Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 1808–1814
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Catalytic dehydrogenation of cyclooctane with neutral iridium(I) complexes

Silke Taubmann, Helmut G. Alt *

Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany

Received 21 December 2007; received in revised form 24 January 2008; accepted 1 February 2008
Available online 7 February 2008

Abstract

A series of new 1,5-cyclooctadiene iridium(I) complexes with chelating ligands has been synthesized. The ligands are naphthoxyimines, carboxylates and alcoholates. The complexes catalyze the homogeneous dehydrogenation of cyclooctane to give cyclooctene and hydrogen without an external hydrogen acceptor up to rates of 75 turnovers. The catalysts are active for at least 48 h at a temperature of 300 °C. The ligand structure has an influence on the activity and selectivity of the corresponding catalysts.

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

1. Introduction

The selective, catalytic activation of chemical bonds remains a challenging and significant goal of modern research in chemistry. An attractive area is the transformation of relatively inexpensive hydrocarbon feedstocks into more useful value-added products by low energy processes [1]. In this respect, catalytic alkane dehydrogenation with coordination compounds is a significant reaction converting alkanes into the corresponding olefins and hydrogen. The products are valuable educts or intermediates for industrial processes.

In the year 1979, Crabtree et al. reported the stoichiometric dehydrogenation of cyclooctene to cyclooctadiene with an iridium phosphine complex [2]. Four years later, Baudry and Ephritikhine described the first catalytic dehydrogenation of cyclooctane with a rhenium polyhydride complex under thermal conditions [3]. This process represents a transfer dehydrogenation reaction, because a "sacrificing" olefin reacts with the generated hydrogen. In the following, transfer dehydrogenation reactions were reported in the literature [4–15]. In the year 2004, Brookhart et al. described turnover numbers of 1000 per 30 min using an iridium bis(phosphinite) *p*-XPCP pincer complex [16]. The disadvantage of this transfer dehydrogenation is the necessity of a hydrogen acceptor, like *tert*-butylethylene, making this reaction uneconomic. CH bond activation reactions without a hydrogen acceptor are very rare [17,18]. The yields of these reactions are mostly lower than the transfer dehydrogenation results [19]. To carry out acceptor less dehydrogenation reactions, neutral iridium(I) complexes with heteroatomic N,O-chelating ligands were synthesized.

2. Results and discussion

2.1. Syntheses of the complexes

The hydroxyimine ligand precursors were synthesized via an acid-catalyzed condensation reaction of 2-hydroxy-1-naphthaldehyde with a phenylamine as reported in the literature [20]. The ligand precursors have to be transformed into the corresponding sodium alcoholates. The typical procedure is the reaction of the ligand precursor with NaH to produce the sodium alcoholate and hydrogen. The reaction of 1 equiv. of the alcoholate with 0.5 equiv. of

* Corresponding author. Tel.: +49 921 55 2555; fax: +49 921 55 2044.
E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.02.003

$[Ir(cod)Cl]_2$ yielded the corresponding, new naphthoxy iridium complexes **1a–d** (Scheme 1). The complexes were obtained with yields of 65–85%.

Similar complexes like the naphthoxyimine iridium(I) compounds are the alcoholate iridium(I) complexes **2a–c** (the hetero atoms nitrogen and oxygen coordinating to iridium). The synthesis was performed as described in Scheme 2. The complexes were obtained as yellow and orange solids.

The complex 1,5-cyclooctadiene 8-oxychinoline iridium(I) (**2d**) was prepared in an analogous manner [21].

The third type with an N,O-chelating ligand are carboxylate iridium(I) complexes. The novel complexes **3a–c** were synthesized from the reaction of $[Ir(cod)(OMe)]_2$ with pyridine 2-acetic acid, 6-methylpyridine 2-carboxylic acid and indol 2-carboxylic acid (Scheme 3).

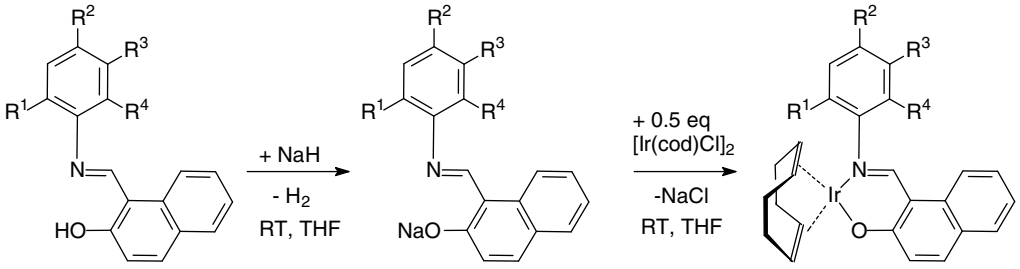
For investigations of structure–efficiency relationships in CH-activation reactions, the known iridium(I) complexes **3d–h** were synthesized. The procedure is known in the literature [22,23].

