Journal of Organometallic Chemistry, 133 (1977) 123–138

Unsaturated Nitrogen-Containing Ligands in Triosmium Clusters Derived from Trimethylamine and N,N-Dimethylbenzylamine*

C. Choo Yin and A. J. Deeming**

Department of Chemistry, University College London, 20 Gordon
Street, London WC1H 0AJ (Great Britain)

(Received March 9th, 1977)

SUMMARY

Trimethylamine and N,N-dimethylbenzylamine react with $Os_3(CO)_{12}$ by elimination of alkane or H_2 to give the compounds $HOs_3(\mu^2$-RC=NMe)(CO) (R = H or Ph), $HOs_3(\mu^2$-C=NMeR)$(CO)_{10}$ (R = Me or $PhCH_2$) and $HOs_3(\mu^3$-HC=NMe)$(CO)_9$. An ortho-metallated product from $PhCH_2NMe_2$, cis-Os(o-C_6H_4CH=NMe)$_2(CO)_2$, also contains an unsaturated ligand and is formed in very low yield, and indeed no products not containing C=N double bonds were observed. Metallation at atoms α to the heteroatom and the formation of unsaturated ligands are almost completely dominant features of the chemistry, the latter being a characteristic of triosmium systems not shared by many others. Some of these products are also formed from benzylidenemethylamine with a mononuclear product, cis-Os(o-C_6H_4CH=NMe)$_2(CO)_2$ in very low yield.

INTRODUCTION

In this paper we will describe some chemistry of trimethylamine and of N,N-dimethylbenzylamine with $Os_3(CO)_{12}$ leading to the triosmium-coordinated unsaturated ligands μ^2-C=NMe$_2$, μ^2-C=NMe(CH$_2$Ph), and μ^2- or μ^3-RC=NMe (R = Ph or H). In direct contrast with trimethyl-phosphine, trimethylamine is notoriously poor as a ligand especially with heavy Group VIII metals, and indeed the reported chemistry of saturated tertiary amines with metal carbonyls is extremely limited.

