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THE SYNTHESIS OF THE ZERO-VALENT NICKEL COMPLEXES VIA DI-π-ALLYLNICKEL

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Summary

A new route to zero-valent nickel complexes, (cycloocta-1,5-diene)duroquinonenickel, (*endo*-dicyclopentadiene)duroquinonenickel, dicycloocta-1,5-dienenickel and bis(tetracyclone)nickel, is described. The synthetic procedure involves the reaction between di-π-allylnickel and duroquinone, cyclic dienes, or tetraphenylcyclopentadienone. The replacement of the π-allyl ligand with duroquinone or a cyclic diene is suggested to follow the associative mechanism. The ^{13}C NMR and mass spectra of the compounds isolated are reported.

Introduction

Transition metal allyl compounds have found wide applications as homogeneous catalysts and precursors in organic synthesis in the past decade. The chemical behaviour of "purely" allyl complexes such as di-π-allylnickel has, however, been studied insufficiently. Carbon monoxide, tertiary phosphines, and hydrogen halides are known to replace the π-allyl ligand in this compound [1]. The action of carbon dioxide [2] and benzaldehyde [3] on di-π-allylnickel leads to insertion of these species at the metal—allyl bond. Data also exist [4] on adducts of di-π-allyl complexes with halogenated *p*-benzoquinones and on the possibility of their use as catalysts in butadiene polymerization.

In 1972, we studied the reaction between di-π-allylnickel and duroquinone and isolated diduroquinonenickel [5], synthesized earlier by treating nickel tetracarbonyl with duroquinone [6]. We now describe the use of di-π-allylnickel as a starting material to synthesize a number of other zero-valent nickel complexes.

Results and discussion

Treatment of a mixture of duroquinone and cycloocta-1,5-diene with a solution of di-π-allylnickel at room temperature results in precipitation of (cycloocta-1,5-diene)duroquinonenickel in a yield of 78% (eq. 1).

$$(\pi\text{-}C_3H_5)_2Ni + C_8H_{12} + DQ \rightarrow (C_8H_{12})(DQ)Ni + C_6H_{10} \qquad (1)$$

(C_8H_{12} = cycloocta-1,5-diene; DQ = duroquinone)

Di-π-allylnickel reacts with dicyclopentadiene and duroquinone under the same conditions to give another (diene)duroquinonenickel complex, (*endo*-dicyclopentadiene)duroquinonenickel, in a 16% yield (eq. 2).

$$(\pi\text{-}C_3H_5)_2Ni + C_{10}H_{12} + DQ \rightarrow (C_{10}H_{12})(DQ)Ni + C_6H_{10} \qquad (2)$$

($C_{10}H_{12}$ = *endo*-dicyclopentadiene)

(Diene)duroquinonenickel complexes are usually made by heating together nickel tetracarbonyl and duroquinone in the presence of a cyclic diene [7]. The route to (diene)duroquinonenickel complexes starting from di-π-allylnickel suggested here requires less drastic reaction conditions and has the advantage of obviating the need to handle highly toxic nickel tetracarbonyl.

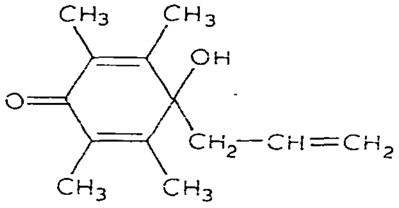
Di-π-allylnickel may also be used as a starting material for the synthesis of nickel diene π-complexes. Thus, di-π-allylnickel reacts with cycloocta-1,5-diene to give dicycloocta-1,5-dienenickel in a 42% yield (eq. 3).

$$(\pi\text{-}C_3H_5)_2Ni + C_8H_{12} \rightarrow (C_8H_{12})_2Ni + C_6H_{10} \qquad (3)$$

The replacement of the π-allyl ligand with duroquinone in ether proceeds only sluggishly. The reaction at room temperature, with stirring for 7 days, gave as little as 29% yield of diduroquinonenickel. The yield increased more than two-fold after 21 days. The replacement of the π-allyl groups in di-π-allylnickel with a cyclic diene took about 25 days.

