

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

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and to the NSF-URP program which supported R. L. H.

Registry No. $[\text{Ni}(\text{en})_3]\text{Cl}_2$, 13408-70-3; $[\text{Ni}(\text{en})_3](\text{Ph}_3\text{B})_2$, 41685-81-8; DMSO-*d*₆, 2206-27-1.

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

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Received March 19, 1973

Nickelocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$, reacts with the square-planar (diphos)NiX₂ 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{diphos})]_2\text{NiX}_4$ 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{NiX}]_2\text{-}\mu\text{-diphos}$ (X = I, CN) as the sole isolable products. With the exception of the cyano complex, acetone solutions of the complexes afford the ionic $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{diphos})]\text{X}$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{diphos})]\text{PF}_6$ 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, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$, 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 $[\text{CpNi-}\mu\text{-X}]_2$ ⁶ (X = P(CF₃)₂, SR) result from the treatment of nickelocene with $\text{HP}(\text{CF}_3)_2$ ⁷ and mercaptans,^{8,9} respectively. High-temperature reaction with diphenylacetylene affords the dimeric $[\text{CpNi}]_2\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$ 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 perfluoro-

benzyne,¹⁷ or ethyl diazoacetate¹⁸ yield products in which addition to one of the cyclopentadienyl rings has occurred.

A related class of transformations involves transfer of a C₅H₅ ligand to another metal, exemplified by the reactions with $\text{Ni}(\text{CO})_4$,¹⁹ $\text{Fe}(\text{CO})_5$,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 $[\text{CpNi}(\text{diphos})]^+$ cation^{22,23} and the complex $[\text{CpNi}(\text{CN})]_2\text{-}\mu\text{-diphos-2C}_6\text{H}_6$ 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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Table I. Physical and Analytical Data

Complex	Color	Mp, °C	Analyses, calcd (found)			
			% C	% H	% P	% nitrogen or halogen
[CpNi(CN)] ₂ -μ-diphos	Green	171-172	65.14 (65.13)	4.86 (4.77)	8.86 (8.80)	4.0 (3.89) (N)
[CpNiI] ₂ -μ-diphos	Deep red	194 dec	48.00 (47.71)	3.78 (4.01)	6.89 (7.14)	28.22 (28.46) (I)
[CpNi(diphos)]I	Green	133 dec	57.45 (56.82)	4.47 (4.71)	9.58 (9.44)	
[CpNi(diphos)]PF ₆	Green	203	56.02 (56.08)	4.36 (4.25)	13.96 (13.76)	
[CpNi(diphos)] ₂ NiCl ₄	Green	122 dec	59.76 (59.25, 59.16)	4.65 (4.74, 4.79)	10.77 (9.58)	11.41 (11.07) (Cl)
[CpNi(diphos)] ₂ NiBr ₄	Green	220 dec	52.29 (52.69, 52.59)	4.08 (4.16, 4.19)	9.42 (8.49)	22.44 (21.50) (Br)

X₂,^{25,26} [(C₆H₅)₂PCH₂P(C₆H₅)₂]₂NiX₂,²⁶ and [(C₆H₅)₂P(CH₂)₂-P(C₆H₅)₂]₂NiX₂²⁶ were prepared by standard literature methods.

Elemental analyses (Table I) were conducted by Galbraith Micro-analytical Laboratories, Knoxville, Tenn. Visible-near-infrared spectra were determined with a Perkin-Elmer Model 450 spectrometer using methylene chloride solvent. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer using potassium bromide plates with the samples in Nujol. A Varian Associates T-60 instrument was utilized for determination of the proton nmr spectra. Chemical shifts (Table II) are reported in ppm downfield from internal tetramethylsilane. The 100-MHz spectra were measured on a Varian Associates HA-100 spectrometer. Phosphorus-31 spectra were determined on a 24.3-MHz Varian Instrument. Conductance measurements were made in methylene chloride solution using approximately 10⁻³ M solutions. The latter operations were conducted in a Vacuum Atmospheres drybox due to the moisture sensitivity of the complexes. Melting points were measured in sealed capillaries and are uncorrected (Table I).

