pathway, a $k_{CO_3^{2-}}$ value of 0.008 M^{-1} sec^{-1} can be calculated. The $k_{OH^-}/k_{CO_3^{2-}}$ ratio for this system would be about 120, comparable to that observed with the ruthenium(III) analogs.

In summary, the data presented in this article demonstrate that for analogous organonitrile complexes of the type $M(NH_3)_5(N{\equiv}CR)^{3+}$ the d^5 Ru(III) species is significantly more reactive toward base hydrolysis to the amido complex than are the d^6 Rh(III) and Co(III) analogs. This effect is presumably due to the relative ability of the Ru(III) center to act as a π acceptor and stabilize the developing negative charge on the ligand which results from rate-determining hydroxide attack on the nitrile carbon atom. The Ru(II) analog in contrast is remarkably unreactive presumably because of this metal center's relative ability to π back-bond into the nitrile ligand.

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Registry No. $[Ru(NH_3)_5(CH_3CONH)](BF_4)_2$, 52843-04-6; $[Ru(NH_3)_5(C_6H_5CONH)](ClO_4)_2$, 52843-06-8; $[Rh(NH_3)_5(CH_3CONH)](ClO_4)_2$, 52843-08-0; $Ru(NH_3)_5(CH_3CONH_2)^{3+}$, 52843-09-1; $Ru(NH_3)_5(C_6H_5CONH_2)^{3+}$, 52843-10-4; $Rh(NH_3)_5(CH_3CONH_2)^{3+}$, 52843-11-5; $(NH_3)_5Ru(CH_3CN)^{3+}$, 44819-54-7; $(NH_3)_5Rh(CH_3CN)^{3+}$, 44819-05-3; $(NH_3)_5Ru(CH_3CN)^{2+}$, 26540-31-8; $(NH_3)_5Ru(C_6H_5CN)^{3+}$, 46343-59-3.

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Dissymmetric Solvent Interactions. Thermodynamic Parameters for the Enantiomerization of Tris(*o*-phenanthroline)nickel(II) Ions in (−)-2,3-Butanediol

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The enantiomerization of solutions of (±)-$Ni(phen)_3^{2+}$ dissolved in (−)-2,3-butanediol has been studied between 4 and 100°. From the temperature dependence of the enantiomerization equilibrium constant the enthalpy of the dissymmetric interaction is evaluated as −119 cal mol^{-1} and the corresponding entropy as −0.28 cal K^{-1} mol^{-1}. A study of the rates of loss of optical activity of solutions of (+)- and (−)-$Ni(phen)_3^{2+}$ in (−)-2,3-butanediol confirms this small chiral discrimination. The origin of the discrimination energy is discussed.

The diastereotopic[1] interactions between chiral molecules have been a matter of continuing interest[2,3] since the early observations of Kuhn[4] and Pfeiffer,[5] who noted that the equilibrium constant between enantiomers could be displaced from unity by the presence of other chiral molecules. Pfeiffer observed that the addition of both chiral cations and anions caused aqueous solutions of labile *o*-phenanthroline– and bipyridyl–metal complexes to develop optical activity which could be ascribed to the preponderance of one enantiomer of the complex over the other. Subsequently, Dwyer[6] suggested that the displacement of the enantiomer equilibrium arose from a differential change in the activity coefficients of the optical antipodes. That enantiomerization,[3,7,8] that is the displacement of the enantiomer equilibrium, does indeed occur was demonstrated by Kirschner,[9] who actually isolated the optically active nickel complexes formed by the induction of *l*-malic acid. These results, although interesting in themselves, suffer from the fact that few quantitative thermodynamic and kinetic data have been obtained which precisely define, in energy terms, the extent of the diastereotopic interactions.

Table I

Temp, °C	K^a	Temp, °C	K^a	Temp, °C	K^a
4.0	1.071^b	49.5	1.047	78.0	1.030
25.0	1.062	64.5	1.037	100	1.020
35.0	1.055				

^{a} The (−) enantiomer predominates at equilibrium. ^{b} This value was not used in the evaluation of $\Delta H°$ and $\Delta S°$ (*vide infra*).