---

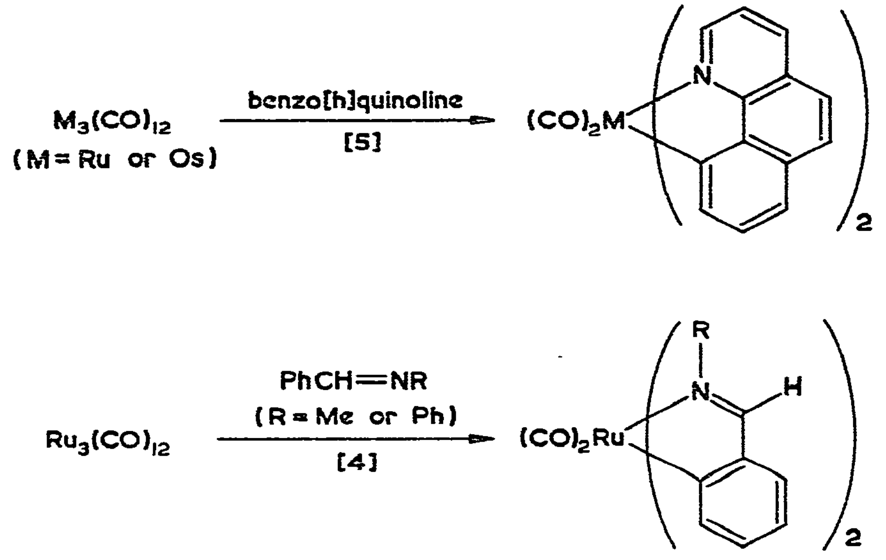
* No reprints available

Nevertheless we have examined the reactions of NMe_3 and of NMe_2CH_2Ph with $Os_3(CO)_{12}$, encouraged by the remarkable transformations of PMe_3 and PEt_3 with this metal carbonyl [1,2] and hoping to make direct comparisons. With $Os_3(CO)_{12}$, trialkylphosphines undergo C-H cleavag and, among other products, the alkene complex $HOs_3(Et_2PC=CH_2)(CO)_9$ a the alkyne complex $HOs_3(PEt_2)(CHCH)(CO)_9$ are generated from PEt_3 [2] This illustrates the dominant tendency to form unsaturated ligands in the chemistry of organic molecules with triosmium clusters. Trialkylamines conform with this, but unlike trialkylphosphines, multiple bonds to the heteroatom are formed. Before we come to this main topic some chemistry of PhCH=NMe with $Os_3(CO)_{12}$ will be describ which is quite unlike its usual ligand behaviour and akin to that of pyridine [3]. Complexes are formed which are the same or directly comparable with those from trialkylamines, justifying their inclusio here.

RESULTS

Triosmium Derivatives of Benzylidenemethylamine.

The compounds PhCH=NR (R = Me or Ph) react with $Ru_3(CO)_{12}$ by ortho-metallation and cluster disintegration to give *cis*-$Ru(CO)_2$(*o*-$C_6H_4CH=$ [4]. This is the normal mode of reaction to give five-membered chela rings and is also found for benzo[h]quinoline with both osmium and ruthenium carbonyls [5] (Scheme 1) and one would expect the chemistr of PhCH=NMe with $Os_3(CO)_{12}$ to be essentially the same. Remarkably, however, $Os_3(CO)_{12}$ reacts with PhCH=NMe under conditions mild enough to recover 20% starting material (refluxing octane under an atmospher of CO, 15 h) to give $HOs_3(PhC=NMe)(CO)_{10}$ (I) (18%), $H_2Os_3(PhC=NMe)_2$(C (II) (5%) and only a 1% yield of *cis*-Os(*o*-$C_6H_4CH=NMe)_2(CO)_2$ (III), each giving yellow crystals after t.l.c. separation. As in most reactions of organic molecules with $Os_3(CO)_{12}$, several products in fairly low yields were obtained, but nevertheless it appears from this result that there is preferential C-H cleavage at carbon next to nitrogen with the aldimine in a *syn*-configuration rather than



Scheme I

o-metallation to give a five-membered chelate ring with an anti-configuration of the aldimine. In the Os_3 cluster, nitrogen coordination at one metal atom allows Os-C formation at an adjacent one.

Compounds I and II are structurally comparable with $HOs_3(NC_5H_4)(CO)_{10}$ (IV) and $H_2Os_3(NC_5H_4)(CO)_8$ (V) which contain bridging 2-pyridyl ligands formed by direct reaction of pyridine with $Os_3(CO)_{12}$ [3]. The strong similarity of the ν(CO) spectra of corresponding compounds (Figure 1) can only mean that the compounds adopt the entirely analogous structures as shown in Scheme 2. The nitrogen ligands in all cases form 3e-donating bridges and since the structure of V has been established by X-ray diffraction [6] we can be confident of the structures in Scheme 2. The ^{1}H n.m.r. spectra confirm that the hydrogen atoms transferred to the metal atoms in I and II are the ones shown (see Table 1) and furthermore in II the metal hydrides (τ 21.18 and 22.68) and the PhC=NMe ligands (τ_{Me} 6.69 and 6.71) are inequivalent just as the hydrides and 2-pyridyl ligands in V. Thus compounds II and V are non-fluxional with apparently the same structures in solution as in the crystal. The bridging ligands are so orientated that the three osmium atoms are

