

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

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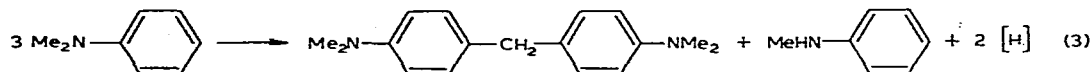
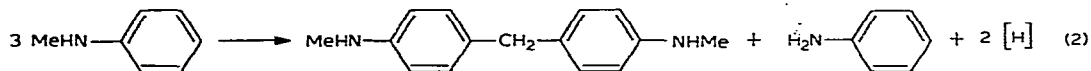
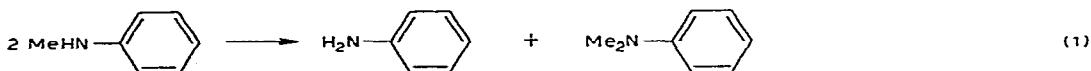
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Summary

$\text{Os}_3(\text{CO})_{12}$ catalyses the conversion of NMe_2Ph to $(4\text{-NMe}_2\text{C}_6\text{H}_4)_2\text{CH}_2$ and NHMePh in refluxing *N,N*-dimethylaniline. This reaction is similarly catalysed by $\text{H}_4\text{Os}_4(\text{CO})_{12}$, while $(4\text{-NHMeC}_6\text{H}_4)_2\text{CH}_2$ 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 $(4\text{-NRR}'\text{C}_6\text{H}_4)_2\text{CH}_2$ (R or $\text{R}' = \text{H}$ or Me) are obtained. The formation of $\text{H}_3\text{Os}_3(\text{CH})(\text{CO})_9$ 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 $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ are also weakly active.

Introduction

In the course of an examination of cluster carbonyl derivatives of alkyl- and aryl-amines, we have found that $\text{Os}_3(\text{CO})_{12}$, or derivatives of this formed in the reaction solution, catalyse the reactions 1 to 3. We do not know the course of



* 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 ($\text{R} = \text{Me}$ or Et) [2,3] in their reactions with $\text{Os}_3(\text{CO})_{12}$. Elimination at the alkylamine gives clusters with ligands containing $\text{N}=\text{C}$ bonds, while elimination at the trialkylphosphines occurs only at the substituent R to give alkene and alkyne complexes. The formation of $\text{HOs}_3(\text{MeN}=\text{CH})(\text{CO})_n$ ($n = 9$ or 10) [1], in addition to $\text{HOs}_3(\text{C}=\text{NMe}_2)(\text{CO})_{10}$, from NMe_3 shows that $\text{N}-\text{C}$ 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 ($\text{E} = \text{P}$ or As) [4,5] which react with $\text{Os}_3(\text{CO})_{12}$ by o -metallation and $\text{E}-\text{aryl}$ cleavage to give $\mu^3\text{-C}_6\text{H}_4$ 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 $\text{N}-\text{alkyl}$ 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 $\text{Os}_3(\text{CO})_{12}$ in NMe_2Ph solution gives $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}_2$ 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 $(4\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{CH}_2$ is initially ca. $46 \text{ mol } [\text{mol Os}_3(\text{CO})_{12}]^{-1} \text{ h}^{-1}$ but this drops to ca. $3 \text{ mol } [\text{mol Os}_3(\text{CO})_{12}]^{-1} \text{ h}^{-1}$ after 30 h, based on the initial $\text{Os}_3(\text{CO})_{12}$ concentration. The overall formation after 63 h is $742 \text{ mol } [\text{mol Os}_3(\text{CO})_{12}]^{-1}$ by which time the reaction is essentially over. No reaction occurs in the absence of $\text{Os}_3(\text{CO})_{12}$ 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 stoichiometry 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 $\text{Os}_3(\text{CO})_{12}$ to give $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and eventually $\text{H}_4\text{Os}_4(\text{CO})_{12}$ [6], it was possible that conversion to these hydrides was the origin of the catalyst decay. However, $\text{H}_4\text{Os}_4(\text{CO})_{12}$ catalyses reaction 3 at rates even somewhat higher than those of $\text{Os}_3(\text{CO})_{12}$ so, far from being inactive, the tetrahydride may be the active catalyst even when $\text{Os}_3(\text{CO})_{12}$ is used and that under CO its formation from $\text{Os}_3(\text{CO})_{12}$ is largely prevented.

