Oxidative Addition of X−H (X = C, N, O) Bonds to $[Ir(PMe_3)_4]Cl$ and Catalytic Hydration of Acetonitrile Using its Peroxo Derivative, $[Ir(O_2)(PMe_3)_4]Cl$, as Catalyst Precursor

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The reactions of $[Ir(PMe_3)_4]Cl$ (**1**) with a variety of substrates (acetonitrile, *p*-aminobenzonitrile, *p*-cyanophenol) containing a nitrile group were examined. Cleavage of the X−H bonds occurred selectively over the coordination of the CN moiety in those substrates, and compounds derived from the corresponding X−H (X = C, N, O) oxidative addition reaction, namely, *cis*-$[IrH(CH_2CN)(PMe_3)_4]Cl$ (**2**), *cis*-$[IrD(CD_2CN)(PMe_3)_4]Cl$ (**3**), *cis*-$[IrH(p\text{-}NHC_6H_4CN)(PMe_3)_4]Cl$ (**4**), and *cis*-$[IrH(p\text{-}OC_6H_4CN)(PMe_3)_4]Cl$ (**6**), were obtained. X-ray diffraction studies have confirmed the structures of **3** and **4**. In the case of **6**, the compound *trans*-$[IrClH(PMe_3)_4][p\text{-}OC_6H_4CN]$ (**5b**), resulting from exchange of Cl and *p*-OC_6H_4CN anions between inner and outer sphere, was also formed, and the solid-state structure (**5b**·HOC_6H_4CN), obtained by X-ray diffraction, contained the hydrogen-bonded $NCC_6H_4O\cdots H\cdots OC_6H_4CN$ anion. The salt $[Ir(PMe_3)_4][BPh_4]$ (**7**) was also prepared, characterized by X-ray diffraction and reacted with *p*-HOC_6H_4CN. Reaction of **1** with acetamide, the product of acetonitrile hydration, was undertaken to gain insight into the nitrile hydration process, and the single-crystal structure of the N−H bond cleavage product, *cis*-$[IrH(NHC(O)Me)(PMe_3)_4]Cl$ (**8**), was determined by X-ray diffraction. The peroxo compound derived from reaction of **1** with O_2, $[Ir(O_2)(PMe_3)_4]Cl$ (**9**), was prepared, characterized by X-ray diffraction, and used as a catalyst precursor for the hydration of acetonitrile using the protio and deuterio mixtures of substrates, CH_3CN/H_2O (A), CD_3CN/D_2O (B), CD_3CN/H_2O (C), and CH_3CN/D_2O (D). Catalysis occurred cleanly at 140 °C, giving d_n-acetamides; the formation of these was monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and GC/MS. *In situ* $^{31}P\{^1H\}$ NMR spectroscopic studies during catalysis confirmed the formation of $O{=}PMe_3$.

Introduction

The coordination and reactivity of nitriles with low-valent late transition metal complexes is of interest because catalytic hydration of nitriles to amides remains a challenging goal.[1] The conversion of nitriles into amides by conventional acid/base strategies usually requires harsh conditions[2] and remains impractical for most purposes due to conversion and selectivity issues,[3] and even more so, due to serious concerns regarding the extensive formation of salts that result from the neutralization of the reaction media, which may account for up to ca. 70 wt % of total wastes.[4a] The development of catalytic reactions that employ transition metal complexes as catalysts under neutral and mild conditions has been proposed[4,5] as a particularly important alternative for the nitrile hydration process to address these issues, and a considerable amount of effort has been expended in this direction.[1b] The majority of these efforts, however, have not succeeded in achieving catalysis,[1−6] and as a result, most of the existing literature concerning transition-metal-promoted hydration of nitriles still refers to stoichiometric reactions.[1a,b]

Relevant to the nitrile hydration, the reactivity of organonitriles with nickel complexes has been examined by Garcia and Jones et al.[7] In this instance, the formation of organometallic compounds containing *side-on* bound RC≡N groups, η^2-coordinated[8] to Ni(0), has been well established by spectroscopic and structural studies including X-ray crystallographic studies of an extensive number of compounds bearing aryl,[7i,j] heteroaryl,[7i] and alkyl substituents.[7g] The reactivity of the

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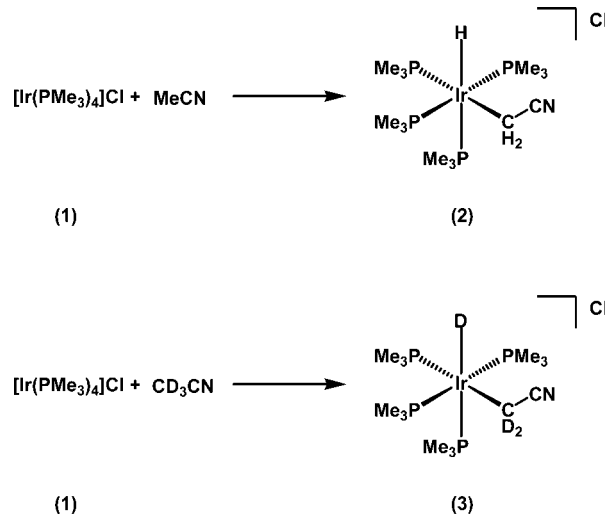
coordinated nitriles toward the addition of water was investigated,[7d,e] and as a result, the feasibility of a catalytic process using Ni(0) catalyst precursors for the hydration of benzonitrile and acetonitrile[7e] and the aryl-dinitriles 1,2-, 1,3-, and 1,4-terephthalonitrile[7d] has been demonstrated. A related study concerned the preparation of η^2-coordinated imines of formula [(dippe)Ni(η^2-*C*(Ph)(H)═*N*(R)] (R = fluorinated benzene ring),[9] resembling an [(L$_2$)Ni(η^2-*C*(R)(OH)═*N*H)] intermediate proposed in the catalytic hydration process, a result of the *N*,*N*-dihydro-*C*-oxo-biaddition of water.[2,10] The σ-coordination and C−C bond cleavage of nitriles at rhodium[11] and iridium[12] centers has been observed by the groups of Brookhart and Bergman, and the possibility of η^2-coordination has been suggested in reaction intermediates. Of additional relevance, the formation of Ir(III) carboxamides, [Cp*(PMe$_3$)Ir(Ph)(NHC(O)R)], has been reported to occur via a bimetallic reaction between [Cp*(PMe$_3$)Ir(Ph)(OH)] and [Cp*(PMe$_3$)Ir(Ph)(NCR)]$^+$;[13] the formation of the latter compound occurred as a result of reaction between [Cp*(PMe$_3$)Ir(Ph)(OTf)] and a number of aromatic (R = −C$_6$H$_4$CH$_3$, −C$_6$H$_5$, and −C$_6$H$_4$CF$_3$) and aliphatic (R = −CH$_3$, −CH(Ph)$_2$) nitriles. Competing C−H activation was observed to take place when attempting the reaction with acetonitrile instead of aromatic nitriles. The use of [Cp*(PMe$_3$)Ir(Ph)(OH)] in the additional presence of acetamide, however, showed the C−H bond activation to be overcome by N−H bond cleavage; the iridium carboxamide [Cp*(PMe$_3$)Ir(Ph)(NHC(O)Me)] and a stoichiometric amount of water were obtained selectively under these conditions. The formation of −NHC(O)R complexes is envisaged as being key to the overall metal-mediated or catalytic conversion of an organonitrile into a free carboxamide, and thus the synthesis of such intermediates is relevant. In the latter case, however, formation of free carboxamides was not achieved in catalysis even using excess water and high temperatures, and thus, protonolysis of bound carboxamides using HCl was required to release the free amides.

Scheme 1. Reaction of [Ir(PMe$_3$)$_4$]Cl (1) with CH$_3$CN and CD$_3$CN



We envisaged [Ir(PMe$_3$)$_4$]Cl (**1**) to be of potential use in the study of the nitrile hydration reaction because the [Ir(PMe$_3$)$_4$]$^+$ cation is known[14a] to oxidatively add water, giving the *cis*-hydrido-hydroxy cation [IrH(OH)(PMe$_3$)$_4$]$^+$, and also to activate acetonitrile. Thus, previous studies of reactions of Ir(I)/Rh(I) systems with acetonitrile by English and Herskovitz[14b] demonstrated not only the C−H oxidative addition of CH$_3$CN to **1** and to [Ir(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$]Cl but also the formal carboxylation of the CH$_2$CN moiety with CO$_2$. The present work provides a more detailed characterization, by high-field NMR spectroscopy and X-ray diffraction studies, of the product of CH$_3$CN C−H oxidative addition to **1**. We also explored **1**, as well as the more electrophilic peroxo compound [Ir(O$_2$)(PMe$_3$)$_4$]Cl (**9**), for the nitrile hydration reaction and show that the latter compound, at a low loading of 0.1 mol %, is a useful catalyst precursor for the hydration of acetonitrile using stoichiometric amounts of water. First, we describe studies of the oxidative addition of C−H, N−H, and O−H bonds to **1**.

