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Catalytic homogeneous CH-activation reactions of cyclooctane with [Ir(cod)LL]X complexes (LL = *N*,*N*-chelating ligands, amines, phosphines; X = Cl, PF_6)

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Abstract

A series of new [Ir(cod)LL]X complexes (LL = chelating ligands, amines, phosphines; X = Cl, PF_6) was synthesized. The complexes catalyzed the selective homogeneous dehydrogenation of cyclooctane to give cyclooctene up to a rate of 61 turnovers. The activity and selectivity depends on the ligand structure of the corresponding coordination compound. The addition of external additives (amines and phosphines) increased the activities up to 100% in case of PCy_3 and $NHPh_2$. The dehydrogenation reaction showed a high temperature dependence.

Keywords: CH bond activation; Homogeneous catalyst; Dehydrogenation; Iridium complexes

1. Introduction

Saturated hydrocarbons are still abundant and inexpensive chemical feedstocks. Therefore it is a challenge and an attractive goal in research to convert alkanes into alkenes in order to use their synthetic potential [1–3]. Olefins are valuable educts and/or intermediates in many industrial processes.

The key step of a catalytic CH-activation reaction is the formation of an electronically and coordinatively unsaturated active species. Low valent transition metal species have the potential to insert into an alkane CH-bond to give an alkyl metal hydride complex (oxidative addition of an alkane at a transition metal). A subsequent β-hydrogen elimination produces the olefin and hydrogen [4]. Crabtree et al. first reported the stoichiometric dehydrogenation of cyclooctene to cyclooctadiene with an iridium phosphine complex [5]. In the early 1980s, examples were discovered of oxidative addition of CH bonds to late transition metal complexes [6,7]. Perhaps the most remarkable report was the one of Baudry and Ephritikhine of the first catalytic dehydrogenation of cyclooctane with a rhenium polyhydride complex by thermal activation [8]. This reaction is a transfer dehydrogenation reaction, which catalyzes the transfer of hydrogen from an alkane to a sacrificial olefinic hydrogen acceptor. In the following many transfer dehydrogenation reactions were reported in the literature [9–20]. Brookhart et al. described turnover numbers higher than 1000 per 30 min [21] using an iridium bis(phosphinite) *p*-XPCP pincer complex. The disadvantage of a transfer dehydrogenation reaction is the necessity of a hydrogen acceptor, like *tert*-butylethylene. This makes such a reaction uneconomic. CH-activation reactions without a hydrogen acceptor are hard to find. The activities of these reaction are mostly lower than the transfer dehydrogenation results [22]. To carry out acceptorless CH-activation reactions [Ir(cod)LL]PF_6 (LL = chelating ligands, amines, phosphines; X = Cl, PF_6) complexes should be promising candidates.

2. Results and discussion

2.1. Syntheses of the complexes

The pyridine imine ligand precursors were synthesized via an acid catalyzed condensation reaction of acetyl pyridine with a phenylamine as reported in the literature [23,24]. The ligand precursors have to be transformed into the corresponding sodium

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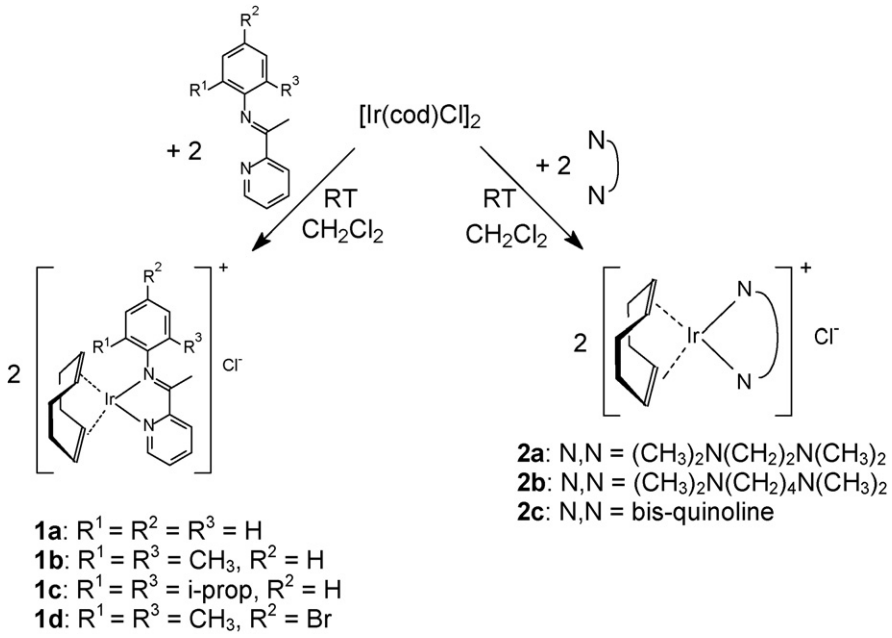


