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Solvent Dependence of the Ring Conformations of the Tris(ethylenediamine)nickel(II) Cation

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The difference in pmr contact shifts for the axial and equatorial methylene protons of $Ni(en)_3^{2+}$, which are partially averaged due to $\delta \longleftrightarrow \lambda$ ring conformational equilibria, is 54 ppm more in DMSO than in H_2O at 25°. Analysis of the temperature dependence of the contact shifts in terms of chelate ring conformational equilibria for $Ni(en)_3Cl_2$ in H_2O gives $\Delta G° = 7.6 \pm 0.1 - (18.2 \pm 0.3)T$ kcal/mol and $\Delta\nu_{eq} = -110$ ppm and $\Delta\nu_{ax} = -63$ ppm as the limiting contact shifts. In DMSO, $Ni(en)_3(Ph_4B)_2$ yields $\Delta G° = 5.8 \pm 0.1 - (11.8 \pm 0.3)T$ kcal/mol and limiting contact shifts of $\Delta\nu_{eq} = -137$ ppm and $\Delta\nu_{ax} = -37$ ppm. The major influence of the solvent is on ring pucker, resulting in a ring 7° more puckered in DMSO than in H_2O, and 23° less puckered in DMSO than in the solid state. The differences in ring pucker as well as the ΔH and ΔS differences are attributed to solvation effects, primarily hydrogen bonding of the solvent to the amino protons of the complex.

Introduction

There has recently been much interest in the study of the conformations of ethylenediamine chelates by nmr[1-3] and a recent review summarizes the present status of knowledge in this field.[4] In the interpretation of these data the role of the solvent has barely been explored and has usually been ignored. In the light of a calculated[5,6] ΔG for the $\delta \longleftrightarrow \lambda$ ring inversion of approximately 0.6 kcal/mol and the reported results of crystal structures having mixed conformations,[7] it seems questionable to neglect the role of the solvent.

Some evidence of a solvent effect upon the ring conformations of ethylenediamine complexes is available. Froebe and Douglas[2] studied $[Co(en)_3]Cl_3$ in D_2O and trifluoroacetic acid. They found a narrower CH_2 nmr line in trifluoroacetic acid which they attributed to enhancement of the δ ring conformation in that solvent. Appleton and Hall[8] examined $J_{Pt-N-C-H}$ for a series of platinum-diamine complexes in various solvents and found a difference of 1.7 Hz in CH_3OH compared to H_2O. If one assumes that such a coupling constant obeys the Karplus relationship (eq 2), then this change in J can be attributed to a change in the extent of ring pucker in the two solvents. On the basis of a molecular orbital study of the angular dependence of the contact shifts of the methylene protons of $Ni(en)_3^{2+}$,[9] it has been proposed that the ethylenediamine rings are much less puckered in aqueous solution than in the solid state. In all cases these solvent effects were attributed to conformational changes in the ethylenediamine rings resulting from hydrogen bonding with the solvent.

Fung[10] has observed that the axial and equatorial N-H pmr signals of $Co(en)_3^{3+}$ occur as a single peak in $D_2O-D_2SO_4$, but that in DMSO two signals are observed which are separated by 0.40 ppm. He attributed the single peak observed in D_2O to fast interchange of the axial and equatorial protons due to rapid ring flexing, while the two peaks in DMSO were thought to be due to slow interchange due to slow ring inversion promoted by strong hydrogen bonding to the DMSO. More recently, Fung, noting that Beattie[4] has concluded that ring inversion has always been found to be fast, pointed out that the two peaks observed in DMSO could be due to an unequal population of δ and λ ring conformations which are exchanging rapidly on the nmr time scale.[11] The observation of two peaks in DMSO could be due to a larger ΔG between the δ and λ ring conformations in DMSO compared to H_2O or to greater ring puckering in DMSO which would make the axial and equatorial N-H protons less alike. In order to investigate these possibilities, we have undertaken a study of the effect of solvent-chelate interactions on the amount of ring pucker and the free energy of ring inversion in $Ni(en)_3^{2+}$.

