

CATIONIC RUTHENIUM AND OSMIUM SYSTEMS

V *. CATIONIC OSMIUM(II) HYDRAZINE AND HYDRAZONE COMPLEXES DERIVED FROM THE POLYMER $[\text{OsCl}_2(\text{COD})]_x$ (COD = CYCLO-OCTA-1,5-DIENE; $x > 2$). THE CRYSTAL STRUCTURE OF $[\text{Os}(\text{COD})(\text{CNBu}^t)_2(\text{NH}_2\text{N}:\text{CMe}_2)_2][\text{BPh}_4]_2 \cdot (\text{ACETONE})_2$

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Summary

The polymer $[\text{OsCl}_2(\text{COD})]_x$ (1; COD = cycloocta-1,5-diene; $x > 2$) and the appropriate hydrazine have been used to prepare the salts $[\text{OsCl}(\text{COD})(\text{N}_2\text{H}_4)_3][\text{BPh}_4]$ (2), $[\text{Os}(\text{COD})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (3) and $[\text{OsCl}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{PF}_6$ (4). Treatment of 3 with *t*-butyl isocyanide produced *mer*- $[\text{Os}(\text{CNBu}^t)_3(\text{N}_2\text{H}_4)_3][\text{BPh}_4]_2$ (5) and *trans*- $[\text{Os}(\text{CNBu}^t)_4(\text{N}_2\text{H}_4)_2][\text{BPh}_4]_2$ (6) from refluxing ethanol and the hydrazone complex $[\text{Os}(\text{COD})(\text{CNBu}^t)_2(\text{NH}_2\text{N}:\text{CMe}_2)_2][\text{BPh}_4]_2$ (7) from refluxing acetone. Reactions of 3 and L {L = CNxylyl, P(OMe)₃, and P(OMe)₂Ph; xylyl = 2,6-dimethylphenyl} in acetone gave *trans*- $[\text{Os}(\text{NH}_2\text{N}:\text{CMe}_2)_2\text{L}_4][\text{BPh}_4]_2$ (8). The crystal structure of $[\text{Os}(\text{COD})(\text{CNBu}^t)_2(\text{NH}_2\text{N}:\text{CMe}_2)_2][\text{BPh}_4]_2 \cdot (\text{Acetone})_2$ (7) has been determined from three-dimensional X-ray counter data and refined to a final *R* (on *F*) of 0.090 based on 3014 reflections. The compound crystallizes in the monoclinic space group *C2/c* with four formula units in a cell of dimensions *a* 24.60(2), *b* 13.31(1), *c* 24.12(2) Å and β 111.51(2)°. The cation has a crystallographically imposed *C*₂ symmetry, with octahedral coordination of the osmium atom, assuming that the COD ligand occupies two adjacent coordination sites. Coordination of the mutually *trans* hydrazone ligands to the osmium atom is through the amino-N atoms rather than through the less basic, more sterically hindered, imino-N

* Part IV. T.V. Ashworth, R.H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, (1978) 1036.

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atoms. Relevant bond distances are: Os–N 2.19(2) (mean), Os–C(COD) 2.19(2) and 2.29(2), and Os–C(isocyanide) 1.93(2) (mean) Å.

Introduction

Considering the large number of transition metal hydrazine compounds that are known, it is surprising that only two osmium hydrazine complexes have been prepared [1,2]. We have been investigating [3] the preparation and reactivity of the ruthenium hydrazine complexes, $[\text{Ru}(\text{COD})(\text{NH}_2\text{NR}_2)_4]\text{X}_2$ ($\text{R} = \text{H}$, $\text{X} = \text{BPh}_4$; $\text{R} = \text{Me}$, $\text{X} = \text{PF}_6$) and $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{PF}_6$ from the insoluble polymer $[\text{RuCl}_2(\text{COD})]_x$ ($x > 2$). In solution these salts react like highly unsaturated ruthenium-diene and ruthenium-diene hydride species due to the lability of the hydrazine ligands. This has led to a range of cationic ruthenium(II) complexes by simple substitution reactions [4,5]. In view of the stability, ease of preparation, and reactivity of the ruthenium cations, we have now investigated the interactions of the osmium polymer $[\text{OsCl}_2(\text{COD})]_x$ ($x > 2$) with hydrazines. Our aims were threefold: (1) To develop a simple and general route to cationic organo-osmium(II) systems, few of which are known [6]; (2) To extend the limited range of osmium hydrazine complexes known [1,2] and, (3) To continue our investigations into the formation and stability of metal-hydrazone complexes [3,7,8], none of which are known for osmium(II).

We report here the first part of this study, namely the preparation of diene-osmium hydrazine salts, their characterization together with IR and ^1H NMR data, and some conversions to osmium-hydrazine and -hydrazone compounds. As part of our investigations of the factors governing the stability of metal hydrazone complexes the crystal structure of $[\text{Os}(\text{COD})(\text{CNBu}^t)_2(\text{NH}_2\text{N}:\text{CMe}_2)_2][\text{BPh}_4]_2 \cdot (\text{acetone})_2$ has been elucidated.

