CP], 53.6 [s, CH_3], 128.8−134.4 [m, C_6H_5], 171.7 [br m, $COOCH_3$]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 40.8.

Dicarbonyl[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Tetraphenylborate (3d). As starting materials, the amounts of 193.5 mg (0.20 mmol) of **3a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ were used. Reaction time: 100 h. Yield: 237.9 mg (93%). Mp: >187 °C (dec). IR (KBr, cm^{-1}): 2233 w ν(CN), 2064 st, 1998 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −10.3 [s]. ^1H NMR (CD_2Cl_2): δ = 3.09−3.45 [m, 6 H, CH_2], 6.87−7.58 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 30.5−30.9 [m, CP], 36.3 [br s, CH_2], 118.3 [br m, CN], 122.1−136.3 [m, C_6H_5], 164.5 [q, $^1J_{CB}$ = 49.3 Hz, *ipso*-$B(C_6H_5)_4^-$], 175.6 [q, $^2J_{PC}$ = 23.1 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 40.1. MS (FD), *m/z*: 960.4 [$M^+ - B(C_6H_5)_4^-$], 931.6 [$M^+ - B(C_6H_5)_4^- - CO$]. Calcd for $C_{71}H_{56}BIrN_3O_2P_3$ (1279.19): C, 66.67; H, 4.41; N, 3.28. Found: C, 66.12; H, 4.47; N, 3.32.

Dicarbonyl[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Chloride (3d′). IR (CH_2Cl_2, cm^{-1}): 2066 st, 1998 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −10.4 [s].

Carbonyl(ethene)[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Tetraphenylborate (1e). A 178.6 mg (0.20 mmol) amount of **1a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ were used as starting materials. Yield: 207.8 mg (86%). Mp: >150 °C (dec). IR (KBr, cm^{-1}): 2025 st-m, ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 21 °C): δ = −27.1 [br s]. ^1H NMR ($CDCl_3$, 21°C): δ = 2.02, 2.80 [AA′XX′, 4 H, C_2H_4], 2.07−2.38 [m, 6 H, CH_aH_e], 2.74−2.87 [m, 3 H, HCP], 6.84−7.44 [m, 50 C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21°C): δ = 20.1 [s, C_2H_4], 22.9 [d, $^1J_{PC}$ = 33.7 Hz, CP], 27.6 [s, CH_2], 121.8−136.3 [m, C_6H_5], 164.5 [q, $^1J_{CB}$ = 49.3 Hz, *ipso*-$B(C_6H_5)_4^-$], 181.1 [q, $^2J_{PC}$ = 22.0 Hz, CO]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 35.9. MS (FAB), *m/z*: 885.2 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{69}H_{63}BIrOP_3$ (1204.2): C, 68.82; H, 5.27. Found: C, 68.30; H, 5.20.

Carbonyl(ethene)[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(I) Tetraphenylborate (2e). The amounts of 213.4 mg (0.20 mmol) of **2a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ were applied. Yield: 228.8 mg (83%). Mp: >183 °C (dec). IR (KBr, cm^{-1}): 2043 st ν(CO), 1726 st ν($COOCH_3$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 21 °C): δ = −13.8 [br s]. ^1H NMR (CD_2Cl_2, 21 °C): δ = 2.10, 2.53 [AA′XX′, *N* = 7.9 Hz, 4 H, C_2H_4], 2.57 [*A*BX$_2$, $^2J_{HH}$ = 17.2, $^3J_{PH}$ = 32.9 Hz, 3 H, CH_aH_e], 3.27 [A*B*X$_2$, $^2J_{HH}$ = 17.2, $^3J_{PH}$ = 9.2 Hz, 3 H, CH_aH_e], 3.46 [s, 9 H, $COOCH_3$], 6.85−7.76 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 24.5 [s, C_2H_4], 34.4 [s, CH_2], 46.3 [d, $^1J_{PC}$ = 14.3 Hz, CP], 53.0 [s, CH_3], 121.5−136.2 [m, C_6H_5], 164.2 [q, $^1J_{CB}$ = 48.6 Hz, *ipso*-$B(C_6H_5)_4^-$], 171.5 [s, $COOCH_3$]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 44.3. MS (FAB), *m/z*: 1067.2 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{75}H_{69}BIrO_7P_3$ (1378.32): C, 65.36; H, 5.05. Found: C, 65.16; H, 5.32.

