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Metallation of 2-methyl-2-thiazoline at a triosmium cluster: X-ray structure of $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH_2C=NCH_2CH_2S)]$

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Abstract

The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-methyl-2-thiazoline at ambient temperature results in the C–H activation of the methyl substituent of the heterocyclic ligand and this gives the new compound $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH_2C=NCH_2CH_2S]$ (8) in 55% yield. Compound 8 undergoes decarbonylation and a further C–H bond activation by thermolysis at 98°C or by treatment with trimethylamine-*N*-oxide to give the dihydrido cluster $[(\mu-H)_2Os_3(CO)_9(\mu-\eta^2-CH_2C=NCH_2CH_2S]$ (9) in 45% yield. Both complexes have been characterized by elemental analyses, IR and ¹H NMR spectroscopy, together with X-ray crystallography for 8. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Osmium; X-ray structures; Metallation

1. Introduction

The study of the reactivity of N and S containing heterocycles with trimetallic clusters of osmium and ruthenium continues to be the subject of considerable interest; this is due to their relevance to modelling the industrially important hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes [1-7]. We have recently reported the thiazolide clusters [$(\mu-H)M_3(CO)_{10}(\mu-2,3-\eta^2 \dot{C}$ =NCMe=CH \dot{S})] (3, M = Os; 4, M = Ru; Scheme 1), with metallation exclusively at the 2-position, from the reactions of $[M_3(CO)_{10}L_2]$ (1, M=Os, L=MeCN; 2, M=Ru, L = CO) with 4-methyl thiazole [1]. We also found that the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with thiazole results in metallation at the 4- and 2-positions, leading to the isomeric compounds $[(\mu-H)Os_3(CO)_{10}(\mu-2,3-\eta^2-\eta^2)]$ C=NCH=CHS (5) and $[(\mu-H)Os_3(CO)_{10}(\mu-3,4 \eta^2$ -HC=NC=CHS)] (6) [2]. In contrast, when reacted with $[Ru_3(CO)_{12}]$, thiazole preferentially metallates at the 2-position yielding $[(\mu-H)Ru_3(CO)_{10}(\mu-2,3-\eta^2-\eta^2)]$ C = NCH = CHS [7] [3].



Pyridine and 2-substituted pyridines react with triosmium and triruthenium clusters by orthometallation to give [(μ -H)M₃(CO)₁₀(μ -L)] (L=C₅H₄N, 2-MeC₅H₃N, 3-MeC₅-H₃N, 2-Et-C₅H₃N) [8–17]. In comparison to the extensive orthometallation chemistry of five- and six-membered heterocyclic rings, examples of the activation of their substituent groups are comparatively rare. An example of the ethenyl group C–H bond activation rather than those at the hetero-

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cyclic ring has been observed when $[Os_3(CO)_{10}(MeCN)_2]$ was reacted with 2-ethenyl pyridine leading to the formation of the open triosmium cluster $[HOs_3(CO)_{10}(NC_5H_4-C=CH)]$ [18]. As part of our interest in the reactivity of N and S containing heterocycles with trimetallic clusters we have investigated the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-methyl-2-thiazoline and report herein a rare example of the C–H activation of the substituent group of the ligand at ambient temperature.

2. Results and discussion

The lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ readily reacts with 2-methyl-2-thiazoline at room temperature to give the novel cluster $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2 CH_2C = NCH_2CH_2S$ (8) in 55% yield (Scheme 2). The compound 8 has been characterized by microanalysis, IR and ¹H NMR spectroscopy as well as X-ray crystallography. The ¹H NMR spectrum of **8** shows four multiplets at δ 3.24, 3.37, 3.89 and 4.18 for the ring protons, which remain intact, and two coupled doublets at δ 1.81 and 2.40 for the 2-CH₂ group along with a high field singlet at $\delta - 14.20$ each integrating for one hydrogen. The coupling of 20.0 Hz between these protons and their chemical shifts imply a coordinated CH₂ group and metallation at the substituent group. The spectroscopic data indicated the activation of the C-H bond of the methyl substituent of the heterocycle and subsequent coordination of the carbon to the metal. The exact nature of the bonding of the organic ligand to the cluster was obtained by a single crystal structure determination for 8.

The structure of a single molecule of **8** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The molecule consists of a triangular cluster of osmium atoms with three distinct metal-metal bonds (Os(1)-Os(2) = 2.9047(8), Os(1)-Os(3) = 2.8858(8) and Os(2)-Os(3) = 2.9414(10) Å). The Os(2)-Os(3) edge which is bridged simultaneously by the hydride and the heterocyclic ligand is significantly longer than the two unbridged edges.





