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ZEROVALENT NICKEL COMPLEXES; NEW PREPARATIVE PROCEDURES, STRUCTURES AND PROPERTIES

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Summary

New simple procedures for preparing zerovalent nickel complexes are described. Three classes of compounds containing two moles of dialkyl maleates or fumarates and a ligand L per atom of nickel have been characterized in which L is acetonitrile, a quaternary ammonium or phosphonium salt, or a monovalent or bivalent metal halide. The X-ray structure of acetonitrile bis(diethyl fumarate)-nickel(0) is reported. A new preparation of dicyclooctadienenickel(0) is also described.

Introduction

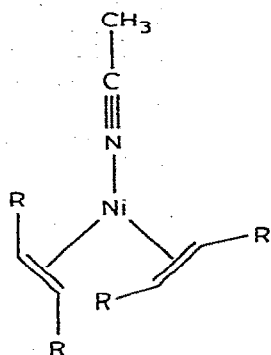
Zerovalent nickel complexes are known to act as catalysts in several organic reactions and are also useful as stoichiometric reagents for organic synthesis [1]. The known procedures for preparing zerovalent nickel complexes require rather laborious and time-consuming operations often involving the use of reagents not easy to handle [2]. We have therefore developed simple methods for preparing some complexes of this kind. In addition, since little is known about the structure and properties of this class of complex, we have tried to extend knowledge of them by preparing unusual compounds containing activated olefins as ligands.

Results and discussion

Reaction of zerovalent nickel with dialkyl fumarates or maleates and ligands L, where L is (a) CH_3CN ; (b) $\text{Br}^-[\text{N}(\text{C}_2\text{H}_5)_4]^+$, $\text{Br}^-[\text{PPh}_4]^+$, LiBr , MnBr_2 , NiBr_2 , MgCl_2 , ZnCl gives complexes of the type bis(dialkyl fumarate or maleate)-ligand-nickel(0).

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(I) $R = \text{COOEt}$

(a) The complexes acetonitrile bis(dimethyl fumarate)nickel(0), acetonitrile bis(diethyl fumarate)nickel(0), acetonitrile bis(dimethyl maleate)nickel(0) and acetonitrile bis(diethyl maleate)nickel(0) are crystalline compounds, soluble in organic solvents, and are sensitive to the oxygen of the air, but stable under an inert atmosphere up to about 110°C . In the IR spectrum the COOR absorbances are only weakly shifted towards lower frequencies, while the characteristic absorption of the CN group is absent. The main features of the structure of acetonitrile bis(diethyl fumarate)nickel(0) as revealed by X-ray analysis [3] may be represented as I. The four carbon atoms of the double bonds and the nitrogen atom are equi-planar and equidistant from the central nickel atom. The two carbons and the nitrogen of the CH_3CN ligand lie on the same axis as in free CH_3CN and with bond distances of the same order of magnitude. The COOEt groups are not coordinated.

(b) Bis(dimethyl fumarate)(tetraethylammonium bromide)nickel(0) and bis(dimethyl fumarate)(tetraphenylphosphonium bromide)nickel(0) complexes are very easily crystallised and have properties analogous to those of the corresponding CH_3CN complexes. In this case also, in the IR spectra only a weak shift of the COOMe absorption is observed.

Complexes which do not have any tendency to crystallise but appear as intensely coloured amorphous powders, soluble only in solvents which can solvate the metal cation, can be obtained with ethyl and methyl fumarate and maleate in the presence of Li^+ , Mn^{2+} , Ni^{2+} , Mg^{2+} , and Zn^{2+} halides. The IR spectrum shows large shifts of the COOR bands, which can be attributed to a coordination of the metal cation to the COOR groups of the fumarate and maleate. Similar band shifts are reported in the literature in the case of esters coordinated to salts of the same type. The amorphous nature, perhaps attributable to polymerisation, is probably due to the formation of bonds between the metal cation and COOR groups belonging to different molecules of the complex.

