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Reaction of π-Allylic Nickel Complexes with Quinones and Their Catalytic Activity[1]

G. Lugli, W. Marconi, A. Mazzei, and N. Palladino

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*The reaction between bis(π-crotyl)Ni and π-crotyl-Ni-Cl with some quinones such as chloranil, bromanil and monochloro-*p*-benzoquinone have been studied. The preferred Ni-quinone mole ratio is one or two depending on the oxidation state of Ni in the starting complex. On the basis of analytical data and infrared spectra, the reaction products may be formulated as charge transfer complexes in which electrons are transferred from Ni to the quinone. All the complexes are brown solids, unstable in the air and insoluble in all solvents, except those in which complete solvolysis takes place, in agreement with a proposed salt-like structure. Catalytic activity of these complexes in the stereospecific polymerization of butadiene is briefly reported and discussed in terms of acceptor-donor properties of both starting Ni and quinone derivatives.*

Introduction

Most quinones form complexes with transition metals,[2] in particular with nickel they may form π-complexes or react yielding salt-like materials which are better formulated[3] as $Ni^{2+}(quinone)_2^{2-}$. These complexes are generally prepared from the reaction between quinones and the metal carbonyl: if the reaction is carried out in the presence of a cyclic olefin, new complexes of nickel with quinone and olefin are obtained.[4a]

All the duroquinone-olefin nickel complexes are diamagnetic, however cyclooctadiene complexes of nickel with 2,5- or 2,6-dimethyl-*p*-benzoquinone are paramagnetic and an intermediate formulation between the π bonded and the ionic form is suggested.[4b]

Also Cobalt, Rhodium and Iridium yield π complexes of the type C_5H_5-Co-Duroquinone.[5]

Calderazzo[6] reported that halopentacarbonyl anions of Molybdenum and Tungsten react with *p*-benzoquinone giving anionic complexes of formula $[MX(quinone)_3]^-$. These have been isolated as lithium salts.

Furthermore it is reported that chloranil (CA) forms well characterized complexes with nickelocene and cobaltocene and not isolable complexes with ferrocene.[7]

On the basis of e.s.r. results these complexes may be formulated as charge transfer complexes such as

$$\pi\text{-}(C_5H_5)_2\text{—}Co^+(CA)^-CA \quad \text{and} \quad \pi\text{-}(C_5H_5)_2\text{—}Ni^{2+}(CA)^{2-}CA$$

Our interest in the catalytic properties of π-complexes of nickel with Lewis acids in the stereospecific polymerization of diolefins, prompted us to investigate the possibility of preparing new complexes starting from π-allyl-Ni derivatives and quinones.[8]

Results

Generally π-allyl-Ni complexes react readily in toluene with quinones to give precipitates insoluble in hydrocarbons.

At –20°C the appearance of the brown precipitate is instantaneous, while at –40°C it takes place after about 30′ and at –78°C all the solid sets down after many hours. The stoichiometric nickel: acceptor mole ratio is 1 : 1 for bis (π-allyl)Ni compounds and 2 : 1 for π-allyl-Ni-halides. In the latter case, starting from equimolecular ratios, half of the quinone is found unreacted in the filtered liquid phase. All the complexes are brown solids, unstable in the air, insoluble in all organic solvents and stable at room temperature. In some experiments a little amount of solvent (1÷3%) firmly remains in the isolated product; in these cases the exact amount of solvent has been determined by means of gas-chromatography on the hydrolysis products of a sample.

1. Complexes with p*-Chloranil (Bromanil).* The dried products from the reaction of bis(π-crotyl-Ni) and π-crotyl-Ni-Cl with chloranil show infrared spectra very different from that of the free *p*-chloranil, see Table I. In particular the absorption of C=O stretching is found at 1410 cm^{-1} with a lowering of about 275 cm^{-1} with respect to the chloranil C=O frequency.

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(1) Paper presented at XIth International Conference on Coordination Chemistry, Haifa, Jerusalem, Sept. 1968.

