Electrochemical Reduction of Dicyanobis(tertiary phosphine)nickel(II) Complexes

By **Gino Bontempelli,*** Istituto di Chimica Analitica, Università di Padova, Via Marzolo 1,35100 Padova, Italy
Benedetto Corain and **Luciano De Nardo**, C.N.R., Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione c/o Istituto di Chimica Analitica, Università di Padova, Padova, Italy

Redox reactions of *trans*-$[Ni(CN)_2L_2]$ complexes [L = PEt_3, PPr_3, PBu^t_3, $PEtPh_2$, PEt_2Ph, or $P(C_6H_{11})_3$] at mercury electrodes in acetonitrile solution have been investigated by cyclic voltammetry, controlled-potential electrolysis, and spectrophotometry. With the exception of $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$, which exhibits different behaviour, all the investigated complexes undergo, at least, two subsequent cathodic processes in which the charge-transfer step leads to unstable and unusual dicyanodi(phosphine)-nickel(I) and -nickel(0) complexes respectively, which both decay in a short time to a dimeric nickel(I) species by two different reaction paths. When the neutral ligands are phosphines with sufficient π-acceptor ability a third cathodic process can be detected in which the dimeric nickel(I) species is further reduced to phosphinenickel(0) complexes not containing cyanide as ligand. Reduction mechanisms are proposed which are consistent with the data. The dependence of the reduction potentials on the nature of the phosphine ligands and the stereochemistry of the primary nickel(I) and nickel(0) reduction products are discussed.

It is well known that nickel(II) complexes containing various neutral and anionic ligands can be reduced to complexes of Ni^I and Ni^0 by numerous chemical reducing agents. For example, $[Ni^{II}(CN)_4]^{2-}$ can be reduced to

$[Ni^{I}_2(CN)_6]^{4-}$ and to $[Ni^{0}(CN)_4]^{4-}$ by potassium in liquid ammonia.[1] The dimeric complexes $[Ni^{II}_2(CN)_4(L{-}L)_3]$ ($L{-}L = Ph_2P[CH_2]_nPPh_2$; $n = 3$ or 4) are easily reduced to $[Ni^{I}_2(CN)_2(L{-}L)_3]$ by $Na[BH_4]$ in ethanol,[2,3] and $[Ni^{II}X_2\{P(C_6H_{11})_3\}_2]$ (X = Cl or Br) undergo reduction either to $[Ni^{I}_2X_2\{P(C_6H_{11})_3\}_4]$ or to $[Ni^{0}\{P(C_6H_{11})_3\}_3]$ by sodium in toluene.[4]

Although electrochemical methods, in many cases, afford the most suitable conditions for obtaining unusual oxidation states and allow a more detailed study of the reductive-oxidative mechanisms, they appear to have been neglected in comparison with chemical techniques. In fact only a few electroanalytical investigations on nickel(II) complexes have been reported: $[Ni^{II}(CN)_4]^{2-}$ was cathodically reduced in water to $[Ni^{I}_2(CN)_6]^{4-}$;[5,6] $[Ni^{II}(dppe)_2]^{2+}$ (dppe = $Ph_2P[CH_2]_2PPh_2$) is known to undergo a two-step reduction in acetonitrile at a mercury electrode to give $[Ni^{I}(dppe)_2]^{+}$ and $[Ni^{0}(dppe)_2]$;[7] and several square-planar nickel(II) complexes of cyclic amines have been reduced to the corresponding nickel(I) in acetonitrile at both platinum and mercury electrodes.[8]

In a previous paper[9] we reported the cathodic behaviour of the complex *trans*-$[Ni(CN)_2(PEt_2Ph)_2]$ in an aprotic medium at a mercury electrode. This complex is reversibly reducible to unstable dicyanodi(phosphine)-nickel(I) and -nickel(0) species depending on the applied potential. These species evolve quite rapidly along two different paths to Belluci's analogous dimeric nickel(I) complex $[Ni_2(CN)_2(PEt_2Ph)_4]$. Furthermore, under suitable conditions, $[Ni^{0}(PEt_2Ph)_4]$ can be obtained by direct reduction of $[Ni(CN)_2(PEt_2Ph)_2]$. In order to ascertain whether the observed behaviour is typical of $[Ni(CN)_2L_2]$ (L = phosphine) complexes, we have undertaken an extensive investigation with the purpose of elucidating the role played by the neutral ligands in the electrochemical reduction.