Results and Discussion

Reactions of [Ir(PMe$_3$)$_4$]Cl (1) with CH$_3$CN and CD$_3$CN. Stoichiometric C−H and C−D oxidative addition was observed when **1** was dissolved in neat CH$_3$CN and CD$_3$CN, respectively, at room temperature (Scheme 1).[14b]

In both cases, the stoichiometric activation of a corresponding C−H or C−D bond occurred in preference to the coordination of the −CN moiety, and thus, the hydrido σ-alkyl compounds *cis*-[IrH(CH$_2$CN)(PMe$_3$)$_4$]Cl (**2**) and *cis*-[IrD(CD$_2$CN)(PMe$_3$)$_4$]Cl (**3**) were obtained in high purity and reasonable isolated yield (56% and 54%) as air-stable, white solids upon crystallization from neat CH$_3$CN or CD$_3$CN solutions, respectively, by addition of toluene.[14]

Compounds **2** and **3** exhibit an octahedral geometry around the Ir center, the corresponding hydride (^{1}H NMR: δ −13.18, ddt, $^2J_{\text{H−P-}trans}$ = 132 Hz, $^2J_{\text{H−P-}cis\text{-}a}$ = 20 Hz, $^2J_{\text{H−P-}cis\text{-}b}$ = 16 Hz) and deuteride (^{2}H{^{1}H} NMR: δ −13.12 br dq, $^2J_{\text{D-P-}trans}$ = 20 Hz, $^2J_{\text{D-P-}cis}$ = 3 Hz) moieties occupying positions *cis* to coordinated CH$_2$CN and CD$_2$CN, respectively, as expected for

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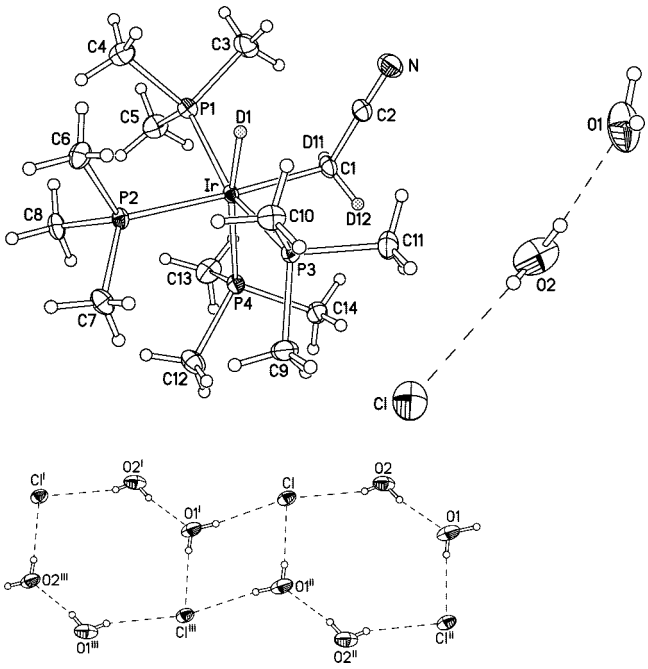

Figure 1. (Top) Molecular structure of $3 \cdot 2H_2O$ (here and henceforth, thermal ellipsoids are drawn at the 50% probability level). (Bottom) Details of the hydrogen-bonding network involving the Cl anion and two water molecules.

a concerted oxidative addition process. The deuteride moiety displayed a *trans* coupling of 20 Hz, 6.6 times smaller than that displayed by the hydride, consistent with the ratio of γ_H/γ_D of 6.51.[15]

The ^{31}P and $^{31}P\{^1H\}$ NMR spectra of both compounds are consistent with the presence of four phosphines in three environments in an octahedral *cis*-IrP_4XY geometry. In the case of **2**, the signal for the P *trans* to the hydride displays a $^2J_{P-H}$ coupling of 132 Hz in the ^{31}P NMR spectrum, matching the value obtained from the ^1H NMR spectrum. While the $^{31}P\{^1H\}$ NMR spectrum of **3** displays a complex multiplet for the P *trans* to D, due to the near equivalence of the $^2J_{P-D}$ and two $^2J_{P-P}$ values, the $^{31}P\{^1H + ^2H\}$ NMR spectrum simplified to a well-resolved quartet with $^2J_{P-P}$ of 20 Hz. Single crystals of compound **3** were obtained and characterized by X-ray crystallography (see Figure 1, Tables 1 and S1), confirming the octahedral geometry around iridium.[16] Details of the molecular structure in the solid state will be deferred to a later section (*vide infra*).

The C−H/C−D activation of acetonitrile described above proceeds very quickly, and we did not observe any precoordination of the nitrile to the metal center via π- or σ-bonding in NMR experiments. This leaves the question of a feasible bonding mode prior to C−H bond activation or a possible hydration reaction of nitriles at iridium open, and therefore, we investigated the coordination properties of *p*-substituted benzonitriles, *p*-XC_6H_4CN (X = CF_3, F, Me, OH, OMe, and NH_2), with increasingly negative Hammett σ_p values, to **1**, thus avoiding competing C−H activation at the α-position.

Reaction of 1 with *p*-Aminobenzonitrile: Formation of *cis*-[IrH(*p*-NHC_6H_4CN)(PMe_3)$_4$]Cl (4). *In situ* NMR spectroscopic studies of the reactions of **1** with a series of benzonitriles with *para* subtituents X = CF_3, F, Me, and OMe showed no evidence for interaction of the nitrile moiety with the iridium center. However, in the case of *p*-aminobenzonitrile, N−H oxidative addition occurred, and the product **4** was thus obtained as an air- and moisture-stable white solid in 41% yield (Scheme 2).

The bound −NH− fragment of compound **4** appeared as a broad singlet at δ 2.0 in the ^1H NMR spectrum, upfield from the respective free ligand (δ 4.3). Four separate doublets of doublets for the aromatic protons appeared at δ 7.23, 7.01, 6.60, and 6.51, the free ligand exhibiting only two doublets at δ 7.35 and 6.62. Importantly, the replacement of one NH proton by the Ir center breaks the 2-fold symmetry of the *p*-aminobenzonitrile moiety, and the observation of four sharp aromatic proton and four C−H carbon signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively, indicates a lack of rotation about the N−C bond, consistent with a trigonal-planar nitrogen involved in strong π-conjugation with the aromatic ring. This is probably enhanced by the presence of the *p*-CN π-acceptor group as well as by the potentially destabilizing π-interaction of the N-lone pair with the filled t_{2g} orbitals on the d^6-Ir(III) center, resulting in a push−pull interaction across the arene ring. The ^{13}C NMR chemical shift of the aryl carbon attached to the CN group appears shielded by ca. 8 ppm from its position in the free *p*-aminobenzonitrile, consistent with a considerable amount of negative charge being located at this center.

The ^{31}P NMR spectrum of **4** confirmed the presence of the phosphine *trans* to the hydride as a broad doublet at δ −55.8 ($^2J_{P-H\text{-}trans}$ = 139 Hz), the other two phosphorus environments appearing as broad multiplets at δ −45 (*trans*-PMe_3) and −57.3 (PMe_3 *trans* to $-NHC_6H_4CN$).

The solid-state structure of compound **4** was confirmed by single-crystal X-ray diffraction (Figure 2, Tables 1 and S1).

Reaction of [Ir(PMe_3)$_4$]Cl (1) with *p*-Cyanophenol. The addition of *p*-cyanophenol to a stirred THF/hexane suspension of **1** led to the precipitation of a 1:1 mixture of *cis*-[IrClH(PMe_3)$_4$][*p*-OC_6H_4CN] (**5a**) and *trans*-[IrClH(PMe_3)$_4$][*p*-OC_6H_4CN] (**5b**). After three weeks at room temperature, this ratio shifted completely in favor of the *cis* compound (Scheme 3).

The identity of the compounds has been confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, HRMS, and elemental analysis.

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(15) The magnetogyric ratios of ^1H and ^2H (γ_H and γ_D) are 26.7522128 and 4.10662791 × 10^7 rad T^{-1} s^{-1}, respectively. See, e.g.: http://www.webelements.com/webelements/elements/text/H/nucl.html.

(16) Crystals of **3** were grown in air, leading to incorporation of water molecules in the lattice. Repeated efforts to grow single crystals of **2** and **3** under an inert atmosphere were unsuccessful, suggesting that incorporation of H_2O may be required for crystal growth.

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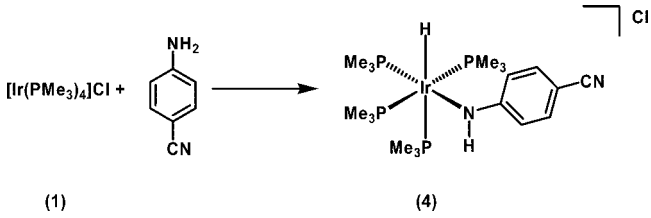
Table 1. Selected Bond Distances (Å)

	3	4	5b	7	8	9a	9b
Ir−P(1)	2.3536(9)	2.3428(8)	2.3460(4)	2.2963(7)	2.3388(7)	2.3667(7)	2.361(1)
Ir−P(2)	2.3254(8)	2.2966(8)	2.3291(4)	2.3056(7)	2.2975(6)	2.2778(7)	2.298(1)
Ir−P(3)	2.3447(8)	2.3491(8)		2.2874(7)	2.3564(7)	2.2833(6)	2.287(1)
Ir−P(4)	2.3897(9)	2.3817(9)		2.3034(8)	2.3969(6)	2.3596(7)	2.356(1)
Ir−Cl			2.4950(5)				
Ir−C(1)	2.177(3)						
Ir−N(1)		2.121(2)			2.098(2)		
Ir−D/H	1.49(4)	1.61	1.45(3)		1.64(3)		
Ir−O(1)						2.056(2)	2.057(3)
Ir−O(2)						2.064(2)	2.073(3)
O(1)−O(2)						1.475(3)	1.481(5)

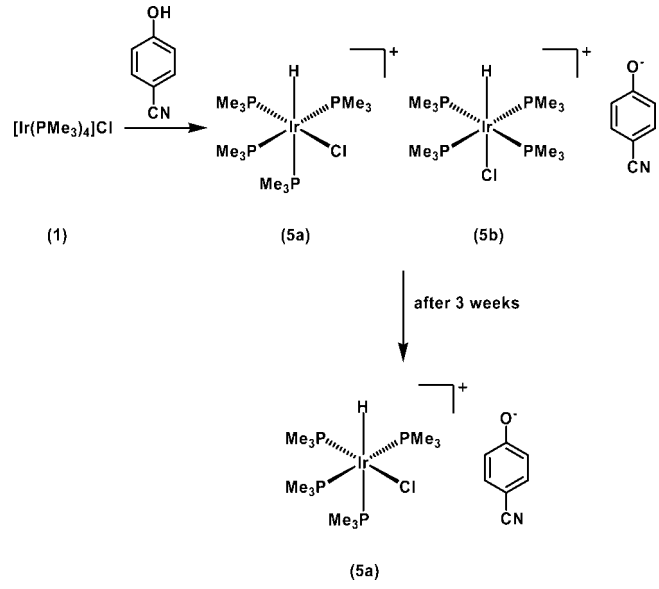
Scheme 2. Oxidative Addition of an N−H Bond of *p*-Aminobenzonitrile to 1



The HRMS-ES+ spectrum displayed a peak at *m*/*z* of 531.11557 Da for the $[IrHCl(PMe_3)_4]^+$ cation. The ^{1}H NMR spectrum displayed a doublet of quartets centered at δ −11.8 ($^2J_{H-P\text{-}trans}$ = 148 Hz, $^2J_{H-P\text{-}cis}$ = 18 Hz) for the hydride of **5a** and a quintet at δ −21.66 ($^2J_{H-P\text{-}cis}$ = 15 Hz) for the *trans* compound **5b** in accordance with a publication by Milstein et al.[17] The two isomers are further distinguished by their ^{31}P NMR spectrum, **5a** displaying signals at δ −45.15 (dt, $^2J_{P-P}$ = 19 Hz, $^2J_{P-P}$ = 11 Hz), δ −46.90 (t, $^2J_{P-P}$ = 19 Hz), and δ −53.60 (td, $^2J_{P-P}$ = 19 Hz, $^2J_{P-P}$ = 11 Hz), while **5b** gives rise to a singlet at δ −45.42. Single crystals of **5b**·HOC_6H_4CN·THF suitable for X-ray diffraction were obtained after recrystallization from THF; the structure (Figure 3) shows the phenolate anion being stabilized by a second molecule of 4-cyanophenol via hydrogen bonding.

