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A dibenz[*a*,*c*]phenazine-supported *N*-heterocyclic carbene and its rhodium and iridium complexes

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ABSTRACT

A new polycyclic *N*-heterocyclic carbene featuring a fused dibenz[*a*,*c*]phenazine moiety was generated *in situ* from the corresponding tetrafluoroborate salt. The synthesis and NMR data of its corresponding precursors, its sulfur adduct and dimer are reported. Complexes of type [MCl(COD)(**1**)] and [MCl(CO)$_2$(**1**)] (M = Rh and Ir, **1** = 1,3-dibutyldibenzo[*a*,*c*]phenazino[11,12-*d*]imidazol-2-ylidene) were prepared and characterized using spectroscopic and crystallographic methods. The electron-releasing capacity of this new carbene was investigated by evaluation of its corresponding IrCl(COD) and IrCl(CO)$_2$ complexes by IR spectroscopy (ν_{av}) and cyclic voltammetry ($E_{1/2}$). These studies revealed that the electron donicity of this ligand is comparable to that of the previously reported naphthoquinone-annulated imidazolin-2-ylidene. Some preliminary studies of the photophysical properties and catalytic activity of these metal complexes are reported.

1. Introduction

Since the isolation and crystallographic characterization of the first stable *N*-heterocyclic carbene (NHC) in early 1991, carbene chemistry has become a very prolific field of research [1]. Owing to their unique electronic and steric properties, NHCs have emerged as a powerful class of carbon-based ligands rivaling the leading status of phosphines as ligands in homogeneous catalysis [2–18]. It was recognized early on that expanding on the structural diversity of NHCs may extend the ability to fine-tune their electronic and steric properties, which is of prime importance for the design of catalysts with enhanced activities. One approach that has been used to modify the electronic properties of these carbenes is annulation of the typical 5-membered ring parent system (Fig. 1, **I**) with aromatic or nonaromatic carbo- and heterocycles. It has been shown that annulation at C_4–C_5 can have a significant impact on the stability and the electronic nature of NHCs [19–21]. With a few exceptions [22–26], the majority of 4,5-annulated imidazol-2-ylidenes reported to date contain a π-system fused to the 5-membered parent ring [27]. Although numerous examples of bicyclic 4,5-annulated imidazol-2-ylidenes have been studied [27,28], reports of more extended aromatic systems (tri- and polycyclic) are scarce, despite their proven utility in catalysis, polymer chemistry and materials science [19,27,29–37]. Among these carbenes, only three of them incorporate a fused polycyclic heteroaromatic moiety (Fig. 1, **II**–**IV**)) [33,38,39].

This contribution reports our investigation toward the synthesis and reactivity of a new polycyclic heteroaromatic carbene: 1,3-dibutyldibenzo[*a*,*c*]phenazino[11,12-*d*]imidazol-2-ylidene (**1**). Our interest in the development of this new carbene stems from its potential application as a fluorescent ligand in homogeneous catalysis [40]. Dibenzo[*a*,*c*]phenazine (DBP) and its derivatives are a class of aromatic compounds with interesting photophysical properties [41–46]. Fusion of such a ring to an imidazolin-2-ylidene provides a promising framework in which the carbene center is a component of an electron-rich, extended aromatic system. This should have a significant effect on the donor properties of the ligand. In addition, the carbene center is tightly coupled to the fluorescent DBP moiety which should lead to useful photophysical properties of the metal complexes that incorporate **1**. Preliminary studies of the catalytic performance of these metal complexes in hydrosilylation of acetophenone are also reported.

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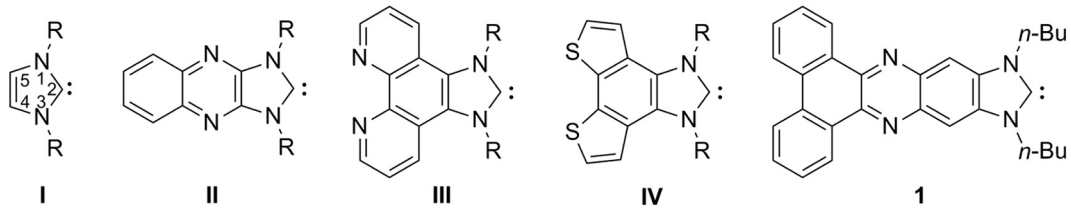


Fig. 1. Examples of NHCs featuring fused polycyclic heteroaromatic moieties.

2. Results and discussion

2.1. Chemical synthesis

2.1.1. Synthesis of the carbene precursor

The most common method used to generate NHCs is the deprotonation of the appropriate imidazolium salt precursors [1]. As summarized in Scheme 1, five steps provided access to imidazolium salt **6** from the commercially available 5-nitrobenzimidazole **2**. First, benzimidazole **2** was nitrated with a mixture of HNO_3/H_2SO_4 following a known procedure [47]. Subsequent alkylation with excess *n*-butyl iodide in the presence of sodium hydroxide yielded 1,3-dibutyl-6-dinitrobenzimidazolium iodide **3**. Reduction of the nitro groups with $SnCl_2$ in methanol afforded **4**. Iodide salt **4** was converted to the tetrafluoroborate salt **5** in order to circumvent potential halide exchange and any subsequent separation problems in reactions involving metal chlorides. The ^{13}C and ^{1}H NMR spectra of **5** are consistent with the proposed structure. In the ^{1}H NMR spectrum, the characteristic imidazolium proton appears at δ 9.13 ppm in d_6-DMSO, shifted upfield by 1.11 ppm in comparison with that of **3**. This shift reflects the electronic properties of the two substituents on the benzene ring (amino *vs.* nitro). The ^{13}C NMR signal of C2 appears at δ 137.51 ppm (d_6-DMSO), 11.04 ppm upfield in comparison with the corresponding signal for **3**. Condensation of **5** with 9,10-phenanthrenedione afforded the desired imidazolium salt **6** in excellent yields. The acidic proton display a signal at δ 10.17 ppm which suggests that the newly formed dibenzoquinoxaline fragment withdraws electrons from the imidazolium ring as strongly as the two nitro groups in **3**. The ^{13}C NMR signal of C2 of **6** appears at δ 148.31 ppm in d_6-DMSO.

