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Note

Reactivity of electron-deficient triosmium quinoline cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ with alkynes

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ABSTRACT

Reactions of the electron-deficient triosmium cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ (**1**) with various alkynes are described. Cluster **1** readily reacts with the activated alkyne dimethyl acetylenedicarboxylate (dmad) upon mild heating (65–70 °C) to give the adduct $[Os_3(CO)_9(\mu\text{-}C_9H_6N)(\mu_3\text{-}MeO_2CCCHCO_2Me)]$ (**2**). In contrast, a similar reaction of **1** with diphenylacetylene affords previously reported compounds $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ (**3**), $[Os_3(CO)_9(\mu\text{-}C_4Ph_4)]$ (**4**) and $[Os_3(CO)_8\{\mu_3\text{-}C(C_6H_4)C_3Ph_3\}(\mu\text{-}H)]$ (**5**) while with 2-butyne gives only the known compound $[Os_3(CO)_7(\mu\text{-}C_4Me_4)(\mu_3\text{-}C_2Me_2)]$ (**6**). The new cluster **2** has been characterized by a combination of spectroscopic data and single crystal X-ray diffraction analysis.

1. Introduction

The chemistry of electron-deficient triosmium clusters is spurred by their excellent reactivity compared to their electron-precise counterparts as most of them are chemically inert under mild conditions [1–3]. Among various types of electron-deficient triosmium clusters, the benzoheterocyclic clusters of the general formula $[Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}(L\text{-}H)\}(\mu\text{-}H)]$ (L = quinoline, benzothiazole, benzimidazole, quinoxaline, benzoxazole, phenanthridine, 5,6-benzoquinoline) are one of the well studied class of unsaturated 46-electron triosmium hydride clusters. Their reactivity has been thoroughly investigated over the past ten years from which it has been found that they are reactive towards a wide range of substrates [4–15]. For examples, reactions of phosphine and amines with this type of clusters result in ligand addition at the metal core along with rearrangements whereas reactions with anionic neocleophiles such as hydride or carbanions results in attack at the carbocyclic ring [4,5,7–12].

The reactivity of this type of clusters so far studied was mainly with neutral two electron donors or carbanions. Surprisingly we found that no reactions of these clusters with alkynes have been reported to date albeit alkynes are an important class of organic ligands with carbon donor atoms. So, we have decided to investigate their reactivity with various alkynes and recently reported that the benzothiazole cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)]$ (**A**) [13], reacts with dmad resulting in the formation of two isomeric alkenyl complexes **B** and **C** (Scheme 1). We also showed that **B** cleanly transformed to **C** under similar conditions thereby established **B** as the kinetic product and **C** as the thermodynamic product (Scheme 1). As part of our study of the reactivity of these unsaturated clusters with alkynes we have now studied the reactions of another triosmium unsaturated cluster of this series namely the quinoline cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ (**1**) with various alkynes the results of which are described herein.

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques but work-up was carried out in air unless otherwise stated. Reagent grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Dimethyl acetylenedicarboxylate, diphenylacetylene and 2-butyne were purchased from Aldrich and used as received. Cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ (**1**) was prepared according to the literature method [4,9]. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Varian Unity Plus 400 instruments. Elemental analyses were performed by BCSIR Laboratories, Dhaka.

2.1. Reaction of 1 with dimethyl acetylenedicarboxylate

To a hexane solution (50 mL) of **1** (150 mg, 0.158 mmol) was added dimethyl acetylenedicarboxylate (110 mg, 0.774 mmol) and the mixture was heated at 65–70 °C for 15 h during which time the colour of the reaction mixture changed from green to

