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Catalytic Hydrocyanation of Olefins by Nickel(0) Phosphite Complexes—Effects of Lewis Acids[†]

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Mechanistic studies on the addition of HCN to olefins using Ni[P(O-*o*-tolyl)$_3$]$_3$ catalyst show that the reactions proceed under mild conditions via (η^1-organo)- or (η^3-organo)nickel cyanide intermediates formed by the insertion of monoenes or dienes into the nickel–hydrogen bond of HNiL$_3$CN. The RNiL$_m$CN intermediates can be identified spectroscopically by NMR and IR in some cases. In the case of very electronegative R groups (formed for example from reactions of HNiL$_3$CN with C$_2$F$_4$ or acrylonitrile), reductive elimination does not occur, and the catalyst is poisoned for olefin hydrocyanation. Improved rates, catalyst lifetimes, and product linearity can be obtained by the addition of Lewis acid (A) cocatalysts. Spectroscopic studies show that Lewis acids can coordinate strongly to the nitrogen lone-electron pair of hydrido cyanide intermediates to form HNiL$_3$CN·A complexes. An explanation of the effects of Lewis acids on hydrocyanation is proposed, which involves increasing the concentration of nickel in catalytic loop species [in the P(O-*p*-tolyl)$_3$ system], accelerating the rate of carbon–carbon coupling to form alkanenitriles from alkylnickel cyanide complexes and destabilizing relatively bulky branched alkyl intermediates relative to less crowded linear ones.

The addition of HCN to olefins by homogeneous nickel catalysts is one of the important success stories in the industrial application of homogeneous catalysis. In spite of the fact that adiponitrile has been produced on a large scale from butadiene for more than 10 years,[1] very little has been published in the scientific literature[2] concerning the mechanism of the reactions, particularly the intriguing roles of the Lewis acid cocatalysts. We have described some related chemistry, including the dissociation of NiL$_4$ complexes to NiL$_3$,[3] the oxidative addition of HCN to NiL$_n$ complexes to give HNiL$_m$CN[4] (L = a phosphorus ligand, n = 3 or 4, m = 2 or 3), and studies of reactions of olefins and nitriles to give (olefin)NiL$_2$[5] and (RCN)NiL$_3$ complexes.[5c,6] Studies on olefin hydrocyanation by homogeneous nickel catalysts have recently been reported from three other laboratories,[7,8a–c] in addition to ours.[8d] We now wish to report some details of our spectroscopic and kinetic studies on catalytic olefin hydrocyanation with L = P(O-*o*-tolyl)$_3$ or P(O-*p*-tolyl)$_3$. We chose P(O-*o*-tolyl)$_3$ for most of the studies because of both its good solubility and its combination of electronic and steric properties,[9] which give high concentrations of many of the catalytic intermediates. The P(O-*o*-tolyl)$_3$ system gives rapid hydrocyanation of many olefins at 25 °C or below even in the absence of added Lewis acid.[10] While some olefins such as ethylene or butadiene (for the first HCN addition) can be satisfactorily hydrocyanated without Lewis acids, the addition of Lewis acids with other olefins and with P(O-*p*-tolyl)$_3$ can give marked improvements, including higher rates, improved distributions of linear products, and longer catalyst life. Better known roles of Lewis acids in organometallic chemistry include their acceleration of alkyl migration (or CO insertion) in metal alkyl carbonyl complexes[11] and their use as cocatalysts in the Fischer–Tropsch reaction[12] and in nickel-catalyzed olefin dimerization by RNiL$_n$X and HNiL$_n$X (X = halogen) complexes.[13]

Hydrocyanation without Lewis Acids. Reaction of excess HCN with Ni[P(O-*o*-tolyl)$_3$]$_3$[14] causes an immediate color change from red to yellow, even at −78 °C, to produce HNiL$_3$CN.[15] Addition of excess ethylene to the chilled solution quantitatively converts the hydride to an ethylnickel complex, EtNiL$_2$CN. The presence of two phosphite ligands is based on the 2:1 relative intensities of the ^{31}P{^{1}H} resonances of equimolar NiL$_4$ and EtNiL$_2$CN[16] observed at −50 °C and the fact that the same intermediate can be generated by the addition of HCN to pure (C$_2$H$_4$)NiL$_2$. The ethyl protons in the ^{1}H NMR spectra appear as a single broad resonance[17] at −50 °C but as a resolved A$_2$B$_3$X$_2$ multiplet at 0 °C.[18] Resonances of EtNiL$_2$CN persist

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[†] Contribution No. 3208.

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(15) Readily identified by its NMR spectra (hydride ^{1}H quartet at δ −15.27 (J_{PH} = 37.5 Hz) and ^{31}P{^{1}H} singlet at 118.6 ppm in toluene-d_8 at −20 °C) and infrared CN stretching vibration at 2126 cm^{-1} in CH$_2$Cl$_2$. See ref 4.

