ChemComm



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COMMUNICATION

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Cite this: Chem. Commun., 2022, 58, 13270

Received 11th October 2022, Accepted 5th November 2022

DOI: 10.1039/d2cc05547c

rsc.li/chemcomm

Electronic, steric and catalytic properties of N-heterocyclic carbene rhodium(1) complexes linked to (metallo)porphyrins[†]

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Electronic and steric properties of NHC ligands functionalized with porphyrins were investigated. When porphyrins are used as NHCwingtips, nickel(II) in the macrocyle significantly improves the catalytic activity of the neighbouring NHC-Rh(I) complex in the conjugate addition of phenylboronic acid to cyclohexen-2-one.

N-Heterocyclic carbenes (NHCs) are ubiquitous ligands in homogenous transition metal catalysis.¹ Rationalizing catalytic properties of NHC-metal complexes mainly consists in investigating electronic and steric properties of NHCs. Imidazol-2-ylidenes are among the most commonly used NHCs in catalysis. Their electronic properties are affected by the substituents on C4 and C5 atoms and by the wingtip groups on N1 and N3 atoms, while their steric properties are mainly affected by the size and the rigidity of the wingtip groups oriented toward the metal centre (Fig. 1).² Descriptors like Tolman electronic parameter (TEP) and percent of buried volumes (% V_{bur}) are routinely used to quantify electronic and steric properties of NHCs, respectively.^{2,3}

Several NHCs linked to porphyrins were reported⁴ and used in organocatalysis⁵ and transition metal catalysis.⁶ Here, we propose to investigate electronic, steric and catalytic properties of three types of NHC-Rh(I) complexes linked to porphyrins, namely M^1 -A- M^2 , M^1 -B- M^2 and M^1 -C- M^2 , where M^1 is the metal in the porphyrin core (2H, Zn or Ni) and M^2 is the outer Rh(cod)Cl (cod = 1,5-cyclooctadiene) or Rh(CO)₂Cl complex (Fig. 1). In complexes M^1 -A- M^2 , porphyrins and NHCs are

separated by benzyl groups. In complexes M¹-B-M², porphyrins and NHCs are fused together and the C4 and C5 atoms of NHCs correspond to two neighbouring β -pyrrolic carbon atoms. This rigid structure ensures that the inner metal M¹ is remote from the outer metal M^2 . In complexes M^1 -C- M^2 , porphyrins are wingtips of NHCs and both are linked together through the formation of C_{meso} -N_{NHC} bonds. In this case, inner metal M^1 and outer metal M^2 are in close proximity (~5-6 Å) and cooperativity between them may be observed. For example, the inner metal M¹ can be used as binding site to fix substrates near the peripheral catalytic site in order to increase catalyst activity and/or selectivity.7 Finally, 1,3-dimethylimidazol-2ylidene ligand IMe is used as reference NHC. (NHC)Rh(cod)Cl and (NHC)Rh(CO)₂Cl complexes were used to assess steric and electronic properties, respectively. Then, catalytic properties of (NHC)Rh(cod)Cl complexes were investigated for the conjugate addition of phenylboronic acid to cyclohexen-2-one.

Imidazolium salts used as NHC precursors were obtained following synthetic strategies depicted in Scheme 1. Imidazolium salts M^1 -A-Cl were obtained by first synthesizing the free-base *meso* 5-(4'-chloromethylphenyl)-10,15,20-tris(mesityl)porphyrin 2H-1.⁸ SN reaction with *N*-methylimidazole afforded imidazolium salt 2H-A-Cl. Then, metalation reactions afforded the corresponding Ni(II) and Zn(II) porphyrins (Ni-A-Cl and Zn-A-Cl). Imidazolium salts M^1 -B-BF₄



Fig. 1 Structures of complexes $M^1\text{-}B\text{-}M^2,\ M^1\text{-}B\text{-}M^2,\ M^1\text{-}C\text{-}M^2,\ \text{IMe-M}^2$ and NiP.

