Inorganica Chimica Acta 364 (2010) 167–171

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Reduction chemistry of the mixed ligand metallocene $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}C_8H_8)$ with bipyridines

Michael K. Takase, Ming Fang, Joseph W. Ziller, Filipp Furche, William J. Evans *

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

ARTICLE INFO

Article history:
Available online 30 July 2010

Dedicated to Professor Arnold Rheingold for his extensive contributions to chemistry and for his extraordinary efforts to make crystallographic data more accessible to everyone.

Keywords:
Non-innocent ligand
Redox
Cyclopentadienyl
Cyclooctatetraenyl
Uranium
Bipyridine

ABSTRACT

The U^{4+} cyclooctatetraenyl complex, $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}C_8H_8)$, **1**, reacts with two equiv of 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) and 2 equiv of 2,2′-bipyridine (bipy) to form 2 equiv of $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)U(Me_2bipy\text{-}\kappa^2N,N')$ and $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)U(bipy\text{-}\kappa^2N,N')$, respectively. X-ray crystallography, infrared spectroscopy, and density functional theory calculations indicate that the products are best described as U^{4+} complexes of bipyridyl radical anions. Hence, only one of the $(C_8H_8)^{2-}$ ligands in **1** acts as a reductant and delivers 2 electrons per equiv of **1**. Since the reduction potentials of uncomplexed $(C_8H_8)^{2-}$, Me_2bipy, and bipy are −1.86, −2.15, and −2.10 V vs SCE, respectively, it is likely that prior coordination of the bipyridine reagents enhances the electron transfer.

1. Introduction

$[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}C_8H_8)$, **1**, is a U^{4+} complex that has recently been studied to define the capacity of ligand based reduction in organoactinide chemistry [1–5]. Complex **1** typically effects two electron reduction chemistry to make U^{4+} products formally using one of its three $(C_8H_8)^{2-}$ ligands as the reducing agent. Scheme 1 shows the formal half reaction and Scheme 2 shows an example with phenazine [2].

The combination of an electron and a $[(C_5Me_5)(C_8H_8)U]^{1+}$ cation in Scheme 1 is formally equivalent to the U^{3+} complex, $(C_5Me_5)(C_8H_8)U$, and it is conceivable that the reductions involving **1** could go through U^{3+} intermediates. The chemistry of cyclopentadienyl cyclooctatetraenyl U^{3+} complexes was originally examined in the 1990s with the solvated complex $(C_5Me_5)(C_8H_8)U(THF)$, **2** [6].

The reaction of **1** with 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) was of interest because it had earlier been reported that **2** reacts with Me_2bipy, not by reduction, but by ligand substitution to make a product formulated as a U^{3+} complex of the neutral bipyridine, $(C_5Me_5)(C_8H_8)U(Me_2bipy)$, **3**, Scheme 3. If **1** made the same product, it would be an example in which the $(C_8H_8)^{2-}$-based reduction resulted in a metal oxidation state change rather than a substrate reduction. Since the $(C_8H_8)^{2-}$ ligands in **1** do not reduce the U^{4+} ions in **1**, this would be a case in which there was a delicate balance in the location of electrons depending on the composition of the specific system.

The reactions of **1** with bipyridines were also of interest since the redox potential for the $C_8H_8/(C_8H_8)^{2-}$ couple is −1.86 V vs SCE [7], whereas the reduction potentials of Me_2bipy and bipy are −2.15 and −2.10 V vs SCE, respectively [8]. On the basis of the redox potentials of these species in the absence of a metal, reduction of the bipyridines by $(C_8H_8)^{2-}$ would not be expected. It has previously been found that **1** does not reduce anthracene (−1.98 V vs SCE) [9], acenaphthylene, (−1.65 V vs SCE) [9], or benzanthracene (−1.58 V vs SCE) [9]. Reduction of bipyridines by **1** would indicate an influence by the metal in the reduction process. To examine this possibility, the reactions of **1** with Me_2bipy and the unsubstituted bipy were performed and the products were analyzed by X-ray crystallography, infrared spectroscopy, and density functional theory calculations.

