J|A|C|S
COMMUNICATIONS

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

Neil J. Findlay, Stuart R. Park, Franziska Schoenebeck, Elise Cahard, Sheng-ze Zhou,
Leonard E. A. Berlouis, Mark D. Spicer,* Tell Tuttle,* and John A. Murphy*

*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building,
295 Cathedral Street, Glasgow, G1 1XL, United Kingdom*

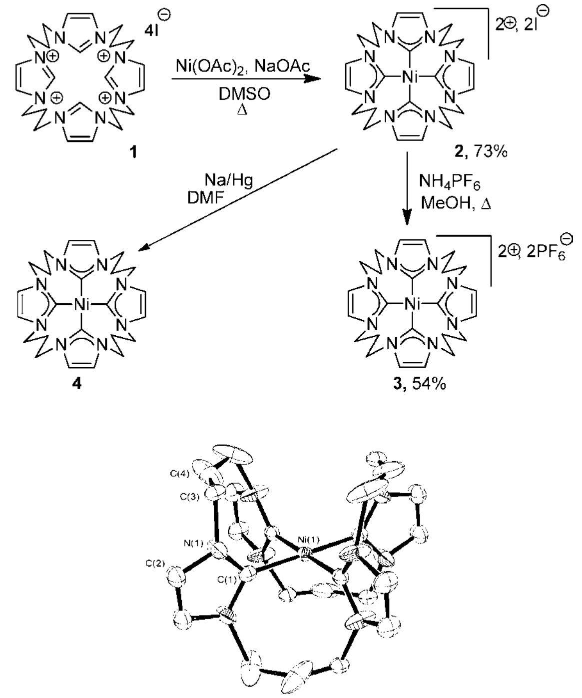
Received March 26, 2010; E-mail: john.murphy@strath.ac.uk

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 arenesulfonamides, 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 reported[1] 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 agents[3,4] and reasoned that reduced metal crown NHC complexes[3h] should be particularly powerful in this regard. Fort and co-workers showed[5] that Ni(0)/imidazolium chloride/NaO*i*Pr and related systems were effective for reducing aryl halides (including aryl fluorides) to arenes. In that case, a standard Ni(0)/Ni(II) cycle, featuring oxidative addition and reductive elimination, was entirely consistent with their results. We now report the synthesis of the Ni(II) crown tetra-NHC complex **2**[6] and its two-electron reduction to the complex **4** which shows remarkable electron transfer chemistry.

Nickel(II) complex **2** was synthesized from macrocycle **1** (Scheme 1) and recrystallized from methanol. The crystal structure of **2** reveals a square planar nickel atom coordinated by all four NHC ligands. The ligand conformation topologically resembles the cover of a tennis ball. To study the redox activity of **2**, it was treated with excess Na/Hg, and an aliquot of the supernatant solution was removed for titration against iodine. A 1 equiv amount of the reduced nickel complex converted 1 equiv of iodine to 2 mol of iodide, indicating that the reduced nickel complex was a two-electron donor.[7] Hence, the reduced complex **4** could be viewed formally as a Ni(0) complex (but see below for a more accurate description).

Scheme 1. Synthesis of Nickel-Containing Complexes and the X-ray Crystal Structure of **2** (Only the Cation Is Shown)



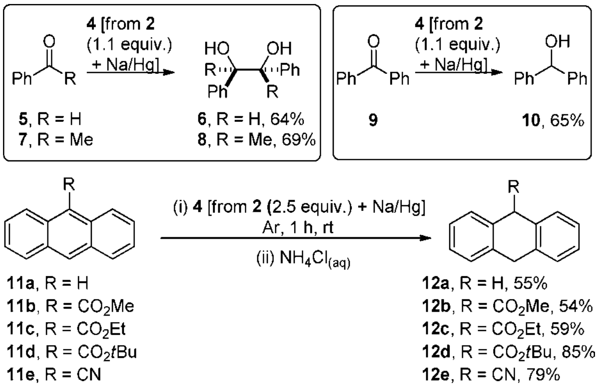
The corresponding PF_6 salt (**3**) was prepared for analysis by cyclic voltammetry (CV).[8] Reduction of the complex revealed an irreversible electron transfer at −2.4 V vs Ag/AgCl corresponding to a single electron transfer (calibrated against Fc/Fc^+). This peak was partly hidden when a Pt cathode 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, **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 benzhydrol **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 NH_3.[14c,d] Reaction of anthracene **11a** with **4** afforded 9,10-dihydroanthracene **12a** (55%) following an inverse quench[14c,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*-