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[†] Electronic supplementary information (ESI) available: Experimental details, synthetic procedures, NMR spectra, mass spectra, computational details and catalytic studies. See DOI: https://doi.org/10.1039/d2cc05547c



and M1-C-PF6 were obtained by first synthesizing the corresponding Ni(II) porphyrins bearing an imidazole ring fused to a pyrrole (Ni-2) or on a meso position (Ni-3) following our reported procedures.⁹ Then, demetalation (TFA/H₂SO₄ 20%) and remetalation with Zn(II)afforded the corresponding free-base porphyrins (2H-2 and 2H-3) and Zn(II) porphyrins (Zn-2 and Zn-3), respectively. SN reactions of these porphyrins with CH₃I and anion metathesis reactions afforded imidazolium salts M^{1} -B-BF₄ and M^{1} -C-PF₆ ($M^{1} = 2H$, Ni or Zn). Complexes M¹-A-Rh(cod)Cl, M¹-B-Rh(cod)Cl and M¹-C-Rh(cod)Cl (M¹ = 2H, Ni or Zn) were obtained by reacting imidazolium salts with tBuOK and [Rh(cod)Cl]₂ (Scheme 1).^{5,6,10} Formation of the C_{NHC}-Rh bonds was confirmed by the absence of the signals of the imidazolium protons in their ¹H NMR spectra and by the characteristic doublets observed at $\delta \sim$ 180–190 ppm in their ¹³C¹H} NMR spectra. Characteristic signals due to coordinated cod ligands were also observed by ¹H NMR spectroscopy.

Measuring CO stretching wavenumbers of (NHC)Rh(CO)₂Cl complexes by FTIR spectroscopy allowed to assess the electronic properties of NHCs and determine their TEP values.¹¹ Complexes M¹-A-Rh(CO)₂Cl, M¹-B-Rh(CO)₂Cl and

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 M^1 -C-Rh(CO)₂Cl were obtained by bubbling CO in solutions of the corresponding (NHC)Rh(cod)Cl complexes in CH₂Cl₂ (Scheme 1, these complexes were generated *in situ* and not isolated). Two CO stretching wavenumbers were observed in the FTIR spectra of (NHC)Rh(CO)₂Cl complexes confirming the *cis* geometry of all Rh(I) complexes (Scheme 1) and allowing the determination of TEP values (Table 1), which are in the same range (2052.6–2053.4 cm⁻¹) and similar to the TEP value of **IMe** (2053.0 cm⁻¹). These data show that the localization of the porphyrin has no or very weak inductive effect on the NHCs. Likewise, porphyrins exert similar inductive electronic effects, irrespective of the nature of the inner metal M¹ used in this study (M¹ = 2H, Ni or Zn). It is thus reasonable to consider that all NHCs presented here transfer similar amounts of electron density to Rh(I).

Steric pressures exerted by NHCs in the primary coordination sphere of Rh(I) were assessed by calculating their V_{Bur} values and their steric maps to figure out ligands anisotropy. For this purpose, DFT calculations were first performed to optimize geometries of complexes **M¹-A-Rh(cod)Cl**, **M¹-B-Rh(cod)Cl** and **M¹-C-Rh(cod)Cl** (see ESI†). Then, V_{bur} values (Table 1) and steric maps presenting the buried space around Rh(I) along the C_{NHC}-Rh(I) axes (Fig. 2 and ESI†) were calculated with SambVca 2.1.¹² NHCs **M¹-A** have V_{bur} values in the range of 30.9–31.0% (Table 1, entries 2–4), but these values should be taken with caution since steric pressure is due to benzyl groups (yellow-orange area on the left side of **Ni-A** in Fig. 2). Indeed, only one conformation is used to calculate V_{bur} values and steric maps, but benzylic sp³ carbon atoms ensure enough flexibility to adapt the steric bulk and

Table 1Electronic, steric and catalytic properties00101010101010101010101010101010101010101010101010101010101010101010101010101010101010101010101010101010101010101010101</

Entry	ligand	(cm^{-1})	$%V_{\rm bur}$	(% yield) 60 °C	(% yield) 100 °C
1	IMe	2053.0	26.0	41 (40)	63 (58)
2	2H-A	2052.6	31.0	38 (26)	55 (38)
3	Zn-A	2053.4	31.0	37 (27)	51 (45)
4	Ni-A	2053.4	30.9	38 (25)	56 (44)
5	2H-B	2053.0	26.9	30 (19)	45 (34)
6	Zn-B	2052.6	27.0	37 (33)	55 (51)
7	Ni-B	2053.4	26.8	33 (26)	52 (46)
8	2H-C	2053.4	32.4	14 (4)	46 (35)
9	Zn-C	2052.6	31.5	13 (7)	58 (52)
10	Ni-C	2053.0	32.0	12 (1)	91 (87)

^{*a*} ν (CO) (cm⁻¹) measured in CH₂Cl₂ and TEP values calculated using the equation: TEP = 0.8001 × ν^{av} (CO) + 420 cm⁻¹, see ref. 10. ^{*b*} N_{bur} values calculated with the SambVca 2.1 tool and the standard inputs given in Fig. 3. ^{*c*} Reaction conditions: 0.5 mmol of cyclohexen-2-one, 1.1 mmol of phenylboronic acid and 0.09 mmol of KOH in 2 mL of toluene with 0.2% mol catalyst loading, 60 or 100 °C, under argon. Conversions (% conv.) and yields (% yield) after 3 hours were determined by gas chromatography (GC) using anisole as internal standard and are the average values of three independent and reproducible experiments.

