Synthesis and characterization of some new complexes of the Vaska-type *trans*-[IrX(CO)L_2] (X = Cl or I; L = phosphite, phosphinite or phosphonite) and the direction of dihydrogen addition to these species

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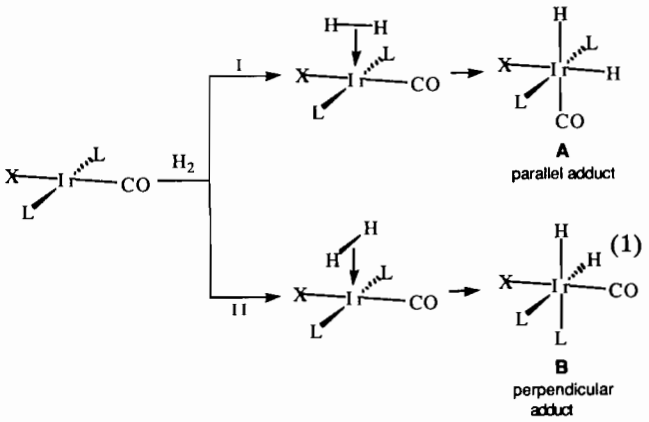
Abstract

A series of new Vaska-type complexes *trans*-[IrX(CO)L_2] (X = Cl, L = $P(OEt)Ph_2$ (**1**), $P(OEt)_2Ph$ (**2**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**3**), $P(OPr^i)_3$ (**4**), $P(OBu^n)_3$ (**5**); X = I, L = $P(OEt)Ph_2$ (**6**), $P(OEt)_2Ph$ (**7**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**8**), $P(OBu^n)_3$ (**9**) are prepared and characterized. In solution complex **8** undergoes slow cyclometallation to give [IrHI(CO){$P(O\text{-}o\text{-}C_6H_3Ph)(O\text{-}o\text{-}C_6H_4Ph)_2$}{$P(O\text{-}o\text{-}C_6H_4Ph)_3$}] (**10**). The oxidative addition of H_2 to **1–9** occurs stereospecifically with *cis* addition of H_2 parallel to the X–Ir–CO axis rather than perpendicular to the axis, leading to *cis, trans*-[$IrH_2X(CO)L_2$] with a *trans* disposition of the two L ligands. This direction of H_2 addition is not in agreement with a prior suggestion based on *ab initio* quantum chemical calculations.

Introduction

The oxidative addition of H_2 to square-planar d^8 iridium(I) complexes of the Vaska-type *trans*-[IrX(CO)L_2] has received intensive investigation [1]. The reaction generally proceeds via a concerted *cis* addition of H_2 along one of the two ligand axes, X–Ir–CO or L–Ir–L, leading to the formation of one of the two possible adducts with different stereochemistry, as shown by pathways I and II in eqn. (1). In the formation of **A** and **B**, the H_2 approaches the square-planar Ir(I) complex with its molecular axis parallel and perpendicular, respectively, to the X–Ir–CO symmetry axis. We will therefore refer to **A** and **B** as the 'parallel' and 'perpendicular' adducts.



(1)

The electronic and steric factors that control the stereochemistry of H_2 oxidative addition in eqn.(1) are not yet fully understood. Mapping out these factors is of fundamental importance and may help elucidate the course of homogeneous hydrogenation, hydroformylation and other catalytic reactions. In general, if X is a halide or pseudohalide and L is a phosphine or arsine, H_2 addition to *trans*-[IrX(CO)L_2] exclusively gives the parallel adduct **A** [2]. On the other hand, the perpendicular adduct **B** can be formed when X is a hydride, alkyl or aryl [3, 4]. For example, in the case of *trans*-[IrX(CO)$(PMe_3)_2$], the parallel and perpendicular adducts are formed, respectively, for X = Cl and X = Me, but for X = Ph, the perpendicular adduct is the kinetic product at −80 °C which upon warming to 25 °C rearranges to the parallel adduct via an H_2 reductive elimination/oxidative addition sequence [4].

In a related system, [IrX(CO)(dppe)], chosen to minimize complications due to differential steric effects associated with the two modes of addition for the case

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of *trans*-[IrX(CO)L_2], Eisenberg and co-workers have found that H_2 addition proceeds under kinetic control with initial stereoselective formation of the parallel adduct (P–Ir–CO axis) which subsequently isomerizes to yield the thermodynamically favored perpendicular adduct [5].