10.1021/ja107703n

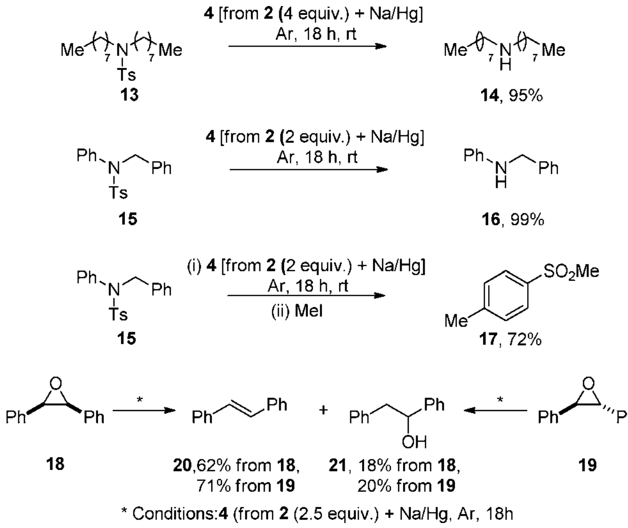
Scheme 2. Reductions of Carbonyl Compounds and of Anthracenes



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 rate[3c] (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_z-orbitals on the carbene C atoms clearly dominate in both the LUMO of **2** (Figure 1) and the SOMO of **22** (Figure 2).

Scheme 3. Reductive Cleavage of Organic Substrates Using Complex **4**



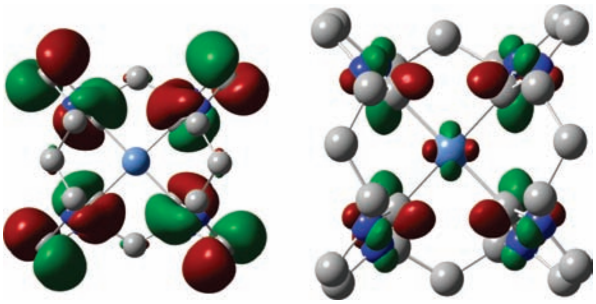


Figure 1. HOMO (left) and LUMO (right) of the Ni(II) crown carbene complex **2**. System charge is 2+.

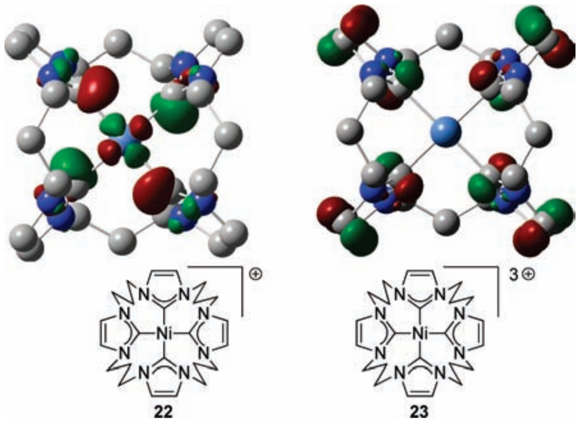


Figure 2. (Left) SOMO of the Ni crown carbene complex **22** [system charge is 1+] and (right) SOMO of the Ni crown carbene complex **23** [system charge is 3+].

