# Synthesis of Transition-metal Carbonyl Derivatives of Magnesium

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*Summary* Novel transition-metal carbonyl derivatives of magnesium can be readily prepared by the reductive cleavage of numerous dimeric transition metal carbonyl complexes with magnesium amalgam in the presence of a Lewis base.

We report the synthesis and properties of a new class of reactive 'mixed metal' complexes containing metal–metal bonds between magnesium and Group VI, VII, and VIII transition metals.

The reductive cleavage of dimeric transition-metal carbonyl complexes with magnesium amalgam in the presence of a Lewis base

$$\text{M–M} + \text{Mg(Hg)} \xrightarrow{\text{Base}} \text{B}_x\text{Mg[M]}_2 \text{ (I)}$$

yields complexes of general formula (I) [M = $Fe(CO)_2C_5H_5$, $Mo(CO)_2(L)C_5H_5$, $Co(CO)_3L$, $Ni(CO)C_5H_5$, $Mn(CO)_4L$ where L = CO, or alkyl- or aryl- phosphine; B = tetrahydrofuran (thf), pyridine (py), or tetramethylethylenediamine (tmeda); and $x = 2$ or 4 when B is considered monobasic], in quantitative yield at ambient temperature. The complexed Lewis base can be supplied by the solvent or by the addition of a slight excess of base to a hydrocarbon reduction medium. The complexes, (I), thus obtained are air- and moisture-sensitive, thermally stable (decomp. *ca.* 150 °C, 10 mmHg), diamagnetic and monomeric in hydrocarbon and ether solvents. The number of complexed bases ($x$) found in (I) was established by n.m.r. and chemical analyses and correlates well with the nucleophilicity of the transition-metal anion.[1] When (M) is a strongly nucleophilic anion, such as $Fe(CO)_2C_5H_5^-$ or $Mo(CO)_2(PR_3)C_5H_5^-$, complexes containing two Lewis bases crystallise from solution, while less nucleophilic anions, such as $Co(CO)_3L^-$ and $Mn(CO)_5^-$, yield magnesium derivatives containing four complexed bases.

The molar conductivities ($\Lambda_M = \Omega^{-1}$ cm$^2$ mol$^{-1}$), of 0·05 M THF solutions of (I) smoothly increase with decreasing anion nucleophilicity. Values of $\Lambda_M$ range between the extremes of 0·010 and 1·60 found for $(py)_2Mg[Fe(CO)_2C_5H_5]_2$ and $(thf)_4Mg[Mn(CO)_5]_2$, respectively. These numbers, when compared to $\Lambda_M = 12·4$ found for an ionized 0·05 M THF solution of $NaCo(CO)_4$,[2] suggest that the magnesium–transition-metal bond is not highly dissociated.

Benzene solutions of $(py)_2Mg[Fe(CO)_2C_5H_5]_2$, (II) and $(thf)_4Mg[Co(CO)_3P(C_4H_9)_3]_2$, (III) exhibit carbonyl stretching frequencies at 2015m, 1921vs, 1854vs, and 1822sh, and at 2046w, 1968s, 1910s, 1888vs, and 1872sh cm$^{-1}$, respectively. These frequencies are intermediate between those exhibited by the corresponding anions[3] and their covalent mercury derivatives.[4,5] The number of carbonyl bands observed for (II) and (III) is well above that predicted by local symmetry arguments[6] and is attributed to vibrational coupling across the M–Mg–M linkage.[7] The i.r. results, together with the molar conductivity data and monomeric behaviour, suggest that the magnesium–transition-metal bond in (I) possesses considerable covalent character.

Because of their excellent hydrocarbon solubility, the complexes (I) are useful metallating agents. For example, $(Ph_3P)_3CuCo(CO)_3P(C_4H_9)_3$ was prepared by the metathetical reaction of $(thf)_4Mg[Co(CO)_3P(C_4H_9)_3]_2$ with $[Ph_3P]_3CuCl$ in hexane solution. In a more conventional preparation employing $NaCo(CO)_3P(C_4H_9)_3$ in THF, only copper metal and $(Ph_3P)_2Cu[Co(CO)_3P(C_4H_9)_3]_2$ were obtained, as the polar solvent assisted the disproportionation of the initially formed Cu$^I$ complex. Thus, in cases where the failure to isolate 'mixed metal' complexes can be attributed to solvent-aided disproportionations, the use of hydrocarbon-soluble, magnesium–transition-metal carbonyl complexes appears very attractive.

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