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# Arene-to-Alkyne Linkage Isomerizations of Diphenylacetylene on Pentaammineosmium

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When $Os(NH_3)_5(CF_3SO_3)_3$ is reduced in the presence of diphenylacetylene, four pentaammineosmium(II) complexes can be isolated and characterized in which the alkyne remains intact. The kinetically favored mononuclear complex features a phenyl group $\eta^2$-bound to the metal center. This species is observed to undergo a linkage isomerization in which the osmium migrates to the alkyne. Through the use of pulse radiolysis, this isomerization was determined to be greatly accelerated by oxidizing the metal to Os(III). The inherent stability of alkyne complexes for both di- and trivalent osmium provides the opportunity to assess the ability of this ligand to act as a $\pi$-donor as well as $\pi$-acceptor.

Our interest in the reactivity of pentaammineosmium(II) with unsaturated organic ligands[1] has prompted us to investigate the affinity of this metal center for acetylenes. As ligands for transition metals, alkynes are of particular interest in that they can function simultaneously as both $\pi$-donors and $\pi$-acceptors.[2] In an attempt to generate a complex with diphenylacetylene, an osmium(II) species was formed in which, contrary to expectation, the metal was found to be $\eta^2$-coordinated to one of the phenyl groups. By variation of the reaction conditions, four different mono- and binuclear pentaammineosmium(II) complexes of the intact ligand were identified.

## Experimental Section

$^1H$ NMR spectra were recorded on a Varian XL-400 spectrometer and are reported as ppm shifts from tetramethylsilane. Electrochemical experiments were performed under anaerobic conditions by using a PAR Model 173 potentiostat driven by a Model 175 universal programmer. All voltammograms, unless otherwise noted, were measured from +1.0 to −1.5 V in a standard three-electrode cell[3] and are reported vs the normal hydrogen electrode. The reference electrode was calibrated with the ferrocene/ferrocenium couple ($E° = 0.55$ V, NHE) as measured in situ.

**Pulse Radiolysis.** Electron-pulse-radiolysis transient-absorption experiments were carried out with the 2-MeV Van de Graaff accelerator at Brookhaven National Laboratory. Radiolytic yields were determined by using the $(SCN)_2$ dosimeter as a standard ($G = 6.13$, $\epsilon_{472\,nm} = 7950$ $M^{-1}\,cm^{-1}$). The experiments were performed on aqueous solutions of $2-5 \times 10^{-5}$ M $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}C_6H_5CCPh)](OTf)_2$ (**1**) in 0.1 M $NaHCO_3$ saturated with $N_2O$. A $G$ value of 6.0 radicals per 100 eV of absorbed energy was used. The concentration of hydroxyl radicals generated in a single experiment was $2-9 \times 10^{-6}$ M. Carbonate radical anion $CO_3^{\bullet-}$ was produced from the reaction of bicarbonate and carbonate ions with the hydroxyl radical as follows:[4]

$$OH^\bullet + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O \qquad k = 8.5 \times 10^6\ M^{-1}\ s^{-1}$$

$$OH^\bullet + CO_3^{2-} \rightarrow CO_3^{\bullet-} + OH^- \qquad k = 3.9 \times 10^8\ M^{-1}\ s^{-1}$$

Subsequent rapid reaction of the carbonate radical anion with **1** yields the osmium(III) intermediate of interest.

**Reagents.** Acetone was purified by vacuum distillation over $B_2O_3$,[5] and $Et_2O$ and 1,2-dimethoxyethane (DME) were purified by distillation over NaK alloy.[6] *N,N*-Dimethylacetamide (DMA) was dried over BaO and refluxed from triphenylsilyl chloride.[7] The amide was then refluxed with $CaH_2$ for 24 h and redistilled to remove traces of HCl. NaOTf (OTf = $CF_3SO_3$) was recrystallized three times from acetone and $Et_2O$, and tetrabutylammonium hexafluorophosphate (TBAH) from methanol and water. Diphenylacetylene (DPA) (Aldrich) and EtOAc (Burdick and Jackson) were used as purchased without further purification. $[FeCp_2]PF_6$ was prepared from ferrocene by air oxidation in sulfuric acid.[8] All solvents were deoxygenated and all reactions carried out under argon in a Vacuum Atmospheres Co. glovebox.

