Journal of Organometallic Chemistry, 420 (1991) 289–292
Elsevier Sequoia S.A., Lausanne
JOM 22040

Preferential attack of the terminal hydrogen in $(\mu\text{-H})Os_3(CO)_{11}H$ by the $(CF_3)_2NO$ radical and X-ray structure of $\{(\mu\text{-H})Os_3(CO)_{11}\}[ON(CF_3)_2]$

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(Received April 5th, 1991)

Abstract

Bis(trifluoromethyl)nitroxyl radical, $(CF_3)_2NO$, has been shown to preferentially attack the terminal hydrogen from the $(\mu\text{-H})Os_3(CO)_{11}H$ cluster to give the derivative $(\mu\text{-H})Os_3(CO)_{11}[(CF_3)_2NO)]$ **1** together with bis(trifluoromethyl)hydroxylamine in quantitative yields. A radical mechanism is proposed. The product **1** represents the first example of a stable metal carbonyl cluster containing the perfluoro $(CF_3)_2NO$ radical, a relatively strong oxidant. The X-ray structure and IR spectra are reported.

Although bis(trifluoromethyl)nitroxyl radical reacts directly with several main group elements to form derivatives [1] containing the $(CF_3)_2NO$ moiety, only a few metal complexes containing the bis(trifluoromethyl)nitroxyl radical have been reported [2–6]. These are dominated by transition metal derivatives co-ordinatively unsaturated containing substituted phosphines and carbon monoxide. Most mono- and dinuclear carbonyls undergo oxidation reactions with $(CF_3)_2NO$ to give metal nitroxides and carbon monoxide. The only transition metal carbonyl compound containing the $(CF_3)_2NO$ moiety was that derived from $MnH(CO)_5$ [4]. We now report a novel reaction between the $(CF_3)_2NO$ radical and a triosmium carbonyl hydrides and the X-ray structure of the metal cluster derivative **1**.

The reactions of $(CF_3)_2NO$ radical and $(\mu\text{-H})Os_3(CO)_{11}H$ in a 2:1 ratio proceeded at room temperature for 10 min to give a complex which can be formulated as $(\mu\text{-H})Os_3(CO)_{11}[(CF_3)_2NO]$ [7*] together with bis(trifluoromethyl)hydroxylamine in quantitative yields. These reactions indicate for the first time

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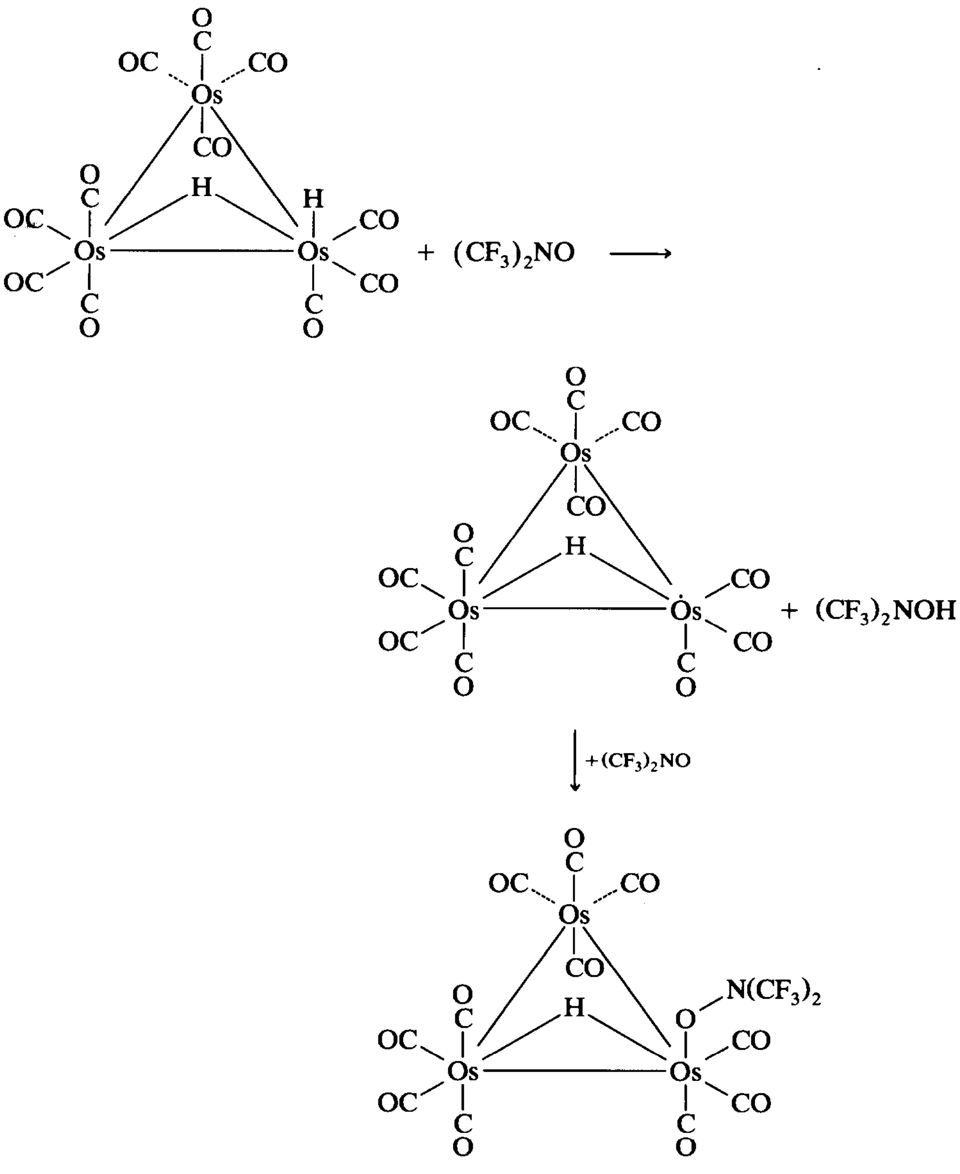
* Reference number with asterisk indicates a note in the list of references.