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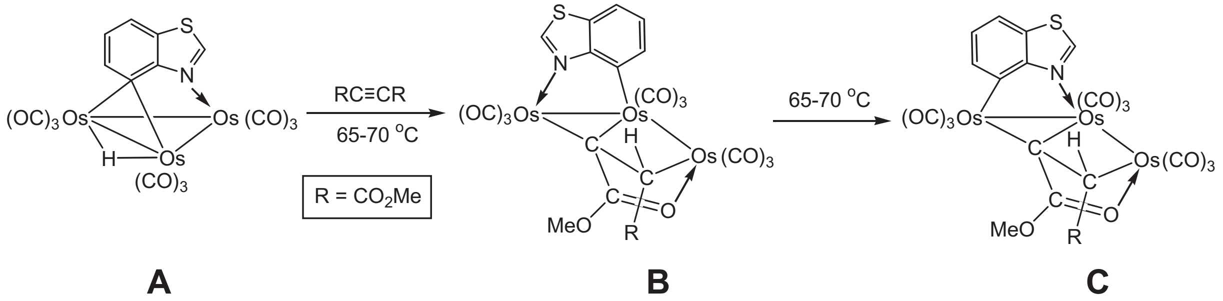


Scheme 1. Reactivity of the benzothiazole cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)]$ (**A**) towards dmad.

yellow. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed two bands. The major band afforded $[Os_3(CO)_9(\mu\text{-}C_9H_6N)(\mu_3\text{-}MeO_2CCCHCO_2Me)]$ (**2**) (64 mg, 37%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 20 °C while the minor band gave unreacted **1** (trace). Spectral data for **2**: *Anal.* Calc. for $C_{24}H_{13}NO_{13}Os_3$: C, 26.35; H, 1.20; N, 1.28. Found: C, 26.62; H, 1.37; N, 1.38%. IR (ν(CO), CH_2Cl_2): 2087 w, 2064 s, 2029 m, 2018 sh, 1993 s,br, 1967 w, 1942 w, 1923 w, 1918 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.21 (m, 1H), 8.20 (m, 1H), 8.13 (m, 1H), 7.09 (m, 3H), 3.73 (s, 3H), 3.58 (s, 3H), 2.48 (s, 1H).

2.2. Reaction of 1 with diphenylacetylene

A heptane solution (50 mL) of **1** (190 mg, 0.199 mmol) and diphenylacetylene (175 mg, 0.972 mmol) was heated to reflux for 6 h. A similar chromatographic separation to that above gave the following compounds in order of elution: $[Os_3(CO)_{10}(\mu\text{-}C_9H_6N)(\mu\text{-}H)]$ (**3**) (24 mg, 12%), $[Os_3(CO)_8\{\mu_3\text{-}C(C_6H_4)C_3Ph_3\}(\mu\text{-}H)]$ (**5**) (33 mg, 14%), $[Os_3(CO)_9(\mu\text{-}C_4Ph_4)]$ (**4**) (30 mg, 13%) and **1** (10 mg).

2.3. Reaction of 1 with 2-butyne

A reaction similar to that above of **1** (100 mg, 0.105 mmol) and 2-butyne (40 mg, 0.741 mmol) in refluxing hexane for 15 h followed by similar chromatographic separation afforded $[Os_3(CO)_7(\mu\text{-}C_4Me_4)(\mu_3\text{-}C_2Me_2)]$ (**6**) (36 mg, 37%).

2.4. X-ray crystallography

Single crystals of **2** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at 20 °C. Crystallographic data were collected at 150(2) K, using Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). All calculations were carried out using the WinGX package [16] and all data sets were corrected for absorption using DIFABS [17]. The structure was solved by direct methods and refined on F^2 by full matrix least-squares using SHELXL [18] using all unique data. All non-hydrogen atoms were directly located from difference Fourier maps and refined using anisotropic displacement parameters without any geometrical restraints. The hydrogen atoms were included in calculated positions (riding model). All pertinent crystal data and other experimental conditions and refinement details are summarized in Table 1.