In a recent *ab initio* quantum chemical study of H_2 addition to *trans*-[IrX(CO)$(PR_3)_2$], Sargent and Hall [6] suggested that the direction of addition is controlled by the interactions between the ligands in the plane of addition and the concentrations of charge around the metal center. The electronic nature of both the X and PR_3 ligands is therefore crucial. Strongly electron-donating X ligands such as H^-, Me^- and Ph^- destabilize the transition state by contributing to the electronic repulsion between the ligands and the metal and so favor the perpendicular addition, whereas weakly electron-donating X ligands such as halides and pseudohalides encourage the parallel addition. The π-accepting ability of PR_3 ligands is also shown to be important in determining the direction of H_2 addition. It was suggested that H_2 addition to Vaska-type complexes *trans*-[IrCl(CO){$P(OR)_3$}$_2$] which contain π-accepting phosphite ligands might give perpendicular adducts.

Our longstanding interest [4, 7] in the oxidative addition of H_2 to transition-metal complexes led us to test this suggestion. In this paper, we describe the synthesis and characterization of a series of new Vaska-type complexes with phosphite and related ligands and the direction of H_2 addition to these species.

Results and discussion

Synthesis and characterization of new Vaska-type complexes trans-[IrX(CO)L_2] (X = Cl or I; L = phosphite, phosphinite or phosphonite)

The syntheses of Vaska-type complexes *trans*-[IrCl(CO)$(PR_3)_2$] have usually been carried out by reduction of Ir(III) or Ir(IV) precursors under CO, often in a refluxing high-boiling alcoholic solvent, followed by addition of phosphine [8]. The preparations are not particularly convenient and sometimes prove erratic and unreliable [9]. In other cases, substitution reactions involving *trans*-[IrCl(CO)$(PPh_3)_2$] or [IrCl$(CO)_3]_x$ are used [8c, 9, 10].

We recently reported a convenient and efficient synthetic route to these complexes starting from the readily available Ir(I) complex [IrCl(cod)]$_2$, as shown in eqn. (2) [11]. In contrast to previous methods, our method involved only room-temperature steps, but it was not clear whether the method would be applicable with phosphite and related ligands or other halides.

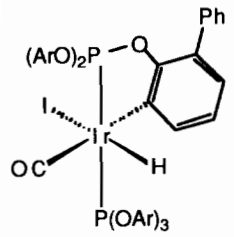
$$[IrCl(cod)]_2 \xrightarrow{PR_3} [IrCl(cod)(PR_3)_2] \xrightarrow{CO} [IrCl(CO)(PR_3)_2] \quad (2)$$

We now find that a series of Vaska-type complexes *trans*-[IrX(CO)L_2] in which X is Cl^- or I^- and L is a phosphite, phosphinite or phosphonite ligand can be synthesized according to a route analogous to that shown in eqn. (2). Treatment of [IrX(cod)]$_2$ with 4 equiv. of L, followed by bubbling a stream of CO through the resulting mixture, produce high yields of the new complexes *trans*-[IrX(CO)$(PR_3)_2$] (X = Cl, L = $P(OEt)Ph_2$ (**1**), $P(OEt)_2Ph$ (**2**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**3**), $P(OPr^i)_3$ (**4**), $P(OBu^n)_3$ (**5**); X = I, L = $P(OEt)Ph_2$ (**6**), $P(OEt)_2Ph$ (**7**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**8**), $P(OBu^n)_3$ (**9**)).

This method appears to be general for the preparation of Vaska-type complexes containing phosphite or related ligands, since we have encompassed a range of L ligands with different electronic and steric properties. However, cyclometallation can sometimes be a problem in the preparation of iodo complexes probably due to the higher basicity of the metal center. For example, complex **8** slowly undergoes cyclometallation in solution to give the six-coordinate Ir(III) complex [IrHI(CO){$P(O\text{-}o\text{-}C_6H_3Ph)(O\text{-}o\text{-}C_6H_4Ph)_2$}{$P(O\text{-}o\text{-}C_6H_4Ph)_3$}] (**10**). Accordingly, compound **8** is invariably contaminated with a small amount of **10** even upon quick isolation. Attempts to prepare *trans*-[IrI(CO){$P(OPr^i)_3$}$_2$] gave a complex mixture containing the desired product, the cyclometallation species and other uncharacterized species.

The IR and NMR spectroscopic data for the new complexes are given in 'Experimental'. In particular, the IR spectra of **1–9** show strong absorption bands at 1940–1990 cm^{-1} assignable to ν(CO) vibrations. The ν(CO) stretching frequencies are somewhat higher than those of the analogous phosphine complexes [8–11], reflecting the decreased Ir to CO π-backdonation in **1–9** due to the stronger π-accepting nature of the L ligands. The $^{31}P\{^1H\}$ NMR spectra show a single resonance as expected from a square-planar structure with a *trans* disposition of the two L ligands.

