Synthesis and Fluxionality of a Tungsten–Triosmium Cluster Compound $CpWOs_3(CO)_{11}(\mu_3$-CTol)

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The reaction of $Os_3(CO)_{10}(NCMe)_2$ with a tungsten alkylidyne $Cp(CO)_2W{\equiv}CTol$ ($Cp = \eta^5$-C_5H_5, $Tol = p$-C_6H_4Me) produces the compound, $CpWOs_3(CO)_{11}(\mu_3$-CTol) (**1**). The structure of compound **1** can be viewed as one in which the metalla-alkyne, $Cp(CO)_2W{\equiv}CTol$, is μ_3-η^2-$\perp$(perpendicular) bound to an $Os_3(CO)_9$ fragment. Variable-temperature ^{13}C NMR spectra of **1** show no evidence for the analogous rotation of the metalla-alkyne molecule as shown alkyne rotation in $Os_3(CO)_9(C_2Tol_2)$ compound. This lack of the metalla-alkyne fluxionality supports the apparent saturated nature of compound **1**.

Introduction

A variety of organotriosmium cluster compounds were prepared from the reactive triosmium complexes with many alkynes.[1] Useful triosmum precursor compounds for this chemistry include the coordinatively unsaturated species $H_2Os_3(CO)_{10}$[2] and the lightly stabilized species, $Os_3(CO)_{10}(NCMe)_2$.[1b,3] These osmium complexes exhibit greatly enhanced reactivity under mild conditions, compared with $Os_3(CO)_{12}$, and appear to be quite adaptable to designed synthesis.

Stone and coworkers have utilized the isolobal relationships[4] between alkynes ($RC{\equiv}CR'$) and metal alkylidyne complexes ($LnM{\equiv}CR$) to prepare a series of mixed metal μ-alkylidyne species. The success of this idea has prompted studies of the reactive triosmium clusters with a tungsten alkylidyne to form tungsten–triosmium (WOs_3) cluster framework.

We have previously reported that the reaction of $H_2Os_3(CO)_{10}$ with the alkyne analogue $Cp(CO)_2W{\equiv}CTol$ revealed rich chemistry of hydrocarbon-substituted tungsten–triosmium mixed metal clusters[5]. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Cp(CO)_2W(CTol)$, has yielded a major product, $CpWOs_3(CO)_{11}(\mu_3$-CTol) (**1**). We now report details of the preparation and fluxional process of compound **1** which can be viewed as that a metalla-alkyne, $Cp(CO)_2W{\equiv}CTol$, is μ_3-η^2-$\perp$(perpendicular) bound to an $Os_3(CO)_9$ fragment.

Experimental

General Comments. Solvents were dried prior to use. Anhydrous Me_3NO (mp 225~230 °C) was obtained from $Me_3NO{\cdot}2H_2O$ (98% Aldrich Chemical Ltd.) by sublimation (three times) at 90~100 °C under vacuum. $Os_3(CO)_{12}$,[6] ^{13}CO-enriched $Os_3(CO)_{12}$[7], and $Cp(CO)_2W(CTol)$[8] were prepared as described in the literature.

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. The progress of the reactions was monitored by analytical thin-layer chromatography (pre-coated tlc plates, Silica Gel 60 F-254, E. Merck). Preparative thin-layer plates were prepared from Silica Gel G (Type 60, E. Merck).

