

## Synthesis of Transition-metal Carbonyl Derivatives of Magnesium

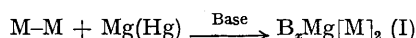
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**Summary** Novel transition-metal carbonyl derivatives of magnesium can be readily prepared by the reductive cleavage of numerous dimeric transition metal carbonyl complexes with magnesium amalgam in the presence of a Lewis base.

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



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.<sup>1</sup> 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 ( $\Lambda_M = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ), of 0.05M 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  $NaCo(CO)_4$ ,<sup>2</sup> 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  $\text{cm}^{-1}$ , respectively. These frequencies are intermediate between those exhibited by the corresponding anions<sup>3</sup> and their covalent mercury derivatives.<sup>4,5</sup> The number of carbonyl bands observed for (II) and (III) is well above that predicted by local symmetry arguments<sup>6</sup> and is attributed to vibrational coupling across the  $M-Mg-M$  linkage.<sup>7</sup> 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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