

shift in the  $\sigma \rightarrow \sigma^*$  transition energy. The same effect is noted for the  $\pi_x^*(b_1)$  orbital which is also forced higher in energy more than  $\sigma^*(b_1)$  giving again a red shift from the trend in  $\pi^* \rightarrow \sigma^*$  energies expected from the ionic model. The  $\pi_y^*(a_2)$  orbital is not of the proper symmetry to interact with the cesium 5p orbitals and its energy would not be affected by inner shell bonding in  $C_{2v}$  symmetry.

Finally, there is a red shift for each  $Br_2^-$  and  $I_2^-$  transition, and the  $Cl_2^-$  and  $F_2^-$  transitions,<sup>18</sup> on going from the argon matrix-isolated  $M^+X_2^-$  species to the  $X_2^-$  color center in the solid alkali halide lattice.<sup>10</sup> The largest difference was found for the  $\sigma \rightarrow \sigma^*$  transition of  $F_2^-$ . These differences in dihalide radical anion spectra must be attributed to the different types and symmetries of the immediate  $X_2^-$  ion environments in the two cases. It may also be possible that charge transfer to the halogen molecule in the  $M^+X_2^-$  species is not quite as complete as for the  $X_2^-$  color center, owing to the induced dipole moment on the intimately involved  $M^+$  ion in the  $M^+X_2^-$  species.

**Matrix Reaction Chemistry.** Although the tungsten lamp photolysis data are not as quantitatively accurate for  $M^+Br_2^-$  and  $M^+I_2^-$  as compared to the lighter species due to overlapping  $Br_2$  absorption and a steeply rising background, a general statement can be made. The two heavier  $M^+X_2^-$  species photodecompose more readily than  $M^+Cl_2^-$ ; however, they are clearly more stable than  $M^+F_2^-$ . Again, the  $Cs^+$  compounds appear to be the most stable.

It is of considerable interest that the  $M^+X_2^-$  intermediates are trapped in the matrix reaction experiments. In earlier crossed-molecular beam work, evidence has been presented for an electron transfer mechanism forming  $M^+...X_2^-$ , which decomposed readily to give the final products of reactions 1 and 2. The role of the  $X_2^-$  ion in these reactions has been described by Herschbach.<sup>26</sup>

Finally, the salt-molecule reactions (3 and 4) proceed readily under the conditions of these experiments. In fact these products increase on sample warming which indicates that reactions 3 and 4 have very little activation energy. This is in accord with the observation of a collision complex in the crossed-molecular beam reaction of  $CsI$  and  $Cl_2$

which persisted for many vibrational periods and then decomposed to give  $CsCl$  and  $ICl$ .<sup>27</sup>

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## References and Notes

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## A New Class of Nickel Hydrides. $HNiL_3CN$

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**Abstract:** Addition of HCN to phosphorus complexes of zerovalent nickel of the type  $NiL_4$  gives a new class of five-coordinate nickel hydride complexes  $HNiL_3CN$ , which have been characterized in solution by  $^1H$  and  $^{31}P$  NMR and ir.  $^1H$  NMR line shape analysis of  $HNi(PEt_3)_3CN$  solutions indicates that  $PEt_3$  exchanges by a dissociative process with  $\Delta G_{300}^\ddagger = 12.0$  kcal/mol. The four-coordinate  $HNiL_2CN$  intermediates can be observed in solution if the ligands L have sufficient steric bulk.

Earlier papers reported that addition of strong acids, such as  $H_2SO_4$ , to  $NiL_4$  complexes (L = phosphorus ligand) causes protonation at the nickel to give cationic five-coordinate hydride complexes  $HNiL_4^+$ .<sup>1,2</sup> Crystalline salts of  $HNi[Ph_2PCH_2CH_2PPh_2]_2^+$  and  $HNiL_4^+$  (L = cyclic or bicyclic phosphite) have been isolated.<sup>3</sup> We now wish to re-

port that addition of the weak acid HCN to  $NiL_4$  (or  $NiL_3$ ) complexes gives a new class of five-coordinate nickel hydride complexes of the type  $HNiL_3CN$ .

Addition of HCN to solutions of  $NiL_4$  (or  $NiL_3$ ) complexes usually causes the solutions to change color rapidly to yellow or orange. Proton NMR spectra at  $-25^\circ$  in non-

