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Preparation, crystal structure and reactivity of bis(methyl acrylate)(pyridine)nickel(0)

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Abstract

The preparation, crystal structure and reactivity of bis(methyl acrylate)(pyridine)nickel(0) are reported. This complex reacts with *E*,*Z*-1-bromo-1-propene in the presence of water to give the conjugate addition product. Complexes of this type seem to be involved in Ni^0 catalysed reactions of olefins with organic halides in the presence of pyridine and water.

Introduction

Nickel(0) catalysed processes constitute an important class of transition-metal mediated reactions in organic synthesis [1]. If these transformations require the presence of ligands, then substituted phosphanes are usually employed. Reactions in the presence of nitrogen ligands are far less common. Recently we developed a reaction of organic halides with electron-deficient olefins in the presence of $NiCl_2 \cdot 6H_2O$, zinc and pyridine (in eq. 1 shown for methyl acrylate as olefin). We assumed that a Ni^0 complex with pyridine as ligand might be involved [2].

This reaction is very flexible in the kind of organic halide that can be used; primary, secondary and tertiary aliphatic bromides and vinylic and aryl chlorides,

$$RX + H_2C{=}CHCO_2Me \xrightarrow[\text{Zn, pyridine, THF}]{NiCl_2 \cdot 6H_2O} RCH_2CH_2CO_2Me \qquad (1)$$

bromides and iodides have been used. At some stage during the reaction there must be oxidative addition of an organic halide to a coordinatively unsaturated Ni^0 complex. As (bipyridine)bis(olefin)nickel(0) complexes (18 electron complexes) did not show any activity in the reaction [3], we reasoned that a nickel(0) complex with two olefins and one pyridine might be involved. Such a complex has now been isolated and characterised, and it does, indeed, show the expected reactivity.

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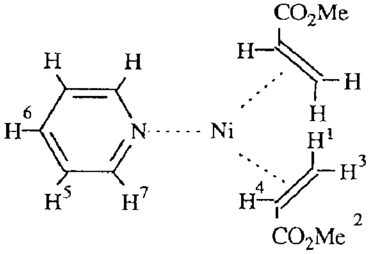
Results and discussion

Bis(methyl acrylate)(pyridine)nickel(0) can be prepared in either of two ways: treatment of a mixture of $NiCl_2 \cdot 6H_2O$ with an excess of methyl acrylate and pyridine in tetrahydrofuran in the presence of zinc leads after several hours to a THF solution of the complex. Separation from the inorganic salts and work-up (see Experimental section for details) gives 70% of **1** as a pale orange powder. The same product is obtained when di-1,5-cyclooctadienenickel(0) is treated with an excess of methyl acrylate and pyridine; this procedure gave the crystals used in the X-ray study.



(1)

The complex was investigated by ^{1}H NMR spectroscopy in toluene-d_8 and in pyridine-d_5. The spectra are highly temperature dependent which points to dynamic behaviour of the complex. At −40 °C in toluene-d_8 the pyridine protons display broad signals at 6.32 ppm (H^5), 6.64 ppm (H^6) and 7.88 ppm (H^7). Compared with the free ligand in toluene-d_8 the signals are shifted ca 0.5 ppm to higher field. The olefinic protons and the methyl group of methyl acrylate are found between 2.9–3.9 ppm. A singlet which can be identified at 3.11 ppm in the multiplet from the olefinic protons (which is not further interpreted) can be assigned to the methyl protons of the methoxycarbonyl groups. Owing to complexation the olefinic protons are found at more than 2 ppm to higher field than those of free methyl acrylate. At lower and higher temperatures than −40 °C the signals are broadened, and above +50 °C the complex decomposes. In pyridine-d_5 the complex is more stable, and the ^{1}H NMR spectra can be recorded even at +80 °C, but the situation is more complicated with this solvent because exchange of free and complexed pyridine can take place, and in principle an additional pyridine molecule might also be added to form an 18 electron complex. The higher stability of **1** in pyridine as solvent or in the presence of pyridine in other solvents could be interpreted in terms of a dissociation/association equilibrium with the dissociated form decomposing faster.

