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REACTIONS OF POLYNUCLEAR COMPLEXES
NOVEL BENZOTRIAZOLE — ALLYLAMINE COBALT COMPLEXES AND THEIR OXIDIZING PROPERTIES*

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Summary

The absorption of oxygen by solutions of bis(triphenylphosphine)cobalt(II) chloride in allylamine in the presence of heterocyclic ligands has been studied. Novel complexes are formed in the presence of benzotriazole. A new class of trinuclear complexes has been discovered and studied by X-ray diffraction. Oxidation of triphenylphosphine takes place catalytically in the presence of oxygen under mild conditions.

Introduction

The important role of cobalt complexes and other transition metal catalysts in the oxidation of various organic compounds (e.g. triphenylphosphine [1], tert-butylcarbylamine [2], cyclohexenes [3], alkylbenzenes [4]) is well established. Many of the complexes act as oxygen carriers, and have been studied extensively as potentially useful selective oxidation catalysts for the preparation of important industrial materials. Since template effects could reasonably be expected, we have investigated the reaction of coordinated unsaturated amines (e.g. allylamine) towards various reactive nitrogen containing molecules (e.g. benzotriazole with UV light, azides). As far as benzotriazole and allylamine are concerned, no specific template reactions were observed but unusual novel complexes were obtained which weakly catalyse the oxidation of triphenylphosphine at room temperature (80% after 3 days), the process being accelerated by UV light. The results contribute to the understanding of the complex reactions which are involved in the oxidation of cobalt compounds. The most striking observation, however, is the formation of a highly symmetri-

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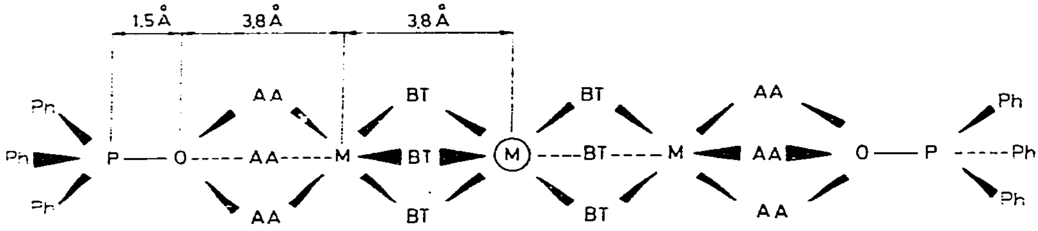
cal trinuclear complex from Co or Ni in which there is a very unusual type of bonding involving two molecules of phosphine oxide as ligands [see structure (III)*]. We describe below the preparation and properties of these complexes; studies of other reactions mentioned are still in progress.



(IIIa) M = Co**
(IIIb) M = Ni*
(IIIc) M = Ni , PPh_3 as ligand instead of Ph_3PO
(M) : centre of symmetry

Results

A. Oxidation of Co—allylamine—benzotriazole complexes

When a complex such as L_x cobalt(II) chloride (L = triphenylphosphine: $x = 2$; L = α,α'-bipyridyl: $x = 1$) is dissolved in allylamine in the presence of varying amounts of benzotriazole, a homogeneous solution (solution A) is obtained if oxygen is rigorously excluded. If oxygen is introduced, a precipitate appears immediately and the ligand L is virtually completely expelled from the complex in every case (see Scheme 1). Analysis of the precipitates for various Co/BTH ratios* shows that their oxygen content decreases markedly as the ratio Co/BTH decreases: in fact when Co/BTH varies from ∞ to 0.17, the oxygen content drops from 7.2 to 0.65% for L = α,α'-bipyridyl. At the same time the chlorine content decreases from 16.4 (Co/BTH = ∞) to 0% (Co/BTH = 0.10). The overall yield of precipitated complex increases considerably with the concentration of BTH, up to 80% for Co/BTH = 0.2.

The composition of the precipitate obtained in the absence of BTH agrees roughly with the empirical formula of (I), but the material is probably a mixture of several peroxidic species: $[Co_2Cl_3C_{18}H_{42}N_6O_3]_2$ (I).