(16) ^{31}P resonances at 129.7 and 118.3 ppm appear after mixing NiL$_3$ with excess HCN and C$_2$H$_4$. The resonances broaden on raising the temperature due to rapid exchange of free and coordinated L. The relative integrated areas of ethyl and total ligand methyl in the ^{1}H spectrum are as expected. ν_{CN} in the IR is 2152 cm^{-1} in CH$_2$Cl$_2$.

(17) δ 0.65, fwhm = 15 Hz, in toluene-d_8. The ^{13}C{^{1}H} resonances do, however, appear separately at 14.1 (CH$_3$) and 11.6 ppm. The number of protons on each was established by APT experiments. For the technique see: Patt, S. L.; Shoolery, J. *J. Magn. Reson.* **1982**, *46*, 535.

(18) CH$_3$ triplet at δ 0.61 (J_{HH} = 6.6 Hz) and CH$_2$Ni multiplet at δ 0.73; integrated intensities 3:2.

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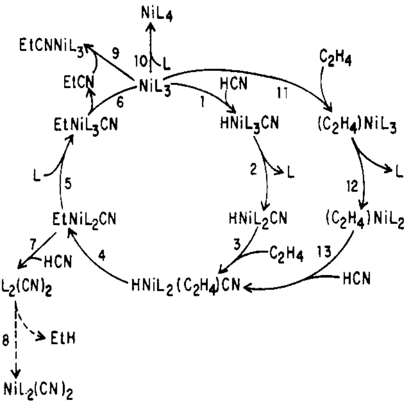
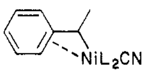


Figure 1. Mechanism of ethylene hydrocyanation by Ni[P(O-*o*-tolyl)$_3$]$_3$, showing formation of EtCNNiL$_3$ and NiL$_4$ and catalyst destruction by HCN.

while propionitrile[19] gradually appears and HCN and ethylene are consumed in a reaction that becomes rapid above 0 °C. When DCN is substituted for HCN, propionitrile is formed in which deuterium is scrambled between α- and β-positions. This indicates that nickel hydride addition to ethylene is reversible and occurs rapidly with respect to irreversible coupling of Et and CN groups to give propionitrile. Warming to 25 °C causes rapid disappearance of the EtNiL$_2$CN intermediate, along with the appearance of small amounts of ethane.[20] This is accompanied by irreversible oxidation of the nickel to nickel(II) dicyanide complexes that precipitate from solution and give a new broad IR band at about 2170 cm^{-1}. Product propionitrile (in CH$_2$Cl$_2$) appears at 2252 cm^{-1} with a shoulder at about 2240 cm^{-1} due to (C$_2$H$_5$CN)NiL$_3$.[6] These observations serve to define the inner catalytic cycle shown in steps 1–6 in Figure 1, which are drawn as shown to be consistent with the 16- and 18-electron rule.[21] We cannot exclude the additional pathway indicated in steps 11–13.[22] We showed earlier that treatment of NiL$_3$ with C$_2$H$_4$ gives (C$_2$H$_4$)NiL$_2$.[5b,23] Addition of excess HCN to pure (C$_2$H$_4$)NiL$_2$ at low temperature gives an immediate and quantitative reaction to give EtNiL$_2$CN, which on warming gives EtCN and HNiL$_3$CN; the additional ligand comes from loss of L from NiL$_2$(CN)$_2$ as Ni(CN)$_2$ precipitates. Reaction 10 in Figure 1 is indicated by earlier work.[3] The fact that EtNiL$_3$CN is less stable than EtNiL$_2$CN while HNiL$_3$CN is more stable than HNiL$_2$CN is attributed to greater steric crowding in the ethyl complexes. An Et group has a cone angle of 102° while H is only 75°.[24]

Addition of propylene to a solution of HNiL$_3$CN gives only partial conversion of the hydride to alkyl intermediates, indicating an unfavorable equilibrium for olefin insertion. Catalytic hydrocyanation of propylene still occurs but at a rate slower than ethylene—by a factor of about 5 in one experiment at 0 °C.[25] NMR and GC analyses of products formed at 0 °C show 72% *n*-butyronitrile and 28% isobutyronitrile, undoubtedly formed via the isomeric intermediates CH$_3$(CH$_2$)$_2$NiL$_2$CN and (CH$_3$)$_2$CHNiL$_2$CN. The higher concentration of the linear product is attributed to more unfavorable steric crowding in the branched alkyl intermediate; *tert*-butylethylene gives exclusively the linear product (CH$_3$)$_3$CCH$_2$CH$_2$CN. Backvall and Andell[7] (using Ni[P(OPh)$_3$]$_4$ and ZnCl$_2$) have shown that addition of DCN to (*E*)-1-deuterio-*tert*-butylethylene occurs stereospecifically cis.

