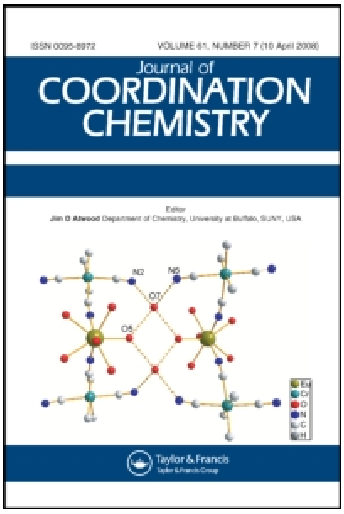

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Influence of Steric Bulk on the Relative Stability and Interchangeability of the Various Oxidation States for Nickel Complexed with 1,2-Bis(Dialkylphosphino)Benzene

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INFLUENCE OF STERIC BULK ON THE RELATIVE STABILITY AND INTERCHANGEABILITY OF THE VARIOUS OXIDATION STATES FOR NICKEL COMPLEXED WITH 1,2-BIS(DIALKYLPHOSPHINO)BENZENE

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The reduction potentials and electrochemical reversibilities of a series of nickel complexes of 1,2-bis(dialkylphosphino)benzene are sensitive to the steric bulk of the alkyl substituents. With very large ligands, electroreduction is accompanied by rapid secondary chemical reaction, and spectroscopic evidence for the intermediacy of a coordinatively unsaturated species is presented. The potentials required for electrooxidation of these complexes are shifted to more positive potentials by increasing bulk of the alkyl substituents on the bisphosphino ligands.

Keywords: Nickel, phosphines, electrochemistry, X-ray structures

INTRODUCTION

Compounds containing trivalent group V atoms readily coordinate with transition metals,[1–3] and those containing phosphorus bind most tenaciously. Complexes containing tertiary phosphine ligands have been employed in numerous homogeneous reactions: hydrogenation,[4,5] hydroformylation,[6,7] polymerization,[8] oxidation,[9] and hydrosilylation.[10] Multidentate (chelating) ligands have proven to be useful in suppressing both irreversible, redox-activated decomposition *via* ligand dissociation and catalyst deactivation *via* oxidative addition of the ligand's C–P bond to the coordinated metal.[11] Studies of metal complexes of polyphosphino ligands therefore provide a valuable supplement to more conventional investigations employing first row coordinating atoms to understand catalytic processes.[12] Systematic investigations of the sensitivity of the redox properties of metal polyphosphino complexes to structural variations are lacking, however, despite the clear importance of such studies, as gauged by the many analogous investigations of substituted amino complexes.

Electrochemical techniques can be used to probe reactivity *in situ*[13,14] and, specifically, to quickly establish the reactive oxidative state of metal complexes. The work presented herein employs electrochemistry in conjunction with more traditional analytical methods to probe the effect of steric bulk on the stability and interchangeability of the various oxidation states for 1,2-bis(phosphino)benzene complexes of nickel. We are most interested in determining the effect of perturbed ligand structure

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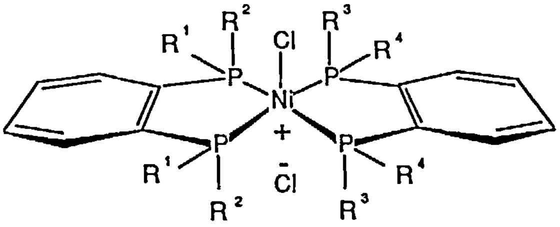
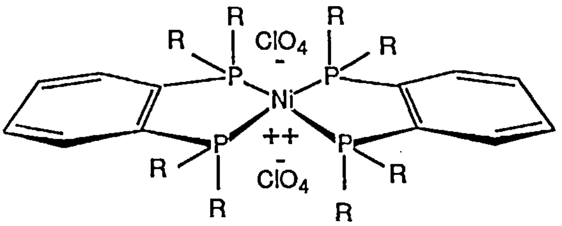
on the stability of the several possible redox levels accessible to nickel phosphine complexes. Such descriptions are important in characterizing the chemical processes activated by different oxidation levels of these complexes and in evaluating the possibility that such complexes might be appropriate catalysts for single or multiple electron redox processes.

RESULTS AND DISCUSSION

Several synthetic routes to multidentate ligands have been reviewed elsewhere.[15–17] Although most studies to date have employed complexes with either per-methyl or per-phenyl substitution at phosphorus, a route previously described by Kyba[17] has been adapted to synthesize six 1,2-(dialkylphosphino)benzene ligands with various alkyl substitution at phosphorus.[18] From these ligands, six complexes with nickel(II) chloride (**1–6**) and three complexes with nickel(II) perchlorate (**7–9**) were prepared. Alkyl substitution was made only at phosphorus in order to minimize electronic perturbation of the arene.[19] The complexes are arranged so that the approximate steric bulk of the alkyl substituent



1 R^1, R^2, R^3, R^4 = Me
2 R^1, R^2 = Me, R^3, R^4 = Et (cis and trans isomers)
3 R^1, R^3 = Me, R^2, R^4 = Et
4 R^1, R^2, R^3, R^4 = Et
5 R^1, R^3 = Et , R^2, R^4 = nPr (cis and trans isomers)
6 R^1, R^2 = Me, R^3, R^4 = iPr



7 R = Me.
8 R = Et
9 R = iPr

on the ligating phosphorus bound to nickel increases along the series (i.e., **1** smaller than **2**, etc.).

Reductive Electrochemistry in Acetonitrile: Ni(II)–Ni(I)–Ni(0)

The electrochemical reduction of the permethylated Ni(II) complex **1** (in acetonitrile), occurs as a single, quasi-reversible two-electron wave (as established by coulometric measurement) accompanied by a peak potential difference of 300mV separating the reduction wave from its reverse oxidation wave. Similar effects have been previously reported for other metal complexes of this ligand.[20,21] Its cyclic voltammogram (CV) is compared in Figure 1 with those of complexes **2** (which resembles that of **3**) and **5** (which resembles that for **4**); although poorer reversibility in the oxidation waves is observed in complexes bearing bulkier alkyl groups, the waves for the reductions (and their associated return oxidations) for the series show reasonable chemical reversibility and quasi-reversible electrochemistry, with the potential of the (Ni(0)→Ni(II)) wave being progressively shifted to a slightly less negative value (**1** = 1.12 V, **2** = −1.07 V, **3** = −1.02 V) as the ligand bulk increases. This quasi-reversibility in the reduction wave is routinely observed in chemically reversible transformations which are accompanied by a geometry change. Here the square planar Ni(II) complex must undergo a structural reorganization to the tetrahedral geometry of the Ni(0) complex (see below).

In complexes **4** and **5**, the electrochemistry changes considerably. The reduction remains a single, two-electron wave, but the peak separation is reduced to 90 mV, as is indicative of improved electrochemical reversibility which is presumably related to the added distortion in the square planar complexes caused by very large substituents borne at the coordinating phosphorus atom. Complex **6** is the only nickel chloride complex which exhibits two one-electron reduction waves in acetonitrile (Figure 2): the first wave is at a potential more positive than any of the other chloride complexes (−0.85 V). This complex is also unique in exhibiting two distinct waves in the return oxidation (Ni(0)→Ni(II)).

Increasing the ligand's steric bulk thus facilitates the reduction of Ni(II) to Ni(I). For complexes **1**–**3**, the reduction of Ni(II)→Ni(I) occurs with an overpotential, *i.e.*, at a potential more negative than the Ni(I)→Ni(0) reduction. The reduction of complexes **4** and **5** also occurs at an overpotential. With **6**, the Ni(II) → Ni(I) conversion occurs at a sufficiently positive potential that it may be observed independently of the Ni(I)–Ni(0) couple.

