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## Reactions of the Zerovalent Complex Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub><sup>1</sup>

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Ligand substitution and oxidative addition reactions of the complex Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> have been investigated. Complete substitution of diphenylphosphine occurs upon reacting Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> with phosphites, L, resulting in the production of NiL<sub>4</sub> in reasonable yields. Reactions of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> with organic halides and with HgX<sub>2</sub> (X = Cl, Br, I, SCN) produce the pentacoordinate species Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>X<sub>2</sub>, while reactions with Hg(CN)<sub>2</sub> form polymeric {Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>](CN)<sub>2</sub>·H<sub>2</sub>O}<sub>n</sub>, with benzoyl cyanide form square-planar Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(CN)<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub>, and with phenyl isothiocyanate form Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>NCS)<sub>2</sub>. Oxidative additions with HgX<sub>2</sub> produce, in most cases, Hg<sub>2</sub>X<sub>2</sub> rather than elemental mercury suggesting that these reactions occur by sequential one-electron oxidations rather than simultaneous two-electron oxidations. The relative ease of these oxidations Cl > Br > I suggests that these oxidations occur by atom transfer without the intermediate formation of Ni-Hg bonds. The organic products of some of the oxidative additions of RX have been isolated and characterized. The nature of the organic products suggests that oxidative addition reactions of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> with RX proceed by radical pathways involving sequential oxidative addition and reductive elimination steps.

### Introduction

There has been considerable interest in recent years in the reactions of zerovalent transition metal complexes<sup>3</sup> since they have been suggested as model systems for the study of relations between homogeneous and heterogeneous catalysts.<sup>4</sup> This idea rests upon the tenet that coordination and chemisorption can be related by similar electronic interactions and that the behavior in solution of some zerovalent metal complexes is essentially that of solvated metal atoms. The mechanisms of oxidative additions have been studied with the hope of explaining the homogeneous catalytic activity of these species.<sup>5</sup> Proposals involving carbonium ions, free radicals, and concerted three-center intermediates have evolved from various kinetic investigations.<sup>5b,c,6</sup>

To date only tertiary phosphine and di(tertiary phosphine) complexes of nickel(0), palladium(0), and platinum(0) have been extensively investigated<sup>3</sup> but no detailed investigations of all the products of these reactions have been reported. All of these complexes have two features in common: they are or they can become coordinatively unsaturated<sup>7</sup> in solution, and the metal is coordinated to "soft" ligands such as phosphines or arsines.

Since the small steric requirements of diphenylphosphine might be expected to enhance the stability of its complexes,<sup>7</sup> an investigation of the reactions of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> was undertaken especially because the complex Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> is readily obtained<sup>8</sup> and easily handled.

### Experimental Section

The complex Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> was prepared by the literature method.<sup>8</sup> It is moderately air sensitive but may be handled briefly in the air and can be kept in a desiccator under vacuum for approximately 2 days before decomposing. Decomposition is accompanied by a color change from lemon yellow to brown.

**A. Oxidative Additions of Alkyl and Aryl Halides.** These reactions were all run similarly either by suspending Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> in

anhydrous benzene under dry nitrogen and adding an excess of the organic reagent or by suspending Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> in the neat reactant in a dry nitrogen atmosphere. The following are typical.

(1) To 4.44 g (5.5 × 10<sup>-3</sup> mol) of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> suspended in 100 mL of dry benzene under a stream of dry nitrogen was added 1.12 mL (1.236 g, 1.1 × 10<sup>-2</sup> mol) of chlorobenzene. The suspension was refluxed for approximately 24 h (until nearly all of the Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> dissolved) with a color change from bright yellow to yellow-brown. Unreacted Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> was removed by filtration and anhydrous diethyl ether was added to the filtrate to precipitate [HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>NiCl<sub>2</sub> as brown crystals (mp 94 °C) which were removed by filtration under a stream of nitrogen. The resultant filtrate was concentrated on a rotary evaporator at 40–50 °C. White crystals were recovered from the filtrate (0.124 g; 10%; mp 70–71 °C) and identified as biphenyl on the basis of melting point, GC analysis, and NMR.

(2) To 4.44 g (5.5 × 10<sup>-3</sup> mol) of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> was added 50 mL of freshly distilled chlorobenzene and the suspension was refluxed under nitrogen until most of the Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> dissolved (~24 h). The solution changed color from yellow to yellow-brown as the Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> dissolved. A minor amount of gelatinous material was removed by filtration and the filtrate was triturated with diethyl ether to yield 0.99 g (26%) of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>Cl<sub>2</sub>. The filtrate was concentrated to 10 mL by distillation and treated with a trace of water to yield 0.13 g of white crystals, mp 71 °C, identified as biphenyl.

