

## An N-Heterocyclic Carbene Ligand with an Oxalamide Backbone

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Scheme 1. Synthesis and Reactivity of Carbene Precursor 1

Summary: The preparation of the novel N-heterocyclic carbene ligand 3 based on an oxalamide backbone is described. Carbene 3 is not stable as a monomeric species at ambient temperature but dimerizes to the olefin 4 in the absence of trapping reagents. Carbene 3 reacts with elemental sulfur, tert-butylisocyanide, or  $[M(COD)Cl]_2 (M = Rh, Ir)$  to give thione 5, ketenimine 6, or complexes [(3)M(COD)Cl] (7), respectively. The dicarbonyl complexes  $[(3)M(CO)_2Cl]$  (8) (M = Rh, Ir) show high-energy CO vibrations. The carbene ligand 3 behaves as a remarkably poor net electron donor compared to other NHC ligands.

## Introduction

Understanding and modifying the electronic structure of N-heterocyclic carbenes (NHCs) is an active field of current research.<sup>1</sup> While NHCs were soon recognized as superb donor ligands, their capability to exert some  $\pi$ -acceptor character as well has been appreciated only recently. The net donor properties of NHCs have been modified, for example, by introduction of electron-releasing or -withdrawing groups to either the N-bonded aryl groups or the C4 and C5 atoms of imidazol-2-ylidene rings.<sup>2</sup> While it is difficult to separate donor and acceptor contributions to the metal–NHC bond from experimental data, various theoretical studies indicate clearly that the acceptor contribution is not negligible.<sup>3</sup> Alternative approaches to modify the electronic properties of NHCs included the evaluation of cationic carbenes based on triazol structures<sup>4</sup> and the introduction

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of carbonyl groups into the backbone, thus to proceed from diamino to diamidocarbenes. The latter approach has been reported independently by the groups of César<sup>5</sup> and Bielawski,<sup>6</sup> respectively, based on easily available six-membered cyclic malonamide derivatives. In addition to the typical NHC behavior as nucleophilic ligands toward transition metal fragments, some electrophilic character was also observed for these diamido carbenes. In this communication we wish to report our own preliminary results concerning the synthesis and properties of a cyclic five-membered diamido carbene based on an oxalamide backbone. In a very recent study Roesler reported attempts to prepare related oxalamide-based NHCs with various N-aryl substituents, which proved elusive.<sup>7</sup> Furthermore, Cesar and Lavigne as well as Glorius reported the preparation and properties of five-ring NHCs with one carbonyl function in the backbone.<sup>8</sup>

## **Results and Discussion**

Reaction of N,N'-dimesitylformamidine with oxalyl chloride in chloroform according to a protocol reported by Richter<sup>9</sup> afforded the neutral five-membered oxalamide 1 in 98% yield as an off-white solid (Scheme 1). The formation of a neutral product with a chlorine atom attached to the C2 atom of the ring is in accord with César's observation in the case of the six-membered malonamide.<sup>5</sup> In contrast, Bielawski reported the formation of a cationic malonamide when chloride was exchanged for the less nucleophilc triflate anion.<sup>6</sup> The C–Cl bond in **1** is highly labile, and upon addition of methanol the 2-methoxy derivative **2** was obtained in nearly quantitative yield and fully characterized by spectroscopic methods (Scheme 1).

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Scheme 2. Synthesis and Reactivity of Carbene 3



Treatment of precursor 1 with NaHMDS (NaHMDS =  $NaN(SiMe_3)_2$ ) in THF at -80 °C leads to deprotonation and chloride elimination with subsequent formation of the neutral diamidocarbene 3, which proved too unstable to be characterized. Instead, after workup the olefin 4 was obtained as a result of carbene dimerization in 70% yield (Scheme 2). Olefin 4 is water-stable and can be handled in air for a short period of time. For the related six-membered malonamide-based carbenes, no dimerization was observed, and some derivatives could be characterized by NMR spectroscopy in solution at low temperature<sup>5,6</sup> and in one case by X-ray diffraction.<sup>6b</sup> Interestingly, Roesler reported that the treatment of molecular precursors analogous to 1 bearing other aryl substituents at nitrogen with bases resulted mainly in decomposition. However, he succeeded in isolating a side product in low yield, which was identified as a dimer connected by a C2-C2 single bond with additional H atoms located at the bridging C atoms.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a solution of 4 in dichloromethane at room temperature. The structure is shown in Figure 1 together with some representative geometric parameters. Olefin 4 is the first structurally characterized tetraamido ethylene. Both rings deviate only slightly from planarity, with a maximum atomic distance from the mean planes of 3.6(2) pm. All oxalamide ring atoms feature  $sp^2$ hybridization with most significant deviations for N1 (sum of angles 355.2°) and N3 (352.7°). In di(imidazolidin-2ylidenes) the N atoms are usually significantly pyramidalized with angle sums of 330-345°.<sup>10</sup> The length of the interannular C-C bond is 135.7(4) pm. The torsion angle between the heterocyclic rings is 19.2(2)°, a significant twist compared to di(imidazolidin-2-ylidenes), which usually feature torsion angles between 0° and 15°.<sup>10,11</sup> The geometrical parameters for both rings are very similar, with mean values for C=O of



