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Electrochemical studies of nickel complexes containing phosphorus(III) ligands and their related Ziegler catalysts

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Abstract

All of the data obtained by electrochemical methods involving the mercury electrode, spectrophotometry and conductometry have showed the stepwise formations of a neutral σ-donor–acceptor pentacoordinated NiX_2L_3 and a cationic tetracoordinated NiL_4^{2+}, associated with a shift in the dissociation–coordination equilibrium owing to an excessive concentration of the ligand in solutions of the binary systems containing Ni^{II} compounds coordinated with acid ligands ($X = Cl^-$, NO_3^-, acac) and the trivalent phosphorus ligands ($L = PBu_3$, PPh_3, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(O\text{-}s\text{-}Bu)_3$, $P(OC_6H_{11})$, $P(OPh)_3$). The complexes have for the first time been prepared for all the phosphines and phosphites studied. $Ni(acac)_2$ was found to enhance coordination by the phosphines and phosphites in acetonitrile. The value of the semiwave potential shift ($\Delta E_{1/2}$, V) towards less negative potentials depends on the number of ligands present in the inner coordination sphere of metal, and was found to be 200–300 and 800–1300 mV for NiX_2L_2 and NiL_4^{2+}, respectively. The electrochemical reduction of NiL_4^{2+} complexes into the zero-valent nickel isostructural complexes is reversible with values similar to that of the nickel formal potential Ni^{2+}/Ni^0 ($E_{1/2} = E_0 = -0.25$ V). For the first time, the homogeneous formations of catalytically active complexes have been studied electrochemically in situ with the tricomponent Ziegler–Natta catalytic systems to give stable Ni^{II} complexes in toluene solutions of $Ni(acac)_2$–$\{PR_3$ or $P(OR)_3\}$–OAC ($Ni/P/Al = 1/4/4$) at $T \leqslant -10\,°C$. These complexes can undergo reversible reductions and determine catalytic activity of the system. They are regarded as ionic and are tentatively assigned the structure of bimetallic complexes $[RNiL_3]^+[AlR_4]^-$. The hydride complexes of divalent nickel $HNiL_4^+$ were found to be as catalytically active as the $Ni(acac)_2$–$P(OR)_3\{R = Et$, i-Pr$\}$–$AlEt_3$ ($Ni/P/Al = 1/4/4$) systems formed in toluene–isopropanol solvent at $T = -10$ to $+25\,°C$. The activating effect by the organic phosphorus ligand on the electronic state of Ni has been found for the first time to decrease the energy levels of the boundary orbitals as the

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coordination sphere becomes saturated with the ligand, thus changing the ligand's environment and configuration of the complex, the degree of alkylation and the degree of stabilization of the catalytically active complexes. In the case of the NiL_4^{2+} complexes, the ligand-to-metal charge transfer energies permitted the estimation of the affinity to the nickel electron inherent to the nickel LUMO energy level in the given complex, that energy being similar to HOMO energy in Ni^0L_4 under the conditions of the reversible electronic process.

Introduction

Intramolecular electronic donor–acceptor interactions represent the basis of catalytic processes and occur in both the primary reaction and in the transition states. In order to study the orbital-controlled processes, electrochemistry and electronic spectroscopy methods are preferred for they can detect the fine changes in the energies of the boundary orbitals, LUMO and HOMO, by way of potentials measured in reversible electrochemical systems, and by changes in absorption measured in the spectrophotometric cell.

Electrochemistry when used to study the investigating reactions of homogeneous catalytic systems, can elucidate the component interaction dynamics, can determine the degree of oxidation of the metal as a complexing agent, and permits estimation of the stability of the different oxidative states and the lifetimes of the catalytically active complexes in solution.

For the oligo- and copolymerization of olefins, dienes, and acetylenes, nickel, as its mixed-ligand complexes such as NiX_2L_2 ($X = Hal, CN, CNS, NO_3$; $L = PR_3$) or in solution as NiX_2 ($X = Hal^-, NO_3^-$, acac, and other acido ligands) containing certain amounts of tertiary phosphines or phosphites, or as the products of reaction with organoaluminium compounds has been widely used. The electron-donor properties of the organophosphorus ligands have been known to be important for stabilizing highly reactive alkyl, hydride, and π-olefin nickel complexes involved in the intricate series of catalytic transformations. The coordination and dissociation of ligand are the keystones for the proper functioning of the catalytic systems, on the basis on transition metal complex, and for their interactions with substrates.

The number of investigations that have been carried out on complexed catalysts by use of electrochemical methods is steadily growing, but up to now the literature has insufficient information available on problems such as: the mutual effects of the central metal atom and ligands, the nature of coordination bondings, the mechanism of the rearrangements in the ligand environmental sphere, the redox properties of various types of complexes, and the state of the coordination–dissociation equilibrium.

Thus, the studies that have recently appeared [1–3] on the electrochemical behaviour of NiX_2L_2 phosphine complexes in solution took little account of the lability of the nickel coordination bondings with both ligand types or their ability to dissociate in polar solvents. The coordination of nickel compounds to trivalent phosphorus ligands was shown only by $Ni(ClO_4)_2$, in the absence of acid ligands possessing donor properties. In real catalytic systems, there were Ni^{II} compounds containing acid ligands that can compete for the coordination sites with the organophosphorus bases (Cl^-, NO_3^-, acac).

Electrochemical research of Ziegler catalytic systems is at the outset of its development. There is one report [4] that covers the problems of the control and prediction of the catalytic activity and of selecting the optimal reaction conditions. However, there remain unstudied the electrochemical properties of hydride, alkyl, π-olefin, and bimetallic ion complexes of di-, mono-, and zerovalent nickel, which have been preparatively isolated from catalytic systems that have yet to be examined.

Here we describe the results of electrochemical studies into the mechanism of the production in situ of di- and tricomponent systems containing compounds of NiX_2 ($X = Cl^-$, NO_3^-, acac), tertiary phosphines or phosphites, and organoaluminium compounds, with respect to the component number, their types and ratios, and preparative conditions (temperature, solvent, time).

We thought that a stepwise approach to solving the problems would be the best:

1. To study the equilibrium of the coordination–dissociation associated with each of the complexes $NiCl_2(PBu_3)_2$, $NiCl_2(PPh_3)_2$, $Ni(NO_3)_2(PPh_3)_2$, compounds NiX_2 ($X = Cl^-$, NO_3^-, acac) with P^{III} ligands (PBu_3, PPh_3, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(O\text{-}s\text{-}Bu)_3$, $P(OC_6H_{11})_3$, $P(OPh)_3$) in acetonitrile and ethanol solution; to study processes taking place at the electrode and to estimate the dependence between the reversibility of the reaction and the structural conformations of redox participants, and that between the extent of changes in type of bonding and the electron state of Ni during saturation of the coordination sphere by an organophosphorus ligand.

2. To study the process of formation and the electrochemical properties of the catalytic complexes formed at $T \leqslant -(10\text{–}25\,^\circ C)$ in the systems (a) $Ni(acac)_2$–$AlEt_3$ (1/4) in toluene; (b) $Ni(acac)_2$–$\{PR_3$ or $P(OR^1)_3\}$–OAC (1/4/4), where R = Bu, Ph; R^1 = Et, i-Pr, s-Bu, C_6H_{11}, Ph; OAC=$AlEt_3$, $Al(i\text{-}Bu)_2Cl$, $Al(i\text{-}Bu)_2H$; in toluene; (c) $Ni(acac)_2$–$P(OR)_3$–$AlEt_3$ (1/4/4), where R = Et, i-Pr; in toluene–isopropyl alcohol (1/2).

Experimental

Chemicals

Thoroughly dried ethanol, methanol, acetonitrile, or a mixture of acetonitrile, toluene, and isopropyl alcohol (by volume) were employed as solvents.

Ethanol of reagent grade quality (96%) was dried by a published procedure [5] with anhydrous $CuSO_4$ and Mg chips, and distilled in a stream of dry argon with the use of an appropriate electrically heated (80 °C) head filled with calcined Al_2O_3 or 4 Å zeolites. The distillate formed was collected into the calcined Schlenk vessel filled with dry argon and provided with a plug to permit solvent removal with a syringe. The content of water in the ethanol was found after this treatment to be 0.40% (as calculated by use of the Fischer method).

Methanol of reagent grade quality (99.9%) was dried with Mg chips [5], distilled in a stream of dry argon, and collected in the calcined Schlenk vessel filled with dry argon and equipped with a plug to permit solvent removal with a syringe. The content of water in the methanol was 0.010% (as calculated by use of the Fischer method).

Acetonitrile of reagent grade quality (99.95%) was dried [5] over CaH_2 and P_2O_5, and slowly distilled in a stream of dry argon. The first portion of the distillate (5%)

was removed. The rest was collected into the calcined Schlenk vessel filled with argon and equipped with a plug to permit solvent removal with a syringe. The content of water in acetonitrile was 0.008% (as calculated by use of the Fischer method).

Toluene of reagent grade quality was purified and dried by distillation over triethylaluminium and was also collected into the Schlenk vessel equipped with a plug to permit solvent removal with a syringe. The content of water in toluene was 0.001% (as calculated by use of the Fischer method). Toluene was mixed with acetonitrile in a 2/3 ratio (by volume) for use as the solvent in the investigations of the real catalytic systems.

Isopropyl alcohol of reagent grade quality (99.0%) was purified by boiling over metallic sodium [6] with further fractional distillation in a stream of dry argon. The fraction b.p. = 82° C was used. The content of water in isopropyl alcohol was 0.01% (as calculated by use of the Fischer method).

The solvents used were deaerated before use by prolonged bubbling of dry argon (2–3 h). The solvent purity was checked from the value of the background current at the Hg dropping electrode with a superimposed potential linear base and from spectrophotometry (e.g. with acetonitrile).

Xylene of reagent grade quality was purified by distillation over metallic sodium and used to prepare a 50% solution of triisobutylaluminium (TIBA) to be used for drying argon.

Argon (bottled) was purified and dried by passage through a system of absorbents: concentrated H_2SO_4, granulated NaOH, calcined Al_2O_3, 4 Å zeolites, a 50% solution of TIBA in absolute xylene, a mixture of zeolites; a Schott filter was used to trap the flying pulverized Al_2O_3 formed because of TIBA decomposition. Argon thus purified was saturated with the relevant solvent vapor and then used to prepare the solutions and to deaerate them in the electrochemical cell.

Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared by neutralization of a 10% aqueous solution of tetrabutylammonium hydroxide with perchloric acid, subsequent recrystallization from absolute methanol, and was further dried in vacuum (1 mm Hg) at 50° C. Bu_4NClO_4 (0.1 *M*) was employed as the indifferent electrolyte, in all experiments.

Acetylacetone was purified by distillation (b.p. 139° C).

Triethylaluminium ($AlEt_3$) as a 87% hydrocarbon solution and purified by distillation in the dry argon flow (b.p. = 68–70° C; 5 mm Hg) [7] was used as a 1.5 *M* solution in absolute toluene.

Diisobutylaluminium hydride (DIBAH) was prepared by heating TIBA for 4–5 h in an oil bath at 140° C. The isobutylene (1 *M*) that separated, was collected in a trap with dry ice, and the remaining DIBAH was distilled under reduced pressure in a stream of dry argon (b.p. = 120–130° C; 1 mm Hg).

Nickel chloride, analytically pure, was dried in vacuum (120° C; 1 mm Hg). No additional purification was necessary to reach constant mass.

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) was used pure and dehydrated in vacuum (50° C, 1 mm Hg) to constant mass.

Bis(acetylacetonato)nickel(II) ($Ni(acac)_2$) was purified by recrystallization from absolute benzene with the subsequent sublimation at reduced pressure (10 mm Hg).

Dry salts were stored in sealed vessels filled with dry argon.

Ligands and complexes of Ni were synthesized by published procedures: triethylphosphite $P(OEt)_3$, triisopropylphosphite $P(O\text{-}i\text{-}Pr)_3$ [8]; tri-s-butylphosphite $P(O\text{-}s\text{-}Bu)_3$, tricyclohexylphosphite $P(OC_6H_{11})_3$, triphenylphosphite $P(OPh)_3$ [9]; n-tributylphosphine PBu_3, triphenylphosphine PPh_3 [10]; dichlorobis(n-tributylphosphine)nickel(II) $NiCl_2(PBu_3)_2$, dichlorobis(triphenylphosphine)nickel(II) $NiCl_2\text{-}(PPh_3)_2$, dinitratobis(triphenylphosphine)nickel(II) $Ni(NO_3)_2(PPh_3)_2$ [11]; acetylacetonatoethyl(triphenylphosphine)nickel(II) $EtNi(acac)PPh_3$ [12]; hydridotris(triphenylphosphine)nickel(II) bromide $(PPh_3)_3Ni(H)Br$, tris(triphenylphosphine)-nickel(I) chloride $[(PPh_3)_3NiCl]_2$ [13]; ethylenebis(triphenylphosphine)nickel(II) $(PPh_3)_2NiC_2H_4$ [14].