The IR spectrum of **10** shows a ν(Ir–H) band at 2052 cm^{-1}, and a ν(CO) band at 2065 cm^{-1} which is significantly higher than the ν(CO) stretching frequency (1994 cm^{-1}) for its Ir(I) precursor **8**, as expected from the decreased electron density on the Ir center and hence decreased Ir to CO π-backdonation in **10** upon cyclometallation. The $^{31}P\{^1H\}$ NMR spectrum of **10** shows two doublet resonances at δ 103.1 and 64.7 with a large $^2J_{PP}$ coupling constant of 855.3 Hz, indicating a *trans* disposition of the two inequivalent phosphorus donors. The higher field resonance is assigned to the unmetallated phosphite ligand by comparison with the ^{31}P NMR data of **18**, the H_2 adduct of **8** (*vide infra*),



10
(Ar = 2-phenylphenyl)

whereas the lower field resonance is assigned to the cyclometallated phosphite ligand and so corresponds to a chelation shift (Δ_R) of +38.4 ppm, which is consistent with the deshielding of the phosphorus atom in a five-membered chelate ring as shown below [12]. The ^{1}H NMR spectrum of **10** shows a doublet of doublets (δ −14.83, ^2J(HP) = 16.0, 13.2 Hz, 1H) in the hydride region. The small ^2J(HP) values confirm that the hydride ligand is *cis* to the two phosphorus donors. The relatively high field chemical shift of the hydride ligand suggests that it is *trans* to the iodide ligand [13], as is expected from thermodynamic considerations which favor orienting the strongly *trans*-influencing hydride ligand *trans* to the π-donating iodide ligand and *cis* to the other strongly *trans*-influencing CO ligand.

Oxidative addition of H_2 to trans-[IrX(CO)L_2]

The availability of a series of *trans*-[IrX(CO)L_2] complexes provides us with an opportunity for a systematic study of the effect of the structure of L on the direction of H_2 addition to these complexes. Complexes **1–9** react slowly (2–24 h) with H_2 (1 atm) in CH_2Cl_2 at room temperature. The reaction has been followed by IR and ^{1}H and ^{31}P NMR spectroscopy. In all cases, the reaction occurs stereospecifically with *cis* addition of H_2 along the X–Ir–CO axis (pathway I in eqn. (1)) to give the six-coordinate *cis* dihydride complexes *cis, trans*-[$IrH_2X(CO)L_2$] (X = Cl, L = $P(OEt)Ph_2$ (**11**), $P(OEt)_2Ph$ (**12**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**13**), $P(OPr^i)_3$ (**14**), $P(OBu^n)_3$ (**15**); X = I, L = $P(OEt)Ph_2$ (**16**), $P(OEt)_2Ph$ (**17**), $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (**18**), $P(OBu^n)_3$ (**19**)) in which the two L ligands maintain their *trans* disposition.

The reaction is slower than that with the Vaska-type complexes containing phosphine or arsine ligands studied previously [2], as is expected from the oxidative character of the reaction and the decreased electron density on the metal center in **1–9** which contain stronger π-accepting L ligands. The reaction is reversible since the resulting H_2 adducts **11–19** lose H_2 slowly *in vacuo* to regenerate **1–9** quantitatively, and undergo exchange with D_2 to give the corresponding dideuteride complexes probably via an H_2 reductive elimination/oxidative addition sequence. On heating under H_2, complexes **11–19** do not isomerize to the perpendicular adduct **B** (pathway II in eqn. (1)). This indicates that **11–19** are probably the thermodynamic products.

The stereochemistry of the H_2 adducts **11–19** is unequivocally assigned from the IR and ^{1}H and ^{31}P NMR spectroscopic data. In each case, the hydride region of the ^{1}H NMR spectrum shows a pair of triplets of doublets with *cis* ^2J(PP) (13–18 Hz) and ^2J(HH) (4–5 Hz) couplings, appropriate for the two inequivalent *cis* hydride ligands coupled to two equivalent *trans* phosphorus donors. The higher field hydride resonance is assigned to the hydride *trans* to the halide, whereas the lower field hydride resonance is assigned to the hydride *trans* to the CO, by analogy with the known [$IrH_2X(CO)(PR_3)_2$] complexes [2, 13].

The IR data of **11–19** further support the stereochemical assignment. In each case, the spectrum shows two ν(Ir–H) bands at 2090–2200 cm^{-1} and a ν(CO) band at 1960–2030 cm^{-1}. The ν(CO) absorption occurs at a significantly higher frequency than that in the precursor, as is expected from an increase in the formal oxidation state upon formation of the dihydride adduct. The ν(CO) band is shifted to a higher frequency in the corresponding dideuteride complex. For example, complex **12** exhibits a ν(CO) band at 1994 cm^{-1}, whereas the dideuteride, **12**-d_2, prepared from **2** and D_2, has a ν(CO) band at 2033 cm^{-1}. This shift of ν(CO) upon deuteration is diagnostic of a *trans* disposition of a CO ligand and a hydride ligand which causes a resonance interaction between the vibration states of the ν(Ir–H) and ν(CO) stretching motions [14].

