Published in final edited form as:

Inorganica Chim Acta. 2008 May 5; 361(6): 1624–1633. doi:10.1016/j.ica.2007.03.059.

Synthesis, structure, photophysical and electrochemical behavior of 2-amino-anthracene triosmium clusters

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Abstract

The reactions of 2-amino-anthracene with $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ have been studied and the products structurally characterized by spectroscopic, X-ray diffraction, photophysical and electrochemical techniques. At room temperature in CH_2Cl_2 two major, isomeric products are obtained $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-(N-C(1))}\text{-NH}_2\text{C}_{14}\text{H}_8)(\mu\text{-H})]$ (**1**, 14%) and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-(N-C(3))}\text{-NHC}_{14}\text{H}_9)(\mu\text{-H})]$ (**2**, 35%) along with a trace amount of the dihydrido complex $[\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-(N-C(3))}\text{-NHC}_{14}\text{H}_8)(\mu\text{-H})_2]$ (**3**). In refluxing tetrahydrofuran only complexes **2** and **3** are obtained in 24% and 28%, respectively. A separate experiment shows that complex **1** slowly converts to **2** and that the rearrangement is catalyzed by adventitious water and involves proton transfer to the anthracene ring. Complex **1** is stereochemically non-rigid; exhibiting edge to edge hydride migration while **2** is stereochemically rigid. Complex **3** is also stereochemically non-rigid showing a site exchange process of the magnetically nonequivalent hydrides typical for trinuclear dihydrides. Interestingly, **2** decarbonylates cleanly to the electronically unsaturated $46e^-$ cluster $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-(N-C(3))}\text{-NHC}_{10}\text{H}_9)(\mu\text{-H})]$ (**4**, 68%) in refluxing cyclohexane, while photolysis of **2** in CH_2Cl_2 yields only a small amount of **3** along with considerable decomposition. The mechanism of the conversion of **1** to **2** and the dependence of the product distribution on solvent are discussed. All four compounds are luminescent with compounds **1–3** showing emissions that can be assigned to radiative decay associated with the anthracene ligand. Complexes **1–3** all show irreversible $1e^-$ reductions in the range of -1.85 – -2.14 V while **4** shows a nicely reversible $1e^-$ wave at -1.16 V and a quasi-reversible second $1e^-$ wave at -1.62 V. Irreversible oxidations are observed in the range from $+0.35$ to $+0.49$ V. The relationship between the cluster ligand configurations and the observed electrochemical and photochemical behavior is discussed and compared with that of the free ligand.

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This paper is dedicated to Professor Piero Zanello on the occasion of his 65th birthday.

⁵Supplementary material

CCDC 636035 and 636036 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

Keywords

Osmium clusters; Electrochemistry; Luminescence; 2-Aminoanthracene

1. Introduction

In recent years we have been studying the reactivity bicyclic nitrogen containing heteroaromatics with $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$. The resulting complexes have proven to be interesting from several points of view. First of all, the formation of formally electron deficient 46e-complexes of the general formula $[\text{Os}_3(\text{CO})_9(\mu_3-\eta^2(\text{L-H}))(\mu\text{-H})]$ (L = quinoline, phenanthridine, 5,6-benzoquinoline, quinoxaline, benzimidazole, benzoxazole, benzothiazole) results in a dramatic change in the reactivity of the coordinated heterocycle relative to the free ligand. Thus nucleophilic attack on the coordinated ligand takes place on the carbocyclic ring while in the free ligand it is invariably on the heterocyclic ring. Moreover, the regio- and stereoselectivity can be controlled in a previously unprecedented way [1–3]. Subsequent density functional theory (DFT) computational studies revealed that it was not the actual electron deficiency in the carbocyclic ring that lead to the observed novel reaction chemistry but rather the ability of the metal core to stabilize the anionic intermediates that are formed after nucleophilic attack [4].

These same complexes also proved to be good electron acceptors and electrochemical or chemical reduction results in the formation of stable radical anions, even in aqueous solutions, which have been studied spectroscopically and modeled with DFT calculations [5–7]. Here again, the ability for the metal core to communicate with the organic ligand via the electron deficient $\mu_3-\eta^2$ -bonding mode proved to be an important factor in determining the overall stability of the radical anions produced by reduction. Recently, it has been shown that this type of bonding mode can result from the reaction of an aromatic carbocycle containing exocyclic amine substituents [8]. Also, there have been recent reports that metal complexes of anthracene are particularly good intercalators into the major groove of DNA [9]. In light of our previous reports regarding the selective binding of triosmium complexes containing aromatic nitrogen heterocycles to DNA we thought it would be interesting to study the reactions of 2-aminoanthracene with $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ [10,11]. We report here the results of these studies including the electrochemical and photophysical properties of the complexes formed as well as their structural characterization by solid state and solution spectroscopic techniques.