Results and discussion

Hydrazine complexes

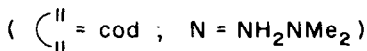
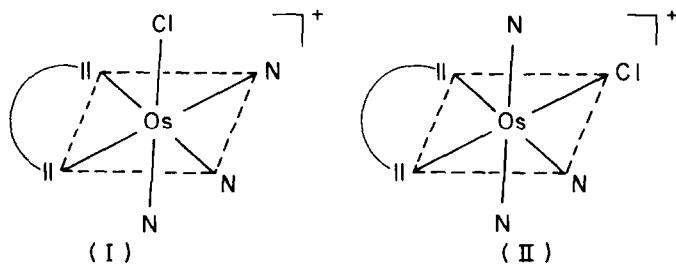
Stirring a suspension of $[\text{OsCl}_2(\text{COD})]_x$ (**1**; COD = cycloocta-1,5-diene) in methanol at room temperature for 20 min with anhydrous hydrazine gave a pale yellow solution from which the pale-yellow salt $[\text{OsCl}(\text{COD})(\text{N}_2\text{H}_4)_3][\text{BPh}_4]$ (**2**) precipitated on addition of NaBPh_4 in methanol. When the above reaction is performed in boiling methanol, the second chloride is labilized, and additions of methanolic NaBPh_4 to the reddish-yellow solution produced the cream product $[\text{Os}(\text{COD})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (**3**). Tetraphenylborate was the only counter anion that effected precipitation and attempts to isolate the cations of **2** and **3** with other anions, e.g. $[\text{PF}_6]^-$ and $[\text{BF}_4]^-$, were unsuccessful. Corresponding reactions of **1** with *N,N*-dimethylhydrazine in refluxing methanol produced only $[\text{OsCl}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{PF}_6$ (**4**) on addition of an aqueous solution of NH_4PF_6 . Attempts to labilize the chloride in **4**, or to convert it to the hydride corresponding to $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{PF}_6$ have so far failed. The chloride in **2** does, however, readily convert to a hydride in refluxing acetone-ethanol mixtures with a range of tertiary phosphorus ligands. This has led to a facile synthesis of a series of new osmium hydride salts [9].

The salts **2–4** are reasonably stable in air and light over a period of ca. 1 week, but for prolonged storage are best kept under an inert atmosphere in the dark.

The IR spectra of complexes **2–4** have characteristic bands in the regions 3120–3340 [$\nu(\text{N-H})$], 1600–1610 (asymmetric N–H bending), 1135–1165 (symmetric N–H bending) and 920–940 cm^{-1} [$\nu(\text{N-N})$]. The low frequencies observed for $\nu(\text{N-N})$ are in the region characteristic for unidentate hydrazine ligands [3].

Complexes **2–4** only had a reasonable solubility in acetone- d_6 . The ^1H NMR spectra for these salts consisted of broad ill-defined multiplets in the region 1.5 to 4.8 ppm for the hydrazine and COD ligands, and a resonance at 3.12 ppm which increased with time. This latter resonance was attributed to water formed from the condensation of acetone- d_6 with hydrazine, and these exchanges could account for the poor resolution observed in the ^1H NMR spectra of these complexes. Also proton resonances for hydrogen atoms attached to nitrogen atoms are notoriously difficult to observe due to broadening effects of the ^{14}N nuclear quadrupole moment [10]. The resonances attributable to the methyl groups in **4** were observed at 2.65 and 2.86 ppm in the ratio of 2/1. The ^{13}C NMR spectra for complexes **2–4** in acetone- d_6 gave large numbers of lines for the COD ligand as a result of the condensation process.

On the evidence available it was thus not possible to distinguish between the two possible isomers for **2** and **4** namely I and II.



Other hydrazine complexes readily form from **2** and **3** by substitution reactions in refluxing ethanol. In the majority of cases, however, mixtures resulted which were difficult to separate. With *t*-butyl isocyanide as a ligand, it was possible to separate the products *mer*- $[\text{Os}(\text{CNBu}^t)_3(\text{N}_2\text{H}_4)_3][\text{BPh}_4]_2$ (**5**) and *trans*- $[\text{Os}(\text{CNBu}^t)_4(\text{N}_2\text{H}_4)_2][\text{BPh}_4]_2$ (**6**) from reactions with **3**, by fractional crystallization.

The IR spectra of **5** and **6** were comparable with $[\text{Ru}(\text{CNBu}^t)_x(\text{N}_2\text{H}_4)_{6-x}][\text{BPh}_4]_2$ ($x = 3$ and 4) [8] in that they contained $\nu(\text{N-H})$, $\delta(\text{N-H})$ and $\nu(\text{N-N})$ vibrational frequencies between 3170–3360, at 1600, and between 920–925 cm^{-1} , respectively. The *mer*- and *trans*-configurations for **5** and **6** were assigned on the basis of the two singlets at 1.52 and 1.55 ppm (ratio 1/2) and the singlet at 1.50 ppm respectively, observed for the butyl methyl resonances in their ^1H NMR spectra. The broad resonances at 3.00 and 6.07 ppm for **5** and 3.60 and 5.93 ppm for **6** were ascribed to the amino protons in these complexes.

Hydrazone complexes

Treatment of the osmium hydrazine salt **3** in refluxing acetone for 19 h with a six molar excess of CNBu^t gave the white crystalline complex $[\text{Os}(\text{COD})-$

(CNBu^t)₂(NH₂N : CMe₂)₂[[BPh₄]₂ · (acetone)₂ (**7**) on addition of ethanol. Recrystallizations of this complex from a variety of solvents resulted in solvent inclusion, of varying degrees, in all cases. With acetone-ethanol mixtures the salt crystallized consistently with two molar equivalents of acetone, allowing reproducible analytical data to be obtained. When reactions of **3** were performed with 2,6-dimethylphenyl isocyanide (xylyl isocyanide), P(OMe)₃, and P(OMe)₂Ph in refluxing acetone, the osmium hydrazones, *trans*-[Os(NH₂N : CMe₂)₂L₄][BPh₄]₂ (**8**; L = CNxylyl, P(OMe)₃, and P(OMe)₂Ph), precipitate from solution on addition of ethanol.

The IR spectra of **7** and **8** contain characteristic azomethine bands of medium intensity in the region 1650–1665, and N–H stretching vibrations between 3160–3300 cm⁻¹. In all cases the asymmetric N–H bending vibrations are obscured by [BPh₄]⁻ vibrational bands. Strong isocyanide stretching vibrations were observed between 2130 and 2210 cm⁻¹, which are in the region typical of terminal isocyanide ligands.

