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Hydride elimination from an iridium(III) alkoxide complex: a case in which a vacant *cis* coordination site is not required

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday in recognition of his outstanding contributions to organometallic chemistry.

Abstract

Decomposition of *trans*-$HIr(OCH_3)(C_6H_5)(PMe_3)_3$ (**2**) formed by oxidative addition of methanol to $Ir(C_6H_5)(PMe_3)_3$ (**1**) was studied in detail. Thermolysis of this complex yields *trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**2**) and formaldehyde. Complex **2** is less stable than its two dihydrido isomers, showing that it is the kinetic product of this reaction. The elimination process follows first order kinetics and exhibits a kinetic isotope effect of $k_H/k_D = 3.2 \pm 0.2$, the observed activation parameters are $\Delta H^{\ddagger}_{obs} = 8.3 \pm 1.0$ kcal mol^{-1}; $\Delta S^{\ddagger}_{obs} = -34 \pm 3.5$ e.u. and $\Delta G^{\ddagger}_{obs\,(298\ K)} = 18.4 \pm 2.0$ kcal mol^{-1}. Catalysis by methanol was observed. The process does not involve a vacant coordination site *cis* to the coordinated methoxide, as shown by labeling experiments and by the lack of exchange with $P(CD_3)_3$. Thus, in this case the *β-hydride elimination process does not follow the usual pathway*. A mechanism, in which following methoxide dissociation, C–H cleavage of free methanol takes place, is suggested.

Keywords: Hydride; Iridium; Elimination; Alkoxide; Mechanism; O–H activation

1. Introduction

Late transition metal alkoxides are suggested as intermediates in various catalytic reactions, such as carbalkoxylation of olefins and alkyl halides, hydrogenation of carbon monoxide, ketones and aldehydes, dehydrogenation of alcohols, transesterification and hydrogen transfer from alcohols to ketones. Decomposition of late transition metal alkoxides to metal hydrides and the corresponding carbonyl compounds is probably the most commonly observed reactivity mode of these complexes [1]. This process is generally believed to involve cleavage of a β-C–H bond of the coordinated alkoxide, with concomitant formation of hydride and η^2-aldehyde (or ketone) ligands, requiring an empty *cis* coordination site [2–4]. We have shown previously [5] that water and alcohols oxidatively add to electron rich Ir(I) complexes and have studied in detail the mechanism of β-H elimination from *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ [2b]. We now report [6] that decomposition of saturated phenyl Ir(III) hydrido alkoxide complex, obtained by oxidative addition of methanol does not take place by the commonly accepted mechanism. Recently, a *binuclear* mechanism involving alkoxide complexes was demonstrated [7].

2. Results and discussion

Oxidative addition of methanol to $Ir(C_6H_5)(PMe_3)_3$ (**1**) [8] in benzene at room temperature leads to quantitative formation of the hydrido alkoxy complex *trans*-$HIr(OCH_3)(C_6H_5)(PMe_3)_3$ (**2**) (Eq. (1)). Its ^{1}H-NMR resonance at 4.12 ppm is typical of protons α to oxygen in late transition metal alkoxides [9]. Water oxidative addition to **1** in THF leads to the analogous, spectroscopically similar hydrido–hydroxo complex *trans*-$HIr(OH)(C_6H_5)(PMe_3)_3$ (**3**). The hydroxide ligand gives rise to a signal at −3.06 ppm in ^{1}H-NMR, which is typical of hydroxo complexes [1]. Complex **3** is con-

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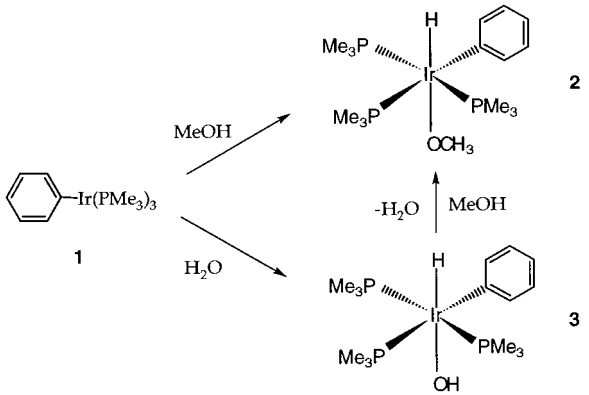


