Chiral Co-ordination of Bridging Formamido-ligands in Clusters of Type $[HOs_3(CO)_{10}(\mu\text{-}RNHCO)]$

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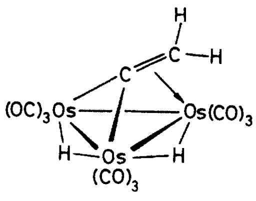
Summary Enantiomers of $[HOs_3(CO)_{10}(\mu\text{-}PhCH_2NHCO)]$ interconvert slowly on an n.m.r. time-scale and diastereomers of $[HOs_3(CO)_{10}(\mu\text{-}PhCHMeNHCO)]$ have been separated by t.l.c. and characterised by their ^1H n.m.r. and c.d. spectra.

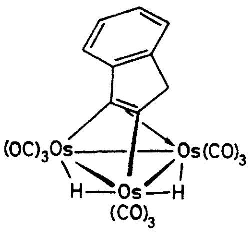
Clusters may be chiral when different metal atoms form the skeleton, as in $[FeCoMoS(C_5H_5)(CO)_8]$ which has recently been resolved.[1] However, many clusters are chiral because of the geometry of attachment of ligands which are themselves achiral, but in many cases fluxionality prevents resolution. For example, the chiral cluster $[H_2Os_3(CO)_9(C{:}CH_2)]$ (**1**) has a time-averaged plane of symmetry resulting from a rapid hydride migration.[2] Hydride migration cannot interconvert the enantiomers of $[H_2Os_3(CO)_9(\mu^3\text{-indene})]$ (**2**), but rapid rotation and flipping of the μ^3-ligand relative to the metal triangle leads to n.m.r. coalescences and time-averaged planes of symmetry through the organic ligand and the cluster as a whole.[3] Clearly, before attempting resolution such fluxionality must be absent.

The cluster $[HOs_3(CO)_{10}(Me_2CHCO)]$ (**3**) gives two sharp Me doublets in the ^1H n.m.r. spectrum up to 120 °C[4] and a rough extrapolation from a rate of enantiomerisation of $<1\ s^{-1}$ at this temperature suggests that resolution of such clusters at room temperature should be feasible. The related compound $[HOs_3(CO)_{10}(\mu\text{-}PhCH_2NHCO)]$ (**4**) is similarly non-dynamic.[5]

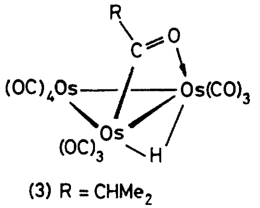
(+)-1-Phenylethylamine reacts with $[Os_3(CO)_{12}]$ in refluxing octane, as does $PhCH_2NH_2$,[5] or at room temperature



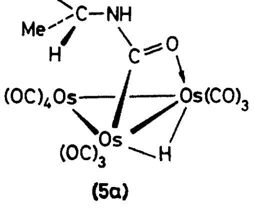
(1)



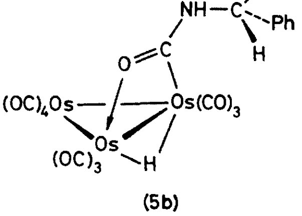
(2)



(3) R = $CHMe_2$
(4) R = $NHCH_2Ph$



(5a)



(5b)

if the neat amine is used.[6] The major product in each case is $[HOs_3(CO)_{10}(PhCHMeNHCO)]$ (**5**) which exists as a mixture of two diastereomers (**5a**) and (**5b**). Exchange is slow enough for each to give separate ^1H n.m.r. signals ($CDCl_3$; 35 °C) at δ 1·43(d) and 1·40(d) (Me) and −14·38(s) and −14·48(s) (hydride). The diastereomers are easily and completely separated into two yellow bands on SiO_2 (preparative t.l.c.; eluant, pentane), the separation being confirmed by their different ^1H n.m.r., but identical $\nu(CO)$ i.r. spectra. There was no detectable interconversion of the isomers even after 20 min at 100 °C in toluene. The c.d. spectra of (**5a**) and (**5b**) in the range 280—500 nm (Figure) are approximate mirror images and since 1-phenylethylamine does not absorb above 280 nm, essentially the whole effect is due to cluster-based asymmetry, *i.e.* of the Os_3CO group of atoms. The pair of diastereomers enantiomeric with (**5a**) and (**5b**) was synthesised similarly from the (−)-amine and likewise separated. We have not established the absolute stereochemistries of the Os_3CO groups, but an *X*-ray structure determination of one of the diastereomers is planned.

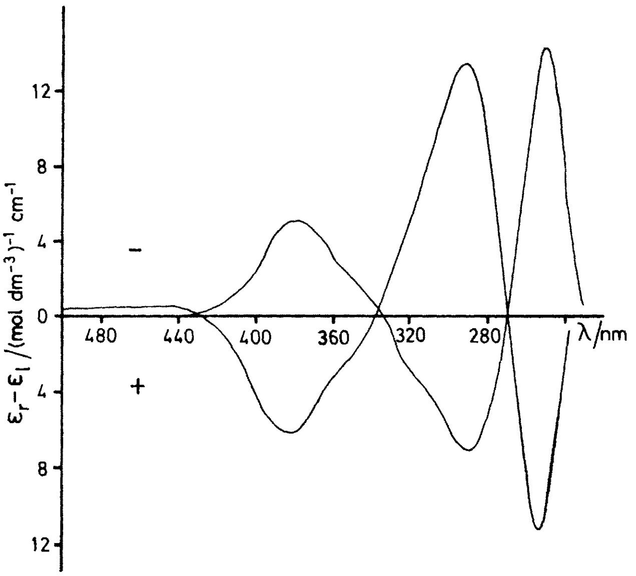


FIGURE. C.D. spectra for diastereomers (**5a**) and (**5b**).

In the reaction of the (+)-amine with $[Os_3(CO)_{12}]$ a significant excess of one diastereomer is apparent from a weak c.d. spectrum for the unseparated mixture of (**5**) and from ^1H n.m.r. intensities. The ratio of isomers for the high temperature reaction is 35 : 65. Attempts to separate the enantiomers of (**4**) are in progress. This compound, prepared by the reaction of a pure diastereomer of (**5**) with neat $PhCH_2NH_2$ at 120—140 °C, did not give a detectable c.d. spectrum; the amine exchange had occurred with racemisation.

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