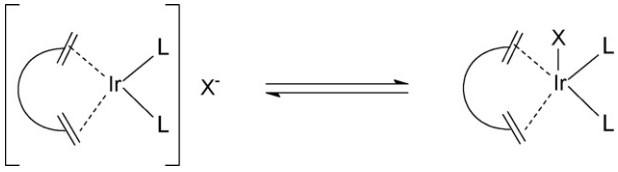
Scheme 1. Synthesis of iridium complexes with *N*,*N*-chelating ligands (**1a**–**d** and **2a**–**c**).

alcoholates, which reacts directly with $[Ir(cod)Cl]_2$ yielding the new pyridine imine iridium complexes **1a**–**d** (Scheme 1). The yields of compounds **1a**–**d** are generally high (95–99.5%). Another kind of iridium complexes with *N*,*N*-chelating ligands are complexes **2a**–**c**. The reaction of 1 equiv. of the corresponding *N*,*N*-chelating ligand precursor with 0.5 equiv. of $[Ir(cod)Cl]_2$ yields the new complexes **2a**–**c** (Scheme 1). These complexes were formed by a breakdown of the dimeric $[Ir(cod)Cl]_2$ complexes. The chlorides formed the anions of the new ionic iridium complexes. Complexes [Ir(cod)bipy]Cl (**2d**) and [Ir(cod)phen]Cl (**2e**) were prepared according to published procedures [25].

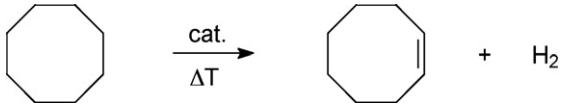
The novel complexes **3a**–**c** and **4a** were prepared from the reaction of $[Ir(cod)Cl]_2$ with $NaPF_6$ and an excess of the amine resp. phosphine (Scheme 2).

The complexes $[Ir(cod)(PR_3)_2]PF_6$ (R = Ph (**4b**), Cy (**4c**), *p*-Tol (**4d**), *m*-Tol (**4e**)) were prepared according to published procedures [26–29].

Jensen postulated coordinatively and electronically unsaturated intermediates as the active species [4]. Therefore ionic complexes as 16 e^- species are promising candidates for dehydrogenation reactions (Scheme 3).



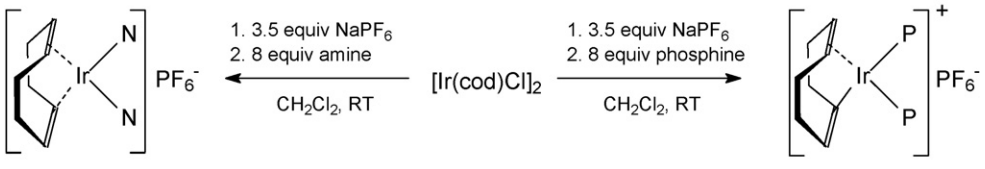
Scheme 3. Equilibrium of tetra- and pentacoordinated species of ionic iridium(I) complexes [29].



Scheme 4. Catalytic activation of cyclooctane.

