Dodecacarbonyltriosmium Anchored on Poly(4-vinylpyridine) †

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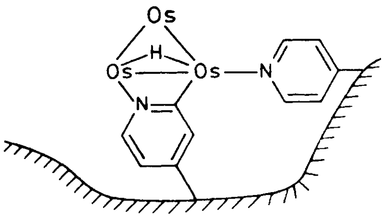
Dodecacarbonyltriosmiun reacts with polystyrene cross-linked poly(4-vinylpyridine) to give polymer-anchored cluster derivatives. The solution ^1H n.m.r. spectrum of the polymer shows that the major species corresponds to one of the isomers of $[Os_3H(CO)_9(NC_5H_4)(py)]$ (py = pyridine).

Carbonyl clusters anchored on organic or inorganic polymers are of interest due to their potential catalytic activity.[1] The characterisation of supported clusters by i.r. spectroscopy poses severe problems since in the majority of cases the spectra contain broad ill defined carbonyl absorptions typical of solid-state spectra. Here we report the synthesis of poly(4-vinylpyridine) (pvpy) supported species derived from $[Os_3(CO)_{12}]$, which can be unambiguously characterised by solution ^1H n.m.r. spectroscopy. The supported material has also been tested as a catalyst for the water-gas shift reaction.

Heating $[Os_3(CO)_{12}]$ with pvpy in *NN*-dimethylformamide (dmf) at 110 °C for 3 h gives the cluster-incorporated polymer (1), showing two strong and broad i.r. bands ‡ centred around 2 040 and 1 940 cm^{-1}. Variation in reaction time or temperature does not cause any observable change in the i.r. spectrum of the resultant material. Reaction of $[Os_3(CO)_{12}]$ with pyridine, studied under a variety of conditions by Yin and Deeming,[2] is known to yield a number of cluster and dinuclear complexes. Since most of these complexes have carbonyl bands around 2 040 and 1 940 cm^{-1}, reliable formulation of (1) on the basis of i.r. data is difficult.

The solubility of pvpy allows the n.m.r. spectrum of (1) to be recorded in $CDCl_3$. Three Os–H signals at δ -10.5, -12.0, and -13.75 were observed where the first one was at least four times as intense as the other two. On the basis of the reported [2] n.m.r. data of pyridine-substituted derivatives of $[Os_3(CO)_{12}]$, three compounds, the two isomers (A) and (B) of $[Os_3H(CO)_9(NC_5H_4)(py)]$ (2) and $[Os_3H_2(CO)_8(NC_5H_4)_2]$ (3), appear to form on the polymer matrix. However, the relative intensities suggest that about 70% of the anchored derivatives in (1) correspond to isomer (B) of (2). It is known that isomerism results from the different substitution positions taken up by the pyridine molecules. The diagram above indicates that coordination by a *second* pyridine molecule must involve flexibility of the polymer chain. For clarity, the CO groups are not shown. It is important to note that $[Os_3H(CO)_{10}(NC_5H_4)]$ (4) is not present to an observable extent in (1), though this is the first complex to be formed in a reaction of $[Os_3(CO)_{12}]$ with pyridine. Chelation by the flexible polymer chain presumably imparts extra stability to (1) which explains why, unlike isomers (A) and (B) of (2), (1) does not react with CO even under high pressures ($\leqslant 600$ lbf in^{-2}) to generate polymer-anchored (4). Similarly, unlike the free isomer (B) of (2), (1) does not undergo decarbonylation to generate (3).



(1)

 = pvpy

The cluster $[Os_3(CO)_{12}]$, as well as $[Os_3(CO)_{12}]$ anchored on polystyrene or polystyrene functionalised with vinyl groups, have been used previously as catalysts in the water-gas shift reaction.[3,4] Although (1), when tested as a water-gas shift catalyst shows reasonably high turnover numbers (~45 d^{-1}), loss of osmium from the polymer is apparent from direct estimations of the metal before and after a catalytic run.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 377 grating spectrophotometer. N.m.r. spectra were recorded on a Nicolet 360-MHz instrument. Gas chromatographic determination of evolved hydrogen in the water-gas shift reaction was carried out with a Pye-Unicam 204 instrument on a Poropak Q column. Osmium estimation was carried out by atomic absorption spectrophotometry using an IL 751 instrument. $[Os_3(CO)_{12}]$ and pvpy with 10% styrene were purchased from Strem Chemicals (U.S.A.) and Aldrich Chemical Company (U.K.) respectively.

Synthesis of (1).—Poly(4-vinylpyridine) (1.0 g) was heated with $[Os_3(CO)_{12}]$ (0.2 g) in dmf (50 cm^3) at 110 °C under CO for 3 h. The solution was cooled and (1) was precipitated by addition of diethyl ether; the product was purified by reprecipitation from dichloromethane–hexane followed by Soxhlet extraction with ether overnight.

Catalytic Experiments.—Compound (1) (0.1 g) was heated with bis(2-methoxyethyl) ether (50 cm^3) and water (2.5 cm^3) under CO at 110 °C. The evolved hydrogen was monitored

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† *Non-S.I. unit employed*: lbf in^{-2} = 6.89 × 10^3 Pa.

‡ The spectrum was recorded in KBr; the limited solubility of the polymer prevented observation of clearly defined carbonyl absorptions.

after 96 and 120 h. Osmium estimation of (1) before and after (120 h) this experiment gave values of 1.3 and 0.6% respectively.

Attempted Carbonylation and Decarbonylation of (1).—These experiments were usually carried out in dmf solutions. Carbonylation was attempted in a Parr pressure reactor at 600 lbf in^{-2} and room temperature. Decarbonylation was attempted by heating the dmf solution at 140 °C under nitrogen.

References

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