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THE PARAMAGNETIC SPECIES PRODUCED IN THE REACTIONS OF TRANSITION METAL CHELATES WITH ORGANOMETALLIC REAGENTS

I. REDUCTION OF NICKEL(II) DIISOPROPYLSALICYLATE WITH GRIGNARD REAGENTS

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Summary

Grignard reagents reduce nickel(II) diisopropylsalicylate. Three different types of EPR signals were found and assigned to Ni^{II}, Ni^{I} and to a ketyl radical of the modified chelate ligand. The presence of the transition metal speeds up the formation of ketyl radicals.

Introduction

The central problem of the preparation of a stereospecific catalyst is the determination of the structure of intermediates formed in the course of reduction of transition metal chelates with organometallic compounds. These intermediates, formed in relatively low concentrations, very often function as catalytically active centres for polymerisation. They frequently possess paramagnetic properties which can advantageously be studied by EPR [1-4]. The location of the unpaired electron depends on the type of the organometallic compound and is explained in different ways. The aim of this work is to determine the influence of the chelate ligand, and of the alkyl and aryl groups respectively of the organometallic compound, on the structure of the paramagnetic products. The reactions of nickel(II) diisopropylsalicylate [$Ni(DIPS)_2$] and nickel(II) acetylacetonate [$Ni(acac)_2$] with different Grignard reagents (RMgX) were investigated with a systematic variation of R. These studies, in addition to clarifying the catalytic mechanism, also give information on the principles of the reduction of transition metal chelates and show the way to the preparation of long-living free radicals.

Experimental

$Ni(DIPS)_2$ and $Ni(acac)_2$ were prepared from $NiCl_2$ and diisopropylsalicylic acid or acetylacetone respectively according to refs. 5 and 6 and dried for two hours in vacuo (90°C/1 Pa). The following solutions were used: 0.5 *M* $Ni(DIPS)_2$ in hexane, 0.5 *M* $Ni(acac)_2$ in benzene, 0.5 *M* diisopropylsalicylic acid and 2 *M* solutions of different Grignard reagents in diethyl ether. The solvents p.a. were rectified and, before use, were dried with a organometallic compound and redistilled. The preparation of the Grignard reagents, the mixing of the reactants and all other operations were caried out under a well purified and dried argon atmosphere. The EPR spectra were obtained with a Varian E-3 X-band spectrometer. The conductivity of the reaction mixture was measured as described previously [7]. The volume of the gases formed during the reaction was determined and the gaseous compounds were identified by gas-chromatography. The reaction mixture was hydrolysed with 2 *M* HCl and the reaction products were separated and investigated by NMR, IR and mass spectrometry.

Results

(a) Nickel(II) diisopropylsalicylate

The paramagnetic properties of the reaction mixture [$Ni(DIPS)_2$ + RMgX] depend on the molar ratio Mg/Ni. There are three regions of molar ratios each with a characteristic EPR signal, as shown in Fig. 1.

At ratios Mg/Ni up to 4/1 a singlet having g_1 = 2.17 was observed. The maximum observed concentration of paramagnetic species corresponds to 5% nickel atoms present in the system. The singlet does not disappear when oxygen is brought into the reaction mixture. The appearance of this singlet is accompanied by the formation of a black precipitate and the whole system becomes jelly-like. The precipitate is soluble in alcohol and the nickel remains in the Ni^{II}

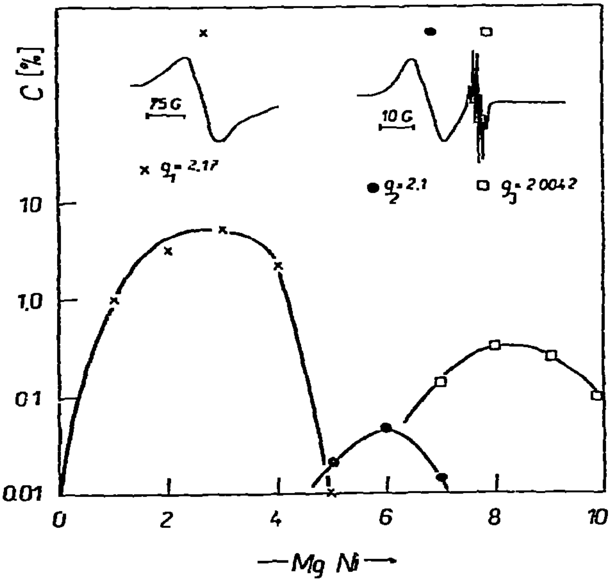


Fig. 1. The concentration of paramagnetic products at different molar ratios Mg/Ni.

state. During reaction with RMgX the hydrocarbon RH (from the corresponding Grignard reagent) is formed. Simultaneously, an absorption band at 1390 cm^{-1} in the IR spectrum, belonging to the phenoxygroup of the salicylate ligand, disappears.