Synthesis of [CpNi(diphos)]₂NiCl₄. The reaction vessel was a 200-ml three-neck flask fitted with reflux condenser, argon inlet, and magnetic stirrer. All glassware was oven-dried (200°, 24 hr) prior to use and purged with dry argon for 30 min prior to initiation of the reaction. Nickelocene (0.57 g, 3.0 mmol), (diphos)NiCl₂ (1.06 g, 2.0 mmol), and approximately 150 ml of benzene were charged to the reaction vessel and the mixture was heated at 50° for 48 hr. During the course of the reaction the yellow-orange (diphos)NiCl₂ slowly dissolved and green crystals formed. The reaction mixture was cooled to room temperature and filtered under argon to afford the green solid product which was washed twice with 50-ml portions of benzene. Recrystallization from methylene chloride-diethyl ether and vacuum-drying yielded 0.91 g of green microcrystalline [CpNi(diphos)]₂-NiCl₄ (75% based on (diphos)NiCl₂). Similar yields are obtained using refluxing methylene chloride, but the formation of decomposition products complicates product purification.

Synthesis of [CpNi(diphos)]₂NiBr₄. The reaction was carried out as described above for the chloride complex with 3.0 mmol of nickelocene and 1.23 g (2.0 mmol) of (diphos)NiBr₂. Recrystallization of the benzene-insoluble product from methylene chloride-diethyl ether and vacuum drying afforded 0.97 g of green crystalline [CpNi(diphos)]₂-NiBr₄ (69% yield). The reaction proceeds more rapidly in refluxing methylene chloride but slightly lower yields are observed.

Synthesis of [CpNiI]₂-μ-diphos. Nickelocene (0.57 g, 3.0 mmol) and (diphos)NiI₂ (2.13 g, 3.0 mmol) and 150 ml of methylene chloride were charged to a 200-ml flask under argon as described above for the chloride and bromide reactions. The reaction mixture was heated at reflux for 1 hr and solvent was then removed by rotary evaporator. The residue was extracted with hexane under argon; the extract was colorless indicating that nickelocene was completely reacted. The product was taken up in 25 ml of methylene chloride and filtered under argon. Dropwise addition of ether to the filtrate brought about precipitation of the product which was rapidly filtered. (The mother liquor quickly attains a green color indicating the presence of [CpNi(diphos)]I.) Yield of the red-purple crystalline product was 1.07 g, 40%. The synthesis may be carried out with equal facility with benzene as the reaction solvent. In this case the product begins to precipitate before reflux temperature is reached. After 1-hr reaction time treatment of the mixture as described above affords 40-50% yields of the product after recrystallization.

Synthesis of [CpNi(CN)]₂-μ-diphos. Three millimoles each of nickelocene and (diphos)Ni(CN)₂ in approximately 150 ml of benzene were refluxed for 48 hr. During the course of the reaction (diphos)Ni(CN)₂ dissolved and the green product slowly precipitated. The reaction mixture was cooled to room temperature and benzene re-

Table II. Nmr Data^a

Complex	δ(C ₆ H ₅)		δ(CH ₂)	
	δ(C ₆ H ₅)	δ(C ₆ H ₅)	δ(CH ₂)	δ(CH ₂)
[CpNi(CN)] ₂ -μ-diphos ^b	5.22 s	7.4 br, m	2.78 d (J _{PH} = 2.0 Hz)	
[CpNi(diphos)]Cl ^c	5.50 s	7.5 br, m	2.74 d (J _{PH} = 18 Hz)	
[CpNi(diphos)]Br ^{c,d}	5.52 s	7.4 br, m	2.75 d (J _{PH} = 18 Hz)	
[CpNi(diphos)]I ^{c,d}	5.58 s	7.6 br, m	2.72 d (J _{PH} = 18 Hz)	
[CpNi(diphos)]PF ₆ ^c	5.55 s	7.5 br, m	2.71 d (J _{PH} = 18 Hz)	
[CpNi(diphos)] ₂ NiCl ₄ ^b	5.40 s	7.4 br, m	2.75 d (J _{PH} = 18 Hz)	

^a Varian Associates T-60 spectrometer; chemical shifts in ppm downfield from internal TMS. Key: s, singlet; d, doublet; m, multiplet; br, broad. ^b Methylene chloride-d₂. ^c Acetone-d₆. ^d Phosphorus-31 resonance at -70 ppm vs. H₃PO₄, broad multiplet.

moved at reduced pressure. The residue was taken up in methylene chloride and filtered, and the product was precipitated by addition of diethyl ether. The yield of product after vacuum drying was 1.40 g, 67%. Unlike the preparations of the other complexes described above, no precautions to exclude moisture are necessary. The complex exhibits ν(C≡N) at 2118 cm⁻¹ and is a nonelectrolyte.

