Metallation of Aniline by Reaction with Dodecacarbonyltriosmium

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Dodecacarbonyltriosmium in refluxing aniline gives $H_2Os_3(HNC_6H_4)(CO)_8(H_2NPh)$ which reacts successively with CO to give $H_2Os_3(HNC_6H_4)(CO)_9$ and $HOs_3(HNPh)(CO)_{10}$. The decacarbonyl in refluxing nonane gives initially $H_2Os_3(HNC_6H_4)(CO)_9$ which then isomerises to $H_2Os_3(NPh)(CO)_9$ which is the main product on heating a hydrocarbon solution of the decacarbonyl in a sealed tube. Corresponding reactions with *p*-fluoro- and *p*-methyl-aniline are compared with those of aniline.

ALCOHOLS (ROH) and thiols (RSH) react with dodecacarbonyltriosmium to give the complexes $HOs_3(OR)(CO)_{10}$[1] or $HOs_3(SR)(CO)_{10}$,[2] examples of which have been studied crystallographically.[3] Alternatively, if there are two hydrogens on the heteroatom both may be transferred to the metal as in the reaction of H_2S with $Os_3(CO)_{12}$ to give $H_2Os_3S(CO)_9$.[4] With this in mind we treated primary amines RNH_2 with $Os_3(CO)_{12}$ expecting to obtain $H_2Os_3(NR)(CO)_9$. Indeed, in the reactions of aniline and certain *para*-substituted anilines with $Os_3(CO)_{12}$ two hydrogens are successively transferred from aniline to the metal, but in certain cases one hydrogen is derived from the *ortho*-position of the arene ring. The transfer of two hydrogens from a molecule to a triosmium cluster is now known for olefins,[4-8] benzene,[4] trialkylphosphines,[9] and hydrogen sulphide[4] and now, as described in this paper, for aniline:

$$H_2X + Os_3(CO)_{12} \longrightarrow H_2Os_3X(CO)_9 + 3CO$$

This might be described as a double oxidative addition and bears a superficial resemblance at least to the interaction of similar molecules with metal surfaces.

Reaction of Dodecacarbonyltriosmium with Aniline.—The main product (59%) obtained by refluxing a solution of $Os_3(CO)_{12}$ in aniline for 1 h is a yellow crystalline complex of apparent formula $Os_3(CO)_8(aniline)_2$, which successively reacts with CO to give derivatives of apparent formulae $Os_3(CO)_9(aniline)$ and $Os_3(CO)_{10}(aniline)$. If the original reaction of $Os_3(CO)_{12}$ with aniline is carried out with CO passing through the solution the decacarbonyl is the main product. These formulae, as established by elemental analyses and mass spectra (for the nona- and deca-carbonyls only) are only apparent since all are hydrido-complexes. One of the aniline ligands in the octacarbonyl complex is simply co-ordinated through the nitrogen atom and is readily displaced by CO to give the nonacarbonyl on bubbling this gas through a refluxing heptane solution. ^1H N.m.r. spectra (Table) of the nonacarbonyl show signals in intensity ratio 1 : 3 (arene region) : 1 (N*H* region) : 2 (metal hydride region) and so we formulate it as $H_2Os_3(HNC_6H_4)(CO)_9$ rather than as $H_2Os_3(NPh)(CO)_9$ which was the expected product. As with many

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[1] B. F. G. Johnson, P. A. Kilty, and J. Lewis, *Chem. Comm.*, 1968, 180; *J. Chem. Soc.* (*A*), 1968, 2859; B. F. G. Johnson, R. D. Johnston, P. A. Kilty, J. Lewis, and I. G. Williams, *Chem. Comm.*, 1968, 861.

[2] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

[3] R. Mason, *Pure Appl. Chem.*, 1973, **33**, 513; R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

[4] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.

[5] A. J. Deeming and M. Underhill, *J.C.S. Chem. Comm.*, 1973, 277.