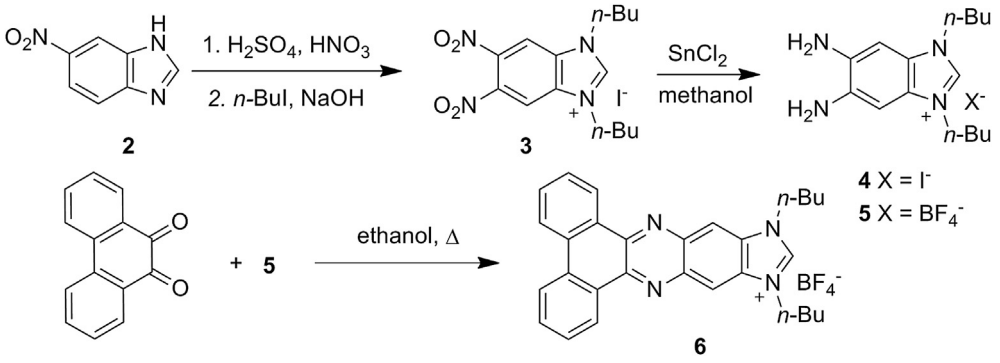
2.1.2. Generation of carbene *1*

The imidazolium salt **6** could be deprotonated with NaH and a catalytic amount of DMSO in THF at room temperature, leading to the neutral carbene **1**, which could be trapped by addition of elemental sulfur to give the thiourea **7** in good yield (Scheme 2). In the ^{13}C NMR spectrum of the thiourea **7**, the signal for the N_2CS carbon atom appears at a typical chemical shift of δ 174.29 ppm. Carbene **1** was found to decompose upon concentration, which precluded its isolation. Our attempt to generate the free carbene through deprotonation of **6** with potassium *t*-butoxide or NaH/DMSO(cat) mixture in THF resulted, upon evaporation of the solvent, in a complex mixture of products, one of which was isolated and identified as being the enetetramine **8**, whose N_2C carbon signal appears at δ 155.21 ppm [48]. However, in an NMR experiment treatment of a dilute solution of **6** with NaH/$DMSO_{(cat)}$ in dry d_8-THF led to immediate disappearance of the acidic proton and the formation of the free carbene **1** as the major product. This carbene was stable enough to be analyzed by ^{13}C NMR spectroscopy [49]. However, all attempts to observe the chemical shift of the carbenic carbon were unsuccessful. Treatment of this NMR solution with elemental sulfur after 24 h led to the formation of the corresponding sulfur adduct **7** as the major product.

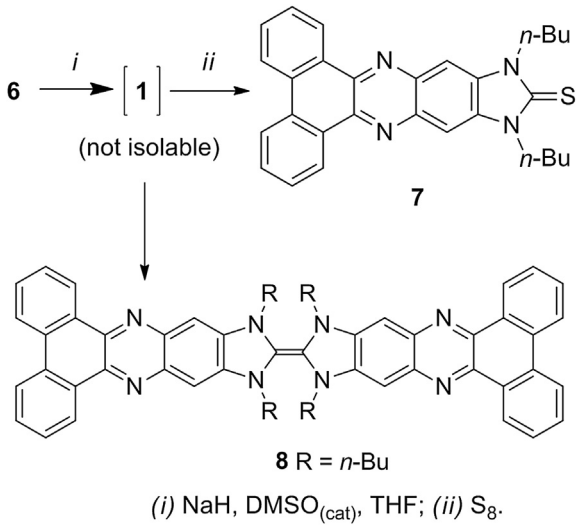
2.1.3. Synthesis of metal complexes

Subsequent efforts were focused on the coordination of the carbene to various transition metals. Rhodium(I) and iridium(I) complexes **9** and **10** were prepared by *in situ* deprotonation of the imidazolium salt **6** with potassium *t*-butoxide in the presence of $[MCl(COD)]_2$ (M = Rh, Ir) at room temperature (Scheme 3). Both complexes are air and moisture stable. No decomposition was observed upon heating the solids under vacuum at 100 °C for 5 days. They are soluble and stable in THF and halogenated solvents (CH_2Cl_2, $CHCl_3$) at room temperature. Their structures were confirmed by analytical and spectroscopic techniques. In the ^{13}C NMR spectra of the Rh complex **9**, the carbenoid carbon appears as a doublet at δ 208.2 ppm ($^{1}J_{Rh\text{-}C}$ = 50.4 Hz), falling in the range previously observed for related Rh complexes of saturated five and six-membered NHCs [50]. The carbons in the COD double bonds of **9** are each coupled with the rhodium atom differently ($^{1}J_{Rh\text{-}C}$ = 6.35, 14.28 Hz), which is consistent with their placement *trans* to different groups. For the iridium complex **10**, the carbenoid carbon occurs as a singlet at δ 201.9 ppm.

Metal-bound carbonyls are useful spectroscopic handles for measuring the electron density at the coordinated metal centers. Many $[IrCl(CO)_2]$ and $[RhCl(CO)_2]$ complexes supported by NHCs



Scheme 1. Synthesis of imidazolium salt **6**.

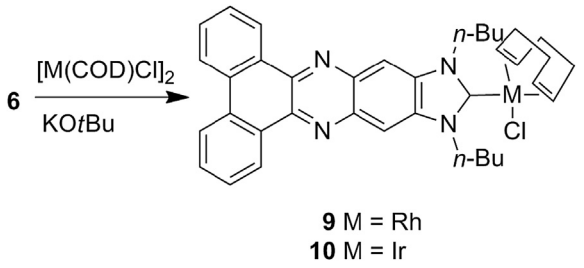


Scheme 2. Synthesis and trapping of carbene **1**.

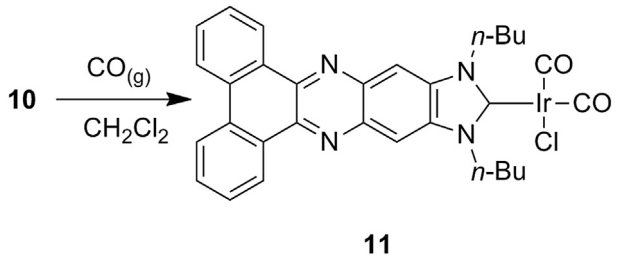
have been prepared and used to determine and compare the electron donating abilities of new NHCs to those of known ligands [51]. To access the [IrCl(CO)$_2$] complex of our carbene, carbon monoxide was bubbled through a CH_2Cl_2 solution of **10**, resulting in a clean conversion to complex **11** (Scheme 4). The complex is air and moisture stable and readily soluble in halogenated solvents.