At molar ratios Mg/Ni = 4-7 the singlet having g_1 = 2.17 is replaced by a new singlet with g_2 = 2.10. The maximum measured concentration of this paramagnetic species corresponds to 0.05% nickel atoms added to the system. Here, the system loses its gelatinous consistency and the evolution of the hydrocarbon RH is complete by the time the molar ratio Mg/Ni $\geqslant$ 6 is reached.

When the molar ratio Mg/Ni > 6 the signal having g_2 characteristic of the transition metal also disappears and a spectrum typical of free radicals with g_3 = 2.004$_2$ is observed. The maximum concentration of these radicals obtained was 10^{-4} *M*, corresponding to 0.3% nickel atoms added to the system. At these ratios, the previously heterogeneous system changes to a dark brown solution. The structure of the radical products having the g_3 value depends on the type of Grignard reagent as well as on the type of chelate ligand. This can be seen from Fig. 2, where the spectra obtained after the reaction of two different nickel chelates [Ni(DIPS)$_2$ and Ni(acac)$_2$] with two different Grignard reagents [CH$_3$MgBr and PhMgBr] are compared. Using one type of nickel chelate we obtained different spectra if different Grignard reagents were applied, and vice versa.

The type and concentration of paramagnetic products at different ratios of Mg/Ni, shown in Fig. 1 for the system Ni(DIPS)$_2$ + n-BuMgBr, are very similar if different Grignard reagents are used. At all molar ratios Mg/Ni the absorption of the carbonyl group, as followed by IR spectroscopy, remains without any considerable change. The relatively low conductivity of Ni(DIPS)$_2$ solution (3 10^{-7} Sm^{-1}) does not increase significantly on the addition of a highly conductive solution of RMgX (10^{-3} Sm^{-1}) at the molar ratio Mg/Ni < 6. At the ratio Mg/Ni > 6 the con-

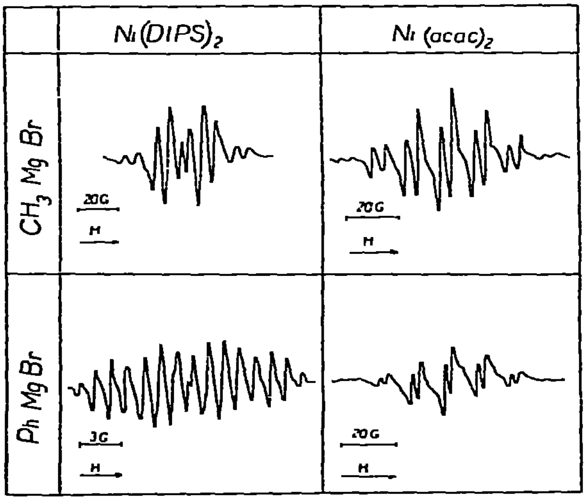


Fig. 2. The ESR spectra obtained by the reaction of two different transition metal chelates [Ni(DIPS)$_2$ and Ni(acac)$_2$] with two different Grignard reagents [CH$_3$MgBr and PhMgBr].

ductivity increases rapidly and the reaction mixture shows IR absorptions characteristic of RMgX.

(b) Diisopropylsalicylic acid (HDIPS)

To elucidate the role of the transition metal in the formation of free radicals, three types of experiments were compared: (i) $Ni(DIPS)_2$ + RMgX; (ii) HDIPS + RMgX (without transition metal); (iii) HDIPS + RMgX (adding definite amounts of transition metal to the reaction mixture).

In experiment (i) the formation of free radicals is always reproducibly observed immediately after mixing the reaction compounds. The concentration of free radicals is about 10^{-4} *M*. In experiment (ii) there is usually no formation of radicals immediately after mixing the reactants and only after one or more days can the radicals be observed. These results are not reproducible. In experiment (iii), i.e. if HDIPS is mixed with RMgX and a definite amount of a transition metal is added to the reaction mixture, radical formation is reproducibly observed immediately after the mixing of the reaction compounds. The spectra of the radicals obtained here are identical to those found in experiment (i); the stationary radical concentration depends on the amount of transition metal added to the reaction mixture, as shown in Fig. 3. The radical concentration is proportional to the transition metal concentration until both have reached a value of about 10^{-4} *M*, then, on increasing the transition metal concentration further, the radical concentration remains without any considerable change. The transition metal compounds used were the chlorides and the acetonates of Fe^{III}, Co^{II} and Ni^{II}.