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 carbenic 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)

Table 1. Selected X-ray Crystallographic and Calculated Structural Parameters for **2**, **4**, **22**, and **23**

	2		4	22	23
	X-ray	Calcd	Calcd	Calcd	Calcd
d(Ni−C), Å	1.900(7)	1.930	1.962	1.963	1.933
		1.930	1.962	1.962	1.957
		1.930	1.962	1.963	1.957
		1.930	1.963	1.963	1.932
∠C−Ni−C, deg (cis)	90	90.01	91.96	90.29	87.50
	90	90.00	92.00	90.40	92.79
	90	90.02	91.95	90.34	87.50
	90	89.96	91.97	90.33	87.10
∠C−Ni−C, deg (trans)	180	179.77	158.57	171.16	178.01
	180	179.82	158.67	171.16	176.86
d(C$_{carbene}$−N), Å	1.331(6)	1.366	1.391	1.377	1.370
		1.366	1.404	1.381	1.370
∠N−C$_{carbene}$−N, deg	102.6(6)	104.2	101.5	103.0	104.7

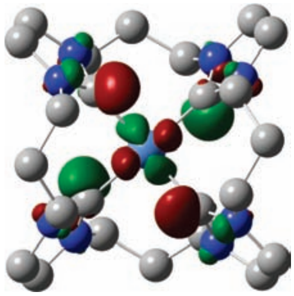


Figure 3. HOMO of the nickel crown carbene complex **4**. System charge is 0.

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 $C_{carbene}-N$ 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),[16] it has not previously been observed in NHC ligands.[17,18]

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−NHC bonds. However, upon optimization, the distorted species immediately collapses back to the stable 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.[19]

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.

References

(1) McKie, R.; Murphy, J. A.; Park, S. R.; Spicer, M. D.; Zhou, S.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 6525–6528.

(2) While NHCs are substantially stronger σ-donors than phosphines, their π-acceptor ability has become more widely acknowledged recently, particularly with electron-rich metals. Computational studies on Ni(0) complexes. (Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350–4358. Radius, U.; Bickelhaupt, F. M. *Coord. Chem. Rev.* **2009**, *253*, 678–686) are particularly relevant.

(3) (a) Murphy, J. A.; Khan, T. A.; Zhou, S.-Z.; Thomson, D. W.; Mahesh, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1356–1360. (b) Murphy, J. A.; Zhou, S. Z.; Thomson, D. W.; Schoenebeck, F.; Mohan, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5178–5183. (c) Schoenebeck, F.; Murphy, J. A.; Zhou, S.-Z.; Uenoyama, Y.; Miclo, Y.; Tuttle, T. *J. Am. Chem. Soc.* **2007**, *129*, 13368–13369. (d) Murphy, J. A.; Garnier, J.; Park, S. R.; Schoenebeck, F.; Zhou, S.-Z.; Turner, A. T. *Org. Lett.* **2008**, *10*, 1227–1230. (e) Garnier, J.; Murphy, J. A.; Zhou, S. Z.; Turner, A. T. *Synlett* **2008**, 2127–2131. (f) Cutulic, S. P. Y.; Murphy, J. A.; Farwaha, H.; Zhou, S. Z.; Chrystal, E. *Synlett* **2008**, 2132–2136. (g) Murphy, J. A.; Schoenebeck, F.; Findlay, N. J.; Thomson, D. W.; Zhou, S. Z.; Garnier, J. *J. Am. Chem. Soc.* **2009**, *131*, 6475–6479. (h) Park, S. R.; Findlay, N. J.; Garnier, J.; Zhou, S. Z.; Spicer, M. D.; Murphy, J. A. *Tetrahedron* **2009**, *65*, 10756–10761. (i) Cutulic, S. P. Y.; Findlay, N. J.; Zhou, S. Z.; Chrystal, E. J. T.; Murphy, J. A. *J. Org. Chem.* **2009**, *74*, 8713–8718.

(4) Mahesh, M.; Murphy, J. A.; Wessel, H. P. *J. Org. Chem.* **2005**, *70*, 4118–4123, and references therein.