[6] A. J. Deeming and M. Underhill, unpublished results.

[7] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **43**, C35.

[8] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **36**, C43.

[9] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727.

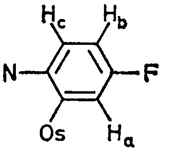
hydrido-cluster complexes of osmium intramolecular hydride exchange occurs rapidly and below the coalescence temperature (between −50 °C and 27 °C) the hydride singlet is converted into two singlets (τ 24·03 and 24·47) so that these ligands are actually non-equivalent. Structure (I) is the most reasonable one we can suggest for this complex with the HNC_6H_4 ligand triply bridging the three metal atoms and acting as a 4e-donor. It is more likely that the nitrogen lone-pair rather than the π-electrons of the arene are used in bonding to the metals. The structure is very similar to that shown for the vinylidene complex $H_2Os_3(CCH_2)(CO)_9$ [4,5] and proposed for the complex $H_2Os_3(Me_2PCH)(CO)_9$ [9] derived from ethylene and PMe_3 respectively. All three complexes show a similar exchange of hydride ligands on the n.m.r. time scale. The mechanism for the vinylidene complex $H_2Os_3(CCH_2)(CO)_9$ most likely involves movement of hydrido-ligands between the bridging sites between the metal atoms.[6]

The octacarbonyl $Os_3(CO)_8(PhNH_2)_2$ is an aniline substituted derivative of the nonacarbonyl, *i.e.* $H_2Os_3(HNC_6H_4)(CO)_8(PhNH_2)$. The substitution position is unknown. In the ^1H n.m.r. spectrum the HNC_6H_4 signals are superimposed as expected on signals due to co-ordinated $PhNH_2$, and there are two N*H* signals not completely resolved but having a total integrated intensity equivalent to three hydrogens. The non-fluxional complex gives two sharp hydride signals at room temperature. Of the complexes described here, this is the only one that does not clearly show the parent ion in its mass spectrum. It is not very volatile and requires probe temperatures in excess of 187 °C to give a spectrum, but this corresponds to $H_2Os_3(HNC_6H_4)(CO)_9$. We believe that thermal decomposition gives