Comparison between experiment and theory

The parallel adduct **A** (pathway I in eqn. (1)) is the sole product observed in H_2 addition to any of the complexes **1–9**. The perpendicular adduct **B** (pathway II in eqn. (1)) is never present, whether the reaction is examined at early reaction times or on completion. We were unable to find conditions which led to rearrangement of **A** to **B** or any other isomer. The simplest and most likely interpretation of the experimental results is that the parallel adduct **A** is both the kinetic and thermodynamic product of the reaction.

We need to exclude the possibility that **B** is first formed as the kinetic product, but subsequently rearranges to **A** as the thermodynamic product. Any such rearrangement would most likely proceed by the same mechanism that we found previously for the phosphine analogues: reductive elimination of H_2 from **B** to regenerate *trans*-[IrX(CO)L_2] via the reverse of pathway II in eqn. (1), followed by oxidative addition of H_2 to *trans*-[IrX(CO)L_2] to give **A** via pathway I of eqn. (1). If this were the case, we would have detected isomer **B** at early reaction times.

Another possible mechanism for rearrangement of **B** to **A** involves dissociation of a ligand (X, L or CO) to give a fluxional five-coordinate species followed by readdition of the ligand. We consider CO dissociation to be unlikely, since it should be the most strongly bound ligand. Facile dissociation of X and L ligands would result in rapid intermolecular exchange of these ligands between complexes with different X and L ligands. To probe this possibility, a mixture of *cis,trans*-$[IrH_2Cl(CO)\{P(OEt)_2Ph\}_2]$ (**12**) and *cis,trans*-$[IrH_2I(CO)\{P(OEt)Ph_2\}_2]$ (**16**) in CD_2Cl_2 was studied by ^1H and ^{31}P NMR spectroscopy. Products resulting from exchange of X or L ligands were not noticeable in 2 h at room temperature. Only after 48 h was a small amount of *cis,trans*-$[IrH_2I(CO)\{P(OEt)_2Ph\}_2]$ (**17**) and *cis,trans*-$[IrH_2Cl(CO)\{P(OEt)Ph_2\}_2]$ (**11**) observed in the mixture, but no mixed L products were observed. Very similar results were observed between complexes with other L ligands. The results require that exchange of L ligands does not occur and that exchange of halide ligands occurs only very slowly. This makes it unlikely that dissociation of X or L ligands is a pathway for rearrangement of **B** to **A**, although we cannot carry out this experiment on the unavailable perpendicular adduct **B**.

Finally, we cannot exclude the possibility that the perpendicular adduct **B** is indeed the kinetically favored product in H_2 addition to **1–9**, but it is thermodynamically unstable with respect to the Ir(I) complex and free H_2 and so no macroscopic amounts of **B** are ever able to build up. This seems unlikely, however, because **B** has been observed to be stable with respect to the Ir(I) complex and free H_2 in a number of systems previously studied [3, 4] and we cannot see any particular reasons why **B** should be unstable in the systems studied here.

The parallel adducts **11–19** therefore seem to be both the kinetic and thermodynamic products. Our results are not in accord with the suggestion, mentioned in 'Introduction', that isomer **B** should be the kinetic product for Vaska-type complexes containing phosphite ligands. It is noteworthy that in the cyclometallation reaction of **8**, the C–H bond also approaches the square-planar Ir(I) complex with its axis parallel to the I–Ir–CO axis, leading to the formation of **10** with a *trans* disposition of the two phosphorus donors.

Conclusions

We have synthesized a series of new Vaska-type complexes *trans*-$[IrX(CO)L_2]$ (X = Cl or I; L = phosphite, phosphinite or phosphonite) from the readily available $[IrX(cod)]_2$. The oxidative addition of H_2 to these complexes proceeds stereospecifically with *cis* addition of H_2 parallel to the X–Ir–CO axis, leading to dihydride products *cis,trans*-$[IrH_2X(CO)L_2]$ in which the two L ligands maintain their *trans* disposition. This direction of H_2 addition is not in agreement with a prior suggestion based on *ab initio* quantum chemical calculations. The reaction of H_2 with **1–9** is slower than that with the Vaska-type complexes containing phosphine or arsine ligands studied previously, as is expected from the oxidative character of the reaction and the decreased electron density on the metal center in **1–9** which contain stronger π-accepting L ligands.

Experimental

General procedures

All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, heptane and tetrahydrofuran were distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over 4-Å molecular sieves. All chemicals were purchased from Aldrich Co. and used without further purification.

^1H and ^{31}P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers in CD_2Cl_2; ^1H chemical shits were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer.

