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New Water-Soluble Iridium(I)−N-Heterocyclic Carbene−Tertiary Phosphine Mixed-Ligand Complexes as Catalysts of Hydrogenation and Redox Isomerization

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Supporting Information

ABSTRACT: Seven new [Ir(NHC)(η^4-cod)(L)] complexes (**4**−**9**, **11**) with NHC = bmim, emim, L = Cl^-, H_2O, or the water-soluble phosphines *m*tppms-Na, *m*tppts-Na_3, and pta were synthesized and characterized. Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) and [Ir(bmim)(η^4-cod)(pta)]Cl (**7**) actively catalyzed hydrogenation of alkenoic and oxo acids in aqueous solution. These catalysts were also found to be active in the hydrogenation of highly substituted C=C bonds (such as those in methylmaleic and methylfumaric acids). The stability of **6** was significantly increased by the addition of formate or oxalate. Under hydrogen, active catalysts were formed in situ from [IrCl(bmim)(η^4-cod)], [IrCl(η^4-cod)(emim)], or [IrCl(η^4-cod)(IMes)] and *m*tppts-Na_3 or pta. In the presence of HCOONa, [IrCl(η^4-cod)(bmim)] + *m*tppts-Na_3 showed a TOF of 150 h^{-1}in the hydrogenation of itaconic acid in water at 60 °C, which is the highest value determined to date for a water-soluble Ir(I) hydrogenation catalyst in an aqueous system. Both **6** and **7** selectively isomerized alk-1-en-3-ols to the corresponding methyl ketones with no need for an external reducing agent such as H_2. Furthermore, Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) was also shown to catalytically decompose aqueous formate to H_2 and bicarbonate.

INTRODUCTION

Iridium complexes play a prominent role in homogeneous catalysis[1] due to their versatility in facilitating reactions such as hydrogenation,[2] hydrogen transfer reactions,[3] hydrosilylation,[4] hydroamination,[5] and C−C bond formation,[6] among others.

An example of a particularly successful Ir-based hydrogenation catalyst is [Ir(η^4-cod)(PCy_3)(py)]BF_4 (PCy_3 = tricyclohexylphosphine, cod = 1,5-cyclooctadiene, py = pyridine), known as Crabtree's catalyst.[2a−c] This complex has the outstanding feature that in noncoordinating solvents, such as dichloromethane, it hydrogenates highly substituted alkenes with high rates even in cases when other homogeneous catalysts are completely inactive. In addition, useful directing effects of already existing substituents in substrate molecules were observed and utilized for stereoselective hydrogenations.[2c] A notable weakness of this catalyst is its instability under hydrogenation conditions, leading to relatively fast deactivation.[1c,2a,d−h]

N-heterocyclic carbenes form stable complexes with catalytically important metal ions such as Pd(II), Rh(I), Ru(II), Ir(I), etc. and are widely used with favorable effects for the replacement of tertiary phosphine ligands.[7] Several groups have performed excellent work on Ir(I)−NHC complexes as catalysts, including those of Nolan,[2e] Buriak,[2g,h] Herrmann and Kühn,[3j,k] and Peris.[3l] Substitution of PCy_3 by various N-heterocyclic carbene ligands in [Ir(η^4-cod)(PCy_3)(py)]BF_4 did not lead to more active catalysts. In fact, in several cases the NHC-ligated complexes were catalytically less active than the parent compounds; however, the catalyst stability was improved remarkably.[2h] In contrast, keeping a tertiary phosphine ligand in the coordination sphere of Ir(I) and replacing pyridine by an N-heterocyclic carbene resulted in a significant increase of hydrogenating activity; the best result could be achieved by optimizing the choice of the phosphine and carbene ligands.[2e−h,k,3j]

Aqueous organometallic catalysis provides a practical means of catalyst recovery and allows the design of green chemical processes by replacing organic solvents with water.[8] So far, only a few studies have appeared on the synthesis and application of water-soluble Ir complex catalysts,[9] and even fewer attempts have been made to obtain water-soluble Ir(I)-based hydrogenation catalysts. A case in point is the synthesis of [Ir(η^4-cod)(PR_3)(py)]PF_6, where PR_3 is the water-soluble PEG-functionalized phosphine PEG-($OC_6H_4PPh_2$)$_2$, derived from poly(ethylene glycol) PEG-3400, and is presumed to coordinate as a monodentate ligand.[2f] This complex actively catalyzed the biphasic hydrogenation of allylbenzene; however, the maximum turnover frequency (TOF = (mol of hydrogenated substrate) (mol of catalyst)$^{-1}$ h^{-1}) was only 23 h^{-1}, while under comparable conditions a TOF of 187 h^{-1} was achieved with [Ir(η^4-cod)(PPh_3)(py)]PF_6 in CH_2Cl_2. Note

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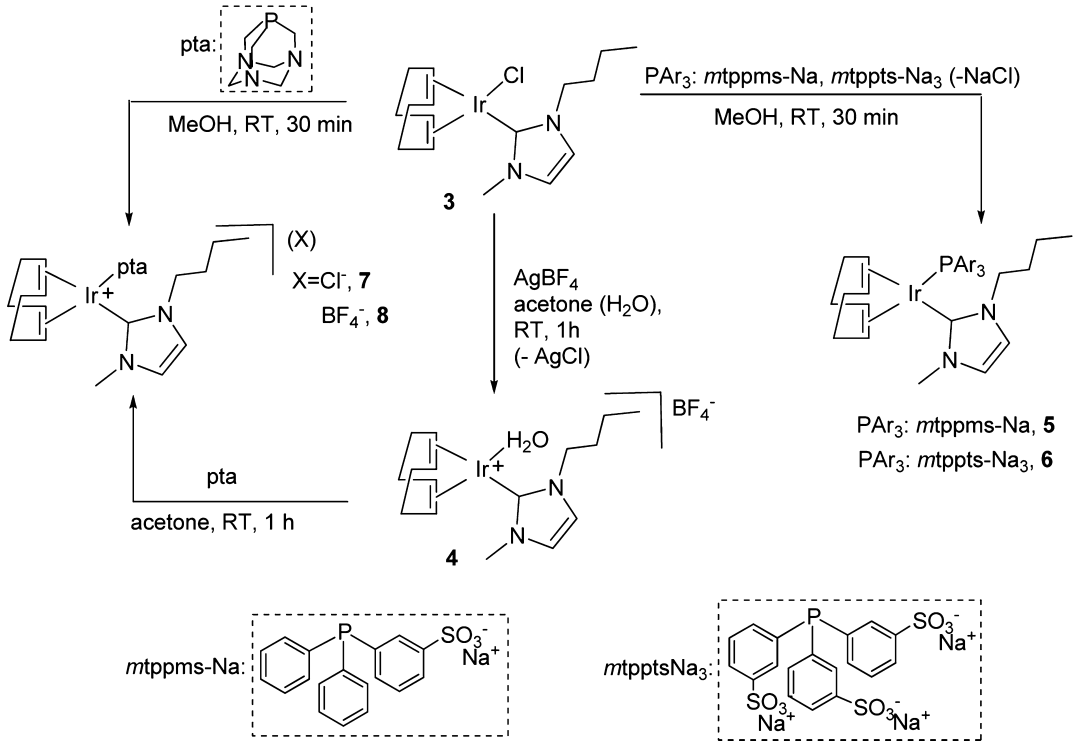
Scheme 1. Synthesis of Complexes 4−8



that, although quite a large number of water-soluble metal complexes containing N-heterocyclic carbene ligands are now known,[10] there have been few such iridium complexes reported.[11]

This lack of aqueous-phase catalysis by iridium−NHC complexes as well as our longstanding interest in aqueous organometallic catalysis[8a] led us to synthesize and study mixed N-heterocyclic carbene/tertiary phosphine complexes of iridium as catalysts in aqueous media (homogeneous solutions and aqueous−organic biphasic systems). The water solubility of such mixed NHC/PR_3 complexes of Ir(I) may be provided either by water-soluble N-heterocyclic carbene or by hydrophilic tertiary phosphine ligands. We have already reported on the synthesis and catalytic application of complexes with water-soluble N-heterocyclic carbene ligands;[10e,f] however, the present work was directed at the study of Ir(I)−NHC−PR_3 complexes with commercially available water-soluble tertiary phosphines. In some cases the ionic nature of the complexes also contributed to their hydrophilicity. With the use of $[IrCl(\eta^4\text{-cod})]_2$ (**1**) and $[Ir(OMe)(\eta^4\text{-cod})]_2$ (**2**) as starting materials, we synthesized [IrCl(bmim)(η^4-cod)] (**3**; bmim = 1-butyl-3-methylimidazol-2-ylidene), $[Ir(H_2O)(bmim)(\eta^4\text{-cod})]BF_4$ (**4**), [Ir(bmim)(η^4-cod)(*m*tppms)] (**5**; *m*tppms-Na = sodium 3-diphenylphosphinobenzenesulfonate), Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**; *m*tppts-Na_3 = trisodium 3,3′,3″-phosphinetriylbenzenesulfonate), and [Ir(bmim)(η^4-cod)(pta)]X (X = Cl^- (**7**), BF_4^- (**8**); pta = 1,3,5-triaza-7-phosphaadamantane = 1,3,5-triaza-7-phosphatricyclo-[3.3.1.$1^{3,7}$]decane). 1-Butyl-3-methylimidazolium-2-ylidene was chosen as the ligand in these complexes because of its relatively small size and good water solubility; furthermore, bmimH^+X^- (X = Cl^- or other anion) is one of the most widely used ionic liquids. For comparison, [IrCl(η^4-cod)(emim)] (**9**; emim = 1-ethyl-3-methylimidazol-2-ylidene) and [IrCl(η^4-cod)(IMes)] (**10**; IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) were also prepared and used for in situ synthesis of hydrogenation catalysts (**11**−**14**) in reaction with *m*tppts-Na_3 or pta under hydrogen. Synthetic procedures and characterizations for **3**−**9** and **11** and the catalytic application of **6** and **7** (and to a smaller extent those of **11**−**14**) in aqueous-phase hydrogenation of alkenoic, alkadienoic, and oxo acids as well as in redox isomerization of allylic alcohols are reported below.