The above generalizations also carry over to the ickel perchlorate complexes **7**–**9**, Figure 3. Complex **7** reduces in a single, two-electron wave (−1.15 V), while **8** is reduced at a less negative potential in two waves (−0.95 V and −1.11 V). Lacking the apical coordination with chloride which obtains in complexes **1** through **6**, the reductions of **7** and **8** occur at potentials positive of those for their chloride analogues (**1** and **4**). The perchlorate complex **9** continues this trend with a reduction wave at −0.82 V. The reduction of **9**, however, involves a more complicated chain of events, including decomplexation–recomplexation, which is discussed below.

The geometries of analogous Ni(II) complexes are usually pentacoordinate[20] with the phosphines being coordinated in a square pyramidal array and a counterion or solvent occupying the apical position. The four phosphorus atoms form a basal plane, and a covalent bound chlorine occupies the axial position. The nickel sits either in the basal plane or slightly above it. The geometry of the analogous perchlorates in solution is square planar: however, in coordinating solvents (*e.g.*, acetonitrile), it is likely that the axial coordination sites are also occupied.

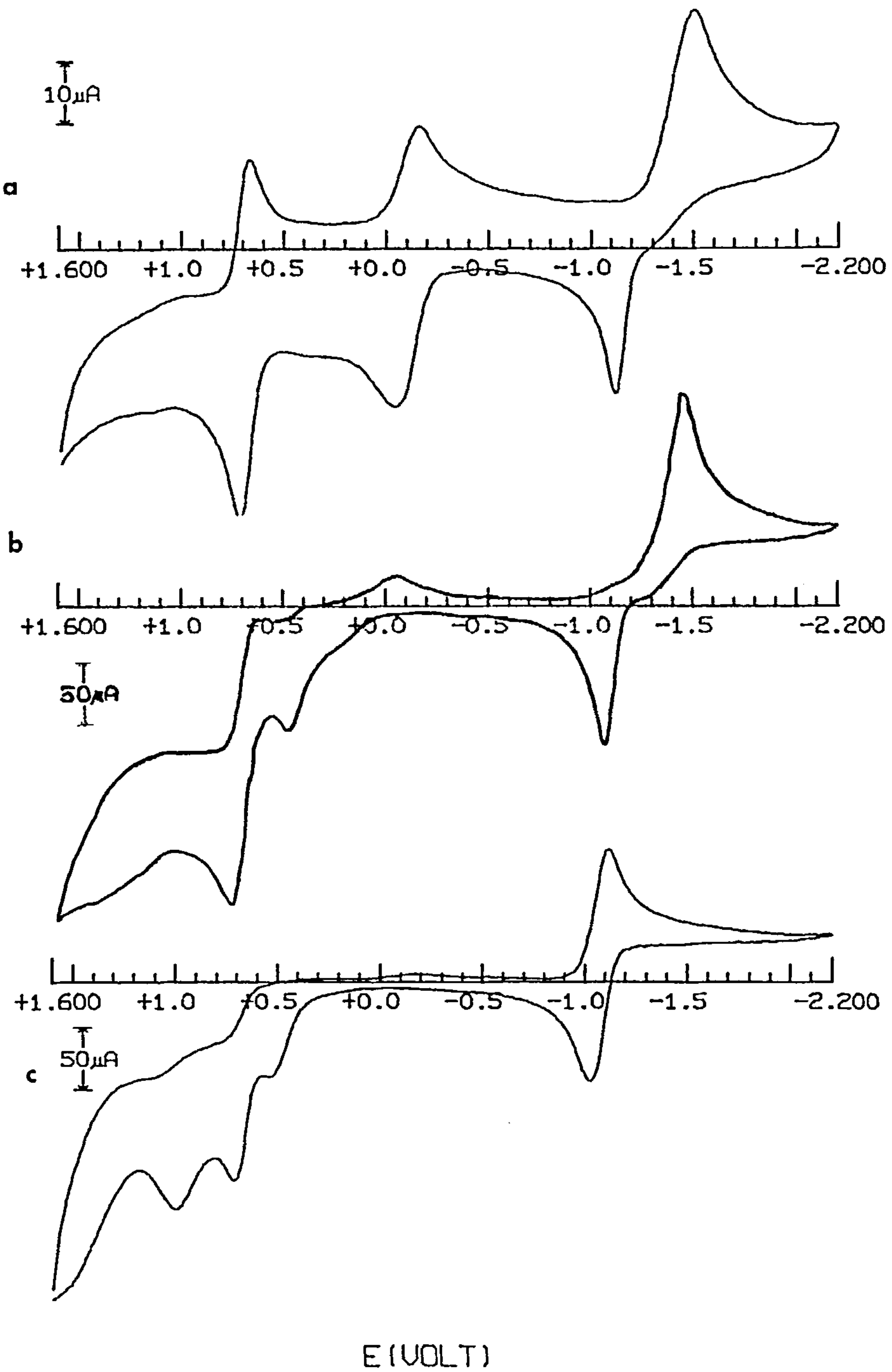


FIGURE 1 Cyclic voltammograms (initial scans) at glassy carbon in acetonitrile, 25°C, 0.2 M TBAP, 100 mV/s: (a) **1**; (b) **2**; (c) **5**.

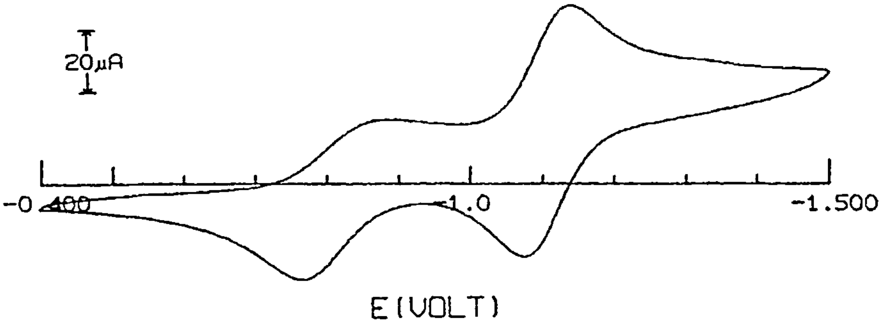


FIGURE 2 Cyclic voltammogram (initial scan) of 6 at glassy carbon in acetonitrile, 25°C, 0.2 M TBAP, 100 mV/s.