Figure 1 displays the structure revealed by the X-ray analysis, and in Tables 1 and 2 the atomic coordinates and selected bond lengths and angles are listed. The carbon atoms of the double bonds and the nitrogen atom of pyridine, together with the nickel atom, are located almost in a plane (torsion angle C^2–C^1–C^5–C^6 11.9 °), resulting in a trigonal planar environment for the nickel atom (sum of angles 360.0 ° : N–Ni–{centre C^1, C^2} 115.0 °, N–Ni–{centre C^5, C^6} 116.1°, (centre C^1, C^2)–Ni–{centre C5, C6}128.9 °). The pyridine ring adopts a position nonorthogonal to the plane C^1, C^2, Ni, C^5, C^6, with an interplanar angle of 114.0 °, thus minimising interference with the methoxycarbonyl groups of the two methyl acrylate groups. The methoxycarbonyl groups are positioned almost perpendicular to the

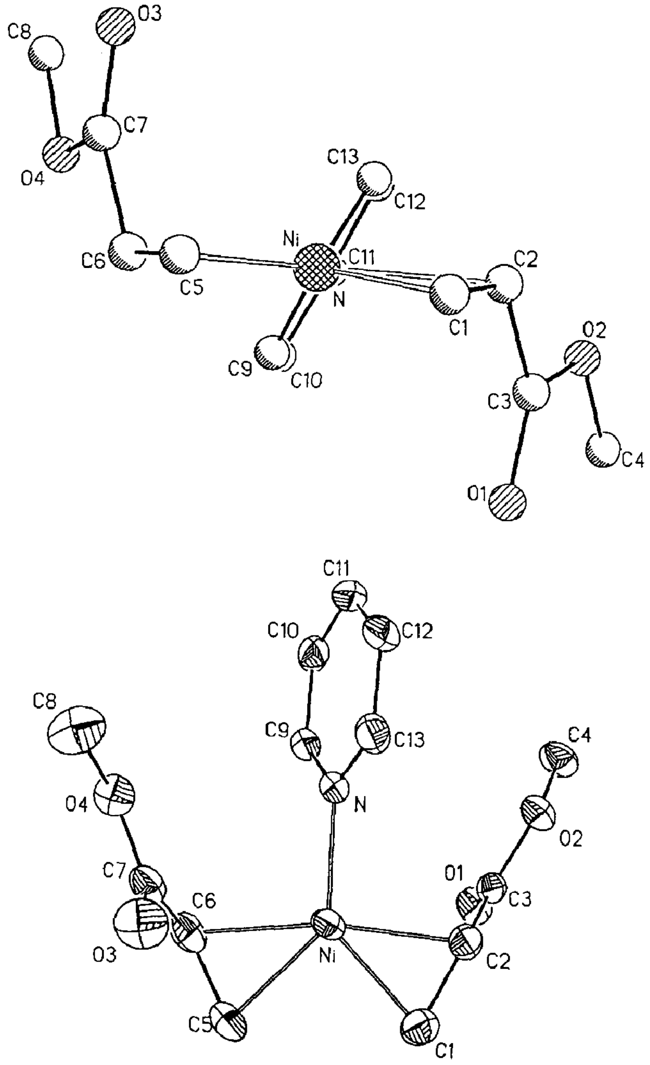


Fig. 1. Two projections of the crystal structure of **1**.

previous plane (plane {Ni, C^1, C^2, C^5, C^6}-plane {O^1, C^3, O^2} 88.3° and plane {Ni, C^1, C^2, C^5, C^6}-plane {O^4, C^7, O^3} 96°), resulting in a slightly distorted C_2-symmetry of the molecule, with its axis penetrating the atoms Ni, N and C^{11}. Reflecting the molecular symmetry the methoxycarbonyl groups are pointing to opposite directions. No intermolecular contact is less than the sum of the relevant van der Waals radii. The Ni–N bond length (194.2(3) pm) is in the range of known Ni–N bond lengths of bipyridinenickel complexes, and the lengths of the double bonds C^1–C^2 and C^5–C^6, 139.3(6) and 138.4(6) pm, respectively, fall in the expected range.

Only a few structures of nickel(0) complexes with nitrogen ligands have been previously determined [4–6]. Two of these are tetrahedral complexes containing bipyridine and two olefinic double bonds, and one is a bis(ethylfumarate)(acetonitrile)nickel(0) complex. The latter comes closest in structure to **1**. The

