

New Synthetic Routes to $[\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ ($\text{M} = \text{Ru}$ or Os)†

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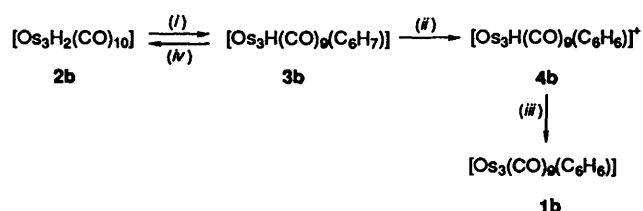
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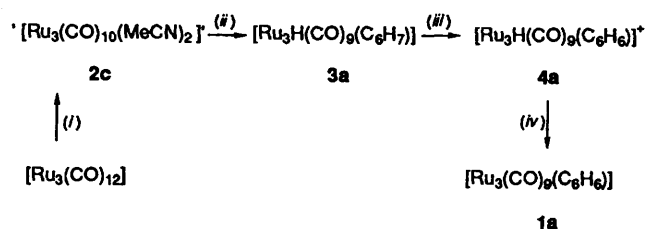
A new, more convenient route to the benzene cluster $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ directly from $[\text{Ru}_3(\text{CO})_{12}]$ has been established. Triruthenium dodecacarbonyl, $[\text{Ru}_3(\text{CO})_{12}]$, undergoes reaction with $\text{Me}_3\text{NO-CH}_2\text{Cl}_2$ in the presence of cyclohexa-1,3-diene to give the clusters $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ and $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ in moderate yield. Triosmium dodecacarbonyl does not react similarly, but from the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with cyclohexa-1,3-diene a key intermediate compound $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$ has been isolated and the solid-state structure of its acetonitrile solvate established by single crystal X-ray diffraction analysis at 150 K. The structure is monoclinic, space group $P2_1/n$, with $a = 8.932(8)$, $b = 17.387(13)$, $c = 14.833(15)$ Å, $\beta = 105.69(6)^\circ$ and $Z = 4$. The three osmium atoms form a regular triangle with a mean Os–Os distance of 2.877(12) Å. Two osmium atoms, Os(1) and Os(2), are co-ordinated to four carbonyl ligands and one, Os(3), co-ordinates to two carbonyl ligands. All carbonyl ligands are terminal and approximately linear. The cyclohexadiene ligand is η^4 co-ordinated to Os(3) *via* the 1,3-diene moiety, donating four electrons in total. On thermolysis, this compound is converted to $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ and then eventually to $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ by established means.

We have previously reported the syntheses and full structural characterisation of the two trinuclear benzene derivatives $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ **1a**^{1,2} and $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ **1b**.^{3,4} These molecules are of special interest because they appear to serve as excellent models for the interactions of benzene with a (111) metal surface.⁵ However, the two compounds were prepared by different synthetic routes. For the osmium compound **1b**, the highly reactive dihydrido cluster $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ **2b** was treated directly with cyclohexa-1,3-diene in octane to form first the dienyl derivative $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3b** and then, on reaction with Ph_3CBF_4 , the cationic hydrido-benzene cluster $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_6)]^+$ **4b**. This cluster **4b** in turn reacts with 1,8-diazabicyclo[5.4.0]undeca-7-ene (dbu) to form the required compound **1b** (Scheme 1). Significantly, the molecular structure of cluster **3b**, which has been established previously from X-ray diffraction studies, contains a C_6H_7 -dienyl entity spanning three osmium atoms and is clearly closely related to **1b**.

In contrast, because the corresponding dihydrido cluster $[\text{Ru}_3\text{H}_2(\text{CO})_{10}]$ **2a** is not available, the activated precursor $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ **2c** was employed in the preparation of the analogous ruthenium derivative $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ **1a**. In this case, reaction of **2c** with cyclohexa-1,3-diene produced the dienyl derivative $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3a** directly. As with the osmium compound, further reaction first with Ph_3CBF_4 and then dbu gave the required product **1a** (Scheme 2). Although this route can lead to moderate yields of **1a**, it is not reliable and difficulty has been encountered by us and others with both steps (ii) and (iv) of Scheme 2. In this paper we wish to report further studies of potential synthetic routes to both **1a** and **1b** and an investigation into the possible mechanism of the formation of **3a** and **3b**.



