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Oxidative Addition of Water and Aliphatic Alcohols by IrCl(trialkylphosphine)$_3$

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Abstract: Oxidative addition of aliphatic alcohols to $(C_8H_{14})IrCl(PMe_3)_3$ in benzene yields the *cis*-hydrido-alkoxo products *mer-cis*-$HIr(OR)Cl(PMe_3)_3$ (R = Me, Et, 1-pentyl, 2-propyl). The analogous hydroxo complex is prepared by oxidative addition of water in THF. The addition rate depends on the nature of the alcohol (methanol > 1-pentanol ≫ 2-propanol and methanol > water). The reaction is retarded in polar media but accelerated by protic cosolvents. Anionic ligand redistribution involving chloride and alkoxide (or hydroxide) competes with the oxidative addition reaction. A detailed kinetic study suggests that the 16-electron $IrCl(PMe_3)_3$ is the species undergoing the oxidative addition, and *mer-cis*-$HIr(OR)Cl(PMe_3)_3$ is the kinetic product. The reaction proceeds by a single-step nucleophilic attack of the metal on the O−H proton. π-Donation by chloride stabilizes the transition state and governs the stereochemical course of the reaction. Protic solvent aggregation in the transition state in an apolar medium is suggested. *mer-cis*-$HIr(OH)Cl(PEt_3)_3$, obtained by water addition to $IrCl(PEt_3)_3$, was crystallographically characterized, showing an unusual hydrophobic cage around the hydride ligand.

Introduction

Water is used in various transformations homogeneously catalyzed by late transition metals, such as oxidations of olefins to aldehydes (Wacker process),[1,2] the water−gas shift reaction,[1] hydrocarbonylations of olefins[1,3] and alkyl halides,[1] and nitrile hydration.[4] Examples for desired but still unobtainable catalytic transformations utilizing water as a substrate include the direct anti-Markovnikov hydration of olefins[5] and the suggested solar energy conversion and storage by water photodissociation.[6] Aliphatic alcohols are used for the carbalkoxylation of olefins and alkyl halides,[1,7] hydrogen transfer from alcohols to ketones,[8] *trans*-esterifications,[9] and alcohol dehydrogenations.[1] The direct addition of alcohols to unactivated olefins is an attractive goal.[10] Catalytic pathways involving oxidative additions of O−H bonds are often suggested to be involved in these transformations. Hydrido-alkoxo complexes may be key intermediates, but examples of such compounds[11,12] or of the hydrido-hydroxo analogues,[11c,12b,c,13,14] generated by O−H oxidative addition, are rare. Unfavorable formation constants, decomposition of the products by β-hydride elimination from the alkoxide and the presumed lability[15] of the M−OR (R = H, alkyl) bond of the late transition metal complexes in polar media are held responsible for their scarcity.

Probably for this reason, very little is known about the mechanism by which the oxidative addition of O−H bonds takes place. A protonation mechanism was indicated for the reversible addition of water to $Pt(PEt_3)_3$[16] and $HRh(P\text{-}i\text{-}Pr_3)_3$,[17] and for

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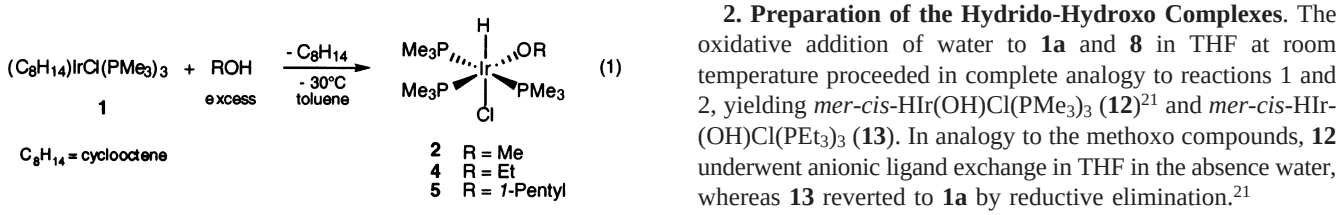
the irreversible addition to $PtMe_2(bpy)$ (bpy = 2,2′-bipyridyl).[18] Calculations suggest a similar protonation mechanism for the water oxidative addition to $PtMe_2\{(N(=CH_2)-NH)_3BH\}]^-$.[19] The cis oxidative addition of water to the postulated 14-electron intermediates $Ir\{C_6H_3\text{-}2,6\text{-}(CH_2P\text{-}t\text{-}Bu_2)_2\}$ and $IrCl(DMSO)_2$ may proceed by a different mechanism.[13g,14d] We now report a detailed mechanistic study of the oxidative addition of alcohols to $(C_8H_{14})IrCl(PMe_3)_3$[20] (**1**) in benzene, leading to *cis*-hydrido-alkoxo products. The oxidative addition is by the 16-electron species $IrCl(PMe_3)_3$ (**1a**). It proceeds by a single-step nucleophilic attack of the metal on the O−H proton. π-Donation by the chloro ligand stabilizes the transition state and governs the stereochemical course of the reaction.

Results

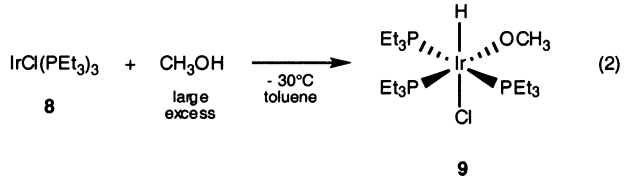
1. Preparation of Hydrido-Alkoxo Complexes. Addition of excess methanol to a toluene solution of $(C_8H_{14})IrCl(PMe_3)_3$-20 (**1**) at −30 °C led within minutes to decoloration and to formation of the *cis*-hydrido-methoxo complex *mer-cis*-$HIr(OCH_3)Cl(PMe_3)_3$ (**2**) (eq 1).[21] Small amounts of *mer-cis*-$HIrCl_2(PMe_3)_3$[22] (**3**) (typically below 5%) were also formed. The off-white products were sensitive to hydrolysis even in the solid state. They were relatively stable in benzene, but disproportionation products (having 2 or 4 phosphine ligands) appeared after a few days. In more polar media (at least 4%, methanol in benzene) β-hydride elimination yielded *mer-cis*-$H_2IrCl(PMe_3)_3$ (**6**).[23]



Oxidative addition of ethanol and 1-pentanol to **1** also proceeded smoothly to yield *mer-cis*-$HIr(OCH_2CH_3)Cl(PMe_3)_3$ (**4**) and *mer-cis*-$HIr(O(CH_2)_4CH_3)Cl(PMe_3)_3$ (**5**), respectively. 2-Propanol did not react at −30 °C, but at room temperature *mer-cis*-$HIr(OCH(CH_3)_2)Cl(PMe_3)_3$ (**7**) was slowly formed.

Compounds **2**, **4**, **5**, and **7** were characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy. The A_2X pattern in the ^{31}P NMR spectrum and the virtual H−P coupling observed in the proton spectrum are consistent with a meridional configuration of the phosphines. A doublet of triplets resonance with small H−P coupling constants ($^2J^d_{H-P,cis} \approx 19-21$ Hz; $^2J^t_{H-P,cis} \approx 13-15$ Hz) was observed at δ −21.5 ppm for each of the hydrides[24] of **2**, **4**, **5**, and **7**, indicating that neither a phosphine nor another strong trans labilizing ligand was located trans to it. The protons on the carbon α to the alkoxo oxygen resonate between 4.1 and 3.8 ppm. These protons were coupled to the trans dispositioned phosphorus ($^4J_{H-P,trans} = 5.6$, 1.4, 1.4, 2.6 Hz for **2**, **4**, **5**, and **7**, respectively), thus establishing the geometry of these complexes. Somewhat unusually, the $^{13}C\{^1H\}$ NMR of **2** and **4** revealed that $^3J_{C-P,trans} < {}^4J_{C-P,trans}$ for the alkoxo ligand (for **2** and **4**, $^3J_{C-P,trans} < 1$ Hz, and for **4**, $^4J^d_{C-P,trans} = 6.7$ Hz).[25] There was no indication in the ^1H NMR or IR spectra for the presence of hydrogen-bonded (or free) alcohol molecules.

The triethylphosphine analogue *mer-cis*-$HIr(OCH_3)Cl(PEt_3)_3$ (**9**) was formed by the addition of excess methanol to $IrCl(PEt_3)_3$[26] (**8**) (eq 2).[21] Small amounts of *mer-cis*-$HIrCl_2(PEt_3)_3$[27] (**10**) were also formed, as in the preparation of **2**. Unlike its PMe_3 analogue **2**, compound **9** underwent β-hydride elimination even at −30 °C (in the presence of methanol) as well as when only traces of methanol were present (at room temperature) to form *mer-cis*-$H_2IrCl(PEt_3)_3$ (**11**).[23,28] Therefore, small quantities of **11** were present in any preparation of **9**. Compound **9** was unambiguously characterized and was assigned the same configuration as that of **2**. The analogous hydroxo complex **13**, having similar frequencies in IR, ^1H, and ^{31}P NMR spectroscopy was crystallographically characterized (see below).



2. Preparation of the Hydrido-Hydroxo Complexes. The oxidative addition of water to **1a** and **8** in THF at room temperature proceeded in complete analogy to reactions 1 and 2, yielding *mer-cis*-$HIr(OH)Cl(PMe_3)_3$ (**12**)[21] and *mer-cis*-$HIr(OH)Cl(PEt_3)_3$ (**13**). In analogy to the methoxo compounds, **12** underwent anionic ligand exchange in THF in the absence water, whereas **13** reverted to **1a** by reductive elimination.[21]

The ^1H NMR signal of **12** at −2.15 ppm, and of **13** at −2.07 ppm is typical of a metal-coordinated hydroxide.[29] The hydroxide presence is evident also from the sharp infrared band at 3463 cm^{-1} of **13**. Otherwise, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **12** and **13** are completely analogous to those of the methoxo complexes **2** and **9**, establishing an identical geometrical arrangement. The structural assignment is based on the A_2X patterns in the $^{31}P\{^1H\}$ NMR spectra, the virtual H−P couplings in the proton spectra, and hydride signals with small proton−phosphorus coupling constants at −21.7 ppm, and the coupling of the hydroxo protons only to a single unique phosphorus atom ($^3J^d_{H-P} \approx 5.5$ Hz).