Procedures and apparatus

The various procedures were applied on the basis of the properties of the chemicals under study, especially with regard to high lability to traces of water and/or oxygen.

Graduated flasks (5 and 10 ml) with ground-glass stopper and branch pipes on polished sections for the introduction of the inert gas (argon) were used to prepare the solutions [15]. A suitable head permitted the purging of the flasks with argon, and the transfer of the solution prepared to the working cell in a stream of argon.

To prepare the Ziegler–Natta catalytic mixtures, a flat-bottom glass cylinder, with a ground-glass stopper and a side-pipe for the introduction of an inert gas and provided with a magnetic stirrer, was used. The reactor was cooled to $-(10\text{–}25\,^\circ C)$ with a mixture of dry carbon dioxide and acetone.

Solutions of the various Ni compounds were prepared in a previously calcined, graduated flask that had been filled with dry argon through a suitable head, provided with a ground-glass stopper, and weighed beforehand on an analytical balance to a constant mass of ± 0.0002 g.

All manipulations were carried out under argon in a glove box.

The flask containing the sample reached constant mass after multiple flushings with argon. Then the flask was charged with a sample of supported electrolyte and the required amount of solvent. The solvent and ligand to be dosed (from 10 μl to 10 ml) were introduced under argon from a graduated syringe. The solutions of σ-alkyl Ni complexes were prepared and studied at $-25\,^\circ C$. The working solution was cooled directly in the flask before it was introduced into the electrochemical cell, which had been cooled and filled with argon.

The tricomponent catalytic systems containing an organoaluminium compound as $Ni(acac)_2\text{–}\{PR_3 \text{ or } P(OR)_3\}\text{–}OAC$ were prepared in a previously calcined and argon-filled vessel. The vessel was charged with $Ni(acac)_2$ (0.1 M), the required amount of solvent (toluene), and organophosphorus ligand (4.0 M). After $Ni(acac)_2$ had dissolved, the reactor was placed into a bath containing a mixture of solid carbon dioxide and acetone at $-(10\text{–}25\,^\circ C)$.

Under continuous stirring (magnetic stirrer) under dry argon, some of the OAC solution in toluene (3–4 M) was added to the cooled vessel from a graduated glass syringe. A sample of the catalyst thus prepared was drawn off by glass syringe under dry argon immediately after mixing. To avoid errors because of dilution, the aliquots taken were less than 0.1 ml. Each of the samples that had been drawn was placed in a graduated flask containing a cooled solution ($-10\,^\circ C$; 0.1 M) of a supported electrolyte in an acetonitrile/toluene mixture in a 3/2 ratio. The contents of the flask were then removed to an argon-filled electrochemical cell through the head under argon.

The tetracomponent catalytic system in protogenic medium containing isopropanol and ethanol was prepared by the dropwise addition of an excess of isopropanol (4–6 ml) from a graduated syringe to the vessel containing the solution of the tricomponent system (−10 °C). The samples were drawn analogously from the vessel.

The electrochemical cell was designed by Mayranovsky and Titov [15], in addition to a novel one designed and made by us. Our cell has two electrodes ($\tau = 0.3$ and 44 s) and provides simultaneously the classic and cyclic voltammograms from the same solution.

The desired temperature (from +25 to −25 °C) in the cell was maintained by use of the ultrathermostat U-10 with ethanol, cooled by dry carbon dioxide circulating in cell jacket. Voltammetry was carried out immediately after the working solution had been introduced into the electrochemical cell. The newly prepared solutions were employed only when necessary.

Voltammetry. LP-60 (Czechoslovakia) and OH-105 (Hungary) instruments were used to register classic polarograms.

The dropping mercury electrodes, with forced drop-separation by a "blade" soldered onto the capillary [15], were found to have the parameters as follows:

(1) $m = 1.8$ mg/s, $\tau = 0.75$ s; (5) $m = 3.9$ mg/s, $\tau = 0.54$ s;
(2) $m = 1.85$ mg/s, $\tau = 0.2$ s; (6) $m = 1.53$ mg/s, $\tau = 0.22$ s;
(3) $m = 1.9$ mg/s, $\tau = 0.3$ s; (7) $m = 0.4$ mg/s, $\tau = 0.48$ s
(4) $m = 1.2$ mg/s, $\tau = 0.8$ s;

An amalgamated silver plate was the reference electrode.

The cyclic voltammograms were recorded on a PO 5122-02A (U.S.S.R.) and set so as to survey cyclic voltammetric curves of the linear-trigonal voltage and 0.125–1.0 V/s scanning rate [16].

The original device, EAP 10-KAI (U.S.S.R.) with a scanning rate of 4 V/s, was used to record the cyclic voltammograms of linear-trigonal stepwise voltage, those commutated at 25–900 Hz frequency, cathodic and anodic voltammograms under polarization with rectangular pulses of the linearly increasing amplitude.

Substantial increases in the response, accuracy, and resolution of measurements as well as for expansion of the sphere of the instrument's utilization are possible because of the three types of polarizing voltage, i.e. trigonal, stepwise, and pulse (for the discrete current measurements), and because there are automated devices that can form and subtract the residual current, register the current and the peak potential, and devices that permit fractional differentiation and compensation of bulk resistance.

Pulse-commutated oscillopolarography with a stationary electrode was used to register the cathodic and anodic branches of an oscillopolarographic curve, which at the same time provides novel ways for "trapping" and investigating unstable elements before they change.

The novel oscillopolarography method presented was used in conjunction with the Kolouseč switch, so that the auxiliary potential corresponded to the anodic limiting current due to product oxidation, associated with the depolarizing electrochemical reduction.

Changes in the duration of the rectangular pulses and the increment in their amplitude permits variation of the commutation frequency, which is limited to 100 Hz when used with the Kolouseč switch and usually at even lower values due to the effect of charging current. The principle of time selection favours the substantial decrease in interference and the expansion of the commutation frequency range (up to 2000 Hz).

The commutated polarograms were also recorded with the Kolouseč switch at 10 Hz frequency according to the commutation scheme (II) [17].

The peak potentials were measured with the P-307 potentiometer to within 0.001 V.

The slowly dropping electrodes in acetonitrile gave the parameters:

(1) $m = 0.3$ mg/s, $\tau = 20$ s;
(2) $m = 0.18$ mg/s, $\tau = 29$ s;
(3) $m = 0.0098$ mg/s, $\tau = 44$ s

The voltammetric curves were analyzed by use of methods published previously [18].

The number of electrons (n_e) involved in the electrochemical reaction was estimated by comparing the limiting current value of the compound under study with that of the limiting diffusion current of reference compounds, viz. the initial salts NiX_2.

The correction for the difference in molecular mass was derived by combining the Il'kovitch and Stoks-Einstein equations:

$$n_x = \frac{(i_{\text{limit}})_x \cdot n_{\text{ref}} \cdot M_x^{1/6} \cdot C_{\text{ref}}}{(i_{\text{limit}})_{\text{ref}} \cdot M_{\text{ref}}^{1/6} \cdot C_x}$$

Spectrophotometry. To study the complexation of the divalent nickel compounds in the presence of excess high concentration of organophosphorus ligands, the electron spectra were recorded by use of a double-beam spectrometer "UV-Vis Specord-40" in range 54000–11000 cm^{-1} (185–900 nm). A quartz cell ($l = 0.997$ cm) with a ground-glass stopper, filled with argon was used for sample measurements. The solutions of bis(acetylacetonato)nickel(II) were prepared at +25 °C by dilutions of the initial $Ni(acac)_2$ solution from aliquots weighed beforehand on an analytical balance to ± 0.0001 g.

The solutions ranging in concentration from 0.00263 *M* to 0.000026 *M*, with a $PBu_3/Ni(acac)_2$ ratio of 4–100, were prepared by volumetric dilution of the stock 0.117 *M* $Ni(acac)_2$ solution. The PBu_3 and $Ni(acac)_2$ aliquots were introduced from a graduated syringe.

Th spectra were recorded in the operating range of 200–900 nm at 2 mm/s and at +25 °C.

The other solutions were prepared analogously.

The electron spectra of complexes $NiX_2(PR_3)_2$ and $NiX_2\{P(OR)_3\}_2$, where $X = Cl, NO_3$, were recorded on a "UV-Vis Specord" instrument, in cells of $l = 0.1$ cm.

Only freshly prepared solutions were used in the study. Acetonitrile of polarographic purity was used as solvent.

Electroconductivity measurements. Electroconductivity of solutions was measured with a Conductivity Meter OK 102/1 (Radelkis, Hungary) at +25 ± 1° C in acetonitrile of polarographic purity. Electroconductivity of the tricomponent system $Ni(acac)_2$–$P(O\text{-}i\text{-}Pr)_3$–$AlEt_3$ was measured by use of smooth platinum electrodes ($S = 1$ cm^2), in toluene of polarographic purity at −10° C.

Results and discussion

Investigation of the coordination–dissociation and the processes taking place at the electrodes involving the Ni^{II} complexes and tertiary phosphines and phosphites

Tetracoordinated phosphine complexes $NiX_2(PR_3)_2$, which in their free states represent typical σ-donor–acceptor complexes, are formed by (preferable) charge transfer from the unshared pair of phosphorus electrons to the metal, and by the less important retrotransfer of charge from the occupied 3*d* orbital of Ni to the free 3*d* or hybrid 3*d*,3*p* orbitals of phosphorus. The donor–acceptor interactions include action by the acid ligands, which have donor properties. The behaviour of such complexes in solution is determined by the strength of Ni coordination bondings with both ligand types and, with the large concentration of tertiary phosphine, by the ability of Ni to undergo an increase in coordination number from 4 to 6. And so, the key reactions of σ-donor–acceptor complexes in solution are represented by the equilibrium reactions of stepwise coordination–dissociation. A shift of that equilibrium as is effected by the presence of excessive organophosphorus ligand can cause it to take either form. The complexes formed with Ni salts are capable of molecular and ionic dissociations and NiX_2Solv_4, $NiXSolv_5{}^+$, $NiSolv_6{}^{2+}$ species are thus formed in their solutions. The reactivity of each species varies depending on the electron transfer and/or coordination reaction. The species form either molecular or cationic σ-donor–acceptor complexes exhibiting separate waves on their polarograms if equilibrium is achieved only after some time. To interpret the intricate polarograms, we carried out preliminary studies of the electrochemical reduction of the anhydrous compounds of NiX_2($NiCl_2$, $Ni(NO_3)_2$, $Ni(acac)_2$) and the tertiary phosphines (PBu_3, PPh_3) and phosphites ($P(OEt)_3$, $P(OPh)_3$, etc.).

Since the σ-donor properties and the bulkiness of the organophosphorus bases are of crucial importance for the processes studied, the results obtained are listed with respect to this type of ligand.

Tributylphosphine. Electroconductivity ($\mu = 70.5$ ohm^{-1} cm^2 M^{-1}) and polarography data reveal complex $NiCl_2(PBu_3)_2$ to be half dissociated in acetonitrile. The polarogram of its 10^{-3} M solution shows one anodic wave, attributable to the Hg dissolved in the presence of Cl^- ions, and three cathodic waves; the first, $E^{I}_{1/2} = -0.78$ V, represents the reduction of the complex, the second, $E^{II}_{1/2} = -1.20$ V, is due to the solvated cations $Ni(MeCN)_6{}^{2+}$, and the third, $E^{III}_{1/2} = -2.75$ V is due to PBu_3 (Fig. 1, curve 2). Dissociation of the complex is suppressed in the presence of a ten-fold excess of PBu_3. In this solution, the polarogram exhibits the only two-electron reversible reduction wave of the stabilized complex with $E_{1/2} = -0.58$ V (Fig. 1, curve 3). The cyclic voltammetry carried out in the linear-trigonal (curve 3′), the linear-stepped (curve 3″) and the 200 Hz commutative (curve 3‴) polarization modes give the cathodic peaks and those of the oxidation of the reduction products ($E_{pa_1} = -0.47$ V; $E_{pa_2} = -0.28$ V), respectively.