No useful information was obtained from the NH and COD resonances in the ¹H NMR spectra of **7** and **8**, which appeared as broad resonances in the usual region (Table 2). The methyl groups in the t-butyl isocyanide ligands in **7** appeared as a singlet at 1.60 ppm, as expected for a *trans*-disposition of isocyanide ligands. The two singlets at 2.19 and 2.22 ppm were assigned to asymmetrical methyl groups on the two magnetically equivalent hydrazone ligands. Pairs of singlets for the azomethine methyls were also observed for the *trans*-bis(hydrazone) complex **8** at 1.88 and 2.10 ppm (L = CNxylyl), 1.93 and 2.02 ppm {L = P(OMe)₃}, and 1.90 and 2.08 ppm {L = P(OMe)₂Ph}. The xylyl methyl ¹H resonances in **8** (L = CNxylyl) appeared as a singlet at 2.63 ppm, whereas the phosphite and phosphonite methyl resonances in **8** (L = P(OMe)₃ and P(OMe)₂Ph) formed the characteristic pattern at 3.96 and 3.46 ppm respectively, for an equatorial planar arrangement of ligands [11].

It was previously found that solutions of [Ru(COD)(N₂H₄)₄][BPh₄]₂ react rapidly with phosphites or phosphonites to form the bis(hydrazone) salts *trans*-[Ru(NH₂N : CMe₂)₂L₄][BPh₄]₂ {L = P(OMe)₃, P[(OCH₂)₃CMe], P[(OCH₂)₃CEt], P(OEt)₃, and P(OMe)₂Ph} in high yields [3]. These hydrazone complexes were found to be exceedingly stable in solution and practically inert to further reactions under reasonable conditions, which was unusual considering the instability of the few known transition metal hydrazone complexes.

From the X-ray crystal structure of [Ru(NH₂N : CMe₂)₂(P(OMe)₃)₄][BPh₄]₂ it was inferred [7] that the inertness to further substitution in these complexes is attributable to strong hydrogen bonding occurring between the amino hydrogen atoms and the phosphite or phosphonite oxygen atoms. The later preparation of the kinetically inert salts *trans*-[Ru(CNR)₄(NH₂N : CMe₂)₂][BPh₄]₂ (R = Bu^t, C₆H₁₁, CH₂Ph, xylyl) [8], in which hydrogen bonding is improbable, cast doubt on the stabilizing effect of this bonding on the inertness to further substitution of the hydrazone complexes. No comparative X-ray structural data is available, however, on the ruthenium-isocyanide hydrazone complexes. It was thus decided to determine the X-ray structure of **7** to confirm the absence of any hydrogen bonding in the complex.

Crystals of [Os(COD)(CNBu^t)₂(NH₂N : CMe₂)₂][BPh₄]₂ · (acetone)₂ (**7**) consist of discrete cations, anions and solvent molecules, separated by distances which approximate to the sum of the Van der Waals radii for the atoms concerned. Bonding parameters for the tetraphenylborate anion, and for the acetone molecule, are normal and require no comment.

The cation has a crystallographically imposed C_2 symmetry. The osmium atom is octahedral with the cycloocta-1,5-diene ligand occupying two coordination sites (Table 4(a)). The hydrazone ligands are mutually *trans* and bonding to the metal atom is through the amino N atoms i.e., further confirmation is provided for a previous suggestion [15] that when imino- and amino-nitrogens compete for the coordination site an amino-linkage is favoured by: (i) a more sterically crowded octahedral or seven-coordinate metal environment; and (ii) the presence of an unsubstituted amino-nitrogen. The isocyanide ligands are *cis* to one another and, as expected, bond to the Os atom through the lone pair on the C atom. In contrast to observations made on the ruthenium-hydrazone compound $[\text{Ru}(\text{NH}_2\text{N}:\text{CMe}_2)_2\{\text{P}(\text{OMe})_3\}_4][\text{BPh}_4]_2$ [7], the cation is not stabilized through H-bonding involving the amino-N atom of a hydrazone ligand e.g., $\text{N}(1) \cdots \text{N}(3)$ 3.83 Å [16].

The metal– NH_2 distances, the metal–N–N angles, and the N–N distances for the $\text{NH}_2\text{N}:\text{CMe}_2$ ligands in complexes whose structures have been determined, are respectively: 2.17 Å, 119°, and 1.46 Å in $[\text{Ru}(\text{NH}_2\text{N}:\text{CMe}_2)_2\{\text{P}(\text{OMe})_3\}_4]^{2+}$ [7]; and 2.27 Å, 112°, and 1.47 Å in $[\text{W}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{NH}_2\text{N}:\text{CMe}_2)]^+$ [15]. Differences in the covalent radii of the metal atoms ($\text{Os} \approx \text{Ru} < \text{W}$) [17] appear to account for the variation of M–N distances, but the variation of M–N–N angles is difficult to explain. Possibly the large M–N–N angle observed for the Ru cation is associated with the intramolecular H-bonding which occurs in this complex. The N–N distance of 1.51 Å for the Os cation is unexplainably long, and certainly falls outside the range of 1.45–1.48 Å reported [1] for N–N bond lengths in complexes containing either unidentate or bridging NH_2NH_2 ligands. Other bonding parameters for the acetone-hydrazone ligands in these complexes compare favourably.

The COD ring has the usual conformation of the four doubly-bonded C atoms within bonding distance of Os (2.29–2.33 Å) and the remaining four C atoms at non-bonding distances (3.22–3.29 Å). C–C bond lengths average 1.46 and 1.58 Å for double and single bonds respectively. Details of the *t*-butyl isocyanide ligand are unexceptional. The sequence of lengths Os–C(4), C(4)–N(3), and N(3)–C(5) is 1.93, 1.19 and 1.52 Å respectively, with angles at the N and C of 173 and 167°.

