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DODECACARBONYLTRIOSMIUM CATALYSED FORMATION OF BIS(4-*N*,*N*-DIMETHYLAMINOPHENYL)METHANE FROM *N*,*N*-DIMETHYLANILINE *

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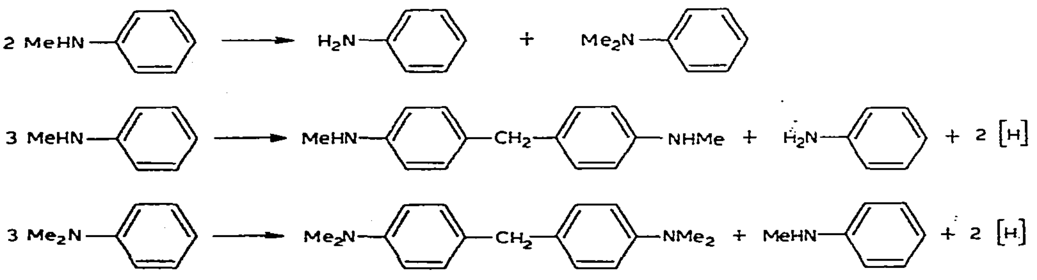
Summary

$Os_3(CO)_{12}$ catalyses the conversion of NMe_2Ph to $(4\text{-}NMe_2C_6H_4)_2CH_2$ and NHMePh in refluxing *N*,*N*-dimethylaniline. This reaction is similarly catalysed by $H_4Os_4(CO)_{12}$, while $(4\text{-}NHMeC_6H_4)_2CH_2$ may be obtained from NHMePh. In this case, however, NMe_2Ph and NH_2Ph are also formed, and after longer reaction times mixed products of type $(4\text{-}NRR'C_6H_4)_2CH_2$ (R or R' = H or Me) are obtained. The formation of $H_3Os_3(CH)(CO)_9$ indicates methyl transfer from nitrogen to osmium which may be a key step in the catalysis, but it does not appear that clusters are essential since $Fe(CO)_5$ and $Cr(CO)_6$ are also weakly active.

Introduction

In the course of an examination of cluster carbonyl derivatives of alkyl- and aryl-amines, we have found that $Os_3(CO)_{12}$, or derivatives of this formed in the reaction solution, catalyse the reactions 1 to 3. We do not know the course of



(1)

(2)

(3)

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* No reprints available.

this catalysis, nor the nature of the catalytic species, but the few organometallic clusters we have isolated suggest possibilities.

Previously we have compared NMe_3 [1] with PR_3 (R = Me or Et) [2,3] in their reactions with $Os_3(CO)_{12}$. Elimination at the alkylamine gives clusters with ligands containing N=C bonds, while elimination at the trialkylphosphines occurs only at the substituent R to give alkene and alkyne complexes. The formation of $HOs_3(MeN{=}CH)(CO)_n$ ($n = 9$ or 10) [1], in addition to $HOs_3(C{=}NMe_2)(CO)_{10}$, from NMe_3 shows that N—C cleavage can be induced as is required for reactions 1—3. We initiated a study of the reactions of NMe_2Ph for comparison with our earlier results on EMe_2Ph (E = P or As) [4,5] which react with $Os_3(CO)_{12}$ by *o*-metallation and E—aryl cleavage to give μ^3-C_6H_4 clusters with the EMe_2 groups remaining intact. It seems that alkyl activation only takes place in these systems when these are the only substituents present. Our results described here show that N—alkyl bonds are cleaved and that *o*-metallation, if it occurs, is not apparent from the nature of the products.

Results and discussion

A refluxing solution (194°C) of $Os_3(CO)_{12}$ in NMe_2Ph solution gives $(4\text{-}Me_2NC_6H_4)_2CH_2$ by reaction 3 in catalytic quantities. Use of NMe_2Ph as the solvent prevented significant occurrence of reactions 1 and 2 as the concentration of NHMePh increased as the reaction proceeded. The rate of formation of $(4\text{-}Me_2NC_6H_4)_2CH_2$ is initially ca. 46 mol $[\text{mol } Os_3(CO)_{12}]^{-1}$ h^{-1} but this drops to ca. 3 mol $[\text{mol } Os_3(CO)_{12}]^{-1}$ h^{-1} after 30 h, based on the initial $Os_3(CO)_{12}$ concentration. The overall formation after 63 h is 742 mol $[\text{mol } Os_3(CO)_{12}]^{-1}$ by which time the reaction is essentially over. No reaction occurs in the absence of $Os_3(CO)_{12}$ either with or without light and carbon monoxide suppresses the catalysed reaction; the rate is reduced by approximately 250 fold on changing from an atmosphere of N_2 (1 atm) to CO (12 atm). This indicates that amine coordination at osmium (not necessarily at an osmium cluster) is necessary for reaction.