The identity of these compounds was confirmed by a low-temperature crystallographic study of **13** (Figure 1). The hydroxo proton is intramolecularly hydrogen-bonded to the chloro ligand, and is unavailable for hydrogen-bonding to the hydride as in $[cis\text{-}HIr(OH)(PMe_3)_4]^+$.[30] However, an unusual hydrophobic cage is revealed around the hydride (Figure 2), in which three

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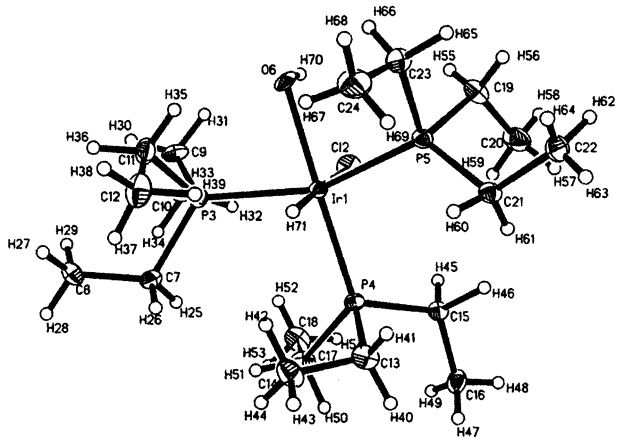


Figure 1. Low-temperature X-ray structure of **13**. Selected bond distances (Å): Ir−Cl 2.490(2), Ir−P(3) 2.341(2), Ir−P(4) 2.259(7), Ir−P(5) 2.338-(2), Ir−O 2.143(9), Ir−H(71) 1.730(1), O−H(70) 0.805(75), C(12)−H(37) 0.939(80), C(12)−H(38) 1.038(81), C(12)−H(39) 1.154(84), C(14)−H(42) 0.971(82), C(14)−H(43) 0.978(79), C(14)−H(44) 0.873(81), C(24)−H(67) 0.9117(90), C(24)−H(68) 0.997(87), C(24)−H(69) 0.968(91), Cl···H(70) 2.417(77), H(39)···H(71) 2.065(91), H(42)···H(71) 2.155(93), H(67)···H(71) 2.384(100). Selected bond angles (degrees): Cl−Ir−P(3) 95.7(1), Cl−Ir−P(4) 93.9(3), Cl−Ir−P(5) 95.9(2), Cl−Ir−O 83.4(3), Cl−Ir−H(71) 177.6-(18), P(3)−Ir−P(4) 103.4(1), P(3)−Ir-P(5) 154.5(1), P(3)−Ir−O 77.4(2) P(3)−Ir−H(71) 84.0(19), P(4)−Ir−P(5) 98.3(1), P(4)−Ir−O 177.3(2), P(4)−Ir−H(71) 85.5(21), P(5)−Ir−O 81.6(21), P(5)−Ir−H(71) 85.5(21), O−Ir−H(71) 98.7(20), Ir−O−H(70) 97.8(58), O−H(70)···Cl, 122.4(687).

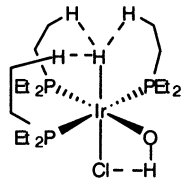
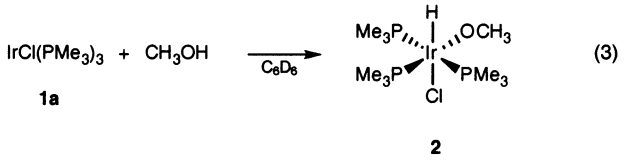


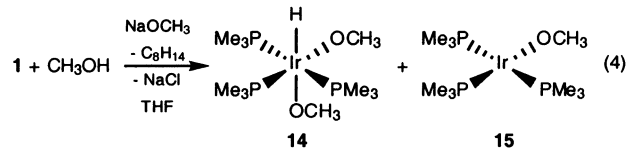
Figure 2. Schematic drawing of **13** emphasizing nonbonding interactions.

methyl protons, one from each PEt_3 group, get as close as 2.15−2.2 Å to the hydride. The C−H bonds of these protons are significantly longer (by 0.1−0.2 Å) than all the other C−H bonds of the complex, as is observed for any X−H bond involved in hydrogen bonding.[31] A recent survey of the Cambridge Structural Database detected M−H···H−C hydrogen-bonding in 18 compounds, half of which involve sp^3 C−H bonds in trialkylphosphines, with H···H distances similar to those we found.[32]

3. Mechanistic Studies of the O−H Oxidative Addition. Addition to IrCl(PMe$_3$)$_3$ (1a). The well-resolved doublet and triplet that comprise the phosphorus NMR spectrum of **1** in THF or toluene at temperatures higher than −10 °C and the $^{13}C\{^1H\}$ and ^1H NMR signals of free cyclooctene indicate that cyclooctene is completely dissociated. Hence, only the square planar $IrCl(PMe_3)_3$ (**1a**) will be considered in the discussion below.



A follow-up of the methanol addition to **1a** (eq 3) at various temperatures (10, 22, 30, and 40 °C) showed that, along with **2** and small amounts of **3**, two additional compounds were formed but disappeared when **1a** was totally consumed. They were identified as *mer-cis*-$HIr(OCH_3)_2(PMe_3)_3$ (**14**) and $Ir(OCH_3)$-$(PMe_3)_3$ (**15**) On the basis of ^{31}P and ^1H NMR. In the presence of 3-fold excess $NaOCH_3$ **14** and **15** turned to be the major products (eq 4).



Compound **14** exhibits ^{31}P and ^1H NMR spectra similar to that of the alkoxo complexes **2**, **4**, **5**, and **7**. Its ^{31}P NMR A_2X pattern and the virtual H−P coupling observed in the proton spectrum are consistent with a meridional configuration. One methoxo group appears at 4.10 ppm in the ^1H NMR and is coupled to the phosphorus trans to it ($^4J_{H-P,trans} = 5.5$ Hz). A slightly broadened singlet at 3.89 ppm with equal intensity is assigned to the methoxo trans to the hydride (these two signals have the same area and grow and disappear together). The hydride appears at −23.09 ppm, in agreement with its being trans to a weak σ-donor. It is coupled to three cis disposed phosphines ($^2J^d_{H-P,cis} = 18.7$ Hz and $^2J^t_{H-P,cis} = 15.9$ Hz).

Compound **15** exhibits a doublet at 3.98 ppm, assigned to a methoxide trans to phosphine ($^4J_{H-P,trans} = 4.1$ Hz). An A_2X pattern in the ^{31}P NMR and the virtual H−P coupling in the proton spectrum indicate three phosphines. Two are trans to each other and their ^{31}P NMR resonance at −15.1 ppm is at least 10 ppm downfield compared to neutral d^6 $Ir(PMe_3)_3XYZ$ (X, Y, and Z are anionic ligands).[22−24,33] For comparison, IrCl-$(PMe_3)_3$ (**1a**) has its equivalent phosphines at −19.1 ppm, supporting the identity of **15** as a d^8 complex.[34]

A typical progress of reaction 3 is shown in Figure 3. The combined concentrations of **14** and **15** do not differ by much from that of **3**. It is likely that **3**, **14**, and **15** are products of anionic ligand redistribution. Alkoxides often undergo facile exchange with other anionic ligands.[9,23,25b,35]

The kinetics suggested that reaction 3 was first-order in **1a** (Figure 4 and Table 1). A best fit for a fourth-order in methanol was obtained (Figure 5), although a third- or fifth-order may not be ruled out. This strong dependence is similar to our findings for other processes involving methanol and a methoxo ligand in apolar media.[11f,23] A strong dependence on methyl iodide concentration was reported for its addition to Vaska's

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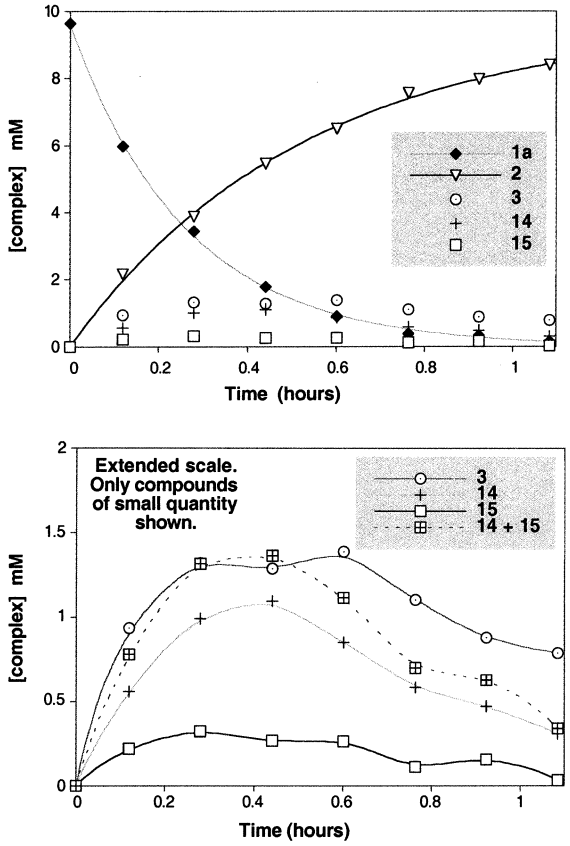

Figure 3. Progress of methanol addition to **1a** in C_6D_6 at 22 °C (eq 3). $[\mathbf{1a}]_0 = 9.6 \pm 0.3$ mM. $[CH_3OH] = 90 \pm 2.5$ mM. Data for **1** and **2** were fit to general exponential decay and formation. Data for **3**, **14**, **15**, and the concentration sum of **14** + **15** were fit by interpolation.

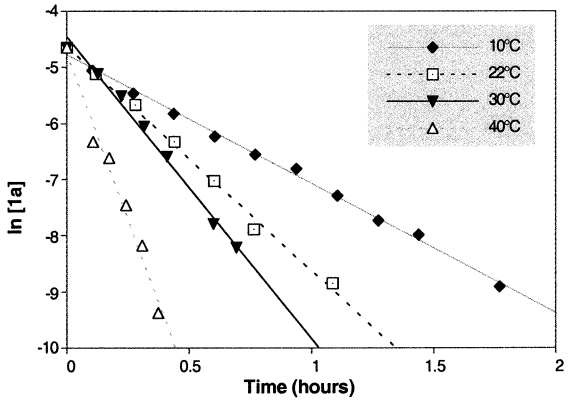

Figure 4. Pseudo-first-order plots for reaction 3.

complex in benzene.[36] The activation parameters obtained for the disappearance of **1a** (Figure 6) were $\Delta H^{\ddagger}_{obs} = 8.7 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{\ddagger}_{obs} = -23 \pm 6$ eu.

Only **1a** and **2** were observed upon follow-up at −30 °C. Heating to 60 °C caused β-hydride elimination, generating **6**.[23] At higher temperatures, phosphine redistribution products were also observed.

The effect of deuterium substitution was determined by comparing the additions of CH_3OH, CH_3OD, and CD_3OD to **1a** at 22 °C. A primary kinetic deuterium isotope effect of $k_{CH_3OH}/k_{CH_3OD} = 2.0 \pm 0.2$ was obtained for the disappearance

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Table 1. Observed Rate Constants for the Addition of Methanol to **1a** in C_6D_6 (eq 3); [**1a**] = 9.6 mM; [Methanol] = 90 mM

T °C ± 0.5	pseudo-first-order k_{obs}[a] s^{-1}	k_{obs}[a] $s^{-1}\,M^{-4}$
10	6.22×10^{-4}	9.87
22	1.20×10^{-3}	19.1
30	1.60×10^{-3}	25.5
40	3.18×10^{-3}	50.5

[a] Largest variation in k_{obs} was 11%. For each single measurement $R^2 > 0.986$ (usually $R^2 > 0.997$).