Experimental

The polymer $[\text{OsCl}_2(\text{COD})]_x$ (1), was prepared as described previously [18]. Hydrazine and methylhydrazine were obtained commercially and were not further purified. All reactions were performed in air. Melting points were obtained on a Kofler hot-stage apparatus and were corrected. Infrared spectra were recorded as Nujol mulls using a Perkin–Elmer model 457 grating spectrophotometer. ^1H NMR spectra were recorded on a Varian EM 390 instrument. Microanalyses were carried out in the NCRL laboratory. Physical and spectroscopic data for the complexes are presented in Tables 1 and 2.

Preparations

Chloro(η^4 -cycloocta-1,5-diene)tris(hydrazine)osmium(II) tetraphenylborate (2)

The complex $[\text{OsCl}_2(\text{COD})]_x$ (1.8 g, 5 mmol) was suspended in methanol (25 ml) and an excess of anhydrous hydrazine (95%, 5 ml, 158 mmol) was added. The suspension was stirred for 1.5 h at room temperature, water (10 ml) then added and

(Continued on p. 440)

TABLE 1
PHYSICAL AND ANALYTICAL DATA FOR THE COMPLEXES

Complex	M.p. ^a (°C)	Analyses (%) ^b		Infrared data (cm ⁻¹) ^c			$\nu(\text{C}\equiv\text{N})$
		C	H	N	$\nu(\text{NH})$	$\delta(\text{NH})$	
					<i>asym</i>	<i>sym</i>	
[OsCl(COD)(N ₂ H ₄) ₃][BPh ₄] ² (2) ^g	155-160	51.54 (51.30)	5.78 (5.92)	11.00 (11.22)	3160- 3330	1610	925, 940
[Os(COD)(N ₂ H ₄) ₄][BPh ₄] ₂ (3)	123-125	63.06 (63.15)	6.88 (6.44)	9.65 (10.52)	3260, 3340	1600	925
[OsCl(COD)(NH ₂ NMe ₂) ₃][PF ₆] ⁴ (4) ^h	120-122	25.63 (25.51)	5.60 (5.51)	12.59 (12.75)	3120, 3170, 3270	1605	920
<i>mer</i> -[Os(CNBu ^t) ₃ (N ₂ H ₄) ₃][BPh ₄] ₂ (5)	> 188 ^d	64.69 (64.44)	6.69 (6.78)	10.13 (10.74)	3280, 3330, 3360	1600	925
<i>trans</i> -[Os(CNBu ^t) ₄ (N ₂ H ₄) ₂][BPh ₄] ₂ (6)	175-180	66.34 (66.66)	6.58 (6.91)	8.91 (9.15)	3170, 3220, 3270	1600	920
[Os(COD)(CNBu ^t) ₂ (NH ₂ N:CMc ₂) ₂][BPh ₄] ₂ (7)	120-122	68.41 (68.71)	7.37 (7.20)	6.20 ^e (6.16)	3250, 3290	/	915
[Os(NH ₂ N:CMc ₂) ₂ L ₄][BPh ₄] ₂ (8) L = CNxylyl	165-175	71.03 (71.45)	6.42 (6.50)	6.84 ^e (6.94)	3160, 3210, 3240	/	925
L = P(OMe) ₃	155-157	53.71 (53.96)	6.55 (6.31)	3.90 (3.81)	3160 3230, 3270	/	915
L = P(OMe) ₂ Ph	> 179 ^d	62.33 (62.47)	6.34 (6.10)	3.26 (3.39)	3240 3300	/	925

^a In air. ^b Calculated values in parenthesis. Additional analyses are given below C, H, N values. ^c Nujol mulls. $\nu(\text{NH})$, $\delta(\text{NH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{NN})$ frequencies are weak. $\nu(\text{C}\equiv\text{N})$ frequencies are strong. Vibrations due to BPh₄⁻ and PF₆⁻ anion observed at 710, 735 and 750 cm⁻¹ and 840 cm⁻¹, respectively. ^d Decompose without melting. ^e C, H and N values calculated with two moles of acetone of crystallization. ^f Not observed, possibly obscured by band at 1580 cm⁻¹ due to BPh₄⁻ anion. ^g Found: Cl, 4.51; calcd.: 4.73%. ^h Found: Cl, 5.36; calcd.: 5.38%.