RESULTS AND DISCUSSION

$[Ir(OMe)(\eta^4\text{-cod})]_2$ (**2**) is a convenient source of Ir(I) for the synthesis of N-heterocyclic carbene complexes. In acetone, it reacted smoothly with bmimH^+Cl^-, yielding [IrCl(bmim)(η^4-cod)] (**3**). Removal of chloride by $AgBF_4$ in wet (undried) acetone resulted in formation of the corresponding aquo complex $[Ir(H_2O)(bmim)(\eta^4\text{-cod})]BF_4$ (**4**). Similar reactions of **3** with the sulfonated tertiary phosphines *m*tppms-Na and *m*tppts-Na_3 afforded the zwitterionic [Ir(bmim)(η^4-cod)(*m*tppms)] (**5**) and Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**), respectively. The reaction of **3** with pta yielded [Ir(bmim)(η^4-cod)(pta)]Cl (**7**). [Ir(bmim)(η^4-cod)(pta)]BF_4 (**8**) was obtained by replacement of the H_2O ligand in **4** with pta. These reactions are summarized in Scheme 1.

Formation of **5** could also be followed by UV−vis spectrophotometry. In methanolic solutions, titration of **3** with *m*tppms-Na resulted in very large spectral changes in the 350−600 nm range (Figure S1, Supporting Information). Molar ratio curves (Figure S2, Supporting Information) constructed for various wavelengths showed exclusive formation of a stable 1:1 complex which was identified as **5** by NMR spectroscopy.

X-ray-quality crystals of **5** and **8** could be obtained from chloroform solutions of these complexes. ORTEP views of the structures of $[Ir(bmim)(\eta^4\text{-cod})(mtppms)]\cdot 1.5H_2O\cdot CHCl_3$ (**5**·

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1.5H_2O·$CHCl_3$) and [Ir(bmim)(η^4-cod)(pta)]BF_4·2$CHCl_3$ (**8**·2$CHCl_3$) are shown in Figures 1 and 2.

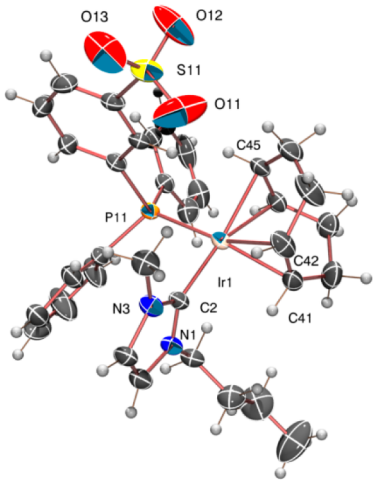

Figure 1. ORTEP view of [Ir(bmim)(η^4-cod)(*m*tppms)]·1.5H_2O·$CHCl_3$ (**5**·1.5H_2O·$CHCl_3$) at the 30% probability level with partial numbering scheme. Solvent chloroform and water molecules are omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ir(1)−C(2) 2.033(11), Ir1(1)-P(11) 2.301(8), Ir(1)−C(η)$_{average}$ 2.194(7), C(2)−N(1) 1.347(16), C(2)−N(3) 1.347(15), S(11)−O(11) 1.361(15), S(11)−O(12) 1.402(15), S(11)−O(13) 1.389(14); P(11)−Ir(1)−C(2) 90.9(4); N(1)−C(2)−Ir(1)−P(11) 87.3, N(3)−C(2)−Ir(1)−P(11) −92.0.

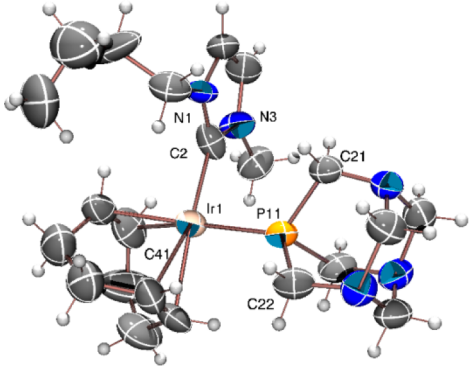

Figure 2. ORTEP view of [Ir(bmim)(η^4-cod)(pta)]BF_4·2$CHCl_3$ (**8**·2$CHCl_3$) at the 30% probability level with partial numbering scheme. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for both complexes of the asymmetric unit: Ir(1)−C(2) 2.052(14), 2.031(15), Ir1(1)-P(11) 2.278(4), 2.279(4), Ir(1)−C(η)$_{average}$ 2.206(7), C(2)−N(1) 1.338(16), 1.373(16), C(2)−N(3) 1.353(17), 1.368(18); P(11)−Ir(1)−C(2) 90.0(4), 89.3(4); N(1)−C(2)−Ir(1)−P(11) −91.16, 90.4, N(3)−C(2)−Ir(1)−P(11) 87.1, −89.8.

Ir−C and Ir−P bond lengths, N−C−Ir and C−Ir−P angles, and N−C−Ir−P torsion angles for these structures are in good agreement with those of other [Ir(bmim)P] and [Ir(η^4-cod)] complexes. In the case of [Ir(bmim)(η^4-cod)(*m*tppms)] (**5**) the structure of the *m*tppms ligand agrees well with those reported earlier.[12] A detailed discussion of the structural features can be found in the Supporting Information.

For comparison purposes we attempted the synthesis of complexes analogous to **6** but with emim (1-ethyl-3-methyl imidazol-2-ylidene) and IMes (1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) as N-heterocyclic carbene ligands. The corresponding imidazolium chlorides reacted cleanly in dry acetone with [Ir(OMe)(η^4-cod)]$_2$, yielding [IrCl(η^4-cod)(emim)] (**9**) and [IrCl(η^4-cod)(IMes)] (**10**), respectively (**10** is a known compound[7f]). Subsequent reaction of [IrCl(η^4-cod)(emim)] with *m*tppts-Na_3 and pta in methanol at room temperature resulted in the instantaneous formation of Na_2[Ir(η^4-cod)(emim)(*m*tppts)] (**11**) and [Ir(η^4-cod)(emim)(pta)]Cl (**12**), respectively, as shown by the appearance of the characteristic red color of the complexes and also by ^{31}P and ^{13}C NMR spectroscopy. However, under similar conditions no interaction of [IrCl(η^4-cod)(IMes)] (**10**) with pta or *m*tppts could be detected by ^{1}H and ^{31}P NMR spectroscopy, presumably due to the steric hindrance of the cod, IMes, and PR_3 ligands.

The new compounds gave the correct elemental analyses, and their infrared spectra displayed absorptions expected for complexes containing bmim, emim, and the relevant phosphine ligands (Figures S3−S10, Supporting Information). Especially characteristic were the sharp and strong IR absorptions of the sulfonate group around 1432, 1335, 1031 cm^{-1} and 1430, 1338, 1036 cm^{-1} displayed by **5**, **6**, and **11**. Complexes **5**−**7** were also subjected to ESI-MS measurements and showed the correct molecular masses and isotope distributions. ^{13}C NMR signals of **3**−**7**, **11**, and **12** appeared in the range of 171.0−179.9 ppm, which is characteristic of carbene carbon. In the cases of mixed phosphine−NHC complexes these signals were doublets, with ^2J(C,P) values of 8.9−11.4 Hz. These data agree well with those reported in the literature for related complexes.[2g,h,7f] For example, Buriak and co-workers reported a carbene ^{13}C NMR signal for [Ir(1,3-dimethylimidazoline-2-ylidene)(η^4-cod)(PPh_3)]PF_6 at δ 174.09 ppm and for [Ir(1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene)(η^4-cod)(P^nBu_3)] PF_6 at δ 175.97 ppm.[2g]

Reactions of Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (6) and [Ir(bmim)(η^4-cod)(pta)]Cl (7) with Hydrogen. Aqueous solutions of **6** and **7** reacted with H_2 at room temperature with an immediate color change from red to yellow. Simultaneously, the resonances of coordinated cod in the 29−32, 49−51, and 79−90 ppm intervals disappeared from the ^{13}C NMR spectra of the hydrogenated complexes. On the other hand, ^{1}H NMR spectra showed numerous resonances in the hydride region between −4 and −27 ppm. The most intense lines (doublet of doublets) were centered at −24.15 ppm, and another doublet signal could be observed at −25.37 ppm (Figures S15 and S16, Supporting Information). At least 14 distinct but badly resolved lines could be observed in the hydride region. Upon ^{31}P{^{1}H} and ^{1}H{^{31}P} decoupling the multiplicity of the signals became simpler; however, the spectra were still not suitable for an exact structure determination of the hydrides formed in the solutions−illustrative spectra are shown in Figure S17 (Supporting Information). Furthermore, ^{1}H−^{1}H COSY measurements (Figures S15 and S16) revealed that the various hydrides are not involved in scalar coupling and therefore multiplicities of their resonances arise from coupling to phosphorus atoms. On the basis of these results, the presence of a mononuclear Ir trihydride cannot be ascertained. Since in **6** and **7** the Ir:P ratio is 1:1, most probably the hydride species in the solution are multinuclear complexes (or clusters) containing more than one iridium and phosphorus. These findings agree with the observations of Buriak[2g,h] and support the assumption that removal of the cyclooctadiene ligand by hydrogenation yields several monomeric and bridged Ir hydrido complexes. (However, in the presence of carboxylato ligands a

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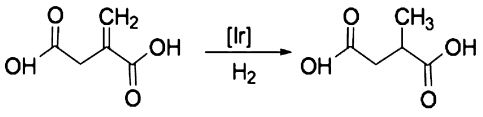
single major hydrido complex could be obtained, as we shall discuss later on.)

