Journal of Organometallic Chemistry, 136 (1977) 259—264

FORMATION OF A NOVEL ALKYLCOBALT DIMER

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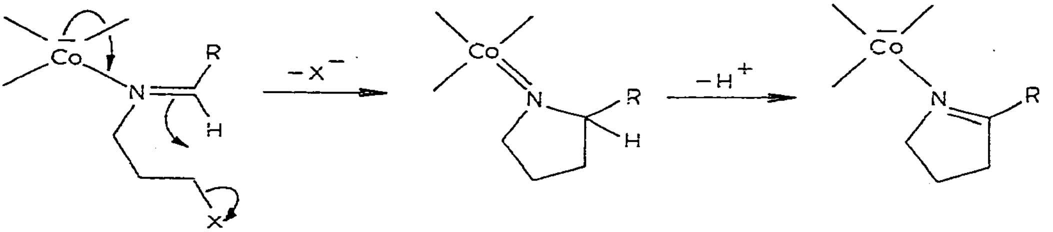
(Received March 2nd, 1977)

Summary

A functionally-substituted derivative (I) of *N,N'*-disalicylalethylenediaminecobalt(II) was synthesized. Reduction of I with lithium naphthalide led to formation of a novel alkylcobalt dimer.

Introduction

Cobalt(I) compounds are powerful nucleophiles and as such react with alkyl halides and certain esters to give alkylcobalt compounds [1,2]. The present work was undertaken to examine the possibility of effecting intramolecular alkylation using reactions delineated by the following sequence (eq. 1).



(1)

Interest in this reaction sequence rested on the possiblity that such a mechanism might exist in the biogenesis of cobalamines and metalloporphyrins and that, if realized, would provide a method of constructing the pyrollidine moiety in these systems.

In order to test this proposal it was necessary to prepare a cobalt complex with a suitably functionalized ligand. Because the necessary diaminobutanol was readily available by known sequence, the synthesis of *N,N'*-disalicylal-2,2-

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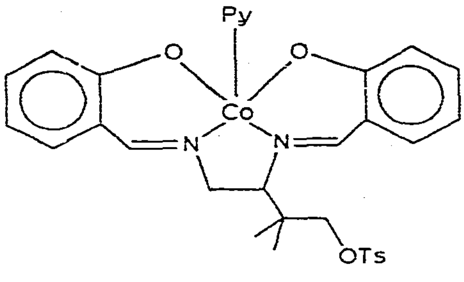
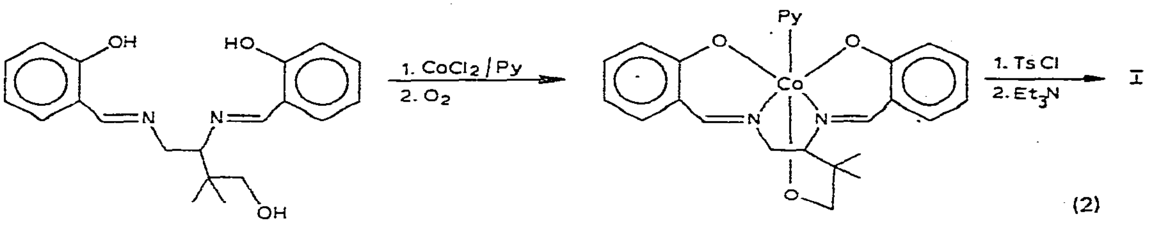
dimethyl-3,4-diaminobutyl-*para*-toluenesulfonatopyridinatocobalt(II) (I), a derivative of the well-known salcomine, was undertaken.



(I)

Results and discussion

The synthesis of I was accomplished by way of the sequence shown in eq. 2.

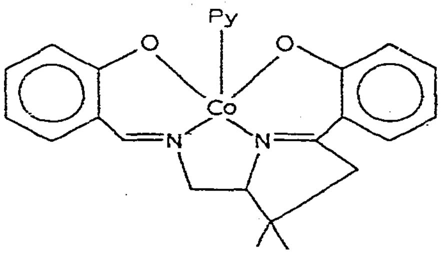


(2)

(II) (III)

The Schiff base II was prepared in high yield from salicylaldehyde and 2,2-dimethyl-3,4-diaminobutanol. Reaction of II with cobaltous chloride, followed by air-oxidation and recrystallization of the product from pyridine, gave the cobalt(III) alkoxide III. Conversion of III to the desired complex I was affected by treatment of III with tosyl chloride followed by reduction with triethylamine. The new structures (I, II, and III) were established by elemental, spectroscopic, polarographic, and magnetic data.

