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Preliminary communication

THE POLYMER $[OsCl_2(cod)]_x$ AS A ROUTE TO HYDRAZINE- AND HYDRAZONE-OSMIUM(II) COMPLEXES; THE CRYSTAL STRUCTURE OF $[Os(cod)(CNBu^t)_2(NH_2N{=}CMe_2)_2](BPh_4)_2 \cdot (ACETONE)_2$

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Summary

The salts, $[OsCl(cod)(NH_2NR_2)_3]X$ (R = H, X = BPh_4: R = Me, X = PF_6) and $[Os(cod)(NH_2NH_2)_4](BPh_4)_2$, formed from $[OsCl_2(cod)]_x$ and hydrazines, can be converted into a range of hydrazine- and hydrazone-osmium(II) complexes with isocyanides and tertiary phosphorus ligands. The crystal structure of $[Os(cod)(CNBu^t)_2(NH_2N{=}CMe_2)_2](BPh_4)_2 \cdot (acetone)_2$ has been elucidated.

The hydrazineruthenium complexes $[RuH(cod)(NH_2NMe_2)_3]PF_6$ (1; cod = 1,5-cyclooctadiene) and $[Ru(cod)(NH_2NHR)_4]X_2$ (2; R = H, X = BPh_4 and R = Me, X = PF_6) [1] are useful precursors to a range of stable hydrazine- and hydrazone-ruthenium complexes [1,2]. As only two hydrazineosmium compounds are known and no hydrazoneosmium complexes have been reported [3,4], we have now investigated the reactions of the corresponding osmium polymer as a viable route to new hydrazine and hydrazone compounds of osmium.

A suspension of $[OsCl_2(cod)]_x$ (3; $x > 2$) in methanol reacts rapidly with hydrazines to give yellow solutions from which the salts, $[OsCl(cod)(NH_2NR_2)_3]X$ (4; R = H, X = BPh_4; R = Me, X = PF_6), precipitate on addition of the respective counteranion. When the reaction is performed in boiling methanol a reddish-brown solution is formed which deposites the dicationic salt,

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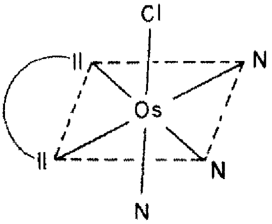
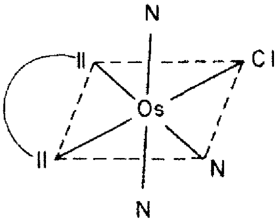
$[Os(cod)(NH_2NH_2)_4](BPh_4)_2$ (5) with $NaBPh_4$. In contrast to the ruthenium system [1], no osmium hydrides corresponding to 1 were obtained with NH_2NMe_2. The stability of 4 and 5 mirror the ruthenium salts 1 and 2 in being air stable and decomposing slowly in light over a period of a week. They were characterized by analytical data and all contained characteristic frequencies in their infrared spectra between 3120—3340 cm^{-1} (ν(N—H)), 1600—1610 cm^{-1} (δ (N—H)$_{asym}$), and 925—940 cm^{-1} (ν(N—N)). Of the two possible isomers for 4, e.g. I and II, I corresponds to that determined for 1 by an X-ray crystal structure determination [5]. In the absence of X-ray data in the osmium case, it is impossible from ^1H and ^{13}C NMR spectra to distinguish between the two possible configurations for 4.



(I)



(II)

(= cod ; N = NH_2NMe_2)

The reactions of 5 with a series of monodentate ligands have given new hydrazineosmium complexes from ethanol and hydrazoneosmium complexes with acetone as solvent. For example 5 and $CNBu^t$ produce *mer*-$[Os(CNBu^t)_3(NH_2NH_2)_3](BPh_4)_2$ (6) and *trans*-$[Os(CNBu^t)_4(NH_2NH_2)_2](BPh_4)_2$ (7) in refluxing ethanol, and $[Os(cod)(CNBu^t)_2(NH_2N{=}CMe_2)_2](BPh_4)_2$ (8) from refluxing acetone. Corresponding reactions of 5 with other monodentate ligands L (L = $P(OMe)_3$, $P(OMe)_2Ph$, and CNxylyl; xylyl = 2,5-dimethylphenyl) in refluxing acetone, gave *trans*-$[Os(NH_2N{=}CMe_2)_2L_4](BPh_4)_2$ (9; L = $P(OMe)_3$, $P(OMe)_2Ph$, and CNxylyl).

