

## Springloaded porphyrin NHC hybrid rhodium(III) complexes: carbene dissociation and oxidation catalysis†

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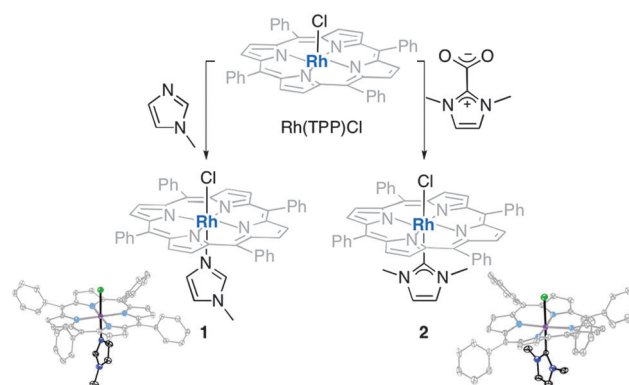
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**Porphyrin rhodium(III) complexes accommodate one or two NHC ligands in the apical position, which leads to severe porphyrin distortion and dearomatization. The strain in the bis(carbene) complex induces facile carbene dissociation and the formation of a catalytically active site for alcohol oxidation.**

The utilization of N-heterocyclic carbenes (NHCs) as ligands has modified the properties of transition metals substantially.<sup>1</sup> Advantageous effects have been, in parts, attributed to the strong metal–carbon bond in NHC complexes,<sup>2</sup> which originate from a relatively high covalent contribution to the overall bonding.<sup>3</sup> As a consequence, NHCs have been combined with a range of other privileged ligand classes in attempts to foster synergies, including for example bipyridine-type scaffolds, phosphine NHC hybrids, and pincer platforms.<sup>4</sup> The combination of NHC ligands with porphyrins is remarkably under-explored,<sup>5</sup> despite the beneficial features of porphyrins such as their photochemical activity.<sup>6</sup> Porphyrins offer the unique added benefit that coordination of a ligand L to a metalloporphyrin will enable its *trans* effect to be fully exploited, as any reaction will involve the distal site *trans* to L. Consideration of the strong *trans* effect of NHCs prompted us to investigate hybrid NHC porphyrin complexes and to evaluate structural and catalytic implications arising from NHC bonding to a rhodium porphyrin unit.

For comparison, two [Rh(TPP)(L)Cl] complexes **1** and **2** were prepared which feature *N*-methylimidazole (**1**) and *N,N'*-dimethylimidazolidene (**2**) as axial ligands, respectively (Scheme 1, TPP = *meso*-tetraphenyl porphyrin). Complex **1** was synthesised from [Rh(TPP)Cl]<sup>7</sup> and an excess (10 equiv.) of 1-methylimidazole. Coordination of one imidazole ligand was unambiguously confirmed by the pertinent integral ratios and

Scheme 1 Synthesis and ORTEP plots of complexes **1** and **2**.

the characteristic deshielding of the imidazole protons induced by the porphyrin ring current ( $\Delta\delta_{\text{H}}$  up to 6.5 ppm).<sup>8</sup>

Complex **2** was prepared by thermal decarboxylation of *N,N'*-dimethylimidazolium carboxylate<sup>9</sup> in the presence of [Rh(TPP)Cl] (Scheme 1). The carbene resonance appeared as a broad signal at  $\delta_{\text{C}}$  143.15 ppm ( $J_{\text{RhC}}$  not resolved), some 40 ppm higher field than in typical rhodium(III) NHC complexes.<sup>10</sup> The <sup>1</sup>H NMR spectrum revealed two singlets at diagnostically high field,  $\delta_{\text{H}}$  4.67 and –0.46 ppm in a 1:3 ratio for the C<sub>NHC</sub>–H and N–CH<sub>3</sub> protons, respectively. The ring current effects are smaller than those observed for **1** and suggest a lower aromaticity<sup>8</sup> of the porphyrin skeleton in **2**. Such a model is further supported by the resonances due to the *ortho* phenyl protons, which appeared as a broad resonance at 8.05 ppm upon NHC coordination (Fig. S1 and S2, ESI†), while in **1** they retain AX multiplicity.† This broadening is temperature-dependent<sup>11</sup> and suggests either inversion of the TPP puckering or rotation about the C<sub>meso</sub>–C<sub>Ph</sub> bond due to an out-of-plane bending of the *meso* substituents.