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Fig. 2 Steric maps and %V_{bur} values of NHCs IMe, Ni-A, Ni-B and Ni-C calculated with SambVca 2.1 with the following standard inputs: bondi radii 1.17 Å, Rh-C_{NHC} 2.00 Å, r_{sphere} = 3.50 Å, mesh spacing 0.10 Å, H atoms excluded, see ref. 11.

conformations with % $V_{\rm bur}$ as low as ~26.5% are possible.¹³ NHCs M^{1} -B possess % V_{bur} values in the range of 26.8–27.0% (Table 1, entries 5–7) and similar to the %V_{bur} value of NHC IMe (26.0%). Steric maps of NHCs M¹-B and IMe are similar because the steric pressure is due to the two N-methyl groups of the NHCs (see Ni-B and IMe in Fig. 2).

As expected, NHCs M¹-C with porphyrin wingtips are more bulky with %Vbur in the range of 31.5-32.4% (Table 1, entries 8-10). The broad greenish areas on the left side of their steric maps are due to the porphyrin cores (see Ni-C in Fig. 2). Thus, it is clear that porphyrins exert similar steric pressure in the primary coordination sphere of Rh(I), irrespective of the nature of the inner metal M^1 used in this study ($M^1 = 2H$, Ni or Zn). However, M¹ may impact the secondary coordination sphere of Rh(1) by modifying the shape of the porphyrin core.¹⁴ To illustrate this point, DFT optimized structures of complexes M¹-C-Rh(cod)Cl are represented in Fig. 3. Porphyrins of complexes 2H-C-Rh(cod)Cl and Zn-C-Rh(cod)Cl are rather flat (free base porphyrin is slightly saddle-shaped), while Ni(II) porphyrin in complex Ni-C-Rh(cod)Cl adopts a ruffled distortion in agreement with X-ray structures of similar NHCs reported by Ruppert, Weiss and coworkers.¹⁵ It is also noticeable that the ruffled distortion of the porphyrin has two major consequences: the Ni(π) porphyrin wraps the Rh(τ) complex along its C5-C15 axis and both metal ions get closer. Indeed, the Rh-Ni distance of ~5.08 Å in complex Ni-C-Rh(cod)Cl is slightly shorter than the Rh-Zn distance of ~ 5.25 Å in complex Zn-C-Rh(cod)Cl (Fig. 3).

Catalytic properties of (NHC)Rh(cod)Cl complexes were investigated in the conjugate addition of phenylboronic acid to cyclohexen-2-one.¹⁶ Reactions were performed for 3 hours in toluene at 60 and 100 °C in the presence of KOH and catalyst loading of 0.2 mol% (Table 1), and were monitored by GC and UV-vis absorption spectroscopy (see ESI[†]). We observed that complexes IMe-Rh(cod)Cl (entry 1), M1-A-Rh(cod)Cl (entries 2-4) and M¹-B-Rh(cod)Cl (entries 5-7) afforded rather similar reaction outcomes and time profiles (see ESI⁺), although slightly better conversion and yield were obtained with IMe-**Rh(cod)Cl.** Thus, porphyrins and their inner metal ions have no or very weak influence on the catalytic properties of the corresponding Rh(I) complexes. It can be explained by the fact that NHCs IMe, M¹-A and M¹-B possess similar electronic properties. Likewise, steric properties of NHCs IMe and M¹-B are also very similar. In the case of NHCs M¹-A, flexibility is ensured by benzylic sp³ carbon atoms to adapt the steric bulk (vide supra) and porphyrins are too far from Rh(1) complexes to modulate the catalytic activity.