In contrast to *tert*-butylethylene and propylene, styrene gives mostly branched product: 9% 3-phenylpropionitrile and 91% 2-phenylpropionitrile. This change in regioselectivity is attributed to stabilization of the branched alkylnickel cyanide intermediate by interaction of the nickel with the aromatic ring, as shown in **1**, or as the extreme π-allyl representation, in **2**.[26] We have not been able to



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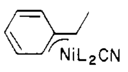

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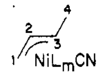
confirm the aromatic interaction by ^{1}H NMR, because of the complexity of the aromatic region.[27] The idea is however supported by the deep red color of the solutions during styrene hydrocyanation, similar to solutions of **3**[28] which we have unambiguously identified by NMR in the reaction of butadiene with HNiL$_3$CN.

The reaction of butadiene to give **3** is essentially irreversible at 25 °C. At higher temperatures carbon–carbon



3

coupling occurs to form 3-pentenenitrile (coupling of CN with C$_1$) and 2-methyl-3-butenenitrile (coupling with C$_3$) in a 2:1 ratio. Hydrocyanation of these initial products is inhibited until all the butadiene is consumed because of the stability of the η^3 intermediate (**3**) relative to the η^1 intermediates formed from the monoenes. Addition of HCN to 3-pentenenitrile and 2-methyl-3-butenenitrile separately, in the absence of butadiene, gives primarily adiponitrile and methyl glutaronitrile, respectively, no doubt via intermediates **4** and **5**.[29] The adiponitrile arises from a combination of isomerization of 3- to 4-pentenenitrile[30] and preferential anti-Markovnikov addition of the second HCN.

Other conjugated and unconjugated dienes can also be hydrocyanated. Spectroscopic studies of reactions of

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(19) CH$_3$ triplet δ 0.34 (J_{HH} = 7.5 Hz) and CH$_2$CN quartet δ 1.04. In the ^{13}C{^{1}H} spectrum, the resonances are accidentally superimposed at 10.5 ppm.

(20) Singlet at δ 0.82 in solution rechilled to −20 °C.

(21) Tolman, C. A. *Chem. Soc. Rev.* **1972**, 1, 337.

(22) This situation is similar to the situation in olefin hydrogenation by RhCl(PPh$_3$)$_3$, where both a "hydride route" and an "unsaturate route" were considered by: Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. We favor the hydride route (steps 1–3 in Figure 1), especially for weakly coordinating olefins like propylene or *tert*-butylethylene, where HNiL$_3$CN is the major Ni species under catalytic conditions, but have no experiments to determine what fraction of the reaction goes via steps 1–3 and what by steps 11–13.

(23) The synthesis of (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$ is described in: Seidel, W. C.; Tolman, C. A. *Inorg. Chem.* **1970**, *9*, 2354. The X-ray crystal structure in: Guggenberger, L. J. *Ibid.* **1973**, *12*, 499.

(24) Reference 9, Appendix C.

(25) Propylene (0.3 M) was added to 0.175 M HNiL$_3$CN. The rate laws are, however, expected to be different: zero order in ethylene but first order in propylene with excess olefin, because of the different predominant form of the nickel under catalytic hydrocyanation conditions.

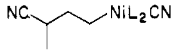
(26) This type of interaction has been established by: Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418, in the X-ray structure of (p-methylbenzyl)CpMo(CO)$_2$.

(27) The aliphatic region in the ^{1}H NMR (in toluene-d_8 at −25 °C) shows the CH$_3$ of **1** as a doublet at δ −0.84 (J_{HH} = 6 Hz). ^{31}P{^{1}H} NMR shows rapid exchange of free and coordinated L. The IR (CH$_2$Cl$_2$ at −25 °C) shows ν_{CN} at 2136 cm^{-1}.

(28) Both *syn*- and *anti*-η^3-CH$_3$C$_3$H$_4$NiL$_m$CN isomers appear in solution with methyl resonances at δ 1.47 and 1.06, respectively. A single ligand methyl resonance (δ 2.11) is consistent with rapid exchange of free and coordinated L. The IR (in CH$_2$Cl$_2$) shows a single ν_{CN} band at 2142 cm^{-1}.

(29) A broad IR band that appears at 2145 cm^{-1} when 4-pentenenitrile is added to a solution of HNiL$_3$CN is assigned to **5**, though some of the branched alkylnickel complex analogous to **7** is probably also present.

(30) One of the intriguing aspects of the system is the more rapid equilibration of 3-pentenenitrile with the less stable 4-isomer rather than with the thermodynamically more stable 2-isomer. This is fortunate, however, because the 2-pentenenitriles are not hydrocyanated but act as inhibitors by forming stable CH$_3$CH$_2$CH$_2$(NC)CHNiL$_m$CN complexes.



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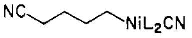

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$HNiL_3CN$ with 1,3- and 1,5-hexadienes at 25 °C in both cases showed formation within 3 min of (1-methyl-3-ethyl-η^3-allyl)nickel cyanide complexes that on standing gradually gave similar heptenenitrile products, identified by GC/MS as $C_6H_{11}CN$. Clearly, rapid olefin double bond isomerization can occur under hydrocyanation conditions. Rapid olefin isomerization by related $HNiL_4^+$ complexes [L = $P(OEt)_3$] was described earlier.[31] Butadiene also acts as a poison in that system, through formation of relatively stable η^3-$C_4H_7NiL_3^+$.

