Electrochemical, Electron Spin Resonance and Nuclear Magnetic Resonance Investigations of Tertiary Phosphine Complexes of Nickel. Part 2.[1] $[Ni^IL_4]^+$, $[Ni^I(L–L)_2]^+$ and their Precursors (L = monodentate phosphine, L–L = bidentate diphosphine)

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The complexes $[Ni(L–L)_2]^{2+}$ and $[NiX(L–L)_2]^+$ [L–L = *cis*-$C_2H_2(PPh_2)_2$-1,2, $C_6H_4(PPh_2)_2$-1,2, $C_6H_4(PMePh)(PPh_2)$-1,2 or $C_6H_4(PBu^nPh)(PPh_2)$-1,2; X = Cl or Br] have been prepared and characterized. Phosphorus-31 NMR spectroscopy reveals the presence of stereoisomers of $[Ni(L–L)_2]^{2+}$ when L–L is unsymmetrically substituted, and the results for the case L–L = $C_6H_4(PBu^nPh)(PPh_2)$-1,2 are presented and analysed. Electrochemical studies of the above complexes in CH_2Cl_2 and of CH_2Cl_2 solutions containing nickel(II) and an excess of ligand L = $PMePh_2$ or PBu^nPh_2 or L–L = $C_6H_4(PMePh)_2$-1,2 have been made. Two successive one-electron metal-based reductions were observed for the $[Ni(L–L)_2]^{2+}$ complexes. The halide-containing complexes showed complex redox behaviour involving loss of halide upon one-electron reduction to form the stable $[Ni^I(L–L)_2]^+$ species. Electron spin resonance studies of nickel(I) complexes obtained upon controlled-potential reduction of these systems have been made. Data from both electrochemical and ESR studies show effects due to variations in the structure of the phosphine ligands. The most important factor is the nature of the interphosphorus linkage, but effects due to changes in the substituents at phosphorus are also observed. The electrochemical and ESR properties of $[Ni(PPh_2R)_4]^+$ are very sensitive to the nature of the alkyl substituent R.

In Part 1[1] we reported a study by cyclic voltammetry and simultaneous electrochemistry and ESR spectroscopy of the redox behaviour of several neutral mixed-ligand nickel(II) dithiolene or dihalogenide complexes containing either two monodentate phosphine ligands or a single bidentate phosphine ligand. It was found that significant variations in redox behaviour occur with changes in the substituents at the phosphorus atom and, in the case of the bidentate phosphines, with changes in the nature of the interphosphorus linkage. In this paper we report a study of the redox behaviour of several cationic nickel(II) complexes with a variety of mono- and bidentate phosphines. This work extends previously reported studies of such systems, which are briefly summarized below.

The cathodic behaviour in acetonitrile of anhydrous nickel(II) perchlorate in the presence of a variety of monodentate phosphorus ligands, PR_3, has been investigated, using electroanalytical and spectrophotometric techniques.[2] In the cyclic voltammograms for the cases $R_3 = Ph_3$ or Ph_2Et a single irreversible two-electron cathodic peak was obtained, followed by two one-electron anodic peaks on the reverse scan. The nickel(II) complex produced *in situ* undergoes an irreversible two-electron reduction to produce a nickel(0) complex which reacts with the former to produce a nickel(I) complex, which may be reduced to a nickel(0) complex at the working potential [equations (1)–(3)].

$$[Ni(PR_3)_2(MeCN)_4]^{2+} + 2PR_3 + 2e^- \longrightarrow [Ni(PR_3)_4] + 4MeCN \quad (1)$$

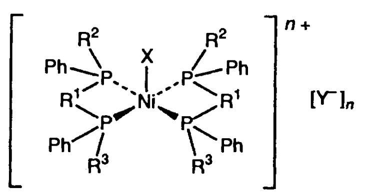
$$[Ni(PR_3)_4] + [Ni(PR_3)_2(MeCN)_4]^{2+} + 2PR_3 \longrightarrow 2[Ni(PR_3)_4]^+ + 4MeCN \quad (2)$$

$$[Ni(PR_3)_4]^+ + e^- \rightleftharpoons [Ni(PR_3)_4] \quad (3)$$

The redox processes involving nickel-(II), -(I) and -(0) complexes of bidentate ligands such as $(CH_2)_2(PPh_2)_2$ (dppe), $(CH_2)_3(PPh_2)_2$ (dppp) and $(CH_2)_4(PEt_2)_2$ (depb) have been investigated using electroanalytical and spectrophotometric techniques.[3,4] The effect of the variation of the $(CH_2)_n$ chain length upon the two successive one-electron reduction potentials of the $[Ni^{II}(L–L)_2]^{2+}$ complexes, L–L = dppe, dppp, depb, *etc.*, was investigated, and it was found that the reduction potential for the Ni^{II}–Ni^I couple decreases with increasing chain length. The factors which influence the separation of redox potentials for successive redox processes in nickel(II) complexes are electronic and steric in origin. They may include changes to the cationic charge following a redox process,[5,6] a change in steric strain in the complex accompanying the redox process,[3] and the influence on the Ni^I–Ni^0 couple of the interphosphorus linkage length for chelate ligands.[3,4]

For the square-planar $[Ni^{II}\{C_6H_4(PMe_2)_2\text{-}1,2\}_2]^{2+}$ complexes an irreversible two-electron reduction to the corresponding tetrahedral $[Ni^0\{C_6H_4(PMe_2)_2\text{-}1,2\}_2]$ species was observed.[7] Electrochemical studies have been reported for a number of complexes of the type $[Ni\{C_6H_4(PR_2)_2\text{-}1,2\}_2]^{2+}$ and $[NiCl\{C_6H_4(PR^1R^2)(PR^3R^4)\text{-}1,2\}_2]^+$ where R, R^1, R^2, *etc.* are alkyl groups (Me, Et, Pr).[8] It was found that the potentials required for the reduction and oxidation of these complexes shifted to more positive values with increasing steric bulk of the substituents.