Interestingly, unlike the experiment involving *p*-aminobenzonitrile, the reaction with *p*-cyanophenol did not yield the primary X−H oxidative addition product. The initial ratio of compounds **5a** and **5b** might result from either protonation of the iridium complex **1** followed by coordination of the chloride

Scheme 3. Reaction of [Ir(PMe$_3$)$_4$]Cl (1) with *p*-Cyanophenol Leading to Two Isomers



anion or oxidative addition of *p*-cyanophenol and subsequent anion substitution. However, the ^{1}H NMR spectrum of the reaction mixture showed traces of an additional product giving rise to a doublet of quartets at δ −11.2 ($^2J_{H-P\text{-}trans}$ = 148 Hz, $^2J_{H-P\text{-}cis}$ = 18 Hz) and a quintet at δ −20.59 ($^2J_{H-P\text{-}cis}$ = 15 Hz). In addition, small amounts of another cation were observed in the HRMS at *m*/*z* = 614.17392, suggesting partial Cl/*p*-

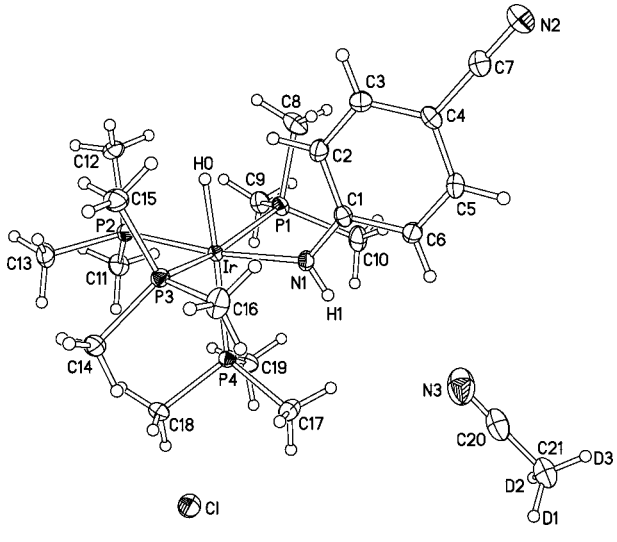


Figure 2. Molecular structure of **4**·CD_3CN (note the absence of hydrogen bonding to the NH group).

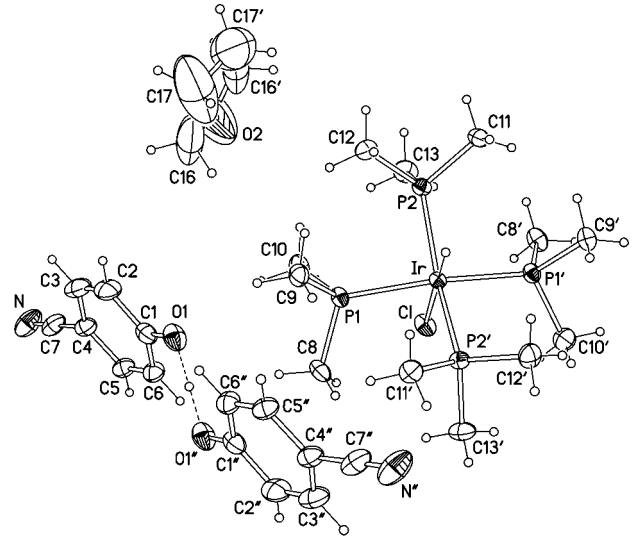


Figure 3. Molecular structure of **5b**·HOC_6H_4CN·THF. Primed atoms are generated by 2-fold axes, double-primed by an inversion center.

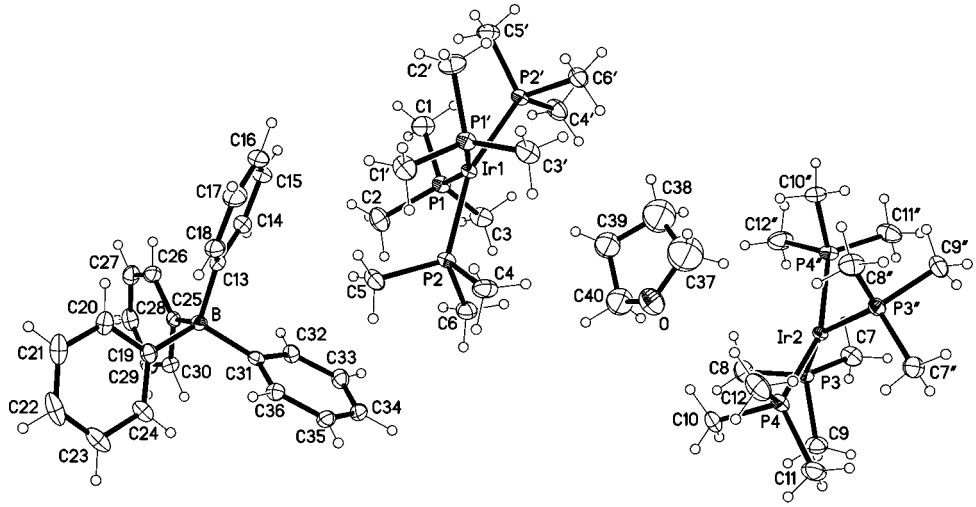


Figure 4. Molecular structure of **7**·THF, showing one of the alternative positions of the THF molecule. Primed atoms are generated by the 2-fold axis.

OC_6H_4CN anion exchange leading to the [IrH(*p*-OC_6H_4CN)-(PMe_3)$_4$] cation. This reaction has been carried out several times, and in some cases, we were able to detect *cis*-[IrH(*p*-OC_6H_4CN)(PMe_3)$_4$]Cl (**6**) as the major product (ca. 75%) giving rise to a doublet of quartets at δ −11.04 ($^2J_{H-P\text{-}trans}$ = 144 Hz, $^2J_{H-P\text{-}cis}$ = 19 Hz) in the ^{1}H NMR spectrum and a signal in the HRMS at *m*/*z* = 614.17392. Whatever the small differences in the conditions of the experiments were is not clear, but it is feasible that a concentration effect or traces of water might influence the reaction pathway through, e.g., hydrogen bonding, as has been found in the crystal (Figure 3) obtained from a reaction mixture employing 2 equiv of *p*-cyanophenol.

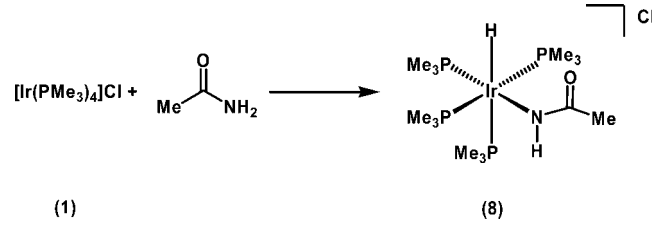
Synthesis of [Ir(PMe_3)$_4$][BPh_4] (7). In order to investigate further the oxidative addition reaction of *p*-cyanophenol to the cation [Ir(PMe_3)$_4$]$^+$ and the influence of the counterion, we prepared and fully characterized [Ir(PMe_3)$_4$][BPh_4] (**7**) and reacted it with *p*-HOC_6H_4CN.

The addition of Na[BPh_4] to a stirred suspension of **1** in THF led to the quantitative formation of **7**. Single crystals of **7** suitable for X-ray diffraction were obtained after recrystallization from THF/hexanes, and the structure is shown in Figure 4.

Unfortunately, the reaction of **7** with *p*-HOC_6H_4CN is very unselective and led to several unidentified products. The NMR experiments indicate that the counterion [BPh_4]$^-$ is partially involved and is thus not completely innocent.

Although we could not find evidence for C≡N coordination of benzonitriles to **1**, and acetonitrile undergoes C−H bond activation, we nonetheless examined **2** and **3** as potential catalyst precursors for the hydration of acetonitrile. In preliminary NMR experiments, with 10 mol % loading of *cis*-[IrH(CH_2CN)-(PMe_3)$_4$]Cl (**2**) or *cis*-[IrD(CD_2CN)(PMe_3)$_4$]Cl (**3**) in d_3-acetonitrile/H_2O (molar ratio 1:1) at 120 °C, the formation of acetamide, the hydration product of CD_3CN, was observed together with stoichiometric amounts of $OPMe_3$ with respect to the iridium complex. Interestingly, ^{13}C NMR spectroscopic and GC/MS investigations clearly indicated incorporation of protons at the methyl group in the final product, as well as incorporation of deuterium at the nitrogen in acetamide, leading to a distribution of several d_n-acetamides. In addition, the GC/MS also revealed that the CD_3CN solvent undergoes H/D exchange with H_2O under the above-mentioned conditions. The same behavior was found on employment of **1** as catalyst precursor for the reaction of acetonitrile with water. In order to understand the origin of the H/D scrambling, we also examined the reactivity of **1** toward acetamide.