Scheme 1. O–H oxidative addition to complex **1**.

verted to **2** by methanol (Scheme 1). The hydride chemical shifts of **2** (− 25.13 ppm) and of **3** (− 23.99 ppm) point to its position *trans* to the methoxide, which is the only weak σ-donor in **2** [10]. Complexes **2** and **3** are uncommon examples of monomeric hydrido–hydroxo and –alkoxo complexes obtained by direct oxidative addition [1,5,11].

Complex **2** cleanly decomposes to the dihydride complex *trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**4**) and formaldehyde (Eq. (1)). The presence of formaldehyde and its oligomers was verified by the chromotropic acid test [12]. Complex **4** was unambiguously characterized spectroscopically. *Trans*-dihydride complexes are uncommon due to the large *trans* effect of the hydride ligand.

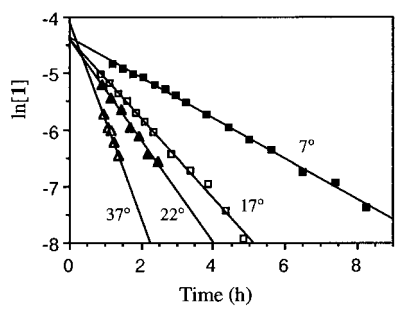


Fig. 1. First order plots for reaction 1. [MeOH] = 98.4 mM; $[\mathbf{1}]_0$ = 12.3 mM.

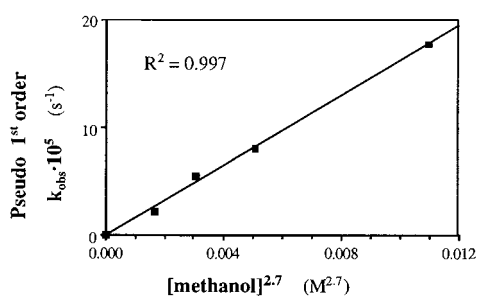
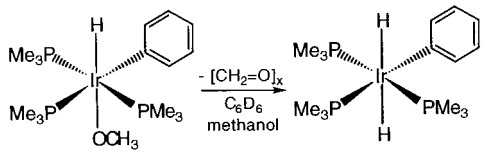


Fig. 2. Dependence of reaction 1 on the methanol concentration in C_6D_6 at 22°C. $[\mathbf{2}]_0$ = 12.3 mM.

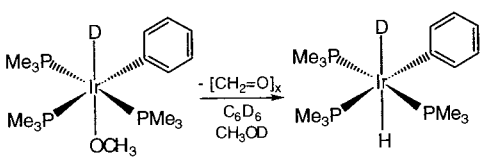
Trans dihydride iridium complexes have been reported [13].



(1)

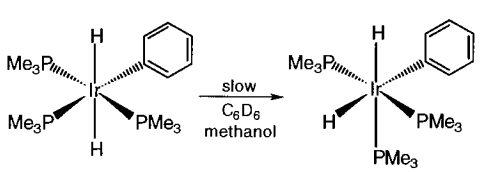
Thermolysis kinetics in C_6D_6 in the presence of methanol (98.4 mM) followed by $^{31}P\{^1H\}$-NMR show that reaction 1 is first order in **2** from 7 to 37°C (Fig. 1). Interestingly, reaction 1 is catalyzed by methanol (Fig. 2). A best fit to the data is obtained with an order of 2.7 in methanol. The activation parameters, $\Delta H^{\ddagger}_{obs} = 8.3 \pm 1.0$ kcal mol^{-1}; $\Delta S^{\ddagger}_{obs} = -34 \pm 3.5$ e.u. and $\Delta G^{\ddagger}_{obs\,(298\ K)} = 18.4 \pm 2.0$ kcal mol^{-1} (Fig. 2), differ substantially from those obtained for β-hydride elimination from the analogous chloro complex *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (**5**) ($\Delta H^{\ddagger}_{obs} = 24.1$ kcal mol^{-1}; $\Delta S^{\ddagger}_{obs} = 0.6$ e.u.; $\Delta G^{\ddagger}_{obs(298\ K)} = 23.9$ kcal mol^{-1}) [2b]. Comparing the decompositions of **2** and of *mer-trans*-$DIr(OCD_3)(C_6H_5)(PMe_3)_3$ (**2a**) at 22°C (in $C_6D_6 + CD_3OD$), yields $k_{obs}(\mathbf{2})/k_{obs}(\mathbf{2a}) = 3.2 \pm 0.2$ at 22°C, implying that the C–H bond cleavage is involved in the rate determining step or precedes it.

