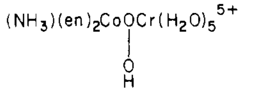
reduction of $Ti(O_2)(edta)^{2-}$ by $Ti(edta)(H_2O)^-$ in this work. Sykes has shown that species **10** is reduced by Cr^{2+} in an



$$(NH_3)(en)_2Co\underset{\substack{| \\ O \\ H}}{O}Cr(H_2O)_5^{5+}$$

10

outer-sphere step.[24] At 35 °C the scavenging of **10** by Cr^{2+} is rapid with a second-order rate constant of $\geq 10^2\ M^{-1}\ s^{-1}$. An intermediate containing an O_2^{3-} bridging ligand of bond order 0.5 is produced (**11**) which has the similar structure shown for **10** but a charge of 4+.[24,31] The intermediate **11** decays by a first-order process with $k \sim 2.1 \times 10^{-2}\ s^{-1}$, forming the hydroxy bridged Co^{III}–Cr^{III} complex **12** with liberation of hydroxyl radical as shown in eq 18. In the presence of excess

$$\underset{\mathbf{11}}{(NH_3)_5Co(O_2H)Cr(H_2O)_5^{4+}} \xrightarrow{H^+} \underset{\mathbf{12}}{(NH_3)_5CoO(H)Cr(H_2O)_5^{5+}} + HO\cdot \quad (18)$$

Cr^{2+}, the hydroxyl radical is rapidly scavenged, forming $CrOH^{2+}$. The steps in the Cr^{2+} reduction of **10** are very similar to the reduction of the peroxo ligand of $Ti(O_2)(edta)^{2-}$ by $Ti(edta)(H_2O)^-$. Step 16 is analogous to the rapid reduction of **10** forming **11**.[28] Indeed both rates are of the order of $10^2\ M^{-1}\ s^{-1}$ although the titanium reaction (eq 16) has the same kinds of thermodynamic and electrostatic advantages as mentioned for the reduction of the superoxo ligand of $Ti(O_2)(edta)^-$. The O_2^{3-} bridging group (protonated as HO_2^{2-} in the Co^{III}/Cr^{III} system) appears to be much more stable since the ejection of hydroxyl radical is detectable in a separate step (eq 18) for Sykes' system while the Ti(IV) complex is much more rapidly reorganized to the final $TiO(edta)^{2-}$ product. The greater stability of **11** might be due to the effect of two withdrawing metal centers. In both cases an oxo ligand is left behind at the metal center which binds peroxo. In the reduction of **10**, the oxo ligand becomes protonated in species (**12**) under the highly acidic conditions required for the Cr^{2+} reagent, while for the Ti(IV) complex at pH ~5 of this study, the oxo ligand exists alone.

It is interesting that the actual reduction step forming either **11** or the Ti(IV) analogue $Ti(O_2)(edta)^{3-}$ occurs at nearly the same rate of $\sim 10^2\ M^{-1}\ s^{-1}$. As mentioned above, the lability of $Ti(edta)(H_2O)^-$ prevents an unambiguous assignment of mechanism for reaction 16; however, the likely conclusion is that the reduction of the peroxo group is an outer-sphere event. The closeness in the rates for the highly dissimilar cases described here suggests that bond reorganization factors within the O_2^{3-} of HO_2^{2-} ligand,[31] and less on the attached metal centers, determine the rate of formation of this species. Once formed, however, the rate of ejection of hydroxyl radical is very sensitive to the charges and number of metal centers to which O_2^{3-} or HO_2^{2-} is attached.

Acknowledgment. We thank the donors from the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $TiO(edta)^{2-}$, 77400-11-4; H_2O_2, 7722-84-1; $Ti(edta)(H_2O)^-$, 74111-14-1; $Ti(O_2)(edta)^{2-}$, 77400-12-5; $TiO(edtaH_2)(H_2O)$, 77400-13-6; $TiO(edtaH)(H_2O)^-$, 77400-14-7; $TiO_2(edta)^-$, 77400-15-8.

(31) The first empty orbital of H_2O_2 or O_2^{2-} has σ^* symmetry: cf. W. L. Jorgenson and L. Salen, "The Organic Chemists' Book of Orbitals", Academic Press, New York, 1973, p 112. The existence of O_2^{3-} or O_2H^{2-} is only likely in the presence of strongly withdrawing groups such as transition-metal centers in high oxidation states.

Contribution from the Istituto di Chimica Analitica, University of Padova, the CNR Laboratorio di Polarografia ed Elettrochimica Preparativa, and the CNR Centro di Studi sulla Stabilità e Reattività dei Composti di Coordinazione, 35100 Padova, Italy

Influence of the Nature of Tricovalent Phosphorus Ligands on the Relative Stability of Nickel(II), Nickel(I), and Nickel(0). An Electroanalytical Approach Providing Thermodynamic and Structural Information

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The cathodic behavior of anhydrous nickel(II) perchlorate in the presence of a variety of tricovalent phosphorus ligands has been investigated in acetonitrile. A combination of electroanalytical and spectrophotometric measurements have made possible the synthesis and the characterization of various nickel(0), nickel(I), and nickel(II) complexes. The employed electroanalytical tools have also made it possible to demonstrate that phosphine ligands such as PPh_3, $PEtPh_2$, PEt_2Ph, PEt_3, and dppe stabilize the +1 oxidation state with respect to the 0 and +2 ones, while the phosphites $P(OPh)_3$ and $P(OEt)_3$ act in the opposite way. The complex $[Ni^I(P(OEt)_3)_4]^+$ can be, however, prepared and accumulated thanks to kinetic reasons. These techniques have allowed also information on the geometric configuration of the synthesized species to be obtained. Moreover, the reversible half-wave potentials relative to the redox processes $Ni^0 \rightleftarrows Ni^I + e^-$ have made possible the ranking of the employed ligands in a thermodynamically well-grounded sequence of ligand properties relative to their ability to stabilize the lower oxidation states of nickel. In the case of $P(OPh)_3$, a bis(phosphite)nickel(0) complex has been clearly identified and synthesized.

Introduction

The +1 oxidation state in nickel complexes could be considered "rare" till about ten years ago.[1] In this last decade the family of nickel(I) complexes has grown a great deal, and the occurrence of the +1 state in the reaction patterns of nickel organometallic species is now well recognized.[2,3] Not surprisingly, a significant number of authentic nickel(I) complexes has been prepared by electrochemical procedures in the last

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1972.

(2) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319–6332.

(3) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547–7560.

