Dearomatization of Furan: Structure of an η^2-Furan Complex and a Survey of Its Reactivity

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Furans, like their nitrogen counterparts, pyrroles, undergo electrophilic substitution preferentially at the α-carbons.[1] Consequently, the convenient synthesis of a β-substituted furan directly from its unsubstituted furan precursor is often preempted by addition or substitution to an α carbon or by polymerization. Recently, the first example of an η^2-furan complex was reported in which an osmium(II) fragment coordinated the heterocycle across C(2) and C(3).[2] We speculated that such coordination could render the bound furan more susceptible to electrophilic additions at the β-carbon (i.e., C(4)). Furthermore, metal-to-ligand back-bonding should render the resulting oxonium intermediate less electrophilic than its organic counterpart and, therefore, less inclined to polymerize. Herein, we report a preliminary study of the chemical reactivity of the η^2-furan complex, $[Os(NH_3)_5(\eta^2\text{-furan})]^{2+}$ (**I**), toward various electrophiles.

The furan complex **I** was prepared according to literature methods[2] from the osmium(III) precursor $Os(NH_3)_5(OTf)_3$.[3] Since structural data for η^2-furan complexes are absent in the literature, a single crystal of **I**-$(OTf)_2$ was grown from CH_3CN, and structurally analyzed.[4] In Figure 1, an ORTEP drawing for the cation **I** shows significant distortions in the furan ligand relative to the uncoordinated heterocycle, consistent with a modest decrease in bond length for C(4) and C(5) (1.31(1) Å; cf. 1.322(6) Å)[5] and a corresponding increase for C(3) and C(4) (1.47(1) Å; cf. 1.428(7) Å).[5] As a result of metal binding, the uncoordinated portion of the furan ring closely resembles a vinyl ether.

Since many of the transformations involving vinyl ethers and electrophiles are conducted under acidic conditions,[6] we felt that it was initially important to establish the reactivity pattern of η^2-furan complexes with protons. The furan complex **I** undergoes a stoichiometric reaction with strong acid (HOTf) in a variety of solvents to give the compound **II**-$(OTf)_3$.[7] Judging from ^{1}H, ^{13}C, DEPT, HETCOR, and electrochemical data, the η^2-furan undergoes cleavage of the O–C(2) bond to give the (3-oxopropyl)-carbyne complex **II**, shown in Figure 2. Diagnostic features for this species include *cis*-ammine resonances shifted *downfield* of the *trans*-ammine signal, and a carbyne ^{13}C resonance at 296.7 ppm.[8] Treatment of **I** (0.13 mmol) with 1 equiv of $BF_3{\cdot}OEt_2$ in CH_3CN immediately consumes the starting material, and only uncharacterized paramagnetic products are recovered. Finally, when a methanol solution of furan complex **I** is treated with a catalytic amount of triflic acid (HOTf, 0.26 equiv), and monitored over a period of 14 days, ^{1}H and ^{13}C NMR data indicate formation of two stereoisomers of the acetal **III**, in a ratio of 2:1 (Figure 2).

Despite the tendency of furan complex **I** to undergo ring-opening or metal oxidation in the presence of strong acids, β-electrophilic additions and substitutions can be accomplished in certain cases

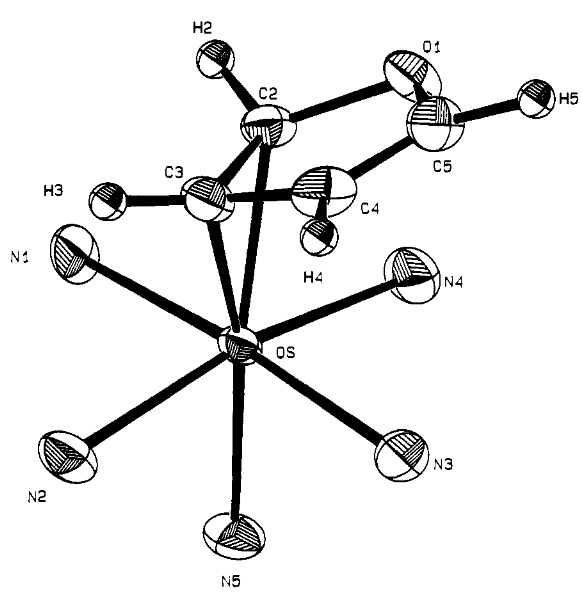

Figure 1. ORTEP drawing of the cation $[Os(NH_3)_5(\eta^2\text{-furan})]^{2+}$: Os–C(2), 2.123(7) Å; Os–C(3), 2.202(8) Å; C(2)–C(3), 1.43(1) Å; C(3)–C(4), 1.47(1) Å; C(4)–C(5), 1.31(1) Å; C(5)–O(1), 1.38(1) Å; O(1)–C(2), 1.432(9) Å; Os–C(2)–O(1), 118.6(5) Å; Os–C(3)–C(4), 118.0(5) Å.

