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Carbynes and Carbenes in Coordination Chemistry: A New Class of Pentaammine and Tetraammine Complexes of Osmium(II)

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Since their discovery by Fischer and co-workers in 1973,[2] the study of transition-metal carbyne complexes and their role in alkyne metathesis has rapidly developed into a mature field.[3] Although carbyne complexes are known for a diverse set of early- and mid-transition metals, the vast majority of these complexes contain carbon or phosphine π-acids, or bulky alkoxide ligands, which limit the coordination number. We wish to report the first example of a carbyne species, as well as several heteroatom-carbene derivatives, in which the metal fragment, $Os^{II}(NH_3)_5$,[4] provides a classical octahedral coordination environment.

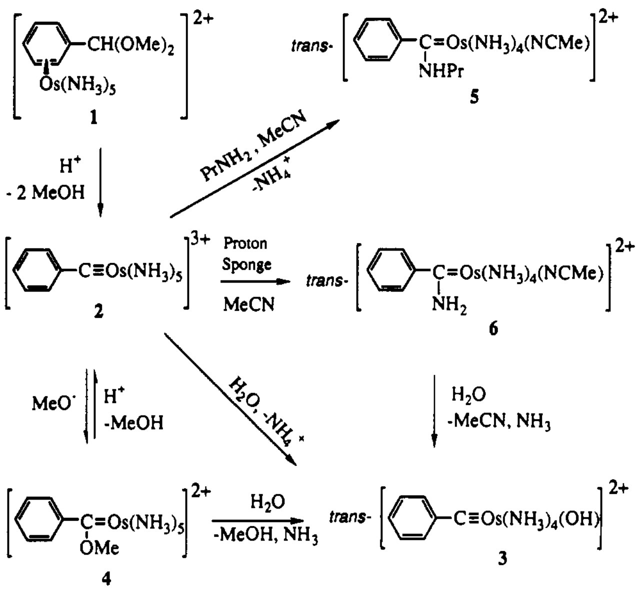

Figure 1. Schematic of the synthesis and reactivity of the osmium(II) pentaammine carbyne **2**.

The carbyne $[Os(NH_3)_5(\equiv CPh)](OTf)_3$ (**2**) is synthesized in two steps from $Os(NH_3)_5(OTf)_3$ and benzaldehyde dimethyl acetal, as shown in Figure 1.[5] Reduction of the Os(III) precursor with Mg^0 in the presence of the acetal generates the complex $[Os(NH_3)_5(\eta^2\text{-}PhCH(OMe)_2](OTf)_2$ (**1**) in which the organic ligand is bound through the arene. ^1H NMR and cyclic voltammetric data are consistent with other η^2-arene complexes of pentaammineosmium(II),[6] the former indicating that the metal is fluxional on the NMR time scale. Treatment of **1** with 1 equiv of triflic acid in methanol yields the carbyne, **2**, in 85–90% yield. ^1H and ^{13}C NMR data (acetone-d_6) for **2** show phenyl and ammine signals, and a ^{13}C resonance at 278 ppm, consistent with that reported for other carbyne carbons.[3] No methoxy signals were detected in either the proton or carbon NMR. Crystals of **2** were obtained from acetone solution, and a structure determination was undertaken.[7] The ORTEP of $[Os(NH_3)_5(\equiv CPh)]^{3+}$ (Figure 2) features a nearly linear (175.3°) Os≡CPh linkage, with the metal–carbon bond length of 1.73 (1) Å, and a significantly lengthened *trans*-NH_3 bond.

Although the pentaammineosmium carbyne **2** is stable in acidic D_2O,[8] over several days in neutral solution **2**, as well as the heterocarbene complexes **4** and **6**, undergo conversion to a common product (**3**). Both ^{13}C and ^1H NMR spectra of **3** are consistent with the formation of a carbyne species similar to **2** but with a hydroxy group replacing the ammine ligand trans to the carbyne.[9] Repeated efforts to isolate **3** in analytically pure form have failed, but trace amounts of a crystalline material, formed from **2** in wet acetone solution, were analyzed by X-ray.[10] Although somewhat disordered, a structure determination confirms the presence of one octahedral carbyne unit and two triflates, consistent with our formulation of **3** as $[Os(NH_3)_4(OH)(\equiv CPh)](OTf)_2 \cdot 0.5(CH_3)_2CO$.

The carbyne **2** readily undergoes nucleophilic addition at the carbyne carbon to give heteroatom carbenes. Reaction of **2** with sodium methoxide in methanol gives the corresponding methoxycarbene, **4** (Figure 1), a species which most likely is an intermediate in the conversion of the benzaldehyde dimethyl acetal

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(1) 1992 Camille and Henry Dreyfus Teacher-Scholar.

(2) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Muller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.*, **1973**, *12*, 564–5.