(3) Excess cyclohexyl iodide was reacted as in part 2. After filtration of the reaction mixture, addition of dry acetone, and isolation of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>I<sub>2</sub> by filtration, the filtrate was distilled. The distillation products were identified as cyclohexane, cyclohexene, and dicyclohexyl by their boiling points and infrared and NMR spectra.

(4) *d*-Bromocamphor was reacted as in part 1. After separation of the crystalline precipitate of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>Br<sub>2</sub>, the solution was treated with 50 mL of hexane and filtered. Excess 2,4-dinitrophenylhydrazine reagent was then added to the filtrate and it was allowed to stand for 12 h. The crystalline product thus formed melted sharply at 168 °C. Though this product was not completely characterized, its infrared spectrum confirmed that it was a 2,3-dinitrophenylhydrazone and the integrated NMR spectrum indicated the presence of two camphoric fragments for every hydrazone group in the molecule, indicating that the camphor had dimerized. The

Table I. Products of the Reactions of  $(\text{Ph}_2\text{PH})_4\text{Ni}$  with Organic Halides

Organic halide	Conditions		Inorganic product (% yield)	Organic product (% yield)
	T, °C	Time, h		
Iodides				
I <sub>2</sub>	25	0.15	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (90)	Complex mixture
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	25	0.15	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (90)	Complex mixture
ICH <sub>2</sub> COOH	25	0.15	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (90)	Complex mixture
HCl <sub>3</sub>	25	0.15	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (90)	Complex mixture
CH <sub>3</sub> I	25	24	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (60)	C <sub>2</sub> H <sub>6</sub>
CH <sub>2</sub> I <sub>2</sub>	25	24	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (60)	Complex mixture
Cyclohexyl iodide	25	24	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (70)	Bicyclohexyl, cyclohexane, cyclohexene
Iodobenzene	25	24	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (60)	Benzene, biphenyl
2-Iodoethylbenzene	25	24	$(\text{Ph}_2\text{PH})_3\text{NiI}_2$ (80)	Ethylbenzene
Bromides				
HCBR <sub>3</sub>	25	0.25	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2 \cdot \text{C}_6\text{H}_6$ (60)	Complex mixture
d-Bromocamphor	25	24	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (65)	Camphor dimer
2-Bromo-2-phenylacetophenone	25	24	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (75)	Complex mixture
Bromobenzene	152	24	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (90)	Biphenyl (90)
Bromobenzene	78	12	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (75)	Biphenyl (75)
Crotyl bromide <sup>a</sup>	97	24	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (60)	2,6-Octadiene, 3-methyl-1,5-heptadiene, 3,4-dimethyl-1,5-hexadiene
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	195	24	$(\text{Ph}_2\text{PH})_3\text{NiBr}_2$ (82)	Bibenzyl (82)
Chlorides				
Benzoyl chloride	193	24	$(\text{Ph}_2\text{PH})_3\text{NiCl}_2$ (15)	Benzil (5)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	172	24	$(\text{Ph}_2\text{PH})_3\text{NiCl}_2$ (15)	Bibenzyl (5)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	78	24	$(\text{Ph}_2\text{PH})_3\text{NiCl}_2$ (5)	
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	98	24	$(\text{Ph}_2\text{PH})_3\text{NiCl}_2$ (83)	4,4'-Dimethylbibenzyl (83)

<sup>a</sup> I. D. Webb and G. T. Borchardt, *J. Am. Chem. Soc.*, **73**, 2654 (1951), provides a system for comparison.

compounds isolated from some of the oxidative addition reactions of various organic halides, their melting points, and their percent yields are given in Table I.

**B. Oxidative Additions of HgX<sub>2</sub>.** These reactions were all carried out in the same manner, the following being typical.

A slurry containing 2.89 g (0.036 mol) of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  and 3.36 g (0.074 mol) of  $\text{HgI}_2$  in 50 mL of dry benzene was refluxed under nitrogen. The yellow precipitate of  $\text{Hg}_2\text{I}_2$  was filtered off and 100 mL of diethyl ether was added to the benzene filtrate. The mixture was again filtered and the filtered solution was reduced to a small volume under vacuum at room temperature causing precipitation of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$ . This was removed by filtration, washed with 20 mL of anhydrous ether and 20 mL of hexane, and dried under vacuum over  $\text{P}_4\text{O}_{10}$  to yield 0.735 g (23.5%) of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$ . The compounds formed, their melting points, and their percent yields are given in Table II.