TABLE 2
¹H NMR DATA FOR THE COMPLEXES

Complexes	¹ H NMR data (ppm) ^a
[OsCl(COD)(N ₂ H ₄) ₃][BPh ₄] ⁽²⁾	1.9–4.3 (br. m, 24H, NH ₂ 's and COD); 6.6–7.5 (m, 20H, Ph)
[Os(COD)(N ₂ H ₄) ₄][BPh ₄] ₂ ⁽³⁾	1.5–4.8 (br. m, 28H, NH ₂ 's and COD); 6.6–7.5 (m, 40H, Ph)
[OsCl(COD)(NH ₂ NMe ₂) ₃][PF ₆] ⁽⁴⁾	1.0–6.0 (br. m, 18H, NH ₂ 's and COD); 2.65 (s, 12H, NMe ₂); 2.86 (s, 6H, NMe ₂)
<i>mer</i> -[Os(CNBu ^t) ₃ (N ₂ H ₄) ₃][BPh ₄] ₂ ⁽⁵⁾	1.52 (s, 9H, Bu ^t); 1.55 (s, 18H, Bu ^t); 3.00 (br. s, 6H, NH ₂); 6.07 (br. s, 6H, NH ₂); 6.7–7.5 (m, 40H, Ph)
<i>trans</i> -[Os(CNBu ^t) ₄ (N ₂ H ₄) ₂][BPh ₄] ₂ ⁽⁶⁾	1.50 (s, 36H, Bu ^t); 3.60 (br. s, 4H, NH ₂); 5.93 (br. s, 4H, NH ₂); 6.7–7.5 (m, 40H, Ph)
[Os(COD)(CNBu ^t) ₂ (NH ₂ N: CMe ₂) ₂][BPh ₄] ₂ ⁽⁷⁾	1.60 (s, 18H, Bu ^t); 2.19 (s, 6H, =CMe ₂); 2.22 (s, 6H, =CMe ₂); 2.53 and 5.42 (br. m, 16H, NH ₂ and COD); 6.7–7.6 (m, 40H, Ph)
[Os(NH ₂ N: CMe ₂) ₂ L ₄][BPh ₄] ₂ ⁽⁸⁾ L = CNxylyl	1.88 (s, 6H, =CMe ₂); 2.10 (s, 6H, =CMe ₂); 2.63 (s, 24H, Me); 6.7–7.5 (2 br. m, 52H, Ph); 8.21 (br. s, 4H, NH ₂)
L = P(OMe) ₃	1.93 (s, 6H, =CMe ₂); 2.02 (s, 6H, =CMe ₂); 3.96 (m, 36H, P(OMe) ₃); 6.40 (br. s, 4H, NH ₂); 6.77 (t), 6.91 (t) and 7.31–7.34 (br. m) (all 40H, Ph)
L = P(OMe) ₂ Ph	1.90 (s, 6H, =CMe ₂); 2.08 (s, 6H, =CMe ₂); 3.46 (m, 24H, P(OMe) ₂); 6.7–7.7 (m and Br. s, 64H, Ph and NH ₂)

^a Relative to TMS. Solvent acetone-*d*₆. s = singlet, br. s = broad singlet, m = multiplet, br. m = broad multiplet.

after a further 20 min stirring, the mixture was filtered. Addition of a filtered solution of Na[BPh₄] (4.1 g, 12 mmol) in methanol (25 ml) to the yellow filtrate produced an immediate yellow precipitate. Filtering and washing the precipitate with water (10 ml), ice-cold ethanol (3 ml) and pentane (5 ml) produced a yield (1.7 g, 2.3 mmol, 46%) of the analytically pure product after vacuum drying. Recrystallization can be effected from an acetone/ethanol solution in the cold to give the product as a yellow powder.

(η⁴-Cycloocta-1,5-diene)tetrakis(hydrazine)osmium(II) bis(tetraphenylborate) (3)

An excess of anhydrous hydrazine (95%, 10 ml, 316 mmol) was added to a suspension of [OsCl₂(COD)]₂ (2.6 g, 7 mmol) in methanol (50 ml) and the suspension was boiled on a steambath for 5 min. Water (10 ml) was then added and the solution was boiled for a further 10 min, and filtered. Addition of a filtered solution of Na[BPh₄] (5.0 g, 15 mmol) in methanol (25 ml) and cooling to 0 °C gave the product as a cream precipitate, which on recrystallization from acetone/ethanol/ether mixtures gave the product as cream prisms (4.4 g, 4 mmol, 57%).

Chloro(η⁴-cycloocta-1,5-diene)tris(N,N-dimethylhydrazine)osmium(II) hexafluorophosphate (4)

A large excess of anhydrous *N,N*-dimethylhydrazine (79%, 25 ml, 329 mmol) and water (7 ml) were added to a suspension of [OsCl₂(COD)]₂ (3.3 g, 9 mmol) in methanol (25 ml). Boiling the suspension for 30 min produced a dark colored solution, from which a cream powder precipitated (2.0 g, 3 mmol, 33%) after addition of a solution of NH₄[PF₆] (3 g, 18 mmol) in water (25 ml). The product so obtained was analytically pure.

mer-Tris(t-butyl isocyanide)tris(hydrazine)osmium(II) bis(tetraphenylborate) (5)

t-Butyl isocyanide (0.8 g, 9.6 mmol) was added to a suspension of [Os(COD)(N₂H₄)₄][BPh₄]₂ (3) (1.6 g, 1.5 mmol) in ethanol (30 ml) and the mixture was refluxed for 19 h. Cooling to 0 °C gave the product as a white powder which on recrystallization from a dichloromethane/ethanol solution gave the product as white prisms (0.35 g, 0.3 mmol, 20%).

trans-Tetrakis(t-butyl isocyanide)bis(hydrazine)osmium(II) bis(tetraphenylborate) (6)

The complex precipitated from the mother liquor of 4 as white prisms (0.06 g, 0.05 mmol, 3%).

Bis(acetone hydrazone)bis(t-butyl isocyanide)(η⁴-cycloocta-1,5-diene)osmium(II) bis(tetraphenylborate) (7)

An acetone solution (30 ml) of [Os(COD)(N₂H₄)₄][BPh₄]₂ (3) (2.5 g, 2.4 mmol) and *t*-butyl isocyanide (1.2 g, 14.5 mmol) was heated under reflux for 19 h. Ethanol (20 ml) was then added, and the acetone removed under reduced pressure till a white precipitate formed. The product was recrystallized from acetone and ethanol as white prisms containing two moles of acetone of crystallization (1.7 g, 1.4 mmol, 58%).

Bis(acetone hydrazone)tetrakis(xylyl isocyanide)osmium(II) bis(tetraphenylborate) (8)
 $[\text{Os}(\text{COD})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (**2**) (0.5 g, 0.5 mmol) and xylyl isocyanide (0.5 g, 3.8 mmol) were dissolved in a 1/1 mixture of acetone and ethanol (20 ml) and the mixture was refluxed overnight. Evaporation of the acetone and addition of ether gave the required product as a fine, white powder. Recrystallization from an acetone/ethanol mixture gave the product as white prisms containing two moles of acetone of crystallization (0.1 g, 0.1 mol, 20%).