Scheme 1 Formation of $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ from $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$: (i) 1,3- C_6H_8 ; (ii) Ph_3CBF_4 ; (iii) dbu; (iv) heating in octane

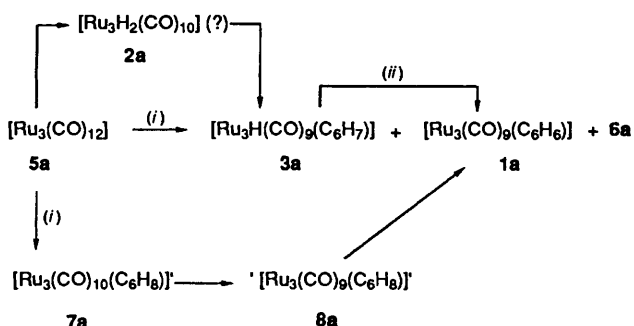


Scheme 2 Preparation of $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ from $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$: (i) $\text{Me}_3\text{NO-CH}_2\text{Cl}_2\text{-MeCN}$; (ii) 1,3- C_6H_8 ; (iii) Ph_3CBF_4 ; (iv) dbu

Results and Discussion

Our earlier observation⁶ that the hexaosmium cluster $[\text{Os}_6(\text{CO})_{18}]$ undergoes reaction with $\text{Me}_3\text{NO-CH}_2\text{Cl}_2$ to form the highly reactive hydrido species $[\text{Os}_6\text{H}(\text{CO})_{17}]^-$ and $[\text{Os}_6\text{H}_2(\text{CO})_{17}]^-$ led us to examine the related reactions of $[\text{Ru}_3(\text{CO})_{12}]$ as a potential *in situ* route to $[\text{Ru}_3\text{H}_2(\text{CO})_{10}]$. We have found that $[\text{Ru}_3(\text{CO})_{12}]$ **5a** in CH_2Cl_2 reacts with Me_3NO in the presence of cyclohexa-1,3-diene to produce moderately good yields of both compounds **1a** and **3a**. In addition, small amounts of a (as yet not fully characterised) cluster **6a** are also formed. The mass spectrum of this material **6a** exhibits a molecular ion

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 3 Formation of $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ from $[\text{Ru}_3(\text{CO})_{12}]$: (i) reaction with $\text{Me}_3\text{NO}\cdot\text{CH}_2\text{Cl}_2$ in the presence of 1,3- C_6H_8 ; (ii) heating in hexane

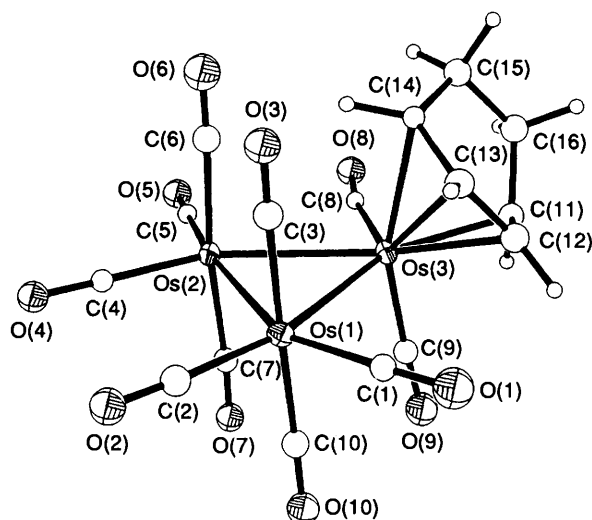
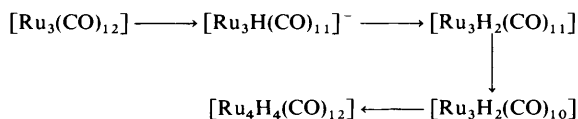


Fig. 1 The molecular structure of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$; in each carbonyl group the C atom bears the same number as the O atom

at $m/z = 627$, which corresponds to the molecular formula $[\text{Ru}_3\text{H}(\text{CO})_6(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_7)]$. So far, attempts to obtain crystals of this intriguing compound suitable for single crystal X-ray analysis have been unsuccessful. On heating, 3a is partly converted to 1a, giving overall yields of 1a approaching 35%.