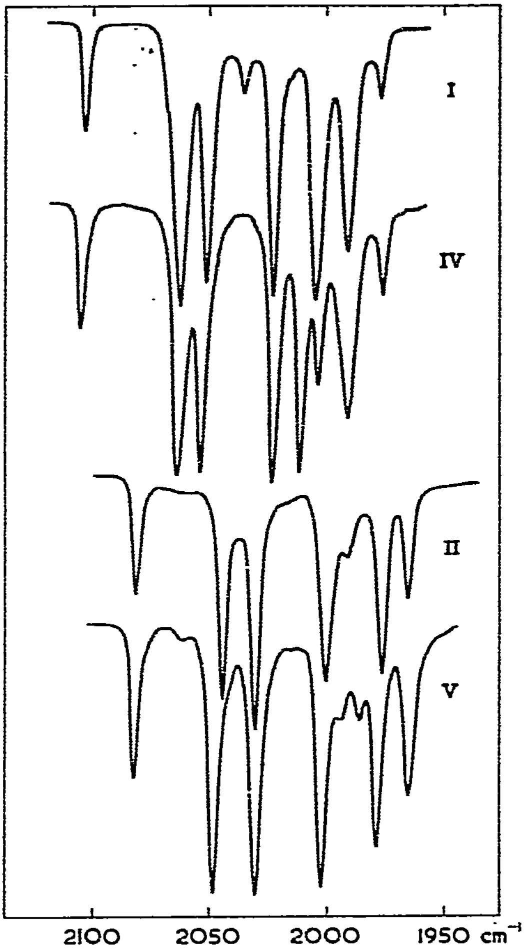
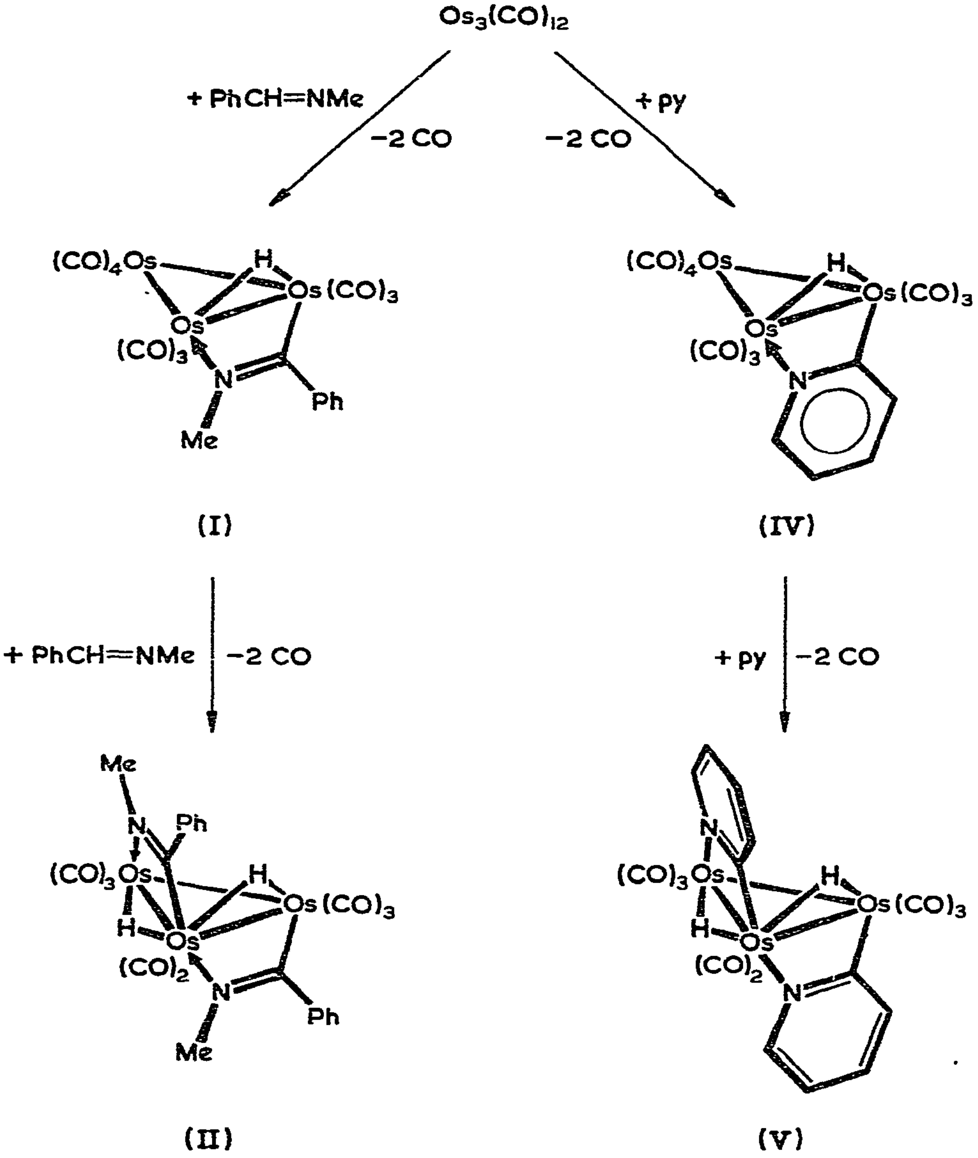


