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Electrochemical Synthesis of *Tetrakis*(triphenylphosphite)cobalt(0) and Its Reduction to Cobalt(−1) Derivative

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The easy obtaining by electrochemical methods, of well characterized monomeric alkylphosphite complexes of zerovalent cobalt of stoichiometry CoL_4, where L = triethyl- and triisopropylphosphite [1,2], has focused our efforts on attempts to prepare, by this procedure, the analogous, previously unreported triphenylphosphite derivative for which chemical reductions had proved inefficient [3,4].

Anodic dissolution (100% current efficiency) of a metallic cobalt foil in dry acetonitrile containing sodium perchlorate as supporting electrolyte and in the presence of excess triphenylphosphite, produces a dark-brown solution showing a two-electron irreversible reduction wave at the dropping mercury electrode, different in shape and half-wave potential ($E_{1/2}$ = −1.10 V *vs.* Ag/0.1 *M* Ag^+ in CH_3CN reference electrode) from that characteristic of the cobalt(II) ion [2]. Potentiostatic reduction at potentials of the plateau of the wave on a mercury pool cathode at low temperature proceeds with the uptake of two electrons. The title compound is obtained as pale yellow bright leaflets which precipitate during the course of the electrolysis leaving a light brown spent catholyte [5]. At the end the precipitate is filtered off, washed with cooled acetonitrile and dried under vacuum. All the operations are performed under carefully deoxygenated argon. The solid is extremely reactive towards air. Elemental analysis agrees with the formula $Co[P(OC_6H_5)_3]_4$ (*I*).

I readily dissolves in THF, 1,2-dimethoxyethane and aromatic solvents, but solutions are so sensitive towards traces of oxygen that molecular weight measurements are not practical. NMR spectroscopic determination of paramagnetic susceptibility in benzene containing 5% of cyclohexane gives a magnetic moment μ = 2.1 B.M., *i.e.* a value consistent with the presence of one unpaired electron. The assignment of a d^9 monomeric metal species in tetrahedral geometry is confirmed by the electronic spectrum displaying a band at 10.0 kK (ϵ = 370) [1,2].

I reacts quickly both in solution and in solid phase with nitrogen oxide to give a yellow-orange product and with carbon monoxide to give a red-brown compound which were identified on the basis of their IR spectra as the already known $(NO)Co[P(OC_6H_5)_3]_3$ [6] and $[Co(CO)_3\{P(OC_6H_5)_3\}]_2$ [7], respectively.

In 1,2-dimethoxyethane containing $NaClO_4$ (0.5 *M*) as supporting electrolyte *I* exhibits a one-electron, fully reversible, reduction process ($E_{1/2}$ = −1.00 V) [8]. Exhaustive controlled potential electrolysis on the plateau of the wave at −30 °C requires one equivalent of electrons per mol of depolarizer affording a quite stable colourless solution from which in time a white crystalline solid precipitates. The recovered compound, which is rapidly destroyed upon exposure to air, is diamagnetic. Satisfactory elemental analyses have been obtained for the formula $Na[Co\{P(OC_6H_5)_3\}_4]$ (*II*).

On treatment with water, *II* immediately gives the known compound $HCo[P(OC_6H_5)_3]_4$ [9] and a strongly alkaline solution. Carbon monoxide at −30 °C operates on *II* the stepwise substitution of the phosphorus ligands to give $Na[Co(CO)_2\{P(OC_6H_5)_3\}_2]$ (ν_{CO} = 1924, 1865 cm^{-1} in CH_3CN soln.) and $Na[Co(CO)_3\{P(OC_6H_5)_3\}]$ (ν_{CO} = 1962, 1874 cm^{-1}). At room temperature full conversion to $Na[Co(CO)_4]$ takes place. This behaviour, while differing from that of the analogous rhodium complex [10], is consistent with the higher affinity for carbon monoxide of the lighter transition metals.

II shows a quite different reactivity even towards pentafluoroiodobenzene: instead of producing the expected organometallic derivative [10], the fast reaction yields a green product identified as $ICo[P(OC_6H_5)_3]_3$ by comparison with an authentic sample prepared by a procedure similar to that reported in the literature [3]. Such d^{10} species are, however, well known to be versatile reagents in the synthesis of organometallic derivatives [11]: the capability of *II* is at present under investigation.

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5 The following synthesis is typical: 6.2 g of triphenylphosphite (20 mmol) are added to 25 ml of a 0.5 *M* $NaClO_4$ CH_3CN solution at room temperature. After 1.0 mmol of Co^{2+} has been produced by anodizing the cobalt electrode at about +0.5 V, the solution is cooled to 0 °C and exhaustively reduced on a Hg pool at about −1.3 V. The yield is 90%.
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electron reduction wave is a common feature for the compounds CoL_4. Since in the available potential range the corresponding hydrides, $HCoL_4$, are not reducible, this could be considered as an analytical tool to make a choice between the two formulations, particularly useful when other techniques are unfeasible.

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