Bis(acetone hydrazone)tetrakis(trimethoxyphosphine)osmium(II) bis(tetraphenylborate) (8)

Trimethoxyphosphine (0.5 g, 4 mmol) was added to an acetone (20 ml) solution of $[\text{Os}(\text{COD})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (**2**) (0.5 g, 0.5 mmol) and the mixture was refluxed for 24 h. Ethanol (20 ml) was added to the reddish-black solution and the acetone was removed under reduced pressure until a white precipitate formed. Complete precipitation was afforded by cooling the solution to 0 °C. The precipitate was filtered and recrystallized from an acetone/ethanol solution to give a white powder (0.3 g, 0.2 mmol, 40%).

Bis(acetone hydrazone)tetrakis(dimethoxyphenylphosphine)osmium(II) bis(tetraphenylborate) (8)

This compound was prepared in a similar way to **8** ($\text{L} = \text{P}(\text{OMe})_3$) as a white powder (0.1 g, 0.05 mmol, 10%).

Crystal data

$[\text{Os}(\text{COD})(\text{CNBu}^1)_2(\text{NH}_2\text{N} : \text{CMe}_2)_2][\text{BPh}_4]_2 \cdot (\text{acetone})_2$ (**7**), $M = 1363.4$, Monoclinic, space group $C2/c$, a 24.60(2), b 13.31(1), c 24.12(2) Å, β 111.51(2)°, $U = 7347.6$ Å³, D_m (by flotation) 1.29, $Z = 4$, D_c 1.23 g cm⁻³, $F(000) = 2816$, Mo- K_α radiation, λ 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ 14.9 cm⁻¹

Colourless platelets of the complex were obtained by crystallization from acetone/ethanol mixtures. The crystals, which slowly collapsed to a powder in air on loss of solvent molecules, were mounted in 0.5 mm Lindemann tubes. A crystal of dimensions 0.43 × 0.36 × 0.09 mm was used for data collection on the Philips PW 1100 four-circle diffractometer at the NPRL, CSIR. Intensity measurements (graphite-monochromatized Mo- K_α radiation) were based on the ω - 2θ scan routine, in the range θ 3–20°. Each reflection was scanned for 30 s and the same time was spent on the background count. 3014-reflections out of 3957 were considered observed on the basis of $I > 3\sigma(I)$. Standard reflections, remeasured every hour, showed no significant variation during the total time of data collection. Corrections were made for Lorentz and polarisation effects but not for extinction or absorption.

Structure solution and refinement

The space group was assumed to be $C2/c$ (rather than Cc), and nothing occurred during solution and refinement to suggest otherwise. Solution of the Patterson function located the Os atom on a crystallographic 2-fold axis. Subsequent electron-difference syntheses revealed the positions of the remaining non-hydrogen atoms. Refinement was carried out using the full-matrix least-squares method, with anisotropic thermal parameters for Os, and individual isotropic thermal parameters for O, N, B, and C (the phenyl C atoms were assigned a common isotropic temperature

(Continued on p. 445)

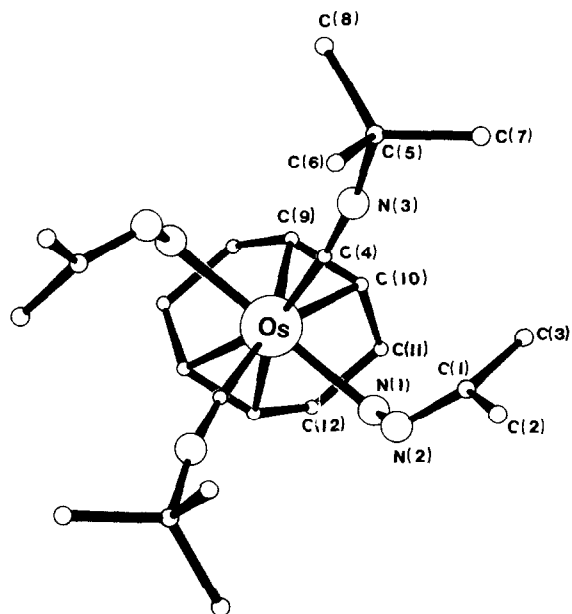


Fig. 1. The cation, viewed down its crystallographically imposed 2-fold axis.