**C. Reaction of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$  with Aqueous Base.**  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$  (0.506 g,  $7.40 \times 10^{-4}$  mol) was slurried with 20 mL of concentrated aqueous ammonia. The solid changed color from dark blue to orange to yellow over the course of a few minutes. The product,  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$ , was removed by filtration, washed with 20 mL of water and 20 mL of acetone, and dried under vacuum over  $\text{P}_4\text{O}_{10}$  to yield 0.232 g (equivalent to 50% of the original nickel). Dimethylglyoxime was added to the filtrate and the resultant precipitate of  $\text{NiC}_8\text{H}_{14}\text{O}_4\text{N}_4$  was dried to constant weight to yield 0.0530 g (equivalent to 40% of the original nickel).  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{X}_2$  (X = Cl, Br) reacted similarly with  $\text{NH}_4\text{OH}$ , as did  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$ , giving  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_4$ ;  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3(\text{NCS})_2$  did not react.

**D. Preparation of Deuterium-Substituted Compounds.** (1)  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_4$  was prepared in 47% yield (mp 174–176 °C) in the same fashion as  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  except that the  $\text{LiP}(\text{C}_6\text{H}_5)_2$  solution in tetrahydrofuran was reacted with a tetrahydrofuran solution containing  $\text{D}_2\text{O}$ ,  $\text{CH}_3\text{COOD}$ , and anhydrous  $\text{NiBr}_2$ .

(2)  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$  was prepared by reacting a slurry containing 0.634 g of  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_4$  in 10 mL of refluxing tetrahydrofuran with excess iodine to yield a deep blue-black solution. A few drops of pentane was added and the mixture cooled under a stream of dry nitrogen. Addition of more pentane completed precipitation of the crystalline product. This was filtered, washed with 20 mL of pentane, and dried under vacuum over  $\text{P}_4\text{O}_{10}$  to give 0.616 g (90%) of  $\text{Ni}[\text{DP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$ .

**E. Oxidative Addition Reactions with HX.** Dry HCl gas was bubbled through a suspension of 6.2 g ( $7.72 \times 10^{-3}$  mol) of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  in 150 mL of dry benzene under nitrogen until most

Table II. Products of the Reactions of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  with  $\text{HgX}_2$ 

X	Products (% yield)	Re- action time, h	Temp, °C
Cl	$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{Cl}_2$ + $\text{Hg}_2\text{Cl}_2$ (65)	0.5	80
Br	$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{Br}_2$ + $\text{Hg}_2\text{Br}_2$ (55)	0.1	25
I	$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{I}_2$ + $\text{Hg}_2\text{I}_2$ (23.5)	0.1	25
CN	$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3(\text{CN})_2 \cdot \text{H}_2\text{O}^a$ + $\text{Hg}$ (75)	0.25	80
SCN	$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3(\text{NCS})_2^b$ + $\text{Hg}_2(\text{NCS})_2$ (59)	0.25	80

<sup>a</sup>  $\nu(\text{CN})$  2150  $\text{cm}^{-1}$ . <sup>b</sup> This complex contains N-bonded thiocyanate on the basis of  $\nu(\text{CN})$  2085  $\text{cm}^{-1}$  and  $\nu(\text{CS})$  775  $\text{cm}^{-1}$ . For comparative data, see J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 231 (1969).

of the nickel complex had dissolved. This solution was filtered and anhydrous ether added to precipitate  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{Cl}_2$ . The complex was removed by filtration and dried under vacuum over  $\text{P}_4\text{O}_{10}$  to yield 4.17 g ( $7 \times 10^{-3}$  mol, 91%) of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{Cl}_2$ , mp 94 °C.

Similarly,  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{X}_2$  (X = Cl, Br, I) was prepared by adding aqueous HX to a benzene suspension of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$ . No hydrides were detected in any of these syntheses.

**F. Ligand Substitutions of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$ .** These reactions were all carried out in a similar fashion and the following is typical.

(1)  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  (8.74 g, 0.011 mol) and 20 mL of triethyl phosphite (0.17 mol) were refluxed under nitrogen in 100 mL of dry benzene to produce a clear, light yellow solution. This solution was reduced to a small volume under vacuum at 50–60 °C and allowed to cool. The colorless crystals which precipitated were filtered, washed with 5 mL of ice-cold methanol, and dried under vacuum over  $\text{P}_4\text{O}_{10}$  to yield 0.98 g (12%) of  $\text{Ni}[\text{P}(\text{OEt})_3]_4$ , mp 106–108 °C; lit. mp 108,<sup>10</sup> 107 °C.<sup>11</sup> The products isolated, their melting points, and their percent yields are given in Table III.