**Preparation of $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}C_6H_5CCPh)](OTf)_2$ (1).** $Os(NH_3)_5(OTf)_3$[9] (350 mg) and DPA (1.4 g) were dissolved in DMA (10 mL). A 1.5-g amount of activated $Mg^0$ turnings was added, and the reaction mixture was stirred for 2.5 h. The solution was then filtered, and the filtrate was added to $Et_2O$ (200 mL), which resulted in the formation of a reddish brown oil. The oil was worked into a solid from acetone and $Et_2O$, and then the solid was collected, washed ($Et_2O$), and dried under vacuum. Attempts to recrystallize this material resulted in the formation of **2**. Yield: 30–50%.

**Characterization of 1.** Anal. Calcd for $C_{16}H_{25}OsS_2F_6O_6N_5$: C, 25.6; H, 3.35; N, 9.32. Found: C, 24.33; H, 3.32; N, 9.37. $^1H$ NMR (acetone-$d_6$, ppm vs TMS; 20 °C): 7.52 (d, 2 H), 7.40 (m, (2 + 1) H), 6.8 (vb, 5 H), 4.84 (b, 3 H), 3.62 (b, 12 H). $^1H$ NMR (acetone-$d_6$, ppm vs TMS; −80 °C): 7.52 (d, 2 H), 7.40 (m, 3 H), 7.35 (dd, 1 H), 6.82 (d, 1 H), 6.58 (dd, 1 H), 5.48 (d, 1 H), 5.26 (dd, 1 H), 4.84 (b, 3 H), 3.62 (b, 12 H). Cyclic voltammetry (100 mV/s; acetone; 1 M NaOTf): $E_{p,a} = 0.25$ V, NHE. (A $\nu(C{\equiv}C)$ absorption was not observed in the IR spectrum.)

**Preparation of $[Os(NH_3)_5(\eta^2\text{-}PhC{\equiv}CPh)](OTf)_2$ (2).** Compound **1** (50 mg) was dissolved in acetone (1 mL) and allowed to stand for 18 h. The reaction mixture was then added to $Et_2O$ (20 mL), which resulted in the formation of a orange solid that was collected, washed ($Et_2O$), and dried under vacuum. Proton NMR measurements showed the final solid to contain approximately 15% of the substitution product $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)](OTf)_2$;[1a] this impurity fully accounts for the low percentage of carbon found by microanalysis. We felt that further purification of **2** was impractical, considering the relative lability of the alkyne ligand.

**Characterization of 2.** Anal. Calcd for $C_{16}H_{25}OsS_2F_6O_6N_5$: C, 25.6; H, 3.35; N, 9.32. Found: C, 22.77; H, 3.37; N, 9.20. $^1H$ NMR (acetone-$d_6$, ppm vs TMS; 20 °C): 7.52 (d, 4 H), 7.41 (t, 4 H), 7.33 (t, 2 H), 5.21 (b, 3 H), 4.16 (b, 12 H). Cyclic voltammetry (100 mV/s; acetone; 1 M NaOTf; $E_\lambda = 1.40$ V; −1.40 V): $E_{1/2} = 0.21$ V, NHE. IR (glaze deposited on KBr disk): 1910 $cm^{-1}$ (m).

**Preparation of a Salt of $[Os(NH_3)_5(\eta^2\text{-}PhC{\equiv}CPh)]^{3+}$ (3).** Compound **2** (36 mg) was treated with $Fe(Cp)_2PF_6$ (17 mg) in 1.0 mL of acetone. The resulting red solution was added dropwise to $Et_2O$ (15 mL), forming an oil which was separated from the ether layer and worked into a solid from acetone and $Et_2O$. The final product was collected, washed ($Et_2O$), and dried under vacuum. We estimate the purity of **3** to be >90%, judging from the electrochemical data.

**Partial Characterization of 3.** Cyclic voltammetry (100 mV/s; acetone; 1 M NaOTf; $E_\lambda = 1.40$ V; −1.40 V): $E_{1/2} = 0.21$ V, NHE. IR (glaze deposited on KBr disk): 1818 $cm^{-1}$ (m).