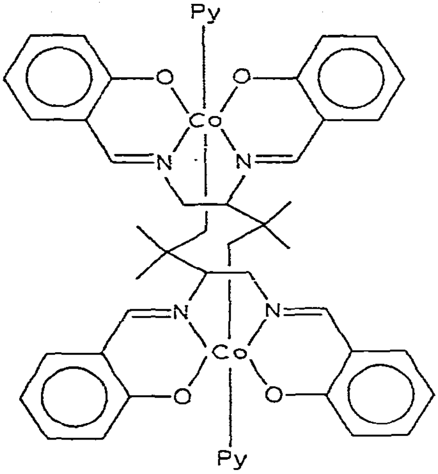
The functionalized complex I was reduced in a nitrogen atmosphere with lithium naphthalide and then exposed to the air. Thin-layer chromatography revealed that a homogeneous colored product had formed. Recrystallization gave a bright-orange diamagnetic solid. Loss of the tosylate group in the reaction was established by the elemental analysis and infrared spectrum of the product. If the postulated reaction sequence (eq. 1) had occurred, it was expected that subsequent air-oxidation would provide the annelated salcomine (IV).



(IV)

Several lines of evidence, based in part by comparison with the closely-related model compound, salcomine, ruled out this structure and indicated that the otherwise interesting reaction postulate had not materialized: (1) the diamagnetism of the product; (2) the electronic spectrum differed irreconcilably with that of salcomine; (3) molecular weight measurement pointed to a dimeric structure.

A structure which can accommodate the foregoing evidence as well as that derived by comparison with a second model compound, methylcobalt salcomine [3], is the novel dimer V. Obvious chemical precedents support such a structure and establish that the reduction step was followed by a conventional nucleophilic displacement of tosylate by cobalt(I).



(V)

In addition to chemical precedent the dimeric structure is supported by other evidence. The electronic spectrum of the product, λ_{max} (EtOH), 377 (6840) and 405 nm (4430) is similar to that reported for methylcobalt salcomine, λ_{max} (THF), 340 (ϵ 9170) and 395 nm (ϵ 5000). Elemental data agree as well as the NMR spectrum, the details of which were as follows: δ(ppm) 8.66 (d, (br), 2H, α protons of pyridine), 6.0—7.8 (m, 13H, remaining aromatic and benzylidene protons), 4.75 (d, *J* 5.5 Hz, 1H, one of the two geminal protons of the cobalt-methylene group), 3.82 (d, *J* 5.5 Hz, 1H, geminal partner of preceding proton), 3.25—3.63 (m, 3H, *N*-methylene, *N*-methine array), 1.05 (s, 3H, methyl), 1.02 (s, 3H, geminal methyl partner of the preceding signal). The relatively small (5.5 Hz) geminal coupling constants of the cobalt-methylene proton-pair is consistent with the fact that such constants diminish as the electronegativity of the substituent bonded to methylene diminishes. This effect is particularly apparent when the methylene group is bonded to metals [4].

Dimeric alkylcobalt compounds with the unique cage structure of V have not, to our knowledge, been reported previously.

Experimental

All melting points are uncorrected. The electronic spectra were recorded on a Cary Model II recording Spectrophotometer and IR spectra on a Perkin—Elmer

Infracord. NMR traces were recorded using deuterochloroform solvent with tetramethylsilane as the internal standard. Magnetic susceptibilities were measured using the NMR method of Evans [5]. A Sargent XXI Polarograph was used to obtain reduction or oxidation potentials, with dimethylsulfoxide as solvent, tetrabutylammonium perchlorate as the support electrolyte, and standard calomel as the reference electrode. Elemental analyses were performed by Huffman Microanalytical Laboratories Wheatridge, Colorado.

Preparation of N,N'-disalicylal-2,2-dimethyl-3,4-diaminobutan-1-ol (II)

A solution containing 5.5 g (0.027 mol) of 2,2-dimethyl-3,4-diaminobutan-1-ol dihydrochloride [6], 10 ml of water, 10 g of sodium acetate trihydrate was added to a hot, stirred mixture of 6.55 g (0.0537 mol) of salicylaldehyde in 250 ml of ethanol. As the solution cooled, yellow crystals precipitated which were filtered and allowed to dry. The product weighed 7.44 g (85%), m.p. 154—156°C. UV spectrum: λ_{max} (CH_3OH): 213 (log ϵ 4.635), 254 (4.304), 370 (3.824), and 403 nm (3.113); strongly resembling the parent Schiff base, *N,N'*-disalicycalethylenediamine [7]. Anal. Found: C, 70.30; H, 7.05; N, 8.17. $C_{20}H_{24}N_2O_3$ calcd.: C, 70.57; H, 7.11; N, 8.23%.

Preparation of N,N'-disalicylal-2,2-dimethyl-3,4-diaminobut-1-oxy-pyridinatocobalt(III) (III)