(2) Exchange reactions were also carried out in sealed NMR tubes in the following manner. A weighed amount of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  and phosphite in a 1:6 mole ratio and approximately 0.3 mL of  $\text{C}_6\text{D}_6$  were added to an NMR tube and the contents chilled in liquid nitrogen.

**Table III.** Zerovalent Nickel Complexes, NiL<sub>4</sub>, Prepared by Ligand Substitutions of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>

L	Mp, °C	Color	% yield
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	149	Colorless	56
P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	106–108	Colorless	12
P(OCH <sub>3</sub> ) <sub>3</sub>	215	Colorless	60
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )	151	Pale yellow	85
C <sub>6</sub> H <sub>5</sub> P(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	134	Pale yellow	77
P(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	118	Pale yellow	62

The tube was then evacuated, sealed, and heated in a boiling water bath for 20 min to produce a clear solution, which was cooled to room temperature, and the NMR spectrum was obtained.

(3) For comparison purposes all of the Ni[P(OR)<sub>3</sub>]<sub>4</sub> complexes were also prepared according to the procedure of Vinal and Reynolds.<sup>10</sup>

(4) To prepare Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>NCS)<sub>2</sub>, phenyl isothiocyanate (3.2 mL) and Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> (4.39 g) were stirred together in 25 mL of dry benzene under nitrogen for 24 h at room temperature. The mixture was filtered to remove unreacted Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> and anhydrous diethyl ether added to the filtrate to precipitate crystals of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>NCS)<sub>2</sub>. These were filtered, washed with ether, and dried under vacuum over P<sub>2</sub>O<sub>10</sub>.

**G. Physical Measurements.** Infrared spectra were obtained as KBr pellets or as neat liquids on Beckman IR-5A and IR-8 recording spectrometers and calibrated against known bands of polystyrene. <sup>1</sup>H NMR spectra were obtained on Varian A-60 or Jeolco 4-H 100 spectrometers as solutions in CDCl<sub>3</sub>, CD<sub>3</sub>C(=O)CD<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>, or C<sub>7</sub>D<sub>8</sub> with TMS as an internal standard. Melting points were determined on a Fisher-Johns melting point apparatus in air and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or Alfred Bernhardt Microanalytisches Laboratorium, Mülheim, West Germany. All compounds gave satisfactory elemental analyses. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5700 A with a Model 7123 A recorder using two columns. These were a 6 ft long, 1/8-in. diameter 10% Carbowax 20 on 80–100 mesh Chromosorb WHP support with a helium carrier gas flow rate of 45–53 cm<sup>3</sup>/min or a 6 ft long, 1/8-in. diameter 10% Apiezon L on 80–100 mesh Chromosorb WHP support with the same carrier gas and flow rate. Details of the chromatograph conditions are given elsewhere.<sup>12</sup>

## Results and Discussion

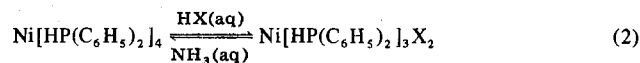
**A. Stability and Reactivity of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>.** It was demonstrated earlier<sup>8</sup> that the yellow diamagnetic compound formed by reaction of diphenylphosphine with nickel halides in protic solvents is the zerovalent complex Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> and not the divalent compound Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> it was originally believed to be.<sup>13</sup> In contrast to the numerous<sup>3</sup> studies of oxidative addition reactions of zerovalent palladium and platinum complexes, few studies have been conducted with nickel complexes though oxidative additions are implicated in numerous catalytic reactions involving nickel species.<sup>14</sup> The limited number of studies is probably due to the general extreme air sensitivity or lack of reactivity of these species. This is due<sup>7</sup> to either a very high (Ni(PR<sub>3</sub>)<sub>4</sub>) or very low value of the equilibrium constant *K* for ligand dissociation according to reaction 1. It is generally believed that the coordinatively