that the $(CF_3)_2NO$ radical preferentially abstracts the terminal hydrogen over the bridging hydrogen followed by radical attack of the osmium cluster radical, as shown by the following equations:



(1)

However, the reactions of $(CF_3)_2NO$ radical and $[PPN][(\mu\text{-H})Os_3(CO)_{11}]$ in a 2:1 ratio afforded **1** in about 3% yield. The same product **1** was obtained in poor yield (~ 3%) when the radical was reacted with $H_2Os_3(CO)_{10}$, also in 2:1 ratio. These results provide clear evidence of the strong preference of the $(CF_3)_2NO$ for the terminal hydrogen.

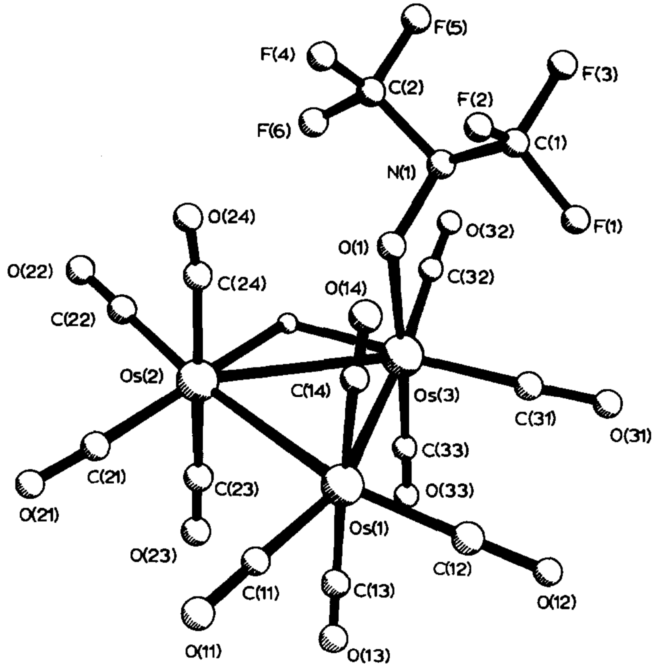


Fig. 1. The crystal and molecular structure of $[Os_3(CO)_{11}ON(CF_3)_2]$ showing the numbering scheme. Selected bond lengths (Å) and bond angles (°): Os(1)–Os(2) 2.901(1), Os(1)–Os(3) 2.845(1), Os(2)–Os(3) 2.999(1), Os(3)–O(1) 2.107(8), O(1)–N(1) 1.419(13), N(1)–C(1) 1.435(16), N(1)–C(2) 1.444(24); O(1)–Os(3)–Os(1) 86.1(2); O(1)–Os(3)–Os(2) 83.6(2).

Unlike the reactions between mononuclear and dinuclear binary metal carbonyls and the $(CF_3)_2NO$ radical which are oxidised to afford only metallic nitroxides, the reactions with $(\mu\text{-H})Os_3(CO)_{11}H$ afford a stable complex **1** without any sign of oxidation. These reactions of the nitroxyl radical with the triosmium carbonyl cluster open up a new synthetic route leading not only to the osmium carbonyl cluster derivatives but also other metal carbonyl cluster derivatives containing $(CF_3)_2NO$ radical. Thus, it appears that there is a possibility of incorporating not only perfluoro species which have strong oxidising properties but also fluorine atoms into the metal cluster.

The X-ray structural determination of **1** shows that the $(CF_3)_2NO$ moiety bonds to an osmium atom [Os(3)] at the axial terminal position (Fig. 1). The structure of the complex **1** is retained upon substitution of the terminal hydrogen by $(CF_3)_2NO$ radical. This is consistent with the fact that $(CF_3)_2NO$ is not only a hydrogen abstractor but also a powerful radical scavenger. The structure is isomorphous with $H_2Os_3(CO)_{11}$ **2** and $Os_3(CO)_{12}$ **3** [8] and nearly isostructural with **2**. Although the differences in geometry between **1** and **3** could not be attributed entirely to the presence or absence of a bridging hydride ligand as between **2** and **3**, the effect of the $(CF_3)_2NO$ moiety is minimal. Thus the bridged Os–Os distance (2.999 Å) in **1** is only 0.01 Å more than that in **2**. The average Os–Os distances in **1** and **2** are very nearly the same, being 2.918 Å and 2.915 Å respectively.

The bulkier $(CF_3)_2NO$ has also brought on effects on the axial carbonyls. Thus the average of Os–Os–CO (axial) (88.4°) and OC–Os–OC (178.5°) are similar for

1 and **3** in comparison to **2**. This would be expected on the basis of the relative sizes of $(CF_3)_2NO$, CO and H. More significantly, the Os(3)–O(1) bond tilts more towards Os(2)–C(24). The bond distance of Os(3)–O(1) is long, presumably due to the electron-withdrawing nature of the CF_3 group.

References and notes

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7 Elementary analysis (calculated values in parentheses) $(\mu\text{-H})Os_3(CO)_{11}[(CF_3)_2NO]$ (**1**) C, 15.15 (14.89); F, 11.30 (10.88). The infrared spectrum in CH_2Cl_2 gave the following peaks: ν(CO): 2145m, 2099s, 2077vs, 2070vs, 2057s, 2037s, 2017s, 1990m; $\nu(CF_3)$: 1217m, 1184m; $\delta(CF_3)$ 703w; ν(NO): 1018w.

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