Reaction 2 yields only **4a**. Integration of its hydrides (vs. the $P(CH_3)_3$ protons) amounted to 50 ± 2% of that expected for the non-deuterated **2** (long relaxation delays of 10 s were given to allow accurate integration), suggesting that the Ir–D bond of **2a** is not involved in its decomposition, and that the C–H cleavage is irreversible (Eq. (2)).

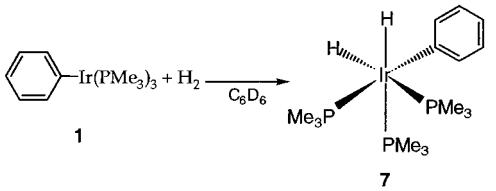


(2)

The *mer-trans* dihydride complex **4** is undoubtedly the kinetic product of reaction 1. It is the least stable isomer of this complex and isomerizes slowly under the conditions of reaction 1 (or in neat C_6D_6) to *mer-cis*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**6**, Eq. (3)). The third isomer, *fac*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**7**) was prepared separately from **1** and hydrogen in benzene and was found stable under the conditions of reaction 1, even at elevated temperatures.



(3)



(4)

The classic β-hydride elimination mechanism predicts incorporation of the eliminated β-H into positions *cis* to that of the methoxide. As **4** is the kinetic product of reaction 1, the *trans* H–Ir–H geometry of **4** provides clear evidence that *the decomposition of* **2** *does not follow that pathway*. Additionally, the reported β-H eliminations require a vacant coordination site *cis* to the alkoxide prior to the C–H cleavage [2–4], unlike our observations for reaction 1. Thermolysis of **2** in the presence of a tenfold excess of $P(CD_3)_3$ resulted in no incorporation of this phosphine into the product, indicating that phosphine dissociation does not take place. The decompositions of the deuterium labeled **2a** and *mer-trans*-$DIr(OCH_3)(C_6H_5)(PMe_3)_3$ (**2b**) showed no incorporation of deuterium into the phenyl ring of the product. Thus, a pentacoordinate intermediate having an η^2-coordinated benzene is not formed during reaction 1.

A binuclear mechanism involving catalysis of reaction 1 by iridium(III) as observed by Bergman [7] is unlikely since it should cause deviation from the observed first order dependence on **2**.

While our evidence indicates clearly that reaction 1 does not proceed by the traditional β-H elimination mechanism, the nature of the operating mechanism is unclear. However, a mechanism in which following dissociation of the methoxide (via a contact ion pair $HIr(C_6H_5)(PMe_3)_3^+CH_3O^-$), C–H cleavage of free methanol takes place (either by oxidative addition generating a formal Ir(V) intermediate or by deprotonation of the η^2-bound C–H bond) [14], is in keeping with our results (Fig. 3). In this very electron rich system, considerable build-up of electron density on the methoxide oxygen is expected, promoting inter-molecular hydrogen bonding [15] and methoxide dissociation. C–H activation by cationic Ir(III) was reported [16]. The stereochemical course predicted by this mechanism indeed leads to the unstable *trans* dihydride geometry of **4**. The 2.7 order in methanol suggests that the C–H bond cleaved may be of a free methanol molecule, and that a hydrogen bonding network (based solely on methanol) is involved for stabilization of the transition state in our otherwise apolar medium. The negative and very large activation entropy and the kinetic deuterium isotope effect may reflect the cleavage of the C–H bond in a multicentered transition state, in addition to contributions from solvent rearrangement. The proposed mechanism may also explain the different reactivities of **2** and *cis*-$[HIr(OMe)(PMe_3)_4]PF_6$ (**8**) [5] which are both kinetically stabilized against dissociation of any but the methoxo ligand. Only the less electron rich **8** is stabilized against thermolysis to the dihydrido species in methanol–THF. Complex **2** is an unusually electron rich Ir(III) complex that may be subject to oxidations uncommon for d^6 iridium species (Scheme 2).