Analytical,[a] infrared,[b] n.m.r.,[c] and other data for the new complexes

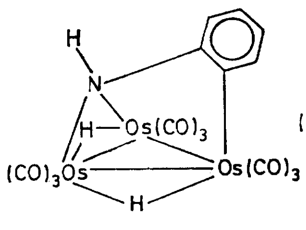
Complex	Colour	M.p. (t/°C)	C	H	N	ν(CO) (cm^{-1})	N.m.r. solvent	τ	Assign.	Coupling constant, *etc.*
$HOs_3(NHPh)(CO)_{10}$ [d]	Orange-red	174—176	20·25 (20·35)	0·7 (0·75)	1·55 (1·5)	2106m, 2069s, 2053s, 2023s, 2006s, 1995s, 1984m, 1976w	$CDCl_3$	2·7—3·3, m 4·2br 24·13, d	Ph N*H* Os*H*	 J(H–H) = 3·1
$HOs_3(HNC_6H_4F)(CO)_{10}$	Orange	194—196	19·9 (20·0)	0·7 (0·65)	1·4 (1·45)	2106m, 2069s, 2054s, 2024s, 2006s, 1995s, 1985m, 1976m	$CDCl_3$	2·7—3·4, m 4·3br 22·51, d	C_6H_4 N*H* Os*H*	 J(H–H) = 2·8
$HOs_3(HNC_6H_4Me)(CO)_{10}$	Orange	166	21·3 (21·3)	0·9 (0·95)	1·5 (1·45)	2104m, 2068s, 2053s, 2035w, 2023s, 2005s, 1995s, 1984m, 1976m	$CDCl_3$	2·99, m 3·31, m 4·2br 7·74, s 24·15, d	C_6H_4 C_6H_4 N*H* Me Os*H*	} AA'BB' spectrum of *p*-subst. ring J(H–H) = 3·1 [k]
$H_2Os_3(HNC_6H_4)(CO)_9$ [e]	Pale yellow	181—182	19·65 (19·65)	0·75 (0·75)	1·6 (1·55)	2118s, 2084s, 2053s, 2043s, 2033s, 2012s, 1996s, 1986m, 1980s	$CDCl_3$	2·51, dd 3·49, m 4·75br 24·03, s 24·47, s	1H } C_6H_4 3H } N*H* Os*H* [l] } Os*H* [l] }	J(H–H) = 3·2, 5·1 At −50 °C
$H_2Os_3(HNC_6H_3F)(CO)_9$ [i]	Orange	182—183	19·0 (19·3)	0·65 (0·65)	1·35 (1·5)	2118m, 2085s, 2054s, 2044s, 2034s, 2013s, 1997s, 1987m, 1981s	$(CD_3)_2CO$	2·70br 2·85, dd 3·44, dd 3·82, m 24·39, s	N*H* H_a H_c H_b OsH [m]	 $J(H_a–F)$ = 8·6; $J(H_a–H_b)$ = 2·8 $J(H_b–H_c)$ = 8·6; $J(H_c–F)$ = 5·2 6 line mult.; $J(H_b–F)$ = 8·6
$H_2Os_3(NPh)(CO)_9$ [f]	Orange	174—176	20·1 (19·7)	0·85 (0·75)	1·50 (1·55)	2115m, 2082s, 2055s, 2036sh, 2032s, 2009s, 1987s, 1977m	$CDCl_3$	2·88, s 28·31, s	Ph Os*H* [n]	
$H_2Os_3(NC_6H_4F)(CO)_9$ [j]						2116m, 2083s, 2056s, 2034s, 2010s, 1987s, 1977m [h]				
$H_2Os_3(NC_6H_4Me)(CO)_9$	Brown	175·5—176·5	20·65 (20·65)	0·9 (1·0)	1·6 (1·5)	2114s, 2082s, 2055s, 2036sh, 2032s, 2009s, 1986s, 1976s	$CDCl_3$	2·92, m 3·10, m 7·72, s 28·33, s	C_6H_4 C_6H_4 Me Os*H* [n]	} AA'BB spectrum for *p*-subst. ring
$H_2Os_3(HNC_6H_4)(CO)_8(PhNH_2)$ [g]	Yellow	>160 (dec.)	24·35 (24·45)	1·6 (1·55)	2·85 (2·85)	2085s, 2046s, 2039s, 2004s, 1989s, 1973s	$CDCl_3$	2·38, dd 2·73, m 3·32, m 4·80br 23·87, s 29·38, s	1H } 3H } arene 5H } 3N*H* Os*H* Os*H*	J(H–H) = 3·6, 5·3 NH + NH_2 not completely resolved
$H_2Os_3(HNC_6H_3F)(CO)_8(FC_6H_4NH_2)$	Yellow	196—206 (dec.)	23·55 (23·6)	1·35 (1·2)	2·55 (2·75)	2086s, 2048s, 2039s, 2006s, 1990s, 1975s	$(CD_3)_2CO$	2·4br 2·84—3·92, m 4·43br 24·24, s 29·67, s	N*H* $C_6H_3 + C_6H_4$ NH_2? Os*H* Os*H*	

[a] % Found with calculated figures in parentheses. [b] Recorded in cyclohexane solution. [c] Recorded at 100 MHz at 27 °C unless otherwise stated; coupling constants in Hz; signal intensities are consistent with assignments. [d] ν(NH) = 3360 cm^{-1}. [e] ν(NH) = 3318, 3258 cm^{-1}. [f] No ν(NH) observed. [g] ν(NH) = 3310, 3220 cm^{-1} (*d*—*g* recorded in $CHCl_3$). [h] Slightly contaminated with $HOs_3(HNC_6H_4F)(CO)_{10}$ as apparent from weak peaks at 2106, 2069, 2023, and 1995 cm^{-1}. [i] Hydrogen assignments:

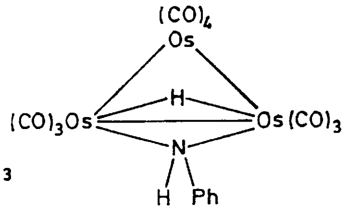


[j] I.r. spectrum only recorded; too little material for full characterisation. [k] Spin decoupling confirmed that this is coupling to the NH proton. [l] At 27 °C a sharp singlet (τ 24·28) integrating for two hydrogens was obtained. [m] The low-temperature spectrum was not recorded to test whether the signal at τ 28·31 (2H) was due to two exchanging protons as expected by analogy with $H_2Os_3(HNC_6H_4)(CO)_9$. [n] Temperature-invariant spectra.

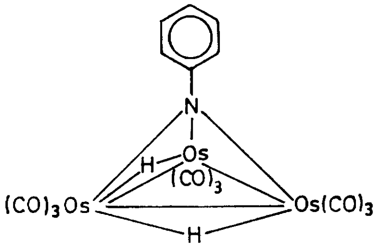
the more volatile nonacarbonyl, a conversion which occurs in low yield on pyrolysis of the octacarbonyl on a preparative scale.



(I)



(II)



(III)

The complex $H_2Os_3(HNC_6H_4)(CO)_9$ reacts further with CO at 125 °C in refluxing octane to give the decacarbonyl, $HOs_3(HNPh)(CO)_{10}$. In this reverse-metallation reaction a C–H bond has been reformed with a CO providing the extra two electrons required by the metals. A coupling of *ca.* 3 Hz between the hydride and the N*H* proton in this complex was confirmed by spin decoupling. The i.r. spectrum near 2000 cm^{-1} is closely similar to that of the known complexes $HOs_3(SR)(CO)_{10}$ [2] or $HOs_3(OR)(CO)_{10}$ [1] and in the light of their known structures [3] we propose that the aniline complex has structure (II). The conversion of the octa- to the nona- and then to the deca-carbonyl complex on treatment with CO is likely to be the reverse of the path whereby $H_2Os_3(HNC_6H_4)(CO)_8(PhNH_2)$ was originally formed. If this were so the decacarbonyl should be converted into the nonacarbonyl when heated.

Action of Heat on $HOs_3(HNPh)(CO)_{10}$.—When nitrogen was passed through a refluxing nonane solution (150 °C) of $HOs_3(HNPh)(CO)_{10}$ a quantitative conversion into $H_2Os_3(HNC_6H_4)(CO)_9$ was observed by following changes in the i.r. spectrum. Thus an initial loss of CO is accompanied by *ortho*-metallation of the arene ring. However, on extended heating further reaction occurred. By a slow isomerisation, $H_2Os_3(NPh)(CO)_9$ was formed together with some decomposition and the two isomers were separated on silica t.l.c. plates. The new isomer is the product we originally expected from the reaction of aniline and dodecacarbonyltriosmium.* The i.r. spectrum near 2000 cm^{-1} is rather similar to that of $H_2Os_3S(CO)_9$ and $H_2Ru_3S(CO)_9$ [10] and accordingly we suggest structure (III) for this aniline derivative. Unlike the isomer of structure (I) only one sharp hydride singlet is obtained even at −50 °C and the hydrido-ligands are most likely equivalent. Thus the *ortho*-metallated complex of structure (I) is formed as the kinetically controlled product and the thermodynamically most-stable compound of structure (III) is only formed by subsequent isomerisation.