We recently showed[7] that the chiral solvent (−)-2,3-butanediol was a remarkably efficient enantiomerizing medium and that solubility measurements[8] could provide precise thermodynamic data on diastereotopic interactions. Further, the recent work by Craig and his collaborators[10] has provided a theoretical basis for the possible origins of diastereotopic interactions in terms of the various kinds of intermolecular forces. It seems opportune, therefore, to reopen the question of the Pfeiffer effect in quantitative terms.

This article provides data on the enantiomerization constants of $[Ni(phen)_3]Cl_2$ in (−)-2,3-butanediol over the temperature range 4–100°.

Results and Discussion

The enantiomerization equilibrium constants are given in Table I from which we calculate $\Delta H° = -119$ cal mol^{-1} and $\Delta S° = -0.28$ cal K^{-1} mol^{-1}, reflecting a slightly greater stability of (−)-$[Ni(phen)_3]^{2+}$ in (−)-2,3-butanediol. Although the energy difference between the two enantiomers in the chiral solvent is small, the values are accurate to ±5% because of the precision of the technique we have used and the extended range of the data. The kinetic implication of these results is that the rate of inversion of the (+)-$[Ni(phen)_3]^{2+}$ ion is faster than that of the (−) isomer. This is confirmed (for (+), $k = 1.67 \times 10^{-2}$ hr^{-1}; for (−), $k = 1.57 \times 10^{-2}$ hr^{-1}, at 28°) and, furthermore, the ratio of these rate constants is equal to the enantiomerization constant at the same temperature.

At 4° the equilibrium constant was reproducible but its value, when included in the log K *vs.* $1/T$ plot, deviated by much more than the experimental error from the line spanning the data at the higher temperatures.

It appears that this is the first set of thermodynamic data for this type of effect despite the large amount of quantitative optical work that has been done. That the diastereotopic interaction energy is small occasions no surprise because the shifts in equilibria, at least for the Pfeiffer effect, have always been of the order of a few per cent. For example, Dwyer,[11] over 20 years ago, performed a classic experiment in which he measured the solubilities of the (+)- and (−)-$[Ru(phen)_3](ClO_4)_2$ enantiomers in aqueous solutions containing 2% ammonium *d*-bromocamphorsulfonate and sodium potassium *d*-tartrate at 25°. He obtained in the former medium the following solubilities: (+) form, 0.2317 g/100 ml; (−) form, 0.2347 g/100 ml. In the latter medium he found the following: (+) form, 0.2145 g/100 ml; (−) form, 0.2197 g/100 ml. Provided Dwyer used identical crystal forms of the two enantiomers, as he almost certainly would have, then the ratio of the solubility products of the two antipodes is equal to the enantiomerization constant.[9] We thus calculate the free energies for enantiomerization of $[Ru(phen)_3]^{2+}$ to be 23 and 42 cal mol^{-1}, respectively, for the two solvents. Thus if $[Ru(phen)_3]^{2+}$ were optically labile, which it is not at 25°, it would enantiomerize but a few per cent. This is typical of Pfeiffer displacements.

In view of these results, our earlier observation[9] that the enantiomerization constant for *cis*-$[Co(en)_2Cl_2]^+$ in (−)-2,3-butanediol is 4 ($\Delta G° = -0.9$ kcal mol^{-1}) is quite remarkable and suggests a more specific type of solute–solvent interaction. It is probable that, in this case, the weakly acidic amino protons form strong hydrogen bonds to the solvent and that the structure of the first solvation sphere is largely constrained by this hydrogen bonding. If, in addition, the structure of the first solvation sphere can extend itself, by hydrogen bonding, into the chiral self-structure of the solvent, we might expect these special structural features in the solvation to add to the diastereotopic discrimination.

The traditional Pfeiffer compounds, with *o*-phenanthroline and 2,2'-bipyridyl ligands, are unlikely to form hydrogen bonds with the solvent, but in the present case, a different type of structural component to the diastereotopic discrimination may be present. It is attractive to view the first solvation sphere of $[Ni(phen)_3]^{2+}$ as having the solvent molecules packed between the phen ligands so that the (solvation) methyl groups are directed toward the metal atom and the hydroxyl groups radiate out to form hydrogen bonds with the chiral bulk solvent (Figure 1). Since the phen molecules are arranged as a (chiral) three-bladed propeller, the solvent molecules packed between them will tend to adopt the same chiral geometry. If this is so, then it is plausible to assume that the structure adopted by the first solvation sphere of one enantiomer will connect better with the chiral bulk solvent structure than that of the other enantiomer.