2.2. Catalytic dehydrogenation of cyclooctane

The synthesized coordination compounds were tested as catalysts for the dehydrogenation of cyclooctane to generate cyclooctene and hydrogen (Scheme 4) in a homogeneous reaction. The catalysts could be used without any activation or additives.

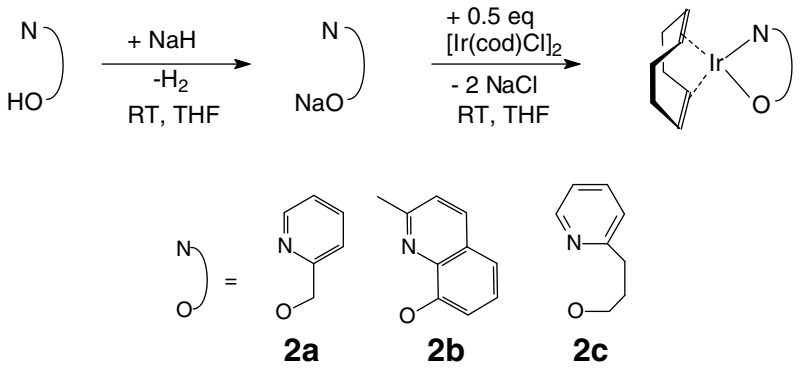
The corresponding coordination compound was dissolved in cyclooctane, the solution was transferred into an autoclave and heated to 300 °C. This temperature is useful because the dehydrogenation of alkanes is an endothermic reaction. At higher temperatures most of the organometallic compounds have no longer their original compositions but they are still catalytically active. Remarkably, the investigations of structure–efficiency relationships of catalysts showed that the nature of the organic ligands has a relevant impact on the activity and selectivity of the corresponding catalyst and its "decomposition product". The identity of the decomposition products is still unclear.

The results of the naphthoxyimine iridium(I) catalysts (Scheme 5) indicated that a *meta*-substitution (**1d**) gave a higher TON (44) than the *ortho*-substituted derivative (**1a**) with 28 turnovers. The highest activity (TON = 75) was obtained for catalyst **1c**. This could be due to the electron withdrawing effect of the *para*-Br substituent. This electronic deficit could favor an oxidative addition reaction of the alkane at the metal which is the starting step of the CH-activation reaction. Catalysts **1a–c** produced 100% cyclooctene.

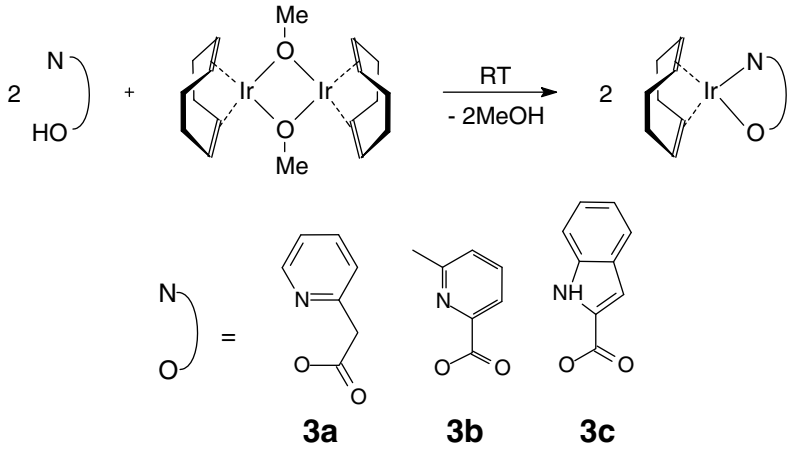


2a R^1, R^4 = Me; R^2, R^4 = H
2b R^1, R^4 = i-prop; R^2, R^4 = H
2c R^1, R^4 = Me; R^2 = H; R^3 = Br
2d R^1, R^2 = Me; R^3, R^4 = H

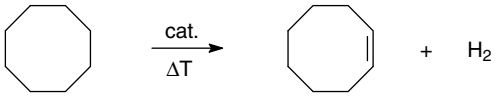
Scheme 1. Synthesis of naphthoxy iridium(I) complexes.



