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Catalysts

Polymeric Schiff's Base Chelates and Their Precursors 8[a], Some Cobalt Chelates as Catalysts for the Isomerization of Quadrycyclane to Norbornadiene

D. Wöhrle and P. Buttner

Organische und Makromolekulare Chemie, Studiengang Chemie, Universität Bremen,
Bibliothekstr. NW 2, D-2800 Bremen 33, Federal Republik of Germany

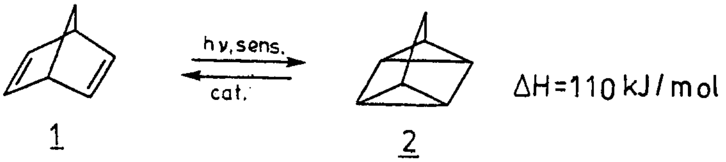
SUMMARY

Starting with Z-2,3-diamino-2-butenedinitrile as diamine component the synthesis of the low molecular N,N,O,O-chelate 3.Co and its ligand 3 is optimized. An easy synthesis of the chelate 8.Co covalently bound on macroreticular resins is presented. The chelates 8.Co are the most active heterogenous catalysts for the valence isomerization of quadricyclane to norbornadiene today.

INTRODUCTION

The cyclic system norbornadiene (1)-quadricyclane (2) is one of the most promising among the abiotic photochemical solar energy storage systems (Ref. 2-4) (Scheme 1). 1 / 2 consist of the sensitized reaction of colourless 1 to 2 and the catalyzed backreaction during which heat is released. For reaching economic use the development of highly effective, especially working (selectivity > 99.5 %) (Ref. 2,4,5) sensitizers and catalysts is necessary. Moreover for practical application the sensitizer and the catalyst must be immobilized.

Scheme 1



Up to the present, low molecular and polymer bound ketones and Cu(II)-compounds as sensitizers have the disadvantage of working only at the lower edge of the UV-VIS spectrum ($\lambda < 315$ nm) (Ref. 3). For the catalyzed backreaction some transition metal complexes (Ref. 4,6-9), mostly square planar, were found, but all exhibit the disadvantage of low activity and/or loss of activity. The most active catalyst up to now is cobalt(III)tetraphenylporphin (Co(III)TPP) (Ref. 8,10,11). However, loss of activity can be traced to a stable cobalt-reactant bond by formation of nortricyclyl-Co(III)TPP (Ref. 11). The few polymer bound catalysts synthesized up to the present show essentially lower activity compared to their low-molecular derivatives (ref. 12-15).

Initial studies proved the catalytic activity of 3.Co for the reaction of 2 to 1 (Ref. 16). This paper presents detailed investigations on the use

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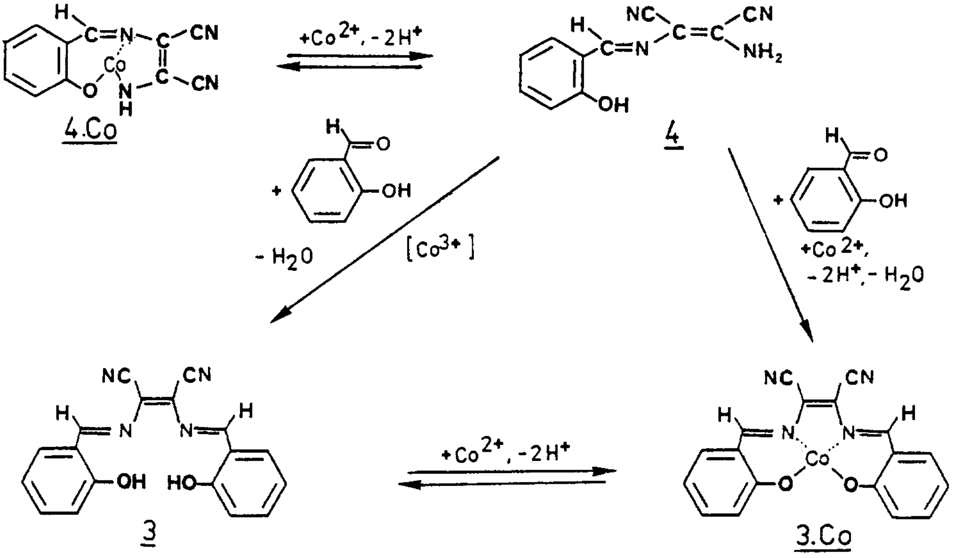
[a] Part 7: Ref. 1

of 3.Co in this reaction. Another main objective is an easy synthesis of 3.Co covalently bound at macroreticular resins.