Infrared spectra were obtained on a Perkin-Elmer 281B spectrophotometer. Both ^1H NMR (360MHz) and ^{13}C NMR (90 MHz) spectra were recorded on a Nicolet NT-360 spectrometer. $Cr(acac)_3$ (*ca.* 0.02 M) was added to ^{13}C sample as a shiftless relaxation reagent. Mass spectra were recorded by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois using Varian MAT CH-5. All *m/z* values are referenced to ^{184}W and ^{192}Os. Microanalytical data were provided by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Preparation of $Os_3(CO)_{11}(NCMe)$. $Os_3(CO)_{12}$ (821.8 mg, 0.906 mmol) was dissolved in 1300 m*l* of dichloromethane containing 100 m*l* of acetonitrile. An acetonitrile solution of trimethylamine oxide (1.05 mmol, 1.1 equiv.) was added dropwise until the $Os_3(CO)_{12}$ had disappeared as monitored by IR spectroscopy. The solvent was removed using a rotary evaporator. The residue was dissolved in hot acetonitrile and recrystallized at −10 °C to yield a bright yellow crystalline product $Os_3(CO)_{11}(NCMe)$ (662.6 mg, 0.721 mmol, 80%).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Cp(CO)_2W(CTol)$. A CH_2Cl_2 (50 m*l*)-MeCN (10 m*l*) solution of $Os_3(CO)_{11}(NCMe)$ (59.4 mg, 0.0646 mmol) was treated with an acetonitrile solution (10 m*l*) of trimethylamine oxide (5.2 mg, 0.069 mmol) to produce $Os_3(CO)_{10}(NCMe)_2$. After evaporation of the solvent *in vacuo*, the $Os_3(CO)_{10}(NCMe)_2$ was redissolved in toluene (60 m*l*) and heated quickly to 110 °C. To this solution was slowly added a cold (−20 °C) toluene solution (20 m*l*) of $Cp(CO)_2W(CTol)$ (54.2 mg, 0.133 mmol) using a cannula. The reaction mixture was heated to reflux for 0.5 h. The solvent was evaporated and the residue was extracted with dichloromethane (*ca.* 2 m*l*). The remaining yellow solid was identified by IR as $Os_3(CO)_{12}$ (21.0 mg, 0.0232 mmol, 36%). The dichloromethane extract was purified by preparative tlc (pentane : dichloromethane, 3:2) to provide red $CpWOs_3(CO)_{11}(\mu_3$-CTol) (**1**, 33.3 mg, 0.0271 mmol, 42%, R_f = 0.25) as a crystalline solid. Recrystallization from pentane-dichloromethane gave an analytically pure sample of **1**. IR(CCl_4) ν (CO) 2078(s), 2039(vs), 2033(vs), 2007(s), 2000(sh), 1982(m), 1975(m) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.46-7.12(m, 4H), 5.52 (s, 5H) 2.27 (s, 3H); MS (70 eV) *m/z* 1236 (M^+), 1236-28X, X = 1-11 (M^+ − XCO). Anal. Calcd. for $C_{24}H_{12}O_{11}WOs_3$: C, 23.42; H, 0.98; W, 14.94; Os, 46.36. Found : C, 23.52; H, 0.90; W, 14.94;Os, 46.56.

Preparation of ^{13}CO-enriched 1. Carbon-13 CO-en-

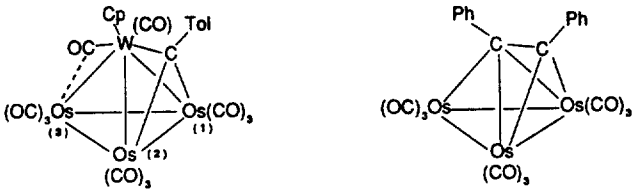

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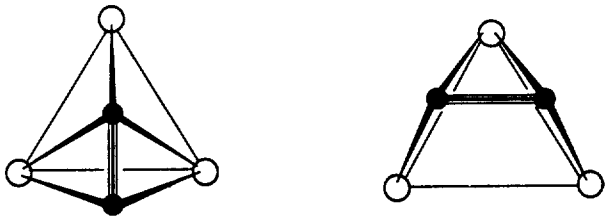
Figure 1. Structure of $CpWOs_3(CO)_{11}(\mu_3$-CTol)(**1**) and $Os_3(CO)_9(C_2Ph_2)$.



I

$\mu_3-\eta^2-\perp$

$Fe_3(CO)_9(C_2Ph_2)$[15]

$Os_3(CO)_9(C_2Ph_2)$[16]

$Cp_2W_2Fe(CO)_6(C_2Tol_2)$[9a]

II

$\mu_3-\eta^2-\parallel$

$Fe_3(CO)_8(C_2Ph_2)_2$[11]

$Os_3(CO)_{10}(C_2Ph_2)$[12]

$Ni_3(CO)_3(C_5H_5)(C_2(CF_3)_2)$[13]

$Cp_2W_2Os(CO)_7(C_2Tol_2)$[14]

$Cp_2W_2Ru(CO)_7(C_2Tol_2)$[9]

