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Metal Carbonyls: An Overview

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Commentary

Metal carbonyls have a history that dates back to 1834, when Justus von Liebig conducted preliminary experiments on the reaction of carbon monoxide with metals. Even then, it was later found that the compound he claimed to be potassium carbonyl was not, in fact, a metal carbonyl at all. Hieber prepared numerous compounds containing metal and carbon monoxide after Schutzenberger in 1868 reported the synthesis of [PtCl₂(CO)₂] and [PtCl₂(CO)]₂, followed by Mond in 1890 reporting the synthesis of [Ni(CO),].

Organometallic compounds are those that contain at least one carbon-metal bond. Metal carbonyls are transition metal coordination complexes with carbon monoxide ligands. Metal carbonyls can be used in organic synthesis as well as catalysts or catalyst precursors in homogeneous catalysis processes such as hydro formylation and Reppe chemistry. Nickel tetra carbonyl is used in the Mond process to produce pure nickel. Metal carbonyls are precursors in organometallic chemistry. These are all Mx(CO) y-type volatile and low-melting compounds that biodegrade on heating into carbon monoxide and metal, with their properties determined by the structure of the carbonyl molecules and the type of chemical bonds in them. In many ways, the carbonyl ligand (CO) distinguishes itself from other ligands. For example, unlike alkyl ligands, the carbonyl (CO) ligand is unsaturated, allowing the ligand to not only donate but also accept electrons in its orbital from d metal orbitals, making the CO ligand acidic. The majority of mononuclear carbonyl complexes are flammable and toxic colourless or pale yellow volatile liquids or solids. Vanadium hexacarbonyl is a blue-black solid that is a unique 17-electron metal carbonyl. Carbonyls that are dimetallic or polymetallic are more deeply coloured.

Metal carbonyl synthesis is a hot topic in organometallic research. Many procedures for the preparation of mononuclear metal carbonyls as well as homo- and heterometallic carbonyl clusters have been developed since the work of Mond and

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then Hieber. Paul Schützenberger created the first true heteroleptic metal carbonyl complex in 1868 by passing chlorine and carbon monoxide over platinum black, resulting in dicarbonyldichloroplatinum (Pt(CO)₂Cl₂). Some metal carbonyls are synthesised by reducing metal halides under high carbon monoxide pressure. Copper, aluminium, hydrogen, and metal alkyls such as triethylaluminium are among the reducing agents used. Metal carbonyls can be mononuclear or polynuclear in structure. Metal atoms in polynuclear carbonyls are directly and, in many cases, indirectly bound to each other via bridging CO-groups. Metal carbonyls have been identified as potential catalysts/catalyst precursors in a number of important organic compound transformations. Metal carbonyls are employed in a variety of industrial processes. The extraction and purification of nickel via nickel tetracarbonyl by the Mond process was possibly the earliest application (see also carbonyl metallurgy). The toxicity of metal carbonyls is due to the toxicity of carbon monoxide, the metal, and because of the complexes' volatility and instability, any underlying toxicity of the metal is generally made much more drastic due to the ease of exposure. Chronic inhalation of nickel tetracarbonyl at low concentrations can cause neurological symptoms such as insomnia, headaches, dizziness, and memory loss. Nickel tetracarbonyl is known to be carcinogenic, but the clinical manifestation of cancer can take 20 to 30 years from the time of exposure.