2. Experimental

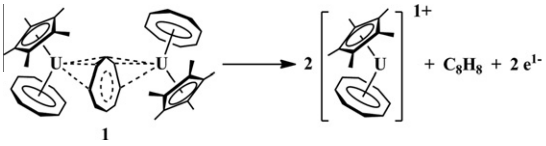
2.1. Materials and methods

The syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using

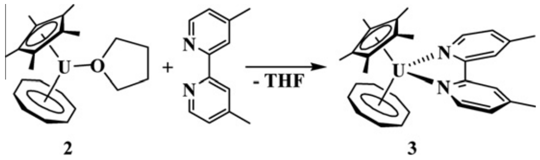
---

* Corresponding author. Tel.: +1 949 8245174; fax: +1 949 8242210.
E-mail address: wevans@uci.edu (W.J. Evans).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.07.074



Scheme 1.



Scheme 3.

glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred prior to use. ^{1}H NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. [(C_5Me_5)(C_8H_8)U]$_2$(μ-C_8H_8), **1**, was prepared as previously described [5]. 4,4′-Dimethyl-2,2′-bipyridine (Me_2bipy) and 2,2′-bipyridine (bipy) were purchased from Aldrich and sublimed before use. Elemental analyzes were performed on a Perkin–Elmer 2400 CHNS elemental analyzer.

2.2. Synthesis of (η^5-C_5Me_5)(η^8-C_8H_8)U(Me_2bipy-κ^2N,N′), 4

A colorless solution of Me_2bipy (35 mg, 0.19 mmol) in benzene was added to a dark brown solution of **1** (100 mg, 0.094 mmol) in benzene (6 mL) and stirred overnight. The solvent was removed under vacuum to yield **4** as a dark brown powder (124 mg, 99%). In an NMR scale experiment, free C_8H_8 was observed at 5.6 ppm in a 1:2 molar ratio with **4** by ^{1}H NMR spectroscopy. To confirm the identity of **4**, crystals suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. The complex crystallized in the space group $P2_1/c$ in a solvate free form. Crystallization of **4** from a toluene/Et_2O mixture at −35 °C gave single crystals of (η^5-C_5Me_5)(η^8-C_8H_8)U(Me_2bipy-κ^2N,N′)·(solvent), **5**, that had solvent in the cell lattice and crystallized in the $Pna2_1$ space group that matched that for (η^5-C_5Me_5)(η^8-C_8H_8)U(Me_2bipy-κ^2N,N')·(Et_2O), **3**·(Et_2O), in the literature [6]. The structure of **5** is isomorphous with **3**·(Et_2O) [6], but the ligands on uranium were disordered and there were high thermal parameters on the lattice solvent that was modeled as toluene. ^{1}H NMR (C_6D_6): δ 103.9 (s, $\Delta\nu_{1/2}$ = 28 Hz, 6H, *Me*$_2$bipy), 2.3 (s, $\Delta\nu_{1/2}$ = 13 Hz, 15H, C_5*Me*$_5$), −13.5 (s, $\Delta\nu_{1/2}$ = 6 Hz, 2H, Me_2*bipy*), −15.9 (s, $\Delta\nu_{1/2}$ = 48 Hz, 8H, C_8*H*$_8$), −52.0 (s, $\Delta\nu_{1/2}$ = 35 Hz, 2H, Me_2*bipy*), −112.3 (s, $\Delta\nu_{1/2}$ = 56 Hz, 2H, Me_2*bipy*). ^{1}H NMR (THF-d_8): δ 100.5 (s, $\Delta\nu_{1/2}$ = 26 Hz, 6H, *Me*$_2$bipy), 1.9 (s, $\Delta\nu_{1/2}$ = 12 Hz, 15H, C_5*Me*$_5$), −11.3 (s, $\Delta\nu_{1/2}$ = 6 Hz, 2H, Me_2*bipy*), −15.9 (s, $\Delta\nu_{1/2}$ = 45 Hz, 8H, C_8*H*$_8$), −52.4 (s, $\Delta\nu_{1/2}$ = 32 Hz, 2H, Me_2*bipy*), −104.8 (s, $\Delta\nu_{1/2}$ = 63 Hz, 2H, Me_2*bipy*). IR: 3030m, 2900s, 2852s, 2197m, 1569s, 1491s, 1469m, 1417s, 1326m, 1268m, 1219w, 1180w, 971m, 959s, 901m, 818w, 771w, 722s, 675w cm^{-1}. *Anal.* Calc. for $C_{30}H_{35}N_2U$: C, 54.46; H, 5.33; N, 4.23. Found: C, 54.89; H, 5.38; N, 4.45%.

