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Monomeric Alkene and Alkyne Complexes of Osmium(II) and Osmium(III)

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Summary: The first examples of osmium(II) alkene and alkyne complexes have been isolated using the precursors *cis*-$Os(bpy)_2Cl_2$ and $Os(bpy)_2CO_3$ (bpy is 2,2′-bipyridine) and the appropriate unsaturated hydrocarbon. Preliminary description of ^{13}C and ^1H NMR spectral properties is included and cyclic voltammetric results for several complexes are described. Of particular importance is the observation of solution stable osmium(III) alkene dications formed by bulk electrolysis.

The synthesis and chemistry of osmium complexes with unsaturated hydrocarbon ligands such as simple alkenes and alkynes has been confined to precursors based on Os(0). Examples include the reaction of ethylene with $Os(PPh_3)_3(CO)_2$[1] or the reactions of a series of unsaturated hydrocarbons with clusters such as $Os_3(CO)_{12}$ or its derivatives.[2] By contrast, there is an extensive chemistry based on Fe(II)[3a,b] and to a lesser degree Ru(II).[3c–f] We have a continuing interest in the reactions of ruthenium(II) and osmium(II) alkene and alkyne complexes, including the recent unique observation of a hydration/disproportionation of terminal alkynes promoted by monomeric Os(II) and Ru(II) complexes.[4]

We report here the first examples of osmium-alkene complexes derived from Os(II) precursors, in this case *cis*-$Os^{II}(bpy)_2Cl_2$ or $Os^{II}(bpy)_2CO_3$ (bpy is 2,2′-bipyridine). We also report that the alkene and alkyne complexes have reversible Os^{III}/Os^{II} redox couples. Electrochemical oxidation of Os(II) to Os(III) gives a series of solution stable Os(III) complexes which are rare examples of odd-electron metal complexes.[5]

In a typical preparation 250 mg (0.49 mM) of *cis*-$Os^{II}(bpy)_2Cl_2$ was allowed to react with 2 mL (0.018 mM) of 3-hexyne in a 1:1 mixture of deoxygenated $EtOH/H_2O$ by heating at reflux for 8 h. After the reflux period the solvent was half removed, and an aqueous solution of NH_4PF_6 was added. The flocculent dark green precipitate was collected, washed with water and ether, and then air-dried. Column chromatography on alumina using toluene–acetonitrile mixtures as previously described[6] gave a dark green band which after removal of the solvent yielded 375 mg (69%) of pure [*cis*-$Os(bpy)_2(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)Cl](PF_6)$.

Table I. Os(III)/Os(II) Reduction Potentials for the Alkene, Alkyne, and Related Complexes of Os(II)

complex	$E_{1/2}$,[a] M
[*cis*-$Os(bpy)_2(CH_3CN)Cl](PF_6)$	0.41
[*cis*-$Os(bpy)_2(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)Cl](PF_6)$	0.47
[*cis*-$Os(bpy)_2(PPh_3)Cl](PF_6)$	0.56
[*cis*-$Os(bpy)_2(\eta^2\text{-}CH_2{=}CHPh)Cl](PF_6)$	0.84
[*cis*-$Os(bpy)_2(\eta^2\text{-}CH_2{=}CHCH_2Ph)Cl](PF_6)$	0.84
[*cis*-$Os(bpy)_2(\eta^2\text{-}CH_2{=}CH_2)Cl](PF_6)$	0.86
[*cis*-$Os(bpy)_2(\eta^2DMAC)Cl]PF_6$	1.05
[*cis*-$Os(bpy)_2(CO)Cl](PF_6)$	1.18
[*cis*-$Os(bpy)_2(\eta^1\text{-}C{=}NMe)_2](PF_6)$	1.44
[*cis*-$Os(bpy)_2(C_7H_8)](PF_6)_2$	1.64[b]
[*cis*-$Os(bpy)_2(NO)Cl](PF_6)_2$	>2.2

[a] Measured in CH_3CN solution with 0.1 M $(NEt_4)ClO_4$ as supporting electrolyte using a Pt bead working electrode. All potentials are referenced to the sodium chloride saturated calomel electrode. Anodic and cathodic peak currents are equal at a scan rate of 200 mV/s unless otherwise noted. [b] Oxidative peak potential at a scan rate of 200 mV/s.