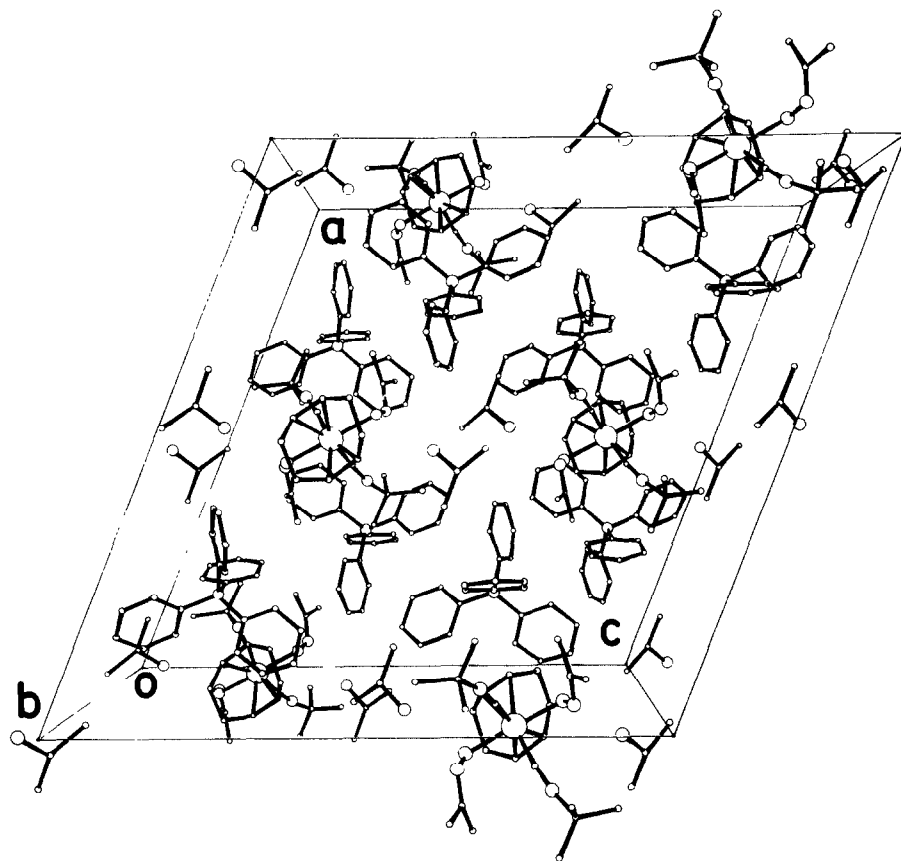


Fig. 2. The unit-cell contents viewed down the *b* axis.

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
<i>(a) [Os(COD)(CNBu^t)₂(NH₂N:CMe₂)₂]²⁺</i>			
Os	0	1191(1)	2500
N(1)	445(6)	1006(12)	1869(7)
N(2)	542(8)	-98(14)	1784(8)
C(1)	1078(10)	-445(17)	2060(10)
C(2)	1148(11)	-1583(20)	1906(12)
C(3)	1614(9)	141(17)	2418(10)
C(4)	518(8)	197(14)	3003(8)
N(3)	834(7)	-362(13)	3361(8)
C(5)	1114(10)	-1191(20)	3810(10)
C(6)	748(15)	-2157(27)	3572(15)
C(7)	1751(17)	-1401(31)	3792(13)
C(8)	997(18)	-899(33)	4414(20)
C(9)	381(9)	2452(15)	3179(9)
C(10)	742(9)	2389(16)	2818(9)
C(11)	720(9)	3104(16)	2325(9)
C(12)	49(9)	3342(17)	1851(10)
<i>(b) [BPh₄]⁻</i>			
B	2006(10)	5093(18)	3529(10)
C(A1)	1537(11)	5403(18)	2840(11)
C(A2)	1736(10)	5295(18)	2370(11)
C(A3)	1332(11)	5455(18)	1742(11)
C(A4)	738(11)	5731(18)	1641(11)
C(A5)	567(10)	5895(18)	2120(11)
C(A6)	961(11)	5715(18)	2734(11)
C(B1)	2620(11)	5778(19)	3638(11)
C(B2)	3174(11)	5341(18)	4021(11)
C(B3)	3703(10)	5982(19)	4114(10)
C(B4)	3648(11)	6944(19)	3877(11)
C(B5)	3087(11)	7365(19)	3506(10)
C(B6)	2569(11)	6781(19)	3397(10)
C(C1)	2166(10)	3876(20)	3589(11)
C(C2)	2245(10)	3377(18)	3100(11)
C(C3)	2436(10)	2303(19)	3190(11)
C(C4)	2485(10)	1790(18)	3713(11)
C(C5)	2379(10)	2289(19)	4182(11)
C(C6)	2199(10)	3378(18)	4101(11)
C(D1)	1753(11)	5425(18)	4048(11)
C(D2)	1214(10)	4894(18)	4028(11)
C(D3)	980(10)	5166(18)	4480(11)
C(D4)	1264(10)	5862(18)	4950(10)
C(D5)	1805(10)	6331(19)	4965(10)
C(D6)	2038(9)	6157(20)	4520(10)
<i>(c) Acetone</i>			
O(1)	228(11)	1627(19)	4386(12)
C(13)	617(32)	2137(51)	4956(31)
C(14)	1256(31)	2261(49)	4927(27)
C(15)	197(37)	2800(67)	5284(36)

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES ^{a,b}(a) [Os(COD)(CNBu')₂(NH₂N.CMe₂)₂]²⁺

Os–N(1)	2.19(2)	C(4)–N(3)	1.19(2)
Os–C(4)	1.93(2)	N(3)–C(5)	1.52(3)
Os–C(9,10)	2.19(2)	C(5)–C(6)	1.55(4)
Os–C(9)	2.29(2)	C(5)–C(7)	1.61(4)
N(1)–N(2)	1.51(2)	C(9)–C(10)	1.46(3)
N(2)–C(1)	1.32(2)	C(10)–C(11)	1.51(3)
C(1)–C(2)	1.58(3)	C(11)–C(12)	1.66(3)
C(1)–C(3)	1.50(3)	C(12)–C(9')	1.57(3)
N(1)–Os–N(1')	167(1)	Os–C(4)–N(3)	173(2)
N(1)–Os–C(4)	89(1)	C(4)–N(3)–C(5)	167(2)
N(1)–Os–C(4')	83(1)	N(3)–C(5)–C(6)	107(2)
N(1)–Os–C(9,10)	95(1)	N(3)–C(5)–C(7)	107(2)
N(1)–Os–C(9',10')	95(1)	N(3)–C(5)–8(8)	106(2)
C(4)–Os–C(4')	93(1)	C(6)–C(5)–(7)	107(3)
C(4)–Os–C(9,10)	92(1)	C(6)–C(5)–C(8)	105(3)
C(4)–Os–C(9',10')	175(1)	C(7)–C(5)–C(8)	124(3)
C(9,10)–Os–C(9',10')	84(1)	C(12')–C(9)–C(10)	124(2)
Os–N(1)–N(2)	110(1)	C(9)–C(10)–C(11)	126(2)
N(1)–N(2)–C(1)	117(2)	C(10)–C(11)–C(12)	114(2)
N(2)–C(1)–C(2)	113(2)	C(11)–C(12)–C(9')	112(2)
N(2)–C(1)–C(3)	128(2)		
C(2)–C(1)–C(3)	119(2)		

