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A mesoionic nitrogen-donor ligand: structure, iridium coordination, and catalytic effects

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A mesoinic pyridylideneamide ligand (PYA) was synthetized and fully characterized and coordinated to an iridium(III) center. This ligand represents the first example of a mesoionic N-donor ligand. Structural and spectroscopic analysis revealed unique properties which were exploited in chemically driven water oxidation catalysis.

Metal-ligand bond interactions serve both to modulate the electronic properties of the metal center and to influence the steric environment of the metal coordination sphere, thus providing excellent control over the structure and reactivity of the coordinated metal center. Therefore, the design and development of new ligand motifs is crucial to advance the area of organometallic chemistry and homogeneous catalysis.¹ A particularly intriguing class of rare ligands are so-called mesoionic compounds, i.e. species which cannot be represented by a neutral Lewis structure, and which feature a formally negative and positive charge that are mutually conjugated.² Mesoionic carbenes (Figure 1a) constitute a class of such mesoionic ligands, in which the ligand is bound to the metal center through a carbenic carbon, which is formally a carbanion that is charge balanced by a conjugated iminium cation.³⁻⁵ These mesoionic carbenes are a subclass of Nheterocylic carbenes and have been extensively studied as strongly donating neutral C-donor ligands during the last decade. Even though nitrogen donor ligands have been widely studied and used in organometallic chemistry, mesoionic Ndonor ligands have not been known so far.

Herein, we describe the first mesoionic N-donor ligand, its coordination ability and its impact for catalytic transformations.

Electronic Supplementary Information (ESI) available: Synthetic procedures, general procedure for catalytic water oxidation, crystallographic details and NMR spectra of all new compounds. CCDC 1582052(2), 1582053(3) and 1582054(4). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



We have been intrigued by the donor ability of so-called pyridylidene amide (PYA) ligands (Fig. 1b), $^{6-12}$ which display a neutral as well as a zwitterionic limiting resonance form. We have demonstrated that depending on various factors (solvent, charge at metal), this PYA ligand adopts its structure and hence provides electronic flexibility.^{13,14} We have now exploited the synthetic versatility of the PYA ligands to modify the donor properties of the PYA unit by changing the position of the amide unit (Fig. 1c) to the meta position. This PYA isomer lacks an uncharged resonance form and therefore represents a mesoionic N-donor ligand system.



Figure 1 Representation of C4-imidazolylidene (I), C4-triazolylidene (II) and pyridylidene (III) as examples of mesoionic ligands (a), limiting resonance structures of a para-PYA unit (b) and a mesoionic meta-PYA unit (c).

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Scheme 1 Synthesis of the mesoionic pyridylidene amide 3 and its iridium complex 4

The synthesis of the meta-pyridinium amide salt as precursor of the mesoionic PYA ligand was accomplished in two simple steps. In analogy to the synthesis of the known para-PYA system.^{15,16} Accordingly, reaction of 3-aminopyridine and the substituted benzoyl chloride yielded the corresponding amide 1 in good yield (85%, Scheme 1).¹⁷ Subsequent methylation with Mel was selective and took place exclusively at the pyridine nitrogen, even when an excess of alkylating agent was used.¹⁸ The pyridinium salt **2** showed the pertinent $[M-I]^{\dagger}$ signal in highresolution MS at 303.1339 (theoretical value 303.1329 amu), and the appearance of a new singlet for the N–CH₃ group (δ_{H} = 4.41) along with a diagnostic downfield shift of the pyridinium protons by about 0.5 ppm when compared to the analogous resonances of the neutral pyridine precursor 1, corroborated the formation of the pyridinium salt 2. An amide N-H bending mode was observed at 1666 cm⁻¹ in the IR spectrum. The molecular structure of pyridinium salt 2 was further confirmed by X-Ray diffraction analysis (Figure 2). Amide deprotonation was accomplished with aqueous NaOH by a simple liquid-liquid extraction with CH₂Cl₂ from a 2 M NaOH solution of the pyridinum salt 2. The organic layer contained the free mesoionic ligand 3, which was isolated as an air-stable yellowish hygroscopic solid in a good yield (60%). Formation of the free PYA was indicated by the disappearance of the amide proton, as well as an upfield shift of about 0.4 ppm for the heterocyclic proton resonances in the ¹H NMR spectrum. In addition, the N-H bending feature was absent in the IR spectrum. The methoxysubstituted mesoionic PYA 3 readily crystallized from CH₂Cl₂ upon slow diffusion of pentane, and the molecular structure was unequivocally confirmed by single X-ray diffraction analysis (Figure 2).