**Preparation of $[\{Os(NH_3)_5\}_2(\mu\text{-}2,3\text{-}\eta^2{:}4,5\text{-}\eta^2\text{-}C_6H_5CCPh)](OTf)_4$ (4).** When $Os(NH_3)_5(OTf)_3$[9] (200 mg), $Mg^0$, and diphenylacetylene (1.0 g) were allowed to react in a less polar solvent medium (10 mL of DME:1

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[1] (a) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223. (b) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. (c) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439. (d) Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917. (e) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101.

[2] (a) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956. (b) Capelle, B.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4662. (c) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

[3] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; J. Wiley & Sons: New York, 1980; p 23. Unless otherwise noted, cyclic voltammograms are recorded at 100 mV/s in a 1 M solution of NaTFMS by using a $Pt^0$ working electrode.

[4] (a) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals in Aqueous Solution*; Radiation Chemistry Data Center, University of Notre Dame: Notre Dame, IN, 1987; Table 8, p 2. (b) Buxton, G. V.; Elliot, A. J. *Radiat. Phys. Chem.* **1986**, *27*, 241–3.

[5] Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.

[6] Purchased from Aldrich Chemicals as an 80% $K^0$ alloy.

[7] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Oxford: New York, 1980.

[8] Yang, E. S.; Chan, M.; Wahl, A. C. *J. Phys. Chem.* **1975**, *79*, 2049.

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

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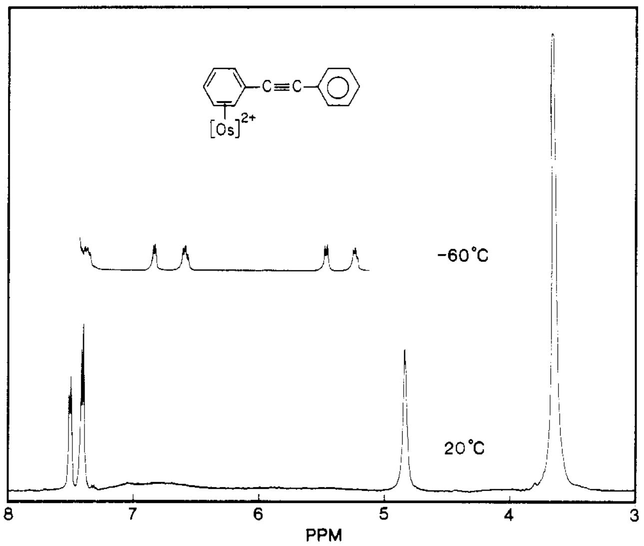

**Figure 1.** $^1H$ NMR spectrum of $[Os(NH_3)_5(\eta^2\text{-}C_6H_5CCPh)]^{2+}$ in acetone-$d_6$.

mL of DMA), the crude solid obtained from $CH_2Cl_2$ was found to contain a significant amount (40%) of a new species, **4**. (The product also contained significant amounts of **1** and an osmium(II) complex that is thought to be an isomer of **4**, in which both arene and alkyne segments of the bridging DPA ligand are coordinated.) This mixture was suspended in EtOAc (5.0 mL) for 5 h and filtered. The precipitate collected was composed of >90% compound **4**.[10]

**Characterization of 4.** $^1H$ NMR (acetone-$d_6$, ppm vs TMS; 20 °C): 7.42 (m, 2 H), 7.36 (m, (2 + 1) H), 4.82 (m, (1 + 1) H), 4.55 (m, (1 + 1) H), 7.04 (d, 1 H), 3.80 (b, (12 + 12) H), 4.97 (b, 3 H), 5.02 (b, 3 H). Cyclic voltammetry (100 mV/s; acetone; 1 M NaOTf; $E_\lambda$ = 1.40 V; -1.40 V): $E_{1/2}$ = 0.41 V; $E_{p,a}$ = 0.85 V, NHE.