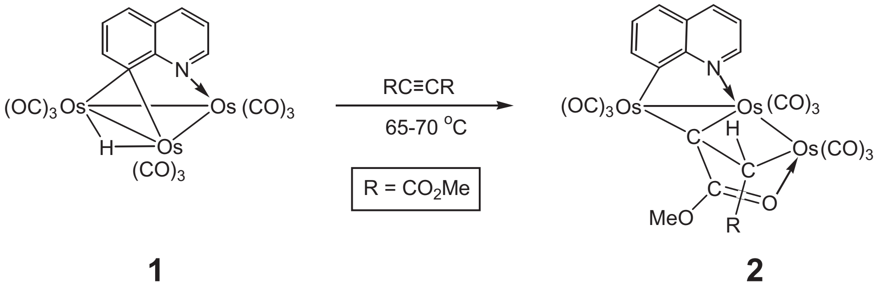
Table 1
Crystallographic data and structure refinement for **2**.

Empirical formula	$C_{24}H_{13}NO_{13}Os_3$
Formula weight	1093.95
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.639(2)
b (Å)	9.927(2)
c (Å)	16.204(4)
α (°)	79.81(2)
β (°)	81.84(3)
γ (°)	62.96(2)
Volume (Å^3)	1355.9(5)
Z	2
Density (calculated) (Mg/m^3)	2.680
Absorption coefficient (mm^{-1})	14.091
F(0 0 0)	992
Crystal size (mm^3)	0.15 × 0.15 × 0.15
θ range for data collection (°)	2.32–24.88
Index ranges	$-10 \leq h \geq 5$ $-11 \leq k \geq 11$ $-17 \leq l \geq 18$
Reflections collected	4701
Independent reflections	3586 (R_{int} = 0.0621)
Refinement method	full-matrix least-squares on F^2
Maximum and minimum transmission	0.2264 and 0.2264
Data/restraints/parameters	3586/228/372
Goodness-of-fit (GOF) on F^2	1.010
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0409, wR_2 = 0.1152
R indices (all data)	R_1 = 0.0475, wR_2 = 0.1166
Largest difference peak and hole (e Å^{-3})	2.343 and −2.232

3. Results and discussion

Treatment of **1** with excess dmad (RC≡CR, R = CO_2Me) at 65–70 °C in hexane furnished $[Os_3(CO)_9(\mu\text{-}C_9H_6N)(\mu_3\text{-}MeO_2CCCH\text{-}CO_2Me)]$ (**2**) in 37% yield (Scheme 2). Apparently, the alkyne ligand is inserted into the metal hydride bond to form alkenyl cluster. The ^1H NMR spectrum of **2** displays resonances for six aromatic protons of the quinoline ligand and six methyl protons of the carboxylate groups of dmad. In addition the absence of any hydride resonance and appearance of a singlet at δ 2.48 (integrated to 1H) indicates that the hydride is transferred to the alkyne moiety which was also observed for **B** and **C** (*vide supra*). The pattern of the IR spectrum of **2** is very similar to those of **B** and **C** that differ by the orientation of the benzothiazole ring. In view of the similarity of spectroscopic data of **2** with those of **B** and **C** it was not possible to identify which isomeric form of **2** was isolated. In order to elucidate the precise nature of **2** an X-ray crystallographic study was carried out the results of which are summarized in Fig. 1.

The molecule consists of an open trinuclear cluster of three osmium atoms with two distinctly different osmium–osmium bonds [Os(1)–Os(2) 2.8138(12) and Os(2)–Os(3) 2.9263(11) Å]. The nine carbonyl atoms are all terminal and equally distributed to three osmium atoms. The quinoline ligand bridges the Os(1)–Os(2) edge so that the nitrogen atom is bonded to the central osmium atom, Os(2), of the open cluster [Os(2)–N(1) 2.249(13) and Os(1)–C(21) 2.133(15) Å] which is also observed in the thermodynamic product **C** obtained from the reaction between **A** and dmad (*vide supra*). The alkenyl ligand is coordinated to the triosmium core in a μ_3–η^2, η^1, κ^1 fashion, i.e., one carbon, C(13), bridges an osmium–osmium



Scheme 2. Reaction of the quinoline cluster [$Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$] (**1**) with dmad.