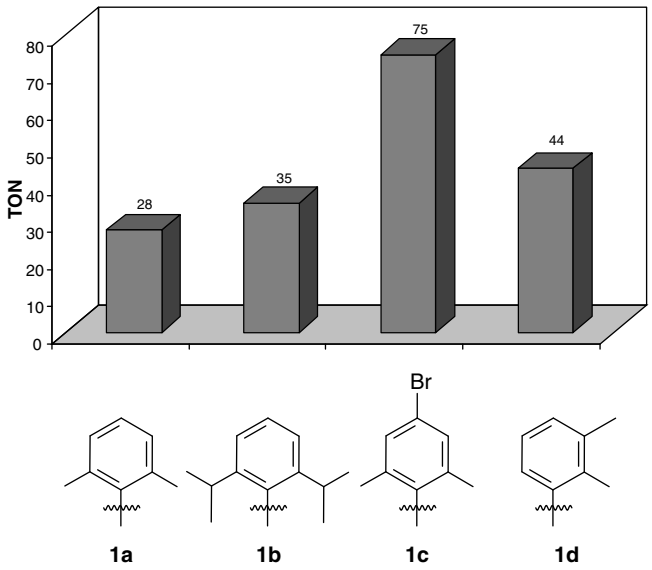
Scheme 2. Synthesis of the alcoholate iridium(I) complexes **2a–c**.



Scheme 3. Synthesis of carboxylate iridium(I) complexes.

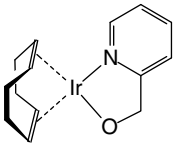
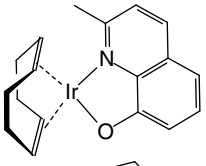
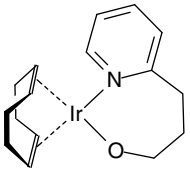
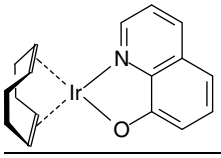


Scheme 4. Catalytic activation of cyclooctane.



Scheme 5. TONs of the dehydrogenation of cyclooctane catalyzed with **1a–d**.

Table 1
TONs and selectivities of the dehydrogenation of cyclooctane catalyzed by **2a–h**

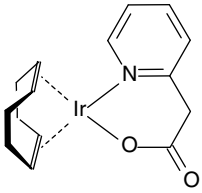
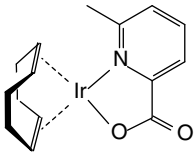
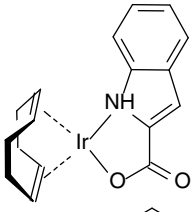
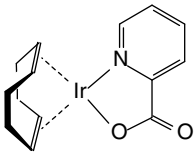
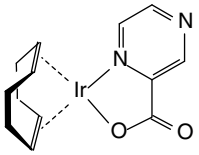
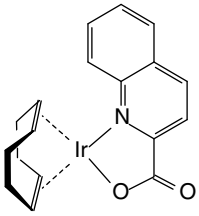
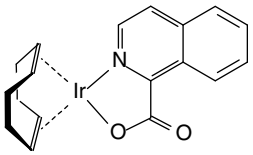
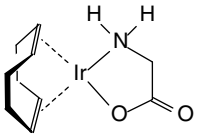
Metal complex	Catalyst no.	TON	Selectivity [%]
	**2a**	14.12	100
	**2b**	10.59	78.4
	**2c**	9.21	55.3
	**2d**	10.34	100

The alcoholate iridium(I) catalysts also achieved a catalytic dehydrogenation reaction of cyclooctane to give cyclooctene and hydrogen. The activities of catalysts **2a–d** were constant within the scope of measuring accuracy (TON = 9–14). Compared with the naphthoxy iridium(I) catalysts, the alcoholate ligands of catalysts **2a–d** showed no influence (Table 1). In contrast to the activities, the selectivities varied depending on the hetero atoms of the ligand. The results in Table 1 show that a substitution at the pyridine (**2b**) reduced the selectivity to produce the monoolefin. Another decrease of selectivity (55.3%) was observed with catalyst **2c**. The unfavorable seven-membered ring of the chelating ligand could be the reason for this behavior.