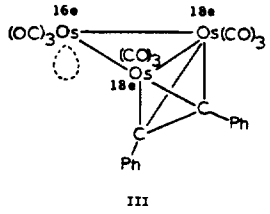
Figure 2. The two common M_3C_2 framework arrangements for an alkyne bonded to an M_3 triangle; ○ = M, ● = C (acetylenic carbon atom).

riched compound **1** was prepared from $Cp(CO)_2$-W(CTol) and ^{13}CO-enriched $Os_3(^*CO)_{10}(NCMe)_2$ [from *ca.* 50% ^{13}CO-enriched $Os_3(^*CO)_{12}$] by the procedure described above.

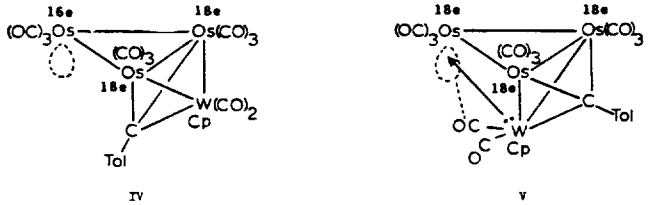
Results and Discussion

Synthesis and Characterization of 1. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Cp(CO)_2W(CTol)$ provides a dark red crystalline product, which is formulated as $CpWOs_3(CO)_{11}(CTol)$, **1**, on the basis of spectroscopic and analytical data. Increasing the reaction temperature results in improved yields, a maximum yield [42%, 66% based on the recovered $Os_3(CO)_{12}$] being obtained by refluxing a toluene solution at 110 °C. $Os_3(CO)_{12}$ was isolated as a coproduct. Simple adduct formation between "$Os_3(CO)_{10}$" species and $Cp(CO)_2W(CTol)$ with loss of a carbonyl ligand apparently gave compound **1** as the major product. After compound **1** was isolated, it was learned that Stone and coworkers had previously isolated the same compound from the reaction of $Os_3(CO)_{10}(C_8H_{14})_2$ with $Cp(CO)_2W(CTol)$ in a low yield (16%, 5days, 25 °C)[9]. Furthermore, they had obtained its X-ray crystal structure. The structure (Figure 1) of compound **1** adopts approximately tetrahedral arrangement of metal atoms with a WOs_2 face capped by the triply-bridging CTol ligand.

This *closo* trigonal bipyramid compound contains six skeletal bond electron pairs with five skeletal atms and therefore obeys skeletal electron pair theory.[10] The tungsten and



III



IV V

Figure 3. Schematic representaion of $Os_3(CO)_9(C_2Ph_2)$ (III) and two possible bonding mode of the tungsten alkylidyne moiety in compound **1** (IV and V).

osmium (3) atoms have formally 19 and 17 electrons, respectively, which probably accounts for the presence of a semi-bridging carbonyl ligand. For the alkyne-three metal atom (M_3C_2) type of interaction, the two isomeric forms are pictorially illustrated in Figure 2. In the form I, the acetylenic carbon atoms symmetrically bridge over two metal atoms and are perpendicular to the M_2 vector($\mu_3-\eta^2-\perp$). The carbon atom which lies above the M_3 center is within bonding distances of all three metal centers. The isomeric form II has the acetylenic C_2 vector above the M_3 plane and almost parallel to an M_2 vector ($\mu_3-\eta^2-\parallel$). Each of the two acetylenic carbon atoms is within bonding distances of two metal atoms. Established trimetallic alkyne clusters are also listed below the two isomeric forms in Figure 2

Compound **1** can be viewed as the sturcture I in which an alkylidyne molecule, $Cp(CO)_2W(CTol)$, is bound to an $Os_3(CO)_9$ fragment. In this respect compound **1** has a sturcture related to that of unsaturated $Os_3(CO)_9(C_2Tol_2)$ as shown in Figure 1. Compound **1** is, therefore, formally two electrons deficient and expected to react readily with various substrates, as has been shown to be the case $Os_3(CO)_9(C_2Ph_2)$.[16] No reaction, however, is observed upon treatment of compound **1** either with carbon monoxide or with dihydrogen in a pressure bottle (45 psig) at room temperature for 5 h (except for slight decomposition of the compound).