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Table I. Peak Potential Values (V) Recorded on a Platinum Microelectrode from Cyclic Voltammograms at a Scan Rate of 0.1 V s^{-1} Quoted vs. an Aqueous SCE

system in CH_3CN	molar ratio	$(E_p)_c$ $Ni^{II} \rightarrow Ni^0$	$(E_p)_a$ $Ni^0 \rightarrow Ni^{II}$	$(E_p)_c$ $Ni^{II} \rightarrow Ni^I$	$(E_p)_a$ $Ni^I \rightarrow Ni^{II}$	$E_{1/2}^{r\,a}$ $Ni^I \rightleftarrows Ni^0$
Ni		−1.10	+0.20			
Ni-PPh_3	⩾1:2	−0.88			+0.20	−0.78
Ni-$PEtPh_2$	⩾1:2	−0.98			+0.10	−0.92
Ni-PEt_2Ph	1:2	−1.06			+0.03	−0.98
	⩾1:4			−0.19	+0.03	−0.98
Ni-PEt_3	1:2	−1.18			−0.26	−1.08
	⩾1:4			−0.48	−0.26	−1.08
Ni-dppe	⩾1:2			−0.25	−0.19	−0.45
Ni-$P(c\text{-}Hx)_3$	⩾1:2	−1.70	+0.15			
Ni-$P(OEt)_3$	⩾1:5	−0.78	+0.62		+0.65	−0.18
Ni-$P(OPh)_3$	1:2	−1.26	−0.05			
	⩾1:4	−1.26	+0.41			
Ni-$P(O\text{-}o\text{-}tol)_3$	⩾1:2	−0.96	−0.05			

[a] Determined as the mean value of $(E_p)_a$ and $(E_p)_c$ for the reversible systems investigated.

decade.[4] However, the influence of the nature of the coordinated ligands on the stability of this oxidation state appears to have not been rationalized so far.

We have recently published a paper dealing with the cathodic behavior of electrogenerated anhydrous nickel perchlorate in acetonitrile in the presence of triphenylphosphine.[4f] In this paper we have reported that $[Ni^I(PPh_3)_4]^+$ can be prepared along different electrochemical routes, and it proves to be a species thermodynamically stable toward valence disproportionation. We have also observed that electrochemical information may be a valuable tool in the reliable estimate of the stability of an "intermediate" oxidation state, as it is in this case of the +1 one.

On the basis of this observation and in the light of our general interest on the chemical and electrochemical behavior of nickel(0) and nickel(I) species,[4f,5] we have studied the cathodic behavior of nickel(II) in the presence of a variety of phosphorus ligands in acetonitrile.

Experimental Section

Chemicals. All the chemicals employed were of reagent grade quality. Reagent grade acetonitrile was further purified by distilling repeatedly from phosphorus pentoxide and stored over molecular sieves (3 Å) under nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from methanol, and dried in a vacuum oven at 50 °C.

Stock solutions of anhydrous nickel(II) perchlorate in acetonitrile were prepared by anodic oxidation of metallic nickel in TBAP–acetonitrile solutions as previously described.[5c]

All the ligands available as liquids were distilled just prior of their use and added to the cell, under nitrogen, with a microsyringe.

The complexes $[Ni(PPh_3)_4]$ and $[Ni(P(OPh)_3)_4]$ were synthesized as reported in the literature.[6] Fully deoxygenated nitrogen, previously equilibrated to the vapor pressure of acetonitrile, was used in the removal of dissolved oxygen.

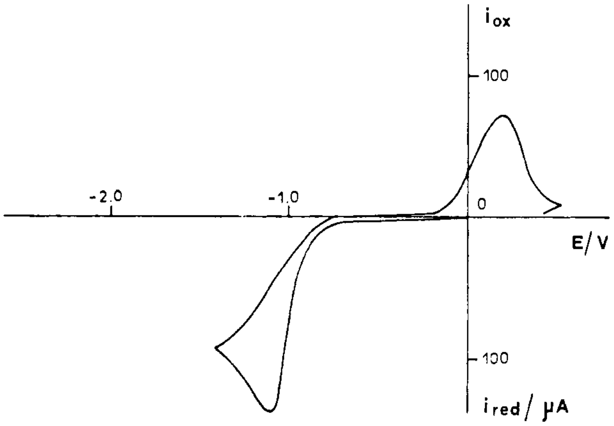

Figure 1. Cyclic voltammetric curve recorded with a platinum microelectrode in a 3 × 10^{-3} M $Ni(ClO_4)_2$, 0.1 M TBAP, CH_3CN solution (scan rate 0.1 V s^{-1}).

Apparatus and Procedure. Voltammetric experiments were carried out in a three-electrode cell. The working electrode was either a platinum or a glassy carbon disk surrounded by a Pt-spiral counterelectrode. 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 a H-shaped cell with cathodic and anodic compartments separated by a sintered glass disk. The working electrode was either a platinum gauze or a glassy carbon bar, while a mercury pool was used as the counterelectrode.

In all cases, an aqueous SCE was used as reference electrode. The employed voltammetric unit was a three-electrode system assembled with the MP-system 1000 equipment in conjunction with a digital logic function generator made in these laboratories.[7] The recording device was either a Hewlett-Packard 7040 A X-Y recorder or a Hewlett-Packard Memory Scope, Type 1201 A.

In the controlled-potential electrolyses, an Amel Model 552 potentiostat was used and the associated coulometer was an Amel integrator Model 558. In the spectrophotometric measurements, a Cary 40 spectrophotometer was employed.

The electroanalytical measurements were performed, unless otherwise stated, at 20 °C.

Results

The voltammetric picture exhibited by electrogenerated nickel(II) perchlorate in acetonitrile is reported in Figure 1. As previously reported by us,[5c] the species $[Ni(CH_3CN)_6]^{2+}$ is cathodically reduced in an irreversible two-electron process to metallic nickel, which can be reoxidized to nickel(II) in the

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(4) See, for example: (a) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611–1621. (b) Martelli, M.; Pilloni, G.; Zotti, G.; Daolio, S. *Inorg. Chim. Acta* **1974**, *11*, 155–158. (c) Geiger, W. E., Jr.; Allen, C. S.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1977**, *16*, 2003–2008. (d) Bowden, W. L.; Holloway, J. D. L.; Geiger, W. E., Jr. *Ibid.* **1978**, *17*, 256–260. (e) Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972–976. (f) Bontempelli, G.; Magno, F.; Corain, B.; Schiavon, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 243–250.

(5) (a) Bontempelli, G.; Corain, B.; Magno, F. *Anal. Chem.* **1977**, *49*, 1005–1008. (b) Bontempelli, G.; Corain, B.; De Nardo, L. *J. Chem. Soc., Dalton Trans.* **1977**, 1887–1891. (c) Corain, B.; Bontempelli, G.; De Nardo, L.; Massocchin, G. A. *Inorg. Chim. Acta* **1978**, *26*, 37–40. (d) Seeber, R.; Mazzocchin, G. A.; Bontempelli, G.; Magno, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *92*, 215–220. (e) Magno, F.; Bontempelli, G.; Corain, B. *J. Chem. Soc., Faraday Trans. 1*, **1979**, *75*, 1330–1336.

(6) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1, pp 105–106.

(7) Magno, F.; Bontempelli, G.; Mazzocchin, G. A.; Patane, I. *Chem. Instrum.* (*N.Y.*) **1975**, *6*, 239–257.

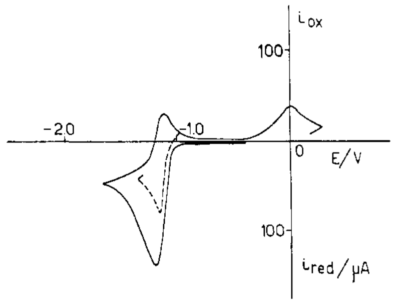

Figure 2. Cyclic voltammetric curves recorded with a platinum microelectrode in a 3×10^{-3} M $Ni(ClO_4)_2$, 0.1 M PPh_3, 0.1 M TBAP, CH_3CN solution (scan rate 0.1 V s^{-1}).

associated anodic peak. The addition of phosphines and phosphites causes profound changes in the observed voltammetric behavior due to the formation of nickel complexes of the metal in low oxidation states.

