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Rhodium and iridium complexes of *N*-heterocyclic carbenes: Structural investigations and their catalytic properties in the borylation reaction ☆

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Abstract

Bridged and unbridged *N*-heterocyclic carbene (NHC) ligands are metalated with $[Ir/Rh(COD)_2Cl]_2$ to give rhodium(I/III) and iridium(I) mono- and biscarbene substituted complexes. All complexes were characterized by spectroscopy, in addition $[Ir(COD)(NHC)_2][Cl,I]$ [COD = 1,5-cyclooctadiene, NHC = 1,3-dimethyl- or 1,3-dicyclohexylimidazolin-2-ylidene] (**1**, **4**), and the biscarbene chelate complexes **12** [(η^4-1,5-cyclooctadiene)(1,1′-di-*n*-butyl-3,3′-ethylene-diimidazolin-2,2′-diylidene)iridium(I) bromide] and **14** [(η^4-1,5-cyclooctadiene)(1,1′-dimethyl-3,3′-*o*-xylylene-diimidazolin-2,2′-diylidene)iridium(I) bromide] were characterized by single crystal X-ray analysis. The relative σ-donor/π-acceptor qualities of various NHC ligands were examined and classified in monosubstituted NHC-Rh and NHC-Ir dicarbonyl complexes by means of IR spectroscopy. For the first time, bis(carbene) substituted iridium complexes were used as catalysts in the synthesis of arylboronic acids starting from pinacolborane and arene derivatives.
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1. Introduction

The selective functionalization of unreactive C–H bonds is one of the largest challenges in metal-organic chemistry [1]. Meanwhile a set of transition metal complexes, in particular complexes of palladium, platinum, rhodium and iridium, were described which are capable of intermolecular C–H activation with saturated and unsaturated hydrocarbons [1,2]. So far, only a few examples of complexes are known which could accomplish the activation of a C–H bond of aromatic substrates.

Recently, several research groups investigated the spectacular synthesis of arylboronic acid ester derivatives via rhodium and iridium catalyzed C–H-borylation of arenes and heteroarenes, by means of bis(pinacolato)diborane (Pin_2B_2) or pinacolborane (PinBH) [3–7]. The C–H-borylation reaction was also established for aliphatic hydrocarbons and vinylic compounds [8,9]. The widely available arylboronic acid ester derivatives can easily be transformed into various functionalized hydrocarbons such as alcohols, amines or alkenes. Also, their possible employment in catalytic C–C coupling reactions, like the Suzuki–Miyaura coupling [10], turns these borylated hydrocarbons into extraordinarily valuable raw materials for organic chemistry [11]. The system published by Miyaura, Ishiyama and

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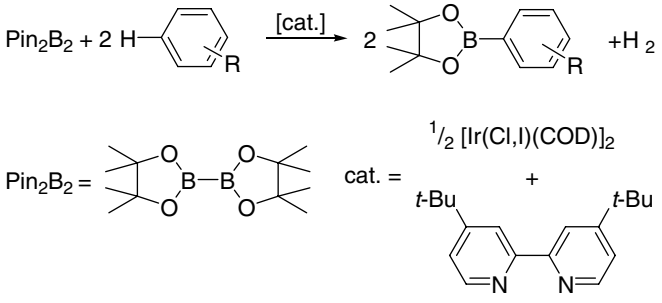
Hartwig possesses particularly high activity, which was further optimized in the course of systematic studies. Thus the combination of $[Ir(\eta^4\text{-COD})(OMe)]_2$ and 4,4′di-*tert*-butyl-2,2′-bipyridine makes the catalytic borylation of aromatics with stoichiometric quantities of bis(pinacolato)diborane in an inert solvent at ambient temperature possible (Scheme 1) [3,4a]. In addition the reaction is regioselective and a wide set of functional groups are tolerated in this reaction [3,6]. Mediated by a transition metal boryl complex, the mechanism of the borylation reaction proceeds via oxidative addition of the C–H bond [4]. The direct synthesis of boronic acid esters via activation and functionalization of an aromatic C–H bond is a clear simplification.

For a long time our group was focused on the employment of stable nucleophilic carbenes, such as the *N*-heterocyclic carbenes [12]. They have the advantageous property of forming strong bonds to metal centers, with little tendency towards dissociation [13–15]. This is particularly beneficial in their use as ligands for organometallic catalysts [16]. The σ-donor strength varies with the constitution of the respective derivative. A large number of new mono- and bi-dentate carbene ligands of imidazolin-2-ylidene and the imidazolidin-2-ylidene types were developed and applied in the synthesis of transition metal complexes [17,18].



Scheme 1. Borylation of hydrocarbons.

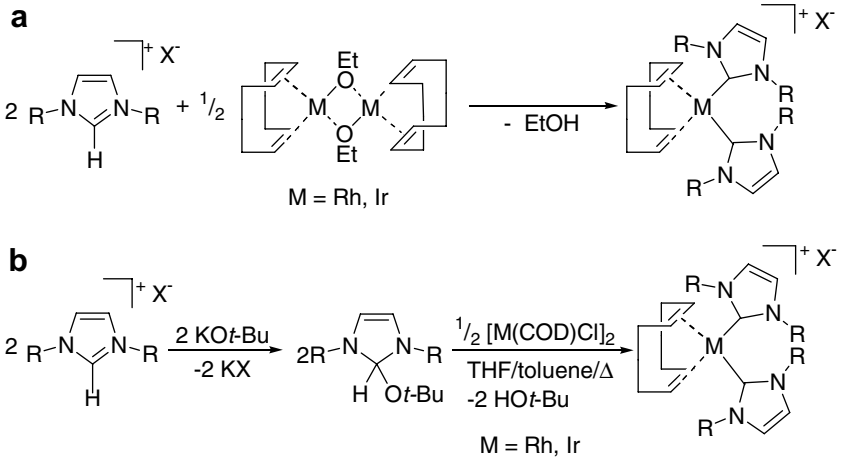
2. Results and discussion

In the present paper we focus on investigations of the activation and functionalization of aromatic C–H bonds [19], using iridium as the catalytically active metal, given the recent success in the borylation of aromatic compounds [3–9]. Therefore, we tried to apply adequate biscarbene complexes for the direct catalytic synthesis of arylboronic acid esters. Convenient cationic biscarbene complexes of rhodium and iridium can be synthesized by in situ deprotonation of the imidazolium salts [20–23]. Substituting the halide bridge in the precursor dimer by an ethoxy bridge, this "internal base" deprotonates the imidazolium salt in situ, leading to the desired complexes (Scheme 2a). The reaction of an alcoholate adduct of the imidazolium salt with the $[M(COD)Cl]_2$ precursor dimer is another possible synthesis route for the formation of the expected biscarbene complexes (Scheme 2b) [12,14,24,25]. These complexes are soluble in most organic solvents and stable towards exposure to air under dry conditions.

Complexes **1**–**4** (Table 1) were prepared according to the procedure shown in (Scheme 2a); for the bridged biscarbene complexes **5**–**12** the synthesis route over the imidazolium alcoholate was used (Scheme 2b, Table 1). Complexes **13** [26,27] and **14** were also prepared according to Scheme 2b. The ^{13}C NMR signals for the carbene carbons of the characterized biscarbene complexes are in the range of $\delta = 172$–182 ppm, and are in agreement with the literature [20,26–31]

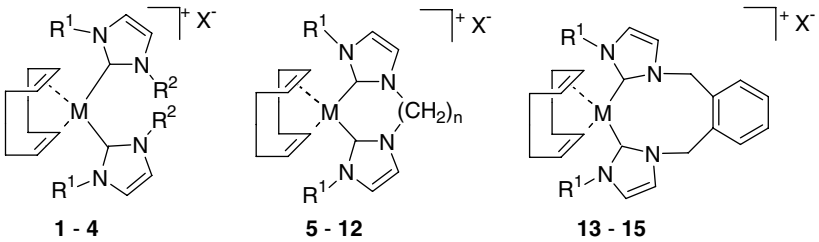
Suitable crystals of complexes **1** (Fig. 1), **4** (Fig. 2), **12** (Fig. 3) and **14** (Fig. 4) for single X-ray diffraction studies were obtained from dichloromethane/*n*-pentane solutions at ambient temperature. A selection of characteristic bond angles and bond distances are given in Table 2.

All complexes favour a slightly disorted square-planar coordination sphere of the iridium center. The iridium–carbene bond lengths of complexes **1** and **4** are marginally longer [(**1**) 2.03, 2.08; (**4**) 2.074(4), 2.076(3)] than the bond lengths of complexes **12** and **14** [(**12**) 2.02, 2.04; (**14**)



Scheme 2. Synthesis of biscarbene substituted iridium and rhodium complexes.

Table 1
Biscarbene substituted iridium and rhodium complexes



Complex	M	R^1	R^2	X^-	*n*	Yield (%)	$\delta C_{carbene}$ (ppm)
1	Ir	Me	Me	I^-	–	86	177.0
2	Rh	*t*-Bu	*t*-Bu	Cl^-	–	70	180.1
3	Ir	*t*-Bu	*t*-Bu	Cl^-	–	67	174.5
4	Ir	Cy	Cy	Cl^-	–	68	173.9
5	Rh	Et	–	I^-	1	48	179.9
6	Ir	Et	–	I^-	1	52	173.7
7	Rh	Cy	–	I^-	1	71	182.0
8	Ir	Cy	–	I^-	1	75	174.2
9	Rh	Me	–	PF_6^-	2	57	178.4
10	Rh	*t*-Bu	–	Br^-	2	74	180.0
11	Ir	*t*-Bu	–	Br^-	2	79	175.1
12	Ir	*n*-Bu	–	Br^-	2	92	175.0
13 [27]	Rh	Me	–	PF_6^-	–	87	180.5
14	Ir	Me	–	Br^-	–	71	175.9
15	Ir	Me	–	PF_6^-	–	71	175.7

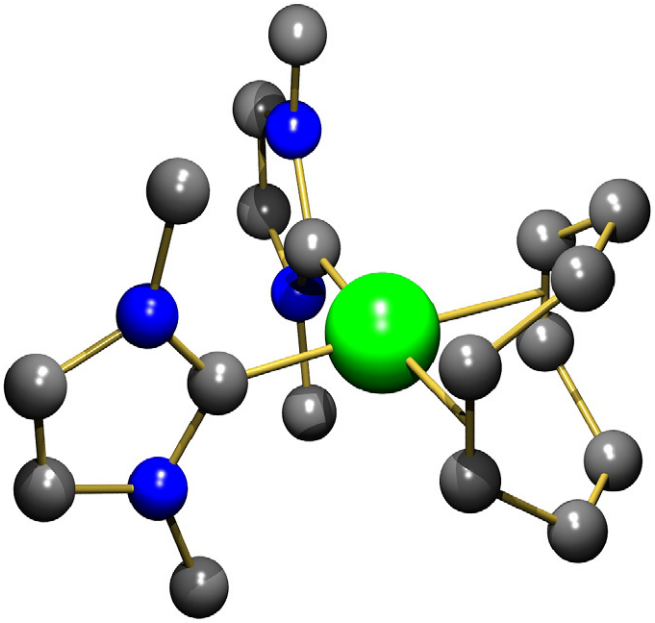


Fig. 1. Ball and stick model of the cationic part of compound **1** in the solid state (for details see Ref. [32a]).