2.2. Assessment of the ligand donating properties of carbene *1*

Several distinctly different methods were developed to quantify the electronic properties of NHCs [52]. Initially, the ligand-donating ability of carbene **1** was investigated by analyzing the carbonyl complex **11** using IR spectroscopy. Complex **11** exhibited *trans* (2078 cm^{-1}) and *cis* (1982 cm^{-1}) carbonyl stretching frequencies consistent with those observed in other known NHC-supported [IrCl(CO)$_2$] complexes [51,53–55]. The average value ν_{av} = 2030 cm^{-1} was used to calculate the Tolman electronic parameter (TEP = 2055.4 cm^{-1}) of **1** [51]. On the basis of this calculated TEP value, carbene **1** appears to be as strong of a donor as a previously reported naphtoquinone-annulated NHC (TEP = 2055.4 cm^{-1}) [19,56]; however, it is a weaker donor than 1,3-dimesitylimidazol-2-ylidene (IMes) (TEP = 2050.7 cm^{-1}) and its saturated analog 1,3-dimesitylimidazolin-2-ylidene (SIMes) (TEP = 2053) [51,54]. While TEPs are commonly used to analyze the electron donicity of NHCs, the measurement is indirect, as it relies upon changes in the stretching frequency of the coordinated carbonyl groups [57,58]. Voltammetry was shown to be a superior approach for the determination of the electron donating properties of NHCs because the metal center is directly bonded to the NHC ligand [59]. The results of the cyclic and differential pulse voltammetry measurements are summarized in Table 1. Complexes **9** and **10** exhibit quasi-reversible redox processes at +0.948 V ($\Delta E_{1/2}$ = 142 mV) and +0.959 V ($\Delta E_{1/2}$ = 126 mV) that are attributed to $M^{I/II}$ couples, and these values are higher than those reported for other non-annulated NHC-supported [MCl(COD)] complexes ($E_{½}$ = 0.648–0.920 V) [59], but comparable to the value reported by Bielawski for the [IrCl(COD)] complex of the naphtoquinone-annulated NHC ($E_{½}$ = 0.95 V) [19,56]. The $Ir^{I/II}$ couple of **11** was shifted beyond the solvent window and could not be observed [56,60]. The collective IR spectroscopy and electrochemical data suggest that the annulation with the DBP moiety of the parent 5-membered parent ring resulted in an attenuated ligand donicity relative to that of the non-annulated counterparts, but comparable to that of the naphtoquinone-annulated NHC reported by Bielawski.



Scheme 3. Synthesis of rhodium and iridium complexes **9** and **10**.



Scheme 4. Synthesis of iridium complex **11**.

2.3. Structural studies

Complex **10** gave X-ray quality crystals upon slow diffusion of methanol into a saturated toluene solution. Selected bond lengths and angles are given in Table 2. Iridium complex **10** crystallizes in the monoclinic space group $P2_1/n$. As shown in the ORTEP plot (Fig. 2), complex **10** adopts a square planar coordination geometry around the iridium. Relative to the [IrCl(COD)] plane, ligand **1** is rotated by 87.5(4)°. The Ir–C2 and Ir–Cl lengths of 2.008(5) and 2.3640(15) Å compare closely with those measured in other [IrCl(COD)(NHC)] complexes, with typical values from 1.99 to 2.091 Å and 2.335 to 2.39 Å, respectively [2,51,59,61–64]. As expected, the average distance between iridium and the olefinic carbons *trans* to **1** [r_{av}(Ir–C34(35) = 2.189 (5) Å] is slightly larger than the average distance between iridium and the double bond carbons *cis* to **1** [r_{av}(Ir–C38(39) = 2.117 (5) Å]. This indicates a stronger *trans*-influence of the carbene and a weaker iridium-(C=C) bond for the carbons *trans* to C2 than *trans* to chloride.

Single crystals of **11** were grown from a saturated dichloromethane solution by vapor diffusion with methanol at room temperature. Complex **11** crystallizes in the triclinic *P*-1 group with square planar coordination geometry around the iridium as depicted in Fig. 3. Selected bonds and angles for **11** are given in Table 2. The asymmetric unit contains two unique molecules. The Ir–C2 distance of 2.065(6) Å and the iridium-carbonyl and C–O bond lengths measured *cis* (1.833(9) and 1.024(11) Å, respectively) and *trans* (1.878(7) and 1.158(9) Å) relative to the carbene moiety are within the ranges reported for other NHC-supported [IrCl(CO)$_2$] complexes [51]. The plane of the carbene is almost perpendicular to

Table 1
Summary of electrochemical data.[a]

	$E_{1/2}$ (V)	ΔE (mV)	E_{pa} (V)	E_{pc} (V)
9	0.948	143	1.020	0.877
10	0.962	127	1.026	0.899

[a] The electrochemical data were obtained in CH_2Cl_2 in the presence of 0.1 M [Bu_4N][PF_6] electrolyte with decamethylferrocene (Fc*) as an internal standard (100 mV s^{-1} scan rate), referenced to SCE.

Table 2
Selected bond lengths (Å) and angles (deg) for **10** and **11**.

	10	**11**[a]
M–C2	2.008(5)	2.065(6)
M–X	2.3640(15)	2.358(2)
M–C34	2.194(5)	1.878(7)
M–C35	2.185(5)	1.833(9)
M–C38	2.133(5)	–
M–C39	2.102(5)	–
C34–O1	–	1.158(9)
C35–O2	–	1.024(11)
C2–N1	1.366(6)	1.341(8)
C2–N3	1.368(7)	1.362(9)
C4–C25	1.410(7)	1.440(9)
C25–N1	1.390(6)	1.387(8)
C4–N3	1.390(6)	1.353(8)
M–C2–N1	126.1(4)	126.4(5)
M–C2–N3	127.5(4)	127.4(5)
N1–C2–N3	105.7(4)	106.2(5)
Cl1–M–C2	87.31(15)	89.26(17)
Cl1–M–C34	92.30(18)	89.9(2)
Cl1–M–C35	89.46(16)	177.8(3)
Cl1–M–C38	163.18(15)	–
Cl1–M–C39	157.35(16)	–

[a] Structural data for one of the two unique molecules in the asymmetric unit.

the iridium coordination plane (interplanar angle 89.7(45)°). In the crystal, the molecules' hexacyclic planes are in face-to-face contact with one another, with an interplanar distance of about 3.4 Å as depicted in Fig. 3 (bottom).

The buried volume (% V_{bur} = 26.4) of **1** was calculated using the crystallographic information files and the software developed by Cavallo and co-workers (r = 3.5 Å, $d_{Ir\text{-}C2}$ = 2.008(5) Å) [65,66]. This value is comparable with the values found for IMes (% V_{bur} = 26) and SIMes (TEP = % V_{bur} = 27) [51].