Fig. 1. X-ray structure of **8**, showing the atom labelling scheme. The ring hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 40% probability level.

able I							
Selected	bond	lengths	(Å)	and	angles	$(^{\circ})$	for 8

$\begin{array}{c} Os(1)-Os(2) \\ Os(2)-Os(3) \\ Os(3)-N(1) \\ Os(2)-H(23) \\ S(1)-C(12) \\ N(1)-C(12) \\ C(11)-C(12) \\ C-O \end{array}$	2.9047(8) 2.9414(10) 2.165(9) 1.77 ^b 1.747(11) 1.284(14) 1.477(13) 1.138 ^a	$\begin{array}{c} Os(1)-Os(3) \\ Os(2)-C(11) \\ Os-C(CO) \\ Os(3)-H(23) \\ S(1)-C(13) \\ N(1)-C(14) \\ C(13)-C(14) \end{array}$	2.8858(8) 2.190(11) 1.923 ^a 1.72 ^b 1.778(11) 1.484(12) 1.48(2)
$\begin{array}{c} C(3) - Os(1) - C(4) \\ C(4) - Os(1) - C(1) \\ C(4) - Os(1) - C(2) \\ C(5) - Os(2) - C(7) \\ C(7) - Os(2) - C(6) \\ C(7) - Os(2) - Os(1) \\ C(11) - Os(2) - Os(1) \\ C(11) - Os(2) - Os(3) \\ C(11) - Os(3) - C(9) \\ C(8) - Os(3) - C(9) \\ C(8) - Os(3) - N(1) \\ C(9) - Os(3) - N(1) \\ C(9) - Os(3) - N(1) \\ C(9) - Os(3) - N(1) \\ C(12) - S(1) - C(13) \\ C(12) - N(1) - Os(3) \\ C(12) - C(11) - Os(2) \\ N(1) - C(12) - S(1) \\ C(14) - C(13) - S(1) \\ Os(2) - H(23) - Os(3) \\ \end{array}$	103.7(4) 90.4(4) 90.4(4) 100.4(5) 92.5(4) 86.1(4) 93.8(3) 84.2(3) 96.1(4) 88.8(4) 93.2(4) 118.9(3) 91.7(6) 126.9(7) 120.1(7) 115.6(8) 107.6(8) 115 ^b	$\begin{array}{c} C(3)-Os(1)-C(1)\\ C(3)-Os(1)-C(2)\\ C(1)-Os(1)-C(2)\\ C(5)-Os(2)-C(6)\\ C(5)-Os(2)-C(11)\\ C(6)-Os(2)-C(11)\\ C(7)-Os(2)-Os(3)\\ C(8)-Os(3)-C(10)\\ C(10)-Os(3)-C(9)\\ C(10)-Os(3)-C(9)\\ C(10)-Os(3)-N(1)\\ N(1)-Os(3)-Os(1)\\ N(1)-Os(3)-Os(2)\\ C(12)-N(1)-C(14)\\ C(14)-N(1)-Os(3)\\ N(1)-C(12)-C(11)\\ C(11)-C(12)-S(1)\\ C(13)-C(14)-N(1)\\ Os-C-O\\ \end{array}$	$\begin{array}{c} 94.4(5)\\89.4(4)\\175.7(5)\\92.3(4)\\84.7(4)\\176.3(4)\\113.2(3)\\90.7(4)\\90.6(4)\\176.2(4)\\91.5(2)\\82.9(2)\\113.2(10)\\119.6(7)\\125.6(10)\\118.9(8)\\110.9(9)\\176.5^{a}\\\end{array}$

^a Average value.

^b Approximate value.

Similar lengthening of the doubly bridged Os-Os edges was also observed in $[(\mu-H)Os_3(CO)_{10}{\mu-2,3-\eta^2}$ $\dot{C} = NC(Me) = CHS$ (2.9340(8)) versus 2.8590(7), 2.8849(8)Å), $[(\mu-H)Os_3(CO)_9{\mu-2,3-\eta^2 C = NC(Me) = CHS) (PPh_3)$ (2.9674(9))versus 2.8619(13), 2.8779(9) Å) and [(µ-H)Os₃(CO)₈{µ-2,3- η^2 -C=NC(Me)=CHS}(PPh_3)₂] (2.9528(6))versus 2.8795(6), 2.9050(6) Å) [1]. The bridging hydride is located close to the plane of the Os₃ triangle, while the heterocyclic ligand is nearly perpendicular to it. The metal atoms Os(3) and Os(2) each contain three linear terminal carbonyl ligands while Os(1) is bonded to four. A notable feature of this structure is that a C-H activation of the methyl