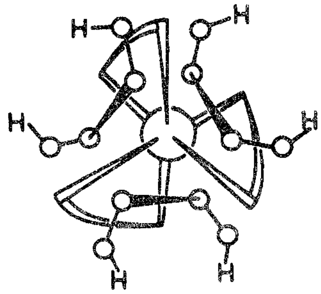

Figure 1. The suggested packing of the (−)-2,3-butanediol molecules around the $[Ni(phen)_3]^{2+}$ ion.

The original Pfeiffer phenomena where both chiral anions and cations induced enantiomerization in cationic *o*-phenanthroline complexes can be explained in a similar way. Thus the solvating water molecules, around both the enantiomerizing (complex) cation and the chiral cation or anion responsible for the induction, take on an inherently chiral structure, thus allowing the propagation of the dissymmetric interaction possibly over several intervening solvent molecules. The possible existence of such solvent cage chirality avoids the problem of direct contact between species of the same charge and may largely account for the "Pfeiffer discriminations" observed in the original case and in the present system.

Although we have attempted to explain the results in terms of chiral steric interactions, it is useful to consider the contributions due to intermolecular forces.[10] The only ones likely to be of significance in the present systems arise from the interaction between the permanent dipole moment of one molecule and the quadrupole moment of the other and dispersive forces[12] generated by the cross-term interaction of the transition electric and magnetic moments. The discriminatory part of the latter is likely to be small, perhaps a few wave numbers in favorable circumstances. The former, however, may reach the range of discrimination observed and can be of the order of a few hundred calories at short distances between molecules possessing fairly large permanent moments. Even so we are inclined to the view that the Pfeiffer effects are largely due to the type of steric interaction we have suggested.

It is, however, possible that the multipolar interactions are significant for the discrimination observed at 4°. The solution at this low temperature is extremely viscous and it is possible that structural changes occur in the solvent which, when pure, melts at 19.7°. It is interesting that the discrimination between enantiomers is *less* at this temperature than is implied from an extrapolation of the higher temperature data. This suggests that as the order in the self-structure of the solvent increases, as it presumably does as the temperature is decreased, the solvent at a certain stage becomes less discriminating. This perhaps would not have been expected, and we are tempted to view the solvation at 4° in a similar way to that suggested[13] for large organic ions, such as Ph_4As^+ dissolved in water. We assume that as the solvent itself becomes more tightly bound, the dissolved ion will tend to be surrounded by a quasi-spherical shell of solvent molecules without the first solvation sphere