2. Experimental

2.1. General methods and materials

Reactions were carried out under a nitrogen atmosphere but were worked up in air using preparative thin layer chromatography (10 × 20 cm plates coated with 1 mm silica gel PF 60₂₅₄-EM Science). Solvents were reagent grade. Tetrahydrofuran was distilled from benzophenone ketyl and methylene chloride and acetonitrile were distilled from calcium hydride. Osmium carbonyl purchased from Strem Chemicals and was used to prepare of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ by oxidation with trimethylamine N-oxide(Aldrich) in acetonitrile

according to the known literature procedures [12]. 2-Aminoanthracene 98% (Aldrich) was used as received.

^1H NMR spectra were obtained on a Varian 400 MHz Unity Plus or a Varian NMR Systems 500 MHz spectrometer. Infrared spectra were obtained on a Thermo-Nicolet 633 FT-IR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Labs, Woodside, NY. Electrochemical methods were performed on a BAS 100 electrochemical analyzer in methylene chloride using tetra-n-butyl ammonium hexafluorophosphate as the carrier electrolyte and are reported referenced to the ferrocene/ferrocenium ion couple. UV-Vis absorption spectra and emission spectra were recorded on a Molecular devices Spectra Max M2 using acetonitrile as the solvent.

2.2. The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 2-aminoanthracene at ambient temperature

The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.220 g, 0.21 mmol) with 2-aminoanthracene (0.08 g, 0.41 mmol) in CH_2Cl_2 (40 mL) at room temperature was carried out for 15hr. The solvent was removed on a rotary evaporator and the residue was thin layer chromatographed on silica. Elution with hexane/ CH_2Cl_2 (4:1 v/v) gave four bands. The fastest moving band was the unreacted starting material (actually $[\text{Os}_3(\text{CO})_{12}]$ because $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ converts to the parent carbonyl with decomposition on silica gel in the absence of acetonitrile). The second band afforded compound $[\text{Os}_3(\text{CO})_{10}(\mu-\eta^2\text{-(N-C(3))}-\text{NHC}_{14}\text{H}_9)(\mu\text{-H})]$ (**2**) as greenish yellow crystals from CH_2Cl_2 /hexane at 4 °C in 14% (0.034 g) yield. Elemental *Anal.* Calc. for $\text{C}_{24}\text{H}_{11}\text{N}_1\text{O}_{10}\text{Os}_3$: C, 27.91; H, 1.03; N, 1.23. Found: C, 27.61; H, 1.06; N, 1.34%. IR in CH_2Cl_2 : 2100(s), 2060(vs), 2049(vs), 2017(s), 2000(s), 1988(sh), 1974(sh); ^1H NMR in CDCl_3 : δ 8.07(s, br, 1H); 7.99(s, 1H); 7.806(m, 1H), 7.66(m, 1H); 7.65(s, 1H); 7.42(m, 3H), 4.12(d, 1H); 3.85(d, 1H); 14.169(s, 1H).

The third band afforded $[\text{Os}_3(\text{CO})_{10}2(\mu-\eta^2\text{-(N-C1)}-\text{NH}_2\text{C}_{14}\text{H}_8)(\mu\text{-H})]$ (**1**) as red crystals from CH_2Cl_2 /hexane at 4 °C in 35% (0.88 g) yield. Elemental *Anal.* Calc. for $\text{C}_{24}\text{H}_{11}\text{N}_1\text{O}_{10}\text{Os}_3$: C, 28.15; H, 0.80; N, 1.19. Found: C, 27.61; H, 1.06; N, 1.34%. IR in CH_2Cl_2 : 2100(s), 2062(vs), 2050(vs), 2018(s), 1998(s), 1988(sh), 1974(sh); ^1H NMR in CDCl_3 : δ 8.02(s, 1H); 7.97(d, 2H); 7.81(s, 1H); 7.54(m, 3H), 4.45(br, 2H); 14.06(br, 1H).