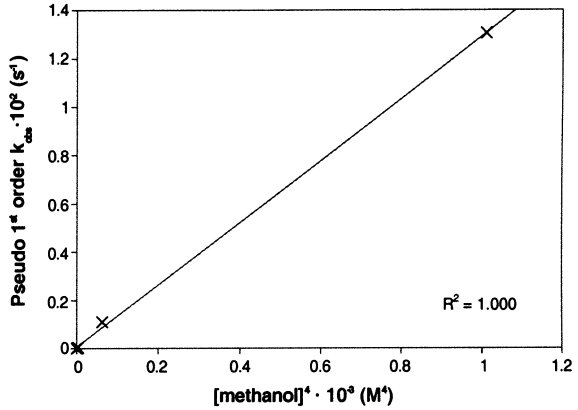

Figure 5. Dependence of reaction 3 on methanol concentration in C_6D_6 at 22 °C. Measurements were at 0, 8.91, 44.6, 89.1, and 178 mM of methanol. [**1a**] = 9.6 mM. The three lower concentration points overlap.

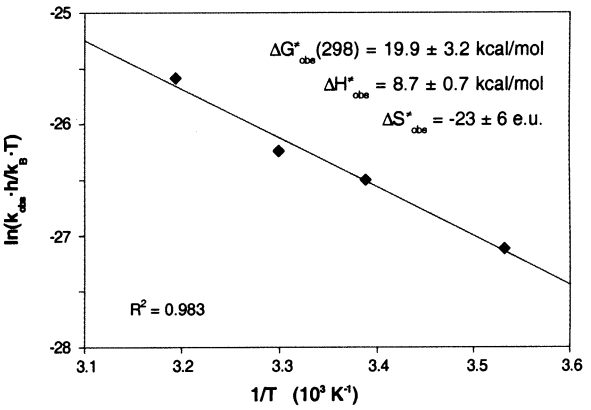

Figure 6. Eyring plot for the oxidative addition of methanol to **1a** in C_6D_6 (eq 3).

of **1a**. The combined primary and secondary isotope effects value found is $k_{CH_3OH}/k_{CH_3OD} = 3.2 \pm 0.3$. We estimate the secondary effect to be 1.17 per β-deuteron for the disappearance of **1a**.

Methanol oxidative addition to **1a** is faster in C_6D_6 than in the aprotic but more polar THF (Table 2). In the even more polar *N*-methyl pyrrolidone (NMP), no product of methanol addition to **1a** was observed.[37]

Methanol addition to **1a** was examined in the presence of a catalytic amount (2% relative to **1a**) of either $HBF_4 \cdot Et_2O$ or *p*-toluenesulfonic acid. In both cases, the reaction rate was the same as that in the absence of acid.

(37) **2** dissolves in NMP but does not revert to **1a** in the absence of methanol. This stability of **2** can be explained by a high barrier for reductive elimination in the absence of bridging, hydrogen-bonded methanol molecules.

Table 2. Pseudo-First-Order Rate Constants for the Oxidative Addition of Alcohols to **1a**

alcohol	solvent	T °C	[**1a**] M	[alcohol] M	k [a] s^{-1}
methanol	C_6D_6	22	9.6×10^{-3}	9.0×10^{-2}	1.20×10^{-3}
1-pentanol	C_6D_6	22	9.6×10^{-3}	9.0×10^{-2}	1.08×10^{-4}
2-propanol	C_6D_6	22	9.6×10^{-3}	9.0×10^{-2}	no reaction
2-propanol	C_6D_6	22	9.6×10^{-3}	1.19	4.39×10^{-5}
methanol	THF	17	1.9×10^{-2}	0.18	3.60×10^{-4}
water	THF	17	1.9×10^{-2}	0.18	8.69×10^{-5}

[a] Largest variation in k was 15%. For each single measurement, $R^2 > 0.978$.

LiCl (14.8 mol equiv) did not affect the rate of oxidative addition to **1a**.[38] The pseudo-first-order rate constant for the disappearance of **1a** at 22 °C was $(1.10 \pm 0.14) \times 10^{-3}$ s^{-1}, as compared with $(1.20 \pm 0.10) \times 10^{-3}$ s^{-1} in the absence of LiCl. The ^{31}P NMR chemical shifts of the disappearing species in the presence of LiCl appeared at −26.5 (d, $^2J_{P-P,cis} = 19.9$ Hz, 2P) and −38.8 (t, 1P), whereas those of **1a** in benzene were at −19.1 (d, $^2J_{P-P,cis} = 23.9$ Hz, 2P) and −41.0 (t, 1P). The d^6 iridium products **3** and **2** were not shifted. It is possible that the compound observed in the presence of excess LiCl is Li-[$IrCl_2(PMe_3)_3$] (**16**). Upon addition of LiCl to a solution of **1** in benzene or in THF, **16** was not observed, because LiCl was insoluble in the absence of methanol. Compound **16** may be viewed as a zwitterion stabilized by lithium chelation.[39]

An attempt to study the influence of added PMe_3 was hindered by the facile formation of sparingly soluble [$Ir(PMe_3)_4$]-Cl,[20] which reacts with methanol and THF to generate *cis*- and *trans*-$[HIrCl(PMe_3)_4]^+$ [40] as well as *cis*-$[H_2Ir(PMe_3)_4]^+$.[41]

The oxidative addition of alcohols to **1a** follows the reactivity order methanol > 1-pentanol ≫ 2-propanol and methanol > water (Table 2). Redistribution of the chloro and alkoxo ligands was observed during the oxidative additions of 1-pentanol and water to **1a**. During the very slow reaction of 2-propanol with **1a** (under higher alcohol concentration), only small amounts of **3** were observed.

Addition to $IrCl(PEt_3)_3$ (8). The oxidative addition of methanol to **8** in C_6D_6 was complicated by its reversibility and by the concomitant β-hydride elimination, liberating formaldehyde and **11**. Observation of $HIrCl_2(PEt_3)_3$ (**10**) indicates that anionic ligand redistribution takes place as well. No reaction between **8** and methanol was observed in THF under otherwise the same conditions. The reaction of **8** with water and methanol is discussed in a separate report.[21] Unlike complex **8**, $(C_2H_4)_2$-$IrCl(PEt_3)_2$[42] (**17**) did not react with methanol in C_6D_6 under the same conditions.

The effect of added phosphine could be examined in this case, since IrL_4^+ is not formed with L = PEt_3. Reaction of **8** with methanol in the presence of 10 equiv of PEt_3 reached equilibrium at the same rate as in the absence of phosphine, and the same ratio between complexes **8** and **9** resulted.

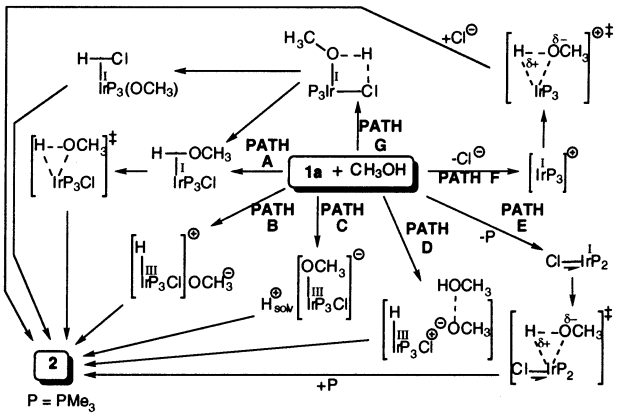

Figure 7. Mechanistic scenarios for reaction 3, which are considered in the text and then discarded. For our suggested mechanism see Figure 9.

Discussion

Reaction 3 proceeds at −30 °C with no observable anionic ligand redistribution. This redistribution is, therefore, not on the direct reaction path between **1a** and **2**. We thus separate the discussion of the anionic ligands redistribution from that of the O−H oxidative addition step.

1. Mechanism of the O−H Oxidative Addition to 1a. Classification of the Operating Mechanism. As discussed below, we conclude that the reaction proceeds by a single-step nucleophilic attack of the metal on the O−H proton. First we consider pathways that can be excluded. The observed pseudo-first-order in **1a** combined with the pronounced solvent dependence of reaction 3 is incompatible with a mechanism involving a radical chain or the formation of a caged radical pair.

A concerted process via an η^2-bound intermediate (pathway A, Figure 7) is often postulated for the oxidative addition of nonpolarized bonds such as H−H, C−H, Si−H, and C−C[43] but is rendered unlikely by the observed stereochemistry of reaction 3. The kinetic product of methanol addition to **1a** in benzene is **2** (see below). Its stereochemistry differs from that of the products we obtained for the hydrogen and triethylsilane addition to **1** (eqs 3, 5). Similarly, Eisenberg observed a different stereochemical course for the addition of hydrogen or $HSiEt_3$ to *cis*-(CO)IrCl(DPPE) (DPPE = 1,2-bisdiphenylphosphinoethane) as compared to HCl addition.[44] Since HCl and MeOH are larger than hydrogen but smaller than the silane, this behavior cannot be due to steric factors only. Considering the trans influence of the various ligands suggests that only in reaction 3 the kinetic product (**2**) is the electronically most stable. It has both poor σ-donors (chloride ≈ methoxide) trans disposed to the best σ-donors (hydride > PMe_3). A trans influence analysis for reaction 5 suggests that ligand arrangements of **6** (analogous to that of **2** upon replacing methoxide by R) and **20** are more stable than that of kinetic products **18** and **19**. Hence, the dissimilarity between reactions 3 and 5 is in the electronic demands of the intermediates, which are, therefore, different. Substantial mechanistic differences between the oxidative addition in benzene of hydrogen[45,46] and of polarized bonds,[45,4748] were demonstrated long ago. The same

(38) Other examples of oxidative addition reactions not affected by added halide anions (a) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813. (b) Basson, S. S.; Leipoldt, J. G.; Nel, J. T. *Inorg. Chim. Acta* **1984**, *84*, 167. (c) Reference 18.
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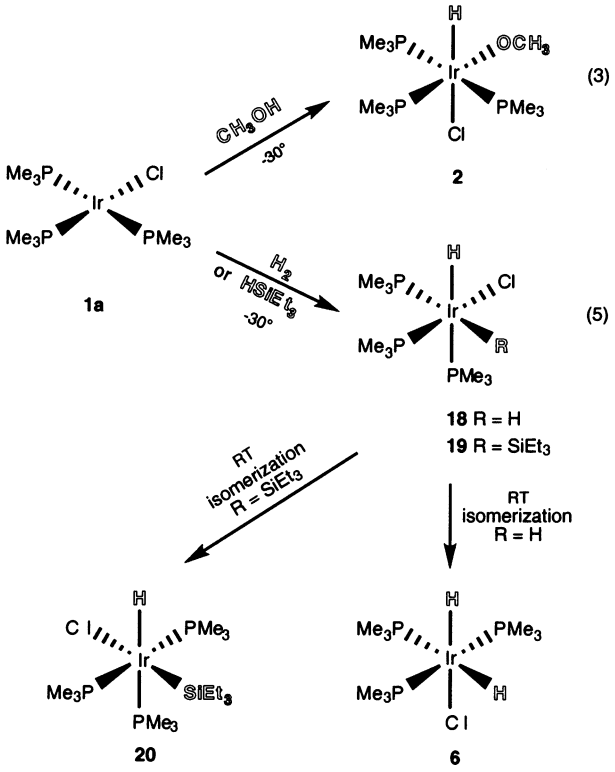
holds for the reverse process of reductive elimination of polar C−O and apolar C−C bonds from d^6 platinum in benzene and THF.[49]



CD_3OD addition to **1a** did not generate signals of Ir−H or Ir−O(CH_3D_{3-n}) ($n = 1-3$) in the ^1H NMR spectrum, confirming that methanol is the only source of the hydride in **2** and that competing C−H activation processes involving the PMe_3 ligands do not occur. Initial C−H cleavage of the alcohol[50] is also excluded, because addition of CH_3OD yields only deuteride-containing products.

