Reductions of Challenging Organic Substrates by a Nickel Complex of a Noninnocent Crown Carbene Ligand

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Abstract: The first crown-tetracarbene complex of Ni(II) has been prepared, and its crystal structure determined. The complex can be reduced by Na/Hg, with an uptake of two electrons. The reduced complex reductively cleaves aranesulfonamides, including those derived from secondary aliphatic amines, and effects Birch reduction of anthracenes as well as reductive cleavage of stilbene oxides. Computational studies show that the orbital that receives electrons upon reduction of the complex 2 is predominantly based on the crown carbene ligand and also that the HOMO of the parent complex 2 is based on the ligand.

We recently reported1 the synthesis of a new family of metal N-heterocyclic carbene (NHC) complexes, consisting of a macrocyclic (crown) tetra-NHC enclosing either a single Pd(II) ion or two ions of Cu(I) or Ag(I). In view of the exceptional σ-donor properties of NHC ligands,2 this macrocyclic tetra-NHC should be able to affect significantly the redox properties of transition metals. We are interested in strong and selective reducing agents3,4 and reasoned that reduced metal crown NHC complexes3h should be particularly powerful in this regard. Fort and co-workers showed5 that Ni(0)/imidazolium chloride/NaOCl was partly hidden when a Pt cathode was used but fully revealed when a glassy carbon electrode was used. A second peak was not observed before the onset of solvent (DMF) reduction. Such a highly negative potential implies that the neutral tetracarbene ligand has extraordinary power to inhibit reduction of the Ni(II) ion, compared to all previous neutral ligands.9,10 No oxidation of the Ni(II) complex was observed in CV in the range 0 to +2.5 V. This shows that the crown carbene ligand spectacularly inhibits both reduction and oxidation at nickel.

To test the reactivity of the reduced complex 4 formed from amalgam reductions, aliquots of the resulting red solution were separated from the amalgam and added to substrates. The carbonyl compounds, PhCHO, PhCHO, 5, and PhCOMe, 7, were reduced exclusively to the (d,l)-isomer of the corresponding pinacol products 6 (64%) and 8 (69%) respectively,7,11 while benzophenone 9 afforded benzhydril 10 (65%) (Scheme 2). These selective reductions contrast with other Ni-based reductions of ketones and aldehydes, where mixtures of pinacol and alcohol products are seen.12,13 Complex 4 did not lead to reduction of aliphatic ketones.

Our attention now turned to one of the most challenging reductive transformations in organic chemistry, the Birch reduction of aromatic rings,14 routinely involving alkali metals in liquid NH3.14c,d Reaction of anthracene 11a with 4 afforded 9,10-dihydroanthracene 12a (55%) following an inverse quench14c,d of the reaction mixture. More electron-deficient 9-substituted anthracenes 11b–e worked well also (54–85%). Complex 4 was also reacted with p-
toluenesulfonamides including 13 and 15, which are among the most difficult functional groups for reduction, despite common application as both protecting and activating groups.15 Even the least reactive toluenesulfonamides, those derived from secondary aliphatic amines, e.g. 13, underwent efficient reductive cleavage, although this required an excess (4 equiv) of the reducing agent to achieve a reasonable rate3c (Scheme 3; see Supporting Information (SI) for further examples). The reductive nature of the cleavages was established by adding iodomethane to the products from reaction of 15. This afforded sulfone 17 (72%) via methylation of the p-toluenesulfinate anion. Finally, complex 4 also reduced cis- and trans-stilbene oxides 18 and 19 respectively to (E)-stilbene 20 and 1,2-diphenylethanol 21.4 The formation of common products from both epoxide isomers is consistent with a common intermediate, as expected for an electron transfer mechanism.

Computational studies reveal the true nature of the redox processes. Complex 2 is formally a Ni(II) complex with the crown carbene ligand. However, the addition of an electron to this system populates the LUMO of 2, which resides primarily on the crown carbene ligand (Figure 1). As such, the monocationic complex (22) can be considered as a Ni(II) species with a radical anion ligand, rather than involving reduction of the metal center. This is confirmed upon inspection of the single occupied MO (SOMO) of 22 (Figure 2), which is closely related to the LUMO of 2. There is a minor difference in the interaction of the Ni d-orbital with the carbene ligands, which is due primarily to the distortion of the geometry of the first coordination sphere. That is, there is a slight deviation from planarity about the metal center upon reduction of the system (Table 1). Nonetheless, the p-orbitals on the carbene C atoms clearly dominate in both the LUMO of 2 (Figure 1) and the SOMO of 22 (Figure 2).

Further reduction of the crown carbene complex results in the addition of a second electron to the crown carbene ligand. The second electron is clearly donated into the half-filled orbital that is predominantly ligand-based, encompassing the carbon of each of the four imidazolylidene rings (Figure 3) with only a small component on the Ni ion; 4 may best be viewed as a ligand dianion complex of Ni(II). The HOMO of the neutral compound 4 (Figure 3) is, to all intents and purposes, identical to the SOMO of 22 (Figure 2). This results in a closed shell system, with the Ni(II)
metal center coupled to the doubly anionic crown carbene ligand. A more pronounced tetrahedral distortion is observed at the metal center in this case. Furthermore, in both 4 and 22 the C_{carbone}−N distances increase by about 0.03 Å and the N−C−N angle becomes more acute by about 2° (with respect to 2), emphasizing the ligand-based nature of the electron transfer (Table 1). While ligand noninnocence has been long-established in square planar nickel chemistry (especially with dithiolene ligands), it has not previously been observed in NHC ligands. In order to test the conformational stability of the reduced complex 4, the geometry of the first coordination sphere was distorted to break one or two of the Ni−N bonds. However, upon optimization, the distorted species immediately collapses back to the square planar arrangement.

Studies of the putative oxidized species 23 (Figure 2) similarly show that the electron transfer is from a ligand-based orbital, rather than the Ni, with the square planar geometry around the metal remaining largely undisturbed. An attempt to stabilize electrons around the metal center in the parent species 2 by coordination expansion, allowing one or two solvent molecules to access the axial sites at the metal center, was also unsuccessful. Attempts to optimize the solvent complexes resulted in their expulsion from the first coordination sphere and formation of outer sphere complexes via electrostatic interactions (Figures S2 and S3 in SI).

Thus, we conclude that the crown carbene ligand spectacularly inhibits the redox processes at the Ni center as a result of (i) inflexibility of the metal coordination sphere, (ii) inability to undergo coordination expansion due to the ligand conformation, and (iii) the low energy of the filled metal-based orbitals relative to the MOs of the crown carbene.

Acknowledgment. We thank EPSRC Mass Spectrometry Centre, Swansea, and EPSRC, WestCHEM, and the Glasgow Centre for Physical Organic Chemistry (GCPOC) for funding.

Supporting Information Available: Experimental procedures, spectroscopic data, cif file for 2 computational results and cyclic voltammetry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA107703N