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Orientational isomerism in bridging 2-pyridyl complexes: orthometallation of (*S*)-nicotine and (*R*)-1-(4-pyridyl)ethanol in triosmium clusters

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Diastereomeric orthometallated products, formed by treating $[Os_3(CO)_{10}(MeCN)_2]$ with (*S*)-nicotine or (*R*)-1-(4-pyridyl)ethanol, have been partially separated by TLC but completely so by HPLC. The two diastereomers of $[Os_3(\mu\text{-}H)\{\mu\text{-}(R)\text{-}NC_5H_3CH(OH)Me\text{-}4\}(CO)_{10}]$ **1** and **2** and four isomers of $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$, **3** to **6**, two diastereomers each for the products of metallation at the 2 and 6 positions respectively, have been separated and characterized by circular dichroism (CD) spectra to obtain their relative configurations. The CD spectra in the 230–500 nm wavelength range are totally characteristic of the configuration of the Os_3CN group at atoms. A crystal structure determination for isomer **2** has allowed absolute configurations of all isomers to be established. There is little enantioselection in the orthometallation process and no detectable interconversion of isomers. The compound $[Os_3(\mu\text{-}H)_2\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}_2(CO)_8]$ was also obtained as a complex isomeric mixture which was not separated.

Introduction

Many transition metal clusters are chiral but are commonly difficult to resolve or little attempt has been made to do so. One of the simplest type of chiral clusters is where a tetrahedron is formed by four different atoms and the cluster $[FeCoMo(\mu_3\text{-}S)(C_5H_5)(CO)_8]$ of this type was resolved nearly 20 years ago.[1] Homometallic clusters may also be chiral if there is an appropriate orientation of suitable ligands. For example, triangular clusters with μ or μ_3 unsymmetrical ligands XY positioned out of the plane or the metal triangle are chiral (Fig. 1). By the addition of chiral amines such as (+)-PhCHMeNH$_2$ to $[Os_3(CO)_{12}]$, we have shown that the product $[Os_3(\mu\text{-}H)(\mu\text{-}PhCHMeNHCO)(CO)_{10}]$ exists as a pair of diastereomers which may be separated by TLC.[2] These diastereomers differ in the orientation of the RNHCO ligand across a pair of metal atoms and their separation depends upon the rigid non-dynamic character of this bridge. In this case there is no detectable interconversion of the separated isomers at room temperature. On the other hand some other ligands are rapidly mobile with respect to the M_3 cluster and isomers are therefore inseparable. For example, the vinyl ligands in the clusters $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_9L]$ (L = CO or tertiary phosphine) rapidly move about the metal triangle.[3] Likewise there is now considerable evidence for the mobility of μ_3-alkynes or μ_3-arynes which would prevent separation of enantiomeric forms or diastereomeric forms if a chiral alkyne is used. An example from our own work is the isopropyl-substituted aryne cluster $[Os_3(\mu\text{-}H)(\mu\text{-}AsMe_2)(\mu_3\text{-}C_6H_3Pr^i)(CO)_9]$ which undergoes rapid rotation and flipping of the unsymmetrical benzyne.[4] There are many cases such as this where ligand mobility would prevent resolution of enantiomers but 2-pyridyl is a good example of a rigidly co-ordinated unsymmetrical ligand.

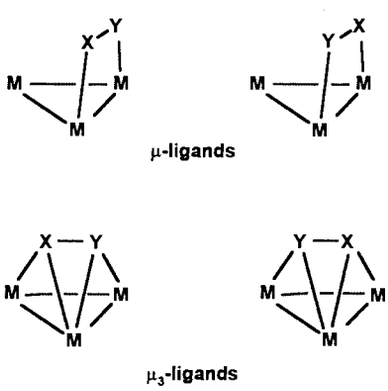


Fig. 1 Enantiomers generated by co-ordination of an unsymmetrical bridging ligand XY to a homometallic M_3 cluster.