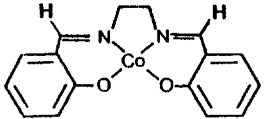
SYNTHESIS

The low molecular compound 3.Co (Ref. 16) precipitates in high yields from 4, 2-hydroxybenzaldehyde and Co(II) in refluxing ethanol. Corresponding to the synthesis of 3.Ni and 3.Cu (Ref. 16), the addition of glacial acetic acid is unnecessary, because 4.Co, existing in equilibrium, is not the end product due to its good solubility in ethanol. Moreover, the demetallization of 3.Co to 3 by acids was observed, followed by the decomposition of 3 to 4 and 2-hydroxybenzaldehyde. 3 was obtained in an improved synthesis compared to Ref. 16. By the addition of Co(II) to 3 in DMF, 3.Co forms immediately (Scheme 2).

Scheme 2

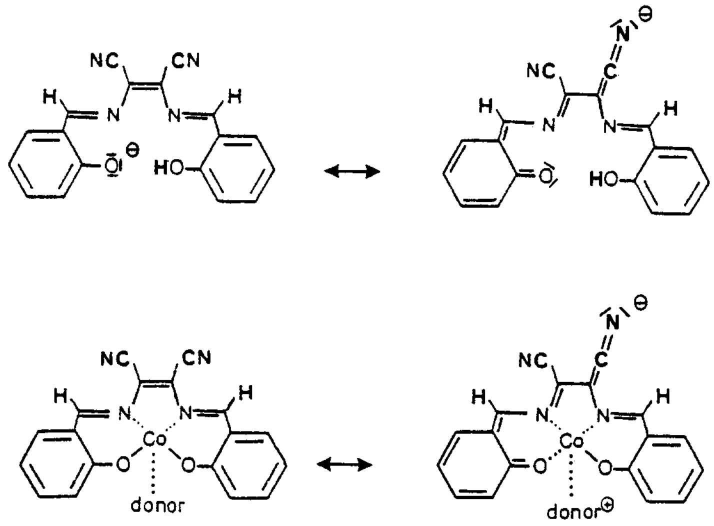


3.Co shows a great tendency for additional complexation with donor ligands. The red-brown form of 3.Co obtained from the synthesis described above and dried at 353 K still contains coordinated solvent. Solvent-free black-violet 3.Co was obtained by heating at 383 K. After crystallization from pyridine, 3.Co coordinates three molecules of pyridine. The coordination of donor ligands alters the UV-VIS spectra (see exp. part), especially the absorption at longest wave lengths is shifted bathochromically. This is not observed for Co(salen) 5.Co. Also the addition of NaOH to the yellow solution of 3 in acetone leads to a deep red solution of the anion of 3 (see exp. part). The dicyanovinylen bridge, which contains groups with strong electron withdrawing effect is responsible for the resonance with the ligand atoms (Scheme 3). Therefore 3.Co contains strongly electrophilic cobalt for the reaction with 2.



5.Co

Scheme 3



Covalently polymer bound chelates were synthesized on macroreticular resins, because neither 1, 2 nor chloroform, the solvent for the catalysis, are good swelling solvents for low crosslinked polystyrene. The resins A and B were first alkylated with 5-chloromethyl-2-hydroxybenzaldehyde giving 6 (Ref. 17,18) (Scheme 4). The degree of alkylation was calculated by elemental analysis after reaction of 6 with 2,4-dinitrophenylhydrazine to 7. The degree of alkylation of about 0.6 mmol per g resin corresponds to yields of 50-60 % related to the inserted 5-chloromethyl-2-hydroxybenzaldehyde. The following reaction of 6 with 4 and Co(II) to the chelates 8.Co succeeds best in ethanol/glacial acetic acid (vol. ratio 3:1). Contrary to Ref. 16, this preparation of polymer bound 3.Co is easier and side reactions with formation of polymer bound 4.Co and accompanying crosslinking can be avoided. The deep blue resins 8.Co exhibit a rest absorption ν C=O at 1650 cm^{-1} originating from unreacted 2-hydroxybenzaldehyde groups. According to cobalt analysis of 8.Co (according to Ref. 20), the resins contain about 0.2 mmol chelate centers per g resin. This corresponds to a yield of 28-44 %, when beginning with 6 (Tab. 1). The yields are comparable with those of the synthesis of 3.Co in ethanol/glacial acetic acid (Ref. 16).

