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Electrochemistry of Coordination Compounds. V. * Electrochemical Reduction of Ni(II), Pd(II), Pt(II) Complexes with 1,2-Bisdiphenylphosphinoethane: A Comparison between Polarographic Data and Nucleophilic Substitution Reactions on d^8 Square Planar Metal Complexes

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The electrochemical reduction of d^8 ionic complexes of nickel, palladium and platinum with 1,2-bisdiphenylphosphinoethane is presented. The obtained thermodynamic data suggest the relevance of the electron uptake ability in the determining the kinetic behaviour in S_N2 reactions on complexes with same configuration. The well known difference between lighter and heavier elements of the same group is once again observed: nickel(II) is reduced in two one-electron steps involving a rare Ni(I) complex while platinum(II), palladium(II) take up two electrons in a single process.

Introduction

Our recent work on the electrochemical behaviour of d^8 cobalt, rhodium and iridium complexes with 1,2-bisdiphenylphosphinoethane (DPE) as ligand has shown that these compounds undergo reversible reduction steps at a dropping mercury electrode[1,2] allowing us to discuss the stabilities of the reduction products in terms of thermodinamic data. Furthermore, electrochemical reduction proved to be superior to chemical methods for the preparation of complexes of the above elements in unusual oxidation states, *e.g.*, the (–1) formal valence in the anionic d^{10} complexes and of the zerovalent d^9 cobalt complex.[2] For these reasons and considering that the reduction of a species at a dropping mercury electrode can be classified as an unusual case of reaction with a nucleophile,[3] we extended the previous work to the analogous d^8 complexes of the nickel, palladium and platinum with the pourpose of: (i) preparing possible new d^9 systems and (ii) obtaining polarographic data which could better explain the behaviour of these d^8 triads in the general field of the nucleophilic substitution reactions.

Experimental

Materials

1,2-bisdiphenylphosphinoethane (DPE) was prepared according to W. Hewertson and H. R. Watson.[4]

The complexes were synthesized and identified as reported in the literature: $[Pt(DPE)_2](ClO_4)_2$[5], $[Pt(DPE)_2]$[6], $[Pd(DPE)_2](ClO_4)_2$[5], $[Pd(DPE)_2]$[7], $[Ni(DPE)_2](ClO_4)_2$[7], $[Ni(DPE)_2]$[7].

All the chemicals employed were of reagent grade quality (R. P. C. Erba and Schuchardt). Reagent grade acetonitrile was further purified by repeated refluxings over anhydrous aluminum chloride, then over lithium carbonate, subsequently over calcium hydride and finally by a careful fractionation.[8]

Owing to the poor solubility of the complexes in perchlorate medium, tetraethylammonium tetrafluoborate was used as supporting electrolyte: in this medium about $1 \times 10^{-3} M$ concentrations can be achieved.

Tetraethylammonium tetrafluoborate (TEATFB) was prepared by the addition of 50% fluoboric acid to an aqueous solution of tetraethylammoniumhydroxide. The solution was concentrated under reduced pressure and the precipitate was crystallized three times from water, dried at 75°C in vacuo and stored over anydrous magnesium perchlorate.

All solution contained $0.1 M$ TEATFB as supporting electrolyte. The water content of these solutions, checked by Karl–Fisher titration, way always less than 1 mM. 99.999% Argon, previously equilibrated to the vapour

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* For previous papers in this series see *J. Electroanal. Chem.*, *40*, 63 (1972); *45*, 483 (1973); *47*, 89 (1973); *50*, 295 (1974).

pressure of acetonitrile, was used to the removal of dissolved oxygen.

Apparatus and Procedure

An Amel (Milan, Italy) model 463 multifunction assembly, connected with an Hewlett–Packard 7040A X–Y recorder was employed for polarographic measurements. All potentials were measured against an aqueous saturated calomel electrode (SCE). The salt bridge which separated the SCE from the working compartment of the electrochemical cell was filled with an acetonitrile solution of the supporting electrolyte. The dropping time was maintained at 1.0s by forced fall of the drop.