Experimental Section

Tris(ethylenediamine)nickel(II) chloride, $Ni(en)_3Cl_2$, was prepared by adding excess ethylenediamine to an aqueous solution of nickel chloride. When the product precipitated out of solution upon addition of acetone it was immediately filtered and dried. Tris(ethylenediamine)nickel(II) tetraphenylborate, $Ni(en)_3(Ph_4B)_2$, was prepared by dissolving $Ni(en)_3Cl_2$ in H_2O and adding a $NaPh_4B$ solution. The product precipitated as a light violet powder which was filtered, washed, and dried. Chemical analyses were done by Chemalytics, Inc., Tempe, Ariz., and were satisfactory.[12]

Electronic spectra obtained on a Cary Model 14 showed absorption maxima for $Ni(en)_3(Ph_4B)_2$ in DMSO at 29,400, 18,700, and 11,400 cm^{-1}. The literature values for solid $Ni(en)_3(ClO_4)$ are 29,000, 18,300, and 11,200 cm^{-1}.[13]

Nmr spectra were obtained using a Varian HA-100 modified to obtain side bands of variable frequency up to 40 kHz. At least three spectra were taken at each temperature, and the average values are reported here. The temperature was monitored with a thermocouple permanently installed in the probe. A Digitec thermometer Series 590 was calibrated with Varian temperature calibration samples and charts were prepared from the work of Van Geet.[14] Contact shifts are reported in parts per million downfield from the diamagnetic $Zn(en)_3^{2+}$.

Solvents used were deuterated DMSO and D_2O obtained from Stohler Isotope Chemicals.

Data Reduction

To obtain values of ΔH and ΔS for ring inversion, and the value

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(1) F. L. Ho and C. N. Reilley, *Anal. Chem.*, 42, 600 (1970).

(2) L. R. Froebe and B. E. Douglas, *Inorg. Chem.*, 9, 1513 (1970).

(3) J. L. Sudmeir and G. L. Blackmer, *Inorg. Chem.*, 10, 2010 (1971).

(4) J. K. Beattie, *Accounts Chem. Res.*, 4, 253 (1971).

(5) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81, 2620 (1959).

(6) J. R. Gollogy, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, 10, 317 (1971).

(7) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 842 (1968).

(8) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 10, 1717 (1971).

(9) R. E. Cramer, *Inorg. Chem.*, 11, 1019 (1972).

(10) B. M. Fung, *J. Amer. Chem. Soc.*, 89, 5788 (1967).

(11) B. M. Fung, S. C. Wei, T. H. Martin, and I. Wei, *Inorg. Chem.*, 12, 1203 (1973).

(12) *Anal.* Calcd for $Ni(en)_3(Ph_4B)_2$: C, 73.92; H, 7.35; N, 9.58. Found: C, 70.89; H, 7.48; N, 9.85. A referee suggested that the Ph_4B^- salt might be contaminated with Cl^-. Analysis indicates "less than 0.1% Cl, if any."

(13) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4, 20 (1965).

(14) A. L. Van Geet, *Anal. Chem.*, 40, 2227 (1968).

$(K_b - K_a)$ for the limiting contact shifts, the equation developed by Reilley and coworkers was used.[11]

$$K_{bb'} - K_{aa'} = (K_b - K_a)(2/(1 + \exp((-\Delta H + T\Delta S)/RT)) - 1) \qquad (1)$$

In this equation, $K_n = T\Delta\nu_n$, where $\Delta\nu_n$ represents the limiting contact shift with $\Delta\nu_{nn'}$ representing the observed shift which results from conformational averaging. Equation 1 assumes a constant ΔH, ΔS, and $K_b - K_a$ over the temperature range studied. A computer program was written to solve for the three variables, ΔH, ΔS, and $K_b - K_a$, using the simplex minimization routine of Chandler,[15] the input being the measured contact shifts $\delta_{aa'}$ and $\delta_{bb'}$ at several different temperatures. Using the data of Ho and Reilley,[1] this program produced results of $K_b - K_a = 46.5 \pm 0.5 \times 10^3$ ppm °K, $\Delta H = 366 \pm 3$ cal/mol, and $\Delta S = 0.21 \pm 0.01$ eu, which are in close agreement with their values.

It should be remembered that while the contact shift is sensitive only to the conformation of a single chelating ring, a complex such as $Ni(en)_3{}^{2+}$ produces three separate equilibria $\Lambda\lambda\lambda\lambda \longleftrightarrow \Lambda\lambda\lambda\delta \longleftrightarrow \Lambda\lambda\delta\delta \longleftrightarrow \Lambda\delta\delta\delta$. Our results therefore can only give us information about the average λ and δ ring conformations.[16]

Results and Discussion

Table I presents the measured values for the contact shifts of $Ni(en)_3Cl_2$ in D_2O and $Ni(en)_3(Ph_4B)_2$ in DMSO, and representative spectra are presented in Figure 1. The values of ΔH, ΔS, ΔG, and $K_b - K_a$ obtained from analysis of the data in Table I are presented in Table II. In Figures 2 and 3 we present plots comparing the observed and calculated experimental parameters. The deviation of high temperature points from the calculated lines in Figures 2 and 3 is due to onset of the $\Delta \longleftrightarrow \Lambda$ metal configurational exchange.[1] These points are not included in the calculation of the values listed in Table II.