The results obtained with ligands displaying similar behavior are reported in the following separate sections.

A. Triphenylphosphine (L = PPh_3) and Ethyldiphenylphosphine (L = $PEtPh_2$). The presence of these ligands modifies in the same way the voltammetric behavior of nickel(II) solutions for any employed ligand to nickel molar ratio higher than 2:1, the only difference being the potentials at which the electrochemical processes take place (see Table I). In both cases a single irreversible two-electron cathodic peak can be observed as shown in Figure 2 for the Ni^{II}–PPh_3 system. The two anodic one-electron peaks observed in the reverse scan were found[4f] to be due to the stepwise oxidation of nickel(0), produced at the electrode surface, to nickel(I) and nickel(II), respectively. By reversing the anodic scan soon after the first anodic peak is traversed, a new cathodic peak, located at potential values slightly less cathodic than that at which the reduction of nickel(II) takes place, can be detected (dashed line in Figure 2). This gives rise to a perfectly reversible system involving the first anodic peak.

We have previously demonstrated[4f] that in the irreversible cathodic process observed in the presence of PPh_3 a fairly unusual EECE mechanism is operative. At these potentials nickel(II) undergoes an irreversible two-electron reduction, giving nickel(0), which reacts with the depolarizer nickel(II) to give a nickel(I) species reducible, in its turn, to nickel(0) at the working potential. In this kind of mechanism the "slow" cathodic reduction of nickel(II) is electrocatalyzed by nickel(0). Moreover, electrochemical results coupled with spectrophotometric (see Table II) and magnetic data indicated that (i) nickel(II) is present as the octahedral complex $[NiL_2(CH_3CN)_4]^{2+}$, (ii) nickel(I) as the tetrahedral species $[NiL_4]^+$ and (iii) nickel(0) as the well-known tetrahedral $[NiL_4]$ complex.

On the basis of these data, the reaction sequence of eq 1–3

$$[NiL_2(CH_3CN)_4]^{2+} + 2e^- \xrightarrow[-4CH_3CN]{+2L} [NiL_4] \qquad (1)$$

$$[NiL_4] + [NiL_2(CH_3CN)_4]^{2+} \xrightarrow[-4CH_3CN]{+2L} 2[NiL_4]^+ \qquad (2)$$

$$[NiL_4]^+ + e^- \rightleftarrows [NiL_4] \qquad (3)$$

could be given for the cathodic process. This sequence shows that nickel(II) is not reduced in steps to nickel(I) and nickel(0) in that its reduction is affected by a large overvoltage so that it occurs at potential values at which nickel(I) is reversibly reduced to nickel(0) (peak reported with a dashed line in Figure 2).

It is well-known that the complexes $[NiL_4]$ undergo partial loss of the phosphine ligand to give generally three-coordinated species $[NiL_3]$.[8] Moreover, with CH_3CN being a ligand of appreciable bonding ability toward nickel(0),[9] it is obvious that the presence of species such as $[NiL_3(CH_3CN)]$ has to be considered in the employed experimental conditions. However, as these equilibria are likely to be fast for the employed phosphines,[8,9] all these mentioned species will be electrochemically "indistinguishable". In other words, although the metal center is stabilized in solution by various coordination shells, a single electrochemical response has to be obtained when the different species containing the same metal center are coexisting in fast chemical equilibria. For this reason we will employ the symbol $[NiL_4]$ for indicating the systems Ni^0, L, CH_3CN.

Table II. Visible and Near-IR Spectral Data

system in CH_3CN	molar ratio	λ_{max}, nm
Ni^{II}–PPh_3	⩾1:2	370 (sh), 590, 990
Ni^{I}–PPh_3	⩾1:4	425 (sh), 1520
Ni^{II}–$PEtPh_2$	⩾1:2	370 (sh), 600, 1.000
Ni^{II}–PEt_2Ph	1:2	355 (sh), 605, 1.020
	⩾1:4	420
Ni^{II}–PEt_3	1:2	348 (sh), 620, 1.030
	⩾1:4	410
Ni^{II}–dppe	⩾1:2	400
Ni^{II}–$P(C\text{-}Hx)_3$	⩾1:2	380 (sh), 600, 1.010
Ni^{II}–$P(OEt)_3$	1:2	360 (sh), 590, 980
	⩾1:5	415
Ni^{II}–$P(OPh)_3$	⩾1:2	370 (sh), 595, 990
Ni^{II}–P(O-*o*-tol)$_3$	⩾1:2	350 (sh), 600, 995

The electrochemical behavior of nickel(II) in the presence of $PEtPh_2$ is found to be the same as that just described for the Ni^{II}–PPh_3 system.

On the basis of these findings, the production of the $[NiL_4]^+$ species, stable in the employed experimental conditions, can be achieved with both PPh_3 and $PEtPh_2$ by means of three different procedures: (i) by anodic oxidation of the corresponding nickel(0) complex (first anodic peak), (ii) by one-electron cathodic reduction of $Ni(ClO_4)_2$ in the presence of L (reactions 1 and 2), and finally (iii) by a chemical comproportionation reaction between nickel(II) and nickel(0) (reaction 2).

It is pertinent to note that $[Ni(PPh_3)_4]^+$ has been recently obtained by carefully controlled chemical reduction of $Ni(ClO_4)_2 \cdot 6H_2O$ with $NaBH_4$ in ethanol in the presence of PPh_3.[10] The near-infrared spectrum of $[Ni(PPh_3)_4]^+$ in CH_3CN (see Table II) is in agreement with the data of ref 10 if one takes into account the different media employed. This spectrum is also consistent with that previously reported[11] for $[Ni(PMe_3)_4]^+$.

B. Triethylphosphine (L = PEt_3) and Diethylphenylphosphine (L = PEt_2Ph). The addition of increasing amounts of free ligand to a solution containing a known amount of $Ni(ClO_4)_2$ causes a progressive lowering of the $[Ni(CH_3CN)_6]^{2+}$ reduction peak reported in Figure 1 and the appearance and concomitant increase of a new peak located at slightly more cathodic potential values in the presence of PEt_3. When PEt_2Ph is employed this peak appears at slightly more anodic potentials. This "conversion" appeared complete for a ligand to nickel(II) molar ratio equal to 2:1 (see Figure 3, dashed line), and the height of the peak obtained under these conditions equals that relative to $[Ni(CH_3CN)_6]^{2+}$, thus indicating that a two-electron process is again involved.

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(8) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53–60.

(9) Tolman, C. A. *Inorg. Chem.* **1971**, *10*, 1540–1541.

(10) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. J. *Can. J. Chem.* **1978**, *56*, 2552–2559.

(11) Gleizes, A.; Dartiguenave, M.; Dartiguenave, Y.; Galy, J.; Klein, H. F. *J. Am. Chem. Soc.* **1977**, *99*, 5187–5189.