**Table I.** Proton NMR<sup>a</sup> and Ir<sup>b</sup> Data on HNiL<sub>3</sub>CN Complexes

Ligand	$-\delta_{\text{H}}$ (ppm)	$J_{\text{HP}}$ (Hz)	$\nu_{\text{CN}}$ (cm <sup>-1</sup> )	$\nu_{\text{CO}}$ (A <sub>1</sub> ) (cm <sup>-1</sup> ) <sup>c</sup>
PEt <sub>3</sub>	19.4	41.5	2098	2061.7
PMe <sub>3</sub>	18.9	46.0	2100	2064.1
PPhMe <sub>2</sub>	18.4	43.0	2102	2065.3
PPh <sub>2</sub> Me	16.4	39.0	2102	2067.0
PPh <sub>3</sub>	18.0	42.3	2108	2068.9
PPh <sub>2</sub> OMe	16.4	38.5	2111	2072.0
PPh(O- <i>i</i> -Pr) <sub>2</sub>	16.4	37.5		2072.2
PPh(OBu) <sub>2</sub>	15.9	34.5		2073.4
PPh(OEt) <sub>2</sub>	15.9	34.0	2113	2074.2
P(O- <i>o</i> -Pr) <sub>3</sub>	17.3	38.0	2116	2075.9
P(OEt) <sub>3</sub>	16.6	34.2	2120	2076.3
P(OCH <sub>2</sub> C-H <sub>2</sub> OCH <sub>3</sub> ) <sub>3</sub>	16.4	33.5		2079.3
P(OMe) <sub>3</sub>	16.6	32.8	2119	2079.5
P(OCH <sub>2</sub> C-H <sub>2</sub> Cl) <sub>3</sub>			2130	2084.0
P(O- <i>o</i> -tolyl) <sub>3</sub>	15.2	38.0	2130	2084.1

<sup>a</sup> In toluene-*d*<sub>8</sub> at  $-25^{\circ}$ . Shifts are given from internal TMS at  $\delta = 0.0$ ; negative values at high field. <sup>b</sup> In toluene at  $+25^{\circ}$ . <sup>c</sup> Values for Ni(CO)<sub>3</sub>L in CH<sub>2</sub>Cl<sub>2</sub> from Ref. 4.

**Table II.** <sup>31</sup>P NMR Data<sup>a</sup> on HNiL<sub>3</sub>CN Complexes

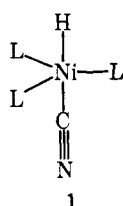
Ligand	$\delta$ (NiL <sub>4</sub> )	$\delta$ (HNiL <sub>3</sub> CN)	$J_{\text{PH}}$ (Hz)
PPh(OEt) <sub>2</sub> <sup>b</sup>	-163.4	-151.5	32
P(OEt) <sub>3</sub> <sup>b</sup>	-157	-138	30
P(O- <i>o</i> -tolyl) <sub>3</sub>	-128.6 <sup>c</sup>	-118.0	39
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> -PPh <sub>2</sub>	-16.4 <sup>d</sup>	-21.5 <sup>e</sup>	>20 <sup>f</sup>

<sup>a</sup> In toluene at  $-25^{\circ}$  unless noted otherwise. Negative shifts are in ppm downfield from external 85% H<sub>3</sub>PO<sub>4</sub>. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> NiL<sub>3</sub> complex. <sup>d</sup> For the [Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>]<sub>2</sub>Ni complex. <sup>e</sup> Coordinated ends of the diphosphines. The free end appeared at +8.2 ppm with one-third the intensity. <sup>f</sup> Apparent coupling with off-resonance CW proton decoupling.

polar solvents (Table I) show a new 1:3:3:1 quartet at high field, indicating formation of a nickel hydrogen bond with coupling to three equivalent phosphorus nuclei. The resonance tends to appear at highest field for the best electron donating ligands, judging donor and acceptor character of L by the  $\nu_{\text{CO}}$  (A<sub>1</sub>) frequencies in Ni(CO)<sub>3</sub>L complexes.<sup>4</sup> The values of  $J_{\text{PH}}$  show less systematic variation. In the HNiL<sub>4</sub><sup>+</sup> complexes<sup>2</sup> the chemical shift showed no systematic variation, while  $J_{\text{PH}}$  increased with the electron acceptor character of L.

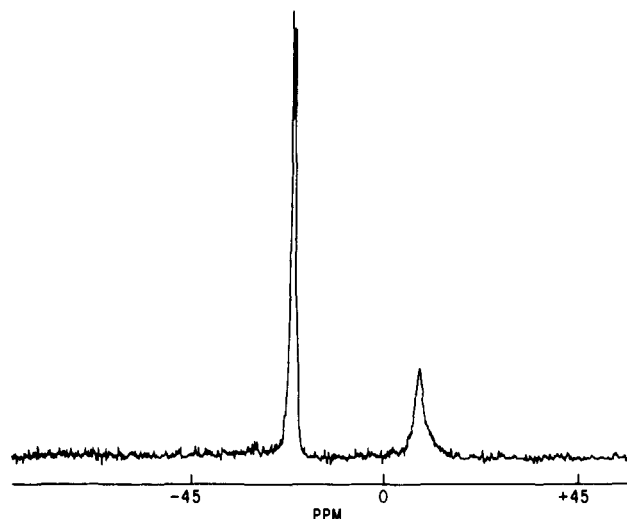
The <sup>31</sup>P NMR spectrum of Ni[PPh(OEt)<sub>2</sub>]<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> changed as HCN was added; the original NiL<sub>4</sub> resonance at -163.4 ppm (H<sub>3</sub>PO<sub>4</sub>) lost intensity and a new doublet ( $J_{\text{PH}} = 32 \pm 3$  Hz) grew in at -151.5, assigned to HNi[PPh(OEt)<sub>2</sub>]<sub>3</sub>CN. The doublet structure indicates that only one hydrogen is bound to nickel. <sup>31</sup>P data on a few complexes are given in Table II.