Not all olefins can be hydrocyanated. Tetrafluoroethylene and acrylonitrile form very stable alkylnickel cyanide complexes $HCF_2CF_2NiL_mCN$[32] and $NC(CH_3)CHNiL_mCN$[33] with high CN stretching frequencies at 2163 and 2164 cm^{-1}; the organic ν_{CN} in the (α-cyano)allylnickel cyanide appears at 2233 cm^{-1}.[34] 2PN behaves much like acrylonitrile, forming a relatively stable (α-cyano)allylnickel cyanide complex and poisoning the system for further olefin hydrocyanation. Thus successful conversion of 3PN to adiponitrile depends on isomerizing it to 4PN and adding the second HCN before isomerization to 2PN (the most stable pentenenitrile) can occur. The absence of C–C coupling in the above cases is attributed to an unfavorable equilibrium constant for the reductive elimination reaction (1). *K* is also very small for R = H,

$$\mathrm{RNiL_3CN} \overset{K}{\rightleftharpoons} \mathrm{RCN} + \mathrm{NiL_3} \qquad (1)$$

favoring oxidative addition of HCN to Ni, but very large for R = C_2H_5, favoring reductive elimination to form the nitrile product. Thus a delicate balance, clearly dependent on the properties of both the olefin and L, must be achieved in order to have efficient catalytic olefin hydrocyanation. The balance is illustrated by the fact that PhCN can be oxidatively added to $Ni(PEt_3)_3$ or $N_2Ni(PCy_3)_2$[35,36] and then reductively eliminated by the addition of phosphites like $P(OEt)_3$.[37,38a]

Hydrocyanation with Lewis Acids. Propylene hydrocyanation was followed in an NMR tube by warming a mixture of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$, HCN, propylene, and Lewis acid ($AlCl_3$, $ZnCl_2$, BPh_3, or none) from −50 °C and following the appearance of *n*-butyronitrile and *sec*-butyronitrile products. The half-lives of product formation depended strongly on the Lewis acid and increased in the series: $AlCl_3$ (10 min at −25 °C) < $ZnCl_2$ (<4 min at 25 °C) < none (60 min at 0 °C, 10 min at 25 °C) < BPh_3 (>60 min at 25 °C). The percentage of linear product was 70–72% for $AlCl_3$, $ZnCl_2$, or no Lewis acid but was 89% with BPh_3.

Table I. Lewis Acid Effects on Product Distribution with $P(O\text{-}o\text{-tolyl})_3$ [a]

	% linear nitrile product	
Lewis acid	styrene	4PN
BPh_3	33	98
B(*o*-tolyl)$_3$	9	74
BCy_3	11	72
none	9	77
$B(OPh)_3$	1	70

[a] Reactions were carried out with 0.05 mmol of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$, 0.05 mmol of Lewis acid, 0.2 mmol of olefin, and 0.2 mmol of HCN in 0.5 cm^3 of toluene for 21 h at 25 °C.

Because of the exceptionally high linearity of the BPh_3 result, we investigated a number of other boron-containing Lewis acids. Results with the substrates styrene and 4-pentenenitrile (4PN) are given in Table I. With no Lewis acid, styrene gave about 10% linear product and 4PN about 75%. Similar results were obtained with B(*o*-tolyl)$_3$, BCy_3, and $B(OPh)_3$. BPh_3 clearly gave superior distributions of linear products, though product formation was considerably slower.

Spectroscopic studies show that Lewis acids form adducts both with the organic nitriles in these solutions and with the cyanide groups on nickel—the latter being generally strongly preferred. The analogous structure of $CpFe(CO)_2CN\cdot BPh_3$ has been established by an X-ray single-crystal study.[38b] In the case of $HNi[P(O\text{-}o\text{-tolyl})_3]_3CN$, the addition of excess BPh_3 causes the immediate disappearance of the ν_{CN} band at 2128 cm^{-1} in the IR and the appearance of a new stronger band at 2184 cm^{-1} assigned to $HNiL_3CN\cdot BPh_3$. The proton NMR spectrum shows the hydride as a high field quartet, with a slightly different chemical shift and P–H coupling constant from the parent $HNiL_3CN$.[39] $HNiL_3CN\cdot B(o\text{-tolyl})_3$ has spectroscopic parameters similar to $HNiL_3CN\cdot BPh_3$; However, in the case of the more sterically hindered acid, the association equilibrium constant K_2 is much smaller, and free $HNiL_3CN$ can be observed even in the presence of excess B(*o*-tolyl)$_3$ (eq 2). While K_2 is too large to measure for

$$\mathrm{HNiL_3CN} + \mathrm{A} \overset{K_2}{\rightleftharpoons} \mathrm{HNiL_3CN\cdot A} \qquad (2)$$