The 2-pyridyl cluster $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ was first synthesized by direct thermal reaction of $[Os_3(CO)_{12}]$ with pyridine, along with other products of further metallation such as $[Os_3(\mu\text{-}H)_2(\mu\text{-}NC_5H_4)_2(CO)_8]$.[5] Later it was synthesized by treating $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$ with pyridine.[6] Thermolysis of $[Os_3(CO)_{11}(py)]$, formed from $[Os_3(CO)_{11}(MeCN)]$, in the presence of an excess of pyridine also gives the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$[6] whereas if no excess of pyridine is added higher clusters including $[Os_5H(C)(\mu\text{-}NC_5H_4)(CO)_{14}]$ and $[Os_{10}(C)(CO)_{24}]^{2-}$ are obtained.[7] The cluster $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ is also formed when various clusters such as $[Os_3\{S{=}C(NMe_2)_2\}(CO)_{11}]$[8] or $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}]$[9] are treated with pyridine. Analysis of the vibrational spectra of $[Os_3(CO)_{11}(py)]$ and of $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ has been particularly helpful in interpreting electron energy loss (EEL) spectra to provide supporting evidence for the conversion of pyridine into 2-pyridyl at Pt(111) surfaces.[10] Other work has been on electrochemical[11] and high-pressure vibrational[12] studies of $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$.

Table 1 500 MHz ^{1}H NMR data for isomeric clusters **1** and **2** containing orthometallated (*R*)-1-(4-pyridyl)ethanol in $CDCl_3$ [a]

Compound	OsH	H^2	H^4	H^5	OH	CH	CH_3
1	−14.837	7.280 (d) (2.0)	6.707 (dd) (5.8, 2.2)	8.052 (d) (5.8)	1.532 (br)	4.700 (dq) (6.5, 2.6)	1.403 (d) (6.5)
2	−14.834	7.302 (d) (1.9)	6.682 (dd) (6.1, 2.0)	8.046 (d) (5.8)	1.528 (br)	4.704 (dq) (6.5, 2.7)	1.411 (d) (6.5)

[a] Hz in parentheses; site positions are based on the Os-bonded carbon as C^1. The free ligand (proligand) has the spectrum: δ 8.48 (AA′ part of AA′BB′ spectrum, H^2,H^6), 7.30 (BB′ part of AA′BB′ spectrum, H^3,H^5), 4.89 (q, J = 6.6, CH), 3.35 (broad, OH) and 1.49 (d, CH_3, J = 6.6 Hz).

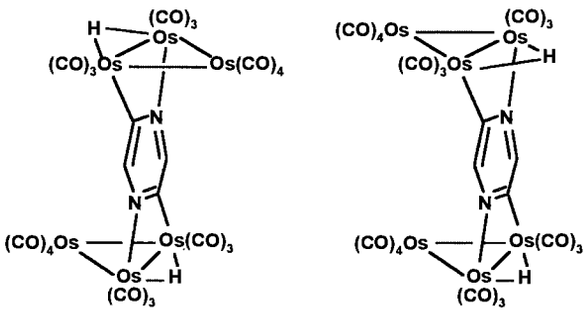
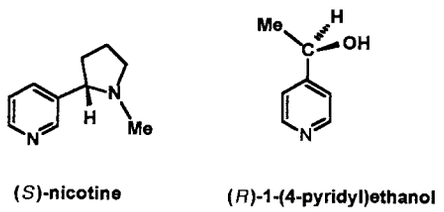


Fig. 2 The *syn* and *anti* forms of the pyrazine derivative [{Os_3(μ-H)$(CO)_{10}$}$_2$(μ_4-$C_4H_2N_2$)].[15]

The rigidity of co-ordination of μ-2-pyridyl ligands is supported by various observations. Extended reaction of $[Os_3(CO)_{12}]$ with pyridine gives trinuclear pyridyl osmium clusters which quantitatively convert into two separable head-to-head and head-to-tail isomers of $[Os_2(\mu\text{-}NC_5H_4)_2(CO)_6]$,[5] the crystal structures of which have been determined.[13] These isomers do not interconvert at 150 °C. The resolution of $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ has been achieved by replacement of one CO ligand with L-alanine ethyl ester, separation of diastereomers by TLC chromatography, and subsequent replacement of the chiral amino-ester by CO to reform the separated enantiomers.[14] Another more recent example of the rigidity of this type of ligand is the isolation of non-interconverting *syn* and *anti* isomers of the doubly ortho-metallated pyrazine derivative [{$Os_3(\mu\text{-}H)(CO)_{10}$}$_2$($\mu_4$-$C_4H_2N_2$)] (Fig. 2).[15]