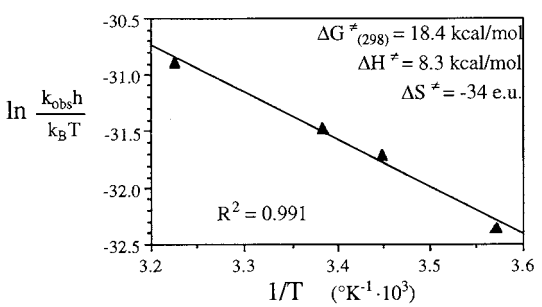
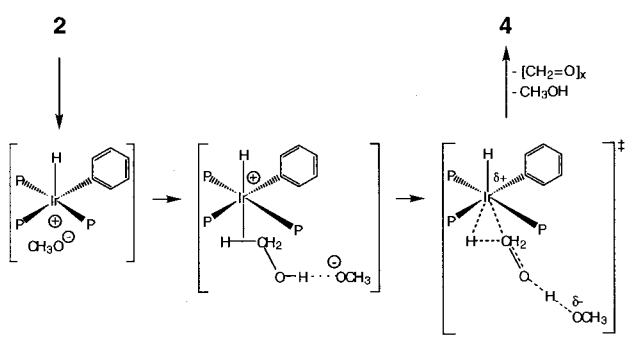


Fig. 3. Eyring plot for reaction 1 in C_6D_6. $[\mathbf{2}]_0 = 12.3$ mM; $[CH_3OH] = 98.4$ mM.



Scheme 2. A possible mechanism of reaction 1. Participation of additional methanol molecules (not drawn) in hydrogen bonding during the reaction is most likely.

3. Experimental

3.1. General

All syntheses and chemical manipulations were carried out under nitrogen in a Vacuum Atmospheres DC-882 dry box, equipped with an oxygen–water scrubbing recirculation MO-40 'Dri-Train' or under argon, using high vacuum and standard Schlenk techniques. The solutions were prepared using standard dilution techniques to avoid weighing small amounts. All solvents were refluxed on the proper drying agents, distilled under argon and stored over activated (150°C under vacuum for 12 h) 4 Å molecular sieves (3 Å for methanol). All deuterated solvents were purchased from Aldrich, degassed and dried over 3 Å molecular sieves for at least 1 week before use. Trimethylphosphine (Aldrich), LiCl and LiBr (Merck) were used as received. Cyclooctene (Merck) was freshly distilled under argon

before use. $P(CD_3)_3$ was prepared according to a literature method [17] using CD_3I (Aldrich). $IrCl_3 \cdot 3H_2O$ was supplied by Engelhardt.

^1H-, ^{31}P-, ^{13}C- and ^2H-NMR spectra were recorded at 400.19, 161.9, 100.6 and 61.4 MHz, respectively, using a Bruker AMX 400 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si (^1H, ^{13}C), $(CD_3)_4Si$ (^2H) and referenced to the residual solvent-h_1 (^1H) natural abundance-d_1 (^2H), and all-d-solvent (^{13}C), or downfield from external H_3PO_4 85% in D_2O (^{31}P).

Spectra were recorded in standard pulsed FT mode using 90° (or less) pulses and at least $5T_1$ periods between pulses to assure reliable quantitative results. When tip angles smaller than 90° were employed, calculated delay times were used.