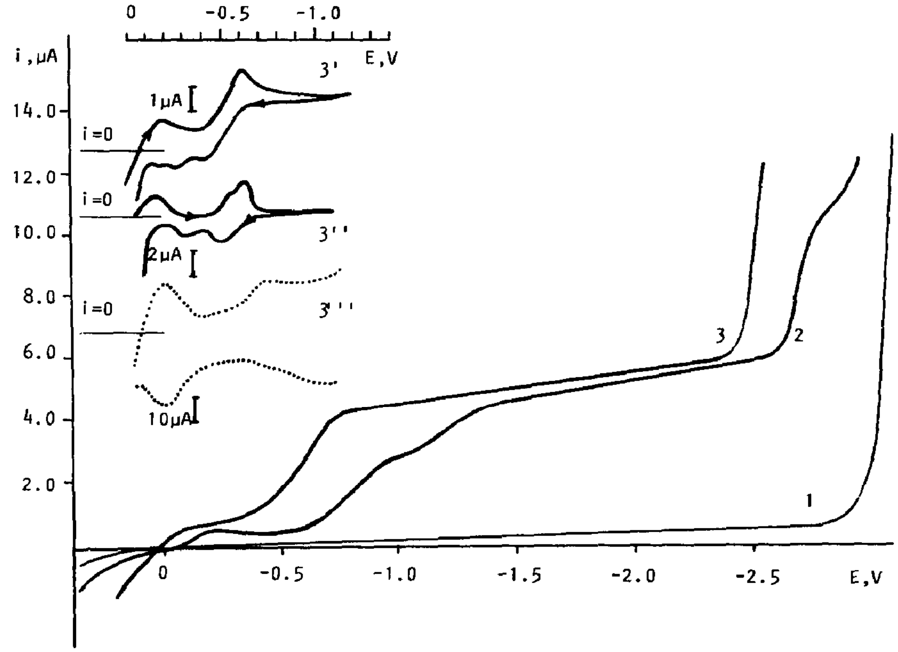


Fig. 1. Classic (2–3), cyclic (3', 3'') ($v = 0.4$ V/s, 4 s delay), and commutative (3''') voltammograms of 10^{-3} M solution of $NiCl_2(PBu_3)_2$ (2) containing 10^{-2} M PBu_3 (3, 3') in MeCN, 0.1 M TBAP (1). Voltage types: 3' – linear-trigonal; 3'' – stepped-trigonal; 3''' – rectangular impulses with a linearly increasing amplitude (4 mV).

The absorption spectrum of that solution shows the charge transfer band, the position ($\lambda = 410$ nm) and intensity ($\epsilon = 10^3$) of which are consistent with earlier assignments made for pentacoordinated complexes of similar structure, viz. $Ni[(CN)_2(PR_3)_3]$ [19].

In the presence of a ten-fold excess of PBu_3 the electroconductivity is decreased to half the usual value ($\mu = 33$ ohm^{-1} cm^2 M^{-1}) and with a 50-fold excess of PBu_3 in the solution, $E_{1/2}$ becomes -0.40 V, the electroconductivity increases to 120 ohm^{-1} cm^2 M^{-1}, and the solution turns an intense yellow. This evidence leads to the suggestion that highly polarized, planar-tetrahedral complexes are present in the solution. To induce further shifts in $E_{1/2}$ to less negative potentials under even higher PBu_3 concentrations in the system is not possible because mercury-phosphine complexes are formed by the reaction of PBu_3 with metallic mercury in the presence of free Cl^- ions in the solution. The presence of these mercury-phosphine complexes is revealed by a cathodic–anodic wave near those potentials at 0–0.3 V thus masking the effect under consideration.

As the Ni^{II} coordination sphere is saturated by PBu_3 molecules, the reversibility at the electrodes increases and the cathodic–anodic peaks become symmetrical and attain equal height. An increase in coordination number from 4 to 6 with a concomitant decrease in symmetry as evidenced also by spectrophotometry can occur only if the ligand environment of Ni^{II} is changed by the ionization of the nickel bonding to the acid ligand and transfer of the latter to the external coordination sphere. In terms of the data obtained for the pentacoordinated complexes, the structure $Ni[(PBu_3)_3Cl]Cl$ is the most appropriate, and for the coordinatively unsaturated complexes that form under a complete equilibrium shift the most probable structure is $Ni[PBu_3)_4]Cl_2$. The cations of these complexes are of planar-tetrahedral structure, typical of σ-donor–acceptor complexes. After their electrochemical reduction no energy is required to reconstruct their coordination spheres and to change their geometries. Thus, the redox-transfers in the pair $Ni(PBu_3)_4{}^{2+}/Ni^0(PBu_3)_4$ are strictly reversible and occur at potentials similar to the conventional potential for the Ni^{II}/Ni^0 pair ($E_0 = -0.25$ V).

The reactions described above for the formation of tetra-, penta-, and hexacoordinated complexes also take place during the interactions of $NiCl_2$ with tributylphosphine (P to Ni molar ratio of 2–100) in ethanol [20].

The coordination of the Ni^{II} salt by tributylphosphine in acetonitrile is illustrated by $Ni(NO_3)_2$, a 10^{-3} M solution of which contains 90% $Ni(MeCN)_6{}^{2+}$ cations ($E_{1/2}^{II} = -1.20$ V) and 10% molecular solvates $Ni(NO_3)_2(MeCN)_4$ ($E_{1/2}^{I} = -0.87$ V).

At 25 ° C, no evidence of any complexation was observed for our system despite the 100-fold excess of PBu_3. The coordination by the components was found to be instantaneous in a solution cooled to 0 ° C. The solution turns yellow if more than a 10-fold excess of PBu_3 is present. Its polarogram reveals three waves ($E_{1/2}^{I} = -0.25$ V; $E_{1/2}^{II} = -0.56$ V; $E_{1/2}^{III} = -0.82$ V) with a total limiting current equal to that of the initial 10^{-3} M $Ni(NO_3)_2$ solution.

Similarly, the cyclic voltammograms show three cathodic peaks ($E_{pc_1} = -0.27$ V; $E_{pc_2} = -0.57$ V; $E_{pc_3} = -0.90$ V) and one anodic peak ($E_{pa_1} = -0.24$ V) and are thus related to the waves in the polarogram. At low temperature, $Ni(NO_3)_2$ fails to dissociate significantly and its solvated molecules are involved in the coordination

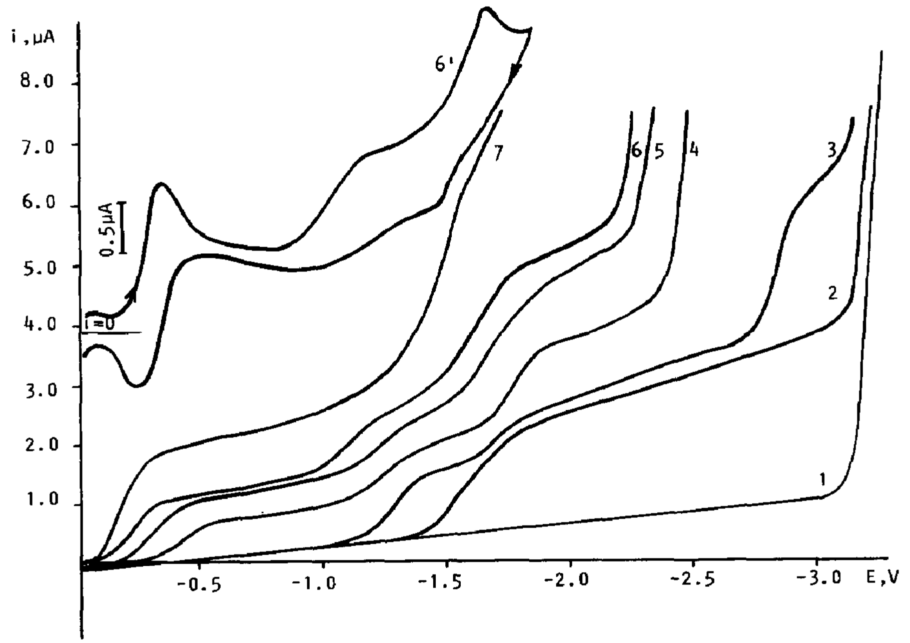


Fig. 2. Classic (2–6) and cyclic (6′) voltammograms ($v = 1$ V/s, 4 s delay) of 10^{-3} M solutions of $Ni(acac)_2$ (2) containing PBu_3 at concentrations of $2 \cdot 10^{-3}$ M (3), 10^{-2} M (4), $3 \cdot 10^{-2}$ M (5), $5 \cdot 10^{-2}$ M (6, 6′), 10^{-1} M (7) in MeCN, 0.1 M TBAP (1).

with PBu_3, thus forming tetra-, penta-, and hexacoordinated complexes $Ni(NO_3)_2(PBu_3)_n$ ($n = 2$–4) as deduced from the reduction potential values.

Bis(acetylacetonato)nickel(II) is being used more frequently to prepare catalytic systems containing either tertiary phosphines or phosphites. Owing to the coordinative unsaturation of that complex in solution, it usually occurs as a trimeric associate in an equilibrium very much low-equilibrated towards the trimeric form, with the monomer.

Only the monomeric molecules undergo the electrochemical reductions and coordinations to organophosphorus bases, those molecules determining the values of limiting current more than three times decreased as compared to the two-electron current value.

The monomerization–trimerization equilibrium is shifted towards monomer by coordinating to $Ni(acac)_2$ ligands of higher field, such as PBu_3. The total limiting reduction current of nickel species then takes on the expected (monomeric) value.

The appearance of octahedral complexes $Ni(acac)_2(PBu_3)_2$ was observed as early as with the stoichiometric ratio of components. The polarogram of this reaction gives a different wave, $E^{I}_{1/2} = -1.25$ V, because of the smaller free $Ni(acac)_2$ ($E^{II}_{1/2} = -1.55$ V) and PBu_3 ($E^{III}_{1/2} = -2.75$ V) waves; the former is represented as curve 3 (Fig. 2).

A 10- to 50-fold increase in the PBu_3 concentration results in an additional reversible wave with its limiting current gradually growing and $E^{I}_{1/2}$ shifting from -0.43 to -0.24 V; the next wave decreases with its $E^{II}_{1/2}$ shifting from -1.25 to -1.16 V; another concomitant wave appears in the discharge potential region of $Ni(acac)_2$ ($E^{III}_{1/2} = -1.60$ V), which is identical in height to the wave of the initial 10^{-3} M $Ni(acac)_2$ (Fig. 2, curves 4–6).

The cyclic voltammogram for 10^{-3} M $Ni(acac)_2$ in the presence of $5 \cdot 10^{-2}$ M PBu_3 (Fig. 2, curve 6′) reveals a pair of symmetric cathode–anode peaks ($E_{pc_1} = -0.32$ V; $E_{pa_1} = -0.25$ V; $i_a/i_c = 1.0$) and two irreversible cathodic peaks ($E_{pc_2} = -1.16$ V; $E_{pc_3} = -1.65$ V).

In the presence of a 100-fold excess of PBu_3, the first wave merges into the second one, and the third wave is masked by the discharge current of free PBu_3 (Fig. 2, curve 7). The appearance of these waves, and changes in their respective parameters with growing PBu_3 concentration may be explained in terms of slow stepwise complexations and the associated changes in geometry and ligand environment of Ni^{II} that take place in solution. Spectrophotometry confirms this suggestion. The complexes $Ni(acac)_2(PBu_3)_2$ formed initially should have the distorted octahedral structure with retention of the acetylacetonate bidentate coordination. This is confirmed by an absorption band of $\lambda = 640$ nm and $\epsilon = 37$. The absorption increases as the PBu_3 concentration is increased, a phenomenon which is inherent in complexes with a lower degree of symmetry ($P/Ni = 10$; $\lambda = 401.1$ nm; $\epsilon = 410$) of either regular pyramidal or trigonal pyramidal structure. They are represented by the molecular complexes $Ni(acac)_2(PBu)_3$, with acetylacetonate monodentate coordination. With a P/Ni mole ratio of > 15, the $\lambda = 640$ nm and $\lambda = 401.1$ nm intensities are lowered and a new absorption band appears at $\lambda = 254.4$ nm ($\epsilon = 10^4$), which is evidence of the formation of highly polarized, square planar complexes $[Ni(PBu_3)_4](acac)_2$ ($E_{1/2} = -0.25$ V), owing to the ionization of nickel-to-acetylacetonate bonding and to the displacement of the latter as an anion into the external coordination sphere.

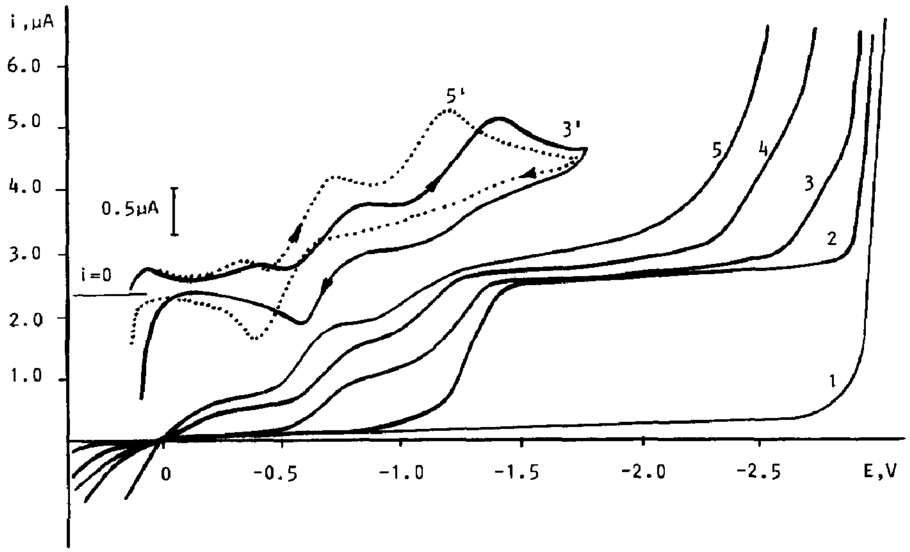


Fig. 3. Classic (2–5) and cyclic (3′, 5′) ($v = 1$ V/s, 4 s delay) voltammograms of 10^{-3} M solutions of $Ni(NO_3)_2$ (2), of $Ni(NO_3)_2(PPh_3)_2$ (3, 3′) containing PPh_3 at concentrations of 10^{-2} M (4), 10^{-1} M (5, 5′) in MeCN, 0.1 TBAP (1) at $T = 6$ °C.