In a 1-liter, 3-necked flask equipped with a mechanical stirrer, reflux condenser, and addition funnel were combined 17.02 g (0.05 mol) of II, 150 ml of water, 4.0 g (0.10 mol) of sodium hydroxide, and 0.25 g of sodium acetate trihydrate. The mixture was stirred and heated with a flame until complete solution was achieved. To the stirred hot solution was added dropwise a hot solution of 11.90 g (0.05 mol) of cobalt(II) chloride hexahydrate in 25 ml of water; a brown precipitate formed during the addition. After the addition was complete, the mixture was stirred for 20 min, then cooled to room temperature. Water (50 ml) was added to the flask. The precipitate was filtered, ground in a mortar, triturated with water, and filtered again. The precipitate was washed with additional water (100 ml) then dried under vacuum at room temperature over phosphorus pentoxide. The crude dried product, a grayish-brown powder, weighed 15.0 g. It was dissolved in boiling pyridine (1.5 l), filtered, and allowed to stand overnight at room temperature. A precipitate formed which was filtered, washed with a small amount of fresh pyridine, followed by ether, then dried under vacuum at room temperature over phosphorus pentoxide. The purified product, a light-brown microcrystalline solid, weighed 3.48 g. A second crop weighed 2.43 g (total yield, 25%). UV spectrum: λ_{max} (EtOH): 256 (log ϵ 4.712) and 387 nm (3.706). The IR spectrum (KBr) showed no OH band. The product is diamagnetic and exhibited $E_{1/2}$ at —0.6 V. Anal. found: C, 62.59; H, 5.41; N, 8.79, Co, 12.76. $C_{25}H_{26}CoN_3O_3$ calcd.: C, 63.16; H, 5.52; Co, 12.37; N, 8.82%.

Preparation of N,N'-disalicylal-2,2-dimethyl-3,4-diaminobutyl-para-toluenesulfonatopyridinatocobalt(II)

In a 250-ml Erlenmeyer flask equipped with a magnetic stirrer were combined 0.382 g (2 mmol) of *p*-toluenesulfonyl chloride and 0.950 g (2 mmol) of

III. Initially, the mixture was heterogeneous due to the limited solubility of the cobalt(III) complex in pyridine. After the mixture was stirred for 30 min, it was homogeneous. The solution was stirred for an additional 90 min then warmed to boiling. To the boiling solution was added sufficient triethylamine to effect slight cloudiness. After an additional brief boiling period (2—3 min), the solution was filtered and allowed to cool slowly in an insulated flask. A crystalline precipitate, consisting of a mixture of deep-brown microcrystals and small colorless prisms, was collected. The colorless fraction, shown by comparison with an authentic sample to be trimethylamine hydrochloride, was easily removed by washing the precipitate with water. The remaining dark-brown fraction, free of chloride, dried under vacuum over phosphorus pentoxide, weighed 338 mg (27%). UV spectrum: λ_{max} (EtOH): 224 (log ϵ 4.658λ, 240 (4.619), 343 (3.724), and 404 nm (3.907). Anal. found: C, 60.74; H, 5.50; N, 6.72; S, 4.49. $C_{32}H_{33}CoN_3O_5S$ calcd.: C, 60.94; H, 5.27; N, 6.66; S, 5.09%.

The oxidation state of the cobalt in this compound is +2 as indicated by its paramagnetic behavior in the NMR spectrum, i.e., broadened weak signals. A magnetic susceptibility measurement using the NMR method of Evans [5] indicated one unpaired electron in the complex. Further confirmation of the +2 oxidation state was found in the polarogram of this compound which showed an oxidation wave ($Co^{2+} \rightarrow Co^{3+}$) at + 0.02 Volt and a reduction wave ($Co^{2+} \rightarrow Co^{+}$) at —1.11 Volts. This polarogram is similar to that recorded for salcomine, oxidation at —0.08 V, reduction at —12.4 V. IR spectrum: 7.36, 7.65, and 8.51 μm, characteristic of alkylsulfonate esters.

Reduction of I with lithium naphthalide: formation of the dimer V

In a 250-ml, three-necked flask equipped with a magnetic stirrer, serum cap, and nitrogen inlet, was placed 1.251 g (2 mmol) of the cobalt(II) tosylate I. Previously purified tetrahydrofuran (20 ml) was distilled from lithiuni aluminum hydride into the flask while the system was purged with nitrogen. The cobalt(II) tosylate did not completely dissolve. The stirred heterogeneous deep-orange mixture was chilled to 0°C and 4 ml of 0.7 *M* (2.8 mmol) lithium naphthalide in tetrahydrofuran was introduced. The flask contents became somewhat brownish in color, which persisted for a few minutes, then the initial orange color was restored, attended by complete homogeneity. The reaction mixture was allowed to warm to room temp. and then opened to the atmosphere; no color change occurred. The solvent was evaporated and the residue dissolved in chloroform. The chloroform solution, intense green, was washed with water and dried with anhydrous magnesium sulfate. The dried solution was filtered and evaporated to dryness. The solid dark-brown residue was triturated with ether then warmed under vacuum to remove any naphthalene present. Recrystallization of the crude product (0.690 g) from aqueous pyridine provided 0.438 g (0.99 mmol, 50% of theory) of bright-orange platelets which decomposed without melting at 180°C. Thin-layer chromatography on Silica-gel G using 15% methanol in chloroform as the eluent indicated that the product was homogeneous. NMR and UV spectra see Results and discussion. Absence of line-broadening in the NMR spectrum indicated a diamagnetic substance. Anal. found: C, 65.29; H, 5.92; Co, 13.24; N, 9.08. $Co_2C_{50}H_{52}N_6O_4$ calcd.: C, 65.35; H, 5.71; Co, 12.83; N, 9.15%. Osmometric weight in pyridine: found: 917; calcd.: 919.

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