In this paper we have extended studies of the type described above to include phosphines with different combinations of substituents at phosphorus and, in the case of complexes with bidentate phosphines, with different combinations of substituents and interphosphorus linkage. The nickel(II) complexes **1**–**8** were prepared and their redox processes studied by cyclic voltammetry and ESR spectroscopy. Also reported is a study of the $[Ni^I(PR_3)_4]^+$ complexes, $R_3 = MePh_2$ and Bu^nPh_2.



	R1	R2	R3	X	Y	n
1	*cis*-1,2-C_2H_2	Ph	Ph	-	BPh_4	2
2	1,2-C_6H_4	Ph	Ph	-	ClO_4	2
3	1,2-C_6H_4	Me	Me	-	ClO_4	2
4	1,2-C_6H_4	Ph	Me	-	ClO_4	2
5	1,2-C_6H_4	Ph	Bu^n	-	ClO_4	2
6	*cis*-1,2-C_2H_2	Ph	Ph	Br	BPh_4	1
7	1,2-C_6H_4	Me	Me	Cl	BPh_4	1
8	1,2-C_6H_4	Ph	Me	Cl	BPh_4	1

Experimental

Instrumental.—Details of the electrochemistry experiments and ESR spectroscopy have been reported in Part 1 of this series.[1] All potentials measured in the cyclic voltammetry experiments were internally referenced to the Ag–AgCl couple using the potential for the one-electron oxidation of ferrocene (0.46 V *vs.* Ag–AgCl). A Bruker AM400 spectrometer was used to record the ^{31}P NMR spectra, with 85% H_3PO_4 as an external standard. Spectra were obtained using a 10 mm broad-band probe with ^1H decoupling.

Syntheses.—Solvents were dried and distilled from sodium under dry oxygen-free nitrogen before use.

$[Ni^I(PR_3)_4]^+$ (R_3 = $MePh_2$ *or* PBu^nPh_2). In order to study these electrogenerated complexes, it was necessary to prepare their precursors *in situ*. For this purpose, the compound $PRPh_2$, R = Me or Bu^n (10 mmol), was added to $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in deoxygenated CH_2Cl_2. The reaction mixture was stirred for 5 min during which time it became intensely red. Cyclic voltammograms were recorded and the *in situ* ESR experiments were performed using these solutions.

Ditertiary phosphines and derivatives. The ditertiary phosphines, *cis*-1,2-bis(diphenylphosphino)ethene, *cis*-$Ph_2PCH{=}CHPPh_2$, 1,2-bis(methylphenylphosphino)benzene, $C_6H_4(PMePh)_2$-1,2, $C_6H_4(PMePh)(PPh_2)$-1,2 and $C_6H_4(PBu^nPh)(PPh_2)$-1,2 were prepared and characterized as previously described.[1]

1,2-*Bis*(*diphenylphosphino*)*benzene*, $C_6H_4(PPh_2)_2$-1,2. This was prepared in a manner analogous to that previously reported.[9]

Bis[cis-1,2-*bis*(*diphenylphosphino*)*ethene*-P,P′]*nickel*(II) *bis*(*tetraphenylborate*), $[Ni\{cis\text{-}C_2H_2(PPh_2)_2\text{-}1,2\}_2][BPh_4]_2$ **1**. To a stirred solution of *cis*-$C_2H_2(PPh_2)_2$-1,2 (0.42 g, 1.06 mmol) in absolute ethanol (50 cm^3) was added dropwise an ethanolic solution of $NiBr_2 \cdot 3H_2O$ (0.14 g, 0.51 mmol). The reaction mixture was stirred for 5 min, and then an ethanolic solution of $NaBPh_4$ (0.50 g, 1.46 mmol) was added. The reaction mixture was stirred for 3 h during which time a yellow solid precipitated. This was filtered off, washed twice with absolute ethanol (20 cm^3) and then recrystallized twice from CH_2Cl_2–diethyl ether and dried *in vacuo* to yield yellow crystals (0.62 g, 81%), m.p. 168 °C (decomp.) (Found: C, 80.7; H, 6.0. $C_{100}H_{84}B_2NiP_4$ requires C, 80.6; H, 5.7%). ^{31}P NMR (CH_2Cl_2): δ 67.6.

Bis[1,2-*bis*(*diphenylphosphino*)*benzene*-P,P′]*nickel*(II)-*diperchlorate*, $[Ni\{C_6H_4(PPh_2)_2\text{-}1,2\}_2][ClO_4]_2$ **2**. This was prepared by a previously described method,[10] using $C_6H_4(PPh_2)_2$-1,2, to yield a yellow solid (Found: C, 61.1; H, 4.7. $C_{60}H_{48}Cl_2NiO_8P_4$ requires C, 62.6; H, 4.2%).