Preparations

$[IrCl(cod)]_2$ [15], $[IrI(cod)]_2$ [16] and $P(O\text{-}o\text{-}C_6H_4Ph)_3$ [17] were prepared according to the literature methods.

trans-Chlorocarbonylbis(ethyl diphenylphosphinite)iridium(I) (trans-[IrCl(CO)\{P(OEt)Ph$_2$\}$_2$] (1))

To a suspension of $[IrCl(cod)]_2$ (282 mg, 0.42 mmol) in hexane (40 ml) was added dropwise a solution of $P(OEt)Ph_2$ (363 μl, 1.68 mmol) in hexane (30 ml) over 1 h. The mixture was filtered to remove a small amount of insoluble pale yellow solid. A stream of CO was then bubbled through the orange filtrate for 40 min. The solvent volume was reduced *in vacuo* to *c.* 5 ml. The resulting yellow solid was filtered off, washed with heptane (3 × 10 ml), and dried *in vacuo*. Yield 475 mg (79%). *Anal.* Calc. for $C_{29}H_{30}ClIrO_3P_2$: C, 48.64; H, 4.22. Found: C, 48.81; H, 4.27%. IR (Nujol): ν(CO) 1962 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.81 (m, 8H, Ph), 7.44 (m, 12H, Ph), 4.28 (td, $^2J(HH) = 7.0$ Hz, $^2J(HP) = 3.6$ Hz, 4H, CH_2), 1.39 (t, $^2J(HH) = 7.0$ Hz, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 99.26.

trans-Chlorocarbonylbis(diethyl phenylphosphonite)iridium(I)
(trans-[IrCl(CO){P(OEt)$_2$Ph}$_2$] (2))

To a suspension of [IrCl(cod)]$_2$ (300 mg, 0.45 mmol) in hexane (40 ml) was added dropwise a solution of P(OEt)$_2$Ph (343 μl. 1.80 mmol) in hexane (30 ml) over 1 h. The resulting orange–yellow solution was treated with a stream of CO for 40 min and then filtered to give a yellow solution. The solution was concentrated *in vacuo* to *c.* 5 ml and cooled to −78 °C, resulting in the precipitation of a yellow solid, which was filtered off, washed with cold heptane (3×5 ml), and dried *in vacuo*. Yield 456 mg (78%). *Anal.* Calc. for $C_{21}H_{30}ClIrO_5P_2$: C, 38.68; H, 4.64. Found: C, 38.82; H, 4.64. IR (Nujol): ν(CO) 1968 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.83 (m, 4H, Ph), 7.48 (m, 6H, Ph), 4.12 (m, 8H, CH_2), 1.32 (t, ^2J(HH) = 7.0 Hz, 12H, CH_3). ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 69.12.

trans-Chlorocarbonylbis(tris(2-phenylphenyl)phosphite)iridium(I)
(trans-[IrCl(CO){P(O-o-C$_6$H$_4$Ph)$_3$}$_2$] (3))

A solution of [IrCl(cod)]$_2$ (140 mg, 0.21 mmol) and P(O-*o*-C$_6$H$_4$Ph)$_3$ (460 mg, 0.86 mmol) in CH_2Cl_2/hexane (1:1 vol./vol., 30 ml) was stirred for 15 min. The resulting orange–yellow solution was treated with a stream of CO for 1 h and then filtered to give a yellow solution. The solution was concentrated *in vacuo* to *c.* 0.2 ml and heptane (20 ml) added, resulting in the precipitation of a yellow solid. After cooling to −78 °C, the solid was filtered off, washed with cold heptane (2×5 ml), and dried *in vacuo*. Yield 222 mg (80%). *Anal.* Calc. for $C_{73}H_{54}ClIrO_7P_2$: C, 65.78; H, 4.08. Found: C, 65.63; H, 4.24. IR (Nujol): ν(CO) 1993 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.4–6.8 (m, 54H, Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 103.00.

trans-Chlorocarbonylbis(triisopropyl phosphite)iridium(I)
(trans-[IrCl(CO){P(OPr^i)$_3$}$_2$] (4))

To a suspension of [IrCl(cod)]$_2$ (160 mg, 0.24 mmol) in hexane (40 ml) was added dropwise a solution of P(OPr^i)$_3$ (251 μl, 1.00 mmol) in hexane (30 ml) over 1 h. The resulting orange–yellow solution was treated with a stream of CO for 1 h and then filtered. The yellow filtrate was concentrated *in vacuo* to *c.* 2 ml and chromatographed on an alumina (neutral, activity I) column (10×1 cm). After elution of cod with hexane, the yellow band of the product was eluted with CH_2Cl_2. Evaporation of the yellow eluent gave a yellow oily product, which is spectroscopically pure. Yield 110 mg (69%). IR (thin film prepared by evaporation of a drop of the CH_2Cl_2 solution on a NaCl plate): ν(CO) 1994 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 4.99 (m, 6H, CH), 1.32 (br d, ^2J(HH) = 6.2 Hz, 36H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 115.36.