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(3) G. N. Schrauzer and H. Thyret, *J. Am. Chem. Soc.*, *82*, 6420 (1960).

(4a) G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, *16b*, 353 (1961); *ibid. 17b*, 73 (1962).

(4b) *Chem. Ber.*, 96, 1755 (1963).

(5) G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, *86*, 3265 (1964).

(6) F. Calderazzo and R. Henzi, *J. Organomet. Chem.*, *10*, 483 (1967).

(7) J. C. Goan, E. Berg, and H. E. Podall, *J. Org. Chem.*, *29*, 975 (1964).

(8) Italian Patent 788.146 to Snam Progetti (dep. 12-7-66); W. A. Kormer *et al.*, Int. Symposium on Makromol. Chem., Prague, Aug-Sept. 1965.

Table I. Infrared Frequencies (cm^{-1})[a]

Ni crotylchloride-chloranil:
3060 (w), 3020 (w), 1420 (vs), 1210 (m), 1185 (m), 1165 (m), 1025 (m), 955 (m), 900 (vs), 710 (ms), 480 (m)

Ni bis(π-crotyl)chloranil:
3060 (w), 3020 (w), 1410 (vs.), 1270 (w), 1200 (m), 1180 (m), 1160 (m), 1030 (m), 952 (m), 920 (s), 720 (ms)

Ni bis(π-crotyl)-chloroquinone:
3060 (w), 3010 (w), 1470 (vs), 1250 (s), 1200 (s), 1030 (m), 915 (m), 820 (vs), 450 (w)

Ni crotyl-chloride-chloroquinone:
3060 (w), 3010 (w), 1470 (vs), 1250 (m), 1200 (s), 1030 (w) 970 (w), 910 (w), 820 (vs)

Chloranil 1685 cm^{-1}

[a] in nujol and exachlorobutadiene

The other important absorptions due to the quinone ligand fall at 1210 (m), 900 (vs), 710 (m). These absorptions compared with the IR data reported for semiquinons radical ion[9] and with IR spectra of bis sodium tetrachlorohydroquinone salt are in agreement with the presence of the quinone dinegative ion. In the infrared spectra, absorptions are also present at 3060 and 3020 cm^{-1}, assigned to CH stretching due to the presence of crotyl residues. Furthermore, absorptions at 1490, 1025, and 480 cm^{-1}, were observed.[10]

The suspicion that the presence of a little amount of toluene in the complexes might also give absorptions at the same wavelengths, prompted us to carry out the reaction in completely deuterated toluene.

In the infrared spectrum of this reaction product there is no more evidence of the band at 1490 cm^{-1}, whereas the absorptions at 3020, 3060, 1025, and 480 cm^{-1}, which are still present, confirm the crotyl group.

Chemical analyses carried out in the reaction product from π-crotyl-Ni-Cl and chloranil are in agreement with an empirical formula $C_{10}H_7O_2Cl_6Ni_2$, and from bis (π-crotyl)Ni and chloranil with $C_{10}H_7O_2Cl_4Ni$.

Attemts to confirm the presence of the π-crotyl by decomposition of the complexes with anydrous HCl or NaOH in alcool, gave chlorobutane and butenes respectively, although not quantitatively with respect to the above mentioned formula.

Similar results are obtained starting from π-crotyl-Ni derivatives and bromanil.

2. *Complexes with Chloro-*p*-Benzoquinone.* The infrared spectra of the precipitates obtained by reaction of bis (π-crotyl)Ni and π-crotyl-Ni-Cl with chloro-*p*-benzoquinone (Table I) are similar to those previously reported for chloranil as far as absorptions at 1490, 1025, and 480 cm^{-1} are concerned. For quinone absorption the strongest bands fall at 1470, 1250, 1200, and 820 cm^{-1}, again in good agreement with the I.R. spectra of the quinone dinegative ion. Chemical analyses carried out on the complexes obtained respectively from bis (π-crotyl)Ni and π-crotyl-Ni-Cl with chloroquinone agree sufficiently with the formula $C_{10}H_7O_2ClNi$ in the former case and with the elemental formula $C_{10}H_7O_2Cl_3Ni_2$ in the latter.