When the amount of benzotriazole is increased, the analysis agrees more closely with a structure such as (II), probably in an associated form involving coordination by the lone-pair of the 3-nitrogen atom of benzotriazole. The compounds were found to be insoluble in all solvents tried. They are related to known complexes of cobalt and benzotriazole such as $[(C_6H_4N_3)_2Co \cdot nH_2O]_x$ [5] in which a (Co—N)σ bond is formed by each coordinated molecule of benzotriazole.

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* Derivative for which complete X-ray analysis has been made [6].

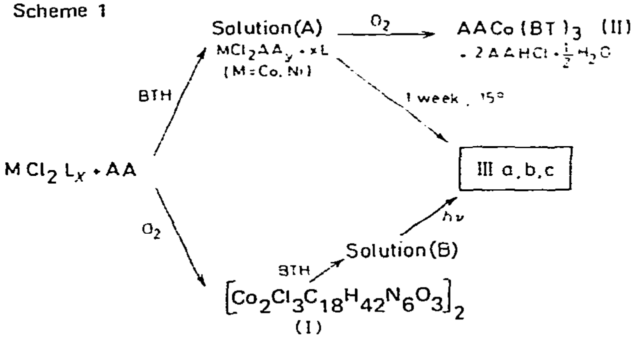
** This complex is isostructural to IIIb as shown by X-ray diffraction [6].

B. Reactions of peroxidic Co—allylamine—benzotriazole complexes

In contrast, when a solution of bis(triphenylphosphine)cobalt(II) chloride was dissolved in allylamine and the solution shaken *under oxygen* a dark precipitate, (I), was formed; this redissolved readily on addition of benzotriazole, to give a deep red solution (B). Irradiation of this solution with UV light (Pyrex filter) gave an orange precipitate, (IIIa). Good crystals of the same product are very slowly formed on storage of solutions (A) or (B) in the dark (see Scheme 1).

The IR spectra and elemental analyses of the various crops of (IIIa) obtained in these two procedures were all identical, and fit the suggested formula.

Scheme 1



M = Co, Ni
L = PPh_3, x = 2; α,α′-bipyridyl, x = 1 ;
AA = allylamine;
BT = benzotriazolyl

Discussion

The results summarised in part *A* indicate the formation of cobalt salts of benzotriazole from a homogeneous solution of ill-defined species. Thin-layer chromatography shows that the presence of allylamine causes the phosphine to be immediately expelled from the complex. It is, however, re-incorporated during the crystallization of complexes of type (III). The formation of the three Co—benzotriazole σ-bonds is explained by the oxidation of Co^{II} to Co^{III} and elimination of HCl from $CoCl_2$ and BTH in the presence of allylamine, the fixation of the third molecule of BTH involving oxidation of the hydrogen atom of BTH to H_2O. Intermolecular coordination of electron pairs of nitrogen from BT to cobalt can account for the insolubility of (II), by completing the coordination sphere of the metal.

The nickel analogue of (I) is not formed under these conditions. As far as part *B* is concerned, the structure of (IIIb), which is isostructural with (IIIa),

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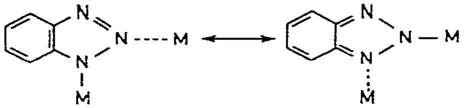
* BT = benzotriazolyl, $C_6H_4N_3$.

has been established by X-ray diffraction [6]. The molecule is linear with respect to both P—O axes of phosphine oxide and to the three metal atoms, and has a ternary axis and a centre of symmetry. The benzotriazole molecules are located between the metal atoms, whereas the six allylamine molecules are symmetrically coordinated with three at each end of the molecule.