Figure 1

Infrared spectra of compounds I, II, IV, and V in the carbonyl absorption region showing the close similarity of I and IV and of II and V.

different; by interchanging the C-Os and N-Os bonds of one of the bridging ligands by turning it round, II and V would have gained C_2 axes. It may be that there are unfavourable concentrations of charge in this symmetrical structure which are avoided in the less symmetrical one. Even so there is no obvious reason for the observed orientations. The compound $Os_2(NC_5H_4)_2(CO)_6$ [3], for example, forms two isomers of similar energy which differ only in the relative orientations of the 2-pyridyl ligands.

There is no evidence for the formation of the species $H_3Os_3L_3(CO)_6$ [L = NC_5H_4 or PhC=NMe (VI)] with the third osmium pair bridged. Although this might seem feasible and would complete the series, it would require at least two bridges on the same side of the osmium plane. Indeed, with PhC=NMe bridges occupying axial sites at the metal atoms as in II and V it is impossible to form VI.



Scheme 2

Compound III, $Os(\underline{o}-C_6H_4CH=NMe)_2(CO)_2$, is the product expected by analogy with the ruthenium work, but the low yield (1%) made characterisation difficult. However, better yields from $PhCH_2NMe_2$ (see later) allowed full characterisation which showed that it is in every way analogous to $Ru(\underline{o}-C_6H_4CH=NMe)_2(CO)_2$ [4]. The CO groups are <u>cis</u> as seen from the two equally intense ν(CO) absorptions at 2002 and 1937 cm^{-1} and the $C_6H_4CH=NMe$ ligands are inequivalent (see ^1H n.m.r. data in Table 1). Accordingly the molecule must have the structure shown with one CO <u>trans</u> to Os-C and the other <u>trans</u> to Os-N. The $\underline{o}-C_6H_4CH=NMe$ ligands in III are sufficiently different to allow a 1.0 p.p.m. separation of the methyl signals in the ^1H n.m.r. with one of the signals (τ 5.77) at an unusually low shift. The two methyl groups are expected to experience quite different shielding by the π-electrons of the other ligand.

<u>Triosmium Derivatives of Tertiary Amines</u>

The two amines we have examined, NMe_3 and $PhCH_2NMe_2$, react very similarly with $Os_3(CO)_{12}$ giving only products with multiple C-N bonds. Various reaction conditions were employed. N,N-Dimethylbenzyl -amine was reacted with $Os_3(CO)_{12}$ in refluxing decane or dekalin with CO bubbling through or in refluxing dekalin under nitrogen. Trimethy -amine was passed through a refluxing solution of $Os_3(CO)_{12}$ in nonane or was condensed with hexane and $Os_3(CO)_{12}$ in a glass tube at -173 °C which was sealed under vacuum and subsequently heated at 170 °C. No method gave anything but poor yields of the compounds in Table 2 (see Experimental Section).

The very minor products $HOs_3X(CO)_{10}$ ($X = NH_2$ or OH) are probab derived from ammonia and water as impurities in the trimethylamine. Water is known to react with $Os_3(CO)_{12}$ to give $HOs_3(OH)(CO)_{10}$ [7] and the reaction with ammonia is like the first step of the reaction of aniline with $Os_3(CO)_{12}$ to give $HOs_3(NHPh)(CO)_{10}$ [8]. Our attempts to react ammonia with $Os_3(CO)_{12}$, however, gave an intractable mixture of osmium compounds which probably contain ligands derived by condensation of NH_3 with CO. All other products in Table 2 are derived from tertiary amines.