With NHMePh reactions 1 and 2 both occur so that pure $(4\text{-NHMeC}_6\text{H}_4)_2\text{CH}_2$ 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, ^1H NMR indicates that these are a mixture of $(4\text{-NR}^1\text{R}^2\text{C}_6\text{H}_4)_2\text{CH}_2$ 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 $(4\text{-NHMeC}_6\text{H}_4)_2\text{CH}_2$.

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

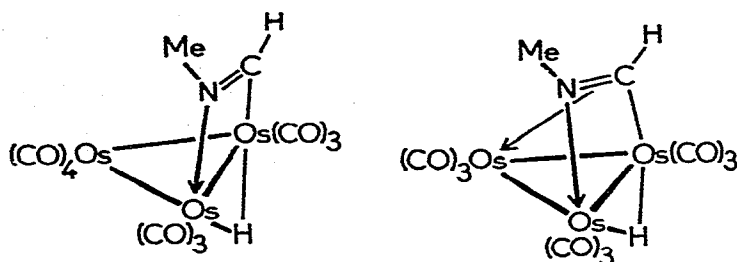


Fig. 1. Probable structures of $\text{HOs}_3(\text{MeN}=\text{CH})(\text{CO})_9$ or 10 .

ysis. Attempting to isolate organometallics formed at early stages of the reaction we treated NRMePh ($\text{R} = \text{H}$ or Me) with $\text{Os}_3(\text{CO})_{12}$ under CO which slows down the catalysis. A complex mixture of carbonyl complexes was obtained but low yields of $\text{H}_3\text{Os}_3(\text{CH})(\text{CO})_9$, when $\text{R} = \text{Me}$, clearly indicate methyl transfer from nitrogen to osmium. This compound has been obtained by thermal treatment of $\text{HOs}_3(\text{CH}_3)(\text{CO})_{10}$, $\text{H}_2\text{Os}_3(\text{CH}_2)(\text{CO})_{10}$ [7], $\text{HOs}_3(\text{OCH}=\text{CH}_2)(\text{CO})_{10}$ or $\text{HOs}_3(\text{COCH}_3)(\text{CO})_{10}$ [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 $\text{PhN}=\text{CH}_2$ which might be stabilised in the compound $\text{HOs}_3(\text{PhN}=\text{CH})(\text{CO})_{10}$ but we were unable to detect this species in the mixture from NMe_2Ph . Imines do react in this way with $\text{Os}_3(\text{CO})_{12}$ since $\text{MeN}=\text{CHPh}$ readily gives $\text{HOs}_3(\text{MeN}=\text{CPh})(\text{CO})_{10}$ [1] and trialkylamines react to give imine derivatives, for example NMe_3 reacts with $\text{Os}_3(\text{CO})_{12}$ to give $\text{HOs}_3(\text{MeN}=\text{CH})(\text{CO})_n$ ($n = 9$ or 10) [1] by loss of the elements of CH_4 . Fig. 1 shows the most likely structures for these compounds. The compound $\text{HOs}_3(\text{PhN}=\text{CH})(\text{CO})_{10}$ was, however, obtained from the reaction of NHMePh with $\text{Os}_3(\text{CO})_{12}$ but here alkyl transfer is not required. Another organometallic compound isolated is $\text{HOs}_3(\text{NHPh})(\text{CO})_{10}$, no doubt formed by reaction of the aniline generated by reaction 1 with $\text{Os}_3(\text{CO})_{12}$ [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 $\text{HOs}_3(\text{CH}_3)(\text{CO})_{10}$, $\text{H}_2\text{Os}_3(\text{CH}_2)(\text{CO})_{10}$ or $\text{H}_3\text{Os}_3(\text{CH})(\text{CO})_9$, are essentially unknown so that these carbon atoms may or may not have electrophilic character. The chemistry is not, however, unique to clusters since $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$ also catalyse reaction 3 but less effectively. Metal carbonyl catalysed routes to $(4\text{-NR}^1\text{R}^2\text{C}_6\text{H}_4)_2\text{CH}_2$ ($\text{R}^1 = \text{R}^2 = \text{Me}$) from $\text{NR}^1\text{R}^2\text{Ph}$ 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 $\text{NR}^1\text{R}^2\text{Ph}$ ($\text{R}^1 = \text{R}^2 = \text{H}$ or Me) [12,13].