In contrast to the solutions of complexes of similar structure containing the anions Cl^- or NO_3^-, in the presence of acac anions, mercury-phosphine complexes do not seem to interfere with development of the $Ni(PBu_3)_4^{2+}$ band.

The electroconductivity value of 112 ohm^{-1} cm^2 M^{-1} (P/Ni = 50) confirms that the ionization of hexacoordinated complexes is complete in the solutions under consideration.

Triphenylphosphine. Poor donor properties and the bulkiness of triphenylphosphine enhances the high lability of its coordination to metal. Polarography and conductometry have indicated that the 10^{-3} M acetonitrile solution of $Ni(NO_3)_2(PPh_3)_2$ is half dissociated. Its polarogram shows three cathodic waves; loss of charge from the complex ($E^{I}_{1/2} = -0.71$ V), and for the solvated cations $Ni(MeCN)_6^{2+}$ ($E^{II}_{1/2} = -1.20$ V) and PPh_3 ($E^{III}_{1/2} = -2.75$ V) (Fig. 3, curve 3). The cyclic voltammogram exhibits a pair of interconnected cathode–anode peaks ($E_{pc_1} = -0.78$ V; $E_{pa_1} = -0.60$ V; $i_a/i_c \cong 1.0$) and an irreversible cathodic peak ($E_{pc_2} = -1.30$ V) (Fig. 3, curve 3′), which are related to the loss of charge from the Ni-containing species. The addition of a large excess of PPh_3 (10- and 100-fold mole excess) results in a $E_{1/2}$ wave shift of complex discharge (from -0.71 to -0.56) and a $Ni(MeCN)_6^{2+}$ wave shift (from -1.20 to -1.05 V), their limiting currents remaining unchanged (Fig. 3, curves 4 and 5, 5′) and the solution electroconductivity decreasing from 87 to 50 ohm^{-1} cm^2 M^{-1}. The above is evidence that both Ni-containing species are involved in the associated coordination reactions in the presence of an excess of PPh_3 to give molecular and cationic complexes according to eqs. 1 and 2

$$Ni(NO_3)_2(PPh_3)_2 + PPh_3 \rightleftharpoons Ni(NO_3)_2(PPh_3)_3 \qquad (1)$$

$$Ni(MeCN)_6^{2+} + 2PPh_3 \rightleftharpoons Ni(PPh_3)_2(MeCN)_4^{2+} + 2MeCN \qquad (2)$$

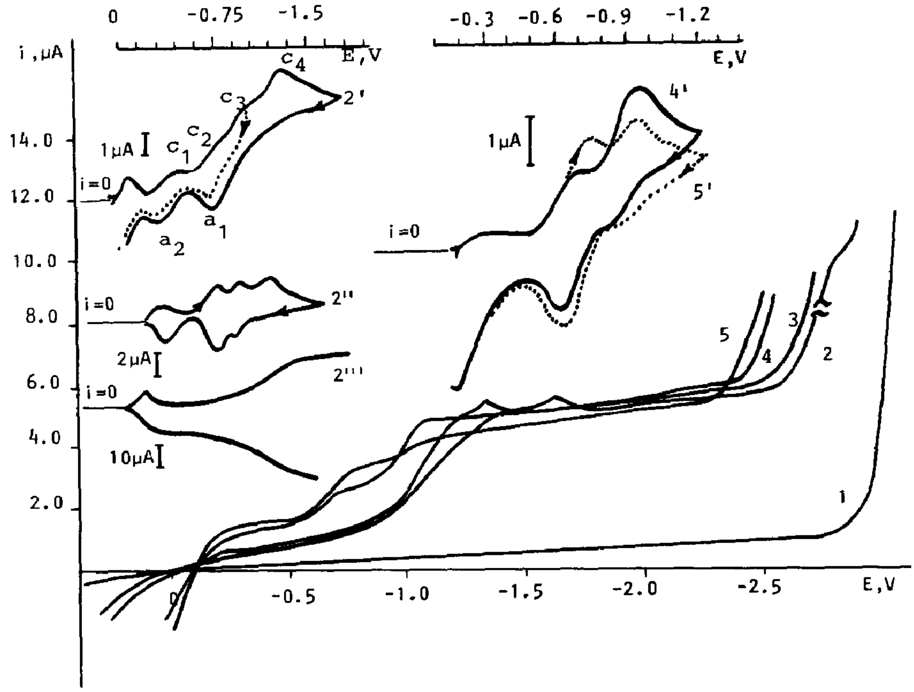


Fig. 4. Classic (2–5) and cyclic (4′, 5′) ($v = 1$ V/s, 4 s delay) voltammograms of 10^{-3} *M* solutions of $NiCl_2(PPh_3)_2$ (2), containing PPh_3 at concentrations of 10^{-2} *M* (3), 10^{-1} *M* (4, 4′), $1.7 \cdot 10^{-1}$ *M* (5, 5′); cyclic (2′, 2″) ($V = 0.4$ V/s, 4 s delay) and commutative (2‴) voltammograms of 10^{-3} *M* solution of $NiCl_2(PPh_3)_2$ in MeCN, 0.1 *M* TBAP (1) at $T = 7\,°C$. Voltage types: 2′ – linear-trigonal; 2″ – stepped-trigonal; 2‴ – rectangular impulses with a linearly growing amplitude (4 mV).

Further increases in the PPh_3 concentration causes no changes in the wave parameters, still a significant increase in the cathodic current of mercury phosphine complexes is observed (Fig. 3, curve 5).

The coordination reactions described here take place in acetonitrile solutions of $Ni(NO_3)_2$, containing an excess of PPh_3. However, a high degree of dissociation such as in the 10^{-3} *M* solution of $Ni(NO_3)_2$ (85%) determines the preferable involvement of $Ni(MeCN)_6^{2+}$ cations ($E_{1/2} = -1.20$ V) into the coordination. These cations are completely bound into the complexes $Ni(PPh_3)_2(MeCN)_4^{2+}$ ($E^{II}_{1/2} = -1.05$ V) in the presence of a two-fold excess of PPh_3. The parameters of the related wave reveal no changes with increased PPh_3 concentration since it is impossible to insert more than two PPh_3 molecules into the coordination sphere of a solvated cation [21]. A small amount of the reversibly discharging molecular complexes $Ni(NO_3)_2(PPh_3)_3$ ($E^{I}_{1/2} = -0.50$ V) are simultaneously formed in the solution.

The polarogram of $NiCl_2(PPh_3)_2$ in acetonitrile is of more intricate character: with zero potential, a small wave at $i_{max} = 0.5$ μA turns out to be an irregular wave with its low maximum on the limiting current site in the potential region of -0.40 to -1.50 V; in addition, a wave due to free PPh_3 ($E_{1/2} = -2.75$ V) (Fig. 4, curve 2) appears before the TBAP discharges.

Cyclic voltammograms of the linear-trigonal and linear-stepped voltage shapes permit the four cathodic and two anodic peaks to be distinguished, the assignments of which have been reported previously [20] (Fig. 4, curves 2′, 2″). The introduction of a 10-fold excess of PPh_3 into the solution causes the shifting of the upper wave section towards its less negative values by 100 mV and, accordingly, the forth peak matched with the third in terms of its potential (Fig. 4, curve 3). In the presence of a 100-fold excess of PPh_3, the polarogram shows three waves ($E^{I}_{1/2} = -0.10$ V; $E^{II}_{1/2} = -0.67$ V; $E^{III}_{1/2} = -0.96$ V). The cyclic voltammogram gives three related peaks: the first one is of the conventional wave shape ($E_{pc_1} = -0.35$ V), and the other two correspond to the potentials of the second and third waves ($E_{pc_2} = -0.70$ V; $E_{pc_3} = -0.95$ V) (Fig. 4, curves 4, 4′). With the direction of potential scanning reversed, two anodic peaks ($E_{pa_1} = -0.62$ V; $E_{pa_2} = -0.25$ V) are observed, which are caused by the oxidation of those products obtained with the second cathodic peak potentials. Further increases of the free PPh_3 concentration in the solution results in an increase in height of the second cathodic peak owing to a smaller third peak and that of the anodic peak ($E_{pa} = -0.62$ V) (Fig. 4, curves 5, 5′). In addition, the total limiting current of nickel-containing complexes is lowered. It is rather difficult to interpret the above described polarograms since we do not have sufficient information concerning the mechanisms of the electrochemical and the associated reactions occurring in the solutions of the complex. Still, in analogy to the above described complexes of similar structure, we are inclined to regard the behaviour of the given complex in acetonitrile as that determined by the reactions of molecular and ion dissociation

$$2PPh_3 + NiCl_2(MeCN)_4 \overset{MeCN}{\leftrightarrows} NiCl_2(PPh_3)_2 \overset{MeCN}{\rightleftharpoons} \tag{3}$$

$$NiCl(PPh_3)_2(MeCN)^+ + Cl^- \overset{MeCN}{\rightleftharpoons} Ni(MeCN)_6{}^{2+} + 2Cl^- + 2PPh_3$$

The existence of various structures and different reactivities of Ni-containing complexes in solution as seen from the stepwise character of polarograms is evidence of their involvement in the stepwise coordination reactions.

A sharp decrease in electroconductivity of the $NiCl_2(PPh_3)_2$ 10^{-3} *M* solution from 85.2 to 5.0 ohm^{-1} cm^2 M^{-1} which occurs when 0.3 *M* PPh_3 is added may indicate the preferable formation of the pentacoordinated molecular complexes. This is further confirmed by the presence of a charge transfer band at $\lambda = 540$ nm ($\epsilon = 10^3$).

The coordination of $NiCl_2$ with triphenylphosphine in acetonitrile is impossible because the salt is insoluble in the solvent. Coordinations are very slow in ethanol.

That $Ni(acac)_2$ complexes with triphenylphosphine was doubted for a long time, however, we have found that the complexes $Ni(acac)_2(PPh_3)_2$ and $[Ni(PPh_3)_4](acac)_2$ can be formed in the solution.

The polarogram of 10^{-3} *M* $Ni(acac)_2$ containing $2 \cdot 10^{-3}$ *M* PPh_3 shows irreversible cathodic waves of the three equilibrium components: that of the complex, $Ni(acac)_2(PPh_3)_2$ ($E^{I}_{1/2} = -1.32$ V), that of $Ni(acac)_2$ ($E^{II}_{1/2} = -1.55$ V), and that of PPh_3 ($E^{III}_{1/2} = -2.75$ V). From the ratio of limiting currents, one can conclude that 80% of monomeric molecules of $Ni(acac)_2$ have been bound into the complex. In the presence of a 10-fold excess of Ph_3, only one wave remains in the polarogram ($E_{1/2} = -1.24$ V) corresponding to that of the initial $Ni(acac)_2$ solution; with a 100-fold excess of PPh_3, it shifts to the less negative potentials ($E_{1/2} = -1.05$ V) and, with the maximum PPh_3 concentration in acetonitrile (0.3 *M*), it separates into two waves ($E^{I}_{1/2} = -0.25$ V and $E^{II}_{1/2} = -1.05$ V).

The cyclic voltammogram of the latter solution contains a pair of symmetric cathode–anode peaks ($E_{pc_1} = -0.28$ V; $E_{pa_1} = -0.24$ V; $i_a/i_c = 1.0$) and an irreversible cathodic peak ($E_{pc_2} = -1.08$ V). With the PPh_3 concentration changed, the electroconductivity varies from 1.12 to 6.5 ohm^{-1} cm^2 M^{-1} and the absorption spectrum shows an intense charge-transfer band ($\lambda = 263$ nm, $\epsilon = 10^4$) typical of that for the cationic complexes, NiL_4^{2+}. The limiting current values and electroconductivity of the solution containing 0.3 *M* PPh_3 reveal that nearly all the bis(acetylacetonato)nickel(II) molecules exist as trimeric associates (60%), the remainder comprises the molecular complexes $Ni(acac)_2(PPh_3)_2$ (30%) and cationic complexes $Ni(PPh_3)_4^{2+}$ (10%) only.