EXPERIMENTAL

Chemicals.—All the chemicals employed were of reagent-grade quality. Reagent-grade acetonitrile was further purified by repeated distilling from phosphorus pentaoxide and stored on molecular sieves (3 Å) under a nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate was prepared from perchloric acid and tetrabutylammonium hydroxide and twice crystallized from methanol. All the complexes investigated, with the exception of $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$, were synthesized as reported in the literature.[10-12]

trans-Dicyanobis(tricyclohexylphosphine)nickel(II) was prepared by stirring at 50 °C a suspension of $[NiCl_2\{P(C_6H_{11})_3\}_2]$ (0.60 g, 1 mmol) and sodium cyanide (0.1 g, 2 mmol) in methanol (50 cm^3) until a limpid yellow solution was obtained (*ca.* 1 h). After concentration to 10 cm^3 *in vacuo* at 0 °C, yellow crystals were obtained which were recrystallized from methanol and dried *in vacuo* (Found: C, 68.65; H, 9.70; N, 4.25. Calc. for $C_{38}H_{66}N_2NiP_2$: C, 67.95; H, 9.85; N, 4.15%). The i.r. spectrum of the complex in Nujol shows a medium-intensity band at 2 110 cm^{-1} [ν(CN)] with a hump at 2 115 cm^{-1} which is not present when the spectrum is recorded for a solution of the complex in CH_2Cl_2. The presence of a single ν(CN) band in solution is consistent with the proposed *trans* geometry.

Stock solutions of the investigated complexes were prepared by dissolving weighed amounts of these reagents in the degassed 0.1 mol dm^{-3} $[NBu_4][ClO_4]$–MeCN solvent. Nitrogen (99.99%), previously equilibrated to the vapour pressure of acetonitrile, was used to remove dissolved oxygen.

Apparatus and Procedure.—Voltammetric experiments were carried out in a three-electrode cell. Either a dropping mercury electrode (d.m.e.) with mechanical control of the drop time or a gold sphere freshly covered with mercury was used as working electrode while the counter electrode was a platinum spiral surrounding the working electrode. The potential of the working electrode was probed by a Luggin-capillary reference-electrode compartment whose position was made adjustable by mounting it on a syringe barrel. Coulometric and preparative tests were carried out in an H-shaped cell with cathodic and anodic compartments separated by a sintered glass disc. Both working and counter electrodes were a mercury pool. In each case an aqueous saturated calomel electrode (s.c.e.) was used as reference. The voltammetric unit was a three-electrode system assembled with MP-System 1000 equipment in conjunction with a digital logic-function generator made up in these laboratories;[13] the recording device was a Hewlett–Packard 7004 B X-Y recorder or 1201 A oscillograph depending on the scan rate employed. In the controlled-potential electrolyses an Amel model 557 SU potentiostat was used and the associated coulometer was an Amel model 558 integrator.

Ultraviolet spectra were recorded with a Perkin-Elmer model 402 spectrophotometer.

For the detection of metallic nickel, suitable amounts of the electrolyzed solutions were filtered through a sintered glass crucible; the recovered precipitate, washed with dichloromethane to remove trace amounts of nickel complexes, was dissolved in the minimum volume of hot concentrated nitric acid. The resulting solution was assayed by the standard dimethylglyoxime test.

RESULTS

The complexes $[Ni(CN)_2L_2]$ (L = substituted phosphine) were studied at a stationary mercury microelectrode in acetonitrile solution by cyclic voltammetry. All the complexes investigated, with the exception of $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$, exhibited at least two cathodic peaks; the corresponding peak potential values are collected in the Table. In order to check the effect of the nature of the anionic ligand on the cathodic reduction, we report also the peak potential values for the complex $[NiCl_2(PPr_3)_2]$.

---

[1] J. W. Eastes and W. M. Burges, *J. Amer. Chem. Soc.*, 1942, **64**, 1187.

[2] B. Corain, M. Bressan, P. Rigo, and A. Turco, *Chem. Comm.*, 1968, 509.

[3] B. Corain, *Gazzetta*, 1972, **102**, 687.

[4] M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.

[5] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1957, **22**, 948.

[6] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1736.