Interestingly, this reactivity can also be observed in the solid state: red powders of **6** or **7** turned yellow when placed under a hydrogen atmosphere at room temperature. Infrared spectra of the yellow solids showed a very strong and broad absorbance in the terminal hydride region at 2236 cm^{-1} (**6**) and 2184 cm^{-1} (**7**) (Figures S8 and S9, Supporting Information). Replacement of H_2 by N_2 led to an almost complete elimination of these infrared absorbances; however, the color of the samples only changed slightly toward pink. Under a fresh H_2 atmosphere, the absorbance at 2236 cm^{-1} of a sample of **6** increased again; however, its intensity was not completely recovered but reached only about 35% of the absorbance in the first cycle (Figure S10, Supporting Information). In conclusion, both the solution NMR measurements and the solid-state IR spectra showed that **6** reacted irreversibly with hydrogen.

Catalysis. We chose two reactions for a study of the catalytic properties of the new hydrophilic Ir(I)−NHC−phosphine complexes: namely (a) hydrogenation of alkenoic, alkadienoic, and oxo acids in homogeneous aqueous solution and (b) redox isomerization of allylic alcohols in aqueous biphasic systems. In most cases Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) and [Ir(bmim)(η^4-cod)(pta)]Cl (**7**) were used as catalysts for these reactions; however, catalysts prepared in reactions of [IrCl(η^4-cod)(emim)] (**9**) and [IrCl(η^4-cod)-(IMes)] (**10**) with pta or *m*tppts-Na_3 under hydrogen were also investigated.

Hydrogenation of Alkenoic, Alkadienoic, And Oxo Acids in Water. Unsaturated aliphatic acids such as crotonic, maleic, fumaric, and similar acids are frequently used for studying the activity of new hydrogenation catalysts in aqueous systems.[13] Such substrates were actively hydrogenated by **7** in aqueous solutions under mild conditions (60 °C, 1 bar of total pressure; i.e. 0.8 bar partial pressure of H_2 above the aqueous solution). The color of the reaction mixture changed characteristically in time: in the first few seconds the solution was red and then turned yellow, and at the end of the reaction it became colorless. Hydrogenation of unsaturated acids was followed by using constant-pressure gas burets and also by ^{1}H NMR spectroscopy (Figure S11, Supporting Information). The time course of the hydrogenation of itaconic (2-methylenesuccinic) acid (Scheme 2) is shown in Figure 3, while characteristic data of hydrogenations of several substrates are collected in Table 1.

Scheme 2. Hydrogenation of Itaconic Acid



The hydrogen uptake diagram suggests that in the specific case of itaconic acid the substrate and catalyst form a stable intermediate complex so that the rate of hydrogenation is independent of substrate concentration until conversions close to 100%. In general, however, hydrogen uptake proceeded with gradually decreasing rate (see e.g. Figure S12, Supporting Information).

The specific activity of **7** (expressed as TOF) is comparable to those of other water-soluble hydrogenation catalysts such as [RuHCl(*m*tppms)$_3$] and [RuH(OAc)(*m*tppms)$_3$].[13b,c] For example, at 60 °C itaconic acid was hydrogenated by

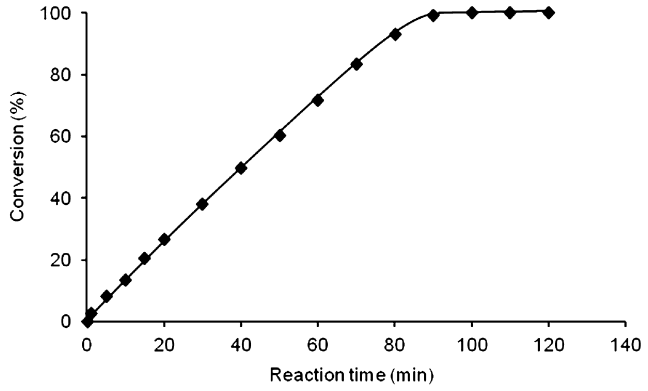


Figure 3. Conversion of itaconic acid as a function of time in hydrogenation catalyzed by **7**. Conditions: 0.01 mmol of **7**, 0.3 mmol of itaconic acid, 3 mL of water, 60 °C, $P(H_2)$ = 0.8 bar.

Table 1. Hydrogenation of C═C and C═O Unsaturated Acids (or Their Salts) In Aqueous Solution with the Catalyst [Ir(bmim)(η^4-cod)(pta)]Cl (7)[a]

entry	substrate	[S]/[C]	conversion (1 h), %	TOF (1 h), h^{-1}
1	*trans*-crotonic acid	50	36.7	18.4
2	maleic acid	50	25.0	12.5
3	citraconic (methylmaleic) acid	50	30.5	15.3
4	fumaric acid	25	39.4	9.9
5	mesaconic (methylfumaric) acid	25	34.1	8.5
6	mesaconic (methylfumaric) acid	50	18.8	9.4
7	itaconic acid	30	79.3	23.8
8	itaconic acid	30	100 (1.5 h)	20.0 (1.5 h)
9	K-sorbate (K-2,4-hexadienoate)	25	31.7	7.9
10	K-sorbate (K-2,4-hexadienoate)	25	100[b] (6.5 h)	7.7 (6.5 h)
11	Na-pyruvate	50	59.7	29.9
12	levulinic acid	50	14.7	7.4

[a]Conditions: 0.01 mmol of **7**, 3 mL of water, 60 °C, $P(H_2)$ = 0.8 bar. Conversion (%) = 100$[S]_{reacted}/[S]_{total}$. TOF ($h^{-1}$) = (mol of H_2 reacted)(mol of catalyst)$^{-1}$ h^{-1}. [b]Both C═C double bonds hydrogenated.

[RuHCl(*m*tppms)$_3$] with TOF = 84 h^{-1}, and the activity of the same catalyst in hydrogenation of maleic acid was 23 h^{-1} (both reactions in 0.1 M aqueous HCl).[13b] Reduction of ketocarboxylic acids to hydroxycarboxylic acids is an important physiological reaction. With catalyst **7**, sodium pyruvate (Na-2-oxopropionate) was hydrogenated to lactate with a TOF of 29.9 h^{-1}, in contrast to the TOF = 115 h^{-1} achieved by using [RuHCl(*m*tppms)$_3$] in 0.1 M HCl as solvent. Hydrogenation of 4-oxovaleric acid (levulinic acid) yielded γ-valerolactone, an important sustainable platform chemical.[14] Since levulinic acid is obtained from biomass in aqueous solution, its hydrogenation in this reaction medium is of high importance.[13b,c,14] With **7** as catalyst, hydrogenation of levulinic acid proceeded smoothly (Figure S12, Supporting Information) but was found slightly slower (TOF = 7.4 h^{-1}) than hydrogenation of the same substrate with [RuHCl(*m*tppms)$_3$] in 0.1 M HCl as solvent (TOF = 13 h^{-1}).[13b]

The catalytic activities of the new water-soluble Ir(I)−NHC−phosphine complexes were compared in the hydro-

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genation of itaconic acid. As mentioned earlier, attempts to synthesize analogues of **6** and **7** by reacting *m*tppts-Na_3 or pta under argon with [IrCl(η^4-cod)(IMes)] (**10**) failed (the same observation was made by Torres et al. in the case of **10** and *m*tppts-Na_3[7f]). However, both phosphines reacted readily with **10** under hydrogen, leading to the formation of homogeneous aqueous solutions of catalytically active Ir(I) complexes **13** and **14**. For comparison, all other catalysts in Table 2 were prepared

Table 2. Hydrogenation of Itaconic Acid with in Situ Prepared [IrCl(η^4-cod)(NHC)] + PR_3 Catalysts in Water[a]

entry	catalyst	TOF (h^{-1})
1	[IrCl(bmim)(η^4-cod)] + *m*tppts-Na_3 (**6**)	27.9
2	[IrCl(bmim)(η^4-cod)] + pta (**7**)	23.8
3	[IrCl(η^4-cod)(emim)] + *m*tppts-Na_3 (**11**)	66.6
4	[IrCl(η^4-cod)(emim)] + pta (**12**)	86.2
5	[IrCl(η^4-cod)(IMes)] + *m*tppts-Na_3 (**13**)	20.0
6	[IrCl(η^4-cod)(IMes)] + pta (**14**)	20.6

[a]Conditions: 0.005 mmol of [IrCl(bmim)(η^4-cod)], [IrCl(η^4-cod)(emim)], or [IrCl(η^4-cod)(IMes)], 0.005 mmol of pta or *m*tppts-Na_3, substrate/catalyst = 30–50, 3 mL of water, 60 °C, $P(H_2)$ = 0.8 bar. TOF (h^{-1}) = (mol of H_2 reacted)(mol of catalyst)$^{-1}$ h^{-1}.

similarly (see also the Experimental Section). In all cases, hydrogen uptake was a linear function of time until full conversion (such as in Figure 3). This refers to the kinetic role of a stable substrate-containing intermediate. Removal of cod from the coordination sphere of Ir(I) by hydrogenation opens up coordination sites which may be filled by the phosphine and chloride or H_2O. It seems reasonable that even at low concentrations itaconic acid replaces the H_2O ligand(s), which can explain the linear H_2 uptake.