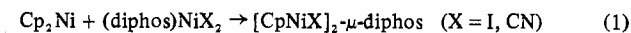
[CpNi(diphos)]X (X = Cl, Br, I). Acetone solutions of [CpNi(diphos)]₂NiX₄ (X = Cl, Br) or [CpNi(I)]₂-μ-diphos afford essentially quantitative yields of the corresponding complexes [CpNi(diphos)]X upon addition of water. All of the complexes may be recrystallized from acetone by dropwise addition of diethyl ether. Thus 0.45 g of (CpNiI)₂-μ-diphos afforded 0.31 g of [CpNi(diphos)]I (96%). The identity of the complexes is confirmed by their metathetical conversion to the hexafluorophosphate salt [CpNi(diphos)]PF₆ as described below, elemental analysis of the iodide salt, and conductivity measurements.

[CpNi(diphos)]PF₆. Addition of saturated aqueous NH₄PF₆ (Ventron) to acetone solutions of any of the complexes reported in this study (with the exception of [CpNi(CN)]₂-μ-diphos) affords the complex [CpNi(diphos)]PF₆ identified by elemental analysis (Table I) and by the characteristic P-F stretching frequencies of the PF₆⁻ ion at 830 and 548 cm⁻¹.²⁷

Attempted Reactions of Nickelocene with Other Bis(phosphine)-nickel Complexes. No isolable products could be obtained from the reactions of nickelocene with [(C₆H₅)₂PCH₂P(C₆H₅)₂]₂NiX₂ or [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂NiX₂ (X = Cl, Br, I) in refluxing benzene or dichloromethane. No color change was noted in the reaction mixtures after 72 hr and 60-70% of the unchanged starting materials could be recovered. Nickelocene and (diphos)Ni(NCS)₂ apparently reacted in refluxing benzene but a pure product could not be isolated. In refluxing methylene chloride no reaction occurred.

Results and Discussion

Nickelocene reacts with (diphos)NiI₂ and (diphos)Ni(CN)₂ according to eq 1 affording high yields of the bridged bimetal-



lic complexes [CpNiX]₂-μ-diphos (X = I and CN, respectively). The syntheses may be conducted in methylene chloride or benzene solvents. The cyano complex is best prepared in refluxing benzene, the reaction requiring approximately 48 hr to go to completion. In either benzene or methylene chloride the production of [(Cp)NiI]₂-μ-diphos is complete in 30-60 min, the reaction mixture rapidly acquiring the deep red color of the product. Fine red needles of the complex begin to precipitate from benzene almost immediately upon mixing starting materials. Both complexes are air stable, crystalline solids, but the iodo complex is extremely

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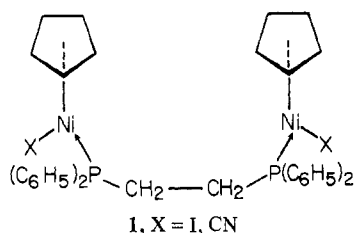
moisture sensitive. The reaction with water occurs rapidly in solution and more slowly in the solid state to afford the green ionic $[(\text{Cp})\text{Ni}(\text{diphos})]\text{I}$ in which both phosphorus atoms of the diphos ligand are coordinated to nickel (*vide infra*). The exact nature of the decomposition is not known, but aqueous extracts from preparative-scale reactions give positive tests for nickel(II). Nickelocene could not be detected among the decomposition products.

The reactions of $(\text{diphos})\text{NiCl}_2$ and $(\text{diphos})\text{NiBr}_2$ with nickelocene proceed in refluxing methylene chloride or benzene according to eq 2, the products precipitating from solution as formed.