Results and discussion

Since the complex $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ exists as the enantiomers shown in Fig. 3, the introduction of an optically pure enantiomer of a chiral pyridine instead of pyridine itself will lead to potentially separable diastereomers. Treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with (*R*)-1-(4-pyridyl)ethanol leads to the orthometallated product $[Os_3(\mu\text{-}H)\{\mu\text{-}(R)\text{-}NC_5H_3CH(OH)\text{-}Me\text{-}4\}(CO)_{10}]$ as the diastereomers **1** and **2** in approximately 50 : 50 mol ratio, that is with negligible enantioselectivity. The IR spectrum around 2000 cm^{-1} is almost identical to that of the unsubstituted analogue $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)\text{-}(CO)_{10}]$.[1] The ^{1}H NMR spectrum of the mixture of **1** and **2** gives 7 signals, one for each proton environment, with virtually no chemical shift separation between the signals for the two diastereomers, although careful analysis of the multiplets confirmed that these 7 signals are the result of 14

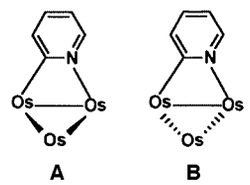
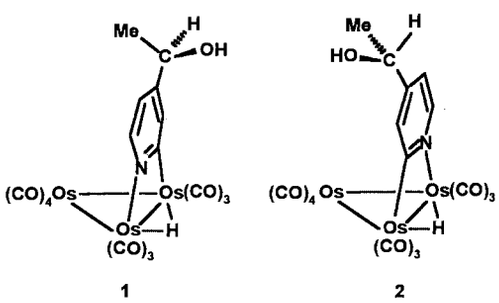


Fig. 3 Enantiomers of $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$.

overlapping achronous signals (Table 1). Notably the hydride signal appeared as a single resonance with only slight evidence for splitting even in the 500 MHz spectrum. There appears therefore to be little chemical recognition between the (*R*)-4-CH(OH)Me groups and the Os_3NC units of different configuration. It was therefore understandable that TLC treatment gave only one yellow band and that careful segmentation of this band gave no evidence for separation or even enrichment of the isomers in the different segments. However, surprisingly we were able to achieve essentially total separation of diastereomers **1** and **2** by HPLC (see Experimental section). Table 1 shows the close similarity of the ^{1}H NMR spectra of **1** and **2**. The IR spectra of the separated isomers are indistinguishable.



The clearest evidence for separation of isomers **1** and **2** came from the CD spectra which are shown in Fig. 4. Absorptions in the wavelength range 230 to 450 nm are essentially due to the Os_3(pyridyl) chromophore and not the (*R*)-4-CH(OH)Me group and therefore the CD spectra are close to true reflections of each other. These CD spectra may be compared with those of the resolved enantiomers of the 2-pyridyl complex $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$.[14,16] The CD spectra we obtained for **1** and **2** are broadly the same as those of the parent pyridyl enantiomers although there are some differences in detail. The absolute configurations of the enantiomers of $[Os_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}]$ were not established. We had some difficulties in growing good large crystals of these compounds but did manage to grow some small crystals of isomer **2**, suitable for structure determination. The structure of isomer **2** (Fig. 5, Table 2) has allowed the absolute configurations of **1** and **2** to be established. The compound forms monoclinic crystals in the chiral space group *C*2. The absolute configuration was given by the determined value of the Flack parameter which is consistent with the known stereochemistry of the $CH(OH)CH_3$ substituent in the starting material (from Aldrich). Selected bond lengths and angles are given in Table 2. The structure is

as expected for a cluster of the type $[Os_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}]$ with the substituted 2-pyridyl bridge above the Os_3 plane and the μ-hydride below it. Although the position of the hydride ligand was not established from diffraction data, application of the energy minimization program HYDEX[17] confirmed the position as shown. The stereochemistry of the Os_3(2-pyridyl) component is as in Fig. 3(B) which corresponds with the structure shown for cluster **2**. Therefore the structure of cluster **1** must also be as shown. Isomers **1** and **2** do not interconvert in solution at room temperature.