Bis[1,2-*bis*(*methylphenylphosphino*)*benzene*-P,P′]*nickel*(II) *diperchlorate*, $[Ni\{C_6H_4(PMePh)_2\text{-}1,2\}_2][ClO_4]_2$ **3**. The high solubility of this complex precluded its isolation as a solid. Solutions in CH_2Cl_2 were prepared *in situ*, when required, by mixing $C_6H_4(PMePh)_2$-1,2 in excess and $Ni(ClO_4)_2 \cdot 6H_2O$ with stirring for 30 min.

Bis[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*-P,P′]*nickel*(II) *diperchlorate*, $[Ni\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2][ClO_4]_2$ **4**. An ethanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.24 g, 0.67 mmol) was added dropwise to a stirred solution of $C_6H_4(PMePh)(PPh_2)$-1,2 (0.53 g, 1.36 mmol) in absolute ethanol (20 cm^3). An intensely red solution initially formed, and then a solid precipitated. This was recrystallized twice from CH_2Cl_2–diethyl ether, and dried *in vacuo* to yield an orange-yellow solid (0.60 g, 60%), m.p. 274–275 °C (Found: C, 56.9; H, 4.8. $C_{50}H_{44}Cl_2NiO_8P_4$ requires C, 58.5; H, 4.3%).

Bis[1-(n-*butylphenylphosphino*)-2-(*diphenylphosphino*)-*benzene*-P,P′]*nickel*(II) *diperchlorate*, $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2][ClO_4]_2$ **5**. A solution of $C_6H_4(PBu^nPh)(PPh_2)$-1,2 (0.38 g, 0.94 mmol) in CH_2Cl_2 (50 cm^3) was added to an aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (2.00 g, 5.47 mmol). The mixture was stirred for 30 min during which time the organic layer became orange. The organic layer was separated, washed with water, and then dried over anhydrous $MgSO_4$. A solid precipitated upon addition of diethyl ether. This was recrystallized from CH_2Cl_2–diethyl ether, and dried *in vacuo* to yield a yellow solid (0.24 g, 49%), m.p. 255–260 °C (Found: C, 60.0; H, 5.5. $C_{56}H_{56}Cl_2NiO_8P_4$ requires C, 60.6; H, 5.1%).

Bis[cis-1,2-*bis*(*diphenylphosphino*)*ethene*-P,P′]*bromonickel*(II) *tetraphenylborate*, $[NiBr\{cis\text{-}C_2H_2(PPh_2)_2\text{-}1,2\}_2][BPh_4]$ **6**. This compound was prepared as previously described,[11] m.p. 180–182 °C (Found: C, 72.2; H, 5.5. $C_{76}H_{64}BBrNiP_4$ requires C, 73.0; H, 5.2%). ^{31}P NMR (CH_2Cl_2): δ 52.9.

Bis[1,2-*bis*(*methylphenylphosphino*)*benzene*-P,P′]*chloronickel*(II) *tetraphenylborate*, $[NiCl\{C_6H_4(PMePh)_2\text{-}1,2\}_2][BPh_4]$ **7**. Solid $NiCl_2$ (anhydrous) (0.40 g, 3.09 mmol) and $NaBPh_4$ (2.35 g, 6.87 mmol) were added to a stirred solution of $C_6H_4(PMePh)_2$-1,2 (2.01 g, 6.23 mmol) in absolute ethanol (20 cm^3). The reaction mixture was stirred for 12 h in an ice-bath. An orange solid gradually precipitated, and was filtered off, washed twice with water (50 cm^3) and then twice with diethyl ether (50 cm^3). Recrystallization from CH_2Cl_2–diethyl ether yielded an orange solid (0.71 g, 30%), m.p. 130–132 °C (Found: C, 72.9; H, 6.2. $C_{64}H_{60}BClNiP_4$ requires C, 72.7; H, 5.7%).

Chlorobis[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)-*benzene*-P,P′]*nickel*(II) *tetraphenylborate*, $[NiCl\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2][BPh_4]$ **8**. A solution of $NiCl_2$ (anhydrous) (0.04 g, 0.34 mmol) in absolute ethanol (20 cm^3) was added dropwise to a stirred solution of $C_6H_4(PMePh)(PPh_2)$-1,2 (0.27 g, 0.70 mmol) in absolute ethanol (20 cm^3) to yield an intensely red solution. Upon addition of a solution of $NaBPh_4$ (0.50 g, 1.46 mmol) in absolute ethanol (20 cm^3) with stirring, a red-brown solid separated. The reaction mixture was stirred for 3 h. The precipitate was filtered off, washed with water (50 cm^3) and then twice with absolute ethanol (50 cm^3). The product was then dissolved in CH_2Cl_2, and slow addition of absolute ethanol, followed by drying *in vacuo*, yielded a red-brown solid (0.18 g, 44%), m.p. 189–191 °C (Found: C, 74.9; H, 5.9. $C_{74}H_{64}BClNiP_4$ requires C, 75.2; H, 5.5%).