The fourth band yielded a small amount of compound $[\text{Os}_3(\text{CO})_9(\mu-\eta^2\text{-(N-C(3))}-\text{NHC}_{14}\text{H}_8)(\mu\text{-H})_2]$ (**3**) as yellow crystals from CH_2Cl_2 /hexane at 4 °C. Elemental *Anal.* Calc. for $\text{C}_{23}\text{H}_{11}\text{N}_1\text{O}_9\text{Os}_3$: C, 26.75; H, 0.85; N, 1.21. Found: C, 27.19; H, 1.09; N, 1.38%. IR in CH_2Cl_2 : 2122(s), 2080(vs), 2049(vs), 2003(s), 1992(sh), 1972(sh); ^1H NMR in CDCl_3 : δ 8.13(s, 1H), 8.06(d, 2H), 7.88(m, 2H), 7.35(m, 2H), 7.04(s, 1H), 5.85(br, 1H) and -14.59(s, 2H).

2.3. The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 2-aminoanthracene at elevated temperature

A THF solution (60 mL) of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.400 g, 0.43 mmol) and 2-aminoanthracene (0.120 g, 0.62 mmol) was refluxed for 3 h during which time the color of the solution changed from yellow to greenish yellow. The solvent was removed on a rotary evaporator and the residue was thin layer chromatographed on silica gel. Elution with hexane/ CH_2Cl_2 (3:1 v/v) generated four bands. The faster moving band was the unreacted

starting material. The second band contained a trace amount of a green compound. The third band gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-C}_{14}\text{H}_9\text{NH})(\mu\text{-H})]$ (**2**) as greenish yellow crystals from CH_2Cl_2 /hexane at 4 °C in 24% (0.107 g) yield. The slowest moving band afforded $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_8\text{NH})(\mu\text{-H})_2]$ (**3**) as yellow crystals from CH_2Cl_2 /hexane at 4 °C in 28% (0.120 g) yield.

2.4. Synthesis of $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_8\text{NH}_2)]$ (**4**)

Thermolysis of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-(N-C(3)C}_{14}\text{H}_9\text{NH})(\mu\text{-H}))]$ (**2**) in refluxing cyclohexane (40 mL) gave a deep green solution. The solvent was removed by rotary evaporator and the residue was purified by TLC on silica gel. Elution by hexane/ CH_2Cl_2 (3:1 v/v) gave two bands. The faster moving band yielded compound $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_{14}\text{H}_9\text{-NH}_2)(\mu\text{-H})]$ (**4**) as green crystals from CH_2Cl_2 /hexane at 4 °C in 68% (0.030 g) yield. Elemental *Anal. Calc.* for $\text{C}_{23}\text{H}_{11}\text{N}_1\text{O}_9\text{Os}_3$: C, 27.40; H, 0.53; N, 1.20. Found: C, 27.19; H, 1.09; N, 1.38%. IR in CH_2Cl_2 : 2102(s), 2063(s), 2052(vs), 2021(s), 2003(s), 1970(w); ^1H NMR in CDCl_3 : 10.67(s, 2H); 8.52(s, 1H); 8.01(s, 1H); 7.86(t, 2H); 7.6(m, 2H); 7.5(t, 1H); 5.33(s, 2H); 14.36(s, 1H).

2.5. Photolysis of **1**

The photolysis of compound **2** was done by irradiating a methylene chloride (70 mL) solution of compound **2** by UV radiation for 2 h. The resulting brown solution was then dried on an evaporator. The chromatographic separation of the residue gave two bands as eluted by hexane/ CH_2Cl_2 (4:1 v/v). The faster moving band was the unreacted compound **2** and the slower moving band yielded compound **3**.

2.6. Crystal structure analysis

Suitable crystals of **2** and **3** were coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo $\text{K}\alpha$ (0.71073 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using SMART [13] software. Frame integration and final cell refinements were done using SAINT [14] software. The final cell parameters were determined from least-squares refinement on 2481 and 5705 reflections, respectively. The SADABS [15] program was used to carry out absorption corrections.