2.4. UV–Vis and fluorescence studies

Further investigation of the spectroscopic properties of the imidazolium salt **6** and metal complexes **9** and **10** revealed key room temperature characteristics that are summarized in Table 3. All compounds absorb UV–Vis light strongly at λ < 500 nm (Fig. 4, log (ε_{abs}) ~ 4.83–4.89 at λ_{max}). A comparison of the absorption spectra of **6, 9** and **10** with the DBP spectrum reveals a close similarity of their spectral features. They all display complex absorption spectra with two major regions: one between 240 and 325 nm and the other between 340 and 500 nm, corresponding to spin-allowed optical transitions of the $^1(\pi-\pi^*)$ type. The most noticeable differences among them are the bathochromic shifts of up to

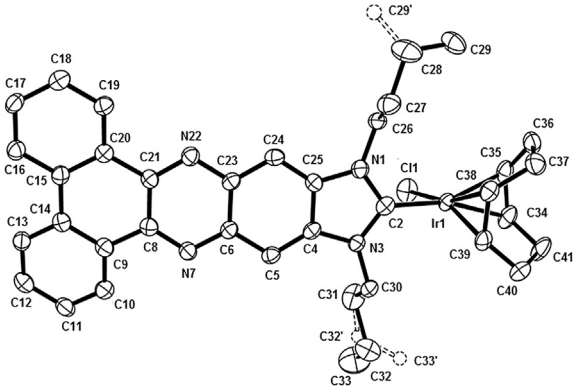


Fig. 2. Molecular structure of complex **10** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. There is some disorder in both butyl chains.

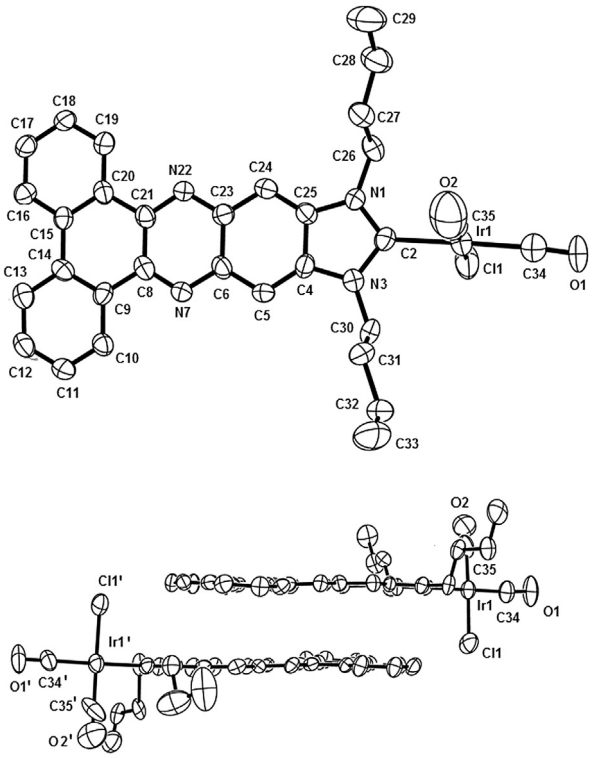


Fig. 3. (Top) Molecular structure of complex **11** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. (Bottom) Lattice view of the molecular network showing the parallel arrangement of the molecules.

39 nm of the absorption maxima to DBP (Table 3). These shifts are consistent with the more delocalized π-systems of **6**, **9** and **10** relative to DBP.

In CH_2Cl_2, **6**, **9** and **10** exhibit fluorescence emissions in the region 400–650 nm (Fig. 5). With excitation at 394 nm, imidazolium salt **6** exhibits emission over three-fold stronger than DBP, while the emission intensity for **9** and **10** are 73% and 44% of that of DBP. The quantum efficiencies (Φ) of **6**, **9** and **10** are 0.02, 1.4 × 10^{-3} and 1.8 × 10^{-3}, respectively, as determined by integration of their emission spectra and comparison to the emission spectrum of riboflavin Refs. [67,68]. The metal complexes **9** and **10** exhibit reduced fluorescence in comparison with imidazolium salt **6**, consistent with literature precedent for related NHC-supported [IrCl(COD)] complexes [35]. The fluorescence quenching is likely

Table 3
Room-temperature UV–Vis and fluorescence spectroscopic properties of **6**, **9**, **10** and DBP.[a]

Compound	λ_{abs} (nm)[b] [log ε]	λ_{em} (nm) [relative Intensity][c]			Φ[d]
6	256 [4.89], 414 [4.36]	**496 [1.00]**			0.02
9	293 [4.83], 424 [4.71]	405 [0.033]	**427 [0.230]**	447 [0.172]	1.4 × 10^{-3}
10	292 [4.86], 431 [4.71]	406 [0.035]	**428 [0.138]**	446 [0.105]	1.8 × 10^{-3}
DBP	254 [4.89], 393 [4.33]	406 [0.266]	**422 [0.313]**	446 [0.239]	3.7 × 10^{-3}

[a] Data obtained for CH_2Cl_2 solutions (2.5 × 10^{-6} mol l^{-1}) under ambient conditions. See also Supporting information.
[b] λ_{max} indicated in bold.
[c] Excitation at 394 nm; emission maximum indicated in bold.
[d] Quantum efficiencies (Φ) were determined relative to riboflavin in water (Φ = 0.23) [67,68].

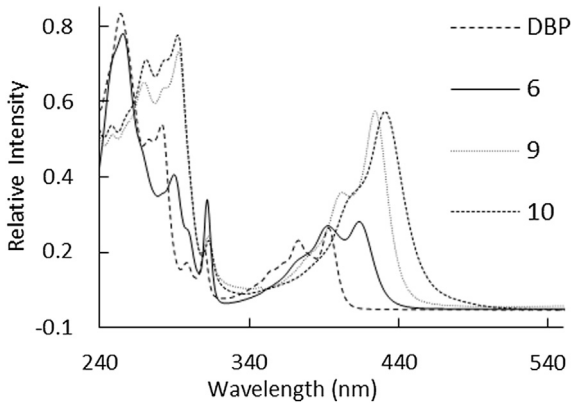


Fig. 4. Normalized UV–Vis absorption spectra of solutions of **6**, **9**, and **10** and DBP in CH_2Cl_2 (2.5×10^{-6} mol l^{-1}) at 22 °C.

caused by the heavy atom effect [69]. The presence of the chlorine atoms could promote a non-radiative decay or intersystem crossover to a non-emissive triplet excited state. The electronic structure of DBP is strongly affected by the annulation of the imidazolium moiety as evidenced not only by the difference in appearance and the relative intensities of the emission bands of **6** and DBP, but also by the difference in their λ_{max} values, where λ_{max} of **6** is bathochromically shifted by as much as 74 nm relative to DBP ($\lambda_{max} = 496$ and 422 nm, respectively). On the other hand, the emission spectra of **9** and **10** resemble the emission spectrum of DBP quite well, emission maxima being red shifted by only 5 and 6 nm relative to DBP (Table 3). These results are promising and suggest that the incorporation of **1** into catalytically relevant metal complexes could facilitate the monitoring of the state of a catalyst during a catalytic process by fluorescence spectroscopy [40].