Phosphites. Complexes of exact stoichiometric compositions such as $NiX_2[P(OR)_3]_2$ were not preparatively made. Their formation in solution was detected by spectrophotometry [22] and polarography [20]. The cations $Ni(Solv)_6^{2+}$ and simple salts $NiCl_2$, $Ni(NO_3)_2$ coordinate with the less bulky phosphites $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$ with the greatest facility. In an acetonitrile solution of 10^{-3} *M* $Ni(NO_3)_2$, the cations $Ni(MeCN)_6^{2+}$ ($E_{1/2} = -1.20$ V) become bonded to the complexes $Ni[P(OEt)_3]_2(MeCN)_4^{2+}$ ($E_{1/2}^{II} = -1.05$ V), and undissociated molecules, in turn, become bonded to the molecular complexes $Ni(NO_3)_2[P(OEt)_3]_2$ ($E_{1/2}^{I} = -1.70$ V) in the presence of as little as $2 \cdot 10^{-3}$ *M* $P(OEt)_3$. The ratio of the cationic to molecular complexes is determined by high degree of dissociation of $Ni(NO_3)_2$ (Fig. 5, curve 3). At a molar ratio of components of P/Ni = 5, three waves appear ($E_{1/2}^{I} = -0.25$ V; $E_{1/2}^{II} = -0.50$ V; $E_{1/2}^{III} = -1.05$ V) on the polarogram where the first and the second waves are growing at the cost of the decreased

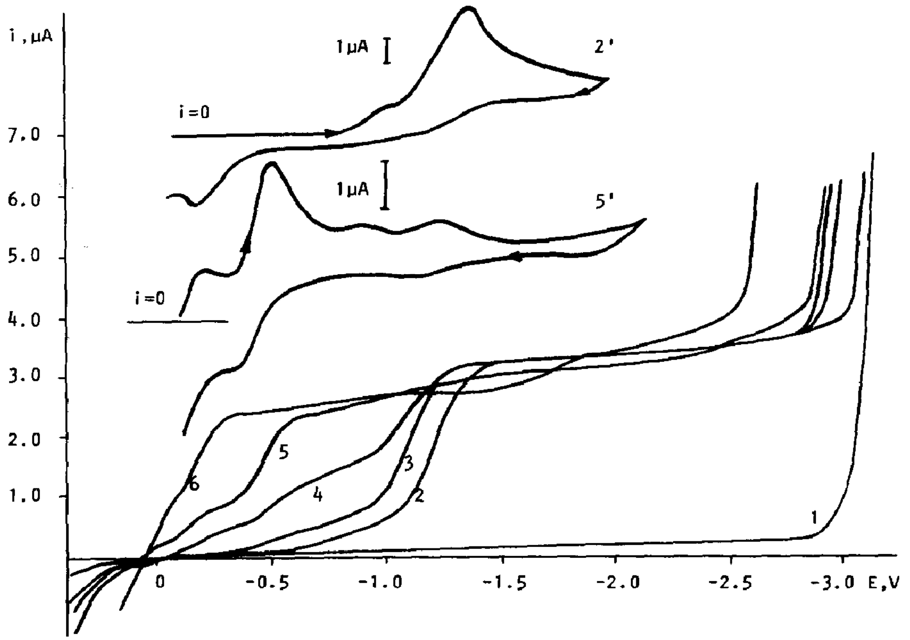


Fig. 5. Classic (2–6) and cyclic (2′, 5′) ($v = 1$ V/s, 4 s delay) voltammograms of 10^{-3} *M* solution of $Ni(NO_3)_2$ (2, 2′) containing $P(OEt)_3$ at concentrations of $2 \cdot 10^{-3}$ *M* (3), $5 \cdot 10^{-3}$ *M* (4), 10^{-2} *M* (5, 5′), 10^{-1} *M* (6) in MeCN, 0.1 *M* TBAP (1) at $T = 6\,°C$.

height of the third (Fig. 5, curve 4). At $P/Ni = 10$, the third wave has almost disappeared and, because of this, the first and the second waves as well as the related cathode–anode peaks become larger (Fig. 5, curves 5, 5′). The absorption spectra of the solution described show a charge transfer band ($\lambda = 435$ nm; $\epsilon = 10^3$) typical of that for pentacoordinated complexes. An increase in the electroconductivity to 216 ohm^{-1} cm^2 M^{-1} indicates that these complexes are highly ionized. The introduction of a 100-fold excess of $P(OEt)_3$ into solution, gives a polarogram with a single reversible wave ($E_{1/2} = -0.18$ V) (Fig. 5, curve 6), which can be assigned to the reduction of cationic complexes $Ni[P(OEt)_3]_4{}^{2+}$ formed by the total ionization of hexacoordinated complexes. The electroconductivity of the solution is increased to 250 ohm^{-1} cm^2 M^{-1}.

The complexation of $NiCl_2$ with triethylphosphite is even more facile: cationic σ-donor–acceptor complexes $Ni[P(OEt_3)]_4{}^{2+}$ predominate in the presence of a 10-fold excess of $P(OEt)_3$ ($E_{1/2} = -0.24$ V; $E_{pc} = -0.30$ V; $E_{pa} = -0.24$ V; $i_a/i_c \cong 1.0$).

$Ni(NO_3)_2$ coordinates with the bulkier phosphite $P(O\text{-}i\text{-}Pr)_3$ to give similar complexes at lower rates. A small excess of $P(O\text{-}i\text{-}Pr)_3$ with $P/Ni = 4$ affords the cationic solvated complexes $Ni[P(O\text{-}i\text{-}Pr)_3]_2(MeCN)_4{}^{2+}$ ($E_{1/2} = -1.05$ V). With the introduction of a 10-fold excess of the same base into the solution, two equal waves are observed ($E^{I}_{1/2} = -0.40$ V; $E^{II}_{1/2} = -1.05$ V). The first one corresponds to the pair of symmetric cathode–anode peaks ($E_{pc} = -0.43$ V; $E_{pa} = -0.37$ V; $i_a/i_c = 1.0$). The appearance of the charge transfer band ($\lambda = 455$ nm; $\epsilon = 10^3$) indicates that an additional type of complex, $Ni(NO_3)_2[O\text{-}i\text{-}Pr)_3]_3$, is formed in the solution. A complete shift of the coordination equilibrium to the hexacoordinated complexes $[Ni\{P(O\text{-}i\text{-}Pr)_3\}_4](NO_3)_2$ may be reached only in the presence of a 300-fold excess of $P(O\text{-}i\text{-}Pr)_3$, the electroconductivity being $\mu = 108$ ohm^{-1} cm^2 M^{-1}.

The Ni^{II} salts show the least ability to coordinate with triphenylphosphite.

A 10^{-3} M solution of $NiCl_2$ in the presence of 10^{-1} M $P(OPh)_3$ showed no changes in its polarogram, either in its color or electroconductivity, but after 10 h, the solution turns a yellow-brown color and its polarogram gives a reversible dielectronic wave ($E_{1/2} = -0.18$ V) and a related pair of symmetric cathode–anode peaks appears in its cyclic voltammogram thus attesting the formation of the hexacoordinated complex $[Ni\{P(OPh)_3\}_4]Cl_2$.

Bis(acetylacetonato)nickel(II) is less able to coordinate to phosphites than simple salts of Ni^{II}. Molecular complexes $Ni(acac)_2\{P(OEt)_3\}_2$ are formed with a stoichiometric component ratio ($E_{1/2} = -1.26$ V). The introduction of a 100-fold excess of $P(OEt)_3$ causes a shift of that wave to lower negative potentials ($E_{1/2} = -0.97$ V) and a slight increase in the total current conducted by the Ni-containing complexes.

The cyclic voltammogram shows an irreversible cathodic peak ($E_{pc} = -1.06$ V) and a related anodic peak ($E_{pa} = -0.40$ V). Repeated scanning from the zero value reveals an additional cathodic peak ($E_{pc} = -0.56$ V) and gives a decrease in height of the subsequent cathodic peak to confirm the stability of zerovalent complexes $Ni^0\{P(OEt)_3\}_4$ formed ($E_{pc} = -1.05$ V). The electrochemical oxidation of the zerovalent complexes to the corresponding cations $Ni[P(OEt)_3]_4{}^{2+}$ becomes apparent with repeated scanning when another cathodic peak ($E_{pc} = -0.56$ V) appears. A significant shift of the coordination equilibrium is realized only with a 400-fold excess of $P(OEt)_3$ to give a reversible wave of $E_{1/2} = -0.45$ V. The absorption spectrum of that solution shows a charge transfer band ($\lambda = 251.9$ nm;

$\epsilon = 10^4$), which may be assigned to the cationic complexes $Ni\{P(OEt)_3\}_4^{2+}$ formed in the solution. The effects of higher $P(OEt)_3$ concentrations were not examined.

Triisopropylphosphite coordinates with $Ni(acac)_2$ in a similar way. The presence of the molecular complexes in the solution is revealed by the wave of $E_{1/2} = -1.22$ V at a molar ratio of P/Ni = 4 and its $E_{1/2}$ shifts to −1.05 V when P/Ni = 600. The coordinatively saturated complexed cations $Ni\{P(O\text{-}i\text{-}Pr)_3\}_4^{2+}$ are formed in the presence of a 1000-fold excess of $P(O\text{-}i\text{-}Pr)_3$ to give a strictly reversible wave ($E_{1/2} = -0.21$ V) and a pair of symmetric cathode–anode peaks ($E_{pc} = -0.30$ V; $E_{pa} = -0.18$ V; $i_a/i_c \cong 1.0$). The absorption spectra of these complexes shows a charge transfer band with $\lambda = 260.2$ nm; $\epsilon = 10^4$).

Tri-s-butylphosphite and $P(OC_6H_{11})_3$ coordinate to $Ni(acac)_2$ in a similar way.

An examination of the experimental data obtained for the equilibrium reactions of the stepwise complexations and dissociations preceding the electrochemical reduction of Ni complexes with trivalent phosphorus ligands lead to the conclusions as follows.

The total of donor–acceptor bondings formed in molecular complexes of the NiX_2L_2 type gives rise to the rearrangements of charges within the coordination sphere to relax the σ-bonding between nickel and acid ligand. As a consequence, the tetracoordinated complexes (σ-DAC) are reduced by potentials that are 200–300 mV less than those for the initial molecules of $Ni(acac)_2$, $NiCl_2$, and for the solvated nickel cations (2 +).

The tetracoordinated complexes in the presence of an excess of the main (neutral) ligand introduced into the solution suppress partly or completely the dissociation such that the equilibrium is shifted towards the stepwise complexation leading to the complete coordinative saturation of Ni^{II}

$$NiX_2L_2 + L \rightleftharpoons NiX_2L_3 + L \rightleftharpoons NiX_2L_4 \tag{4}$$

The saturation of an Ni^{II} coordination sphere with the higher field ligands, such as tertiary phosphines and phosphites, results in the metal being oversaturated with electrons and in a delicate difference developing between the energy levels of Ni^{II} HOMO and acid ligand LUMO to give energy gain by their interactions in excess of the total energy required for removal of the acid ligand as an anion. So, a homogeneous intramolecular one-electron transfer distinctive for σ-DAC occurs, thus completely ionizing the hexacoordinated complex

$$NiX_2L_4 \rightleftharpoons NiL_4^{2+} + 2X^- \tag{5}$$

The shift of the equilibrium towards the cationic complexes NiL_4^{2+} depends on the basicity and bulkiness of σ-donor as well as on the strength of nickel-to-acid ligand bonding. Thus, the shift of the coordination equilibrium with the cationic tributylphosphine complexes formed can be observed by use of a 100–500-fold excess of ligand irrespective of the acid ligand nature. The formation of the cations $Ni\{P(OEt)_3\}_4^{2+}$ depends on the acid ligand type: in solutions of $NiCl_2$ they are found to exist with a 50-fold excess of the ligand, in $Ni(NO_3)_2$ with a 100-fold excess, and in $Ni(acac)_2$ solution, even a 400-fold excess of $P(OEt)_3$ is insufficient. Some other alkyl phosphites usually require a 1000-fold excess of the σ-ligand present in solution.

The cationic complexes NiL_4^{2+} are iso-structural analogues of the related coordinatively saturated complexes of zerovalent nickel Ni^0L_4 with similar bonding

Table 1

Spectral and energetic assignments of NiL_4^{2+} cationic complexes

No.	L	λ (nm)	$h\nu$ (eV)	J_D^P (eV)	E_A (LUMO Ni) (eV)
1.	PBu_3	254.4	4.87	8.0	3.13
2.	PPh_3	263.0	4.71	8.20	3.49
3.	$P(OEt)_3$	251.9	4.92	8.50	3.58
4.	$P(O\text{-}s\text{-}Bu)_3$	259.9	4.77	8.43	3.67
5.	$P(O\text{-}i\text{-}Pr)_3$	260.2	4.77	8.46	3.69

lengths and valence angles. With such a pair of complexes, electron transfer requires no activation energy to rearrange the coordination sphere and is strictly reversible at potentials similar to those of the conventional potential of that pair, Ni^{2+}/Ni^0 ($E_0 = -0.25$ V).

The cationic complexes, NiL_4^{2+}, have been prepared with Ni^{II} coordinating to the aliphatic or aromatic phosphines, or phosphites; their stability in solution has been confirmed by use of three independent methods, i.e. by cyclic voltammometry, electronic spectroscopy, and electroconductivity measurements. The semi-empirical estimation after Mallikon's equation affords the calculations of the affinity energy to the LUMO complex by the energy band of charge transfer from phosphorus to nickel

$$h\nu = J_D + E_A$$

The data listed in Table 1 show that the electron affinity energy correlates to the steric and electronic parameters of Tolman [23].