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors (pm^2 $\times 10^{-1}$)

	x	y	z	U_{eq} [a]
Ni	7464(1)	589(1)	299(1)	23(1)
N	7401(3)	−1301(3)	−341(2)	23(1)
O(1)	5462(3)	−934(3)	1686(2)	31(1)
O(2)	6891(3)	−2746(3)	1580(2)	27(1)
O(3)	9483(3)	1884(4)	−1234(2)	39(1)
O(4)	8118(2)	592(3)	−2073(2)	30(1)
C(1)	7486(5)	1225(5)	1585(3)	33(1)
C(2)	7619(4)	−322(5)	1526(3)	26(1)
C(3)	6540(3)	−1312(4)	1611(3)	22(1)
C(4)	5906(4)	−3833(5)	1600(3)	33(1)
C(5)	7452(5)	2739(5)	−36(3)	35(1)
C(6)	7328(4)	1869(5)	−809(3)	28(1)
C(7)	8423(4)	1465(4)	−1374(3)	27(1)
C(8)	9135(4)	33(7)	−2608(3)	43(2)
C(9)	6356(4)	−1705(5)	−772(3)	28(1)
C(10)	6225(5)	−3077(5)	−1189(3)	35(1)
C(11)	7210(4)	−4053(5)	−1181(3)	37(1)
C(12)	8277(5)	−3644(5)	−746(3)	37(1)
C(13)	8359(4)	−2263(5)	−328(3)	30(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Bond lengths (pm) and selected angles (°)

Ni–N	194.2(3)	Ni–C(1)	196.8(4)
Ni–C(2)	198.7(4)	Ni–C(5)	197.6(4)
Ni–C(6)	199.0(4)	N–C(9)	134.8(5)
N–C(13)	134.3(5)	O(1)–C(3)	121.3(5)
O(2)–C(3)	133.7(5)	O(2)–C(4)	143.9(5)
O(3)–C(7)	122.2(5)	O(4)–C(7)	133.3(5)
O(4)–C(8)	143.0(6)	C(1)–C(2)	139.3(6)
C(2)–C(3)	146.5(6)	C(5)–C(6)	138.4(6)
C(6)–C(7)	147.7(6)	C(9)–C(10)	137.8(6)
C(10)–C(11)	137.4(7)	C(11)–C(12)	137.1(7)
C(12)–C(13)	138.2(6)		
Ni–Ni–C(1)	135.5(2)	Ni–Ni–C(2)	94.6(2)
C(1)–Ni–C(5)	87.8(2)	Ni–Ni–C(5)	136.6(2)
N–Ni–C(6)	95.8(2)	C(2)–Ni–C(6)	169.6(2)
Ni–N–C(9)	119.7(3)	Ni–N–C(13)	121.4(3)
C(9)–N–C(13)	118.8(3)	C(3)–O(2)–C(4)	116.0(3)
C(7)–O(4)–C(8)	115.6(3)	Ni–C(2)–C(3)	104.5(3)
C(1)–C(2)–C(3)	120.9(4)	O(1)–C(3)–O(2)	122.7(3)
O(1)–C(3)–C(2)	126.7(4)	O(2)–C(3)–C(2)	110.7(3)
Ni–C(6)–C(7)	104.6(3)	C(5)–C(6)–C(7)	120.9(4)
O(3)–C(7)–O(4)	123.3(4)	O(3)–C(7)–C(6)	124.9(4)
O(4)–C(7)–C(6)	111.8(3)	N–C(9)–C(10)	122.5(4)
C(9)–C(10)–C(11)	118.5(4)	C(10)–C(11)–C(12)	119.2(4)
C(11)–C(12)–C(13)	120.2(4)	N–C(13)–C(12)	120.8(4)

structure of a bis(ethylene)(tricyclohexylphosphane)nickel(0) complex has also been reported [7].

The assumption that **1** must be involved in the reaction of methyl acrylate with organic halides in the presence of $NiCl_2 \cdot 6H_2O$, zinc, pyridine and water was tested. Thus a solution of bis(methyl acrylate)(pyridine)nickel(0) in THF was treated with a 1 molar ratio of a mixture of *E*- and *Z*-1-bromo-1-propene in the presence of water. The solution becomes green in colour within minutes at room temperature showing the high reactivity of **1**.

$$\underset{(1)}{(MeO_2CHC{=}CH_2)_2Ni(C_5H_5N)} + H_3CCH{=}CHBr \xrightarrow{THF}$$

$$H_3CHC{=}CH_2CH_2CO_2Me + Ni(OH)Br + H_2C{=}CHCO_2CH_3 + C_5H_5N \qquad (2)$$

After separation from the insoluble salts an *E*,*Z*-mixture of 4-hexenecarboxylic acid methyl ester was isolated in 72%. **1** exhibits the same reactivity towards organic halides as the intermediate that is generated in situ by the reduction of $NiCl_2 \cdot 6H_2O$ with zinc in the presence of pyridine and water. Indeed, in many cases the reaction of an organic halide with olefins can be carried out more easily by first isolating **1** and then treating it with the halides. In our earlier work [2] we showed that pure *Z*-1-bromo-1-propene yields *Z*-4-hexenecarboxylic acid ethyl ester exclusively. Thus oxidative addition and insertion of the olefin take place stereospecifically.