As was shown earlier [5], di-π-allylnickel reacts with duroquinone at a lower temperature to give an unstable adduct of the composition diallylnickel/duroquinone 1/1. It seems likely that the replacement of the π-allyl ligand in di-π-allylnickel with duroquinone and cyclic dienes follows the associative mechanism typical for reactions of square-planar transition metal complexes [8].

We isolated for the first time 1-hydroxy-2,3,5,6-tetramethyl-1-allylcyclohexa-2,5-dien-4-one (I) as a by-product of the interaction of di-π-allylnickel with duroquinone and dicyclopentadiene or cycloocta-1,5-diene. The yields



(I)

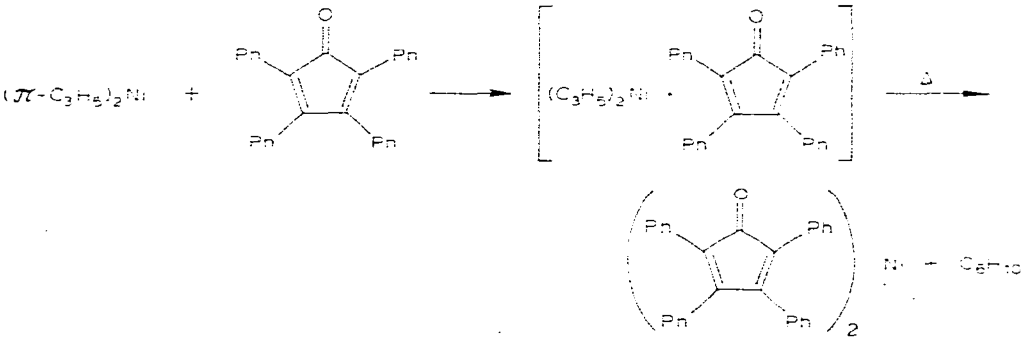
were 8 and 1%, respectively. Such an alkylation of *p*-benzoquinones at the carbonyl group is usually carried out with organomagnesium or organozinc compounds [9].

Recently, Hegedus [10] applied di-π-allylnickel halides to alkylated ketones, aldehydes, and anthraquinone. However, this author showed for a large number of reactions [11] that diallylnickel halides allylate substituted *p*-benzoquinones at the site of the highest spin density in the corresponding anion radicals rather than at the quinone carbonyl group. He failed to make duroquinone react with di-π-allylnickel halides [11].

The structure of I was determined by elemental analysis and spectral methods. The proton NMR spectrum of its solution in CCl_4 contained two singlet signals from methyl protons at δ 1.71 and 1.99 ppm, a slightly broadened signal from the hydroxyl proton at δ 3.39 ppm, a doublet signal from the methylene protons at δ 2.47 ppm, showing a characteristic coupling with the nearest methyl group proton (J = 5.5 Hz), and lastly, a multiplet from the three vinyl protons of the allyl fragment at 5.06 ppm, resolved only poorly at 60 MHz. The signal intensity ratio was in excellent agreement with the proposed structure of allylated duroquinone (I). The ^{13}C NMR spectrum contained two quadruplet signals due to the two different methyl groups at δ 14.5 ppm with $J(^{13}C—^{1}H)$ = 127.5 Hz and δ 11.1 ppm with $J(^{13}C—^{1}H)$ = 128.5 Hz and singlet signals from the carbonyl carbon atom (δ = 184.4 ppm). The two non-equivalent carcon atoms at the olefinic bonds of the six-membered ring (δ = 153.8 and 130.6 ppm) and the key carbon atom directly bonded to the hydroxyl and allyl groups (δ = 73.5 ppm). The other signals observed in the ^{13}C NMR spectrum were: a doublet from the allyl group central carbon atom at δ = 131.5 ppm with $J(^{13}C—^{1}H)$ = 159.2 Hz, and two triplets at δ 117.4 ppm with $J(^{13}C—^{1}H)$ = 158.1 Hz and 41.2 ppm with $J(^{13}C—^{1}H)$ = 128.0 Hz, assigned to the terminal carbon atom at the olefinic bond and to the carbon atom linked with the ring, respectively. Naturally, all these signals appeared as singlets in the $^{13}C\{^{1}H\}$ spectrum.

The scope of the reaction discovered was broadened by the preparation of tetraphenylcyclopentadienonenickel complexes. Like duroquinone, tetraphenylcyclopentadienone (tetracyclone) contains a low-energy vacant orbital and thus may form stable transition metal π-complexes [12].