The approach suggested for the estimation of redox potentials of nickel complexes with t-phosphines and t-phosphites in the lowest oxidation state of the metal (Ni^0L_4) eliminates the errors due to the instability of the complexes in solution. The redox potentials obtained for the NiL_4^{2+}/Ni^0L_4 pair were found to be slightly influenced by the type of phosphorus ligands and, therefore, their values are determined by the MO energies, most predominantly by the Ni atomic orbitals (t_{2g}).

Values of $E_{1/2}$ given in the literature for oxidized Ni^0L_4 differ by 1500 mV [2]. The experimental results on the above described simulations of coordination–dissociation equilibria, and of stepwise coordinative saturation, illustrated by individual molecular compounds by use of the equilibrium-shift method, are of special interest.

The acid ligands selected permitted the elucidation of the mechanism of the trivalent phosphorus ligand complexation, effected by the specific nickel(II)-to-acid ligand coordination bonding in solution:

(1) Ni^{II} salts and non-coordinative acid ligand as $Ni(ClO_4)_2$ [2] only form the cationic types of σ-DAC, by partial or complete substitution of the solvent molecules in heterogeneous solvated cations $Ni(Solv)_6^{2+}$ for organophosphorus ligands. With the stoichiometric ratio ($P/Ni = 2$) for all ligand types, only cationic complexes of the octahedral structure $NiL_2(Solv)_4^{2+}$ are reduced irreversibly. With larger, and excessive quantities of σ-ligand, the equilibrium may be partially shifted towards total saturation of the coordination sphere by that ligand only in cases of

less bulky t-phosphines and t-phosphites. We believe that the polarograms register two types of cationic σ-DAC, i.e. NiL_4^{2+} and $NiL_2(Solv)_4^{2+}$, the first being reversibly discharged at −0.25 V and the second being quasireversibly discharged at −1.00 V. Reports [2,3] attribute these waves to a two-step reduction according to eq. 6

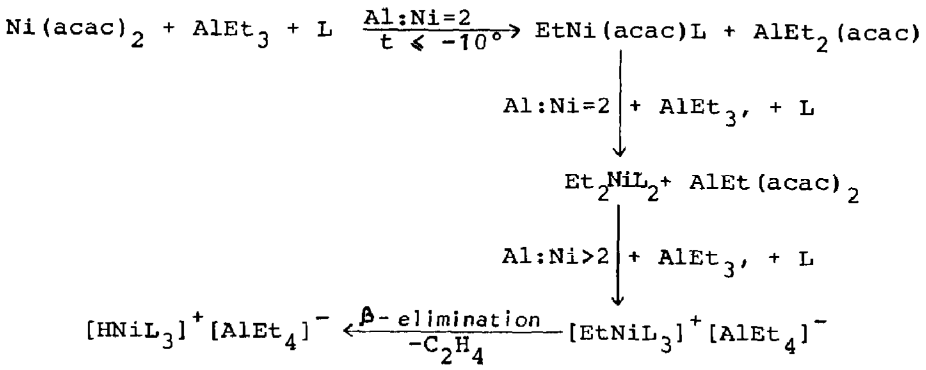
$$NiL_4^{2+} \overset{+e}{\rightleftharpoons} NiL_4^{+} \overset{+e}{\rightleftharpoons} Ni^0L_4 \qquad (6)$$

(2) Acid ligands are involved in formation of σ-donor–acceptor complexes with the trivalent phosphorus ligands (NO_3^- reveals its low coordinative ability) in solutions of Ni^{II} salts, the acid ligands of which possess σ-donor properties (Cl^-, NO_3^-). With regard to the high degree of dissociation of these salts in acetonitrile, in the presence of an excess of organophosphorus compounds in solution, molecular σ-DAC of the type NiX_2L_n ($n = 2$–4) is observed, which, because of complete coordination saturation, dissociates to eliminate the acid ligand as an anion, and the reversibly discharged NiL_4^{2+} is subsequently formed.

(3) In coordinations of trivalent phosphorus ligands to bis(acetylacetonato)-nickel(II), which tends to form associates, they are partially or totally destroyed. With P/Ni = 2, the coordination spheres of the square-planar monomeric molecules are transformed to octahedral structure, with ca. 20% of $Ni(acac)_2$ monomeric molecules remaining unbonded. The molecular σ-DACs formed, $Ni(acac)_2 \cdot L_2$, are typical for all the t-phosphines and t-phosphites tested. They are irreversibly reduced in the region $E_{1/2} = -(1.00$–$1.20)$ V. An increase in the number of organophosphorus ligands from two to four is most facile with interactions of $Ni(acac)_2$ and stronger bases such as tributylphosphine. With P/Ni = 50, the ratio of $Ni(acac)_2(PBu_3)_2$ to $Ni(PBu_3)_4^{2+}$ is 1/1; with P/Ni = 100, the equilibrium is completely shifted towards $Ni(PBu_3)_4^{2+}$. The partial formation of the analogous triphenylphosphine complex is observed with only a 300-fold excess of that ligand. It is much more difficult to shift the equilibrium of stepwise complexation of σ-DAC to $Ni(acac)_2 \cdot L_2$ towards the NiL_4^{2+} with aliphatic phosphites. Only with a 1000-to-1500-fold excess does it become possible to stabilize the cationic σ-DAC, as $Ni\{P(OR)_3\}_4^{2+}$, in solution.

The mobile chemical equilibria involved in the formation and dissociation of the complexed species with the metal in an unchanged oxidized state are usually accompanied by a cathodic $E_{1/2}$ shift. Use of the Nernst equation permits the shift value to be estimated from the ratio of stability constants for the oxidized and reduced metal forms, from the difference in coordination numbers, and from the equilibrium constant values. For the irreversibly discharged complexes, estimation of the shift value, in addition, involves the charge overvoltage value. The $E_{1/2}$ shift will take place if the reduced metal gives a more stable complex than the oxidized metal.

However, the zerovalent nickel phosphine and phosphite complexes such as $Ni^0L_3(Solv)$ and Ni^0L_4 also become interconnected by the slow establishment of coordination–dissociation equilibria. Thus an increase in the organophosphorus base concentration results in the concomitant shifting of interconnected cathode–anode peaks, and in the improvement of the Nicholson-Schein reversibility criteria. The one-stepped transfer of two electrons becomes strictly reversible with the formation of NiL_4^{2+} complexes in solution. For the NiL_4^{2+} (L = dppe, PEt_3,



Scheme 1

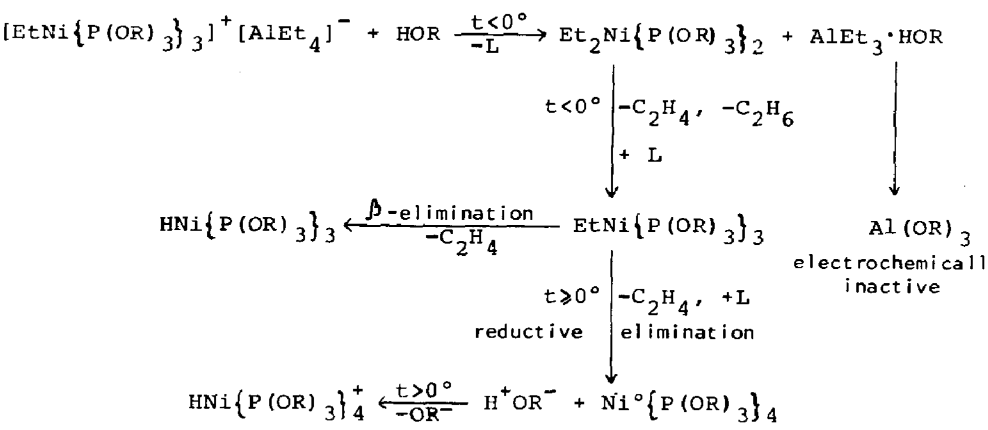
PEt$_2$Ph) cations, Bontempelli and coworkers [2] regard the reversible process to be two-stepped and that the second reaction step [$NiL_4{}^+ \rightleftharpoons Ni^0L_4 + e$] is common to both the phosphine and phosphite complexes. We attribute the reversible character of electrodic processes at the electrodes to the similar geometries of both types of complexes as the criterion of reversibility for all the electrochemical systems. Our observations have shown that an increase in the electrode process reversibility, so resulting in a fall in the negative potential value, is inherent in octahedral complexes Ni(acac)$_2$L$_2$ that are reduced irreversibly at potentials 300–500 mV less than those for free Ni(acac)$_2$, as well as to the cationic solvated complexes $NiL_2(MeCN)_4{}^{2+}$ which are reduced irreversibly at 200 mV less than potentials for $Ni(MeCN)_6{}^{2+}$, and to the tetracoordinated complexes NiX$_2$L$_2$ (X = Cl, NO$_3$; L = PR$_3$, P(OR)$_3$) reduced at 200–400 mV less than potentials for NiX$_2$. Therefore, the higher reversibilities of the electrodic processes involving Ni^{II} and Ni^0 complexes are due to the lowering of the boundary orbital levels caused by the total metal–ligand DA interactions.

The processes forming active complexes in Ziegler-type catalytic systems

1. [Ni(acac)$_2$–AlEt$_3$] in toluene (Al/Ni = 4; T = −25°C). The cyclic voltammogram of this system exhibits a cathodic peak ($E_{pc_1} = -1.70$ V), the height of which corresponds to the formal consumption of 1.5 electrons calculated for a Ni atom, and a pair of cathodic–anodic peaks in the more negative potential region ($E_{pc_2} = -2.24$ V; $E_{pa_1} = -2.04$ V; $i_a/i_c = 0.8$).

The spectrophotometry data [25] for the system at 25°C shows the monoalkylation reaction to yield EtNi(acac) and AlEt$_2$(acac), the former being stabilized by triethylaluminium. At much lower temperatures (−25°C) and in the absence of ligands capable of stabilizing Ni^{II} dialkyl derivatives, the alkylation is clearly slowed in its first step. Of the two reaction products, diethylaluminium acetylacetonate reveals its higher stability and can be obtained from the reaction of acetylacetone with triethylaluminium. Its addition to the catalytic system solution leads to an increase in the pair of cathode–anode peaks of E_{pc_2} to −2.24 V and of E_{pa_1} to −2.04 V, thus the first cathodic peak ($E_{pc_1} = -1.70$ V) can be assigned to EtNi(acac) reduced.

2. Ni(acac)$_2$–{PR$_3$ or P(OR)$_3$}–AlEt$_3$ (and some other organoaluminium compounds) (Ni/P/Al = 1/4/4; T = −(10–25)°C. The classic polarogram of the



Scheme 2

Ni(acac)$_2$–P(OEt)$_3$–AlEt$_3$ system contains an irreversible wave ($E_{1/2} = -1.68$ V) at the same place as another smaller wave that is masked by the discharge current of free P(OEt)$_3$ (Fig. 6, curve 2). The limiting current constant for the first wave corresponds to the formal consumption of 1.8 electrons for a Ni atom (found by the comparison with the limiting current constant of Ni(acac)$_2$ with $n_e = 0.6$ [24].

The polarogram depicted in Scheme 2 shows the anodic current of the initial reduction product that is oxidized ($i_a/i_c \cong 0.4$), indicating the quasi-irreversible nature of the process at the electrode (Fig. 6, curve 2′). In the same potential region, a pair of symmetric cathode–anode peaks ($E_{pc_1} = -1.72$ V; $E_{pa_1} = -1.60$ V;

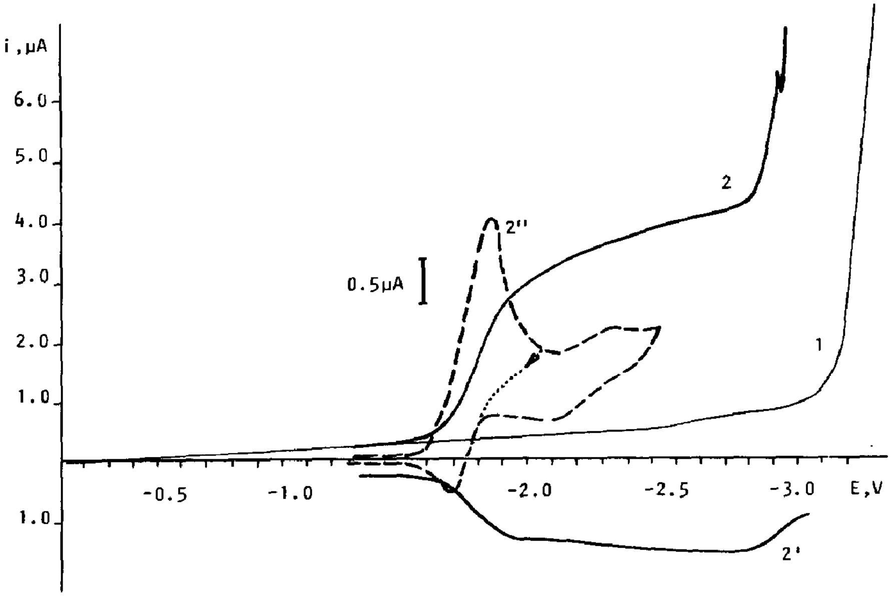


Fig. 6. Classic (2), commutative (2′), and cyclic (2″) ($v = 1$ V/s, 4 s delay) voltammograms of 10^{-3} M solution of the tricomponent system Ni(acac)$_2$–P(OEt)$_3$–AlEt$_3$ with Ni/P/Al = 1/4/4 in MeCN–PhMe (3/2), 0.1 M TBAP (1) at $T = -10$ °C.