Treatment of $[Os_3(CO)_{12}]$ with (*S*)-nicotine for 30 min in refluxing octane gave a mixture of four isomers of $[Os_3(\mu\text{-H})(\mu\text{-NC}_5H_3C_4H_7NMe)(CO)_{10}]$. The same four isomers were obtained under milder conditions by treating $[Os_3(CO)_{10}(MeCN)_2]$ with (*S*)-nicotine in refluxing dichloromethane. The isomeric mixture gave four ^{1}H NMR hydride singlets at δ −14.388, −14.474, −14.833 and −14.840 (Table 3) in intensity ratio of approximately 0.20:0.20:0.30:0.30. Although the ^{1}H NMR spectrum of the mixture was complex, analysis of the region between δ 6.5 and 8.2 clearly showed that two isomers had resulted from metallation at the 2 position of the pyridine ring and the other two from metallation at the 6 position. Attempts to separate the isomers by TLC were only partially successful since only fractions enriched in particular isomers were obtained. However, by optimizing conditions for HPLC separation it was possible to achieve essentially total separation of all four isomers. Fig. 6 shows an example of an HPLC trace showing the efficiency of the separation. In practice it was convenient to collect the first two bands and the third and fourth bands as two fractions using semipreparative HPLC and then to separate each fraction into two isomers by further HPLC. Fig. 7 shows the ^{1}H NMR spectra in the hydride region for the mixture as synthesized and the corresponding spectra of the four fractions after HPLC. The signals around δ −14.4 correspond to isomers **3** and **4** which are metallated at the 2 position while those with signals at δ −14.8 are for the 6-metallated isomers **5** and **6**. Note that there is a larger chemical shift difference ($\Delta\delta = 0.086$) when the pyridine ring substituent is closer to the Os_3 ring (isomers **3** and **4**) than when it is more remote ($\Delta\delta = 0.007$) (isomers **5** and **6**). However, there is a better separation of isomers **5** and **6** by HPLC (Fig. 6). The CD spectra of isomers **3** to **6** are shown in Fig. 8. The pattern of

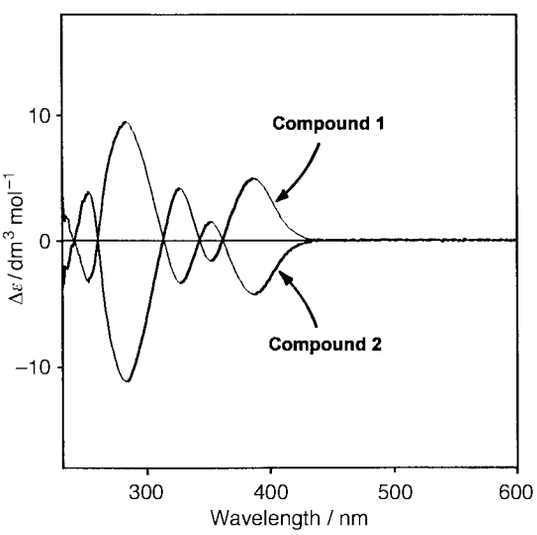


Fig. 4 The CD spectra for the diastereomers **1** to **2** of $[Os_3(\mu\text{-H})\{\mu\text{-}(R)\text{-NC}_5H_3CH(OH)Me\text{-}4\}(CO)_{10}]$ (0.075 mg cm^{-3} in CH_2Cl_2).

Table 2 Selected bond lengths (Å) and angles (°) for the cluster $[Os_3(\mu\text{-H})\{\mu\text{-}(R)\text{-NC}_5H_3CH(OH)Me\text{-}4\}(CO)_{10}]$, diastereomer **2**

Os(1)–Os(2)	2.9049(8)	Os(2)–C(4)	1.968(12)
Os(1)–Os(3)	2.8680(10)	Os(2)–C(5)	1.921(14)
Os(2)–Os(3)	2.8882(7)	Os(2)–C(6)	1.913(14)
Os(1)–N(1)	2.147(11)	Os(3)–C(7)	1.944(11)
Os(2)–C(11)	2.122(11)	Os(3)–C(8)	1.927(12)
Os(1)–C(1)	1.932(12)	Os(3)–C(9)	1.904(13)
Os(1)–C(2)	1.901(12)	Os(3)–C(10)	1.955(14)
Os(1)–C(3)	1.902(12)		
Os(1)–Os(2)–C(11)	68.3(3)	Os(1)–N(1)–C(11)	110.3(7)
Os(3)–Os(2)–C(11)	88.8(3)	Os(1)–N(1)–C(15)	126.9(8)
Os(2)–Os(1)–N(1)	68.5(2)	Os(2)–C(11)–N(1)	112.7(8)
Os(3)–Os(1)–N(1)	88.2(2)	Os(2)–C(11)–C(12)	128.4(8)