Figure 1. Molecular structure of olefin 4 (ellipsoids drawn at 30% probability; H atoms and the solvating  $CH_2Cl_2$  molecule omitted for clarity). Selected distances (pm) and angles (deg): C1-C4 135.7(4), C1-N1 142.9(3), C1-N2 143.1(3), C2-N1 138.6(3), C3-N2 138.0(4), C2-O1 120.8(3), C3-O2 120.6(3), N1-C1-N2 104.7(2).

120.7 pm and OC-CO of 148.2 pm, longer C-N bonds to the olefinic C (142.8 pm), and shorter C-N bonds to C=O carbons (138.4 pm). The N-bonded mesityl groups are in a pairwise parallel orientation, with interplanar angles between respective planes of  $10.0(2)^{\circ}$  (rings containing C11 and C31) and  $4.4(2)^{\circ}$  (rings containing C21 and C41).

The formation of the carbene 3 as an intermediate species was corroborated by further trapping reactions. Addition of elemental sulfur to a solution of carbene 3 prepared in situ resulted in the formation of the expected thione 5, which was fully characterized by spectroscopic methods. Furthermore, carbene 3 also reacted cleanly with tert-butylisocyanide to afford the respective ketenimine 6 in good yield. Usually, the formation of ketenimines from isonitriles is observed only for highly electrophilic carbenes, available for example from diazoalkanes, and not for diamino NHCs characterized by a large HOMO-LUMO gap due to the stabilization exerted by the N atoms. Bielawski reported recently the formation of ketenimines from a malonamide-type carbene and attributed this reactivity to an energetically low-lying LUMO centered on the carbone carbon atom, providing this diamidocarbene with significant electrophilic character.<sup>6c</sup> In addition, the malonamide NHC studied by Bielawski reversibly formed a ketene upon reaction with CO and inserted into a secondary isopropyl C-H bond of a diisopropylphenyl group bound to the N atom.<sup>6a</sup> These latter two reactions were again taken as evidence for the electrophilicity of the malonamide NHC. In contrast, the oxalamide NHC 3 did not produce the respective ketene when exposed to CO. Instead, the olefin 4 was formed as the only product under these reaction conditions.

The propensity of the new NHC **3** to act as a ligand toward transition metal fragments was also evaluated. When a carbene solution was treated with a solution of  $[M(COD)Cl]_2$  (M = Rh, Ir) in THF at -80 °C, the complexes [(3)M(COD)Cl] **7a** (M = Rh) and **7b** (M = Ir) were isolated in 65% and 59% yield after chromatographic workup (Scheme 3). In contrast, treatment of the olefin **4** with  $[Rh(COD)Cl]_2$  did not result in the formation of complex **7a**.

The most prominent spectroscopic feature of the Rh complex 7a is the low-field carbene resonance in the <sup>13</sup>C NMR spectrum at 248 ppm, which appears as a doublet (54.6 Hz) due to the coupling to the Rh nucleus. For the analogous Rh complex with the six-membered malonamide NHC ligand, the resonance for the carbene-C was found at

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Scheme 3. Formation of Carbene Metal Complexes



245 ppm.<sup>5b</sup> The <sup>1</sup>H NMR spectrum of complex **7a** shows two signals for the olefinic protons of the COD ligand at 3.62 and 5.12 ppm. The spectroscopic properties of the Ir complex 7b are quite similar to those of the Rh analogue 7a. In addition, crystals of 7b suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution. The molecular structure of complex 7b is depicted in Figure 2 together with some geometrical parameters. The Ir atom is in a square-planar environment with a remarkably short Ir-C(NHC) distance of 193.1(9) pm. In (COD)IrCl complexes bearing NHCs derived from imidazole or imidazolidine the Ir-C(NHC) distance is usually found in the range 201–208 pm.<sup>12</sup> The bonds between Ir and the COD C atoms trans to the NHC are fairly long (228.0(9) and 225.6(8) pm) compared to other (NHC)Ir(COD)Cl complexes, where they are usually found in the range 217-219 pm.<sup>12c</sup> The Ir-C(COD) bonds *trans* to the chloride are significantly shorter (215.1(9) and 218.2(9) pm), as is usually observed. The C=C bond lengths of the COD ligand are also strongly affected by the groups bound in *trans* position to Ir: the C=C bond *trans* to NHC is short (136.3(15) pm), while the one trans to Cl is considerably longer (141.1(13) pm).