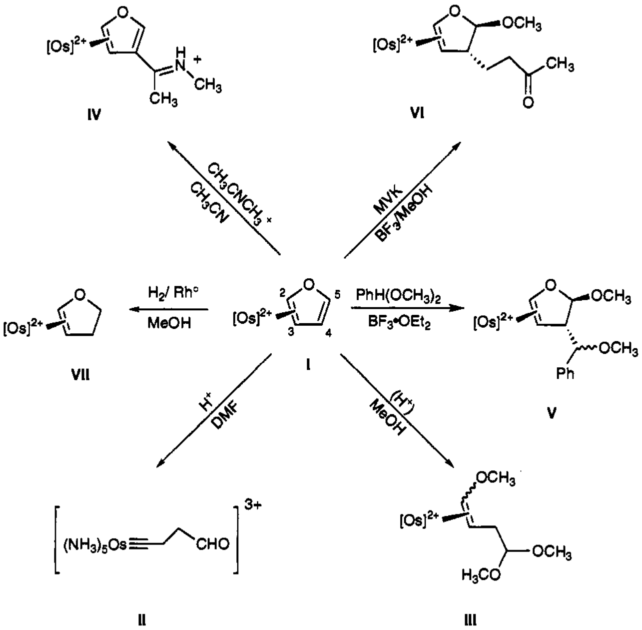

Figure 2. Reaction scheme for the cation $[Os(NH_3)_5(\eta^2\text{-furan})]^{2+}$. Stereochemical assignments are based on NOESY and coupling data.

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[1] Sargent, M. V.; Dean, F. W. In *Comprehensive Heterocycle Chemistry*; Katritzky, E. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Part 3, Vol 4.

[2] Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.

[3] Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

[4] Crystallographic data for **I**-$(OTf)_2{\cdot}3CH_3CN$: M = 764.71; triclinic, space group $P\bar{1}$ (No. 2); a = 13.388(4) Å, b = 13.949(4) Å, c = 7.672(3) Å, α = 94.37(3)°, β = 93.90(3)°, γ = 106.47(2)°; V = 1364 Å^3; Z = 2. The structure was solved by direct methods in TEXSAN 5.0 and refined to $R(F)$ = 0.034 and $R_w(F)$ = 0.057 for 4171 absorption-corrected reflections with $I > 3\sigma(I)$ measured up to 2θ = 50° on a Rigaku AFC6S diffractometer (Mo Kα radiation = 0.710 69 Å, T = –120 °C).

[5] Fourme, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 2984.

[6] Fisher, P. In *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues*; Patai, S., Ed.; J. Wiley & Sons: New York, 1980; Suppl. E, Part 2.

[7] Synthesis and characterization of **II**: A solution of triflic acid (132 mg, 0.883 mmol) in anhydrous DMF (210 mg) was added to a solution of **I**-$(OTf)_2$ (112 mg, 0.175 mmol) in DMF (1.04 g). Yield after precipitation with CH_2Cl_2: 106 mg, 77%. ^{1}H NMR (CD_3CN): δ 9.74 (s, 1 H, CHO), 4.64 (br s, 12 H, *cis*-NH_3), 3.19 (br s, 3 H, *trans*-NH_3), 3.19 (t, J = 6.3 Hz, 2H, CH_2), 2.51 (t, 2H, J = 6.3 Hz, CH_2). ^{13}C NMR (CD_3CN): δ 296.7, 202.4, 47.8, 36.9. CV (CH_3CN/TBAH/100 mV/s): $E_{p,c}$ = –0.82 V (NHE). Anal. ($C_7H_{20}N_5O_{10}S_3OsF_9$) H, N; C: calcd, 10.62; found, 11.49.

[8] An analogous compound, the phenylcarbyne, was recently reported. See: Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371.