3.2. Generation of *mer-trans*-$HIr(OCH_3)(C_6H_5)(PMe_3)_3$ (2)

C_6D_6 (400 μl) containing $(C_6H_5)Ir(PMe_3)_3$ [7] (**1**, 3 mg, 6.18×10^{-3} mmol) were taken from a stock solution, placed in a 5 mm NMR tube and let to freeze at −30°C. C_6D_6 (150 μl) containing methanol (2 μl, 4.94×10^{-2} mmol) were taken from another stock solution and placed on top of the frozen solution. The NMR tube was kept in liquid N_2 until it was transferred to a thermostated NMR spectrometer, where the two solutions were let to mix. Within an hour at room temperature, **1** was completely consumed, **2** was formed and only small amounts of *mer-trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**4**) were present. Complex **2** was not isolated as a solid since it decomposes upon removal of the solvent. It also undergoes β-C–H cleavage in solution even at −30°C yielding **4**, thus preventing its separation by low temperature crystallization. Hence, **2** was always freshly prepared in situ. Its characterization in solution is unequivocal. Note: Free methanol in our solution appears at 3.14 ppm (3H) and 1.41 ppm (1H).

2: ^1H-NMR (400 MHz, in C_6D_6 with 0.36% methanol): 8.41 (tt (apparent), $J^t = 6.4$ Hz, $J^t = 1.3$ Hz, $1H_{ortho}$), 7.59 (ddt (apparent), $J^d = 7.2$ Hz, $J^d = 5.9$ Hz, $J^t = 1.3$ Hz, $1H_{ortho}$), 7.40 (tt (apparent), $J^t = 7.4$ Hz, $J^t = 1.6$ Hz, 1H, H_{meta} or H_{para}), 7.18 (tt (apparent), $J^t = 7.2$ Hz, $J^t = 1.3$ Hz, 1H, H_{meta} or H_{para}), 7.07 (tt (apparent), $J^t = 7.2$ Hz, $J^t = 1.6$ Hz, 1H, H_{meta} or H_{para}), 4.12 (s, 3H, OCH_3), 1.25 (d, $^2J^d_{H-P} = 7.6$ Hz, 9H, $P(CH_3)_3$), 1.06 (t, $^{virtual}J^t_{H-P} = 3.4$ Hz, 18H, $2P(CH_3)_3$), −25.13 (td, $^2J^t_{H-P,cis} = 17.7$ Hz, $^2J^d_{H-P,cis} = 13.6$ Hz, 1H, Ir–*H*). $^{31}P\{^1H\}$-NMR: −42.2 (d, $^2J^d_{P-P,cis} = 20.3$ Hz, 2P), −48.2 (t, $^2J^t_{P-P,cis} = 20.2$ Hz, 1P).

3.3. Preparation of *mer-trans*-$HIr(OH)(C_6H_5)(PMe_3)_3$ (3)

Water (100 μl) was added to an orange THF (3 ml) solution of $(C_6H_5)Ir(PMe_3)_3$ (**1**, 70 mg, 0.144 mmol) resulting in rapid bleaching. The solvents were removed after an hour yielding pure **3**.

3: ^1H-NMR (C_6D_6): 7.99 (tt (apparent), $J^t = 6.1$ Hz, $J^t = 1.3$ Hz, $1H_{ortho}$), 7.70 (tt (apparent), $J^t = 6.4$ Hz, $J^t = 1.3$ Hz, $1H_{ortho}$), 7.28 (tt (apparent), $J^t = 7.4$ Hz, $J^t = 1$ Hz, 1H, H_{para}), 7.15 (tt (apparent), $J^t = 7.1$ Hz, $J^t = 1.3$ Hz, 1H, H_{meta}), 7.04 (t (apparent), $J^t = 7.3$ Hz, 1H, H_{meta}), 1.27 (d, $^2J^d_{H-P} = 7.7$ Hz, 9H, $P(CH_3)_3$), 1.00 (t, $^{virtual}J^t_{H-P} = 3.4$ Hz, 18H, $2P(CH_3)_3$), −3.06 (s (slightly broadened), 1H, IrO*H*), −23.99 (td, $^2J^t_{H-P,cis} = 16.7$ Hz, $^2J^d_{H-P,cis} = 12.9$ Hz, 1H, Ir–*H*). $^{31}P\{^1H\}$-NMR: −40.4 (d, $^2J^d_{P-P,cis} = 21.4$ Hz, 2P), −50.2 (t, $^2J^t_{P-P,cis} = 21.5$ Hz, 1P).