The most striking feature of the structure of (IIIb) is the absence of direct bonding between the phosphine oxide molecules and the metal atom: they are symmetrically connected to the rest of the molecule, probably via hydrogen bonding from the amino groups [*d*(N—O) 3.0 Å]. Thus, the oxidation of the phosphine takes place in solution via an entity which is different from (IIIa), probably a cobalt peroxide species, as indicated by the presence of a weak signal at 2 G.s^{-1} * in the EPR spectra of the oxidized solutions (A) and (B). This signal is not observed for complex (IIIa). The benzotriazole molecules are linked symmetrically through the 1- and 2-nitrogen atoms to the adjacent nickel atoms [*d*(Ni—N) 2.2 Å]. The equivalence of the Ni—N bonds shows that no distinction is possible between σ and dative bonds (from the electron pairs of BT): this can be accounted for by mesomerism of the benzotriazolyl anion. In fact, the charges may be delocalised throughout the whole chain of metal atoms and ligands, and this could contribute to stabilization of the bonding of the PO entity to the allylamine molecules.



Previous results suggest that the 3-nitrogen atom of 1-substituted benzotriazole is a stronger nucleophile than the other nitrogen atoms [8], but the type of bonding in such a large molecule is strongly influenced by steric factors. Coordination with the 3- instead of the 2-nitrogen atom would lead to overcrowding of the electron pairs of three 2-nitrogen atoms and to prohibitive angular strains in the Ni—BT—Ni bonds.

When (IIIa) is formed from the oxidized solution (B), reduction of paramagnetic cobalt species (probably such as Co^{II}OO·) takes place, as shown by EPR spectroscopy, and this reduction is accelerated by UV light. At the same time the coordinated phosphine in (IIIa) is oxidized to its oxide, as shown by analysis and thin-layer chromatography of the ligand (after destruction of the complex by HCl).

The similar complex (IIIb) is obtained from $NiI_2(PPh_3)_2$ and benzotriazole in allylamine; analysis shows that the ligand is triphenylphosphine when the reaction is carried out under nitrogen, but the phosphine oxide is formed on working up in air, as shown by X-ray diffraction examination. Moreover a solution of triphenylphosphine in allylamine is not so easily oxidized to its oxide in the presence of the nickel complexes as in that of their cobalt analogues.

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* EPR spectra were recorded by Dr. Derouane, University of Liège.

Experimental

All the syntheses were carried out with allylamine freshly distilled over calcium hydride under pure argon. Benzotriazole was purified by recrystallization from ethanol followed by chromatography on silica gel.

Bis(triphenylphosphine)cobalt(II) chloride was prepared in alcohol from $CoCl_2.6H_2O$ and triphenylphosphine, and thoroughly dried under vacuum. α,α'-Bipyridylcobalt(II) chloride was similarly prepared from α,α'-bipyridyl, and bis(triphenylphosphine)nickel(II) iodide was similarly prepared from nickel iodide and triphenylphosphine.

Preparation of complexes (I) and (II)

The flask containing the cobalt complex L_xCoCl_2 ($L = PPh_3 : x = 2$; $L = \alpha,\alpha'$-bipyridyl, $x = 1$) (0.69 mmol) was dried in vacuum and flushed with argon. Allylamine (3 ml) was added from a syringe. The colour of the complex turned from blue to pink. Benzotriazole (0.69 - 6.9 mmol) dissolved in allylamine (1 ml) was introduced into the reaction mixture, and rapid dissolution of the pink complex occurred to give a homogeneous solution (solution A) (purple when Co/BTH > 1, yellow when Co/BTH < 1).

This solution readily absorbed oxygen to give an orange precipitate which was filtered off, washed with allylamine and dried in vacuum. All the complexes decomposed above 150° without melting. Since they were insoluble they could not be recrystallized, and analysis showed that the compounds were contaminated by traces of ligand L (e.g. PPh_3). In the case where Co/BTH = 0.1, the analysis of the complex after correction for the phosphine is: C, 54.0; H, 5.0; Co, 12.0; N, 29.0. ($C_{21}H_{19}N_{10}Co$ (II) calcd.: C, 53.6; H, 4.0; Co, 12.5; N, 29.8%).