2.5. Catalytic studies

The catalytic hydrosilylation of acetophenone with diphenylsilane was chosen as a model reaction to evaluate the catalytic potential of complexes **9** and **10**. For comparative purposes the catalyst loading was fixed at 2.5 mol%. All catalytic experiments

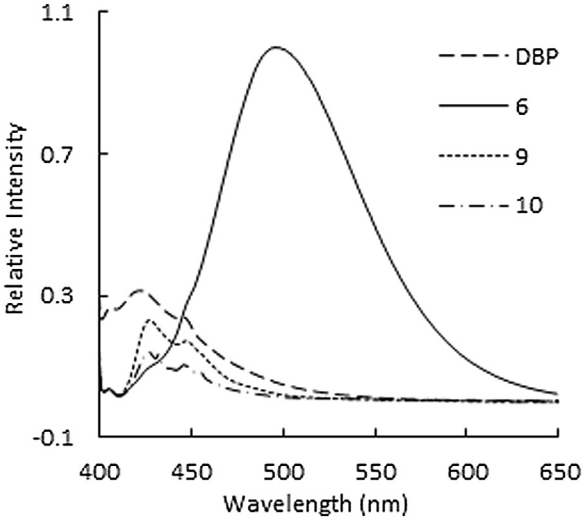
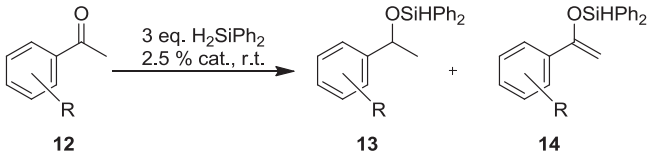


Fig. 5. Normalized emission spectra of CH_2Cl_2 solutions (2.5×10^{-6} mol l^{-1}) of **6**, **9**, and **10** and DBP at 22 °C after excitation at 394 nm.

Table 4
Hydrosilylation of acetophenone derivatives **12** with complex **9** and **10**.[a]



Entry	Catalyst	R	Time (h)	NMR yield **13**	NMR yield **14**
1[b]	**9**	H	3	80%	11%
2[b]	**10**	H	3	98%	2%
3[c]	**9**	H	3	80%	10%
4[c]	**10**	H	3	90%	2%
5[c]	**9**	4-CH_3	6	88%	5%
6[c]	**10**	4-CH_3	2	98%	2%
7[c]	**9**	2-OMe	4	76%	13%
8[c]	**10**	2-OMe	2	100%	0%
9[c]	**9**	4-OMe	3	83%	8%
10[c]	**10**	4-OMe	1	100%	0%
11[c]	**9**	2-Cl	10	30%	26%
12[c]	**10**	2-Cl	10	88%	3%
13[c]	**9**	4-F	5	83%	10%
14[c]	**10**	4-F	5	92%	1%
15[c]	**9**	4-Cl	5	92	8%
16[c]	**10**	4-Cl	5	98	2%
17[c]	**9**	4-Br	8	80%	13%
18[c]	**10**	4-Br	22	97%	2%

[a] Initial concentration: 0.083 M of **12**. Yields calculated by ^{1}H NMR spectroscopy as averages of two runs using 1,3,5-trimethoxybenzene as internal standard.
[b] In dichloromethane-d_2.
[c] In benzene-d_6.

were carried out at room temperature in the presence of 3 equivalents of Ph_2SiH_2 and an initial 0.083 M concentration of **12**. The reactions were monitored by ^{1}H NMR spectroscopy. The yield of silyl ether **13** was calculated by comparing the integration values of the CH_3 doublet and the CH quartet with that of the OCH_3 singlet of the internal standard, 1,3,5-trimethohybenzene. The yield of **14** was calculated by comparing the integration values of the two vinylic CH doublets with that of the OCH_3 singlet of the internal standard. The results are summarized in Table 4. Hydrosilylation of acetophenone (R = H) was found to proceed with comparable yields in both benzene-d_6 and dichloromethane-d_2 (entries 1–4). The identity of the metal proved to have a significant effect on the outcome of the reaction, with the iridium complex being more active than the rhodium complex in all studied reactions. In the presence of iridium complex **10**, 4- and 2-methoxyacetophenones were converted quantitatively into **13** within 1–2 h.

3. Conclusion

In summary, a novel dibenz[*a*,*c*]phenazine-fused imidazol-2-ylidene was generated *in situ* by deprotonation at room temperature of the corresponding imidazolium tetrafluoroborate **6**. Salt **6** was obtained by a five-step synthesis from commercial starting materials. Details on the chemistry of this ligand with respect to its ability to support catalytically relevant metal complexes were provided. A series of metal complexes that incorporate **1** have been synthesized, fully characterized, and their solid state molecular structures have been determined by X-ray diffraction studies. The buried volume of **1** was calculated as being % $V_{bur} = 26.4$, comparable with that found for IMes and SIMes. Electrochemical and IR spectroscopic analyses of complexes **9**–**11** revealed that carbene **1** is among the weakest σ-donors in the unsaturated series of Arduengo-type carbenes, and that its donicity is comparable to that displayed by the previously reported naphthoquinone-annulated imidazolin-2-ylidene. The UV–Vis absorption and emission

spectra of **6**, **9** and **10** were determined and compared to that of DBP. The results show that the dibenz[*a*,*c*]phenazine fused NHCs are suitable ligands for rhodium and iridium catalysts in the hydrosilylation of acetophenones. Further studies of these new fluorescent compounds and their analogs with respect to their possible use as fluorescent catalysts are underway.