group of 2-methyl-2-thiazoline occurs during the reaction. The organic ligand is η^2 -coordinated to the longest Os(2)– Os(3) edge through a metal–carbon σ bond from C(11) to Os(2) and a two-electron donor bond from N(1) to Os(3). The Os(2)–C(11) bond length of 2.190(11) Å and Os(3)– N(1) bond length of 2.165(9) Å are comparable to those of the related compounds $[(\mu-H)_2Ru_3(CO)_9(\mu_3-\eta^2-\eta^2)]$ CH(Me)C=NCH₂CH₃)}] and $[(\mu-H)_2Os_3(CO)_9(\mu_3-\eta^2-\eta^2-\eta^2)]$ $CHC = NCH_2CH_2CH_2$ [19]. The C(12)-N(1) bond length of 1.284(14) Å is typical of carbon nitrogen double bonds in the related triosmium and triruthenium complexes [20-22], while the C(14)-N(1) bond length of 1.484(12) Å is close to that expected for a C–N single bond (1.47 Å)[23]. The S–C distances (1.747(11)–1.778(11), average 1.763 Å) are only slightly smaller than the value expected for a S–C single bond (1.81 Å) [23]. The Os–C(CO) distances (1.897(11)-1.954(12)), average 1.923 Å) and the Os-C-O angles (171.3(10)-179.6(9), average 176.54°) are comparable to the corresponding values in triosmium decarbonyl compounds containing a 3, 3, 4 carbonyl ligand distribution and in which the heterocyclic ligand and the hydride bridge the same Os–Os edge [1,2,20,22].

Thermolysis of **8** in refluxing heptane at 98°C gives the dihydrido cluster $[(\mu-H)_2Os_3(CO)_9(\mu_3-\eta^2-CHC=NCH_2CH_2S)]$ (**9**) in 45% yield (Scheme 1). The compound has been characterized on the basis of elemental analysis, IR and ¹H NMR spectroscopic data. A direct analog of **9** was obtained from the reaction of the μ_3 -imidoyl compound $[(\mu-H)Os_3(CO)_9(\mu_3-\eta^2-C=NCH_2CH_2CH_2)]$ (**10**) with diazomethane (Scheme 3) [19]. The ν (CO) frequencies of **9** are very similar to those of **11**, indicating that they have very similar distribution of the carbonyl ligands.

The aliphatic region of the ¹H NMR spectrum of **9** contains a doublet at δ 4.24 (J=1.2 Hz) and three multiplets at δ 3.74, 3.47 and 3.17 in a relative intensity ratio of 1:1:1:2. The hydride region shows a doublet at $\delta - 14.48$ (J=1.6 Hz) and a doublet of doublets at $\delta - 14.61$ (J = 1.6 and 1.2 Hz) in a relative intensity of 1:1. The doublet at δ 4.24 is due to the methyne proton and it exhibits coupling to one of the hydrides which appears as a doublet of doublets at $\delta - 14.61$. Irradiation of the methyne proton results in a collapse of the hydride doublet of doublets at δ – 14.61 to a doublet. The hydride chemical shifts, their multiplicity and the long-range coupling between the methyne proton and one of the hydrides are almost identical with those reported for 11 (δ – 14.30 (d, J=1.7 Hz), -14.56 (dd, J=1.7 and 0.8 Hz)) whose structure was established by X-ray diffraction studies [19]. The analytical data and spectroscopic features of 9 are thus in agreement with the proposed structure.

In order to examine whether the double bond of the heterocyclic ligand in **8** would exhibit the ability to coordinate to the rare metal atom yielding a μ_3 -imidoyl type compound, the compound was treated with Me₃NO. Contrary to expectation, we observed a preferred reaction that involved a further C–H activation of the coordinated methylidyne ligand accompanied by a CO loss.



In conclusion, we have demonstrated herein an unusual C– H activation of the methyl substituent of 2-methyl-2-thiazoline at a triosmium centre to give $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH_2\overline{C=NCH_2CH_2S})]$ (8) which undergoes a further C–H activation to afford $[(\mu-H)_2Os_3(CO)_9(\mu-\eta^2-CH\overline{C=NCH_2CH_2S})]$ (9). Decarbonylation of 8 using Me₃NO also gives 9 instead of the expected μ_3 -imidoyl type product, indicating that C–H activation is more amenable than coordination of the double bond of the heterocycle to the rear metal atom.