L = $P(O\text{-}o\text{-tolyl})_3$ and A = BPh_3, it can be determined from spectrophotometric measurements[40] of equilibria 3 and 4, where L′ = $P(O\text{-}p\text{-tolyl})_3$. Subtracting (3) from (4) gives

$$\mathrm{HCN} + \mathrm{NiL'_4} \rightleftharpoons \mathrm{HNiL'_3CN} + \mathrm{L'} \quad K_3 = 4 \times 10^{-4} \qquad (3)$$

$$\mathrm{HCN} + \mathrm{NiL'_4} + \mathrm{BPh_3} \rightleftharpoons \mathrm{HNiL'_3CN\cdot BPh_3} + \mathrm{L'} \quad K_4 = 20\,\mathrm{M^{-1}} \qquad (4)$$

$K_2 = 5 \times 10^4$ M^{-1}. Greatly increasing the concentration of nickel in the catalytic cycle explains the accelerating effect of BPh_3 on overall rate of olefin hydrocyanation in the $P(O\text{-}p\text{-tolyl})_3$ system, where the rate is close to first order in added [BPh_3].[41]

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[31] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6785; **1972**, *94*, 2994.

[32] The broad ^{19}F resonance 140.4 ppm upfield of internal $CFCl_3$ in C_6D_6 can be compared with 132.3 ppm for free C_2F_4 and 127.9 ppm J_{PF} = 40 Hz) in $(C_2F_4)NiL_2$.

[33] An olive gel precipitated when HCN was added to a CH_2Cl_2 solution of $(C_2H_3CN)NiL_2$. After being washed with methanol and dried, the material had an analysis corresponding approximately to $NC(CH_3)CHNiL_{0.6}CN$: Ni, 19.6; P, 5.3; C, 57.0; H, 4.8; N, 8.0. Found: Ni, 17.5; P, 5.4; C, 55.6; H, 4.8; N, 7.9.

[34] This can be compared with 2210 and 2200 cm^{-1} reported for ν_{CN} in $NC(CH_3)CHM$ complexes formed in the reactions of acrylonitrile with $HFeCp(CO)_2$ and $HCo(CN)_5^-$, respectively, in Ariyaratne, J. K. P.; Green, M. L. H. *J. Chem. Soc.* **1963**, 2976. Halpern, J.; Wong, L.-Y. *J. Am. Chem. Soc.* **1968**, *90*, 6665.

[35] Favero, G.; Morvillo, A.; Turco, A. *Gazz. Chim. Ital.* **1979**, *109*, 27.

[36] Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.

[37] Favero, G.; Gaddi, M.; Morvillo, A.; Turco, A. *J. Organomet. Chem.* **1978**, *149*, 395.

[38] (a) A similar reductive eliminating of PhCN from $PhNi(PPh_3)_2CN$ by addition of $P(OPh)_3$ was found earlier in these laboratories by R. Cramer (unpublished results). (b) Laing, M.; Kruger, G.; duPreez, A. L. *J. Organomet. Chem.* **1974**, *82*, C40.

[39] In toluene-d_8 at −25 °C: δ −15.24 (J(P–H) = 33.5 Hz) for $HNi[P(O\text{-}o\text{-tolyl})_3]_3CN\cdot BPh_3$; δ −15.27 (J(P–H) = 37.5 Hz) for $HNi[P(O\text{-}o\text{-tolyl})_3]_3CN$.

[40] In benzene at 25 °C. Extinction coefficients were assumed to be the same for complexes with $P(O\text{-}p\text{-tolyl})_3$ as with $P(O\text{-}o\text{-tolyl})_3$, where the reactions go to completion.

[41] For a large number of catalytic cycles the concentration of HCN in solution should be kept low. (While hydrocyanation is first order in [HCN], irreversible catalyst oxidation is second order.) Under these conditions, with most of the nickel present as $Ni[P(O\text{-}p\text{-tolyl})]_4$, hydrocyanation is also first order in $[BPh_3]_3$. The turnover number can also be increased by adding excess $P(O\text{-}p\text{-tolyl})_3$, though this does slow the hydrocyanation rate.

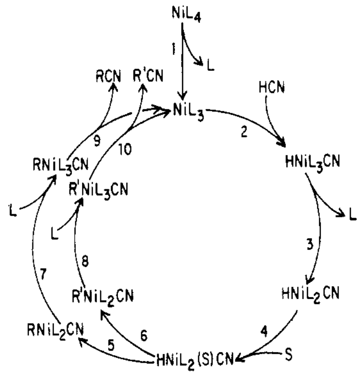

Figure 2. Simplified mechanism of hydrocyanation of a terminal olefin substrate (S) in the absence of a Lewis acid. R and R′ refer to linear and branched alkyl groups, respectively; L is a phosphorus donor ligand. Olefin isomerization and catalyst deactivation are not shown.