2.044(5), 2.044(5)], where the carbene ligand acts as a bischelate. These bond lengths show no indication for different donor strength of the carbene ligands due to the similar properties of these ligands. The iridium–carbene bond lengths in complexes **12** and **14** are on average 0.03 Å shorter than the bond lengths of complexes **1** and **4**, caused by the rigid coordination of the bischelate. In all complexes the N–C–N angles of the carbene ligands are in accordance with coordinated azole rings reported in the literature [33,34].

To form biscarbene substituted rhodium(III) complexes, a synthetic route first described by Peris in 2003 was used (Scheme 3) [27]. Starting from the $[Rh(COD)Cl]_2$ precursor the first step of the reaction is oxidation by passing air through the reaction solution to increase the yield of the desired complexes. The addition of KBr at the end of the reaction is in order to form only the perbrominated complexes **16** and **17**. In the ^{13}C NMR spectrum, the carbene signals are observed as doublets at $\delta = 175.8$ ppm (**16**) and 176.9 ppm (**17**) with coupling constants of $^1J_{Rh,C} = 34.1$ Hz (**16**) and 33.9 Hz (**17**). The chemical shift of the carbene is very similar to the *n*-butyl substituted complex synthesized by Poyatos et al. in 2003 [27].

Monosubstituted carbene complexes of rhodium and iridium are known now from nearly every carbene type. The variety of such complexes is nowadays enormous and varies from the classical Öfele-Wanzlick-Arduengo carbenes [35], (NHCs) [17,21,23,25,28,29,34,36–38], to acyclic varieties [39,40] and alternative carbene derivatives [41,42].

To form mono carbene rhodium and iridium (COD) complexes three different synthesis routes are well established (Schemes 4 and 6). First the reaction of a free carbene with the dimeric precursor $[M(COD)Cl]_2$ (M = Rh, Ir) (Scheme 4a). This method is used for bulky substituents such as adamantyl or *tert*-butyl groups in 1,3-position of cyclic azolin-2-ylidene and acyclic carbenes to give monosubstituted carbene rhodium complexes by cleaving the

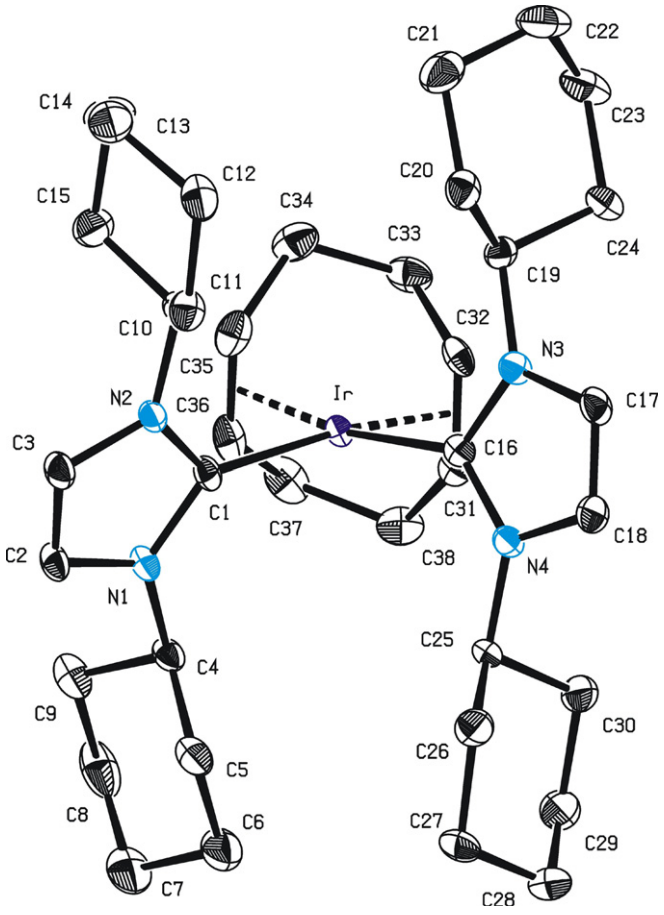


Fig. 2. ORTEP style plot of the cationic part of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ir–C1 2.074(4), Ir–C16 2.076(3), Ir–C31 2.161(3), Ir–C32 2.206(3), Ir–C35 2.171(3), Ir–C36 2.200(4), N1–C1 1.368(5), N1–C2 1.384(4), N1–C4 1.471(5), N2–C1 1.369(4), N2–C3 1.388(5), N2–C10 1.473(5), N3–C16 1.366(5), N3–C17 1.382(4), N3–C19 1.468(5), N4–C16 1.363(4), N4–C18 1.393(5), N4–C25 1.471(5); C1–Ir–C16 97.9(1), Ir–C1–N1 124.7(2), Ir–C1–N2 131.1(3), N1–C1–N2 103.5(3), Ir–C16–N3 124.7(2), Ir–C16–N4 131.2(3), N3–C16–N4 103.8(3).

chloro bridge of the dimeric COD complexes during the reaction [28,36,37,39]. Applying imidazolium alcoholate precursors, (Scheme 4b) preparation is very similar to the synthesis of the analogous biscarbene complexes [25].

According to a synthetic route from Denk and Herrmann, where the first metal-complex of rhodium and iridium with an acyclic carbene was synthesized [39], we attempted to increase the variety of this type of complexes with a similar acyclic carbene. The deprotonation of **27** to form the free acyclic carbene **28** was performed according to a procedure published by Alder et al. where LDA (lithiumdiisopropylamide) was used for deprotonation (Scheme 5) [43]. Complex **25** was first published by our group [40] and was prepared according to a procedure published recently [44].

The third preparation pathway for mono carbene substituted COD complexes was used for the iridium complexes **22** and **24** via a silver intermediate [45]. The use of silver

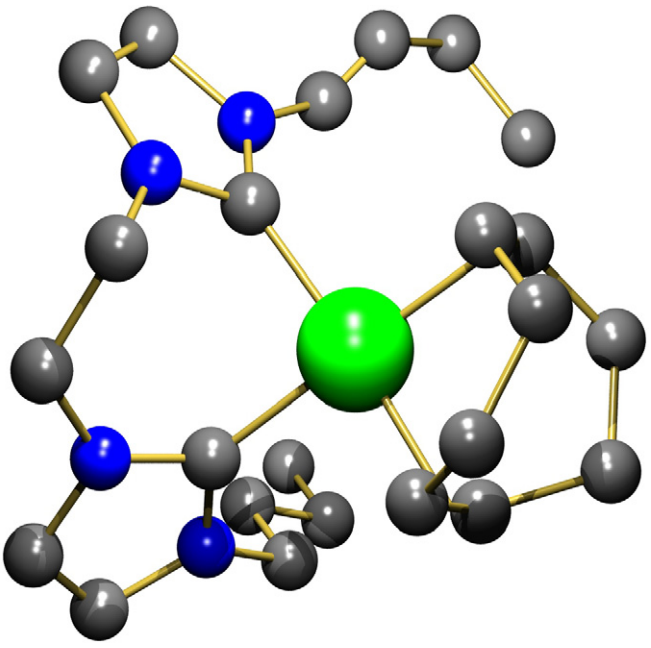


Fig. 3. Ball and stick model of the cationic part of compound **12** in the solid state (for details see Ref. [32b]).

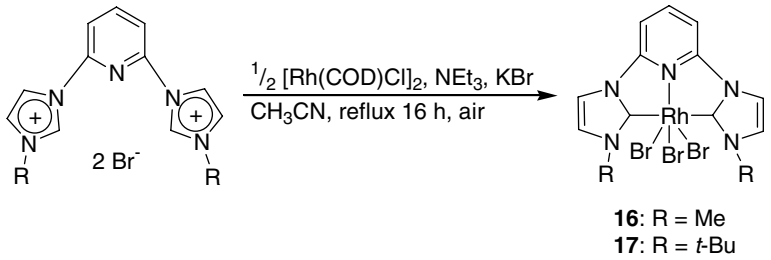
carbene complexes as carbene transfer reagents has proven to be an effective method for the synthesis of other transition metal carbene complexes (Scheme 6) [38,45,46].

The imidazolium salts were treated with Ag_2O at room temperature to form the corresponding silver carbene complexes. The reaction of the silver salts with $[Ir(COD)Cl]_2$ at room temperature readily gave the desired yellow metal carbene complexes **22** and **24**.

A summary of the prepared mono carbene rhodium and iridium complexes is shown in Table 3.

The corresponding carbonyl substituted rhodium and iridium complexes **29**–**32** were obtained by passing carbon monoxide through a dichloromethane solution of the COD substituted complexes **18**, **21**, **22**, **24** at room temperature (Scheme 7). The products **29**–**32** were formed within 30 min, evidenced by a color change from light to dark yellow. Due to the strong donor capability of the NHC ligands the cyclooctadiene ligand can be completely substituted by stronger acceptor ligands such as carbon monoxide [28].