Scheme 4. Iridium-Mediated N−H Bond Cleavage of Acetamide



N−H Oxidative Addition of Acetamide to 1. The reaction of acetamide with **1** at room temperature, in THF suspension (Scheme 4), resulted in the cleavage of an N−H bond in preference to a C−H bond in the same molecule, the activation of the former being envisioned as the reverse of the final step in the catalytic hydration of acetonitrile.[18] The reaction required 72 h, after which time, *cis*-[IrH(NHC(O)Me)(PMe_3)$_4$]Cl (**8**) was isolated as a white, air-stable solid in 55% yield. Its ^{1}H NMR spectrum displayed a broad signal centered at δ 3.9 and a sharp singlet at δ 1.95, consistent with a bound −NH and a $-CH_3$ group of the coordinated −NHC(O)Me moiety. The chemical shift for the −NH fragment is shielded from the corresponding $-NH_2$ protons in free acetamide (δ 6.1, 5.9). The Ir−H resonance was observed at δ −11.3 as a broad doublet; coupling to the *cis*-phosphines was not resolved. The ^{31}P{^{1}H} NMR spectrum of **8** confirmed the presence of three phosphorus environments consistent with a *cis* octahedral geometry. The structure of compound **8**, cocrystallized with a water molecule, was obtained by X-ray diffraction studies (Figure 5, Tables 1 and S1).

Compound **8** should be the last key intermediate in the iridium-mediated hydration reaction of acetonitrile and provides various possible pathways for H/D exchange, i.e., protonation of the metal-bound nitrogen by H_2O or CD_3CN, exchange of the hydrido ligand at iridium prior to reductive elimination, etc.

The observed C−H and N−H bond activation of acetonitrile and of the hydration reaction product acetamide, respectively,

(18) For the use of [Cp*(PMe_3)Ir(Ph)(OH)] in reactions involving the preparation of a series of carboxamido complexes, including one with acetamide, see ref 13.

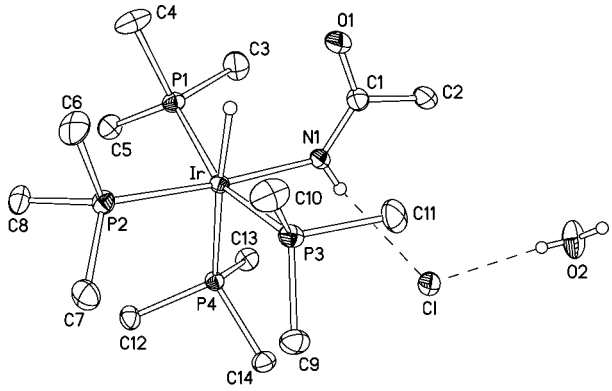


Figure 5. Molecular structure of *cis*-[IrH(NHC(O)Me)(PMe$_3$)$_4$]Cl (**8**)·H$_2$O.

providing possibilities for H/D exchange, led us to investigate the synthesis and catalytic properties of a more electrophilic Ir(III) species incapable of undergoing oxidative addition and thus potentially favoring coordination of nitrile C≡N groups.

Reaction of [Ir(PMe$_3$)$_4$]Cl (1) with O$_2$. Bubbling dry dioxygen for a period of 4 h through an orange THF suspension of **1** gave *cis*-[Ir(O$_2$)(PMe$_3$)$_4$]Cl (**9**) as a white precipitate, which was recrystallized from CH$_3$CN/Et$_2$O and isolated in 82% yield. The green-yellow crystals were suitable for X-ray diffraction, and crystal structures were obtained for two different pseudo-polymorphs (**a** and **b**), as shown in Figures 6 and 7. It is noteworthy that when the product is dried *in vacuo*, it is colorless, while a solvent effect leads to the colored crystals. Scheme 5 illustrates the reaction; the formation of d^6 complexes with formula [M(L)$_4$(O$_2$)]$^+$ (M = Co, Rh, Ir)[19] containing η^2-coordinated dioxygen,[14d] and their analogues, [M(L$_2$)$_2$(O$_2$)]$^+$ (M = Rh, Ir),[20] is well-known.

Discussion of the Crystal Structures of 3, 4, 5b, and 7−9. Crystal data and other experimental details are listed in Table S1, and selected bond distances are given in Table 1.

The single crystals for X-ray diffraction studies were grown by solvent diffusion of toluene/acetonitrile mixtures without precautions to eliminate exposure to air; thus, incorporation of water molecules in the crystal lattice was observed in several cases. This finding underlines the stability of the products to oxygen and water at ambient temperature.

The asymmetric units in crystals of **3**, **4**, and **8** (Figures 1, 2, and 5) contain one complex cation and one chloride anion. That of **3** also contains two water molecules, which, with the anions, form an infinite hydrogen-bonded double chain [ribbon] parallel to the crystal axis *x* (Figure 1, bottom). The asymmetric unit of **8** contains one water molecule; the cations related via the inversion center (1/2, 0, 1/2) are linked by a pair of hydrogen-bonded bridges, N−H···Cl···H−O−H···O(1). The asymmetric unit of **4** contains one molecule of deuterated acetonitrile, forming a weak hydrogen bond, C−D···Cl (D···Cl 2.69 Å). Surprisingly, the −NH group forms no hydrogen bond in the presence of good potential acceptors.

The cation in each case shows a distorted *cis*-octahedral coordination of Ir and approximate local mirror symmetry (plane "*m*" through Ir, P(2), P(4), and C(1) or N(1) atoms). The positions of hydride (deuteride in **3**) ligands were revealed in the electron density map (and in **3** and **8** also refined by least-squares) to lie in this plane within experimental error. Ir−P distances are consistent with the succession of *trans*-influence, H/D > PMe$_3$ > CH$_2$CN > NHC(O)Me. In **3**, the linear C(1)C(2)N group is *syn* to the deuteride ligand but is rotated out of the *m* plane by 9° to the side of P(3). The CD$_2$−CN bond distance (1.451(4) Å) is typical of that found for alkyl-CH$_2$CN derivatives (mean 1.465(7) Å),[21] and the Ir−C (2.177(3) Å) bond is slightly longer than in [(Me$_3$P)$_4$Ir(H)Me]-[CpMo(CO)$_3$] (2.04(2) Å),[22] PPN[(OC)$_2$Ir(CH$_2$CN)$_2$] (2.138(8) Å),[23] and [(Me$_3$P)$_4$Ir(H)CH$_2$OH]PF$_6$ (2.134(5) Å).[14a] In cation **8**, the planar acetamido ligand forms a dihedral angle of 15° with the *m* plane. The N(1)−C(1) bond is shorter (1.322(3) Å) and the C(1)−O(1) bond longer (1.262(3) Å) than in R−NH−C(O)Me analogues, e.g., with R = 1-adamantyl (1.345(2) and 1.235(2) Å, respectively)[24] or R = 4-fluorocuban-1-yl (1.336(1) and 1.234(1) Å),[25] indicating a shift toward the $^+$N=C−O$^-$ structure. In cation **4**, the angle between the *m* plane and the benzene ring plane equals 10°, the coordination plane of the N(1) atom being inclined to these planes by 4° and 6°, respectively. The arene ring shows a significant quinoid distortion, the C(2)−C(3) and C(5)−C(6) bonds being ca. 0.03 Å shorter than the remaining four C−C bonds (mean 1.377(3) vs 1.410(4) Å). The only structurally characterized *p*-NC-C$_6$H$_4$NHR derivative with an unconjugated R group, bis(4-cyanophenyl)-cyclohexanediamine,[26] shows a similar difference in the ring bond distances (Δ = 0.031, esd 0.005 Å) as well as C(ar)−NH and C(ar)−CN distances (1.362(4) and 1.433(5) Å) similar to those in **4** (1.354(3) and 1.433(3) Å), and consistent with a degree of C(ar)−NH multiple bond character resulting in the lack of rotation about this bond in solution, *vide supra*. Two iridium complexes (five- and six-coordinate) with PhNH ligands[27] also show marginal quinoidal distortions (Δ = 0.018, esd 0.003 Å); the Ir−N bond in the six-coordinate (PCP)Ir(H)-(NHPh)(CO) is *trans* to the Ir−C σ-bond and is slightly longer (2.142(2) Å) than in **4**.

In the structure of **5b** (Figure 3), the cation is situated on a crystallographic 2-fold axis (passing through the Ir, Cl, and hydride H atoms) and thus has a distorted *trans*-octahedral coordination. The *p*-NCC$_6$H$_4$O$^-$ anion and its symmetrical equivalent via an inversion center must be linked by a hydrogen bond (and thus constitute a {(NCC$_6$H$_4$O)$_2$H}$^-$ monoanion), as indicated by the short O···O″ distance of 2.438(3) Å, cf. 2.471(5) Å in [PhOHOPh]NBu$_4$[28] and 2.44 Å in [(*p*-OC$_6$H$_4$O)(*p*-HOC$_6$H$_4$OH)](NH$_2$Et$_2$)$_2$.[29] Indeed, a peak of electron density

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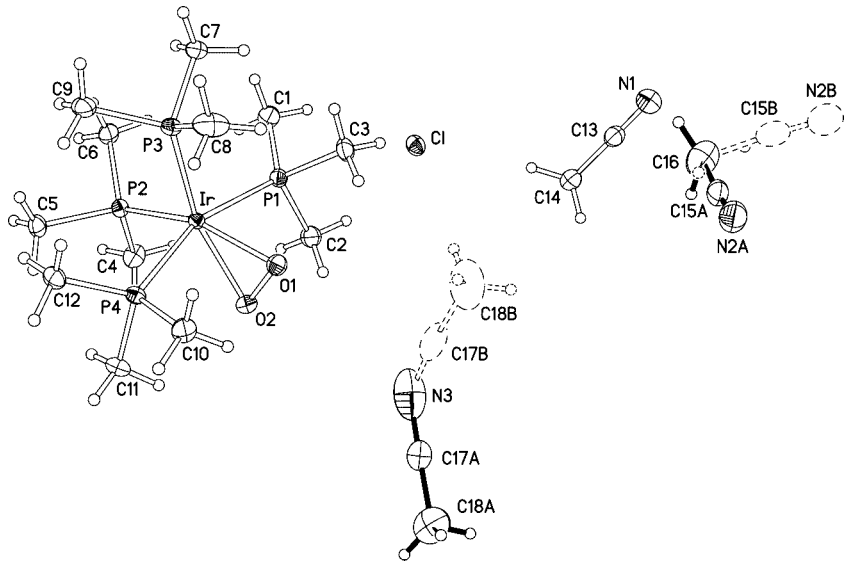


Figure 6. Molecular structure of **9a**·3CH_3CN, showing the disorder of the acetonitrile of crystallization.