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where the oxonium species resulting from β-electrophilic addition may be stabilized by nucleophilic addition to C(5) or deprotonation at C(4). For example, treatment of **I** with methylacetonitrilium triflate (CH_3CN) generates the corresponding iminium derivative of the 4-acetylfuran, **IV** (74%).[9] Here, the imine resulting from electrophilic addition is sufficiently basic to deprotonate the oxonium intermediate at the β-carbon. Over a 5-day period in D_2O, **IV** hydrolyzes to its 4-acetylfuran derivative.[10]

Lewis acids can be used to facilitate electrophilic addition at C(4) provided that a moderate nucleophile is present. For example, when a solution of **I** is treated with an excess of benzaldehyde dimethyl acetal in the presence of 1 equiv of $BF_3{\cdot}OEt_2$, substitution on the acetal carbon and subsequent addition of methoxide to C(5) generates the dihydrofuran complex **V** in 76% yield.[11] Similarly, when methyl vinyl ketone (MVK) is used as the electrophile, conjugate addition at C(4) and methoxide addition at C(5) provide the 5-methoxy-4-(3-oxobutyl)-4,5-dihydrofuran complex **VI** (89%).[12] Acetals **V** and **VI** show well-defined stereochemistry at C(4) consistent with the electrophile approaching the furan ring from the exo face, *anti* to the osmium. In contrast, the stereochemistry at C(5) is governed by a thermodynamic preference for the methoxy oxygen to point toward the pentaammineosmium(II) group; such an orientation allows a hydrogen-bonding interaction with the moderately acidic ammine ligands.[13] NOESY and coupling data support the stereochemical assignments shown in Figure 2.

Finally, furan complex **I** may be selectively hydrogenated (1 atm of H_2) in the presence of 5% Rh^0/C in methanol solution.[14] The reduced product **VII** shows two methylene and two methine carbons (DEPT), as expected for a 4,5-dihydrofuran analog. In order to confirm this assignment, $Os(NH_3)_5(OTf)_3$ was reduced in the presence of 2,3-dihydrofuran. The isolated product is spectroscopically identical to compound **VII**.

The vicinal difunctionalization of furans by their η^2-complexation to a transition metal may ultimately prove to be a versatile tool for heterocyclic synthesis, and efforts are underway in our laboratories to make such a process practical. Similar vicinal-difunctionalization sequences have been realized for the corresponding η^2-pyrrole and arene systems.[15]

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Supplementary Material Available: Additional information on the synthesis and characterization of compounds **I–VII** and tables of experimental details, atomic position parameters, thermal parameters, bond distances and angles and ORTEP drawings for compound **I** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(9) Synthesis and characterization of **IV**: A solution of methylacetonitrilium triflate (100 mg, 0.478 mmol) in acetonitrile (598 mg) was added to a solution of **I**-$(OTf)_2$ (125 mg, 0.195 mmol) in acetonitrile (2.90 g). The reaction mixture was stirred (80 min), treated with pyridine (120 mg, 1.52 mmol), and then added to CH_2Cl_2 (150 mL) (121 mg, 74%). ^1H NMR (CD_3CN): δ 10.0 (br s, 1 H, NH), 8.17 (s, 1 H, C5), 7.71 (d, $J = 3.6$ Hz, 1 H, C2), 5.13 (d, $J = 3.6$ Hz, 1 H, C3), 4.33 (br s, 3 H, *trans*-NH_3), 3.26 (s, 3 H, NCH_3), 3.16 (br s, 12 H, *cis*-NH_3), 2.43 (s, 3 H, CH_3). ^{13}C NMR (CD_3CN): δ 176.5, 163.5, 125.5, 102.8, 37.9, 33.4, 17.6. Anal. ($C_{10}H_{25}N_6O_{10}S_3OsF_9$) H, N; C: calcd, 14.19; found, 14.84 .

(10) ^1H NMR data for $[Os(NH_3)_5((2,3\text{-}\eta^2)\text{-4-acetylfuran})](OTf)_2$: 7.95 (s, 1 H, C5), 7.73 (d, 1 H, $J = 3.6$ Hz, C2), 5.37 (d, 1 H, $J = 3.6$ Hz, C3), 4.76 (br, 3 H, *trans*), 3.57 (br, 12 H, *cis*), 2.27 (s, 3 H, CH_3).