The NMR data are in accord with a trigonal bipyramidal structure **1**. This type of structure has been found in the iso-



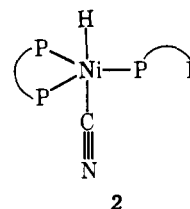
electronic HCo[PPh<sub>3</sub>]<sub>3</sub>(N<sub>2</sub>) by x-ray diffraction.<sup>5</sup>

Five-coordinate hydridocyanides can also be formed from



**Figure 1.** The 36.43-MHz <sup>31</sup>P{<sup>1</sup>H} CW decoupled spectrum of a solution of 2:1 HCN:Ni[Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>]<sub>2</sub> in benzene at  $20^{\circ}$ .

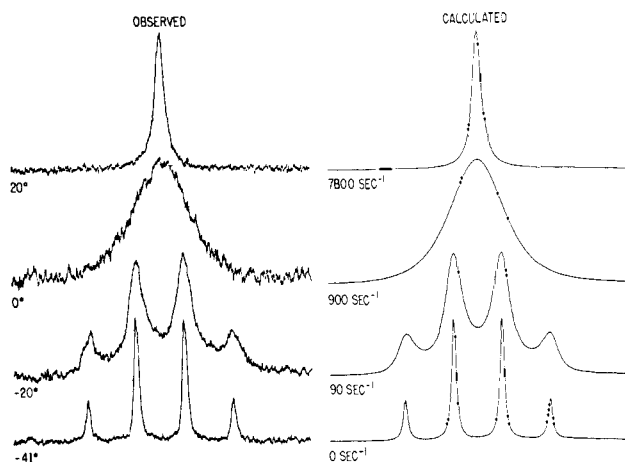
complexes containing chelating diphosphines. The <sup>31</sup>P{<sup>1</sup>H} spectrum of Ni[Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>]<sub>2</sub> (0.1 M in benzene,  $20^{\circ}$ ) showed a single resonance at -16.4 ppm. Addition of HCN in a ratio of 2:1 HCN:Ni eliminated the original resonance and gave two new ones in a 3:1 intensity ratio at -21.5 and +8.2 ppm. A spectrum with CW proton decoupling is shown in Figure 1. The decoupling frequency was adjusted to maximize decoupling of the non-hydridic protons. The low field resonance is clearly to be assigned to the coordinated <sup>31</sup>P nuclei in complex **2**; chemical shifts of bi-



dentate and bound monodentate phosphines are accidentally equal. The weaker high field resonance is due to the free end of one diphosphine. The chemical shift of uncoordinated diphosphine is +17.1 ppm. The 220-MHz <sup>1</sup>H spectrum of a similar solution at  $-31^{\circ}$  showed a quartet hydride resonance at -19.4 ppm with  $J = 36$  Hz, confirming the five-coordinate structure of the hydridocyanide.

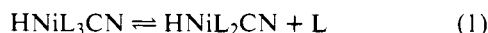
Corain and co-workers<sup>6</sup> reported that HCN reacts rapidly with Ni[Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>]<sub>2</sub>. Though no H<sub>2</sub> was evolved, they were unable to find a hydride resonance in the proton NMR spectrum and concluded that the product was a binuclear Ni(I) complex: Ni<sub>2</sub>(CN)<sub>2</sub>dph<sub>3</sub> (dph = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>). Our work shows that the compound is the Ni(II) hydridocyanide complex **2**. The reported olefin isomerization<sup>7</sup> in the presence of the complex is then readily understandable in terms of the metal hydride addition-elimination mechanism established for HNi[P(OEt)<sub>3</sub>]<sub>4</sub><sup>+</sup>.<sup>8</sup>

The difficulty encountered by Rigo, Corain, and Turco<sup>6</sup> in identifying the <sup>1</sup>H hydride resonance is probably attributable to the rapid intermolecular phosphine exchange shown by many of the HNiL<sub>3</sub>CN complexes. The left side of Figure 2 shows temperature dependent 220-MHz spectra of HNi[PEt<sub>3</sub>]<sub>3</sub>CN, prepared by the 1:1 addition of HCN to a solution of Ni[PEt<sub>3</sub>]<sub>4</sub>. In the low temperature limit the spectrum consists of a binomial quartet ( $J_{\text{PH}} = 41.5$  Hz at  $-30^{\circ}$ ). As the temperature is raised the H-P coupling constant decreases slightly and the spectrum begins to broaden. At still higher temperatures the spectrum collapses to a



**Figure 2.** The 220-MHz  $^1\text{H}$  hydride region spectra of  $\text{HNi}(\text{PEt}_3)_3\text{CN}$  in toluene- $d_8$  at various temperatures.

sharp single line as a result of a fast intermolecular exchange process which removes H-P coupling. The  $^1\text{H}$  NMR line-shapes are observed to be invariant to added ligand. This indicates the dissociative exchange process shown in eq 1.