3. *Butadiene Polymerization.* The reaction products described under 1. and 2. were tested as catalysts in the stereospecific polymerization of butadiene, Table II.

The case of chloro-*p*-benzoquinone with bis(π-crotyl) Ni is not listed because it exhibited no catalytic activity.

A few similar catalyst systems were also tested: a negligible amount of high molecular weight polymer is obtained using catalysts consisting of the reaction product between bis(π-crotyl)Ni and *p*-benzoquinone, duroquinone and 2,3-dimethyl-*p*-benzoquinone. Very low activity is found also employing dichlorodicyano-*p*-benzoquinone.

Discussion

The exact characterization of the products formed by the reaction of bis(π-crotyl)Ni or π-crotyl-Ni-chloride with quinones is difficult owing to their insolubility in all solvents except in those in which complete solvolysis takes place. Chemical analyses also

Table II. Polymerization of Butadiene

Ni derivs.	Quinone	Polym. Time hr	Temp. °C	Polymer yield	I.R. Analysis		
					c	*t*	v
1. bis(π-allyl)Ni	Chloranil	48	50	15	88	9	3
2. bis(π-methallyl)Ni	Chloranil	35	50	75	84	3	3
3. bis(π-crotyl)Ni	Chloranil	48	25	60	95	3	2
4. bis(π-crotyl)Ni	Bromanil	48	25	73.5	94.5	2.5	3
5. (π-crotyl NiCl$)_2$	Chloranil	48	25	83	94	3	3
6. (π-crotyl NiCl$)_2$	Bromanil	48	25	80	93.5	4	2.5
7. (π-crotyl NiCl$)_2$	2,6-dibromo *p*-benzoquinone	48	40	35	93.5	4	2.5
8. (π-crotyl NiCl$)_2$	2-chloro-*p*-benzoquinone	48	40	30	94	4.0	2
9. (π-crotyl NiBr$)_2$	Chloranil	80	15	34	93	4.5	2.5
10. (π-crotyl NiJ$)_2$	Chloranil	60	15	20	51	46	3
11. bis(π-crotyl)Ni	Chloranil	20	25	87	94	3.5	2.5
12. bis(π-crotyl)Ni	Chloranil	60	15	47	93	4	3

Conditions: benzene 50 ml; 0.5 mmole Ni derivatives; Ni: quinone mole ratio 1 : 1 in all runs; 20 g butadiene; polybutadiene microstructure $c = \%$ 1,4-*cis*, $t = \%$ 1,4-*trans*, $v = \%$ 1,2. The catalyst was preformed in the absence of monomer, except for run 11. Run 12 was carried out in diethyl ether benzene 1 : 1.

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(9) Y. Matsunaga, *J. Chem. Phys.*, *41*, 1609 (1964).

(10) H. P. Fritz, *Chem. Ber.*, *94*, 1217 (1961).

suffer from the impossibility of crystallization and from the difficulty of eliminating all traces of solvent. These features are however indicative of a salt-like structure of these substances meaning that extensive charge transfer has occurred in the reaction.

The infrared evidence indicates, in all cases examined, that the quinone moiety of the complex is in the form of a dinegative ion. The presence of the original crotyl groups is also suggested by the infrared absorptions in the 3000, 1000, and 500 cm^{-1} range, which have been shown to be due to groups coming from the reactants alone, in the experiment with *p*-chloranil in a completely deuterated solvent.

These facts together with the analyses are consistent with a formulation of these compounds in which electrons are transferred from Ni atoms to the quinone, and suggest a formulation of the two products as shown in Figure 1 and 2. The variation in the quinone-nickel molar ratios could be justified, in our opinion, on the basis of the different electron acceptor-donor properties of the two systems.