2.2. Dehydrogenation of cyclooctane

Various coordination compounds were tested as catalysts for the dehydrogenation of cyclooctane to form cyclooctene and hydrogen (Scheme 4) in a homogeneous reaction. The catalysts were used without any activation.



Scheme 2. Syntheses of bis(amine)-1,5-cyclooctadiene iridium complexes and bis(phosphine)-1,5-cyclooctadiene iridium complexes.

Table 1
TONs and selectivities of complexes **1a–d**

Catalyst no.	Products	TON	Selectivity (%)
1a	Cyclooctene, toluene	3.4	55.4
1b	Cyclooctene	21.5	100
1c	Cyclooctene	13.9	100
1d	Cyclooctene	7.9	100

Table 2
TONs and selectivities of complexes **2a–e**

Catalyst no.	Products	TON	Selectivity (%)
2a	Cyclooctene	32.5	100
2b	Cyclooctene	40.1	100
2c	Cyclooctene	20.5	100
2c	Cyclooctene	18.9	100
2d	Cyclooctene	12.9	100
2e	Cyclooctene	10.7	100

For CH-activation reactions the corresponding complex was dissolved in degassed cyclooctane. The solution was transferred into an autoclave and heated to 200–400 °C. The standard reaction temperature was 300 °C. After the reaction period, the autoclave was cooled to room temperature. The reaction gas and the reaction solution were characterized by GC analysis. The selectivity for the dehydrogenation reaction was calculated by the conversion of cyclooctane to cyclooctene.

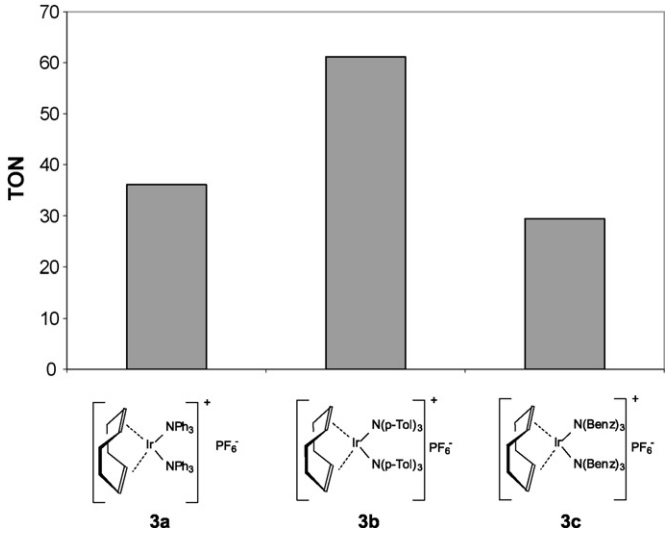
At high temperatures most of the organometallic compounds do no longer have the original composition. Remarkably, structure-efficiency relationships showed that the nature of the organic ligands has a relevant impact on the activity and selectivity of the corresponding catalyst.

Complexes **1a–d** converted cyclooctane to cyclooctene in a catalytic reaction with TONs between 3.4 and 21.5 (Table 1). The selectivities were 100% with the exception of complex **1a** which produced toluene as secondary product.

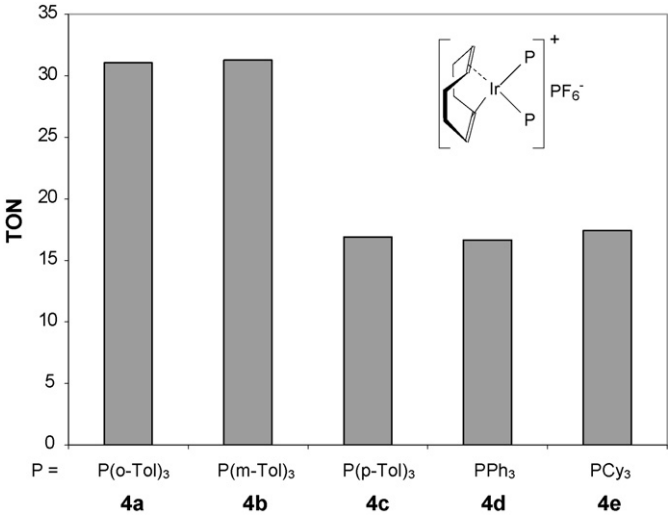
The complexes **2a–e**, especially **2a** and **2b**, showed a high dehydrogenation potential for homogeneous dehydrogenation reactions without a hydrogen acceptor (Table 2). The high TONs of **2a** and **2b** can be interpreted with the more flexible ligand backbone of the chelating ligand.