A kinetic study of reaction 4 shows that the rate of formation of $HNi[P(O\text{-}p\text{-tolyl})_3]_3CN{\cdot}BPh_3$, under conditions where the final equilibrium lies far on the right, is first order in [NiL'_4], and zero order in [HCN] and [BPh_3]. The half-life of 1 h at 25 °C is the same as that measured[5d] in the reaction of maleic anhydride with $Ni[P(O\text{-}p\text{-tolyl})_3]_4$, where the rate-limiting step is ligand dissociation to give the 16-electron NiL'_3 complex. Thus reaction 4 proceeds in elementary steps shown in (5) consistent with the 16- and 18-electron rule.

$$NiL'_4 \xrightarrow[L]{} NiL'_3 \xrightarrow[HCN]{Fast} HNiL'_3CN \xrightarrow[BPh_3]{Fast} HNiL'_3CN{\cdot}BPh_3 \qquad (5)$$

We mentioned earlier that BPh_3 *slows* the rate of propylene hydrocyanation by $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ but markedly improves product butyronitrile linearity. During the reaction, the only loop species observable is $HNiL_3CN{\cdot}BPh_3$,[42] the alkyl intermeidates being too unstable to detect. Hydrocyanations of ethylene and styrene are also greatly slowed by BPh_3 in the $P(O\text{-}o\text{-tolyl})_3$ system; alkyl intermediates, which were easily observable in the absence of Lewis acid, are no longer seen, and $HNiL_3CN{\cdot}BPh_3$ is the only observable loop species. Thus K_1 is significantly smaller than the corresponding equilibrium constant in the absence of Lewis acid (eq 6).

$$\text{Olefin} + HNiL_3CN{\cdot}BPh_3 \overset{K_6}{\rightleftharpoons} RNiL_2CN{\cdot}BPh_3 + L \qquad (6)$$

An explanation of this effect and of the improved product distribution in the hydrocyanation of terminal olefins is that coordination of the moderately bulky Lewis acid BPh_3, through what Brown has called a buttressing effect or B-strain,[43] increases the steric crowding around nickel and increases the strain energy associated with larger R groups.[44] Cone angles of H, Et (or Pr), and *i*-Pr are 75°, 102°, and 114°, respectively, based on CPK models.[22] Very bulky Lewis acids like $B(o\text{-tolyl})_3$ or BCy_3 (Table I) are unable to coordinate strongly, and an improved product distribution is not observed because the reaction goes through the more rapid Lewis free hydrocyanation loops indicated in Figure 2. Figure 3 shows a three-dimensional representation of a terminal olefin hydrocyanation system. The loops in the upper A_0 plane are just those shown in Figure 2. The A_1 plane is the same except for replacing each CN by CN·A.[45] With excess BPh_3, essentially all hydrocyanation is forced to occur in the A_1 plane. Figures 2 and 3 are oversimplified in not showing pathways for catalyst destruction, olefin coordination prior to HCN, olefin isomerization, or formation of more than two products. In addition, coordination of nitrile ligands can be competitive with coordination of phosphorus ligands and could thus possibly influence selectivities via both steric and electronic effects.

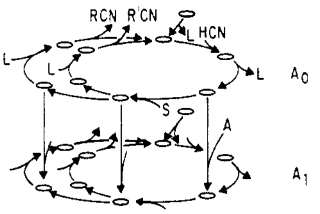

Figure 3. A simplified three-dimensional mechanism of terminal olefin hydrocyanation in the presence of a Lewis acid (A). For simplicity only a few of the paths connecting the A_0 plane (no Lewis acid) with the A_1 plane (one Lewis acid on each CN) are shown.

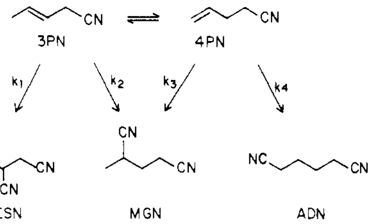

Figure 4. Scheme showing the isomerization of 3PN to 4PN and the formation of dinitriles with relative rate constants k_i.

Table II. Lewis Acid Effects on Steady-State Concentrations and Relative Hydrocyanation Rates of Pentenenitriles[a]

Lewis acid	([4PN]/ [3PN])$_{SS}$[b]	k_1	k_2	k_3	k_4	([C3PN]/ [T3PN])$_{SS}$[b]
$AlCl_3$	0.5/99.5	1.0	0.9	365	678	0.08
$ZnCl_2$	3.0/97.0	1.0	1.5	220	1470	0.17
BPh_3	7.0/93.0	1.0	1.1	39	1260	0.19

[a] At 68 °C in neat pentenenitrile solvent with $Ni[P(O\text{-}p\text{-tolyl})_3]_4$, $P[O\text{-}p\text{-tolyl}]_3$, Lewis acid, and PN in the mole ratio of 1:10:2:240. HCN was fed continuously at a rate of 30 mol of HCN/mol of Ni/h. [b] Pentenenitrile ratios at steady state as determined by GC.