An ethereal solution of di-π-allylnickel does in fact react with tetracyclone to give a yellow crystalline solid practically insoluble in organic solvents and



(4)

TABLE 1

CHEMICAL SHIFTS, δ ^{13}C (PPM FROM $(CH_3)_4Si$), IN NICKEL COMPLEXES AND INITIAL LIGANDS [a]

Compound	Solvent	T (°C)	C=C	CH	CH_2	CH_3	C=O	C_6H_5
Duroquinone	$CHCl_3$	22	139.0			11.3	185.9	
Cycloocta-1,5-diene	$CHCl_3$	22	127.0		27.2			
endo-Dicyclopentadiene	$CHCl_3$	33	131.3; 131.5; 131.6; 135.5	41.0; 44.9; 45.9; 54.6	34.4; 49.9			
Di-duroquinonenickel	$CHCl_3$	22	113.0			11.0		
Dicycloocta-1,5-dienenickel	C_6H_6	10	89.6		30.9			
(Cycloocta-1,5-diene)-duroquinonenickel	$CHCl_3$	22	$\frac{100.5}{112.2}$		29.0	$\frac{\text{—}}{12.1}$	$\frac{\text{—}}{153.5}$	
(*endo*-Dicyclopentadiene)-duroquinonenickel [b]	$CDCl_3$	50	$\frac{100.1;\ 103.2}{114.3}$ $\frac{106.4;\ 112.1}{117.4}$	$\frac{43.4;\ 46.2}{\text{—}}$ $\frac{52.3;\ 56.1}{\text{—}}$	$\frac{34.0;\ 61.4}{\text{—}}$	$\frac{\text{—}}{12.8}$	$\frac{\text{—}}{151.8;\ 157.6}$	
Bis(tetracyclone)nickel	$CDCl_3$	30	98.1; 108.2				164.0	127.3; 127.5; 127.8; 128.4; 128.7; 130.5; 130.9; 131.0

[a] The values above and below the lines correspond to the diene and duroquinone ligands, respectively. [b] The ^{13}C NMR spectrum of this compound was measured on a Bruker WH-180 instrument at 45.28 MHz.

stable in air. According to the analytical data, the adduct composition is 1/1. When heated to 180° C it decomposes to the diallyl and a deep-brown solid, bis(tetracyclone)nickel (eq. 4). The structure of the latter product was determined by its IR and ^{13}C NMR spectra (see Table 1). According to the literature data, this compound may be prepared from tetracarbonylnickel and tetracyclone or diphenylacetylene [13]. It should be noted that thermal decomposition of the adduct from di-π-allylnickel and duroquinone proceeds likewise [5]. Heating the adduct in a sealed tube at 100—150° C leads to the evolution of diallyl and formation of diduroquinonenickel.

The isolated nickel complexes were studied by ^{13}C NMR and mass spectrometry. The mass spectra were dominated by free ligand molecular ions or fragment ions derived from them. This may be explained by thermal decomposition of the complexes, as their mass spectra can only be measured when the direct inlet system temperatures approach their decomposition points. The intense decomposition of diduroquinonenickel under the conditions of mass spectrometry was the reason why we failed to observe the corresponding molecular ion (M^+) earlier [5] using an instrument of lower sensitivity. We shall discuss here only those metal-containing ions whose contribution to the total ion current does not exceed 25%.

The molecular ions were present in the mass spectra of all the complexes studied except for bis(tetracyclone)nickel (Table 2). Their major fragmentations involved the loss of duroquinone to give (diene)Ni$^+$. This indicates a higher stability of the (diene)Ni$^+$ compared to (DQ)Ni$^+$. Further decomposition of (diene)Ni$^+$ led to fragments of the type (C_nH_m)Ni$^+$.