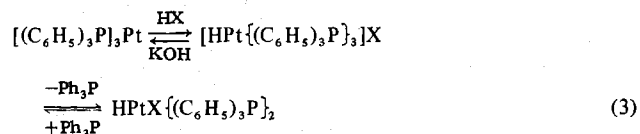
unsaturated species ML<sub>3</sub> and ML<sub>2</sub> are the reactive intermediates in reactions of the ML<sub>4</sub> species. Using the ligand cone angle value of  $\theta = 128^\circ$  quoted by Tolman<sup>15</sup> for HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> one can estimate that *K* for Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> will be on the order of 10<sup>-10</sup>. This leads to the conclusion that Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> should be as dissociatively stable as the Ni[P(OR)<sub>3</sub>]<sub>4</sub> species<sup>7</sup> and also as unreactive. Our own experience with both species, however, demonstrated that these species do not have similar stabilities. The Ni[P(OR)<sub>3</sub>]<sub>4</sub> species are stable for weeks or longer in a desiccator whereas Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> is only stable for about 2 days.

This difference in stability coupled with the fact that diphenylphosphine produces pentacoordinate nickel(II) com-

plexes of the type<sup>9</sup> NiL<sub>3</sub>X<sub>2</sub> whereas phosphites generally produce pentacoordinate complexes of the type Ni[P(OR)<sub>3</sub>]<sub>5</sub><sup>2+</sup> suggested that Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> might undergo oxidative addition reactions of an associative nature rather than the more common dissociative oxidative additions. In concert with this idea reaction 2 was found to occur without P–H bond cleavage



which surely would result if large amounts of free diphenylphosphine were present in these solutions. This result should be compared with those obtained for an analogous platinum system<sup>3</sup> as illustrated in reaction 3.



Complete ligand exchange can however be promoted by reaction with phosphites in which case reaction 4 occurs.

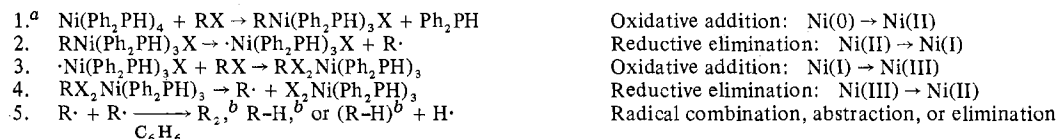


Similar reactions occur with Pt{(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P}<sub>4</sub>.<sup>17</sup> The products of these reactions and their properties are given in Table III. Only partial substitution of HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> occurs upon reaction with the carbon monoxide source Fe(CO)<sub>5</sub> to produce<sup>8</sup> HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ni(CO)<sub>3</sub> and HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Fe(CO)<sub>4</sub>.

From these results as well as the results of oxidative addition reactions with organic halides, Table I (vide infra), it is concluded that under these conditions Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> does not undergo measurable dissociation in solution. This may well account for its low solubility in solvents with which it does not react.

**B. Oxidative Addition Reactions with Organic Halides.** A plethora of oxidative addition reactions<sup>3–6</sup> have been studied with the primary emphasis devoted to the inorganic products. Products of the types RMX(R<sub>3</sub>P)<sub>2</sub> and MX<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub> (M = Pd, Pt), with the latter predominating, have in general been formed. With Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>X<sub>2</sub><sup>9</sup> is the exclusive inorganic product of the reaction of all alkyl and aryl halides herein investigated. These products were identified by elemental analyses, by melting points, by infrared and NMR spectroscopy, and by comparison with authentic samples prepared by the method of Hayter.<sup>9</sup> In addition, the organic products of several of these reactions were either isolated or identified by gas chromatography. When isolated, the products were identified by IR, NMR, melting point or boiling point, and comparison with authentic samples. The results of these reactions are given in Table I. In addition to the reactants listed in Table I, C<sub>3</sub>H<sub>5</sub>N·ICl, propargyl bromide, allyl bromide, bromine, *N*-bromosuccinimide, PBr<sub>3</sub>, CCl<sub>4</sub>, and CHCl<sub>3</sub> all reacted vigorously with Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> but dark, air-sensitive solutions and/or tars were formed in each case and no characterizable products could be isolated. Some generalizations can however be made regarding the reactions of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> with organic halides. Both the rate of reaction and the isolated yield of organic products are a function of the halide increasing in the order Cl < Br < I. The rate and yield generally increase with an increase in temperature and an increase in the concentration of the organic substrate. Reactions proceed faster in neat reactant than in benzene solution.  $\alpha$ -Chloro-*p*-xylene reacted faster and with higher yield than  $\alpha$ -chlorotoluene; this is the same order of reactivity as found for the coupling of the analogous Grignard reagents,<sup>18</sup> a reaction which has been shown to proceed via a radical pathway.<sup>18</sup>

