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Slow epimerization of stereochemically rigid diastereomers of the equatorially substituted cluster $[Os_3H_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$

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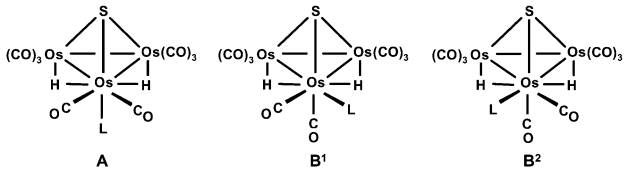
Received (in Cambridge, UK) 12th April 2002, Accepted 12th August 2002
First published as an Advance Article on the web 5th September 2002

Turnstile rotation is suppressed in the equatorially substituted cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$ which was separated by HPLC into two diastereomers which do not interconvert at room temperature and epimerize only slowly at 90 °C.

Two features of the fluxionality of metal carbonyl clusters are turnstile rotation of $M(CO)_3$ and $M(CO)_2L$ sub-units and the ability of hydride ligands to hop between metal–metal edges. Both can be rapid enough to give NMR coalescences. The dynamics of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ **1**[1] involve rapid hydride motion between osmium–osmium edges to give time-averaged C_{3v} symmetry.[2] In this case turnstile rotation of the $Os(CO)_3$ groups occurs much more slowly.

We have now studied the substitution of **1** by amines and phosphines and have observed that the mono-substituted products $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(L)]$ exist as the isomers **A**, **B¹** and **B²** depending upon which ligand L is used. For tertiary



phosphines all three isomers are formed in equilibrium, but only isomers **B¹** and **B²** have been detected for amines. With simple achiral monodentate ligands, isomers **B¹** and **B²** are enantiomers.

N-donor ligands bind exclusively in equatorial sites, whether the ligand is bulky or not.† Thus $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(L)]$ shows just two hydride ^{1}H NMR signals ($CDCl_3$ solutions; signals sometimes resolved as narrow doublets) at δ −19.70 and −24.73 (MeCN),[3] δ −18.85 and −25.57 (NMe_3),[3] δ −19.19 and −25.52 (NEt_3), δ −19.43 and −24.38 ($NH_2{}^iPr$), δ −9.31 and −24.88 ($NHEt_2$), δ −19.29 and −24.39 (NH_2CH_2Ph). There is no evidence for the axial isomer **A** in any case, even with the most bulky amines such as NEt_3, and the rate of interconversion of the enantiomers **B¹** with **B²** is too slow to result in NMR coalescence. The NH_2CHMe_2, $NHEt_2$, NEt_3 and NH_2CH_2Ph ligands in these clusters all show diastereotopic groups as appropriate for co-ordination of the amine to a stereochemically rigid chiral cluster. For example, the $NH_2{}^iPr$ ligand shows signals at δ 3.11 (sept., CH), 1.241 (d, J = 4.0 Hz, Me), 1.225 (d, J = 4.0 Hz, Me), 3.01 (br, NH), 2.53 (br, NH). The isopropylamine cluster is rigid in ^{1}H NMR spectra up to 100 °C with no line broadening at this temperature. Turnstile rotation of the $Os(CO)_2L$ group is therefore slow. This suggests the possibility of separation of enantiomers of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(L)]$ or diastereomers if a chiral ligand L is used.

As predicted the complex $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$ demonstrates clearly the presence of two diastereomers in the ^{1}H NMR spectrum ($CDCl_3$); there are hydride signals at δ −19.39, −19.47, −24.48 and −24.51, broad NH signals at δ 3.49, 3.28, 2.99 and 2.85, and Me doublets at δ 1.57 and 1.55 with a diastereomeric ratio of 0.54 : 0.46 at room temperature. Attempts to fractionate the yellow product by TLC on SiO_2 led to only slight isomer enrichment but HPLC separation of **B¹** and **B²** was very effective and gave the two diastereomers in 100 and 95% isomeric purity, respectively.

The structure of the isomer **B¹** was determined by single-crystal XRD (Fig. 1).‡ The equatorial co-ordination of (S)-$PhCHMeNH_2$ leading to the two ^{1}H NMR signals at δ −19.39 and −24.51 was confirmed. The hydride giving the signal at δ −19.39 is that *cis* to the amine. The amine has a smaller *trans* influence than CO on the Os–Os distances which are 2.8647(13) and 2.8846(14) Å *trans* to amine and *cis* to CO and 2.9155(12) and 2.9050(12) Å *cis* to amine and *trans* to CO, compared with 2.908(1) and 2.922(1) Å for the hydride-bridged edges in $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ **1**, although in essence the structure is closely similar to that of cluster **1**.[1] Note that the cluster is equatorially substituted unlike $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}Se)(CO)_8(PPh_3)]$ which contains an axial phosphine.[4]

The final confirmation that the isomers are indeed **B¹** and **B²** came from their CD spectra which are shown in Fig. 2. The ligand (S)-$PhCHMeNH_2$ does not absorb significantly in the range 300 to 400 nm so that the cluster itself is the chromophore in this region and there is a strong inverse relationship between the CD spectra totally consistent with cluster-centred chirality. We believe that this is the first time isomeric clusters related by a trigonal twist of a $M(CO)_2L$ group have been separated and shown to interconvert only very slowly.