While the stoicheiometry of reaction 3 was not precisely established, NHMePh is formed in significant amounts so that *N*-methyl groups are undoubtedly the origin of the central CH_2 of the product. Formally H_2 is lost in the reaction (we did not test for its formation) and, since H_2 reacts with $Os_3(CO)_{12}$ to give $H_2Os_3(CO)_{10}$ and eventually $H_4Os_4(CO)_{12}$ [6], it was possible that conversion to these hydrides was the origin of the catalyst decay. However, $H_4Os_4(CO)_{12}$ catalyses reaction 3 at rates even somewhat higher than those of $Os_3(CO)_{12}$ so, far from being inactive, the tetrahydride may be the active catalyst even when $Os_3(CO)_{12}$ is used and that under CO its formation from $Os_3(CO)_{12}$ is largely prevented.

With NHMePh reactions 1 and 2 both occur so that pure $(4\text{-}NHMeC_6H_4)_2CH_2$ can only be obtained after short reaction times (1 h). Longer reaction times give greater yields of substituted diphenylmethanes but, while these were not separated, ^{1}H NMR indicates that these are a mixture of $(4\text{-}NR^1R^2C_6H_4)_2CH_2$ where NR^1R^2 is NMe_2, NHMe or NH_2. It may be that these are formed from the different amino compounds generated by reaction 1, but more likely a reaction analogous to 1 is occurring with $(4\text{-}NHMeC_6H_4)_2CH_2$.

We can present very little evidence to support any mechanism for the catal-

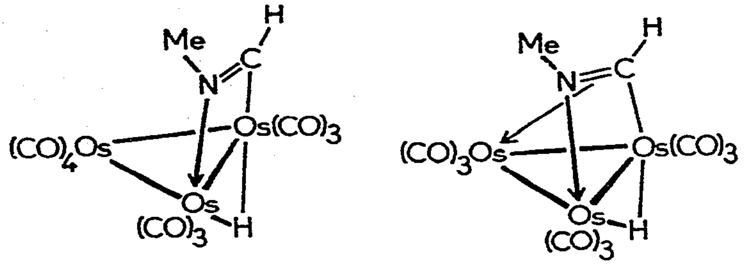

Fig. 1. Probable structures of $HOs_3(MeN{=}CH)(CO)_9$ or 10.

ysis. Attempting to isolate organometallics formed at early stages of the reaction we treated NRMePh (R = H or Me) with $Os_3(CO)_{12}$ under CO which slows down the catalysis. A complex mixture of carbonyl complexes was obtained but low yields of $H_3Os_3(CH)(CO)_9$, when R = Me, clearly indicate methyl transfer from nitrogen to osmium. This compound has been obtained by thermal treatment of $HOs_3(CH_3)(CO)_{10}$, $H_2Os_3(CH_2)(CO)_{10}$ [7], $HOs_3(OCH{=}CH_2)(CO)_{10}$ or $HOs_3(COCH_3)(CO)_{10}$ [8] so that transfer of a methyl group to an Os_3 cluster is likely to give the CH compound at high temperatures. The residual organic fragment after loss of the elements of CH_4 is expected to be $PhN{=}CH_2$ which might be stabilised in the compound $HOs_3(PhN{=}CH)(CO)_{10}$ but we were unable to detect this species in the mixture from NMe_2Ph. Imines do react in this way with $Os_3(CO)_{12}$ since MeN=CHPh readily gives HOs_3 $(MeN{=}CPh)(CO)_{10}$ [1] and trialkylamines react to give imine derivatives, for example NMe_3 reacts with $Os_3(CO)_{12}$ to give $HOs_3(MeN{=}CH)(CO)_n$ (n = 9 or 10) [1] by loss of the elements of CH_4. Fig. 1 shows the most likely structures for these compounds. The compound $HOs_3(PhN{=}CH)(CO)_{10}$ was, however, obtained from the reaction of NHMePh with $Os_3(CO)_{12}$ but here alkyl transfer is not required. Another organometallic compound isolated is $HOs_3(NHPh)(CO)_{10}$, no doubt formed by reaction of the aniline generated by reaction 1 with $Os_3(CO)_{12}$ [9].

