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Preliminary communication

SYNTHESIS AND REACTIVITY OF TRIOSMIUM CLUSTERS CONTAINING A 2-SUBSTITUTED PYRIDINE MOIETY

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Summary

2-Substituted pyridines react with $[Os_3(CO)_{10}(NCMe)_2]$ to form clusters in which the ligand is bound to the osmium cluster either by ortho-metallation of the pyridine ring, via the substituent group only or, via both the pyridine nitrogen and the substituent group; the thermal stability of each category of cluster is discussed.

The observation that 2(1*H*)-pyridone could be coordinated to a triosmium system [1] led us to investigate the synthesis and reactivity of triosmium clusters containing 2-substituted pyridine ligands. A series of clusters were prepared from the appropriate pyridines and $[Os_3(CO)_{10}(NCMe)_2]$* (Scheme 1).

In three cases cited the 2-substituent of the pyridine did not participate in coordination (Fig. 1)**. The 2-methylpyridine derivative (III) in heptane was unchanged after 3 h at 180°C under either an inert atmosphere (argon) or under CO (40 atm)*** reflecting the stability of orthometallated *N*-heterocycles on triosmium; such stability has also been observed for similar triosmium clusters containing pyrrazole, imidazole, benzimidazole and benzoxazole ligands [3].

In contrast to the above results pyridine-2-carboxaldehyde (X = CHO) metal-

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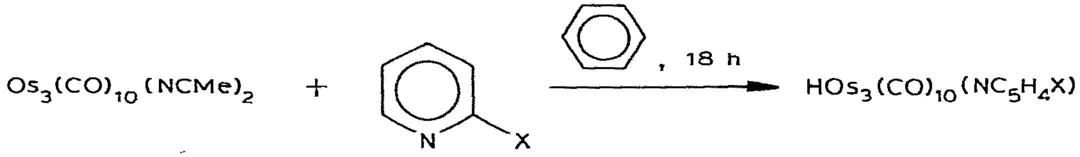
*1.1 Equivalents of the pyridine in 1 cm^3 of benzene for every 1 mg of $Os_3(CO)_{10}(NCMe)_2$. In each case the product was isolated by TLC and recrystallized from $CH_2Cl_2/n\text{-}C_6H_{14}$ mixtures.

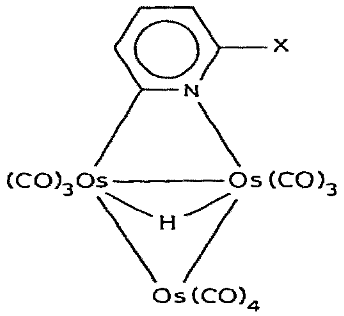
**Satisfactory C, H, and N analyses and appropriate molecular ions were found for all compounds reported in this paper. The carbonyl IR spectra of clusters I—III compare closely with that reported for $HOs_3(CO)_{10}(NC_5H_4)$ e.g., X = Cl (hexane solution throughout): 2105 (w), 2065 (st), 2053 (st), 2024 (st), 2008 (st), 1996 (md), 1992 (md), 1976 (w) cm^{-1} and the ^1H NMR of these complexes were similar e.g., X = Cl (20°C, CD_2Cl_2 at 80 MHz in δ (ppm) throughout): 7.38—6.86 (m, 3 H) −14.49 (s, 1 H).

***High pressure infrared apparatus as described previously [2].

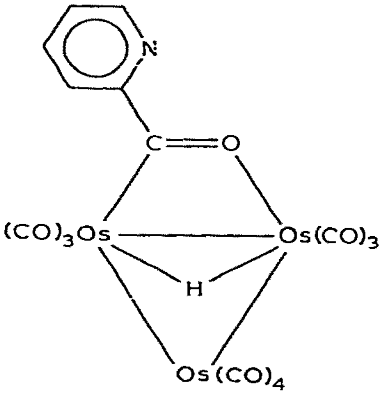


SCHEME 1. Reaction of 2-substituted pyridines with [$Os_3(CO)_{10}(NCMe)_2$].

lated on the aldehyde carbon without involving the pyridine nitrogen atom in coordination to the osmium cluster (IV)*; this compound is analogous to the clusters [$HOs_3(CO)_{10}(COR)$] (R = alkyl, aryl) that have previously been reported [1,4].



(I, X = Cl; 66% yield; at 45 °C.
II, X = CN; 43% yield; at 45 °C.
III, X = Me; 22% yield; at 20 °C)



(IV, 45% yield; at 40 °C)

Fig. 1. *Ortho*-metallated pyridines (I—III) and a pyridine bonded via the aldehydic CO (IV).

At 90°C in heptane after 1 h cluster IV was observed to eliminate the "aldehydic" CO to form the known [5] ortho-metallated system [$HOs_3(CO)_{10}$-(NC_5H_4)] in high yield. Similar decarbonylation of an acyl ligand has been reported [4] for the cluster [$HOs_3(CO)_{10}(COPh)$] which, on heating, loses both the aldehydic CO and a carbonyl ligand to form the "benzyne" cluster [$H_2Os_3(CO)_9(C_6H_4)$].

2-Aminopyridine and 2(1*H*)-pyridinethione (pyridine-2-thiol) were found to bond to triosmium decarbonyl in the same way as the 2(1*H*)-pyridone in cluster V.