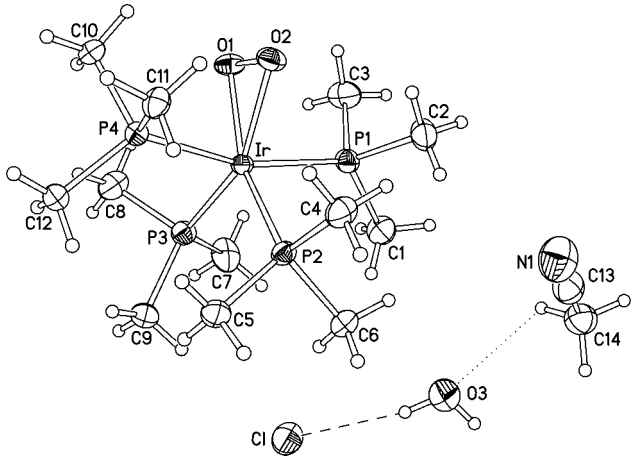
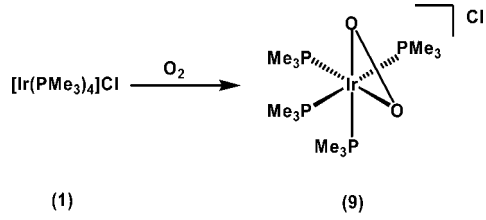


Figure 7. Molecular structure of **9b**·H_2O·CH_3CN.

Scheme 5. Formation of the Peroxo Compound *cis*-[Ir(O_2)(PMe_3)$_4$]Cl (9)



was located at the inversion center and successfully refined as a hydrogen atom. The THF molecule of crystallization is located on a crystallographic 2-fold axis.

Complex **5b** is the third structurally characterized $IrHP_4Cl$ complex and the second one with a *trans*-configuration, after $[HIr(depe)_2C1]^+[CH(CN)_2]^-$.[30] While in the latter complex the angles at Ir deviate little from octahedral, and in the cations of **3**, **4**, and **8** adjacent phosphines are tilted toward the smallest (hydride) ligand, in **5b** the four phosphine ligands adopt a peculiar pseudotetrahedral arrangement. With respect to a plane perpendicular to the 2-fold (i.e., Cl−Ir−H) axis and passing through the Ir atom, P(1) and its symmetric equivalent P(1′) are tilted by 0.45 Å toward the Cl atom, while P(2) and P(2′) are tilted by 0.26 Å toward the hydride ligand. In either case, one methyl group of the phosphine ligand is eclipsed with the ligand (H or Cl) from which the phosphine is tilted away.

The asymmetric unit of **7** contains two symmetrically nonequivalent $[Ir(PMe_3)_4]^+$ cations, both Ir atoms lying on a crystallographic 2-fold axis. The THF molecule is disordered between two positions related via the same axis, while the $[BPh_4]^-$ anion occupies a general position (Figure 4). The crystal is isomorphous with that of $[Rh(PMe_3)_4][BPh_4]$·1/2C_6H_6.[31] The metal coordination is distorted from square-planar toward tetrahedral, with pseudo-*trans* angles P(1)−Ir(1)−P(1′) 158.55(4)°, P(2)−Ir(1)−P(2′) 160.40(4)°, P(3)−Ir(2)−P(3′) 152.82(4)°, P(4)−Ir(2)−P(4′) 158.87(4)° considerably reduced from 180°. However, in $[Ir(PMe_3)_4]PF_6$ (the only *nonchelated* IrP_4 complex reported previously), these angles are even smaller, 149.3(1)° and 150.3(1)°; thus the coordination must be fairly responsive to outer-sphere influences.

Crystallizations of **9** gave two pseudopolymorphs, both containing one cation and one anion per asymmetric unit, that of **9a** contains three molecules of acetonitrile (two of them disordered), and that of **9b**, one acetonitrile and one water molecule. Thus, incidentally, **9b** has exactly the composition for the catalytic process. The anions and water molecules are hydrogen-bonded into an infinite chain (spiraling around the 2_1 screw axis) to which the acetonitrile molecules are attached through weak C−H···O and C−H···Cl hydrogen bonds. The cations in **9a** and **9b** have essentially identical geometries, which could be described as trigonal-bipyramidal, with the Ir, P(2), P(3), O(1), and O(2) atoms lying in the equatorial plane, although, as the P(2)−Ir−P(3) angle = 94.63(2)° in **9a** and 99.66(4)° in **9b**, a distorted octahedral description seems more appropriate. As usual, "axial" Ir−P bonds are longer than "equatorial" ones. Compared with the isostructural cation $[Ir(O_2)(PMe_2Ph)_4]^+$, Ir−P distances in **9** are shorter by ca. 0.03

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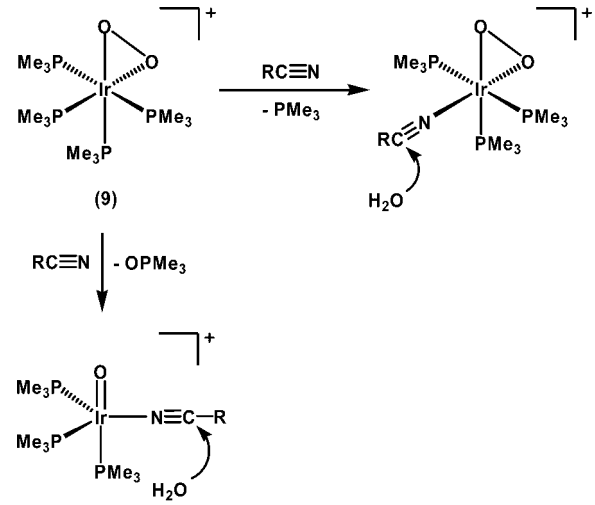
Å, but the geometry of dioxygen bonding is essentially the same, confirming the absence of straightforward structural relationships.[32]

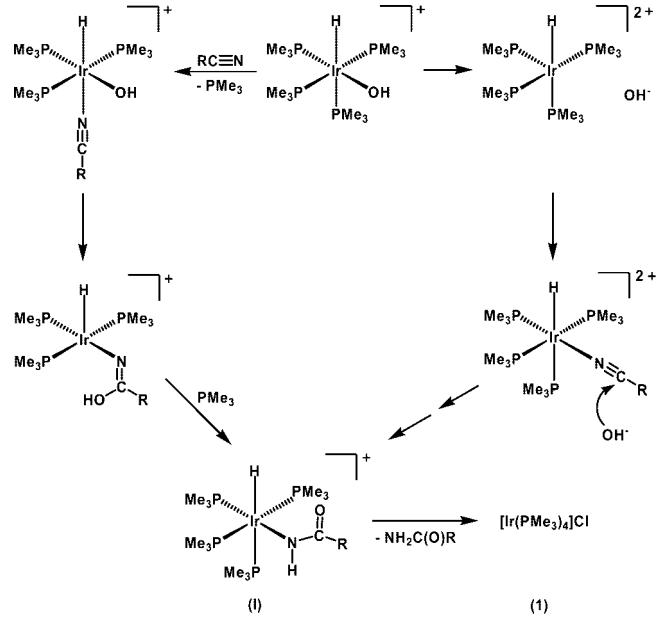
Catalysis Experiments. The peroxo compound *cis*-[Ir(O$_2$)(PMe$_3$)$_4$]Cl (**9**) was employed as catalyst precursor at 0.1 mol % loading for the reaction of acetonitrile with water at 140 °C for 200 h to yield acetamide with >800 turnovers and an isolated yield of 82%. The activity of the iridium catalyst in terms of TON is comparable to those of nickel, platinum, and palladium systems using phosphines as auxiliary ligands. A series of experiments were subsequently conducted at 1 mol % catalyst loading to gain insight into the reaction mechanism. The experiments included the reagent combinations CH$_3$CN/H$_2$O (A), CD$_3$CN/D$_2$O (B), CD$_3$CN/H$_2$O (C), and CH$_3$CN/D$_2$O (D).

In the same manner as the original run to yield acetamide (A), perdeuterated d_5-acetamide can be obtained on employment of CD$_3$CN and D$_2$O (B) as demonstrated by GC/MS and ^{13}C NMR spectroscopy (see Figure S3). Interestingly, the reactions of CD$_3$CN/H$_2$O (C) and CH$_3$CN/D$_2$O (D) did not give the expected single products CD$_3$C(O)NH$_2$ and CH$_3$C(O)ND$_2$, but rather a statistical distribution of various isotopomers of acetamide with different deuterium content ranging from d_0 to d_5 was observed. The GC/MS results indicate for C that d_3-acetamide and for D, that d_2-acetamide were major products with ca. 32% abundance, although further signals at ±1 mass units appear with 21−27% abundance (see Figures S5 and S7). The resonances in the ^{13}C NMR spectra at δ 21.5 for the acetamide methyl group produced in reactions C and D show overlapping singlets, triplets, quintets, and septuplets with coupling constants of $^1J_{C-D} = 20$ Hz, thus proving the presence of CH$_3$, CH$_2$D, CHD$_2$, and CD$_3$ groups in the final products. Substantial evidence for competitive C−H and C−D activation of acetonitrile and therefore a feasible explanation for the above-mentioned observations was obtained on investigation of the reaction mixtures by ^{13}C NMR spectroscopy and GC/MS. The resonance at δ 0.8 for the CH$_3$/CD$_3$ group in "unreacted" acetonitrile appears as several overlapping multiplets. The GC/MS indicates for run D CH$_2$DCN (m/z = 42) and CHD$_2$CN (m/z = 43) as the major species, although loss of deuterium from CD$_3$CN to give CD$_2$CN (m/z = 42) as a fragment ion cannot be entirely excluded. The data for experiment C show, besides CH$_2$DCN as the major isotopomer, further deuterium incorporation pointing to the presence of CHD$_2$CN and CD$_3$CN (see Figures S6 and S8). In an *in situ* ^{31}P NMR spectrum of a catalytic reaction mixture, the formation of O=PMe$_3$ was observed together with the formation of an {Ir(PMe$_3$)$_3$} species displaying a doublet at δ −33.8 ($^2J_{P-P}$ = 20 Hz) and a triplet at δ −51.0 ($^2J_{P-P}$ = 20 Hz) in addition to signals for other species in small quantities. The ^{1}H NMR spectrum of the reaction mixture displayed several resonances in the hydride region between δ −11 and −25. It is feasible that during the catalytic conversion an Ir(I) species is generated that undergoes C−H/C−D/O−H/O−D activation of acetonitrile and water, promoting the H/D exchange. Milstein et al. reported the formation of *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$ upon addition of water to [Ir(PMe$_3$)$_4$]PF$_6$.[14a] The high basicity of the hydroxo ligand leads to H/D exchange to give *cis*-[IrH(OD)(PMe$_3$)$_4$]PF$_6$. We have shown in this publication that [Ir(PMe$_3$)$_4$]Cl is also capable of activating the N−H bond in acetamide, and thus an intermediate iridium hydrido-acetamido complex would provide another route for H/D incorporation at the amino group of the initial product. Further evidence supporting the existence of an Ir(I) species capable of C−H/O−H activation, and hence scrambling, arises from the above-mentioned preliminary NMR experiments reacting [Ir(PMe$_3$)$_4$]Cl (**1**), *cis*-[IrH(CH$_2$CN)(PMe$_3$)$_4$]Cl (**2**), or *cis*-[IrD(CD$_2$CN)(PMe$_3$)$_4$]Cl (**3**) with water in CD$_3$CN at elevated temperature, giving d_n-acetamide according to ^{1}H NMR and ^{13}C NMR spectroscopy and GC/MS. In both experiments the formation of O=PMe$_3$ was observed, although no O$_2$ was present, and thus water must be the source of the oxygen atom.