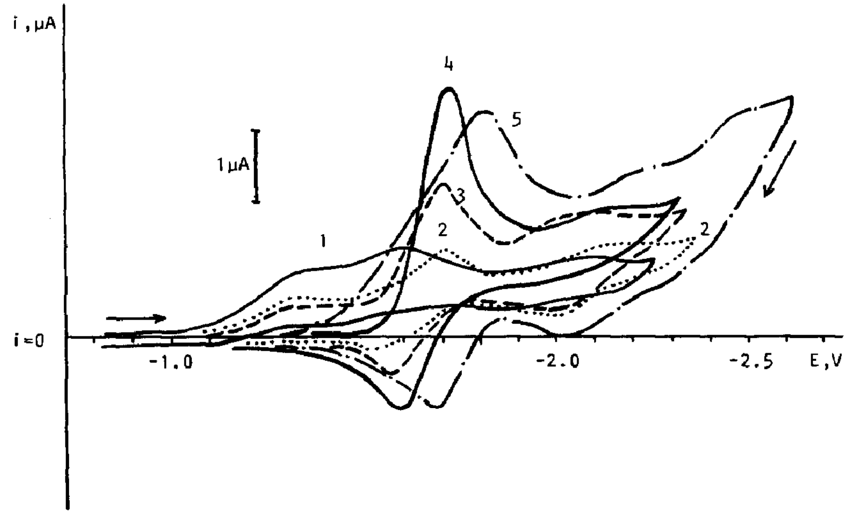


Fig. 7. Cyclic voltammograms ($v = 1$ V/s, 4 s delay) of solutions of the 10^{-3} M binary system, $Ni(acac)_2$–$P(OEt)_3$, and of the tricomponent system, $Ni(acac)_2$–$P(OEt)_3$–$AlEt_3$, in MeCN–PhMe (3/2), 0.1 M TBAP at $T = -10$°C. 1 – Ni/P = 1/4; 2 – Ni/P/Al = 1/4/0.7; 3 – Ni/P/Al = 1/4/1.5; 4 – Ni/P/Al = 1/4/4; 5 – Ni/P/Al = 1/4/6.

$i_a/i_c \cong 0.4$) and a small cathode peak with more negative potentials ($E_{pc_2} = -2.24$ V) (Fig. 6, curve 2″) are observed in the cyclic voltammogram. The parameters of those waves and peaks are accurately reproducible, for the samples selected, every 30 min for 5 h after the catalysts were prepared. During that time, the maximum catalyst activity was retained in light of the yield of olefin oligomerization products.

The formation of the complexes responsible for that catalytic activity has been observed in systems containing 10^{-3} M $Ni(acac)_2$, $4 \cdot 10^{-3}$ M $P(OEt)_3$, to which $AlEt_3$ is gradually added (from $0.7 \cdot 10^{-3}$ M to $6 \cdot 10^{-3}$ M).

Figure 7 shows the changes in the cyclic voltammograms during the interactions with $AlEt_3$. Curve 1 shows the equilibrium state in the binary system: the first cathodic peak ($E_{pc_1} = -1.25$ V) corresponds to $Ni(acac)_2\{P(OEt)_3\}_2$ reduced and the second ($E_{pc_2} = -1.60$ V) to free $Ni(acac)_2$ discharged. With a steady increase in the $AlEt_3$ concentration from $0.7 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$ M, these peaks diminish and eventually disappear and, at the same time, a pair of symmetric cathode–anode peaks in the more negative potential region ($E_{pc} = -1.72$ V; $E_{pa} = -1.60$ V; $i_a/i_c \cong 0.4$) appear and become larger. The cathodic current of that new pair of peaks exceeds by 2.5 times the total limiting current of Ni-containing complexes existing in the $Ni(acac)_2$–$P(OEt)_3$ system with P/Ni = 4.

This result indicates the destruction of the reaction initial associates $[Ni(acac)_2]_3$ and $[AlEt_3]_2$ as the monomeric molecules of both components are involved in the subsequent reactions. With $AlEt_3$ concentrations above $4 \cdot 10^{-3}$ M, the activity of the system falls abruptly and the polarogram becomes distorted in the region of the pair of symmetric cathode–anode peaks characteristic of the catalytically active complexes, which elucidates the main role of $AlEt_3$ during catalyst formation.

To provide electrochemical identifications of intermediates we used the same conditions to study the tricomponent systems of similar structure but with different

Table 2

Electrochemical assignments of nickel complexes detected in situ for tricomponent catalytic systems (Ni/P/Al = 1/4/4) in MeCN-PhMe (3/2), 0.1 *M* TBAP, $T = -10\,^{\circ}\mathrm{C}$

No.	NiX_2	L	OAC	E_{pc} V	E_{pa} (V)	ΔE_{pca} (mV)	Colour
1	$Ni(acac)_2$	PBu_3	$AlEt_3$	−1.58	−1.47	110	brick-red
2	$Ni(acac)_2$	PPh_3	$AlEt_3$	−1.12 −1.79	−1.01 −1.69	110 100	yellow
3	$Ni(acac)_2$	PPh_3	$Al(i\text{-}Bu)_2Cl$	−1.72	−1.64	80	dark-green
4	$Ni(acac)_2$	$P(OEt)_3$	$AlEt_3$	−1.72	−1.59	130	yellow
5	$Ni(acac)_2$		$Al(i\text{-}Bu)_2Cl$	−1.87	−1.73	130	yellow
6	$Ni(acac)_2$		$Al(i\text{-}Bu)_2H$	−2.09	−2.05	40	yellow
7	$Ni(acac)_2$	$P(O\text{-}i\text{-}Pr)_3$	$AlEt_3$	−1.62	−1.42	200	yellow
8	$Ni(acac)_2$	$P(O\text{-}s\text{-}Bu)_3$	$AlEt_3$	−1.48	−1.29	190	yellow
9	$Ni(acac)_2$	$P(OC_6H_{11})_3$	$AlEt_3$	−1.68	−1.48	200	yellow
10	$Ni(acac)_2$	$P(OPh)_3$	$AlEt_3$	−1.95	−1.91	40	yellow
11	$NiCl_2$	PPh_3	$AlEt_3$	−2.12	−1.95	170	crimson

organophosphorus bases and organoaluminium compounds with Ni/P/Al = 1/4/4 at $T = -10\,^{\circ}\mathrm{C}$,

$Ni(acac)_2\text{–}P(O\text{-}i\text{-}Pr)_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}P(O\text{-}s\text{-}Bu)_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}P(OC_6H_{11})_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}P(OPh)_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}P(OEt)_3\text{–}Al(i\text{-}Bu)_2Cl$
$Ni(acac)_2\text{–}P(OEt)_3\text{–}Al(i\text{-}Bu)_2H$
$Ni(acac)_2\text{–}PBu_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}PPh_3\text{–}AlEt_3$
$NiCl_2\text{–}PPh_3\text{–}AlEt_3$
$Ni(acac)_2\text{–}PPh_3\text{–}Al(i\text{-}Bu)_2Cl$

For all the above systems, symmetric cathode–anode peaks were observed in the potential region of $-(1.50 \div 2.20)$ V (Table 2, Fig. 8, curves 1–10). The durability of the intermediates registered is of the same high value as that for the $Ni(acac)_2\text{–}P(OEt)_3\text{–}AlEt_3$ system (1/4/4) and so exist in solution to ensure the optimal catalytic activity of the system.

The above results clearly indicate that most of the initial divalent nickel in those systems at low temperature undergoes no profound reduction to yield corresponding zerovalent nickel complexes with tertiary phosphines and phosphites. It was reported in [4] that the $Ni(acac)_2\text{–}Al(i\text{-}Bu)_2H$ system with P/Ni = 1 even at 23°C was reduced after 24 h. According to present-day ideas, with respect to the conditions employed, i.e. solvent type, temperatures, and component types and ratio, the Ziegler-type Ni catalysts may be represented by Ni^0, Ni^I, and Ni^{II}

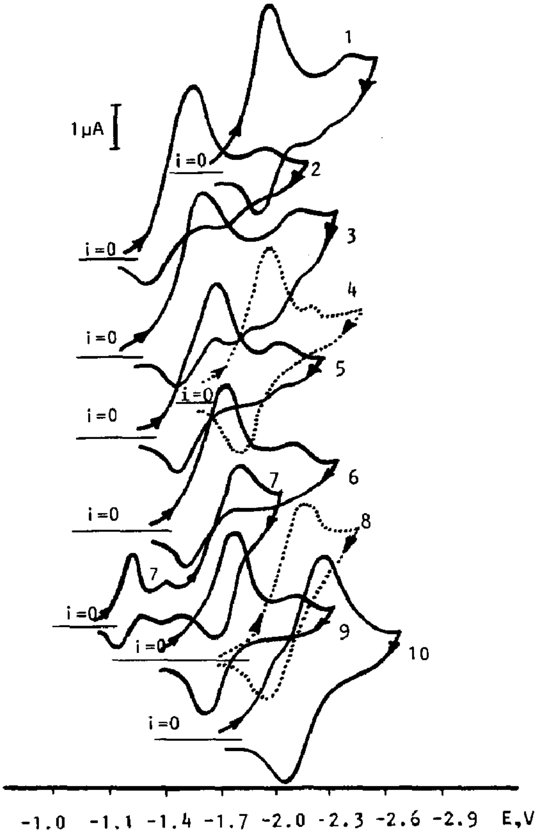


Fig. 8. Cyclic voltammograms ($v = 1$ V/s, 4 s delay) of 10^{-3} *M* solutions of tricomponent systems with Ni/P/Al = 1/4/4 in MeCN–PhMe (3/2), 0.1 *M* TBAP at $T = -10$ ° C. 1 – $Ni(acac)_2$–$P(OPh)_3$–$AlEt_3$; 2 – $Ni(acac)_2$–$P(O$-s-$Bu)_3$–$AlEt_3$; 3 – $Ni(acac)_2$–PBu_3–$AlEt_3$; 4 – $Ni(acac)_2$–$P(OEt)_3$–$Al(i$-$Bu)_2Cl$; 5 – $Ni(acac)_2$–$P(O$-i-$Pr)_3$–$AlEt_3$; 6 – $Ni(acac)_2$–$P(OC_6H_{11})_3$–$AlEt_3$; 7 – $Ni(acac)_2$–PPh_3–$AlEt_3$; 8 – $NiCl_2$–PPh_3–$AlEt_3$; 9 – $Ni(acac)_2$–PPh_3–$Al(i$-$Bu)_2Cl$; 10 – $Ni(acac)_2$–$P(OEt)_3$–$Al(i$-$Bu)_2H$.

complexes, where the ligand environment (hydrides, alkyls, substrates, organoaluminium and -phosphorus compounds) is the deciding factor. To identify the intermediate types, detected electrochemically in situ, we investigated the electrochemical properties of some complexes isolated from systems such as $EtNi(acac)PPh_3$ (I), $Ni(H)Br(PPh_3)_3$ (II), $[(PPh_3)_3NiCl]_2$ (III), and $(PPh_3)_2Ni(C_2H_4)$ (IV). Their lability in acetonitrile demanded that the working solutions were prepared under inert atmosphere at −25 ° C.

Electrochemical assignments of complexes I–IV are given in Table 3.

The polarogram of complex IV with formally zerovalent Ni reveals a cathode current which may be due to its coordinative unsaturation (16e), and its peculiar structure of the double bond in ethylenic ligand distorted as a cyclopropane ring.

The four complexes under study can be reduced at more negative potentials and, thus, there is no reason to assume that they are the intermediate analogues detected in situ in tricomponent systems.