Carbonyl(ethene)[*cis,cis*-1,3,5-tricyano-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) Tetraphenylborate (3e). Application of 193.5 mg (0.20 mmol) of **3a** and 75.3 mg (0.22 mmol) of $NaBPh_4$ with a reaction time of 240 h gave a 220.0 mg (86%) yield. Mp: >183 °C (dec). IR (KBr, cm^{-1}): 2233 w ν(CN), 2055 st ν(CO). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 21 °C): δ = −19.1 [br s]. ^1H NMR (CD_2Cl_2, 21 °C): δ = 2.40, 2.91 [AA′XX′, *N* = 7.6 Hz, 4 H, C_2H_4], 3.15 [*A*BX$_2$, $^2J_{HH}$ = 15.9, $^3J_{PH}$ = 26.3 Hz, 3 H, CH_aH_e], 3.30 [A*B*X$_2$, $^2J_{HH}$ = 15.9, $^3J_{PH}$ = 7.6 Hz, 3 H, CH_aH_e], 6.85−7.34 (m, 50 H, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21°C): δ = 27.1 [s, C_2H_4], 31.1 [d, $^1J_{PC}$ = 18.1 Hz, CP], 35.8 [s, CH_2], 118.4 [s, CN], 121.0−136.0 [m, C_6H_5], 164.1 [q, $^1J_{CB}$ = 50.0 Hz, *ipso*-$B(C_6H_5)_4^-$]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 40.3. MS (FAB), *m/z*: 960.0 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{72}H_{60}BIrN_3OP_3$ (1279.24): C, 67.60; H, 4.73; N, 3.29. Found: C, 66.69; H, 4.99; N, 2.92.

Carbonylhydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) Tetraphenylborate (1f). To a suspension of **1a** (178.6 mg, 0.20 mmol) in 50 mL of benzene was added $NaBPh_4$ (75.3 mg, 0.22 mmol). After stirring of the reaction mixture at 85°C for 15 h, it was allowed to cool down to room temperature. After the solution had been separated from NaCl and residual $NaBPh_4$, the volume of the solution was reduced to 3 mL and 50 mL of *n*-pentane was added. The resulting off-white precipitate was filtered out, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure. Yield: 185 mg (79%). Mp: >155 °C (dec). IR (KBr, cm^{-1}): 2077 w ν(IrH), 2025 m ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -90.6$ [dd, $^2J_{PP} = 27.8$, Hz $^2J_{PP} = 16.3$ Hz, P *ortho*-C), -30.5 [dd, $^2J_{PP} = 16.3$ Hz, $^2J_{PP} = 16.3$ Hz, P *trans* to H], -26.6 [dd, $^2J_{PP} = 27.8$ Hz, $^2J_{PP} = 16.3$ Hz, P]. ^1H NMR ($CDCl_3$): $\delta = -7.81$ [dddd, $^2J_{PH} = 119.8$ Hz, $^2J_{PH} = 11.0$ Hz, $^2J_{PH} = 11.0$ Hz, $^4J_{HH} = 2.6$ Hz, 1 H, IrH], 1.84−3.35 [m, 9 H, C_6H_9], 9.95−7.95 [m, 49 H, C_6H_5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.0$, 21.7, 23.2 [d, $^1J_{PC} = 27.0$, 27.9, 31.6 Hz, CH], 26.0, 26.7, 27.2 [s, CH_2], 122.0−137.0 [m, C_6H_5], 164.5 (q, $^1J_{CB} = 50.0$ Hz, *ipso*-$B(C_6H_5)_4^-$]. Λ_M (CH_2Cl_2, 25 °C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 25.6. MS (FAB), *m/z*: 857.6 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{67}H_{59}BIrOP_3$ (1176.2): C, 68.42; H, 5.06. Found: C, 67.85; H, 5.49.

