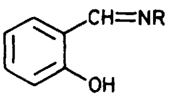
Three Isomeric Triosmium Clusters containing Bridging Ligands derived from the Salicylaldimine $PhCH_2N=CHC_6H_4OH$-2

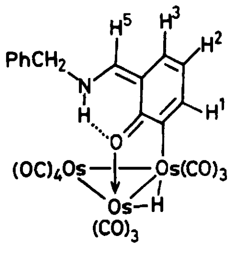
Alejandro J. Arce, Antony J. Deeming,* and Richa Shaunak
Department of Chemistry, University College, London, 20 Gordon Street, London WC1H 0AJ

$[Os_3(CO)_{10}(MeCN)_2]$ reacts in refluxing benzene with the salicylaldimine $PhCH_2N=CHC_6H_4OH$-2 to give the decacarbonyl cluster $[Os_3H(CO)_{10}(\mu\text{-}OC_6H_3CH=NHCH_2Ph)]$ by metallation at the position *ortho* to the phenolic group. Thermolysis of this compound in refluxing heptane gives three isomers: $[Os_3H(CO)_9(\mu_3\text{-}OC_6H_3CH=NHCH_2Ph)]$, $[Os_3H(CO)_9(OC_6H_4CH=NCH_2Ph)]$ in which the salicylaldiminate ligand chelates in a classical manner, and $[Os_3H_2(CO)_9(\mu_3\text{-}OC_6H_2CHNHCH_2Ph)]$ in which the organic ligand is bound to the metal through carbon atoms only. The last named isomer is directly analogous to the known *o*-phenylene compound $[Os_3H_2(CO)_9(C_6H_4)]$. The structures of these compounds are discussed on the basis of ^1H n.m r. and i.r. data and the consequences of replacing $PhCH_2$ by the asymmetric PhCHMe group are described.

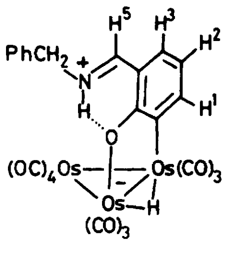
We describe here the syntheses of several triosmium clusters derived by oxidative addition of the salicylaldimes H_2L^1 and H_2L^2. Our initial objectives in this work were to prepare chiral clusters such as $[Os_3H(CO)_{10}(R'C=NR)]$ ($R' = C_6H_4$-OH-2) known to be formed from the imines R'CH=NR,[1,2] and to attempt their resolution. Using optically pure H_2L^2, separation of diastereomers followed by hydrolysis of the imine could generate enantiomerically pure clusters. Our work has not progressed so far yet, but we report here the complexes of general form $[Os_3(CO)_{10}(H_2L)]$ and three isomers of $[Os_3(CO)_9(H_2L)]$ where H_2L is either H_2L^1 or H_2L^2. The isomeric nonacarbonyls are all hydrido-species; one contains an *ortho*-metallated ring, another a ring which is both *ortho*- and *meta*-metallated, and the third isomer contains a ligand bound through O and N atoms only.



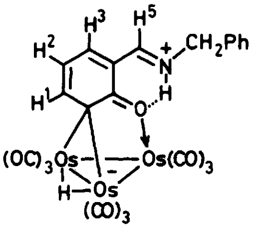
H_2L^1; R = CH_2Ph
H_2L^2; R = CHMePh



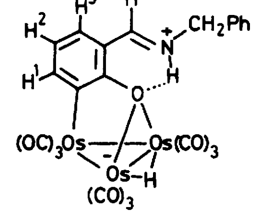
(1a)



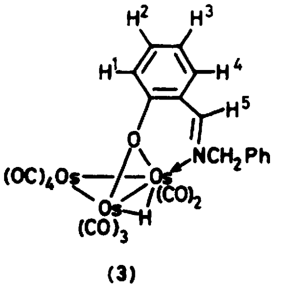
(1b)



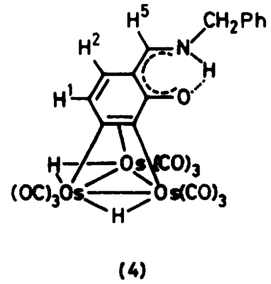
(2a)



(2b)



(3)



(4)