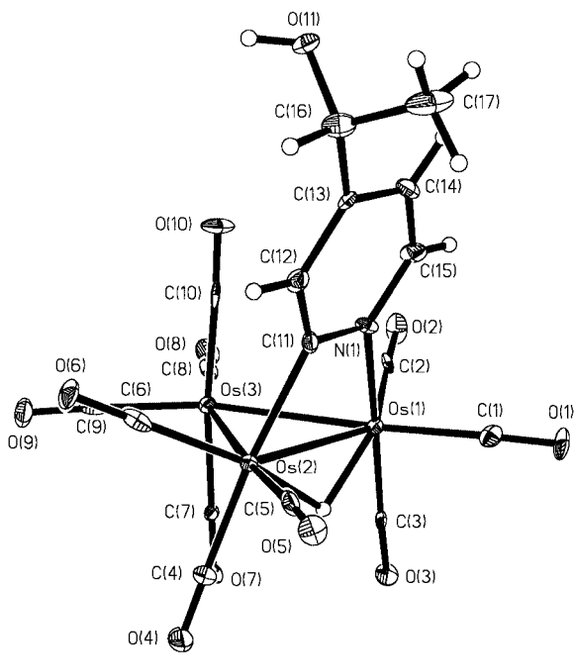


Fig. 5 Molecular structure of isomer **2** of $[Os_3(\mu\text{-H})\{\mu\text{-}(R)\text{-NC}_5H_3\text{-}CH(OH)Me\text{-}4\}(CO)_{10}]$.

Table 3 Selected ^{1}H NMR data for nicotine and the isomeric nicotinyl clusters $[Os_3(\mu\text{-H})\{\mu\text{-}(S)\text{-NC}_5H_3C_4H_7NMe\}(CO)_{10}]$, **3** to **6**

Compound	OsH	H^2	H^3	H^4	H^5	H^6	CH_3
(*S*)-Nicotine		8.54 (d) (2.2)		7.71 (dddd) (7.8, 1.7, 2.2, 0.5)	7.28 (dddd) (7.8, 4.7, 0.9, 0.3)	8.45 (dd) (4.7, 1.7)	1.56 (s)
3	−14.388 (s)		8.10 (dd) (1.7, 5.5)	6.70 (dd) (5.5, 7.9)	7.69 (dd), 1.6, 7.8) (1.6, 7.8)		2.17 (s)
4	−14.474 (s)		8.11 (dd) (1.7, 5.4)	6.72 (dd) (5.5, 7.9)	7.68 (dd) (1.6, 7.9)		2.12 (s)
5	−14.833 (s)		8.15 (d) (1.4)		7.18 (dd) (1.8, 7.7)	7.28 (d) (7.8)	2.09 (s)
6	−14.840 (s)		8.09 (d) (1.4)		7.23 (dd) (1.8, 7.7)	7.30 (d) (7.8)	2.05 (s)

[a] *J*/Hz in parentheses.

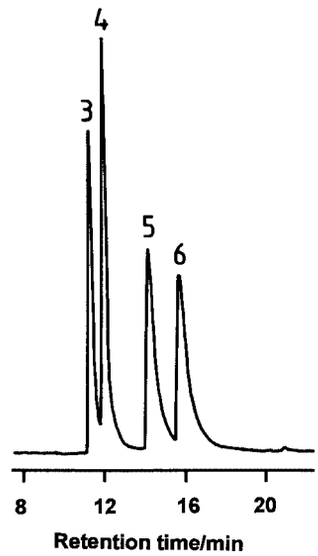


Fig. 6 Analytical HPLC trace showing the separation of the diastereomers **3** to **6** of $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ (see Experimental section for conditions).