3.4. β-C–H elimination from *mer-trans*-$HIr(OCH_3)(C_6H_5)(PMe_3)_3$ (2)

3.4.1. Kinetic follow up of the decomposition of 2

As **2** was always prepared in situ from $(C_6H_5)Ir(PMe_3)_3$ (**1**) and methanol in benzene, and as this oxidative addition is by an order of magnitude faster than the subsequent decomposition to yield *mer-trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**4**), we could study the kinetics of both reactions on the same reaction mixture. A C_6D_6 solution of **2** was partitioned among several NMR tubes such that each tube contained **2** (3 mg, 6.18×10^{-3} mmol) in 400 μl of C_6D_6. The NMR tubes were kept frozen (−30°C) in the drybox. Before the measurement, 150 μl of a C_6D_6 solution containing 2 μl of methanol (49.4×10^{-3} mmol) were added on top of the frozen solution in the dry box. The tube was kept frozen (liquid N_2) for a few more minutes, then warmed to room temperature (1.5 min) and placed in the thermostated NMR probe. The oxidative addition was followed by $^{31}P\{^1H\}$-NMR as described above until completion of the process and subsequently the much slower β-C–H cleavage from the product was studied on the same reaction mixture.

This procedure was repeated at 7, 17, 22 and 37°C. In all experiments, the compounds observed were **2**, and **4** (at 37°C small amounts of the consequent isomerization product *mer-cis*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**6**) were also seen). All values were reproducible (twice) with a surprisingly low inconsistency (less than 5%).

4: ^1H-NMR (C_6D_6 with 0.36% methanol): 8.34 (apparent ddt, $^3J^d_{H-H} = 6.6$ Hz, $^4J^d_{H-P,trans} = 5.5$ Hz, $^4J^t_{H-H} = 1.3$ Hz (actually two doublets), $2H_{ortho}$), 7.12 (tt, $^3J^t_{H-H} = 7.0$ Hz, $J^t_{H-H} = 1.4$ Hz, $1H_{para}$), 7.08 (apparent tt, $^3J^d_{H-H} = 7.0$ Hz, $^4J^t_{H-H} = 1.4$ Hz, $2H_{meta}$), 1.33 (d, $^2J^d_{H-P} = 7.5$ Hz, 9H, $P(CH_3)_3$ *trans* to phenyl), 1.24 (t, $^{virtual}J^t_{H-P} = 3.3$ Hz, 18H, $2P(CH_3)_3$ mutually *trans*), −10.67 (td, $^2J^t_{H-P,cis} = 17.4$ Hz, $^2J^d_{H-P,cis} = 16.5$ Hz, 2H, *H*–Ir–*H*). $^{31}P\{^1H\}$-NMR: −47.3 (d, $^2J^d_{P-P,cis} = 22.6$ Hz, 2P), −59.3 (t, $^2J^t_{P-P,cis} = 22.6$ Hz, 1P). Elemental analysis: Anal. Calc. C, 36.07%; H, 6.81%: Obs. C, 35.71%; H, 6.49%.

3.5. Decomposition of *mer-trans*-$DIr(OCD_3)(C_6H_5)(PMe_3)_3$ (**2a**)

3.5.1. Kinetic deuterium isotope effect in the decomposition of **2**

The decompositions of **2** and of *mer-trans*-$DIr(OCD_3)(C_6H_5)(PMe_3)_3$ (**2a**) were compared at 22°C. The procedure described above was used here as well. After repeating these experiments twice (and mathematically correcting for 1% non-deuterated methanol), the value of k_H/k_D obtained was 3.17 ± 0.07. This value includes contributions from both primary and secondary kinetic deuterium isotope effects, but it is sufficiently large to render the existence of a substantial primary effect beyond doubt.