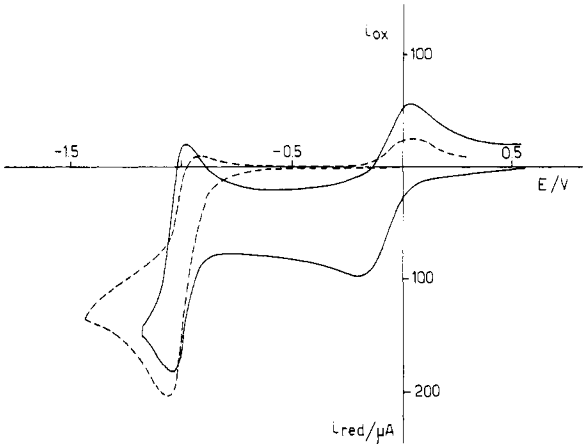

Figure 3. Cyclic voltammetric curves recorded with a platinum microelectrode in a 4.5×10^{-3} M $Ni(ClO_4)_2$, 0.1 M TBAP, CH_3CN solution after addition of (---) 9×10^{-3} M PEt_2Ph and (—) 2.5×10^{-2} M PEt_2Ph (scan rate 0.1 V s^{-1}).

Further increase of the ligand to nickel(II) concentration ratio up to 4:1 causes a moderate lowering of the emerged peak, with an associated very small shift to more anodic potentials. Moreover, a new peak located at much more positive potential values appears as shown in Figure 3 (full line) for the case of PEt_2Ph. The corresponding peak potential values found with both ligands are shown in Table I. When the free ligand to nickel ratio is increased up to 100:1, no further change in the voltammetric picture can be observed.

These findings clearly indicate that different ligand to nickel(II) ratios make possible the existence of two different metal complexes. Spectrophotometric measurements carried out in parallel to the voltammetric ones reveal that at the 2:1 ratio an octahedral species,[1] namely, $[NiL_2(CH_3CN)_4]^{2+}$ as in the cases of PPh_3 and $PEtPh_2$, is the only species present. At the 4:1 or higher ratios the square-planar $[NiL_4]^{2+}$ complexes are the only nickel(II) species to be detected. The square-planar structure of the $[NiL_4]^{2+}$ complexes is proposed on the basis of the close analogy of their vis-UV spectra with that of the well-known square-planar species $[Ni(dppe)_2]^{2+}$.[12]

The relevant spectroscopic data are reported in Table II. Figure 3 shows that in the 2:1 condition two anodic peaks are associated with the single cathodic one as found in the case of PPh_3 and $PEtPh_2$. The rather low height of the anodic peaks observed in this condition is attributed to the low stability of the nickel(0) complexes with PEt_3 and PEt_2Ph when the ligand to nickel ratios are less than 4:1.

When controlled-potential coulometric experiments are carried out at potential values corresponding to the cathodic peak at the 2:1 ratio, both the consumption of 2 mol of electrons/mol of nickel(II) and the formation of appreciable amounts of metallic nickel are observed. The voltammetric analysis of the electrolyzed solutions indicates unambiguously that $[NiL_4]$ is also present in the solution as the anodic peaks observed under this condition are the same as those observed in voltammetric tests performed on nickel(II) solutions containing an excess of the free ligands (see later).

The measurements of the height of the cathodic peaks obtained when the L:Ni^{II} molar ratio is 4:1 or higher (see Figure 3) indicate clearly that both processes involved are one-electron and controlled-potential coulometric experiments carried out at the corresponding potentials are in full agreement with this estimate. The two redox systems depicted in Figure 3 are attributed, therefore, to the processes nickel(II) $\rightleftarrows$ nickel(I) and nickel(I) $\rightleftarrows$ nickel(0), respectively. On the basis of the usual criteria employed in linear sweep and cyclic voltammetry ($E_p - E_{p/2}$ and $(E_p)_a - (E_p)_c$), the less cathodic system is found to be quasi-reversible and the more cathodic one appears to be reversible in character.

In line with the arguments developed by us in a previous paper,[4f] we account for these findings by suggesting that the square-planar $[NiL_4]^{2+}$ complex is reduced to an essentially tetrahedral species $[NiL_4]^+$ (quasi-reversible process) and the latter to the tetrahedral compound $[NiL_4]$ (reversible process).

In the experimental conditions now described, solutions of electrogenerated $[NiL_4]^+$ and $[NiL_4]$ appear to be indefinitely stable (under nitrogen) and the formation of metallic nickel is never observed.

The substantial identity of the voltammetric behavior exhibited by nickel(II) in the presence of PEt_3 and PEt_2Ph in a L:Ni^{II} molar ratio equal to 2:1 and that displayed by nickel(II) in the presence of PPh_3 or $PEtPh_2$ demonstrates that it is just the profound difference in geometry and composition of the coordination sphere of the redox partners which is the major source of the irreversibility observed for the nickel(II) reduction process.

C. 1,2-Bis(diphenylphosphino)ethane (L = $^1/_2$dppe) and Tricyclohexylphosphine (L = $P(c\text{-}Hx)_3$). The ligand $Ph_2P(CH_2)_2PPh_2$(dppe) is known to give the square-planar species $[Ni^{II}(dppe)_2]^{2+}$,[12] the distorted tetrahedral $[Ni^{I}(dppe)_2]^+$,[4b] and the tetrahedral complex $[Ni^0(dppe)_2]$.[12] Moreover, $P(c\text{-}Hx)_3$ is known to exhibit electron-donor acceptor properties rather similar to those of PEt_3[13] but a steric bulkiness which is even greater than that of PPh_3.[13] For these reasons we carried out, with these ligands, experiments quite similar to those reported above for PEt_3, PEt_2Ph, $PEtPh_2$, and PPh_3 with the purpose of gaining support for the correlation, proposed in the previous section, between the reversibility exhibited by the redox processes and the stereochemical features of the redox partners involved.

Cyclic voltammetric tests performed on the Ni^{II}–dppe system reveal that, for any ligand to nickel ratio (even for dppe:Ni^{II} less than 2), the only phosphinenickel(II) complex which appears to be formed is $[Ni(dppe)_2]^{2+}$. This complex is reducible in two one-electron and appreciably reversible steps to give nickel(I) and nickel(0) complexes, respectively. The appreciable reversibility exhibited by both processes is in agreement with the occurrence of the electrode reactions

$$[NiL_4]^{2+} + e^- \rightleftarrows [NiL_4]^+ \qquad (4)$$

$$[NiL_4]^+ + e^- \rightleftarrows [NiL_4] \qquad (5)$$

in which the coordination number of the species involved does not change. Moreover, their geometric configuration changes gradually from square-planar ($[Ni(dppe)_2]^{2+}$) to tetrahedral ($[Ni(dppe)_2]$), on passing through the "square-planar–tetrahedral" structure of $[Ni(dppe)_2]^+$ suggested in the literature for the nickel(I) complex.[4b]

The voltammetric picture exhibited by $P(c\text{-}Hx)_3$-containing nickel(II) solutions appears to be rather peculiar in the series of phosphine ligands employed in this work. For any ligand to nickel ratio, in fact, the usual combination of voltammetric and spectrophotometric data indicates that only the complex $[NiL_2(CH_3CN)_4]^{2+}$ is formed. Moreover, the irreversible two-electron reduction of this species to nickel(0) is observed as in the case of PPh_3 and $PEtPh_2$. For this ligand, however, no evidence for the formation of Ni^I species can be obtained for any employed experimental condition, and this fact makes the system Ni–$P(c\text{-}Hx)_3$ surprisingly similar to the nickel-phosphite ones (see later).