## Results

In consideration of the ability for pentaammineosmium(II) to interact with arenes,[1b] the ligand diphenylacetylene offers a variety of coordination sites for this metal center. Consistent with expectation, six different coordination environments for pentaammineosmium(II) are detected by $^1H$ NMR when this intermediate and the ligand react in a nonpolar solvent.[11] Previously, we have reported the tendency of mononuclear $\eta^2$-arene complexes to form binuclear species in which the arene acts as a bridging ligand.[1b,12] The suppression of binuclear compounds such as compound **4** was achieved by reducing Os(III) in a polar solvent (DMA) with an excess of organic ligand. By limiting the reaction time, we isolated a mononuclear diphenylacetylene complex (**1**) that displays exclusively arene coordination. At room temperature, the $^1H$ NMR spectrum (Figure 1) for this complex in acetone-$d_6$ shows resonances for the ammine and uncoordinated phenyl protons only. The extreme broadening of the coordinated ring resonances is the result of a fluxional process in which the metal center migrates around the arene ring. When the temperature is lowered to -80 °C, this process is sufficiently retarded such that these signals are easily resolved. A homonuclear decoupling experiment performed at this temperature shows that the osmium is located solely at the 2,3-$\eta^2$-position. As observed for other monosubstituted benzene complexes of pentaammineosmium(II),[12] the $\alpha$ protons[13] are displaced to higher field (5.48, 5.26 ppm) relative to those of the free ligand. Like the other resonances of the coordinated ring, the para proton (7.35 ppm) has significantly broadened at 20 °C, indicating that the 2,3-$\eta^2$-species is no longer the dominant isomer at this temperature.[14]

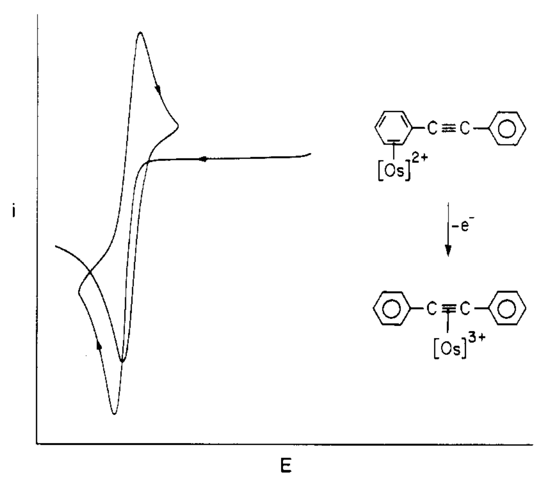

**Figure 2.** Cyclic voltammogram of $[Os(NH_3)_5(\eta^2\text{-}C_6H_5CCPh)]^{2+}$ in acetone ($v$ = 100 mV/s).

When this acetone solution is heated to 55 °C, the peaks associated with the arene isomer are gradually replaced ($t_{1/2}$ = 15 min) by a new set of resonances that correspond to the formation of **2**. Ammine signals for this complex at 4.12 and 5.20 ppm are shifted about 0.4 ppm downfield with respect to the arene precursor, this observation suggesting a decrease in the metal center electron density upon arene-to-alkyne isomerization. Unlike its precursor (**1**) or the free ligand, the mononuclear acetylene complex (**2**) displays an active infrared band at 1910 $cm^{-1}$ which corresponds to the alkyne C–C stretch.

The cyclic voltammogram of **2** features a single couple that is reversible in a variety of solvents. In acetone (1 M NaOTf) this occurs with an $E_{1/2}$ = 0.21 V, NHE, a value which is displaced positive to that of the parent acetylene complex[15] by about 300 mV as a result of the electron-withdrawing nature of the phenyl groups. Under identical cell conditions, a solution of **1** on first scan displays an anodic wave at $E_{p,a}$ = 0.25 V, NHE. The return scan, at first glance, appears to indicate a chemically reversible couple. However, close inspection reveals that upon oxidation the Os(III) arene complex isomerizes to form a new species showing electrochemistry consistent with that of the alkyne complex **2** (Figure 2). An arene-to-alkyne isomerization on Os(III) is confirmed by performing an experiment in which samples of both **1** and **2** are chemically oxidized.[16] The infrared spectra for these oxidation products are identical and feature a medium-intensity absorption at 1815 $cm^{-1}$, a value consistent with a variety of electron-deficient diphenylacetylene complexes.[17] Cyclic voltammetric data are also in agreement for these products ($E_{1/2}$ = 0.21 V). Further support for the assignment of $[Os(NH_3)_5(\eta^2\text{-}PhC{\equiv}CPh)]^{3+}$ as the oxidation product (**3**) of either **1** or **2** comes from the observation that an acetone-$d_6$ solution of this material, when treated with the reducing agent $CoCp_2$, displays an NMR spectrum identical with that of **2**.

