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Preliminary communication

Synthesis of halo metal carbonyls by the reductive carbonylation of halides and oxyhalides of molybdenum and tungsten

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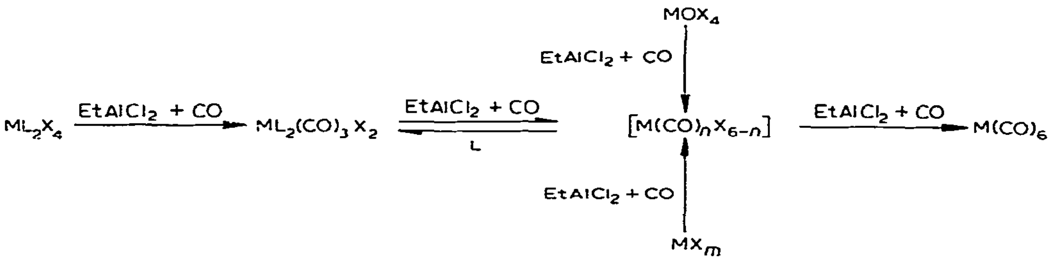
Several examples have been described for the synthesis of $Mo(CO)_6$ and $W(CO)_6$ by 'reductive carbonylation'[1] but the halo carbonyl derivatives of Mo and W have been prepared up to now only from the appropriate hexacarbonyls[2,3]. We report now a direct method for the synthesis of the halo metal carbonyls of molybdenum and tungsten.

$W(CO)_6$ is formed when WPy_2Cl_4 or $W(Ph_2PC_2H_4PPh_2)_2Cl_3$ reacts with $EtAlCl_2$ in chlorobenzene under 1 atm of carbon monoxide[4,5]. Halides and oxyhalides react similarly. Ether, which is the favoured solvent in the high pressure synthesis of $W(CO)_6$[1], inhibits the reaction. Using hydrocarbons as solvents and $WOCl_4$ as starting material, a 30% yield of $W(CO)_6$ was obtained. Halo carbonyl complexes were also formed and being insoluble in hydrocarbons could be easily separated. When these complexes were dissolved in acetone and an acetone solution of triphenylphosphine was added, $W(CO)_3(PPh_3)_2Cl_2$ separated out. Starting from WCl_6 and using a 4/1 Al/W molar ratio, the yield of $W(CO)_3(PPh_3)_2Cl_2$ was 30%. The corresponding $AsPh_3$ derivative was prepared analogously.

The method may also be applied to preparation of molybdenum derivatives. Thus, 150 mg $Mo(PPh_3)_2Cl_4$ was suspended in 3 ml heptane and treated with 0.2 ml $EtAlCl_2$ in 10 ml heptane (Al/Mo 10/1) under carbon monoxide for 3 h. The solid portion of the products was separated and dissolved in a small quantity of acetone, and an acetone solution of PPh_3 was added. $Mo(PPh_3)_2(CO)_3Cl_2$, precipitated as yellow powder (yield 23%). When this experiment was repeated with an Al/Mo molar ratio of 2/1, the solid part of the reaction mixture consisted mainly of $Mo(PPh_3)_2(CO)_3Cl_2$, which after washing with acetone, was obtained in 32% yield; no more of this complex was separated when PPh_3 was added.

To our knowledge, this is the first case in which intermediate halo carbonyls have been isolated from reductive carbonylation of the Group VIA metals to their hexacarbonyls:



The unsubstituted halo carbonyls are obtained as a mixture as shown by their IR spectrum, and presumably $M(CO)_4X_2$ is the species which is transformed into $ML_2(CO)_3X_2$ on the addition of L, while the others apparently lose carbon monoxide.

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