The structure was solved using the Patterson method and difference Fourier techniques (SHELXTL, V6.12) [16]. Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij} 's related to the atom's ridden upon. The bridging hydrides were positioned by using XHYDEX [17]. All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the International Tables for X-ray Crystallography [18]. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

3. Results and discussion

3.1. Compound synthesis and reaction pathways

The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 2-aminoanthracene in CH_2Cl_2 at room temperature yielded $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-(N-C(1))}\text{-NH}_2\text{C}_{14}\text{H}_8)(\mu\text{-H})]$ (**1**) and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-(N-C(3))}\text{-NHC}_{14}\text{H}_9)(\mu\text{-H})]$ (**2**) in 35% and 14% yield, respectively, along with trace amounts of $[\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-(N-C(3))}\text{-NHC}_{14}\text{H}_8)(\mu\text{-H})_2]$ (**3**) (Scheme 1). When the same reaction is performed in refluxing THF only **2** and **3** in 24% and 28% yield, respectively, are obtained along with a trace amount of a dark green compound which was subsequently identified as $[\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C}_{14}\text{H}_8\text{NH})(\mu\text{-H})]$ (**4**) (vide infra) (Scheme 1). In a separate experiment red crystals of **1** were dissolved in CDCl_3 and monitored by ^1H NMR. The initially red solution gradually turns yellow and the proton resonances associated with **2** gradually appear. Thus it appears that C–H activation at the 1- and 3-positions of the anthracene ring is competitive at room temperature but that **2** is more thermodynamically stable than **1**. The structures of **2** and **3** based on the NMR, IR and elemental analysis were verified by solid state structure determinations. The thermal instability of **1** precluded obtaining good single crystals and is based on its ^1H NMR and the observed dynamical behavior of the hydride ligand (vide infra). It would appear that if activation of the C–H bond at the 3-position takes place this intermediate goes on to form **3** but if activation at the 1-position occurs than the initially formed **1** is unstable with respect to conversion to **2**.

The rearrangement of **1** to **2** involves an overall transfer of a proton from the amine nitrogen to the 1-position of the anthracene ring along with reductive elimination of the initially activated C(1)–H bond. The disruption of the aromatic by the proton transfer to C(1) results in formation of a C(2)=N bond (Scheme 1). We noticed that conversion of **1** to **2** was accelerated by the addition of water. When D_2O is added to a solution of **1** in CD_2Cl_2 the onset of the conversion to **2** is noted immediately (Fig. 1). In addition to the appearance of the hydride peak associated with **2** and the corresponding AB pattern for the C(1) methylene group we noted an additional broad singlet at δ 4.79 that is not present in either **1** or **2**. This resonance gradually disappears along the resonances associated with **1** and conversion to **2** is >90% complete in 6 days (Fig. 1). We can assign this peak to a C(1)HD group formed by initial deuteration of C(1) by D_2O followed by reductive elimination (Scheme 1). The disappearance of this peak with time and the simultaneous appearance of the C(1) H_2 of **2** indicates that these steps are reversible and that a thermodynamic isotope effect is operative due to the presence of H_2O in the sample (in our hands it was not possible to avoid the introduction of water during the preparation of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ and/or during TLC purification). We suggest here that steric crowding at the osmium atom bound to the C(1) in **1** leads to an elongated Os–C(1) bond, negatively polarized toward C(1) which activates this position towards protonation by adventitious water. The proposed steric crowding arises from the disposition of the anthracene ring relative to the carbonyl groups on the Os bound to C(1). Clearly there are alternative possibilities for the proton catalyzed conversion of **1** to **2** but the pathway presented in Scheme 1 represents the most straightforward one based on the data at hand. As expected at higher temperature the conversion of **1** to **2** is much faster and therefore only compounds **2** and **3** observed.

Initial activation at C(3) leads to a less sterically encumbered adduct which then goes on to form **3** via N–H activation-decarbonylation. There is ample precedent for the room temperature formation of nonacarbonyl dihydrides from the reaction of aromatic hydrocarbons containing amine functionalities with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ [19].

In our previous studies on the reactivity of decacarbonyl triosmium complexes of aromatic nitrogen heterocycles we found that decarbonylation either thermally or photochemically leads to the formation of nonacarbonyl complexes containing a $\mu_3\text{-}\eta^2$ bonding mode for the nitrogen heterocycle with the osmium bound carbon involved in a 3-center-2-electron bond [1,2]. This is not the case for **2** where only thermolysis leads to decarbonylation while photolysis leads only to the formation of **3** along with nonspecific decomposition (Scheme 3). The reasons for this difference probably lie in the larger size and “vertical” orientation of the anthracene ring in **2**. Our recent computational studies on the transition states involved in the decarbonylation of related complexes revealed that considerable motion of the heterocyclic ring is involved in the reaction coordinate [20]. Thermal excitation of the large and vertically oriented anthracene ring is therefore required to access the decarbonylation pathway. This is thermally accessible for the smaller ring systems at ambient temperatures and thus decarbonylation can take place both thermally and photochemically.