The puzzling observation that BPh_3 slows hydrocyanation with L = $P(O\text{-}o\text{-tolyl})_3$ but promotes it with $P(O\text{-}p\text{-tolyl})_3$ is a result of the 10^8 times larger value of K for ligand dissociation from NiL_4 in the former. With L = $P(O\text{-}o\text{-tolyl})_3$ and excess HCN, essentially all of the Ni is present as loop species in Figure 3, in the A_0 plane in the absence of BPh_3 (primarily as $EtNiL_nCN$ with excess S = C_2H_4) and in the A_1 plane (primarily as the slower reacting $HNiL_3CN{\cdot}BPh_3$) with excess BPh_3. With $P(O\text{-}p\text{-tolyl})_3$, especially with excess L′ and low [HCN], most of the Ni is present off the loops as NiL'_4, so that the concentration of $HNiL'_3CN{\cdot}BPh_3$ (and the rate of hydrocyanation) is proportional to [BPh_3].

Figure 4 shows the net result of hydrocyanation of (3PN) 3-pentenenitrile[46] and 4-pentenenitrile to give ethyl-

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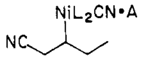
(42) With excess BPh_3, cyanide solids did not precipitate, presumably because of BPh_3 coordination to the dead catalyst.

(43) Brown, H. D. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; pp 71 and 102.

(44) The increased linearity of hydrocyanation on increasing the steric bulk of the hydridocyanide (by Lewis acid) is conceptually similar to the increased linearity observed in olefin hydroboration on going from diborane to disiamylborane, for example. See ref 43, p 282.

(45) This way of representing complex mechanisms in three dimensional figures has also been used in: Tolman, C. A.; Faller, J. "Mechanistic Studies of Catalytic Reactions Using Spectroscopic and Kinetic Techniques" Pignolet, L. H., Ed.; Plenum Press: New York, in press.

succinonitrile (ESN), methylglutaronitrile (MGN), and adiponitrile (ADN). Lewis acids affect both the rate of isomerization relative to hydrocyanation and the relative rates of formation of dinitrile products, as shown in Table II. The relative observed rate constants k_i (whose absolute values depend on several factors including temperature, Lewis acid type and concentration, concentration of added L, and HCN feed rate) were determined from the product distributions measured with a steady-state distribution of 4PN and 3PN's, and starting with pure 4PN and extrapolating back to $t = 0$.[47] The steady-state ratio ([3PN]/[4PN])$_{SS}$ is farthest away from equilibrium (7.5/92.5)[48] with $AlCl_3$ and closest with BPh_3. The same is true for ([C3PN]/[T$_3$PN])$_{SS}$, where the equilibrium value is 0.24. These results show that the rate of hydrocyanation relative to isomerization is highest with $AlCl_3$ and decreases in the order $AlCl_3 > ZnCl_2 > BPh_3$ and also that C3PN is hydrocyanated in preference to T3PN. The relative rate constants in Table II show that there is little selectivity (k_2/k_1) in forming MGN or ESN from 3PN (suggesting similar steric crowding in the intermediates **7** and **6**) but substantial selectivity (k_4/k_3) in forming ADN or MGN from 4PN via **8** and **7**.



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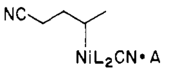

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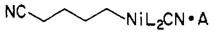

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Relative rates of HCN addition to 4PN and 3PN [$(k_3 + k_4)/(k_1 + k_2)$] are similar and in the range of 510–620 for all three Lewis acids. This selectivity can be compared with 212 for the relative binding constants of the olefins 4PN and T3PN to Ni(0).[49] The reason for the much poorer product distribution with $AlCl_3$ (47.7% ADN) compared to $ZnCl_2$ (81.8%) and BPh_3 (95.0%) is partly due to the lower value of $k_4/(k_3 + k_4)$ and partly to the very low concentration of 4PN relative to 3PN at steady state.

While steric effects are very important in determining the product distribution, electronic effects are also important, particularly in accelerating the rates of the carbon–carbon coupling reactions. If L is a phosphite, these reductive elimination reactions are not reversible in most cases[50] but are reversible if an allylic cyanide is produced.[51] Experiments with allyl cyanide and $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ show that olefin and nitrile complexes of Ni(0) form rapidly at room temperature and that oxidative addition is very slow in the absence of Lewis acids.[5a] In the presence of Lewis acids, however, especially $AlCl_3$ and $ZnCl_2$, reaction 7 is instantaneous on mixing. This acceleration of C–C coupling and cleavage is quite analogous to the effects of Lewis acids with transition-metal alkyl carbonyls.[9–11]

$$CH_2{=}CHCH_2CN{\cdot}A + NiL_3 \rightleftharpoons \eta^3\text{-}C_3H_5NiL_2CN{\cdot}A + L \qquad (7)$$

The role of Lewis acids in increasing catalyst lifetime and turnover number is less clear than its other roles. In the case of 3PN hydrocyanation, isomerization of 3PN to conjugated 2PN may be slowed relative to isomerization to 4PN; this helps because 2PN acts as a catalyst poison.[30] Decreasing the electron density on nickel by coordination of Lewis acid to the cyanide nitrogen, increased steric crowding about nickel, and reduced steady-state concentrations of nickel alkyl intermediates no doubt help also in reducing the attack of HCN with concomitant formation of alkane and nickel dicyanide.