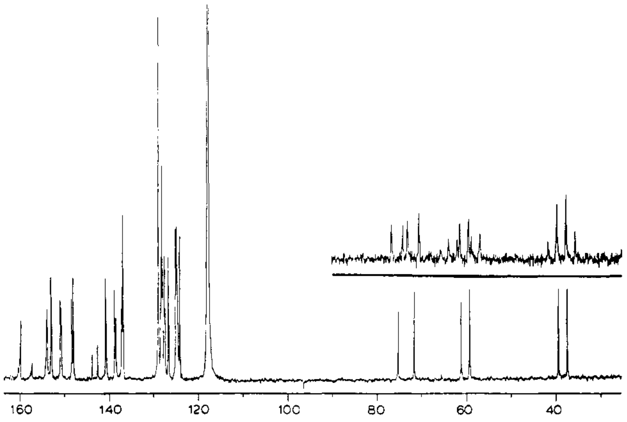

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of [*cis*-$Os^{II}(bpy)_2(\eta^2\text{-}CH_2{=}CHCH_2Ph)Cl](PF_6)$ taken in CH_3CN/CD_3CN (2:1 by volume) recorded at 30 °C. Inset shows ^{13}C proton-coupled region of the olefinic and methylene carbon resonances.

The reaction appears to proceed through the monoaquo complex (eq 1) followed by displacement of the aquo ligand

$$cis\text{-}Os^{II}(bpy)_2Cl_2 + H_2O \rightleftharpoons [cis\text{-}Os^{II}(bpy)_2(H_2O)Cl]^+ + Cl^- \quad (1)$$

$$[cis\text{-}Os^{II}(bpy)_2(H_2O)Cl]^+ + \text{alkene} \rightarrow [cis\text{-}Os^{II}(bpy)_2(\text{alkene})Cl]^+ + H_2O \quad (2)$$

by the hydrocarbon (eq 1 and 2). The synthetic procedure has led to the preparation of products which contain styrene, ethylene, allylbenzene, 3-hexyne, and dimethyl acetylenedicarboxylate (DMAC) (see Table I). The dicationic, diolefin complex, $[Os(bpy)_2C_7H_8]^{2+}$ (C_7H_8 is 2,5-norbornadiene) was prepared by using similar conditions but on the basis of the carbonato complex $Os(bpy)_2CO_3$, as shown in eq 3 and 4.

$$Os^{II}(bpy)_2CO_3 + 2H^+ + H_2O \rightarrow cis\text{-}Os^{II}(bpy)_2(H_2O)_2{}^{2+} + CO_2 \quad (3)$$

$$cis\text{-}Os^{II}(bpy)_2(H_2O)_2{}^{2+} + C_7H_8 \rightarrow Os^{II}(bpy)_2(C_7H_8)^{2+} + 2H_2O \quad (4)$$

Characterization of all of the products was achieved by ^1H and ^{13}C NMR spectroscopy, elemental analyses,[7] cyclic

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[2] See, for example, Hanson, B. E.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1852. Gambino, O.; Voglio, G. A.; Ferrari, R. P.; Cetini, G. *J. Organomet. Chem.* **1971**, *30*, 381.

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voltammetry, and in some cases, field desorption mass spectrometry or infrared spectroscopy.

Both ^1H and ^{13}C NMR spectroscopy clearly show the presence of a dynamic behavior associated with the osmium(II)-alkene or -alkyne bond. For example, Figure 1 shows the ^{13}C NMR spectrum of [*cis*-$Os^{II}(bpy)_2(\eta^2$-CH_2=$CHCH_2Ph)Cl](PF_6)$ taken in CD_3CN. In this case the carbon atoms of the allyl of group (CH_2CH=CH_2) show *six* resonances of equal intensity in the $^{13}C\{^1H\}$ NMR spectrum. The proton-coupled spectrum confirms that the six resonances are due to isomeric forms of the allylbenzene complex. The $^{13}C\{^1H\}$ and ^1H NMR spectra show evidence for only a cis bpy geometry, ruling out cis-trans isomers of the complex. One possible form of isomerism is through alkene- or alkyne-based rotamers which are magnetically distinct due to the asymmetry of the ring currents from the bpy ligands. For the allylbenzene complex (Figure 1) the rotamers interconvert very slowly at room temperature. However, the $^{13}C\{^1H\}$ NMR spectrum of the 3-hexyne complex in the region of the alkyne carbon atoms demonstrates that interconversion occurs at room temperature, as evidenced by the appearance of only *one* carbon resonance, at −70 °C. The single resonance is split into two magnetically inequivalent lines at 25 °C. The dynamics of the interconversion process are currently under investigation.