The iridium complexes **3a–c** showed catalytic dehydrogenation activities (Scheme 5). The dehydrogenation results of the $[Ir(cod)NN]PF_6$ catalysts indicated that a *para*-substitution (**3b**) of the amino phenyl group has a positive effect on the activity (TON = 61). The TON of **3b** describes a thoroughly active iridium catalyst in a homogeneous dehydrogenation reaction without any hydrogen acceptor. The catalysts **3a–c** produced cyclooctene with a selectivity of 96–100%.

The $[Ir(cod)PP]PF_6$ (P = P(*o*-Tol)$_3$, P(*m*-Tol)$_3$, P(*p*-Tol)$_3$, PPh_3, PCy_3) complexes yielded cyclooctene in catalytic amounts (Scheme 6). The activities of complexes **4a–e** are generally lower than the activities of amine containing complexes (**3a–c**). Only the complexes **4a** (TON = 31) and **4b** (TON = 31) showed TONs in the range of the activities of $[Ir(cod)NN]PF_6$ complexes.



Scheme 5. TONs of bis(amine) 1,5-cyclooctadiene iridium(I) complexes (**3a–c**).



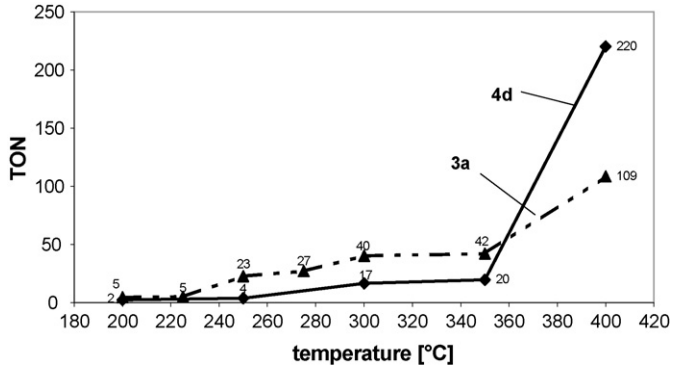
Scheme 6. TONs of bis(phosphine) 1,5-cyclooctadiene iridium(I) complexes (**4a–e**).

2.3. Temperature dependence of dehydrogenation reactions

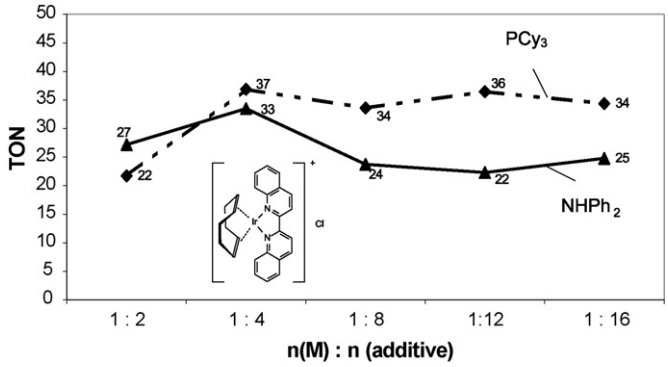
The CH-activation reaction is an endothermic process. Therefore a temperature dependence can be expected. In the temperature range from 200 to 350 °C a continuous increase of the activity can be observed with the catalysts $[Ir(cod)(NPh_3)_2]PF_6$ (**3a**) and $[Ir(cod)(PPh_3)_2]PF_6$ (**4d**). Remarkably, the activities showed a sudden increase at a reaction temperature of 350 °C (Scheme 7). This suggests that a new active species is formed. In this process the ligands are involved. Obviously the phosphine (**4d**) is better than the amine ligand (**3a**) forming such a catalytic species at higher temperatures in a homogeneous system.