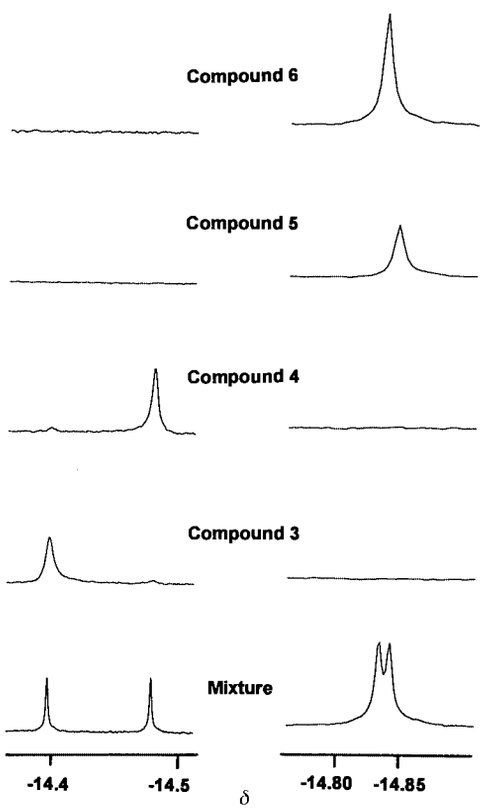
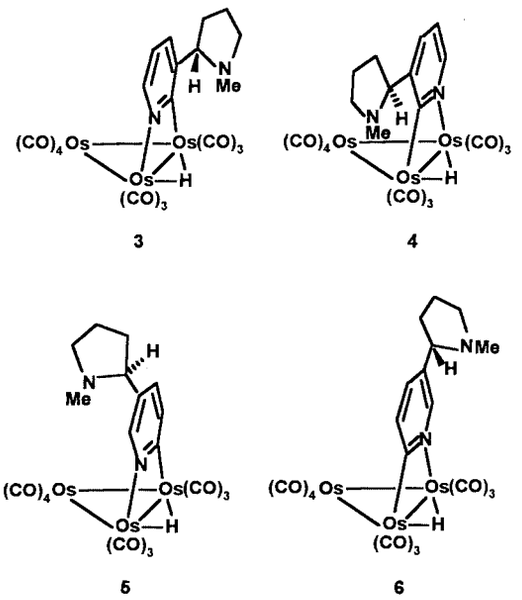


Fig. 7 The ^1H NMR spectra for the diastereomers **3** to **6** of $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ in $CDCl_3$.

these spectra are closely similar to those of **1** and **2** in Fig. 4, consistent with these spectra being largely the result of the Os_3CN configuration (**A** or **B** in Fig. 3) and not that of the organic substituent at the pyridine. By comparison of the CD spectra with those of **1** and **2** of known absolute configuration it has been possible to assign the configurations of isomers **3** to **6**.

More forcing treatment of $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3(CO)_{12}]$ with (*S*)-nicotine in refluxing toluene gave a small amount of the mixture of **3** to **6** but the major product was a mixture of isomers of $[Os_3(\mu\text{-}H)_2\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}_2(CO)_8]$ **7** containing two orthometallated ligands. The IR spectrum of mixture **7** is very similar to that of the 2-pyridyl



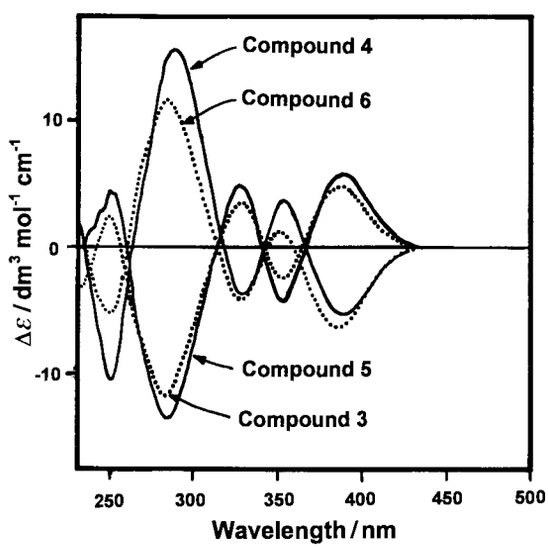


Fig. 8 The CD spectra for the diastereomers **3** to **6** of $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ (0.075 mg cm^{-3} in CH_2Cl_2).

derivative $[Os_3(\mu\text{-}H)_2\{\mu\text{-}NC_5H_4\}_2(CO)_8]$ and almost certainly therefore they are based on the same structure.[5] The 2-pyridyl complex has non-equivalent pyridine rings resulting from their relative orientation, and shows non-equivalent hydride and pyridyl signals in the ^1H NMR spectra. As a consequence, cluster **7** should exhibit four isomers and the NMR spectrum is accordingly complex. Careful TLC treatment gave a set of poorly resolved bands giving mixtures except for one band which gave isomerically pure cluster **7a**. The was shown to contain one 2-metallated and one 6-metallated nicotinyl ligand and two different hydride ligands (δ −10.753 and −12.819) corresponding to the signals at δ −10.80 and −12.47 we reported for $[Os_3(\mu\text{-}H)_2\{\mu\text{-}NC_5H_4\}_2(CO)_8]$.[5] We have not studied compound **7a** further and have not determined its absolute configuration.