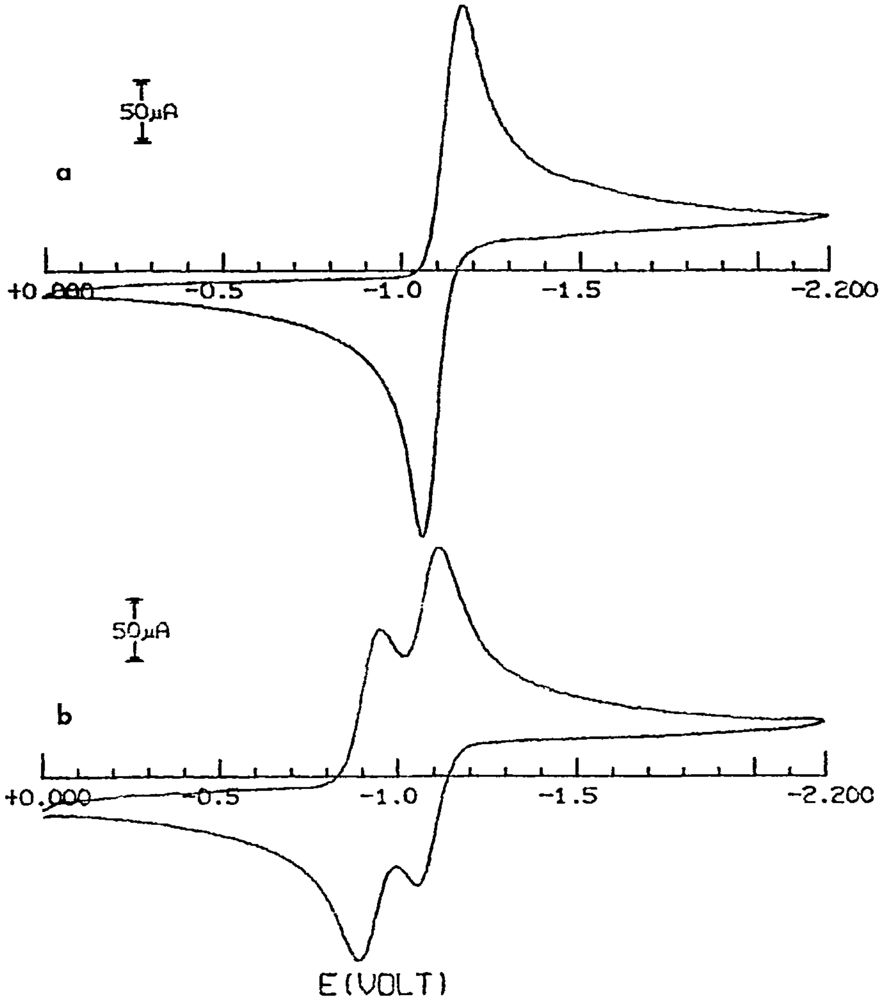


FIGURE 3 Cyclic voltammograms (initial scans) at glassy carbon in acetonitrile, 25°C, 0.2 M TBAP, 100 mV/s; (a) 7 and (b) 8.

Complexes **1–9** undergo two types of sterically induced geometric distortion. Increasing a ligand's steric bulk forces the coordinating phosphorus atoms to reside further from the metal. This distortion causes the metal's $dx^2–y^2$ orbital (with which the phosphorus atoms directly overlap) to be lowered in energy.

A second type of distortion, caused by van der Waals interaction between the bulky ligands, is an enhanced elevation of the metal atom above the basal plane. This allows the axial ligand to evade crowding by the equatorial alkyl groups. Rossi and Hoffmann have pointed out that in square pyramidal complexes, the $dx^2–y^2$ orbital is lowered in energy as the L_{basal}–metal–L_{basal} angle decreases.[22]

These distortions produce similar results. Since **1–8** are all low spin complexes, stabilization of the vacant $dx^2–y^2$ orbital results in a more electronically favourable reduction. When steric crowding is increased, the resulting destabilization of the Ni(II) oxidation state diminishes the overpotential for reduction. This implies that the transition state for the Ni(II)→Ni(I) conversion is more easily reached when the initial square planar geometry is destabilized by torsional strain derived from ligand steric bulk. This explanation is experimentally equivalent to one in which the electroreduction is coupled with a rapid conversion to a pseudo-tetrahedral form wherein ligand bulk increases the rate of stereochemical change. This is reasonable, since a "square-planar-to-tetrahedral" geometry (which similar Ni(I) complexes are known to possess[23]) more easily accommodates bulky ligands. Crowding should also expedite expulsion of the axial ligand, which is a prerequisite for conversion to the tetrahedral geometry.

TABLE I

Molar conductivity, UV absorption and ^{31}P nmr for complexes **1–9**.

		Λ_M[a]	$\lambda_{max}(\varepsilon)$[a]	^{31}P[b]
1	$[Ni(C_6H_4(PMe_2)_2)_2]Cl_2$	117	326 (2791) 398 (1096)	41.4 (s)
2	$[Ni(C_6H_4(PMe_2)_2)_2C_6H_4(PEt_2)_2]Cl_2$	121	406 (1035)	67.9 (t), J = 74 Hz 35.7 (t), J = 4 Hz
3	$[NiC_6H_4(PMe,Et)_2)_2]Cl_2$	117	412 (1035)	50.8 (s)[c] 50.2 (s)
4	$[Ni(C_6H_4(PEt_2)_2)_2]Cl_2$	113	426 (1316)	57.1 (s)
5	$[NiC_6H_4(PEt,nPr)_2)_2]Cl_2$	107	428 (1196)	55.1 (s)
6	$[Ni(C_6H_4(PMe_2)_2C_6H_4(P\ iPr_2)_2]Cl_2$	103	438 (934)	79.1 (t), J = 69 Hz 27.1 (t), J = 69 Hz
7	$[Ni(C_6H_4(PMe_2)_2)_2](ClO_4)_2$	229	376 (935)	39.8 (s)
8	$[Ni(C_6H_4(PEt_2)_2)_2](ClO_4)_2$	230	384 (617)	63.7 (s)
9	$[Ni(C_6H_4(P\ iPr_2)_2)_2](ClO_4)_2$	267	380 (- - - - -)[d] 436 (439)[e]	91.2 (s) 73.3 (s)[e]

[a] Molar conductivities ($ohm^{-1}\,cm^2\,mol^{-1}$) and electronic spectra were measured in acetonitrile ($\approx 10^{-3}$ M). [b] ^{31}P nmr (proton decoupled) are referenced to phosphoric acid: complexes **1** to **6** were measured in $CDCl_3$, complexes **7–9** in CH_3CN. [c] Two isomers present. [d] Absorption due to the 1:1 complex. [e] Measurement made using 1,2-dichloroethane as solvent.

In this series, steric bulk does not appear to alter the geometry at Ni(II). For pentacoordinate d^8 nickel complexes (**1–6**), the trigonal bipyramidal and square pyramidal geometries are very close in energy, and tetracoordinate d^8 nickel complexes (7–9) with strong field ligands generally favour a square planar geometry over a tetrahedral one. Consistent with this explanation, ^{31}P nmr data (*i.e.*, multiplicity and diamagnetism) indicate that in the Ni(II) oxidation states of **1–9**, the phosphorus atoms remain coplanar. The energy required to stabilize the square pyramidal and square planar geometries is derived from enhanced phosphorus-nickel orbital overlap. The ^{31}P nmr data (Table I) shows that the phosphorus-phosphorus coupling constants for **2** and **6** are very similar, in contrast to the expectation if the geometry of **6** were very different from that of **2**.[24]

X-ray Crystal Structural Characterization of the Complexes

Molar conductivity measurements (Table I) confirm that in acetonitrile each nickel chloride complex exists as a 1:1 electrolyte and that each of the perchlorate complexes is a 2:1 electrolyte.[25]

The perethyl-substituted complexes **4** and **8** reduce more readily than their less bulky permethyl-substituted analogues (**1** and **6**). A possible explanation for this difference in electrochemical behaviour is that steric bulk of the alkyl substituent alters the ligand–metal–ligand dihedral angle. Complexes containing bulkier ligands reduce more readily because the geometries for the Ni(II) and Ni(0) oxidation states more closely resemble one another (*i.e.*, a least-motion argument). In order to probe this issue, the structures of **4** in the Ni(II) and Ni(0) states were determined by X-ray crystallography.

In the Ni(II) oxidation state, the geometry about the nickel atom is clearly square pyramidal[26] as expected for a typical Ni(II) complex; the four phosphorus atoms form the basal plane with a chlorine at the apex (see Supplementary Material). The ligand–metal–ligand dihedral angle (*ca* 10°), the ligand bite angle (*i.e.*, P3–Ni–P4 angle, *ca* 85°), and the phosphorus-nickel bond length (2.2 Å) give little indication of sterically induced distortions. The geometry of **4** appears to be dictated by the ligand field and not by steric bulk.