2.4. Influence of additives on the dehydrogenation reaction of cyclooctane

Since the positive influence of the heteroatomic ligands was obvious from numerous experiments, it made sense to add exter-



Scheme 7. Temperature dependence of the activities of catalysts **3a** and **4d**.



Scheme 8. Activities of complex **2c** depending on different additive amounts.

nal additives (amines and phosphines) in order to increase the activities. The complex [Ir(cod)dichinolin)]PF_6 (**2c**) was suspended in 20 ml cyclooctane and the respective additive was added in a ratio of metal:additive = 1:4.

The TON of complex **2c** (without additive) was 19.7. The catalysts **5a** and **5c**–**e** showed lower TONs than **2c** (Table 3). The phosphine additive PCy_3 was responsible for a decrease of the activity with the exception of catalyst **5b** (Table 3). The addition of PCy_3 increased the TON to 36.9 (100% higher than **2c**).

The amine additives (catalysts **6a**–**h**) showed generally an increase of the activities (TON = 19.9–33.5) in comparison to catalyst **2c** (TON = 19.7). The highest TON was obtained for catalyst **6c**, which contained 4 equiv. $NHPh_2$ (Table 4). The amines proved as better additives than phosphines. In all cases, catalysts **6a**–**h** showed selectivities of 100% for the production of cyclooctene.

In another series of experiments the amount of additives was varied with metal:additive ratios of 1:2, 1:4, 1:8, 1:12 and 1:16. The ideal additive concentration was 4 equiv. (Scheme 8). The increase of the additive concentration gave no higher TON. $NHPh_2$ ratios of 1:8, 1:12 and 1:16 decreased the TON. These experiments with Lewis basic additives are another argument for the formation of a new active species in the process.

3. Summary and conclusions

Novel complexes of the type [Ir(cod)LL]X (LL = pyridine imine (**1a**–**d**), *N*,*N*-chelating ligand (**2a**–**c**), amine (**3a**–**c**), phosphine (**4a**); X = Cl, PF_6) were synthesized. The advantage of these complexes is an existing equilibrium between penta- and tetra-coordinated species. Because of this dynamic equilibrium which depends on the anion and the solvent, these complexes are promising candidates as dehydrogenation catalysts for alkanes. The prepared complexes catalyzed the dehydrogenation of cyclooctane at a reaction temperature of 300 °C. The catalysts showed relatively high activities (maximum of

Table 3
TONs and selectivities depending on phosphine additives

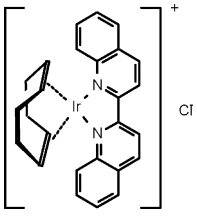
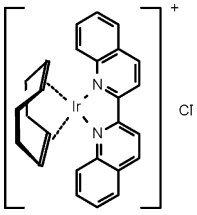
Coordination compound	Catalyst no.	Additive [M:additive]	TON	Selectivity (%)
	**5a**	PPh_3 [1:4]	14.1	100
	5b	PCy_3 [1:4]	36.9	100
	5c	P(*p*-Tol)$_3$ [1:4]	18.0	93.5
	5d	P(*n*-Bu) [1:4]	7.1	53.0
	5e	PH(*t*-Bu) [1:4]	4.2	57.8

Table 4
TONs and selectivities depending on amine additives

Coordination compound	Catalyst no.	Additive [M:additive]	TON	Selectivity (%)
	**6a**	NPh_3 [1:4]	24.1	100
	6b	NEt_3 [1:4]	29.7	100
	6c	$NHPh_2$ [1:4]	33.5	100
	6d	NH_2Ph [1:4]	26.5	100
	6e	NH_2pyr [1:4]	19.9	100
	6f	NH(*i*-prop)$_2$ [1:4]	24.1	100
	6g	$NHCy_2$ [1:4]	25.7	100
	6h	NMe_2Et [1:4]	27.4	100