Bis(methyl or diethyl fumarate)(nickel dibromide)nickel(0) and bis(dimethyl or diethyl maleate)(nickel dibromide)nickel(0) complexes appear to be identical to those described in the literature as monovalent nickel complexes, viz.: bromo(dimethyl or diethyl fumarate)nickel and bromo(dimethyl or diethyl maleate)nickel [5]. We regard these as, in fact, zerovalent nickel complexes by analogy with those formed with other ligands (LiBr , MnBr_2 , MgCl_2 , ZnCl_2) showing similar properties.

All the complexes may be prepared by adding two moles of dimethyl (or diethyl) fumarate or dimethyl (or diethyl) maleate in a suitable solvent to one mole of dicyclooctadienenickel(0) in the presence of the appropriate ligand L. In addition, complexes with $L = CH_3CN$ may be prepared directly by reduction with a Mn/Fe alloy * of a solution of $NiBr_2$ in MeOH/CH in the presence of dimethyl (or diethyl) maleate or dimethyl (or diethyl) fumarate. All the other complexes can be easily obtained from those with CH_3CN .

Although these complexes are very sensitive to the oxygen of the air both in the solid state and in solution, they dissolve in water with varying ease without decomposing.

Dicyclooctadienenickel(0) was made by a completely new method of preparation **, which is described in the Experimental Section. This method has the advantage of not requiring the use of alkylaluminiums or other hazardous reagents [2].

Experimental

The organic starting materials were pure Merck products. The manganese metal was a pure C. Erba material, and was powdered before use. The manganese/iron alloy was a commercial product containing 79% Mn, 16% Fe, 1.46% C, and was powdered before use (0.040–0.025 mm).

The products were identified by elemental analysis, and by IR (Perkin—Elmer) and NMR (Jeol A60) spectroscopy.

Preparation of the complexes with $L = CH_3CN$

(a) 0.8 g (2.9 mmol) of dicyclooctadienenickel(0), 0.95 g (6 mmol) of dimethyl fumarate, and 1 ml of acetonitrile were successively added to 5 ml of 1,5-cyclooctadiene under an inert atmosphere. The mixture was stirred until the reagents dissolved and an orange-red solution was obtained then it was allowed to stand for 1–2 h. The complex (90%) separated as fine orange-red crystals. In the case of diethyl fumarate, a mixture of 2.5 ml of n-hexane and 2.5 ml of cyclooctadiene was used as solvent because of the higher solubility of the complex formed. For equivalent amounts of dimethyl (or diethyl) maleate a mixture of 7 ml of diethyl ether and 1 ml of cyclooctadiene was used as solvent.

Acetonitrile bis(dimethyl fumarate)nickel(0). Found: 15.05. $C_{14}H_{19}NO_8Ni$ calcd.: Ni, 15.12%. IR (Nujol) 1695 cm^{-1} (vs). The molar ratio between esters and nitrile was determined by NMR and by GLC of the ligands after oxidation of the complex with air or iodine.

Acetonitrile bis(diethyl fumarate)nickel(0). Found: Ni, 13.1 $C_{18}H_{27}NO_8Ni$ calcd.: Ni, 13.21%. IR (Nujol): 1725 and 1695 cm^{-1} (s); molecular weight by cryoscopy in benzene 366–370, calcd. 444.05 (the complex is probably slightly dissociated in benzene).

Acetonitrile bis(dimethyl maleate)nickel(0). Found: Ni, 14.94. $C_{14}H_{19}NO_8Ni$ calcd.: Ni, 15.12%. IR (Nujol) 1710 and 1695 cm^{-1} (s).

Acetonitrile bis(diethyl maleate)nickel(0). Found: Ni, 13.01. $C_{18}H_{27}NO_8Ni$ calcd.: Ni, 13.21%. IR (Nujol) 1720 and 1690 cm^{-1} (s).