The *cis*-conformation of the carbonyl ligands in complexes **29**–**32** was consistently indicated by IR- and NMR-spectra. The IR spectra exhibit two strong ν(CO)-bands. The ^{13}C NMR-spectra contain three signals between $\delta = 167$ and 187 ppm, two for the carbonyl and one for the carbene-carbons. All carbonyl complexes are air-stable in the solid state, but decompose in solution under air within some hours. They are all soluble in polar solvents such as chloroform, dichloromethane, DMSO, and THF and less soluble in less polar solvents such as diethyl ether, *n*-hexane or *n*-pentane. The CO-stretching frequencies of each complex were recorded in dichloromethane solution and are listed in Table 4.



Scheme 3. Synthesis of biscarbene substituted rhodium(III) complexes.

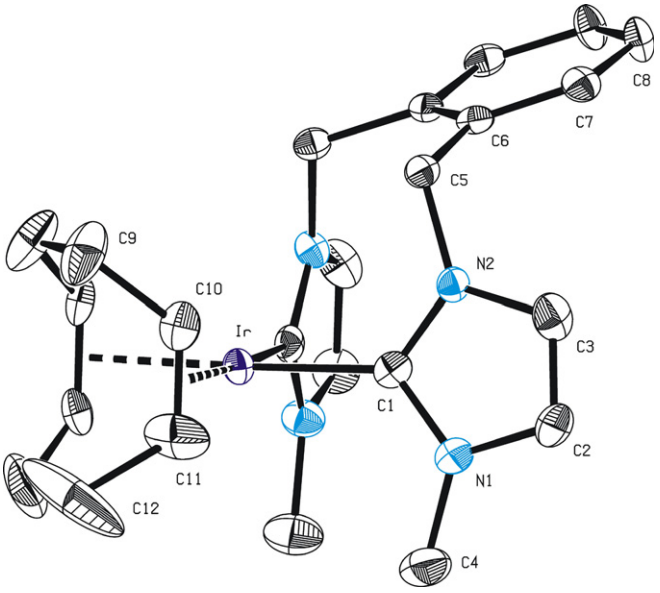
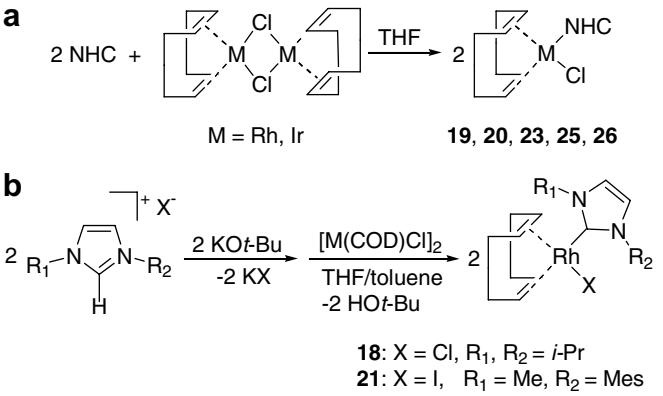


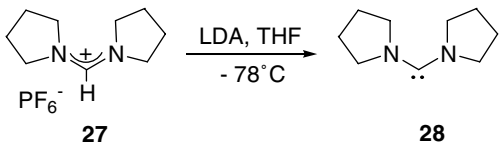
Fig. 4. ORTEP style plot of the cationic part of compound **14** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ir–C1 2.044(5), Ir–C10 2.190(5), Ir–C11 2.191(4), N1–C1 1.342(6), N1–C2 1.399(7), N1–C4 1.458(6), N2–C1 1.343(5), N2–C3 1.386(6), N2–C5 1.469(6); C1–Ir–C1_a 92.1(2), Ir–C1–N1 127.8(3), Ir–C1–N2 127.0(3), N1–C1–N2 105.1(4). Symmetry operation to equivalent atom positions _a: $-x, y, z$.

The relevant IR data differ for each metal only by five wave numbers and correlate very well with further published results for imidazolin-2-ylidene complexes [44]. Also the chemical shifts of the carbene carbons are in the expected range, as mentioned before for such complexes [21,25,28,29,36,38a,39,42].

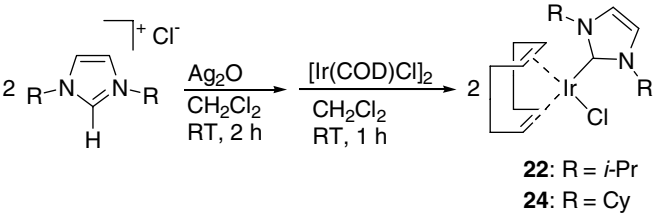
For catalytic experiments we used the complexes **1**, **4**, **8**, **12** and **14** as catalysts [19]. The catalytically active systems (**1a**, **4a**, **8a**, **12a**, **14a**) were generated by exchange of the coordinating anions with the non-coordinating trifluoroacetate (TFA) (Scheme 8). The aromatic substrate was used as solvent and for the boron source pinacolborane was selected for several reasons: when bis(pinacolato)diborane is used, only one boron equivalent is converted to the



Scheme 4. Synthesis of monocarbene substituted iridium and rhodium complexes.



Scheme 5. Preparation of the free acyclic carbene **28**.

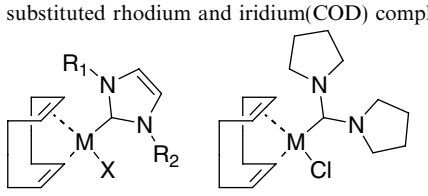


Scheme 6. Synthesis of monosubstituted NHC–Iridium complexes using the silver transmetalation route.

Table 2
Selected bond distances (Å) bond and torsion angles (°) for the complexes **1**, **4**, **12** and **14**

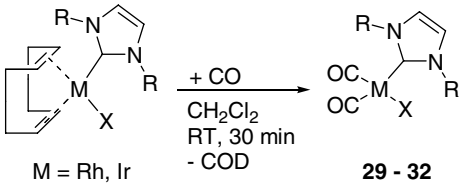
Complex	Ir–$C_{carbene}$ (Å)	N–$C_{carbene}$–N (°)	$C_{carbene}$–Ir–$C_{carbene}$ (°)
1	2.03 2.08	103.5 106.8	93.4
4	2.074(4) 2.076(3)	103.5(3) 103.8(3)	97.9(1)
12	2.02 2.04	103.6 104.5	85.4
14	2.044(5) 2.044(5)	105.1(4) 105.1(4)	92.1(2)

Table 3
Monocarbene substituted rhodium and iridium(COD) complexes



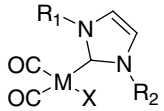
18-24 **25, 26**

Complex	M	R^1	R^2	X	Yield (%)	$\delta C_{carbene}$ (ppm)
18	Rh	*i*-Pr	*i*-Pr	Cl	73	179.9
19	Rh	*t*-Bu	*t*-Bu	Cl	38	177.9
20	Rh	Ad	Ad	Cl	69	183.0
21	Rh	Me	Mes	I	71	182.1
22	Ir	*i*-Pr	*i*-Pr	Cl	66	177.9
23	Ir	*t*-Bu	*t*-Bu	Cl	41	179.8
24	Ir	Cy	Cy	Cl	73	178.1
25	Rh	–	–	Cl	49	216.2
26	Ir	–	–	Cl	53	214.7



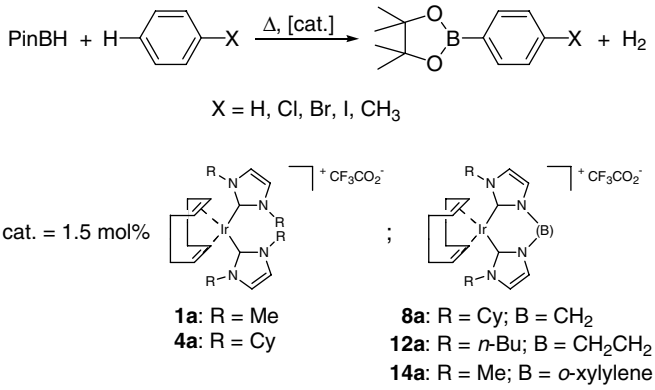
Scheme 7. Synthesis of monocarbene substituted iridium and rhodium carbonyl complexes.

Table 4
Monocarbene substituted iridium and rhodium carbonyl complexes



Complex	M	R^1	R^2	X	ν(CO) sym.	ν(CO) asym.	Yield (%)	$\delta C_{carbene}$ (ppm)
29	Rh	*i*-Pr	*i*-Pr	Cl	2078	1997	95	170.2
30	Rh	Me	Mes	I	2073	2000	91	174.3
31	Ir	*i*-Pr	*i*-Pr	Cl	2066	1982	93	171.0
32	Ir	Cy	Cy	Cl	2064	1982	94	171.2

favored product, however bis(pinacolato)diborane is much more expensive than pinacolborane. The latter offers easy accessibility from the inexpensive reducing agent sodium borohydride. Identification of the formed products and the yield rates was possible by GC-MS. The results of our experiments are presented in Scheme 8 and Table 5. It soon appeared during the conversion of benzene that the desired product was obtained in high selectivity; in this case phenylboronic acid pinacol ester was detected as the



Scheme 8. Borylation of benzene derivatives with biscarbene iridium complexes.

Table 5
Conversion of aryls with pinacolborane to the corresponding arylboronic acids

Complex	Entry	Aryl	Cat. (mol%)	*T* (°C)	*t* (h)	Yield (%)
1a, **12a**, **14a**	1	Benzene	1.5	40	12	100
	2	Toluene	1.5	40	12	100
	3	Chlorobenzene	1.5	40	12	100
	4	Bromobenzene	1.5	40	12	100
	5	Iodobenzene	1.5	40	12	100
4a	6	Benzene	1.0	40	10	100
	7	Toluene	1.0	40	10	100
	8	Chlorobenzene	1.0	40	10	100
	9	Bromobenzene	1.0	40	10	100
	10	Iodobenzene	1.0	40	10	100
	11	2-Chlorotoluene	1.0	40	10	92
	12	*ortho*-Xylene	1.0	40	10	93
8a	13	Benzene	1.5	45	9	100
	14	Toluene	1.5	45	9	100
	15	Chlorobenzene	1.5	45	9	100
	16	Bromobenzene	1.5	45	9	100
	17	Iodobenzene	1.5	45	9	100
14a	18	2-Chlorotoluene	1.5	40	12	90
	19	3-Chlorotoluene	1.5	40	12	89
	20	*ortho*-Xylene	1.5	40	12	94

only product after 10–12 h by full conversion, according to pinacolborane for all used catalysts (Table 5, Entries 1, 6, 13). When using toluene and halogen aromatics of conversions up to 100% were obtained.