61 turnovers) for homogeneous dehydrogenation reactions. The activity and selectivity depends on the heteroatomic ligand. For most ligands selectivities of 100% monoolefin were obtained. In the homogeneous system the catalysts with amine ligands achieved the highest TONs with selectivities of 100%. At higher temperatures most catalysts have no longer the original compositions. Obviously the ligands of the original organometallic compound contribute to the formation of the new active species. The formation of a new active species using the heteroatomic ligand is supported by experiments with external additives. The addition of amine additives increased the activities of the corresponding catalysts. The ideal additive concentration proved as metal:additive = 1:4. The activities of the ionic iridium(I) complexes also depend on the reaction temperature and show a sudden increase at a temperature >350 °C. This result is another argument for the formation of a new active species at elevated temperatures. Its composition is still unknown.

4. Experimental

4.1. General considerations

All manipulations were carried out using standard Schlenk techniques under argon, which was purified by passage through columns of BTS catalyst and 4 Å molecular sieves. NMR spectra were measured on a Bruker ARX250 instrument. Chemical shifts (δ, ppm) were recorded relative to the residual solvent peak at $\delta = 7.26$ ppm for chloroform-*d*. The multiplicities were assigned as follows: s, singlet; m, multiplet. $^{13}C\ \{^1H\}$ NMR spectra were fully proton decoupled and the chemical shifts (δ, ppm) are relative to the solvent peak (77.0 ppm). The gas chromatograph Agilent 6890 was used to monitor the dehydrogenation reactions. The identification of dehydrogenation products and the reaction control were carried out by a FOCUS DSQ instrument (Thermo). Elemental analyses were performed using a VarioEl III instrument.

4.2. Materials

Tetrahydrofuran, *n*-pentane and toluene were distilled from Na/K alloy. Diethylether was distilled from $LiAlH_4$ and methylene chloride from P_2O_5. All solvents were stored under argon. Cyclooctane (COA) was degassed and stored under argon. $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ were synthesized in analogy to known procedures [26,30–32]. The organic starting materials were purchased from Aldrich or Arcos.

4.3. General synthesis of the pyridine imine iridium(I) complexes (*1*)

0.5 mmol $[Ir(cod)Cl]_2$ were dissolved in 20 ml CH_2Cl_2. After addition of 1 mmol of the respective pyridine imine, the mixture was stirred at RT for 2 h. The solvent was reduced in vacuo and the remained suspension was filtered. The solid was washed with pentane and dried in vacuo. The products were obtained as dark blue solids.

(**1a**). From 196 mg (1 mmol) of 1-(2-pyridyl)-2-phenyl-2-aza-ethene and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 519 mg (0.98 mmol, 98%) of **1a** as a dark blue powder. MS data for **1a**: 495 ($M^{\bullet+} - Cl$) (24), 493 (20), 295 (10), 269 (4), 195 (61), 181 (37), 118 (85), 77 (100).

(**1b**). From 224 mg (1 mmol) of 1-(2-pyridyl)-2-(2,6-dimethylphenyl)-2-aza-ethene and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 539 mg (0.96 mmol, 96%) of **1b** as a dark blue powder. MS data for **1b**: 524 ($M^{\bullet+} - Cl$) (25), 412 (11), 295 (17), 269 (4), 224 (31), 209 (100), 146 (45), 105 (24), 77 (31).