Considering the projections shown for **B¹** and **B²** below, the turnstile rotation is basically a Bailar twist and known to occur very slowly if at all for octahedral complexes. Note that, if we

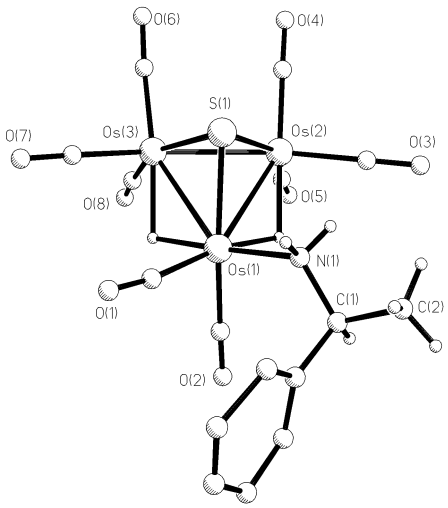
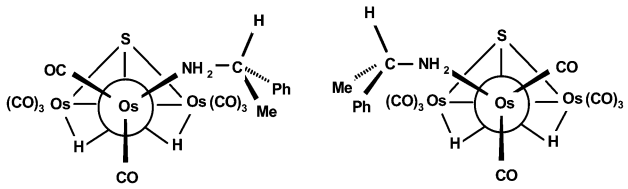


Fig. 1 Molecular structure of one of two independent molecules in the unit cell of the diasteromer B¹ of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$. Selected bond lengths (Å): Os(1)–Os(2) 2.9155(12), Os(2)–Os(3) 2.7723(12), Os(1)–Os(3) 2.8647(13), Os(1)–S(1) 2.404(6), Os(2)–S(1) 2.391(6), Os(3)–S(1) 2.390(6), Os(1)–N(1) 2.17(3).

DOI: 10.1039/b203611h



consider only the ligand positions and not the metal–metal vectors, then the substituted osmium atom is closely octahedral.

The situation with tertiary phosphines is very different to that with amines. Thus we have observed mixtures of **A** and **B¹**/**B²** for each of the tertiary phosphines we have used: PPh_3, PCy_3, PEt_3, PMe_2Ph with an increased preference for isomer **A** with the more bulky phosphines.§ The crystal structure of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}Se)(CO)_8(PPh_3)]$ shows that the structure **A** is adopted in the solid state.[4] However, we have now shown that $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(PPh_3)]$ exists in solution as a mixture of the equatorial isomers (**B¹**/**B²**) and the axial isomer (**A**) as do all the other tertiary phosphine complexes of this type we have studied. The mol ratio **A**:**B¹**/**B²** varies from 7.16:1 (P^iPr_3), 3.92:1 (PPh_3), 1.25:1 (PEt_3) to 0.67:1 (PMe_2Ph) at room temperature in the order of Tolman cone angles [170° PCy_3, 145° PPh_3, 132° PEt_3, 122° PMe_2Ph]. The cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(PMe_2Ph)]$ probably crystallizes as the isomer **B¹**/**B²** because this is the dominant isomer initially on dissolving in $CDCl_3$ [mol ratio **A**:**B¹**/**B²** = 0.12:1] but the equilibrium mixture [mol ratio **A**:**B¹**/**B²** = 0.67:1] is formed over 27 hours at 20 °C. Our studies on the mechanism of interconversion of isomers and hydride exchange show that hydride migration is faster than phosphine or CO movement but that the interconversion of isomers can be detected by EXSY methods and by NMR dynamic line broadening at temperatures around 100 °C in the ^{1}H and ^{13}C NMR spectra. Kinetic details will be published elsewhere.[5]

A preliminary theoretical study has shown that the isomers **A** and **B¹**/**B²** of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(PH_3)]$ are almost equal in energy whereas the equatorial isomers **B¹**/**B²** of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(NH_3)]$ are lower in energy than the unobserved isomer **A**, consistent with our observations.[6]

Epimerization is very slow. There is a 26% conversion of isomer **B¹** to **B²** in chloroform over 142 days in the dark at room temperature. However, if a solution of predominantly diastereomer **B¹** in heptane is kept at 96 °C, there is significant conversion to the **B¹**/**B²** mixture within 15 min and after 45 min the composition is 0.52:0.48, close to the composition of the synthesised mixture. If a similar treatment of one diastereomer of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$ in refluxing heptane solution is carried out in the presence of isopropylamine, there is some conversion to the **B¹**/**B²** mixture (*i.e.* some epimerization) but most of the reaction proceeds by substitution to the isopropylamine cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(Me_2CHNH_2\}]$. Thus, after 30 min reaction in refluxing heptane, a sample of **B¹** and **B²** (initial mol ratio 0.10:0.90) gave a mixture of **B¹**, **B²** and the isopropylamine substituted product in mol ratio 0.04:0.24:0.72. Epimerization and substitution occur at similar rates under the same conditions. We are currently carrying out a more detailed kinetic study of both the epimerization and substitution processes. Preliminary results indicate that epimerization is about 4 times faster than substitution.[7] Intramolecular turnstile rotation and Os–N bond cleavage are therefore very finely balanced.