3.2. Solid state structures of compounds **2** and **3**

The solid state structure of **2** is shown in Fig. 2, crystal data are given in Table 1 and selected distances and angles are given in Table 2. The structure consists of an approximately equilateral triangle of osmium atoms with the 2-amino anthracene ligand bound to one edge of the triangle via the nitrogen atom and C(3) of the ring (C(24) in Fig. 2). The ligand resides in a plane approximately perpendicular to the plane of the Os_3 triangle ($\text{N}(1)\text{--Os}(3)\text{--Os}(2) = 92.49(12)^\circ$ and $\text{C}(24)\text{--Os}(1)\text{--Os}(2) = 90.65(14)^\circ$). The $\text{N}(1)\text{--C}(11)$ ($\text{C}(3)$) bond length is $1.296(6)\text{\AA}$ is consistent with this being a double carbon–nitrogen bond and the adjacent carbon–carbon bonds can be viewed as carbon–carbon single bonds ($\text{C}(11)\text{--C}(24) = 1.467(7)$, $\text{C}(11)\text{--C}(12) = 1.500(7)$, $\text{C}(12)\text{--C}(13) = 1.508(7)\text{\AA}$). The $\text{C}(23)\text{--C}(24)$ bond length of $1.357(7)\text{\AA}$ is suggestive of double bond localization as a result of disruption of the aromaticity of the cluster bound ring while the carbon–carbon bonds in the remaining anthracene rings are all around $1.42\text{\AA}$.

The solid state structure of **3** is shown in Fig. 3 crystal data are given in Table 1 and selected distances and bond angles are given in Table 3. The structure consists of an isosceles triangle of osmium atoms with one elongated edge ($\text{Os}(1)\text{--Os}(2) = 2.9881(3)\text{\AA}$) and two shorter approximately equal edges ($\text{Os}(1)\text{--Os}(3) = 2.8102(3)$, $\text{Os}(2)\text{--Os}(3) = 2.8030(3)\text{\AA}$). The longer edge has an in plane bridging hydride, H2H, as determined by the program XHYDEX [17]. The doubly bridged edge has the calculated position of the hydride, H1H tucked well below the plane of the Os_3 triangle at 79.9° and as expected directly *trans* to two carbonyl groups on Os(1) and Os(3). The 2-amino anthracene ligand is approximately perpendicular to the Os_3 plane and the symmetrical nitrogen bridge across the $\text{Os}(1)\text{--Os}(3)$ edge $\text{Os}(10)\text{--N}(1) = 2.131(4)$ and $\text{Os}(3)\text{--N}(1) = 2.139(4)\text{\AA}$ results in the ligand bisecting this edge. There is evidence for double bond localization for the double bond associated with the nitrogen atom and the one involving the carbon atom bound to Os(2) ($\text{C}(1)\text{--C}(2) = 1.359(7)$ and

C(13)–C(14) = 1.370(8) Å but the C–N bond is clearly a single bond (C(1)–N(1) = 1.439(7) Å). The overall geometry of the complex is very similar to that observed for related dihydrides where nitrogen is part of the aromatic ring system [19].

3.3. Hydride ligand dynamics for 1 and 3

Although the monohydride complex **2** is stereochemically rigid the related complex **1** exhibits a dynamical process which we interpret as simple edge to edge migration of the hydride ligand which averages the major isomer where the hydride bridges the same edge as the anthracene ligand, as in **2**, with a minor isomer where the bridge is either to the carbon bound osmium atom or the nitrogen bound osmium atom and the Os(CO)₄ group (Scheme 2 and Fig. 4). The ratio of the two isomers is 6.1:1 with the major isomer appearing at δ –14.06 and the minor isomer appearing at δ –13.02 as a broad signal at –4 °C. Similar edge hopping processes have been observed for Os₂(CO)₁₀(L)(μ -H) systems where L is a nitrogen containing ligand [21].

