

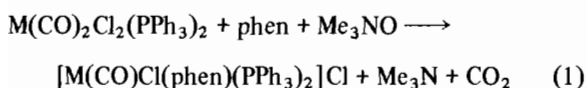
Trimethylamine Oxide Induced Decarbonylation of $M(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ ($M = \text{Ru}, \text{Os}$) Complexes

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(Received May 12, 1988)

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) $\text{Ru}(\text{CO})_2\text{X}_2(\text{PPh}_3)_2$ complexes ($\text{X} = \text{Cl}, \text{Br}$) undergo selective monodecarbonylation with Me_3NO to give neutral $\text{Ru}(\text{CO})\text{X}_2(\text{py})(\text{PPh}_3)_2$ complexes [2]. A similar reaction involving $M(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ ($M = \text{Ru}, \text{Os}$) has now been studied under more vigorous conditions (refluxing 2-methoxyethanol), and in the presence of 1,10-phenanthroline (phen) yields the cationic $[M(\text{CO})\text{Cl}(\text{phen})(\text{PPh}_3)_2]^+$ complexes (**I**) as the major products (reaction (1))



In addition, reaction (1) ($M = \text{Ru}$) also results in the formation of the hydrido complex $[\text{HRu}(\text{CO})(\text{phen})(\text{PPh}_3)_2]^+\text{Cl}^-$ (**II**) as a minor product.

The $[M(\text{CO})\text{Cl}(\text{phen})(\text{PPh}_3)_2]^+$ cationic complexes are prepared by heating under reflux a suspension of $M(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ (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 $[M(\text{CO})\text{Cl}(\text{phen})(\text{PPh}_3)_2](\text{PF}_6)$ (65% yield for $M = \text{Ru}$; 60% for $M = \text{Os}$). On standing, the mother liquor (for $M = \text{Ru}$) deposits orange crystals of $[\text{HRu}(\text{CO})(\text{phen})(\text{PPh}_3)_2](\text{PF}_6) \cdot \text{EtOH}$ (10%). The analogous triphenylarsine derivatives of **I** and **II** (for $M = \text{Ru}$) were similarly prepared. The complexes were characterized by elemental analyses (C, H, N), IR and ^1H NMR spectroscopy. The previously reported complexes **I** ($M = \text{Os}$, prepared by carbonylation of a mixture of $\text{Os}(\text{phen})\text{Cl}_4$ and PPh_3 in ethylene glycol) [5] and **II** (prepared by reacting $\text{RuHCl}(\text{CO})(\text{phen})(\text{PPh}_3)_2$ with NaBPh_4 in methanol) [6] had similar spectroscopic properties to the reported values. Spec-

troscopic 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 $[M(\text{phen})_2(\text{PPh}_3)_2]^{2+}$ is not observed. The failure of **I** to undergo further decarbonylation may be attributed to its low $\nu(\text{CO})$ absorption (*ca.* 1950 cm^{-1}) and the fact that Me_3NO induced decarbonylations are generally restricted to complexes with $\nu(\text{CO}) > 2000 \text{ cm}^{-1}$ [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** ($M = \text{Ru}$) into **II** by reacting **I** with phen in refluxing methoxyethanol have been unsuccessful. This observation and the fact that the related complex $[\text{Os}(\text{CO})\text{Cl}(\text{bpy})\text{L}_2]^+$ (*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 $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ during reaction (1). In the absence of Me_3NO , the dicarbonyl starting complexes $M(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ 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.

Acknowledgement

This work was funded by the AUM Grant-in Aid program.

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