[7] M. Martelli, G. Pilloni, G. Zotti, and S. Daolio, *Inorg. Chim. Acta*, 1974, **11**, 155.

[8] D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.

[9] G. Bontempelli, B. Corain, and F. Magno, *Analyt. Chem.*, 1977, **49**, 1005.

[10] P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, 1967, **6**, 1636.

[11] P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, 1968, **7**, 1623.

[12] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

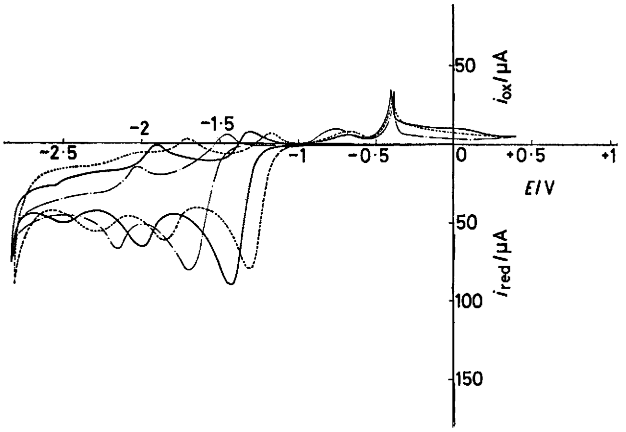
[13] F. Magno, G. Bontempelli, G. A. Mazzocchin, and I. Patanè, *Chem. Instr.*, 1975, **6**, 239.

All the dicyano-complexes in the Table, except that containing $P(C_6H_{11})_3$, exhibit anodic peaks associated with the first two cathodic ones even at scan rate of 0.05 V s^{-1}, thus indicating a significant degree of stability of the reduction products. As typical cyclic-voltammetric pictures obtained on the investigated complexes, the Figure shows the cathodic behaviour exhibited by acetonitrile solutions of $[Ni(CN)_2(PEt_3)_2]$, $[Ni(CN)_2(PEt_2Ph)_2]$, and $[Ni(CN)_2(PEtPh_2)_2]$ respectively. When the scan rate was <30 V s^{-1} the ratio between the height of the anodic peak and that of the corresponding cathodic peak was $<1:1$ both for the first and the second process and for all the complexes (1)—(6), thus indicating that the primary reduction products undergo fast chemical decay under the employed experimental conditions.

Reduction potentials (V) for $[Ni(CN)_2L_2]$ complexes at a mercury electrode. Peak potentials from cyclic voltammograms at a scan rate of 0.2 V s^{-1} are quoted *versus* an aqueous s.c.e.

Complex *	$E_p(c_1)$	$E_p(c_2)$	$E_p(c_3)$
trans-$[Ni(CN)_2(PBu^t_3)_2]$ (1)	-2.06	-2.54	
trans-$[Ni(CN)_2(PPr_3)_2]$ (2)	-1.89	-2.26	
trans-$[Ni(CN)_2(PEt_3)_2]$ (3)	-1.75	-2.15	-2.70
trans-$[Ni(CN)_2(PEt_2Ph)_2]$ (4)	-1.44	-2.00	-2.60
trans-$[Ni(CN)_2(PEtPh_2)_2]$ (5)	-1.38	-1.86	-2.20
cis-$[Ni(CN)_2(dppe)]$ (6)	-1.26	-1.57	-2.00
trans-$[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$ (7)	-2.00		
trans-$[NiCl_2(PPr_3)_2]$ (8)	-1.05	-1.25	-1.50

* The complexes $[Ni_2(CN)_4\{Ph_2P(CH_2)_4PPh_2\}_3]$ and $[Ni_2(CN)_4\{Ph_2P(CH_2)_3PPh_2\}_3]$ mentioned in the introduction are too insoluble in acetonitrile.