The IR spectrum showed the absence of the benzotriazole band at 1620 cm^{-1} which is attributed to the N—H bond, and this showed the formation of the Co—N bond in the complexes. Comparison of the relative intensities of the bands due to the coordinated benzotriazole (1210 cm^{-1}) and allylamine (920 cm^{-1}) showed that the proportion of the ligands in the complex depended on the ratio Co/BTH, and became constant for low values of this ratio.

In the absence of BTH, the analysis of the dark violet precipitate obtained after treatment with oxygen fits approximately with a formula $[Co_2Cl_3C_{18}H_{42}N_6O_3]_n$ (I). (Found: C, 38.8; H, 7.3; Cl, 15.7; Co, 17.6; N, 13.7; O, 7.2. Calc.: C, 35.1; H, 6.8; Cl, 17.2; Co, 19.0; N, 13.6; O, 7.8%.) The product is, of course, impure and ill-defined.

Preparation of (IIIa)

(a). From solution (A). The solution was prepared as described above. Small orange crystals (6 mg) appeared on storage of the solution in the dark for one week at 15° under argon. These crystals were obtained from solutions containing Co/BTH ≈ 0.3 and were isolated by working up in air. (Found: C, 60.6; H, 5.4; Co, 9.9; N, 18.8; P, 3.5. $C_{90}H_{96}Co_3N_{24}O_2P_2$ (IIIa) calcd.: C, 61.1; H, 5.4; Co, 10.0; N, 19.0; P, 3.5%.)

(b) From solution (B). Bis(triphenylphosphine)cobalt(II) chloride (0.168 mmol) in allylamine (5 ml) was shaken under oxygen until no further absorp-

tion was observed (≈ 24 h). A dark blue precipitate appeared and benzotriazole (0.168 - 1.00 mmol) in allylamine (2 ml) was then added. The precipitate redissolved immediately, to give a clear deep-red solution (solution B). EPR spectroscopy indicated the presence of $Co^{II}OO\cdot$ radicals [9]. When this solution was irradiated with UV light under argon, an orange precipitate appeared readily. The $Co^{II}OO\cdot$ signals could no longer be detected, and the powder had the same IR spectrum and elemental analysis as the crystals obtained from solution (A) (see above). The yield was much better (≈ 90%) than in the first example.

The same reaction took place more slowly in the dark. The reduction of $Co^{II}OO\cdot$ to Co^{II} is the key step of this reaction, whereas a slow rearrangement of ligand occurs in the other method.

Preparation of (IIIb) [the nickel analogue of (IIIa)]

This complex was obtained by mixing equivalent amounts of benzotriazole with a solution of $NiI_2(PPh_3)_2$ in allylamine. Blue crystals separate slowly from the solution.

(Found: C, 61.2; H, 5.1; Cl, 0; N, 19.8; Ni, 10.5; P, 3.7. $C_{90}H_{96}N_{24}Ni_3P_2$ (IIIb) calcd.: C, 61.7; H, 5.5; Cl, 0; N, 19.2; Ni, 10.1; P, 3.55%.)

Other crops of crystals which were prepared and stored in the air contained Ph_3PO as shown by thin-layer chromatography and X-ray diffraction analysis [6].

Molecular weight determination by osmometry in DMF shows that the two molecules of Ph_3PO are displaced from the molecule of (IIIc) by the solvent (mol.wt. found: 540; calculated for (IIIc) : 1786, calculated for the dissociated complex : 595); thin layer chromatography of the complex (IIIc) dissolved in DMF shows the presence of free Ph_3PO. This is expected from the proposed structure, since the Ph_3PO ligands are obviously arly weakly bound.

Oxidation of triphenylphophine

Oxidation of triphenylphosphine took place when the solutions of the complexes reported above were shaken under oxygen ((p 1 atm). For example a solution of type (A), (Co/BTH = 3, [Co] = 8.10^{-3} mol/l in allylamine) containing triphenylphosphine (0.18 mol/l, including the phosphine originally present in L_2CoCl_2) was shaken under oxygen at room temperature in the presence of precipitate. After three days, triphenylphosphine oxide was isolated in 80% yield.

UV irradiation, as described above, caused quantitative oxidation of the triphenylphosphine.

Acknowledgement

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