The calculated line shapes shown on the right in Figure 2 assume negligible dissociation of  $\text{HNi}[\text{PEt}_3]_3\text{CN}$  over the  $-41^\circ$  to  $+20^\circ$  temperature range. The kinetic data obtained from Figure 2 and from spectra at other temperatures not shown can be fitted by the Arrhenius expression

$$k_1(T) = 10^{15.5} e^{15700/RT}$$

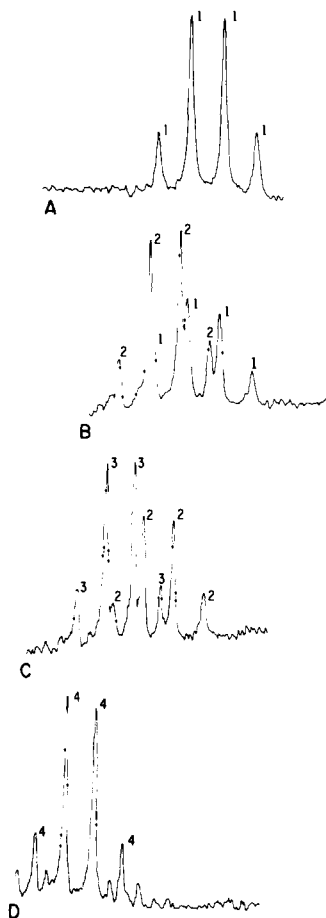
The corresponding Eyring parameters are  $\Delta G_{300}^\ddagger = 12.0$  kcal/mol,  $\Delta H_{300}^\ddagger = 15.1$  kcal/mol, and  $\Delta S_{300}^\ddagger = 10.3$  eu. The small positive entropy of activation is consistent with a dissociative process. Dissociative exchange in  $\text{NiL}_3(\text{CN})_2$  complexes has been established in NMR studies by Grimes and Pearson,<sup>9</sup> who obtained similar parameters, for example,  $\Delta H_{298}^\ddagger = 15.1$  kcal/mol and  $\Delta S_{298}^\ddagger = 8.7$  eu when  $\text{L} = \text{P}(\text{OEt})_3$ .

A variety of hydridocyanides was generated in solution by phosphorus ligand exchange. Figure 3 shows a series of  $^1\text{H}$  NMR spectra obtained by adding increasing increments of  $\text{P}(\text{OEt})_3$  to a solution of  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_3\text{CN}$ . All stages of substitution represented by eq 2 to 4 are clearly visible.



NMR data in Table I were obtained in this way for  $\text{L}' = \text{PPhMe}_2$ ,  $\text{PPh}(\text{O}-i\text{-Pr})_2$ ,  $\text{PPh}(\text{OBu})_2$ , and  $\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_3)_3$ , since we did not have the starting  $\text{NiL}_4$  complexes.

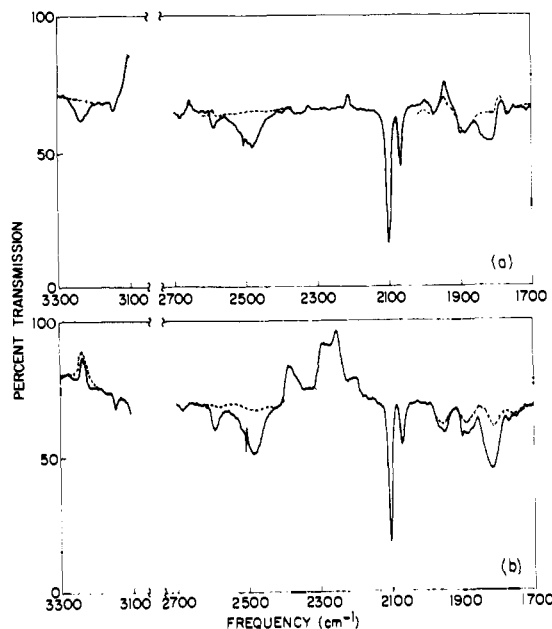
When excess  $\text{P}(i\text{-Pr})_3$  was added to a solution of  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_3\text{CN}$  at  $-25^\circ$  a triplet resonance was observed at  $-15.4$  ppm ( $J_{\text{HP}} = 60$  Hz) assigned to  $\text{HNi}[\text{P}(i\text{-Pr})_3]_2\text{CN}$ . The same quantity of  $\text{PEt}_3$  in a similar experiment gave only the five-coordinate  $\text{HNi}[\text{PEt}_3]_3\text{CN}$ . This indicates that equilibrium 1 can favor four-coordinate hydridocyanide complexes if the phosphorus ligands are sufficiently bulky. Green and co-workers<sup>10</sup> have reported the isolation of  $\text{HNi}[\text{P}(\text{C}_6\text{H}_{11})_3]_2\text{CN}$  (hydride triplet at  $-15.3$ ,  $J_{\text{HP}} = 64.5$  Hz), by metathesis from the hydridochloride.