Cyclic-voltammetric curves recorded at a mercury-covered gold microelectrode in 0.1 mol dm^{-3} $[NBu_4][ClO_4]$–MeCN solutions of: (– – – –) 4.4×10^{-3} mol dm^{-3} $[Ni(CN)_2(PEtPh_2)_2]$, (——) 5×10^{-3} mol dm^{-3} $[Ni(CN)_2(PEt_2Ph)_2]$, and (— · — · —) 4.5×10^{-3} mol dm^{-3} $[Ni(CN)_2(PEt_3)_2]$. Scan rate, 0.2 V s^{-1}. The cycles start from 0.0 V and proceed towards negative potentials

The transfer coefficient α relative to the first cathodic process was found to be 0.50 ± 0.05 (assuming $n = 1$) for complexes (1)—(7) of the Table. The αn values were estimated by three different methods: measuring the ΔE_p values between the cathodic and the associated anodic peaks [with the exception of complex (7)]; measuring the difference between the E_p and the $E_{p/2}$ values relative to each of the cathodic peaks; and logarithmic analysis of the polarographic waves recorded on the same solution employed for the other measurements. Attribution of the value 1 to n is based on a comparison of the peak heights measured for solutions of complexes (1)—(3) and (5)—(7) with that of $[Ni(CN)_2(PEt_2Ph)_2]$ for which the occurrence of a one-electron reduction process has been shown unambiguously.[9] On the basis of the constancy of the α value for all the investigated complexes, it seems worthwhile to point out that this finding makes possible a reliable correlation of the reduction potentials and the effect of the neutral ligands.

For the complex $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$, only a single cathodic peak with no associated anodic partner, in the same potential region, could be observed even at a very high scan rate (100 V s^{-1}).

As already found for $[Ni(CN)_2(PEt_2Ph)_2]$,[9] we have ascertained that the two anodic peaks located at *ca.* -0.5 V (see Figure), observed for all the complexes (1)—(7), are due to mercury oxidation in the presence of free cyanide ions released in the previously mentioned chemical decay of the primary reduction products. A check of this last statement was made by cyclic voltammetry in which the explored potential range was suitably limited in order to avoid the involvement of the second cathodic reduction.

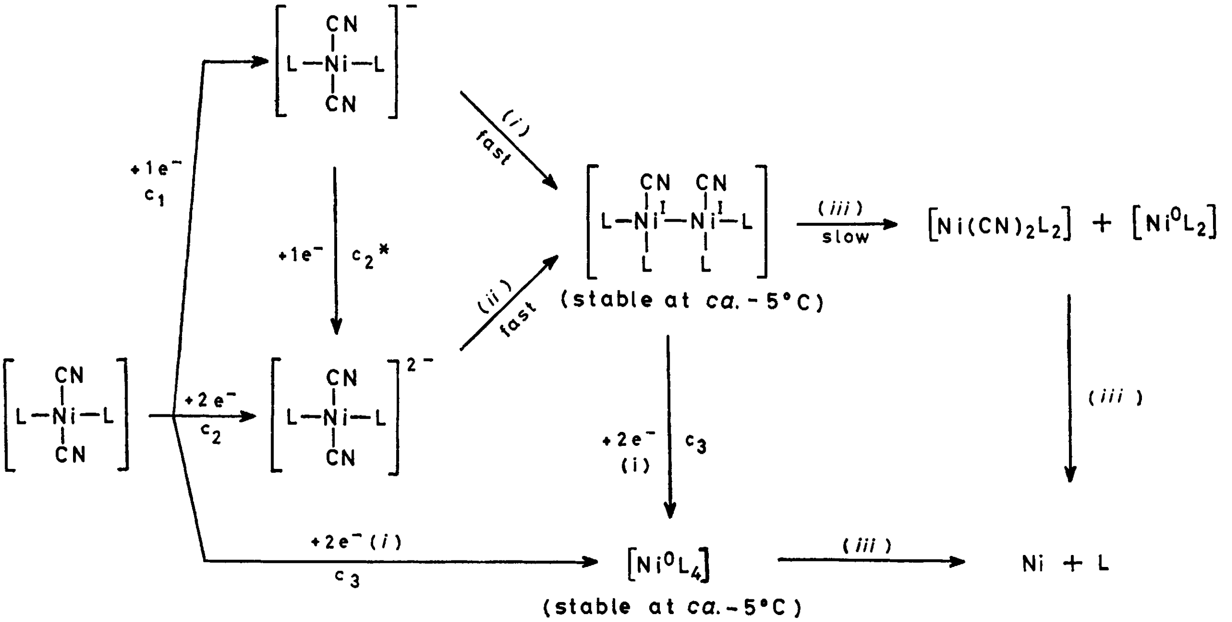
Controlled-potential coulometric experiments carried out both at room temperature and at -5 °C for each cathodic process for solutions of each of the complexes (1)—(3), (5), and (6), coupled with cyclic-voltammetric tests performed at various times after completion of the electrolyses, gave the same results as those obtained for $[Ni(CN)_2(PEt_2Ph)_2]$.[9]