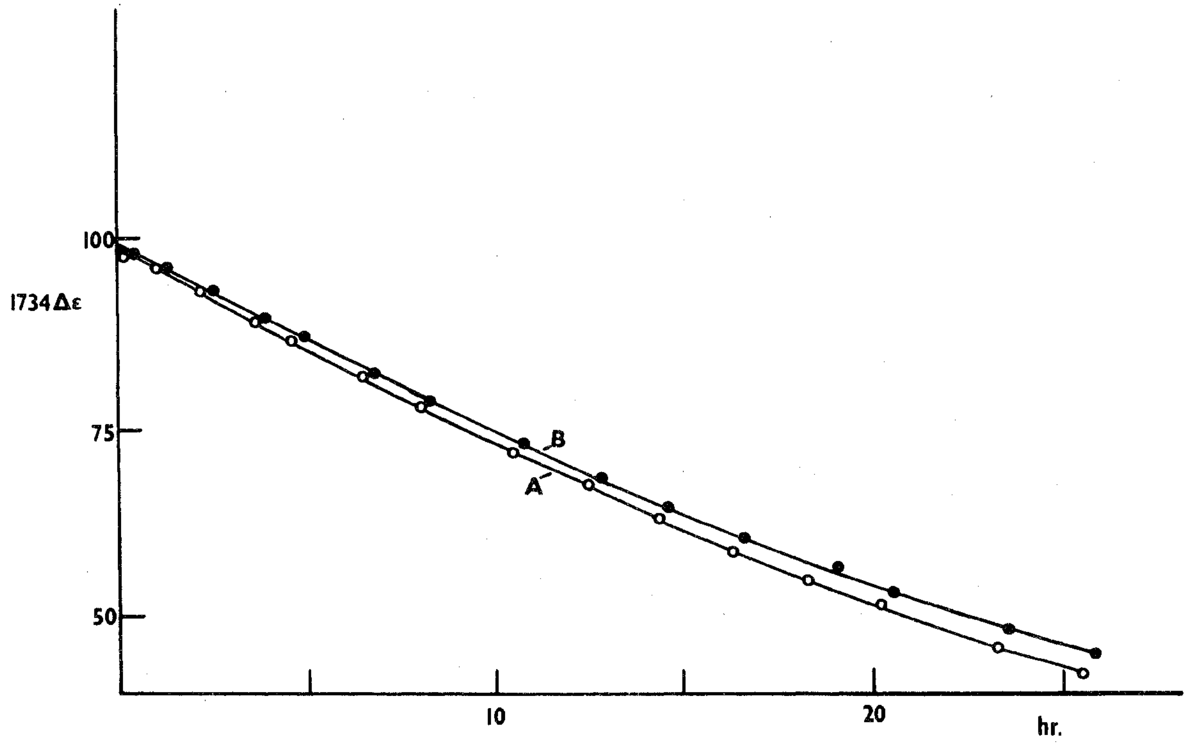

Figure 2. Plot of decreasing $\Delta\epsilon_t$ against time (hr) for (A) (+)-Ni(phen)$_3{}^{2+}$ and (B) (−)-Ni(phen)$_3{}^{2+}$ in (−)-2,3-butanediol at *ca.* 28°.

adopting any particular defined structure. If, as it were, the $[Ni(phen)_3]^{2+}$ ion is surrounded by a solvent "bubble," the steric factors would be minimized and discrimination due to multipolar interactions would tend to dominate.

Finally, the small negative entropy points to order production as the (−) enantiomer predominates over its isomer, and if both $\Delta H°$ and $\Delta S°$ were temperature independent, the data imply that the enantiomerization constant would become unity at 152°.

Experimental Section

The chloride salts of the $[Ni(phen)_3]^{2+}$ ion were prepared in order to obtain adequate solubility in (−)-2,3-butanediol.

(±)-[Ni(phen)$_3$]Cl$_2$·CH$_3$OH·H$_2$O. Solid *o*-phenanthroline monohydrate (3.0 g) was added to a warm solution of $NiCl_2·6H_2O$ (1.2 g) in methanol (25 ml). The mixture was gently warmed and stirred to complete the reaction. Ether was then slowly added to the cooled reaction mixture to precipitate the product as fine salmon pink needles. They were recrystallized from methanol by the slow addition of ether (3.0 g).

Anal. Calcd for Ni(phen)$_3$Cl$_2$·CH$_3$OH·H$_2$O: Ni, 8.0; C, 60.1; H, 4.3; N, 11.4; Cl, 9.6. Found: Ni, 8.0; C, 59.4; H, 4.2; N, 11.4; Cl, 9.7.

The methanol of crystallization was confirmed by nmr in DMSO-*d*$_6$.

(+)- and (−)-[Ni(phen)$_3$]Cl$_2$·2CH$_3$OH·2H$_2$O. The resolved[14] (+)- and (−)-[Ni(phen)$_3$](ClO$_4$)$_2$·3H$_2$O salts ([α]D ±1470°; lit.[14] ±1476°) were converted to their chloride salts as follows. The optically active perchlorate salt (1 g) was suspended in methanol (10 ml) and stirred with methanol-washed Dowex 2-X8 anion-exchange resin (8.0 g, Cl$^-$ form) until solution was obtained. The resin was collected and the filtrate was treated again with 8 g of resin. The resulting solution was reduced to about 10 ml on a rotary evaporator at 25° and the chloride salt was precipitated by the slow addition of ether. A second crystallization from methanol–ether gave the pure products as fine pink needles (0.4 g).

Anal. Calcd for (+)-Ni(phen)$_3$·2CH$_3$OH·2H$_2$O: Ni, 7.6; C, 59.2; H, 4.7; N, 10.9; Cl, 9.2. Found: Ni, 7.6; C, 59.9; H, 4.4; N, 10.9; Cl, 9.5. Found for the (−) form: Ni, 7.6; C, 59.6; H, 4.4; N, 11.1; Cl, 9.5.