Carbonylhydrido[*cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]iridium(III) Tetraphenylborate (2f). To a solution of **2a** (213.4 mg, 0.20 mmol) in 100 mL of dichloromethane was added $NaBPh_4$ (75.3 mg, 0.22 mmol). After being stirred at room temperature for 15 h, the reaction mixture was separated from NaCl and residual $NaBPh_4$. The solution was concentrated in volume to 3 mL, 50 mL of *n*-pentane was added, and the resultant off-white precipitation was filtered out, washed three times with 10 mL of *n*-pentane each, and dried under reduced pressure. Yield: 224.1 mg (83%). Mp: >180 °C (dec). IR (KBr, cm^{-1}): 2085 w ν(IrH), 2048 st ν(CO), 1728 st $\nu(COOCH_3)$. IR ($CHCl_3$, cm^{-1}): 2086 w ν(IrH), 2056 st ν(CO), 1731 st $\nu(COOCH_3)$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -81.7$ [dd, $^2J_{PP} = 22.7$ Hz, $^2J_{PP} = 18.1$ Hz, P], -9.4 [dd, $^2J_{PP} = 18.1$ Hz, $^2J_{PP} = 18.1$ Hz, P *trans* to H], -6.2 [dd, $^2J_{PP} = 22.7$ Hz, $^2J_{PP} = 18.1$ Hz, P]. ^1H NMR (CD_2Cl_2): $\delta = -8.48$ [ddd, $^2J_{PH} = 130.0$ Hz, $^2J_{PH} = 14.2$ Hz, $^2J_{PH} = 10.4$ Hz, 1 H, IrH], 2.58−3.10 [m, 5 H, CH_2], 3.49, 3.57, 3.82 [s, 9 H, $COOCH_3$], 3.84−3.96 [m, 1 H, CH_2], 6.60−7.73 [m, 49 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 33.5−35.8 [m, CH_2], 40.3, 45.1, 48.9 [d, $^1J_{PC} = 23.1$, 12.1, 17.9 Hz, CP], 53.2, 53.3, 54.9 [s, CH_3], 122.0−136.7 [m, C_6H_5], 148.6 [ddd, $^2J_{PC} = 61.0$ Hz, $^2J_{PC} = 5.6$ Hz, $^2J_{PC} = 5.6$ Hz, IrC], 164.3 [q, $^1J_{CB} = 49.3$ Hz, *ipso*-$B(C_6H_5)_4^-$], 170.3 [m, CO], 170.0, 170.7, 170.8 [d, $^2J_{PC} = 6.5$, 5.5, 5.7 Hz, $COOCH_3$]. Λ_M (CH_2Cl_2, 25°C, $cm^2\ \Omega^{-1}\ mol^{-1}$): 43.7. MS (FD), *m/z*: 1031.9 [$M^+ - B(C_6H_5)_4^-$]. Calcd for $C_{73}H_{65}BIrO_7P_3$ (1350.26): C, 64.94; H, 4.85. Found: C, 64.35; H, 5.18.

X-ray Diffraction Study. Single crystals of **3d** and **2f** were grown from THF by slow evaporation of the solvent (**3d**) and by diffusion of ether into a THF solution of **2f**. Both crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer. Rotation photographs were taken, and a photosearch was performed to find a suitable reduced cell (graphite-monochromated Mo Kα radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-square methods. The final cell parameters and specific data collection parameters for **3d** and **2f** are collected in Table 3. Intensities were collected with the ω-scan technique with scan speed varying from 5 to 20° min^{-1} and 8 to 30° min^{-1} in ω, respectively. Scan ranges for **3d** and **2f** were 0.7 and 1.2, respectively. For both structures empirical absorption corrections were performed (ψ-scan, maximal and minimal transmissions 0.477 and 0.408 (**3d**) and 0.657 and 0.488 (**2f**)). All structures were solved by Patterson methods[34] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 1.012 and −0.686 $eÅ^{-3}$ (**3d**) and 1.393 and −0.650 $eÅ^{-3}$ (**2f**), respectively. The asymmetric unit of compound **3d** contains three molecules of THF. Final atomic coordinates are collected in the Supporting Information.

Table 3. Experimental Data for the X-ray Diffraction Studies of the Complexes 3d and 2f

	3d	2f
formula	$C_{83}H_{80}BIrN_3O_5P_3$	$C_{73}H_{65}BIrO_7P_3$
fw	1495.42	1350.17
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a, Å	16.577(3)	9.103(3)
b, Å	19.972(4)	26.834(6)
c, Å	21.355(4)	24.852(5)
β, deg		91.36(2)
V, $Å^3$	7070(2)	6069(3)
Z	4	4
d_{calcd}, g cm^{-3}	1.405	1.478
F(000)	3064	2744
cryst size, mm	0.40 × 0.30 × 0.20	0.20 × 0.10 × 0.10
μ(Mo Kα) mm^{-1}	2.012	2.336
diffractometer	Siemens P4	
2θ range, deg	4−50	4−50
temp, K	173(2)	173(2)
no. of data collcd	26488	18645
no. of unique data with $I \geq 2\sigma(I)$	10419	5672
no. of params refined	866	767
S	1.885	1.085
$R1^a$	0.052	0.032
$wR2^b$	0.115	0.066

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

Acknowledgment. We thank the DEGUSSA AG for a loan of $IrCl_3 \cdot xH_2O$ and the Fonds der Chemischen Industrie, Frankfurt/Main, Germany, and the University of Tübingen for financial support. Prof. W. C. Kaska, University of California, Santa Barbara, CA, and Prof. E. Lindner, University of Tübingen, for helpful discussions and support are also greatly acknowledged.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and data collection parameters (23 pages). Ordering information is given on any current masthead page.

OM960006Q

---

(34) Sheldrick, G. M. SHELXTL 5.03 program; University of Göttingen, Germany, 1995.