Results and Discussion

^{31}P *NMR Studies.*—The complexes **3**–**5**, **7** and **8** are expected to exist in a number of stereoisomeric forms. These have been studied in detail in the case of **7**, where the substituents on the two phosphorus atoms of the diphosphine are the same.[12] The complexes **4**, **5** and **8** in which the substitution patterns at the two phosphorus atoms in the ligand are different, present a significantly different situation. In order to investigate the possibility of the existence of stereoisomeric forms of these complexes ^{31}P NMR studies were carried out. As expected the resulting spectra were quite complex as a result of the existence of several isomeric forms, each of which gives rise to a non-first-order spectrum. However, $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2][ClO_4]_2$ **5** yielded a spectrum in which there was no overlap between the spectra of the different isomeric forms and the results for this are presented here. The ^{31}P-{^{1}H} NMR spectrum is shown in Fig. 1(*a*). It consists of separate contributions from two distinct AA'BB' spin systems. The simulated spectra for each are compared with the experimental spectrum. The ^{31}P NMR parameters which were used in the simulations are given in Table 1.

Compound **5** may consist of a mixture of a maximum of four diastereoisomers **I**–**IV**, Fig. 2. Of these, **I** exists as an internally compensated mesomeric complex whilst **II**–**IV** are racemic mixtures. The *E* and *Z* forms of each of the *cis* and *trans* isomers differ in the relative orientations of the *n*-butyl substituents with regard to the square plane of the molecule. Such a difference is spatial and the *E* and *Z* types of either of the *cis* and *trans* forms would be expected to exhibit different ^{31}P NMR spectra. Such differences in NMR parameters of metal complexes arising from spatial differences in substituents on the two nuclei of ditertiary phosphines were the subject of a previous investigation.[1] Further, spatial differences as exhibited in diastereoisomers of similar complexes produce significant differences in their ^{1}H NMR spectra.[12–14] These considerations suggest that four different ^{31}P NMR spectra should have been observed, one for each diastereoisomer. All four isomers contain two sets of two symmetrically related phosphorus atoms, so each would give rise to an AA'BB' spin system. However, spectra due to only two such spin systems were observed experimentally.

Two different kinds of explanation for this observation can be considered. First, it may be that only one diastereoisomer in each pair of diastereoisomers **I**, **II** and **III**, **IV** is formed in the synthesis of $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2][ClO_4]_2$. That is, one of each is a thermodynamically preferred product. Hence only two AA'BB' spectra are exhibited by the diastereoisomeric mixture. The second type of explanation is that all four diastereoisomers may be present in solution and there is a dynamic process, fast on the NMR time-scale, which results in interconversion between pairs of diastereoisomers. Thus a process which interconverts **I** and **II**, and **III** and **IV**, would produce two time-averaged spectra for the two pairs. However, such a rearrangement necessitates Ni–PBu^{n}Ph bond cleavage and inversion of the substituent configuration at phosphorus, which seems unlikely on energetic grounds. Another possible dynamic process is one in which the diastereoisomers **I** and **II** are rearranged into **IV** and **III** respectively by twisting through a tetrahedral intermediate. Some related complexes show a tetrahedral distortion from square-planar geometry,[4] and so the existence of a tetrahedral intermediate would not seem to be unreasonable. This process has been reported for similar compounds in the presence of co-ordinated halide ions.[12] This type of process in the present system would produce two time-averaged spectra for the pairs **I**, **IV** and **II**, **III**. In this case, the distinction between the *cis* and *trans* forms disappears, as one form is changed into the other by this process. This is not consistent with the fact that excellent fits to the observed spectra are obtained by using parameters which are characteristic of *cis* and *trans* structures (see below).

Of the six coupling constants between the four phosphorus nuclei in structures **I**–**IV** there are two pairs whose members are equal by symmetry. The largest coupling constants are expected to be those between phosphorus atoms which are mutually *trans* to each other. These have values in the range 180–200 Hz in the present systems (Table 1). The two *trans* coupling constants are symmetrically equivalent in the *trans* structures, but are not equivalent in the *cis* structures. The best fits to the observed spectra were obtained with the parameters shown in Table 1,

Table 1 The ^{31}P NMR parameters for the two AA'BB' spin systems observed in the spectrum of $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2][ClO_4]_2$ **5** in CDCl$_3$ (Fig. 1). Chemical shifts δ, coupling constants *J*/Hz; 1,2,3,4 refer to the nuclei A,A',B,B' respectively

Parameter	System 1	System 2
δ(1), δ(2)	51.81	53.83
δ(3), δ(4)	57.95	54.35
J(1,3), *J*(2,4)	−37.52	−39.23
J(1,4), *J*(2,3)	184.65	−50.95
J(1,2)	−48.43	188.67
J(3,4)	−48.41	195.32