4. Experimental section

4.1. General procedures

All solvents were reagent grade, except THF which was dried and distilled prior to use. Reactions with air- or moisture-sensitive compounds were conducted under a nitrogen atmosphere using a glove box or Schlenk techniques. Reagents were purchased from commercial sources and used as supplied. NMR spectra were recorded on a Bruker DPX 300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz). Chemical shifts are described in parts per million downfield shifted from $SiMe_4$. UV–visible absorption and fluorescence emission spectra were acquired using 2.5×10^{-6} M solutions in CH_2Cl_2 under ambient conditions on a Cary 4000 UV–Vis spectrophotometer and a PTI QuantaMaster spectrofluorimeter, respectively. Room temperature quantum yields were determined relative to a 2.5×10^{-6} M solution of riboflavin in water ($\Phi = 0.230$) [67,68], as described in Supplementary information. Electrochemical experiments were conducted on an Epsilon Electrochemical Workstation from BAsi using a three electrode cell under an atmosphere of nitrogen at room temperature. The cell was equipped with platinum working and counter-electrodes, as well as a Ag/AgCl reference electrode containing aqueous 3 M KCl. Measurements were performed in dry CH_2Cl_2 with 0.1 M [tetra-*n*-butylammonium][PF_6] as the electrolyte and decamethylferrocene [Fc*] as the internal standard. All potentials were determined at a 100 mV s^{-1} scan-rate and referenced to SCE by shifting $[Fc^*]^{0/+}$ to −0.057 V [70].

4.2. Synthesis

4.2.1. Synthesis of 1,3-dibutyl-5,6-dinitrobenzimidazolium iodide (**3**)

To a solution of 5,6-dinitro-benzimidazole [47] (6.00 g, 28.8 mmol) in 120 mL acetonitrile were added 4.75 mL of a 6.25 M aqueous NaOH solution. The reaction mixture was stirred at room temperature for 30 min. After addition of butyl iodide (14.4 mL, 126 mmol), the reaction was stirred at room temperature for another 25 min. The temperature was increased to 90 °C, and the reaction mixture was stirred at this temperature for 10 days. The reaction progress was monitored by ^{1}H NMR spectroscopy. The solvent was then removed, and the residue was taken up in CH_2Cl_2 and filtered. The volatiles were removed from the filtrate and the solid residue was further purified by trituration with ethyl acetate to give **3** after filtration (11.51 g, 89% yield). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 10.24 (s, 1H, C2*H*), 9.24 (s, 2H, Ar*H*), 4.56 (t, 4H, $J = 7.3$ Hz, NCH_2), 1.88 (p, 4H, $J = 7.4$ Hz, NCH$_2$CH_2), 1.35 (sextet, 4H, $J = 7.4$ Hz, CH_2CH$_3$), 0.92 (t, 6H, $J = 7.43$ Hz (CH_3). ^{13}C NMR (d_6-DMSO, 75.5 MHz): δ 148.55 (N*C*N), 140.53 (Ar*C*), 132.58 (Ar*C*), 113.24 (Ar*C*), 47.69 (NCH$_2$), 30.60 (NCH$_2$CH$_2$), 19.04 (CH$_2$CH$_3$), 13.45 (CH$_3$). Anal. Calcd. for $C_{15}H_{21}N_4O_4I$ (448.25): C, 40.19; H, 4.72; N, 12.49. Found: C, 40.09; H, 4.74; N, 12.48.

4.2.2. Synthesis of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (**4**)

Compound **3** (6.00 g, 13.4 mmol) was dissolved into methanol (190 mL) under nitrogen to give an orange solution. This solution was heated at 95 °C and $SnCl_2$ (41.5 g, 184 mmol) was added in small portions. The reaction mixture became colorless within minutes and the heating was continued for 24 h. The volatiles were removed and the residue was basified with 2 M aqueous sodium hydroxide. The product was extracted into CH_2Cl_2. After drying with $MgSO_4$ and evaporation of the volatiles, pure **4** was obtained as an off-white solid (4.74 g, 91.3% yield). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 9.15 (s, 1H, C2*H*), 6.84 (s, 2H, Ar*H*), 5.21 (s, 4H, NH_2), 4.22 (t, 4H, $J = 7.1$ Hz, NCH_2), 1.78 (p, 4H, $J = 7.3$ Hz, NCH$_2$CH_2), 1.26 (sextet, 4 H, $J = 7.3$ Hz, CH_2CH$_3$),0.89 (t, 6H, $J = 7.3$ Hz, CH_3). ^{13}C NMR (d_6-DMSO, 75.5 MHz): δ 137.17 (N*C*N), 135.59 (Ar*C*), 123.92 (Ar*C*), 94.15 (Ar*C*), 45.87 (NCH$_2$), 30.27 (NCH$_2$CH$_2$), 19.13 (CH$_2$CH$_3$), 13.40 (CH$_3$). Anal. Calcd. for $C_{15}H_{25}N_4I$ (388.29): C, 46.39; H, 6.48; N, 14.42. Found: C, 46.25; H, 6.52; N, 14.46.

4.2.3. Synthesis of 1,3-dibutyl-5,6-diaminobenzimidazolium tetrafluoroborate (**5**)

Imidazolium salt **4** (4.74 g, 12.2 mmol) was dissolved in methanol (100 mL). An aqueous solution of $Pb(BF_4)_2$ (2.7 mL, 50% wt., 6.1 mmol) was added to form a yellow precipitate immediately. The mixture was stirred at room temperature for 2 h and filtered through Celite. The filtrate was evaporated to give the product **5** (4.09 g, 96.2% yield). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 9.13 (s, 1H, C2*H*), 6.83 (s, 2H, Ar*H*), 5.21 (s, 4H, NH_2), 4.22 (t, 4H, $J = 7.1$ Hz, NCH_2), 1.78 (p, 4H, $J = 7.3$ Hz, NCH$_2$CH_2), 1.26 (sextet, 4 H, $J = 7.3$ Hz, CH_2CH$_3$),0.89 (t, 6H, $J = 7.3$ Hz, CH_3) ^{13}C NMR (d_6-DMSO, 75.5 MHz): δ 137.51 (N*C*N), 136.06 (Ar*C*), 124.36 (Ar*C*), 94.65 (Ar*C*), 46.28 (NCH$_2$), 30.68 (NCH$_2$CH$_2$), 19.54 (CH$_2$CH$_3$), 13.81 (CH$_3$). Anal. Calcd. for $C_{15}H_{25}N_4BF_4$ (348.19): C, 51.74; H, 7.23; N, 16.09. Found: C, 51.58; H, 7.46; N, 15.99.