The high irreversibility observed in this case for the reduction of nickel(II) resembles closely that exhibited by the

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(12) Chatt, J.; Hart, F. A.; Watson, H. R. *J. Chem. Soc.* **1962**, 2537–2545.

(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

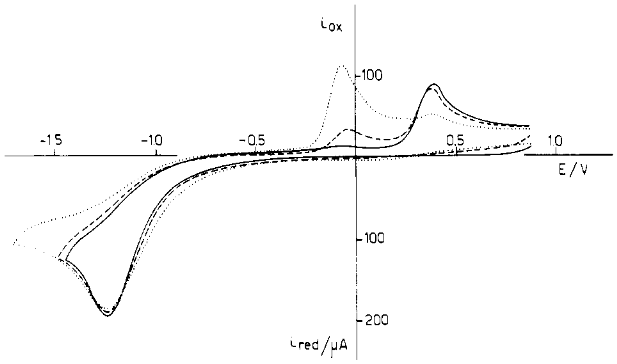

Figure 4. Cyclic voltammetric curves recorded with a glassy carbon microelectrode in a 4 × 10^{-3} M $Ni(ClO_4)_2$, 0.1 M TBAP, CH_3CN solution after addition of (···) 8 × 10^{-3} M $P(OPh)_3$, (- - -) 4 × 10^{-2} M $P(OPh)_3$, (—) 1.2 × 10^{-1} M $P(OPh)_3$ (scan rate 0.1 V s^{-1}).

Ni^{II}–PPh_3 system and stresses that steric features rather than electronic ones have to be the major source of overvoltage in the mentioned process.

D. Triphenyl Phosphite (L = $P(OPh)_3$). Voltammetric tests carried out on nickel(II) solutions containing increasing concentrations of added ligand show that the cathodic peak relative to the reduction of $[Ni(CH_3CN)_6]^{2+}$ decreases, while a new cathodic one located at more negative potentials (see Table I) arises; this peak "conversion" appears to be complete for the L:Ni^{II} ratio equal to 2:1. The cathodic picture is not affected by further addition of L up to ratios of 35:1, thus indicating (see section A) that only two ligand molecules enter the coordination sphere of nickel(II). Parallel spectrophotometric measurements show the presence of an octahedral nickel(II) complex for a L:Ni^{II} ratio equal or higher to 2:1 (see Table II). The combination of these data clearly indicates that, as in the cases of PPh_3, $PEtPh_2$, and $P(c\text{-}Hx)_3$, nickel(II) is present in solution as $[NiL_2(CH_3CN)_4]^{2+}$ even in the presence of large excess of L.

The addition of free ligand, on the contrary, strongly affects the response obtained in the reverse scan, i.e., the associated anodic behavior which can be observed only on glassy carbon electrodes. This behavior cannot be observed on Pt or Hg electrodes owing to their apparent poisoning.

Figure 4 shows the cyclic voltammograms for solutions containing different L:Ni^{II} molar ratios. The only result caused by the excess of free ligand is the conversion of the first anodic peak into the second more anodic one; at the same time, the two-electron cathodic peak appears totally unaffected. It has been possible to attribute the second anodic peak to the two-electron oxidation process of $[NiL_4]$ as it is practically identical with that exhibited by CH_3CN–C_6H_6 solutions (50% v/v) of the same compound chemically prepared. ($[Ni(P(OPh)_3)_4]$ is known to be slightly soluble in CH_3CN.[14])

Cyclic voltammetric tests carried out on solutions in which the L:Ni^{II} ratio is 2:1 indicate that the lowering of the temperature down to −30 °C causes the total disappearance of the second anodic peak in favor of the first one. The same effect is observed by increasing the scan rate, at room temperature, up to 1 V s^{-1}.

The data suggest that the reduction of $[NiL_2(CH_3CN)_4]^{2+}$ occurs by an EC mechanism involving the preliminary formation of a bis(phosphite)nickel(0) complex which subsequently undergoes either a ligand disproportionation reaction (for L:Ni^{II} = 2:1) or a ligand addition reaction (for L:Ni^{II} ≥ 4:1), giving in both cases $[NiL_4]$ according to the sequence of eq 6–8.

$$[NiL_2(CH_3CN)_4]^{2+} + 2e^- \rightarrow [NiL_2(CH_3CN)_2] + 2CH_3CN \quad (6)$$

$$[NiL_2(CH_3CN)_2] \rightarrow {}^{1}/{}_{2}Ni + {}^{1}/{}_{2}[NiL_4] + 2CH_3CN \ (L:Ni^{II} = 2:1) \quad (7)$$

$$[NiL_2(CH_3CN)_2] + 2L \rightarrow [NiL_4] + 2CH_3CN \ (L:Ni^{II} \geq 4:1) \quad (8)$$

The EC pattern depicted in eq 6–8 is fully confirmed by controlled-potential electrolyses. The relevant results are, in fact, the following: (i) for any ligand to nickel(II) ratio employed, the reduction process occurring at the cathodic peak involves always 2 mol of electrons/mol of Ni^{II}; (ii) the reduction of solutions containing L:Ni^{II} ratios equal or greater than 4:1 gives a white precipitate which was identified as $[Ni(P(OPh)_3)_4]$ by voltammetric tests (see above) and melting point; (iii) the reduction of nickel(II) in solutions containing L:Ni^{II} molar ratios equal to 2:1 at −30 °C gives perfectly clean very pale yellow solutions in which only the first anodic peak (see Figure 4) can be observed; (iv) the addition of excess of free ligand to this last electrolyzed solution causes the immediate precipitation of $[NiL_4]$, while letting the temperature of the electrolyzed solution rise gradually up to room temperature allows the concomitant precipitation of metallic nickel and $[NiL_4]$ to be observed. The addition of benzene to this last suspension up to 50% (v/v) increases remarkably the solubility of the obtained nickel(0) complex, thus making possible its coulometric estimate by controlled-potential oxidation. The obtained figures are perfectly consistent with the ligand disproportionation reaction 7.

The results described in this last point leave no doubt that a bis(phosphite)nickel(0) complex can be obtained in suitable experimental conditions.

It is worthwhile to point out that the slowness of the ligand association (or ligand exchange) equilibrium between nickel(0) complexes (eq 7 and 8) is not surprising with triphenyl phosphite as ligand in view of the relative inertness generally exhibited by nickel(0)–phosphite complexes in this kind of reaction.[15] In this connection, we wish to emphasize that in contrast with the case presented in section A, two different anodic peaks are here obtained for species containing the same metal center as they coexist in slow equilibrium.

As far as the irreversible character of both the cathodic and the anodic processes is concerned, this has to be the consequence of the structural changes occurring in the nickel(II) ⇄ nickel(0) conversion. As we have emphasized in previous cases, in fact, this conversion results in a profound change both in the geometric configuration and in the nature of the ligand set; consequently a remarkable overvoltage is observed.

In conclusion, it is pertinent to remember that rather similar electrochemical behavior has been described by us for the Ni^{II}, Ni^{0}–$P(O\text{-}o\text{-}tol)_3$ system in acetonitrile,[5c] the only difference being the apparent absence of equilibria like those depicted in reactions 7 and 8.