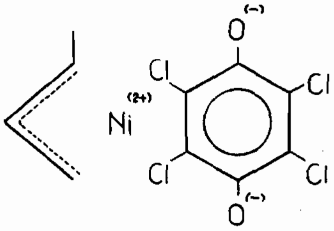

Figure 1.

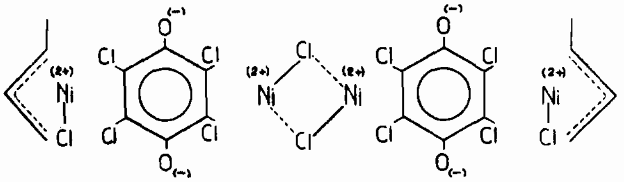

Figure 2.

The same structures may be also drawn in the bromanil and monochloro-*p*-benzoquinone cases.

It has been reported[8] that π-allyl-Ni-halides themselves give a low yield of polybutadiene whose microstructure is mixed *cis-trans* for the bromide and predominant 1,4-*trans* for the iodide.

Our results in the polymerization of butadiene are in agreement with the results of Sharaev *et al.*:[11] the presence of the quinone moiety in the catalyst increases enormously the activity and changes the stereospecificity of the bromide and iodide containing systems, favouring the formation of the *cis* polymer. It would seem difficult to assess the important factors in determining the choice of the *cis* form, this being possibly due to the steric requirements of the quinone and/or to the very different electronic situation of the metal atom. What is certainly apparent is that the effect of the halide atom, while still present, is much less important than in the absence of quinone.

The enhancement of overall catalytic activity is to be attributed with almost absolute confidence to the effect of the charge transfer from metal to quinone.

In agreement with above mentioned authors[11] we see that the enhancement in activity parallels the oxidizing power of the quinone. Thus in the case of Cl-*p*-benzoquinone, which is a weaker acceptor than chloranil, a catalytically active complex is formed only when starting from allylic nickel-halides and not from nickel-bis-crotyl. In the former case less charge transfer is necessary because some has already occurred toward the halogen.

Nevertheless, when better acceptors than chloranil, such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were employed with bis(π-crotyl)Ni and π-crotyl-Ni-Cl, complexes of quite low activity occurred. We feel that the catalytic activity is connected with a delicate balance between the acceptor properties of the quinone and the donor properties of nickel in the starting complex.

Experimental Section

The complexes were prepared by mixing dry toluene solutions of quinone and crotyl-Ni-derivative and filtering the precipitated products. These were washed with additional toluene and dried in high vacuum at room temperature. All operations were carried out under dry inert atmosphere.

Gas-chromatographic analyses were carried out with a C. Erba mod. C apparatus; infrared spectra of the complexes were recorded by a Perkin-Elmer 125 spectrophotometer in nujol and hexachlorobutadiene. Chemical analyses were made by standard methods; in particular for chlorine the best results were obtained with Vieböck method.[12]

(π-crotyl)$_2$Ni and chloranil (1 : 1). This complex was quantitatively obtained by adding a toluene solution of quinone (5 mmole) to a stirred solution of bis-crotyl-Ni[13] and cooling at −20°C. The brown precipitate was filtered at −20°C through a sintered glass filter G4 and washed several times with fresh solvent cooled at the same temp. Nickel and chlorine were absent in the liquid phase, and 80% of the crotyl groups coming from the reaction were recovered as diolefins (2,6-octadiene and 3-methyl-1,5-heptadiene). The solid was dried at room temp. for 20 hr at 10^{-4} mm Hg; in these conditions 1.6% of toluene is firmly retained and it was exactly determined by decomposition of a sample (388 mg) with anhydrous ethyl alcohol (5 ml) at room temp. for 8 hr, analyzing the solution by gas-chromatography.