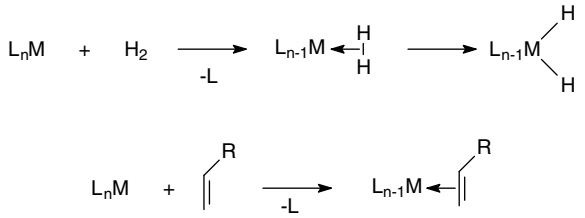
The carboxylate iridium(I) complexes **3a–h** achieved excellent selectivities (100%). Depending on the organic ligand, the activities of complexes **3a–h** varied between 5 and 35 turnovers (Table 2).

Complexes **3a** with a six-membered ring of chelating ligand and metal showed the highest catalytic activity (TON = 35). The NH-structure unit reduced the activity of catalysts **3c** and **3h**. A steric influence of the isochinoline

Table 2
TONs and selectivities of the dehydrogenation of cyclooctane catalyzed with **3a**–**h**

Metal complex	Catalyst no.	TON	Selectivity [%]
	**3a**	34.53	100
	**3b**	17.41	100
	**3c**	4.88	100
	**3d**	28.02	100
	**3e**	18.81	100
	**3f**	25.02	100
	**3g**	20.57	100
	**3h**	10.09	100

and the quinoline carbonic acid ligand could not be observed. The simpler the structure of hetero atomic ligands (pyridine carboxylate) the higher the activities (complexes **3a** and **3d**). In a similar manner also cationic iridium complexes of the type [Ir(cod)LL]X (LL = chelating ligand; X = Cl, PF_6) are able to activate cyclooctane in homogeneous solution [24].



Scheme 6. Coordination of an alkene and hydrogen at the metal center of the active species.

2.3. Time dependence of homogeneous dehydrogenation

The catalytic dehydrogenation of alkanes produces alkenes and hydrogen. These products are potential ligands (Scheme 6) and can block the first step of the CH-activation reaction.

In a homogeneous system, the reaction products cannot be isolated or separated from the catalytic centers. This explains the time dependence of the TONs of catalyst **3a** (Scheme 7). The curve is indicative of a permanent reduction of the dehydrogenation reaction. The catalyst performed 29 turnovers in 8 h. An extension of the reaction time of 48 h gave 43 turnovers. In spite of the activity decrease, catalyst **3a** was still active after 48 h.