The TOF data in Table 2 show that among the various Ir–NHC–phosphine catalysts the emim-containing complexes have the highest activity in hydrogenation of itaconic acid, and in the case of [IrCl(η^4-cod)(emim)] + pta this is higher than the activity displayed by [RuHCl(*m*tppms)$_3$] under comparable conditions (TOFs 86.2 vs 84 h^{-1}[13b]). This catalyst (**12**) contains the smallest carbene and phosphine ligands, but otherwise the size of the ligands does not make much difference.

In general, the catalytic hydrogenation activity of the new water-soluble Ir–NHC–PR_3 complexes **6**–**14** (TOF in the 7–86 h^{-1} range, Tables 1 and 2) is comparable to that of [Ir(η^4-cod)(PR_3)(py)]PF_6 (PR_3 = water-soluble PEG-($OC_6H_4PPh_2$)$_2$) studied by Crabtree et al. in the aqueous–organic biphasic hydrogenation of allylbenzene (TOF = 23 h^{-1}).[2f] In fact, **11** and **12** (Table 2) are the most active Ir(I)-based catalysts to date for olefin hydrogenation in aqueous solution. However, two important effects should be considered. First, water is a strongly coordinating solvent and Crabtree's unmodified catalyst is most effective in a noncoordinating solvent such as dichloromethane.[1c,2a–c] Second, replacement of PCy_3 in [Ir(η^4-cod)(py)(PCy_3)]BF_4 by an aromatic phosphine, such as PPh_3, is known to result in a significant decrease of hydrogenation activity.[1c] On the other hand, **7** was found to be suitable for the hydrogenation of olefins such as citraconic (methylmaleic) and mesaconic (methylfumaric) acids, containing highly substituted carbon–carbon double bonds; in fact, the turnover frequencies are very close to or even higher than those determined with the less substituted substrates maleic and fumaric acids (Table 1, entries 2 vs 3 and 4 vs 5).

Crabtree's catalyst and its NHC-containing analogues are known to be unstable under hydrogenation conditions.[1c,2a,d–h] In the hydrogenation of itaconic acid we have also found that, after 100% conversion of the first batch of substrate, addition of another portion of itaconic acid led to a slower second cycle and in subsequent cycles the catalyst gradually lost its activity. Interestingly, in the presence of sodium formate the catalyst could be recycled with a fairly constant activity (Figure 4).

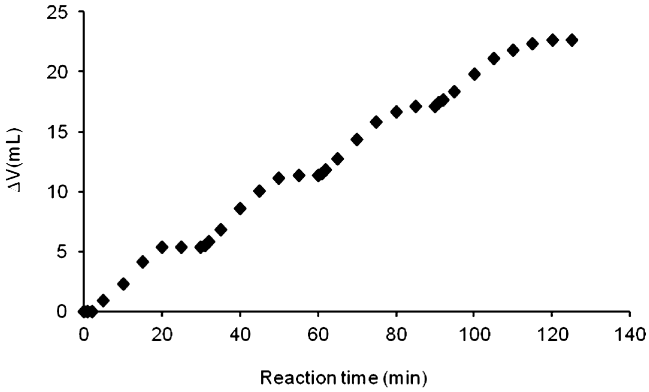

Figure 4. Hydrogenation of itaconic acid in the presence of formate in repeated cycles. After complete conversion of the substrate (determined by ^{1}H NMR) new batches of itaconic acid (0.25 mmol) were added at 30, 60, and 90 min. Conditions: 0.005 mmol of Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**), 0.5 mmol of HCOONa, 3 mL of water, 60 °C, $P(H_2)$ = 0.8 bar.

Figure 4 also reveals two very interesting properties of the catalyst. First, the rate of hydrogenation was found to be substantially higher in the presence of formate than in its absence. In the first cycle 100% conversion was achieved in 20 min (checked by ^{1}H NMR), corresponding to a TOF of 150 h^{-1} in comparison to 27.9 h^{-1} in the absence of formate, as shown in Table 2. Second, although the calculated decrease in the volume of the gas phase in the hydrogenation of 1 mmol of itaconic acid in aqueous solutions at 60 °C is 34.05 mL, it can be seen from Figure 4 that in the presence of formate this expectation is not fulfilled; only 22.6 mL of gas was consumed for 4 × 0.25 mmol of itaconic acid at 125 min, i.e. 11.45 mL less than that expected, despite the 100% hydrogenation in each cycle. It may be assumed that reduction of itaconic acid takes place—in part—by direct hydrogen transfer from HCOONa + H_2O. This reaction leads to formation of CO_2, and since the reaction mixtures are acidic (pH 3.86), the latter is released to the gas phase. Indeed, CO_2 was detected in the gas phase above the reaction mixture by gas chromatography (Figure S13, Supporting Information). However, in independent experiments the rate of direct hydrogen transfer under an argon atmosphere was found to be slow, and only 8% conversion of itaconic acid was determined by ^{1}H NMR instead of 100% in reductions with HCOONa/H_2 under otherwise identical reaction conditions. Consequently, we do not consider the contribution of this side reaction to the diminished gas uptake to be extensive. On the other hand, in aqueous solution, formate can be catalytically decomposed[15] to H_2 + HCO_3^- and protonation of bicarbonate yields CO_2, which accumulates in the gas phase in our closed systems (gas burets, Schlenk tubes). In the reaction under study (Figure 4) decomposition of approximately 67% of the initial amount of formate (0.5 mmol) is sufficient to supply the 11.45 mL of CO_2 required to

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rationalize the diminished gas uptake. Under the conditions of Figure 4, decomposition of $NaHCO_2$ was indeed observed but resulted in only a 1.1 mL volume increase in 30 min (Figure S14, Supporting Information). However, when succinic acid was added to mimic the situation in the presence of itaconic acid (similar pH, presence of a prospective dicarboxylate ligand), a fast gas evolution was observed, yielding an additional 15.7 mL of volume increase in 150 min (Figure S14). This is entirely sufficient to explain the reduced amount of gas uptake in the hydrogenation experiments. Since in acidic solutions Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) does not catalyze the hydrogenation of CO_2 once all the formate has decomposed, its stabilizing effect on the catalyst can no longer be observed. Therefore, although the formate substantially increased the rate of hydrogenations catalyzed by **6**, and temporarily made the catalyst considerably more stable, it could not be regarded as an ideal stabilizing agent.

Concerning the effect of the formate, we reasoned that, after the elimination of cod from the coordination sphere of Ir(I) by hydrogenation, the formate is coordinated as a bidentate ligand and this is what improved the stability of the catalyst. At the same time the reaction of **6** and $HCOO^-$ may facilitate the formation of a catalytically important hydride species, which leads to the large increase in the rate of hydrogenation.

On the basis of this concept, we carried out hydrogenations of itaconic acid in the presence of K-oxalate (Figure 5). As

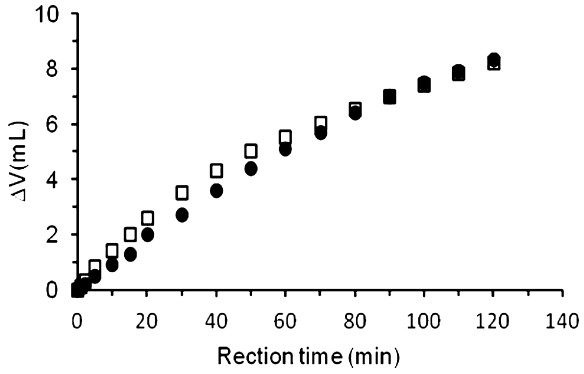


Figure 5. Hydrogenation of itaconic acid catalyzed by Na_2[Ir(bmim)(cod)(*m*tppts)] (**6**) in the presence of 1 equiv of K-oxalate: (□): experiment 1, 0.005 mmol of Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**), 0.005 mmol of K-oxalate, 0.25 mmol of itaconic acid, 3 mL of water, 60 °C, $P(H_2)$ = 0.8 bar; (●) experiment 2, addition of a new batch of 0.25 mmol of itaconic acid to the reaction mixture from experiment 1 at 120 min and measurements of gas uptake started again.

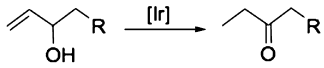
expected for the absence of a reactant (e.g., formate) that would produce gaseous byproducts, the observed gas uptake (8.3 mL in 120 min) closely approached the calculated value (8.51 mL), in complete agreement with the ^{1}H NMR measurements (98% conversion). From the average conversion obtained in 1 h a TOF value of 31.1 h^{-1} can be calculated. This is certainly lower than that determined in the presence of HCOONa (150 h^{-1}). However, the stability of the catalyst was remarkably improved and no decrease of the rate of hydrogenation was observed in repeated runs (Figure 5).

As mentioned earlier, the ^{1}H NMR spectrum of **6** in aqueous solution under H_2 showed several badly resolved resonances. However, in the presence of oxalate the spectrum became clear with two strongly overlapping doublets in the hydride region at δ −24.50 ppm (J_{HP} = 31.14 Hz) and −24.58 ppm (J_{HP} = 31.14 Hz) (Figure S18a, Supporting Information). This indicates the formation of an Ir(III) dihydride with the two hydride ligands in trans (apical) positions and with the *m*tppts and bmim ligands coordinated cis-meridionally. The bidentate oxalate ligand completes the meridional plane. In the presence of itaconic acid the two hydride doublets slightly move apart, showing coordination of itaconic acid already at room temperature (δ −24.51 ppm, J_{HP}= 31.14 Hz and δ −24.58 ppm, J_{HP} = 29.59 Hz; Figure S18b, Supporting Information). Similar spectral changes were observed in solutions of **6**, K-oxalate, and citraconic acid.