trans-Chlorocarbonylbis(tri-n-butyl phosphite)iridium(I)
(trans-[IrCl(CO){P(OBu^n)$_3$}$_2$] (5))

This complex was prepared analogously to **4** by using [IrCl(cod)]$_2$ (160 mg, 0.24 mmol) and P(OBu^n)$_3$ (264 μl, 0.98 mmol) and was isolated as a yellow oil. Yield 131 mg (73%). IR (thin film): ν(CO) 1993 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 4.12 (m, 12H, OCH_2), 1.67 (qn, ^2J(HH) = 7.0 Hz, 12H, CH_2), 1.41 (sextet, ^2J(HH) = 7.4 Hz, 12H, CH_2), 0.93 (t, ^2J(HH) = 7.3 Hz, 18H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 85.42.

trans-Iodocarbonylbis(ethyl diphenylphosphinite)iridium(I)
(trans-[IrI(CO){P(OEt)Ph$_2$}$_2$] (6))

To a suspension of [IrI(cod)]$_2$ (162 mg, 0.19 mmol) in hexane (20 ml) was added dropwise a solution of P(OEt)Ph$_2$ (164 μl, 0.76 mmol) in hexane (15 ml) over 1 h. A stream of CO was then bubbled through the resulting orange–yellow suspension for 40 min. The yellow solid was filtered off, washed with hexane (3×10 ml), and dried *in vacuo*. Yield 282 mg (92%). *Anal.* Calc. for $C_{29}H_{30}IIrO_3P_2$: C, 43.13; H, 3.74. Found: C, 43.31; H, 3.62%. IR (Nujol): ν(CO) 1952 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.80 (m, 8H, Ph), 7.48 (m, 12H, Ph), 4.09 (m, 4H, CH_2), 1.43 (t, ^2J(HH) = 7.0 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 83.31.

trans-Iodocarbonylbis(diethyl phenylphosphonite)iridium(I)
(trans-[IrI(CO){P(OEt)$_2$Ph}$_2$] (7))

To a suspension of [IrI(cod)]$_2$ (188 mg, 0.22 mmol) in hexane (20 ml) was added dropwise a solution of P(OEt)Ph$_2$ (169 μl, 0.88 mmol) in hexane (15 ml) over 1 h. The resulting orange solution was treated with a stream of CO for 40 min, evaporated *in vacuo* to *c.* 5 ml and cooled to −78 °C. The yellow solid was filtered off, washed with cold heptane (3×5 ml), and dried *in vacuo*. Yield 216 mg (66%). *Anal.* Calc. for $C_{21}H_{30}IIrO_5P_2$: C, 33.92; H, 4.07. Found: C, 34.06; H, 4..09%. IR (Nujol): ν(CO) 1943 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.80 (m, 4H, Ph), 7.48 (m, 6H, Ph), 4.15 (m, 8H, CH_2), 1.36 (t, ^2J(HH) = 6.8 Hz, 12H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 103.86.

trans-Iodocarbonylbis(tris(2-phenylphenyl) phosphite)iridium(I)
(trans-[IrI(CO){P(O-o-C$_6$H$_4$Ph)$_3$}$_2$] (8))

This complex was prepared analogously to **3** by using [IrI(cod)]$_2$ (126 mg, 0.15 mmol) and P(O-*o*-C$_6$H$_4$Ph)$_3$ (325 mg, 0.60 mmol) and was isolated as a yellow solid. Yield 174 mg (83%). *Anal.* Calc. for $C_{73}H_{54}IIrO_7P_2$: C,

61.56; H, 3.82. Found: C, 61.45; H, 3.95%. IR (Nujol): ν(CO) 1994 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.4–6.8 (m, 54 H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 103.41.

trans-Iodocarbonylbis(tri-n-butyl phosphite)iridium(I) (trans-[IrI(CO){P(OBu^n)$_3$}$_2$] (9))

This complex was prepared analogously to **4** by using $[IrI(cod)]_2$ (188 mg, 0.22 mmol) and $P(OBu^n)_3$ (243 μl, 0.90 mmol) and was isolated as a yellow oil. Yield 138 mg (74%). IR (thin film): ν(CO) 1997 cm^{-1}. ^1H NMR (CD_2Cl_2: δ 4.08 (m, 12H, OCH_2), 1.67 (qn, ^2J(HH) = 7.0 Hz, 12 H, CH_2), 1.41 (sextet, ^2J(HH) = 7.4 Hz, 12H, CH_2), 0.93 (t, ^2J(HH) = 7.3 Hz, 18H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 120.99.

