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Electrochemical Behaviour of the Triple-Decker Sandwich Cobalt and Nickel Complexes with *cyclo*-Triphosphorus and *cyclo*-Triarsenic

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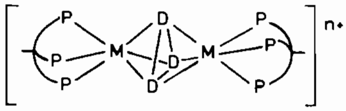
The triple-decker dinuclear metal complexes containing the *cyclo*-P_3 or the *cyclo*-As_3 unit as internal slice, having the general formula $[(\text{triphos})M\text{-}\mu(\eta^3\text{-}D_3)M(\text{triphos})]^{n+}$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; M = Co, Ni; N = 1, 2) were recently synthesized in this Laboratory [1]. These compounds represent a unique class of double sandwich metal complexes with 31 to 34 valence electrons, in agreement with the MO treatment by Hoffmann and coworkers [2] which predicts also the existence of stable 30-electron complexes:



M = Co; D = P : Co_2P
D = As : Co_2As
M = Ni; D = P : Ni_2P
D = As : Ni_2As

The 31- and 33-electron dications Co_2P^{2+}, Co_2As^{2+}, Ni_2P^{2+} and Ni_2As^{2+} are formed by reaction of the appropriate hydrated metal salt, usually tetrafluoroborate, with the ligand triphos and with white P_4 or yellow As_4 under nitrogen, followed by recrystallization in the presence of air. By reaction with $NaBH_4$ the corresponding singly charged 32- and 34-electron cations are obtained. With the aim of collecting more information on the redox behaviour of these compounds and to try to generate 30-electron species electrochemically, we decided to investigate the electrochemistry of these metal complexes.

Preliminary work on the cobalt complexes indicated that reversible three-step voltammograms (a one-electron oxidation and two one-electron reduction processes) can be obtained at the platinum electrode for Co_2P^{2+} and Co_2As^{2+} in acetonitrile using Et_4NBF_4 as electrolyte [3]. The CV curve obtained with Co_2P^{2+} is reported in Fig. 1. Bulk electrolysis of Co_2P^{2+} (Number of Valence Electrons 31) at the potential of the first reduction step generates, as expected, a solution of Co_2P^+ (NVE 32) which was previously prepared by chemical means; this was confirmed by its spectral and magnetic properties. Bulk oxidation of Co_2P^{2+} at controlled potential generates a bright green solution of Co_2P^{3+}. This novel species is diamagnetic** as expected by locating its 30 valence electrons into the 15 lowest energy orbitals of the previously outlined MO diagram [1c, 2]. The arsenic analogue Co_2As^{2+} displays an analogous three-step electrochemical behaviour, small differences being observed in the $E_{1/2}$ values: +2/+3: Co_2P, +0.22 V; Co_2As, +0.16 V; +2/+1: Co_2P, −0.47 V; Co_2As, −0.51 V; +1/0: Co_2P, −1.61 V; Co_2As, −1.58 V; *vs.* $Ag/AgNO_3$, 0.01 *M*, 0.1 *M* Et_4NBF_4 at 25 °C.

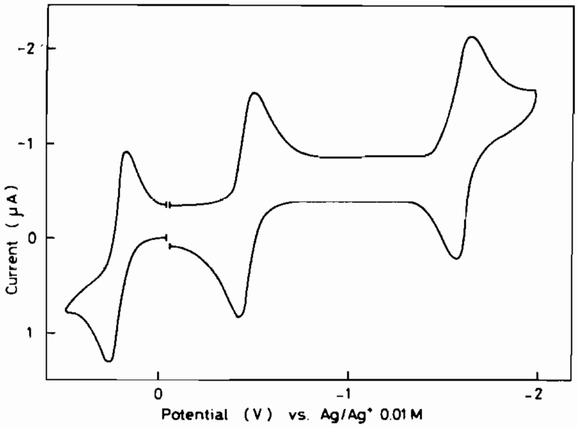


Fig. 1. Cyclic voltammogram at the platinum microsphere of a 5 × 10^{-4} solution of $[(\text{triphos})Co\text{-}\mu(\eta^3\text{-}P_3)Co(\text{triphos})](BF_4)_2$, in acetonitrile, which was 0.1 *M* in Et_4NBF_4.

A similar study could not be carried out for the nickel derivatives Ni_2P^{2+} and Ni_2As^{2+}, due to their instability in acetonitrile. Similar instability was found to occur also in DMSO as well as in DMF. We performed, therefore, an electrochemical study in acetone where both double sandwich cobalt and nickel cations are stable. The electrochemical range in acetone is remarkably less extended towards both oxidation and reduction limits than in acetonitrile. As a consequence, for Co_2P^{2+} and Co_2As^{2+} only the oxidation and the first reduction processes are detected at the platinum electrode, the second reduction step being preceded by the cathodic solvent discharge. In all cases, the species produced by controlled potential electrolysis, +1 and +3 cations, correspond to those obtained in acetonitrile, as shown by the close similarity of the visible spectra.