The mechanism by which this sequence of reactions occurs (Scheme 3) is not altogether clear, but we suspect the dihydrido cluster $[\text{Ru}_3\text{H}_2(\text{CO})_{10}]$ is formed initially and functions as a key intermediate. We find that reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with $\text{Me}_3\text{NO}\cdot\text{CH}_2\text{Cl}_2$ in the absence of cyclohexa-1,3-diene produces good yields of the tetrahydrido-tetraruthenium cluster $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ as the only identifiable product. This observation is consistent with the suspected reaction sequence given below.



Thus, the overall reaction sequence (Scheme 3) is, in part, similar to that observed for osmium (Scheme 1), except we find that on heating the derivative 3b the major product is $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ and only a very small amount of the required product 1b is produced. However, there is no doubt that this new one-step synthetic route to compound 1a is considerably more convenient than that employed earlier.^{1,2} We also find that the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with Me_3NO in the presence of benzene does not yield compound 1a; however, addition of benzene to the reaction mixture $[\text{Ru}_3(\text{CO})_{12}]$ - Me_3NO - C_6H_6 does lead to improved yields of 1a. On the basis of these observations we consider that the reaction with $[\text{Ru}_3(\text{CO})_{12}]$

Table 1 Bond lengths (Å) and bond angles (°) for compound 7c

Os(1)-Os(2)	2.8645(9)	C(1)-O(1)	1.156(22)
Os(1)-Os(3)	2.8884(9)	C(2)-O(2)	1.146(22)
Os(2)-Os(3)	2.8790(9)	C(3)-O(3)	1.125(22)
Os(1)-C(1)	1.890(17)	C(4)-O(4)	1.164(20)
Os(1)-C(2)	1.912(18)	C(5)-O(5)	1.147(20)
Os(1)-C(3)	1.954(18)	C(6)-O(6)	1.076(23)
Os(1)-C(10)	1.929(18)	C(7)-O(7)	1.113(21)
Os(2)-C(4)	1.867(16)	C(8)-O(8)	1.122(20)
Os(2)-C(5)	1.917(16)	C(9)-O(9)	1.153(22)
Os(2)-C(6)	2.013(18)	C(10)-O(10)	1.146(22)
Os(2)-C(7)	1.983(17)	C(11)-C(12)	1.48(3)
Os(3)-C(8)	1.906(15)	C(11)-C(16)	1.52(3)
Os(3)-C(9)	1.844(17)	C(12)-C(13)	1.44(3)
Os(3)-C(11)	2.203(18)	C(13)-C(14)	1.495(24)
Os(3)-C(12)	2.203(18)	C(14)-C(15)	1.474(24)
Os(3)-C(13)	2.245(18)	C(15)-C(16)	1.50(3)
Os(3)-C(14)	2.342(16)		
Os(2)-Os(1)-Os(3)	60.056(22)	Os(1)-Os(2)-Os(3)	60.383(22)
Os(1)-Os(3)-Os(2)	59.560(22)	C(12)-C(11)-C(16)	117.5(15)
C(11)-C(12)-C(13)	112.6(15)	C(12)-C(13)-C(14)	115.3(15)
C(13)-C(14)-C(15)	121.3(15)	C(14)-C(15)-C(16)	110.5(15)
C(11)-C(16)-C(15)	114.2(15)		

goes *via* the intermediacy of both $[\text{Ru}_3\text{H}_2(\text{CO})_{10}]$ and $[\text{Ru}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$ 7a and that the reaction sequence in Scheme 3 is essentially the same as that described in Scheme 1.

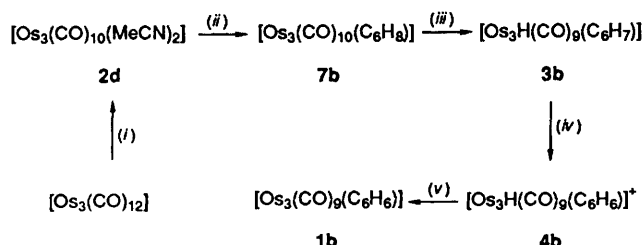
In contrast to these reactions of $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Os}_3(\text{CO})_{12}]$ does not undergo reaction with $\text{Me}_3\text{NO}\cdot\text{CH}_2\text{Cl}_2$ directly, but some reaction does occur in the presence of cyclohexa-1,3-diene to produce small amounts of the 1,3-diene derivative 7b.