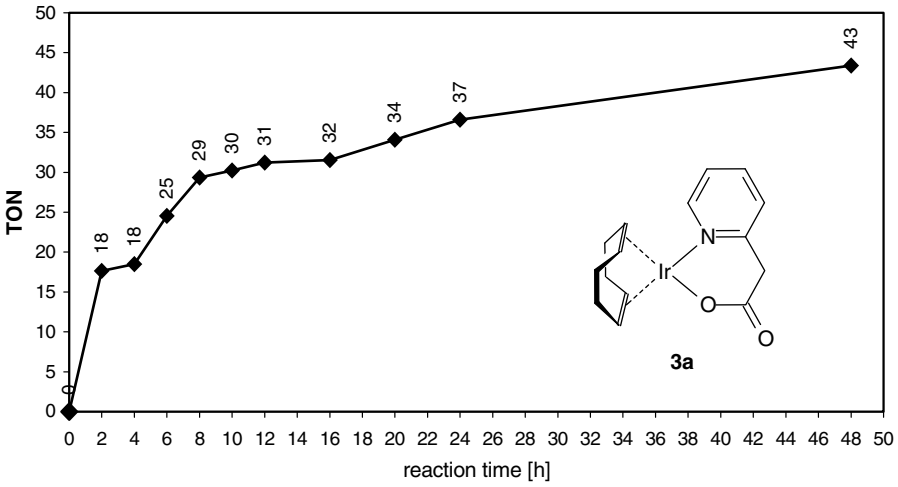
3. Summary and conclusion

Novel naphthoxyimine (**1a**–**d**), alcoholate (**2a**–**d**) and carboxylate iridium(I) complexes (**3a**–**c**) have been synthesized. The hydroxyimine ligand precursors can be prepared from relatively inexpensive starting materials. The alcoholates and carboxylic acid ligand precursors are commercially available. The prepared complexes catalyzed the homogeneous dehydrogenation of cyclooctane without a "sacrificing" olefin at a reaction temperature of 300 °C (maximum of 75 turnovers). The activity and selectivity depends on the nature of the heteroatomic ligand. For most ligands a selectivity of 100% monoolefin was obtained. The naphthoxyimine ligand with a *para*-bromine-substituent (**1c**) gave the highest conversion, obviously because of the electron pulling effect of the ligand favoring the oxidative addition of alkanes at the iridium atom. The time dependence of the homogeneous dehydrogenation reaction of catalyst **3a** was almost a parabolic curve. This is indicative of a permanent reduction of the activity. The reason for this behavior is primarily the contamination of the catalysts by its own products (hydrogen and alkene) in a closed system. In order to gain more information it is planned to perform these reactions in open systems (fixed bed reactor) at various temperatures.

4. Experimental

4.1. General considerations

Air- and moisture-sensitive reactions were carried out under an atmosphere of argon employing standard Schlenk



Scheme 7. Time dependence of the dehydrogenation of cyclooctane in a closed system catalyzed with **3a**.

techniques. NMR spectra were measured on a Bruker ARX 250 instrument. Chemical shifts (δ, ppm) were recorded relative to the residual solvent peak ($\delta = 7.24$ ppm for chloroform-*d*). The multiplicities were designated as follows: s = singlet; d = doublet; m = multiplet. $^{13}C\{1H\}$ NMR spectra were fully proton decoupled and the chemical shifts (δ, ppm) are relative to the solvent peak ($\delta = 77.0$ ppm). Elemental analyses were performed using a VarioEl III instrument. A gas chromatograph Agilent 6890 was used to register the dehydrogenation reaction products. The identification of dehydrogenation products and the reaction control were carried out by FOCUS DSQ (Thermo) mass spectrometer.

4.2. Materials

Tetrahydrofuran, *n*-pentane, diethylether, methylenechloride and toluene were refluxed over the appropriate drying agents and distilled under argon. NaH was washed with toluene and pentane before use to remove mineral oil. $CDCl_3$ was stored over molecular sieves. Cyclooctane (COA) was degassed and stored under argon. $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ were synthesized in analogy to known procedures [25–28]. The organic starting materials were purchased from Aldrich or Arcos.

4.3. General procedure for the synthesis of the complexes *N,O*-imine-Ir(cod) (*1*)

To a THF solution (30 ml) of the respective hydroxyimine (1 mmol) was added 1 mmol of NaH. The mixture was stirred for 2 h at RT. A solution of 0.5 mmol of $[Ir(cod)Cl]_2$ in 20 ml THF was then added and the mixture was stirred for 2 h at RT. After evaporation of the solvent in vacuo, the residue was dissolved in CH_2Cl_2. The solution was filtered over Na_2SO_4, the solvent was then removed in vacuo. The crude product was washed with pentane and dried in vacuo. The complexes were obtained as yellow powders.

4.3.1. Compound *1a*

From 275 mg (1 mmol) of 1-[(2,6-dimethylphenyl) imino]methylenyl]-2-naphthalenol, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 372 mg (0.65 mmol, 65%) of **1a** as an orange powder. Spectroscopic data for **1a**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 9.04 (s, 1H), 7.89–7.03 (9H), 4.46–4.41 (m, 2H), 2.66–2.56 (m, 2H), 2.30 (s, 6H), 2.21–2.09 (m, 4H), 1.80–1.62 (4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 166.5 (C_q), 157.5 (CH), 150.2 (C_q), 136.2 (CH), 134.7 (C_q), 130.8 (C_q), 129.2 (CH), 128.3 (CH), 127.5 (CH), 127.3 (C_q), 126.3 (CH), 125.3 (CH), 122.8 (CH), 118.9 (CH), 110.2 (C_q), 69.1 (CH), 57.4 (CH), 32.5 (CH_2), 29.5 (CH_2), 18.7 (CH_3). MS data for **1a**: 575 ($M^{\cdot+}$) (100), 573 (60), 545 (9), 463 (17), 295 (6), 77 (7).