Small differences can be noted in the shifts reported here for $Ni(en)_3Cl_2$ compared to those of Ho and Reilley.[1] These could be due to the presence in their solution of a small amount of excess ethylenediamine, which could alter the ring conformations, or the equilibria between them, by hydrogen bonding to the coordinated ligands. This postulate is supported by the fact that the average shift is identical in the two studies, but in all cases our results show a wider separation of the observed shifts.

While our contact shift values in H_2O are a little different from those reported by Ho and Reilley,[1] the values listed in Table II are quite different. For a given set of data the simplex error minimization routine we are using often produces several fits of the observed data, with the particular solution which one obtains dependent upon the initial guess for the calculated parameters. Many of these solutions can be rejected because they are in fact poor fits of the experimental data producing positive errors at high temperature and negative errors at low temperature or vice versa. These poor solutions readily show up when one plots the observed points *vs.* the calculated line. In the case of Ho and Reilley's data, we find several acceptable solutions, one of which corresponds to the values they have published and one of which corresponds to the solution we report here. The solution we report fits their data somewhat better than their solution, with average errors for the two solutions of 0.3 and 0.8%, respectively. As the number of data points and the temperature range increase, the number of possible solutions decreases. As a result, for our full data set, which spans a temperature region of some 60°, we find that the only acceptable solution is that reported in Table II. Our results are comparable in magnitude to those reported for 2,3-diaminobutane, a study which included a larger number of points and a wider temperature range.[16]

Table I. Temperature Dependence of the Observed Contact Shifts[a] of $Ni(en)_3{}^{2+}$ in H_2O and DMSO

$Ni(en)_3Cl_2$ in D_2O			$Ni(en)_3(Ph_4B)_2$ in DMSO		
Temp, °C	$\Delta\nu_{aa'}$	$\Delta\nu_{bb'}$	Temp, °C	$\Delta\nu_{aa'}$	$\Delta\nu_{bb'}$
0.2	−72.8	−123.2	20.1	−45.2	−136.1
6.4	−71.5	−120.2	27.1	−43.8	−132.6
13.4	−69.1	−116.7	31.2	−43.7	−129.8
21.8	−67.5	−112.5	35.6	−44.8	−131.4
34.7	−65.3	−107.4	40.5	−44.8	−129.6
38.8	−64.8	−105.7	44.9	−44.1	−125.6
44.0	−64.0	−103.9	50.5	−44.1	−122.9
48.5	−63.8	−102.6	53.1	−45.6	−122.9
53.2	−63.1	−100.4	57.2	−44.5	−119.4
57.9	−62.6	−98.6	62.5	−44.0	−117.9
61.3	−62.2	−96.8	64.9	−44.5	−116.1
64.8	−61.5	−94.8	68.2	−44.2	−115.4
68.2	−61.6	−93.9	73.3	−44.7	−111.1
72.1	−61.7	−91.8	78.7	−43.6	−109.6
75.0	−61.8	−90.0	83.1	−45.6	−109.3
			88.3	−44.6	−105.8
			94.2	−46.3	−102.2
			99.5	−48.1	−99.9
			103.5	−50.8	−98.6

[a] Reported in parts per million from $Zn(en)_3{}^{2+}$.

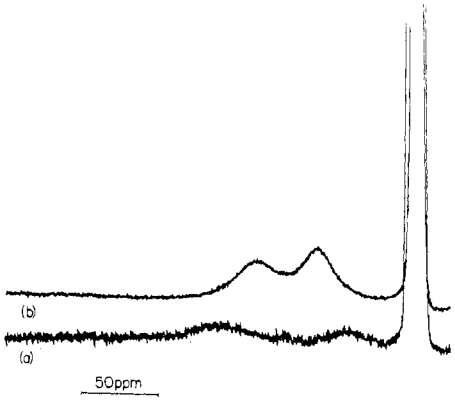

Figure 1. Ambient temperature nmr spectra of (a) $[Ni(en)_3](Ph_4B)_2$ in DMSO-d_6 and (b) $[Ni(en)_3]Cl_2$ in D_2O. The low quality of spectrum (a) is due to the low solubility of this complex in DMSO.