Anal. Calcd. for $C_{10}H_7Cl_4O_2Ni$; C, 33.36; H, 1.95; Cl, 39.48; Ni, 16.32;. Found: C, 33.40; H, 2.20; Cl, 39.00; Ni, 17.90.*

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(11) O. K. Sharaev, A. V. Alferov, E. I. Tiniakova, B. A. Dolgoplosk, V. A. Kormer, and A. D. Babitskij, *Doklady Acad. Nauk SSSR, 177,* 140 (1967).

(12) F. Viebock, Ber. 65, 493 (1932).

(13) Prepared accordingly to G. Wilke, and B. Borgdanovic, Angew. Chem. 73, 756 (1961).

(*) Mean value obtained from several analyses. The Ni content is generally slightly higher than the theoretical one probably because of the presence of a little amount of metallic Ni coming from the instability of the starting bis-crotyl-Ni.

π-Crotyl-Ni-Chloride[14] *and Chloranil* (*2 : 1*). Use of a 2 : 1 mole ratio of the reactants at room temp. resulted in the precipitation of a brown solid in quantitative yield. The product was washed and dried at room temp. for 10 hr. at 10^{-4} mm Hg, after that toluene was present for 2,4%.

Anal. Calcd. for $C_{10}H_7Cl_6O_2Ni_2$ C, 24.52; H, 1.43; Cl, 43.53; Ni, 23.98. Found: C, 24.10; H, 1.60; Cl, 42.50; Ni, 25.00.

The same reaction was carried out in perdeutero toluene, in order to assign with certainty infrared absorptions of crotyl groups. The dried product retains 4% of solvent, its infrared spectrum shows the same absorptions reported in Table I for the complex obtained from toluene.

(*π-crotyl*)$_2$*Ni and Monochloro-*p*-benzoquinone* (*1*: *1*. Following the above mentioned preparation method 10.5 mmoles of bis-crotyl-Ni were mixed in toluene with the stoichiometric amount of chloroquinone. The obtained solid was filtered and washed several times with fresh solvent. All operations were carried out at –30°C to avoid partial decomposition of the starting Ni derivative. The complex was dried at room temp. for 10 hr at 10^{-4} mm Hg.

Anal. Calcd. for $C_{10}H_{10}ClO_2Ni$ C, 46.84; H, 3.90; Cl, 13.86; Ni, 22.91. Found: C, 46.81; H, 4.20; Cl, 14.11; Ni, 21.70.

*π-Crotyl-Ni-Chlorid and Monochloro-*p*-benzoquinone* (*2 : 1*). 4.02 mmoles of quinone dissolved in toluene were added to a solution of 8.04 mmoles of crotyl-Ni-Cl, at room temp. The obtained precipitate was filtered, washed and dried for 10 hr at 10^{-4} mm Hg.

Anal. Calcd. for $C_{10}H_{10}Cl_3O_2Ni_2$ C, 31,09; H, 2.59; Cl, 27.59; Ni, 30.42. Found: C, 31.55; H, 2.96; Cl, 26.38; Ni,29.32.

Decomposition Reactions

1. *Cleavage with alcoholic NaOH.* 200 mg of reaction product obtained from bis-crotyl-Ni and chloro-*p*-benzoquinone were reacted at 60°C with 5 ml of a 2 Mol. solution of NaOH in ethyl alcohol.

Gaseous products were analysed by mass-spectroscopy and identified as 1-butene and 2-butenes with a small amount of butadiene. The same olefins were found in the liquid alcoholic phase. Nevertheless, the yield of C_4 products was about 30% of the theoretical.

2. *Cleavage with ethanol.* 300 mg of the same complex were hydrolyzed with 3 ml of ethyl alcohol at 60°C. The gas evolved (40% of the theoretical) consisted of butenes and small amount of diolefins was recovered in the alcoholic phase.

3. *Cleavage with anhydrous HCl.* Different results were obtained depending on the reaction medium: in toluene about 70% of the crotyl groups were recovered as octanes and octenes (mass-spectrometry) while decompositions carried out without any solvent gave 2-chlorobutane, with 20% yield.

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[14] Netherland Patent Appl. 6409180 to Studiengesellschfat Kolc (1965).