The lack of reactivity in compound **1** can be rationalized as shown in Figure 3. Two isomers (IV and V) are possible for $Os_3(CO)_9[Cp(CO)_2W{\equiv}CTol]$. The structure IV (not the observed isomer) would be, expected to be as reactive as $Os_3(CO)_9(C_2Ph_2)$ (III) due to unsaturation. In the alternative structure V (the observed isomer), however, a lone pair electron on the tungsten atom can act as a donor to the electron deficient osmium center, leading to overall saturation of the cluster compound. This donor-acceptor bond is further supported by a semibridging carbonyl ligand in compound **1** as was observed for other compounds such as $Os_3(CO)_{10}(C_2Ph_2)$[12] and $Fe_2(CO)_6(C_4R_4)$[17].

Solution Dynamics of 1. The solution dynamics of compound **1**, $CpWOs_3(^*CO)_{11}$ (μ_3-CTol), have been examined by variable-temperature ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum at -80 °C (see Figure 4) form a 1/1/1/1/3/3/1 pattern at δ 218.4, 202.1, 187.9, 181.4, 181.0, 179.8

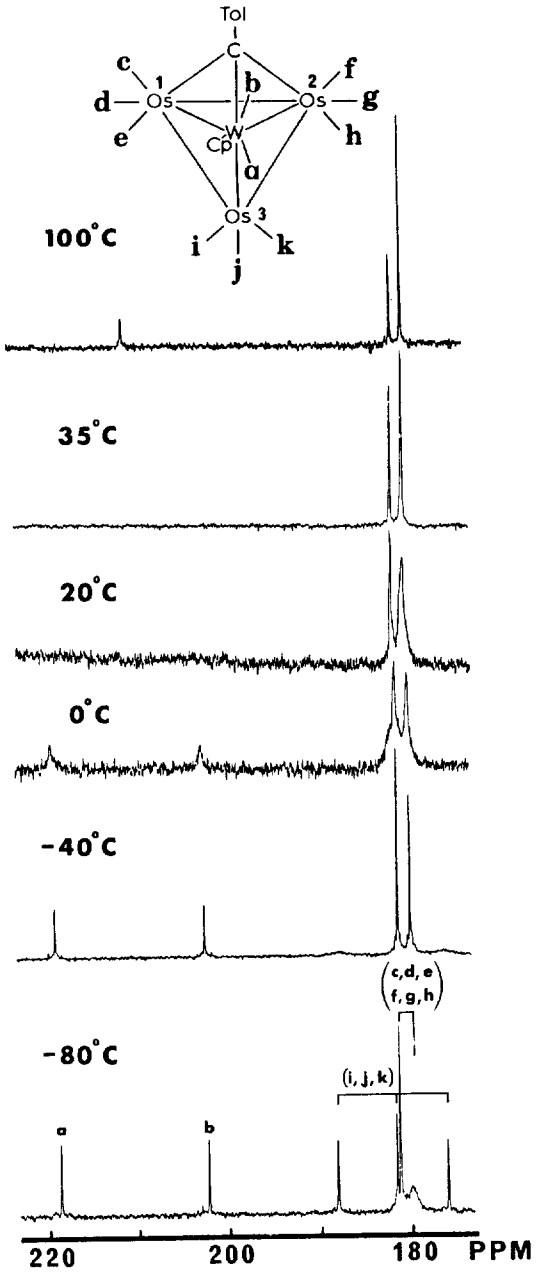


Figure 4. Variable-temperature ^{13}C NMR spectra (90 MHz) of $CpWOs_3(^*CO)_{11}(\mu_3$-CTol) (**1**) in CD_2Cl_2.

(broad), and 175.8. The two resonances at δ 218.4 and 202.1 are assigned to carbonyl ligands on the tungsten atom *a* (J_{WC} = 131.9 Hz) and *b* (J_{WC} = 143.3 Hz), respectively, on the basis of ^{183}W-satellites and the fact that bridging carbonyls generally appear further downfield than terminal carbonyls.