Thus chloro-, bromo- and iodobenzene were also converted in good yields into the corresponding boronic acid ester (Table 5) [3a,47]. It became evident from the GC-MS-analysis that exclusive C–H activation took place while the C–X bonds were not attacked at all. Analogous reactions were performed with the corresponding rhodium complexes. Under the same conditions which were used for the iridium complexes, no conversion of pinacolborane could be detected within 12 h with benzene, toluene, chloro- or bromobenzene by using the corresponding rhodium complexes. However, it should be mentioned that in

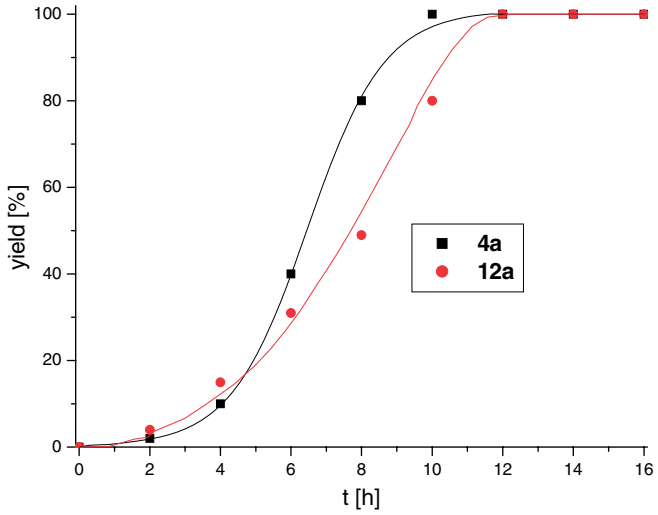


Fig. 5. Catalytic borylation of benzene with pinacolborane at 40 °C applying iridium complexes **4a** and **12a**.

the last two cases again the C–X bonds were not attacked during the reactions.

In Fig. 5 the catalytic properties of complexes **4a** and **12a** are monitored in the borylation reaction of benzene with pinacolborane. Compared to complex **12a**, complex **4a** has a much more intense induction period. Both complexes show a full conversion after 12 h.

3. Conclusion

We were able to show that *N*-heterocyclic carbene complexes of iridium(I) show significant catalytic performance in the direct borylation of arenes. This is in accordance with the previous observation that complexes with strong donor ligands provide good catalytic activities in this reaction [3]. GC-MS analysis revealed that the reaction occurs with high chemo-selectivity via activation of a C–H bond while C–X bonds are not attacked. Furthermore, high regioselectivity is observed, since only one borylated product is detected. This is the first example for the application of *N*-heterocyclic carbene complexes in the catalytic activation and functionalization of aromatic C–H-bonds. Currently, the further use of various *N*-heterocyclic carbene complexes and substrates is under investigation in our laboratory. From these initial results it seems possible that other functionalized arylboronicacid esters will be accessible via this one-pot-synthesis.

4. Experimental

4.1. General comments

The imidazolium salts [48] and the corresponding carbenes were prepared according to the reported procedures. The formamidinium salt **27** was prepared according to the literature [49]. The metal dimer precursors $[M(COD)Cl]_2$ (M = Rh, Ir) were synthesized as reported in the literature [25,50]. The silver carbene complexes were prepared according to the literature [51].

All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at room temperature and referenced to the residual ^1H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. IR spectra were recorded on a FTS 575C BIO-RAD or Jasco 460 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using the CI or FAB technique. Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli).

4.2. 1,1′-Di-tert-butyl-3,3′-ethylene-diimidazolium dibromide (*33*)

Tert-butylimidazole (6.25 g, 50 mmol), 1,2-dibromoethane (4.69 g, 25 mmol) and 5 mL THF were heated in an ACE pressure-tube under reflux conditions for 48 h. The light yellow precipitate was collected by filtration and washed three times with 5 mL THF. The hygroscopic solid can be recrystallized from a dichloromethane solution to give pure **33**. Yield: 9.26 g (85%). mp: 262 °C (dec.). IR (KBr): 3131, 3092, 2976, 2883, 2083, 1749, 1636, 1552, 1474, 1407, 1378, 1335, 1317, 1288, 1239, 1205, 1132, 846, 762, 689, 657, 635, 566, 489, 460 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.51$ (s, 2H, NCHN), 7.12 (s, 2H, NCHCHN), 6.75 (s, 2H, NCHCHN), 3.84 (s, 4H, NCH_2CH_2N), 1.59 (s, 18H, $NC(CH_3)_3$). ^{13}C NMR (100.5 MHz, DMSO-d_6): $\delta = 135.3$ (NCHN), 122.8, 120.5 (NCHCHN), 59.8 (NCH_2CH_2N), 48.4 ($NC(CH_3)_3$), 28.9 ($NC(CH_3)_3$). MS (FAB): $m/z = 355.3$ [M^+], 275.3 [M^{2+}]. Anal. Calc. for $C_{16}H_{28}N_4Br_2$ (436.23): C, 44.05; H, 6.47; N, 12.84. Found: C, 43.81; H, 6.45; N, 12.69%.

4.3. Di-N-pyrrolidylmethylidene (*28*)

A suspension of 1.2 mmol pyrrolidine-1-ylmethylidene-pyrrolidinium hexafluorophosphate (**27**) in 10 mL THF was mixed at −78 °C with a solution of 1.2 mmol LDA in 5 mL THF. After removing the cooling bath the solution was stirred for 45 min at ambient temperature. A clear light yellow solution was observed. All volatile components were removed in high vacuo. Afterwards the residual solid was extracted three times with 15 mL *n*-hexane. After removing the solvent in vacuo and sublimation the free carbene was received as a colorless crystalline solid. Yield: 138 mg (75%). ^1H NMR (C_6D_6): $\delta = 3.05$ (s, 4H, NCH_2), 2.60 (s, 4H, NCH_2), 1.76 (s, 4H, CH_2), 1.25 (s, 4H, CH_2). ^{13}C NMR (C_6D_6): $\delta = 241.9$ (s,

N*C*N), 49.6 (s, NCH_2), 32.9 (s, NCH_2), 25.9 (s, CH_2), 24.0 (s, CH_2).

4.4. General procedure for the preparation of biscarbene complexes

NaH (55 mg, 2.29 mmol) was dissolved in 10 mL ethanol and slowly added to a suspension of 0.34 mmol $[M(COD)Cl]_2$ (M = Rh, Ir) in 15 mL ethanol. The reaction mixture was stirred for 30 min at room temperature and 1.70 mmol of the imidazolium salt was added. After stirring between 90 min and 72 h at room temperature the solvent was reduced in vacuo. The solid was washed twice with 5 mL ice-cold diethyl ether. The complexes can be recrystallized from a dichloromethane/*n*-hexane solution.

4.4.1. (η^4-1,5-cyclooctadiene)bis(1,3-dimethylimidazolin-2-ylidene)iridium(I) iodide (**1**)

Yield: 91 mg (86%). ^{1}H NMR ($CDCl_3$): $\delta = 7.06$ (s, 4H, NC*H*C*H*N), 3.94 (s, 12H, NCH_3), 3.77 (s, 4H, COD_{vinyl}), 2.29 (m, 4H, COD_{allyl}), 1.94 (m, 4H, COD_{allyl}). ^{13}C NMR ($CDCl_3$): $\delta = 177.0$ (N*C*N), 123.1 (N*C*H*C*HN), 76.7 (COD_{vinyl}), 38.3 (N*C*H_3), 30.9 (COD_{allyl}). MS (FAB) $m/z = 493$ (M^+). Anal. Calc. for $C_{18}H_{28}N_4IIr$ (619.57): C, 34.89; H, 4.56; N, 9.04. Found: C, 35.39; H, 4.82; N, 8.96%.

4.4.2. (η^4-1,5-cyclooctadiene)bis(1,3-tert-butylimidazolin-2-ylidene)rhodium(I) chloride (**2**)

Yield: 72 mg (70%). ^{1}H NMR (DMSO-d_6): $\delta = 7.73$ (s, 4H, NC*H*C*H*N), 4.26 (s, 4H, COD_{vinyl}), 3.28 (m, 8H, COD_{allyl}), 1.85 (m, 36H, C(CH_3)). ^{13}C NMR (DMSO-d_6): $\delta = 180.1$ (N*C*N), 121.6 (N*C*H*C*HN), 60.5 (COD_{vinyl}), 56.8 (*C*$(CH_3)_3$), 30.0 (COD_{allyl}), 19.6 (C(*C*$H_3)_3$). Anal. Calc. for $C_{30}H_{52}N_4ClRh$ (607.12): C, 59.35; H, 8.63; N, 9.23. Found: C, 60.23; H, 8.92; N, 9.87%.

4.4.3. (η^4-1,5-cyclooctadiene)bis(1,3-tert-butylimidazolin-2-ylidene)iridium(I) chloride (**3**)

Yield: 80 mg (67%). ^{1}H NMR (DMSO-d_6): $\delta = 7.98$ (s, 4H, NC*H*C*H*N), 4.30 (m, 4H, COD_{vinyl}), 3.38 (s, 8H, COD_{allyl}), 1.91 (m, 36H, C(CH_3)). ^{13}C NMR (DMSO-d_6): $\delta = 174.5$ (N*C*N), 120.4 (N*C*H*C*HN), 59.6 (COD_{vinyl}), 55.9 (*C*$(CH_3)_3$), 29.1 (COD_{allyl}), 18.6 (C(*C*$H_3)_3$). Anal. Calc. for $C_{30}H_{52}N_4ClIr$ (696.43): C, 51.74; H, 7.53; N, 8.04. Found: C, 51.95; H, 7.82; N, 8.59%.