(Continued on p. 133)

Table 1

Infrared[a] and Analytical[b] Data for Osmium Compounds.

Compound	$\nu(CO)^{a}/cm^{-1}$			C	H	N
$HOs_3(PhC{=}NMe)(CO)_{10}$ I	2104(4) 2025(10) 1977(2)	2063(10) 2005(10)	2052(10) 1991(7)	22.3 (22.3)	0.9 (0.95)	1.5 (1.45)
$H_2Os_3(PhC{=}NMe)_2(CO)_8$ II	2082(5) 2001(9) 1966(5)	2045(9) 1992(4)	2031(10) 1977(9)	28.2 (27.9)	1.9 (1.75)	2.75 (2.7)
$Os(\underline{o}\text{-}C_6H_4CH{=}NMe)_2(CO)_2$ III	2002(10)	1937(10)		44.1 (44.8)	3.55 (3.35)	5.4 (5.8)
$HOs_3(HC{=}NMe)(CO)_{10}$ VII	2105(3) 2025(10) 1992(9)	2064(10) 2008(10) 1978(3)	2053(9) 2006sh(8)	16.85 (16.15)	0.85 (0.55)	1.7 (1.55)
$HOs_3(C{=}NMe_2)(CO)_{10}$ VIII	2100(3) 2019(10) 1987(8)	2057(10) 2002(10) 1980(5)	2048(8) 1990(5)	19.25[c] (17.2)	1.15 (0.8)	1.35 (1.55)
$HOs_3(HC{=}NMe)(CO)_9$ IX	2096(3) 2017(10) 1974(3)	2069(9) 2006(6)	2043(10) 1998(9)	15.85 (15.25)	0.5 (0.6)	1.5 (1.6)
$HOs_3(NH_2)(CO)_{10}$[d] X	2106(1) 2022(10) 1982(3)	2068(10) 2005(9) 1974(1)	2053(8) 1994(9)	15.3[c] (13.85)	0.65 (0.35)	1.65 (1.6)

Table 1 (contd).

Compound	$\nu(CO)^a$/ cm^{-1}			C	H	N
$HOs_3\{C{=}NMe(CH_2Ph)\}(CO)_{10}$ XII	2100(3) 2019(10) 1987(7)	2057(9) 2001(10) 1980(6)	2048(9) 1991(5)	23.0 (23.2)	1.15 (1.15)	1.4 (1.4)

a. Recorded in cyclohexane; intensities relative to the strongest peak (10) are in parentheses.

b. Calculated figures in parentheses.

c. Sample is probably contaminated with high boiling hydrocarbon; all other evidence supports the formulation.

d. $\nu(NH)$ recorded in hexachlorobutadiene; 3415, 3360 cm^{-1}

Table 1 (contd).

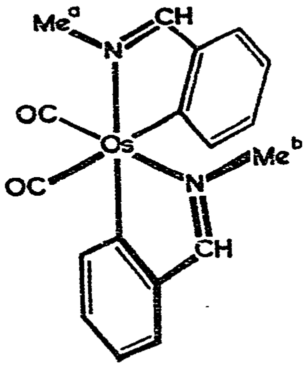
Compound	$\nu(CO)^a$/ cm^{-1}			C	H	N
$HOs_3\{C{=}NMe(CH_2Ph)\}(CO)_{10}$ XII	2100(3) 2019(10) 1987(7)	2057(9) 2001(10) 1980(6)	2048(9) 1991(5)	23.0 (23.2)	1.15 (1.15)	1.4 (1.4)

a. Recorded in cyclohexane; intensities relative to the strongest peak (10) are in parentheses.

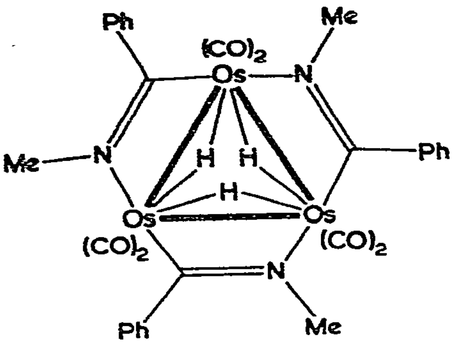
b. Calculated figures in parentheses.

c. Sample is probably contaminated with high boiling hydrocarbon; all other evidence supports the formulation.

