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Electrochemical Synthesis of Tetrakis(triisopropylphosphite)cobalt(0). Evidence for the Reversible Formation of π-Bonded Organonitrile Complexes

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As a part of our study on the electrochemical behaviour of cobalt phosphite complexes we previously reported on the electrochemical preparation and properties of the new Co(0) derivative, $Co[P(OEt)_3]_4$, [1]. At the same time a monomeric triisopropylphosphite derivative of Co(0) was prepared by sodium amalgam reduction [2]. We now report the preparation of the title compound by electrochemical reduction, as a simple and reliable alternative procedure to the chemical one, of cobalt perchlorate in acetonitrile solvent in the presence of excess phosphite and its reaction with acetonitrile and benzonitrile affording the nitrile complexes of zerovalent cobalt.

The solution of anhydrous cobalt perchlorate generated in the electrochemical cell by anodic dissolution of a metallic cobalt foil in acetonitrile with 100% current efficiency, when treated with excess triisopropylphosphite turns from pink to green-brown. At the same time two one-electron, reversible waves ($B_{1/2}$ = –0.51 V and –1.45 V *vs* Ag|0.1 *M* Ag^+ in CH_3CN reference electrode), resulting from the single two-electron, irreversible step ($E_{1/2}$ = –1.00 V) of the cobalt(II) ion, appear in the polarogram. Potentiostatic reduction on the plateau of the second wave (≅ –1.8 V) proceeds with the uptake of two electrons. The reduction is carried out in the presence of 0.5 *M* $NaClO_4$ as supporting electrolyte and on a mercury pool cathode. The product is obtained as a white powder [3] which precipitates during the course of the electrolysis leaving a final pale green solution [4]. The yield is 85%, but the remaining portion can be recovered from the spent catholyte on cooling to –20 °C. At the end the precipitate is filtered off, washed with cold acetonitrile and dried under vacuum. All the operations are performed under carefully deoxygenated argon. The solid reacts quickly and spectacularly with the atmosphere. Elemental analysis agrees with the formula $Co[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (I).

(I) readily dissolves in hydrocarbons or other apolar solvents, but solutions are so sensitive to traces of oxygen that cryoscopic determinations of molecular weight have yielded no meaningful results. NMR spectroscopic determination of the paramagnetic susceptibility in 1,2-dimethoxyethane [5] gives a magnetic moment μ = 1.7 B.M., the value expected for a d^9 complex. The electronic spectrum is also consistent with the assignment of a d^9 metal ion in tetrahedral geometry displaying a band at 9.1 kK (ϵ = 290) [1].

When acetonitrile is added to a colourless solution of (I) in 1,2-dimethoxyethane a green colour almost immediately develops and gradually darkens with time. The final stage is reached for concentrated solutions (≅5 × 10^{-2} *M*) after about two hours. Three $d \rightarrow d$ transitions are now observed in the near infrared and visible regions at 17.10 kK (42), 12.65 kK (135) and 8.8 kK (80), while the IR spectrum exhibits, in addition to the phosphite ligand and free acetonitrile bands, a new strong absorption at 1790 cm^{-1} which is tentatively assigned to ν(CN) vibration of an acetonitrile molecule π-bonded to cobalt(0). No detectable change of magnetic susceptibility is observed upon addition of acetonitrile. Introduction of triisopropylphosphite produces a discharge of the colour and shifts the bands of the electronic and IR spectra back towards those characteristic of (I) [6]. Since the changes produced by acetonitrile can be completely reversed by phosphite we assume the following equilibrium (L = triisopropylphosphite):

$$CoL_4 + CH_3CN \rightleftharpoons CoL_3(\pi\text{-}CH_3CN) + L \qquad (1)$$

Spectrophotometric measurements confirm the stoichiometry of reaction (1) and give for the equilibrium constant a value of 0.1 ± 0.01 at 25 °C.

Once again, using benzonitrile similar changes occur and the electronic and IR spectra can be obtained. Two $d \rightarrow d$ transitions are now observed in the electronic spectrum at 12.90 kK (145) and 8.9 kK (80) (the third highest energy transition is obscured by a charge transfer transition responsible also for the brown-red colour of the solution) accompanied by the appearance of a sharp infrared band at 1755 cm^{-1}, thus providing additional evidence for the formation of a π-bonded nitrile complex. Introduction of phosphite restores the original spectra. The benzonitrile adduct displays a considerably higher dissociative stability than the corresponding acetonitrile complex as inferred by the equilibrium constant value (12 ± 1 at 25 °C).

Solutions of (I) react quickly and irreversibly with one equivalent of acrylonitrile producing a deep blue colour (bands at 17.24 kK (75) and 10.87 kK (150)). The IR spectra show a strong absorption at 2204 cm^{-1} assignable to the CN stretching vibration which is only 26 cm^{-1} lower than that of free acrylonitrile. No absorption band is observed in the 1900–

1700 cm^{-1} region. The limited lowering of this absorption upon complexation is a good indication of the coordination of this ligand through the carbon double bond [7].

On the other hand the observed decreases in $\nu(CN)$ for the coordinated acetonitrile ($\Delta\nu_{CN}$ = 466 cm^{-1}) and benzonitrile ($\Delta\nu_{CN}$ = 474 cm^{-1}) suggest that these ligands are π-bonded to cobalt. These decreases are much larger than those observed with most other metal systems [8, 9] and indicate extensive back-donation from the metal into the nitrile π^*-orbitals. This increased back-donation is consistent with the zero-valent state of cobalt and the weak π-acceptor properties of the triisopropylphosphite ligand. It is noteworthy that Co(0) derivatives with less bulky phosphite ligands, such as $Co[P(OMe)_3]_4$ and $Co[P(OEt)_3]_4$ [1], show no evidence of complex formation with acetonitrile even when present in large excess, suggesting that steric requirements could play an important role.

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3 The compound described in ref. 2 is orange-red.

4 The following synthesis is typical: triisopropylphosphite (4 g) was added to a stirred solution of cobalt perchlorate (0.04 *M*) in 0.5 *M* $NaClO_4/CH_3CN$ (25 ml) at 25 °C and the electrolysis performed in a two-compartment cell.

5 This solvent has been chosen because of its transparence in the 1950–1600 cm^{-1} region and suitability to electrochemical studies.

6 ^1H NMR tests in C_6D_6 /CD_3CN solvent mixture clearly indicate the presence of uncoordinated phosphite

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