**Figure 3.** The 90-MHz  $^1\text{H}$  hydride region spectra of a solution of 0.1 M  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_3\text{CN}$  with added  $\text{P}(\text{OEt})_3$  in toluene- $d_8$  at  $25^\circ$ .  $\text{P}(\text{OEt})_3$  is (A) 0 M, (B)  $\sim 0.075$  M, (C)  $\sim 0.15$  M, and (D)  $\sim 0.3$  M. The assignment is: (1)  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_3\text{CN}$ , (2)  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_2[\text{P}(\text{OEt})_3]\text{CN}$ , (3)  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3][\text{P}(\text{OEt})_3]_2\text{CN}$ , (4)  $\text{HNi}[\text{P}(\text{OEt})_3]_3\text{CN}$ .

Formation of hydridocyanide complexes in solution could be followed by infrared spectroscopy. Addition of HCN to a toluene solution of  $\text{Ni}(\text{PEt}_3)_4$  in a 1:1 mole ratio gave a clear yellow solution with a strong band at  $2098\text{ cm}^{-1}$  assigned to  $\nu_{\text{CN}}$  of  $\text{HNi}[\text{PEt}_3]_3\text{CN}$ ; the same spectrum was obtained with an equivalent amount of DCN. No bands assignable to  $\nu_{\text{NiH}}$  or  $\nu_{\text{NiD}}$  were observed. With excess HCN a gummy residue formed, the  $2098\text{-cm}^{-1}$  band decreased in intensity, and a new sharp band appeared at  $2108\text{ cm}^{-1}$  assigned to  $\text{HNi}(\text{PEt}_3)_2\text{CN}$ . Bands of free HCN ( $3225$  and  $2086\text{ cm}^{-1}$ ) were not seen until the ratio of HCN:Ni reached  $\sim 3:1$ . Apparently excess HCN removes  $\text{PEt}_3$  to form gummy residue and leave  $\text{HNi}(\text{PEt}_3)_2\text{CN}$ . Adding  $\text{PEt}_3$  to the solution caused the  $2098\text{-cm}^{-1}$  band to grow in intensity at the expense of the  $2108\text{-cm}^{-1}$  band. The absence of  $\text{HNi}[\text{PEt}_3]_2\text{CN}$  until excess HCN was added indicates that  $K_1$  is very small, as assumed in the NMR line shape analysis. A shift of  $\sim 10\text{ cm}^{-1}$  between five- and four-coordinate complexes has also been observed in *trans*- $\text{NiL}_3(\text{CN})_2$  and  $\text{NiL}_2(\text{CN})_2$  complexes.<sup>11</sup>

Phosphorus ligand exchange experiments of the type shown in Figure 3 were also followed in the infrared. Addition of excess  $\text{PEt}_3$  to a solution of  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3]_3\text{CN}$  gave complete conversion to  $\text{HNi}[\text{PEt}_3]_3\text{CN}$ . Excess  $\text{P}(i\text{-Pr})_3$  in a similar experiment gave mostly  $\text{HNi}[\text{P}(i\text{-Pr})_3]_2\text{CN}$  ( $\nu_{\text{CN}} = 2108\text{ cm}^{-1}$ ) with only a little  $\text{HNi}[\text{P}(i\text{-Pr})_3]_3\text{CN}$ . Excess  $\text{P}(t\text{-Bu})_3$  gave a band at  $2115\text{ cm}^{-1}$ , assigned to  $\text{HNi}[\text{P}(\text{O}-o\text{-tolyl})_3][\text{P}(t\text{-Bu})_3]\text{CN}$ , but no lower frequencies even in 0.5 M phosphine.