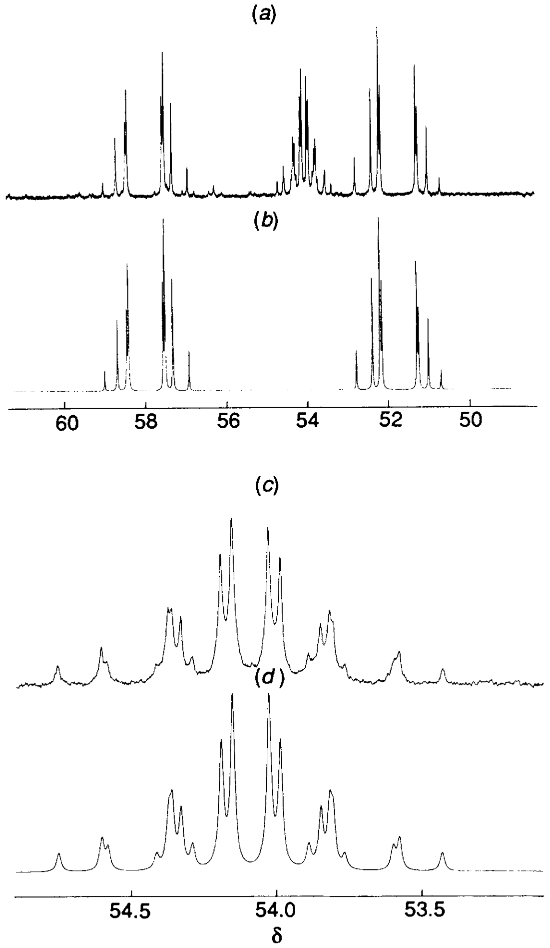


Fig. 1 The ^{31}P-{^{1}H} NMR spectra of $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2]^{2+}$ **5**: (*a*) experimental, CDCl$_3$ solution; (*b*) simulation of AA'BB' system 1; (*c*) expansion of centre component of the experimental spectrum; (*d*) simulation of AA'BB' system 2. Simulations carried out using the parameters in Table 1 with linewidths of 3 Hz

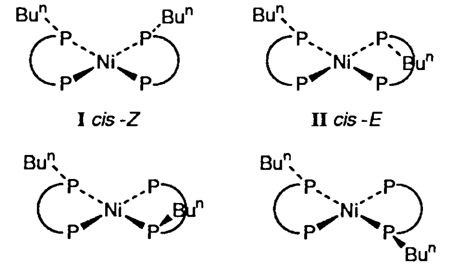


Fig. 2 Diastereoisomers of $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2]^{2+}$ **5**. The *cis* or *trans* notation refers to the proximity of the PBu^{n}Ph groups, whilst the *E* or *Z* notation refers to the relative position of the PBu^{n}Ph groups in regard to the square plane of the complex

which correspond to a *cis* configuration for system 1 and a *trans* configuration for system 2. Thus, the ^{31}P NMR data indicate the presence of at least two stereoisomers for complex **5** in solution. The parameters obtained are similar in magnitude and have the same signs as those determined from the AA'BB' spectra observed for nickel(II) complexes containing two different bidentate diphosphine ligands.[4]

Electrochemical and ESR Studies.—The cyclic voltammetry parameters for the redox processes observed for the nickel(II) complexes in CH_2Cl_2 solution are given in Tables 2 and 3. In most cases the formation of a nickel(I) product upon reduction was confirmed by observation of its ESR spectrum in solution at ambient temperature and in frozen solution at *ca*. 90 K. The ESR parameters for the nickel(I) species are given in Table 4.

$[Ni^I(PR_3)_4]^+$ (R_3 = $MePh_2$ *or* Bu^nPh_2). The cyclic voltammogram of a 10:1 mole ratio mixture of $PMePh_2$ and $Ni(ClO_4)_2 \cdot 6H_2O$ in CH_2Cl_2 showed behaviour similar to that of the corresponding PPh_3 system in MeCN (Table 2), but the single irreversible reduction occurs at a considerably higher potential in the present case. By analogy with the PPh_3 case, the cathodic wave is attributed to the formation of $[Ni^0(PMePh_2)_4]$ *via* equations (1)–(3), and the two anodic waves to the formation of $[Ni^I(PMePh_2)_4]^+$ and $[Ni^{II}(PMePh_2)_4]^{2+}$, the latter product undergoing rapid dissociation. Controlled-potential electrolysis in the *in situ* ESR cell at a potential below −0.59 V resulted in a product which exhibited a single broad ESR line at g = 2.152 in solution at room temperature and an anisotropic pattern in its frozen-solution spectrum (Fig. 3). Hyperfine coupling to four equivalent ^{31}P nuclei is evident in the frozen-solution spectrum. This spectrum is therefore assigned to $[Ni^I(PMePh_2)_4]^+$. The presence of this species is attributed to a comproportionation reaction, (2).

The cyclic voltammogram of a 10:1 mole ratio mixture of PBu^nPh_2 and $Ni(ClO_4)_2 \cdot 6H_2O$ in CH_2Cl_2 exhibited two cathodic processes. Controlled-potential electrolysis of the product in the *in situ* ESR cell at a potential below the first of

Table 2 Cyclic voltammetry parameters for solutions of nickel(II) perchlorate in CH_2Cl_2 solution in the presence of an excess of phosphine ligand L at *ca*. 273 K and 200 mV s^{-1} scan rate

L	E_{pc}/V	E_{pa}/V	$\Delta_{1,2}{}^a/V$
$PPh_3{}^b$	−1.20	−1.12	
		0.02	1.14
$PMePh_2$	−0.59	−0.54	
		−0.02	0.56
PBu^nPh_2	−0.74		
	−1.54		0.80

[a] $\Delta_{1,2}$ is the difference in the E_{pa} values for the peaks assigned to Ni^{II}–Ni^I and Ni^I–Ni^0 couples. [b] Ref. 2; in MeCN solution, *vs*. saturated calomel electrode (SCE), scan rate 100 mV s^{-1}.