The methanol solvate was confirmed by nmr. These complexes showed equal and opposite circular dichroism ($\Delta\epsilon_{max} = \pm 0.0572$ at 565 mμ) in (−)-2,3-butanediol. The specific rotations in methanol solution were $[\alpha]_{589}$ +1578 and −1560° and equal to the perchlorate salts on a molar basis. The complex with the positive rotation gave positive circular dichroism at 565 mμ and both complexes gave the same extinction coefficient ϵ_{max}(524 mμ) 11.6 M^{-1} cm^{-1} in (−)-2,3-butanediol.

(a) Equilibrium Measurements. A 0.165 mol l.$^{-1}$ solution of racemic [Ni(phen)$_3$]Cl$_2$·CH$_3$OH·H$_2$O in freshly distilled (−)-2,3-butanediol ([α]D −11.14° neat)[15] containing 0.0235 mol l.$^{-1}$ of *o*-phenanthroline was equilibrated at 4, 25, 35, 49.5, 64.5, 78.5, and 100°. At the higher temperatures, the solutions were cooled as quickly as possible to quench the enantiomerization reaction ($t_{1/2} \approx 33$ hr at 25° and $t_{1/2} \approx 10$ sec, 100°).[16] We found that without the excess phen a small, slowly attained, change in the optical density occurred presumably because of solvolysis. With excess phen, a freshly prepared solution and one allowed to stand at room temperature for 15 weeks had identical spectra. Solutions of rather high concentrations were used in order to obtain adequate instrument deflections at equilibrium. Thus a deflection of −31.5 ± 0.5 mm at 565 mμ for a 2.5-cm cell was obtained at 35° ($K = 1.055$). The optical density at 565 mμ was about 3.0. To average the instrument noise, the recorder of the Dichrographe was run for 15 min at a constant wavelength (565 mμ) and the average value taken. The form of the circular dichroism spectrum in the visible region obtained at equilibrium was identical with that obtained for the independently resolved complex.

The equilibrium circular dichroism could be reestablished by returning the solutions to any temperature and the results were reproducible. The correlation coefficient for the plot of log *K vs.* $1/T$ for all temperatures, except the data at 4°, was 0.999 and the estimated maximum possible error in log *K* at 35° is $\pm 0.4 \times 10^{-3}$ ($\log K = 23.2 \times 10^{-3}$).

(b) Kinetic Measurements. In order to show the small difference in inversion rates of the two enantiomers of the $[Ni(phen)_3]^{2+}$ ion in the chiral solvent the following technique was adopted. Identical 0.0173 mol l.$^{-1}$ solutions of the two enantiomers of [Ni(phen)$_3$]Cl$_2$ were made up in (−)-2,3-butanediol containing 0.0235 mol l.$^{-1}$ of phen. The two solutions, in matching 5-cm silica cells, were then transferred to the cell compartment of the Dichrographe and the two racemization reactions followed at 565 mμ for 1.5 half-lives (26 hr). The temperature became constant at 28° after 6 hr. The rate difference is clearly seen in Figure 2.

It is readily shown that the integrated rate expressions for the (+) and (−) forms racemizing in the chiral solvent are identical and that a plot of ln ($\Delta\epsilon_t - \Delta\epsilon_\infty$) *vs.* time, where $\Delta\epsilon_t$ = CD at time *t* and $\Delta\epsilon_\infty$ = CD at equilibrium, will give straight lines of identical slope equal to the sum of the two inversion rate constants. Because of the much lower concentrations used in the kinetic experiments (dictated by the high activity of the resolved complexes), the $\Delta\epsilon_\infty$ value could not be obtained with high precision. It was calculated from the equilibrium data and we find that the observed rate constants for approach to equilibrium are identical for the two isomers (3.25×10^{-2} hr^{-1}). A least-squares treatment of the data between 6 and 26 hr gave a correlation coefficient of 0.999 for all 10 points. The two rates of inversion are, for (+), 1.67×10^{-2} hr^{-1} and, for (–), 1.57×10^{-2} hr^{-1}. This 6% difference is also obtained by extrapolating the data in Figure 2 to zero time where the kinetics are controlled only by the forward inversion rates of the two enantiomers.