For the catalytic reactions 2 and 3 a source of electrophilic carbon is required. This may be either a methyl group transferred to osmium from nitrogen or a nitrogen-bound carbon of an imine residue. The chemistries of $HOs_3(CH_3)(CO)_{10}$, $H_2Os_3(CH_2)(CO)_{10}$ or $H_3Os_3(CH)(CO)_9$ are essentially unknown so that these carbon atoms may or may not have electrophilic character. The chemistry is not, however, unique to clusters since $Cr(CO)_6$ and $Fe(CO)_5$ also catalyse reaction 3 but less effectively. Metal carbonyl catalysed routes to $(4\text{-}NR^1R^2C_6H_4)_2CH_2$ ($R^1 = R^2$ = Me) from NR^1R^2Ph may now be added to free-radical routes from NMe_2Ph initiated by $t\text{-}BuO_2\text{-}t\text{-}Bu$ [10], photochemical reactions of NMe_2Ph in acidic solutions [11] and acid-catalysed condensation of formaldehyde with NR^1R^2Ph ($R^1 = R^2$ = H or Me) [12,13].

Experimental

Action of $Os_3(CO)_{12}$ with N,N-dimethylaniline

1. Reaction under reflux. A solution of $Os_3(CO)_{12}$ (0.100 g) in NMe_2Ph (462 cm^3, freshly distilled, pure by GLC) was heated under reflux under N_2 for 63 h. The NMe_2Ph, removed under reduced pressure, was shown to contain

NHMePh. The solid residue (20.8 g), although essentially one compound, was obtained analytically pure by extraction with a large volume of petroleum ether (b.p. <40°C) and, following treatment with activated charcoal, this extract was concentrated to give bis(4-*N*,*N*-dimethylaminophenyl)methane as colourless crystals, m.p. 89—90°C (Found: C, 80.2; H, 8.6; N, 11.1. $C_{17}H_{22}N_2$ calcd.: C, 80.25; H, 8.7; N, 11.0%); ^1H NMR ($CDCl_3$): symmetrical AA'BB' signals at δ (ppm) 7.03 and 6.67 (C_6H_4), 3.79 s (CH_2) and 2.89 s (CH_3). The yields of $(4\text{-}NMe_2C_6H_4)_2CH_2$ after various reflux times were estimated from the mass of dry residue of samples: 0.51 g (1 h), 2.55 g (2 h), 5.2 g (4 h), 17.8 g (20 h), 18.6 g (36 h) and 20.8 g (63 h). Maximum mol product/mol catalyst (R) = 742. A blank reaction carried out in the absence of $Os_3(CO)_{12}$ gave no product.

2. *Isolation of organometallic compounds.* CO was passed through a refluxing solution of $Os_3(CO)_{12}$ (0.179 g) and NMe_2Ph (2 cm^2) in dekalin (25 cm^3) for 6 h. The solid residue after evaporation was separated by layer chromatography (silica) using $CHCl_3$/pentane (30/70 v/v) as eluant to give $H_3Os_3(CH)(CO)_9$ as the only characterisable organometallic product (0.007 g, 4%), identical spectroscopically with that prepared by an alternative route [8].

3. *Sealed tube reaction.* A stainless steel autoclave (100 cm^3 capacity) with a glass liner containing $Os_3(CO)_{12}$ (0.180 g), NMe_2Ph (10 cm^3) and decane (10 cm^3) was evacuated, charged with CO, sealed and heated at 194°C for 34 h (12 atm at this temperature). After cooling, the solution was decanted from unreacted $Os_3(CO)_{12}$ (0.162 g). Layer chromatography of the decanted liquid gave $(4\text{-}NMe_2C_6H_4)_2CH_2$ (0.134 g, R = 2.7).

4. *Other metal carbonyls.* Other metal carbonyls in refluxing NMe_2Ph under N_2 for 3 h also gave $(4\text{-}NMe_2C_6H_4)_2CH_2$ [R = 237, $H_4Os_4(CO)_{12}$; R = 15.4, $Ru_3(CO)_{12}$; R = 0.4, $Fe(CO)_5$; R = 1.1, $Cr(CO)_6$].