Rather different behaviour is observed if the pyrolysis of $HOs_3(HNPh)(CO)_{10}$ is carried out in a sealed glass tube. The decacarbonyl was heated in decalin in an n.m.r. tube at 197 °C and after *ca.* 24 h a mixture of complexes was formed which was essentially the same after being heated for a further 188 h. The mixture contained the starting decacarbonyl (*ca.* 70%), nonacarbonyl of structure (III) (*ca.* 30%), and only traces of the other isomer. At this higher temperature the thermodynamically most-stable isomer is favoured and the incomplete conversion into the nonacarbonyl in a closed system must be due to the reversibility of the decarbonylation. Indeed, we have already described the carbonylation of the isomer of structure (I) and the other isomer was also shown to be converted into the decacarbonyl. However, their rates of reaction with CO (1 atm) in refluxing hydrocarbon are different. $H_2Os_3(HNC_6H_4)(CO)_9$ was almost completely converted on CO treatment for 20 min at 150 °C, whereas $H_2Os_3(NPh)(CO)_9$ showed no reaction at this temperature after 3½ h; at 175 °C 10—20% conversion after 14 h took place and at 195 °C *ca.* 50% conversion after 10 h. If the decacarbonyl decarbonylates by a preliminary dissociation of CO, the intermediate, probably $HOs_3(NHPh)(CO)_9$, is likely to be the same as that for the isomerisation of the nonacarbonyl as shown in the following Scheme:

$$\begin{tikzcd}
 & HOs_3(NHPh)(CO)_{10} \arrow[d, shift left, "-CO"] & \\
H_2Os_3(NHC_6H_4)(CO)_9 \arrow[r, shift left, "\text{fast}"] & \text{Intermediate} \arrow[l, shift left, "\text{fast}"] \arrow[u, shift left, "+CO"] \arrow[r, shift left, "\text{slow}"] & H_2Os_3(NPh)(CO)_9 \arrow[l, shift left, "\text{slow}"] \\
\text{Isomer of structure (I)} & \{\text{possibly } HOs_3(NHPh)(CO)_9\} & \text{Isomer of structure (III)}
\end{tikzcd}$$

SCHEME

Related Studies with p-*Fluoro- and* p-*Methyl-anilines*.—The related reactions with *p*-fluoro- and *p*-methylaniline have also been studied in an attempt to assess factors causing the initial formation of the product, $H_2Os_3(NHC_6H_4)(CO)_9$, rather than the more-stable isomer, $H_2Os_3(NC_6H_5)(CO)_9$, on controlled pyrolysis of the decacarbonyl. Broadly our results show that ring metallation was not observed for *p*-toluidine derivatives but two isomers of the nonacarbonyl were found with *p*-fluoroaniline as with aniline itself.

Reaction of $Os_3(CO)_{12}$ in refluxing p-$FC_6H_4NH_2$ gave three products, $H_2Os_3(NHC_6H_3F)(CO)_9$, $H_2Os_3(NHC_6H_3F)(CO)_8(NH_2C_6H_4F)$, and $HOs_3(NHC_6H_4F)(CO)_{10}$ all analogous to the aniline derivatives (see

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* *Note added in proof:* The ruthenium analogue $H_2Ru(NPh)(CO)_9$ has recently been reported to be formed by hydrogenation of $Ru_3(NPh)(CO)_{10}$ which is derived from nitrobenzene and $Ru_3(CO)_{12}$. E. Sappa and L. Milone, *J. Organometallic Chem.*, 1973, **61**, 383.

[10] A. J. Deeming, R. Ettorre, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1971, 1797 and 2701.

Table). The ^1H n.m.r. spectrum of $H_2Os_3(NHC_6H_3F)(CO)_9$ is particularly notable in that it positively supports *ortho*-metallation. All three ring hydrogen signals are clearly visible and couplings can be assigned. Heating an octane solution of the decacarbonyl in a sealed glass tube (186—194 °C) gave both isomers of the nonacarbonyl, $H_2Os_3(NHC_6H_3F)(CO)_9$ and $H_2Os_3(NC_6H_4F)(CO)_9$, and therefore the chemistry of the *p*-fluoro-compounds is not significantly different from that of the aniline derivatives.