Complex **2** also shows a dynamical process common to hydrido triosmium clusters. At room temperature a single sharp hydride resonance of relative intensity **2** is observed at δ –14.62. Given that the two hydride ligands in **2** are not magnetically equivalent in the solid state structure there must be an exchange process which passes through a symmetrical intermediate (Scheme 3). As the temperature is lowered to –12.5 °C the resonance at δ –14.62 broadens and is resolved into two resonances at δ –14.56 and δ –14.69 of equal intensity (Fig. 5). This type of hydride edge hopping is quite common for nonacarbonyl dihydrido triosmium clusters [19].

3.4. Photophysical properties of 1–4

The complexes **1–4** all show several absorption bands in the near UV–Vis region 260–430 nm and in addition **1** shows a band in the visible at 470 nm and **4** shows a band at 615 nm (Table 4). The similarity between the spectra in the 260–430 nm region and that of the free ligand, 2-amino anthracene, suggest that the absorptions in this region are due to π to π^* transitions. This is further born out by the emission spectra of the complexes where almost identical emissions are observed for **1–4** and for 2-amino anthracene in the range of 476–490 nm when they are irradiated in the π to π^* region (Table 4). Excitation spectra of the complexes and of 2-aminoanthracene show that the major contributions to the emissions are from the bands at 261 nm and in the 385–430 nm range. The major difference between the emissions of the complexes and the emission of the free ligand is that the intensity of the emission is significantly attenuated with respect to the free ligand. This is not surprising in that binding of the ligand to the cluster would be expected to mix in metal orbitals with π and/or π^* ligand MO's thereby decreasing the π to π^* transition probability. Irradiation of **1** at 470 nm led to no emission and irradiation of **4** at 615 nm also led to no emission. We assign the later to an n to σ^* transition based on its similar wavelength and intensity compared with the large series of previously reported complexes with similar bonding modes to **4** [22]. Thus it appears that the overall photophysical properties of the anthracene ligand undergo only slight modification on binding to the triosmium cluster in a variety of bonding modes.

3.5. Electrochemical behavior of 1–4

Complexes **1–3** all show irreversible $1e^-$ reductions in the range of -1.85 to -2.14 V while **4** shows a nicely reversible $1e^-$ wave at -1.16 V ($E^{1/2} = 39$ mV at scan rates of 50 – 800 mV/s) and a quasi-reversible second reduction at -1.62 V ($E^{1/2} = 200$ mV at a scan rate of 400 mV/s; Table 5, Fig. 6). The large $E^{1/2}$ and lower peak area for this second reduction suggest that reaction/decomposition of the resulting dianion is rapid on the chemical and electrochemical time scale. Indeed at scan rates less than 400 mV/s this second reduction becomes irreversible while the peak to peak separation for the first reduction remains the same at scan rates of 50 – 800 mV/s. In CH_2Cl_2 no reduction of 2-amino anthracene is observed up to -2.45 V (relative to Fc^+/Fc). The irreversible reduction potentials observed for **2** and **3** are similar to that observed for anthracene (-2.07 V) in CH_3CN but apparently significantly lower than the free ligand in CH_2Cl_2 [23,24]. This is in spite of the fact that in the case of **2** the aromaticity has been interrupted by the proton transfer to the ring (vide supra). This suggests some significant delocalization of electron density onto the cluster in the radical anion but unlike the free ligand, where the reduction is reversible, the resulting radical goes on to react further [23,24]. The slightly lower reduction potential observed for **1** is consistent with the proposed structure where the aromaticity of the anthracene ligand is preserved. The oxidation potentials for **1** and **3** are slightly more positive than for the free ligand again consistent some delocalization of ligand electron density while **2** shows a slightly less positive oxidation potential possibly because on the replacement of a CO by the better electron donors NH and H.

The first reversible $1e^-$ reduction observed for **4** is reminiscent of the previously reported trisium cluster complexes of aromatic nitrogen heterocycles containing a formally 3-center-2-electron bond with a carbocyclic ring in a $46e^-$ species [6,22] and generalizes the electron acceptor properties of this bonding mode to complexes containing exocyclic as well as endocyclic amine groups [8]. However, within this class of molecules only one example of a complex that has two reversible reductions exists; a 4-carboxaldehyde quinoxaline complex while the behavior of **4** is distinctly different in that the second reduction only approaches reversibility at CV scan rates of 400 mV/s [6]. The lower reduction potential of **4** relative to the other complexes and to the free ligand also reflects this electron deficiency.