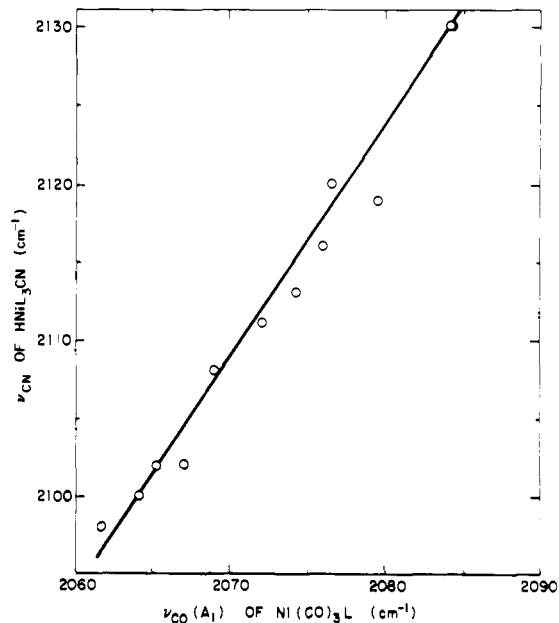


**Figure 4.** Infrared spectra of solutions of 2:1 DCN (70% isotopic purity) and  $\text{Ni}[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]_2$  in (a)  $\text{C}_6\text{H}_6$  and (b)  $\text{C}_6\text{D}_6$ . Dashed curves were obtained before DCN addition.

Reaction of HCN with  $\text{NiL}_3$  or  $\text{NiL}_4$  in most cases gave  $\nu_{\text{CN}}$  of  $\text{HNiL}_3\text{CN}$  but not  $\text{HNiL}_2\text{CN}$ . The reaction of HCN with free phosphine which occurred with  $\text{PET}_3$  took place to a lesser extent with  $\text{PMe}_3$ , but not with the other phosphorus ligands shown in Table I. There were, however, other bands in the infrared spectra. The case of  $\text{Ni}[\text{dpb}]_2$  is typical. Addition of HCN caused the  $\text{HNiL}_3\text{CN}$  band at  $2100\text{ cm}^{-1}$  to grow until the ratio of HCN:Ni exceeded 1:1. With more HCN, bands of free HCN appeared at  $3225$  and  $2086\text{ cm}^{-1}$  and another band appeared at  $2068\text{ cm}^{-1}$ . The excess HCN did not change the position or intensity of the  $2100\text{-cm}^{-1}$  band. DCN gave identical spectra over the range  $4000\text{--}1000\text{ cm}^{-1}$  until the ratio of DCN:Ni exceeded 1:1; then bands of free DCN appeared at  $2500$  and  $1910\text{ cm}^{-1}$  and other broad bands appeared at  $2400$  and  $1820\text{ cm}^{-1}$ . Figure 4 shows spectra with DCN (70% isotopic purity) and  $\text{Ni}[\text{dpb}]_2$  in a 2:1 ratio in  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$ . Frequencies of the additional bands with excess HCN or DCN and other complexes were similar and quite insensitive to the phosphorus ligand involved. We conclude that the extra bands at  $\sim 2070\text{ cm}^{-1}$  for HCN and  $\sim 2400$  and  $\sim 1820\text{ cm}^{-1}$  for DCN arise from a second molecule of HCN (or DCN) hydrogen bonded to the  $\text{HNiL}_3\text{CN}$ . The position of attachment is not likely to be at the NiCN or on the nickel itself because (a)  $\nu_{\text{CN}}$  of  $\text{HNiL}_3\text{CN}$  does not change with excess HCN; (b) the position of the additional bands does not depend on the electronic character of L; and (c) the additional bands are unaffected in most cases by addition of excess L. Corain<sup>6</sup> et al. also concluded that the  $2068\text{-cm}^{-1}$  band observed with  $\text{Ni}[\text{dpb}]_2$  and excess HCN was due to hydrogen-bonded HCN. With DCN they reported the  $1820\text{-cm}^{-1}$  band of  $\nu_{\text{CN}}$  in hydrogen-bonded DCN but did not report the  $\nu_{\text{CD}}$  band at  $2480\text{ cm}^{-1}$ .

The frequency of  $\nu_{\text{CN}}$  in the  $\text{HNiL}_3\text{CN}$  complexes increases regularly as the phosphorus ligands become more electron withdrawing, as shown in Figure 5. This behavior is consistent with a reduced ability of the nickel to back-bond into the cyanide  $\pi^*$  orbitals, and has been observed previously for  $\nu_{\text{CN}}$  in  $\text{NiL}_3(\text{CN})_2$  and  $\text{NiL}_2(\text{CN})_2$  complexes.<sup>11,12</sup>

Formation of  $\text{HNiL}_3\text{CN}$  complexes is rapid and quantitative in most cases; however, there are some exceptions.



**Figure 5.** Correlation of  $\nu_{\text{CN}}$  of  $\text{HNiL}_3\text{CN}$  complexes with  $\nu_{\text{CO}}(\text{A}_1)$  of  $\text{Ni}(\text{CO})_3\text{L}$  (ref 4).

Reaction of  $\text{Ni}[\text{P}(\text{OEt})_3]_4$  in toluene required several hours at  $75^\circ$  with excess HCN to convert most of the nickel to  $\text{HNi}[\text{P}(\text{OEt})_3]_3\text{CN}$ . This behavior can be contrasted with that of the more sterically crowded  $\text{Ni}[\text{P}(\text{O}-i\text{-Pr})_3]_4$ , which reacted rapidly and quantitatively. Earlier studies<sup>13</sup> showed much more extensive dissociation of the  $\text{P}(\text{O}-i\text{-Pr})_3$  in eq 5.