* For preparation of complexes using powdered iron or manganese/iron alloys see ref. 6

** A similar procedure has been applied to bis(acrylonitrile)nickel [8].

(b) A solution of 5.46 g (25 mmol) of NiBr_2 (anhydrous) in a mixture of 10 ml MeOH and 10 ml CH_3CN was refluxed for 15–20 min. The mixture was cooled and then kept at room temperature in a water bath, and 7.25 g (50 ml) of dimethyl fumarate 30 ml of CH_3CN and 2.75 g of the finely powdered Fe/Mn alloy were added under an inert atmosphere with stirring. After a short induction period the reaction began, as indicated by a change in the colour from blue-green to red. (The process of the reduction, which is initially fast and exothermic, may be monitored by iodometric titration of the complex in solution.) After 1 h, the reaction was practically complete (nickel(0) \geq 95%), so the excess alloy was filtered off and the solution evaporated under vacuum at room temperature. The residue was extracted twice with 25–30 ml of diethyl ether, to leave a brown-red powder consisting essentially of the complex bis(dimethyl fumarate)(manganese dibromide)nickel(0). The residue was dissolved with a mixture of 30 ml of CH_3CN and 10 ml of air-free H_2O and the solution is transferred to separatory funnel to which 30 ml of a water-saturated solution was transferred to separatory vigorous stirring, the lower aqueous layer was separated. The process was repeated with 20 ml, and twice with 10 ml of the NaCl solution. The intensive red coloured organic solution was evaporated under vacuum. The solid obtained (9–9.3 g) consisted of the almost pure acetonitrile bis(dimethyl fumarate)-nickel(0) complex. It sometimes contained quantities of free fumarate and NaCl (as a result of incomplete separation in the preceding stages). The product can be crystallised from toluene, diethyl ether, etc.

An analogous process was followed for diethyl fumarate, dimethyl and diethyl maleate complexes. In the presence of maleate, the amount of NiBr_2 involved in the complex after 1 h of reaction is 85–86%; nevertheless, it is inconvenient to prolong the reduction, which becomes very slow at this point.

Maleate complexes may be recrystallised by dissolving the product in CH_3CN (as little as possible) and dilution with 3–4 volumes of diethyl ether. After cooling for 1–2 h at -30°C light yellow crystals are obtained.

Preparation of the complexes with L = quaternary salt

To 1.43 g of acetonitrile bis(dimethyl fumarate) nickel(0) dissolved in 40 ml of ethyl acetate was added tetraethyl ammonium bromide in excess (6g), and the mixture was stirred. After a short induction period a sudden precipitation of the complex as light brown needles was observed. After 15 min it was redissolved by heating with a water bath at $50\text{--}60^\circ\text{C}$. The residual undissolved quaternary salt was filtered off quickly, and the complex allowed to crystallise out again. It was subsequently washed with ethyl acetate and ether, then dried under vacuum to give 1 g of bis(dimethyl fumarate)(tetraethylammonium bromide)nickel(0). The tetraphenylphosphonium bromide complex was prepared by the same procedure, but in this case the stoichiometric amount of phosphonium salt could be used. Similar results were obtained by using dicyclooctadienenickel(0), dimethyl fumarate and quaternary salts in equivalent amounts, in place of the acetonitrile complex.

Bis(dimethyl fumarate)(tetraethylammonium bromide)nickel(0). Found: Ni, 10.3; N, 2.15; Br, 13.99. $\text{C}_{20}\text{H}_{36}\text{NO}_8\text{BrNi}$ calcd.: Ni, 10.53; N, 2.51; Br, 14.34% IR (Nujol) 1680 cm^{-1} (vs).

Bis(dimethyl fumarate)(tetraphenylphosphonium bromide)nickel(0). Found:

Ni, 7.55; P, 3.93; Br, 10.42. $C_{36}H_{36}O_8PBrNi$ calcd.: Ni, 7.65; P, 4.04; Br, 10.42. IR (Nujol) 1690 cm^{-1} (vs).