3.5.2. No H/D scrambling

No H/D scrambling is observed during this decomposition. The ^{1}H-NMR hydride signals of *mer-trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**4**, at -10.67 ppm) and of *mer-trans*-$HDIr(C_6H_5)(PMe_3)_3$ (**4b**, at -10.49) do not overlap. It was therefore possible to determine that **4** is not generated upon decomposition of **2a**. The integration ratios of the hydride versus both $P(CH_3)_3$ signals indicates that *mer-trans*-$D_2Ir(C_6H_5)(PMe_3)_3$ (**4a**) was not formed as well (as a ratio very close to one hydride vs. each nine $P(CH_3)_3$ protons was found).

When this procedure was repeated in non deuterated benzene with the appropriate CH_3OH amounts, only a single hydride signal was observed in the ^{2}H-NMR spectrum. The spectrum also shows no deuteride incorporation into either the phenyl ring or the $P(CH_3)_3$ groups.

3.6. Isomerization of *mer-trans*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**4**) to *mer-cis*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**6**)

The reaction mixture in which the decomposition of **2** to **4** was studied, was left for an additional 48 h at room temperature. While only **4** was observed at the beginning, **6** was the only complex observed at the end.

6: ^{1}H-NMR (C_6D_6 with 0.36% methanol): 7.99 (dm, $^3J^d_{H-H} \approx 6.6$ Hz, 2H, $2H_{ortho}$), 7.20 (m, 1H, $1H_{para}$), 7.18 (ddd (apparent dt), $^3J^d_{H-Hortho} = {}^3J^d_{H-Hpara} = 5.3$ Hz, $^4J^d_{H-Hmeta} = 1.6$ Hz, 2H, $2H_{meta}$), 1.35 (dd $^2J^d_{H-P} = 7.1$ Hz, $^4J^d_{H-H,trans} = 0.7$ Hz, 9H, $P(CH_3)_3$ *trans* to hydride), 1.31 (t, $^{virtual}J^t_{H-P} = 3.3$ Hz, 18H, $2P(CH_3)_3$ mutually *trans*), -11.61 (dtdd, $^2J^d_{H-P,trans} = 134.7$ Hz, $^2J^t_{H-P,cis} = 22.6$ Hz, $^2J^d_{H-H,cis} = 5.0$ Hz, $^4J^d_{H-H,trans} = 0.7$ Hz, 1H, Ir–*H trans* to phosphine), -14.21 (tdd, $^2J^t_{H-P,cis} = 18.0$ Hz, $^2J^d_{H-P,cis} = 17.7$ Hz, $^2J^d_{H-H,cis} = 5.0$ Hz, 1H, Ir–*H trans* to phenyl). $^{31}P\{^1H\}$-NMR: -47.3 (d, $^2J^d_{P-P,cis} = 22.3$ Hz, 2P), -56.2 (t, $^2J^t_{P-P,cis} = 22.2$ Hz, 1P). Elemental analysis: Anal. Calc. C, 36.07%; H, 6.81%: Obs. C, 35.77%; H, 6.52%.

3.7. Synthesis of *fac*-$H_2Ir(C_6H_5)(PMe_3)_3$ (**7**)

Complex **1** (20 mg) was dissolved in 3 ml of benzene and transferred to a Schlenk tube. The solution was frozen (liquid N_2) and the nitrogen atmosphere was replaced by ca. 1 atmosphere of H_2. The reaction mixture was left to warm up to room temperature and the excess pressure (above 1 atmosphere) of H_2 was released. An almost immediate color change (red–yellow) occurred. The solution was stirred for 30 min after which the hydrogen was released and the solvent was stripped off under high vacuum, yielding complex **7** as a white solid.