The configurations of 6 and 7 were assigned from the 1/2 and singlet Bu^t resonances respectively, observed in their ^1H NMR spectra, and 9 (L = $P(OMe)_3$ and $P(OMe)_2Ph$) by comparing their ^1H NMR virtually coupled patterns with those of the corresponding known ruthenium compounds [1,6].

As no hydrazoneosmium compounds have previously been reported, and as part of our interest [6] in factors determining the stability of hydrazonemetal complexes, the crystal structure of 8 was determined.

$[Os(cod)(CNBu^t)_2(NH_2N{=}CMe_2)_2](BPh_4)_2 \cdot (acetone)_2$ (8) crystallizes from acetone/ethanol in the monoclinic system with a 24.60(2), b 13.31(1), c 24.12(2) Å, β 111.51(2)°, $Z = 4$, space group $C2/c$.

Intensity data were collected on a Hilger and Watts four-circle diffractometer using Mo-K_α radiation and a total of 3014 reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier methods and has been refined to $R = 0.091$.

Figure 1 shows the coordination geometry of the cation and some bond distances (Å) and angles (°). The cation has a crystallographically imposed two-fold axis and if one considers the 1,5-cyclooctadiene ligand to occupy two coordination sites (the midpoints of the C(1)—C(2) and C(1′)—C(2′) bonds), then the coordination around the osmium atom is octahedral. The hydrazone ligands are mutually *trans*, and bonding to the metal atom is through the protonated nitrogen atoms N(1) and N(1′); the isocyanide ligands are *cis*, and coordinate essentially linearly through carbon atoms C(3) and C(3′). In contrast to observations made on the ruthenium hydrazone complex $[Ru(NH_2N{=}CMe_2)_2\{P(OMe)_3\}_4](BPh_4)_2$ [6], the cation is not stabilized through hydrogen bonding involving the protonated nitrogen atom of a hydrazone ligand; for example N(1)...N(2) 3.85(5) Å [6,7]. Thus whilst we cannot comment on the electronic factors governing the inertness to further substitution of the complex, it is apparent that factors other than the hydrogen bonding of the type observed in the ruthenium complex play a role in the osmium complex.

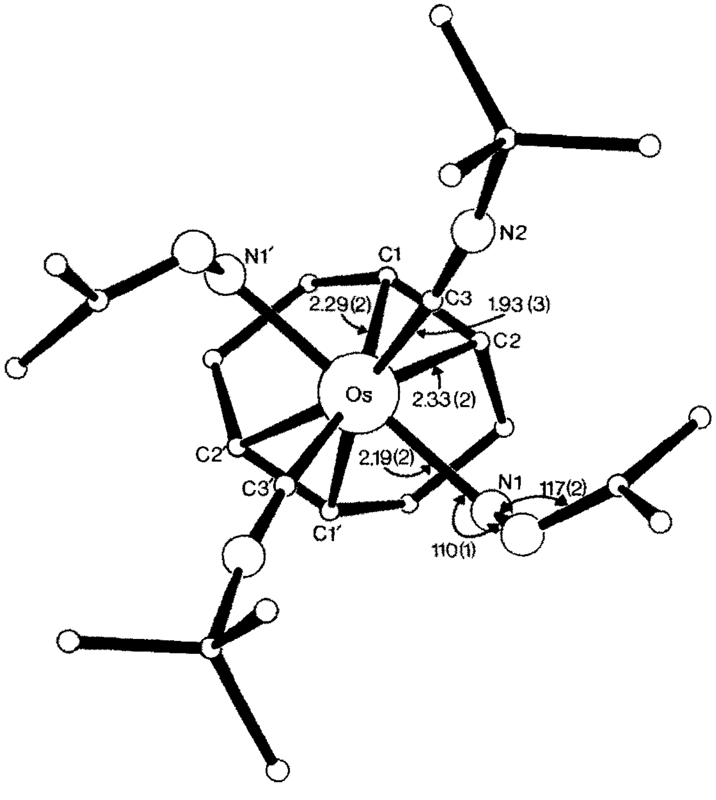


Fig. 1. Coordination geometry of the cation of 8 and some distances (Å) and angles (°).

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