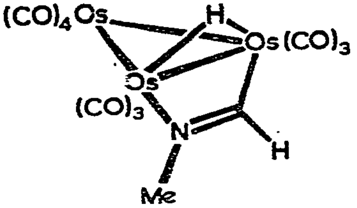
d. ν(NH) recorded in hexachlorobutadiene; 3415, 3360 cm^{-1}



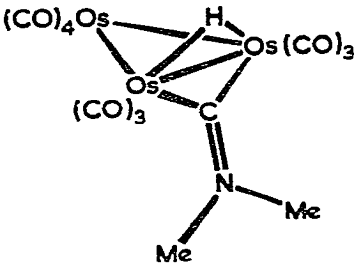
(III)



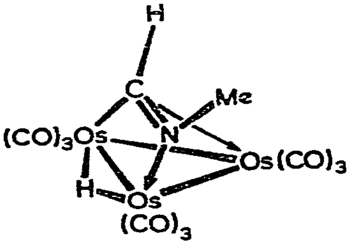
(VI)



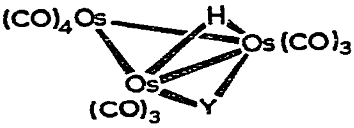
(VII)



(VIII)



(IX)



(X) Y = NH_2

(XI) Y = OH

Table 2

^{1}H n.m.r. Data[a] for Osmium Compounds

Compound	τ	Assignment
$HOs_3(PhC{=}NMe)(CO)_{10}$ I	2.50-2.80m 3.23dd	$C_6\underline{H}_5$
	6.80s	$C\underline{H}_3$
	25.02	$Os\underline{H}$
$H_2Os_3(PhC{=}NMe)_2(CO)_8$ II	2.70m	$C_6\underline{H}_5$
	3.19m	$C_6\underline{H}_5$
	6.69s	$NC\underline{H}_3$
	6.71s	$NC\underline{H}_3$
	21.18s	$Os\underline{H}$
	22.68s	$Os\underline{H}$
$Os(o\text{-}C_6H_4CH{=}NMe)_2(CO)_2$[b] III	1.13m	$C\underline{H}{=}N$
	1.53m	$C\underline{H}{=}N$
	2.02m 2.39-3.21m 3.47m	$(C_6\underline{H}_4)_2$
	5.77s	$NC\underline{H}_3$
	6.76s	$NC\underline{H}_3$
$HOs_3(C{=}NMe_2)(CO)_{10}$ VIII	6.16s	$N(C\underline{H}_3)_2$
	26.75s	$Os\underline{H}$
$HOs_3(HC{=}NMe)(CO)_9$ IX	0.29s	$C\underline{H}$
	6.26s	$C\underline{H}_3$
	28.00s	$Os\underline{H}$
$HOs_3(NH_2)(CO)_{10}$[d] X	25.42d	$Os\underline{H}$
HOs_3 $C{=}NMe(CH_2Ph)$ $(CO)_{10}$ XII	2.52-288m	$C_6\underline{H}_5$
	4.65d 4.85d	$C\underline{H}_2$(AB quartet)[e]
	6.32s	$C\underline{H}_3$
	26.58s	$Os\underline{H}$

a. Recorded in $CDCl_3$ at 100 MHz at 27 °C

b. Recorded in CD_3COCD_3 for direct comparison with the ruthenium analogue.

c. $HRu_3(C{=}NMe_2)(CO)_{10}$ gives singlets at τ 6.1 and 24.9

d. NH_2 signal not observed in $CDCl_3$ or CD_3COCD_3; signal probably too broad to be observed. $Os\underline{H}$ proton couples (3.1 Hz) with only one NH_2 proton.

e. $\underline{J}$(H, H) = 14.2 Hz for the AB quartet.