Action of $Os_3(CO)_{12}$ with N-methylaniline

1. *Reaction under reflux.* A solution of $Os_3(CO)_{12}$ (0.250 g) in NHMePh (50 cm^3, freshly distilled) was heated under reflux under N_2 for 1 h. The orange-brown solution was evaporated under reduced pressure to give a viscous brown oil which was extracted with chloroform (ca. 50 cm^3). $H_4Os_4(CO)_{12}$ (0.110 g, 36%) remained as a buff-coloured solid. The chloroform extract was reduced to dryness and the residue extracted with pentane. Layer chromatography (silica) of the extract, eluting with $CHCl_3$/pentane (70/30 v/v), gave two colourless bands which gave NHMePh and $(4\text{-}NHMeC_6H_4)_2CH_2$ as colourless crystals (0.062 g, m.p. 54—55°C) (Found: C, 79.35; H, 7.95; N, 12.05. $C_{15}H_{18}N_2$ calcd.: C, 79.6; H, 8.0; N, 12.35%); ^1H NMR ($CDCl_3$) δ (ppm) 6.84, 6.30 (AA'BB' signals, C_6H_4), 3.69 s (CH_2), 3.28 br (NH) and 2.71 (NCH_3). The diacetylated derivative of this, $[4\text{-}NMe(COMe)C_6H_4]_2CH_2$, was obtained as pale-yellow crystals (59%), m.p. 93—94°C; (Found: C, 73.55; H, 6.95; N, 8.90. $C_{19}H_{22}N_2O_2$ calcd.: C, 73.5; H, 7.15; N, 9.05%); ^1H NMR ($CDCl_3$): δ (ppm) 7.16 (C_6H_4), 4.01 s (CH_2), 3.18 s (NCH_3) and 1.80 ($COCH_3$).

Extended reaction times gave more products. For example, $Os_3(CO)_{12}$ (0.050 g) in refluxing NHMePh (50 cm^3) for 5.25 h gave NHMePh (ca. 52%), NMe_2Ph (ca. 12%) and NH_2Ph (ca. 16%) (estimated by GLC) and a viscous orange residue (10.2 g) which defied separation but by ^1H NMR was shown to contain mainly a mixture of type $(4\text{-}NR^1R^2C_6H_4)_2CH_2$ (R^1 and R^2 = H or Me).

2. Isolation of organometallic compounds. CO was passed through a refluxing solution of $Os_3(CO)_{12}$ (0.218 g) in NHMePh (20 cm^3) for 6.25 h. After removal of the excess of NHMePh under reduced pressure, layer chromatography (silica; eluant, pentane) gave two broad bands. One gave colourless crystals of $(4\text{-}NHMeC_6H_4)_2CH_2$ (0.3 g) and the other a mixture of organometallic compounds. Crystallisation from pentane gave orange crystals of $HOs_3(NHPh)(CO)_{10}$ (0.019 g, 8%), m.p. 185—187°C (Found: C, 20.3; H, 0.75; N, 1.55. $C_{16}H_7NO_{10}Os_3$ calcd.: C, 20.35; H, 0.75; N, 1.5%), spectroscopically identical with an authentic sample. Evaporation of the pentane mother liquors gave an incompletely characterised compound believed to be $HOs_3(PhN{=}CH)(CO)_{10}$ (0.019 g, 8%); ν(CO) (cyclohexane) 2105(5), 2065(10), 2054(10), 2025(10), 2011(10), 2005(9), 1994(9), 1978(4) cm^{-1} (relative intensities in brackets); ^{1}H NMR ($CDCl_3$), δ (ppm) 10.98 (CH); 7.07 (C_6H_5) and —14.86 s (OsH).

3. Sealed tube reactions. Two clean dry glass tubes charged with $Os_3(CO)_{12}$ (0.205 g), NHMePh (10 cm^3) and octane (40 cm^3) were degassed, sealed under vacuum and heated at 140 and 170°C, respectively, for 100 h. Most of the $Os_3(CO)_{12}$ (0.200 g) was recovered from the tube heated at 140°C, while the other tube gave $H_4Os_4(CO)_{12}$ (0.135 g, 54%) and $HOs_3(NHPh)(CO)_{10}$ (0.010 g).

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