Experimental

The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared by a published method[16] and (*S*)-nicotine and (*R*)-1-(4-pyridyl)ethanol were used as supplied by Aldrich. The NMR spectra were acquired on Bruker AC300 and DRX500 spectrometers, FAB mass spectra on a ZAB spectrometer using 3-nitrobenzyl alcohol matrices, IR spectra on a Nicolet 280 FTIR spectrometer and

CD spectra on a JASCO J600 spectrometer (using solutions of concentration 0.075 mg cm^{-3}) at King's College London using the University of London Intercollegiate Research Service (ULIRS). Solvents used in the syntheses were dried and distilled by standard methods prior to use.

Reactions

Treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with (*R*)-1-(4-pyridyl)-ethanol. A solution of equimolar quantities of $[Os_3(CO)_{10}(MeCN)_2]$ (0.130 g) and (*R*)-1-(4-pyridyl)ethanol (0.028 g) in dry THF (25 cm^3) was refluxed under nitrogen for 1 h. The solvent was removed under reduced pressure to give a yellow residue. Careful TLC treatment (SiO_2, 2 mm Merck 1045; eluent dichloromethane–hexane, 3:7 by volume) gave only one yellow band. This produced a yellow solid which was shown spectroscopically to be an approximately 50:50 mixture of isomers **1** and **2** of $[Os_3(\mu\text{-}H)\{\mu\text{-}(R)\text{-}NC_5H_3CH(OH)Me\text{-}4\}(CO)_{10}]$ (0.125 g, 80%) (Found: C, 21.0; H, 0.8; N, 1.4. $C_{17}H_9NO_{11}Os_3$ requires C, 21.9; H, 1.0; N, 1.4%). $\tilde{\nu}$(CO)/cm^{-1} (cyclohexane): 2104w, 2063vs, 2053s, 2022s, 2010s, 2003m, 1990m and 1975vw. FAB MS showed the parent molecular ion (obs. for centre of isotope envelope *m*/*z* 974, calc. 974). Optimum separation of the mixture of **1** and **2** obtained from the TLC separation dissolved in dichloromethane (0.050 g cm^{-3}) was established using an analytical HPLC SiO_2 column, eluting with an isocratic propan-2-ol–*n*-hexane mixture (2.5:97.5 by volume). Baseline resolution was achieved. Scaling up to a semi-preparative column (5 μm mesh SiO_2, column length 20 cm, internal diameter 10 mm) with an identical isocratic solvent (injection volumes, 0.150 cm^3; flow rate, 4 cm^3 min^{-1}) gave acceptable resolution. Isomers **1** and **2** (>95% isomerically pure) gave indistiguishable IR spectra and similar but distinguishable ^{1}H NMR spectra (Table 1).

$[Os_3(CO)_{12}]$ with (*S*)-nicotine in refluxing octane. A solution of $[Os_3(CO)_{12}]$ (0.180 g) and (*S*)-nicotine (0.160 g) in *n*-octane (30 cm^3) was refluxed under nitrogen for 30 min and the solvent removed under reduced pressure. Chromatography of the residue (TLC, SiO_2; eluent pentane–diethyl ether, 10:1 by volume) gave unchanged $[Os_3(CO)_{12}]$ (0.020 g) and $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ (0.086 g, 62% based on carbonyl complex consumed) as a broad band giving a yellow solid shown spectroscopically to be a mixture of isomers **3** to **6** (Found: C, 23.5; H, 1.55; N, 2.7. $C_{20}H_{14}N_2O_{10}Os_3$ requires C, 23.7; H, 1.5; N, 2.7%). $\tilde{\nu}$(CO)/cm^{-1} (cyclohexane): 2105m, 2063vs, 2053s, 2023s, 2011s, 2004ms, 1990ms and 1976w. Rechromatography (TLC) with careful segmentation of the broad yellow band gave fractions which all contained various amounts of the isomers, none of which could be obtained pure.