No evidence was obtained for the formation of dimeric bridged complexes analogous to the iodo and cyano derivatives. The complexes $[\text{CpNi}(\text{diphos})]_2\text{NiX}_4$ are also decomposed by water, forming $[\text{CpNi}(\text{diphos})]\text{X}$. This observation is consistent with the lability of the NiX_4^{2-} anions ($\text{X} = \text{Cl}, \text{Br}$) in donor solvents.^{28,29} Addition of aqueous ammonium hexafluorophosphate to acetone solutions of $[\text{CpNi}]_2-\mu\text{-diphos}$, $[\text{CpNi}(\text{diphos})]\text{NiX}_4$, or $[\text{CpNi}(\text{diphos})]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) results in essentially quantitative conversion to $[\text{CpNi}(\text{diphos})]\text{PF}_6$.

While this work was in progress, the synthesis of $[\text{CpNi}(\text{diphos})]\text{Cl}\cdot\text{C}_6\text{H}_6$ from $\text{CpNi}[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$ and diphos was reported, but no spectral data were given.²³ This complex reacts with aqueous sodium cyanide to afford $[\text{CpNi}(\text{CN})]_2-\mu\text{-diphos}\cdot 2\text{C}_6\text{H}_6$ ²⁴ analogous to the cyano complex reported here. We have, however, encountered no problems with solvent incorporation in the present study. Salzer and Werner²² have isolated $[\text{CpNi}(\text{diphos})]\text{BF}_4$ from the reaction of $[\text{Cp}_3\text{-Ni}_2]\text{BF}_4$ with the diphos ligand. The synthetic process described here would seem to be superior to those reported by the above routes in terms of overall yield and economy of operation.

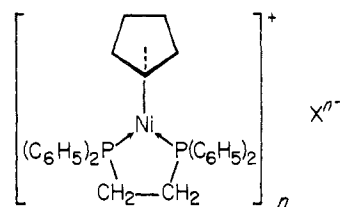
The complexes $[\text{CpNiX}]_2-\mu\text{-diphos}$ ($\text{X} = \text{CN}, \text{I}$) can be reasonably assigned the structure 1. The proton nmr spectrum



of the dimeric complex $[\text{CpNiCN}]_2-\mu\text{-diphos}$ shows phenyl, C_5H_5 , and methylene resonances of the expected relative intensities 20:10:4, respectively. No splitting of the C_5H_5 resonance by phosphorus-31 was observed, but the methylene protons appear as a doublet, $J_{\text{PH}} = 2.0$ Hz. All attempts at obtaining a definitive nmr spectrum of $[\text{CpNiI}]_2-\mu\text{-diphos}$ were unsuccessful, presumably due to its extreme moisture sensitivity. Broad resonances were observed, and relative intensities were intermediate between those expected for the complex and its decomposition product $[\text{CpNi}(\text{diphos})]\text{I}$. All of the ionic derivatives show nmr patterns consistent with the presence of the $[\text{CpNi}(\text{diphos})]^+$ cation and are assigned the general structure 2. The relative intensities of the phenyl, C_5H_5 , and

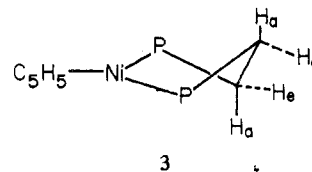
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2, $n = 1$, $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{PF}_6$; $n = 2$, $\text{X} = \text{NiCl}_4, \text{NiBr}_4$

methylene resonances are equal to the expected 20:5:4 ratio within experimental error (Table II). The methylene resonances of the ionic derivatives occur as doublets separated by 18 Hz in the 60-MHz proton spectrum. This is explained on the basis of phosphorus-31 coupling, although much smaller values of J_{PH} are generally encountered in alkylphosphine complexes.^{30,31} An alternative explanation is that the "doublet" is actually two singlets arising from different environments of pairs of methylene protons in a rigid puckered chelate ring such as that shown by 3. That this is not the case was



