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PRELIMINARY NOTE

The Nitrene $\text{OsF}_5(\text{NCl})$

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SUMMARY

Reaction between OsF_6 and $(\text{CH}_3)_3\text{Si}(\text{NCO})$, followed by oxidation of the product with ClF_3 , yields a mixture which contains $\text{OsF}_5(\text{NCl})$. The nitrene is purified by recrystallisation from anhydrous HF.

Recently the nitride fluoride ReNF_4 and the nitrene derivatives $\text{ReF}_5(\text{NF})$ and $\text{ReF}_5(\text{NCl})$ were prepared and characterised in this laboratory [1]. Here we report the synthesis of a novel nitrene fluoride of osmium, $\text{OsF}_5(\text{NCl})$.

Osmium hexafluoride reacts with $(\text{CH}_3)_3\text{Si}(\text{NCO})$ in Genetron 113 solution to give a dark oily product which solidifies on standing to a brown solid which is believed on i.r. evidence to contain isocyanato-derivatives such as $\text{OsF}_5(\text{NCO})$ or $\text{OsF}_4(\text{NCO})$. Treatment with successive small quantities of gaseous ClF_3 ($\sim 100\text{mm}$) (CAUTION) leads to a brown solid which dissolves in excess of liquid ClF_3 to give a red solution from which a red-brown solid is isolated after evaporation of the solvent. After warming to 85° under a dynamic vacuum a small proportion of a yellow sublimate appears; the remaining puce coloured solid has a prominent i.r. peak at 1215 cm^{-1} , and

shows a mass spectral pattern which includes the ions OsF_4N^+ and OsF_3N^+ as well as Cl_2^+ . The purple solid dissolves in anhydrous HF and evaporation of the solution yields white, orange and red crystals. The mass spectrum of the red crystals includes OsO_3N^+ and OsO_2N^+ peaks, and, interestingly a strong peak at 69, which may be assigned to CF_3^+ ; the IR spectrum shows frequencies at 1301(m), 1290(w) (CF) 1210(m), (Os-N), and others associated with Os-O and Os-F. This product has not yet been characterised. The white crystals have been identified as the new 'nitrene' $\text{OsF}_5(\text{NCl})$, corresponding to the known $\text{ReF}_5(\text{NCl})$ [1].

$\text{OsF}_5(\text{NCl})$ (mp. 170-4°) is a white, air sensitive solid which gives a mass spectrum showing the parent ion $\text{OsF}_5(\text{NCl})^+$, the ions $\text{OsF}_4(\text{NCl})^+$, $\text{OsF}_3(\text{NCl})^+$, OsF_nN ($n = 4, 3, 2$), and OsF_n ($n = 4$ to 0). In addition strong peaks appear characteristic of Cl_2 , as well as OsO_n ($n = 4$ to 0) from hydrolysis in the mass spectrometer. The IR spectrum shows frequencies at 1215 cm^{-1} (m) (Os-N), and at 660(vs) (Os-F), 625 (vs,br) (Os-F), 495(w) (?N-Cl) and 425(w). $\text{OsF}_5(\text{NCl})$ is much less volatile than $\text{ReF}_5(\text{NCl})$, but the most striking feature is the absence of a strong colour, in contrast to the purple Re compound. The compound appears to be stable to at least the melting point.

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- 1 J. Fawcett, R. D. Peacock and D. R. Russell, J. Chem. Soc. (Chem. Commun.), (1982) 958 .