The ligands we have obtained are of two types: (A) RN=CR' (in I, VII, and IX) formally derived by elimination of alkane and a hydrogen atom transfer from the tertiary amine to the metal atoms and (B) RR'N=C (in VIII and XII) in this case derived by elimination of H_2 and a hydrogen atom transfer to osmium. This is reminiscent of the formation of the clusters $H_2Os_3(C_2RR')(CO)_9$ containing either RC=CR' or RR'C=C formed by dehydrogenation of alkenes [9]. (A) and (B) can act as three electron donors as in the decacarbonyls I, VII, VIII and XII while MeN=CH in the nonacarbonyl IX is presumably a 5e-donor, donating π-electrons from the C=N bond to the metal as well as the nitrogen lone-pair of electrons. Bonding in this way, it fits into a series of triply-bridging ligands RC=CR', RC=NR' and RN=NR' donating 4e, 5e and 6e respectively. The ligand PhC=NMe formed from PhCH=NMe as descibed earlier is of type (A), while (B) ligands have been identified previously in $HM_3(CNMe_2)(CO)_{10}$ (M = Fe [10] or Ru [11]), and data given in Tables 1 and 2 for VIII are very similar to those for the iron and ruthenium compounds. The $CNMe_2$ ligand in the iron compound was formed from dimethylformamide by oxygen atom loss, while the ruthenium one was obtained from $Me_2NCH_2SnMe_3$ and $Ru_3(CO)_{12}$. Ours is apparently the first example of a direct formation from trimethylamine. The structure of the ruthenium compound determined crystallographically [11] is like that shown for VIII with an approximately planar arrangement of the NC_3 atoms and the two bridged osmium atoms. The slightly stepped arrangement in this group does not involve significant deviation from planarity. The C=N multiple bond implied by the bond length and nitrogen planarity would require a moderately large energy barrier to rotation about this bond and this is indicated in $HOs_3\{C{=}NMe(CH_2Ph)\}(CO)_{10}$, XII. This molecule contains non-equivalent benzylic hydrogen atoms appearing as an AB quartet in the n.m.r. spectrum. A 180° rotation about the C=N bond would give the enantiomer with H_a and H_b with interchanged sites (Scheme 3). The observation of a sharp AB quartet at 30 °C supports a significantly hindered rotation as expected.

Table 3

Products from reactions of tertiary amines with $Os_3(CO)_{12}$

NMe_3:	$HOs_3(CH{=}NMe)(CO)_{10}$	(VII)
	$HOs_3(C{=}NMe_2)(CO)_{10}$	(VIII)
	$HOs_3(CH{=}NMe)(CO)_9$	(IX)
	$HOs_3(NH_2)(CO)_{10}$	(X)
	$HOs_3(OH)(CO)_{10}$	(XI)
$PhCH_2NMe_2$:	$HOs_3(PhC{=}NMe)(CO)_{10}$	(I)
	$HOs_3\ C{=}NMe(CH_2Ph)\ (CO)_{10}$	(XII)
	$HOs_3(CH{=}NMe)(CO)_9$	(IX)
	$Os(\underline{o}\text{-}C_6H_4CH{=}NMe)_2(CO)_2$	(III)
	$(PhCH_2)_2NMe$	

EXPERIMENTAL

All the compounds in the tables gave good mass spectra with parent molecular ions in accord with their formulations and fragmentation ions were also as expected. All high temperature reactions were carried out in the absence of oxygen, but chromatography and isolation of compounds were carried out in air. All compounds were indefinitely stable in air under normal condidions.

Reaction of $Os_3(CO)_{12}$ with N-Benzylidenemethylamine.

A solution of PhCH=NMe (2 cm^3) and $Os_3(CO)_{12}$ (0.197 g) in octane (23 cm^3) was heated under reflux under CO for 5 h. After cooling, the solution was decanted from crystallised $Os_3(CO)_{12}$ (0.040 g) which was washed with a little chloroform. Solvent was removed from the combined solution and washings and the residue separated by layer chromatography on silica using petroleum ether (b.p. below 40 °C) as eluant followed by a petroluem ether/chloroform mixture (up to 50% by volume) to give three yellow bands which gave compounds I (0.037 g, 18%), m.p. 152-5 °C, II (0.011 g, 5%), m.p. 176-9 °C, and III (0.004 g, 1%), all as yellow solids.