4.4.4. (η^4-1,5-cyclooctadiene)bis(1,3-dicyclohexylimidazolin-2-ylidene)iridium(I) chloride (**4**)

Yield: 93 mg (68%). ^{1}H NMR ($CDCl_3$): $\delta = 7.15$ (s, 4H, NC*H*C*H*N), 5.70 (s, 2H, CH_{Cy}), 5.30 (s, 2H, CH_{Cy}), 4.89 (br, 4H, COD_{vinyl}), 3.67 (br, 8H, COD_{allyl}), 2.26–1.94 (m, 32H, C$H_{2,Cy}$), 1.43 (m, 8H, C$H_{2,Cy}$). ^{13}C NMR ($CDCl_3$): $\delta = 173.9$ (N*C*N), 119.6 (N*C*H*C*HN), 73.9 (COD_{vinyl}), 59.7 (NCH_{Cy}), 33.7 (COD_{allyl}), 32.3 (COD_{allyl}), 25.6, 25.3, 24.8 (*C*$H_{2,Cy}$). MS (FAB) $m/z = 765.6$ (M^+). Anal. Calc. for $C_{38}H_{60}N_4ClIr$ (800.58): C, 57.01; H, 7.55; N, 7.00. Found: C, 56.62; H, 7.48; N, 6.65%.

4.5. Preparation of chelating biscarbene complexes

NaH (40 mg, 1.70 mmol) was dissolved in 10 mL ethanol and slowly added to a suspension of 0.34 mmol $[M(COD)Cl]_2$ (M = Rh, Ir) in 10 mL ethanol. The reaction mixture was stirred for 30 min at room temperature and 0.85 mmol of the bis(imidazolium) salt was added. After stirring for 48–72 h at room temperature the solvent was removed in vacuo. The solid was washed twice with 10 mL ice-cold diethyl ether.

4.5.1. (η^4-1,5-cyclooctadiene)(1,1′-diethyl-3,3′-methylene-diimidazolin-2,2′-diylidene)rhodium(I) iodide (**5**)

Yield: 44 mg (48%). ^{1}H NMR (DMSO-d_6): $\delta = 8.12$ (s, 4H, NC*H*C*H*N), 6.23 (br, 2H, NCH_2N), 4.03 (br, 4H, COD_{vinyl}), 4.32 (d, 4H, NCH_2), 3.07 (br, 8H, COD_{allyl}), 1.41 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): $\delta = 179.9$ (N*C*N), 122.8 (N*C*H*C*HN), 75.4 (COD_{vinyl}), 59.7 (N*C*H_2N), 44.6 (N*C*H_2), 34.4 (COD_{allyl}), 14.5 (*C*H_3).

4.5.2. (η^4-1,5-cyclooctadiene)(1,1′-diethyl-3,3′-methylene-diimidazolin-2,2′-diylidene)iridium(I) iodide (**6**)

Yield: 55 mg (52%). ^{1}H NMR (DMSO-d_6): $\delta = 7.89$ (s, 4H, NC*H*C*H*N), 6.43 (br, 2H, NCH_2N), 4.21 (br, 4H, COD_{vinyl}), 4.04 (d, 4H, NCH_2), 3.12 (br, 8H, COD_{allyl}), 1.62 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): $\delta = 173.7$ (N*C*N), 122.1 (N*C*H*C*HN), 75.9 (COD_{vinyl}), 59.5 (N*C*H_2N), 44.4 (N*C*H_2), 34.3 (COD_{allyl}), 13.1 (CH_3). Anal. Calc. for $C_{19}H_{28}N_4IIr$ (631.57): C, 36.13; H, 4.47; N, 8.87. Found: C, 36.91; H, 4.58; N, 9.37%.

4.5.3. (η^4-1,5-cyclooctadiene)(1,1′-dicyclohexyl-3,3′-methylene-diimidazolin-2,2′-diylidene)rhodium(I) iodide (**7**)

Yield: 78 mg (71%). ^{1}H NMR (DMSO-d_6): $\delta = 8.32$ (s, 4H, NC*H*C*H*N), 6.04 (s, 2H, NCH_2N), 5.72 (br, 2H, CH_{Cy}), 4.11 (br, 4H, COD_{vinyl}), 3.10 (br, 8H, COD_{allyl}), 2.04 (m, 16H, C$H_{2,Cy}$), 1.14 (m, 4H, C$H_{2,Cy}$). ^{13}C NMR (DMSO-d_6): $\delta = 182.0$ (N*C*N), 123.2 (N*C*H*C*HN), 74.4 (COD_{vinyl}), 60.2 (N*C*H_2N), 55.1, 54.2 (N*C*H_{Cy}), 34.2 (COD_{allyl}), 25.0, 24.6, 23.8 ($CH_{2,Cy}$).

4.5.4. (η^4-1,5-cyclooctadiene)(1,1′-dicyclohexyl-3,3′-methylene-diimidazolin-2,2′-diylidene)iridium(I) iodide (**8**)

Yield: 95 mg (75%). ^{1}H NMR (DMSO-d_6): $\delta = 8.53$ (s, 4 H, NC*H*C*H*N), 6.19 (s, 2H, NCH_2N), 6.03 (br, 2H, CH_{Cy}), 4.36 (br, 4H, COD_{vinyl}), 3.26 (br, 8H, COD_{allyl}), 2.31 (m, 16H, C$H_{2,Cy}$), 1.57 (m, 4H, C$H_{2,Cy}$). ^{13}C NMR (DMSO-d_6): $\delta = 174.2$ (N*C*N), 123.7 (N*C*H*C*HN), 74.8 (COD_{vinyl}), 60.3 (N*C*H_2N), 55.9, 55.8 (NCH_{Cy}), 34.8 (COD_{allyl}), 25.3, 25.0, 24.8 (*C*$H_{2,Cy}$). Anal. Calc. for $C_{27}H_{40}N_4IIr$ (739.75): C, 43.84; H, 5.45; N, 7.57. Found: C, 44.12; H, 5.86; N, 7.97%.

4.5.5. (η^4-1,5-cyclooctadiene)(1,1′-dimethyl-3,3′-ethylene-diimidazolin-2,2′-diylidene)rhodium(I) bromide (**9**)

Yield: 124 mg (57%). ^{1}H NMR (DMSO-d_6): $\delta = 7.39$ (s, 2H, NC*H*C*H*N), 6.92 (s, 2H, NC*H*C*H*N), 5.92 (s, 4H,

NCH_2CH_2N), 4.42 (s, 2H, COD_{vinyl}), 4.28 (s, 2H, COD_{vinyl}), 3.86 (s, 6H, NCH_3), 2.32 (m, 8H, COD_{allyl}). ^{13}C NMR (DMSO-d_6): $\delta = 178.4$ (d, $^1J =$ 49.0 Hz, N*C*N), 124.2, 123.8 (N*C*H*C*HN), 66.5, 65.1 (COD_{vinyl}), 38.6 (NCH_3), 32.6 (NCH_2*C*H_2N), 31.8, 31.5 (COD_{allyl}).

4.5.6. (η^4-1,5-cyclooctadiene)(1,1′-di-tert-butyl-3,3′-ethylene-diimidazolin-2,2′-diylidene)rhodium(I) bromide (**10**)

Yield: 71 mg (74%). ^{1}H NMR (DMSO-d_6): $\delta = 7.29$ (s, 2H, NC*H*C*H*N), 6.86 (s, 2H, NC*H*C*H*N), 5.41 (s, 4H, NCH_2CH_2N), 4.57 (s, 2H, COD_{vinyl}), 4.34 (s, 2H, COD_{vinyl}), 2.48 (m, 8H, COD_{allyl}), 1.03 (s, 18H, NC(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): $\delta = 180.0$ (d, $^1J_{Rh-C} =$ 52.0 Hz, N*C*N), 126.4, 126.1 (N*C*H*C*HN), 67.0, 64.9 (COD_{vinyl}), 55.9 (N*C*(CH$_3$)$_3$), 31.4 (NCH_2*C*H_2N), 31.2, 31.1 (COD_{allyl}), 18.6 (s, NC(*C*H$_3$)$_3$). Anal. Calc. for $C_{24}H_{38}N_4BrRh$ (565.39): C, 50.98; H, 6.77; N, 9.91. Found: C, 51.31; H, 6.89; N, 10.12%.

4.5.7. (η^4-1,5-cyclooctadiene)(1,1′-di-tert-butyl-3,3′-ethylene-diimidazolin-2,2′-diylidene)iridium(I) bromide (**11**)

Yield: 88 mg (79%). ^{1}H NMR (DMSO-d_6): $\delta = 7.84$ (s, 2H, NC*H*C*H*N), 6.95 (s, 2H, NC*H*C*H*N), 5.62 (s, 2H, NCH_2CH_2N), 5.51 (s, 2H, NCH_2CH_2N), 4.58 (s, 2H, COD_{vinyl}), 4.12 (s, 2H, COD_{vinyl}), 1.39 (s, 8H, COD_{allyl}), 0.98 (s, 18H, NC(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): $\delta = 175.1$ (s, N*C*N), 126.1, 125.6 (N*C*H*C*HN), 66.4, 64.2 (s, COD_{vinyl}), 55.6 (NCH_2*C*H_2N), 31.0 (s, N*C*(CH$_3$)$_3$), 30.6, 30.1 (COD_{allyl}), 18.2 (s, NC(*C*H$_3$)$_3$).

4.5.8. (η^4-1,5-cyclooctadiene)(1,1′-di-n-butyl-3,3′-ethylene-diimidazolin-2,2′-diylidene)iridium(I) bromide (**12**)

Yield: 102 mg (92%). ^{1}H NMR (CD_2Cl_2): $\delta = 6.97$ (s, 4H, NC*H*C*H*N), 4.85 (m, 4H, COD_{vinyl}), 4.30 (m, 4H, NCH_2CH_2N), 4.19 (4H, NCH_2(CH$_2$)$_2$CH$_3$), 2.38 (m, 4H, COD_{allyl}), 2.21 (m, 4H, COD_{allyl}), 1.74 (m, 8H, NCH$_2$(CH_2)$_2$CH$_3$), 1.02 (m, 6H, CH_3). ^{13}C NMR (CD_2Cl_2): $\delta = 175.0$ (N*C*N), 124.1, 123.5, 122.1, 120.4 (N*C*H*C*HN), 77.2, 73.5 (s, COD_{vinyl}), 50.1, 48.2 (N*C*H$_2$*C*H$_2$N), 33.7 (s, N*C*H$_2$(CH$_2$)$_2$CH$_3$), 31.9, 31.3 (s, COD_{allyl}), 20.0, 19.6 (s, NCH$_2$(*C*H$_2$)$_2$CH$_3$), 13.4 (s, CH$_3$). Anal. Calc. for $C_{24}H_{38}N_4BrIr$ (654.72): C, 44.03; H, 5.85; N, 8.56. Found: C, 44.34; H, 6.09; N, 8.95%.