(3) Nugent, W. A.; Mayer, J. A. *Metal Ligand Multiple Bonds*; Wiley Interscience: New York, 1988; pp 310–1.

(4) In this paper we shall use the formalism $Os(II)/CR^+$ and $Os(II)/CR_2{}^0$ for carbyne and carbene complexes, respectively, as opposed to the equally acceptable formalism $Os(VI)/CR^{3-}$ and $Os(IV)/CR_2{}^{2-}$. All cations reported are $CF_3SO_3^-$ salts.

(5) Synthesis of **1**: Benzaldehyde dimethyl acetal (1.76 g, 11.5 mmol) and $[Os(NH_3)_5OTf]OTf_2$ (0.685 g, 0.949 mmol) were dissolved in 3.0 g of *N,N*-dimethylacetamide (DMAc). Activated Mg^0 powder (1.46 g) was added and the reaction mixture stirred. After 45 min, the solution was filtered into 150 mL of CH_2Cl_2. Addition of 200 mL of Et_2O caused the formation of a red precipitate, which was isolated, washed (Et_2O), and dried. Yield: 0.567 g (0.782 mmol, 82%). Characterization of **1** is as follows. CV (acetonitrile, TBAH, v = 100 mV/s): $E_{p,a} = +0.60$ V (NHE). ^1H NMR (acetone-d_6; 25 °C): 5.1–7.3 (br, 5H, Ph); 5.01 (s, 1H, CH); 3.40 (s, 6H, OMe); 4.73 (bs, 3H, trans-NH_3); 3.47 (bs, 12H, cis-NH_3). Synthesis of **2**: Triflic acid (74.3 mg, 0.495 mmol) was dissolved in 2.15 g of MeOH. This solution was added directly to **1** (268 mg, 0.370 mmol) with stirring. After 5 min, Et_2O was added (15 mL), and the precipitate was filtered out, washed (Et_2O), and dried. Isolated yield: 258 mg (0.318 mmol, 86%). Characterization of **2** is as follows. CV (MeCN, TBAH, 100 mV/s): $E_{p,c} = -0.87$ V (NHE). ^1H NMR (acetone-d_6, 25 °C): 8.34 (d, 2H); 8.08 (t, 1H); 7.62 (t, 2H) (Ph); 5.73 (bs, 12H, cis-NH_3); 4.15 (bs, 3H, trans-NH_3). ^{13}C NMR (acetone-d_6; 25 °C): 129.21, 132.39, 136.20, 146.22 (Ph); 277.96 (C≡Os). Anal. Calcd ($C_{10}H_{20}N_5S_3F_9O_9Os$): C, 14.80; H, 2.48; N, 8.63. Found: C, 14.12; H, 2.65; N, 8.87.

(6) (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555. (b) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

(7) Crystals of **2** were grown from acetone by vapor diffusion of Et_2O into the solution. Crystallographic data are as follows: $C_{10}H_{20}F_9N_5O_9S_3Os \cdot 1.5(CH_3)_2CO$; $M = 898.78$; triclinic, space group $P\bar{1}$ (No. 2); a = 13.337 (4) Å, b = 15.411 (3) Å, c = 8.346 (3) Å; α = 93.88 (3)°, β = 102.68 (3)°, γ = 114.35 (2)°, V = 1505 (2) Å^3; Z = 2, d_{calcd} = 1.983 cm^3. The structure was solved by heavy-atom techniques using TEXAN 5.0. Full-matrix least-squares refinement yielded the final R of 0.044 (R_w = 0.053) for 3941 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a Rigaku AFC6S diffractometer up to 2θ = 50° (Mo Kα radiation, λ = 0.710 69 Å, T = −100 °C).

(8) ^1H NMR of **2** in D_2O (0.08 M HOTf): 7.58 (t, 2H); 7.96 (d, 2H); 8.06 (t, 1H); 5.43 (bs, 12H); 3.78 (bs, 3H).

(9) Characterization of **3** is as follows. ^1H NMR (D_2O): 7.95 (t, 1H); 7.86 (d, 2H); 7.56 (t, 2H). ^{13}C NMR (D_2O): 129.47, 130.32, 135.07, 146.30 (Ph); 267.92 (C≡Os).

(10) Unit cell for **3**: $P\bar{1}$ (No. 2), a = 10.779 (3) Å, b = 14.625 (5) Å, c = 8.366 (2) Å, α = 98.97 (2)°, β = 97.50 (2)°, γ = 111.06 (2)°, V = 1190 (6) Å^3. R = 0.043 (R_w = 0.058). Os≡C = 1.74 (1) Å. The phenyl ring was found to be disordered between two different orientations. An ORTEP drawing and structural parameters of **3** are available as supplementary material. Consistent with the interpretation of **3** as a hydroxy carbyne, the metal–ligand bond trans to the carbyne unit (i.e. the O–Os bond) is significantly shorter (2.121 (7) Å) than the corresponding Os–N bond of **2** (2.245 (8) Å).

