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NEW TRIOSMIUM METAL CLUSTERS DERIVED FROM THE REACTIONS BETWEEN $[Os_3(CO)_{10}(NCMe)_2]$ AND AMIDES

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Summary

Triosmium clusters of the type $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)]$ (**1**; R = H, Me, Ph, Et or Pr) are formed in high yields form the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ (**2**) with amides. The nature of the products formed from thermolysis of **1** depend on the group, R.

Introduction

The synthetic utility of employing the bis-acetonitrile complex $[Os_3(CO)_{10}(NCMe)_2]$ (**2**) as precursor to new triosmium clusters of the type $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)]$ (**1**; R = H, Me, Ph, Et or Pr) using the appropriate amides may be attributed to the ease of displacement of the MeCN ligand (eq. 1)

$$[Os_3(CO)_{10}(NCMe)_2] + RCONH_2 \rightarrow [Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)] + 2MeCN \quad (1)$$

Complex **2** has also been shown to react smoothly with aldehydes [1] to form new cluster derivatives of the type $[Os_3(CO)_{10}(\mu\text{-}H)(COR)]$ (**3**; R = Me, Ph, CH_2Ph or C_6H_{13}).

The clusters **1** and **3** pose some very interesting structural problems. In particular, knowledge of the nature of the CO bonding mode is crucial in our understanding of the chemistry of the coordinated carbonyl group especially its catalytic hydrogenation by transition metal clusters. The nature of the bonding of the COR group in clusters **3** has been established [1] by a single crystal X-ray analysis of $[Os_3(CO)_{10}(\mu\text{-}H)(COCH_2Ph)]$ (**3**; R = CH_2Ph) in which the CO fragment was found to bond to the second atom in the osmium triangle via the lone pair of electrons on the oxygen. Strong support for this structural assignment was provided by the C–O bond length of 1.26(2) Å which is close to the expected double bond value. A preliminary report on the synthesis of clusters **1** and **3** via $[Os_3(CO)_{10}(NCMe)_2]$ has appeared [1].

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TABLE 1

IR AND ^{1}H NMR SPECTRA OF [$Os_3(CO)_{10}(\mu$-H)(NHCOR)] DERIVATIVES

R	IR ν(CO) (cm^{-1})[a]	^{1}H NMR (τ)[b]
H	2110mw, 2070s, 2059s, 2024s, 2013s, 2001m, 1988sh, 1985mw, 1979mw. 1597 (amide)	2.07 (C*H*,d) 4.41 (N*H*,br) 21.84 (OsH,s)
Me	2109mw, 2069s, 2057s, 2023s, 2009s, 1999m, 1986sh, 1983mw, 1977mw. 1576 (amide)	4.71 (N*H*) 8.06 (CH_3,s) 21.90 (OsH,s)
Ph	2110mw, 2070s, 2059s, 2023s, 2012s, 1999m, 1987sh, 1984mw, 1977mw. 1590 (amide)	2.58 (Ph,s) 3.94 (N*H*,br) 21.60 (OsH,s)
Et	2109mw, 2069s, 2058s, 2023s, 2011s, 1999m, 1987sh, 1984mw, 1977mw. 1570 (amide)	7.81 (CH_2,q) 9.03 (CH_3,t) 21.80 (OsH,s)
Pr	2108mw, 2068s, 2056s, 2022s, 2010s, 1998m, 1985sh, 1982mw, 1976mw. 1570 (amide)	7.80 (CH_2,m) 8.48 (CH_2,m) 9.15 (CH_3,t, *J* 7 Hz) 21.76 (OsH,s)

[a] In cyclohexane. [b] In CD_2Cl_2 at room temperature.

Results and discussion

The reaction of complex **2** with amides in refluxing cyclohexane affords the new triosmium derivatives [$Os_3(CO)_{10}(\mu$-H)(NHCOR)] (R = H, Me, Ph, Et or Pr) in yields ranging from 50–70%. These yellow microcrystalline products are stable in air, soluble in most organic solvents and exhibit a singlet resonance at τ ca. 22 (CD_2Cl_2) in their ^{1}H NMR spectra indicating the presence of a bridging hydride ligand. Their

TABLE 2

MASS SPECTRAL AND MICROANALYTICAL RESULTS FOR [$Os_3(CO)_{10}(\mu$-H)(NHCOR)] DERIVATIVES

R	m/e[a]	Microanalysis (Found (calcd.) (%))[b]		
		C	H	N
H	901	15.4	0.95	1.86
		(14.8)	(0.34)	(1.56)
Me	915	16.2	1.06	1.56
		(15.8)	(0.55)	(1.54)
Ph	977	21.1	0.88	1.34
		(21.0)	(0.73)	(1.44)
Et	929	17.0	0.80	1.57
		(16.9)	(0.76)	(1.52)
Pr	943	18.1	1.20	1.66
		(17.9)	(0.97)	(1.49)

[a] Based on ^{192}Os. [b] Determined in Cambridge.