4.5.9. (η^4-1,5-cyclooctadiene)(1,1′-dimethyl-3,3′-o-xylylene-diimidazolin-2,2′-diylidene)iridium(I) bromide (**14**)

Yield: 78 mg (71%). ^{1}H NMR (DMSO-d_6): $\delta = 6.83$ (m, 2H, C*H*), 6.61 (s, 2H, NC*H*C*H*N), 6.40 (m, 2H, C*H*), 6.22 (s, 2H, NC*H*C*H*N), 5.29 (s, 2H, NCH_2), 5.26 (s, 2H, NCH_2), 4.13 (s, 2H, C*H*, COD_{vinyl}), 4.09 (s, 2H, C*H*, COD_{vinyl}), 2.89 (s, 3H, NCH_3), 2.79 (s, 3H, NCH_3), 1.49 (m, 4H, COD_{allyl}), 0.89 (m, 4H, COD_{allyl}). ^{13}C NMR (DMSO-d_6): $\delta = 175.9$ (N*C*N), 135.4, 131.7, 129.1, 123.3, 120.9 (N*C*H*C*HN, C_{Ar}), 76.4, 74.9 (COD_{vinyl}), 49.8 (NCH$_2$), 37.2 (NCH_3), 30.8, 30.7 (s, COD_{allyl}). MS (FAB) $m/z = 567.3$ (M^+). Anal. Calc. for $C_{24}H_{30}N_4BrIr$ (646.65): C, 44.58; H, 4.68; N, 8.66. Found: C, 44.64; H, 5.03; N, 8.79%.

4.5.10. (η^4-1,5-cyclooctadiene)(1,1′-dimethyl-3,3′-o-xylylene-diimidazolin-2,2′-diylidene)iridium(I) hexafluorophosphate (**15**)

The anion was exchanged by addition of 1.4 equiv. NH_4PF_6 into the solution of complex **14** in CH_2Cl_2. The desired complex **15** was filtered and dried in vacuo.

Yield: 86 mg (71%). ^{1}H NMR (DMSO-d_6): $\delta = 6.85$ (m, 2H, C*H*), 6.64 (s, 2H, NC*H*C*H*N), 6.42 (m, 2H, C*H*), 6.23 (s, 2H, NC*H*C*H*N), 5.31 (s, 2H, NCH$_2$), 5.28 (s, 2H, NCH_2), 4.17 (s, 2H, COD_{vinyl}), 4.13 (s, 2H, COD_{vinyl}), 2.91 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 1.51 (m, 4H, COD_{allyl}), 0.72 (m, 4H, COD_{allyl}). ^{13}C NMR (DMSO-d_6): $\delta = 175.7$ (N*C*N), 135.4, 131.7, 129.1, 123.3, 120.9 (N*C*H*C*HN, C_{Ar}), 76.4, 74.9 (s, COD_{vinyl}), 49.9 (NCH$_2$), 37.2 (NCH_3), 30.8, 30.7 (s, COD_{allyl}). Anal. Calc. for $C_{24}H_{30}N_4IrPF_6$(711.70): C, 40.50; H, 4.25; N, 7.87. Found: C, 40.87; H, 4.62; N, 7.93%.

4.6. Preparation of rhodium(III) complexes **16** and **17**

A mixture of $[Rh(COD)Cl]_2$ (100 mg, 0.21 mmol), 2 equiv. of the corresponding imidazolium salt (0.41 mmol), KBr (150 mg, 1.25 mmol) and NEt_3 (0.25 mL, 1.8 mmol) were refluxed in 7.5 mL acetonitrile for 12 h. The mixture was aerated several times during the reaction. The reaction mixture was filtered and the solvent of the filtrate was removed in vacuo. The resulting solid was purified via column chromatography. Elution with methylenechloride afforded the separation of $[Rh(COD)Cl]_2$. The product was obtained by further elution with a gradient of methylenechloride/acetone (5:1).

4.6.1. (1,1′-Di-methyl-3,3′-pyrimidinyldiimidazolin-2,2′-diylidene)rhodium(III) bromide (**16**)

Yield: 122 mg (51%). ^{1}H NMR (DMSO-d_6): $\delta = 8.48$ (t, $^3J_{H,H} = 8.1$ Hz, 1H, pyridine-*H*), 8.30 (d, $^3J_{H,H} = 2.3$ Hz, 2H, NC*H*), 7.98 (d, $^3J_{H,H} = 8.1$ Hz, 2H, pyridine-*H*), 7.71 (d, $^3J_{H,H} = 2.3$ Hz, 2H, NC*H*), 3.85 (s, 6H, NCH_3). ^{13}C NMR (DMSO-d_6): $\delta = 176.9$ (d, $^1J_{Rh,C} = 34.1$ Hz, N*C*N), 150.1 (C-*ipso*), 146.7 (C-*ortho*), 126.2 (N*C*H), 117.7 (C-*meta*), 109.2 (N*C*H), 39.1 (NC*C*H$_3$).

4.6.2. (1,1′-Di-tert-butyl-3,3′-pyrimidinyldiimidazolin-2,2′-diylidene)rhodium(III) bromide (**17**)

Yield: 134 mg (49%). ^{1}H NMR (DMSO-d_6): $\delta = 8.53$ (t, $^3J_{H,H} = 7.9$ Hz, 1H, pyridine_*H*), 8.42 (d, $^3J_{H,H} = 1.8$ Hz, 2H, NC*H*), 8.01 (d, $^3J_{H,H} = 7.9$ Hz, 2H, pyridine_*H*), 7.82 (d, $^3J_{H,H} = 1.8$ Hz, 2H, NC*H*), 1.84 (s, 18H, NC(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): $\delta = 175.8$ (d, $^1J_{Rh,C} = 33.9$ Hz, N*C*N), 149.9 (C-*ipso*), 142.9 (C-*ortho*), 123.3 (N*C*H), 116.2 (C-*meta*), 108.1 (im-C), 62.8 (N*C*(CH$_3$)$_3$), 30.1 (NC(*C*H$_3$)$_3$).

4.7. Preparation of mono carbene substituted rhodium complexes

A solution of KO*t*-Bu (0.22 mmol, 2.2 equiv.) in THF (20 mL) was added dropwise to a stirred suspension of the imidazolium halide (0.22 mmol, 2.2 equiv.) in THF (30 mL) at room temperature. The azolium salt was slowly dissolved and the colour of the reaction mixture turned to light yellow. After stirring for 1 h at room temperature, $[Rh(COD)Cl]_2$ (50 mg, 0.1 mmol, 1.0 equiv.) in toluene (20 mL) was added. The reaction mixture was stirred at 80 °C for 1 h. After removing the volatile compounds in vacuo the product was extracted with *n*-hexane (3×10 mL) and dried in vacuo.

4.7.1. Chloro(η^4-1,5-cyclooctadiene)(1,3-di-isopropylimidazolin-2-ylidene)rhodium(I) (**18**)

Yield: 58 mg (73%). ^{1}H NMR ($CDCl_3$): $\delta = 6.86$ (s, 2H, NC*H*C*H*N), 5.73 (sept., $^3J_{H,H} = 6.8$ Hz, 2H, C*H*(CH_3)$_2$), 4.98 (br, 2H, COD_{vinyl}), 3.30 (br, 2H, COD_{vinyl}), 2.36 (m, 4H, COD_{allyl}), 1.91 (m, 4H, COD_{allyl}), 1.47 (t, $^3J_{H,H} = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$). ^{1}H NMR (DMSO-d_6): $\delta = 7.02$ (s, 2H, NC*H*C*H*N), 5.12 (br, 2H, COD_{vinyl}), 4.99 (m, 2H, C*H*(CH_3)$_2$), 4.67 (s, 2H, COD_{vinyl}), 2.16 (m, 4H, COD_{allyl}), 1.43 (d, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 179.9$ (d, $^1J_{Rh-C} = 50.8$ Hz, N*C*N), 116.8 (s, N*C*H*C*HN), 98.0 (d, $^1J_{Rh-C} = 8.8$ Hz, COD_{vinyl}), 67.5 (d, $^1J_{Rh-C} = 14.6$ Hz, COD_{vinyl}), 52.6 (*C*H(CH_3)$_2$), 33.0, 29.8, 28.9 (COD_{allyl}), 24.3, 23.3 (CH(*C*H$_3$)$_2$). MS (FAB) *m*/*z* (%) = 397.6 (55, [M^+]), 362.7 (65, [M^+−Cl]), 320.7 (51, [M^+−(Cl + C_3H_7)]), 153.0 (100, [carbene]). Anal. Calc. for $C_{17}H_{28}N_2ClRh$ (398.78): C, 51.20; H, 7.08; N, 7.02. Found: C, 51.27; H, 7.00; N, 6.46%.