Following the sequence established for ruthenium (Scheme 2) we have examined the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ 2d with cyclohexa-1,3-diene. We find that the reaction proceeds smoothly to generate good yields of the cyclohexadiene cluster $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$ 7b. This compound has been fully characterised on the basis of its spectroscopic and analytical data and the structure of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]\cdot\text{MeCN}$ 7c has been confirmed by single crystal X-ray analysis.

Structure of $[\text{Os}_3(\text{CO})_{10}(1,3\text{-C}_6\text{H}_8)]\cdot\text{MeCN}$.—Suitable crystals of compound 7c were grown from toluene solution at 243 K. Due to their tendency to decompose under ambient conditions, transfer to the diffractometer was effected by coating the crystal in a film of mineral oil cooled by dry ice. The molecular structure of compound 7c is depicted in Fig. 1. Relevant structural parameters are given in Table 1.

The compound is characterised by the presence of a 1,3- C_6H_8 fragment η^4 bonded to a single osmium atom at one corner of a triangular metal framework. The three osmium atoms form a regular triangle with a mean Os-Os distance of 2.877(12) Å, which is close to that observed for the parent binary carbonyl $[\text{Os}_3(\text{CO})_{12}]$. However, the significant variation in these distances from 2.865 [Os(1)-Os(2)] to 2.879 Å [Os(2)-Os(3)] should be noted. Two osmium atoms, Os(1) and Os(2), coordinate to four carbonyl ligands and the other, Os(3), coordinates to two carbonyl ligands and the 1,3- C_6H_8 unit. All carbonyl ligands are terminal and approximately linear. The 1,3- C_6H_8 ligand is η^4 co-ordinated to Os(3) *via* atoms C(11)-C(14), donating four electrons in total. Within the 1,3- C_6H_8 moiety the C-C bond distances fall in the range 1.44-1.52 Å, but all are equivalent at the 3σ confidence level.

On heating in octane under reflux cluster 7b is converted to the dienyly cluster 3b in low yield. This may then be readily converted to compound 1b by the process outlined in Schemes 1 and 4. This method offers no significant advantage over the route established previously.^{3,4} The isolation of the key intermediate 7b is, however, of some interest. Recent work on the related chemistry of Ru_5C and Ru_6C has shown that



Scheme 4 Preparation of $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ from $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$: (i) $\text{Me}_3\text{NO}-\text{MeCN}$; (ii) 1,3- C_6H_8 ; (iii) heating with octane under reflux; (iv) Ph_3CBF_4 ; (v) dbu

benzene may adopt terminal- and face-bridging modes. We suspected, on the basis of detailed structural analyses of several of these Ru_5C and Ru_6C derivatives, that the face-bridging mode followed from a precursor in which the cyclohexa-1,3-diene had formed a bridge between two metal atoms, thereby providing an attractive route first to a face-bonded diene- and then to a face-capped arene-unit. In this work it is clear that, at least for M_3 units, this hypothesis is incorrect, since the complex **7b** contains the diene bonded to a single osmium atom.

On the basis of these observations, we believe that the reaction of $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$ with cyclohexa-1,3-diene also proceeds *via* a similar intermediate, *viz.* $[\text{Ru}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$ **7a**, but that it is less stable than the corresponding osmium compound **7b**, first eliminating CO to form the coordinatively unsaturated compound $[\text{Ru}_3(\text{CO})_9(\eta^4\text{-C}_6\text{H}_8)]$ and then undergoing C-H bond cleavage to generate **3a**.

Conclusions

It is clear that the reaction of $\text{Me}_3\text{NO}-\text{CH}_2\text{Cl}_2$ with carbonyl clusters is proving to be an extremely attractive and convenient method of producing highly reactive intermediates in the formation of diene- and arene-cluster complexes. In this work we have been able to establish a highly efficient and surprisingly simple one-stage synthesis of $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$.

Experimental

All reactions were carried out under an atmosphere of nitrogen, using dry, freshly distilled solvents. Subsequent work-up of products was carried out by thin-layer chromatography on plates supplied by Merck, with a 0.25 mm layer of Kieselgel 60F-254. Trimethylamine *N*-oxide was sublimed immediately prior to use.

Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer in CH_2Cl_2 , using NaCl cells (0.5 mm path length). Fast atom bombardment mass spectra were obtained on a Kratos MS50TC using CsI as calibrant and ^1H NMR spectra were recorded in CDCl_3 using a Bruker WP200 instrument calibrated with SiMe_4 .