Both the osmium(II) alkene and alkyne complexes undergo ligand displacement reactions, as shown, for example, for the substitution of styrene by acetonitrile in eq 5.

$$[cis\text{-}Os^{II}(bpy)_2(\eta^2\text{-}CH_2{=}CHPh)Cl]^+ + CH_3CN \xrightarrow[3\ h]{\Delta} [cis\text{-}Os^{II}(bpy)_2(CH_3CN)Cl]^+ + CH_2{=}CHPh \quad (5)$$

Even more important is the exchange reaction between the 3-hexyne complex and other unsaturated ligands (eq 6)

$$[cis\text{-}Os^{II}(bpy)_2(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)Cl]^+ + CH_2{=}CHPh \xrightarrow[30\ min]{1,2\text{-}C_6H_4Cl_2} [cis\text{-}Os^{II}(bpy)_2(\eta^2\text{-}CH_2{=}CHPh)Cl]^+ + CH_3CH_2C{\equiv}CCH_2CH_3 \quad (6)$$

since it can serve as a preparative route to complexes which are inaccessible by the reaction shown in eq 1. For the example shown in eq 5, complete substitution by styrene in 50-fold excess occurs in 30 min in refluxing *o*-dichlorobenzene.

Cyclic voltammetry and controlled potential electrolysis experiments provide evidence for solution stable Os(III) complexes derived from both [*cis*-$Os^{II}(bpy)_2(\eta^2$-$CH_3CH_2{\equiv}CCH_2CH_3)Cl]^+$ and [*cis*-$Os^{II}(bpy)_2(\eta^2$-CH_2=$CH_2Ph)Cl]^+$. A cyclic voltammogram of [*cis*-$Os^{II}(bpy)_2$-(η^2-CH_2=$CHPh)Cl](PF_6)$ in CH_3CN with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte is shown in Figure 2a. In the voltammogram a reversible one-electron oxidation appears at $E_{1/2}$ = 0.84 V vs. the saturated calomel electrode (SCE). From the voltammogram in Figure 2b recorded 1.5 h after electrolytic oxidation of Os(II) to Os(III), ca. 40% of the original osmium(III) styrene complex was converted into [*cis*-$Os^{III}(bpy)_2(CH_3CN)Cl]^{2+}$ ($E_{1/2}$ = 0.41 V). By contrast, solutions of [*cis*-$Os^{III}(bpy)_2(\eta^2$-CH_2=$CHPh)Cl]^{2+}$ prepared by electrolytic oxidation in CH_2Cl_2 are stable for 1.5 h as shown by the voltammetric traces in Figure 2c and by electronic spectral measurements on the Os(II) form after electrolytic reduction at +0.2 V.

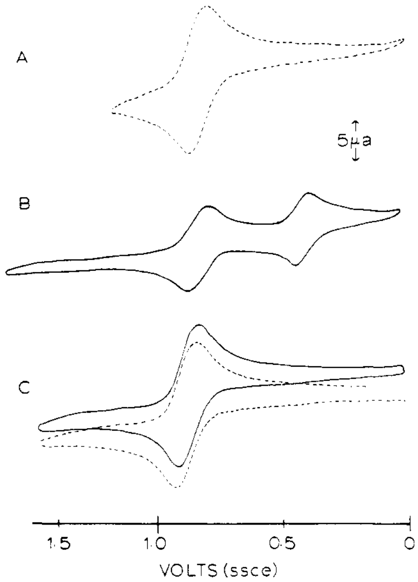

Figure 2. (A) Cyclic voltammogram of [*cis*-$Os^{II}(bpy)_2(\eta^2$-CH_2=$CHPh)Cl](PF_6)$ in CH_3CN with 0.1 M TEAP as supporting electrolyte using a Pt bead as working electrode. (B) Cyclic voltammogram of the same complex 1.5 h after controlled potential electrolysis at +1.10 V (vs. SCE). (C) Cyclic voltammogram of the same complex taken in 0.1 M tetrabutylammonium hexafluorophosphate in CH_2Cl_2 taken before electrolysis (solid line) and 1.5 h after electrolysis at +1.10 V (dashed line).