(b) [BPh₄][−]

B–C(A1)	1.69(3)	C(B5)–C(B6)	1.43(3)
B–C(B1)	1.70(3)	C(B6)–C(B1)	1.44(3)
B–C(C1)	1.66(3)	C(C1)–C(C2)	1.43(3)
B–C(D1)	1.65(3)	C(C2)–C(C3)	1.50(3)
C(A1)–C(A2)	1.40(3)	C(C3)–C(C4)	1.40(3)
C(A2)–C(A3)	1.49(3)	C(C4)–C(C5)	1.41(3)
C(A3)–C(A4)	1.44(3)	C(C5)–C(C6)	1.51(3)
C(A4)–C(A5)	1.39(3)	C(C6)–C(C1)	1.39(3)
C(A5)–C(A6)	1.46(3)	C(D1)–C(D2)	1.49(3)
C(A6)–C(A1)	1.41(3)	C(D2)–C(D3)	1.45(3)
C(B1)–C(B2)	1.46(3)	C(D3)–C(D4)	1.43(3)
C(B2)–C(B3)	1.50(3)	C(D4)–C(D5)	1.46(3)
C(B3)–C(B4)	1.39(3)	C(D5)–C(D6)	1.41(3)
C(B4)–C(B5)	1.45(3)	C(D6)–C(D1)	1.47(3)
C(A1)–B–C(B1)	106(2)	C(B3)–C(B4)–C(B5)	122(2)
C(A1)–B–C(C1)	112(2)	C(B4)–C(B5)–C(B6)	119(2)
C(A1)–B–C(D1)	112(2)	C(B5)–C(B6)–C(B1)	119(2)
C(B1)–B–C(C1)	110(2)	C(C6)–C(C1)–C(C2)	122(2)
C(B1)–B–C(D1)	108(2)	C(C1)–C(C2)–C(C3)	117(2)
C(C1)–B–C(D1)	110(2)	C(C2)–C(C3)–C(C4)	121(2)
C(A6)–C(A1)–C(A2)	121(2)	C(C3)–C(C4)–C(C5)	121(2)
C(A1)–C(A2)–C(A3)	121(2)	C(C4)–C(C5)–C(C6)	119(2)
C(A2)–C(A3)–C(A4)	118(2)	C(C5)–C(C6)–C(C1)	120(2)
C(A3)–C(A4)–C(A5)	120(2)	C(D6)–C(D1)–C(D2)	121(2)
C(A4)–C(A5)–C(A6)	122(2)	C(D1)–C(D2)–C(D3)	117(2)
C(A5)–C(A6)–C(A1)	119(2)	C(D2)–C(D3)–C(D4)	123(2)

TABLE 4 (continued)

C(B6)–C(B1)–C(B2)	123(2)	C(D3)–C(D4)–C(D5)	118(2)
C(B1)–C(B2)–C(B3)	115(2)	C(D4)–C(D5)–C(D6)	122(2)
C(B2)–C(B3)–C(B4)	121(2)	C(D5)–C(D6)–C(D1)	119(2)
<i>(c) Acetone</i>			
C(13)–O(1)	1.52(6)	C(13)–C(15)	1.75(9)
C(13)–C(14)	1.57(7)		
O(1)–C(13)–C(14)	111(6)	C(14)–C(13)–C(15)	133(7)
O(1)–C(13)–C(15)	111(6)		

^a Primed atoms are related by the crystallographic 2-fold axis. ^b C(9,10) designates the midpoint of the line joining C(9) and C(10).

factor). H atoms were not located. The residual, *R*, converged to 0.090 with unit weights assigned to the observations. Very high thermal parameters for the methyl groups of the CNBu¹ ligand and for the acetone molecule suggest that these groups are disordered; bonding parameters, based on mean positions, are nevertheless reasonable (Table 4). A final difference synthesis had a maximum peak height of 1.1 e Å⁻³ and revealed no regions of significant electron density.

All the calculations were made on the IBM 370/158 computer at the University of the Witwatersrand using 'SHELX 76' [12]. Complex neutral-atom scattering factors were employed [13]. Figures were drawn by the ORTEP program of Johnson [14]. Observed and calculated structure factors are available upon request from J.S.F. Atomic coordinates are listed in Table 3, bond lengths and angles in Table 4 and thermal parameters in Table 5. Figure 1 gives the numbering system in the cation while Fig. 2 shows the packing of the unit cell contents viewed down *b*.

TABLE 5

THERMAL PARAMETERS (Å²) FOR [Os(COD)(CNBu¹)₂(NH₂N:CM_e₂)₂][BPh₄]₂·(ACETONE)₂

Atom	<i>U</i> ₁₁ ^a	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Os	0.0185(6)	0.0157(6)	0.0384(8)	0	0.0027(5)	0
Atom	<i>U</i> ^b		Atom	<i>U</i>		
N(1)	0.098(5)		C(8)	0.261(19)		
N(2)	0.113(6)		C(9)	0.098(6)		
C(1)	0.107(7)		C(10)	0.098(6)		
C(2)	0.143(9)		C(11)	0.104(7)		
C(3)	0.108(7)		C(12)	0.117(7)		
C(4)	0.082(5)		O(1)	0.223(10)		
N(3)	0.105(5)		C(13)	0.345(30)		
C(5)	0.120(7)		C(14)	0.365(32)		
C(6)	0.192(13)		C(15)	0.483(47)		
C(7)	0.233(15)		B	0.087(7)		
			C(phenyl) ^c	0.123(17)		

^a Anisotropic vibrational amplitudes in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$. ^b Isotropic vibrational amplitudes *U*. ^c The phenyl carbon atoms were assigned a single overall isotropic temperature factor.

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