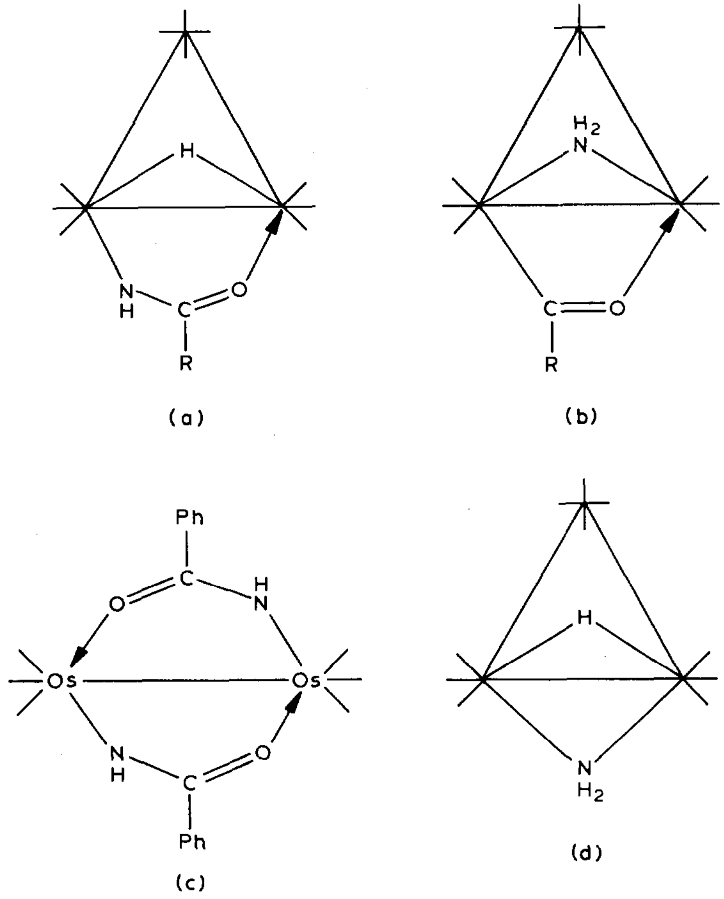

Fig. 1. Proposed structures for new triosmium derivatives (terminal CO ligands are excluded for clarity).

IR and ^{1}H NMR spectra are collected in Table 1 while their mass spectral and microanalytical results are given in Table 2. The decrease in ν(CO)(amide) by ca. 60–90 cm^{-1} (Table 1) compared to that in the free ligands is consistent with coordination of the CO group to the Os_3 triangle (Fig. 1a). These results clearly support the structure given in Fig. 1a for these new amido cluster derivatives, $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)]$ (**1**) and it is likely that the CO fragment is bonded to the second atom in the osmium triangle via the lone pair of electrons on the oxygen atom as already established [1] for the aldehydo analogues **3**.

Some minor products were isolated during the synthesis of clusters **1** and characterised from IR, ^{1}H NMR and mass spectral measurements as $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (**1**; R = H synthesis) and $[Os_3(CO)_{10}(NH_2)(COR)]$ (**4**) (**1**; R = Ph, Et or Pr synthesis). The cluster **1** ($R = CH_3$) was isolated in 75% yield with very little of the minor product **4**. The orange brown products **4** which were isolated in 10% yield for R = Ph, Et or Pr showed the same molecular ion as their precursors **1** but had no detectable metal hydride ligand in their ^{1}H NMR spectra. In addition, their IR spectra varied considerably from those of clusters **1** indicating rearrangement products of the type $[Os_3(CO)_{10}(NH_2)(COR)]$ as illustrated in Fig. 1b. A third minor product isolated in 5% yield from the synthesis of **1** (R = Ph) was characterised as $[Os_2(CO)_6(NHCOPh)_2]$ (Fig. 1c) on the basis of its IR and mass spectral measurements. The fall in ν(CO) (amide) band by ca. 60 to 1597 cm^{-1} compared to the free ligand indicates coordination of the carbonyl group to the metal as proposed in the dimeric structure shown in Fig. 1c. This product showed identical features as that of an authentic sample [2].

Thermolysis of **1** (R = H) in refluxing nonane (40 h) under a dinitrogen atmosphere gave a yellow product (ca. 50 %) with *m/e* 873 (^{192}Os) indicating loss of a CO fragment from the parent cluster. Spectroscopic and microanalytical measurements of this decarbonylated product suggest the molecular formulation $[Os_3(CO)_{10}(\mu\text{-}H)(NH_2)]$ (**5**) although the NH_2 signal was not immediately apparent in the ^{1}H NMR spectrum. The structure of **5** has been established [3] by a single crystal X-ray analysis and it clearly demonstrates that the CO fragment of the amido group in the clusters **1** is more labile than those attached to the metal triangle. Thus the bridging amido group is completely replaced by the amino group by some rearrangement process involving the loss of the CO ligand (Fig. 1d). Thermolysis of **1** (R = CH_3) in nonane (24 h) gave $Os_6(CO)_{18}$ as the only product in 75% yield while the clusters (**1**: R = Ph (45 h), Et or Pr (24 h)) gave $Os_6(CO)_{18}$ and $[Os_3(CO)_{10}(NH_2)(COR)]$ (**4**) in 30 and 10% yields, respectively. An additional product from the R = Ph thermolysis was tentatively assigned the structure $[H_4Os_4(CO)_{11}(PhC)_2]$ on the basis of its mass and IR spectra (Found: *m/e* 1258 (^{192}Os); IR ν(CO) in cyclohexane: 2104mw, 2074s, 2044s, 2018m, 2003sh, 1998mw, 1971w cm^{-1}.