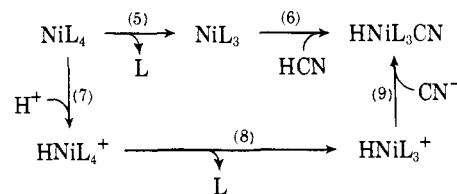


The dissociation of  $\text{P}(\text{OEt})_3$  has been shown to be very slow in a kinetic study by Meier, Basolo, and Pearson.<sup>14</sup>

The reaction of  $\text{Ni}[\text{P}(\text{OEt})_3]_4$  with HCN in methanol was much faster than in toluene, going to equilibrium in about an hour. Proton NMR spectra of methanol solutions show resonances due to both  $\text{HNiL}_4^+$ <sup>1,2</sup> and  $\text{HNiL}_3\text{CN}$ , the concentration of the neutral complex growing with time at the expense of the cation.

Among the pathways for formation of  $\text{HNiL}_3\text{CN}$  which might be considered, two are shown in Scheme I: a nonionic

#### Scheme I

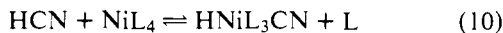


route, consisting of steps 5 and 6, with (5) rate determining; and an ionic route—steps 7–9. Protonation of  $\text{Ni}[\text{P}(\text{OEt})_3]_4$  is very fast,<sup>15a</sup> and dissociation of  $\text{P}(\text{OEt})_3$  is much more rapid from  $\text{HNi}[\text{P}(\text{OEt})_3]_4^+$ <sup>15b</sup> than from  $\text{Ni}[\text{P}(\text{OEt})_3]_4$ .<sup>14</sup>

$\text{Ni}[\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_4$  reacted slowly in toluene to give much less  $\text{HNiL}_3\text{CN}$  than with  $\text{Ni}[\text{P}(\text{OEt})_3]_4$ ;  $\text{HNi}[\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_3\text{CN}$  was identified by a weak band at  $2130\text{ cm}^{-1}$  in the infrared. It is clear that electronic factors play a role in the formation of  $\text{HNiL}_3\text{CN}$  complexes.  $\text{P}(\text{OEt})_3$  and  $\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$  are sterically similar and probably have similar values of  $K_5$ , since they compete about equally for coordination positions on  $\text{Ni}(0)$ .<sup>16</sup>  $K_6$  must, however, be much smaller with  $\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$ , in-

dicating that oxidative addition of HCN becomes less favorable as the electron density on nickel decreases.<sup>17</sup>

Steric factors also play an important role. Ni[P(O-*o*-tolyl)<sub>3</sub>]<sub>4</sub> reacts rapidly and quantitatively with HCN. The electronically similar but sterically less crowded Ni[P(O-*p*-tolyl)<sub>3</sub>]<sub>4</sub> reacted more slowly and to a much smaller extent; the initially colorless solutions turned yellow in the presence of HCN. A value of  $K_{10} \sim 4 \times 10^{-4}$  (benzene, 25°) for  $L = \text{P}(\text{O}-p\text{-tolyl})_3$  was estimated by assuming the same uv extinction coefficients as found for HNi[P(O-*o*-tolyl)<sub>3</sub>]<sub>3</sub>CN (shoulders at 300 mμ ( $\epsilon 6.2 \times 10^3$ ) and 345 ( $3.6 \times 10^3$ )). Note that  $K_{10} = K_5K_6$ .



We expect that equilibrium constants  $K_6$  are very similar for these two ligands; however,  $K_5$  for the smaller ligand is smaller by a factor of  $\sim 10^8$  at 25°.<sup>13</sup>

Four-coordinate platinum complexes HPt[PEt<sub>3</sub>]<sub>2</sub>CN and HPt[PPh<sub>3</sub>]<sub>2</sub>CN have been known for some time.<sup>19</sup> No hydridocyanide complexes of Pd have been reported, though they have been proposed as intermediates in olefin hydrocyanation by Pd[P(OPh)<sub>3</sub>]<sub>4</sub>.<sup>20</sup> Hydrocyanation of  $\alpha$ -olefins by Ni[P(O-*p*-tolyl)<sub>3</sub>]<sub>4</sub> in the presence of ZnCl<sub>2</sub> has been reported by Taylor and Swift.<sup>21</sup>