(c) Instrumentation. The instruments used were a Roussel-Jouan Dichrographe, maximum sensitivity 1×10^{-5}, a Varian T-60 nmr spectrometer, a Unicam SP800A spectrophotometer, and a Perkin-Elmer Model 141 electric polarimeter.

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Registry No. $Ni(phen)_3^{2+}$, 17085-38-0; (+)-$Ni(phen)_3^{2+}$, 31933-96-7; (–)-$Ni(phen)_3^{2+}$, 23385-79-7; (–)-2,3-butanediol, 7225-57-2.

References and Notes

(1) By diastereotopic interaction we mean the difference in interaction between each enantiomer and another chiral molecule of the same or different chemical species; thus it only includes that part of the total interaction which is discriminatory. It is important to make this distinction between the total interaction and the discriminatory part for it is only the latter which causes enantiomerization.

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(16) These values are calculated from our kinetic results and the racemization activation energies of $[Ni(phen)_3]^{2+}$ in ethylene glycol (N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 24, 1325 (1954)).

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Equilibrium Thermodynamics and Mechanism of Cis–Trans Isomerization for Diazidobis(methyldiphenylphosphine)palladium(II) and Diazidobis(dimethylphenylphosphine)palladium(II)

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The complexes $[(C_6H_5)_2PCH_3]_2Pd(N_3)_2$ and $[(CH_3)_2PC_6H_5]_2Pd(N_3)_2$ were prepared and characterized by nuclear magnetic resonance (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$), infrared, and electronic spectroscopy and conductometric methods. It is shown that the magnitude of the phosphorus–phosphorus coupling constant, $^2J_{PP}$, is greater for the azido complexes than for the analogous chloro complexes. These complexes are cis in the solid state but spontaneously isomerize to produce equilibrium mixtures of the cis and trans isomers in a variety of solvents. Equilibrium energetics for the isomerizations were determined by variable-temperature ^1H nmr and compared with the results obtained for the analogous chloride and tetrazole complexes. The mechanism of base-catalyzed and uncatalyzed isomerization was ascertained. Evidence is presented for nonionic five-coordinate intermediates in solutions containing the complexes and amines or phosphines.

Introduction

The cis–trans isomerization of square-planar bis(phosphine)(transition metal) complexes has recently received considerable attention.[2-11] One reason for this interest is the importance of these and similar complexes as catalysts. It is well known that bis(phosphine)platinum(II) complexes are robust and isomer interconversion normally requires either extended periods of refluxing or catalysis by excess phosphine. It is not as widely known that the analogous palladium(II) complexes are so labile that often mixtures of the isomers exist in solution simultaneously and that isomerization occurs spontaneously requiring only a few minutes with no heating and no catalysis.[6-8]

It has been shown that the gross geometry of bis(phosphine)palladium(II) complexes of phosphines containing α-methyl or -methylene groups can be determined by ^1H nmr as the phosphines are virtually coupled.[5-8,11-14] More recently, it has also been shown that, at least for some complexes, the gross geometry can be determined by $^{13}C\{^1H\}$ nmr.[8,11,15-19] The spin systems for these complexes are $A_nXX'A'_n$ or $[A_nX]_2$[20] for ^1H nmr and AXX' or $A[X]_2$ for $^{13}C\{^1H\}$ nmr of the phosphine methyl or methylene groups. The shape of the multiplets in the ^1H and $^{13}C\{^1H\}$ nmr arising from these groups is dependent upon the magnitude of $^2J_{PP}$,[21,22] and $^2J_{PP}$ is different for the cis and trans isomers[22] so that it is possible to determine from the nmr spectra whether the phosphines are mutually cis or trans. Although, many complexes containing halide ions have been investigated in this manner, few containing pseudohalides, especially azide, have.

The chemistry of coordinated azides[23] has received increased attention in recent years primarily due to the multifarious reactions which these complexes undergo. For example, it has been shown that coordinated azides react with metal hydrides to produce amino complexes[24] and with oxygen to produce coordinated nitrites.[25] They are also precursors to molecular nitrogen complexes.[26] The relatively weak N–N bond of the azide moiety (the bond between the middle nitrogen and the nitrogen coordinated to the metal) leads to the conversion of N_3^- to NCO^- [27] by reaction with carbon monoxide and to a coordinated triphenylphosphoimido group[28] by reaction with