Examination of either Figure 1 or Table I reveals large differences in the shifts observed in DMSO and D_2O at ambient temperature. At 35° we observe contact shifts of −65.3 and −107.4 ppm in water, but in DMSO we observe −44.8 and −131.4 ppm. This large difference upon change of solvent could be due to either more ring pucker in DMSO or a greater ΔG between the δ and λ rings in DMSO.

Examination of the values given in Table II shows that ΔG is virtually identical in DMSO and D_2O, but the limiting value of $K_b - K_a$ is quite different in the two solvents. These results suggest that the rings are more puckered in DMSO. Examination of models shows that as the rings become more puckered, the amino protons become more accessible for hydrogen bonding. Since we expect greater hydrogen bonding in DMSO than in H_2O,[10] the greater puckering in DMSO is in agreement with the postulate that ring pucker increases with the strength of hydrogen bonding.[9]

An earlier conclusion, that the chelate rings are nearly flat in solution, is supported by some recent work by Wandiga, Sarmeski, and Urbach[17] who report a contact shift of −300

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(15) J. A. Nelder and R. Mead, *Comput. J.*, 9, 308 (1965).

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Table II. Thermodynamic and Contact Shift Parameters for the $\delta \leftrightarrow \lambda$ Ring Inversion in $Ni(en)_3^{2+}$

Solvent	$K_b - K_a \times 10^{-3}$	ΔH, kcal/mol	ΔS, eu	$\Delta\nu_{eq}$,[b] ppm	$\Delta\nu_{ax}$,[b] ppm	ΔG,[c] kcal/mol
DMSO	30.0 ± 0.3	5.8 ± 0.1	11.8 ± 0.3	−136.8 ± 1	−36.8 ± 1	2.3 ± 0.2
D_2O	13.9 ± 0.1	7.6 ± 0.1	18.2 ± 0.3	−109.6 ± 0.4	−63.2 ± 0.4	2.2 ± 0.2
D_2O	46.4 ± 1.5[a]	0.36 ± 0.03[a]	0.2 ± 0.02[a]	−164 ± 5[a]	−9 ± 5[a]	0.3 ± 0.03[a]

[a] Data taken from ref 1. [b] Values for the "frozen" configurations at 25°. [c] At 25°.

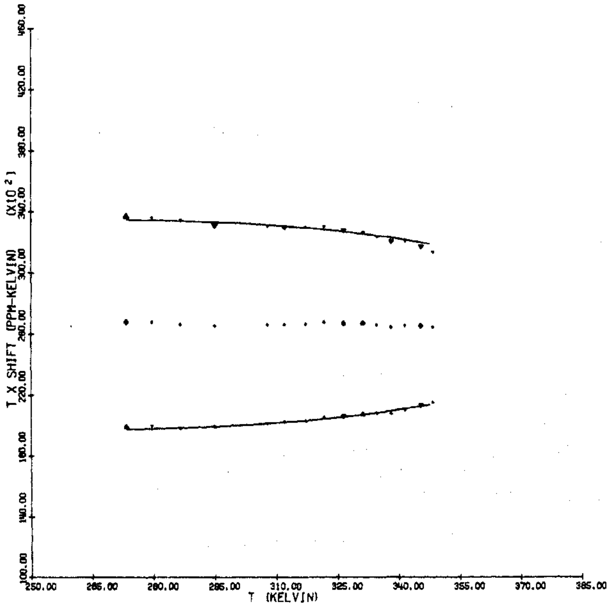

Figure 2. Plot of the product $T\Delta\nu$ *vs.* T for $[Ni(en)_3]Cl_2$ in D_2O. The points are observed data while the lines are calculated using the parameters in Table II. The central line is not observed but represents the average of the two observed peaks. The standard deviations of the data are represented by the size of the symbols.