(5) (a) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2002**, *21*, 1554–1559. (b) Kuhl, S.; Schneider, R.; Fort, Y. *Adv. Synth. Catal.* **2003**, *345*, 341–344. (c) For other Ni(0) reactions with carbene ligands, see: Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, *42*, 5689–5692.

(6) For a dicarbene,dipyridine-crown nickel complex, see: Baker, M. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *Organometallics* **2002**, *21*, 2674–2678.

(7) Blank reactions showed that (i) the Ni(II) complex did not react with iodine; (ii) in the absence of any nickel complex, an aliquot of supernatant liquid from a stirred mixture of sodium amalgam and DMF gave no reaction either with the anthracene (**11d**) or with acetophenone (**7**); and (iii) treatment of macrocycle (**1**) with Na/Hg did not lead to reduction of the anthracene (**11d**) [see SI for further information].

(8) Complex **3**; 0.01 M soln in 0.1 M Bu_4NPF_6/DMF; glassy carbon working electrode, Pt counter electrode, Ag/AgCl/KCl(sat.) reference electrode. CV operated at 50 mV/s.

(9) (a) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109–3118. (b) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392–400.

(10) (a) Esteves, A. P.; Ferreira, E. C.; Medeiros, M. J. *Tetrahedron* **2007**, *63*, 3006–3009. (b) Mubarak, M. S.; Peters, D. G. *J. Electroanal. Chem.* **1992**, *332*, 127–134.

(11) (a) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61–63. (b) Chatterjee, A.; Joshi, N. N. *Tetrahedron* **2006**, *62*, 12137–12158.

(12) A computational investigation of the reaction complex between **4** and **5** shows no direct interaction between the metal center and the substrate.

(13) (a) Kashiwagi, Y.; Kikuchi, C.; Kurashima, F.; Anzai, J. *J. Organomet. Chem.* **2002**, *662*, 9–13. (b) Radivoy, G.; Alonso, F.; Yus, M. *Tetrahedron* **1999**, *55*, 14479–14490, and references therein.

(14) (a) Birch, A. J. *J. Chem. Soc.* **1944**, 430–436. (b) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579–1603. (c) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283–4288. (d) Rabideau, P. W.; Huser, D. L.; Nyikos, S. J. *Tetrahedron Lett.* **1980**, *21*, 1401–1404. (e) For Sm(II) induced Birch reduction, see: Ankner, T.; Hilmersson, G. *Tetrahedron* **2009**, *65*, 10856–10862.

(15) (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; J. Wiley & Sons: New York, 1991. (b) Kocieński, P. J. *Protecting Groups*; Georg Thieme Verlag: Stuttgart, NY, 1994.

(16) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483–1489. (b) For an overview of noninnocence in transition metal dithiolene chemistry, see: Ray, K.; Petrenko, T.; Wieghardt, K.; Neese, F. *Dalton Trans.* **2007**, 1552–1566, and references therein.

(17) For redox processes on free NHCs (a) reduction, see: Enders, D.; Breuer, K.; Raabe, G.; Simonet, J.; Ghanimi, A.; Stegmann, H. B.; Teles, J. H. *Tetrahedron Lett.* **1997**, *38*, 2833–2836. (b) For oxidation, see: Siemeling, U.; Farber, C.; Leibold, M.; Bruhn, C.; Mucke, P.; Winter, R. F.; Sarkar, B.; von Hopffgarten, M.; Frenking, G. *Eur. J. Inorg. Chem.* **2009**, 4607–4612.

(18) For another interpretation of noninnocence in carbenes, see: Romain, C.; Miqueu, K.; Sotiropoulos, J. M.; Bellemin-Laponnaz, S.; Dagorne, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 2198–2201.

(19) In nickel dithiolene systems $[Ni(dth)_2]^{n-}$ ($n = 2, 1, 0$)[15] the ligand π-orbitals are also at higher energies than the metal-based orbitals and reduction results in population of predominantly ligand-based orbitals.

JA107703N