Experimental

Synthesis of $Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)$ (1) derivatives

(i) *R = H*: A solution of the complex $[Os_3(CO)_{10}(NCMe)_2]$ (**2**) (0.1 g) and freshly distilled methanamide (0.6 cm^3) in cyclohexane (30 cm^3) was refluxed for 2.5 h under a dinitrogen atmosphere. The solvent was removed at reduced pressure and the residue dissolved in minimum volume of CH_2Cl_2 followed by chromatography (TLC) using CH_2Cl_2/hexane (20/80) as eluant. The slow moving band was extracted with CH_2Cl_2 to give an oily yellow product. However, upon dissolution in cyclohexane and removal of solvent, $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOH)]$ was obtained as a microcrystalline yellow solid. The crystals of this product were deposited from hexane in ca. 50% yield. The much faster moving purple band was identified as $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ on the basis of its IR, ^{1}H NMR and mass spectral measurements.

(ii) *R = CH_3*: An analogous preparation to that above using complex **2** (0.1 g) and ethanamide (0.02 g) in refluxing cyclohexane (4 h) afforded $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOCH_3)]$ as greenish-yellow crystals (75% yield) after repeated elution with CH_2Cl_2/hexane (20/80) and crystallisation from pentane.

(iii) *R = Ph*: An analogous preparation as in (i) above using 0.1 g of complex **2** and 0.04 g of benzamide in refluxing cyclohexane (4 h) gave $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOPh)]$ as yellow crystals (70% yield) after elution with 20% CH_2Cl_2/hexane and crystallisation from hexane. The much slower moving product was repeatedly eluted with 10% CH_2Cl_2/hexane and the usual work-up afforded orange-brown $[Os_3(CO)_{10}(NH_2)(COPh)]$ (**4**: R = Ph) and yellow $[Os_2(CO)_6(NHCOPh_2)]$ (Fig. 1c). Both crystalline solids were characterised on the basis of their IR, ^{1}H NMR and mass-spectral measurements. Thus complex **4** (R = Ph) showed 977 mass units in its mass spectrum; ^{1}H NMR (CD_2Cl_2): τ 2.32 (Ph,m), 5.73 (NH_2br); IR: ν(CO) in cyclohexane: 2088m, 2057s, 2034s, 2003s, 1986s, 1964m cm^{-1}.

(iv) *R = CH_2CH_3*: Similar preparative route as in (i) above using 0.1 g of complex **2** and 0.024 g of propionamide in refluxing cyclohexane (15 cm^3) afforded $[Os_3(CO)_{10}(\mu\text{-H})(NHCOEt)]$ after 4 h. Crystallisation from pentane gave the pure yellow complex in 70% yield.

(v) *R = $CH_2CH_2CH_3$*: An analogous preparation as in (i) using 0.1 g of complex **2** and 0.028 g of n-butyramide in refluxing cyclohexane (15 cm^3) gave $[Os_3(CO)_{10}(\mu\text{-H})(NHCOPr)]$ after 4 h. Yellow crystals of this product were obtained in 70% yield from hexane. The slow moving orange-brown products from (iv) and (v) (10% yield) were characterised as the corresponding $[Os_3(CO)_{10}(NH_2)(COR)]$ (R = Et or Pr) derivatives on the basis of their IR, ^{1}H NMR and mass spectra.

Thermolysis of $[Os_3(CO)_{10}(\mu\text{-H})(NHCOH)]$ (**1**: R = H) in refluxing nonane for 40 h under a dinitrogen atmosphere gave the yellow product $[Os_3(CO)_{10}(\mu\text{-H})(NH_2)]$ (Fig. 1d) in ca. 50% yield: (Found: C, 14.4; H, 0.48; N, 1.88. $C_{10}H_3Os_3O_{10}N$ calcd.: C, 13.8; H, 0.35; N, 1.61%] ^{1}H NMR (CD_2Cl_2): τ 25.4 (Os–H). ν(CO) in cyclohexane: 2105w, 2067s, 2052m, 2022s, 2005m, 1993m, 1981w cm^{-1}; *m/e* based on ^{192}Os: 873.

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References

1 B.F.G. Johnson, J. Lewis, T.I. Odiaka and P.R. Raithby, J. Organomet. Chem. 216 (1981) C56.
2 A.L. Mann, Ph.D. Thesis, University of Cambridge, 1981, and personal communication.
3 T.I. Odiaka, P.R. Raithby, B.F.G. Johnson and J. Lewis, unpublished work.