As *p*-toluidine is a solid, different reaction conditions were necessary for reaction with $Os_3(CO)_{12}$. The two compounds reacted in a sealed evacuated tube to give exclusively $HOs_3(NHC_6H_4Me)(CO)_{10}$ in good yield. Pyrolysis of this compound gave only $H_2Os_3(NC_6H_4Me)(CO)_9$ with no evidence of ring metallation to give the other isomer. However, at the higher temperatures required for the decarbonylation to take place (210 °C) the initially formed ring-metallated compound might have isomerised. Thus we have no clear evidence to show whether electron-poor or electron-rich aromatic rings are more readily metallated in these systems.

Conclusions.—Metallation at the *ortho*-position of the aniline ring might be compared to metallation of amines in other systems. In single metal atom compounds a dominating feature is the preference for five-membered ring formation [11] and aniline or aniline derivatives do not normally metallate. The ready metallation of aniline with dodecacarbonyltriosmium almost certainly occurs at the metal atom which is not bonded to the nitrogen and so five-membered ring formation may still operate here. However, there is metallation at the α-position to the heteroatom rather than at the β-position for triethylphosphines in triosmium systems (four-membered ring formation) [9] and this is also possible in nitrogen systems since pyridine reacts with $Os_3(CO)_{12}$ to give $HOs_3(o\text{-}C_5H_4N)(CO)_{10}$.[12]

EXPERIMENTAL

All reactions were carried out under nitrogen unless stated otherwise. The products are indefinitely stable at room temperature in air so separation procedures were carried out in the atmosphere using preparative t.l.c. plates made up with silica gel (E. Merck; HF_{254}, type 60). Eluants were pentane with just sufficient chloroform or dichloromethane to give satisfactory movement of bands, which were finally extracted with dichloromethane.

Reactions of Triosmium Dodecacarbonyl with Aniline or p-*Substituted Anilines.*—*Aniline.* A solution of $Os_3(CO)_{12}$ (0·266 g) in freshly distilled aniline (20 ml) was refluxed for 1¼ h. The solvent was removed from the yellow-brown solution under reduced pressure and the residue chromatographed with chloroform–pentane as eluant to give a broad yellow band which gave $H_2Os_3(NHC_6H_4)(CO)_8(NH_2Ph)$ as yellow crystals from chloroform–pentane (0·169 g, 59%). Other products in very low yield were not isolated.

p-*Fluoroaniline.* A solution of $Os_3(CO)_{12}$ (0·200 g) in *p*-fluoroaniline (2·5 ml) was refluxed for 1¼ h and a similar work up to that above gave three yellow bands on chromatography. The first band gave yellow crystals from dichloromethane–pentane of $HOs_3(NHC_6H_4F)(CO)_{10}$ (0·091 g, 41%); the second yellow crystals from dichloromethane–pentane of $H_2Os_3(NHC_6H_3F)(CO)_9$ (0·025 g, 12%); and the third $H_2Os_3(NHC_6H_3F)(CO)_8(NH_2C_6H_4F)$ as yellow crystals (0·031 g, 13%).

p-*Toluidine.* A sealed evacuated glass tube containing $Os_3(CO)_{12}$ (0·231 g) and $p\text{-}MeC_6H_4NH_2$ (0·572 g) was heated at 186—189 °C for 7 h. The cooled mixture was washed from the tube with dichloromethane, the solvent distilled, and the *p*-toluidine sublimed at 0·1 mmHg and *ca.* 50 °C. The involatile residue was chromatographed to give yellow crystals from pentane of $HOs_3(NHC_6H_4Me)(CO)_{10}$ (0·163 g, 65%).

Action of Carbon Monoxide on $H_2Os_3(NHC_6H_4)(CO)_8(NH_2Ph)$.—Carbon monoxide was bubbled through a refluxing heptane solution of the octacarbonyl complex (0·100 g) for 3 h. After removal of the solvent under reduced pressure the residue was separated by chromatography into two yellow crystalline species. One was shown spectroscopically to be starting material (0·035 g, 35%), while the other was $H_2Os_3(NHC_6H_4)(CO)_9$ (0·060 g, 63%).