[IrHI(CO){P(O-o-C$_6$H$_3$Ph)(O-o-C$_6$H$_4$Ph)$_2$}{P(O-o-C$_6$H$_4$Ph)$_3$}] (10)

$[IrI(CO)\{P(O\text{-}o\text{-}C_6H_4Ph)_3\}_2]$ (**8**) (100 mg. 0.07 mmol) was dissolved in acetone (20 ml) and stirred at room temperature for 3 days. The solvent was evaporated *in vacuo* to *c*. 0.1 ml. Addition of heptane (20 ml) afforded a yellow solid. After cooling to −78 °C, the solid was filtered off, washed with cold heptane (2×5 ml), and dried *in vacuo*. Yield 92 mg (92%). *Anal.* Calc. for $C_{73}H_{54}IIrO_7P_2$: C, 61.56; H, 3.82. Found: C, 61.69; H, 3.70. IR (Nujol): ν (Ir–H) 2152 cm^{-1}; ν(CO) 2065 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.2–6.6 (m, 53H, Ph), −14.83 (dd, ^2J(HP) = 16.0, 13.2 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 103.10 (d, ^2J(PP) = 855.3 Hz, 1 P), 64.66 (d, ^2J(PP) = 855.3 Hz, 1 P).

cis,trans-Dihydridochlorocarbonylbis(ethyl diphenylphosphinite)iridium(III) (cis,trans-[IrH$_2$Cl(CO){P(OEt)Ph$_2$}$_2$] (11))

A solution of $[IrCl(CO)\{P(OEt)Ph_2\}_2]$ (**1**) (10 mg) in CD_2Cl_2 (0.4 ml) at 25 °C in a septum-capped 5-mm NMR tube was purged with H_2 for 5 min and then kept under H_2 (1 atm) for 2 h. The solution turned from yellow to colorless with the formation of **11**. IR (thin film): ν(Ir–H) 2183, 2092 cm^{-1}; ν(CO) 1969 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.87 (m, 4H, Ph), 7.78 (m, 4H, Ph), 7.40 (m, 12H, Ph), 3.99 (m, 4H, CH_2), 1.35 (t, ^2J(HH) = 6.9 Hz, 6H, CH_3), −7.77 (td, ^2J(HP) = 17.4 Hz, ^2J(HH) = 4.9 Hz, 1H, Ir–H), −18.78 (td, ^2J(HP) = 14.5 Hz, ^2J(HH) = 4.9 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 90.32.

Other H_2 adducts **12–19** were similarly prepared from the reactions of **2–9** with H_2. The various lengths of time required for the completion of the reactions and spectroscopic data of the adducts are reported below.

cis,trans-Dihydridochlorocarbonylbis(diethyl phenylphosphonite)iridium(III) (cis,trans-[IrH$_2$Cl(CO){P(OEt)$_2$Ph}$_2$] (12))

Prepared from the reaction of **2** with H_2 for 4 h. IR (thin film): ν(Ir–H) 2194, 2095 cm^{-1}; ν(CO) 1994 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.80 (m, 4H, Ph), 7.48 (m, 6H, Ph), 3.8–4.2 (m, 8H, CH_2), 1.34 (t, ^2J(HH) = 6.6 Hz, 6H, CH_3), 1.33 (t, ^2J(HH) = 6.6 Hz, 6H, CH_3), −8.53 (td, ^2JHP) = 17.2 Hz, ^2J(HH) = 4.9 Hz, 1H, Ir–H), −19.09 (td, ^2J(HP) = 14.4 Hz, ^2J(HH) = 4.9 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 93.92.

cis,trans-Dihydridochlorocarbonylbis(tri(2-phenylphenyl) phosphite)iridium(III) (cis,trans-[IrH$_2$Cl(CO){P(O-o-C$_6$H$_4$Ph)$_3$}$_2$] (13))

Prepared from the reaction of **3** with H_2 for 24 h. IR (Nujol): ν(Ir–H) 2185, 2120 cm^{-1}; ν(CO) 2029 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5–6.8 (m, 54H, Ph), −9.69 (td, ^2J(HP) = 18.2 Hz, ^2J(HH) = 4.5 Hz, 1H, Ir–H), −19.12 (td, ^2J(HP) = 16.4 Hz, ^2J(HH) = 4.5 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 86.36.

cis,trans-Dihydridochlorocarbonylbis(triisopropyl phosphite)iridium(III) (cis,trans-[IrH$_2$Cl(CO){P(OPr^i)$_3$}$_2$] (14))

Prepared from the reaction of **4** with H_2 for 12 h. IR (thin film): ν(Ir–H) 2206, 2100 cm^{-1}; ν(CO) 2001 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.78 (m, 6H, CH), 1.30 (dt, ^2J(HH) = 6.4 Hz, ^4J(PH) = 3.7 Hz, 36H, CH_3), −8.74 (td, ^2J(HP) = 18.2 Hz, ^2J(HH) = 5.4 Hz, 1H, Ir–H), −19.65 (td, ^2J(HP) = 15.2 Hz, ^2J(HH) = 5.4 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 90.62.