shown by recording the spectrum at 100 MHz. The spacing between the lines remains constant at 18 Hz, δ 2.75 ppm, demonstrating that the doublet pattern is the result of phosphorus-hydrogen coupling rather than a nonequivalence in chemical shifts. Thus while puckering of the chelated diphos ring has been demonstrated in X-ray studies,^{32,33} it would seem in the present case that either the ring is rapidly flipping to equilibrate proton environments or the chemical shifts of "axial" and "equatorial" protons are very nearly equivalent. Similar doublet patterns have been observed for the methylene protons of $[(h^3\text{-C}_4\text{H}_7)\text{Pd}(\text{diphos})]\text{PF}_6$ ³⁴ and $[(\text{CH}_3)_2\text{-PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]\text{Fe}(\text{CO})_3$ ³⁵ but the origin of this pattern was not commented upon.³⁶ The complex $[\text{CpNi}(\text{diphos})]_2-\text{NiCl}_4$ exhibited a proton nmr spectrum in which chemical shifts and line shapes were virtually identical with those of the $[\text{CpNi}(\text{diphos})]\text{X}$ complexes (Table II). The presence of the paramagnetic NiCl_4^{2-} ion might have been expected to lead to a shifting or broadening of the cation resonances, as is observed for 0.1–0.25 M solutions of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2-\text{NiCl}_4$.³⁷ Recent studies³⁸ have shown, however, that in CH_2Cl_2 solvent these effects decrease considerably as the concentration of the complex decreases. The solubility limitations (approximately 10^{-3} M) imposed by $[\text{CpNi}(\text{di}$

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phos)₂NiCl₄ make it highly unlikely that we would be able to observe either paramagnetic shifts or broadening in this case.

The presence of the tetrahedral NiCl₄²⁻ and NiBr₄²⁻ anions in their respective complexes was shown unequivocally by visible-near-ir spectroscopy. The chloro complex showed its characteristic^{28,29} absorptions at 15,500 cm⁻¹ (ε 206) and 14,500 cm⁻¹ (ε 200). The NiBr₄²⁻ complex showed the expected^{28,29} absorptions at 14,600 cm⁻¹ (ε 280) and 13,600 cm⁻¹ (ε 272). The [CpNi(diphos)]⁺ cation is transparent in this region, allowing unambiguous assignment of these bands.

Infrared spectroscopy was a definitive means of characterization only for [CpNi(CN)]₂-μ-diphos and [CpNi(diphos)]-PF₆. The former complex exhibited a C-N stretching band at 2118 cm⁻¹, typical of coordinated cyanide³⁹ while the latter complex showed characteristic²⁷ P-F stretches at 830 and 548 cm⁻¹. Conductance data for the complexes in methylene chloride are shown in Table III. (The complex CpNi[P(C₆H₅)₃]Cl is included as a reference nonelectrolyte.) The [CpNi(diphos)]X and [CpNi(diphos)]₂NiX₄ complexes afford values of Λ_m consistent with their formulation as ionic species. In the concentration range studied here dichloromethane solutions of (C₆H₅)₄AsCl exhibit a molar conductance value of 78.0 ohm⁻¹ cm² mol⁻¹,⁴⁰ which is taken as the reference value for a 1:1 electrolyte.^{40,41} Unfortunately, dichloromethane is a very poor solvent for discriminating between 1:1 and 2:1 electrolytes in which the cation is a group VIII metal complex containing chelating ligands. This effect is presumably due to ion pairing^{40,41} which could also explain our observations (Table III). The use of solvents in which ion pairing is less important, e.g., acetone or ethanol, is of course precluded by the substitution lability of the NiX₄²⁻ ions in these solvents.^{28,29} Interestingly, the conductance observed for the cyano derivative is very near the reference nonelectrolyte value, while meaningful data for [CpNi(I)]₂-μ-diphos could not be obtained due to its decomposition to [CpNi(diphos)]I during the time required to prepare the sample and measure its conductance. These differences in behavior serve to point up once again the tremendous differences in moisture sensitivity between the cyano and iodo derivatives and suggest that decomposition of the iodo complex may be initiated by dissociation of I⁻ and subsequent attack at nickel by water.