Scheme 6. Nucleophilic Attack of Water at a Nitrile Group Coordinated to an Ir(III) Center



Scheme 7. Nitrile Insertion into the Metal Hydroxo Bond (Left) or External Attack of Hydroxide on Coordinated Nitrile (Right)



Various general mechanisms for the hydration of nitriles are possible, two of which involve nucleophilic attack of water upon coordination of the nitrile group or insertion into a metal−hydroxo bond, aspects of which are illustrated in Schemes 6 and 7. *End-on* coordination of the nitrile group should be favored at a coordinatively unsaturated Ir(III) center, not being able to undergo facile oxidative addition, which could be formed by either dissociation of phosphine ligands or intramolecular reaction of the PMe$_3$ with the oxygen bound to the metal at elevated temperature, forming O=PMe$_3$ and an electrophilic

(32) Blum, O.; Calabrese, J. C.; Frolow, F.; Milstein, D. *Inorg. Chim. Acta* **1990**, *174*, 149–151.

Ir(III) cation (Scheme 6). The insertion reaction might yield an Ir(I) species after reductive elimination of the acetamide (Scheme 7), in turn participating in the various H/D exchange mechanisms. The latter case can proceed via two different reaction pathways, one involving dissociation of a hydroxo ligand and the formation of an iridium dication with subsequent nucleophilic attack of OH^- on coordinated nitrile, the other occurring by dissociation of PMe_3 and intramolecular migration of the OH^- ligand to the coordinated nitrile. Both pathways would give the same intermediate I (Scheme 7) after tautomerism.

As mentioned above, the reactions of **1** with degassed water in CD_3CN and **2** or **3** in degassed H_2O/CD_3CN also produce $O{=}PMe_3$, giving rise to a different mechanism of phosphine oxidation involving water as the oxygen source instead of *cis*-$[Ir(O_2)(PMe_3)_4]Cl$ (**9**).[33] The great variety of different feasible mechanisms for metal-mediated H/D exchange and for the catalytic hydration of the nitrile makes it very difficult to determine the reaction pathways and the active species. However, we have prepared and investigated *cis*-$[Ir(O_2)(PMe_3)_4]Cl$ (**9**) as an air- and moisture-stable catalyst precursor that generates *in situ* an active catalyst for the hydration of acetonitrile to give acetamide.

Conclusions

In this paper we report reactions of the electron-rich complex $[Ir(PMe_3)_4]Cl$ (**1**) with nitriles, in which the employment of CH_3CN and *p*-X-C_6H_4CN (X = HO, H_2N) led to C−H/O−H/N−H activation, with no spectroscopic evidence for nitrile coordination to the metal center. An NMR spectroscopic investigation of the reactions of other *para*-substituted benzonitriles *p*-X-C_6H_4CN (X = CF_3, F, Me, OMe) with **1** also did not show any evidence of nitrile coordination. We reacted **1** with acetamide, the product of acetonitrile hydration, to gain insight into the nitrile hydration process, and we isolated the N−H oxidative addition product *cis*-$[IrH(NHC(O)Me)(PMe_3)_4]Cl$ (**8**), which can be seen as being a model for the penultimate intermediate in the catalytic process.

The iridium complexes **1**, **2**, and **3**, as well as the peroxo derivative *cis*-$[Ir(O_2)(PMe_3)_4]Cl$ (**9**), were catalyst precursors for acetonitrile hydration at 140 °C, with **9** giving up to 800 turnovers under the conditions examined. The activity of the iridium catalyst is comparable to those of nickel, ruthenium, palladium, and platinum systems using phosphines as auxiliary ligands. The reaction of CH_3CN with D_2O and CD_3CN with H_2O using **9** as catalyst precursor led to acetamides containing 0−5 D per molecule, indicative of H/D scrambling. NMR spectroscopic follow-up of the reaction also revealed C−H/D scrambling in the acetonitrile.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were performed using standard Schlenk and glovebox techniques under an inert atmosphere. An Innovative Technology Inc. glovebox was used under nitrogen (BOC), and VAC and MBraun gloveboxes were used under argon (Praxair). All protio solvents (Fisher Scientific and J.T. Baker) were reagent grade and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 solvent purification system; THF was also distilled from purple benzophenone ketyl solutions. Water was purified by distillation and was deoxygenated using the freeze−pump−thaw method. CH_3CN and CD_3CN were purchased from Aldrich, refluxed over and vacuum transferred from calcium hydride. THF-d_8 and D_2O were purchased from Cambridge Isotope Laboratories and were also deoxygenated using the freeze−pump−thaw method. All deuterated organic solvents were stored over 3 Å molecular sieves in a glovebox for at least 24 h prior to their use. $[Ir(PMe_3)_4]Cl$ (**1**) was prepared following the literature procedure,[34] *p*-aminobenzonitrile (98%), *p*-tolunitrile (98%), *p*-fluorobenzonitrile (99%), and acetamide (99%) were purchased from Alfa-Aesar, Avocado, or Lancaster, and *p*-methoxybenzonitrile (99%) and *p*-cyanophenol (95%) were purchased from Aldrich. All other chemicals, filter aids, and chromatographic materials were reagent grade and were used as received. ^1H (399.9 or 499.8 MHz), ^{31}P, $^{31}P\{^1H\}$ (161.9 or 202.3 MHz), and $^{13}C\{^1H\}$ (100.6 or 125.7 MHz) NMR spectra were recorded at ambient temperature using Varian Mercury-400, Bruker Avance-400, or Varian Inova-500 spectrometers; all $^2H\{^1H\}$ (76.7 MHz) and $^{31}P\{^1H+^2H\}$ (202.3 MHz) NMR spectra were recorded using the latter spectrometer. ^1H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent, while $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent. $^{31}P\{^1H\}$ and ^{31}P NMR spectra are reported relative to external 85% H_3PO_4. ^2H NMR experiments are reported relative to TMS and were referenced via the residual deuterium resonance in the corresponding protio solvent. The NMR samples in this work were handled under nitrogen or argon using Wilmad NMR tubes equipped with J. Young valves unless otherwise specified. Unit mass and high-resolution mass spectrometric (MS and HRMS, respectively) determinations were obtained by means of electrospray (ES^+) using acetonitrile solutions and a Thermo-Finnigan LTQ FT spectrometer. Elemental analyses were obtained using an Exeter Analytical Inc. CE-440 elemental analyzer. GC/MS analyses were performed using a LECO-Pegasus 4D equipped with an Agilent 6890N gas chromatograph and a time-of-flight mass analyzer or using an Agilent 6890N gas chromatograph equipped with an Agilent 5973 mass selective detector operating in EI mode.

Structure Determinations. Full spheres of diffraction data were measured at $T = 120$ K on Bruker 3-circle diffractometers with CCD area detectors SMART 1K (for **3**, **4**, **7**, **8**, and **9a**) or SMART 6K (for **5b**), or a Rigaku R-Axis SPIDER diffractometer with cylindrically curved imaging plate (for **9b**), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Data were corrected for absorption by a semiempirical method based on Laue equivalents (**3**, **4**) or by numerical integration based on crystal face-indexing (**5b**, **7**, **8**, **9a**, and **9b**) using the SADABS program[35] (for **9b**, NUMABS[36]). The structures were solved by Patterson (**3**, **8**, **9a**) or direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software.[37] Non-hydrogen atoms were refined in anisotropic approximation (isotropic for disordered carbon atoms in **9b**). All deuterium atoms in **3**, H atoms bonded to Ir (except in **4**), N or O (except in **9b**) atoms were refined in isotopic approximation. Methyl groups were treated as rigid bodies, and other H atoms were treated using a "riding" model.

***cis*-[IrH(CH$_2$CN)(PMe$_3$)$_4$]Cl (2).** $[Ir(PMe_3)_4]Cl$ (**1**) (0.050 g, 0.094 mmol) was dissolved in acetonitrile (1 mL) and stirred at room temperature overnight. The orange solution turned pale yellow. Addition of toluene precipitated the product as a white, crystalline solid, which was collected by filtration, washed with Et_2O (3 × 10 mL), and dried overnight *in vacuo*. Yield: 0.030 g (56.6%). Anal. Calcd (%) for $C_{14}H_{39}ClIrNP_4$: C, 29.34; H, 6.86; N, 2.44. Found: C, 29.07; H, 6.92; N, 2.19. HRMS-ES^+: calcd for $C_{14}H_{39}{}^{191}IrNP_4$ ($[M]^+$) 536.16336 Da, found 536.16334 Da. NMR (CD_3CN): ^1H δ 1.75 (d, $^2J_{H-P}$ = 3 Hz, 18H, mutually *trans*

(33) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890–1901.

(34) Herskovitz, T. *Inorg. Synth.* **1982**, 99–103.