Experimental

Bis(methyl acrylate)(pyridine)nickel(0). To 4.7 g (20 mmol) of $NiCl_2 \cdot 6H_2O$, 5.0 ml (55 mmol) of methyl acrylate and 5.0 ml (61 mmol) of pyridine in 50 ml THF were added 5.0 g (76 mmol) of zinc powder. The suspension was heated to 60 °C and the further heating then stopped. After 2 h the mixture had cooled to room temperature and it was filtered and the solid residue washed 3 times with 15 ml of THF. After removal of the solvent in vacuo extraction with 50 ml of diethyl ether left behind the insoluble zinc salts. Filtration and evaporation of the extract in vacuo gave a red oil which was treated with n-hexane to dissolve the excess of pyridine and methyl acrylate. The n-hexane layer was discarded and the residual oil dissolved in 50 ml of diethyl ether. Cooling to -18 °C gave 4.3 g (14 mmol, 70%) of a pale orange powder, which decomposes at 80 °C.

Elemental analysis: Found: C, 50.23; H, 5.53; N, 4.41. $C_{13}H_{17}NNiO_4$ (310.0) calcd.: C, 50.37; H, 5.52; N, 4.52%. ^1H NMR (toluene-d_8): δ 3.11(s), 2.9–3.9 (m)[12 H], 6.32 (2H), 6.64 (1H), 7.88(2H). ^1H NMR (C_5D_5N): δ 3.37 (d, 2H), 3.52 (s, 6H), 3.93 (d, 2H), 4.29 (dd, 2H), 7.20 (2H), 7.56 (1H), 8.,71 (2H).

Bis(methyl acrylate)(pyridine)nickel(0) (alternative procedure). A mixture of 1.0 ml (12 mmol) of pyridine and 1.1 ml (12 mmol) of methyl acrylate in 10 ml of THF was added dropwise during 5 min to a 0 °C solution of 1.65 g (6.0 mmol) of di-1,5-cyclooctadienenickel(0) in 50 ml of THF. After 2 h at room temperature the solvent was removed in vacuo. Single crystals of **1** were obtained from the resulting red oil by keeping it at -18 °C.

*Reaction of **1** with E,Z-1-bromo-1-propene.* To a solution of 1.04 g (3.35 mmol) of bis(methyl acrylate)(pyridine)nickel(0) in 5 ml THF was added 65 μl of degassed water. The solution was stirred vigorously at room temperature and 0.30 ml (3.5

mmol) of *E*,*Z*-1-bromo-1-propene was added. The mixture turned green and became heterogeneous. Centrifugation after 10 min and distillation of the residual solution gave a mixture of *E*,*Z*-4-hexenecarboxylic acid methyl ester and pyridine. The latter was removed by addition of $NiCl_2 \cdot 2H_2O$ and the product was purified by sublimation in vacuo. Yield 310 mg (72%).

Experimental X-ray structure analysis

A single crystal of the approximate dimensions $0.32 \times 0.27 \times 0.18$ mm^3 was sealed in a capillary and studied on a Nicolet R3-mV-four-circle diffractometer with graphite monochromized Mo-K_α-radiation at 130 K. The cell dimensions were refined from the diffractometer angles of 37 automatically indexed reflexions in the range $20° \geq 2\theta \geq 25°$, a 1078.2(3), b 894.4(3), c 1466.4(5) pm, $\alpha = \gamma = 90$, β 89.32(4)°, $Z = 4$, d_{calc} 1.45 g/cm^3, μ 1.39 mm^{-1}, monoclinic symmetry established by axial photos, space group $P2_1/c$. 3260 independent ($2\theta_{max}$ 60°) and 2449 observed intensities ($F_o \geq 4\sigma(F)$) were used for the structure solution by Patterson methods and refinement with full matrix least squares (SHEXTL-Plus) of 220 parameters, resulting in $R = 0.051$, $R_w = 0.050$, $w^{-1} = (\sigma^2(F_o) + 0.00048F_o^2)$, with all non-hydrogen atoms given anisotropic temperature parameters, rigid models assigned to methyl groups, and unique isotropic temperature parameters used for each group of hydrogen atoms. The maximum residual electron density was 0.53 e/pm$^3 \times 10^6$ at a distance of 92 pm from the nickel atom.

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