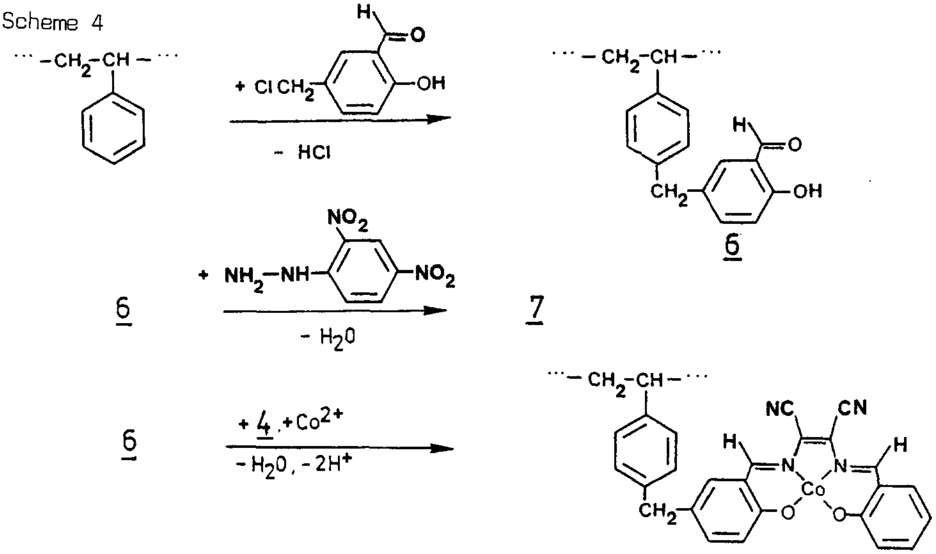
Tab. 1. Introduction of functional groups into the polymers A and B

resin	alkylation of resin A,B to 6		reaction of 6 to 8.Co	
	mmol R-CHO/g polymer[a]	conversion (%)	mmol 8.Co/g polymer[b]	conversion (%)
A	0.55	50	0.21	44
B	0.65	60	0.18	28

[a] from nitrogen analysis of 7

[b] from cobalt analysis of 8.Co

Scheme 4



CATALYSIS

The chelates 3.Co and 8.Co show high catalytic activity in the reaction of 2 to 1 in uncoordinating solvents like chloroform, dichloromethane and benzene. The use of solvents like acetone, DMF, DMSO, THF, Pyridine which contain Lewis-base groups or their addition to the unpolar solvents leads to a retardation or inhibition of the catalytic reaction. These results are in agreement with the retardation of the catalysis by N-heterocycles in the case of CoTPP as catalyst (Ref. 7,11). Furthermore, 3.Co must be solvent-free (dried at 383 K) to achieve sufficient solubility in uncoordinating solvents. Also the solvent had to be well dried. Water in commercial $CDCl_3$ leads already to precipitation of $3.Co{\cdot}H_2O$ - and therefore to an inhibition of catalysis. For the polymeric chelates 8.Co, only the addition of greater amounts of water (> 0.2 %) leads to a loss of activity. The reaction of 2 to 1 was studied in $CDCl_3$ at 293 K and monitored by ^{1}H-NMR. Evaluating the results in terms of a pseudo-first order reaction (Ref. 8), a decrease of the reaction rate is obtained (Fig. 1). Since the UV-VIS spectra of 3.Co also changes when 2 is added and since the IR-spectrum too is altered after isolating the catalyst we suppose that a side reaction of 2 with 3.Co under deactivation of 3.Co is responsible for the decreased reaction rate. Addition of 1 does not alter the spectra and has no influence on the catalytic activity. So a reaction of 3.Co with norbornadiene similar to the reaction CoTPP undergoes is not the reason for the loss of activity. Explaining the nature of this side reaction is the aim of subsequent investigations.