Since little dissociation of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> occurs in solution, these results collectively suggest a mechanism of the

Scheme I. Reaction Mechanism for Oxidative Addition of Organic Halides to  $(\text{Ph}_2\text{PH})_4\text{Ni}$ 

<sup>a</sup> A referee has suggested that the radicals could be generated by an electron-transfer process such as  $\text{Ni}(\text{Ph}_2\text{PH})_4 + \text{RX} \rightarrow \text{Ni}(\text{Ph}_2\text{PH})_4^+ + \text{R}\cdot + \text{X}\cdot$ . We thank the referee for this highly plausible suggestion which is consistent with the results of C. H. Bamford and E. O. Hughes, *Proc. R. Soc. London, Ser. A*, **326**, 469, 489 (1972). <sup>b</sup>  $\text{R}_2$  = dimer of R, R-H = alkane or arene formed by hydrogen abstraction, and (R-H) = alkene formed by H<sup>•</sup> elimination from R<sup>•</sup>.

sort outlined in Scheme I. Though many of these steps must remain speculative at present, the nature of the organic products isolated, particularly the coupling products, clearly demonstrates that the oxidative additions of organic halides to  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  proceed via radical pathways. Which, if any, of the species depicted in Scheme I are intermediates or transition states remains to be seen. The fact that no P-H exchange occurs involving either free or coordinated diphenylphosphine suggests that any homolytic cleavage of  $\text{RNi}$  bonds does not result in any long-lived free radicals as radical exchange as illustrated in reactions 5 should surely occur with



long-lived radicals.<sup>19</sup>

It is also likely that these reactions involve sequential one-electron oxidations<sup>20</sup> rather than concerted two-electron oxidations. This thesis is consistent with the results obtained for reactions of mercuric halides (vide infra).

**C. Oxidative Addition Reactions with Mercuric Halides and Pseudohalides.** It has proven possible to synthesize complexes containing metal-metal bonds via reactions of zerovalent complexes with metal halide derivatives.<sup>3</sup> Through reactions of this sort, compounds containing Pt-Sn, Pt-Cu, Pt-Au, and Pt-Hg bonds have been obtained. The reactions of mercuric halides are fundamentally the simplest of these reactions and the likely reduction products— $\text{Hg}_2\text{X}_2$  and/or  $\text{Hg}^0$ —are easily characterized. For these reasons  $\text{HgX}_2$  (X = Cl, Br, I, CN, and NCS) were reacted with  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  in dry benzene. In no case was a compound containing a mercury-nickel bond obtained. The results of these reactions are given in Table II. In each case except for  $\text{Hg}(\text{CN})_2$ ,  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{X}_2$  was the nickel-containing product and  $\text{Hg}_2\text{X}_2$  the major mercury-containing product. Traces of mercury metal were also evident in each reaction. These results suggest that these reactions proceed by sequential one-electron-transfer steps since the product of a two-electron transfer should be mercury metal only. The fact that mercury metal is the product of the reaction of  $\text{Hg}(\text{CN})_2$  is consistent with this hypothesis since  $\text{Hg}_2(\text{CN})_2$  is not known to exist.<sup>21</sup> It is interesting to note that neither the rate nor the yield of these reactions correlates with the solubilities of  $\text{Hg}_2\text{X}_2$  and hence the reduction potentials of  $\text{HgX}_2$  or the stabilities of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_3\text{X}_2$ .<sup>9</sup> This suggests that electron transfer occurs by atom transfer in these reactions.

**D. Ligand Substitution Reactions.** A common reaction of zerovalent complexes of the nickel triad is ligand substitution,<sup>3</sup> and we<sup>8</sup> utilized this reaction previously to demonstrate that  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  is in fact the zerovalent complex rather than a divalent species. This reaction has now been extended to include additional phosphites and the results are listed in Table III. In general this reaction provides a good synthetic method for preparing zerovalent nickel complexes in reasonable yield. However, no reaction occurs with carbon monoxide at atmospheric pressure and ambient temperatures over a 72-h period in benzene. The yield generally increases as the solubility of the  $\text{Ni}[\text{P}(\text{OR})_3]_4$  species decreases. Each of these