On the basis of these close analogies between the electrochemical behaviour of complexes (1)—(3), (5), and (6), and that of $[Ni(CN)_2(PEt_2Ph)_2]$ (4), we propose that all the electrode and chemical events undergone by the complexes in the course of the controlled-potential electrolyses can be summarized in the Scheme [for the sake of simplicity, the stoicheiometric coefficients have been neglected; complex (6) has a *cis* structure]. The formation of the dimeric complexes $[Ni_2(CN)_2L_4]$ in the chemical decay of $[Ni(CN)_2L_2]$ is proposed on the basis of the concomitant cyanide release, and of the correspondence between the voltammetric-analysis results (scan rate and temperature effect) obtained for complexes (1)—(3), (5), and (6), and those obtained for (4) for which the dimeric nature of the reaction product was supported by spectrophotometric analysis.[9] The slow disproportionation reaction which the $[Ni_2(CN)_2L_4]$ complexes undergo at room temperature has been checked by following voltammetrically the spontaneous reformation of $[Ni(CN)_2L_2]$ in solutions obtained by exhaustive electrolyses carried out at potentials corresponding to the first reduction process. Obviously the third cathodic process reported in this Scheme does not refer to complexes (1) and (2) (see Table), as the solvent discharge reasonably occurs at less negative potentials than that required for these processes.

When the electrochemical data imply that nickel(0) species are formed, as a consequence either of the disproportionation of $[Ni_2(CN)_2L_4]$ species or of the exhaustive electrolyses corresponding to the third cathodic process [complexes (3)—(6)], we found only finely divided metallic nickel and free phosphine at room temperature. These observations apparently indicate that the relevant nickel(0) complexes are unstable under the experimental conditions employed.

The disproportionation reaction between $[Ni(CN)_2L_2]^{2-}$, generated at cathodic peak c_2, and the depolarizer, $[Ni(CN)_2L_2]$, present in the bulk of the solution and which diffuses towards the electrode surface, must be admitted on the basis of the relative values of the redox potentials of these species. The electrode oxidation of the nickel(0) species occurs, in each case, at more negative potentials than those at which the parent nickel(II) complex is reduced. Moreover, the voltammetric picture obtained after exhaustive electrolyses both at c_1 and at c_2 (see Scheme) was qualitatively and quantitatively the same.

Some experiments carried out at potentials corresponding to the single cathodic process displayed by solutions of $[\mathrm{Ni(CN)_2\{P(C_6H_{11})_3\}_2}]$ gave an n_{e^-} value of 1 as found for the first cathodic process of the other cyano-complexes. However, in contrast to the red-orange colour of the clear solutions obtained when complexes (1)—(6) were reduced, a pale yellow turbid solution was obtained starting from $[\mathrm{Ni(CN)_2\{P(C_6H_{11})_3\}_2}]$. The visible spectrum of this last solution, recorded at *ca.* 0 °C, displayed a weak tail into the u.v. with no resemblance to the spectrum observed for $[\mathrm{Ni_2(CN)_2(PEt_2Ph)_4}]$.[9]



Scheme (*i*) $-[\mathrm{CN}]^-$; (*ii*) $+[\mathrm{Ni(CN)_2L_2}]$; (*iii*) *ca.* 20 °C
This reduction step is relevant only to cyclic-voltammetric experiments

Voltammetric analysis of acetonitrile solutions of $[\mathrm{NiCl_2(PPr_3)_2}]$ indicated that this complex is dissociated to some extent, as free chloride ions were detected in anodic scans even when the first cathodic peak was not traversed. Moreover, the three reduction processes appear to occur in a remarkably narrow potential range and the products generated corresponding to the first two cathodic peaks appear to decay more rapidly than in the case of the dicyano-complexes, as indicated by the very low height of the associated anodic peaks.