The molecular structure of the mesoionic PYA reveals an almost co-planar arrangement of the pyridylidene unit and the amide group, as indicated by the small $C_{CO}-N-C_{\beta'}-C_{\alpha'}$ angle of 13.7°. The bond lengths within the pyridyl heterocycle do not show a distinct alteration, indicating a conjugated system with substantial aromatic character. A similar bonding situation was noted for the precursor pyridinium salt 2, with essentially equal C-C bonds within the heterocycle (average C-C bond is 1.383(13) Å in 2 and 1.383(15) Å in 3, Table 1). In contrast, the analogous para-PYA shows marked bond length alteration with short C_{α} -C_B bonds (average 1.36 Å) and long C_{β} -C_v bonds (average 1.43 Å).¹⁵ While the free para-PYA therefore demonstrates substantial diene character, the mesoionic meta-PYA 3 is predominantly aromatic. In agreement with this notion, the N_{PYA}-C_{pyr} bond in the mesoionic PYA 3 is substantially longer than in the free para-PYA ligand (1.381(2) Å vs 1.353(2) Å), which indicates a higher single-bond character as expected for a mesoionic structure.

Metal coordination of the mesoionic *N*-donor ligand **3** was demonstrated with an iridium(III) precursor. Addition of the free mesoionic PYA **3** to $[Ir(Cp)*Cl_2]_2$ in the presence of NaOAc induced also cyclometalation,^{19–21} and afforded the iridium complex **4** as an air-stable solid that was purified by column chromatography and obtained in 77% yield. Cyclometallation was evidenced by the split of the resonances due to the OMe groups into 3 distinct singlets in the ¹H NMR spectrum. Single crystal X-ray diffraction analysis yielded a molecular structure of complex **4** that shows the classical three-legged piano-stool Published on 06 December 2017. Downloaded by University of Newcastle on 07/12/2017 08:26:20

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Figure 1 ORTEP representation of pyridinium salt 2, PYA free ligand 3 and iridium complex 4 (50% probability; hydrogen atoms and cocrystallized solvent omitted for clarity).

geometry with the iridium center in a pseudo-tetrahedral geometry (Fig. 2). The bond lengths and angles around the iridium center are essentially identical to the metrics of similar PYA iridium complexes.^{15,16} As noted for the free ligand, also in the complex the $N_{\text{PYA}}\text{-}C_{\text{pyr}}$ bond length is considerably larger (1.394(4) Å) than in the isomeric para PYA complex (1.378(3) Å), suggesting a more pronounced single bond character of this bond in the mesoionic N-donor. It is worth noting that the bond lengths in the pyridylidene ring do not alter and are identical to those of the free PYA 3, suggesting very little perturbation of the pyridylidene unit of this N-donor ligand upon metal coordination. Such behavior supports a mesoionic notion, while the pyridylidene substituent in the para-PYA responds to metal coordination by a partial loss of the diene configuration. Moreover, the pyridyl ring is markedly twisted out of the amide plane in complex 4, as demonstrated by the large $C_{CO}-N_{PYA}-C_{B'} C_{\alpha'}$ dihedral angle of 49.374°. This large angle suggests negligible π electron density overlap between the amide and the pyridylidene residues.²² In contrast, this dihedral angle in the pyridinum salt 2 (22.560°) and especially the free mesoionic ligand 3 (13.668°) are much smaller.[†] Presumably, steric repulsion with the Cp* ligand forces the tilting of the pyridylidene ring.

 Table 1
 Bond length distances (Å) and angles (°) around the PYA moiety of pyridinium salt 2, mesoionic free base 3, and mesoionic PYA complex 4.