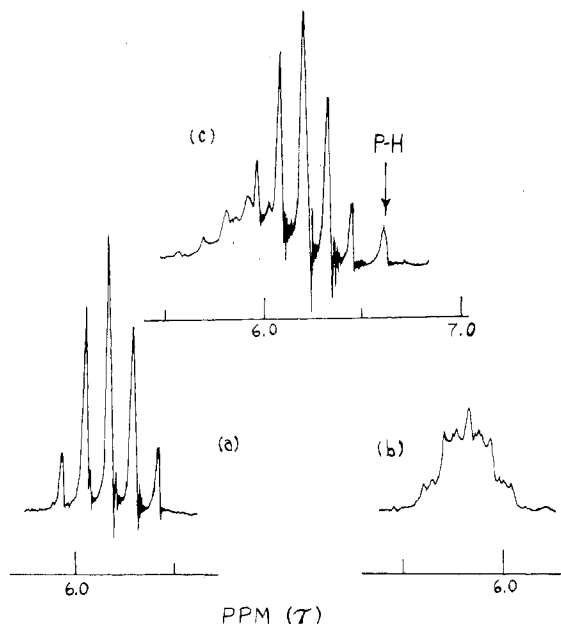


Figure 1. The 60 MHz  $^1\text{H}$  NMR spectrum of the methylene region of (a)  $\text{P}(\text{OC}_2\text{H}_5)_3$ , (b)  $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ , and (c) a mixture produced by reaction of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  with excess  $\text{P}(\text{OC}_2\text{H}_5)_3$  in  $\text{C}_6\text{D}_6$ .

reactions was also conducted in a sealed NMR tube containing a weighed amount of  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  and an excess of  $(\text{RO})_3\text{P}$ . In each case integration of the NMR resonances demonstrated that complete substitution of diphenylphosphine by phosphite occurred. The only species present in the final solutions were  $\text{Ni}[(\text{RO})_3\text{P}]_4$ ,  $\text{HP}(\text{C}_6\text{H}_5)_2$ , and  $(\text{RO})_3\text{P}$ , with the complete absence of phosphates, once again demonstrating that the diphenylphosphine complex is in fact a zerovalent species. The results of a typical experiment are illustrated in Figure 1.

Ligand substitution reactions were also conducted with phenyl isothiocyanate and with carbon disulfide. With phenyl isothiocyanate the red-brown diamagnetic compound  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_5\text{NCS})_2]$ , mp 176–177 °C, was obtained in which the phenyl isothiocyanate is  $\pi$  bound to the nickel through the C=S double bond. This was concluded from a comparison of the infrared spectrum with that reported for  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{C}_6\text{H}_5\text{NCS})_2$ <sup>22</sup> which contains one  $\pi$ - and one  $\sigma$ -bound isothiocyanate. The S-bonded phenyl isothiocyanate exhibits<sup>22</sup> a strong  $\nu(\text{NCS})$  at 2155  $\text{cm}^{-1}$  and a medium-intensity  $\nu_{\text{sym}}(\text{NCS})$  at 925  $\text{cm}^{-1}$ . The complex  $\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_2(\text{C}_6\text{H}_5\text{NCS})_2$  exhibits a strong band at 926  $\text{cm}^{-1}$  which could be assigned to  $\nu_{\text{sym}}$  but no absorption is present in the 2100- $\text{cm}^{-1}$  region. A very strong band is present at 1553  $\text{cm}^{-1}$  which is attributable to  $\nu(\text{CN})$ , while a band at 803  $\text{cm}^{-1}$  might be assigned to  $\nu(\text{C-S})$ . The platinum complex  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\text{C}_6\text{H}_5\text{NCS})$  which contains<sup>22</sup> a  $\pi$ -bonded phenyl isothiocyanate has bands at 1643 and 782  $\text{cm}^{-1}$ .

$\text{Ni}[\text{HP}(\text{C}_6\text{H}_5)_2]_4$  reacted quickly with  $\text{CS}_2$  to give vile smelling solutions from which no pure product could be

isolated. Elemental analyses on several preparations were not reproducible even though other zerovalent phosphine complexes of nickel or palladium<sup>23</sup> give stable adducts with CS<sub>2</sub>.

A suspension of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> in dry benzene was refluxed with excess benzoyl cyanide to give the yellow-orange square-planar diamagnetic complex *trans*-[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Ni(CN)<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub> (mp 143–145 °C;  $\nu(\text{CN})$  2145 cm<sup>-1</sup>) in 81% yield. This complex was further characterized by NMR and elemental analyses. When the reaction was run in toluene or anisole, toluene and anisole solvates were formed. This reaction occurred much more slowly than the analogous reaction with benzoyl chloride. The large difference in reactivity between benzoyl chloride and cyanide can be attributed to the relative strengths of the carbon-carbon and carbon-chlorine bonds in these two compounds.