(35) Sheldrick, G. M. *SADABS 2006/1*; Bruker-Nonius AXS: Madison, WI, 2006.

(36) *NUMABS*; Rigaku Inc.: Tokyo, Japan, 2007.

phosphines), 1.74 (d, $^2J_{H-P}$ = 2 Hz, 9H, PMe$_3$ *trans* to hydride), 1.46 (d, $^2J_{H-P}$ = 8 Hz, 9H, PMe$_3$ *trans* to CH$_2$CN), 1.27 (tdd, J_1 = 9 Hz, J_2, J_3 = 6 Hz, 2H, CH$_2$CN), −13.2 (ddt, $^2J_{H-P\text{-}trans}$ = 132 Hz, $^2J_{H-P\text{-}cis\text{-}a}$ = 21 Hz, $^2J_{H-P\text{-}cis\text{-}b}$ = 16 Hz, 1H, Ir-H); ^{13}C{^{1}H} δ 133.24 (br d, $^3J_{C-P\text{-}trans}$ = 11 Hz, CN), 23.76 (ddd, $^1J_{C-P}$ = 35 Hz, $^3J_{C-P\text{-}cis\text{-}a}$ = 4 Hz, $^3J_{C-P\text{-}cis\text{-}b}$ = 2 Hz, PMe$_3$ *trans* to hydride), 21.1 (tdt, $^1J_{C-P}$, $^3J_{C-P\text{-}trans\text{-}PMe3}$ = 20 Hz, $^3J_{C-P\text{-}cis\text{-}a}$ = 3 Hz, $^3J_{C-P\text{-}cis\text{-}b}$ = 2 Hz, mutually *trans* phosphines), 18.75 (dq, $^1J_{C-P}$ = 29 Hz, $^3J_{C-P}$ = 2 Hz, PMe$_3$ *trans* to CH$_2$CN), −32.9 (br d, $^2J_{C-P\text{-}trans}$ = 60 Hz, CH$_2$CN); ^{31}P δ −53.4 (br m, mutually *trans* phosphines), −59.2 (br m, PMe$_3$ *trans* to CH$_2$CN), −60.5 (br d, $^2J_{P-H\text{-}trans}$ = 132 Hz, PMe$_3$ *trans* to hydride); ^{31}P{^{1}H} δ −53.4 (*t*, *J* = 20 Hz, mutually *trans* phosphines), −59.2 (dt, J_1 = 18 Hz, J_2 = 20 Hz, PMe$_3$ *trans* to CH$_2$CN), −60.55 (dt, J_1 = 18 Hz, J_2 = 20 Hz, PMe$_3$ *trans* to hydride).

***cis*-[IrD(CD$_2$CN)(PMe$_3$)$_4$]Cl (3).** [Ir(PMe$_3$)$_4$]Cl (**1**) (0.050 g, 0.094 mmol) was dissolved in CD$_3$CN (1 mL) and stirred at room temperature overnight. The orange solution turned pale yellow. Addition of toluene precipitated the product as a white, crystalline solid, which was collected by filtration, washed with Et$_2$O (3 × 10 mL), and dried overnight *in vacuo*. Yield: 0.030 g (54.7%). Anal. Calcd (%) for C$_{14}$H$_{36}$D$_3$ClIrNP$_4$: C, 29.19; H, 7.35, N, 2.43. Found: C, 29.14; H, 6.85; N, 2.14. MS-ES$^+$: 541 Da ([M]$^+$). NMR (CD$_3$CN): ^{1}H δ 1.75 (d, $^2J_{H-P}$ = 4 Hz, 18H, mutually *trans* phosphines), 1.74 (d, $^2J_{H-P}$ = 2 Hz, 9H, PMe$_3$ *trans* to deuteride), 1.45 (d, $^2J_{H-P}$ = 8 Hz, 9H, PMe$_3$ *trans* to CD$_2$CN); ^{2}H{^{1}H} δ 1.23 (br s, 2D, CD$_2$), −13.1 (br dq, $^2J_{D-P\text{-}trans}$ = 20 Hz, $^2J_{D-P\text{-}cis}$ = 3 Hz, 1D, Ir-D); ^{13}C{^{1}H} δ 133.2 (br d, $^3J_{C-P\text{-}trans}$ = 11 Hz, CN), 23.7 (d, $^1J_{C-P}$ = 35 Hz, PMe$_3$ *trans* to deuteride), 21.1 (vt, $^1J_{C-P}$, $^3J_{C-P\text{-}trans}$ = 20 Hz, mutually *trans* phosphines), 18.7 (d, $^1J_{C-P}$ = 30 Hz, PMe$_3$ *trans* to CD$_2$CN), −32.9 (br m, CD$_2$); ^{31}P δ −52.5 (br m, mutually *trans* phosphines), −58.3 (br m, PMe$_3$ *trans* to CD$_2$CN), −59.6 (br m, PMe$_3$ *trans* to deuteride); ^{31}P{^{1}H} δ −52.5 (*t*, *J* = 20 Hz, mutually *trans* phosphines), −58.3 (q, *J* = 20 Hz, PMe$_3$ *trans* to −*C*D$_2$CN), −59.6 (tq, J_1 = J_2 = 20 Hz, PMe$_3$ *trans* to deuteride); ^{31}P{^{1}H + ^{2}H}: δ −52.5 (t, *J* = 20 Hz, mutually *trans* phosphines), −58.3 (q, *J* = 20 Hz, PMe$_3$ *trans* to CD$_2$CN), −59.6 (q, *J* = 20 Hz, PMe$_3$ *trans* to deuteride).

***cis*-[IrH(*p*-NHC$_6$H$_4$CN)(PMe$_3$)$_4$]Cl (4).** To a stirred suspension of **1** (0.050 g, 0.094 mmol) in THF (1 mL) was added *p*-aminobenzonitrile (0.011 g, 0.094 mmol) at room temperature. The mixture was left to react overnight, and the precipitate gradually turned from orange to white. CH$_3$CN was added to dissolve the precipitate, which crystallized upon addition of toluene. Yield: 0.025 g (41%). Anal. Calcd (%) for C$_{19}$H$_{42}$ClIrN$_2$P$_4$: C, 35.10; H, 6.51, N, 4.31. Found: C, 35.32; H, 6.48; N, 4.94. HRMS-ES$^+$: calcd for C$_{19}$H$_{42}$^{191}IrN$_2$P$_4$ ([M]$^+$) 613.18991 Da, found 613.19043 Da. NMR (CD$_3$CN): ^{1}H δ 7.23 (dd, J_{H-H} = 9, 2 Hz 1H, Ar), 7.01 (dd, J_{H-H} = 9, 2 Hz, 1H, Ar), 6.60 (dd, J_{H-H} = 9, 2 Hz, 1H, Ar), 6.51 (dd, J_{H-H} = 9, 2 Hz, 1H, Ar), 2.24 (br s, 1H, NH), 1.77 (d, $^2J_{H-P}$ = 10 Hz, 9H, PMe$_3$ *trans* to hydride), 1.6 (d, $^2J_{H-P}$ = 8 Hz, 9H, PMe$_3$ *trans* to NHC$_6$H$_4$CN), 1.56 (vt, $^2J_{H-P}$, $^4J_{H-P\text{-}trans}$ = 4 Hz, 18H, mutually *trans* phosphines), −11.52 (dq, $^2J_{H-P\text{-}trans}$ = 139 Hz, $^2J_{H-P\text{-}cis}$ = 18 Hz, 1H, Ir-H); ^{13}C{^{1}H} δ 161.7 (s, C, Ar), 135.1 (s, CH, Ar), 133.7 (s, CH, Ar), 123.2 (s, CN), 115.6 (*s*, CH, Ar), 115.2 (s, CH, Ar), 91.5 (s, C, Ar), 23.45 (d, $^1J_{C-P}$ = 41 Hz, PMe$_3$ *trans* to hydride), 20.6 (vtd, $^1J_{C-P}$, $^3J_{C-P\text{-}trans}$ = 20 Hz, $^3J_{C-P\text{-}cis}$ = 34 Hz, mutually *trans* phosphines), 18.0 (d, $^1J_{C-P}$ = 29 Hz, PMe$_3$ *trans* to NHC$_6$H$_4$CN); ^{31}P δ −45 (br m, mutually *trans* phosphines), −55.8 (br d, $^2J_{P-H\text{-}trans}$ = 139 Hz, PMe$_3$ *trans* to hydride), −57.3 (br m, PMe$_3$ *trans* to NHC$_6$H$_4$CN); ^{31}P{^{1}H} δ −45 (br t, J_{P-P} = 20 Hz, mutually *trans* phosphines), −55.8 (q, J_{P-P} = 20 Hz, PMe$_3$ *trans* to hydride), −57.3 (q, J_{P-P} = 20 Hz, PMe$_3$ *trans* to NHC$_6$H$_4$CN).

***cis*- and *trans*-[IrClH(PMe$_3$)$_4$][*p*-OC$_6$H$_4$CN] (5a/5b).** [Ir(PMe$_3$)$_4$]Cl (**1**) (102 mg, 0.192 mmol) and *p*-hydroxybenzonitrile (23 mg, 0.193 mg) were suspended in a mixture of THF and hexane (0.5 mL/1 mL) and stirred at room temperature overnight. A white precipitate formed, which was collected by filtration and dried *in vacuo* to give a white solid. Yield: 125 mg (100%). ***cis*-[IrClH(PMe$_3$)$_4$][*p*-OC$_6$H$_4$CN] (5a)**, NMR (CD$_3$CN): ^{1}H δ 7.10 (br d, J_{H-H} = 9 Hz, 2H, Ar), 6.18 (br d, J_{H-H} = 9 Hz, 2H, Ar), 1.8 (br d, $^2J_{H-P}$ = 10 Hz, 9H, PMe$_3$ *trans* to chloride), 1.74 (vt, J_{H-P} = 4 Hz, 18H, PMe$_3$, mutually *trans* phosphines), 1.56 (dd, $^2J_{H-P}$ = 8 Hz, $^4J_{H-H}$ = 1 Hz, 9H, PMe$_3$, *trans* to hydride), −11.8 (dq, $^2J_{H-P\text{-}trans}$ = 148 Hz, $^2J_{H-P\text{-}cis}$ = 18 Hz, 1H, Ir−H); ^{31}P{^{1}H} δ −45.2 (td, $^2J_{P-P}$ = 20 Hz, $^2J_{P-P}$ = 11 Hz, 1P, PMe$_3$ *trans* to Cl), −46.9 (t, $^2J_{P-P}$ = 20 Hz, 2P, mutually *trans* PMe$_3$), −53.6 (td, $^2J_{P-P}$ = 20 Hz, $^2J_{P-P}$ = 11 Hz, PMe$_3$ *trans* to H). ***trans*-[IrClH(PMe$_3$)$_4$][*p*-OC$_6$H$_4$CN] (5b)**, NMR (CD$_3$CN): ^{1}H δ 7.10 (br d, *J* = 9 Hz, 2H, Ar), 6.18 (br d, J_{H-H} = 9 Hz, 2H, Ar), 1.69 (*s*, PMe$_3$), −21.87 (quint, $^2J_{H-P\text{-}cis}$ = 15 Hz, 1H, Ir-H); ^{31}P{^{1}H} δ −45.4 (s, PMe$_3$). Anal. Calcd (%) for C$_{19}$H$_{41}$NClIrOP$_4$: C 35.03, H 6.35, N 2.15. Found: C 34.57, H 6.27, N 2.47. HRMS-ES$^+$: calcd for C$_{12}$H$_{37}$^{35}Cl^{193}IrP$_4$ ([M]$^+$) 531.11583, found 531.11557.