As several other monosubstituted benzene complexes have been shown to undergo an isomerization from the arene to a site on the substituent upon oxidation,[18] we felt it would be useful to obtain

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(10) The purity of compound **4** is estimated on the basis of $^1H$ NMR and cyclic voltammetric data. The structure for compound **4** is assigned by comparison of the binuclear benzene analogue.

(11) These reaction conditions are specified in the text under "Preparation of **4**".

(12) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

(13) As defined in ref 12, the $\alpha$ protons are those adjacent to metal coordination.

(14) A tautomerization between the 2,3- and 5,6-$\eta^2$-positions would not affect the position of the para proton.

(15) The complex $[Os(NH_3)_5(\eta^2\text{-}C_2H_2)](OTf)_2$ is considerably less stable than the diphenylacetylene analogue but has been synthesized at subambient temperature by utilizing the procedures outlined in ref 1d. $^1H$ NMR (acetone-$d_6$): 5.72 (s, 2 H), 4.78 (b, 3 H), 3.80 (b, 12 H). Cyclic voltammetry (acetone/NaOtf): $E_{1/2}$ = 0.11 V. IR (deposited on a KBr disk as an acetone glaze): 1898 $cm^{-1}$.

(16) $FeCp_2PF_6$ is used as the oxidant.

(17) Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983**, *22*, 2416. Also see ref 2a,b.

(18) For the complex $[Os(NH_3)_5L]^{2+}$, see the following. (a) L = aniline: Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403. (b) L = benzonitrile: Sekine, M.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3604. (c) L = 2,2-dimethylpropiophenone: ref 1c. (d) L = anisole, $CF_3Ph$: Harman, W. D.; Ph.D. Dissertation, Stanford University, 1987.

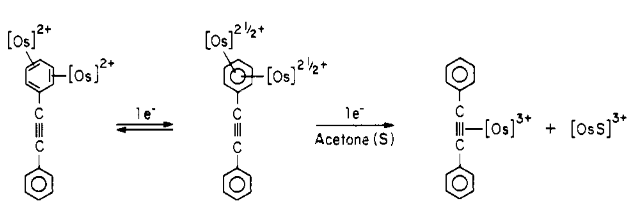

**Figure 3.** Electrochemical oxidation of $[(Os(NH_3)_5)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_5CCPh)]^{4+}$.

a value of the specific rate ($k_1$) for the arene-to-alkyne rearrangement on Os(III). Although arene complexes containing electron-donating substituents isomerize on a time scale that can be conveniently measured by cyclic voltammetry,[18] we have found that for electron-withdrawing groups this rate is significantly increased. Pulse radiolysis provides a convenient way to investigate these faster isomerization rates.

Oxidation of the osmium(II)–arene isomer (**1**) by $CO_3^{\bullet-}$ was observed over a concentration range of 20–50 μM in this complex by following carbonate radical disappearance at 600 nm and the appearance of the osmium(III) intermediate, $[Os(NH_3)_5(\eta^2\text{-}C_6H_5CCPh)]^{3+}$, in the region between 300 and 400 nm. The oxidation reaction was found to proceed with a second-order rate constant of $(9.0 \pm 0.1) \times 10^9$ $M^{-1}$ $s^{-1}$. Subsequent conversion of the osmium(III) arene-bound intermediate to the alkyne complex (**3**) occurs with a rate constant of $k_1 = (1.8 \pm 0.1) \times 10^4$ $s^{-1}$.

**Formation of a Binuclear Arene Complex.** In accord with behavior reported for other arene complexes,[12] $\eta^2$-coordination of the arene in compound **1** activates it toward additional ligation. Thus, when $Os(NH_3)_5(OTf)_3$ is reduced in DME in the presence of low concentrations of diphenylacetylene, the major product is the compound $[\{Os(NH_3)_5\}_2(\mu\text{-}2,3\text{-}\eta^2{:}4,5\text{-}\eta^2\text{-}C_6H_5CCPh)](OTf)_4$ (**4**). The $^1H$ NMR spectrum of **4** features five resonances corresponding to the coordinated arene, four of which are shifted about 2 ppm upfield from their free ligand value. In addition, signals appear for the five aromatic protons and the ammines. A cyclic voltammogram of **4** is similar to that of the benzene derivative reported previously;[1b] scanning to $E_\lambda = 0.60$ V reveals a reversible couple at 0.41 V, indicating the stability of the mixed-valence complex. When the switching potential is raised to 1.0 V, the anodic scan produces a 5+/6+ oxidation wave at $E_{1/2} = 0.85$ V. Subsequent cycling reveals the formation of a 1:1 ratio of **3** and $[Os(NH_3)_5((CH_3)_2CO)]^{3+}$ upon full electrochemical oxidation of **4** (Figure 3).[19]