Table 3 Cyclic voltammetry parameters for $[Ni(L–L)_2]^{2+}$ in CH_2Cl_2 solution at *ca*. 273 K and a scan rate of 200 mV s^{-1}

Compound	$E_{p/2}/V$	$\Delta_{1,2}{}^a/V$	$\Delta E_{pp}/V$
$[Ni\{C_2H_4(PPh_2)_2\text{-}1,2\}_2]^{2+\,b}$	−0.23		0.09
	−0.52	0.29	0.09
1	−0.07		0.10
	−0.44	0.37	0.12
2[c]	−0.08		0.08
	−0.52	0.44	0.07
3[d]	−0.32		0.25
	−0.65	0.33	0.21
4	−0.39		0.03
	−0.55	0.16	0.05
5	−0.24		0.28
	−0.55	0.31	0.25

[a] $\Delta_{1,2}$ is the difference in the $E_{p/2}$ values for the Ni^{II}–Ni^I and Ni^I–Ni^0 couples. [b] Ref. 15. [c] Ref. 4; scan rate 100 mV s^{-1}. [d] Prepared *in situ*.

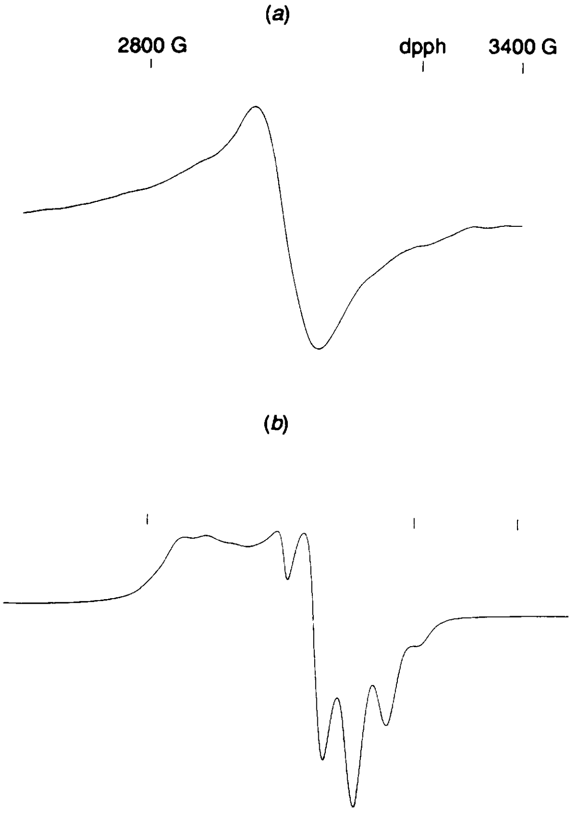


Fig. 3 The ESR spectra of the electrogenerated $[Ni^I(PMePh_2)_4]^+$ complex in CH_2Cl_2: (*a*) solution spectrum at *ca*. 298 K; (*b*) frozen-solution spectrum at *ca*. 90 K. dpph = Diphenylpicrylhydrazyl; G = 10^{-4} T

Table 4 The ESR parameters for the electrogenerated nickel(I) species in CH_2Cl_2 solution. Isotropic and anisotropic parameters were obtained from spectra run at *ca*. 298 and *ca*. 90 K respectively

Complex	g_{iso}	g_1	g_2	g_3	$A_{iso}/10^{-4}\ cm^{-1}$	$A_1/10^{-4}\ cm^{-1}$	$A_2/10^{-4}\ cm^{-1}$	$A_3/10^{-4}\ cm^{-1}$
$[Ni(PMePh_2)_4]^+$	2.152	2.270	2.068	2.068	45[a]	25	53	57
$[Ni(PBu^nPh_2)_4]^{+\,b}$	—	2.153	—	—	—	—	—	—
$[Ni\{C_2H_4(PPh_2)_2\text{-}1,2\}_2]^{+\,c}$	2.074	2.134	2.030	2.030	59	48	64	64
$[Ni\{cis\text{-}C_2H_2(PPh_2)_2\text{-}1,2\}_2]^+$	2.072	2.110	2.030	2.030	60	30	70	70
$[Ni\{C_6H_4(PPh_2)_2\text{-}1,2\}_2]^+$	2.066	2.090	2.032	2.018	63	60	70	70
$[Ni\{C_6H_4(PMePh)_2\text{-}1,2\}_2]^+$	2.065	2.095	2.031	2.019	60	35	60	80
$[Ni\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2]^{+\,d}$	2.066	2.105	2.033	2.021	59	50	60	80
$[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2]^+$	2.072	2.112	2.041	2.030	60	54	60	65

[a] $A_{iso} = (A_1 + A_2 + A_3)/3$. [b] No solution spectrum is exhibited; frozen-solution spectrum is a broad line. [c] Ref. 16. [d] Electrogenerated from $[NiCl\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2]^+$ **8**

these resulted in a product which exhibited no ESR spectrum at room temperature, but a single broad line at $g = 2.153$ in its frozen-solution spectrum. These results are similar to those reported previously for $[Ni^I(PMe_3)_4]^+$,[17] $[Ni^I(PPh_3)_4]^+$,[18] and the tetrahedral bis(cycloocta-1,5-diene)nickel(I) complex.[19] It is not clear why two separate cathodic peaks are seen in this case compared to the single peak in the case of the other monodentate phosphines discussed above. We tentatively attribute these to Ni^{II}–Ni^I (−0.74 V) and Ni^I–Ni^0 (−1.54 V) couples, and assign the $[Ni^I(PBu^nPh_2)_4]^+$ species as the product of the first cathodic process which gives rise to the observed ESR spectrum.