[Ir(PMe$_3$)$_4$][BPh$_4$] (7). [Ir(PMe$_3$)$_4$]Cl (**1**) (60 mg, 0.113 mmol) and Na[BPh$_4$] (39 mg, 0.113 mmol) were suspended in THF (2.5 mL) and stirred overnight at room temperature. A dark red solution with a colorless precipitate formed. After filtration, the volatiles were removed *in vacuo*, and the red residue was redissolved in THF (2 mL). Slow diffusion of hexane into the solution yielded a red, crystalline solid. Yield: 63 mg (68%). NMR (THF-d_8): ^{1}H δ 7.27 (br m, 8H, Ar), 6.85 (br t, J_{H-H} = 9 Hz, 8H, Ar), 6.70 (br t, J_{H-H} = 9 Hz, 4H, Ar), 1.54 (br s, 36H, PMe$_3$); ^{31}P{^{1}H} δ −27.1 (*s*, PMe$_3$). Anal. Calcd (%) for C$_{36}$H$_{56}$BIrP$_4$: C 52.97, H 6.92. Found: C 51.84, H 6.94.

***cis*-[IrH(NHC(O)Me)(PMe$_3$)$_4$]Cl (8).** Acetamide (0.006 g, 0.094 mmol) was added to a stirred suspension of **1** (0.050 g, 0.094 mmol) in THF (1 mL). The orange suspension turned pale white, and after 72 h, the resulting white residue was dissolved *in situ* by dropwise addition of acetonitrile and crystallized by careful addition of toluene. The crystalline solid was collected by filtration, washed with THF (3 × 20 mL), and vacuum-dried overnight. Yield: 0.030 g (54.7%). Anal. Calcd (%) for C$_{14}$H$_{41}$ClIrNOP$_4$: C, 28.45; H, 6.99, N, 2.37. Found: C, 28.80; H, 7.11; N, 2.36. HRMS-ES$^+$: calcd for C$_{14}$H$_{41}$^{191}IrNOP$_4$ ([M]$^+$) 554.17392 Da, found 554.17394 Da. NMR (CD$_3$CN): ^{1}H δ 3.9 (br s, 1H, NH), 1.95 (br s, 3H, Me), 1.7 (br d, $^2J_{H-P}$ = 9 Hz, 9H, PMe$_3$ *trans* to hydride), 1.6 (vt, $^2J_{H-P}$, $^4J_{H-P\text{-}trans}$ = 4 Hz, 18H, mutually *trans* phosphines), 1.5 (br d, $^2J_{H-P}$ = 8 Hz, 9H, PMe$_3$ *trans* to NHC(O)Me), −11.3 (br d, $^2J_{H-P\text{-}trans}$ = 143 Hz, 1H, Ir-H); ^{13}C{^{1}H} δ 175.2 (br d, $^3J_{C-P\text{-}trans}$ = 4 Hz, C═O), 25.7 (d, $^4J_{C-P\text{-}trans}$ = 5 Hz, Me), 23.5 (br dm, $^1J_{C-P}$ = 43 Hz, PMe$_3$ *trans* to hydride), 20.6 (vtd, $^1J_{C-P}$ = $^3J_{C-P\text{-}trans}$ = 20 Hz, $^3J_{C-P\text{-}cis}$ = 4 Hz, mutually *trans* phosphines), 19.0 (d, $^1J_{C-P}$ = 29 Hz, PMe$_3$ *trans* to NHC(O)Me); ^{31}P δ −45.7 (br m, mutually *trans* phosphines), −56.6 (br m, PMe$_3$ *trans* to NHC(O)Me), −57.3 (br m, PMe$_3$ *trans* to hydride); ^{31}P{^{1}H} δ −45.7 (m, mutually *trans* phosphines), −56.64 (overlapping m, PMe$_3$ *trans* to NHC(O)Me), −57.3 (overlapping m, PMe$_3$ *trans* to hydride).

Preparation of [Ir(O$_2$)(PMe$_3$)$_4$]Cl (9). 1 (0.050 g, 0.094 mmol) was suspended in THF (50 mL), and dry dioxygen (Linde-Praxair) was bubbled through the stirred suspension for a period of 3 h. The reaction mixture was stirred for a further 24 h, and the orange suspension turned colorless. The volatiles were evaporated *in vacuo*, and the gray residue was recrystallized from acetonitrile/Et$_2$O to yield green-yellow crystals suitable for X-ray analysis. Upon drying *in vacuo*, a white solid was obtained. Yield: 227 mg (82%). Anal. Calcd (%) for C$_{12}$H$_{36}$ClIrO$_2$P$_4$: C, 25.56; H, 6.43. Found: C, 25.75; H, 6.32. HRMS-ES$^+$: calcd for C$_{12}$H$_{36}$^{191}IrO$_2$P$_4$ ([M]$^+$) 527.12664 Da, found 527.12671 Da. NMR (CD$_3$CN): ^{1}H δ 1.76 (d, $^2J_{H-P}$ = 10 Hz, 18H, PMe$_3$ *trans* to oxygen), 1.46 (vt, $^2J_{H-P}$, $^4J_{H-P\text{-}trans}$ = 4 Hz, 18H, mutually *trans* phosphines); ^{13}C{^{1}H} δ 21.26 (d, $^1J_{C-P}$ = 38 Hz, PMe$_3$ *trans* to oxygen), 13.58 (vt, $^1J_{C-P}$ = $^3J_{C-P\text{-}trans}$ = 20

Hz, mutually *trans* phosphines); $^{31}P\{^1H\}$ δ −27.62 (t, J = 16 Hz, PMe_3 *trans* to oxygen), −51.25 (t, J = 16 Hz, mutually *trans* phosphines).

Catalysis Experiments. NMR tubes equipped with J Young valves were charged with **9** (0.0054 g, 0.0096 mmol, 0.1 mol %), CH_3CN or CD_3CN (9.6 mmol), and H_2O or D_2O (9.6 mmol). The sealed tubes were heated to 140 °C in a silicone oil bath and periodically monitored by NMR spectroscopy over a period of 200 h, at which point substantive crystallization of acetamide produced *in situ* hampered the acquisition of NMR spectra at ambient temperature. Acetamide was recovered from the tubes in the air, dissolving the products in acetone and filtering them through a small bed of silica. The solvent was evaporated, and the remaining white solid was left to dry overnight.

(**A**) **CH_3CN/H_2O**, conversion = 81.5%, TON = 846 cycles, TOF = 4.2 cycles/h. $MeC(O)NH_2$. GC/MS: 59 ($[M]^+$). (**B**) **CH_3CN/D_2O**, overall conversion = 74.8%, TON = 777 cycles, TOF = 3.9 cycles/h. NMR (D_2O+MeCN): ^1H δ 7.88 (br s, NH), 7.15 (br s, NH), 2.37 (s, Me), 2.36 (t, $^2J_{H\text{-}D}$ = 2 Hz, CH_2D), 2.35 (br m, CHD_2); $^{13}C\{^1H\}$ δ 176.01 (s, C═O), 175.95 (s, C═O), 22.29 (q, $^3J_{C\text{-}D}$ = 4 Hz, Me), 22.02 (tq, $^1J_{C\text{-}D}$ = 20 Hz, $^3J_{C\text{-}D}$ = 4 Hz, CH_2D), 21.86 (overlapping m, CHD_2/CD_3). GC/MS: 59 (Int.(%) = 6), 60 (Int.(%) = 20), 61 ($[M]^+$, Int.(%) = 32), 62 (Int.(%) = 27), 63 (Int.(%) = 12), 64 (Int.(%) = 3). (**C**) **CD_3CN/H_2O**, overall conversion = 85.1%, TON = 884 cycles, TOF = 4.4 cycles/h. NMR (CD_3CN+H_2O): ^1H δ 7.33 (br s, 1H, NH), 6.64 (br s, 1H, NH), 1.84 (overlapping br m, CHD_2/CH_2D); $^{13}C\{^1H\}$ δ 175.40 (*s*, C═O), 21.45 (overlapping m, $^1J_{C\text{-}D}$ = 20 Hz, $CH_2D/CHD_2/CD_3$). GC/MS: mass = 60 (Int.(%) = 8), 61 (Int.(%) = 21), 62 ($[M]^+$, Int.(%) = 32), 63 (Int.(%) = 27), 64 (Int.(%) = 11). (**D**) **CD_3CN/D_2O**, overall conversion = 67.3%, TON = 699 cycles, TOF = 3.5 cycles/h. $CD_3C(O)ND_2$, GC/MS: 64 ($[M]^+$, Int.(%) = 100). NMR (D_2O+CD_3CN): $^{13}C\{^1H\}$ δ 175.42 (s, C═O), 21.09 (sept, $^1J_{C\text{-}D}$ = 20 Hz, CD_3).

(37) Sheldrick, G. M. *SHELXTL, version 6.14*; Bruker AXS: Madison, WI, 2003.

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