The ^{13}C NMR parameters of (*endo*-dicyclopentadiene)duroquinonenickel and related complexes are given in Table 1. The striking difference in the shielding of the methylene groups of the *endo*-dicyclopentadiene ligand ($\Delta\delta$ = 27 ppm) is probably due to a significant difference between the respective metal—carbon distances. The lack of symmetry in the *endo*-dicyclopentadiene ligand is responsible for the difference in the shielding of the duroquinone carbonyl ($\Delta\delta$ = 5.79 ppm) and olefinic ($\Delta\delta$ = 3.12 ppm) carbon atoms. It is of interest that the complex formation effects on the duroquinone ligand manifest themselves by upfield shifts of the signals from olefinic carbon atoms by 26 ppm in diduroquinonenickel, 26.8 ppm in (cycloocta-1,5-diene)duroquinonenickel, and 21.6 and 24.7 ppm in (*endo*-dicyclopentadiene)duroquinonenickel, that is, they vary very little from one compound to another. As shown earlier [14], these effects are far smaller (by ca. 10 ppm) than those observed for the

TABLE 2

RELATIVE ION INTENSITIES IN MASS SPECTRA OF NICKEL π-COMPLEXES

Compound	M^+	(DQ)Ni$^+$	(Diene)Ni$^+$	Ni$^+$	ΣC_nH_mNi
Diduroquinonenickel	37	100	—	—	100
(Cycloocta-1,5-diene)-duroquinonenickel	9	—	100	18	5
(*endo*-Dicyclopentadiene)-duroquinonenickel	2	—	50	—	100
Bis(tetracyclone)nickel	—	—	2	—	100

corresponding ligand in dicycloocta-1,5-dienenickel. It should be stressed that the complex formation effects in duroquinone derivatives give rise to practically identical shifts of the signals due to olefinic carbon atoms and to carbonyl carbon, which indicates the important role played by all duroquinone ring atom in bonding with nickel.

Experimental

The proton NMR spectra were obtained with a Hitachi—Perkin—Elmer R-20 instrument at 60 MHz. The ^{13}C NMR spectra were measured on a Bruker HX-90 spectrometer (22.635 MHz) with TMS as reference. The IR spectra were obtained on an UR-20 spectrophotometer.

The mass spectra were measured with an AEI MS-30 instrument equipped with a DS-50 data processing system. The conditions were: direct inlet system temperature 175—200° C, ionization chamber temperature 250° C, ionizing electron energy 70 eV. The GLC analyse were made with a Tsvet-5 chromatograph equipped with a flame-ionizing detector using a 90 m steel column (0.25 mm I.D.), NPTA as stationary phase and helium as carrier gas. The analyses were performed under isothermal conditions at 100° C.

The syntheses were carried out under argon using absolute solvents distilled under argon prior to use.

Di-π-allylnickel was prepared by the action of an ethereal solution of allylmagnesium bromide on anhydrous $NiBr_2$ [15]. The concentrations of di-π-allylnickel in the initial solutions were determined by complexonometric titration [16]. Di-π-allylnickel was added to the reaction mixtures at —30° C.

(1) Reaction of di-π-allylnickel with cycloocta-1,5-diene and duroquinone

A solution of di-π-allylnickel (3.67 g, 26 mmol) in ether was added to a solution of duroquinone (8.56 g, 52.2 mmol) and 20 ml cycloocta-1,5-diene in 150 ml ether. The reaction mixture was stirred at room temperature for 5 days and then evaporated to dryness under vacuum. The solvent distilled off contained diallyl (GLC). The solid residue was extracted with chloroform in air. $CHCl_3$ was then removed and the solid product was repeatedly washed with ether and reprecipitated from CH_2Cl_2 with pentane. The yield of (cycloocta-1,5-diene)-duroquinonenickel was 6.23 g. The combined mother liquor and washes were evaporated to dryness and the residue was chromatographed on Al_2O_3 to give duroquinone (4.68 g, eluted with petroleum ether), a mixture containing I and diduroquinone (0.13 g, eluted with ether) and (cycloocta-1,5-diene)duroquinonenickel (0.46 g, eluted with $CHCl_3$). The total yield of (cycloocta-1,5-diene)duroquinonenickel was 6.69 g (78%), m.p. 205° C (dec.), ν(CO) 1553 cm^{-1} (KBr) [7].

The mixture of I and diduroquinone was separated by crystallization from ether. Diduroquinone, m.p. 205° C [17], was identified by comparing its IR spectrum with the spectrum of a known sample. 1-Hydroxy-2,3,5,6-tetramethyl-1-allylcyclohexa-2,5-dien-4-one, m.p. 91—92° C: Anal.: Found: C, 75.31; H, 8.74. $C_{13}H_{18}O_2$ calcd.: C, 75.69; H, 8.79%.