E. Triethyl Phosphite (L = $P(OEt)_3$). Nickel(II) solutions containing a suitable excess of free ligand exhibit the cyclic voltammetric picture reported in Figure 5. A two-electron irreversible cathodic peak (c_2) is observed with which two one-electron anodic ones are associated. Peak a_2 is seen to be irreversible, while peak a_1 is associated with a cathodic one which is displayed when the potential scan is reversed soon after this anodic peak has been traversed. The so-obtained redox system is found to be reversible ($(E_p)_a - (E_p)_c$ = 60 mV).

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(14) The circumstance that, in spite of the low solubility of $[Ni(P(OPh)_3)_4]$, the anodic peak due to its oxidation can be easily observed in the reverse anodic scan in nickel(II) solutions is apparently due to the fact that the cathodically generated $[NiL_4]$ is present at a supersaturated concentration in the close environment of the electrode surface.

(15) Meier, M.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1969**, *8*, 795–801.

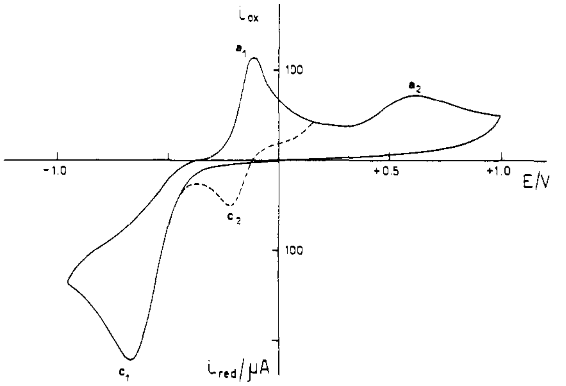

Figure 5. Cyclic voltammetric curve recorded with a platinum microelectrode in a 9×10^{-3} M $Ni(ClO_4)_2$, 4.5×10^{-2} M $P(OEt)_3$, 0.1 M TBAP, CH_3CN solution (scan rate 0.1 V s^{-1}).

This picture is remarkably similar to that exhibited by the Ni–PPh_3 system (see Figure 2). However, in contrast with the cases of PPh_3 and $PEtPh_2$, controlled-potential electrolyses carried out at c_1 reveal that the species responsible of the first anodic peak is obtained even for n_e values equal to 1. In the cases of PPh_3 and $PEtPh_2$, only the species responsible of the second anodic peak can be observed, in fact, when n_e is just equal to 1 (reactions 1 and 2 occur quantitatively).

The complex formed in the two-electron reduction can be oxidized in a one-electron process by controlled-potential electrolysis at the potentials of a_1. The oxidation product can be either oxidized in a further one-electron process at a_2 (renewing the initial nickel(II) concentration) or reduced in a one-electron process at c_2 (restoring the nickel(0) species oxidizable at a_1). These data are easily interpreted by eq 9–12.

$$\text{(peak } c_1\text{)} \quad Ni^{II} + 2e^- \rightarrow Ni^0 \qquad (9)$$

$$\text{(peak } a_1\text{)} \quad Ni^0 \rightleftarrows Ni^I + e^- \qquad (10)$$

$$\text{(peak } a_2\text{)} \quad Ni^I \rightarrow Ni^{II} + e^- \qquad (11)$$

$$\text{(peak } c_2\text{)} \quad Ni^I + e^- \rightleftarrows Ni^0 \qquad (12)$$

As we have seen, nickel(I) is not formed during the reduction of nickel(II) at c_1. Moreover, when the nickel(I) solutions obtained by oxidizing nickel(0) at a_1 are left to stand at room temperature, a gradual disproportionation to Ni^{II} and Ni^0 is observed (voltammetric tests with periodic renewal of the diffusion layer). This reaction is complete in about 30 h.

The occurrence of this disproportionation indicates clearly that the redox potential of the Ni^{II}/Ni^I couple is less positive than that of the Ni^I/Ni^0 one. This observation leads to the conclusion that the nickel(I) complex does not exist with $P(OEt)_3$ for thermodynamic reasons. On this basis, therefore, the nickel(I) species can be obtained and accumulated by electrochemical oxidation of nickel0) (peak a_1) only thanks to its remarkable kinetic inertness.

As to the nature of the Ni^{II}, N^I, and Ni^0 species, the nickel(II) is apparently present as $[NiL_5]^{2+}$ (see the spectral data of Table II and ref 16) while nickel(0) has to be present as the well-characterized $[NiL_4]$ complex which is known to be particularly stable toward the ligand dissociation.[8] Moreover, the reversibility of the redox system relative to the $Ni^0 \rightleftarrows Ni^I$ conversion (Figure 5) strongly suggests that the unstable nickel(I) species has to be $[NiL_4]^+$ having very nearly a tetrahedral configuration.

Discussion

The results reported in this paper are summarized in Table I and in the schemes shown in Figure 6. They can be sectioned in the following findings: (i) straightforward or stepwise reduction of nickel(II) to nickel(0) in the presence of phosphines as a function of the bulkiness of the ligands; (ii) stability of the +1 oxidation state with reference to the type of the ligands present in the coordination sphere of the metal; (iii) electrosynthesis of the thermodynamically unstable but kinetically inert species $[Ni^I(P(OEt)_3)_4]^+$ and $[Ni^0(P(OPh)_3)_2(CH_3CN)_2]$; (iv) dependence of redox potentials on the basicity of the employed ligands.

Nickel(II) can be reduced in steps to nickel(I) and nickel(0) only in the presence of the smaller phosphine ligands PEt_3, PEt_2Ph, and dppe,[13] i.e., those which give $[Ni^{II}L_4]^{2+}$ species having the same coordination number as the corresponding nickel(I) and nickel(0) complexes.

In the cases of the bulkier ligands PPh_3 and $PEtPh_2$, the reduction of nickel(II) is affected by a large overvoltage so that it occurs at potential values at which nickel(I) is also reversibly reduced to nickel(0). The high degree of irreversibility which affects the nickel(II) cathodic reduction results from the fact that the uptake of one electron by the nickel(II) complex to give nickel(I) must be accompanied by ligand exchange and structural changes. Four molecules of CH_3CN must be substituted, in fact, by two molecules of L, while the octahedral arrangement around the nickel atom is changed into a tetrahedral one. We feel that the major contribution to the observed overvoltage has to be attributed to the required entrance of two molecules of these rather bulky phosphine ligands per nickel atom into the activated complex corresponding to the transition state. This activated complex is expected to resemble more or less closely the structure of the parent nickel(II) species, which we have seen to be very reluctant, in these cases, to accommodate more than two molecules of L.

In this connection, our results leave little doubt that the estimation of the reversibility of an electrode process involving coordination compounds can be profitably used as an analytical criterion for gaining information on the structural features of the redox partners.

As to the general problem of the thermodynamic stability of nickel(I) toward disproportionation, the results contained in the schemes of Figure 6 appear to be particularly eloquent. The existence of stable nickel(I) complexes is made possible when phosphines are present in the coordination sphere of nickel, with the significant exception of the very bulky $P(c\text{-}Hx)_3$ ligand. For the nickel(I) complexes containing the phosphines with the lower steric hindrance (PEt_3, PEt_2Ph, dppe),[13] the available data (see Table I) make possible the estimation of the comproportionation constant, thanks to the appreciable reversibility character exhibited by the processes $Ni^{II} + e^- \rightleftarrows Ni^I$ and $Ni^I + e^- \rightleftarrows Ni^0$ ($\log K = \Delta E_{1/2}{}^r/59.15$).