The products obtained after hydrolysis of the reaction mixture from exper-

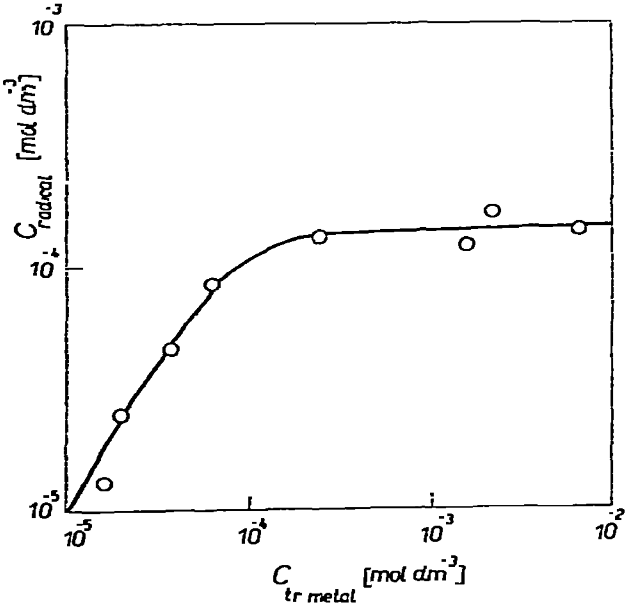


Fig. 3. The dependence of the radical concentration on the concentration of the transition metal added to the reaction mixture.

iments (i), (ii) and (iii) were compared. As the Grignard reagent, n-BuMgBr, was used in the ratio Mg/(salicylate ligand) = 5/1 the reaction was run for 3 days at 20°C. In experiments (i) and (iii), (i.e. if transition metal is present) in addition to the radical generation already described, formation of an aldehydic product was observed, in contrast to experiment (ii) (without transition metal) where no aldehyde was found. NMR analysis of the reaction mixture showed that aldehyde VII (see Scheme 1 below) was formed from salicylate with a yield of 3%. The yield of product IX was 5% and product X 12%.

Discussion

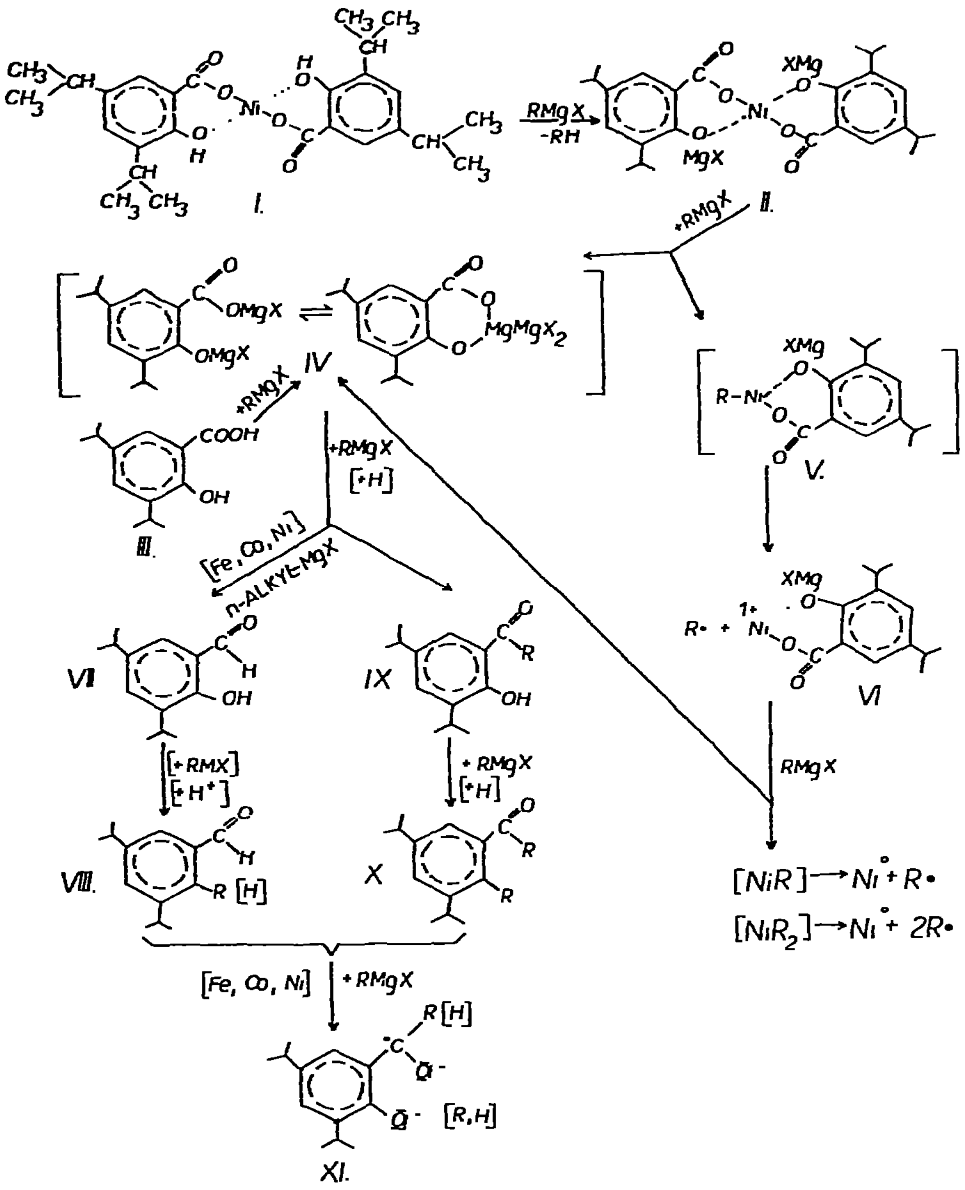
The formation of paramagnetic products during the reaction of $Ni(DIPS)_2$ with RMgX can be explained by means of Scheme 1. At the molar ratio Mg/Ni < 4 the preferred reaction is that of RMgX with the hydrogen of the salicylic phenoxyl group with formation of product II and hydrocarbon RH. The diamagnetic compounds entering the reaction change to the paramagnetic products. From the high g_1 value 2.17 it is evident that the unpaired electron is localized on the transition metal. In the case of nickel the EPR resonance is associated with the d^8 or d^9 configurations and the ferromagnetic resonance of nickel with d^{10} configuration. In view of the fact that at these molar ratios Mg/Ni the valency of nickel remains Ni^{II} and that the paramagnetic product behaves indifferently to the oxygen brought into the reaction mixture, the paramagnetism can be attributed to the d^8 configuration of nickel. The conversion of the diamagnetic compound I to the paramagnetic II can be explained as a consequence of the changes in the ligand field, which are connected with the rearrangement of the d^8 electrons from the low to the high spin configuration.