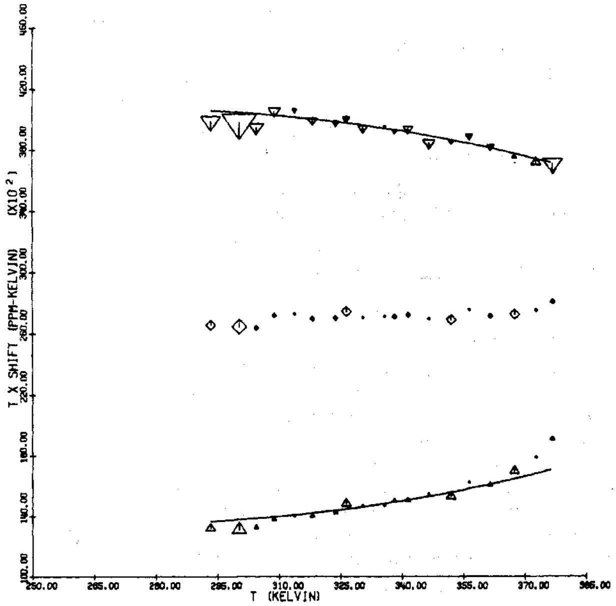

Figure 3. Plot of the product $T\Delta\nu$ *vs.* T for $[Ni(en)_3](Ph_4B)_2$ in DMSO-d_6 on the same scale as Figure 2. The points are observed data while the lines are calculated using the parameters in Table II. The central line is not observed but represents the average of the two observed peaks. The standard deviations of the data are represented by the size of the symbols.

ppm for an α-imino proton for which θ_{eq} is constrained to be 180°. From our earlier work[9] we had estimated the coupling constant for an ethylenediamine radical cation as 22.7 G for $\theta_{eq} = 180°$, but only 12.8 G when $\theta_{eq} = 198°$. The ratio of these two numbers, 22.7/12.8 = 1.77, is in fair agreement with the ratio, −300/−137 = 2.20, of the contact shift of an α-imino proton to that of the equatorial proton observed for $Ni(en)_3^{2+}$ in DMSO. On the other hand, if the chelate ring were as puckered in solution as in the solid state, *i.e.*, $\theta_{eq} = 180°$, then the limiting contact shift should be about −300 ppm, which it is not. We are thus led to the earlier conclusion[9] that the ethylenediamine rings are much flatter in solution than in the solid state.

From our results in Table II the ratio $\Delta\nu_{eq}/\Delta\nu_{ax}$ falls between 0.5 and 3.7. These values occur far out on the wings of the curve of $\Delta\nu_{eq}/\Delta\nu_{ax}$ *vs.* θ_{ax} which has been published[9] and therefore it is not useful to use that curve to determine ring pucker. However, since the values of θ are not near 90° it is appropriate[9] to determine θ from the relation

$$\Delta\nu = \beta_0 + \beta_2 \cos^2 \theta \qquad (2)$$

Assuming $\beta_0 \approx 0$ and using the −300-ppm value of Wandiga, Sarmeski, and Urbach[17] at $\theta_{eq} = 180°$, we can find a value for β_2 in eq 2. Then using this β_2 we can calculate values for θ_{eq} and θ_{ax} from the values of $\Delta\nu_{eq}$ and $\Delta\nu_{ax}$ in Table II. This gives $\theta_{eq} = 225°$ and $\theta_{ax} = 110°$ in DMSO solution. In H_2O, the values are $\theta_{eq} = 232°$ and $\theta_{ax} = 117°$. These angles are similar to those reported in the theoretical study, although the H_2O data reported here lead to a slightly less puckered ring than that which was reported earlier.[9] It is interesting to note that the difference $\theta_{eq} - \theta_{ax}$ is 115° in both solvents, a value which is close to the expected 120° for tetrahedral HCH angles, thus indicating that the above analysis is valid. The values of θ_{eq} and θ_{ax} reported in the solid state are $\theta_{eq} = 183°$ and $\theta_{ax} = 83°$ for $Ni(en)_3SO_4$,[18] which indicate a much more puckered ring in the solid state. Note that the change of nearly 25 ppm in the methylene contact shifts of the frozen conformations translates into a change of ring pucker of only 7°.

Models show that the equatorial NH protons encounter more steric hindrance in the $\Lambda\lambda\lambda\lambda$ conformation than in the $\Lambda\delta\delta\delta$ conformation and it is this steric interference which has been cited for the decreased stability of the former.[5] This steric interference decreases the ability of these amino protons to hydrogen bond to the solvent in the $\Lambda\lambda\lambda\lambda$ conformation and thus we would expect less solvation in this conformation. Some solvation of the complex would then be lost upon ring inversion, consistent with the positive ΔH and ΔS values observed in both solvents. The larger ΔH and ΔS in H_2O is probably due to a greater solvation of the $\Lambda\delta\delta\delta$ isomer in H_2O than in DMSO since the smaller size of H_2O makes it less sensitive to steric crowding than DMSO.