Of considerable interest are the electronic effects of the hydrocarbon ligand on the metal and, ultimately, the effect of the metal on the chemical properties of the ligand. Two experimental probes into the nature of the metal-ligand interaction are the shifts in $\nu(C{\equiv}C)$ for the alkynes, $\Delta\nu$, where $\Delta\nu$ = ν(hydrocarbon) − ν(complexed hydrocarbon), and Os(III)/Os(II) reduction potentials for both the alkene and alkyne complexes. For $[Os^{II}(bpy)_2(\eta^2$-$CH_3CH_2C{\equiv}CCH_2CH_3)Cl]^+$ $\nu(C{\equiv}C)$[8] is 1980 cm^{-1} ($\Delta\nu$ = 127 cm^{-1}) while for $[Os^{II}(bpy)_2(\eta^2$-DMAC$)Cl]^+$ $\nu(C{\equiv}C)$ is 1884 cm^{-1} ($\Delta\nu$ = 373 cm^{-1}). The values of $\Delta\nu$ are more typical of values found for "weakly" bound cases as in complexes of Pt^{II} and Ru^{II} than of "strongly" bound cases as in Pt(0) complexes[9] where $\Delta\nu$ can be as large as 500 cm^{-1}. In the latter cases, ^{13}C NMR studies have been interpreted as indicating a large contribution from a metallocyclopropene ring structure.[10] Unfortunately, there appear to be no IR data on alkyne complexes derived from formal Os(0) precursors with which we can compare our data.

The Os(III)/Os(II) redox potential is a sensitive probe of the relative stabilization of the two oxidation states by the σ-donating and π-accepting properties of the ligands. Taube has presented evidence for osmium(II) ammine complexes which suggests that $d\pi(Os(II))$−π^*(ligand) back-bonding interactions are the predominant determinant of relative redox potentials for Os(III)/Os(II) couples.[11] Based on his argument and assuming that variations in solvation energies between complexes are small, it is possible to use the Os(III)/Os(II) potentials (see Table I) to construct a relative ordering of π-acceptor properties of the hydrocarbon ligands compared to other π-accepting ligands which is as follows: NO^+ > CO > DMAC > alkenes

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(7) For example, Anal. Calcd for $[Os(bpy)_2(\eta^2$-CH_2=$CHPh)Cl](PF_6)$: C, 42.73; N, 7.14; H, 3.07. Found: C, 42.53; N, 7.04; H, 2.75. Anal. Calcd for $[Os(bpy)_2(C_7H_8)](PF_6)_2$: C, 36.65; N, 6.33; H, 2.71. Found: C, 37.19; N, 6.41; H, 2.67.

(8) This complex, although pure by elemenetal analysis, field desorption mass spectrometry, and ^1H NMR spectroscopy, shows another IR stretch at 1960 cm^{-1} the nature of which is under investigation.

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$> C{=}NCH_3 > PPh_3 >$ 3-hexyne $> CH_3CN$.

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Structural Versatility of Ru_4 Butterflies. The Molecular Structures of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)\cdot{}^1/_2C_6H_{14}$. Clusters with Almost Planar Metal Frameworks

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Summary: The synthesis and structural characterization of two new 64-electron butterfly clusters of ruthenium $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)\cdot{}^1/_2C_6H_{14}$ are described. The former crystallizes in space groups $P2_1/n$ with a = 8.941 (1) Å, b = 10.209 (2) Å, c = 39.753 (6) Å, β = 95.62° and Z = 4. The latter crystallizes in space group $P\bar{1}$ with a = 11.954 (1) Å, b = 15.459 (2) Å, c = 19.830 (4) Å, α = 97.19 (1)° β = 74.35 (1)°, and γ = 71.26 (1)°, and Z = 2. These electron-rich clusters have almost planar Ru_4 frameworks with two or three elongated Ru–Ru bonds. The influence of electron count and ligand donation to the Ru_4 core on stereochemistry are discussed.