Yamamoto and his coworkers [26] investigated the components interacting in the $Ni(acac)_2$–PEt_3–$AlEt_2(OEt)$ and $Ni(acac)_2$–$P(OEt)_3$–$AlMe_2(OEt)$ systems in ether

Table 3

Electrochemical assignments of Ni^{II}, Ni^{I}, and Ni^{0} triphenylphosphine complexes in MeCN–PhMe (3/2), 0.1 *M* TBAP at $T = -25\,°C$

Complex	$E_{1/2}$ (V)	E_{pc} (V)	E_{pa} (V)	i_a/i_c	n_e
I	−2.20	−2.48	–	–	1.8
	−2.52	−2.76	–	–	
II	−2.40	−2.48	−2.39	0.7	2.3
III	−2.31	−2.32	−2.19	0.7	2.5
IV [a]	−1.86	−1.97	−1.68	0.7	1.5

[a] In the presence of PPh_3.

at $-30\,°C$ in order to isolate the Ni–Al binary ionic complexes as the main products to which the following structures were assigned: $[NiEt(PEt_3)_3]^+[AlEt_3OEt]^-$ and $[NiMe\{P(OEt)_3\}_3]^+[AlMe_3OEt]^-$, respectively, by IR and PMR spectroscopy, and conductometry methods.

The bimetallic structure of intermediate complexes formed at low temperature in the $Ni(acac)_2$–$P(OEt)_3$–$AlEt_3$ and analogous systems ($T \leqslant -10\,°C$) may be substantiated on the basis of the experimental results reported below.

The reversible electrochemical reduction is due to Ni^{II} cationic complexes with three organophosphorus ligands requiring no activation energy to rebuild the coordination sphere with the corresponding Ni^{0} complexes formed. The yellow solution is also indicative of the low symmetry in the Ni chemistry.

The electroconductivity of the $Ni(acac)_2$–$P(O\text{-}i\text{-}Pr)_3$ ($Ni/P = 1/4$; $\varkappa = 4.6 \cdot 10^{-7}$ $ohm^{-1}\ cm^{-1}$) system in toluene solution compared with that of the tricomponent system containing additional $AlEt_3$ ($Ni/P/Al = 1/4/4$; $\varkappa = 6.0 \cdot 10^{-6}$ ohm cm^{-1}) indicates a significant rise in the degree of ionization of the tricomponent system. The course of homogeneous reactions generating bimetallic ion complexes at low temperature as in [27] may be described as follows.

The first reaction step gives Ni^{II} monoalkylderivatives stabilized by the organophosphorus ligand (L)

$$Ni(acac)_2 + AlEt_3 + L \xrightarrow{Al/Ni = 2} EtNi(acac)L + AlEt_2(acac) \tag{7}$$

An excess of $AlEt_3$ promotes the next alkylation step

$$EtNi(acac)L + AlEt_3 + L \xrightarrow{Al/Ni > 2} Et_2NiL_2 + AlEt(acac)_2 \tag{8}$$

Subsequent migration of an ethyl ligand from nickel to aluminium results in the bimetallic ion complexes formed and stabilized in solution

$$Et_2NiL_2 + AlEt_3 + L \rightarrow [EtNiL_3]^+[AlEt_4]^- \tag{9}$$

In the presence of olefins and dienes, those complexes are readily transformed by β-elimination to the corresponding hydride bimetallic complexes $[HNiL_3]^+[AlEt_4]^-$ directly involved in catalysis (Scheme 1).

3. $Ni(acac)_2$–$P(OR)_3$–$AlEt_3$ (R = Et, i-Pr; Ni/P/Al = 1/4/4) in the mixture of isopropanol and toluene. The catalytic systems prepared at $-(10\text{–}25)\,°C$ by reaction of $Ni(acac)_2$ with triethylaluminium in the presence of alkyl phosphites in toluene, and then further transferred into a solvent containing 60–70% by volume of isopropanol show high thermostability and effectiveness in norbornene and

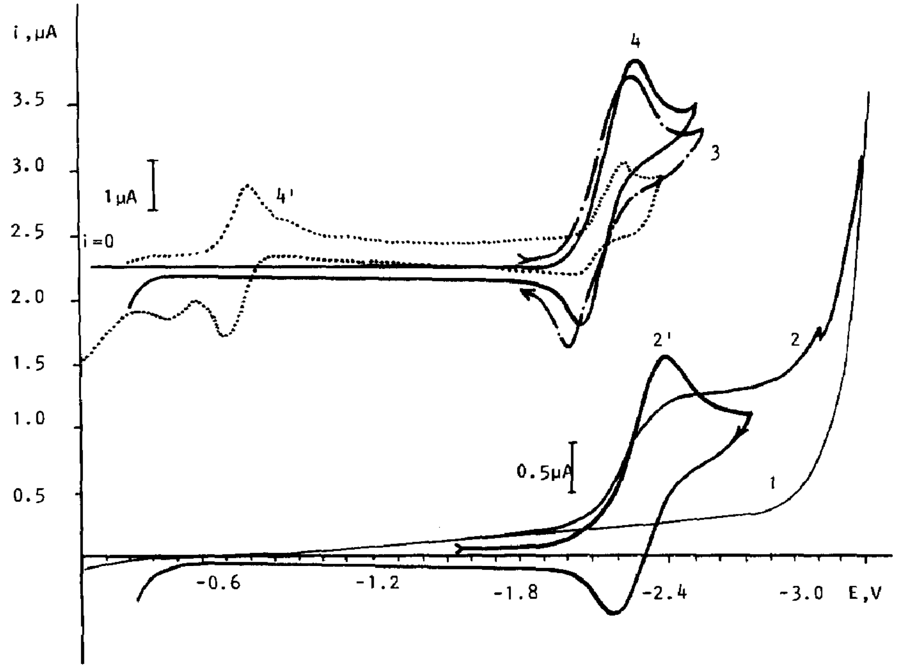


Fig. 9. Classic (2) and cyclic (2', 3, 4, 4') ($v = 1$ V/s, 4 s delay) voltammograms of (2 and 2') – $0.4 \cdot 10^{-3}$ *M* solution of the system $\mathrm{Ni(acac)_2}$–$\mathrm{P(O\text{-}i\text{-}Pr)_3}$–$\mathrm{AlEt_3}$ (Ni/P/Al = 1/4/4) – [A]; (3) – $8 \cdot 10^{-4}$ *M* solution of the system $\mathrm{Ni(acac)_2}$–$\mathrm{P(OEt)_3}$–$\mathrm{AlEt_3}$ (Ni/P/Al = 1/4/4) – [B] in a mixture of PhMe–i-PrOH (1/2); (4) – 10^{-3} *M* solution of system [B] containing monomer and diene – [C]; (4') – 10^{-3} *M* solution of system [C] after 24 h at room temperature in MeCN–PhMe (3/2), 0.1 *M* TBAP (1) at $T = -10\,^\circ$C, T[A] = $-25\,^\circ$C.

norbornadiene co-oligomerizations with allyl acetate [28]. Isopropanol introduced into the catalytic system at $-(10\text{–}25)\,^\circ$C favours the formation of novel Ni complexes. The cyclic voltammograms indicated that the solution had changed, in that they showed the disappearance of a pair of cathode–anode peaks due to the bimetallic ion complexes, and the appearance of a new pair of cathode–anode peaks at much more negative potentials.

For the $\mathrm{Ni(acac)_2}$–$\mathrm{P(OEt)_3}$–$\mathrm{AlEt_3}$ (Ni/P/Al = 1/4/4) system, the pair of cathode–anode peaks ($E_{\mathrm{pc}_1} = -1.72$ V and $E_{\mathrm{pa}_1} = -1.60$ V, $i_\mathrm{a}/i_\mathrm{c} = 0.4$) disappear, and a pair of interconnected peaks of similar height ($E_{\mathrm{pc}_2} = -2.23$ V; $E_{\mathrm{pa}_2} = -2.00$ V; $i_\mathrm{a}/i_\mathrm{c} = 0.7$) (Fig. 9, curve 3) develop.

For the $\mathrm{Ni(acac)_2}$–$\mathrm{P(O\text{-}i\text{-}Pr)_3}$–$\mathrm{AlEt_3}$ (Ni/P/Al = 1/4/4) system, the peaks with $E_{\mathrm{pc}_1} = -1.62$ V, $E_{\mathrm{pa}_1} = -1.42$ V, and $i_\mathrm{a}/i_\mathrm{c} \cong 0.4$ vanish and peaks with $E_{\mathrm{pc}_2} = -2.35$ V, $E_{\mathrm{pa}_2} = -2.12$ V, and $i_\mathrm{a}/i_\mathrm{c} \cong 0.7$ appear (Fig. 9, curves 2, 2').

The cathodic current for the complexes formed in a protic medium corresponds to the formal consumption of 1.8 electrons for a Ni atom (as compared to the limiting current of equimolar $\mathrm{Ni(acac)_2}$).

According to present-day ideas concerning the routes of reactions involving bimetallic ion complexes in protic media, the formation of the novel complexes may be represented as follows according to Scheme 2.

$$[\mathrm{EtNi}\{\mathrm{P(OR)_3}\}_3]^+[\mathrm{AlEt_4}]^- + \mathrm{HOR} \xrightarrow[-\mathrm{L}]{T<0\,^\circ\mathrm{C}} \mathrm{Et_2Ni}\{\mathrm{P(OR)_3}\}_2 + \mathrm{AlEt_3} \cdot \mathrm{HOR} \qquad (10)$$

With the temperature increased, Ni dialkyl derivatives are transformed readily into the monovalent nickel monoalkyl derivatives

$$\mathrm{Et_2Ni\{P(OR)_3\}_2 \xrightarrow[+L]{-C_2H_4,\ -C_2H_6} EtNi\{P(OR)_3\}_3} \qquad (11)$$

This step is marked by the precipitation of a product soluble in the mother liquor at $T > -10\,^{\circ}\mathrm{C}$ (its composition has been corroborated by elemental analysis data and molecular weight measurements [28]). Its catalytic properties begin to show at temperatures above 20 °C. $\mathrm{EtNi\{P(OR)_3\}_3}$ is stabilized at $T > -10\,^{\circ}\mathrm{C}$ by two ways, i.e. by the reduction elimination and β-elimination

$$\begin{tikzcd} \mathrm{EtNi\{P(OR)_3\}_3} \arrow[r, "-C_2H_4"] \arrow[d, "-C_2H_4,\ -C_2H_6"] & \mathrm{HNi\{P(OR)_3\}_3} \\ \mathrm{Ni^0\{P(OR)_3\}_4} & \end{tikzcd}$$

Alcohols and acids can protonate the zerovalent nickel complexes to result in the divalent nickel hydride cationic complexes [29]

$$\mathrm{Ni^0\{P(OR)_3\}_4 + H^+OR^-} \xrightarrow{T>0\,^{\circ}\mathrm{C}} \mathrm{HNi\{P(OR)_3\}_4{}^+ + OR^-} \qquad (13)$$

Similar hydride complexes have been obtained in acetonitrile by the reaction of the zerovalent nickel complex with protonated phosphines and phosphites (acid employed as a proton donor). Complex $\mathrm{HNi\{P(OEt)_3\}_4{}^+}$ undergoes reduction with an E_{pc} of -2.40 V [30], which is similar to the reduction potential of the intermediates registered in a protic medium.

The hydride complexes of mono- and divalent Ni are redox partners with respect to each other, $\mathrm{HNiL_4{}^+/HNiL_3}$, and so, both types may be formed in equal proportions in protic solutions. Their ratio should depend on the conditions of the catalyst formation.

In the presence of monomers, the type and electrochemical properties of these complexes undergo no significant changes (Fig. 9, curve 4). After completion of the monomer co-oligomerization the cyclic voltammogram shows a decrease in the height of the cathodic peak assigned to the hydride cationic complex $\mathrm{HNi\{P(OEt)_3\}_4{}^+}$ reduced, and a new pair of symmetric cathode–anode peaks with much less negative potentials ($E_{\mathrm{pc}} = -0.65$ V; $E_{\mathrm{pa}} = -0.59$ V; $i_{\mathrm{a}}/i_{\mathrm{c}} = 1.0$) (Fig. 9, curve 4′) appears.

The new complexes have yet to be characterized.

Therefore, with fine-electrochemical experiments conducted at low temperatures, $\mathrm{Ni^{II}}$ was not found to undergo fast and significant reduction to the relative phosphine and phosphite complexes of $\mathrm{Ni^0}$ in the reaction of its acetylacetonate with organoaluminium compounds in the presence of the ligands mentioned above. Electrochemical control of the intricate reaction cycle in solutions of these triple systems with an OAC concentration that is gradually increasing, indicated that a Ni/P/Al ratio of 1/4/4 provides the maximum catalytic effect system; the Ni oxidation state is +2 in the stable complexes formed under the conditions employed. These ionic complexes were assumed as $\mathrm{[RNiL_3]^+[AlR_4]^-}$.

Cyclic voltammetry can be usefully applied to monitor the generation and catalytic activity of Ziegler–Natta catalysts (Ni/P/Al = 1/4/4) formed at low temperatures. The scheme was suggested for the formation in situ of ionic catalytic complexes. A number of active Ni complexes, which were isolated from the tricomponent catalytic systems, were thoroughly investigated to determine their electrochemical behaviour.

The tricomponent catalytic system (Ni^{II} acetylacetonate–tertiary phosphite–triethylaluminium) in the optimal ratio, in a mixture of toluene and isopropanol, was found to give Ni^{II} hydride complexes as $HNiL_4^+$ from bimetallic ion intermediates.

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