Preparation of $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3a and $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ **1a**.**—Triruthenium dodecacarbonyl (0.1 g) was dissolved in CH_2Cl_2 (100 cm^3), cyclohexa-1,3-diene (1 cm^3) added and the solution cooled to -78°C . A solution of Me_3NO (38 mg, 3.2 mol equivalent) in CH_2Cl_2 (10 cm^3) was then added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for a further 1 h. The solvent was evaporated *in vacuo* and the products separated by thin-layer chromatography using CH_2Cl_2 -hexane (3:7 v/v) as eluent, resulting in the isolation of $[\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3a** (36%), $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ **1a** (24%) and $[\text{Ru}_3\text{H}(\text{CO})_6(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_7)]$ ($\approx 1\%$).

Conversion of Compound **3a to Compound **1a**.**—Compound **3a** (0.05 g) was dissolved in hexane (100 cm^3) and heated under reflux for 3 h. The solvent was removed *in vacuo* and purification by thin-layer chromatography using CH_2Cl_2 -hexane (3:7 v/v) as eluent afforded $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ (32%)

Table 2 Fractional atomic coordinates with standard deviations for compound **7c**

Atom	x	y	z
Os(1)	0.237 50(7)	0.323 13(4)	0.534 07(4)
Os(2)	0.165 55(7)	0.408 15(4)	0.362 28(4)
Os(3)	0.245 23(7)	0.247 73(4)	0.361 87(4)
C(1)	0.301 4(19)	0.232 9(10)	0.605 2(11)
O(1)	0.337 6(15)	0.174 8(8)	0.642 8(9)
C(2)	0.218 9(20)	0.398 3(10)	0.624 5(12)
O(2)	0.215 7(15)	0.444 6(7)	0.679 0(9)
C(3)	0.452 1(20)	0.354 7(10)	0.546 6(12)
O(3)	0.577 8(15)	0.370 8(7)	0.558 1(9)
C(4)	0.142 8(18)	0.496 0(9)	0.429 7(11)
O(4)	0.135 3(14)	0.549 3(7)	0.475 8(8)
C(5)	0.102 3(18)	0.446 4(9)	0.236 4(11)
O(5)	0.061 1(14)	0.466 7(7)	0.160 1(9)
C(6)	0.390 0(21)	0.431 4(10)	0.371 4(12)
O(6)	0.505 7(16)	0.447 1(8)	0.369 6(9)
C(7)	-0.051 5(20)	0.373 7(10)	0.347 0(11)
O(7)	-0.176 3(14)	0.358 9(7)	0.336 4(8)
C(8)	0.206 7(17)	0.287 1(9)	0.237 8(10)
O(8)	0.190 9(14)	0.298 3(7)	0.161 3(9)
C(9)	0.049 6(19)	0.240 4(10)	0.349 0(12)
O(9)	-0.070 9(15)	0.178 8(7)	0.335 4(9)
C(10)	0.025 4(20)	0.290 0(10)	0.516 5(12)
O(10)	-0.099 2(15)	0.270 4(7)	0.511 2(9)
C(11)	0.309 9(20)	0.140 0(10)	0.303 7(12)
C(12)	0.371 4(20)	0.139 4(10)	0.406 8(12)
C(13)	0.478 3(20)	0.201 3(10)	0.440 9(12)
C(14)	0.509 5(18)	0.252 7(9)	0.367 2(11)
C(15)	0.531 8(20)	0.221 2(10)	0.279 5(12)
C(16)	0.424 7(21)	0.154 4(10)	0.246 6(12)
C(1S)	0.127(4)	-0.016 6(22)	0.542(3)
C(2S)	0.050(5)	0.017(3)	0.581(3)
N(1S)	0.199(6)	-0.057(3)	0.493(3)
N(2S)	-0.051(6)	0.063(3)	0.613(3)

as the major product. Spectroscopic data for compounds **1a** and **3a** are in agreement with the literature values.¹

Preparation of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ **2d.**—Triosmium dodecacarbonyl (0.5 g) was suspended in CH_2Cl_2 (70 cm^3) and MeCN (35 cm^3) and Me_3NO (105 mg, 2.5 mol equivalent) dissolved in MeCN (50 cm^3) was added dropwise over a period of 1 h. The resulting solution was stirred for a further 2 h and then filtered through a short silica column (4 cm) to remove any unreacted Me_3NO . The product was used without further purification.