## Discussion

The measured value of $k_1 = 1.8 \times 10^4$ $s^{-1}$ for an arene-to-alkyne isomerization on Os(III) is in good agreement with the values obtained for other pentaammineosmium complexes incorporating electron-withdrawing substituents, these rates being 2 to 3 orders of magnitude greater than those found for ligands such as aniline or anisole, which contain electron-donating groups.[18,20] Presumably the increase in stability of the osmium(III)–arene isomer for the latter complexes arises from the better σ-donating properties of the organic ligand. The observation that $k_1$ is several orders of magnitude greater than that for the corresponding isomerization on Os(II) testifies to the large back-bonding interaction in the divalent complex.

**π-Donation from Diphenylacetylene to Os(III).** Alkynes are unique in their ability to act simultaneously both as good π-accepting and π-donating ligands.[2] Tatsumi et al.[17] have compared a series of Mo(II) complexes with diphenylacetylene in which both the coordination geometry and number are varied. A second report[2b] features two Co(I) complexes differing only in coordination number. In both cases, the alkyne is considered to "donate" from two to four electrons depending on the environment of the metal center.[21] The present results are complementary to these studies, as they offer a comparison between complexes in which the oxidation state is varied while the coordination environment is conserved. Although crystal structures of these complexes would be most informative, insight may be gained through consideration of the C≡C stretching frequencies. For the $d^6$ complex $[Os(NH_3)_5(PhCCPh)](OTf)_2$, ligand π-donation can be considered negligible as the pseudo $t_{2g}$ orbitals are fully occupied in a formal sense. The displacement in the C≡C stretch of $\Delta\nu = 313$ $cm^{-1}$ is therefore a result solely of the $\pi_\parallel$ and $\pi^*_\parallel$ interaction (i.e. the traditional Dewar–Chatt–Duncanson model).[22] Counter to what might be expected, the one-electron oxidation product of this material (**3**) results in a *decrease* in stretching frequency ($\Delta\nu = 405$ $cm^{-1}$) even though the metal center is significantly less π-basic. This can be accounted for by invoking strong π-donation from the $\pi_\perp$ orbital from the diphenylacetylene ligand. A $\Delta\nu$ of 405 $cm^{-1}$ is typical of those reported for diphenylacetylene complexes incorporating an electron-deficient metal center.[2]

Although attempts to isolate $[Os(NH_3)_5(HCCH)](OTf)_2$ in pure form have thus far been unsuccessful, this species has been generated, isolated in crude form, and partially characterized.[15] $E_{1/2}$ for this complex in acetone (0.11 V, NHE) is about 300 mV negative to that of its ethylene analogue.[18d] This dramatic shift may also be attributed to acetylene π-donation, which stabilizes Os(III), and has no counterpart for the case of the olefin.

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**Registry No.** **1**, 120609-97-4; **2**, 120609-99-6; **3**$(PF_6)_3$, 120610-01-7; **4**, 120610-03-9; $Os(NH_3)_5(OTf)_3$, 83781-30-0; $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)](OTf)_2$, 105164-48-5; $Fe(Cp)_2PF_6$, 11077-24-0; $[Os(NH_3)_5(\eta^2\text{-}C_2H_2)](OTf)_2$, 120610-05-1.

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(19) The formation of $[Os(NH_3)_5(CH_3)_2CO)]^{3+}$ is inferred from the appearance of a cathodic wave at $E_p = -0.45$ V, NHE. See ref 1a.

(20) L = dimethylpropiophenone: $k = 9.0 \times 10^4$ $s^{-1}$. L = $CF_3Ph$: $k > 6 \times 10^3$ $s^{-1}$ (in acetone).

(21) Following precedent, two- or four-electron donor refers to the two limiting cases of metal–alkyne bonding. The terms are not to be taken literally.

(22) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71–79. Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.