The X-ray structure of **4** in the Ni(0) oxidation state reveals a slightly distorted tetrahedral geometry (Figure 4). Each unit cell contains 16 molecules, four each of four slightly different tetrahedra in which the ligand–metal–ligand dihedral angle varies between 72° and 80°. The ligand bite angle and phosphorus-nickel bond length are 91° and 2.15 Å, respectively. The absorption spectra of **4** in the crystalline state and in solution correlate for both the Ni(II) and Ni(0) forms.[27] Therefore, structural information from X-ray crystallography should also pertain to solution species. These results verify the contention that the ligands in complexes **1–9** change from planar to tetrahedral coordination upon reduction.

Absorption Spectra

Gray has formulated a detailed electronic structural model to rationalize the absorption spectra of the arsine analogues of **1** and **7**.[28] At 77 K, all three spin allowed transitions for a low-spin, square-pyramidal d^8 complex ($z^2 \rightarrow x^2-y^2$; $xz,yz \rightarrow x^2-y^2$ and $xy \rightarrow x^2-y^2$) were observed: however, the ordering of orbital energies is different from that of typical C_{4v} square-pyramidal complexes. Our own experiments indicate that Gray's interpretation of the arsine spectra similarly applies to the phosphine complexes.

The electronic spectra of the chloride complexes **1–6** show only one band in the visible region at 300 K. This band is assigned to the symmetry-allowed $^1A_1 \rightarrow {}^1E$

(xz,yz→x^2–y^2). Compounds **1** and **4** were also examined at 77 K, but additional bands were not resolved. As with Gray's arsine complexes, the dominant band sharpens considerably upon cooling and shifts to a longer wavelength (which in part may be caused by a shift in the equilibrium position of the chloride). The integrated area of the peak should have remained constant with temperature but did not, because upon cooling, the λ_{max} shifts closer to a neighbouring charge transfer band.

Unfortunately, low temperature measurements fail to resolve the $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2-y^2$) or $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2-y^2$) bands. Both bands are symmetry-forbidden. Additional barriers to their detection were (1) the superposition of a charge-transfer band over the region that might be expected to contain the $^1A_1 \rightarrow {}^1A_2$ band and (2) the fact that the axial halide does not mix strongly with the metal d-orbitals, which renders the $^1A_1 \rightarrow {}^1B_1$ band very weak.

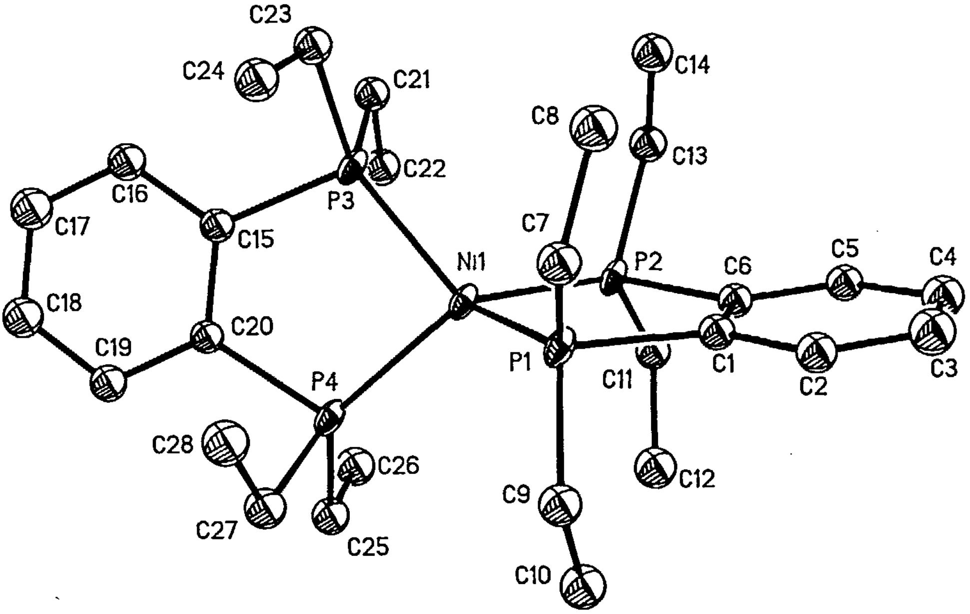


FIGURE 4 ORTEP of complex 4 in the nickel(0) oxidation state. The structure is one of four variations packed into each crystal cell. All of the variants exhibit tetrahedral coordination about the nickel atom.

The perchlorate complexes **7–9** also exhibit only one band in the visible region. This band is assigned to the xz,yz→x^2–y^2 transition as well, which transforms as $^1A_{1g} \rightarrow {}^1E_g$ for D_{4h} symmetry. As a result of this symmetry, the extinction coefficients are considerably smaller (parity forbidden) for the perchlorate complexes (**7–9**) than for the chlorides (**1–6**).

Advancing through the series **1** to **6**, λ_{max} for the $^1A_1 \rightarrow {}^1E$ (xz,yz→x^2–y^2) transition shifts to longer wavelengths (398 to 438 nm), Table I. Similarly, λ_{max} for the $^1A_{1g} \rightarrow {}^1E_g$(xz,yz→$x^2$–$y^2$) transition in **7–9** also shifts to longer wavelengths with increasing ligand bulk (376 to 436 nm), as is consistent with the supposition that increasing steric bulk lowers the x^2–y^2 energy and thus decreases the gap between xz,yz and x^2–y^2 orbitals. Additional support for this idea may be taken from studies of Ni(II) complexes with dimethylethylenediamine (dimen) and diethylethylenediamine (dieen).[29] The bulkier dieen complex exhibited much weaker in-plane and out-of-plane field strengths and a similar shift in λ_{max}.

Solvent Effects on Reductive Electrochemistry

In acetonitrile, the large overpotentials of **1** toward electrochemical reduction have been attributed to the very high thermodynamic stability of the Ni(II) oxidation state. Performing the reduction of **1–3** in a nonpolar, non-coordinating solvent (such as methylene chloride or 1,2-dichloroethane) has little effect on the observed potentials. In contrast, however, changing solvent greatly affects compounds **4** and **5**. As shown in Figure 5 for **5**, this decrease in solvent coordination causes the Ni(II)→Ni(0) reduction to shift from a single, two-electron wave to two one-electron waves. The reduction waves for **4** and **5** in 1,2-dichloroethane thus bear a striking resemblance to that of **6** in acetonitrile (Figure 2).

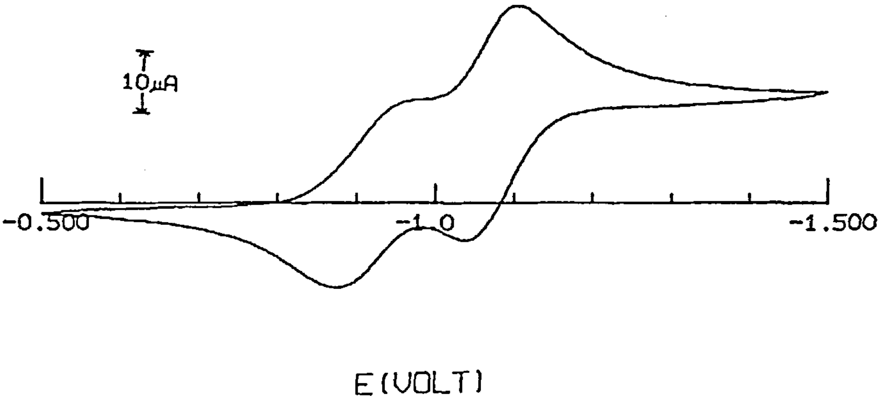


FIGURE 5 Cyclic voltammogram (initial scan) of 5 at glassy carbon in 1,2-dichloroethane, 25°C, 0.2 M TBAP, 100 mV/s.