4.3.2. Compound *1b*

From 331 mg (1 mmol) of 1-[(2,6-diisopropylphenyl)imino]methylenyl]-2-naphthalenol, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 530 mg (0.84 mmol, 84%) of **1b** as a yellow powder. Anal. Calc. for $C_{31}H_{36}NOIr$ (**1b**): C, 58.93; H, 5.90; N, 2.22. Found: C, 59.06; H, 6.10; N, 2.30%. Spectroscopic data for **1b**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 9.09 (s, 1H), 7.90–7.22 (m, 9H), 4.46–4.44 (m, 2H), 3.43–3.37 (m, 2H), 2.77–2.74 (m, 2H), 2.24–2.16 (m, 4H), 1.77–1.66 (m, 4H), 1.35 (d, 6H, $^3J(H,H) = 6.86$ Hz), 1.02 (d, 6H, $^3J(H,H) = 6.80$ Hz). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 166.5 (C_q), 157.5 (CH), 157.4 (CH), 146.9 (C_q), 136.3 (CH), 134.5 (C_q), 129.2 (CH), 127.7 (CH), 127.4 (CH), 127.2 (C_q), 125.4 (CH), 125.2 (CH), 123.3 (CH), 122.8 (CH), 118.5 (CH), 109.5 (C_q), 69.2 (CH), 57.4 (CH), 32.3 (CH_2), 29.5 (CH_2), 27.8 (CH_3), 22.4 (CH_3). MS data for **1b**: 631 ($M^{\cdot+}$) (100), 629 (72), 519 (28), 295 (12).

4.3.3. Compound **1c**

From 354 mg (1 mmol) of 1-[(4-brom-2,6-dimethylphenyl)imino]methylenyl]-2-naphthalenol, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 490 mg (0.75 mmol, 75%) of **1c** as a yellow powder. Spectroscopic data for **1c**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 9.00 (s, 1H), 7.90–7.22 (m, 8H), 4.48 (s, br, 2H), 2.62–2.53 (m, 2H), 2.28 (s, 6H), 2.20–2.14 (m, 4H), 1.80–1.64 (m, 4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 166.6 (C_q), 157.5 (CH), 149.0 (C_q), 136.6 (CH), 134.3 (C_q), 131.1 (CH), 129.3 (CH), 127.8 (CH), 127.3 (C_q), 125.5 (CH), 123.2 (CH), 119.3 (C_q), 118.9 (CH), 110.4 (C_q), 70.4 (CH), 68.9 (CH), 32.8 (CH_2), 29.7 (CH_2), 18.6 (CH_3), 18.5 (CH_3). MS data for **1c**: 653 ($M^{\bullet+}$) (100), 623 (7), 573 (7), 541 (10), 295 (9).

4.3.4. Compound **1d**

From 275 mg (1 mmol) of 1-[[(2,3-dimethylphenyl) imino]methylenyl]-2-naphthalenol, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 488 mg (0.85 mmol, 85%) of **1d** as a yellow powder. Spectroscopic data for **1d**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 9.13 (s, 1H), 7.89–6.89 (m, 9H), 5.49–4.42 (m, 2H), 3.19–3.16 (m, 2H), 2.67–2.61 (m, 4H), 3.34 (s, 3H), 2.21 (s, 3H), 1.78–1.59 (m, 4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 166.3 (C_q), 157.4 (CH), 151.1 (C_q), 137.6 (C_q), 136.3 (CH), 129.2 (CH), 134.4 (C_q), 129.8 (C_q), (C_q), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.4 (C_q), 125.4 (CH), 122.9 (CH), 122.1 (CH), 119.1 (CH), 110.0 (C_q), 69.0 (CH), 56.7 (CH), 32.4 (CH_2), 29.6 (CH_2), 20.6 (CH_3), 14.3 (CH_3). MS data for **1d**: 575 ($M^{\bullet+}$) (100), 573 (70), 545 (8), 463 (25), 295 (17), 77 (10).

4.4. General procedure for the synthesis of N-alcoholate iridium complexes (**2**)

A Schlenk tube was charged with 1 mmol of the respective alcoholate and 5 ml THF. After addition of 1 mmol NaH, the mixture was stirred for 2 h at RT. The suspension was slowly added to a solution of 0.5 mmol $[Ir(cod)Cl]_2$ in 10 ml THF and stirred for 1 h at RT. The solvent was removed in vacuo and the crude product was dissolved in CH_2Cl_2. After filtration through Na_2SO_4, the solvent was reduced in vacuo until a solid precipitated. The solid was washed with pentane and diethylether and dried in vacuo. The products were obtained as yellow and orange powders.

