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

B. LACHELE FOLEY, C. ANNE SMITH
and NICHOLAS C. THOMAS

Chemistry Department, Auburn University at Montgomery, Montgomery, Ala. 36193, U.S.A.

(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) $Ru(CO)_2X_2(PPh_3)_2$ 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))

$$M(CO)_2Cl_2(PPh_3)_2 + phen + Me_3NO \longrightarrow [M(CO)Cl(phen)(PPh_3)_2]Cl + Me_3N + CO_2 \quad (1)$$

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 ν(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.

Acknowledgement

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

References

1 T-Y. Luh, *Coord. Chem. Rev., 60,* 255 (1984).
2 D. St. C. Black, G. B. Deacon and N. C. Thomas, *Inorg. Chim. Acta, 54,* L143 (1981).
3 D. St. C. Black, G. B. Deacon and N. C. Thomas, *Inorg. Chim. Acta, 65,* L75 (1982).
4 N. C. Thomas, *Inorg. Chim. Acta, 120,* L7 (1986).
5 B. P. Sullivan, J. V. Caspar, S. R. Jonson and T. J. Meyer, *Organometallics, 3,* 1241 (1984).
6 S. Gopinathan and C. Gopinathan, *Synth. React. Inorg. Met.-Org. Chem., 16,* 1395 (1986).
7 D. J. Blumer, K. W. Barnett and T. L. Brown, *J. Organomet. Chem., 173,* 71 (1979).
8 H. D. Kaez and R. B. Sailant, *Chem. Rev., 72,* 231 (1972).
9 A. D. Harris and S. D. Robinson, *Inorg. Chim. Acta, 42,* 25 (1980).

0020-1693/88/$3.50