Results and Discussion

The bis-acetonitrile complex $[Os_3(CO)_{10}(MeCN)_2]$ reacts readily with H_2L^1 in refluxing benzene to give mainly the decacarbonyl compound $[Os_3H(CO)_{10}(HL^1)]$ (1). Subsequent treatment of (1) in refluxing heptane gave three isomeric compounds which were separated on silica: the green compound $[Os_3H(CO)_9(HL^1)]$ (2) (6%), the yellow compound $[Os_3H(CO)_9(HL^1)]$ (3) (8%), and the orange compound $[Os_3H_2(CO)_9L^1]$ (4) (30%). The three thermolysis products all have the apparent formula $[Os_3(CO)_9(H_2L^1)]$. ^1H N.m.r. and v(CO) data (Tables 1 and 2 respectively) were used to establish the nature of the ligands HL^1 and L^1 and their probable modes of attachment to the three metal atoms. Compounds (5), (6), and (7) are derived from the imine H_2L^2 and correspond directly with the compounds (1), (2), and (3).

Salicylaldimines are commonly used as bidentate ligands forming six-membered rings but the compounds (1)—(4) illustrate that in clusters a greater variety of bonding is possible and only in (3) is there a six-membered chelate ring. The ^1H n.m.r. spectrum of compound (1) shows quite clearly that only three hydrogen atoms remain on the phenolic ring. The signals for the C_6H_5 protons are between δ 7.3 and 7.5 while

Table 1. Hydrogen-1 n.m.r. data [a]

Compound	H^1	H^2	H^3	H^4	H^5	NH	CH_2		OsH
H_2L^1					8.30 s		4.70 s		
(1)	8.10 dd	6.47 dd	6.72 dd		7.85 d	12.48 br	4.82 dd	4.71 dd	−12.43 s
	(1.7, 6.9)	(6.8, 8.0)	(1.5, 7.9)		(13.4)		(5.2, 14.8)	(6.2, 14.8)	
(2)	7.94 dd	6.31 t	7.73 dd		8.03 d	12.50 br	4.92 br		−12.37 s
	(1.6, 7.2)	(7.2)	(2.1, 7.3)		(11.2)				
(3)	*b*	*b*	*b*	*b*	8.19 s		5.42 d	5.50 d	−10.77 s
							(13.4)	(13.4)	
(4)	6.82 d	6.44 d			7.52 d	12.2 dt [c]	4.62 d		−21.03 br [d]
	(8.2)	(8.2)			(12.6)	(4.8, 12.6)	(4.8)		−17.56 br [d]

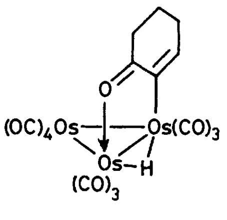
[a] In $CDCl_3$, 200 MHz, 30 °C, δ values with couplings (Hz) in parentheses. [b] Unassigned signals between δ 7.0 and 7.5. [c] Double triplet is just resolved. [d] Recorded at −30 °C; broad singlet at δ −19.3 at 45 °C.

Table 2. Infrared spectroscopic data

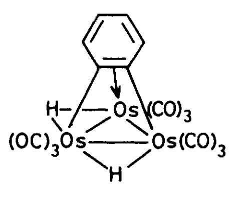
Compound	ν(CO) */cm^{-1}			
(1)	2 099m	2 056s	2 048s	2 014vs
	2 004s	1 995m	1 985m	1 977w
	1 965w			
(2)	2 073m	2 042s	2 018s	1 988s
	1 970m	1 951w	1 942w	
(3)	2 096m	2 056s	2 013vs	2 002s
	1 991m	1 984m	1 975m	1 939m
(4)	2 105m	2 079s	2 054s	2 031m
	2 023s	2 005s	2 003sh	1 985sh
	1 980m			
(5)	2 100m	2 057s	2 049s	2 016vs
	2 006s	1 995m	1 985m	1 978w
	1 967w			
(6)	2 074m	2 044s	2 020s	1 988s
	1 970m	1 952w	1 940w	
(7)	2 096m	2 056s	2 013vs	2 001s
	1 991m	1 983m	1 975m	1 937m

* In cyclohexane solution.