Preparation of $[\text{Os}_3(\text{CO})_{10}(\eta^4\text{-C}_6\text{H}_8)]$ **7b.**—Compound **2d** (0.45 g) was dissolved in CH_2Cl_2 (100 cm^3) and cyclohexa-1,3-diene (1.5 cm^3) added. The reaction mixture was then stirred for 1 h. The solvent was removed *in vacuo* and purification by thin-layer chromatography using CH_2Cl_2 -hexane (2:3 v/v) as eluent afforded the cluster **7b**, which was then crystallised from toluene (yield 90%). IR (CH_2Cl_2) 2110m, 2060s, 2023s, 2004m and 1975 (sh) cm^{-1} . ^1H NMR (CDCl_3): δ 5.27 (m, 2H), 3.77 (m, 2H) and 1.86 (m, 4H).

Preparation of $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3b.**—The cluster **7b** (0.40 g) was heated in octane (100 cm^3) under reflux at 125°C . After removal of the solvent *in vacuo* the remaining solid residue was extracted into dichloromethane (10 cm^3). After purification by thin-layer chromatography with CH_2Cl_2 -hexane (2:3 v/v) as eluent, the complexes $[\text{Os}_3\text{H}(\text{CO})_9(\text{C}_6\text{H}_7)]$ **3b** ($\approx 5\%$) and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ **2b** ($\approx 5\%$) were obtained. The spectroscopic data for these compounds were identical to the reported values.

X-Ray Structure Determination.—*Crystal data.* $\text{C}_{16}\text{H}_8\text{O}_{10}\text{Os}_3\text{C}_2\text{H}_3\text{N}$, $M = 971.8$, monoclinic, space group $P2_1/n$, $a = 8.932(8)$, $b = 17.387(13)$, $c = 14.833(15)$ Å, $\beta = 105.69(6)^\circ$,

$U = 2218 \text{ \AA}^3$ [from 2θ values of 27 reflections measured at $\pm \omega$ ($2\theta = 25\text{--}30^\circ$, $\lambda = 0.71073 \text{ \AA}$)], $Z = 4$, $D_c = 2.910 \text{ g cm}^{-3}$, $T = 150 \pm 0.1 \text{ K}$, yellow tabular crystal $0.97 \times 0.66 \times 0.39 \text{ mm}$, $\mu = 17.23 \text{ mm}^{-1}$, $F(000) = 1736$.

Data collection and processing. All X-ray measurements were made on a Stöe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,⁷ graphite-monochromated Mo-K α X-radiation, $T = 150 \text{ K}$, ω -2 θ scans, 3013 unique data collected ($2\theta_{\text{max}} 45^\circ$, $h -9$ to 9 , $k 0$ – 18 , $l 0$ – 15), semi-empirical absorption correction⁸ applied (minimum and maximum transmission factors 0.0182 and 0.0568 respectively), giving 2381 reflections with $F \geq 4\sigma(F)$ for use in all calculations. A correction for linear isotropic crystal decay (4.4%) was incorporated in the data reduction.

Structure solution and refinement. The osmium atoms were located by automatic direct methods⁹ and subsequent iterative cycles of least-squares refinement and Fourier difference synthesis located all non-H atoms.¹⁰ At isotropic convergence, final corrections (minimum 0.788, maximum 1.402) for absorption were applied using DIFABS.¹¹ A region of disorder was resolved into two partly-overlapping MeCN solvates, each of which is half-occupied. The Os atoms were then refined (by least-squares on F)¹⁰ with anisotropic thermal parameters, with C and O atoms allowed only isotropic thermal motion. Solvent H atoms were omitted while those of the diene were included at fixed, calculated positions. At final convergence R , $R' = 0.0440$, 0.0557 respectively, $S = 0.970$ for 149 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 2.5 or below -3.0 e \AA^{-3} , the major features lying near the Os atoms. A secondary extinction parameter refined to $9(3) \times 10^{-9}$, the weighting scheme $w^{-1} = \sigma^2(F) + 0.00048 F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{\text{max}}$ was 0.05. Atomic scattering factors were inlaid,¹⁰ or taken from ref. 12. Molecular geometry calculations utilised CALC¹³ and Fig. 1 was produced using SHELXTL PC.¹⁴ Fractional atomic coordinates are reported in Table 2.

Additional material available from the Cambridge Crystallo-

graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond angles.

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