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Preliminary communication

Preparation and some reactions of a nickel Grignard reagent

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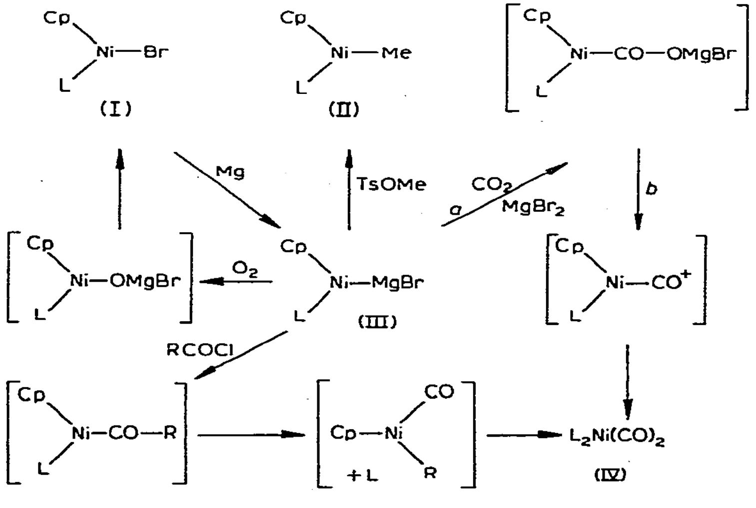
Grignard reagents are used far more extensively in organic chemistry than are the corresponding organo-sodium and -potassium compounds. It is therefore striking to note that the situation at present in transition metal chemistry is exactly the opposite. The vast majority of transition metal nucleophiles are sodium or potassium salts of transition metal anions stabilised by acceptor ligands like CO, as indeed are the very few known compounds containing magnesium–transition metal (Mn, Fe, Co, Mo, W) bonds[1,2]. Here we report the preparation and some reactions of a magnesium–nickel system with ligands other than CO.

Treatment of a solution of the bromide I in ether/THF with excess magnesium turnings gave a dark brown solution, about one mole of magnesium being consumed. A similar solution was obtained when the reaction was carried out in ether/benzene. Analysis of the ether/THF solution showed the presence of approx-



SCHEME 1 ($L = PPh_3$; $Cp = \pi\text{-}C_5H_5$)

imately equimolar quantities of nickel, magnesium and bromine (found: Ni/Mg/Br, 1.0/1.4/1.1) and its ^{1}H NMR spectrum, after evaporation, [(C_6D_6) τ2.3–3.3 (Ph); 3.57 (Cp); 6.3; 8.6 (THF); ratio of areas: $C_5H_5/C_6H_5/C_4H_8O$ = 5/20/26] indicated the formation of a new Cp complex (70% yield with respect to PPh_3). The signal of the Cp protons is at very low field [*cf.* I: τ4.9 (Cp)], similar to that recently reported for the compound $Cp_2Mg{\cdot}2THF$ in C_6D_6, [τ3.8 (Cp); 6.8, 8.8 (THF)][3]. This, and the reactions described below, strongly suggest that these solutions contain a nickel Grignard reagent probably best formulated as III, rather than as $CpLNi^-MgBr^+$ (the compound is readily soluble in benzene).

It was hoped that hydrolysis of these solutions would give the corresponding hydride π-$C_5H_5Ni(PPh_3)H$, but we were unable to isolate this from the reaction mixture. With methyl *p*-toluenesulphonate (2 days at 50°), however, the nickelmethyl complex II[4,5] was obtained in 25% yield★. In the latter reaction, the nickelphenyl complex π-$C_5H_5Ni(PPh_3)Ph$ (15%)[5] and the di-μ-(diphenylphosphido) complex [π-$C_5H_5NiPPh_2]_2$ (15%)[6] were also formed.

Furthermore, these solutions reacted with air to reform the bromide I, presumably by the route indicated in the scheme (yield 20% in ether/benzene). Acetyl chloride and benzoyl chloride with III in ether/benzene gave dicarbonylbis(triphenylphosphine)nickel IV, along with a small amount of tricarbonyltriphenylphosphinenickel (combined yield about 20%); methane and ethane and some bromide I were also formed in the acetyl chloride reaction. Benzoyl chloride and III in ether/THF also led to the dicarbonylnickel complex IV.

Treatment of III in ether/benzene with carbon dioxide, in the presence of added magnesium bromide, led to the same nickel carbonyl complex IV (40% yield); in ether/THF (a more basic solvent) the yield was much lower. This appears to be the first time carbon dioxide has been reduced by a homogeneous transition metal system. Possible intermediates in the formation of IV are shown in Scheme 1. The role of the Lewis acid (magnesium bromide) could be either to activate the carbon dioxide towards nucleophilic attack by III in reaction *a*, or to assist the elimination of $OMgBr^-$ in reaction *b*; the latter reaction presents analogies with the acid cleavage of methoxycarbonyldicarbonyl-π-cyclopentadienyliron to the tricarbonyl-π-cyclopentadienyliron cation[7].

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★All the yields mentioned are with respect to the starting bromide I.

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