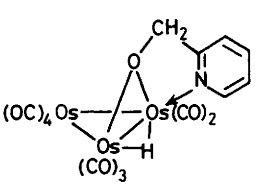
those for the remaining eight hydrogen atoms are all well separated, and their couplings have been analysed. Hydrogen atoms have been displaced from the OH group, and from the position *ortho* to it, and transferred to the N and Os atoms. Spin-decoupling experiments clearly show that the NH proton (broad signal at δ 12.48) is coupled to the aldimine CH proton (J = 13.4 Hz) and to each of the diastereotopic CH_2 protons (J = 5.2 and 6.2 Hz respectively). Descriptions (1a) and (1b) would both fit this arrangement of atoms in the ligand. The ν(CO) spectrum of (1) is very similar to that of compound (8) [3] except that the absorptions are at lower wavenumber by up to 10 cm^{-1}. Much greater lowering would be expected for the zwitterionic form (1b), so we believe (1a) has a more important contribution than (1b). This *ortho*-metallation product (1) gives compounds (2)—(4) on heating in heptane. The major product, compound (4), has only two hydrogen atoms of the original four remaining on the phenolic ring. Spectroscopically, (4) relates closely to the *o*-phenylene compound $[Os_3H_2(CO)_9(C_6H_4)]$ (9): [4] *e.g.* ν(CO) data for (9), with those for (4) in parentheses, are 2 110 (2 105), 2 084 (2 079), 2 058 (2 054), 2 038 (2 031), 2 026 (2 023), 2 011 (2 005), 2 002 (2 003), 1 985 (1 985, 1 980) cm^{-1}. The shift of about 5 cm^{-1} indicates very little extra negative charge at the metal atoms of (4). Another similarity is that the ^1H n.m.r. signals for the hydrides of (4) (δ −17.56 and −21.03 at −30 °C) are coalesced at room temperature as are those for (9) (δ −17.01 and −20.91 at −140 °C), although the rate of hydride exchange is much lower for (4). We prefer to allocate a hydrogen atom at N, rather than O, in (4) in view of its strong coupling to H^5 and the CH_2 protons. We propose the structure shown for compound (3); the ν(CO) i.r. absorption pattern is consistent with a 4,3,2-distribution of CO ligands at the osmium atoms rather than the more common 3,3,3-distribution: *e.g.* ν(CO) for (10),[5] with those for (3) in parentheses, 2 099 (2 096), 2 056 (2 056), 2 016 (2 013), 1 991 (2 002, 1 991), 1 981 (1 984), 1 975 (1 975), 1 936 (1 939) cm^{-1}. The ^1H n.m.r. spectrum for (3) is not as straightforward as for (2) and (4) but the observed singlet for H^5 confirms the absence of a hydrogen atom at N.



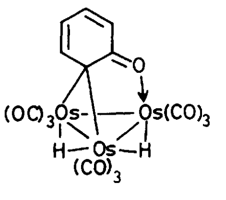
(8)



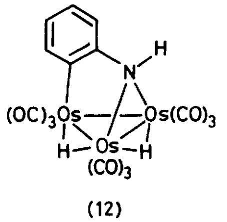
(9)



(10)



(11)



(12)

On the basis of similar spectroscopic evidence we can show that the organic ligand in (2) has the same order of atoms as in (1). The ν(CO) absorptions for (2) are *ca.* 35—45 cm^{-1} lower than for $[Os_3H_2(CO)_9(C_6H_4O)]$ (11), derived from phenol,[6,7] or for $[Os_3H_2(CO)_9(C_6H_4NH)]$ (12), derived from aniline.[7,8] This is consistent with a considerable build-up of negative charge at the metal atoms of (2) such as shown for (2a) or (2b). In view of the different structures adopted by (11) and (12) we feel that it is unwise to decide between structures (2a) and (2b) on our present evidence, although we prefer (2a) on the basis of the chemical shifts for H^1—H^3.

Compounds (1), (3), and (4) are chiral but (2) is not. As expected, when the $PhCH_2$ group is replaced by PhCHMe, compound (5), analogous to (1), exists as a pair of diastereomers; as does compound (7) which is analogous to (3). For example, the 400 MHz ^1H n.m.r. spectrum of (5) has a similar overall appearance to that of (1) except that each signal is composed of two almost identical but slightly displaced signals of intensity ratio 43 : 57, corresponding to the two diastereomers. Hydride singlets at δ —12.35 and −12.38 for (5) correspond to that at δ −12.43 for (1). Attempts to separate diastereomers of compounds (5) and (7) were unsuccessful. In contrast, compound (6), the PhCHMe analogue of the achiral compound (2), shows only a single set of ^1H n.m.r. resonances.

Conclusions

Two general points arise from the work described in this paper. The imines H_2L^1 and H_2L^2 have two co-ordinating functional groups (OH and CH=NR), in addition to the arene rings, for bonding to the metal triangle. Lack of specificity is indicated by the formation of isomers with the ligands bound respectively through O and C, O and N, or just through C atoms. Indeed, the major isomer (4) is that in which the normally co-ordinating heteroatoms are not directly bonded to metal at all. This lack of specificity is an interesting but complicating feature of organometallic cluster chemistry. The second conclusion is that even with polyfunctional ligands the same type of ligand to cluster bonding appears as in simple systems. A few structural arrangements of ligands in cluster such as those found in (9)—(12) are expected to be frequently encountered.