The same calculation, on the contrary, is precluded in the cases of PPh_3 and $PEtPh_2$, owing to the high irreversibility described in this paper for the Ni^{II}–Ni^I process with these ligands. Also in these cases, however, the data reported by us show unambiguously that a phosphine ligand set appears to be suitable for stabilization of the +1 oxidation state toward disproportionation.

Nickel(I) appears to be, on the contrary, fully destabilized when phosphite ligands are involved in the coordination sphere of the metal. Thus, we find that for $P(O\text{-}o\text{-}tol)_3$ and $P(OPh)_3$ the +1 state is inaccessible through the routes useful in the cases of the phosphine ligands and listed in the section A. For $P(OEt)_3$ the synthesis of the nickel(I) complex, which survives for some time thanks to kinetic reasons, is possible only by controlled-potential oxidation of the corresponding nickel(0) species.

Our data on the Ni^I–PR_3 and Ni^I–$P(OR)_3$ systems are in full agreement with the dearth of examples of nickel(I)–

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(16) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1–106.

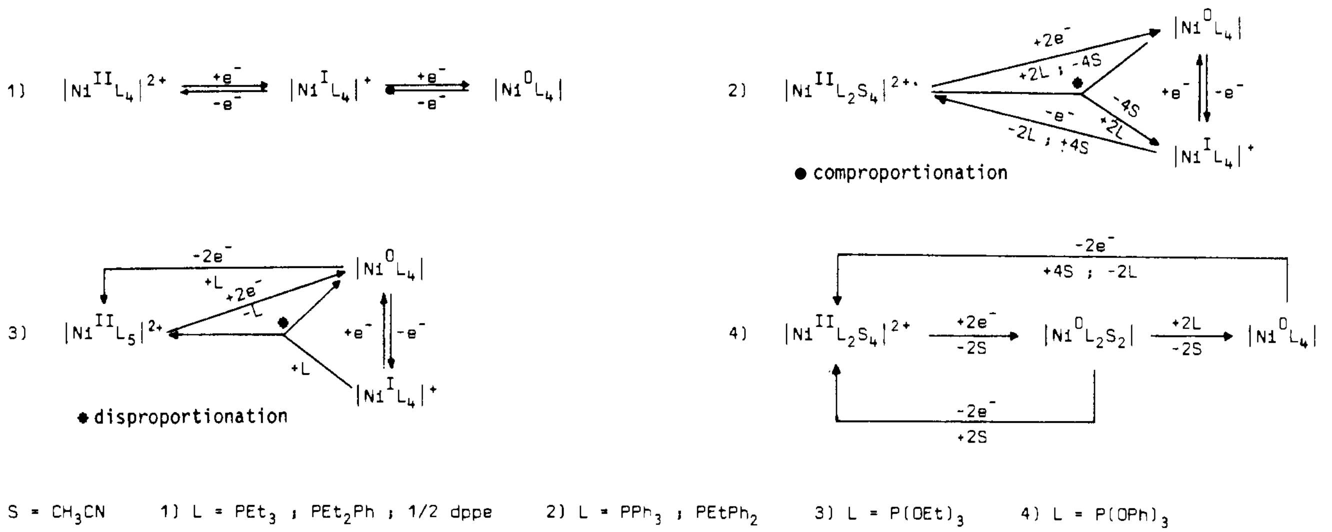

Figure 6. Reaction schemes.

phosphite complexes appearing in the literature. Moreover, they rationalize a previous report[17] on the preparation of the $[Ni^{I}(PPh_3)_3X]$ (X = Cl, Br, I) complexes by comproportionation of the corresponding nickel(II) and nickel(0) compounds as well as the valence disproportionation observed when $P(OPh)_3$ was reacted with the mentioned Ni^{I} species.

The quite different behavior exhibited by nickel(I) when it is accommodated in a phosphine or in a phosphite ligand set has to be concerned with the quite different electronic features (i.e., bonding ability) of these two families of ligands. In fact the +1 oxidation state appears to be stabilized toward the +2 and 0 only when ligands bearing properly balanced σ-donor–π-acceptor abilities (as the phosphines) are present in the coordination sphere of the metal.

As far as the transient existence of the $[Ni^{I}(P(OEt_3)_4]^+$ complex is concerned, the very slow rate of its disproportionation reaction can be easily explained by suggesting that it occurs through a dissociative mechanism and that $P(OEt)_3$ exhibits in nickel(I) complexes the same poor leaving-group character as it is known to display when it is coordinated to nickel(0).[15]

As we have pointed out above for the phosphine complexes of nickel(0), we suggest that in the actual composition of the coordination sphere of the $[Ni^{I}L_4]^+$ complexes, acetonitrile as a ligand can be involved when L = phosphine. When L = $P(OEt)_3$, on the contrary, the poor leaving-group character of this ligand and the circumstance that it is generated by oxidation of $[Ni(P(OEt)_3)_4]$ (see above) suggest that CH_3CN is not involved in the coordination sphere of nickel(I).

As to the bis(triphenyl phosphite)nickel(0) complex, we wish to point out that this species should not be considered as an actual biscoordinate complex (it would be the second example of such nickel(0) species after $[Ni(P(c\text{-}Hx)_3)_2]$[18]). It is generated, in fact, by reducing the corresponding bis(phosphite)tetrakis(acetonitrile)nickel(II) complex in a solvent which is known to exhibit appreciable bonding ability toward nickel(0). The survival of the moiety $[Ni(P(OPh)_3)_2]$ is thus hardly conceivable in this solvent. Hence, the composition of this nickel(0) complex appears to be reasonably $[Ni(P(OPh)_3)_2(CH_3CN)_2]$. The certainly weaker $Ni–CH_3CN$ bond strength with respect to that of $Ni–P(OPh)_3$ suggests, however, that this complex can be considered a "coordinatively unsaturated" nickel(0) species which may offer appreciable synthetic perspectives.

As far as point iv is concerned, the figures reported in Table I suggest a precise correlation between the redox potentials and the basicity of the employed tricovalent phosphorus ligands. The $E_{1/2}{}^{r}$ values relative to the process $Ni^0 \rightleftarrows Ni^I + e^-$ enables one to rank the majority of the employed ligands in the sequence $P(OEt)_3 > dppe > PPh_3 > PEtPh_2 > PEt_2Ph > PEt_3$, which is indicative of their ability to stabilize the O oxidation state with respect to the +1 state. Our data indicate that the more basic ligands (better σ donors) tend to destabilize the 0 state in favor of the +1 state. On the other hand, it appears obvious that the importance of the π-acceptor ability of the ligands has to increase with the decrease of the oxidation state of the metal, while that of the σ-donor ability correspondingly has to decrease.

Some attempts to rank tricovalent phosphorus ligands in series on the basis of their electronic properties have been reported in the literature. Thus, with this purpose, a particularly interesting series of "electron donor–acceptor properties"[19] has been proposed on the basis of spectroscopic measurements. A limitation of this series lies in the fact that it is based on a technique suitable for giving direct information on the metal-coordinated ligands and only indirect ones on the coordinating metal. Moreover, doubts on the usefulness of this spectroscopically grounded series with reference to its employment in "the measure of the extent of π back-bonding in the metal-ligand bond" have been raised recently.[20] As far as this last point is concerned, we feel that the remarkable agreement between the sequence found by us and the "electron donor–acceptor properties" series should dispel any doubt on its usefulness. We think however that in the evaluation of the electronic properties of a ligand and their effect on the metal our approach is, in principle, more reliable than any other one based on the measurement of physical effects induced by these ligands through the mediation of the metal.[19] Moreover, we feel that a conceptual approach like that employed in this work should be profitable for a correct estimate of the actual oxidation state of a metal in a homogeneous catalyst as a function of the ligand set present in its coordination sphere.