The addition of catalytic amounts of acid should accelerate the oxidative addition to **1a**, if it occurs by protonation (pathway B, Figure 7). Addition of an anion source should accelerate reaction 3 if it takes place by initial coordination of alkoxide (pathway C, Figure 7).[51] Since neither strong acids nor LiCl affected the oxidative addition rate, we conclude that the O−H cleavage is mediated by the metal and does not occur prior to the interaction between **1a** and the alcohol. This holds true only when the solvent allows for acid and salt ionization and disfavors contact ion-pair formation.

A mechanism involving contact ion pairs formed by deprotonation of methanol (pathway D, Figure 7) seems highly unlikely. We suggested that methanol addition to $PhIr(PMe_3)_3$ under the conditions of reaction 3 takes place via contact ion-pair formation,[11f,52] and the same was demonstrated for Me_3-Sn-halide addition to *cis*-$Me_2Pt(Bu_2BPY)$.[53] Both reactions yield trans addition kinetic products, and have unusually low $\Delta H^{\ddagger}_{obs}$ (<1 kcal mol^{-1}) that originates from the negative $\Delta H°$ of the ion-pair formation. For the methanol addition to $PhIr(PMe_3)_3$ we also found k_H/k_D of 6.6.[52] For reaction 3 we obtained a cis addition kinetic product (see below), $\Delta H^{\ddagger}_{obs}$ of 8.7 ± 0.7 kcal mol^{-1} and a primary kinetic isotope effect of 2.0 ± 0.2.

The rate dependence on the alcohol type for a contact ion-pair mechanism should correlate with pK_a. The published pK_a scale most relevant to our conditions (0.36% alcohol in C_6D_6 or in THF) is in DMSO.[54] Bordwell's[54a,b] values are methanol 29.0, ethanol 29.8, 2-propanol 30.25, and water 31, whereas according to Arnett and Small[54c] they are water 27.5, methanol 27.9, 1-pentanol 28.0, ethanol 28.2, and 2-propanol 29.3. Bordwell's scale justifies the slower reaction of **1a** with water as compared to that with methanol. Both scales justify the trends in the alcohols addition rates, but not the ratios found (370:33:≪1 for methanol, 1-pentanol and 2-propanol respectively). We expected 2-propanol to react much faster. Steric factors explain our observations better. They account for similar alkyl halide reactivity trends with d^8 complexes taking place by nucleophilic attack of the metal on carbon.[55] A combination of the above evidence with the unlikelihood of a trans intermediate between **1a** and **2** (see below) leads us to consider this mechanism unlikely.

2. Details of the Nucleophilic Attack Mechanism. An oxidative addition by nucleophilic attack of iridium on the proton of methanol seems the most conceivable mechanism for reaction 3. The term nucleophilic attack on proton was used in the past to describe the oxidative addition of acids instead of the better-known acid−base terminology.[56] The steric demands of the reaction and the fact that no multiple bonds are formed are inconsistent with base-initiated organic elimination reactions, justifying this terminology.

Identity of the Species Undergoing the O−H Oxidative Addition. Trialkylphosphine dissociation (pathway E, Figure 7) is not on the pathway of reactions 2 and 3. Excess PEt_3 does not affect the rate of methanol addition to **8**, indicating that reaction 2 does not involve reversible phosphine dissociation. This must hold true also for the less bulky PMe_3 in reaction 3. A mechanism initiated by rate-determining phosphine dissociation will also show no rate dependence on phosphine concentration. This mechanism is inconsistent with the primary kinetic deuterium isotope effect of 2.0 ± 0.2 for reaction 3.

A scenario involving irreversible ligand dissociation (phosphine or chloride) followed by cleavage of the added bond, oxidation of the metal, and ligand reassociation is the microscopic reverse of the mechanism suggested for the reductive elimination of N−H[57] and aryl-halide[58] bonds. It seems unlikely for reactions 2 and 3. $IrCl(PEt_3)_3$ (**8**) and $(C_2H_4)_2IrCl(PEt_3)_2$ (**17**) react with ammonia at the same rate, yielding the same product.[42] Both compounds lose neutral ligands in the process. Under the conditions of reaction 2, **17** did not react with methanol. On the other hand, complex **1a** activates methanol

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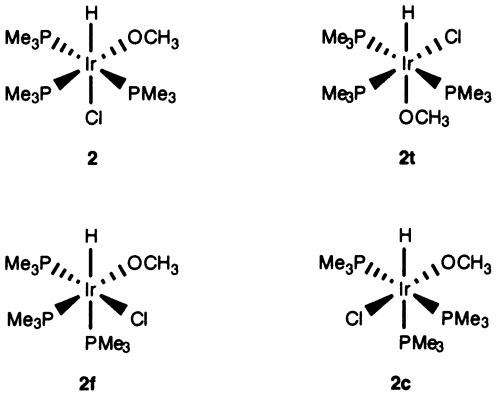
through reaction 3 but does not cleave the ammonia N−H bond.[59] This alone suggests a difference between the reactivities of methanol and ammonia toward **8**. The inactivity of **17** toward methanol may be due either to insufficient nucleophilicity of the postulated $IrCl(PEt_3)_2$ intermediate or to instability of the postulated chloro- or alkoxo-bridged product. A linear relationship between the relative L_nM-X and H−X bond strengths was found for terminal covalently bound ligands,[35a,60] and extended also for bridging amido and alkoxo ligands of palladium.[61] The H−X bond enthalpies for ammonia and methanol are very similar: 107[62] and 104 kcal mol^{-1},[63] respectively, indicating that a product of methanol addition to **17** should be stable. We suggest that unlike $IrCl(PEt_3)_3$ (**8**), the 14-electron $IrCl(PEt_3)_2$ is not nucleophilic enough to activate the methanolic O−H bond. Generation of a 14-electron complex is not required also for the oxidative addition of HCl,[64] alkyl halides,[38a,65] benzyl halides,[66] and propiolactone.[33b]

Chloride does not dissociate from d^8 iridium (pathway F, Figure 7) during reactions 2 and 3. Excess LiCl had very little effect on the product-formation rate, suggesting that reaction 3 does not involve reversible chloride dissociation. Also, if chloride dissociation were on the pathway of methanol addition, $IrCl(PMe_3)_3$ (**1a**) and $[Ir(PMe_3)_4]PF_6$[67] should have reacted at the same rate, having the same $[Ir(PMe_3)_3]^+$ reactive intermediate cleaving the O−H bond. This is inconsistent with the much faster reaction of **1a**, despite our observation that phosphine dissociation is not rate-determining for the oxidative addition by $[Ir(PMe_3)_4]PF_6$ ($k_H/k_D = 7.8 \pm 0.6$ with water).[68] The ruling-out of chloride dissociation is supported also by the reduced rate of methanol oxidative addition with increased solvent polarity according to C_6D_6 > THF ≫ NMP, suggesting that the transition state is less polarized than the reagents.[69] Since the reagents are neutral, a cationic transition state is unlikely. We actually expect the chloride to facilitate reaction 3. It keeps the reagent neutral and therefore a better nucleophile than the cationic product of its dissociation. These conclusions are fully consistent with the mechanism that we elucidated for the microscopic reverse O−H reductive elimination from **2** and **9**.[21]

It is unlikely that alcohol coordination (pathway G, Figure 7) is on the pathway of reactions 2 and 3. Such coordination to a *neutral*, low-valent complex with basic ligands is expected to be weak.[70] Indeed, complexes with coordinated alcohols and water are mostly cationic.[71] Alcohol ligation to the 16-electron IrP_3Cl would also result in saturation. The oxidative addition of ammonia to **8** does involve pre-coordination of the nitrogen to the metal center,[42,72] but in contrast to the reactions with alcohols and water, concomitant dissociation of PEt_3 was implicated.[42,72a] When **1a** binds ammonia, saturation is obtained, and further reactivity to cleave the N−H bond does not take place.[59]

Identity of the Kinetic Product. No other isomer of **2** was observed during reaction 3 at any of the conditions tested. An intermediacy of **2f**, **2c**, or **2t** must imply their facile isomerization to **2**. We concluded that PMe_3 or chloride dissociation is not on the pathway of reaction 3. Methoxide dissociation from **2** under the conditions of reaction 3 ($k = 1.03 \times 10^{-5}\ s^{-1}$) was 2 orders of magnitude slower than the methanol oxidative addition to **1a** ($1.21 \times 10^{-3}\ s^{-1}$). Since the trans effect on the methoxide in **2f** and **2c** is not larger than in **2**, it is improbable that the isomerization of **2f** or **2c** to **2** via methoxide dissociation will be faster than the oxidative addition to **1**. For **2t** the methoxo ligand exchange may be somewhat faster. However, the electronic and steric differences between **2t** and **2** seem too small to bring upon 2 orders of magnitude acceleration of methoxide dissociation from **2t** as compared to that from **2**. In a concerted nucleophilic attack mechanism, in which the O−H bond is not broken prior to the rate-determining step the intermediacy of the trans addition product **2t** is geometrically impossible.



Nondissociative isomerizations within octahedral complexes are uncommon, and $\Delta G^{\ddagger}_{(298)}$ of such transformation is higher than that of reaction 3.[73] Such facial to meridional isomerization of *fac*-$H_2IrCl(PMe_3)_3$ (**18**) took 9 days to reach completion in methanol/benzene. Since the electronic driving force for a nondissociative isomerization of **2t**, **2f**, and **2c** to **2** is smaller or similar to that of **18** to **6**, it will be slow too. Hence, we can rule out an intermediacy of **2t**, **2f**, or **2c** for a concerted nucleophilic attack pathway from **1a** to **2**. Other polarized bonds also undergo cis oxidative addition in aromatic solvents.[11e,13b,24b,44,55d,74]

Effect of Solvent. Because polar solvents retard reaction 3, the high order in methanol is due to its protic nature, and not to its polarity. Hydrogen bonding of free methanol to the addendum may weaken the O−H bond prior to cleavage and stabilize the basic oxygen on the forming product. We found

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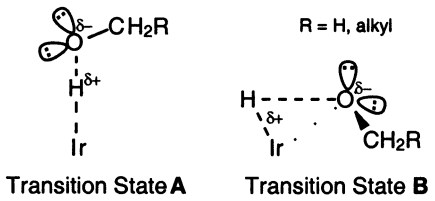
no evidence for hydrogen bonding of methanol to the final product.[13c,25,35c,75] In analogy to our finding, a chain of three hydrogen-bonded water molecules spanning between chloride and a cis-disposed ligand is suggested by calculations to reduce the energy barrier for transformations involving O−H cleavage within the Wacker process.[76] We observed a high order in methanol also for the β-hydride elimination from **2**[23] and from *mer-trans*-HIr(OCH$_3$)(C$_6$H$_5$)(PMe$_3$)$_3$.[11f]

Slower methanol oxidative addition with increased solvent polarity (C$_6$D$_6$ > THF ≫ NMP) was surprising, because we expected the transition state to be stabilized in polar media (it involves charge separation, see below). However, it may be that dilute methanol is stabilized by aprotic polar solvents such as NMP to the extent that it does not participate in the entropically expensive stabilization of the transition state. In the less polar solvents, the implied hydrogen bonding by free methanol probably acts to reduce the transition-state polarity.