2.3. Synthesis of (η^5-C_5Me_5)(η^8-C_8H_8)U(bipy-κ^2N,N′), 6

A colorless solution of bipy (30 mg, 0.19 mmol) in benzene was added to a dark brown solution of **1** (100 mg, 0.094 mmol) in benzene (6 mL) and stirred overnight. The solvent was removed under vacuum to yield **6** as a dark brown powder (115 mg, 96%). In an NMR scale experiment, free C_8H_8 was observed at 5.6 ppm in a 1:2 molar ratio with **6** by ^{1}H NMR spectroscopy. Crystals of **6** suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. ^{1}H NMR (C_6D_6): δ 2.8 (s, 15H, C_5*Me*$_5$), −15.9 (s, 8H, C_8*H*$_8$), −62.8 (s, 2H, *bipy*), −116 (s, 2H, *bipy*), −118 (s, 2H, *bipy*). IR: 3030s, 2969s, 2946s, 2896s, 2851s, 2613m, 2187m, 1501s, 1453s, 1411s, 1374m, 1349m, 1297m, 1257w, 1222w, 1150m, 1083m, 1019m, 949s, 754w, 720s, 683w cm^{-1}. *Anal.* Calc. for $C_{28}H_{31}N_2U$: C, 53.08; H, 4.93; N, 4.42. Found: C, 52.72; H, 4.86; N, 4.40%.

2.4. X-ray crystallographic data

Information on X-ray data collection, structure determination, and refinement for **4**, **5**, and **6** are given in Table 1. Details are given in the Supplementary material.

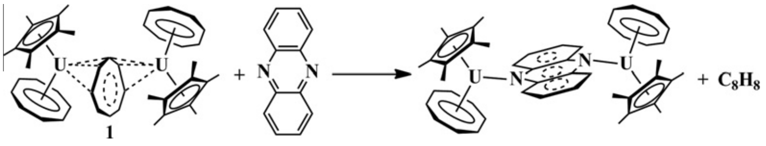
2.5. Computational details

The structures of **4** and **6** were initially optimized using the TPSSH [10] hybrid meta-GGA functional and split valence basis sets with polarization functions on non-hydrogen atoms (SV(P)) [11]. TPSSH was chosen due to its established performance for transition metal compounds [12,13]. Relativistic small-core pseudopotentials [14] were employed for U. Fine quadrature grids (size m4) [15] were used throughout. The multipole-accelerated resolution of the identity (MARI-J) approximation for the Coulomb energy was used throughout [16]. All structures were found to be minima.

Table 1
X-ray data collection parameters for (η^5-C_5Me_5)(η^8-C_8H_8)U(Me_2bipy-κ^2N,N′), **4**, (η^5-C_5Me_5)(η^8-C_8H_8)U(Me_2bipy-κ^2N,N′)·(toluene), **5**, and (η^5-C_5Me_5)(η^8-C_8H_8)U(bipy-κ^2N,N′), **6**.

Empirical formula	$C_{30}H_{35}N_2U$ **4**	$C_{30}H_{35}N_2U\cdot C_7H_8$, **5**	$C_{28}H_{31}N_2U$ **6**
Formula weight	661.63	753.76	633.58
T (K)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_1/n$
a (Å)	12.8073(7)	10.0141(7)	9.9021(8)
b (Å)	11.4579(6)	21.7886(15)	16.7155(13)
c (Å)	18.1385(10)	13.8893(9)	13.8869(11)
α (°)	90	90	90
β (°)	110.5770(10)	90	91.4970(10)
γ (°)	90	90	90
V (Å^3)	2491.9(2)	3030.6(4)	2297.8(3)
Z	4	4	4
ρ_{calc} (mg/m^3)	1.764	1.652	1.831
μ (mm^{-1})	6.534	5.384	7.082
R_1 [$I > 2.0\sigma(I)$][a]	0.0273	0.0369	0.0165
wR_2 (all data)[a]	0.0647	0.0945	0.0402

[a] Definitions: $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$, $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.



Scheme 2.