The molecular structure of complexes **1** and **2** indicates a staggered orientation of the apical heterocyclic ligand with respect to TPP, and its *ortho* substituents point towards the *meso* carbons, indicating negligible Rh–L  $\pi$ -bond interaction.<sup>12</sup>

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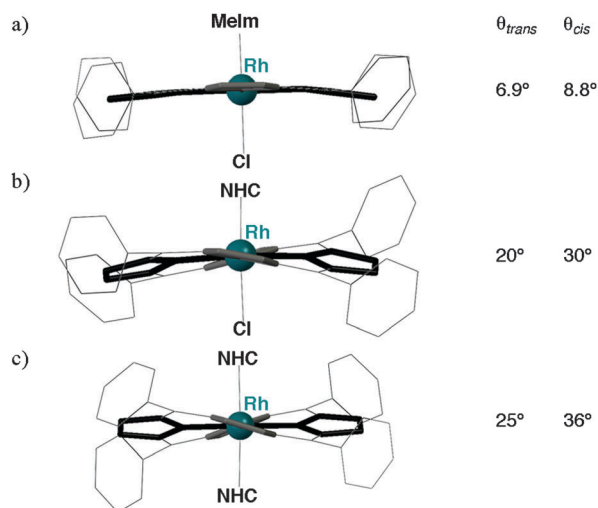
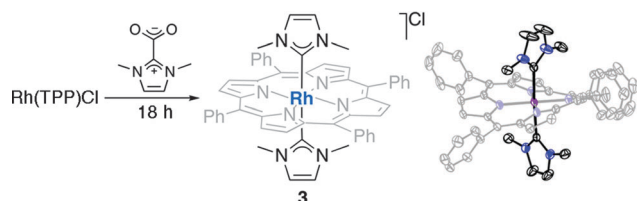


Fig. 1 Distortion of the porphyrin macrocycle and out of plane deviation of *meso* phenyl groups in complexes **1**, **2**, and **3** ( $\theta_{trans}$  and  $\theta_{cis}$  are averaged dihedral angles between pyrrole rings in mutual *cis* and *trans* positions, respectively).

The macrocycle is essentially undistorted and planar in **1** (Fig. 1). In contrast, complex **2** features a strongly ruffled porphyrin and the octahedral distortion parameter,<sup>13</sup>  $\Sigma = 19.82^\circ$ , is significantly larger than in **1** ( $\Sigma = 7.2^\circ$ ). The rhodium center resides 0.08 Å out of the porphyrin plane (towards the NHC ligand) and the *meso*-carbons deviate from this plane by 0.204–0.439 Å.<sup>†</sup> Such distortion reduces aromaticity, in good agreement with structural analysis from solution NMR data.

Even though the methyl substituents of the NHC ligand induce significant distortion of the TPP macrocycle, the Rh–carbene bond length is identical to the Rh–imidazole bond length in **1**, Rh–C<sub>NHC</sub> 2.051(2) Å vs. Rh–N<sub>Melm</sub> 2.058(2) Å. The similar distances and the loss of aromaticity of the TPP ligand indicate a remarkably strong Rh–C bond, which is also demonstrated by the 0.1 Å longer Rh–Cl bond in complex **2** than in **1** (2.4290(4) Å vs. 2.3302(6) Å). Moreover, attempts have been unsuccessful thus far to coordinate 1,2,4,5-tetramethylimidazole, a ligand that is isosteric to the carbene in **2** but featuring *N*- rather than *C*-bonding. Presumably the apical Rh–N bond is not strong enough to compensate for the steric deformation and associated reduction of aromaticity of the porphyrin while the Rh–C<sub>NHC</sub> bond strength counterbalances this loss and yields complex **2**.

The cationic bis-NHC complex **3** was isolated as a by-product during the formation of **2** and was separated by column chromatography (Scheme 2). The yield of **3** was markedly increased when the reaction time of Rh(TPP)Cl with the



Scheme 2 Synthesis of bis(NHC) complex **3**.

imidazolium carboxylate was extended from 3 to 18 h. Using a stoichiometric 2 : 1 ligand/metal ratio afforded **3** with several side products which could not be removed even by column chromatography. The <sup>1</sup>H NMR spectrum of **3** showed the diagnostic upfield shifts of the NHC signals, though the ring current and hence the aromaticity of the porphyrin ring are slightly less pronounced than in the monocarbene analogue **2**. Likewise, the doublet of the carbene carbon is less shielded ( $\delta_C$  153.15 ppm,  $J_{Rh-C} = 35$  Hz).

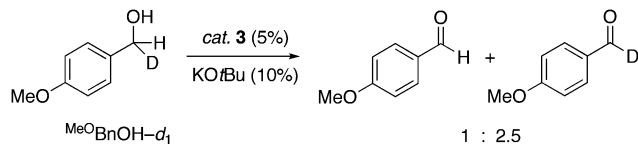
X-ray crystallography confirmed a substantial distortion of the TPP ligand. For example, the *meso* carbons deviate from the porphyrin mean plane by 0.533–0.639 Å (Fig. S4, ESI<sup>†</sup>), significantly more than even in **2**, and the pyrrole rings are substantially twisted out of plane ( $\Sigma = 11.8^\circ$ ). The two NHCs are mutually perpendicular. Despite the strong Rh–C<sub>NHC</sub> bonds, indicated *inter alia* by the substantial porphyrin deformation, the Rh–C<sub>NHC</sub> distances are significantly larger (2.141(2) and 2.124(2) Å) than in the less distorted complex **2** (2.051(2) Å) and indicate a high *trans* influence of the NHCs.