Coordinating solvents readily bind to vacant axial sites, as is generally evidenced by small shifts in λ_{max} (2–8 nm). Even weakly coordinated apical ligands, however, must be expelled during a reduction involving conversion from a pentacoordinate to tetracoordinate complex. Thus complexes **4–6** (and **8**) are more readily reduced in weakly coordinating solvents, *e.g.*, 1,2-dichloroethane or methylene chloride, than in acetonitrile or tetrahydrofuran.

The reason that complexes **1** and **7** were only slightly affected by solvent is that the small permethyl-substituted ligand gives rise to an extremely strong in-plane ligand field. Weak axial coordination contributes little to the existing overpotential arising from the stabilizing effect of the phosphine ligands.

Solvent effects serve to underscore the uniqueness of **9**. In acetonitrile, **9** is the only compound in which the 2:1 complex is in equilibrium with 1:1 complex and free ligand ($K_{eq} \approx 38$ in favour of the 2:1 complex at 25°C, as seen by ^{31}P nmr: 2:1 complex 130 ppm, 1:1 complex 75.5 ppm, and free ligand −3.6 ppm). Monitoring the uv absorption spectrum of **9** at 2 sec intervals after the addition of acetonitrile (1%) to a methylene chloride solution shows that the original absorption at 436 nm decreases in intensity as a new one at 380 nm grows, establishing that acetonitrile is thus able to compete effectively with the bisphosphinobenzene ligands for coordination sites.

The CV of 9 in acetonitrile shows three reduction waves on the first scan (Ni(II)→Ni(I) (2:1 complex) at 0.82 V, Ni(I)→Ni(0) (2:1 complex) at −1.2 V, and Ni(II)→Ni(0) (1:1 complex) at −1.55 V). Subsequent scans exhibit a very weak fourth reduction wave at −0.55 V: although this wave appears in a likely potential range for a Ni(II)→Ni(I) reduction from the tetrahedral complex formed during the first scan, the observed scan rate and relative peak intensities would require a half-life of about 10 seconds for this unstable state, and no evidence for a species with such a half-life could be found in spectroelectrochemical experiments. If excess free ligand is added to the solution, the reduction peak for the 1:1 complex disappears (Figure 6), and the ratio of the Ni(II)→Ni(I) and Ni(I)→Ni(0) peaks changes. The CV of 9 in 1,2-dichloroethane is similar, with one two-electron reduction wave on the first scan (−1.24 V), but on subsequent scans a second reduction wave (−0.42 V) appears. The new wave is highly reversible, which is consistent with a Ni(II)→Ni(I) transition from a tetrahedral geometry. ^{31}P nmr confirms the absence of the 2:1–1:1 equilibrium in 1,2-dichloroethane and explains the disappearance of a reduction peak for the 1:1 complex in this solvent.

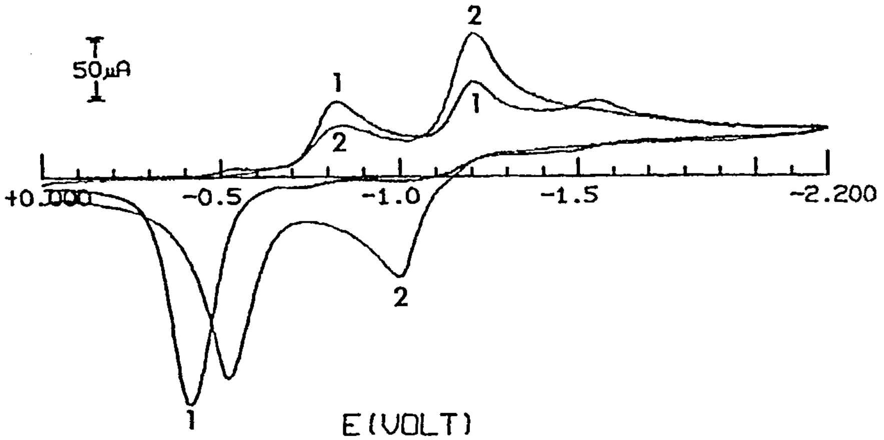


FIGURE 6 Cyclic voltammograms (initial scans) at glassy carbon in acetonitrile, 25°C, 0.2M TBAP, 100 mV/s; (1) Complex 9 alone and (2) in the presence of excess free ligand.

The fact that the Ni(II)→Ni(I) reduction of 9 occurs more readily in acetonitrile than in 1,2-dichloroethane contrasts with the behaviour observed for the other complexes. This difference in solvent effects may arise from an alternative reduction pathway. Steric bulk weakens the ligand field stength of 9 to such a great extent that in acetonitrile, the 2:1 complex is only 2 kcal mol^{-1}* more stable than the 1:1 complex (calculated from K_{eq} at 25°C). In the Ni(I) oxidation state, a planar 2:1 complex would be less stable than the 1:1 complex. Therefore, during reduction, a bisphosphinobenzene ligand may dissociate from the activated complex. After the initial reduction, a bisphosphinobenzene ligand re-enters the coordination sphere to give 2:1 tetrahedral Ni(I) and/or Ni(0) species. Further evidence for this will be presented below.

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* 1 kcal = 4.184 J.

Oxidation of the Ni(0) state of **9** to its original Ni(II) state occurs in two steps, without an immediate geometry change. The Ni(II) oxidation state is most stable when square planar, but in order to achieve that geometry, an activation barrier must be overcome. This activation barrier is probably associated with rotating the bulky phosphine groups past one another. Because this process is slow, a reduction peak for $\mathrm{Ni(II)_{tetrahedral}}$ is observed at scan rates as low as 25 mV/s.

The Contrast Between the Reductive Electrochemistry of Monodentate Tertiary Phosphine Complexes of Ni(II) and 1,2-Bis(dialkylphosphino)benzene–Ni(II) Complexes (1–8) in Acetonitrile

Bontempelli and coworkers have studied the electrochemical reduction of Ni(II) perchlorate in the presence of excess monodentate tertiary phosphine.[30–33] He also found a correlation between ligand bulk and the overpotential for the Ni(II)→Ni(I) process, but the trends of this system are exactly opposite ours. The bulky triphenylphosphine ligand caused a large reductive overpotential (Ni(II)→Ni(I)), while the considerably smaller triethylphosphine ligand does not. In fact, with triethylphosphine, the metal could be reduced in steps (Ni(II)→Ni(I)→ Ni(0)).