The broad ESR lines for $[Ni^I(PR_3)_4]^+$ species, R_3 = Me_3, Ph_3 or Bu^nPh_2, in their solution and frozen-solution spectra may be attributed to the tetrahedral geometry which the complex adopts.[15,17] For such complexes the $^2T_2$ electronic states are sufficiently close that the low-lying excited states allow spin–lattice relaxation to occur *via* spin–orbit coupling, which results in short spin–lattice relaxation times and broad anisotropic ESR signals at most temperatures.[20] The observation of linewidths which are sufficiently narrow to allow resolution of the ^{31}P hyperfine coupling, as observed in the present study for $[Ni^I(PMePh_2)_4]^+$, is unique for the series of $[Ni^IL_4]^+$ complexes reported to date.

The above results indicate that the electrochemical and electronic properties of $[Ni^IL_4]^+$ complexes involving monodentate phosphine ligands L are very sensitive to changes in the nature of the substituents at the phosphorus atom. This parallels recent findings concerning the effect of ligand-bite size on the properties of $[Ni^I(L–L)_2]^+$ species which have been attributed to differing degrees of tetrahedral distortion.[4] The considerable changes in the ESR linewidths with change in phosphine substituent which are observed in the present study indicate a similar degree of structural variation in the $[Ni^IL_4]^+$ species.

$[Ni^{II}(L–L)_2]^{2+}$ **1–5**. The $[Ni^{II}(L–L)_2]^{2+}$ complexes reported herein are four-co-ordinate nickel(II) species in CH_2Cl_2 solution, probably with square-planar geometries as shown in the case of **5** by ^{31}P NMR spectroscopy (see above). The cyclic voltammograms of these complexes (Table 3) show two separate quasi-reversible reductions, similar to those reported previously for $[Ni^{II}\{C_2H_4(PPh_2)_2\text{-}1,2\}_2]^{2+}$ in acetonitrile.[3] By analogy with these earlier results, these are assigned as successive Ni^{II}–Ni^I and Ni^I–Ni^0 one-electron reductions. This is supported by observation of the appropriate nickel(I) species at the appropriate potential by ESR spectroscopy (see below). Inspection of the $E_{p/2}$ values for the first reduction process (Table 3), and comparison of these with the E_{pa} values for the one-electron oxidations of the electrogenerated $[Ni^I(PR_3)_4]^+$ complexes (Table 2), shows that the factor which has the greatest influence on these parameters is the nature of the interphosphorus linkage between the co-ordinating phosphorus atoms. The redox potential for the Ni^{II}–Ni^I couple increases in the order: no linkage < ethene < ethane < *o*-phenylene.

For complexes which contain a particular type of interphosphorus linkage there is also a dependence of the potential of the Ni^{II}–Ni^I couple on the nature of the substituent at the phosphorus atom. In cases such as **4** and **5**, where the ligands differ only in the size of an alkyl substituent, we observe the same trend as that reported by other workers for similar complexes with *o*-phenylene linkages, *viz*. an increase in the first reduction potential with increasing bulk of the alkyl substituent.[8]

Controlled-potential electrolysis of the $[Ni^{II}(L–L)_2]^{2+}$ complexes in the *in situ* ESR cell at potentials below that of the first reduction process exhibited in the cyclic voltammograms resulted in solution and frozen-solution ESR spectra which showed axially symmetric *g* tensors characteristic of d^9 nickel(I) complexes exhibiting hyperfine coupling of the unpaired electron to four equivalent ^{31}P nuclei. The ESR data are given in Table 4 and the spectra for the case L–L = C_6H_4-(PBu^{n}Ph)(PPh$_2$)-1,2 are shown in Fig. 4. The ESR results are consistent with the formation of a stable four-co-ordinate $[Ni^I(L–L)_2]^+$ species, supporting the assignment of the two successive reduction processes to one-electron transfers. The complex for which L–L = $C_6H_4(PMePh)(PPh_2)\text{-}1,2$ produced no observable ESR-active species following electrolysis. However $[Ni^I\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2]^+$ was identified following controlled-potential electrolysis of the complex $[NiCl\{C_6H_4(PMePh)(PPh_2)\text{-}1,2\}_2]^+$ as noted below. Similarities between the cyclic voltammograms of **4** and **7**, as noted below, allow the assignment of redox couples for the successive reductions of compound **4** as Ni^{II}–Ni^I and Ni^I–Ni^0.