4.7.2. Iodo(η^4-1,5-cyclooctadiene)(1-mesityl-3-methylimidazolin-2-ylidene)rhodium(I) (**21**)

Yield: 76 mg (71%). ^{1}H NMR ($CDCl_3$): $\delta = 7.04$ (s, 1H, *m*-C*H*), 7.00 (d, $^3J_{H,H} = 2.0$ Hz, 1H, NCHC*H*N), 6.89 (s, 1H, *m*-CH), 6.75 (d, $^3J_{H,H} = 2.0$ Hz, 1H, NCHCHN), 5.10 (m, 1H, COD_{vinyl}), 4.97 (m, 1H, COD_{vinyl}), 3.65 (m, 1H, COD_{vinyl}), 3.21 (m, 1H, COD_{vinyl}), 4.19 (s, 3H, NC*H*$_3$), 2.55–2.32 (m, 2H, COD_{allyl}), 2.45 (s, 3H, *o*-C*H*$_3$), 2.36 (s, 3H, *o*-C*H*$_3$), 2.13–1.92 (m, 2H, COD_{allyl}), 1.82–1.61 (m, 2H, COD_{allyl}), 1.79 (s, 3H, *p*-CH_3), 1.44–1.35 (m, 2H, COD_{allyl}). ^{13}C NMR ($CDCl_3$): $\delta = 182.1$ (d, $^1J_{Rh-C} = 50.0$ Hz, N*C*N), 138.8, 137.1, 136.1, 134.6, 129.8, 128.2 (C_{Ar}), 123.9, 122.4 (N*C*H*C*HN), 95.3 (d, $^1J_{Rh-C} = 6.9$ Hz, COD_{vinyl}), 95.3 (d, $^1J_{Rh-C} = 8.6$ Hz, COD_{vinyl}), 71.1 (d, $^1J_{Rh-C} = 13.9$ Hz, COD_{vinyl}), 70.1 (d, $^1J_{Rh-C} = 13.9$ Hz, COD_{vinyl}), 40.4 (N*C*H$_3$), 34.3, 30.5, 30.4, 28.2 (COD_{allyl}), 21.9, 21.1 (*o*-CH_3), 17.9 (*p*-CH_3). MS (FAB) *m*/*z* (%) = 537.5 (6, [M^+]), 410.8 (88, [M^+−I]), 302.8 (19, [M^+−(I + COD)]), 201.1 (47, [carbene]), 147 (100). Anal. Calc. for $C_{21}H_{28}N_2IRh$ (538.27): C, 46.86; H, 5.24; N, 5.20. Found: C, 47.02; H, 5.49; N, 5.04%.

4.8. General preparation of iridium and rhodium complexes via the free carbene route

The free carbene (0.22 mmol) was added at −78 °C to a stirred solution of $[M(COD)Cl]_2$ (M = Rh, Ir)] (0.1 mmol) in anhydrous THF (15 mL). A colour change was observed from light to dark yellow for the rhodium complexes (iridium from light red to orange). After the reaction mixture was stirred for 6 h at room temperature, the solvent was removed in vacuo. The precipitate was washed twice with *n*-hexane and diethyl ether (10 mL). After the solvent was decanted, the resulting solid was dried in vacuo. The compounds are soluble in THF and DCM.

4.8.1. Chloro(η^4-1,5-cyclooctadiene)(1,3-di-tert-butylimidazolin-2-ylidene)rhodium(I) (**19**)

Yellow powder; Yield: 32 mg (38%). ^{1}H NMR ($CDCl_3$): $\delta =$ 7.10 (s, 2H, NC*H*C*H*N), 4.90 (br, 2H, COD_{vinyl}), 3.14 (br, 2H, COD_{vinyl}), 2.37 (m, 4H, COD_{allyl}), 1.80 (s, 18H, C(C*H*$_3$)), 1.71 (m, 4H, COD_{allyl}). ^{13}C NMR ($CDCl_3$): $\delta = 177.9$ (d, $^1J_{Rh-C} = 49.0$ Hz, N*C*N), 119.9 (N*C*H*C*HN), 92.7 (d, $^1J_{Rh-C} = 7.7$ Hz, COD_{vinyl}), 68.1 (d, $^1J_{Rh-C} = 15.4$ Hz, COD_{vinyl}), 59.3 (*C*(CH_3)$_3$), 32.9 (C(*C*H$_3$)$_3$), 32.2 (COD_{allyl}), 28.7 (COD_{allyl}). MS (FAB) *m*/*z* (%) = 425.8 (42, [M^+]), 390.8 (11, [M^+−Cl]), 281.9 (48, [M^+−COD]), 181.1 (100, [carbene]).

4.8.2. Chloro(η^4-1,5-cyclooctadiene)(1,3-diadamantylimidazolin-2-ylidene)rhodium(I) (**20**)

Yield: 137 mg (69%). ^{1}H NMR (DMSO-d_6): $\delta = 7.26$ (s, 2H, NC*H*CH*N*), 5.13 (br, 2H, COD_{vinyl}), 4.42 (s, 2H, COD_{vinyl}), 2.43 (m, 4H, COD_{allyl}), 2.01 (m, 4H, COD_{allyl}), 1.94 (d, 12H, (CH_2)$_{ad}$), 1.38 (m, 12H, (CH_2)$_{ad}$), 0.95 (m, 6H, (C*H*)$_{ad}$). ^{13}C NMR (DMSO-d_6): $\delta = 183.0$ (d, $^1J_{Rh-C} = 50.0$ Hz, N*C*N), 120.2 (s, N*C*H*C*HN), 96.1, 72.9 (COD_{vinyl}), 55.9 (N(*C*R$_3$)$_{ad}$), 44.9, 36.8, 30.9 (C_{ad}), 33.2, 30.1 (COD_{allyl}). MS (FAB) *m*/*z* = 547.5 (M^+).

4.8.3. Chloro(η^4-1,5-cyclooctadiene)(1,3-di-tert-butylimidazolin-2-ylidene)iridium(I) (**23**)

Yellow powder; Yield: 42 mg (41%). ^{1}H NMR ($CDCl_3$): $\delta = 7.13$ (s, 2H, NC*H*C*H*N), 4.50 (m, 2H, COD_{vinyl}), 2.72 (m, 2H, COD_{vinyl}), 2.18 (m, 4H, COD_{allyl}), 1.96 (s, 12H, C(CH_3)), 1.53 (m, 4H, COD_{allyl}). ^{13}C NMR ($CDCl_3$): $\delta = 179.8$ (N*C*N), 119.5 (N*C*H*C*HN), 78.1 (COD_{vinyl}), 59.1 (COD_{vinyl}), 51.3 (*C*(CH_3)$_3$), 33.4 (C(*C*H$_3$)$_3$), 32.8 (COD_{allyl}), 29.1 (COD_{allyl}). MS (FAB) *m*/*z* = 515.7 (M^+).

4.8.4. Chloro(η^4-1,5-cyclooctadiene)(di-N-pyrrolidylmethylylidene)rhodium(I) (**25**)

Yield: 39 mg (49%). ^{1}H NMR ($CDCl_3$): $\delta = 4.73$ (2H, COD_{vinyl}), 3.85 (2H, COD_{vinyl}), 3.59 (br, 4H, C*H*$_2$), 3.43 (br, 4H, C*H*$_2$), 3.36 (br, 4H, COD_{allyl}), 3.13 (2H, CH_2), 2.58 (2H, C*H*$_2$), 2.39 (br, 4H, COD_{allyl}), 1.76 (br s, 4H, C*H*$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 216.2$ (N*C*N), 96.1 (COD_{vinyl}), 89.6 (COD_{vinyl}), 47.5, 45.6 (*C*H$_2$N), 30.8, 24.5 (COD_{allyl}),

25.1 (CH_2). Anal. Calc. for $C_{17}H_{28}N_2ClRh$ (398.78): C, 51.20; H, 7.08; N, 7.02. Found: C, 51.63; H, 7.25; N, 7.41%.

4.8.5. Chloro(η^4-1,5-cyclooctadiene)(di-N-pyrrolidylmethylylidene)iridium(I) (**26**)

Yield: 52 mg (53%). ^{1}H NMR ($CDCl_3$): $\delta = 4.93$ (2H, COD_{vinyl}), 3.98 (2H, COD_{vinyl}), 3.86 (br, 4H, CH_2), 3.69 (br, 4H, CH_2), 3.62 (br, 4H, COD_{allyl}), 3.47 (2H, CH_2), 2.82 (2H, CH_2), 2.61 (br, 4H, COD_{allyl}), 1.88 (br s, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 214.7 (NCN), 96.3 (COD_{vinyl}), 88.3 (COD_{vinyl}), 47.7, 45.7 (CH_2N), 30.9 (COD_{allyl}), 25.3 (CH_2).

4.9. Preparation of complexes **22** and **24** via the corresponding silver carbene complexes

To a solution of the silver carbene complex (0.20 mmol) in 20 mL CH_2Cl_2, $[Rh(COD)Cl]_2$ (0.1 mmol) was added, the mixture was stirred for six hours at room temperature. The yellow suspension was concentrated in vacuo. The product was purified by column chromatography (1:2 AcOEt/*n*-pentane).

4.9.1. Chloro(η^4-1,5-cyclooctadiene)(1,3-di-iso-propylimidazolin-2-ylidene)iridium(I) (**22**)

Yield: 64 mg (66%). ^{1}H NMR ($CDCl_3$): $\delta = 6.87$ (s, 2H, NC*H*C*H*N), 5.51 (sept., $^3J_{H,H} = 6.4$ Hz, 2H, NC*H*(CH_3)$_2$), 4.54 (m, 2H, COD_{vinyl}), 2.94 (m, 2H, COD_{vinyl}), 2.19 (m, 4H, COD_{allyl}), 1.71 (m, 2H, COD_{allyl}) 1.59 (m, 2H, COD_{allyl}), 1.46 (d, $^3J_{H,H} = 6.4$ Hz, 6H, CHCH_3), 1.41 (d, $^3J_{H,H} = 6.4$ Hz, 6H, CHCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 177.9$ (N*C*N), 116.5 (N*C*H*C*HN), 83.7 (COD_{vinyl}), 52.3, 51.1 (COD_{vinyl}, N*C*H(CH_3)$_2$), 33.7 (COD_{allyl}), 29.8 (COD_{allyl}), 24.1 (CH*C*H_3), 23.4 (CH*C*H_3). MS (FAB) *m/z* (%) = 487.6 (24, [M^+]), 448.7 (53, [$M^+-C_3H_5$]), 338.7 (53, [M^+-(COD + C_3H_5)]), 146.9 (100, [carbene]).

4.9.2. Chloro(η^4-1,5-cyclooctadiene)(1,3-dicyclohexylimidazolin-2-ylidene)iridium(I) (**24**)

Yield: 83 mg (73%). ^{1}H NMR ($CDCl_3$): $\delta = 6.83$ (s, 2H, NC*H*C*H*N), 5.51 (tt, $^3J_{H,H} = 12.0$, 3.6 Hz, 2H, NCH_{Cy}), 4.57 (br, 2H, COD_{vinyl}), 2.93 (br, 2H, COD_{vinyl}), 2.20–1.24 (m, 8H, COD_{allyl}, 20H, $CH_{2,Cy}$). ^{13}C NMR ($CDCl_3$): $\delta = 178.1$ (N*C*N), 116.5 (N*C*H*C*HN), 83.4 (COD_{vinyl}), 60.0 (COD_{vinyl}), 50.8 (N*C*H_{Cy}), 34.4($CH_{2,Cy}$), 34.3 ($CH_{2,Cy}$), 33.9 (COD_{allyl}), 29.8 (COD_{allyl}), 26.2 ($CH_{2,Cy}$), 25.9 ($CH_{2,Cy}$), 25.5 ($CH_{2,Cy}$).