7: ^{1}H-NMR (C_6D_6): 8.09 (apparent ddd, $^3J^d_{H-H} \approx 7.5$ Hz, $^4J^d_{H-P,trans} \approx 5.8$ Hz, $^4J^d_{H-H} \approx 1.8$ Hz, 2H, $2H_{ortho}$), 7.17 (m, (mostly hidden by H_{meta} and residual C_6HD_5 peaks), 1H, $1H_{para}$), 7.14 (m, (partly hidden by residual $C_6HD_5 + H_{para}$ peaks), 2H, $2H_{meta}$), 1.31 (d, $^2J^d_{H-P} = 7.9$ Hz, 9H, $P(CH_3)_3$ *trans* to phenyl), 1.23 (d, $^2J^d_{H-P} = 7.2$ Hz, 18H, $2P(CH_3)_3$ *trans* to hydride), -10.78 (dm, $^2J^d_{H-P,trans} \approx 140$ Hz, 2H, 2Ir–*H trans* to phosphine. No phosphine ligands are mutually *trans*, as no virtual H–P coupling is observed. It is not clear why a ddd splitting (instead of ddt) was observed for H_{ortho}. $^{31}P\{^1H\}$-NMR: -56.1 (d, $^2J^d_{P-P,cis} = 15.0$ Hz, 2P), -58.3 (t, $^2J^t_{P-P,cis} = 14.9$ Hz, 1P). Elemental analysis: Anal. Calc. C, 36.07%; H, 6.81%: Obs. C, 35.86%; H, 6.55%.

3.8. Stability of **7**

Complex **7** (10 mg) was dissolved in a solution identical to that in which the decomposition of **2** to **4** was studied i.e. 550 μl C_6D_6 containing 2 μl methanol. No isomerization of **7** to either **4** or **6** was observed neither after 1 week at room temperature, nor after 6 h at 60°C.

3.9. Decomposition of **2** in the presence of excess $P(CD_3)_3$

Methanol (15 μl, 0.370 mmol) was added to a C_6D_6 (530 μl) solution of **1** (6 mg, 1.24×10^{-2} mmol) in a NMR tube at room temperature. When all of **1** was consumed but only less than 5% of **2** decomposed to **4**, $P(CD_3)_3$ (12.8 μl, 0.124 mmol) was added by a syringe. $^{31}P\{^1H\}$- and ^{1}H-NMR spectra were recorded periodically. No release of $P(CH_3)_3$ into the solution was observed by $^{31}P\{^1H\}$-NMR (the $^{31}P\{^1H\}$ signal of $P(CH_3)_3$ appears at -62 ppm, and that of $P(CD_3)_3$ at -64 ppm.). Integration of the ^{1}H-NMR $P(CH_3)_3$ signals versus the hydrides and the aromatic peaks shows no $P(CD_3)_3$ incorporation into **4**.

3.10. Examination of a solution of *mer-trans*-$HIr(OH)(C_6H_5)(PMe_3)_3$ (**3**) and $P(CH_3)_3$ by saturation transfer

A solution of **3** (26 mg, 5.16×10^{-2} mmol), $P(CH_3)_3$ (5.4 μl, 5.2×10^{-2} mmol) and water (1 μl, 5.55×10^{-2}

mmol) in C_6D_6 was prepared in an NMR tube, and placed at 22°C in the 500 MHz NMR magnet. Irradiating each time only one of the $^{31}P\{^1H\}$ signals using a DANTE pulse sequence revealed that there is no exchange between the free phosphine and any of the coordinated phosphines. Repeating the experiment with various parameters for the DANTE sequence and at different temperatures (between 22 and 60°C) led to the same conclusion.

3.11. Generation of **2** from **3** and methanol

Complex **3** (12 mg, 2.32×10^{-2} mmol) was dissolved in a solution containing toluene-d_8 (540 ml) and methanol (10 ml). The gradual generation of **2** and the disappearance of **3** were observed by $^{31}P\{^1H\}$-NMR.

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