Although the most common skeletal stereochemistry for homotetranuclear metal clusters is tetrahedral, a substantial number of M_4 species have now been characterised in which the metal framework has a "butterfly" configuration derived from the tetrahedron by cleavage of one metal–metal bond.[1,2] Moreover, interest in the butterfly geometry has been greatly stimulated by the observation of enhanced reactivity for exposed carbidic carbon atoms bound in multisite fashion within the open nest-like frameworks of the butterfly clusters $[HFe_4(\mu_4\text{-}C)(CO)_{12}^-]$, $Fe_4(\mu_4\text{-}C)(CO)_{12}^{2-}]$,[3] and $[Fe_4(CO)_{13}C]$[4] and of highly coordinated carbon monoxide in $Fe_4(CO)_{13}^{2-}$.[5,6] It is possible that the butterfly configuration of tetrametal fragments may play a subtle role in facilitating reactions of ligands bound between the "wings" of the butterfly since in principle an exceedingly wide range of dihedral angles ϑ and M–M nonbonding distances c (Figure 1) can be tolerated for any particular M_4 fragment. For the known Fe_4 clusters[3-8] there are some indications that the dihedral angle may be sensitive to electronic structure but unfortunately the range of compounds, dihedral angles, and electron counts is relatively small. We have recently characterised by X-ray diffraction several tetranuclear ruthenium clusters including two new compounds $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ with highly unusual, almost planar, Ru_4 frameworks which are described herein. These tetraruthenium clusters show unprecedented variations in butterfly geometry. Our results, together with other scattered data in the literature, suggest that electron donation from the ligands can play a major role in influencing butterfly geometry, with higher electron counts favoring larger dihedral angles, flattening of the Ru_4 butterfly, and Ru–Ru bond lengthening. These steps may be part of a logical sequence of stereochemical changes leading from a tetrahedral (60 electrons, six M–M bonds) geometry through a butterfly (62 electrons, five M–M bonds) core to a metal skeleton with only four M–M bonds. The results, which indicate the versatility of the butterfly structural unit, may have important ramifications for the modification and reactivity of clusters.

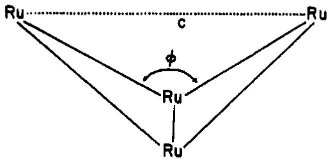

Figure 1. Definition of c, the nonbonding Ru···Ru distance and ϕ, the dihedral angle for an Ru_4 butterfly.

Structural data for the new butterfly structures,[9,13] together with a selection of other data for Ru_4 and mixed

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[9] $Ru_4(CO)_{13}$ $(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ was synthesized in ~10% yield as one product of the controlled decomposition of $Ru_3(CO)_{11}$ $(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$.[10] A dark blue band separated on Florisil (eluant benzene–heptane) afforded red-brown crystals when evaporated to dryness and recrystallized under a CO atmosphere [ν(CO) C_6H_{12}, 2076 (m), 2060 (m), 2041 (s), 2034 (vs), 2023 (vs), 2010 (m), 1998 (s), 1985 (m), 1972 (m), cm^{-1}]. $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ was obtained as a minor product (~10%) from the pyrolysis of $Ru_3(CO)_9(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_3$[11] in toluene. The last red band eluted (3:1 benzene–heptane) from a Florisil column gave red crystals (ν(CO) 2034 (vs), 2014 (s), 1984 (m), 1973 (m), 1967 (s), 1950 (s), 1938 (w) cm^{-1}]. The phosphinidene derivative $Ru_4(CO)_{13}(PPh)$ (red crystals from heptane–benzene) is the major product (~50%) of thermolysis of the coordinately unsaturated cluster $Ru_3(CO)_9(\mu\text{-}PPh_2)(H)$.[12] Full details of the synthesis and spectroscopic properties of these clusters will be presented elsewhere.

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