4.2.4. Synthesis of 1,3-dibutyldibenzo[a,c]phenazino[11,12-d] imidazolium tetrafluoroborate (**6**)

A mixture of 9,10-phenanthrenequinone (0.770 g, 3.73 mmol) and **5** (1.30 g, 3.73 mmol) in ethanol (90 mL) was heated for 24 h at 95 °C. The reaction mixture was filtered and dried *in vacuo* to obtain pure **6** (1.82 g, 94% yield). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 10.17 (s, 1H, C2*H*), 9.19 (d, 2H, $J = 7.9$ Hz, Ar*H*), 9.00 (s, 2H, Ar*H*), 8.75 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.91 (t, 2H, $J = 7.5$ Hz, Ar*H*), 7.82 (t, 2H, $J = 7.5$ Hz, Ar*H*), 4.66 (t, 4H, $J = 7.3$ Hz, NCH_2) 2.04 (p, 4H, $J = 7.4$ Hz, NCH$_2$CH_2), 1.48 (sextet, 4H, $J = 7.4$ Hz, CH_2CH$_3$), 1.00 (t, 6H, $J = 7.3$ Hz, CH_3). ^{13}C NMR (d_6-DMSO, 75.5 MHz): δ 148.31 (N*C*N), 142.52 (Ar*C*), 138.49 (Ar*C*), 133.10 (Ar*C*), 131.89 (Ar*C*), 131.59 (Ar*C*), 129.01 (Ar*C*), 128.56 (Ar*C*), 125.77 (Ar*C*), 123.86 (Ar*C*), 112.21 (Ar*C*), 47.01 (NCH$_2$), 30.45 (NCH$_2$CH$_2$), 19.29 (CH$_2$CH$_3$), 13.56 (CH$_3$). Anal. Calcd. for $C_{29}H_{29}N_4BF_4$ (348.19): C, 66.93; H, 5.61; N, 10.76. Found: C, 66.70; H, 5.49; N, 10.85.

4.2.5. Synthesis of (1,3-dibutyldibenzo[a,c]phenazino[11,12-d] imidazole-2-thione (**7**)

To a mixture of imidazolium salt **6** (0.100 g, 0.19 mmol), NaH (10 mg, 0.4 mmol), and S_8 (10 mg, 0.31 mmol) was added under inert conditions anhydrous THF (6 mL) and a catalytic amount of DMSO. The reaction mixture was stirred at room temperature for 12 h. The mixture was evaporated and the residue was purified by flash chromatography (silica, 7:4 hexane:CH_2Cl_2 mixture) to give **7** as a yellow solid (0.084 g, 94.3% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.29 (d, 2H, $J = 7.8$ Hz, Ar*H*), 8.54 (d, 2H, $J = 7.4$ Hz, Ar*H*), 7.75 (s, 2H, Ar*H*), 7.76 (m, 4H, Ar*H*), 4.35 (t, 4H, $J = 7.3$ Hz, NCH_2), 1.90 (pentet, 4H, $J = 7.6$ Hz, NCH$_2$CH_2), 1.53 (sextet, 4H, $J = 7.4$ Hz, CH_2CH$_3$), 1.04 (t, 6H, $J = 7.3$ Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 174.29 (N$_2$C*S*), 141.21 (Ar*C*), 139.47 (Ar*C*), 135.61 (Ar*C*), 131.84 (Ar*C*), 130.34 (Ar*C*), 130.20 (Ar*C*), 128.04 (Ar*C*), 126.02 (Ar*C*), 123.13 (Ar*C*), 104.94 (Ar*C*), 45.13 (NCH$_2$), 29.86 (NCH$_2$CH$_2$), 20.53 (CH$_2$CH$_3$), 14.10 (CH$_3$). Anal. Calcd. for $C_{29}H_{28}N_4S$ (464.64): C, 74.96; H, 6.07; N, 12.05. Found: C, 74.74; H, 6.22; N, 12.06.

4.2.6. Synthesis of enetetramine **8**

To imidazolium salt **6** (0.050 g, 0.096 mmol) in anhydrous THF (5 mL), a suspension of KO*t*-Bu (13 mg 0.12 mmol) in THF (2 mL) was added dropwise under inert conditions. The reaction mixture was stirred at room temperature for 2 h. The mixture was evaporated and the residue, which showed five different spots by TLC, was purified by flash chromatography (silica, CH_2Cl_2) to give **8** as a yellow solid (0.011 g, 27% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.34 (d, 4H, J = 6.9 Hz, Ar*H*), 8.58 (d, 4H, J = 7.1 Hz, Ar*H*), 7.76 (m, 8H, Ar*H*), 7.64 (s, 4H, Ar*H*), 4.00 (t, 8H, J = 7.3 Hz, NCH_2), 1.87 (pentet, 8H, J = 7.5 Hz, NCH$_2$CH_2), 1.49 (sextet, 8H, J = 7.5 Hz, CH_2CH$_3$), 1.03 (t, 12H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 155.21 (NCN), 140.39 (ArC), 139.78 (ArC), 134.51 (ArC), 131.74 (ArC), 130.63 (ArC), 129.83 (ArC), 127.98 (ArC), 125.84 (ArC), 123.12 (ArC), 103.74 (ArC), 41.65 (NCH$_2$), 30.30 (NCH$_2$CH$_2$), 20.41 (CH$_2$CH$_3$), 13.99 (CH$_3$). Anal. Calcd. for $C_{58}H_8H_{56}CH_2Cl_2$ (950.05): C, 74.58; H, 6.15; N, 11.74. Found: C, 74.22; H, 6.31; N, 11.43.

4.2.7. Synthesis of (1,3-dibutyldibenzo[a,c]phenazino[11,12-d] imidazolin-2-ylidene)rhodium(1,5-cyclooctadiene) chloride (**9**)