Preparation of the complexes with L = LiBr

A mixture of 0.44 g (5 mmol) of LiBr, and 10 ml of CH_3CN was stirred and 2.1 g (5 mmol) of acetonitrile bis(dimethyl fumarate)nickel(0) were added to give an intense dark-red solution. This was evaporated under vacuum, and the residue was treated with 20 ml of anhydrous diethyl ether, then evaporated to dryness. Repetition of the process two or three times gave a very dark powder insoluble in non-coordinating solvents. The preparation was also carried out using dicyclooctadienenickel(0), dimethyl fumarate and LiBr, in equivalent amounts, with CH_3CN as solvent. All the other complexes may be prepared by both procedures.

For the preparation of complexes with $NiBr_2$ and $MnBr_2$ it is convenient to transform the insoluble anhydrous salts into $MnBr_2 \cdot 2 CH_3CN$ and $NiBr_2 \cdot 2 CH_3CN$.

The IR spectra of the complexes with L = salt MX_2 in Nujol show two carbon-yl absorption bands with variable relative intensities. Typical examples are:
 Bis(diethyl maleate)(manganese dichloride)nickel(0): 1730m, 1645s cm^{-1}
 Bis(diethyl maleate)(manganese dibromide)nickel(0): 1730w, 1650s cm^{-1}
 Bis(dimethyl fumarate)(magnesium dichloride)nickel(0): 1712s, 1660s cm^{-1}
 Bis(dimethyl fumarate)(manganese dibromide)nickel(0): 1689s, 1639s cm^{-1}
 Bis(diethyl fumarate)(manganese dibromide)nickel(0): 1715s, 1620s cm^{-1}

With LiBr only one strong band at 1670 cm^{-1} is observed, as for quaternary ammonium or phosphonium salts.

Solutions of bis-fumarate(metal dihalide)nickel(0) complexes in acetonitrile are intensely brown-red in colour, whereas those of the corresponding maleates are permanganate-violet. Acetonitrile solutions of the same complexes without MX_2 are orange-red.

Preparation of dicyclooctadienenickel(0)

24 g of anhydrous $NiBr_2$ were dissolved in 150 ml of ethyleneglycol monomethyl ether(methyl cellosolve) by refluxing. The solution was cooled and 50 ml of 1,5-cyclooctadiene and 20 ml of quinoline added. The mixture was cooled to $-10^\circ C$ and 8 g of finely powdered manganese were added under nitrogen with stirring. After a short induction period, the solution turned orange-red (an intermediate complex with quinoline is formed) and after 15–20 min dicyclooctadienenickel(0) began to precipitate. The reaction was continued for about 1 h with stirring, the temperature of the bath being kept between -5 and $-10^\circ C$. The mixture was filtered under nitrogen then washed first with cold ($0^\circ C$) methyl cellosolve until the filtrate remained colourless (100–150 ml of solvent), and then with ether cooled at $-30^\circ C$. The bright yellow solid obtained was dried and consisted of a mixture of dicyclooctadienenickel(0) and residual metallic manganese.

To remove the metal, dicyclooctadienenickel(0) may be crystallised as follows. The crude product is placed on a Buchner funnel (G III) under nitrogen and washed with a toluene solution (250 ml) containing 1–2 ml of quinoline and 5–10 ml of cyclooctadiene, kept at $90^\circ C$ and added in small amounts (80 ml) to the Buchner without sucking; the precipitate was agitated with a glass rod and filtra-

tion then carried out by applying a gentle nitrogen pressure. The process was repeated until the filtrate remained colourless. The combined filtrates were placed in a flask under nitrogen and immersed in a bath at -70°C . The dicyclooctadinenickel(0) formed was filtered off, extensively washed with cold ether (at -30°C) and dried under vacuum. The total yield was about 14.5 g (60%).

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