Finally, it is worth mentioning that with substrates of low aqueous solubility such as hexene-1 and cyclohexene disappointingly low hydrogenation rates were observed in aqueous−organic biphasic systems using **7** as catalyst. However, allylic alcohols, for example oct-1-ene-3-ol, underwent substantial hydrogenation in addition to redox isomerization when the reaction was run under a hydrogen atmosphere (see data in Table 4 below). This allows the conclusion that high rates of hydrogenations with **6** and **7** as catalysts do not require the presence of a carboxylate group in the substrate.

Redox Isomerization of Allylic Alcohols in Aqueous Systems. Redox isomerization of allylic alcohols (Scheme 3)

Scheme 3. Redox Isomerization of Allylic Alcohols



is a fully atom-economical reaction and has great potential in organic synthesis. As a result, considerable attention has been devoted to the study of this transformation since the seminal discoveries of Blum and co-workers[16a,b] and Trost and Kulawiec.[16c] Although there are three major mechanistic pathways suggested in the literature, formally the reaction can be regarded as a catalytic internal hydrogen transfer. It is not surprising, therefore, that many (albeit not all) of the good hydrogen transfer catalysts perform well in the transposition of allylic alcohols as well.

In aqueous or in aqueous−organic biphasic systems redox isomerization of allylic alcohols can form the basis of eco-friendly procedures, provided that isolation of the products does not require harmful organic solvents. Very active water-soluble catalysts have been prepared recently, mostly based on Ru(II);[17] however, other metal ions such as Rh(I) and Pd(II) have also proved useful. Iridium-based catalysts have rarely been investigated in redox isomerizations,[2b,3,5,18] although many iridium complexes were found to be outstandingly active in the catalysis of hydrogen transfer (some of them in aqueous systems).[3,19]

In the biphasic systems composed of oct-1-en-3-ol and water or 0.2 M aqueous phosphate buffer, both **6** and **7** proved active for the catalysis of redox isomerization (Table S1, Supporting Information). Under argon the exclusive product of the reaction was octan-3-one. Importantly, the catalysts did not move into the organic phase. When 0.2 M phosphate buffer was used as the aqueous phase, the rate of the reaction catalyzed by **6** showed a slight variation as a function of the pH. Interestingly, when the aqueous phase was plain, unbuffered water, the conversion reached 91% in contrast to 50% with buffer (pH 7). This may indicate an interaction of the catalyst with components of the phosphate buffer, similar to earlier observations.[20,21]

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In several cases the catalysts of redox isomerization need activation by reducing agents (H_2, 2-propanol, formates, etc.) presumably to facilitate formation of the catalytically active hydride species.[16c,17a] Catalyst **6** has the advantage that no such activation is necessary. The time course of the reaction of hex-1-en-3-ol (Figure 6) shows an induction period, which may indicate the formation of such hydrides in the reaction of the catalyst with the substrate.

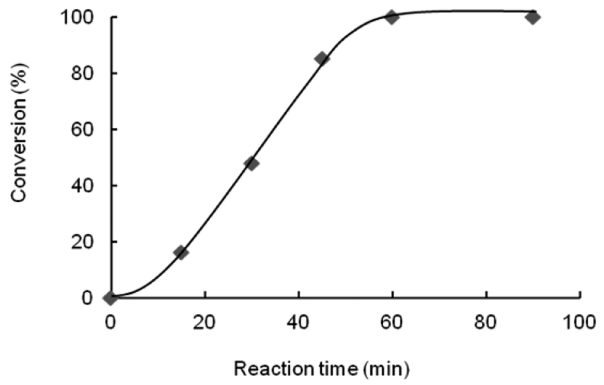

Figure 6. Redox isomerization of hex-1-en-3-ol catalyzed by **6** under an argon atmosphere. Conditions: 0.01 mmol of Ir, [S]/[Ir] = 100, 3 mL of water, T = 80 °C.

Several allylic alcohols were isomerized in water under argon using **6** as catalyst (Table 3). Under the reaction conditions pent-1-en-3-ol and the longer-chain allylic alcohols formed biphases with the aqueous catalyst solution, while but-1-en-3-ol and prop-2-en-1-ol (allyl alcohol) dissolved into the aqueous phase. On the basis of the assumption that catalysis needs at least one free coordination site on Ir, we also checked the effect of a coordinating anion (chloride) on the catalytic activity. However, under the reaction conditions employed, chloride did not effect the redox isomerization of hex-1-en-3-ol (Table 3, entry 3 vs 4).

Table 3. Redox Isomerization of Various Allylic Alcohols to the Corresponding Alkan-3-ones Catalyzed by 6 under an Argon Atmosphere[a]

entry	substrate	conversion, %
1	oct-1-en-3-ol	91
2	hept-1-en-3-ol	93
3	hex-1-en-3-ol	96
4[b]	hex-1-en-3-ol	98
5	pent-1-en-3-ol	97
6	but-1-en-3-ol	100
7[c,d]	prop-2-en-1-ol	100

Conditions: 0.01 mmol of Ir, [S]/[Ir] = 100, 3 mL of water, T = 80 °C, t = 1 h. [a]Yields determined by gas chromatography. [b]0.1 mmol of KCl added. [c]yields determined by NMR spectroscopy. [d]product is propanal.

It can be seen from the data of Table 3 that the various allylic alcohols showed similar reactivities. Since the conversions are close or equal to 100% in all cases, only minimum values of turnover frequencies can be obtained as TOF = 91−100 h^{-1}. Iridium(I) complexes have not been applied earlier for the catalysis of redox isomerization of allylic alcohols in aqueous biphasic systems. Ru(II) complexes were more frequently utilized; however, the majority of the water-soluble Ru(II)-based catalysts have been characterized by TOFs of a few hundred h^{-1} or less.[17a,18a] As an example, [$RuCl_2$(bmim)(η^6-*p*-cymene)] (*p*-cymene = 4-isopropyltoluene) catalyzed the isomerization of oct-1-en-3-ol to octan-3-one in water at 80 °C with an initial TOF value of 65 h^{-1}.[17h] Only a few catalysts are known which displayed substantially higher activities in *aqueous systems*, such as the bis(allyl)−ruthenium(IV) catalyst [RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)]$_2$ (oct-1-en-3-ol, 75 °C, TOF = 2000 h^{-1})[17a,d] and [RuCl(Cp)(*m*tppms-Na)$_2$] (oct-1-en-3-ol, 80 °C, TOF = 2226 h^1; Cp = cyclopentadienyl).[17f]

Hydrogen may influence the reaction by facilitating the formation of catalytically active hydrido species; therefore, the effect of H_2 was also studied. Indeed, under the conditions of Table 3, but under a H_2 atmosphere, the reaction speeded up and reached 100% conversion in all cases (either in water or in 0.2 M phosphate buffer of pH 7) with both catalysts. However, now the product contained a considerable amount of octan-3-ol (Table 4), the relative amount of which could reach 50%.

CONCLUSION

[IrCl(bmim)(η^4-cod)] (**3**) and [IrCl(η^4-cod)(emim)] (**9**) reacted smoothly with the hydrophilic phosphines *m*tppts-Na_3 and pta, affording the respective water-soluble complexes Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**), [Ir(bmim)(η^4-cod)(pta)]Cl (**7**), Na_2[Ir(η^4-cod)(emim)(*m*tppts)] (**11**), and [Ir(η^4-cod)(emim)(pta)]Cl (**12**). Similar reactions of [IrCl(η^4-cod)(IMes)] (**10**) with *m*tppts-Na_3 or pta could not be observed under argon; however, under an H_2 atmosphere active hydrogenation catalysts (**13** and **14**) were obtained with both phosphine ligands. The catalytic properties of **6**, **7**, and **11**−**14** in hydrogenation and redox isomerization reactions in water were studied and compared to those of related complexes in nonaqueous media. The main finding is that these complexes are active catalysts for the hydrogenation of water-soluble olefinic substrates (such as maleic, fumaric, and itaconic acids) and that highly substituted C=C double bonds (such as those in methylmaleic and methylfumaric acids) are also actively

Table 4. Redox Isomerization of Oct-1-en-3-ol Catalyzed by 6 and 7 under H_2[a]

entry	cat.	solvent	time, h	conversion, %	octan-3-one, %	octan-3-ol, %
1	**6**	water, pH 6.5[b]	1	99	49	50
2	**6**	buffer, pH 7.0	1	99	63	36
3	**6**	buffer, pH 7.0	5	100	60	40
4	**6**	buffer, pH 7.0	8	100	65	35
5	**7**	water, pH 6.6[b]	1	100	58	42
6	**7**	buffer, pH 7.0	1	100	51	49

[a]Conditions: 0.01 mmol of Ir, [S]/[Ir] = 100, $P(H_2)$ = 0.8 bar, 3 mL of water or 0.2 M aqueous phosphate buffer, T = 80 °C, t = 1 h. [b]pH of the catalyst solution.