4.4.1. Compound **2a**

From 109 mg (1 mmol) of hydroxymethylpyridine, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 91 mg (0.23 mmol, 23%) of **2a** as a yellow powder. Spectroscopic data for **2a**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.76 (d, 1H), 8.09 (d, 1H), 7.81 (dd, 1H), 7.05 (d, 1H), 4.61 (s, 2H), 4.17 (s, 2H), 3.10 (s, 2H), 2.21–2.14 (m, 4H), 1.62–1.57 (m, 4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 148.1 (CH), 136.9 (CH), 121.7 (CH), 120.0 (CH), 68.4 (CH), 63.7 (CH_2), 53.3 (CH), 31.4 (CH_2), 30.5 (CH_2). MS data for **2a**: 409 ($M^{\bullet+}$) (17), 407 (20), 375 (39), 296 (20), 269 (9), 108 (100).

4.4.2. Compound **2b**

From 146 mg (1 mmol) of 8-hydroxyquinaldine, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 305 mg (0.73 mmol, 73%) of **2b** as an orange powder. Spectroscopic data for **2b**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.00 (d, 1H), 7.27 (dd, 1H), 7.01 (dd, 1H), 6.93 (dd, 1H), 6.78 (dd, 1H), 4.43 (s, 2H), 4.11 (s, 2H), 2.50 (s, 3H), 2.29–2.21 (m, 4H), 1.61–1.50 (m, 4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 161.7 (C_q), 144.3 (C_q), 140.0 (CH), 129.4 (CH), 128.7 (C_q), 124.1 (CH), 115.8 (CH), 113.5 (CH), 67.2 (CH), 55.4 (CH), 33.8 (CH_2), 29.6 (CH_2), 23.8 (CH_3). MS data for **2b**: 459 ($M^{\bullet+}$) (100), 457 (75), 429 (55), 294 (13), 269 (6).

4.4.3. Compound **2c**

From 137 mg (1 mmol) of 3-pyridinepropanol, 24 mg (1 mmol) of NaH, and 336 mg (0.5 mmol) $[Ir(cod)Cl]_2$ was obtained 196 mg (0.45 mmol, 45%) of **2c** as an orange powder. Spectroscopic data for **2c**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.35–8.33 (m, 1H), 7.55–7.43 (m, 1H), 7.05–7.02 (m, 1H), 7.00–6.95 (m, 1H), 3.55 (t, 2H), 3.27 (s, 2H), 2.81 (t, 2H), 2.35 (s, 2H), 1.85–1.81 (m, 2H), 1.37 (s, 4H), 1.11 (s, 4H).

4.5. General procedure for the synthesis of N-carboxylate iridium complexes (**3**)

The respective carbonic acid (1 mmol) was dissolved in 10 ml THF by heating. The solvent was added to a solution of 0.5 mmol $[Ir(cod)(OMe)]_2$ in 10 ml THF. The mixture was stirred for 3 h at RT. A color change from yellow to red resp. brown was observed. After reducing the solvent in vacuo, the precipitated solid was filtered, washed with pentane and diethylether and dried in vacuo. The products were obtained as red and brown powders.

4.5.1. Compound **3a**

From 486 mg (2.5 mmol) of 2-pyridine acetic acid and 662 mg (1 mmol) $[Ir(cod)OMe]_2$ was obtained 859 mg (0.98 mmol, 98%) of **3a** as an orange powder. Spectroscopic data for **3a**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.40 (d, 1H), 7.82 (dd, 1H), 7.40–7.36 (m, 1H), 7.05–7.02 (m, 1H), 4.61 (s, 2H), 4.18–4.16 (m, 2H), 3.11–3.09 (m, 2H), 2.21–2.14 (m, 4H), 1.62–1.57 (m, 4H). ^{13}C $\{^1H\}$ (62 MHz, 21 °C, $CDCl_3$): 171.0 (C_q), 156.0 (C_q), 148.5 (CH), 139.2 (CH), 126.3 (CH), 125.2 (CH), 79.2 (CH), 46.1 (CH_2), 45.1 (CH_2). MS data for **3a**: 453 ($M^{\bullet+}-H$) (3), 297 (100), 295 (98), 269 (26), 91 (4), 77 (7).

4.5.2. Compound **3b**

From 137 mg (1 mmol) of 6-picolinic-acid and 331 mg (0.5 mmol) $[Ir(cod)OMe]_2$ was obtained 415 mg (0.95 mmol, 95%) of **3b** as an orange powder. Spectro-

scopic data for **3b**: MS data for **3b**: 437 ($M^{\cdot+}$) (59), 391 (83), 389 (90), 387 (100), 296 (38), 294 (38), 269 (14).