Interesting catalytic properties were observed for the three complexes M¹-C-Rh(cod)Cl (Table 1, entries 8-10). At 60 °C, they are significantly less active compared to the other catalysts (lower conversions and yields) and it may be attributed to the stronger steric pressure induced by the porphyrin wingtips. At 100 °C, catalytic activity of complexes M1-C-Rh(cod)Cl depends on the nature of M^1 in the order 2H < Zn < Ni (see time profiles of the reactions in Fig. 4(a)). Complex Ni-C-Rh(cod)Cl is surprisingly more active with conversion and yield of 91% and 87%, respectively (Table 1, entry 10). This complex is approximately two times more active than complex 2H-C-Rh(cod)Cl. Rate enhancement is only observed when the $Ni(\pi)$ porphyrin is used as NHC wingtip. Indeed, there is no significant rate enhancement if the Ni(II) porphyrin and the NHC are not connected together (see reaction catalysed by IMe-Rh(cod)Cl + NiP vs. reaction catalysed by IMe-Rh(cod)Cl alone in the ESI⁺) or if they are connected but distant from each other.

Thermodynamic stability of complexes 2H-C-Rh(cod)Cl and Ni-C-Rh(cod)Cl presenting the lowest and highest catalytic activities, respectively, was investigated. For this purpose, they were treated with KOH (100 eq.) in toluene at 100 °C and reaction mixtures were analyzed by ${}^{13}C_1^{1}H$ NMR spectroscopy (see ESI[†]). Complex 2H-C-Rh(cod)Cl is stable and no significant change could be observed after 3 hours. Its lower catalytic



Fig. 3 DFT optimized structures of complexes M1-C-Rh(cod)Cl with M¹ = 2H, Zn and Ni (meso p-tolyl groups and H omitted for clarity).



Fig. 4 (a) Time-dependant reaction profiles of the conjugate addition of phenylboronic acid to cyclohexen-2-one catalysed by M¹-C-Rh(cod)Cl (M¹ = Ni in red, Zn in blue and 2H in green) in toluene at 100 °C. (b) PM3minimized molecular modelling of a plausible transition state of Ni-C-Rh(cod)Cl with phenyl and cyclohexen-2-one bonded to Rh(I) and Ni(II), respectively

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activity does not therefore seem to be due to its lower thermodynamic stability although its decomposition in the presence of the reaction substrates (phenylboronic acid and cyclohexen-2one) cannot be totally excluded to explain the significant drop in catalytic activity after 1 hour. Complex **Ni-C-Rh(cod)Cl** is also stable for at least 30 minutes suggesting that its high initial catalytic activity is due to its kinetic activity. We also observed that complex **Ni-C-Rh(cod)Cl** slowly decomposed over time. Indeed, characteristic signals of carbene and cod ligands disappeared after 3 hours. This gradual decomposition may also explain the redshift of the Soret absorption band observed by UV-vis absorption spectroscopy after 1 hour reaction (see ESI†).

It is obvious that Ni(π) plays a significant role in the enhancement in the reaction rate, but this effect cannot be attributed to changes in inductive electronic effects or steric pressures exerted by NHCs, as previously shown. Although the exact mechanism of this cooperative effect between Rh(π) and Ni(π) remains unclear at this stage, we believe that the ruffled porphyrin core and the short Rh–Ni distance of ~5 Å play significant roles in substrate-preorganization and reaction rate enhancement (Fig. 4(b)).¹⁷ Extending the scope of the reaction to other substrates and detailed kinetic studies will further be needed to understand the exact role of Ni(π) in this reaction.

In summary, catalytic properties of molecular systems combining porphyrins and (NHC)Rh(cod)Cl complexes were investigated in the conjugate addition of phenylboronic acid to cyclohexen-2one. Preliminary data show that catalytic activity of Rh(I) complexes is modulated by the metal in the porphyrin core when the macrocycle is used as NHC wingtip. In this case, we have shown that NHCs with free-base, $Zn(\pi)$ and $Ni(\pi)$ porphyrin wingtips transfer similar amount of electron density to Rh(1) and exert similar steric pressure in the primary coordination sphere of Rh(I). However, we found that $Ni(\pi)$ in the porphyrin macrocycle dramatically increases the catalytic activity of the neighbouring Rh(1) complex. NHC-metal complexes with porphyrin wingtips are thus capable of cation-tunable reactivity and additional studies are underway to understand this phenomenon. Supramolecular catalysis and fine tuning of the catalytic activity of other NHC-metal complexes with porphyrins in close proximity are also actively explored in our group.18,19

We are grateful for the financial support of the French Agence Nationale de la Recherche (Grants ANR-19-CE07-0009 and ANR-19-CE07-0039), the University of Montpellier, the University of Rennes 1 and the Centre National de la Recherche Scientifique (CNRS). S. Scoditti is grateful for the financial support of Calabria Region (project POR Calabria-FSE/FESR 2014–2020).

Conflicts of interest

There are no conflicts to declare.

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