To a mixture of imidazolium salt **6** (0.30 g, 0.57 mmol) and [RhCl(COD)]$_2$ (0.15 g, 0.30 mmol) in anhydrous THF (20 mL), a suspension of KO*t*-Bu (86 mg, 0.76 mmol) in THF (6 mL) was added dropwise under inert conditions. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered and the resulting solid was extracted with CH_2Cl_2 to remove KBF_4. The organic extract was evaporated to give 0.23 g of pure product. Additional product was recovered from the initial filtrate upon evaporation. The resulting solid was dissolved in a small amount of CH_2Cl_2 and precipitated with hexane. The total yield was 0.33 g (77% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.27 (d, 2H, J = 7.8 Hz, Ar*H*), 8.48 (d, 2H, J = 7.4 Hz, Ar*H*), 7.95 (s, 2H, Ar*H*), 7.73 (m, 4H, Ar*H*), 5.27 (bs, 2H, CH_{COD}), 5.07–4.90 (m, 4H NCH_2), 3.52 (bs, 2H, CH_{COD}), 2.58–2.42 [m, 4H, (CH_2)$_{COD}$], 2.34 (m, 2H, NCH$_2$CH_2), 1.96–2.16 [m, 4H (CH_2)$_{COD}$ and 2H NCH$_2$CH_2], 1.68 (sextet, 4H, J = 7.3 Hz, CH_2CH$_3$), 1.18 (t, 6H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 208.2 (d, $J_{Rh\text{-}C}$ = 50.4 Hz), 142.20 (ArC), 138.32 (ArC), 137.16 (ArC), 132.12 (ArC), 130.56 (ArC), 130.32 (ArC), 128.17 (ArC), 126.25 (ArC), 123.21 (ArC), 106.58 (ArC), 101.75 (d, $J_{Rh\text{-}C}$ = 6.35 Hz, CH_{COD}) 69.36 (d, $J_{Rh\text{-}C}$ = 14.28 Hz, CH_{COD}) 49.46 (NCH$_2$), 33.20 (NCH$_2$CH$_2$), 31.44 ((CH$_2$)$_{COD}$), 29.01 ((CH$_2$)$_{COD}$), 20.90 (CH$_2$CH$_3$), 14.15 (CH$_3$). Anal. Calcd. for $C_{37}H_{40}N_4RhCl$ (679.1023): C, 65.43; H, 5.93; N, 8.25. Found: C, 65.27; H, 5.97; N, 8.28.

4.2.8. Synthesis of (1,3-dibutyldibenzo[a,c]phenazino[11,12-d] imidazolin-2-ylidene)iridium(1,5-cyclooctadiene) chloride (**10**)

To a mixture of imidazolium salt **6** (0.30 g, 0.57 mmol) and [IrCl(COD)]$_2$ (0.193 g, 0.287 mmol) in anhydrous THF (30 mL), a suspension of KO*t*-Bu (73 mg, 0.85 mmol) in dry THF (10 mL) was added dropwise under inert conditions. The reaction mixture was stirred at room temperature overnight. The mixture was then evaporated and the residue was purified by flash chromatography (silica, CH_2Cl_2, R_f = 0.34) to give **10** as a yellow solid (0.35 g, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.37 (d, 2H, J = 7.6 Hz, Ar*H*), 8.56 (d, 2H, J = 7.8 Hz, Ar*H*), 7.78 (m, 4H, Ar*H*), 4.99–4.77 (m, 4H NCH_2 and 2H CH_{COD}), 3.13 (bs, 2H, CH_{COD}), 2.37–2.22 and 2.08–1.81 [two multiplets, 6H each, (CH_2)$_{COD}$ and NCH$_2$CH_2], 1.67 (sextet, 4H, J = 7.3 Hz, CH_2CH$_3$), 1.16 (t, 6H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 90.5 MHz): δ 201.99 (NCN), 142.04 (ArC), 138.47 (ArC), 137.57 (ArC), 132.06 (ArC), 130.49 (ArC), 130.32 (ArC), 128.14 (ArC), 126.22 (ArC), 123.17 (ArC), 106.59 (ArC), 88.90 (CH$_{COD}$), 53.32(CH$_{COD}$), 49.02 (NCH$_2$), 33.80 (NCH$_2$CH$_2$), 31.37 ((CH$_2$)$_{COD}$), 29.53 ((CH$_2$)$_{COD}$), 20.78 (CH$_2$CH$_3$), 14.08 (CH$_3$). Anal. Calcd. for $C_{37}H_{40}N_4IrCl$ (768.41): C, 57.83; H, 5.24; N, 7.29. Found: C, 57.69; H, 5.25; N, 7.37.

4.2.9. Synthesis of (1,3-dibutyldibenzo[a,c]phenazino[11,12-d] imidazolin-2-ylidene)iridium(CO)$_2$ chloride (**11**)

Complex **10** (75 mg, 0.097 mmol) was dissolved in CH_2Cl_2 (10 mL) and placed under an atmosphere of $CO_{(g)}$ for 2 h. The solvent was removed and the resulting solid was triturated with hexane to remove residual COD. The remaining solid was dried *in vacuo* to yield **11** as a light yellow powder (66 mg, 96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.28 (d, 2H, J = 7.8 Hz, Ar*H*), 8.50 (d, 2H, J = 7.8 Hz, Ar*H*), 8.10 (s, 2H, Ar*H*), 7.81 (t, 2H, J = 7.2 Hz, Ar*H*), 7.73 (t, 2H, J = 7.2 Hz, Ar*H*), 4.81 (dd, 1H, J = 9.6, 6.3 Hz, NCH_2), 4.87 (dd, 1H, J = 9.6, 6.4 Hz, NCH_2) 4.64 (dd, 1H, J = 9.6, 5.7 Hz, NCH_2) 4.59 (dd, 1H, J = 9.6, 5.7 Hz, NCH_2) 2.10 (m, 4H, NCH$_2$CH_2), 1.60 (sextet, 4H, J = 7.1 Hz, NCH_2CH$_3$), 1.09 (t, 6H, J = 7.35 Hz, CH_3) ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 191.01 (NCN) 180.65 (CO), 167.67 (CO), 142.11 (ArC), 137.85 (ArC), 135.47 (ArC), 131.64 (ArC), 130.34 (ArC), 129.38 (ArC), 127.63 (ArC), 125.84 (ArC), 122.62 (ArC), 108.03 (ArC), 48.88 (NCH$_2$), 30.69 (NCH$_2$CH$_2$), 19.91 (CH$_2$CH$_3$), 13.45 (CH$_3$). IR: ν_{CO} (cm^{-1}): 2078, 1982. Anal. Calcd. for $C_{31}H_{28}N_4O_2IrCl$ (716.25): C, 51.98; H, 3.94; N, 7.82. Found: C, 51.81; H, 3.87; N, 7.73.

4.3. Catalytic studies (Table 4)

Rhodium or indium complexes **9** and **10** (1.0 μmol) and 1,3,5-trimethoxybenzene (internal standard, 6.9 mg, 41.4 μmol) were weighted into an NMR tube. Deuterated benzene (0.48 mL) was added and the tube was inverted until the metal complex dissolved. Diphenylsilane (21 μL, 0.112 mmol) and one of the acetophenones **11** (40 μmol) were then added. The reaction was monitored by ^{1}H NMR spectroscopy. The yield of **13** was calculated by comparing the integration values of the CH_3 doublet and the CH quartet with that of the OCH_3 singlet of the internal standard, 1,3,5-trimethohybenzene. The yield of **14** was calculated by comparing the integration values of the two vinylic CH doublets with that of the OCH_3 singlet of the internal standard.

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Appendix A. Supplementary material

CCDC 899151 and 899152 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.09.034.

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