The Transition State. Since we concluded that no intermediate exists between **1a** and **2** in reaction 3, we relate the activation parameters and the kinetic isotopic effect to the nature of the transition state. As the equilibrium lies heavily toward the product,[21] reaction 3 is exothermic, and the transition state resembles the reagents according to the Hammond postulate. The small primary k_H/k_D value of 2.0 ± 0.2 and the small $\Delta H^{\ddagger}_{obs}$ of 8.7 ± 0.7 kcal mol^{-1} fit a mechanism, in which the O−H bond is only slightly stretched in an early transition state. The large and negative $\Delta S^{\ddagger}_{obs}$ is typical of oxidative additions postulated to proceed via a concerted nucleophilic attack mechanism in apolar media.[45,47,64,74b,77]

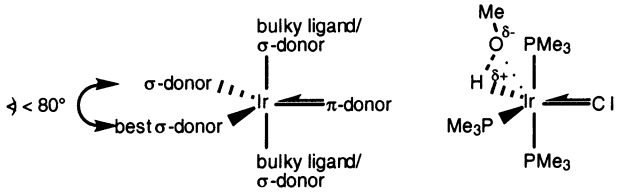
The nature of the transition state in concerted oxidative additions taking place by nucleophilic attack is still being debated.,[45,65c,77b−e,78−80] A linear structure analogous to **A**, in which the addendum is η^1-bound, and an asymmetric three-centered transition state analogous to **B** were suggested. (**B** differs from the transition state of pathway A in Figure 7 by the development of charge separation). We prefer structure **B** over **A**, because only in **B** steric factors seem important.[55] The site of steric difference in **A** is four bonds away from the metal center and the crowding around it (Ir···H−O−C−R, R = H, *n*-Bu or Me). In **B**, the site of steric difference is only three bonds away from the metal center (Ir···O−C−R). Additionally, the alkyl group in **B** is less favorably oriented than in **A**.

Stereochemical Course of the Reaction. Apart from reactions 2 and 3, there are only a few cases in which the identity of the kinetic product of polarized bond oxidative addition is known.[11e,44,74,81,82] In all of them, irrelevant of the spatial



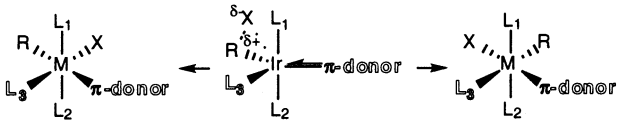
Transition State **A** Transition State **B**

arrangement of the different ligands, the polarized bond added across the axis containing the π-donor (the only exception being allyl-halides[83]). σ-Donors or π-acceptors do not affect the stereochemistry in any of the examples we cite, in contrast to reports about hydrogen and silane oxidative additions.[84,85] *We suggest that the stabilization imparted by the π-donating ligand to the transition state*[21] *accounts for this phenomenon.* Without a π-donor (as in [Ir(PMe$_3$)$_4$]PF$_6$,[21,68] PhIr(PMe$_3$)$_3$,[11f,52] *trans*-RM(CO)(PMe$_3$)$_2$ (M = Ir, Rh, R = alkyl, aryl),[84,86,87] and Me$_2$-Pt(bpy)$_2$ [53]), polarized bonds oxidatively add by other mechanisms, which are multistep.



C **D**

Generalized structure **C** is derived from crystallographic studies of coordinatively unsaturated, 16-electron d^6 compounds with a single π-donor.[88] Based on it is **D**, our suggested structure for the transition state of reaction 3. We expect a similar transition state **E** for the rest of the oxidative additions of polarized bonds R−X mentioned above (R = H, alkyl; X = OH, *O*-alkyl, OC(O)CF$_3$, halide, *S*-aryl).[11e,44,74,81,82] The collapse of **D** and **E** to the final product should involve a concomitant weakening of the polarized bond and a rearrangement that enables coordination of X. Rearrangements within the equatorial plain have the lowest activation energies.[88a,89] Because X enters cis to R, the only possible products are **F** and **G**. Since the



F **E** **G**

neutral ligand L$_3$ (L$_2$ in oxidative addition to *cis*-(CO)Ir(halide)-(DPPE)) has a higher trans effect than the π-donor, the R group

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Table 3. Possible Products of RX Oxidative Addition after Rearrangement within the Equatorial Plain of the Transition State E and Coordination of X (R, R′ = H, Alkyl; X = OR′, $OC(O)CF_3$, Halide, *S*-Aryl)

complex	L	π-donor	ref
$H(OR')IrCl(PMe_3)_3$	$L_1 = L_2 = L_3 = PMe_3$	Cl	this work
$RX(halide)(PPh_3)_2(CO)$	$L_1 = L_2 = PPh_3$, $L_3 = CO$	halide	73,80
$HBrIrCl(PEt_2Me)_2(CO)$	$L_1 = L_2 = PEt_2Me$, $L_3 = CO$	Cl	73a
$RXOsCl(P\text{-}i\text{-}Pr_3)_2(NO)$	$L_1 = L_2 = P\text{-}i\text{-}Pr_3$, $L_3 = NO$	Cl	11e
$HXIr(halide)(DPPE)(CO)$	$L_1 = L_2 =$ DPPE, $L_3 = CO$	Br or I	43
$HRh(SC_6H_5)_2(PMe_3)_3$	$L_1 = L_2 = L_3 = PMe_3$	SC_6H_5	81

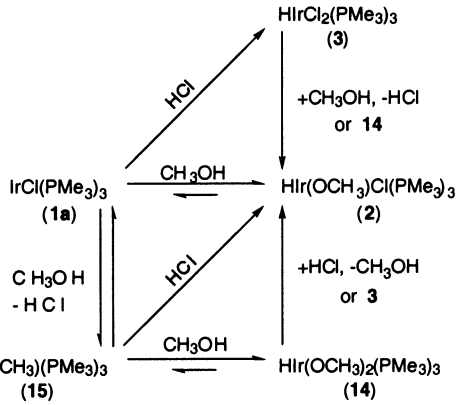

Figure 8. Anionic ligand redistributions during reaction 3.

will enter trans to the π-donor, leading to type **F** products exclusively (Table 3).

This idea is best demonstrated in the oxidative addition of thiophenols to $Rh(SAr)(PMe_3)_3$.[82] Unlike all other examples cited, the type **G** product is more stable here due to steric reasons (thiophenolates are bulkier than PMe_3). Nevertheless, the type **F** compound was the kinetic product observed. It slowly isomerized to the type **G** compound.[82]

3. Redistribution of the Chloro and Alkoxo Ligands. Elucidating the mechanism by which $Ir(OCH_3)(PMe_3)_3$ (**15**) is formed seems key to understanding the redistribution reactions involving **1a**, **15**, **2**, **3**, and **14**. Complex **15** is not the product of dehydrochlorination of **2**, because the formation of **2** and **15** is inversely correlated. The faster **2** is formed, the less we obtain of **15**. Complex **15** is, therefore, the product of an anionic ligand exchange with methanol (eq 6), in similarity to the well-studied alcohol−alkoxide exchanges. This exchange is probably assisted by hydrogen bonding between the weak acid and the anionic ligand.[9,25a,35] A similar mechanism, involving hydrogen bonding to chloride may be operating here, but alcohol coordination to Ir(I) followed by proton exchange between ligands and HCl elimination is also possible. Anionic ligand exchange by reversible bridging of two complexes was reported.[90] The presence of **1a**, **15**, methanol, and HCl in the reaction mixture gives a straightforward explanation to the observation of **3** and **14** along with **2** (Figure 8).

$$\underset{\textbf{1a}}{IrCl(PMe_3)_3} + CH_3OH \rightleftharpoons \underset{\textbf{15}}{Ir(OCH_3)(PMe_3)_3} + HCl \qquad (6)$$

Conclusions

$(C_8H_{14})IrCl(PMe_3)_3$ (**1**) and $IrCl(PEt_3)_3$ (**8**) in benzene afford the *cis*-hydrido-alkoxo and -hydroxo products *mer-cis*-$HIr(OR)(Cl)(PR'_3)_3$ [R′ = Me, R = Me (**2**), Et (**4**), 1-pentyl (**5**), 2-propyl (**7**), H (**12**); R′ = Et, R = Me (**9**), H (**13**)]. These are the kinetic and the only alkoxo or hydroxo products of the reaction. The plausible mechanism of the oxidative addition step is depicted in Figure 9. $IrCl(PMe_3)_3$ (**1a**) is the reactive species. Alcohol coordination to the metal is not on the reaction coordinate. The alcohol approaches the metal in such a way that its O−H bond parallels the Cl−Ir−PR'_3 axis, with the OR group close to the less sterically demanding chloride. The O−H bond is *not* cleaved prior to formation of the Ir−H bond. An asymmetric three-centered transition state involving charge separation is indicated. The transition state is stabilized by π-donation from chloride. Hydrogen bonding of free alcohol molecules to the addendum is suggested to assist the O−H cleavage. Rearrangement to the final product in the plane including chloride, hydride, and phosphine is governed by the strong trans effect of the hydride and phosphine.

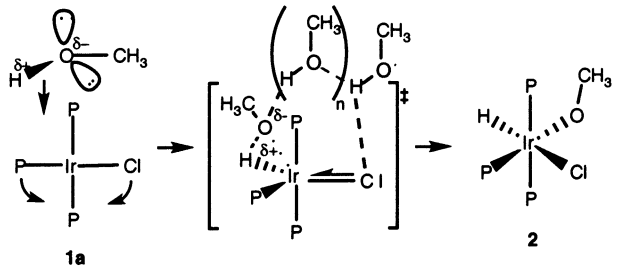

Figure 9. Suggested mechanism of methanol oxidative addition to **1a**. P = PMe_3. n = 0, 1, 2.

Comparing our results to those obtained for the oxidative additions of other polarized bonds such as *C*-halide,[44,76] *H*-halide (in apolar media),[64] H-SAr,[74b] and C−O[24a,33b,91] reveals many similarities. We therefore believe that some of our mechanistic conclusions regarding the factors contributing to the activation energies, the stereochemistry of the addition, the identity of the kinetic product, and the shape of the transition state may be true for oxidative addition of other polarized bonds as well, although the oxidative additions of ammonia and alcohols to $IrCl(PEt_3)_3$ (**8**) proceed by different mechanisms.[42,72a]

Experimental Section

General Considerations. All syntheses and chemical manipulations were carried out under nitrogen in a Vacuum Atmospheres DC-882 drybox, equipped with an oxygen/water scrubbing recirculation MO-40 "Dri-Train" or under argon, using vacuum and standard Schlenk techniques. Solutions were prepared using a Mettler PM200 (1 mg) balance, and standard dilution techniques whenever less than 30 mg of a solid were needed. Liquids were measured with Gilson pipets (5 and 1 mL, 200 and 20 μL). Dilution techniques were used for amounts smaller than 20 μL.