The formation of the bridged iodo and cyano complexes parallels the isolation of the covalent CpNi(L)X derivatives from the reaction of nickelocene with [R₃P]₂NiX₂ complexes (X = halogen).^{20,21} The complexes [CpNi(diphos)]₂NiX₄ (X = Cl, Br) were quite unexpected products of their respective reactions and some attempt at explaining the marked anion dependence of these reactions seems in order. Unfortunately, the reactions are heterogeneous, with reactants and/or products being insoluble in the various solvents utilized, and meaningful kinetic studies are thus precluded. It is clear from control experiments, however, that the dimeric complex [CpNi]₂-μ-diphos is not formed by attack of iodide ion on the ionic [CpNi(diphos)]I. The [CpNi(diphos)]⁺ cation is also inert to attack by Cl⁻ and Br⁻ under the reaction conditions employed here. The addition of excess sodium cyano-

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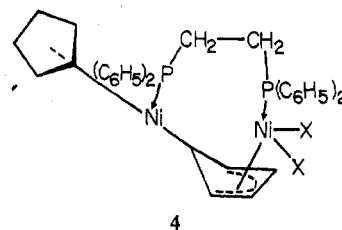
Table III. Conductance Data^a

Complex	Λ _m , ohm ⁻¹ cm ² mol ⁻¹	Complex	Λ _m , ohm ⁻¹ cm ² mol ⁻¹
[CpNi(diphos)]PF ₆	56.3	[CpNi(diphos)] ₂ NiCl ₄	33.6
[CpNi(diphos)]Cl	45.0	[CpNi(diphos)] ₂ NiBr ₄	39.5
[CpNi(diphos)]Br	39.3	[CpNi(CN)] ₂ -μ-diphos	1.7
[CpNi(diphos)]I	51.2	CpNi[P(C ₆ H ₅) ₃]Cl	0.4

^a All complexes ~10⁻³ M in methylene chloride.

nide to solutions of the cation does lead to the formation of [CpNi(CN)]₂-μ-diphos,²⁴ but the quantities isolated from this reaction are not sufficient to account for the yields obtained in our direct synthesis. The precipitation of the [CpNiI]₂-μ-diphos and [CpNi(diphos)]₂NiX₄ complexes (X = Cl, Br) from their respective reaction mixtures is no doubt a dominant factor in their isolation. Control experiments have shown that nickelocene does not react with diphos under the conditions employed here, nor do the (diphos)NiX₂ complexes disproportionate to (diphos)₂Ni²⁺NiX₄²⁻. These processes would seem to be ruled out as important features of the observed reactions.

In accord with mechanisms proposed for other reactions in which a cyclopentadienyl ligand is transferred to or from a nickel complex,^{42,43} we suggest that the reaction is initiated by attack of the 20-electron nickelocene complex on the coordinatively unsaturated (diphos)NiX₂ complexes to afford an intermediate such as 4. This intermediate could collapse



directly to give the dimeric complex or could collapse by a series of steps to afford [CpNi(diphos)]₂NiX₄. While this mechanism is plausible, there are obviously other possibilities which cannot be excluded at present. We are continuing our studies of these and related systems to clarify the mechanistic details of these reactions. The results of these investigations as well as our studies of the reactions of nickelocene with other coordinatively unsaturated metal complexes will be the subjects of future reports.

Acknowledgements. The authors are indebted to Dr. Joyce Y. Corey and Dr. David W. Larsen for several valuable discussions and to Mr. R. E. Miller and Dr. K. Moedritzer of the Monsanto Co. for their assistance in obtaining the phosphorus-31 and 100-MHz proton nmr spectra.

Registry No. [CpNi(diphos)]₂NiCl₄, 41517-22-0; [CpNi(diphos)]₂NiBr₄, 41517-23-1; [CpNiI]₂-μ-diphos, 41517-24-2; [CpNi(CN)]₂-μ-diphos, 38467-34-4; [CpNi(diphos)]Cl, 36683-49-5; [CpNi(diphos)]-Br, 41517-27-5; [CpNi(diphos)]I, 41517-40-2; [CpNi(diphos)]PF₆, 41517-41-3; (h⁵-C₅H₅)₂Ni, 1271-28-9; (diphos)NiCl₂, 14647-23-5; (diphos)NiBr₂, 14647-21-3; (diphos)NiI₂, 15629-91-1; (diphos)Ni(CN)₂, 41538-98-1.

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