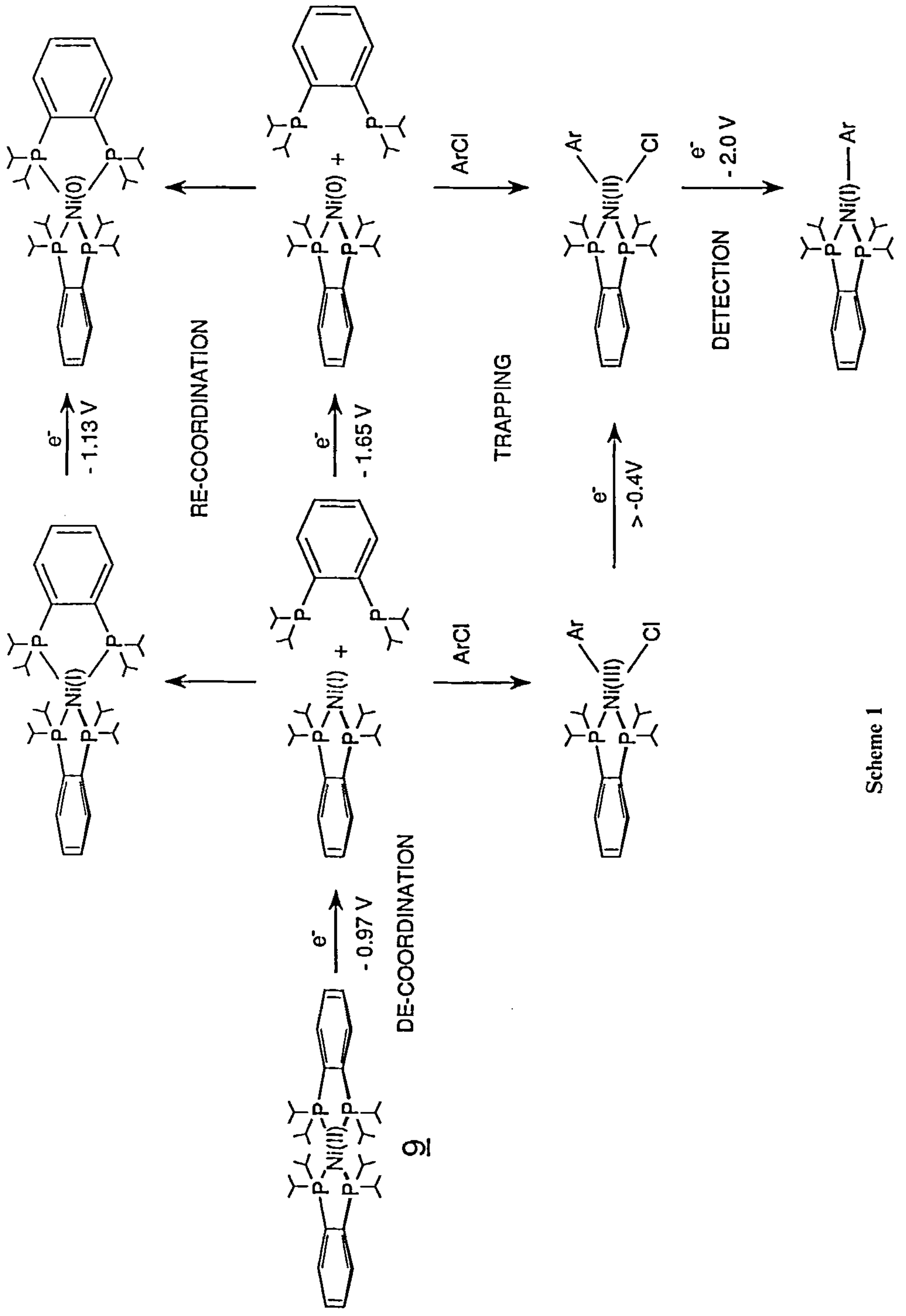
Bontempelli explained these results as follows: in acetonitrile, two triphenylphosphines and four acetonitriles complex with Ni(II) in an octahedral geometry. Reduction to Ni(I) requires the expulsion of four acetonitriles and the entry of two more triphenylphosphines into the activated complex's coordination sphere, concomitantly with a difficult geometry change. In contrast, four of the less bulky triethylphosphines and two acetonitriles complex with Ni(II). Reduction of this complex is easier because it requires only the expulsion of two acetonitriles and a geometry change.

An important feature of our compounds is that steric bulk could be changed without altering the coordination pattern. As a result, the electrochemical consequences are very different from those with Bontempelli's complexes. Only the extremely hindered complex (**9**) shows any indication of changing coordination (approx. 18% of a 1:1 complex in acetonitrile).

Spectroelectrochemistry

Potential step experiments were performed on several complexes. The reduction of **4** to the Ni(0) complex is typical for these complexes; reduction of Ni(II) occurs simultaneously with the formation of Ni(0) ($\lambda_{max} = 401$ nm). A band attributable to Ni(I) could not be resolved. A similar experiment performed with **8** produced nearly identical results.

Reduction of **9** was not accompanied by an immediate appearance of a Ni(0) species. Instead, the growth of the absorption attributed to Ni(0) occurred slowly. In addition, the rate for electrolysis of **9** is ten times slower than for **8** at -1.91 V. When excess free ligand was added, the rate of electrolysis changed very little. However, the rate of appearance of the Ni(0) absorption was accelerated (*ca* two times faster). Since the presence of excess free ligand should have no impact on the rate at which Ni(0) appears, decomplexation–recomplexation must accompany reduction.


RE-COORDINATION
TRAPPING
DETECTION
DE-COORDINATION
Ni(0)
Ni(I)
Ni(II)
Ni(III)
9
e⁻
- 0.97 V
- 1.13 V
- 1.65 V
> -0.4V
- 2.0 V
ArCl
Ar
Cl
P
+

Scheme 1

Trapping Coordinatively Unsaturated Nickel-bisphosphino-benzene Intermediates with Chlorobenzene

The coordinatively unsaturated intermediate, formed when complex 9 temporarily dislocates a bisphosphinobenzene ligand, can be trapped in the presence of chlorobenzene by oxidative addition in competition with ligand recoordination (Scheme I). Coordinatively unsaturated Ni(0)-phosphine complexes are known to undergo rapid oxidative addition with aryl halides,[34-40] (*1*). The resulting aryl nickel(II) complex may subsequently be reduced to Ni(I),[41] (*2*).

$$(PR_3)_2Ni(0) + ArX \longrightarrow (PR_3)_2Ni(II)\begin{smallmatrix}\nearrow Ar\\ \searrow X\end{smallmatrix} \tag{1}$$

$$(PR_3)_2Ni(II)\begin{smallmatrix}\nearrow Ar\\ \searrow X\end{smallmatrix} \xrightarrow[-2.0\ V\ vs\ SCE]{e^-} (PR_3)_2Ni(I){-}Ar + X^- \tag{2}$$

$$(PR_3)_2Ni(I) + ArX \longrightarrow (PR_3)_2Ni(III)\begin{smallmatrix}\nearrow Ar\\ \searrow X\end{smallmatrix} \tag{3}$$

Coordinatively unsaturated Ni(I) phosphine complexes are also reported to undergo oxidative additions with aryl halides,[41,42] (*3*). Reactions (*1*)-(*3*) may be used to sequentially trap and detect coordinatively unsaturated nickel intermediates formed during the cyclic voltammetry of complex 9.

Cyclic voltammetry of 9 in the presence of chlorobenzene (Figure 7) clearly shows evidence for an ece (electrochemical-chemical-electrochemical) reaction sequence during reduction. Besides the reduction waves for 9 (E_p = 1.0 V and −1.2 V), an additional wave at −2.0 V appears. This new reduction wave correlates well with the reported reduction potentials for various Ni(II) aryl halide complexes.[43,44] Furthermore, the wave forms a multi-electron plateau: evidence for the onset of electrocatalytic coupling of aryl halide to biphenyl.