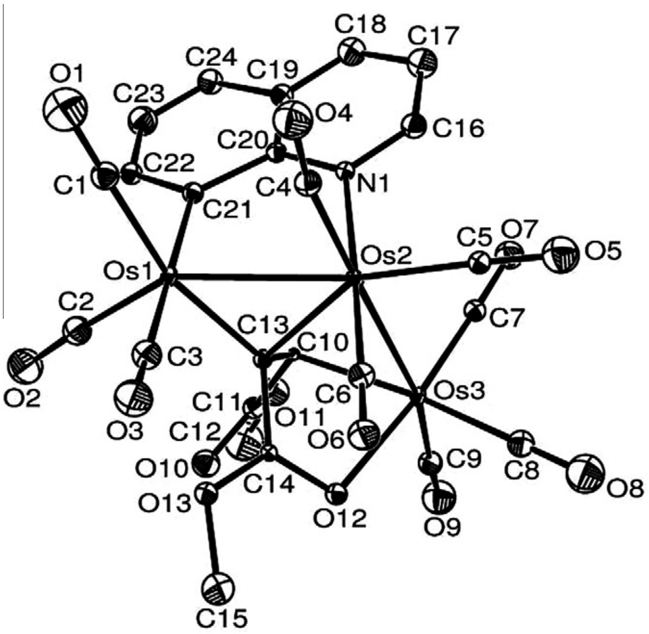
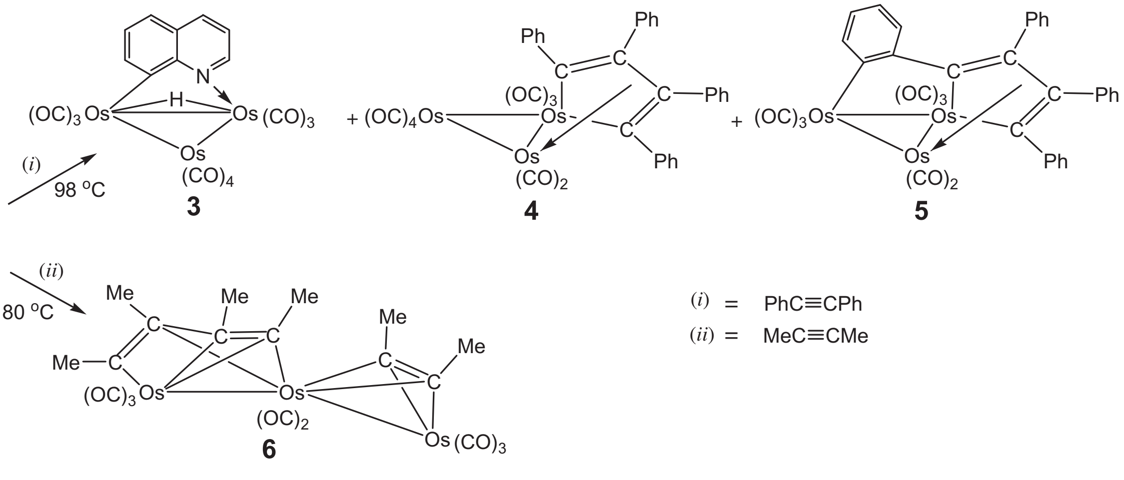


Fig. 1. The solid-state molecular structure of **2**. The thermal ellipsoids were drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Os(1)–Os(2) 2.8137(12), Os(2)–Os(3) 2.9263(11), Os(3)–O(12) 2.164(10), Os(2)–N(1) 2.248(12), Os(1)–C(21) 2.132(15), Os(1)–C(13) 2.106(16), Os(2)–C(13) 2.227(16), Os(3)–C(10) 2.175(16), C(10)–C(13) 1.531(19), Os(1)–Os(2)–Os(3) 107.09(4), C(14)–O(12)–Os(3) 103.8(9), C(13)–C(10)–Os(3) 89.2(9), Os(1)–C(13)–Os(2) 80.9(5), C(10)–C(13)–Os(1) 128.0(11), C(10)–C(13)–Os(2) 108.0(10).