4.5.3. Compound *3c*

From 403 mg (2.5 mmol) of indol-2-carbonic-acid and 662 mg (1 mmol) $[Ir(cod)OMe]_2$ was obtained 424 mg (0.46 mmol, 46%) of **3c** as an orange powder. Anal. Calc. for $C_{17}H_{18}NO_2Ir$ (**3c**): C, 45.75; H, 3.84; N, 2.96. Found: C, 45.27; H, 3.85; N, 2.85%. Spectroscopic data for **3c**: ^1H NMR (250 MHz, 21 °C, $CDCl_3$): 8.92 (s, 1H), 7.71–7.11 (m, 5H), 4.38 (s, breit, 4H), 2.83 (s, breit, 4H), 2.22 (s, breit, 4H).

4.6. Homogeneous dehydrogenation of cyclooctane

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

Acknowledgment

We thank ConocoPhillips, Bartlesville, USA, for the financial support of the project.

References

[1] R.H. Crabtree, J. Chem. Soc., Dalton Trans. (2001) 2437.
[2] R.H. Crabtree, J.M. Mihelcic, J.-M. Quirk, J. Am. Chem. Soc. 101 (1979) 7738.
[3] D. Baudry, M. Ephritikhine, H. Felkin, R. Holmes-Smith, J. Am. Chem. Soc. (1983) 788.
[4] M.J. Burk, R.H. Crabtree, C.P. Parnell, R.J. Uriarte, Organometallics 3 (1984) 816.
[5] H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith, J. Zakrzewski, Tetrahedron Lett. 25 (1984) 1999.
[6] M.J. Burk, R.H. Crabtree, D.V. McGrath, J. Chem. Soc., Chem. Commun. (1985) 1829.
[7] M. Gupta, C. Hagen, R.J. Flesher, W.C. Kaska, C.M. Jensen, Chem. Commun. (1996) 2083.
[8] R.H. Crabtree, C.P. Parnell, Organometallics 4 (1985) 519.
[9] M.J. Burk, R.H. Crabtree, J. Am. Chem. Soc. 109 (1987) 8025.
[10] J.A. Maguire, W.T. Boese, A.S. Goldman, J. Am. Chem. Soc. 111 (1989) 7088.
[11] J.A. Maguire, A.S. Goldman, J. Am. Chem. Soc. 113 (1991) 6706.
[12] J.A. Maguire, A. Petrillo, A.S. Goldman, J. Am. Chem. Soc. 114 (1992) 9492.
[13] J. Belli, C.M. Jensen, Organometallics 15 (1996) 1532.
[14] P. Braunstein, Y. Chauvin, J. Nahring, A. DeCian, J. Fischer, A. Tiripicchio, F. Ugozzoli, Organometallics 15 (1996) 5551.
[15] J.A. Miller, L.K. Knox, J. Chem. Soc., Chem. Commun. (1994) 1449.
[16] I. Göttker, gen. Schnetmann, P. White, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 1804.
[17] T. Aoki, R.H. Crabtree, Organometallics 12 (1993) 294.
[18] F. Liu, A. Goldman, Chem. Commun. (1999) 655.
[19] W.-W. Xu, G.P. Rosini, M. Gupta, C.M. Jensen, W.C. Kaska, K. Krogh-Jespersen, A.S. Goldman, Chem. Commun. (1997) 2273.
[20] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song, W.-H. Sun, J. Organomet. Chem. 689 (2004) 936.
[21] G.S. Rodman, K.R. Mann, Inorg. Chem. 27 (1988) 3338.
[22] L. Carlton, J.J. Molapisi, J. Organomet. Chem. 609 (2000) 60.
[23] C. Potvin, L. Davignon, G. Pannetier, Bull. Soc. Chim. Fr. (1975) 507.
[24] Silke Taubmann, J. Mol. Catal. A: Chem., in press.
[25] R.H. Crabtree, G.E. Morris, J. Organomet. Chem. 135 (1977) 395.
[26] R.H. Crabtree, J.M. Quirk, H. Felkin, T. Fillebeen-Khan, Synth. React. Inorg. Met.-Org. Chem. 12 (1982) 407.
[27] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.
[28] S.D. Robinson, B.L. Shaw, J. Am. Chem. Soc. (1965) 4997.