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hydrogenated. Sodium formate largely increased the activity of **6**, presumably by facilitating the formation of the catalytically active intermediate(s); the TOF determined in hydrogenation of itaconic acid (150 h^{-1}) is the highest to date for an Ir(I) complex catalyst in aqueous hydrogenation. In aqueous solution formate was catalytically decomposed by **6** to yield H_2 and bicarbonate. In the presence of oxalate Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) showed high stability under H_2, which is an important improvement with relation to Ir(I)-based hydrogenation catalysts. **6** and **7** catalyzed the redox isomerization of allylic alcohols under mild conditions (80 °C). No activation by H_2 was necessary, and the reactions proceeded with no need for a base additive, which is an advantageous feature of the process. Under an argon atmosphere the reactions were fully selective to the corresponding ketone or aldehyde. In summary, the results show that the incorporation of hydrophilic phosphine ligands into mixed Ir(I)−NHC−phosphine complexes is a successful approach to the synthesis of active and versatile water-soluble Ir(I)-based catalysts.

EXPERIMENTAL SECTION

[IrCl(η^4-cod)]$_2$ (**1**),[22] [Ir(OMe)(η^4-cod)]$_2$ (**2**),[23] [IrCl(η^4-cod)(IMes)] (**10**),[7f] *m*tppms-Na,[24] *m*tppts-Na_3,[25] and pta[26] were prepared as described in the literature.

^{1}H, ^{13}C, and ^{31}P NMR spectra were referenced to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt), TMS (tetramethylsilane), and 85% phosphoric acid and to residual solvent peaks. IR spectra were recorded in KBr disks.

Thermogravimetric measurements were made on a MOM Derivatograph-C (MOM, Budapest, Hungary) instrument at atmospheric pressure of static air in the 25−350 °C temperature range with a heating rate of 5 °C/min, using a Pt/Pt−Rh thermocouple and an open sample holder (Al_2O_3). Data were referenced to Al_2O_3 calcinated at 1000 °C.

Hydrogen uptake by water-soluble substrates was followed using constant-pressure gas burets, and the extent of hydrogenation was regularly checked also by ^{1}H NMR spectroscopy. Redox isomerization of allylic alcohols was studied in Schlenk tubes under a hydrogen or argon atmosphere, respectively, and the reaction mixtures were analyzed by gas chromatography (HP-5, 30 m × 0.25 mm × 25 μm, carrier gas N_2, FID 300 °C). The products were identified by ^{1}H and ^{13}C NMR spectroscopy and by comparison of retention times to those of known compounds. All catalytic reactions were run at constant temperature controlled by using circulators. Conversions were reproduced within a range of ±3%.

Synthesis of Complexes 3−9 and 11. *Synthesis of [IrCl(bmim)(η^4-cod)] (**3**).* This compound is known[7e] but was previously prepared by the Ag−NHC metathesis method. The synthesis described here is straightforward and affords the product in high yield. [Ir(OMe)(η^4-cod)]$_2$ (50 mg, 0.075 mmol) was dissolved in 5 mL of acetone, and 1-butyl-3-methylimidazolium chloride (27 mg, 0.15 mmol) was added as a solution in 3 mL of acetone. The reaction mixture was stirred for 4 h at 40 °C. No color change was observed. The solvent was removed by vacuum, and the oily residue was washed three times with small amounts of diethyl ether and finally with pentane (twice). The yellow product was dried under vacuum. Yield: 60.0 mg, 83%. Analytically pure product was obtained by recrystallization from benzene. NMR spectra: Figures S22 and S23 (Supporting Information).

^{1}H NMR (360 MHz, C_6D_6): δ/ppm 0.85 (t, ^3J(H,H) = 7.3 Hz, 3H; $NCH_2CH_2CH_2CH_3$), 1.09−1.30 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.47−1.68 (m, 4H; $CH_{2,cod}$), 1.70−1.80 (m, 2H; $NCH_2CH_2CH_2CH_3$), 2.11−2.29 (m, 4H; $CH_{2,cod}$), 2.85−2.96 (m, 2H; CH_{cod}), 3.42 (s, 3H; CH_3N), 3.90 (ddd, ^2J(H,H) = 14.4 Hz, ^3J(H,H) = 9.2 Hz, 5.9 Hz, 1H; $NCH_2CH_2CH_2CH_3$), 4.27 (ddd, ^2J(H,H) = 14.4 Hz, ^3J(H,H) = 9.2 Hz, 5.9 Hz, 1H; $NCH_2CH_2CH_2CH_3$), 5.02−5.11 (m, 2H; CH_{cod}), 5.96 (s, 1H; NCHCHN), 6.07 (s, 1H; NCHCHN). ^{13}C NMR (90 MHz, $CDCl_3$): δ/ppm 13.77 (s, $-CH_2CH_3$), 19.96 (s, $NCH_2CH_2CH_2$), 29.22 (s, $CH_{2,cod}$), 29.91 (s, $CH_{2,cod}$), 32.98 (s, $CH_{2,cod}$), 33.19 (s, $CH_{2,cod}$), 33.94 (s, NCH_2CH_2), 37.43 (s, N-CH_3), 50.13 (s, NCH_2), 51.02 (s, CH_{cod}), 51.64 (s, CH_{cod}), 83.78 (s, CH_{cod}), 84.18 (s, CH_{cod}), 119.84, 121.67 (s, NCH=CHN), 179.93 ppm (s, NCN). IR (KBr): $\tilde{\nu}$/cm^{-1} 3152, 3118, 3098, 3016, 2966, 2938, 2880, 2832 (CH, alkyl); 1696, 1594, 1570 (=CH, cod); 1460, 1410, 1234, 754 (=CH, bmim). Anal. Calcd for $C_{16}H_{26}N_2ClIr$ (474.06): C, 40.54; H, 5.53; N, 5.91. Found: C, 40.46; H, 5.53; N, 5.87. MS (ESI): *m*/*z* for [2M − Cl]$^+$ calcd 913.312, found 913.320.

*Synthesis of [Ir(H_2O)(bmim)(η^4-cod)]BF_4 (**4**).* [IrCl(bmim)(η^4-cod)] (30.0 mg, 0.06 mmol) was dissolved in 10 mL of undried acetone in a Schlenk flask wrapped in aluminum foil. To this solution was added an equivalent quantity (12.3 mg, 0.06 mmol) of $AgBF_4$, and the mixture was stirred for 1 h at room temperature and finally filtered through Hyflo Super Cel filter aid to remove AgCl. The solvent was removed by vacuum, leaving behind an oily red residue that solidified upon addition of pentane. This solid was washed several times with pentane, yielding a yellow-orange product that could be stored in the freezer without decomposition. Yield: 34.5 mg, 95%. The complex dissolves well in water, methanol, and chloroform but is insoluble in diethyl ether. NMR spectra: Figures S24−S26 (Supporting Information).

^{1}H NMR (360 MHz, C_6D_6): δ/ppm 0.74 (s, br, 2H; H_2O), 0.99 (t, ^3J(H,H) = 7.3 Hz, 3H; $NCH_2CH_2CH_2CH_3$), 1.32−1.50 (m, 2H; $NCH_2CH_2CH_2CH_3$; m, 3H, 0.5 $(CH_3)_2CO$), 1.50−1.91 (m, 4H; $CH_{2,cod}$; m, 2H; $NCH_2CH_2CH_2CH_3$), 2.30−2.40 (m, 4H; $CH_{2,cod}$), 3.05−3.10 (m, 2H; CH_{cod}), 3.56 (s, 3H; CH_3N), 3.99−4.08 (m, 1H; $NCH_2CH_2CH_2CH_3$), 3.40−4.70 (m, 1H; $NCH_2CH_2CH_2CH_3$), 5.16−5.30 (m, 2H; CH_{cod}), 6.06 (s, 1H; NCHCHN), 6.18 (s, 1H; NCHCHN). ^{13}C NMR (90 MHz, CD_2Cl_2): δ/ppm 13.45 (s, $-CH_2CH_3$), 19.89 (s, $NCH_2CH_2CH_2$), 28.39 (s, $CH_{2,cod}$), 29.02 (s, $CH_{2,cod}$), 32.72 (s, $CH_{2,cod}$), 33.02 (s, $CH_{2,cod}$), 33.51 (s, NCH_2CH_2), 37.26 (s, NCH_3), 50.27 (s, NCH_2), 51.22 (s, CH_{cod}), 52.14 (s, CH_{cod}), 83.80 (s, CH_{cod}), 84.11 (s, CH_{cod}), 120.73, 122.72 (s, NCH=CHN), 175.45 ppm (s, NCN). IR (KBr): $\tilde{\nu}$/cm^{-1} 3396 cm^{-1} (O−H, water); 3174, 3140, 2960, 2930, 2878 (CH, alkyl); 1682, 1652, 1574 (=CH, cod); 1070 (BF, BF_4); 1466, 1408, 1232, 740, 520 (=CH, bmim). Anal. Calcd for $C_{16}H_{28}N_2OBF_4Ir{\cdot}0.5(CH_3)_2CO$ (572.47): C, 36.70; H, 5.47; N, 4.89. Found: C, 36.55; H, 5.53; N, 4.58. $(CH_3)_2CO$ (% w/w): calcd 4.02; found (^{1}H NMR, C_6D_6) 3.95. MS (ESI): *m*/*z* for [M + Na$^+$] calcd 480.170, found 480.250.

*Synthesis of [Ir(bmim)(η^4-cod)(mtppms)] (**5**).* An 84 mg (0.21 mmol) amount of *m*tppms-Na in powdered form was added to a solution of [IrCl(bmim)(η^4-cod)] (100 mg, 0.21 mmol) in dry methanol (20 mL). The yellow color of the solution of **3** quickly changed to red. The solution was stirred at room temperature for 30 min and finally filtered through Hyflo Super Cel filter aid to remove NaCl. The solvent was removed by vacuum. The flask was cooled in liquid N_2, and the product was solidified by addition of diethyl ether. The red powder was washed another three times with diethyl ether, dried under vacuum, and stored in the freezer under Ar. Yield: 130 mg, 67%. The product is insoluble in water but soluble in organic solvents such as methanol, acetone, and dichloromethane. X-ray-quality crystals were obtained by diffusion of hexane/ether into a $CHCl_3$ solution of **5** at −18 °C. NMR spectra: Figures S27−S29 (Supporting Information).