edge, Os(1)–Os(2), which is also bridged by the benzoheterocyclic ligand while the other carbon of the alkenyl moiety, C(10), is bonded to the third osmium, Os(3), which is also bound to a carbonyl oxygen of one of the carboxylate group and a hydrogen atom. The doubly bridged osmium–osmium edge is shorter than the other. The carboxylate groups of the hydrocarbyl ligand are in *cis*-orientation with respect to each other and located on the opposite face of the Os_3 triangle relative to the benzoheterocyclic ligand. The C(10)–C(13) distance of 1.53(2) Å is similar to the carbon–carbon single bond distances formed by using sp^3 hybrid orbitals which clearly indicates the presence of a single bond between them. The formation of only one product (**2**) in this reaction which resembles the thermodynamic product (**C**) obtained from the reaction between **A** and dmad suggesting that the kinetic product of this reaction (product analogous to **B**) is thermally unstable under the reaction conditions which readily convert to **2** after its formation. This also implies that the benzothiazole binds more strongly to the cluster compare to quinoline as bond rearrangement is necessary for this isomeric conversion. This phenomenon was also observed by Rosenberg and coworkers during their study relating to the displacement of these heterocycles by acetonitrile from cluster surface after functionalization [5]. Later they also showed that the nitrogen atom of the five-membered heterocyclic ring is more basic than that of six-membered heterocyclic ring thereby the former forms stronger bond with metals [10]. Apart from **C**, Lin and Leong also reported a triosmium cluster namely [$Os_3(CO)_9(\mu\text{-}\gamma\text{-}C_5H_3O_2)(\mu_3\text{-}MeO_2CCCHCO_2Me)$] akin to **2** which was obtained from the reaction between the γ-pyrone cluster [$Os_3(CO)_{10}(\mu\text{-}\gamma\text{-}C_5H_3O_2)(\mu\text{-}H)$] and dmad [19].

To gain more insight into the reaction of **1** and alkynes we have investigated its reaction with diphenylacetylene and 2-butyne.



Scheme 3. Reactions of the quinoline cluster [$Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$] (**1**) with diphenylacetylene and 2-butyne.

Heating a heptane solution of **1** and diphenylacetylene at 98 °C resulted in the isolation of three known compounds $[Os_3(CO)_{10}(\mu\text{-}C_9H_6N)(\mu\text{-}H)]$ (**3**) (12%), $[Os_3(CO)_9(\mu\text{-}C_4Ph_4)]$ (**4**) (13%) and $[Os_3(CO)_8\{\mu_3\text{-}C(C_6H_4)C_3Ph_3\}(\mu\text{-}H)]$ (**5**) (14%) (Scheme 3). Cluster **3** [9] is the parent decacarbonyl cluster of **1** while compound **4** was reported by Ferraris et al. from the reaction between $Os_3(CO)_{12}$ and PhC_2Ph and **5** from the thermal decarbonylation of **4** followed by subsequent C–H activation of one of the phenyl groups of the coordinated C_4Ph_4 ligand [20,21]. A similar reaction of **1** with 2-butyne gave only $[Os_3(CO)_7(\mu\text{-}C_4Me_4)(\mu_3\text{-}C_2Me_2)]$ (**6**) (37%) (Scheme 3) which was also documented by Johnson et al. from the reaction between $Os_3(CO)_{12}$ and MeC_2Me [22]. Both these alkynes knocked out the quinoline ligand from the cluster surface whereas dmad adds to the cluster. Apparently the nucleophilicity of these electron rich alkynes are sufficient to displace quinoline from the cluster core but the exact reason behind this reactivity difference is not clear from the present study.

In conclusion, the reaction of the electron-deficient triosmium cluster **1** which carries a $\mu_3\text{–}\eta^2$-quinoline ligand with dmad led to retention of the quinoline ligand and metal–metal bond scission, resulting in the formation of the monosubstituted dmad product. In contrast, with diphenylacetylene the previously reported alkyne only derivatives **4** and **5** were obtained. Furthermore, the reaction between **1** and 2-butyne followed a different course to those describe above affording **6** incorporating both mono and dimerized alkyne.

Acknowledgements

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Appendix A. Supplementary material

CCDC 785241 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.023.

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