(**1c**). From 280 mg (1 mmol) of 1-(2-pyridyl)-2-(2,6-diisopropylphenyl)-2-aza-ethene and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 578 mg (0.995 mmol, 99.5%) of **1c** as a dark blue powder. Spectroscopic data for **1c**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.25 (d, breit, 1H), 8.08–8.03 (m, 1H), 7.70–7.65 (m, 4H), 7.25–7.20 (m, 1H), 3.64 (s, breit, 2H), 3.30–3.19 (m, 4H), 2.24–2.18 (m, 4H), 1.84 (s, 3H), 1.72–1.63 (m, 4H), 1.26 (d, 6H), 1.02 (d, 6H). $^{13}C\ \{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 169.9 (C_q), 157.5 (C_q), 146.9 (CH), 142.2 (C_q), 140.6 (C_q), 136.6 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 124.2 (CH), 63.3 (CH), 31.8 (CH_2), 27.4 (CH), 25.1 (CH_3), 20.7 (CH_3). MS data for **1c**: 580 ($M^{\bullet+}$) (3), 565 (1), 468 (5), 280 (6), 265 (18), 237 (100), 202 (12).

(**1d**). From 303 mg (1 mmol) of 1-(2-pyridyl)-2-(4-brom-2,6-dimethylphenyl)-2-aza-ethene and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 607 mg (0.95 mmol, 95%) of **1d** as a dark blue powder. MS data for **1d**: 602 ($M^{\bullet+} - HCl$) (45), 492 (17), 303 (43), 295 (20), 287 (71), 223 (99), 208 (100), 145 (63), 104 (88).

4.4. General procedure for the synthesis of iridium complexes with N,N-chelating ligands (*2*)

A suspension of the *N*,*N*-chelating ligand (2.5 mmol) in 30 ml of THF was added to a solution of 1 mmol $[Ir(cod)Cl]_2$ in 30 ml THF. The mixture was stirred at RT for 2 h. A color change from red to yellow resp. ocher was observed. The solvent was reduced to 30 and 50 ml pentane were added. The precipitated solid was filtered, washed with pentane and diethylether and dried in vacuo. The products were obtained as yellow and ocher solids.

(**2a**). From 290 mg (2.5 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethyldiamine and 671 mg (1 mmol) $[Ir(cod)Cl]_2$ was obtained 670 mg (0.74 mmol, 74%) of **2a** as a yellow powder. Spectroscopic data for **2a**: $^{13}C\ \{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 67.3 (CH), 63.4 (CH_2), 59.7 (CH_3), 50.2 (CH_3), 32.0, 30.4 (CH_2).

(**2b**). From 361 mg (2.5 mmol) of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-butanediamine and 671 mg (1 mmol) $[Ir(cod)Cl]_2$ was obtained 494 mg (0.51 mmol, 51%) of **2b** as a yellow powder. Spectroscopic data for **2b**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 4.07 (s, breit, 4H), 2.96–2.95 (m, 4H), 2.43 (s, 6H), 2.29 (s, 6H), 2.08–2.01 (m, 8H), 1.34–1.15 (m, 4H). $^{13}C\ \{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 65.1 (CH_2), 59.1 (CH_2), 49.2 (CH_2), 45.0 (CH_3), 31.8 (CH_2), 30.5 (CH_2).

(**2c**). From 641 mg (2.5 mmol) of 2,2′-biquinoline and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 1150 mg (0.97 mmol, 97%) of **2c** as a ocher powder. MS data for **2c**: 592 ($M^{\bullet+}$) (5), 296 (5), 256 (100), 128 (18).

*4.5. General synthesis of bis(amine) iridium(I) complexes (**3**)*

A suspension of $NaPF_6$ (3.5 mmol) in 20 ml of H_2O was added to a solution of 1 mmol $[Ir(cod)Cl]_2$ in 30 ml THF. After addition of 8 mmol of the respective amine, the mixture was stirred at RT for 4 h. The solvent was removed in vacuo and the remaining solid was suspended in pentane. The solid was filtered, washed with pentane, toluene and H_2O and dried in vacuo. The complexes were obtained as light yellow and orange, voluminous powders.