In order to use IR spectroscopy to evaluate the electronic properties of the NHC ligand 3, the carbonyl complexes 8a,b were prepared from the COD complexes by bubbling a slow stream of CO through a solution of complexes 7a,b (Scheme 3). The carbonyl derivatives 8 are much more sensitive than the COD complexes, and only the Rh derivative 8a could be obtained in analytically pure form by chromatography. In the <sup>13</sup>C NMR spectrum of the Rh complex 8a the signals for the carbene-C and amide-C atoms are observed at 242 and 152 ppm, respectively, while the signals for the carbonyl C atoms are found at 181 and 184 ppm. For the Ir complex 8b the signal for the NHC carbon appeared at 229.8 ppm and the signals for the CO ligands were detected at 167.4 and 179.5 ppm. The IR spectra of 8a,b show two strong CO stretching vibrations at  $^{2}$ 017 and 2103 cm<sup>-1</sup> (**8a**,  $\nu_{av} = 2060$  cm<sup>-1</sup>) and 2003 and 2089 cm<sup>-1</sup> (**8b**,  $\nu_{av} = 2046$  cm<sup>-1</sup>), respectively. Compared to other  $M(CO)_2Cl$  (M = Rh, Ir) complexes bearing NHC ligands, the stretching vibrations of complexes **8a**,**b** are located at very high wavenumbers. Specifically, in the case of Rh complexes Bielawski reported CO bands located at 2017 and 2099 cm<sup>-1</sup> for the complex with the 4,5-dicyanoimidazol-2-ylidene ligand, which was shown to exert a reasonable degree of  $\pi$ -acceptor character.<sup>2c</sup> For the related complex with a malonamide NHC ligand,  $v_{av}$ (CO) was found to be 2045 cm<sup>-1.5b</sup> Usually, Rh-(CO)<sub>2</sub>Cl complexes with diaminocarbenes based on imidazolor imidazolidin-2-ylidene have their  $v_{av}(CO)$  in the range



**Figure 2.** Molecular structure of Ir complex **7b** (ellipsoids drawn at 30% probability; H atoms omitted for clarity). Selected distances (pm) and angles (deg): Ir1–Cl1 235.9(2), Ir1–Cl1 193.1(9), Ir1–C22 215.1(9), Ir1–C23 218.2(9), Ir1–C26 225.6(8), Ir1–C27 228.0(9), N1–C1–N2 105.1(7), C1–Ir1–Cl1 95.8(2).

2030-2045 cm<sup>-1</sup>.<sup>13,8b</sup> In a very interesting study, César reported a series of complexes bearing five-membered NHCs, derived from a mixed amino-amido heterocycle with a CO-CH<sub>2</sub> backbone. This species can act either as a neutral NHC ligand or, after deprotonation, as an anionic enolate, or as a neutral enolether after O-functionalization of the enolate with appropriate electrophiles. The Rh(CO)<sub>2</sub>Cl complexes of all three ligand types were examined, and  $\nu_{av}(CO)$  values were found to be 2048.5, 2029.5, and 2037 cm<sup>-1</sup>, respectively.<sup>8b</sup> All experimental data indicate that the oxalamide NHC 3 acts as one of the poorest net electron donors among the N-heterocyclic carbenes. Moreover, theoretical work carried out recently by Roesler indicates that oxalamide-based NHCs feature a quite small HOMO-LUMO gap and, in particular, a low-lying LUMO, which endows these ligands with considerable  $\pi$ -acceptor character,<sup>7</sup> much more pronounced than in the majority of imidazole- and imidazolidine-based NHCs.<sup>2</sup> The exceptionally short Ir-C(NHC) bond (vide supra) may thus be considered as arising from this pronounced  $\pi$ -acceptor contribution. The fact that carbene 3 is not stable as a monomeric species but dimerizes to the olefin 4 can be regarded as additional evidence for the small HOMO-LUMO gap as well.<sup>14</sup>

In conclusion, we have prepared a novel type of N-heterocyclic carbene ligand, 3, based on an oxalamide backbone. While the carbene is not stable as a monomeric species at ambient temperature, it gives rise to the formation of the olefin 4 as a result of dimerization in the absence of trapping reagents. In the presence of either elemental sulfur or tertbutylisocyanide the carbene thione 5 and the ketenimine 6 are obtained, respectively. NHC 3 also reacts cleanly with the dimeric species  $[M(COD)Cl]_2$  (M = Rh, Ir) to afford the complexes [(3)M(COD)Cl] (7). The dicarbonyl complexes  $[(3)M(CO)_2Cl]$  (8) show high-energy CO vibrations, which proves the poor net electron donor property of the carbene ligand 3, while theoretical work indicates that this character is at least partly due to a considerable  $\pi$ -acceptor contribution. Further work to evaluate the reactivity of the new ligand type is currently in progress.

**Supporting Information Available:** Experimental details for the preparation of the reported compounds and crystallographic data (CIF files) for compounds **4** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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