### Experimental Section

Solutions were prepared in inert atmospheres of nitrogen or argon in Vacuum Atmospheres, Inc., dryboxes. Solvents were deoxygenated by bubbling in the box. The NiL<sub>4</sub> or NiL<sub>3</sub> compounds were prepared as described earlier.<sup>16</sup> HCN was added by volume (39 μl/mmol) to serum-capped NMR tubes using a 50-μl Hamilton syringe which had been chilled to 0° by immersing a dry test tube containing the syringe in ice. The serum-capped vial containing the HCN supply was also maintained at 0°. *Caution. HCN is extremely toxic and should be used only in a well-ventilated hood. Heavy rubber gloves should be worn and any contact with skin or clothing carefully avoided.*

Infrared spectra were recorded using 0.1-mm NaCl cells (Barnes Engineering, Inc.) in a Perkin-Elmer 221 spectrometer. Spectra were calibrated with CO gas (2143 cm<sup>-1</sup>); reported frequencies are accurate to  $\pm 3$  cm<sup>-1</sup>.

Proton NMR spectra were recorded using 5-mm tubes on Varian HA-100 and 220-MHz instruments, measuring chemical shifts from internal tetramethylsilane (Me<sub>4</sub>Si); negative values are upfield. <sup>31</sup>P NMR spectra were recorded using 5-mm tubes in a Varian HA-100 at 40.5 MHz or 10-mm tubes in a Bruker HFX-90/Digilab FTS/NMR-3 system at 36.43 MHz. Chemical shifts are reported with respect to external 85% H<sub>3</sub>PO<sub>4</sub>, with upfield shifts considered positive.

The NMR line shape analysis for the hydride region <sup>1</sup>H spectrum of HNi[PEt<sub>3</sub>]<sub>3</sub>CN was carried out using a density matrix equation of motion very similar to that used in mutual exchange.<sup>22-24</sup> The negligible dissociation assumed for the five-coordinate complex was verified by infrared spectra of similar solutions. The NMR line shape analysis was carried out assuming that the concentration of the four-coordinate HNi(PEt<sub>3</sub>)<sub>2</sub>CN intermediate is vanishingly small. The density matrix equation of motion used to analyze the hydride region <sup>1</sup>H NMR spectra is<sup>25,26</sup>

$$\frac{d\rho}{dt} = 2\pi_i[\rho, \mathcal{H}] + \left(\frac{d\rho}{dt}\right)_{\text{relax}} + \sum_i (P_i\rho P_i - \rho)/2\tau_i \quad (11)$$

where  $\rho$  is the spin density matrix and  $\mathcal{H}$  is the high resolution NMR Hamiltonian.  $P_i$  represents the spin flip matrix for the  $i$ th <sup>31</sup>P spin and  $\tau_i$  is the preexchange lifetime for the  $i$ th <sup>31</sup>P spin. Because of the similarity of eq 11 to the equations used for simulating the NMR spectra for systems undergoing mutual exchange, existing programs for mutual exchange can readily be modified for this type of intermolecular exchange. The final expression for the NMR line shapes has the same form as the equation given by Sack<sup>27</sup> for exchange of a single line spectrum between several sites of different frequency.

$$I(\omega) = -\text{Re}[\mathbf{1} \cdot (\mathbf{A} - \mathbf{E}i\omega)^{-1} \cdot \mathbf{1}] \quad (12)$$

In the above equation,  $I(\omega)$  is the absorption intensity at angular frequency  $\omega$  under conditions of slow passage and weak radiofrequency fields.  $\mathbf{1}$  is the unit vector of dimension equal to the sum of the number of transitions in the observed part of the spectrum (hydride region <sup>1</sup>H NMR spectrum).  $\mathbf{A}$  is a complex non-Hermitian matrix given by  $\mathbf{A} = \mathbf{X} + \mathbf{B}$  where  $\mathbf{X}$  is the exchange matrix and  $\mathbf{B}$  is a diagonal matrix whose elements are given by  $B_{ji} = i\omega_i - 1/T_{2i}$ . The  $\omega_i$  are the transition frequencies in angular frequency units and the  $T_{2i}$  are the transverse relaxation times which determine the line widths in the absence of exchange;  $\mathbf{E}$  is the unit matrix.

The equation is solved using the numerical method developed by Gordon and McGinnis,<sup>28</sup> Binsch,<sup>29</sup> and Shirmer, Noggle, and Gaines<sup>30</sup> which avoids inverting the matrix  $(\mathbf{A} - \mathbf{E}i\omega)$  by diagonalizing  $(\mathbf{A} - \mathbf{E}i\omega)$  at some particular  $\omega$  and by using the fact that the transformation which diagonalizes  $(\mathbf{A} - \mathbf{E}i\omega)$  at some particular  $\omega$  diagonalizes  $(\mathbf{A} - \mathbf{E}i\omega)$  at all  $\omega$ 's. We have previously discussed the solution of equations of this type<sup>24</sup> and have demonstrated the advantages of numerical factoring for the case of mutual exchange. Unfortunately, little or no factoring is possible for the case of intermolecular exchange and the magnitude of the numerical problems increases rapidly with increasing number of spins.

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