In a similar experiment at higher temperatures (refluxing octane, 125 °C, 6 h) the octacarbonyl starting material (0·090 g) was completely converted into two yellow crystalline products which were isolated by chromatography and shown to be $HOs_3(NHC_6H_5)(CO)_{10}$ (0·033 g, 43%) and $H_2Os_3(NHC_6H_4)(CO)_9$ (0·016 g, 21%). This decacarbonyl complex could be more conveniently prepared (70% yield) by passing CO through a refluxing aniline solution of $Os_3(CO)_{12}$ for 1 h.

Action of Heat on the Complexes $HOs_3(NHAr)(CO)_{10}$.—*In refluxing alkane.* A solution of $HOs_3(NHC_6H_5)(CO)_{10}$ (0·040 g) in nonane (70 ml) was refluxed and changes in the i.r. spectrum near 2000 cm^{-1} were observed. There was *ca.* 90% conversion into $H_2Os_3(NHC_6H_4)(CO)_9$ after 3 h but 19 h reflux gave significant decomposition. Removal of the solvent and chromatography of the residue gave three pure components, two of which were identified by comparison of their spectra with those of authentic samples as $HOs_3(NHC_6H_5)(CO)_{10}$ (0·002 g) and $H_2Os_3(NHC_6H_4)(CO)_9$ (0·008 g). The third yellow crystalline complex was shown to be $H_2Os_3(NC_6H_5)(CO)_9$ (0·005 g).

Similarly with the *p*-fluoro-analogue, $HOs_3(NHC_6H_4F)(CO)_{10}$ (0·023 g), in nonane (30 ml) complete conversion into $H_2Os_3(NHC_6H_3F)(CO)_9$ was observed (by i.r. spectroscopy) after 5 h. After 19 h under reflux the considerably decomposed mixture yielded yellow crystals of $H_2Os_3(NHC_6H_3F)(CO)_9$ (0·10 g) as the only isolable complex.

The *p*-methyl analogue gave gradual decomposition under similar conditions and no products were isolated.

In Sealed Tubes.—A solution of $HOs_3(NHPh)(CO)_{10}$ (0·040 g) in degassed decalin (1 ml) was heated at 196—198 °C. The hydride n.m.r. signal (τ 28·3) due to $H_2Os_3(NC_6H_5)(CO)_9$ was observed to form and its ratio to that due to the decacarbonyl (*ca.* 0·3) remained constant from 24 to 212 h at this temperature. Significant quantities of the isomeric complex were absent at any stage. The solution yielded $H_2Os_3(NC_6H_5)(CO)_9$ (*ca.* 0·004 g) and $HOs_3(NHC_6H_5)(CO)_{10}$ (0·021 g) after separation.

A solution of $HOs_3(NHC_6H_4F)(CO)_{10}$ (0·026 g) in octane (5 ml) was heated in a sealed tube. Whereas at 167—168 °C no significant reaction was observed, at 186—194 °C (8 h) the following complexes were obtained after chromato-

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[11] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[12] A. J. Deeming and C. Choo Yin, unpublished results.

graphy: starting material (0·014 g); $H_2Os_3(NC_6H_4F)(CO)_9$ (0·003 g) which was identified only by the close similarity of its i.r. spectrum, ν(CO), to that of the corresponding aniline derivative; and $H_2Os_3(NHC_6H_3F)(CO)_9$ (0·006 g).

The complex $HOs_3(NHC_6H_4Me)(CO)_{10}$ (0·163 g) showed little reaction below 210 °C. After 4 h at this temperature chromatography yielded starting material (0·088 g) and $H_2Os_3(NC_6H_4Me)(CO)_9$ (0·036 g). There was no indication of the presence of a ring-metallated isomer.

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