	2	3	4
Ir–N _{PYA}	-	-	2.093(3)
Ir–C _{Ph}	-	-	2.050(4)
Ir–Cl	-	-	2.4141(10)
$N_{PYA}-C_{\beta'}$	1.405(2)	1.381(2)	1.394(4)
N _{pyr} –C _a	1.352(2)	1.339(2)	1.351(4)
$N_{pyr} - C_{\alpha'}$	1.344(2)	1.354(2)	1.349(4)
$C_{\alpha} - C_{\beta}$	1.366(3)	1.368(2)	1.371(5)
$C_{\alpha'} - C_{\beta'}$	1.384(3)	1.396(2)	1.390(5)
$C_{\beta}-C_{\gamma}$	1.385(2)	1.373(2)	1.376(5)
$C_{\beta'} - C_{\gamma}$	1.397(2)	1.396(2)	1.395(5)
$C(O)-N-C_{\beta'}-C_{\alpha'}$	22.560	13.668	49.374

Infrared spectroscopic analysis of compounds **2–4** showed identical energies for the C=O stretch band ($v_{CO} = 1585\pm1 \text{ cm}^{-1}$), suggesting no perturbation of the C=O moiety upon deprotonation or metalation. Similarly, little perturbation of the amide C=O bond was noted for the *para*-PYA analogues although these compounds display two bands in this region, which were attributed to carbonyl and imine C=N vibrations ($v_{CE} = 1642\pm3 \text{ cm}^{-1}$ and 1590±5 cm⁻¹; E = O, N).

We have exploited the properties of this unique mesoionic N-donor ligand in the iridium-catalyzed water oxidation, one of the current bottle necks for the development of efficient artificial photosynthetic processes. Water oxidation was driven by $(NH_4)_2[Ce(NO_3)_6]$ (CAN) as sacrificial chemical oxidant, which is inactive on its own in the oxidation of water. Catalytic application is promoted by the good solubility of the mesoionic PYA iridium complex 4 in water. Upon addition of CAN immediate gas formation was observed and quantified dynamically with a home-built pressure transducer setup and calibrated by GC.²³ Quantitative analysis revealed turnover frequencies up to 1500 h⁻¹ (Table 2, entry 1) which is faster than most previously evaluated C,N-bidentate chelated or monodentate iridium complexes,²⁴ though not record-high.^{25,26} The catalyst demonstrates excellent robustness and utilizes CAN quantitatively, reaching almost the theoretical turnover limit with 4600 TON at 20 μ M catalyst concentration (entry 2).²⁷

 Table 2 Preliminary catalytic water oxidation data using complex 4.^a

Entry	[4]/µM	CAN/complex	TON	TOF_{max}/h^{-1}
1	49.9	7360	1810	1500
2	19.9	18440	4600	1210

^aMeasurements were performed in a sealed 40 mL EPA vial containing 10 mL 0.40 M CAN solution buffered in 1M HNO₃ and complex **4**. O₂ evolution was dynamically monitored with digital manometry and end points were calibrated by gas chromatography; TOF_{max} values were determined by calculating the rate of change of the generated oxygen over time from the kinetic trace.

In summary, we have synthetized, isolated and fully characterized the first mesoionic nitrogen-donor ligand. Modulation of the pyridylidene ring in a simple pyridylidene amide ligand by changing the amide position from the known *para*- to the *meta*-position afforded an air-stable *meta*-PYA

Journal Name

ligand, which represents a new class of *N*-donor system. Structural and spectroscopic analysis reveal the mesoionic properties of this ligand. While we have exploited the specific properties of this ligand in iridium-catalyzed water oxidation, the mesoionic properties are expected to have much wider impact on a variety of redox reactions. In particular the synthesis of the pyridinium salt precursor is highly convenient and allows for introducing a variety of functional features. This diversity combined with the facile accessibility of the free base ligand provides interesting opportunities for application in first row transition metal catalysis and for assisting single electron transfer pathways.

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Conflicts of interest

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There are no conflicts to declare.

Notes and references

- ⁺ The X-ray structure analysis are not unambiguous in justifying the term mesoionic for this type of ligands. From consideration of the bonding situation in the pyridyl heterocycle (no C-C bond length alteration) suggest as a prevailing polar structure a cationic charge on the pyridine nitrogen (or more exactly on its methyl substituent), and a negative charge on N_{PYA}. The representation with one polar structure would argue in favor of a zwitterionic terminology, and not a mesoionic system. In contrast, the flexibility of the C–N_{PYA} bond length (cf Table 1), and the distinct dihedral angles of the amide and the pyridine heterocycle suggest nonnegligible charge delocalization and hence supports a mesoionic terminology. Complementary studies in solution and the solid state will be needed to shed further light on the (de)localization of charges in this ligand system.
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A first example of a mesoionic ligand with a nitrogen coordination site was prepared by a simple and robust synthesis and is shown to have excellent properties for promoting iridium-catalyzed water oxidation.