The rate constant K_{obs} - and the comparable K_m - was calculated from the velocity at the beginning of the catalysis (Tab. 2). These results show that the activity of 3.Co is comparable to that of CoTPP (Ref. 8,10,11), while 8.Co is a heterogenous catalyst with the best activity known today. The main reason for the lower activity of 8.Co compared to 3.Co appears to be diffusion of the substrate 2 into the cavities of the macroreticular resins. The catalytic activity of resin B increases tenfold by grinding the particles.

Subsequent investigations should clarify the interdependence of catalytic activity, deactivation and the structure of inactive cobalt chelates.

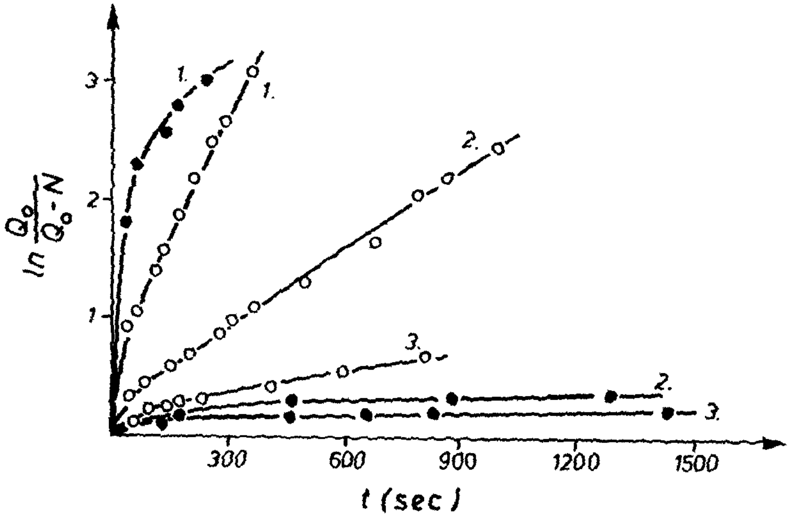


Fig. 1 Isomerization of 2 (0.5 $mol \cdot l^{-1}$) to 1 with low molecular 3.Co (3.8·10⁻⁴ $mol.l^{-1}$) resp. polymer 8.Co (resin A, 8.5·10⁻⁴ $mol \cdot l^{-1}$ chelate centers) at 293 K in $CDCl_3$.
●: 3.Co; o: 8.Co; numbers 1,2,3 specily run 1, run 2, run 3.

Tab. 2. Isomerization of 2 (0.5 $mol \cdot l^{-1}$) to 1 in $CDCl_3$ at 293 K

catalyst(mol%[a], $mol \cdot l^{-1}$)	method	run	K_{obs} (sec^{-1})	K_m ($l \cdot mol^{-1} cm^{-1}$)[b]	$t_{1/2}$ (sec)[c]
3.Co[d] (0.075, $3.8 \cdot 10^{-4}$)	1	1	$5.0 \cdot 10^{-2}$	133	13.8
	1	2	$3.7 \cdot 10^{-4}$	1.0	1873
	1	3	$9.7 \cdot 10^{-5}$	0.25	7145
3.Co[e] (1.06, $5.3 \cdot 10^{-3}$)	2	1	$1.6 \cdot 10^{-4}$	0.03	4359
5.Co[d] (0.49, $2.5 \cdot 10^{-3}$)	1	1	$7.7 \cdot 10^{-5}$	0.03	8978
8.Co, resin A[e] (0.17, $8.5 \cdot 10^{-4}$)	2	1	$1.8 \cdot 10^{-3}$	16.1	38
	2	2	$2.3 \cdot 10^{-3}$	2.4	301
	2	3	$6.6 \cdot 10^{-4}$	0.7	1050
8.Co, resin A[a] (0.42, $2.1 \cdot 10^{-3}$)	2	1	$4.4 \cdot 10^{-2}$	18.4	15.7
	2	2	$3.0 \cdot 10^{-2}$	12.4	23
	2	3	$8.0 \cdot 10^{-3}$	3.4	86
	2	4	$1.6 \cdot 10^{-3}$	0.6	433
8.Co, resin B[e] (0.13, $6.5 \cdot 10^{-4}$)	2	1	$7.0 \cdot 10^{-4}$	1.1	990
8.Co, resin B[e,f] (0.13, $6.5 \cdot 10^{-4}$)	2	1	$6.8 \cdot 10^{-3}$	10.4	102