cis,trans-Dihydridochlorocarbonylbis(tri-n-butyl phosphite)iridium(III) (cis,trans-[IrH$_2$Cl(CO){P(OBu^n)$_3$}$_2$] (15))

Prepared from the reaction of **5** with H_2 for 10 h. IR (thin film): ν(Ir–H) 2193, 2098 cm^{-1}; ν(CO) 2000 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.00 (m, 12H, OCH_2), 1.65 (qn, ^2J(HH) = 6.9 Hz, 12H, CH_2), 1.41 (sextet, ^2J(HH) = 7.3 Hz, 12H, CH_2), 0.93 (t, ^2J(HH) = 7.3 Hz, 18H, CH_3), −9.05 (td, ^2J(HP) = 18.2 Hz, ^2J(HH) = 5.5 Hz, 1H, Ir–H), −19.57 (td, ^2J(HP) = 15.7 Hz, ^2J(HH) = 5.5 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 95.46.

cis,trans-Dihydridoiodocarbonylbis(ethyl diphenylphosphinite)iridium(III) (cis,trans-[IrH$_2$I(CO){P(OEt)Ph$_2$}$_2$] (16))

Prepared from the reaction of **6** with H_2 for 2 h. IR (thin film): ν(Ir–H) 2183, 2092 cm^{-1}; ν(CO) 1992 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.85 (m, 4H, Ph), 7.75 (m, 4H, Ph), 7.44 (m, 12H, Ph), 3.96 (m, 4H, CH_2), 1.34 (t, ^2J(HH) = 6.9 Hz, 6H, CH_3), −9.53 (td, ^2J(HP) = 17.2 Hz, ^2J(HH) = 4.8 Hz, 1H, Ir–H), −16.04 (td, ^2J(HP) = 13.8 Hz, ^2J(HH) = 4.8 Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 87.33.

cis,trans-Dihydridoiodocarbonylbis(diethyl phenylphosphonite)iridium(III)
(cis,trans-[$IrH_2I(CO)\{P(OEt)_2Ph\}_2$] (17))

Prepared from the reaction of **7** with H_2 for 3 h. IR (neat film): ν(Ir–H) 2174, 2098 cm^{-1}; ν(CO) 1998 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.75 (m, 4H, Ph), 7.45 (m, 6H, Ph), 3.8–4.1 (m, 8H, CH_2), 1.34 (t, $^2J(HH) = 6.7$ Hz, 6H, CH_3), 1.32 (t, $^2J(HH) = 6.7$ Hz, 6H, CH_3), −10.28 (td, $^2J(HP) = 16.2$ Hz, $^2J(HH) = 4.8$ Hz, 1H, Ir–H), −16.57 (td, $^2J(HP) = 13.3$ Hz, $^2J(HH) = 4.8$ Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 107.07.

cis,trans-Dihydridoiodocarbonylbis(tris(2-phenylphenyl) phosphite)iridium(III)
(cis,trans-[$IrH_2I(CO)\{P(O\text{-}o\text{-}C_6H_4Ph)_3\}_2$] (18))

Prepared from the reaction of **8** with H_2 for 15 h. IR (thin film): ν(Ir–H) 2188, 2127 cm^{-1}; ν(CO) 2033 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.4–6.7 (m, 54H, Ph), −11.26 (td, $^2J(HP) = 18.8$ Hz, $^2J(HH) = 4.7$ Hz, 1H, Ir–H), −16.55 (td, $^2J(HP) = 15.5$ Hz, $^2J(HH) = 4.7$ Hz, 1H, Ir–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 78.38.

cis,trans-Dihydridoiodocarbonylbis(tri-n-butyl phosphite)iridium(III)
(cis,trans-[$IrH_2I(CO)\{P(OBu^n)_3\}_2$] (19))

Prepared from the reaction of **9** with H_2 for 12 h. IR (thin film): ν(Ir–H) 2176, 2101 cm^{-1}; ν(CO) 2003 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.97 (m, 12H, OCH_2), 1.66 (qn, $^2J(HH) = 7.5$ Hz, 12H, CH_2), 1.42 (sextet, $^2J(HH) = 7.5$ Hz, 12H, CH_2), 0.94 (t, $^2J(HH) = 7.3$ Hz, 18H, CH_3), −10.89 (td, $^2J(HP) = 18.2$ Hz, $^2J(HH) = 4.5$ Hz, 1H, Ir–H), −17.02 (td, $^2J(HP) = 14.6$ Hz, $^2J(HH) = 4.5$ Hz, 1H, Ir–H). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2: δ 89.79.

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