Materials. Solvents were refluxed on the proper drying agent, distilled under argon, and stored over activated 4Å molecular sieves (3Å for methanol). Deuterated solvents (Aldrich) were degassed and dried over 3Å molecular sieves for at least a week before use. Trimethylphosphine (Aldrich), LiCl, and LiBr (Merck) were used as received. Cyclooctene (Merck) was freshly distilled under argon. $NaOCH_3$ was prepared from sodium and methanol under nitrogen (excess methanol was removed under vacuum at 70 °C during 48 h). $IrCl_3 \cdot 3H_2O$ was from Engelhardt. $P(CD_3)_3$,[92] [(cyclooctene)$_2$Ir(μ-Cl)],[93]

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$IrCl(PEt_3)_3$,[26,42] (**8**) and $(C_2H_4)_2IrCl(PEt_3)_2$[42] (**17**) were prepared according to literature.

Physical Measurements. Infrared spectra were recorded with a Nicolet Spectrometer using NaCl plates as either Nujol mulls or neat films. ^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).

Solutions for the kinetic experiments were prepared in a drybox using standard dilution techniques. Gilson pipets were used to add the solutions at room temperature to 5-mm Pyrex NMR tubes, and the height of the solution in the tubes was checked for consistency. Additional solvent was added to attain the desired solvent volume (usually 550 μL).

Spectra were recorded in standard pulsed FT mode using 90° (or less) pulses and at least five T_1 periods between pulses to ensure reliable quantitative results. When tip angles smaller than 90° were employed, delay times were recalculated.[94] ^{31}P spin−lattice relaxation times (T_1, s) were determined by standard spin inversion/recovery methods for compound **2**. Only the faster-relaxing phosphorus trans to phosphorus signals were used as data sources. These signals are also larger and less split than the triplets of the unique phosphorus. In each set of experiments, the acquisition parameters were constant.

$(C_8H_{14})IrCl(PMe_3)_3$ (1). A modified literature procedure[20] was employed. A solution of PMe_3 (0.509 g, 6.7 mmol) in toluene (10 mL) was placed in a dropping funnel equipped with an external cooling jacket (−78 °C) and added dropwise during 30 min to a stirred (−78 °C) suspension of $[(C_8H_{14})_2Ir(\mu\text{-}Cl)]_2$ (C_8H_{14} = cyclooctene; 1.00 g, 1.12 mmol) in toluene (100 mL). Thirty minutes later, the temperature was allowed to rise to room temperature during 4−5 h. Filtration removed insoluble red $[Ir(PMe_3)_4]Cl$,[20] and the solvent was evaporated under vacuum. The product was recrystallized from cold (−30 °C) toluene (15 mL) and cyclooctene (0.75 mL), washed with cold toluene, and vacuum-dried, yielding 0.67 g (53%) of yellow crystals.

***mer-cis*-HIr(OCH$_3$)Cl(PMe$_3$)$_3$ (2).** Cold (−30 °C) methanol (1.0 mL) was added to a cold (−30 °C) solution of **1** (100 mg, 0.18 mmol) in 5 mL of toluene. After 1 h at −30 °C, the solvents were stripped off at the same temperature. The off-white residue contained 93% (by ^1H and $^{31}P\{^1H\}$ NMR) of **2** as a highly hygroscopic solid. Also present were **3** and **6**. ^1H NMR (C_6D_6) 4.09 (d, $^4J^d_{H-P,trans}$ = 5.6 Hz, 3H, OCH_3, 1.40 (t, $^{virt.}J_{H-P}$ = 3.6 Hz, 18H, 2P(CH_3)$_3$), 1.13 (d, $^2J_{H-P}$ = 10.5 Hz, 9H, P(CH_3)$_3$), −21.56 (dt, $^2J^d_{H-P}$ = 19.2 Hz, $^2J^t_{H-P}$ = 14.7 Hz, 1H, Ir-*H*). $^1H\{^{31}P\}$ NMR (C_6D_6) 4.09 (s, 3H), 1.40 (s, 18H), 1.13 (s, 9H), −21.56 (s, 1H). $^{31}P\{^1H\}$ NMR −30.9 (d, $^2J_{P-P,cis}$ = 18.5 Hz, 2P), −50.6 (t, $^2J_{P-P,cis}$ = 18.5 Hz, 1P). $^{13}C\{^1H\}$ NMR (C_6D_6) 65.3 (br s, O*C*H$_3$), 21.2 (d, $^1J_{C-P}$ = 37 Hz, P(*C*H$_3$)$_3$), 16.2 (t, $^{virt.}J_{C-P}$ = 18 Hz, 2P(*C*H$_3$)$_3$). IR (neat): 2165 (s, νIr−H), 1077 (s, νC−O). Upon exposure to air, the C−O peak was immediately replaced by a broad O−H signal at 3400 cm^{-1}.

***mer-cis*-HIr(OCH$_2$CH$_3$)Cl(PMe$_3$)$_3$ (4)** was prepared as **2**, using ethanol. ^1H NMR (C_6D_6) 4.01 (qd, $^3J^q_{H-H}$ = 6.8 Hz, $^4J^d_{H-P,trans}$ = 1.4 Hz, 2H, OCH_2CH$_3$), 1.51 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, OCH$_2$CH_3), 1.39 (t, $^{virt.}J_{H-P}$ = 3.6 Hz, 18H, 2P(CH_3)$_3$), 1.11 (d, $^2J_{H-P}$ = 9.4 Hz, 9H, P(CH_3)$_3$), −21.52 (dt, $^2J^d_{H-P,cis}$ = 19.3 Hz, $^2J^t_{H-P}$ = 14.4 Hz, ^1H, Ir-*H*). $^1H\{^{31}P\}$ NMR (C_6D_6) 4.01 (q, $^3J_{H-H}$ = 6.8 Hz, 2H), 1.51 (t, $^3J_{H-H}$ = 6.8 Hz, 3H), 1.39 (s, 18H), 1.11 (s, 18H), −21.52 (s, ^1H). $^{31}P\{^1H\}$ NMR −31.5 (d, $^2J_{P-P,cis}$ = 18.6 Hz, 2P), −51.7 (t, $^2J_{P-P,cis}$ = 18.5 Hz, 1P). $^{13}C\{^1H\}$ NMR (C_6D_6) 72.5 (s, O*C*H$_2$*C*H$_2$), 23.6 (d, $^4J_{C-P,trans}$ = 6.7 Hz, OCH$_2$*C*H$_3$, 21.2 (d, $^1J_{C-P}$ = 36.1 Hz, P(*C*H$_3$)$_3$), 16.1 (t, $^{virt.}J_{C-P}$ = 18.2 Hz, 2P(*C*H$_3$)$_3$). IR (neat) 2159 (s, νIr−H), 1116 (m, νC−O), 1050 (m, νC−O).). Upon exposure to air, the C−O peak was immediately replaced by a broad O−H signal at 3400 cm^{-1}.

***mer-cis*-HIr(O(CH$_2$)$_4$CH$_3$)Cl(PMe$_3$)$_3$ (5)** was prepared as **2**, using 1-pentanol. ^1H NMR (C_6D_6) 3.93 (td, $^3J^t_{H-H}$ = 7.0 Hz, $^4J^d_{H-P,trans}$ = 1.6 Hz, 2H, OCH_2CH$_2$), 1.88 (tt, $^3J_{H-H}$ = 7.5 Hz, $^3J_{H-H}$ = 7.1 Hz, 2H, OCH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.6(0) (m, 2H, CH_2 of the pentoxide, γ or δ to oxygen), 1.40 (t, $^{virt.}J_{H-P}$ = 3.6 Hz, 18H, 2P(CH_3)$_3$), 1.3(8) (m, 2H, CH_2 of the pentoxide, γ or δ to oxygen), 1.17 (d, $^2J_{H-P}$ = 9.5 Hz, 9H, P(CH_3)$_3$), 1.01 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, O(CH$_2$)$_4$CH_3), −21.53 (dt, $^2J^d_{H-P,cis}$ = 19.0 Hz, $^2J^t_{H-P,cis}$ = 14.7 Hz, 1H, Ir-*H*). $^{31}P\{^1H\}$ NMR −30.9 (d, $^2J_{P-P,cis}$ = 18.8 Hz, 2P), −50.7 (t, $^2J_{P-P,cis}$ = 18.8 Hz, 1P). IR (neat) 2156 (s, νIr−H), 1138 (m, νC−O), 1105 (w, νC−O). Upon exposure to air, the C−O peak was immediately replaced by a broad O−H signal at 3400 cm^{-1}.

***mer-cis*-HIr(OCH(CH$_3$)$_2$)Cl(PMe$_3$)$_3$ (7).** An attempt to prepare this complex using the procedure above (−30 °C) resulted in recovery of the starting material. **7** was generated slowly at room temperature in neat 2-propanol along with the β-hydride elimination product **6** and small amounts of **3**. The mixture was dried under vacuum. ^1H NMR (C_6D_6) 3.80 (heptet·d, $^3J_{H-H}$ = 5.9 Hz, $^4J^d_{H-P}$ = 2.6 Hz, 1H, Ir−OCH(CH$_3$)$_3$), 1.51 (d, $^3J_{H-H}$ = 5.8 Hz, 6H, OCH(CH_3)$_2$), 1.42 (t, $^{virt.}J_{H-P}$ = 3.6 Hz, 18H, 2P(CH_3)$_3$), 1.09 (d, $^2J_{H-P}$ = 9.3 Hz, 9H, P(CH_3)$_3$), −21.32 (dt, $^2J^d_{H-P,cis}$ = 20.8 Hz, $^2J^t_{H-P,cis}$ = 12.8 Hz, 1H, Ir-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6) −32.4 (d, $^2J_{P-P,cis}$ = 19.7 Hz, 2P), −51.7 (t, $^2J_{P-P,cis}$ = 19.7 Hz, 1P). IR (neat) 2156 (s, νIr−H), 1121 (w, νC−O), 1077 (s, νC−O)). Upon exposure to air, the C−O peak was immediately replaced by a broad O−H signal at 3400 cm^{-1}.

***mer-cis*-HIr(OCH$_3$)Cl(PEt$_3$)$_3$ (9)** was prepared as the PMe_3 analogue **2** using **8**, but the solvents were stripped off after 5 min. The products include more than 85% of **9**, along with the β-hydride elimination product **11**, **10**, and small amounts of the starting complex **8**. **9** undergoes β-H elimination in solution, even at −30 °C. ^1H NMR (C_6D_6) 4.01 (d, $^4J_{H-P,trans}$ = 5.7 Hz, 3H, OCH_3), 2.09 (m, (= d·q·virt.·t), J = 3.7 Hz, 6H, 2P(*H*-C(H)-CH$_3$)$_3$, 1.71 (m, (= d·q·virt. t), J = 3.7 Hz, 6H, 2P(H-C(*H*)-CH$_3$)$_3$, 1.67 (dq, $^2J_{H-P}$ = $^2J_{H-H}$ = 7.2 Hz, 6H, P(CH_2-CH$_3$)$_3$), 1.11 (tt (apparent quintet), $^{virt.}J_{H-P}$ = $^3J_{H-H}$ = 7.4 Hz, 18H, 2P(CH$_2$CH_3)$_3$), 0.86 (dt, $^3J_{H-P}$ = 14.4 Hz, $^3J_{H-H}$ = 7.6 Hz, 9H, P(CH$_2$CH_3)$_3$), −21.60 (dt, $^2J^d_{H-P,cis}$ = 16.7 Hz, $^2J^t_{H-P,cis}$ = 14.6 Hz, ^1H, Ir-*H*). $^{131}P\{^1H\}$ NMR −6.9 (d, $^2J_{P-P,cis}$ = 16 Hz, 2P), −20.4 (t, $^2J_{P-P,cis}$ = 16 Hz, 1P).