By further reaction of compound II with RMgX the chelate ligand is transferred to magnesium and compound IV is formed (compound IV is also formed by the reaction of HDIPS (III) with RMgX); simultaneously, further alkylation of nickel takes place. The unstable Ni—C bond splits and the final product of the nickel alkylation is Ni^0. The singlet having g_2 = 2.10 was assigned to Ni^I, an intermediate product, which could be represented by the compound VI. The formation of Ni^I as an intermediate between the two oxidation states of Ni^{II} and Ni^0 is probable, because this paramagnetic product appears at a very advanced stage of the nickel reduction and, from the relatively high value of g_2, it is evident that the unpaired electron is localized on the transition metal. This paramagnetic product is destroyed in contact with oxygen or other oxidizing agents. The problem of Ni^I was discussed in our previous paper [8].

The reduction of the carboxyl group to a ketone with RMgX and the substitution of phenoxyl group for an alkyl R are common reactions; the products IX and X correspond to this type of reaction. Also, the formation of aldehydes by the reduction of the carboxyl group with n-alkyl-MgX is known and it is explained by means of β-addition of the hydrogen from the n-alkyl moiety. The formation of an aldehyde by β-addition should be expected in all our experiments (i), (ii) and (iii) with equal probability. It is therefore remarkable that the aldehyde VII was found only in experiments (i) and (iii), i.e. if transition metal had been added to the reaction mixture. This means that the transition metal facilitates the transfer of hydrogen with consequent aldehyde formation. This effect

SCHEME 1

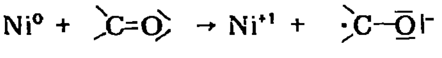
REACTION OF NICKEL(II) DIISOPROPYLSALICYLATE WITH GRIGNARD REAGENTS



can not be attributed to a pure β-addition, so we suppose that the hydride of the transition metal is formed intermediately, and that this facilitates hydrogen transfer from n-alkyl to the carboxyl group with the formation of the aldehyde.

During the last stage of the reaction the formation of free radicals having $g_3 = 2.004_2$ is observed. The radical structure depends on the type of alkyl R in the Grignard reagent and can be formulated as a ketyl radical derived from compound XI. The measured spectra and a detailed discussion of the radical structure is given in part II [9]. Radicals of identical structure are obtained by reaction of Grignard reagent with $Ni(DIPS)_2$ and with HDIPS. In both cases transfer of the unpaired electron from the Grignard reagent to the carbonyl group is speeded up by the presence of the transition metal. In the case of nickel, radical formation is also accelerated if the Ni^{II} has been reduced to Ni^0 before mixing the reactants. Therefore it can be assumed that the transfer of the electron from the alkyl R^- to the carbonyl group is mediated by Ni^0 and Ni^I, according to the following reaction scheme:

$$Ni^{+1} + R^- \rightarrow Ni^0 + R^\bullet$$



$$Ni^0 + \,>C{=}O \rightarrow Ni^{+1} + \,\cdot\!>C{-}O^-$$

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