These rhodium(III) porphyrin complexes were used as catalyst precursors for alcohol oxidation (Table 1).<sup>†14</sup> With benzyl alcohol as a model substrate, the monocarbene complex **2** showed a significantly higher activity than the imidazole-containing analogue **1** (72% vs. 19%, entries 2 and 3). The imidazole had an inhibiting effect, as complex **1** was less active than the simple [Rh(TPP)Cl] precursor salt (45%, entry 1). The bis-NHC complex **3** shows initial activity that is comparable to **2**, though it remains active over a longer time period and achieves essentially quantitative conversions (entry 4). The high activity of the bis(carbene) complex **3** is remarkable when considering that the rhodium center is coordinatively saturated and suggests the substitution of (at least) one carbene ligand with a substrate alcohol or alkoxide in order to initiate  $\beta$ -hydrogen elimination.<sup>15</sup> Indeed, a substoichiometric experiment using a 3 : 1 ratio of alcohol and complex **3** revealed the quantitative formation of the monocarbene complex **2**.<sup>†</sup> As a direct implication, the notion of carbenes as robust spectator ligands requires caution.<sup>2</sup> Carbene dissociation<sup>16</sup> is presumably

Table 1 Catalytic aerobic oxidation of benzylalcohol by rhodium(III) porphyrin complexes<sup>a</sup>

Entry	Cat.	NMR yields (%)	
		1 h	24 h
1	[Rh(TPP)Cl]	20	45
2	[Rh(TPP)(Melm)Cl] <b>1</b>	2	19
3	[Rh(TPP)(NHC)Cl] <b>2</b>	38	72
4	[Rh(TPP)(NHC) <sub>2</sub> ]Cl <b>3</b>	43	92
5	[Rh(TPP)(NHC)(PF <sub>6</sub> )]	30	58
6 <sup>b</sup>	[Rh(TPP)(NHC) <sub>2</sub> ]Cl <b>3</b>	55	>95

<sup>a</sup> General conditions: benzyl alcohol (0.5 mmol), KOtBu (0.05 mmol) and catalyst precursor (0.025 mmol) were stirred in dichlorobenzene (2.5 mL) at 150 °C for 24 h; yields determined by <sup>1</sup>H NMR spectroscopy, average of at least two runs. <sup>b</sup> Irradiation using a xenon lamp.



Scheme 3 Oxidation of monodeuterated  $\text{MeO-BnOH-}d_1$ .

triggered by the high kinetic *trans* effect of the distal NHC as well as by re-aromatization of the porphyrin macrocycle and alleviation of the strain imparted by the methyl substituents of the NHC ligand. The distorted porphyrin in the bis(carbene) complex **3** may thus be considered as a spring-loaded system that discharges electronically and structurally by carbene dissociation and rearomatization. Attempts to facilitate the formation of the putative five-coordinate intermediate by the addition of  $\text{AgBF}_4$  to induce either  $\text{Cl}^-$  abstraction (with **2**, entry 5) or carbene transfer (with **3**) did not result in any rate enhancement, pointing towards the role of  $\text{AgBF}_4$  beyond simple halide abstraction. A significant kinetic isotope effect  $\text{KIE} = 2.5$  was determined when using the monodeuterated methoxy-substituted benzyl alcohol  $\text{MeO-BnOH-}d_1$  as a substrate (Scheme 3), suggesting rate-limiting C–H bond activation.

Interestingly, the catalytic activity of **3** is photochemical sensitive and an increase in initial catalytic activity was observed in runs performed with complex **3** under irradiation (Xe lamp; entry 6). Such photochemical stimulation doubled the initial performance, and up to 40% conversion was accomplished in 0.5 h (*cf.* 1 h for the same conversion in the dark).<sup>†</sup> At higher conversions, the amplification gradually vanishes. Such synergistic effects of the porphyrin spectator ligand are attractive and current work is directed towards generalizing this principle in NHC porphyrin hybrids.

Rhodium porphyrin synthons accommodate up to two apical NHC ligands. The high *trans* effect of the NHC ligand enhances the catalytic activity of the rhodium(III) center in oxidation catalysis. Substoichiometric experiments and reaction profiles demonstrate that the catalytic activity of the coordinatively saturated bis-NHC complex **3** is imparted by carbene dissociation. Facile breaking of the (typically strong)  $\text{Rh-C}_{\text{NHC}}$  bond is promoted by the high *trans* effect of the distal NHC ligand and by the distorted and considerably dearomatized porphyrin. Such sterically and electronically spring-loaded NHC-porphyrin hybrids are highly attractive for generating novel pre-catalysts with low activation barriers.

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