***mer-cis*-HIr(OH)Cl(PMe$_3$)$_3$ (12).** Excess water (0.5 mL) was added to a solution of **1** (100 mg) in dioxane (5 mL). After 1 h at room temperature, the solvents were stripped off. The off-white residue contained **12** (95%) and **3** (3%). ^1H NMR (C_6D_6) 1.36 (t, $^{virt.}J_{H-P}$ = 3.6 Hz, 18H, 2P(CH_3)$_3$), 1.19 (d, $^2J_{H-P}$ = 9.6 Hz, 9H, P(CH_3)$_3$ trans to Cl), −2.15 (d, $^3J_{H-P,trans}$ = 5.8 Hz, 1H, Ir−O*H*), −21.73 (dt, $^2J^d_{H-P,cis}$ = 17.7 Hz, $^2J^t_{H-P,cis}$ = 16.8 Hz, 1H, Ir-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6) −33.0 (d, $^2J_{H-P,cis}$ = 18 Hz, 2P), −49.3 (t, $^2J_{H-P,cis}$ = 18 Hz, 1P). IR (Nujol) 2157 (m, νIr−H). νO−H was not observed.

Preparation of *mer-cis*-HIr(OH)Cl(PEt$_3$)$_3$ (13). The procedure above was repeated, using **8**. The residue included **13** (> 90%) and **8**. ^1H NMR (C_6D_6) 2.10 (m (13 lines), $J_{apparent}$ = 3.6 Hz, 6H, 2 P(C(*H*)-HCH$_3$)$_3$ trans to P), 1.73 (m (13 lines), $J_{apparent}$ = 3.6 Hz, 6H, 2 P(C(H)-*H*CH$_3$)$_3$ trans to P), 1.61 (apparent quintet, the weighed average of $^2J^d_{H-P}$ and $^3J^q_{H-H}$ = 8.0 Hz, 6H, P(CH_2CH$_3$)$_3$ trans to OH), 1.09 (m (apparent quintet), $J_{apparent}$ = 7.4 Hz, 18H, 2 P(C(H)HCH_3)$_3$ trans to P), 0.89 (dt, $^3J^d_{H-P}$ = 14.7 Hz, $^3J^t_{H-H}$ = 7.5 Hz, 9H, P(CH$_2$CH_3)$_3$ trans to OH), −2.07 (d, $^3J^d_{H-P,trans}$ = 5.5 Hz, 1H, Ir−O*H*), −21.72 (dt, $^2J^d_{H-P,cis}$ = 17.6 Hz, $^2J^t_{H-P,cis}$ = 15.3 Hz, 1H, Ir-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6) −17.4 (t, $^2J_{P-P,cis}$ = 15 Hz, 1P), −8.0 (d, $^2J_{P-P,cis}$ = 15 Hz, 2P). IR (Nujol) 3463 (m, νO−H), 2184 (m, νIr−H). The complex is highly hygroscopic. Upon exposure to air, a broad O−H signal at 3400 cm^{-1} appears.

X-ray Structure of 13. Crystals suitable for low-temperature X-ray examination were obtained by slow evaporation of a 1:1 benzene/pentane solution. Crystal data: 0.1 × 0.1 × 0.1 mm^3, monoclinic, $P2_1/c$

(93) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.
(94) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. *Practical NMR Spectroscopy*; Hyden: London, 1980; p 353.

(no. 14), $a = 15.084(4)$ Å, $b = 10.997(2)$ Å, $c = 15.745(4)$ Å, $\beta = 106.24(4)°$, $V = 2503.0(9)$ Å^3, $M_r = 600.162$, $Z = 4$, $D_c = 1.593$ g cm^{-3}, $\mu = 56.16$ cm^{-1}. Data collection and treatment: Rigaku AFC5 diffractometer, rotating anode Rigaku RU300 source, 0.5×10 mm^2 filament, Load of 40 KV, 250 mA, Mo Kα radiation ($\lambda = 0.70926$ Å), $\omega/2\Theta$ scan method, $\theta_{max} = 54°$, scan speed 16°/min, 5383 reflection collected (from which 4915 were unique). The structure was solved by automated Patterson analysis (SHELXS-86) and Fourier method (SHELX-76). Hydrogenous were found from a difference Fourier map. $R_{sym} = 0.01$. Final $R = 0.037$, $R_w = 0.034$.

Reactions of 1 with Methanol and LiCl. (a) The preparation of **2** was repeated at −30 °C with 15 mg of **1** in 750 μL toluene. LiCl (5.6 mg, 5 mol equiv) was dissolved in methanol (150 μL) prior to the addition. Two phases were formed upon mixing. After 1 h, during which the reaction vessel was periodically shaken, the solvent was removed at −30 °C under vacuum. **3** was the only product. (b) The above procedure was repeated in THF instead of toluene. A single phase was formed. Only **3** was obtained. (c) Procedure a was repeated at room temperature, using dioxane instead of toluene, giving a single phase. After 10 min only **3** was observed.

Reaction of 1 with Methanol and $NaOCH_3$ at −30 °C. A solution of $NaOCH_3$ (5.8 mg, 0.11 mmol) and methanol (100 μL) in THF (400 μL) was cooled to −30 °C and added to a cold (−30 °C) solution of **1** (20 mg, 3.5×10^{-2} mmol) in THF (600 μL). After 1 h, the solvents were stripped off under vacuum. Extraction with benzene yielded a yellow solution containing 56% of *mer-cis*-$HIr(OMe)_2(PMe_3)_3$ (**14**), 24% of $Ir(OCH_3)(PMe_3)_3$ (**15**), 17% of trimethylphosphine disproportionation products {[*cis*-$H_2Ir(PMe_3)_4$]Cl,[41] an unidentified product containing two trans phosphines, possibly $[H_2Ir(PMe_3)_2(\mu\text{-}OCH_3)]_2$}, and 3% of other compounds. **14** and **15** decomposed in either THF/methanol or C_6D_6, generating more of the PMe_3 disproportionation products as well as $HIr(PMe_3)_4$[95] and $[(CO)Ir(PMe_3)_4]^+$.[96] Due to their instability, **14** and **15** were characterized by ^{1}H and ^{31}P NMR only.

14: ^{1}H NMR (C_6D_6) 4.10 (d, $^4J_{H-P,trans} = 5.5$ Hz, 3H, OCH_3 trans to PMe_3), 3.89 (s, 3H, OCH_3 trans to H), 1.36 (t, $^{virt.}J_{H-P} = 3.5$ Hz, 18H, 2P(CH_3)$_3$), 1.13 (d, $^2J_{H-P} = 9.4$ Hz, P(CH_3)$_3$), −23.09 (dt, $^2J^d_{H-P,cis} = 18.7$ Hz, $^2J^t_{H-P,cis} = 15.9$ Hz, 1H, Ir-*H*). ^{31}P{^{1}H} NMR (C_6D_6) −29.4 (d, $^2J_{P-P,cis} = 19.6$ Hz, 2P), −52.8 (br m (apparent t), 1P).

15: ^{1}H NMR (C_6D_6) 3.98 (d, $^4J_{H-P,trans} = 4.1$ Hz, 3H, OCH_3), 1.28 (t, $^{virt.}J_{H-P} = 3.0$ Hz, 18H, 2P(CH_3)$_3$), 1.21 (d, $^2J_{H-P} = 8.0$ Hz, 9H, P(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6) −15.1 (d, $^2J_{P-P,cis} = 18.9$ Hz, 2P), −47.2 (t, $^2J_{P-P,cis} = 18.9$ Hz, 1P).

Reaction of 8 with Methanol and LiCl at −30 °C. A cold (−30 °C) solution of LiCl (2.8 mg, 66×10^{-3} mmol) in methanol (50 μL) and THF (200 μL) was added to a solution of **8** (10 mg, 17×10^{-3} mmol) in THF (300 μL). After 30 min, the solvents were stripped off under vacuum; 52% **10** and 48% of **11** were observed in the C_6D_6 extract.

***fac*-$H_2IrCl(PMe_3)_3$ (18).** A solution of 50 mg of **1** in 3 mL of benzene in a Schlenk tube was frozen (liquid N_2), and the nitrogen atmosphere was replaced by ca. 1 atm of H_2. The mixture was warmed to room temperature. An almost immediate change from red to yellow occurred. After the mixture stirred for 30 min, the hydrogen was released, and the solvent was stripped off under vacuum, yielding a yellowish solid. It was recrystallized from toluene/pentane at −30 °C. Yield was almost quantitative. ^{1}H NMR (C_6D_6) 1.30 (d, $^2J_{H-P} = 7.6$ Hz, 18H, 2P(CH_3)$_3$ trans to H), 1.18 (d, $^2J_{H-P} = 10.2$ Hz, 9H, P(CH_3)$_3$ trans to Cl), −10.33 (second-order dm, $^2J_{H-P} \approx 163$ Hz, 2H, *H*-Ir-P). ^{31}P{^{1}H} NMR −43.2 (t, $^2J_{P-P,cis} = 9$ Hz, 1P), −51.1 (d, $^2J_{P-P,cis} = 9$ Hz, 2P). Elemental analysis: calculated: C 23.61, H 6.38; found: C 23.87, H 6.45. Complex **18** remained unchanged in benzene for a month at room temperature. In a 1:10 methanol:benzene solution, the isomerization of facial **18** to meridional **6** took 9 days to reach completion.

(95) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580.
(96) Labinger, J. A.; Osborn, J. A. *Inorg. Synth.* **1978**, *18*, 62.