$[Os_3(CO)_{10}(MeCN)_2]$ with (*S*)-nicotine in refluxing dichloromethane. A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.100 g) and an excess of (*S*)-nicotine (0.010 cm^3) in dichloromethane (25 cm^3) was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure and TLC of the residue on SiO_2 [eluent: dichloromethane–*n*-hexane, 3:7 by volume] gave as a broad yellow band yielding $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ as a mixture of the isomers **3** to **6**. Following analytical HPLC procedures to optimize conditions, separation on a semipreparative silica column with injection volumes of 0.500 cm^3 and isocratic eluent propan-2-ol–*n*-hexane (3:97 by volume) gave a good separation into two components (**3** + **4**) and (**5** + **6**). These two mixtures were further separated on a semipreparative scale to yield essentially pure samples of isomers **3** to **6**.

$[Os_3(CO)_{10}(MeCN)_2]$ with (*S*)-nicotine in refluxing toluene. A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.220 g) and an excess of (*S*)-nicotine (0.40 cm^3) in toluene (35 cm^3) was refluxed under nitrogen for 2 h. The solvent was removed from the orange solution under reduced pressure and TLC of the residue on SiO_2 [eluent: pentane–diethyl ether, 10:4 by volume] gave two major yellow bands yielding $[Os_3(\mu\text{-}H)\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}(CO)_{10}]$ as a mixture of the isomers **3** to **6** (0.050 g) and $[Os_3(\mu\text{-}H)_2\{\mu\text{-}(S)\text{-}NC_5H_3C_4H_7NMe\}_2(CO)_8]$ **7**, also as a complex mixture of the isomers (0.120 g) (Found: C, 31.65; H, 2.5; N, 4.85. $C_{28}H_{28}N_4O_8Os_3$ requires C, 31.5; H, 2.45; N, 4.9%). $\tilde{\nu}$(CO)/cm^{-1} (cyclohexane): 2082m, 2048s, 2029s, 2001s, 1993(sh), 1986w, 1976s and 1960m, almost identical to the spectrum of the 2-pyridyl analogue $[Os_3(\mu\text{-}H)_2(\mu\text{-}NC_5H_4)_2(CO)_8]$.[5] A HPLC separation was not attempted. Further TLC separation of **7** gave several overlapping bands but the main band gave a single pure isomer **7a**. ^{1}H NMR (CD_2Cl_2): δ −10.753 (s, OsHOs), −12.819 (s, OsHOs), 8.17 (d), 7.16 (d), 7.28 (dd) (6-metallated ring), 8.06 (dd), 6.59 (dd), 7.59 (dd) (2-metallated ring), 2.12 (s, Me) and 2.14 (s, Me).

Crystal structure determination

Yellow crystals of compound **2** were obtained by cooling a dichloromethane–hexane solution. A suitable crystal was mounted in an oil droplet which solidified at the data collection temperature of 100(2) K. The crystal was indexed and data collection strategy determined by the Nonius Collect program.[19] Data were integrated and merged, corrected for Lorentz-polarization effects and for the effects of absorption using the programs DENZO-SMN and Scalepack.[20] The structure was solved by direct methods (SHELXS 97).[21] All non-hydrogen atoms of the cluster were refined anisotropically (SHELXL 97)[21] while hydrogen atoms were included in calculated positions and allowed to ride on the atoms to which they were attached, with thermal parameters tied to those of the parent atom. Some ill defined solvent peaks tentatively attributed to hexane were located and modelled in terms of four isotropic carbon atoms, C(1S) to C(4S), each of site occupancy 0.5.

Crystal data for $C_{19}H_9NO_{11}Os_3$ 2·solvent. M_f = 997.87, monoclinic, space group *C*2, a = 21.937(4), b = 11.741(2), c = 9.166(2) Å, β = 93.680(3)°, V = 2355.8(8) $Å^3$, Z = 4, D_c = 2.814 g cm^{-3}, λ(Mo-Kα) = 0.71070 Å, μ = 16.120 mm^{-1}, F(000) = 1784. 5017 Independent reflections were measured in the θ range 2.23 to 27.49°. All data were used in refining 308 parameters to give R = 0.0414 and R' = 0.0859, 0.0377 and 0.0847 for data with $I_o > 2\sigma(I_o)$.

CCDC reference number 186/1517.

See http://www.rsc.org/suppdata/dt/1999/3289/ for crystallographic files in .cif format.

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