DISCUSSION

The results show that $[\mathrm{Ni(CN)_2L_2}]$ complexes, except $[\mathrm{Ni(CN)_2\{P(C_6H_{11})_3\}_2}]$, can be electrochemically reduced in steps to unstable and unusual four-co-ordinate nickel(I) and nickel(0) complexes. The chemical decay of these primary reduction products affords other more stable nickel(I) and nickel(0) complexes (see Scheme). The high degree of reversibility displayed by the electrochemical processes $\mathrm{Ni^{II}} \rightleftharpoons \mathrm{Ni^{I}}$ and $\mathrm{Ni^{I}} \rightleftharpoons \mathrm{Ni^{0}}$ (peaks c_1 and c_2) is a remarkable finding which suggests structural implications. These charge-transfer processes may be accompanied by significant structural changes (*i.e.* geometric modifications of the redox partners). If such changes do not occur, the nickel(I) and nickel(0) complexes obtained at the electrode surface should possess an essentially square-planar structure. On the other hand if these modifications do occur they can take place either after or before the electron-transfer step. In other words the electron taken up in the first cathodic process, for instance, can be accommodated in the undistorted nickel(II) complex and the resulting nickel(I) species subsequently undergoes a square planar–tetrahedral isomerization; alternatively the nickel(II) complex can undergo this isomerization in the electric double layer before the electron uptake.

It should be pointed out that high degrees of reversibility displayed in the cathodic reduction of all the $[\mathrm{Ni(CN)_2L_2}]$ complexes investigated are found to be associated with activation energies $\leqslant 3$ kcal mol^{-1} (work in progress) and this value appears to be important in discussing the processes reported. In fact the hypothesis of a preliminary tetrahedral distortion can be ruled out as such a process would certainly require an activation energy far greater than 3 kcal mol^{-1}, as the ligand set $(\mathrm{CN})_2\mathrm{L}_2$ is known to produce only nickel(II) complexes with square-planar geometry both in the solid state and in solution.[14]

A square planar–tetrahedral isomerization following the electron-transfer step would be accompanied by a decrease in free energy. This ΔG value has to range from zero to that of the activation free energy $\Delta G^{\ddagger}$ [if the activated state is just the square-planar nickel(I) complex] of the reduction process. Hence for the

---

[14] P. Rigo and A. Turco, *Co-ordination Chem. Rev.*, 1974, **13**, 133.

isomerization $[Ni^{I}(CN)_2L_2]^-$(planar) $\rightleftharpoons$ $[Ni^{I}(CN)_2L_2]^-$(tetrahedral) a value ranging from 1 to *ca.* 10^2 is expected for the equilibrium constant. As a consequence of these arguments it can be concluded that the four-co-ordinate nickel(I) species, formed in the first cathodic process, should have either a square-planar structure or a not very much more stable tetrahedral configuration.

As far as the four-co-ordinate nickel(0) structure is concerned, similar arguments to those used for the parent nickel(I) species can be used if the latter is square planar. However, in this case, the possibility of a preliminary isomerization of the parent nickel(I) species in the electric double layer cannot be ruled out as it is not known whether the ligand set $(CN)_2L_2$ is able to stabilize the square-planar structure in nickel(I) complexes as in the case of Ni^{II}. On the other hand, if the parent nickel(I) complex is tetrahedral, the high degree of reversibility exhibited by the second cathodic process can be simply interpreted in terms of the formation of a nickel(0) complex displaying a tetrahedral geometry, which is the only known structure for four-co-ordinate nickel(0) complexes reported in the literature.[15]

As regards the chemical reactions following the charge transfer steps, the disproportionation reaction leading to $[Ni_2(CN)_2L_4]$ through the reaction path corresponding to c_2 is the obvious consequence of the electrode oxidation of $[Ni(CN)_2L_2]^{2-}$ at potentials lower than those at which $[Ni(CN)_2L_2]$ is found to be reduced (see Figure). A quite similar redox reaction has been used by Heimbach [16] to prepare the complexes $[NiX(PPh_3)_3]$ ($X = Cl$, Br, or I). The chemical decay of the species $[Ni(CN)_2L_2]^-$, generated in the first cathodic process, is likely to occur, in our opinion, through a simple dissociative mechanism, which implies 'slow' release of one cyanide ion followed by 'fast' coupling of the $Ni(CN)L_2$ radical formed to give the corresponding dimeric nickel(I) complex. Alternatively, the cyanide-ion release could occur through a solvent-assisted mechanism which we do not prefer as it should require the formation of a probably energetically unfavourable five-co-ordinate activated complex.