(2) Reaction of di-π-allylnickel with dicyclopentadiene and duroquinone

A solution of di-π-allylnickel (1.55 g, 11 mmol) in ether was added to a solution of duroquinone (2.50 g, 15.2 mmol) and 7 ml dicyclopentadiene in 150 ml ether. The mixture was stirred at room temperature for 7 days. Further treatment of the reaction mixture was as for (1).

(*endo*-Dicyclopentadiene)duroquinonenickel was obtained in a 0.61 g yield (16%), m.p. 137° C (dec.) (after reprecipitation from CH_2Cl_2), ν(CO) 1553 cm^{-1} (KBr) [7]. The yield of diduroquinonenickel was 0.12 g (4%), m.p. 205° C (dec.), the IR spectrum was identical with that of a known sample [6]. 1-Hydroxy-2,3,5,6-tetramethyl-1-allylcyclohexa-2,5-dien-4-one was isolated in a 0.25 g yield (8%), m.p. 91—92° C. 1.92 g of duroquinone was recovered, m.p. 110° C [18].

(3) Reaction of di-π-allylnickel with duroquinone

A mixture of duroquinone (5.00 g, 30.5 mmol) and di-π-allylnickel (1.49 g, 10.6 mmol) was stirred in 150 ml ether at room temperature for 21 days. The solvent was then removed under vacuum and the dry residue was extracted with chloroform in air. After evaporating $CHCl_3$, diduroquinonenickel was repeatedly washed with ether and recrystallized from chloroform. The yield was 2.55 g (62%), m.p. 205° C (dec.), ν(CO) 1577 cm^{-1} (KBr) [6].

(4) Reaction of di-π-allylnickel with cycloocta-1,5-diene

A solution of di-π-allylnickel (2.82 g, 20 mmol) in ether was added to 12 ml of cycloocta-1,5-diene. The reaction mixture was maintained at room temperature for 25 days. The dark yellow precipitate formed was filtered, washed with ether and dried under vacuum to give a dicycloocta-1,5-dienenickel (2.28 g, 42%); proton NMR spectrum (in benzene): δ 2.08(CH_2); 4.28(CH) ppm [19].

(5) Reaction of di-π-allylnickel with tetracyclone

A mixture of tetracyclone [20] (3.50 g, 9 mmol) and di-π-allylnickel (2.54 g, 18 mmol) was stirred at room temperature for 8 h. The yellow precipitate was filtered, repeatedly washed with ether and dried under vacuum to give the adduct, diallylnickel · tetracyclone (3.03 g, 63%). Anal.: Found: C, 79.26; H, 6.23; Ni, 10.80. $C_{35}H_{30}NiO$ calcd.: C, 80.02; H, 5.75; Ni, 11.17%.

(6) Bis(tetracyclone)nickel

The adduct diallylnickel · tetracyclone (1.26 g, 2.4 mmol) was placed in a branched sealed tube and heated at 150—180° C for 1 h. During heating, the colour of the solid changed from yellow to black. The liquid products condensing in the branch contained diallyl (GLC). The black residue was chromatographed on Al_2O_3 (3 × 17 cm). The mixture was eluted with ether/benzene 1/1 and then with chloroform to give tetracyclone (0.04 g, 4%) and ditetracyclonenickel (0.92 g, 94%). The IR spectrum of the nickel compound isolated contained an absorption band at 1609 cm^{-1} (KBr) [13].

(7) Thermal decomposition of the adduct, diallylnickel · duroquinone

Thermal decomposition of the adduct diallylnickel · duroquinone (1.58 g, 5.2 mmol) obtained as recommended in ref. 5, was carried out as for (6) at 100—150° C. According to the GCL data the liquid phase contained diallyl. The solid residue was repeatedly washed first with ether and then with chloroform.

After evaporating away the ether and recrystallizing the residue from ethanol, duroquinone (0.58 g, 69%) was isolated, m.p. 110°C [18]. The chloroform solution gave diduroquinonenickel (0.15 g, 15%), m.p. 205°C (dec.), ν(CO) 1577 cm^{-1} (KBr) [6].

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