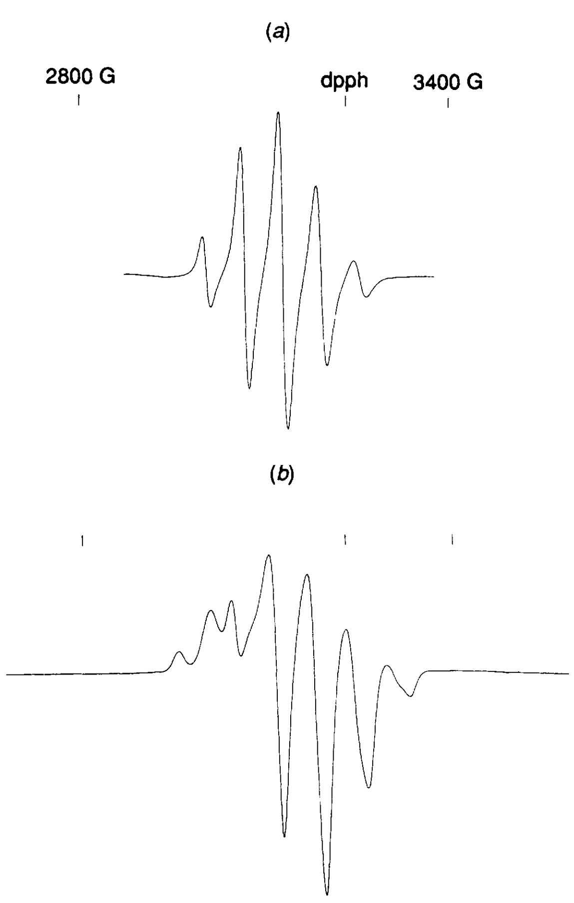


Fig. 4 The ESR spectra of the electrogenerated $[Ni^I\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2]^+$ complex in CH_2Cl_2. Details as in Fig. 3

The occurrence of a second one-electron reduction process at a potential more negative than that of the first reduction indicates that the nickel(I) species with d^9 electronic configurations previously discussed are reduced to nickel(0) species with d^{10} electronic configurations, and that the nickel(0) complex is less stable than the nickel(I) species. The separations $\Delta_{1,2}$ of the successive redox potentials for the Ni^{II}–Ni^I and Ni^I–Ni^0 couples for the various complexes studied are given in Table 3. The values are similar and there is no obvious correlation with the nature of the ligand.

Although the ^{31}P NMR results show that CH_2Cl_2 solutions of the complex $[Ni\{C_6H_4(PBu^nPh)(PPh_2)\text{-}1,2\}_2]^{2+}$ **5** contain at least two stereoisomeric forms, the cyclic voltammetry and ESR results indicate that the electronic structure and redox behaviour of these are very similar, as separate redox processes and products which could be assigned to different stereoisomers were not detected.

$[NiX(L–L)_2][BPh_4]$ **6–8**. The cyclic voltammograms of CH_2Cl_2 solutions of compounds **6–8** exhibit both cathodic and anodic processes as summarized in Table 5. Controlled-potential electrolysis in the *in situ* ESR cell at a potential more

Table 5 Cyclic voltammetry data for the cathodic processes and accompanying anodic processes of $[\mathrm{NiX(L{-}L)_2}]^+$ in $\mathrm{CH_2Cl_2}$ solution at *ca.* 273 K and a scan rate of 200 mV s^{-1}

Complex	E_{pc}/V	E_{pa}/V
6	−0.17	−0.09
	−0.57	−0.44
7	−1.42	−0.42
8	—	−0.27
	−0.80	−0.42

negative than that of the first cathodic process resulted in products which exhibited observable ESR spectra only for compounds **6** and **8**. The solution and frozen-solution ESR spectra obtained were characteristic of nickel(I) species exhibiting hyperfine coupling of the unpaired electron to four equivalent ^{31}P nuclei. The ESR parameters for the product from **6** are identical to those of compound **1**, and the parameters for the product from compound **8** are given in Table 4.

The cyclic voltammetry results for complex **6** are similar to those for the corresponding halide-free complex **1**, *i.e.* two waves are observed on the cathodic sweep which can be assigned to successive $\mathrm{Ni^{II}} \longrightarrow \mathrm{Ni^{I}}$ and $\mathrm{Ni^{I}} \longrightarrow \mathrm{Ni^{0}}$ reduction processes. The potentials for these processes are slightly more negative than those for **1**, reflecting the effect of the co-ordinated bromide. However, on the time-scale of the *in situ* electrolysis the nickel(I) complex must undergo loss of Br$^-$ since its ESR spectrum is identical to that of $[\mathrm{Ni^{I}}\{cis\text{-}\mathrm{C_2H_2(PPh_2)_2}\text{-}1,2\}_2]^+$, the product of the controlled-potential electrolysis of **1**. The cyclic voltammetry and ESR results for **7** and **8** are considerably different from those of the corresponding halide-free complexes **3** and **4**. Whereas the latter show two successive reduction waves, the chloro-complexes **7** and **8** show only a single reduction wave. This is consistent with the formation of the respective $[\mathrm{Ni^{0}(L{-}L)_2}]$ species from the precursor by an irreversible reduction followed by dissociation of the halide ion, in an electrochemical–chemical mechanism. At the requisite reduction potential the $[\mathrm{Ni^{I}(L{-}L)_2}]^+$ species is immediately reduced to $[\mathrm{Ni^{0}(L{-}L)_2}]$. The latter is ESR inactive and this explains why the product from **7** was not observed in the ESR spectrum. The reason for the observation of a nickel(I) product for **8** is probably the same as in the case of the $[\mathrm{Ni^{I}L_4}]^+$ complexes discussed above, *i.e.* a comproportionation reaction between the nickel(0) and unreacted nickel(II) species in solution. The reason why this is observed for **8** and not for **7** is probably associated with the much more cathodic potential required to reduce **7**. At this potential the nickel(I) species may be much less stable, and any such species formed would be rapidly reduced to the diamagnetic nickel(0) state.

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