Experimental

Action of $\text{Os}_3(\text{CO})_{12}$ with *N,N*-dimethylaniline

1. *Reaction under reflux.* A solution of $\text{Os}_3(\text{CO})_{12}$ (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. $<40^{\circ}\text{C}$) and, following treatment with activated charcoal, this extract was concentrated to give bis(4-*N,N*-dimethylaminophenyl)methane as colourless crystals, m.p. $89\text{--}90^{\circ}\text{C}$ (Found: C, 80.2; H, 8.6; N, 11.1. $\text{C}_{17}\text{H}_{22}\text{N}_2$ 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 $(4\text{-NMe}_2\text{C}_6\text{H}_4)_2\text{CH}_2$ 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 $\text{Os}_3(\text{CO})_{12}$ gave no product.

2. *Isolation of organometallic compounds.* CO was passed through a refluxing solution of $\text{Os}_3(\text{CO})_{12}$ (0.179 g) and NMe_2Ph (2 cm^3) in dekaline (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 $\text{H}_2\text{Os}_3(\text{CH})(\text{CO})_9$ 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 $\text{Os}_3(\text{CO})_{12}$ (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 $\text{Os}_3(\text{CO})_{12}$ (0.162 g). Layer chromatography of the decanted liquid gave $(4\text{-NMe}_2\text{C}_6\text{H}_4)_2\text{CH}_2$ (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 $(4\text{-NMe}_2\text{C}_6\text{H}_4)_2\text{CH}_2$ [R = 237, $\text{H}_4\text{Os}_4(\text{CO})_{12}$; R = 15.4, $\text{Ru}_3(\text{CO})_{12}$; R = 0.4, $\text{Fe}(\text{CO})_5$; R = 1.1, $\text{Cr}(\text{CO})_6$].

*Action of $\text{Os}_3(\text{CO})_{12}$ with *N*-methylaniline*

1. *Reaction under reflux.* A solution of $\text{Os}_3(\text{CO})_{12}$ (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). $\text{H}_4\text{Os}_4(\text{CO})_{12}$ (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 $(4\text{-NHMeC}_6\text{H}_4)_2\text{CH}_2$ as colourless crystals (0.062 g, m.p. $54\text{--}55^{\circ}\text{C}$) (Found: C, 79.35; H, 7.95; N, 12.05. $\text{C}_{15}\text{H}_{18}\text{N}_2$ 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 (NCH₃). The diacetylated derivative of this, $[4\text{-NMe}(\text{COMe})\text{C}_6\text{H}_4]_2\text{CH}_2$, was obtained as pale-yellow crystals (59%), m.p. $93\text{--}94^{\circ}\text{C}$; (Found: C, 73.55; H, 6.95; N, 8.90. $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$ 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 (NCH₃) and 1.80 (COCH_3).

Extended reaction times gave more products. For example, $\text{Os}_3(\text{CO})_{12}$ (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 $(4\text{-NR}^1\text{R}^2\text{C}_6\text{H}_4)_2\text{CH}_2$ (R^1 and R^2 = H or Me).

2. *Isolation of organometallic compounds.* CO was passed through a refluxing solution of $\text{Os}_3(\text{CO})_{12}$ (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- NHMeC_6H_4) $_2\text{CH}_2$ (0.3 g) and the other a mixture of organometallic compounds. Crystallisation from pentane gave orange crystals of $\text{HOs}_3(\text{NHPh})(\text{CO})_{10}$ (0.019 g, 8%), m.p. 185–187°C (Found: C, 20.3; H, 0.75; N, 1.55. $\text{C}_{16}\text{H}_7\text{NO}_{10}\text{Os}_3$ 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 $\text{HOs}_3(\text{PhN}=\text{CH})(\text{CO})_{10}$ (0.019 g, 8%); $\nu(\text{CO})$ (cyclohexane) 2105(5), 2065(10), 2054(10), 2025(10), 2011(10), 2005(9), 1994(9), 1978(4) cm^{-1} (relative intensities in brackets); ^1H 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 $\text{Os}_3(\text{CO})_{12}$ (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 $\text{Os}_3(\text{CO})_{12}$ (0.200 g) was recovered from the tube heated at 140°C, while the other tube gave $\text{H}_4\text{Os}_4(\text{CO})_{12}$ (0.135 g, 54%) and $\text{HOs}_3(\text{NHPh})(\text{CO})_{10}$ (0.010 g).

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