(11) Synthesis and characterization of **V**: A CH_3CN solution of **I**-$(OTf)_2$ (81.2 mg, 0.127 mmol) was treated with $PhCH(OMe)_2$ (1.93 g, 12.7 mmol). $BF_3{\cdot}OEt_2$ (9.5 mg, 0.067 mmol) was added, and the solution was stirred (1 h). After addition of pyridine (70.0 mg, 0.886 mmol), the reaction product was precipitated with Et_2O (180 mL) (76.8 mg, 76%). By ^1H NMR, **V** is a mixture of two isomers in 3:2 ratio. NMR (CD_3CN): isomer 1, ^1H, δ 7.29–7.25 (m, 5 H, Ph), 6.28 (d, $J = 3.9$ Hz, 1 H, C2), 5.31 (d, $J = 3.0$ Hz, 1 H, C5), 4.28 (d, $J = 8.4$ Hz, 1 H, PhCH), 3.94 (br, 3 H, *trans*-NH_3), 3.24 (s, 3 H, OCH_3), 3.20 (s, 3 H, OCH_3), 3.19 (d, $J = 3.9$ Hz, 1 H, C3), 2.93 (br, 12 H, *cis*-NH_3), 2.28–2.25 (m, 1 H, C4); ^{13}C, δ 141.2, 129.4–128.2 (5 C), 113.6, 96.4, 86.5, 57.2–56.5 (3 C), 38.97; isomer 2, ^1H, δ 7.29–7.25 (m, 5 H, Ph), 6.28 (d, $J = 3.9$ Hz, 1 H, C2), 5.02 (d, $J = 4.2$ Hz, 1 H, C5), 4.31 (d, $J = 8.4$ Hz, 1 H, PhCH), 3.97 (br, 3 H, *trans*-NH_3), 3.83 (d, $J = 3.9$ Hz, 1 H, C3), 3.19 (s, 3 H, OCH_3), 2.99 (s, 3 H, OCH_3), 2.99 (br, 12 H, *cis*-NH_3), 2.28–2.25 (m, 1 H, C4); ^{13}C, δ 140.4, 129.4–128.2 (5 C), 113.4, 96.4, 86.2, 57.2–56.5 (3 C), 40.5. CV (CH_3CN/TBAH/100 mV/s): $E_{p,a} = 0.80$ V. Anal. ($C_{15}H_{31}N_5O_9S_2OsF_6$): C, H, N.

(12) Synthesis and characterization of **VI**: A solution of **I**-$(OTf)_2$ (155 mg, 0.242 mmol), MVK (1.02 g, 14.5 mmol), and CH_3OH (1.52 g) was added to $BF_3{\cdot}OEt_2$ (35.7 mg, 0.252 mmol). After 5 min, the reaction mixture was treated with Et_2O (100 mL) (160 mg, 88%). ^1H NMR (DMSO-d_6): δ 6.21(d, $J = 3.6$ Hz, 1 H, C2), 4.91 (d, $J = 3.0$ Hz, 1 H, C5), 4.28 (br, 3 H, *trans*-NH_3), 3.27 (br, 12 H, *cis*-NH_3), 3.18 (s, 3 H, OCH_3), 3.15 (d, $J = 3.9$ Hz, 1H, C3), 2.49 (t, $J = 6.6$ Hz, 2 H, CH_2), 2.09 (s, 3 H, CH_3), 1.82 (m, 1 H, C4), 1.73 (m, 2 H, CH_2). ^{13}C NMR: 208.1, 115.4, 94.3, 55.9, 47.2, 40.8, 40.3, 29.75, 29.4. CV (CH_3CN/TBAH/100 mV/s): $E_{1/2} = 0.67$ V. Anal. ($C_{11}H_{29}N_5O_9S_2OsF_6$): C, H, N.

(13) An analogous hydrogen bond has been observed in the crystal structure of a methoxycyclohexene complex of pentaammineosmium(II). See: Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.

(14) Synthesis and characterization of **VII**: A mixture of 5% Rh^0/C (230 mg) and methanol (6 mL) was stirred under 1 atm of hydrogen for 1 h and then combined with **I**-$(OTf)_2$ (100 mg, 0.156 mmol). The reaction mixture was stirred (2 h), filtered, and treated with Et_2O (50 mL). Yield: 63.2 mg, 63%. ^1H NMR (CD_3CN): δ 6.11 (d, $J = 3.9$ Hz, 1 H, C2), 4.02 (dt, $J = 9.6$, 4.2 Hz, 1 H, C5), 3.99 (br, 3 H, *trans*-NH_3), 3.49 (t, $J = 4.2$ Hz, 1 H, C3), 3.02 (br, 12 H, *cis*-NH_3), 2.97 (q, $J = 9.0$ Hz, 1 H, C5), 2.75–2.62 (m, 1 H, C4), 1.81 (ddd, $J = 13.5$, 8.4, 4.5 Hz, 1 H, C4). ^{13}C NMR: δ 95.4, 69.4, 37.6, 30.0. CV (CH_3CN/TBAH/100 mV/s): $E_{1/2} = 0.63$ V (NHE). Anal. ($C_6H_{21}N_5O_7S_2OsF_6$): C, H, N.

(15) Hodges, L. M.; Koontz, J. I.; Gonzalez, J.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1993**, *58*, 4788. Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857.