Two reversible one-electron steps, associated with the +2/+3 and +2/+1 redox changes, were detected

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**The magnetic susceptivity of the solution has been measured by the NMR method.

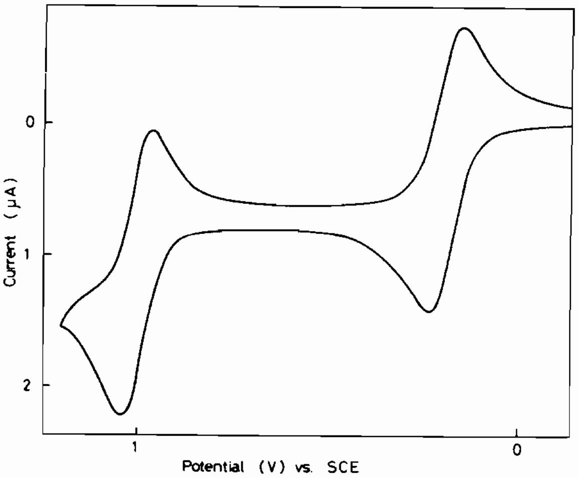

Fig. 2. Cyclic voltammogram at the platinum microsphere of a 5 × 10^{-4} solution of [(triphos)Ni-μ(η^3-P_3)Ni(triphos)]-$(BF_4)_2$ in acetone, which was 0.1 *M* in Et_4NBF_4.

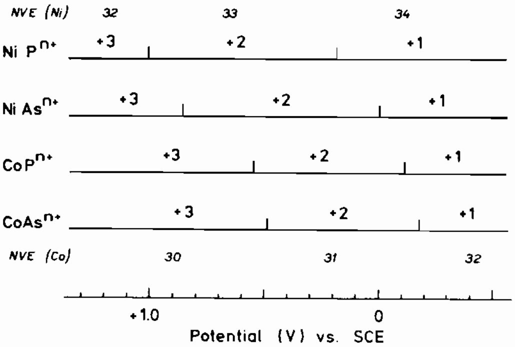

Fig. 3. Electrode potentials for the redox changes of the triple decker complexes in acetone 0.1 *M* Et_4NBF_4, at 25 °C.

voltammetrically also for the nickel derivatives (the CV curve for Ni_2P^{2+} is reported in Fig. 2). However, whereas the monocations, cathodically as well as chemically generated, are stable in acetone, coulometric experiments indicated that the trications Ni_2P^{3+} and Ni_2As^{3+} are reduced to the corresponding dications by the solvent or by the impurities possibly present. The electrochemical preparation of these trications is thus precluded.

The electrode potential values associated with the redox steps occurring in acetone are reported in Fig. 3. Two main features are evident: i) both +1/+2 and +2/+3 oxidation processes occur at higher potential for the nickel complexes than for the cobalt analogues. This behaviour reflects the trend in the series of the Ionization Energies of the individual gaseous cations: $M^{+}_{(g)}/M^{2+}_{(g)}$: Ni, 18.1; Co, 16.6; $M^{2+}_{(g)}/M^{3+}_{(g)}$: Ni, 35.2; Co, 33.5 eV, *i.e.* cobalt and nickel cations behave similarly both in the gaseous state and as cores in a triple decker sandwich complex; ii) for the same metal, the oxidation processes (+1/+2 and +2/+3) are easier for *cyclo*-As_3 than for *cyclo*-P_3 derivatives.

According to the MO scheme previously outlined [1c, 2], the two-fold degenerate 6e orbitals, which contain the electrons involved in the redox changes, are non-bonding towards the η^3-D_3 moiety. However, the different oxidation potentials found for the η^3-P_3 and η^3-As_3 derivatives suggest that the energy of the redox levels is in some way affected by the nature of the *cyclo*-D_3 unit.

It is noticeable that the number of valence electrons of all the electrochemically identified complexes range between 30 and 34, in agreement with Hoffman's prediction [2].

References

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2 J. W. Lauher, M. Elian, R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98,* 3219 (1976).
3 In the CV experiments the $i_{p.c.}/i_{p.a.}$ ratio is unity and the $i_p/\sqrt{\nu}$ ratio (ν, potential scan rate ranging from 50 to 500 mV s^{-1}) is a constant [4]. The one-electron stoichiometry was ascertained by coulometric measurements on chosen redox steps.
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