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[a] refered to 2 = 100 %. [b] $v = K_{obs}[2] = [cat][2]$. [c] calculated values. [d] dried at 383 K.
[e] dried at 343 K. [f] grinded.

EXPERIMENTAL

Used instruments: IR (Perkin Elmer 577), UV-VIS (Perkin-Elmer 544), ^{1}H-NMR (Varian MAT EM 360, 60 MHz).

If necessary, all reactions were carried out under argon in dried, distilled solvents with purified reagents.

Starting resins: resin A: macroreticular polystyrene with 30 % crosslinking, pore diameter 210 Å, pore volume 1.2 ml/g, 50-150 mesh (Ref. 19).
Resin B: macroreticular polystyrene with 30 % crosslinking. Pore diameter 800 Å, pore volume unknown, 22-50 mesh (Aldrich Nr. 9003-53-6).

Quadricyclane 2: Prepared from norbornadiene 1 in a photoreactor according to Ref. 12.

Cobalt analyses were carried out as described in Ref. 20.

[2,2'-Dicyanovinylenebis(nitrilomethylidyne)diphenolato]cobalt (II) (3.Co): A suspension of 0.64 g (2.6 mmol) Co(II)acetate·4 H_2O in 50 ml hot ethanol was given to a hot solution of 1.0 g (8.2 mmol) 2-hydroxybenzaldehyde in 30 ml ethanol. Then a hot solution of 0.53 g (2.5 mmol) 4 (Ref. 16) in 80 ml ethanol was added to this mixture. The red solution was refluxed for 30 min. After cooling the precipitate was filtered off and washed with water, ethanol and acetone. Yield: 0.63 g (67 %). Drying at 353 K over P_2O_5 i.vac. yields a red-brown product, which turns violet-black at 383 K.

$C_{18}H_{10}CoN_4O_2$ (373.24) Calc: C 57.93 H 2.70 N 15.01
Found: C 57.91 H 2.86 N 15.11

UV-VIS ($CHCl_3$): λ_{max}/nm (logε/l·mol^{-1}cm^{-1})= 244 (4.44), 312 (4.35), 348 (4.26), 360 (4.26), 420 (4.09), 500 (4.16)
(acetone)= 364 (4.33), 542 (4.19)
(DMSO)= 261 (4.34), 313 (4.28), 373 (4.36), 455 (sh 3.98), 570 (4.19)

3.Co·H_2O: A solution of 3.Co in CH_2Cl_2 was mixed with H_2O, the red-brown precipitate was filtered off and dried at 333 K.

$C_{18}H_{10}CoN_4O_2\cdot H_2O$ (391.25) Calc: C 55.26 H 3.09 N 14.32
Found: C 55.66 H 3.19 N 14.64

3.Co·py_3: 3.Co was recrystallized under argon from pyridine, the violet shining crystals were washed with a small amount of ether and dried at 333 K.

$C_{18}H_{10}CoN_4O_2\cdot(C_5H_5N)_3$ (610.54) Calc: C 64.92 H 4.13 N 16.06 Co 9.65
Found: C 64.96 H 4.17 N 16.34 Co 10.2

2,3-Bis(2-hydroxybenzylideneimino)-2,3-butenedinitrile 3: 0.1 g (0.46 mmol) 4 (Ref. 16) was dissolved in 50 ml ethanol. Then one drop conc. H_2SO_4, 0.116 g (0.95 mmol) 2-hydroxybenzaldehyde and 0.17 g (0.5 mmol) Co(III)acetylacetonat was added. The green solution was stirred at ambient temperature for a few days, during which the solution turns violet and yellow crystals of 3 precipitated. These were washed with ethanol and dried at 383 K over P_2O_5 i.vac. Yield 0.037 g (25 %), analytic data corresponding Ref. 16.