In this connection, we point out that during the study of the process 13 (L = dppe, $PEtPh_2$, PEt_2Ph, PEt_3, PPr_3, PBu_3),[5b]

$$[Ni^{I}L_2(CN)_2]^- \rightleftarrows [Ni^{II}L_2(CN)_2] + e^- \qquad (13)$$

the same approach allowed us to find a ligand sequence similar to that reported above. In this case a one-electron process

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[17] Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 648.

[18] (a) Jolly, P. W.; Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 731–732. (b) Jonas, K.; Wilke, G. *Ibid.* **1969**, *8*, 519–520.

[19] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956.

[20] Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755–1759.

involving two oxidation states higher than those considered above was inspected. On the other hand, also the data reported in Table I for the nonreversible processes $Ni^{I} \rightleftarrows Ni^{II} + e^-$ appear in agreement with our reasoning, provided all these investigated processes exhibit comparable irreversibility degrees.

Registry No. $Ni(ClO_4)_2$, 13637-71-3; PPh_3, 603-35-0; $PEtPh_2$, 607-01-2; PEt_2Ph, 1605-53-4; PEt_3, 554-70-1; dppe, 1663-45-2; $P(c\text{-}Hx)_3$, 2622-14-2; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; $P(O\text{-}o\text{-}tol)_3$, 2622-08-4.

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Enhanced Stability of Ternary Complexes in Solution[1,2] through the Participation of Heteroaromatic N Bases. Comparison of the Coordination Tendency of Pyridine, Imidazole, Ammonia, Acetate, and Hydrogen Phosphate toward Metal Ion Nitrilotriacetate Complexes

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So that our understanding of the selectivity observed in biological systems could be mimicked and improved, mixed-ligand complexes of the type M(Nta)(A), where $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}, or Zn^{2+}, Nta^{3-} = nitrilotriacetate, and A = pyridine, imidazole, NH_3, CH_3COO^-, or HPO_4^{2-}, have been studied by potentiometric pH titrations ($I = 0.1$, $NaNO_3$; 25 °C); the mentioned monodentate ligands are the simplest models for the corresponding ligating groups often occurring in nature. The change observed in stability by mixed-ligand complex formation is quantified by $\Delta \log K_M = \log K^{M(Nta)}_{M(Nta)(A)} - \log K^{M}_{M(A)}$, which corresponds to the equilibrium $M(Nta)^- + M(A^n)^{2+n} \rightleftharpoons M(Nta)(A)^{n-1} + M^{2+}$. For A = pyridine and $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}, or Zn^{2+} $\Delta \log K_M$ = 0.04, 0.31, 0.54, and 0.22, respectively; with A = imidazole the values are 0.02, 0.02, 0.25, and 0.16, respectively. Hence, for these systems *positive* $\Delta \log K_M$ values are observed in contrast to common experience and the statistical expectation. However, for the ternary systems with A = NH_3, CH_3COO^-, or HPO_4^{2-}, $\Delta \log K_M$ is *negative*. Both the discrimination and the enhanced stabilities in the formation of the ternary complexes depend on the participation of a heteroaromatic N base such as pyridine or imidazole. The cooperative effect between the imidazole and the O donors is suggested as being one of the sources used by nature to achieve selectivity; indeed this combination of ligating groups is observed in many metalloenzymes.

The phosphate, carboxylate, amino, and imidazole groups are important metal ion binding sites in biological systems.[4] Among these groups the imidazole residue is especially versatile,[4-6] and due to its relatively low basicity ($pK_a \approx 7$), it is far more accessible for many metal ions than the amino group ($pK_a \approx 9.5$), for which the competition with the proton is much larger in the physiological pH region.[4]

For the imidazole group, it was in addition suggested,[7] on the basis mainly of results obtained with 2,2′-bipyridyl, histamine, and other heteroaromatic N bases, that mixed-ligand complexes formed by a metal ion of the second half of the 3d series, the imidazole residue, and O donors should be especially stable. As this behavior imparts also discriminating properties between different ligands, the formation of mixed-ligand complexes may be one of the tools of nature to achieve selectivity. Although this view had been questioned,[8] it was reaffirmed,[9] and its importance for biological systems again emphasized.

As the increased stability of such mixed-ligand complexes depends on the π-accepting properties of the heteroaromatic N base,[10] the "pyridine" nitrogens occurring in pyrimidines and purines[11,12] may as potent metal ion binding sites impart similar qualities.

The simplest ligands which may allow further elucidation of the properties of the mentioned natural binding sites are the corresponding monodentate ligands hydrogen phosphate, acetate, ammonia, imidazole, and pyridine. We have therefore measured the stability of the ternary complexes formed by Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}, the tetradentate nitrilotriacetate (Nta^{3-}), and the listed monodentate ligands.

The stability of these mixed-ligand complexes may be quantified[7,13] by determining the position of equilibrium 1.

$$M(Nta)^- + M(A^n)^{2+n} \rightleftharpoons M(Nta)(A)^{n-1} + M^{2+} \quad (1)$$

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[1] This is part 37 of the series "Ternary Complexes in Solution".[2]

[2] Part 36: Sigel, H.; Prijs, B.; Martin, R. B. *Inorg. Chim. Acta*, in press. For part 35 see ref 38a.

[3] Done during a leave of absence from the Department of Chemistry of the University of Calcutta to the University of Basel.

[4] Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201–208.

[5] Freeman, H. C. In "Inorganic Biochemistry"; Eichorn, G. L., Ed.; Elsevier: Amsterdam, London, and New York, 1973; Vol. 1, Chapter 4.

[6] Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471–517.

[7] (a) Sigel, H. *Chimia* **1967**, *21*, 489–500. (b) Sigel, H. *Met. Ions Biol. Syst.* **1973**, *2*, 63–125. (c) Sigel, H. *Angew. Chem.* **1975**, *87*, 391–400; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394–402. (d) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489–4496. (e) Sigel, H. "Plenary Lecture"; Conference Volume of the XXth International Conference on Coordination Chemistry; Banerjea, D., Ed.; published by I.U.P.A.C. through Pergamon Press, Oxford, 1980.

[8] Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527–1531.

[9] Sigel, H. *Inorg. Chem.* **1980**, *19*, 1411–1413.

[10] (a) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945–947. (b) Huber, P. R.; Sigel, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27*, 1319–1323. (c) Walker, F. A.; Sigel, H.; McCormick, D. B. *Inorg. Chem.* **1972**, *11*, 2756–2763. (d) Fischer, B. E.; Sigel, H. *Ibid.* **1979**, *18*, 425–428.

[11] Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 57–124.

[12] Scheller, K. H.; Hofstetter, F.; Mitchell, P. R.; Prijs, B.; Sigel, H. *J. Am. Chem. Soc.* **1981**, *103*, 247.

0020-1669/81/1320-2586$01.25/0