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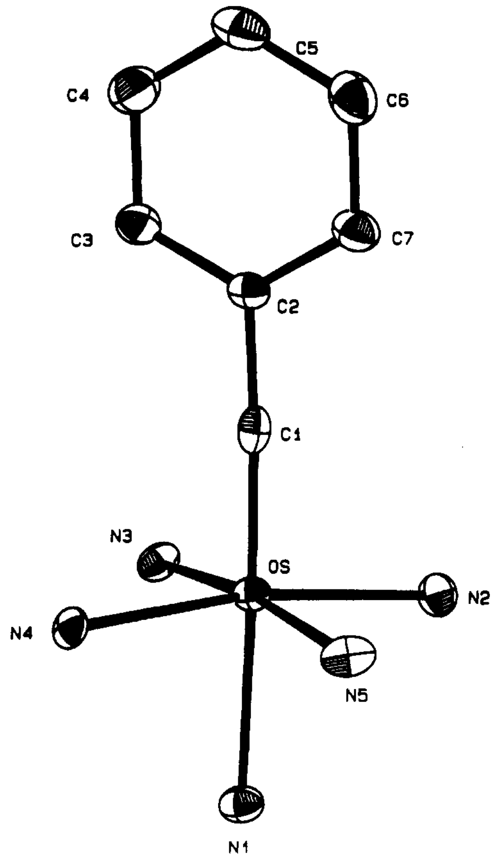

Figure 2. ORTEP for the cation $[Os(NH_3)_5(\equiv CPh)]^{3+}$ (**2**). Selected bond distances (Å) and angles (deg): C1–Os = 1.73 (1), C1–C2 = 1.45 (1), Os–N1 = 2.245 (8), Os–N2 = 2.142 (8), Os–N3 = 2.131 (8), Os–N4 = 2.125 (8), Os–N5 = 2.138 (8); Os–C1–C2 = 175.3 (8), N1–Os–C1 = 177.2 (4).

(**1**) to the carbyne (**2**).[11] Consistent with this interpretation, the carbyne **2** can be regenerated by treatment of **4** with a methanolic solution of triflic acid.

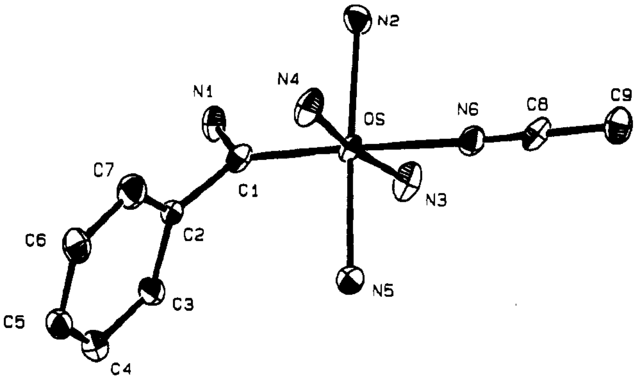

Figure 3. ORTEP for the cation *trans*-$[Os(NH_3)_4(=C(NH_2)Ph)(CH_3CN)]^{2+}$ (**6**). Selected bond distances (Å) and angles (deg): C2–C1 = 1.48 (1), C1–Os = 1.96 (1), C1–N1 = 1.32 (1), Os–N6 = 2.11 (1), N6–C8 = 1.16 (1), C8–C9 = 1.46 (1), C2–C1–Os = 121.0 (1), N1–C1–Os = 127.4 (8).

The reaction of the carbyne **2** in acetonitrile with 1 equiv of the nonhindered amine *n*-propylamine gives *trans*-$[Os(NH_3)_4(=C(NHPr)Ph)(CH_3CN)](OTf)_2$ (**5**) (Figure 1).[12] In this case, the ammonia trans to the carbene is labile and acetonitrile is readily incorporated. When the the carbyne (**2**) is treated with 1 equiv of the hindered base Proton Sponge, the liberated ammonia ligand serves as the nucleophile for unreacted **2**, and *trans*-$[Os(NH_3)_4(=C(NH_2)Ph)(CH_3CN)](OTf)_2$ (**6**) is generated in good yield.[13] The crystal structure for **6** (Figure 3)[14] reveals bond lengths and angles (summarized in the legend) about the carbene which are typical for Fisher carbenes, and ^1H NMR data recorded at room temperature show two resolved resonances for the amino group. However, coalescence experiments show the rotational barrier of the amino group to be only 16.5 kcal/mol, a value which is considerably less than that for typical Fischer aminocarbenes[15] and which suggests that the majority of π electron density in the heteroatom-carbene system is confined to the M–C bond. While the trans acetonitrile is resistant toward substitution in acetone, rapid exchange ($t_{1/2} < 1$ min) is observed by ^1H NMR in CD_3CN. Cyclic voltammograms of the Os(II) aminocarbenes **5** and **6** show reversible couples ($E_{1/2} = +0.34$ V; 50 mV/s) in CH_3CN, an observation which indicates that the Os(III)–carbene analogs to **5** and **6** are also modestly stable.