***fac*-$HIr(SiEt_3)Cl(PMe_3)_3$ (19).** A cold (−30 °C) solution of $HSiEt_3$ (20 μL, 0.125 mmol) in toluene (500 μL) was added dropwise to a cold (−30 °C) solution of **1** (18 mg, 3.18×10^{-2} mmol) in toluene (500 μL), resulting in bleaching within minutes. After 15 min the solvent was stripped off under vacuum at −30 °C, yielding an off-white solid of the pure product. ^{1}H NMR (C_6D_6) 1.47 (dd (apparent t), $^3J_{H-H} = 7.7$ Hz, $^3J_{H-H} = 7.5$ Hz, 9H, Si(H−C(H)CH_3)$_3$), 1.38 (dqd, $^2J^d_{H-H} = 13.9$ Hz, $^3J^q_{H-H} = 7.7$ Hz, $^4J^d_{H-P,trans} = 1.9$ Hz, 3H, Si(H−C(*H*)CH$_3$)$_3$), 1.27 (d, $^2J_{H-P} = 7.4$ Hz, 9H, P(CH_3)$_3$), 1.23 (d (slightly broadened), $^2J_{H-P} = 7.6$ Hz, 9H, P(CH_3)$_3$ trans to H), 1.17 (d, $^2J_{H-P} = 9.9$ Hz, 9H, P(CH_3)$_3$), 1.07 (dqd, $^2J^d_{H-H} = 13.9$ Hz, $^3J^q_{H-H} = 7.5$ Hz, $^4J^d_{H-P,trans} = 1.5$ Hz, 3H, Si(*H*-C(H)CH$_3$)$_3$), −10.66 (ddd (apparent dt), $^2J^d_{H-P,trans} = 144.7$ Hz, $^2J^d_{H-P(1),cis} = {}^2J^d_{H-P(2),cis} = 19.3$ Hz, 1H, Ir-*H*). ^{31}P{^{1}H} NMR (C_6D_6) −44.9 (dd, $^2J_{P-P,cis} = 13$ Hz, $^2J_{P-P,cis} = 9$ Hz, 1P), −51.4 (dd, $^2J_{P-P,cis} = 23$ Hz, $^2J_{P-P,cis} = 13$ Hz, 1P), −57.6 (dd, $^2J_{P-P,cis} = 23$ Hz, $^2J_{P-P,cis} = 9$ Hz, 1P).

***mer*-$HIr(SiEt_3)Cl(PMe_3)_3$ (20). 19** isomerizes to **20** (Si trans to Cl) at room temperature in benzene within hours. ^{1}H NMR (C_6D_6) 1.51 (t, $^{virt.}J_{H-P} = 3.6$ Hz, 18H, 2P(CH_3)$_3$ trans to each other), 1.22 (dd, $^2J_{H-P} = 7.4$ Hz, $^4J_{H-H,trans} = 0.8$ Hz, 9H, P(CH_3)$_3$ trans to H), 1.18 (t, $^3J_{H-H} = 7.8$ Hz, 9H, Si(CH$_2$CH_3)$_3$), 0.78 (q, $^3J_{H-H} = 7.8$ Hz, 6H, Si(CH_2-CH$_3$)$_3$), −10.38 (ddd (apparent dt), $^2J^d_{H-P,trans} = 133.7$ Hz, $^2J^d_{H-P(1),cis} = {}^2J^d_{H-P(2),cis} = 20.4$ Hz, 1H, Ir-*H*). ^{31}P{^{1}H} NMR (C_6D_6) −46.5 (d, $^2J_{P-P,cis} = 22$ Hz, 2P trans to each other), −48.5 (t, $^2J_{P-P,cis} = 22$ Hz, 1P trans to H). Elemental analysis: calculated: C 31.49, H 7.57; found: C 31.42, H 7.72.

Kinetic Experiments

Oxidative Addition of Methanol to $(C_8H_{14})IrCl(PMe_3)_3$ (1). A C_6D_6 solution of **1** was partitioned among several NMR tubes. Each tube contained **1** (3.0 mg, 5.3×10^{-3} mmol) in 400 μL of C_6D_6. The tubes were kept frozen (−30 °C) in the drybox. Before the measurement, 150 μL of a C_6D_6 solution containing 2.0 μL methanol (49×10^{-3} mmol) was added on top of the frozen solution. (A methanol-to-complex ratio of 9.3:1 was used, allowing measurement of the pseudo-first-order rate constants, while keeping low-to-medium polarity—only 0.36% methanol in the solution.) The tube was kept frozen (liquid N_2) after removal from the box, warmed to room temperature (1.5 min), and placed in the thermostated NMR probe. The oxidative addition was monitored by ^{31}P{^{1}H} NMR until its completion. This procedure was repeated at 10, 22, 30, and 40 °C. The 22 °C reaction was monitored by ^{1}H NMR as well. The compounds **1a**, **2**, **3**, **14**, and **15** were observed at all temperatures ([**15**] is too small to be observed at 10 °C), but at the end, only **2** and small amounts of **3** were present. All values were reproducible (at least twice) with less than 11% inaccuracy.

At −30 °C a tripled methanol amount (6.0 μL, 150×10^{-3} mmol) was used to speed up the addition. Only **1a**, **1**, and **2** were observed during the reaction progress.

Kinetic Deuterium Isotope Effects in the Oxidative Addition of Methanol to 1a. The reactions of CH_3OH, CH_3OD (99% D), and CD_3OD (99% D) were compared at 22 °C using the procedure described above. Experiments were repeated three times. The values obtained (mathematically correcting for 1% nondeuterated methanol) were: $k_{CH_3OH}/k_{CH_3OD} = 2.0 \pm 0.2$ for **1a** and 1.75 ± 0.15 for the combined concentrations of **1a** and **15**. $k_{CH_3OH}/k_{CH_3OD} = 3.2 \pm 0.3$ for **1a** and 3.05 ± 0.25 for **1a** and **15** combined. The final solutions were analyzed also by ^{1}H and ^{2}H NMR (deuteride region only in the ^{2}H NMR).

Effect of Methanol Concentration on the Oxidative Addition rate to 1a. The procedure used for monitoring the methanol addition to **1a** in benzene was repeated at 22 °C, using 4, 2, 1, and 0.2 μL (1 mol equiv) of methanol. The reaction with 4 μL of methanol was complete in 5 min, whereas no oxidative addition was observed for days with 0.2 μL of methanol. The reaction with 1 μL of methanol was very slow, and the amounts of **15** and **3** generated were much larger than in the presence of 2 μL of methanol.

Oxidative addition of 1-pentanol to 1a was monitored as the methanol was added to **1a** at 22 °C with 3.0 mg of **1** (5.3×10^{-3} mmol), 5.4 μL of 1-pentanol (49×10^{-3} mmol), and 545 μL of C_6D_6.

Oxidative addition of 2-propanol to 1a was monitored as the methanol was added to **1a** at 22 °C with 3.0 mg of **1** (5.3×10^{-3} mmol), 3.8 μL of 2-propanol (49×10^{-3} mmol), and 546 μL of C_6D_6. No reaction was observed. Data were acquired at a higher concentration of 2-propanol (50 μL, 0.65 mmol in 500 μL of C_6D_6).

Oxidative addition of methanol to 1a in NMP was monitored as the methanol was added to **1a** at 22 °C using NMP as solvent. Because NMP does not freeze at −30 °C, the methanol-containing solution was added on top. No reaction was observed for more than a week. The same refers to a solution of 1-to-1 NMP with C_6D_6.

Comparison of the oxidative addition of methanol and water to 1a in THF was monitored as the methanol addition to **1a**, using THF. As THF is not frozen at −30 °C, the cold (−30 °C) methanol containing solution was added on top, and the tube was transferred within 25 s into a liquid nitrogen container outside of the glovebox. The reactions were monitored at 17 °C. For methanol we had 6.0 mg of **1** (10.5×10^{-3} mmol) and 4 μL of methanol (99×10^{-3} mmol) in 546 μL of THF. The reaction behaved as in C_6D_6, but considerably less of **3** was formed. For water we had 6.0 mg of **1** (10.5×10^{-3} mmol), 1.8 μL water (99×10^{-3} mmol), and 548 μL THF.[21]

Oxidative Addition of Methanol to 1a in the Presence of LiCl. A THF (350 μL) solution containing 2.0 μL of methanol (49×10^{-3} mmol) and 3.3 mg of LiCl (78×10^{-3} mmol) was added to a NMR tube on top of a liquid nitrogen frozen solution of **1** (5.3×10^{-3} mmol) in 200 μL of a THF. After a few minutes, the tube was warmed until the THF melted (1 min) and placed in the NMR probe (22 °C). The oxidative addition was monitored by ^{31}P NMR until its completion. Compound **3** was the major product. Smaller amounts of unidentified products were observed, but they were not formed at higher methanol concentrations. The $^{31}P\{^1H\}$ NMR doublet of the d^8 reactant is shifted 7 ppm upfield, and the triplet 2 ppm downfield: −26.5 (d, $^2J_{P-P,cis} =$ 19.9 Hz, 2P), −38.8 (t, 1P). This compound has no hydrides (the ^{1}H NMR hydride region was examined for the nondeuterated reaction mixture). It may be $Li[IrCl_2(PMe_3)_3]$ (**16**).

Methanol oxidative addition to 1a in the presence of 2% acid was monitored as the methanol was added to **1a** at 22 °C, using 3.0 mg of **1** (5.3×10^{-3} mmol) and 547 μL toluene; 2% (vs [**1a**]) of *p*-toluene sulfonic acid hydrate (0.02 mg 0.11×10^{-3} mmol) was added with the methanol. The disappearance rate of **1a** was the same as that without the acid. The same results were obtained with $HBF_4 \cdot Et_2O$ (85% in ether, 0.02 mg, 0.11×10^{-3} mmol).

Reaction of 1a with methanol in the presence of PMe_3 was monitored as the methanol was added to **1a** at 22 °C, but PMe_3 (0.55 μL, 5.3×10^{-3} mmol, 1 mol equiv) was added with the methanol. Red $[Ir(PMe_3)_4]Cl$[20] precipitated immediately, consuming most of **1a**. In the remaining solution *cis*-$[H_2Ir(PMe_3)_4]^+$,[41] and $[HIrCl(PMe_3)_4]^+$ [40] (cis and trans) slowly formed.

Exchange of 2 with Methanol. A solution of 2 μL of methanol-d_4 (4.92×10^{-2} mmol) in 48 μL of benzene-d_6 was added to a NMR tube containing a frozen solution of **2** (3 mg, 5.96×10^{-3} mmol) in benzene (500 μL). Diminishing of the methoxo peak normalized to the constant area under the aliphatic phosphines was monitored by ^{1}H NMR at 22 °C. Because the exchange rate was very slow, the reaction was followed for only one half-life of **2**. First-order dependence on [**2**] was observed. A very slow exchange of the hydride to a deuteride was observed as well.

Oxidative Addition of Methanol to $IrCl(PEt_3)_3$ (8) in the Presence of PEt_3. Two NMR tubes were loaded each with a solution of **8** (3.0 mg, 5.1×10^{-3} mM) in C_6D_6 (300 μL). The solutions were frozen (−30 °C). C_6D_6 solution (145 μL) containing 5.0 μL (0.12 mmol) of methanol and 7.6 μL (5.1×10^{-2} mmol) of PEt_3 were added to one tube. A solution containing 150 μL of C_6D_6, 5.0 μL (0.123 mmol) of methanol, and no PEt_3 was added to the other. Both tubes were kept in liquid nitrogen until they were put into the thermostated (22 °C) NMR probe. The disappearance of **8** and the generation of **9**, **11**, and small amounts of **10** and other products were observed. These processes took place at the same rate and yielded the same product distribution.

Oxidative Addition of Methanol to 8 in THF. The above procedure was repeated with THF as solvent (and no PEt_3). No reaction was observed within 8 h. With a 22 times higher methanol concentration (110 μL, 0.75 mM), **11** slowly accumulated, but **9** was not observed.

Reaction of $(C_2H_4)_2IrCl(PEt_3)_2$ (17) with Methanol. The above procedure was repeated with **17** in C_6D_6. No reaction was observed within 8 h.

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Supporting Information Available: X-ray data for **13** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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