The remarkably higher lability of the anion $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]^-$ suggests that the above mechanism is not operative in this case, as the general properties of $P(C_6H_{11})_3$ do not appear to be so much different from those of the other phosphines employed to justify the observed dramatic change in the lability of the reduction product. A possible alternative chemical decay of $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]^-$ could be based on the release of both $P(C_6H_{11})_3$ and cyanide ions. On the other hand, the visible–u.v. spectra of the electrolyzed solutions clearly indicate that the complex $[Ni_2(CN)_2\{P(C_6H_{11})_3\}_4]$ is not formed, thus indicating that other products are produced in the chemical decay of the anionic nickel(I) complex.

As a brief comment on the voltammetric behaviour of $[NiCl_2(PPr_3)_2]$ it can be observed that the cathodic processes occur at potentials less cathodic than those found for the dicyano-complexes (1)—(6), and in particular at far less negative values than those corresponding to $[Ni(CN)_2(PPr_3)_2]$. These findings strongly suggest that the electrochemical behaviour of $[NiCl_2(PPr_3)_2]$ is similar to that exhibited by complexes (1)—(6), the major difference being the easier reducibility of the nickel species involved, reasonably due to their presence in solution as co-ordinatively unsaturated species, as a consequence of dissociative processes preceding the electron uptake {as ascertained for a solution of $[NiCl_2(PPr_3)_2]$ for which the presence of free chloride ions has been detected}.

The potentials corresponding to the three cathodic processes for complexes (1)—(5) (Table) appear to depend markedly on the nature of the neutral ligands co-ordinated to Ni^{II} and Ni^{I} respectively. The observed trends indicate unambiguously that, with increasing π-acceptor ability of the phosphines, the reduction of $[Ni(CN)_2L_2]$ to $[Ni(CN)_2L_2]^-$ [$E_p(c_1)$] and of $[Ni(CN)_2L_2]^-$ and $[Ni_2(CN)_2L_4]$ to Ni^0 [$E_p(c_2)$ and $E_p(c_3)$ respectively] becomes easier. The phosphine ligands employed yield the following sequence of ease of electron uptake in the cathodic processes investigated: $PEtPh_2 > PEt_2Ph > PEt_3 > PPr_3 > P(C_6H_{11})_3 > PBu_3$. This sequence is in agreement with that of the decreasing π-acceptor ability estimated on the basis of spectroscopic data by Tolman,[17] with the exception of $P(C_6H_{11})_3$ which is expected to be the worst π-acceptor ligand of those reported.[15] The mutual positions of $P(C_6H_{11})_3$ and PBu_3 can be justified on considering that in the case of the complex $[Ni(CN)_2\{P(C_6H_{11})_3\}_2]$ the charge transfer is followed by an irreversible and very fast chemical reaction, the ΔG of which is expected to produce a significant shift of $E_p(c_1)$ to less negative potentials.

The values of the reduction potential relative to the complex *cis*-$[Ni(CN)_2(dppe)]$ are very close to those found for *trans*-$[Ni(CN)_2(PEtPh_2)_2]$, as expected on the basis of the very similar electronic nature of the moiety Ph_2PCH_2 compared with the phosphine $PEtPh_2$. The less negative values observed for complex (6) apparently indicate that the *trans* complexes are significantly more stable against reduction than the corresponding *cis* isomers.

As a final comment it can be observed that the destiny of the primary reduction product of four-co-ordinate nickel(II) complexes depends markedly on the presence of anionic ligands in the co-ordination sphere of Ni^{II}. Thus the reduction products of $[Ni(CN)_4]^{2-}$ (refs. 5 and 6) and of $[Ni(CN)_2L_2]$ evolve to more stable dimeric nickel(I) species through an easy release of one anionic ligand, while species like $[Ni(dppe)_2]^{2+}$ (ref. 7) are reduced to complexes which are reluctant to release one neutral ligand (or one co-ordination arm) to give three-co-ordinate species able to undergo the subsequent dimerization.

We thank C.N.R. (Rome) for partial support.

[7/209 *Received, 7th February,* 1977

---

[15] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1.

[16] P. Heimbach, *Angew. Chem.*, 1964, **76**, 586.

[17] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2953.