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**Registry No.** (Ph<sub>2</sub>PH)<sub>3</sub>NiI<sub>2</sub>, 16102-67-3; (Ph<sub>2</sub>PH)<sub>3</sub>NiBr<sub>2</sub>, 38199-79-0; (Ph<sub>2</sub>PH)<sub>3</sub>NiCl<sub>2</sub>, 38199-78-9; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>](CN)<sub>2</sub>, 62059-29-4; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>(NCS)<sub>2</sub>, 62066-86-8; Ni[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 14221-00-2; Ni[P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 14839-39-5; Ni[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>, 14881-35-7; Ni[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)]<sub>4</sub>, 62066-87-9; Ni[C<sub>6</sub>H<sub>5</sub>-P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 62066-88-0; Ni[P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 62066-89-1; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 31410-77-2; Ni[DP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 62066-90-4; Ni[DP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>I<sub>2</sub>, 62066-91-5; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>NCS)<sub>2</sub>, 62066-92-6; *trans*-[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(CN)<sub>2</sub>, 62066-85-7; HClI<sub>3</sub>, 75-47-8; CH<sub>3</sub>I, 74-88-4; CH<sub>2</sub>I<sub>2</sub>, 75-11-6; cyclohexyl iodide, 626-62-0; iodo-benzene, 591-50-4; 2-iodoethylbenzene, 103-63-9; HCB<sub>3</sub>, 75-25-2; *d*-bromocamphor, 25619-71-0; 2-bromo-2-phenylacetophenone,

1484-50-0; bromobenzene, 108-86-1; crotyl bromide, 4784-77-4; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, 100-39-0; benzoyl chloride, 98-88-4; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl, 100-44-7; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl, 104-82-5; P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, 122-52-1; I<sub>2</sub>, 7553-56-2; CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>I, 27636-85-7; ICH<sub>2</sub>COOH, 64-69-7.

## References and Notes

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## Equilibrium Energetics of Cis-Trans Isomerization for a Series of Palladium(II) Isocyanate-Phosphine Complexes. Study of Phosphine Electronic Effects. 2<sup>1</sup>

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Equilibrium thermodynamics for the cis-trans isomerization of the para-substituted phosphine complexes [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> (*n* = 1; Z = Cl, H, CH<sub>3</sub>, CH<sub>3</sub>O; *n* = 2, Z = Cl, H, CH<sub>3</sub>) have been determined in several solvents by variable-temperature proton NMR spectroscopy. The cis isomer is generally thermodynamically more stable than the trans isomer, and the nature of the solvent greatly influences the relative isomer population, the cis isomer being favored by polar solvents. The complexes all contain N-bonded isocyanate under all conditions studied both in the solid state and in solution. All complexes are cis in the solid state except [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>, Z = CH<sub>3</sub> and Cl, which are trans. The isomerization process is not entropy controlled and probably occurs via a solvent-association mechanism. Linear correlations of both  $\Delta H$  and  $\Delta S$  with Hammett  $\sigma$  constants of Z are found. The enthalpy and entropy of the reaction *cis*-[ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>  $\rightleftharpoons$  *trans*-[ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> both decrease as the basicity of the phosphine increases. This is opposite to the increase in enthalpy and entropy with increasing basicity observed for the (Ar<sub>2</sub>PCH<sub>3</sub>)<sub>2</sub>Pd(NCO)<sub>2</sub> complexes and all of the analogous azide and chloride complexes. Reasons for this reversal in behavior are suggested. The rates of isomerization of the isocyanate complexes are considerably slower than those of the corresponding chloride and azide complexes. Phosphine exchange in the isocyanate complexes is much slower than for the corresponding cyanide, azide, and chloride complexes.

### Introduction

Several studies of the cis-trans isomerization of square-planar palladium(II) complexes of the type (R<sub>3</sub>P)<sub>2</sub>PdX<sub>2</sub> have recently been reported.<sup>1-7,10</sup> It has been demonstrated in these studies that the rate of the isomerization process, the mechanism, and the relative isomer population are all in-

fluenced by the size and basicity of the phosphine, the nature of the anionic ligand, and the nature of the solvent.<sup>4-7,10</sup> The relative magnitudes of the various contributing terms to  $\Delta H$  and  $\Delta S$  have been discussed<sup>1,4,10</sup> and it has been established that the enthalpy and entropy of solvation are the most important factors influencing the isomer population.<sup>1,4,10</sup>