Reaction of $Os_3(CO)_{12}$ with N,N-Dimethylbenzylamine.

CO was passed through a refluxing solution of $Os_3(CO)_{12}$ (0.198 g) and N,N-dimethylbenzylamine (2 cm^3) in refluxing decane (23 cm^3) for over 48 h until changes in the infrared spectrum around 2000 cm^{-1} showed that most of the $Os_3(CO)_{12}$ had reacted. After evaporation to dryness under reduced pressure the residue was separated by layer chromatography (silica) using pentane as eluant. The two most intense yellow bands and the material on the base line were treated further as follows. The top yellow band was rechromatographed to give I (0.024 g, 11%) containing traces of $Os_3(CO)_{12}$. The solid residue from the second yellow band was washed with a small amount of cold pentane until the washings were no longer intense yellow. The solid yellow material remaining was compound XII (0.016 g, 6%) while the washings contained IX. The material on the base line after rechromatography gave $(PhCH_2)_2NMe$ (0.003 g), identified by elemental analysis and ^1H n.m.r.

A similar reaction under CO in refluxing dekalin gave traces of I, XII (13%), and III (6%). Under N_2 a similar treatment gave traces of I, XII (15%), and III (8%). Little or no reaction of $PhCH_2NMe_2$ with $Os_3(CO)_{12}$ was observed in refluxing octane or nonane.

Reaction of $Os_3(CO)_{12}$ with Trimethylamine.

Method 1

Trimethylamine was passed over KOH pellets and through a refluxing solution of $Os_3(CO)_{12}$ (0.166 g) in nonane (25 cm^3) for 7 h by which time the infrared spectrum indicated that most of the $Os_3(CO)_{12}$ had reacted. The reaction solution was decanted from a brown solid which was washed with chloroform. Solvent was removed from the combined solution and washings and the residue chromatographed as above to give IX (0.004 g, 3%), VIII (0.011 g, 7%), and XI (0.008 g, 6

Method 2

Hexane (10 cm^3) and $Os_3(CO)_{12}$ (0.160 g) were degassed in a glass sleeve within a stainless steel bomb which was finally sealed under vacuum. Trimethylamine (about 5 cm^3) was distilled into the bomb which was resealed and heated at 170 ± 3 °C for 2 h. The infrared spectrum of the solution indicated that little reaction had occurred so the vessel was reloaded and heating continued for a further 7 h. Treatment of the product mixture as above gave $Os_3(CO)_{12}$ (0.006 g), VII (0.002 g), VIII (0.006 g) and X (0.004 g). We obtained nothing but poor yields in our work.

ACKNOWLEDGEMENTS

We would like to thank the S.R.C. for a studentship (to C. C. Y.) and Johnson Matthey Ltd. for a loan of OsO_4 used in this work.

REFERENCES

1. A. J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1973), 2727
2. A. J. Deeming, J. Organometal. Chem., in press.
3. C. Choo Yin and A. J. Deeming, J. Chem. Soc. Dalton, (1975), 2091.
4. R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, J. Chem. Soc. Dalton, (1972), 1787.
5. M. I. Bruce, B. L. Goodall, and F. G. A. Stone, J. Organometal. Chem., 60 (1973), 343.
6. M. B. Hursthouse and L. New, personal communication.
7. C. R. Eady, B. F. G. Johnson, and J. Lewis, J. Organometal. Chem., 57 (1973), C84.
8. C.Choo Yin and A. J. Deeming, J. Chem. Soc. Dalton, (1974) 1013.
9. A. J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1974),1415 and references therein.

10. R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, Chem. Commun., (1970), 1193.

11. M. R. Churchill, B. G. DeBoer, F. J. Rotella, E. W. Abel and R. J. Rowley, J. Amer. Chem. Soc., 97, (1975), 7158 and M. R. Churchill, B. G. DeBoer, and F. J. Rotella, Inorg. Chem., 15, (1976), 1843.