MS (FAB) *m/z* (%) = 567.4 (28, [M^+]), 528.5 (15, [$M^+-C_3H_5$]), 146.9 (100). Anal. Calc. for $C_{23}H_{36}N_2ClIr$ (568.22): C, 48.62; H, 6.39; N, 4.93. Found: C, 49.15; H, 6.58; N, 4.52%.

4.10. General procedure for carbonyl derivatives

CO gas (1 bar, 15 mL/min) was passed through a solution of the COD-complexes (0.17 mmol) in 15 mL dichloromethane at room temperature for 15 min. A colour lightening was observed. The solution was reduced to 5 mL in vacuo and *n*-hexane was added to precipitate the carbonyl complexes in high yields.

4.10.1. Dicarbonylchloro-(1,3-di-iso-propylimidazolin-2-ylidene)rhodium(I) (**29**)

Yield: 33 mg (95%). IR (CH_2Cl_2): $\nu = 2078$, 1997 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.02$ (s, 2H, NC*H*C*H*N), 5.19 (sept., $^3J_{H,H} = 6.8$ Hz, 2H, C*H*(CH_3)$_2$), 1.47 (d, $^3J_{H,H} = 6.8$ Hz, 6H, CH(*C*H_3)$_2$), 1.39 (d, $^3J_{H,H} = 6.8$ Hz, 6H, C*H*(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 184.6$ (d, $^1J_{Rh-C} = 53.2$ Hz, CO), 181.8 (d, $^1J_{Rh-C} = 74.8$ Hz, CO), 170.2 (d, $^1J_{Rh-C} = 43.1$ Hz, N*C*N), 116.6 (N*C*H*C*HN), 52.3 (N*C*H(CH_3)$_2$), 22.3, 22.2 (NCH(*C*H_3)$_2$). MS (FAB) *m/z* (%) = 310.7 (10, [M^+-Cl]), 254.9 (35, [M^+-(2CO + Cl)]), 153.0 (100, [carbene]).

4.10.2. Dicarbonyliodo-(1-mesityl-3-methylimidazolin-2-ylidene)rhodium(I) (**30**)

Yield: 44 mg (91%). IR (CH_2Cl_2): $\nu = 2073$, 2000 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.15$ (d, $^3J_{H,H} = 1.6$ Hz, 1H, NCHC*H*N), 6.95 (s, 2H, m-C*H*), 6.94 (d, $^3J_{H,H} = 1.6$ Hz, 1H, NCHCH*N*), 3.96 (s, 3H, NCH_3), 2.34 (s, 3H, *p*-CH_3), 2.09 (br s, 6H, *o*-CH_3). ^{13}C NMR ($CDCl_3$): δ = 186.9 (d, $^1J_{Rh-C} = 52.3$ Hz, *C*O), 181.6 (d, $^1J_{Rh-C} = 77.6$ Hz, *C*O), 174.3 (d, $^1J_{Rh-C} = 42.3$ Hz, N*C*N), 139.5, 135.2, 129.4 (C_{Ar}), 123.9, 123.4 (N*C*H*C*HN), 40.1 (N*C*H_3), 21.2, 19.0 (Ar–*C*H_3). MS (FAB) *m/z* (%) = 457.4 (16, [M^+-CO]), 429.5 (30, [M^+-2CO]), 330.7 (18, [M^+-(CO + I)]), 302.7 (45, [M^+-(2CO + I)]), 201.0 (100, [carbene]). Anal. Calc. for $C_{15}H_{16}N_2IO_2Rh$ (486.11): C, 37.06; H, 3.36; N, 5.76. Found: C, 37.35; H, 3.36; N, 5.62%.

4.10.3. Dicarbonylchloro-(1,3-di-iso-propylimidazolin-2-ylidene)iridium(I) (**31**)

Yield: 41 mg (93%). IR (CH_2Cl_2): $\nu = 2066$, 1982 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.03$ (s, 2H, NC*H*C*H*N), 5.27 (sept., $^3J_{H,H} = 6.8$ Hz, 2H, NC*H*(CH_3)$_2$), 1.45 (d, $^3J_{H,H} = 6.8$ Hz, 12H, CHCH_3). ^{13}C NMR ($CDCl_3$): δ = 181.2 (*C*O), 171.0 (N*C*N), 167.3 (*C*O), 116.3 (N*C*H*C*HN), 53.1 (N*C*H(CH_3)$_2$), 23.0 (CH(*C*H_3)$_2$). MS (FAB) *m/z* (%) = 436.6 (22, [M^+]), 400.6 (40, [M^+-Cl]), 372.7 (100, [M^+-(CO + Cl)]). Anal. Calc. for $C_{11}H_{16}N_2ClIrO_2$ (435.93): C, 30.31; H, 3.70; N, 6.43. Found: C, 30.98; H, 3.53; N, 6.12%.

4.10.4. Dicarbonylchloro-(1,3-dicyclohexylimidazolin-2-ylidene)iridium(I) (**32**)

Yield: 49 mg (94%). IR (CH_2Cl_2): $\nu = 2064$, 1982 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 6.99$ (s, 2H, NC*H*C*H*N), 4.83 (m, 2H, NCH_{Cy}), 2.02–1.11 (m, 20H, $CH_{2,Cy}$). ^{13}C NMR ($CDCl_3$): $\delta = 181.7$ (CO), 171.2 (N*C*N), 168.3 (*C*O), 118.0 (N*C*H*C*HN), 60.5 (*C*H_{Cy}), 34.1 ($CH_{2,Cy}$), 33.7 ($CH_{2,Cy}$), 25.6 ($CH_{2,Cy}$), 25.4 ($CH_{2,Cy}$), 25.3 ($CH_{2,Cy}$). MS (FAB) *m/z* (%) = 515.4 (7, [M^+]), 488.5 (4, [M^+-CO]), 448 (46, [M^+- C_3H_5]), 418.6 (75, [M^+-(2CO + C_3H_5)]).

Anal. Calc. for $C_{17}H_{24}N_2ClIrO_2$ (516.05): C, 39.57; H, 4.69; N, 5.43. Found: C, 39.50; H, 4.53; N, 5.31%.

4.11. General procedure for the borylation reaction

The reactions for the borylation catalysis were typically conducted as follows: 2 mmol pinacolborane, and 1.0–1.5 mol% of the catalyst (**1a**, **4a**, **8a**, **12a**, and **14a**) were dissolved in 50 mmol aryl substrate. The solution was stirred and heated at 40–45 °C for 9–12 h. The reaction progress was monitored by removal of a small aliquot of the reaction mixture, which was analyzed by GC-MS. The solvent was removed under vacuum at room temperature and the residue was chromatographed over silica gel, eluting with CH_2Cl_2 to yield the product. The products were also analyzed via NMR [3a,47].

4.12. Single crystal X-ray structure determination of compounds $4 \cdot 2(CH_2Cl_2)$ and $14 \cdot 2(CH_2Cl_2)$

Crystal structure analysis of compound $\mathbf{4 \cdot 2(CH_2Cl_2)}$: $C_{40}H_{64}Cl_5IrN_4$, $M_r = 970.42$, red fragment ($0.31 \times 0.36 \times 0.43\ mm^3$), triclinic, $P\bar{1}$ (No.: 2), $a = 12.8837(1)$, $b = 13.7657(2)$, $c = 14.5709(2)$ Å, $\alpha = 70.3607(4)°$, $\beta = 66.4431(5)°$, $\gamma = 65.7350(9)°$, $V = 2113.40(5)$ Å^3, $Z = 2$, $d_{calc} = 1.525\ g\ cm^{-3}$, $F_{000} = 988$, $\mu = 3.508\ mm^{-1}$. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 143 K within the Θ range of $1.56° < \Theta < 25.37°$. A total of 30 570 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.044$), 7764 (all data) and 7057 [$I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 451 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with $R_1 = 0.0250$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0545$ (all data), GOF = 1.042, and shift/error < 0.001. The final difference-Fourier map shows no striking features ($\Delta e_{min/max} = +1.30/-0.87$ e Å^{-3}) [52].

Crystal structure analysis of compound $\mathbf{14 \cdot 2(CH_2\ Cl_2)}$: $C_{26}H_{34}BrCl_4IrN_4$, $M_r = 816.49$, orange fragment ($0.05 \times 0.13 \times 0.15\ mm^3$), orthorhombic, $Cmc2_1$ (No.: 36), $a = 9.8497(1)$, $b = 19.3527(3)$, $c = 15.9019(2)$ Å, $V = 3031.19(7)$ Å^3, $Z = 4$, $d_{calc} = 1.789\ gcm^{-3}$, $F_{000} = 1592$, $\mu = 6.098\ mm^{-1}$. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 123 K within the Θ range of $2.10° < \Theta < 25.31°$. A total of 34 023 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.059$), 2735 (all data) and 2700 [$I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 180 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0192$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0467$ (all data), GOF = 1.102, and shift/error < 0.001. The final difference-Fourier map shows no striking features ($\Delta e_{min/max} = +0.48/-0.52$ e Å^{-3}) [52].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 618422 and 618423 contain the supplementary crystallographic data for [$\mathbf{4 \cdot 2(CH_2Cl_2)}$] and [$\mathbf{14 \cdot 2(CH_2Cl_2)}$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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(b) **12**: $C_{24}H_{38}BrN_4Ir$, $M_r = 654.72$, red fragment, monoclinic, $P2_1/c$ (No.: 14), $a = 11.3631(4)$, $b = 11.1937(5)$, $c = 19.9978(8)$ Å, $\beta = 102.238(3)$, $V = 2485.8(2)$ Å^3, $Z = 4$. Only a basic substructure could be refined. All crystals show strong diffuse streaks in the reciprocal space. Large anisotropic displacement parameters for one n-butyl chain are indicative of disorder, attempts to refine such a model failed.

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