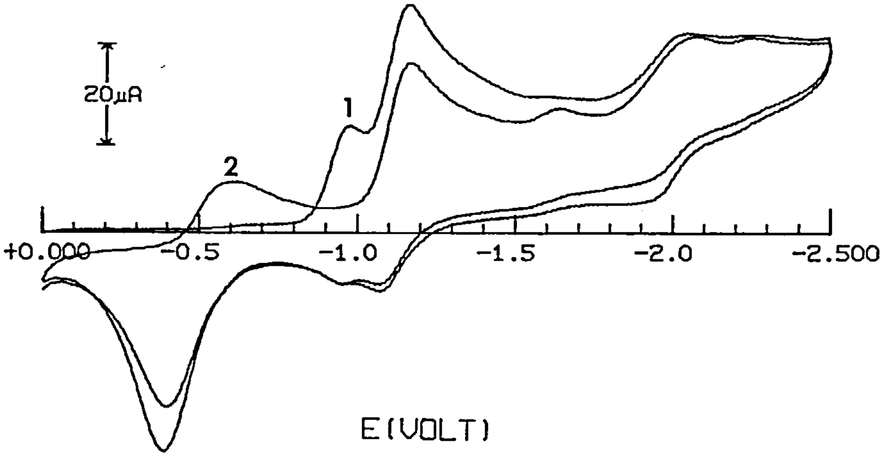


FIGURE 7 Cyclic voltammogram of complex 9 at glassy carbon in acetonitrile and chlorobenzene, 25°C, 0.2 M TBAP, 100 mV/s: (1) first cycle; (2) second cycle.

During the second cycle, a new wave at −0.6 V (attributed to reduction of the tetrahedral Ni(II) complex) emerges, while the reduction wave from the first scan (−1.0 V) disappears. Upon oxidation, a complex which fails to decoordinate a ligand can neither change geometry (tetrahedral to planar) nor be trapped. It therefore survives to be re-reduced during subsequent scans (*i.e.*, −0.6 V). Geometry changes associated with dislocation of a ligand are inhibited by chemical trapping: the return to a planar Ni(II) species is therefore inhibited (*i.e.*, no reduction wave at −1.0 V). Reversibility improves slightly if the electrochemical cycle is conducted in the presence of chloride, suggesting the possible formation of coupling product (biphenyl) on reoxidation and formation of a Ni(II) complex.

The above observations could be alternatively interpreted as an associative substitution between chlorobenzene and a 2:1 bisphosphinobenzene–nickel intermediate. This event, however, is highly unlikely; Ni(0)(diphos)$_2$ and similar coordinatively saturated complexes are known to be unreactive toward aryl halides.[45,46]

Also worth considering is the possibility that the small amount of 1:1 bisphosphinobenzene–nickel(II) complex initially present (in equilibrium with the 2:1 complex) undergoes reduction to Ni(I), and is responsible for the observed formation of Ni(II) aryl halide complex (−2.0 V). To a small extent, this must occur; however, the amount of 1:1 complex present (15%) cannot account for the large Ni(II) aryl halide complex reduction current observed. Furthermore, the addition of excess free ligand (3 mol. equiv.) virtually eliminates the 1:1 complex, yet only slightly suppresses the peak at −2.0 V. Ligand dislocation is most consistent with all of the experimental observations.

Oxidative Electrochemistry: Ni(II–Ni(III)–Ni(IV)

The redox behaviour of **1** (Ni(II)↔Ni(III)) has been described as irreversible.[47] Warren and Bennett originally pointed out that in going from Ni(II) to Ni(III), an additional chloride ligand must enter the coordination sphere.[20] The addition of excess chloride (*e.g.*, tetraethylammonium chloride) makes this step more favourable, and therefore more electrochemically reversible. With increasing ligand steric bulk, however, reversibility is lost, as is consistent with the required additional ligand entering the sixth coordination site being blocked by bulky ligands.

Besides blocking this site, bulky ligands reduce the oxidation potential of the ligands themselves by induction. Thus, as bulky ligands hinder metal-centred oxidations, ligand-centred oxidations[48] intervene. In this way, the two reversible metal-centred electrochemical oxidations observed for **1** (Figure 1) give way to a fairly complicated array of metal and ligand-centred processes (*e.g.*, **4–6**). The perchlorate complexes fail to undergo these oxidations reversibly because they lack the stabilizing axial ligand which is essential to the stability of the higher oxidation states.

CONCLUSIONS

Increasing steric bulk in the series (**1–9**) alters neither the geometry nor the stoichiometry of the coordination of the (dialkylbisphosphino)benzene ligands with nickel(II). Steric bulk does, however, greatly influence the strength of the in-plane ligand binding and the ease of structural reorganization. These effects are manifest in the complexes' electrochemical behaviour.

In complexes **1–8**, changes in electrochemical reducibility arise from a destabilization of the Ni(II) complex (*i.e.*, weaker crystal field strength) and not from any effects on geometry interchangeability. X-ray crystal structures for a complex in both the Ni(II) and Ni(0) oxidation states verify that a geometry change accompanies reduction. The ease of expulsion of axial ligands relates to ligand bulk.

When the ligand becomes very large (*e.g.*, **9**, the Ni(II)→Ni(I) reduction is accompanied by decomplexation of a bisphosphine ligand. Evidence for the production of a coordinatively unsaturated intermediate was obtained by spectroelectrochemical and trapping experiments. Coordinating solvents assist reduction and complicate the mechanism.

The electrochemical production of higher oxidation states (Ni(III) and Ni(IV)) is hampered by steric bulk. Bulky ligands block the sixth coordination site and interfere with contraction of the coordination sphere, so that ligand-centred oxidation becomes kinetically competitive with metal-centred oxidation.

Since the Ni(I)→Ni(0) transformation exhibits electrochemical behaviour which is sensitive to the steric bulk of the ligand, these effects constitute "tunable" behaviour. Solvent effects also constitute a form of "tunability". The oxidations, on the other hand (formation of Ni(III) and Ni(IV) species), cannot be easily altered; here bulky ligands only serve to exacerbate the situation.

EXPERIMENTAL

General

Phosphorus-31 nmr spectra were obtained on either a Varian FT80 or General Electric GN-500 spectrometer. Chemical shifts are given in parts per million relative to phosphoric acid. Absorption spectra were measured on a Hewlett-Packard 8154A diode array spectrophotometer. Measurements at 77K were carried out in a 2:1 ethanol-diethyl ether mixture. This solvent mixture provided satisfactory solubility of compounds **1–6** and usually formed crack-free glasses. Conductivity measurements were made using a Yellow Springs Instrument (YSI Model 32) conductivity bridge. X-ray analyses were performed using a Syntex $P2_1$ auto-diffractometer. A single crystal was affixed to a glass fibre, placed in the diffractometer, and maintained under a cold stream of nitrogen (−110°C).

Unless noted otherwise, all manipulations involving phosphines were conducted under dry nitrogen or argon, and solvents were used as received (spectroscopic grade from Fisher Scientific or Mallinckrodt).

Electrochemical experiments were performed using a Bioanalytical Systems BAS-100 Electrochemical Analyzer equipped with a Houston International DMP-40 digital plotter. Cyclic voltammograms were recorded in a one-compartment cell equipped with a glassy carbon disk working electrode, a silver–silver nitrate in acetonitrile reference electrode, and a platinum auxiliary electrode. In other solvents, a silver wire quasi-reference electrode was used and whose potential was calibrated after the completion of the electrochemical measurements against added ferrocene. The reference electrode was separated from the test solution by a glass frit. Electrolyte solutions (0.2 M tetrabutylammonium perchlorate (TBAP)) were prepared just prior to use and were deaerated by bubbling argon through the solution. After a cyclic voltammogram of the electrolyte solution was obtained to ensure the absence of electroactive impurities, the nickel complex was added ($\approx 10^{-3}$ M).

Positive feedback was utilized in all CV experiments to compensate for IR drop between the working and reference electrodes. The observed potentials were calibrated after the electrochemical measurements by addition of ferrocene. Coulometric measurements were conducted on a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer.