UV-VIS (acetone): λ/nm ($\log\varepsilon$ /l·mol^{-1}cm^{-1})= 348 (4.42), 425 (sh,4.55), 444 (4.60)
($3.86\cdot10^{-5}$ mol·l^{-1} 3 and $3.84\cdot10^{-4}$ mol·l^{-1} NaOH in acetone): 360 (4.24), 416 (4.08), 570 (4.39)

Polymer 6: The synthesis of polymer 6 was described in Ref. 18. The composition of 6 was deduced after reaction to 7 (Tab. 1).

Polymer 7: To 0.04 g 2,4-dinitrophenylhydrazine in 5 ml methanol was added as much conc. H_2SO_4 as necessary for obtaining complete solution. Then 0.1 g polymer 6 was added and the mixture was refluxed for 16 h. After isolation the resin was carefully treated with methanol in a Soxhlet apparatus. After drying at 353 K i.vac. over P_2O_5 approximately 0.1 g of red polymer 7 w obtained.

IR (KBr, cm^{-1}): 3400 (w,OH), 1600 (s,C=N), 1580 (s,NO_2), 1333 (s,NO_2) and absorptions of polystyrene.

7 (resin A) $[(C_8H_8)_9(C_{10}H_{10})_{4.3}(C_{22}H_{18}N_4O_5)]_n$ $(1913.7)_n$
Calc: C 85.9 H 7.00 N 2.92
Found: C 84.53 H 7.08 N 2.63

7 (resin B) $[(C_8H_8)_8(C_{10}H_{10})_{3.8}(C_{22}H_{18}N_4O_5)]_n$ $(1753.7)_n$
Calc: C 85.31 H 6.93 N 3.19
Found: C 83.83 H 6.93 N 3.00

Polymer 8.Co: 0.2 g 6 (resin A) or 0.17 g 6 (resin B) containing 0.11 mmol 2-hydroxybenzaldehyde groups was added to a hot solution of 0.16 g (0.75 mmol) 4 in 30 ml ethanol/glacial acetic acid (vol. ratio 3:1). After the addition of 0.2 g (0.8 mmol) Co(II)acetate·4 H_2O) suspended in 30 ml hot ethanol/glacial acetic acid (vol. ratio 3:1), the mixture was refluxed for 8 h. The deep-blue coloured resins were isolated, thoroughly washed with ethanol, hot DMF and acetone and dried at 353 K over P_2O_5 i.vac. Yields about 0.2 g (resin A) or 0.17 g (resin B).

IR (KBr, cm^{-1}): 2200 w(CN), 1680 (w-m, C=O, 1880 (C=N) and absorptions of polystyrene.

8.Co (resin A)
$[(C_8H_8)_9(C_{10}H_{10})_{4.3}(C_{16}H_{14}O_2)_{0.56}(C_{27}H_{18}CoN_4O_2)_{0.44}]_n$ $(1806.28)_n$
Calc: C 89.02 H 7.15 N 1.36 Co 1.43
Found: C 85.29 H 7.63 N 1.84 Co 1.42

8.Co (resin B)
$[(C_8H_8)_8(C_{10}H_{10})_{3.8}(C_{16}H_{14}O_2)_{0.72}(C_{27}H_{18}CoN_4O_2)_{0.28}]_n$ $(1611.23)_n$
Calc: C 89.87 H 7.22 N 0.97 Co 1.02
Found: C 88.54 H 7.45 N 1.28 Co 1.07

CATALYSIS

Method 1: The catalyst was dissolved in $CDCl_3$, the concentration of the solution was estimated photometrically. 0.5 ml of this solution was put into a NMR-tube. Then, 25 µl of quadricyclane 2 was added with a syringe. After shaking the tube the ^{1}H-NMR-spectrum was immediately recorded.

Method 2: The catalyst was weighed and placed into the NMR tube. Then 0.5 ml of 2, dissolved in $CDCl_3$ (0.5 mol·l^{-1}) was added. The mixture was shaken and the spectrum recorded.

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