

Abstract

The molybdenum(II) and tungsten(II) halocarbonyls, $[\text{M}(\text{CO})_4\text{X}_2]_2$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}$) react with a large excess of the nitrogen bases, 1-methylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine and 2-ethylpiperidine to give aminocarbonyl complexes of the type $\text{M}(\text{CO})_3\text{L}_3$ ($\text{L} =$ alkylamine). Excess piperidine reacts with the tungsten halocarbonyls, $[\text{W}(\text{CO})_4\text{X}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}$), to give the trans isomer of the complex, $\text{W}(\text{CO})_3(\text{C}_5\text{H}_{11}\text{N})_3$. The halogens were recovered as the ammonium salts, amine, HX . The oxidized amine dimerized to form a yellow product which was recovered as an oily liquid but in very small amounts. However, in the reaction between $\text{Mo}(\text{CO})_4\text{Br}_2$ and 1-ethylpiperidine, a yellow crystalline solid, with a melting point of 224°C was recovered in sufficient amounts for elemental analysis, melting point and spectral data. Its mass spectrum showed a molecular ion peak at $m^+/z = 222$, a clear evidence that the oxidized amine dimerizes. The cyclic dibasic amine piperazine, $\text{C}_4\text{H}_{10}\text{N}_2$ is not, however, oxidized by these halocarbonyls but rather it reacts by substituting some CO groups to form products of the type, $\text{M}(\text{CO})_3(\text{C}_4\text{H}_{10}\text{N}_2)_2\text{X}_2$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}$). Products were characterized by elemental analysis, IR, UV, ^1H NMR and mass spectrometry.