As the temperature is raised to −40 °C, resonances at 187.9, 181.4 and 175.8 due to carbonyls *i, j,* and *k* on the unique osmium atom collapse, indicating the occurrence of three-fold carbonyl exchange localized on the Os(3) center. The two resonances at δ 181.0 and 179.8 with a ratio of 3:3 are due to the six carbonyl ligands (*c*~*h*) on Os(1) and Os(2) centers. Definitive assignment of these carbonyls to a specific osmium atom cannot be made. At −40 °C the two osmium centers undergo fast threefold exchanges localized at each atom. The activation barrier on one osmium center is higher than that on the other as indicated by the δ 179.8 (broad) resonance at −80 °C.

When the solution is warmed from −40 °C, the δ 181.0 and 179.8 resonances broaden and coalesce at approximately 20 °C into a single resonance. The two resonances due to carbonyls *a* and *b* broaden and those of *i, j,* and *k* coalesce to a single resonance. This implies that in this temperature range the tungsten and osmium (3) centers undergo slow and fast exchanges of ligands, respectively. Further warming to 100 °C leads to three sharp signals with 2:3:6 intensity ratios. The high temperature fluxional processes are due to a time-averaged symmetrical configuration with a mirror plane through μ_3-C, W and Os(3), which arises from localized ligand exchange on each metal center and equilibration of the six carbonyl ligands *c*~*h*. The activation barriers for localized carbonyl exchange increase as Os(1), Os(2)<Os(3)<W.

Using variable-temperature ^1H NMR, Clauss and Shapley have recently established that $Os_3(CO)_9(C_2Tol_2)$ adopts structure I in solution and the alkyne ligand undergoes rotation resulting in exchange of the two acetylenic ends.[16b] As detailed above, however, no evidence has been observed for the analogous rotation of the metalla-alkyne molecule in compound **1**. This lack of fluxionality supports the apparent saturated nature of cluster **1**.

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Proteolysis of Glucagon Bound to Dimyristoylphosphatidylcholine Vesicle

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Glucagon was found to interact with DMPC vesicles electrostatically and hydrophobically. It appears that glucagon bound irreversibly to the vesicles through hydrophobic interaction was partially protected from the proteolysis by trypsin. Out of three possible sites, only the peptide bond preceded by Arg-18 was cleaved by a prolonged trypsin treatment. α-chymotrysin did not affect the vesicle-bound glucagon. Based on these observations, possible structure of irreversibly bound glucagon on the vesicle surface is discussed.

Introduction

Many mammalian glucagons have an identical amino acid sequence consisted of 29 amino acid residues as shown below. This protein,

His – Ser – Glu – Gly – Thr – Phe – Thr – Ser – Asp – Tyr – Ser –
Lys – Tyr – Leu – Asp – Ser – Arg – Arg – Ala – Glu – Asp –
Phe – Val – Glu – Trp – Leu – Met – Asn – Thr

like many other peptide hormones, have a high potential of forming amphiphilic helical structures[1,2]. The amphiphilicity of parts of the sequence is a common feature among peptide hormones, enabling them to form stable complexes with lipid vesicles. The capacity of assuming an amphiphilic secondary structure accompanying hormone-membrane interaction may have physiological roles as suggested by Tayler and Kaiser[2]. For example, an amphiphilic α-helix or a β-strand may interact with a complementary site on a receptor protein in a manner analogous to its interaction with phospholipid[3]. A second possibility is that amphiphilic secondary structures may facilitate interaction between peptide hormones and receptors through two dimensional diffusion on cell surface[4,5]. Also, the peptide hormone binding to membrane surface may either protect the peptides from attack by soluble proteolytic enzymes or lead to more rapid and specific breakdown by membrane-associated proteases[6]. Pasta *et al.*[7] observed that micelles of various surfactants prolonged the hydrolysis of glucagon by trypsin and α-chymotrypsin. However, they obtained an identical set of products from the digestion of glucagon with or without the presence of micelles. Here we have focused on the interaction of the glucagon with dimyristoylphosphatidylcholine (DMPC) vesicles and the effect of the vesicles on the mode of proteolysis of the peptide hormone by trypsin and α-chymotrypsin. It was found that a certain peptide bonds are protected from the proteolysis by trypsin when glucagon is bound to vesicles. The vesicle-bound glucagon was completely protected from α-chymotrypsin.

Experimental

Materials. Glucagon (extracted from mixture of bovine and porcine pancreas), trypsin (from bovine pancreas, tre-