4. Conclusions

Perhaps the most interesting result of this study is the observation of the proton transfer reaction involved in the conversion of **1** to **2**. This represents a disruption of the aromatic ring of anthracene under very mild conditions. The pathway proposed for this conversion is by no means a unique explanation of this observation but the increased rate of the conversion in the presence of D_2O and the detection of what appears to be a deuterium containing peak seems to at least point to water as the catalyst for this process. The formation of **4** from **2** and its reversible $1e^-$ electrochemical behavior further illustrates the generality of the electron acceptor properties of the $\mu_3\text{-}\eta^2$ -electron deficient bonding mode [2,8]. Overall the photophysical properties and the electrochemical properties of the reported complexes do not differ drastically from the free ligand except in the case of **4**.

Acknowledgements

Support for this research by the Department of Energy (E.R., Grant DE-FG02-01ER45869), the National Science Foundation (J.B.A.R., MCB-0517644) and the National Center for Research Resources, a component of NIH (RR-15583; for use of the core spectroscopy facility) is gratefully acknowledged.

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Fig. 1. 400 MHz ^1H NMR in CD_2Cl_2 showing the room temperature conversion of **1** to **2** before and after the addition of D_2O in the hydride (a) and aliphatic proton (b) regions (* indicates a trace impurity).

Fig. 2.
Solid state structure of **2** showing the 90% probability thermal ellipsoids and the calculated positions of the hydride and hydrogen atoms.

Fig. 3. Solid state structure of **3** showing the 90% probability thermal ellipsoids and the calculated positions of the hydride and hydrogen atoms.

Fig. 4. 500 MHz ¹H NMR of **1** in the hydride region at ambient temperature and -4.5 °C (* indicates a trace impurity).

Fig. 5.
Variable temperature 500 MHz ¹H NMR of **3** in the hydride region.

Fig. 6. Cyclic voltammograms for **4**: (a) the first reversible $1e^-$ reduction at a scan rate of 50 mV/s ($E^{1/2} = 39$ mV); (b) the first reversible ($E^{1/2} = 39$ mV) and second quasi-reversible electron reduction ($E^{1/2} = 200$ mV) at a scan rate of 400 mV/s.

Scheme 1.

Scheme 2.

Scheme 3.

Table 1

Crystal data and structure refinement for **2** and **3**

Compound	3	2
Empirical formula	C ₂₃ H ₁₁ NO ₉ OS ₃	C ₂₄ H ₁₁ NO ₁₀ Os ₃
Formula weight	1015.93	1044.95
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	8.9379(6)	8.4517(10)
<i>b</i> (Å)	14.2536(10)	8.5215(10)
<i>c</i> (Å)	19.0453(12)	20.125(2)
α (°)	90	92.056(3)
β (°)	93.805(2)	90.265(3)
γ (°)	90	119.334(2)
Volume (Å ³)	2421.0(3)	1262.4(3)
<i>Z</i>	4	2
<i>D</i> _{calc} (Mg/m ³)	2.787	2.749
Absorption coefficient (mm ⁻¹)	15.760	15.119
<i>R</i> (000)	1824	942
Crystal size (mm)	0.19 × 0.12 × 0.08	0.20 × 0.12 × 0.02
θ Range for data collection (°)	1.79–28.34	2.03–28.33
Index ranges	–11 ≤ <i>h</i> ≤ 8, –18 ≤ <i>k</i> ≤ 19, –23 ≤ <i>l</i> ≤ 23	–11 ≤ <i>h</i> ≤ 11, –11 ≤ <i>k</i> ≤ 11, –26 ≤ <i>l</i> ≤ 26
Reflections collected	16646	17528
Independent reflections (<i>R</i> _{int})	5862 (0.0304)	6285 (0.0343)
Completeness to $\theta = 28.34^\circ$ (28.33°) (%)	97.2	99.5
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.3654 and 0.1537	0.7519 and 0.1519
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5862/0/325	6285/0/343
Goodness-of-fit on <i>F</i> ²	1.076	1.077
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0280, <i>wR</i> ₂ = 0.0611	<i>R</i> ₁ = 0.0297, <i>wR</i> ₂ = 0.0681
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0631	<i>R</i> ₁ = 0.0337, <i>wR</i> ₂ = 0.0697
Largest difference in peak and hole (e Å ⁻³)	2.162 and –0.841	2.037 and –1.288