^{1}H NMR (360 MHz, $CDCl_3$): δ/ppm 1.08 (t, ^3J(H,H) = 5.9 Hz, 3H; $NCH_2CH_2CH_2CH_3$), 1.38−1.50 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.50−1.66 (m, 4H; $CH_{2,cod}$), 2.10−2.20 (m, 2H; $NCH_2CH_2CH_2CH_3$), 2.21−2.28 (m, 2H; CH_{cod}), 2.28−2.51 (m, 4H; $CH_{2,cod}$), 3.80 (s, 3H; CH_3N), 3.55−3.63 (m, 1H; $NCH_2CH_2CH_2CH_3$), 4.31−4.37 (m, 1H; $NCH_2CH_2CH_2CH_3$), 4.40−4.60 (m, 2H; CH_{cod}), 7.00 (s, 1H; NCHCHN), 7.14 (s, 1H; NCHCHN), 7.04−8.53 (m, Ar-$CH_{phosphine}$). ^{13}C NMR (90 MHz, CD_3OD): δ/ppm 12.66 (s, $-CH_2CH_3$), 19.64 (s, $NCH_2CH_2CH_2$), 29.48, (s, $CH_{2,cod}$), 30.13 (s, $CH_{2,cod}$), 30.37 (s, $CH_{2,cod}$), 31.00 (s, $CH_{2,cod}$), 31.51 (s, NCH_2CH_2), 36.41 (s, NCH_3), 50.15 (s, NCH_2), 79.76 (s, CH_{cod}), 80.06 (s, CH_{cod}), 85.79 (d, CH, *J*(C,P) = 10 Hz, CH_{cod}), 86.97 (d, *J*(C,P) = 10 Hz, CH_{cod}), 121.15, 123.77 (s, NCH=CHN), 128.27−145.8 (m, Ar-CP), 172.83 (d, NCN, ^2J(C,P) = 9.9 Hz). ^{31}P NMR (146 MHz, CD_3OD): δ/ppm 19.22 ppm (s). IR (KBr): $\tilde{\nu}$/cm^{-1} 3427 (OH, water/crystal); 3164, 3105, 3056,

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2956, 2930, 2872 (CH, alkyl); 1630, 1397, 1384 (=CH, aromatic); 1585, 1571 (=CH, cod); 1227, 1198 cm^{-1} (S=O); 1432, 1335, 1031, 696, 533 (=CH, bmim). Anal. Calcd for $C_{34}H_{40}N_2O_3SPIr·H_2O·CHCl_3$ (917.84): C, 45.82; H, 4.73; N, 3.05. Found: C, 45.40; H, 4.52, N, 3.05. MS (ESI): *m/z* for $[M + Na^+]$ calcd 803.200, found 803.205.

*Synthesis of Na_2[Ir(bmim)(η^4-cod)(mtppts)] (**6**).* This complex was obtained by the same procedure as **5**, but using 122 mg (0.21 mmol) of *m*tppts-Na_3 instead of *m*tppms-Na, as a red powder. Yield: 184 mg, 80%. The complex is soluble in water, methanol, and dimethyl sulfoxide but insoluble in diethyl ether, hexane, acetone, chloroform, dichloromethane, and ethanol. NMR spectra: Figures S30–S32 (Supporting Information).

^{1}H NMR (360 MHz, D_2O): δ/ppm 0.83 (t, ^3J(H,H) = 7.3 Hz, 3H; $NCH_2CH_2CH_2CH_3$), 1.22–1.30 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.30–2.00 (m, 4H; $CH_{2,cod}$), 1.84–2.10 (m, 2H; $NCH_2CH_2CH_2CH_3$), 2.28–2.41 (m, 2H; CH_{cod}; m, 4H; $CH_{2,cod}$), 3.56 (s, 3H; CH_3N), 3.49–3.51 (m, 1H; $NCH_2CH_2CH_2CH_3$), 4.16–4.21 (m, 1H; $NCH_2CH_2CH_2CH_3$), 4.32–4.58 (m, 2H; CH_{cod}), 6.84 (s, 1H; NCHCHN), 6.86 (s, 1H; NCHCHN), 7.10–8.14 (m, Ar-$CH_{phosphine}$). ^{13}C NMR (90 MHz, CD_3OD): δ/ppm 13.10 (s, $-CH_2CH_3$), 19.71 (s, $NCH_2CH_2CH_2$), 29.72 (s, $CH_{2,cod}$), 30.36 (s, $CH_{2,cod}$), 30.45 (s, $CH_{2,cod}$), 31.14 (s, $CH_{2,cod}$), 31.91 (s, NCH_2CH_2), 36.89 (s, NCH_3), 50.34 (NCH_2), 79.91 (s, CH_{cod}), 80.86 (s, CH_{cod}), 87.44 (d, J(C,P) = 11 Hz, CH_{cod}), 88.84 (d, J(C,P) = 11 Hz, CH_{cod}), 121.45, 124.27 (s, NCH=CHN), 128.64–145.58 (m, Ar-CP), 171.96 (d, NCN, ^2J(C,P) = 9.9 Hz). ^{31}P NMR (146 MHz, CD_3OD): δ/ppm 20.0 ppm (s). IR (KBr): $\bar{\nu}$/cm^{-1} 3458 (OH, water/crystal); 2957, 2930, 2872 (CH, alkyl); 1638, 1465, 1399 cm^{-1} (=CH, aromatic); 1572 (=CH, cod); 1199 (S=O); 1430, 1338, 1036, 694, 535 (=CH, bmim). Anal. Calcd for $C_{34}H_{38}N_2O_9S_3Na_2PIr·6H_2O$ (1092.13): C, 37.24; H, 4.04; N, 2.55. Found (%) C, 37.34; H, 4.13, N, 2.55. H_2O (% w/w): calcd 9.90; found (thermogravimetry) 5.70. MS (ESI): *m/z* for $[M + Na^+]$ calcd 1007.079, found 1007.080.

*Synthesis of [Ir(bmim)(η^4-cod)(pta)]Cl (**7**).* This complex was obtained by the same procedure as **5**, but using 33 mg (0.21 mmol) of pta instead of *m*tppms-Na, as a red powder. Yield: 103 mg, 74%. The complex is soluble in water, methanol, dimethyl sulfoxide, chloroform, and dichloromethane but insoluble in acetone, hexane, diethyl ether, and ethanol. NMR spectra: Figures S33–S35 (Supporting Information).

^{1}H NMR (360 MHz, CD_3OD): δ/ppm 1.02 (t, ^3J(H,H) = 7.3 Hz, 3H; $NCH_2CH_2CH_2CH_3$), 1.44–1.56 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.72–2.35 (m, 2H; $NCH_2CH_2CH_2CH_3$; m, 2H; CH_{cod}; m, 4H; $CH_{2,cod}$; m, 4H; $CH_{2,cod}$), 3.82 (s, 3H; CH_3N), 3.98 (s, 6H, NCH_2P_{pta}), 4.04–4.61 (s, 6H, NCH_2N_{pta}; m, 2H; $NCH_2CH_2CH_2CH_3$, m, 2H; CH_{cod}), 7.32 (s, 1H; NCHCHN), 7.38 (s, 1H; NCHCHN). ^{13}C NMR (90 MHz, CD_3OD): δ/ppm 14.06 (s, $-CH_2CH_3$), 19.85 (s, $NCH_2CH_2CH_2$), 29.74 (s, $CH_{2,cod}$), 30.67 (s, $CH_{2,cod}$), 30.95 (s, $CH_{2,cod}$), 31.94 (s, $CH_{2,cod}$), 32.41 (s, NCH_2CH_2), 36.40 (s, NCH_3), 49.94 (s, CH_{cod}), 50.1 (s, CH_{cod}), 50.15 (s, $NCH_{2,bmim}$) 71.63 (d, ^3J(C,P) = 7 Hz, $PCH_{2,pta}$), 74.77 (d, ^2J(C,P) = 25 Hz, $NCH_{2,pta}$) 87.78 (d, ^3J(C,P) = 11 Hz, CH_{cod}), 89.20 (d, ^3J(C,P) = 11 Hz, CH_{cod}), 121.15, 123.62 (s, NCH=CHN), 172.12 (d, NCN, ^2J(C,P) = 11.4 Hz). ^{31}P NMR (146 MHz, CD_3OD): δ/ppm −64.2 ppm (s). IR (KBr): $\bar{\nu}$/cm^{-1} 3272, 1986 (CH, alkyl-pta); 3192, 3064, 2936, 2846, 2832 (CH, alkyl); 1618 (=CH, cod); 1428, 1280, 1246, 744 (=CH, bmim). Anal. Calcd for $C_{22}H_{38}N_5PClIr·1.5H_2O$ (658.24): C, 40.14; H, 6.28; N, 10.64. Found: C, 40.24; H, 6.29; N, 10.37. H_2O (% w/w): calcd 4.11, found (thermogravimetry) 4.16. MS (ESI): *m/z* for $[M - Cl]^+$ calcd 596.249, found 596.255.

