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Electrochemical Preparation of *Tetrakis*(triethylphosphite)cobalt(0). Reactions with Some Small Molecules

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Paramagnetic cobalt(0) complexes having phosphines as ligands have been known for many years [1, 2] while only diamagnetic phosphite complexes have so far been prepared [3 - 5].

However, we have been able to obtain the paramagnetic $Co[P(OEt)_3]_4$ (I) by an electrochemical method. In studying the electrochemical behaviour of cobalt phosphite complexes [6] we have found that the reduction of $\{Co[P(OR)_3]_5\}^+$ (R = CH_3 or C_2H_5) proceeds with a single, two-electron, irreversible uptake to yield the final $\{Co[P(OR)_3]_4\}^-$, whereas the oxidation of this last species back to the d^8 complex occurs in two well defined one-electron steps, *i.e. via* a stable zerovalent intermediate.

In particular, the first oxidation wave of $\{Co[P(OR)_3]_4\}^-$ corresponds to that of an uncomplicated reversible one-electron transfer process. The strong similarity to the oxidation pattern of the isoelectronic and isostructural d^{10} $[Co(DPE)_2]^-$ which forms the d^9 zerovalent complex [7] has strongly suggested the formation of the previously unknown $Co[P(OR)_3]_4$ in monomeric form.

Controlled potential electrolysis at –0.9 V *vs.* SCE on the Hg anode at –30 °C of $(Et_4N)Co[P(OEt)_3]_4$ in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte produced the precipitation of a white crystalline solid. At the end of the electrolysis the precipitate was separated, washed with cooled acetonitrile and dried under vacuum. All the operations were performed under carefully deoxygenated argon. The solid reacts quickly and spectacularly with the atmosphere. It readily dissolves in hydrocarbons or other apolar solvents, but solutions were so sensitive to traces of oxygen that cryoscopic determinations of molecular weight have yielded no meaningful results.

NMR spectroscopic determination of the paramagnetic susceptibility [8] in benzene at 33 °C gave a magnetic moment μ = 1.4 B.M., a little less than that expected for the d^9 configuration in a tetrahedral ligand field. This result could be understood by considering a metal–metal interaction: $2Co[P(OEt)_3]_4 \rightleftharpoons \{Co[P(OEt)_3]_4\}_2$. The establishment of this equilibrium in solution can also be supported by the occurrence of the reaction of $\{Co[P(OEt)_3]_4\}^-$ with $\{Co[P(OEt)_3]_4\}^+$ in acetonitrile [6]. Under these conditions precipitation of (I) occurs in a short time. However, such an equilibrium must be very fast to account for the voltammetric behaviour.

The intense EPR signal in acetonitrile matrix at 100 °K clearly demonstrates the monomeric nature of the complex by the presence of eight resolved hyperfine splittings from a single Co nucleus. The electronic spectrum in benzene solution displays a band at 9.6 kK (ϵ = 240). It is comparable to the spectra of essentially tetrahedral (Ni(I) complexes [9].

(I) shows a reactivity typical of zerovalent complexes, giving 1:1 adducts with NO, CS_2, SO_2, O_2.

Solutions of (I) rapidly absorb one equivalent of nitric oxide with the formation of the diamagnetic nitrosyl *tris*(triethylphosphite)cobalt (ν_{NO} = 1710 cm^{-1}, Nujol), analogous to the already known trimethylphosphite derivative [10].

Compound (I) readily dissolves in carbon disulphide giving a deep green solution, whose i.r. spectrum shows, in addition to the phosphite ligand bands, a strong absorption at 1140 cm^{-1} which is characteristic of a π-carbon disulphide complex [11]. On cooling to –60 °C and adding petroleum ether, a dark green solid precipitates. The recovered compound, which is rapidly destroyed upon exposure to air, is paramagnetic both in the solid state and in solution. Analytical data are consistent with the formulation $(\pi\text{-}CS_2)Co[P(OEt)_3]_3$.

Compound (I) reacts quickly both in solution and in solid phase with SO_2 to give a red–brown paramagnetic air-unstable derivative. Two strong infrared bands (CH_3CN soln.) are found at 1260 (broad) and 550 cm^{-1}. These absorptions can be assigned to the ν_3(asym str.) and ν_2(bend) of the coordinated SO_2 molecule (the 1000–1100 cm^{-1} region is obscured by triethylphosphite bands). The high frequency of the band, which we assign to the asymmmetric S–O stretching, suggests a planar arrangement of the Co–SO_2 fragment [12] rather than a bent coordination [13].

When an equivalent amount of oxygen is added to an acetonitrile suspension of (I) at –30 °C, a clear deep-blue solution is almost immediately obtained, while one mol of triethylphosphite *per* mol of cobalt is released (voltammetric tests). No oxidation of phosphite to phosphate takes place under these conditions. It is worth noting that the same colour developed during the preparation of (I), when commercial (99.999%), not further purified argon was used. As the temperature is raised, already at –20 °C the blue colour fades while a dark-brown solid, which we believe to be CoO_2, precipitates. The i.r. spectrum of the blue solution (at –30 °C) shows a strong band at 860 cm^{-1} readily assignable to an

O–O stretching vibration of a coordinated O_2 molecule. The dioxygen adduct gives a strong EPR signal in acetonitrile matrix at 100 °K, with a hyperfine structure due to the cobalt nucleus. The two observed *g* factors are almost identical with those of (I). Thus, the stoichiometry of the reaction strongly suggests for this species the formulation $Co[P(OEt)_3]_3O_2$. I.r. [14] and EPR [15] data are consistent with the oxygen molecule apparently bonded as a peroxide or as a π-complex.

The complex (I) does not react with molecular hydrogen. It reacts with carbon monoxide giving a mixture of carbonylated cationic and anionic species [6].

In conclusion, the results of our investigation furnish unambiguous evidence concerning the existence of stable, paramagnetic cobalt(0) compounds with alkylphosphite ligands. It is of particular interest that such compounds can produce a wide variety of adducts with small molecules while retaining their paramagnetic valence state.

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