Spectroelectrochemical experiments employed a previously described thin layer cell.[49] The cells were constructed with pyrex slides, Teflon spacers, and 1000 wire/inch gold minigrid (working electrode). Typically, the inside wall-to-wall separation was 100 μ. Air and moisture were excluded by enclosing the thin layer cell inside an air-tight cuvette. A platinum grid auxiliary electrode and a platinum or silver wire quasi-reference electrode were used. A Hewlett-Packard 8154A diode array spectrophotometer permitted continuous monitoring over a range of wavelengths during potential step experiments.

Preparation of Complexes 1–9

Previously described procedures for preparation of the symmetric ligands employed in this study[15,17] were directly adapted to the preparation of the dissymmetric ligands. Spectral properties of the new ligands are presented. Both the ligands and complexes proved to be sensitive to air, with decomposition occurring over a period of months when the crystals were stored in capped vials under nitrogen.

1,2-Bis(ethyl-n-propylphosphino)benzene[15,17]

Distillation produced a 81% yield of product: a clear, colourless liquid, b.p. 114–117°C (70 μm): ^{31}P nmr ($CDCl_3$): δ −33.2 (s). Elemental analysis (calc. for $C_{16}H_{28}P_2$): C, 68.06; H, 10.00; P, 21.94%. Found: C, 67.85; H, 9.80; P, 21.98%.

1,2-Bis(methyl ethylphosphino)benzene[15,17]

Distillation produced a 78% yield of product: clear, colourless liquid, b.p. 110–113°C (70 μm): ^{31}P nmr ($CDCl_3$): δ −32.75 (s). Elemental analysis (calc. for $C_{12}H_{20}P_2$): C, 63.7; H, 8.9%. Found: C, 65.1; H, 9.1%.

Symmetric Complexes 1, 3–5, 7, and 8

Symmetric complexes in which all four phosphorus atoms possess equal substitution (compounds **1**, **3–5**, **7** and **8**) were prepared by adding the pertinent ligand in degassed methylene chloride to a methanolic solution of nickel(II) chloride or nickel(II) perchlorate (in a molar ratio of 2:1 ligand:metal) under Ar. (**Hazard: the usual precautions for handling metal perchlorate salts are necessary**). The mixtures were stirred for 10 min.–12 h at room temperature, producing red-orange precipitates. Solvent was removed from the contacting red solutions to give additional crops of crystals. The products were dried under vacuum for 24 h at 60°C. Anhydrous nickel chloride and nickel perchlorate, as well as their hexahydrates, were used for complexation: no difference could be detected. Compounds 1 and 4 have been previously described.[15,17] Spectral characteristics of the new compounds 3 and 5 are reported below.

Chlorobis(1,2-bis(methylethylphosphino)benzene)nickel(II) chloride (3)

The title compound was obtained in 72% yield as red-orange crystals: ^{31}P nmr ($CDCl_3$): δ 50.8 (s), 50.2 (s). Elemental analysis (calc. for $C_{24}H_{40}P_4NiCl_2$): H, 6.93; C, 49.52%. Found: H, 7.22; C, 49.00% (H_2O may be present).

Chlorobis(1,2-bis(ethyl-n-propylphosphino)benzene)nickel(II) chloride (5)

The title compound was obtained in 63% yield as red-orange crystals: ^{31}P nmr ($CDCl_3$): δ 55.1 (s). Elemental analysis (calc. for $C_{32}H_{56}P_4NiCl_2$): H, 8.13; C, 55.36%. Found: H, 8.10; C, 54.86%.

Disymmetric Complexes 2,6 and 9

In the first method, dichloro(1,2-bis(dimethylphosphino)benzene)nickel was prepared by the method of Chatt and Hart.[50] The resulting square planar complex (yellow crystals, ^{31}P nmr ($CDCl_3$): δ 41.37 (s)) was added to a solution of methylene chloride containing one molar equivalent of 1,2-bis(diethylphosphino)benzene or 1,2-bis(diisopropylphosphino)benzene to form the desired complexes **2** and **6** respectively, as a mixture of *cis-* and *trans*-isomers.

Alternatively, these complexes were prepared by rapidly combining (in 1:1 molar ratios) either 1,2-bis(diethylphosphino)benzene or 1,2-bis(diisopropylphosphino)-benzene (dissolved in methylene chloride) with nickel chloride or nickel perchlorate (dissolved in methanol). (**Hazard: the usual precautions for handling metal perchlorate salts are necessary**). Following the removal of solvent, the 1:1 complexes were isolated as yellow crystals. Addition of 1:1 complexes to methanolic solutions containing one equivalent of 1,2-bis(dimethylphosphino)benzene resulted in the formation of the 2:1 complexes.

Upon standing in solution, **6** was found to form a mixture of three species: **1**, 1,2-bis(diisopropylphosphino)benzene present as 1:1 complex with nickel chloride, and 1,2-bis(diisopropylphosphino)benzene as free ligand. This process is slow at room temperature, but as a precaution, **6** was usually prepared *in situ* and immediately before electrochemical experiments were performed. Controlling stoichiometry does not permit facile preparation of pure dichloro(1,2-bis(dimethylphosphino)benzene)-nickel. Regardless of the complexation conditions used, large amounts of the 2:1 complex (**1**) were also formed.

Spectral properties of complexes **2** and **6** derived from the new ligands are reported. Both complexes are air-sensitive and hydroscopic, so obtaining precise elemental analyses, even for solids shown by spectroscopic methods after preparation to be pure as sent to the Analysis Lab, proved to be difficult. Complex **9**, which proved to be too unstable as a solid for satisfactory elemental analysis, was studied immediately as it was formed from the pure ligand and metal salt.

Chloro(1,2-bis(dimethylphosphino)benzene–1,2-bis(diethylphosphino)benzene)-nickel(II) chloride (2)

The title compound was obtained in 63% yield as red-orange crystals: ^{31}P nmr ($CDCl_3$): δ 67.9 (t) J = 74 Hz, 35.7 (t) J = 74 Hz. Elemental analysis (calc. for $C_{24}H_{40}P_4NiCl_2$): H, 6.93; C, 49.52%. Found: H, 6.89; C, 50.99%.

Chloro(1,2-bis(dimethylphosphino)benzene–1,2-bis(di-2-propylphosphino)benzene)-nickel(II)chloride (6)

The title compound was obtained in 43% yield as red-orange crystals: ^{31}P nmr ($CDCl_3$): δ 79.1 (t) J = 69 Hz, 27.1 (t) J = 69 Hz. Elemental analysis (calc. for $C_{28}H_{48}P_4NiCl_2$): H, 7.58; C, 52.7%. Found: H, 7.72; C, 51.67%.

X-ray Crystallography

Crystals of **4** in the Ni(0) oxidation state were large, red blocks which were slightly air-sensitive. Crystals of **4** in the Ni(II) oxidation state were orange needles. Space groups for both compounds were determined by systematically absent reflections. The details of the X-ray structural interpretation are described in Supplementary Material. The structures were solved by direct method and were refined by full matrix least-squares procedures. For the Ni(0) complex, only the Ni and P atoms were refined anisotropically. The H atoms were calculated in idealized positions and refined isotropically. For the Ni(II) complex, all non-H atoms were refined anisotropically. The H atoms were also calculated in idealized positions and refined isotropically. The H atoms of the water molecule could not be located in a difference map and were not included in the final refinement.

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SUPPLEMENTARY MATERIAL

Full lists of atomic positions, thermal parameters, bond lengths and angles, and observed and calculated structure factors are available from M.A.F. ORTEP diagrams of **4** in the nickel(II) oxidation state are also available.

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