3. Experimental

All reactions were carried out under a dry and oxygen-free atmosphere of N_2 by using standard Schlenk techniques. Reagent grade solvents were freshly distilled from the appropriate drying agents. ¹H NMR spectra were recorded on a Varian Unity Plus 400 MHz spectrometer. Infrared spectra were recorded on a FTIR 8101 spectrophotometer. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the known procedure [24].

3.1. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-methyl-2thiazoline

To a dichloromethane solution (40 cm³) of $[Os_3(CO)_{10}-(MeCN)_2]$ (0.188 g, 0.201 mmol) was added 2-methyl-2thiazoline (0.102 g, 1.0 mmol) and the reaction mixture was stirred at room temperature for 20 h. The solvent was removed in vacuo and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (7:3, v/v) gave one major band which afforded $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH_2C=NCH_2CH_2S)]$ (8) (0.105 g, 55%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at $-20^{\circ}C$. *Anal.* Found: C, 17.82; H, 0.89; N, 1.59. C₁₄H₇NO₁₀Os₃S requires: C, 17.66; H, 0.74; N, 1.47%. IR (ν (CO), hexane): 2103 m, 2061 vs, 2050 vs, 2022 vs, 2002 m, 1996 m, 1990 m, 1973 w cm⁻¹. ¹H NMR (CDCl₃): δ 1.81 (d, 1H, *J*=20.0 Hz), 2.40 (d, 1H, *J*=20.0 Hz), 3.24 (m, 1H), 3.37 (m, 1H), 3.89 (m, 1H), 4.18 (m, 1H), -14.24 (s, 1H).

3.2. Thermolysis of $[(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH_2\overline{C=NCH_2CH_2S})]$ (8)

A solution of **8** (0.070 g, 0.073 mmol) in heptane (20 cm³) was heated to reflux for 22 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (7:3,

v/v) developed three bands. The fast moving band gave $[Os_3(CO)_{12}]$ (0.008 g, 12%). The second band gave a too small amount (~0.002 g) for complete characterization. The third band gave $[(\mu-H)_2Os_3(CO)_9(\mu-\eta^2-CHC=NCH_2CH_2S)]$ (9) (0.030 g, 45%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at -20° C. *Anal.* Found: C, 17.10; H, 0.82; N, 1.62. C₁₃H₇NO₉Os₃ requires: C, 16.90; H, 0.76; N, 1.51%. IR (ν (CO), CH₂Cl₂): 2103 s, 2076 vs, 2049 vs, 2019 vs, 2002 s, 1993 m, 1976 m cm⁻¹. ¹H NMR (CDCl₃): δ 3.21 (m, 2H), 3.47 (m, 1H), 3.74 (m, 1H), 4.24 (d, 1H, J=1.2 Hz), -14.48 (d, 1H, J=1.6 Hz), -14.61 (dd, 1H, J=1.6, 1.2 Hz).

3.3. Reaction of 8 with Me_3NO

To a dichloromethane solution (20 cm^3) of **8** (0.070 g, 0.073 mmol) was added dropwise a CH₂Cl₂ solution (5 cm³) of Me₃NO (0.011 g, 0.146 mmol) over a period of 15 min. The reaction mixture was stirred at room temperature for 20 h. A similar work-up to that above followed by a similar chromatographic separation of the residue gave **9** (0.024 g, 35%).

3.4. X-ray crystallography

Crystal data for **8**: $C_{14}H_7NO_{10}Os_3S$, M=951.87, monoclinic, C2/c, a=28.526(6), b=7.758(2), c=17.506(4) Å, $\beta=90.08(3)^\circ$, U=3873(2) Å³, Z=8, $D_c=3.265$ g cm⁻³, μ (Mo K α) = 197.98 cm⁻¹, λ = 0.71073 Å, T=150 K, crystal size $0.22 \times 0.15 \times 0.12$ mm.

Intensity data were recorded on a FAST area detector diffractometer [25], the structure solved by direct methods (SHELXS-86) [26], and refined on F^2 by full-matrix leastsquares (SHELXL-96) [27] using all 2903 unique data and 262 parameters to final $wR_2 = 0.0645$ (on F^2 , all data) and $R_1 = 0.0286$ (on *F*, 2484 data with $F_o^2 > 2\sigma(F_o^2)$). The bridging hydride was located from a difference map but not refined.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk), CCDC ref. no. 139497.

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