# Trimethylamine Oxide Induced Decarbonylation of $M(CO)_2Cl_2(PPh_3)_2$ (M = Ru, Os) Complexes

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Trimethylamine oxide ($Me_3NO$) has been used as a versatile decarbonylating reagent in inorganic and organometallic chemistry [1], and previously we have demonstrated its synthetic utility in reactions of ruthenium(II) carbonyl complexes [2–4]. For instance, under mild conditions (in pyridine at room temperature) $Ru(CO)_2X_2(PPh_3)_2$ complexes (X = Cl, Br) undergo selective monodecarbonylation with $Me_3NO$ to give neutral $Ru(CO)X_2(py)(PPh_3)_2$ complexes [2]. A similar reaction involving $M(CO)_2Cl_2(PPh_3)_2$ (M = Ru, Os) has now been studied under more vigorous conditions (refluxing 2-methoxyethanol), and in the presence of 1,10-phenanthroline (phen) yields the cationic $[M(CO)Cl(phen)(PPh_3)_2]^+$ complexes (I) as the major products (reaction (1))

$$M(CO)_2Cl_2(PPh_3)_2 + phen + Me_3NO \longrightarrow$$

$$[M(CO)Cl(phen)(PPh_3)_2]Cl + Me_3N + CO_2 \qquad (1)$$

In addition, reaction (1) (M = Ru) also results in the formation of the hydrido complex $[HRu(CO)(phen)(PPh_3)_2]Cl$ (**II**) as a minor product.

The $[M(CO)Cl(phen)(PPh_3)_2]^+$ cationic complexes are prepared by heating under reflux a suspension of $M(CO)_2Cl_2(PPh_3)_2$ (0.26 mmol), phen (0.56 mmol) and $Me_3NO$ (1.1 mmol) in 2-methoxyethanol (25 ml) under nitrogen for 2 h. Addition of excess aqueous $KPF_6$ to the hot solution produces an orange–yellow precipitate. After cooling the solution to 0 °C, the precipitate is filtered and recrystallized from acetone/ethanol giving yellow microcrystals of $[M(CO)Cl(phen)(PPh_3)_2](PF_6)$ (65% yield for M = Ru; 60% for M = Os). On standing, the mother liquor (for M = Ru) deposits orange crystals of $[HRu(CO)(phen)(PPh_3)_2](PF_6)\cdot EtOH$ (10%). The analogous triphenylarsine derivatives of **I** and **II** (for M = Ru) were similarly prepared. The complexes were characterized by elemental analyses (C, H, N), IR and $^1H$ NMR spectroscopy. The previously reported complexes **I** (M = Os, prepared by carbonylation of a mixture of $Os(phen)Cl_4$ and $PPh_3$ in ethylene glycol) [5] and **II** (prepared by reacting $RuHCl(CO)(phen)(PPh_3)_2$ with $NaBPh_4$ in methanol) [6] had similar spectroscopic properties to the reported values. Spectroscopic data for all complexes indicate a *trans* arrangement for the phosphine and arsine ligands.

The formation of **I** during reaction (1) results from nucleophilic attack of $Me_3NO$ at CO, followed by coordination of phen and displacement of the *cis* chloride ligand. Despite the presence of excess phen and $Me_3NO$, complete decarbonylation to yield $[M(phen)_2(PPh_3)_2]^{2+}$ is not observed. The failure of **I** to undergo further decarbonylation may be attributed to its low $\nu$(CO) absorption (*ca.* 1950 $cm^{-1}$) and the fact that $Me_3NO$ induced decarbonylations are generally restricted to complexes with $\nu(CO) > 2000$ $cm^{-1}$ [7]. The formation of the hydrido complex **II** may be explained in terms of the generally accepted mechanism for hydride formation in alcoholic solvents [8]. In addition, the presence of weak bases has been shown to assist hydride abstraction from solvents [9]. Thus, the presence of excess phen may assist removal of the alcoholic protons to give an alkoxo complex which rearranges to form **II**. Attempts to convert **I** (M = Ru) into **II** by reacting **I** with phen in refluxing methoxyethanol have been unsuccessful. This observation and the fact that the related complex $[Os(CO)Cl(bpy)L_2]^+$ (bpy = 2,2′-bipyridyl; L = trialkylphosphine) fails to form hydrides in alcoholic solvents [8] would suggest that **II** does not form from **I**, but rather directly from $Ru(CO)_2Cl_2(PPh_3)_2$ during reaction (1). In the absence of $Me_3NO$, the dicarbonyl starting complexes $M(CO)_2Cl_2(PPh_3)_2$ remain unchanged when treated with phen in refluxing methoxyethanol. Thus the presence of $Me_3NO$ is required to initiate the formation of both **I** and **II**. The reactivity of the dicarbonyl and monocarbonyl complexes is presently being studied further.

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