*Synthesis of [Ir(bmim)(η^4-cod)(pta)]BF_4 (**8**).* [Ir(bmim)(η^4-cod)-(pta)]Cl (**7**; 60 mg, 0.095 mmol) was dissolved in acetone (5 mL) followed by addition of $AgBF_4$ (18.5 mg, 0.095 mmol). The solution was stirred in the dark for 1 h. The precipitate that (AgCl) formed during this time was filtered (using a pad of Hyflo Super Cel), and the solvent was removed by vacuum. The oily residue was treated with diethyl ether to yield a red solid product that was dried under vacuum. Yield: 56 mg, 83%. In solution, the ^{1}H, ^{31}P, and ^{13}C NMR parameters of this complex are identical with those of [Ir(bmim)(η^4-cod)(pta)]Cl (**7**). NMR spectra: Figures S33–S36 (Supporting Information).

^{19}F NMR (338 MHz, CD_3OD): δ/ppm −170.3 (BF_4). IR (KBr): $\bar{\nu}$/cm^{-1} 3442 (OH, water), 2933, 2871, 2828 (CH, alkyl), 1654, 1570 (=CH, cod), 1294,1243, 1228, 901, 773, 533 (=CH, bmim), 1198 cm^{-1} (BF, BF_4). Anal. Calcd for $C_{22}H_{38}N_5PBF_4Ir·1.5H_2O$ (709.58): C, 37.24; H, 5.82; N, 9.87. Found: C, 36.98; H, 5.52; N, 9.52. MS (ESI): *m/z* for $[M - BF_4]^+$ calcd 596.249, found 596.255.

*Sample Preparation of [Ir(bmim)(η^4-cod)(pta)]BF_4 (**8**) for X-ray Structure Determination.* **4** (20 mg) was dissolved in $CHCl_3$ (2 mL) followed by addition of an equivalent amount of pta (5.8 mg). This solution was stored under an acetone layer at −18 °C for 2 months. Red crystals of [Ir(bmim)(η^4-cod)(pta)]$BF_4·2CHCl_3$ separated, suitable for X-ray analysis.

*Synthesis of [IrCl(η^4-cod)(emim)] (**9**).* $[Ir(OMe)(\eta^4\text{-cod})]_2$ (150 mg, 0.23 mmol) was dissolved in acetone (10 mL), and 1-ethyl-3-methylimidazolium chloride (66 mg, 0.46 mmol) was added as a solution in acetone (5 mL).

The reaction mixture was stirred for 4 h at 40 °C. No color change was observed. The solvent was removed by vacuum, and the oily residue was washed three times with small amounts of diethyl ether. The orange product was dried under vacuum. Yield: 160.0 mg, 79%. NMR spectra: Figures S37 and S38 (Supporting Information).

^{1}H NMR (360 MHz, $CDCl_3$): δ/ppm 1.47 (t, ^3J(H,H) = 6.5 Hz, 3H; NCH_2CH_3), 1.57–2.98 (m, 4H; $CH_{2,cod}$; m, 4H; $CH_{2,cod}$; m, 2H; CH_{cod}), 3.96 (s, 3H; CH_3N), 4.31–4.48 (m, 1H; NCH_2CH_3; m, 1H; NCH_2CH_3; m, 2H; CH_{cod}), 6.83 (s, 1H; NCHCHN), 6.85 (s, 1H; NCHCHN). ^{13}C NMR (90 MHz, $CDCl_3$): δ/ppm 16.49 (s, $-CH_2CH_3$), 29.52 (s, $CH_{2,cod}$), 29.61 (s, $CH_{2,cod}$), 33.57 (s, $CH_{2,cod}$; s, $CH_{2,cod}$), 37.41 (s, NCH_3), 45.21 (s, NCH_2), 51.39 (s, CH_{cod}), 51.47 (s, CH_{cod}), 84.02 (s, CH_{cod}), 84.25 (s, CH_{cod}), 119.29, 121.87 (s, NCH=CHN), 179.88 ppm (s, NCN). IR (KBr): ν^-/cm^{-1}: 3152, 3120, 3096, 3018, 2964, 2878, 2830 (CH, alkyl); 1676, 1598, 1570 (=CH, cod); 1464, 1264, 1226, 1134, 962, 754, 710 (=CH, emim). Anal. Calcd for $C_{14}H_{22}N_2ClIr$ (447.01): C, 37.62; H, 5.19; N, 6.27. Found: C, 37.42; H, 5.04; N, 5.81. MS (ESI): *m/z* for $[2M + Na]^+$ calcd 846.290, found 846.330.

*Synthesis of Na_2[IrCl(η^4-cod)(emim)(mtppts)] (**11**).* This complex was obtained by the same procedure as for **6**, but using [IrCl(η^4-cod)(emim)] (**9**; 95 mg, 0.21 mmol) instead of [IrCl(bmim)(η^4-cod)] (**3**). Red powder. Yield: 89 mg, 83%. The complex is soluble in water and methanol and insoluble in diethyl ether, hexane, acetone, and ethanol. NMR spectra: Figures S39–S41 (Supporting Information).

^{1}H NMR (360 MHz, D_2O): δ/ppm 1.03 (t, ^3J(H,H) = 6.5 Hz, 3H; NCH_2CH_3), 1.88–2.38 (m, 4H; $CH_{2,cod}$; m, 4H; $CH_{2,cod}$), 3.45 (s, 3H; CH_3N), 3.50–3.65 (m, 2H; CH_{cod}), 3.81–3.88 (m, 1H; NCH_2CH_3) 4.12–4.22 (m, 1H; NCH_2CH_3), 4.40–4.65 (m, 2H; CH_{cod}), 6.85 (s, 1H; NCHCHN), 6.93 (s, 1H; NCHCHN), 7.26–8.08 (m, Ar-$CH_{phosphine}$). ^{13}C NMR (90 MHz, D_2O): δ/ppm 14.15 (s, $-CH_2CH_3$), 29.53 (s, $CH_{2,cod}$), 29.95 (s, $CH_{2,cod}$), 30.53 (s, $CH_{2,cod}$) 31.14 (s, $CH_{2,cod}$), 36.69 (s, NCH_3), 45.19 (s, NCH_2), 80.23 (s, CH_{cod}), 80.56 (s, CH_{cod}), 89.32 (d, J(C,P) = 11 Hz, CH_{cod}), 90.03 (d, J(C,P) = 11 Hz, CH_{cod}), 120.85, 124.01 (s, NCH=CHN), 128.20–143.31 (m, Ar-CP), 171.35 ppm (d, NCN, ^2J(C,P) = 8.9 Hz). IR (KBr): $\bar{\nu}$/cm^{-1} 3451 (OH, water), 2918, 2880 (CH, alkyl), 1635 (=CH, cod), 1465, 1398, 1337 (=CH, aromatic), 1147, 1096 (S=O), 997, 869, 797, 533 (=CH, bmim). Anal. Calcd for $C_{32}H_{34}N_2PS_3O_9Na_2Ir·6H_2O$ (1064.121): C, 36.12; H, 4.36; N, 2.63. Found: C, 35.70; H, 3.98; N, 2.35. H_2O (% w/w): calcd 10.16, found (thermogravimetry) 10.58. MS (ESI): *m/z* for $[M + H^+]$ calcd 957.067, found 957.670.

General Procedure of Hydrogenation of Unsaturated Substrates in Water. In a Schlenk tube under an argon atmosphere, 0.005 mmol of [IrCl(bmim)(η^4-cod)] (**3**), [IrCl(η^4-cod)(emim)] (**9**), or [IrCl(η^4-cod)(IMes)] (**10**) was dissolved in 3 mL of MeOH together with 0.005 mmol of pta or *m*tppts-Na_3. In the case of **3** and **9** the solutions turned deep red, with both phosphines showing the presence of Na_2[Ir(bmim)(η^4-cod)(*m*tppts)] (**6**) and [Ir(η^4-cod)-(bmim)(pta)]Cl (**7**) as well as that of Na_2[Ir(η^4-cod)(emim)-(*m*tppts)] (**11**) and [Ir(η^4-cod)(emim)(pta)]Cl (**12**; ^{31}P NMR −60.64 ppm (s); ^{13}C NMR 172.08 ppm (d, $^2J_{CP}$ = 11.4 Hz)). Conversely, with **10** and *m*tppts-Na_3 or pta no new resonances were observed in the ^{31}P and ^{13}C NMR spectra. The solutions were stirred

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for 20 min at room temperature and then evaporated to dryness. A 2.8 mL portion of H_2O was added to the solid residue, and the solution (fine suspension in the case of **10**) was transferred by using a hypodermic syringe to an atmospheric gas buret equipped with a silicon rubber septum inlet and filled with hydrogen at 60 °C. Clear yellow solutions were obtained in a few seconds. After thermal equilibration, a solution of 0.25 mmol of itaconic acid in 0.2 mL of H_2O was injected through the septum and hydrogen uptake readings were taken at appropriate reaction times. Under these conditions the partial pressure of H_2 inside the gas buret is 0.8 bar.

General Procedure of Catalytic Isomerization of Allylic Alcohols. Under an argon atmosphere, 0.01 mmol of **6** or **7** was dissolved in 3 mL of deoxygenated water. The solution was heated to 80 °C, and then 1.0 mmol of allylic alcohol was added. The reaction mixture was rapidly stirred for 1 h and was subsequently cooled to room temperature and extracted with 1 mL of toluene. The separated organic phase was filtered through a short silica column and was subjected to gas chromatography.

Crystal Structure Data. CCDC 964298 (**5**) and CCDC 964299 (**8**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving experimental details of the X-ray structure determination of **5** and **8**, a discussion of X-ray structures, ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra of complexes **3**−**9** and **11**, infrared spectra of complexes **3**−**7**, **9**, and **11** and interaction of **6** and **7** in the solid state with H_2, and data for the hydrogenation and redox isomerization activity of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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