Controlled potential electrolysis was carried out using an Amel model 557/SU potentiostat. The amounts of electricity consumed were obtained from an Amel model 558 electronic integrator. The working electrode was a mercury pool (area 10 cm^2). The counter electrode was external, the connection being made by an appropriate salt bridge. Cyclic voltammograms were obtained using an Amel model 448 oscillographic polarograph. A Metrohm E–410 hanging drop assembly was used.

All the experiments were carried out at 25.0±0.1 °C.

Results

The polarographic reduction of $[M(DPE)_2](ClO_4)_2$ (M = Ni, Pd, Pt) in CH_3CN, 0.1*M* TEATFB shows reversible and diffusion controlled waves, which are not affected upon addition of free DPE. In particular, the reduction occurs in two one-electron steps for the nickel complex and in a single two-electron step for the palladium and platinum compounds.

The reversibility of the processes was also established by cyclic voltammetric measurements and by controlled potential electrolysis (contemporary presence of a cathodic–anodic wave) in the potential range of every plateau.

The number of electrons utilized at each polarographic step was confirmed *via* the same electrolysis, in the same range of potentials. The two-electron reduction products, obtained as crystalline solids in the reaction medium, were identified as the known $[Ni(DPE)_2]$, $[Pd(DPE)_2]$, $]Pt(DPE)_2]$ by means of their elemental analysis and m.p., which were identical with those of authentic samples prepared as reported in the literature.[6–7] In the case of the nickel complex there is a reversible uptake of one electron and the cyclic voltammetric profile corresponds to that of an uncomplicated reversible one-electron transfer, *i.e.*, in particular, $E_p - E_{p/2} = 60$ mV, E_p being independent of the scan rate in the range between 40 mV s^{-1} and 40 V s^{-1} and on the concentration of $[Ni(DPE)_2]^{2+}$ over the achievable range (10^{-4}–10^{-3}*M*). A constant ratio of anodic to cathodic peak currents is observed in the same ranges.

The strong similarity with the reduction pattern of the isoelectronic and isostructural d^8 $[Co(DPE)_2](ClO_4)$ which forms the d^9 zerovalent complex, strongly suggests the formation of the not previously known $[Ni(DPE)_2]^+$ in monomeric form.

To support this formulation we tried direct measurements of paramagnetic moment. Owing to the impossibility to isolate the product (see later), we resorted to the NMR technique. Unfortunately the highest achievable Ni(I) concentration is too low to give a meaningful result.

Although no signal was present in the ESR spectrum, this result is not in contrast with the previous formulation. Nevertheless, while we have been unable to obtain direct evidence of the type previously reported in similar paramagnetic Ni(I) phosphine complexes,[9] the suggested monomeric formulation provides, to date, the best fit with our cyclic voltammetric results.

The electronic spectrum in CH_3CN solution has a band at 9.2 and a slight shoulder at 22.7 kK. It is comparable with the spectra of distorted tetrahedral halogeno-Ni(I) complexes with 1,1,1-tris(diphenylphosphinomethyl)ethane[10] rather than with those of the diphosphine compounds $Ni(diphos)_{1.5}CN$(diphos = 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane)[11] which have been assigned a squareplanar structure.

Since such a Ni(I) complex can both be reduced and oxidized in reversible steps ($\Delta E_{1/2} = 200$ mV), the disproportionation equilibrium

$$2[Ni(DPE)_2]^+ \rightleftarrows [Ni(DPE)_2]^{2+} + [Ni(DPE)_2]$$

must be considered ($pK_{eq} = \Delta E_{1/2}/59.15 = 3.38$).

The rapid establishement of this equilibrium in solution can be deduced from the reaction of $[Ni(DPE)_2]^{2+}$ with a suspension of the equivalent amount of $[Ni(DPE)_2]$ in CH_3CN.

Under these conditions a clear orange solution of $[Ni(DPE)_2]^+$ is obtained in a short time. The same result, of course, has been achieved allowing one equivalent of electrons *per* mol of complex to pass, in the controlled potential electrolysis of $[Ni(DPE)_2]^{2+}$ on the diffusion plateau of the second wave.