The carbyne **2** fails to react with 2-pentyne (75 °C; CH_3CN) over several hours, and the aminocarbene **6** is equally impotent with norbornene under these conditions. However, given the ease with which ligands may be substituted in a position trans to the carbon, the accessibility of the Os(III) oxidation state, and the simplicity of the ancillary ligands, these osmium(II) ammine complexes offer a new perspective for the study of carbene and carbyne species.

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Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles and ORTEP drawings for **2**, **3**, and **6** (25 pages). Ordering information is given on any current masthead page.

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(11) Characterization of **4** is as follows. CV (MeCN, TBAH, 50 mV/s): $E_{1/2} = +0.65$ V (NHE). ^1H NMR (acetone-d_6, 25 °C): 7.42 (t, 2H); 7.21 (t, 1H); 7.11 (d, 2H), 4.00 (bs, 12H, cis-NH_3), 4.05 (bs, 3H, trans-NH_3), 3.55 (s, OMe). ^{13}C NMR (acetone-d_6, 25 °C): 246.90 (C═Os); 157, 128.75, 126.68, 118.38 (Ph); 58.56 (OMe).

(12) Characterization of **5** is as follows. ^1H NMR (acetone-d_6): 8.78 (bs, 1H, NH); 7.44 (t, 2H); 7.12 (t, 1H); 6.93 (d, 2H), 3.52 (bs, 12H, cis-NH_3); 2.96 (dt, 2H); 1.52 (m, 2H); 0.78 (t, 3H) (Pr), 2.77 (s, 3H, MeCN). ^{13}C NMR (acetone-d_6, 25 °C): 235.37 (C═Os); 154.16, 129.23, 125.88, 119.59 (Ph); 54.40, 23.48, 11.12 (Pr); 3.66 (ligated MeCN, quat carbon unassigned).

(13) Synthesis of **6**: A solution of Proton Sponge (65.4 mg, 0.306 mmol) in acetonitrile (1.37 g) was added to **2** (204.1 mg, 0.251 mmol). After 5 min, the red/brown solution was added to CH_2Cl_2 (60 mL), and the precipitate was isolated, washed (CH_2Cl_2/Et_2O), and dried. Isolated yield: 153.1 mg, 0.218 mmol, 87%. Characterization of **6** is as follows. ^1H NMR (acetone-d_6, 25 °C): 9.09 (bs, 1H), 8.66 (bs, 1H) (NH_2); 7.36 (t, 2H); 7.18 (t, 1H); 7.08 (d, 2H), 3.62 (bs, 12H, cis-NH_3); 2.78 (s, 3H, MeCN). ^{13}C NMR (acetone-d_6, 25 °C): 235.45 (C═Os); 158, 129.06, 126.61, 120.96 (Ph); 3.62 (ligated MeCN, quat carbon unassigned). IR: C≡N stretch at 2268 cm^{-1}. Anal. Calc for *trans*-$[Os(NH_3)_4(=C(NH_2)Ph)(MeCN]^{2+}$, $C_{11}H_{22}N_6O_6S_2F_6Os$: C, 18.80; H, 3.16; N, 11.96. Found: C, 17.65; H, 3.04; N, 11.31.

(14) Crystals of **6** were grown from acetonitrile by vapor diffusion of Et_2O into the solution. Crystallographic data are as follows: $C_{11}H_{22}F_6N_6O_6S_2Os \cdot CH_3CN$, $M = 743.69$; triclinic, space group $P\bar{1}$ (No. 2); $a = 12.120$ (5) Å, $b = 14.831$ (6) Å, $c = 7.838$ (3) Å; $\alpha = 103.99$ (4)°, $\beta = 106.07$ (3)°, $\gamma = 97.77$ (4)°, $V = 1282$ (2) Å^3; $Z = 2$, $d_{calcd} = 1.926$ cm^3. The structure was solved by heavy-atom techniques using TEXAN 5.0. Full-matrix least-squares refinement yielded the final R of 0.044 ($R_w = 0.062$) for 3729 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a Rigaku AFC6S diffractometer up to $2\theta = 50°$ (Mo Kα radiation, $\lambda = 0.710\ 69$ Å, $T = -120$ °C).

(15) Fischer, H.; Kreissl, F. R. in *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983; p 71.