An alternative structure (A) is also compatible with the spectral data** but seems less probable since the carbonyl IR pattern for compounds V—VII is unlike that found for clusters in which the Y function bridges an Os—Os bond e.g. [$HOs_3(CO)_{10}(\mu^2\text{-SPh})$] [6]. An X-ray crystallographic study of compound VI is in progress.

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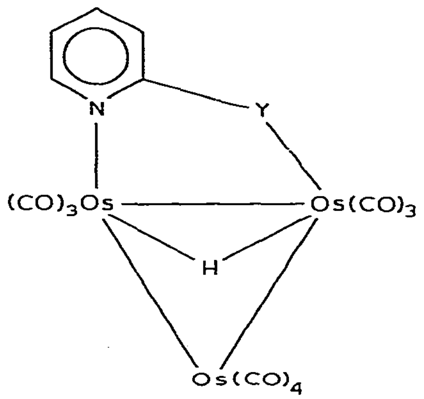
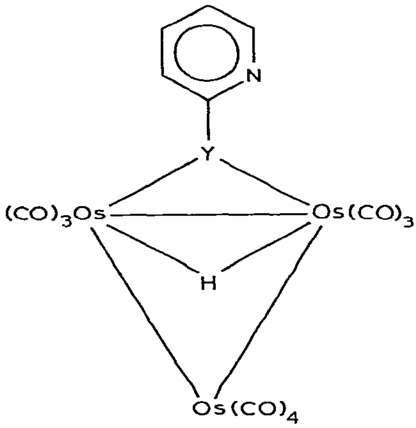
*IR: 2107 (w), 2067 (st), 2055 (st), 2026 (st), 2010 (st), 1997 (st), 1989 (w), 1978 (w), 1591 (w) cm^{-1}. ^{1}H NMR: 8.93 (d, J = 3 Hz, 1H), 8.04—7.27 (m, 4H), −12.48 (s, 1H).

**e.g. Y = S (VI) IR: 2108 (w), 2068 (st), 2058 (md), 2021 (st), 2014 (md), 2000 (md), 1983 (w) cm^{-1}. ^{1}H NMR: 8.54 (d, J = 3 Hz, 1 H), 7.83—7.46 (m, 2 H), 7.23 (d, J = 3 Hz, 1 H), −17.09 (s, 1 H).



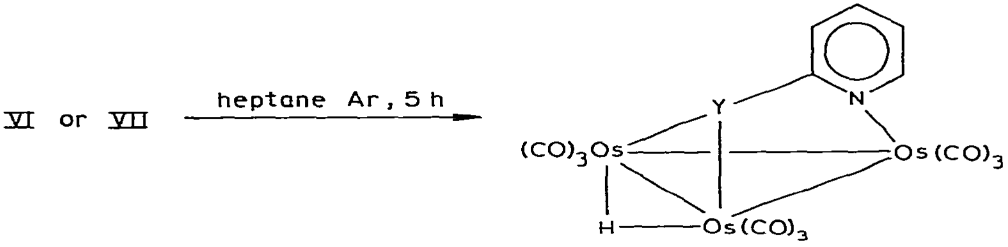
(V, Y = O; 36% yield; at 20°C.
VI, Y = S; 62% yield; at 20°C.
VII, Y = NH; 35% yield; at 20°C)



(A)

Fig. 2. Pyridines coordinated via both the ring nitrogen and the 2-functionality.

The 2(1*H*)-pyridone cluster was stable in heptane under argon to 200°C but the thiol (VI) and amine (VII) analogues were decarbonylated at lower teperatures (Scheme 2). The thermal stability of clusters V—VII therefore seems to be inversely related to the capacity of the function Y to bridge an Os—Os bond; similar trends have been observed in other systems [7]. The ^{1}H NMR data* for cluster VIII are also consistent with an alternative structure (Fig. 3) but this seems less plausible on the basis of differences observed between the carbonyl IR patterns of VIII and that for known clusters with a capping atom e.g.



(Y = O; not formed at 200°C.
VIII, Y = S; 67% yield; at 160°C.
IX, Y = NH; 90% yield; at 68°C)

SCHEME 2. Synthesis of [HOs$_3$(CO)$_9$(SC$_5$H$_2$N)] and [HOs$_3$(CO)$_9$(NHC$_5$H$_2$N)].

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*e.g. Y = S (VIII): IR: 2086 (md), 2056 (st), 2036 (st), 2002 (st), 1990 (s), 1966 (w), 1962 (w) cm^{-1}. ^{1}H NMR: 9.09 (d, J = 6 Hz, 1 H), 7.65—7.04 (m, 3 H), −15.10 (s, 1 H).

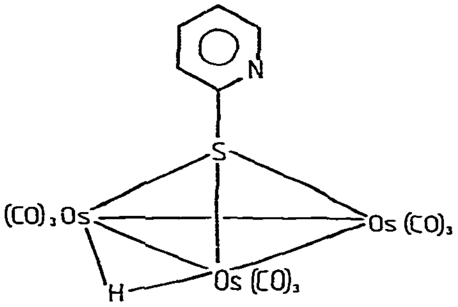

Fig. 3. An alternative structure for $[HOs_3(CO)_9(SC_5H_4N)]$.

$[H_2Os_3(CO)_9(\mu^3\text{-NPh})]$ [8]. An X-ray crystallographic study of the 2(1*H*)-pyridinethione cluster (VIII) is in progress.

Thus, 2-substituted pyridines can bind to osmium clusters via the pyridine nitrogen and/or the substituent group thereby facilitating the introduction of various organic fragments onto a triosmium cluster face.

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