Furthermore, the existence of this equilibrium also accounts for the unsuccessful attempts to isolate the d^9 Ni(I) complex even by addition of large amounts of ClO_4^- or BPh_4^-. In these cases only precipitation of an equimolar mixture of the sparingly soluble $[Ni(DPE)_2]$ and $[Ni(DPE)_2](ClO_4)_2$ or $[Ni(DPE)_2](BPh_4)_2$ occurs.

As far as the palladium and platinum complexes are concerned, the stepwise reduction is not present and it implies that palladium(I) and platinum(I) are unstable and that the experimental $E_{1/2}$ of the two-

TABLE I. Polarographic Properties of $[M(DPE)_2](ClO_4)_2$ in CH_3CN, 0.1*M* Et_4NBF_4, at 25.0° C.

Complex	Conc./m*M*	$E_{1/2}$/V	Slope/mV[a]	I_d[b]
$[Ni(DPE)_2](ClO_4)_2$	1.00	−0,23, −0.43	60	2.3
$[Pd(DPE)_2](ClO_4)_2$	0.68	−0.59	32	4.2
$[Pt(DPE)_2](ClO_4)_2$	0.71	−0.77	32	4.2

[a] Logarithmic analysis. [b] $I_d = i_d/Cm^{2/3}t^{1/6}$, where i_d is expressed in μA, C in mmol l^{-1}, m in mg s^{-1}, t in s.

electron reduction is the average of the two unknown half-wave potentials of the single one-electron steps. Since the $E_{1/2}$ of the single steps for the nickel complex are known, free energy arguments allow to calculate a "theoretical" value (−0.33V), comparable with the previous ones, for a two-electron reversible step.

The polarographic properties of the complexes are summarized in Table I.

Discussion

The d^8 complexes we studied differ only in the metal and are reduced under the same experimental conditions reversibly and without any change in the composition. As a consequence the difference in the half-wave potentials offers a measure of the ability of the depolarizing particle to uptake electrons in the reaction medium.

One observes an increasing ease of reduction in the order Pt<Pd<Ni(Table I) which parallels the tendency of these metal complexes to add a fifth ligand.[12] To a first approximation it is reasonable to expect a similar trend also for the bimolecular nucleophilic displacements (S_N2) on d^8 square-planar complexes, since the formation of pentacoordinated species has been proposed as transition states in such reactions.[13] In fact the k_2 values of the S_N2 reactions of analogous Ni(II), Pd(II), Pt(II) complexes are approximately 10^{7-8}: 10^{5-6}: 1.[14] Furthermore the few comparable data available for reactions of planar Rh(I) and Ir(I) are also consistent with this trend. The $E_{1/2}$ for the reversible reduction of Rh(I) and Ir(I) with DPE[1] are almost identical (−1.71V for rhodium, −1.70V *vs.* S.C.E. for iridium) as well as the values of the second order CO exchange reaction ($k_2 = 2M^{-1}$ s^{-1}) on $Rh(CO)_2$ (*p*-anisidine)Cl and $Ir(CO)_2$(*p*-toluidine)Cl.[15]

Unfortunately no kinetic data have been reported on the Co(I) system.

If this correlation is not fortuitous, these comparisons seem to indicate that the electron uptake ability of the d^8 transition metal ion in a planar complex can play an important role in the free energy changes going from the four-coordinate ground state to the five-coordinate transition state in the S_N2 reactions at the same systems.

Furthermore, our results provide another example of the previously[2] noted difference between lighter and heavier elements of the same group; *i.e.,* nickel (II) accepts two electrons in two one-electron steps and platinum(II), palladium(II) take up two electrons in a single process without a stable state in between. Such behaviour seems to be a rule in these d^8 systems and probably reflects different electronic effects now under investigation, particularly as far as the influence of the ligands is concerned. Finally, the disproportionation constant value of d^9 nickel(I) system in CH_3CN solution, accounts for the contemporary presence of nickel(II) and nickel(0) significant amounts in equilibrium with nickel(I). This result indicates that it would be particularly worthwhile to extend the study of the nickel(I) system to the field of the homogeneous catalysis and detailed studies in this area are in progress.

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