Table 2Selected distances (Å) and angles (°) for compound **2**^a

<i>Bond distances (Å)</i>			
Os(1)–Os(3)	2.9007(4)	C(11)–N(1)	1.296(6)
Os(1)–Os(2)	2.9098(4)	C(11)–C(24)	1.467(7)
Os(2)–Os(3)	2.8992(4)	C(11)–C(12)	1.500(7)
Os(3)–N(1)	2.112(4)	C(12)–C(13)	1.508(7)
Os(1)–C(24)	2.148(5)	C(23)–C(24)	1.357(7)
Os–CO ^b	1.918(6)	C(13)–C(22)	1.426(7)
C–O ^b	1.138(7)		
<i>Bond angles (°)</i>			
Os(1)–Os(2)–Os(3)	59.912(7)	N(1)–C(11)–C(24)	120.3(5)
Os(1)–Os(3)–Os(2)	60.225(10)	N(1)–C(11)–C(12)	118.5(5)
Os(2)–Os(2)–Os(3)	59.863(9)	C(24)–C(11)–C(12)	121.4(4)
N(1)–Os(3)–Os(2)	92.49(12)	C(11)–C(12)–C(13)	115.0(4)
N(1)–Os(3)–Os(1)	81.10(11)	C(11)–C(24)–C(23)	114.5(5)
C(24)–Os(1)–Os(2)	90.65(14)	C(22)–C(23)–C(24)	126.8(5)
C(24)–Os(1)–Os(3)	84.37(14)	Os–C–O ^b	176.2(5)

^aNumbers in parentheses are average standard deviations.^bAverage values.

Table 3Selected distances (Å) and angles (°) for compound 3^a

<i>Bond distances (Å)</i>			
Os(1)–Os(3)	2.8102(3)	C(1)–N(1)	1.439(7)
Os(1)–Os(2)	2.9881(3)	C(1)–C(2)	1.359(7)
Os(2)–Os(3)	2.8030(3)	C(1)–C(14)	1.431(7)
Os(1)–N(1)	2.131(4)	C(2)–C(3)	1.420(8)
Os(3)–N(1)	2.139(4)	C(13)–C(14)	1.370(8)
Os(2)–C(14)	2.135(6)	C(12)–C(13)	1.411(8)
Os–CO ^b	1.914(6)		
C–O ^b	1.136(7)		
<i>Bond angles (°)</i>			
Os(1)–Os(2)–Os(3)	57.954(7)	N(1)–C(1)–C(2)	119.8(5)
Os(1)–Os(3)–Os(2)	64.327(8)	N(1)–C(11)–C(12)	117.0(5)
Os(2)–Os(1)–Os(3)	57.719(8)	C(2)–C(1)–C(14)	123.2(5)
N(1)–Os(3)–Os(2)	77.48(11)	C(13)–C(14)–C(1)	116.4(5)
N(1)–Os(1)–Os(2)	73.40(11)	C(12)–C(13)–C(14)	122.6(5)
C(14)–Os(2)–Os(1)	82.39(14)	C(2)–C(3)–C(12)	117.6(5)
C(14)–Os(2)–Os(3)	83.27(15)	Os–C–O ^b	177.2(5)

^aNumbers in parentheses are average standard deviations.^bAverage values.

Table 4UV-Vis absorption and emission data for **1–4** and 2-amino anthracene

Compound	$\pi-\pi^*$ (nm)	MLCT (nm)	$n-\sigma^*$ (nm)	Excitation (nm)	Emission (nm)	Lifetime (ns)
2-Amino anthracene	261, 316, 334, 352, 405			410	488	
1	261, 324, 364, 383	470		324	485	
2	260, 320, 352, 385, 434			434	490	7.5
3	269, 312, 353, 372, 395			395	476	5.8
4	268, 310, 386		615	386	480	

Table 5Polarographic half wave potentials (in V vs. FeCp₂/FeCp₂⁺ in CH₂Cl₂) for complexes **1–4**

Compound	Oxidation	Reduction
2-Amino anthracene	+0.35 (E_{IRR}), +0.85 (E_{IRR})	>−2.45 ^a
1	+0.42 (E_{IRR})	−1.85 (E_{IRR})
2	+0.35 (E_{IRR})	−2.14 (E_{IRR})
3	+0.42 (E_{IRR})	−2.05 (E_{IRR})
4	+0.49 (E_{IRR})	−1.16 (E_{REV}), −1.62 (E_{QREV})

^aThe limit of the solvent, CH₂Cl₂, is −2.45 V.