In conclusion, it is apparent from our experimental results that the solvent plays an important role in the conformations of ethylenediamine rings in metal complexes. From an analysis of the data we conclude that the degree of ring pucker is the parameter most altered by solvent, but the

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large ΔH and ΔS values observed suggest that solvation of the complex plays a very important role in the conformational equilibria. The mechanism of the solvent effect is attributed to the sensitivity of the hydrogen bonding ability of the amino protons to ring conformation as suggested by Raymond, Corfield, and Ibers.[7]

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Ligand-Transfer Reactions of Nickelocene with 1,2-Bis(diphenylphosphino)ethanenickel(II) Complexes

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Nickelocene, $(h^5\text{-}C_5H_5)_2Ni$, reacts with the square-planar $(diphos)NiX_2$ complexes [diphos = 1,2-bis(diphenylphosphino)-ethane; X = Cl, Br, I or CN] in organic solvents to afford monocyclopentadienylnickel complexes, the nature of the products depending markedly on the anionic ligand in the diphos nickel(II) starting material. The chloro and bromo complexes yield novel ionic $[(h^5\text{-}C_5H_5)Ni(diphos)]_2NiX_4$ complexes which contain nickel(II) cations and anions of different coordination geometries. The corresponding reactions of the iodo and cyano derivatives yield the bridged dimeric compounds $[(h^5\text{-}C_5H_5)NiX]_2\text{-}\mu\text{-diphos}$ (X = I, CN) as the sole isolable products. With the exception of the cyano complex, acetone solutions of the complexes afford the ionic $[(h^5\text{-}C_5H_5)Ni(diphos)]X$ or $[(h^5\text{-}C_5H_5)Ni(diphos)]PF_6$ derivatives upon addition of water or aqueous ammonium hexafluorophosphate, respectively. Proton nmr, infrared, and visible spectra and conductometric data for the new compounds are presented.

Introduction

The chemistry of nickelocene, $(h^5\text{-}C_5H_5)_2Ni$, is dominated by reactions in which the cyclopentadienyl ligands are lost or altered in some fashion.[1,2] Reactions with phosphorus donor ligands afford derivatives of the formula NiL_4[3-5] [L = a trivalent phosphorus ligand], the fate of the displaced cyclopentadienyl ligands being uncertain. Dimeric products of the type $[CpNi\text{-}\mu\text{-}X]_2$[6] (X = $P(CF_3)_2$, SR) result from the treatment of nickelocene with $HP(CF_3)_2$[7] and mercaptans,[8,9] respectively. High-temperature reaction with diphenylacetylene affords the dimeric $[CpNi]_2C_6H_5C_2C_6H_5$[10] in which the acetylene is bonded to both nickel atoms.[11] Reactions with molecular hydrogen,[12] fluoroolefins,[13] acetylenes containing electron-withdrawing substituents,[14-16] perfluorobenzyne,[17] or ethyl diazoacetate[18] yield products in which addition to one of the cyclopentadienyl rings has occurred.

A related class of transformations involves transfer of a C_5H_5 ligand to another metal, exemplified by the reactions with $Ni(CO)_4$,[19] $Fe(CO)_5$,[10] and L_2NiX_2[20,21] complexes (L = a tertiary phosphine, X = halide). The latter reactions suggest that nickelocene might be a useful reagent for the synthesis of a variety of cyclopentadienylmetal complexes not readily accessible by more conventional routes. We have begun a systematic study to test this hypothesis and report herein the results of our study of the reactions of nickelocene with $(diphos)Ni^{II}$ complexes [diphos = 1,2-bis(diphenylphosphino)ethane]. While this work was in progress, salts of the $[CpNi(diphos)]^+$ cation[22,23] and the complex $[CpNi(CN)]_2\text{-}\mu\text{-diphos}\cdot 2C_6H_6$[24] have been prepared by other workers using indirect methods.

Experimental Section

All operations were conducted under nitrogen or argon atmospheres, including admission of argon to evacuated flasks. Methylene chloride was dried by refluxing over phosphorus pentoxide, distilled under argon, and stored over Linde 3A molecular sieves. Benzene was distilled from sodium and ether from lithium aluminum hydride. Nickelocene and phosphorus ligands (Strem Chemical Co.) were purified by sublimation and recrystallization from ethanol-benzene, respectively. Nickel salts were obtained from standard commercial sources and used without purification. The complexes (diphos)Ni-

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