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

Juan Olguín, Helge Müller-Bunz and Martin Albrecht

Porphyridium(IIII) 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. Advantageous effects have been, in parts, attributed to the strong metal-carbon bond in NHC complexes, which originate from a relatively high covalent contribution to the overall bonding. 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. The combination of NHC ligands with porphyrins is remarkably under-explored, despite the beneficial features of porphyrins such as their photochemical activity. 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 prophyrin unit. For comparison, two [Rh(TPP)(L)Cl] complexes 1 and 2 were prepared which feature N-methylimidazole (1) and N,N’-dimethylimidazolidinylidene (2) as axial ligands, respectively (Scheme 1, TPP = meso-tetraphenyl porphyrin). Complex 1 was synthesised from [Rh(TPP)Cl] and excess (10 equiv) of 1-methylimidazole. Coordination of one imidazole ligand was unambiguously confirmed by the pertinent integral ratios and the characteristic deshielding of the imidazole protons induced by the porphyrin ring current (Δδ1 up to 6.5 ppm).

Complex 2 was prepared by thermal decarboxylation of N,N’-dimethylimidazolidinylidene carboxylate in the presence of [Rh(TTP)Cl] (Scheme 2). The carbene resonance appeared as a broad signal at δC 143.15 ppm (JRhC not resolved), some 40 ppm higher field than in typical rhodium(III) NHC complexes.10 The 1H NMR spectrum revealed two singlets at diagnostically high field, δH 4.67 and –0.46 ppm in a 1:3 ratio for the C-NHC–H and N–CH3 protons, respectively. The ring current effects are smaller than those observed for 1 and suggest a lower aromaticity 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), while in 1 they retain AX multiplicity.† This broadening is temperature-
dependent and suggests either inversion of the TPP puckering or rotation about the $C_{\text{meso}}$–$C_{\text{Rh}}$ 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 π-bond interaction. 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, $\Sigma = 19.82^\circ$, 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. 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 in 1, Rh–C$_{\text{NHC}}$ 2.051(2) Å vs Rh–N$_{\text{Melm}}$ 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$_{\text{NHC}}$ 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 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 $^1$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 is slightly less pronounced than in the monocarbene analogue 2. Likewise, the doublet of the carbene carbon is less shielded ($\delta_C = 153.15$ ppm, $J_{\text{Rh-C}} = 35$ 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), significantly more than even in 2, and the pyrrol rings are substantially twisted out of plane ($\Sigma = 11.8^\circ$). The two NHCs are mutually perpendicular. Despite the strong Rh–C$_{\text{NHC}}$ bonds, indicated inter alia by the substantial porphyrin deformation, the Rh–C$_{\text{NHC}}$ 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). With benzyl alcohol as model substrate, the monocarbene complex 2 showed a significantly higher activity than the imidazole-containing analogue 1 (72% vs 19%, entries 2,3). 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 has initial activity that is comparable to 2, though it remains active over a longer time period and reaches essentially quantitatively 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 β-hydrogen elimination. Indeed, a substoichiometric experiment using a 3:1 ratio of alcohol and complex 3 revealed the quantitative formation of the monocarbene complex 2. As a direct implication, the notion of carbennes as robust spectator ligands requires caution. Carbene dissociation is presumably 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 formation of the putative five-coordinate intermediate by the addition of AgBF$_4$ to induce either Cl$^-$ abstraction (with 2, entry 5) or carbene transfer (with 3) did not result in any rate enhancement, pointing towards a role of AgBF$_4$ beyond simple.
halide abstraction. A significant kinetic isotope effect KIE = 2.5 was determined when using the monodentated methoxy-substituted benzyl alcohol $^{18}$O-BnOH-$d_1$ as substrate (Scheme 4), suggesting rate-limiting C–H bond activation.

### Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic, catalytic, and crystallographic details. See DOI: 10.1039/c000000x/
11. $T_{\text{coa}} = 25^\circ \text{C}$ and $k_{\text{cat}} = 230 \pm 40 \text{s}^{-1}$ (Ag = 59.3 ± 0.5 kJ mol$^{–1}$).

### Conclusions

Rhodium porphyrin synths 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 impeded by carbene dissociation. Facile breaking of the (typically strong) Rh–C$_{\text{NHC}}$ bond is promoted by the high trans’ effect of the distal NHC ligand and by the distorted and considerably deametallated 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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New hybrid NHC porphyrin rhodium(III) complexes are active alcohol oxidation catalysts; their activity is entailed by carbene dissociation is significantly enhanced upon irradiation.