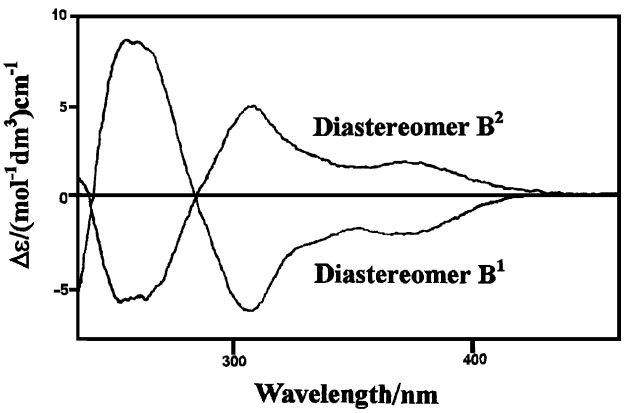


Fig. 2 CD spectra of isomers B^1 and B^2 of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$.

We thank the Royal Society and the Swedish Academy of Sciences for supporting collaborative work with Dr E. Norlander (Lund University) on catalysis by chiral transition metal clusters. We also thank the University of London Intercollegiate Research Service for CD spectra provided by the chiroptical service at King's College London (Dr A. F. Drake and Dr G. Siligardi).

Notes and references

† Typical synthesis of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(L)]$ for amines L: Cluster **1** (0.06 mmol) in dichloromethane (30 cm^3) was treated with $Me_3NO{\cdot}2H_2O$ (0.24 mmol) and the amine L (0.5 cm^3) under nitrogen. After 10 min the reaction mixture was separated on silica (TLC, eluent = light petroleum spirit–dichloromethane eluent) to give traces of **1** and the yellow product (19 to 40%). ν(CO)/cm^{-1} (cyclohexane, L = ^{i}PrNH$_2$): 2085m, 2049vs, 2030vs, 2004vs,1989s, 1968m, 1964m. Satisfactory elemental analyses were obtained.

‡ Crystallographic data for $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8\{(S)\text{-}PhCHMeNH_2\}]$: $C_{16}H_{13}NO_8Os_3S$, M = 949.93, monoclinic, space group $P2_1$, a = 9.4018(4), b = 20.5782(11), c = 11.5621(5) Å, β = 95.605(3)°, V = 2226.25(18) Å, Z = 4, D_c = 2.834 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 17.213 mm^{-1}, F(000) = 1696. 11460 independent reflections were measured in the θ range 1.77 to 24.99°. 526 parameters were refined to give R [$I > 2\sigma(I)$] = 0.0683 and $wR2$ (all data) = 0.1781. The structure was solved by direct methods and refined (SHELXL-97) with all non-H atoms anisotropic. H-atoms were included using a riding model except the hydrides which were located using HYDEX.[8] Flack parameter = 0.01(2). The two independent molecules in the unit cell do not differ significantly. CCDC 183148. See http://www.rsc.org/suppdata/cc/b2/b203611h/ for crystallographic files in CIF or other electronic format.

§ Typical synthesis of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(L)]$ for tertiary phosphines L: a solution of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(MeCN)]$ (0.192 g) and PMe_2Ph (0.035 g) in toluene (75 cm^3) was refluxed under nitrogen for 8.5 h. Removal of the solvent, preliminary column chromatography on silica, and final purification by TLC (eluent: CH_2Cl_2–pentane; 1:6 v/v) gave $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_8(PMe_2Ph)]$ (0.102 g) as the main product. ν(CO)/cm^{-1} (cyclohexane): 2081s, 2045s, 2038(sh), 2001s, 1997(sh), 1986s, 1981(sh), 1977(sh), 1961m. Hydride ^{1}H NMR ($CDCl_3$): isomer **A**: δ −20.62 (d, J_{PH} = 11.5 Hz, J_{OsH} = 30.4 Hz); isomers **B¹**/**B²**: δ −19.99 (d, J_{PH} = 27.5 Hz, *trans* to PMe_2Ph, J_{OsH} = 29.2, 37.4 Hz), δ −21.42 (d, J_{PH} = 8.5 Hz, *cis* to PMe_2Ph, J_{OsH} = 29.6 Hz).

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