Experimental

The salicylaldimines $RN=CHC_6H_4OH$-2 (R = CH_2Ph or CHMePh) were prepared from salicylaldehyde and benzylamine or (+)-$PhCHMeNH_2$ by standard methods.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* $PhCH_2N=CHC_6H_4$-OH-2.—This bis-acetonitrile complex was prepared from $[Os_3(CO)_{12}]$ (0.374 g) by treatment with Me_3NO in CH_3CN–CH_2Cl_2 as reported previously.[9] Excess of Me_3NO was removed by passing the solution down a silica column. The compound $[Os_3(CO)_{10}(MeCN)_2]$, after removal of the solvent under vacuum, was treated with the imine (0.085 g) in benzene (50 cm^3). The solution was refluxed under nitrogen for 1 h to give a deep red solution with a small amount of brown solid which was removed by filtration. Removal of the solvent and chromatography on silica (t.l.c.) eluting with diethyl ether–light petroleum (b.p. 30—40 °C) (20 : 80 v/v) gave three bands. A minor yellow band was discarded, a bright orange band gave $[Os_3H(CO)_{10}(C_{14}H_{12}NO)]$ (1) as orange crystals (0.129 g) from hexane (Found: C, 27.7; H, 1.5; N, 1.1. $C_{24}H_{13}NO_{11}Os_3$ requires C, 27.15; H, 1.25; N, 1.3%). A green slow-moving band gave $[Os_3H(CO)_9(C_{14}H_{12}NO)]$ (2) as a green solid (0.014 g) shown to be the same as that formed by thermolysis of compound (1).

Thermolysis of Compound (1).—A solution of compound (1) (0.110 g) in heptane (25 cm^3) was heated in nitrogen under reflux for 2.5 h. The solvent was removed under vacuum and the residue chromatographed on silica (t.l.c.), eluting with diethyl ether–light petroleum (b.p. 30—40 °C) (20 : 80 v/v) to give four bands. The slowest band gave $[Os_3H(CO)_9(C_{14}H_{12}NO)]$ (2) as dark green crystals (0.006 g) (Found: C, 26.75; H, 1.35; N, 1.3. $C_{23}H_{13}NO_{10}Os_3$ requires C, 26.7; H, 1.25; N, 1.35%). The next slowest band gave a mixture (0.019 g) and the next an orange compound (0.012 g); neither of these was characterised. The fastest band was rechromatographed to give two bands which gave $[Os_3H(CO)_9(C_{14}H_{12}NO)]$ (3) as yellow crystals (0.009 g) (Found: C, 26.85; H, 1.35; N, 1.25%) and $[Os_3H_2(CO)_9(C_{14}H_{11}NO)]$ (4) as orange crystals (0.033 g) (Found: C, 27.3; H, 1.4; N, 1.6%). Both are isomeric with compound (2).

Derivatives of $PhCHMeN=CHC_6H_4OH$-2.—Using the salicylaldimine derived from (+)-$PhCHMeNH_2$ we were able to obtain $[Os_3H(CO)_{10}(C_{15}H_{14}NO)]$ (5), analogous to compound (1) (Found: C, 29.0; H, 1.9; N, 1.35. $C_{25}H_{15}NO_{11}Os_3$ requires C, 27.9; H, 1.4; N, 1.3%); compound (6) (trace), analogous to compound (2); and compound (7), analogous to compound (3).

Acknowledgements

We thank the S.E.R.C. for assistance and Johnson Matthey for a loan of osmium tetraoxide.

References

1 C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.*, 1977, **133**, 123.
2 R. D. Adams and N. M. Golembeski, *Inorg. Chem.*, 1978, **17**, 1969; R. D. Adams and J. P. Selegue, *ibid.*, 1980, **19**, 1791.
3 K. A. Azam, A. J. Deeming, and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1981, 91.
4 A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1974, 1415.
5 A. J. Deeming and R. Peters, unpublished work.
6 K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J. Chem. Soc., Chem. Commun.*, 1978, 1086.
7 K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 2039.
8 C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1973, 1013.
9 B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.*, 1978, **145**, C4; J. R. Shapley and M. Tachikawa, *J. Organomet. Chem.*, 1977, **124**, C19.

Received 21*st September* 1982; *Paper* 2/1622