(**3a**). From 1.96 g (8 mmol) of tri-phenylamine and 671 mg (1 mmol) $[Ir(cod)Cl]_2$ was obtained 1.58 g (0.84 mmol, 84%) of **3a** as apricot, voluminous powder. Spectroscopic data for **3a**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 7.18–6, 90 (m, 30H), 4.16 (s, breit, 4H), 2.26–2.15 (m, 4H), 1.48–1.42 (m, 4H). $^{13}C\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 147.9 (C_q), 129.2 (CH), 124.2 (CH), 122.7 (CH), 62.2 (CH), 31.8 (CH_2).

(**3b**). From 1.15 g (4 mmol) of tri-(*p*-toluyl)amine and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 723 mg (0.71 mmol, 71%) of **3b** as yellow solid. Spectroscopic data for **3b**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 7.32–6.96 (m, 24H), 4.27 (s, 4H), 2.31 (s, 18H), 1.57–1.53 (m, 8H). $^{13}C\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 145.7 (C_q), 131.7 (C_q), 129.7 (CH), 123.9 (CH), 62.8 (CH), 31.8 (CH_2), 20.8 (CH_3).

(**3c**). From 1.15 g (4 mmol) of tri-benzylamine, 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ and 588 mg (3.5 mmol) $NaPF_6$ was obtained 300 mg (0.29 mmol, 29%) of **3c** as light yellow powder. Anal. Calcd for $C_{50}H_{54}N_2PF_6Ir$ **3c**: C, 58.87; H, 5.34; N, 2.75. Found: C, 57.30; H, 5.32; N, 2.92. Spectroscopic data for **3c**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 7.39–7.33 (m, 30H), 4.23 (s, breit, 4H), 3.97 (s, 12H), 2.27–2.23 (m, 4H), 1.55–1.46 (m, 4H). $^{13}C\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 129.5 (CH), 129.1 (CH), 62.2 (CH), 57.6 (CH_2), 31.7 (CH_2).

*4.6. Synthesis of 1,5-cyclooctadiene bis(phosphine) iridium(I) complex (**4a**)*

To a THF solution (30 ml) of $[Ir(cod)Cl]_2$ $[Ir(cod)Cl]_2$ (0.5 mmol) was added 1.75 mmol $NaPF_6$, dissolved in 20 ml H_2O. After addition of 3 mmol tri-(*ortho*-toluyl)-phosphine under stirring, the mixture was stirred at RT for 2 h. The solvent was removed in vacuo and the crude product suspended in pentane. The solid was filtered off, washed with pentane, toluene and H_2O and dried in high vacuum. The reaction yielded 430 mg complex (0.41 mmol, 41%) as an orange powder. Spectroscopic data for **4a**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 7.47–7.04 (m, 24H), 4.22 (s, br, 4H), 2.47 (s, 18H), 2.36–2.24 (m, 8H). $^{13}C\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 133.0 (CH, $^2J(C,P) = 13.0$ Hz), 132.1 (CH, $^3J(C,P) = 4.6$ Hz), 131.7 (CH, $^3J(C,P) = 4.3$ Hz), 130.4 (CH), 62.2 (CH), 31.8 (CH_2), 22.0 (CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, 21 °C, $CDCl_3$): 20.17.

4.7. Addition of external additives (amines, phosphines)

To test the influence of additives on the activities of the metal complexes, a four molar ratio of the respective additive was added directly to a solution of complex **2c** and 20 ml cyclooctane resulting in the formation of the phosphine resp. amine containing catalysts **5a–e** and the amine containing catalysts **6a–h**. The corresponding mixture was used for dehydrogenation experiments (see Section 4.8).

4.8. Homogeneous dehydrogenation of cyclooctane

The respective complex was dissolved resp. suspended in 20 ml cyclooctane. The mixture was transferred into a 250 ml autoclave. The autoclave was closed gastight and heated to 200–400 °C, the standard temperature was 300 °C. After the desired reaction time (4 h), the autoclave was removed from the oven and cooled to room temperature. The gas and the solution were analyzed by GC.

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