Experimental Section

Compounds and Solvents. Because of the air sensitivity of the nickel compounds used in these studies, all preparations of compounds and their solutions were carried out under nitrogen in Vacuum Atmospheres dryboxes. Procedures previously reported were used for preparation of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$,[14] $Ni[P(O\text{-}p\text{-tolyl})_3]_4$,[52] $(C_2H_4)Ni[P(O\text{-}o\text{-tolyl})_3]_2$,[23] and $Ni[P(OEt)_3]_4$.[52] The Lewis acids $ZnCl_2$ and $AlCl_3$ were obtained from Aldrich Chemical Co. and were handled under nitrogen to avoid contamination with moisture. BPh_3 and BCy_3 were obtained from Orgmet Chemical Co. $B(OPh)_3$ and $B(O\text{-}o\text{-tolyl})_3$ were prepared from boric acid and phenol or *o*-cresol by azeotropic removal of water in refluxing toluene. HCN can be obtained from Fumico, Inc. *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 should be carefully avoided.* DCN was prepared by slow addition of a solution of NaCN in D_2O to a stirred solution of D_3PO_4 in D_2O, maintained at 0 °C. The DCN vapor formed was passed through a tube containing P_2O_5 to remove D_2O and was condensed and stored at 0 °C. All solvents were dried over molecular sieves, degassed with nitrogen, and stored under nitrogen. The pentenenitrile solvents were prepared by $Ni[P(O\text{-}p\text{-tolyl})_3]_4$-catalyzed hydrocyanation of butadiene.[53] Individual pentenenitrile isomers can also be prepared by literature procedures and be purified by distillation. References to preparation procedures and isomer boiling points are as follows: T3PN (144 °C),[54] C3PN (147 °C),[54] 4PN (144 °C),[55] T2PN (143 °C),[56] C2PN (128 °C),[56] and 2Me3BN (126 °C).[57]

Instrumentation. Proton NMR spectra were determined on a Varian HA-100 spectrometer at 100 MHz or on a Nicolet NT 360 WB spectrometer. Fluorine-19 spectra were measured on a Varian A56-60 at 56.4 MHz. Phosphorus-31 spectra were recorded on a Bruker HFX-90 at 36.43 MHz. Infrared spectra were recorded by using a Perkin-Elmer 221 spectrometer. Mass spectra were determined using a Du Pont 21-490 mass spectrometer, coupled to a Varian 1400 gas chromatograph for compound separations. GC chromatographic separations of nitrile products used a 10 ft × $^1/_8$ in. column containing 10% UV 210 Chromosorb WHP, 80/100 mesh.

Typical Experimental Procedures. Addition of HCN to 3PN Using $ZnCl_2$ and $Ni[P(O\text{-}p\text{-tolyl})_3]_4$. A glass 50-mL, three-neck, round-bottom flask was arranged in a hood with a thermometer, Teflon-coated stirring bar, electric heating mantle, nitrogen inlet tube, and an outlet tube connected to a dry ice cold trap to condense unreacted HCN vapor. To the nitrogen inlet tube was connected a 10-mL bubbler which was charged with about 5 mL of liquid HCN. The bubbler was maintained in a wet-ice bath. The bubbler contained stopcocks that permitted nitrogen either to pass through the HCN and into the reactor or to bypass the bubbler. A needle valve and flow meter were placed in the nitrogen line to permit flow rates to be used that gave desired HCN feed rates. The reactor was first charged under nitrogen with 24.3 mL (249 mmol) of 3PN,[58] 3.2 mL (8.3 mmol)

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(46) 3PN represents the sum of the cis and trans isomers C3PN and T3PN, respectively.

(47) See the supplementary Material.

(48) These ratios were determined by GC analysis after 2 days of isomerizing each of the pure isomers to equilibrium at 60 °C using 0.05 mmol of $Ni[P(OEt)_3]_4$ and 0.05 mmol of H_2SO_4 in 5 mmol of neat pentenitrile. 2PN's also slowly formed to give an mixture of approximately 0.10:0.24:1.0:1.0:1.0 4PN–C3PN–T3PN–C2PN–T2PN.

(49) For the reaction Ol + $NiL_3 \rightleftharpoons$ (Ol)NiL_2 + L in benzene at 25 °C for L = $P(O\text{-}o\text{-tolyl})_3$ as reported in ref 5c.

(50) Oxidative addition of alkyl or aryl cyanides to Ni(0) can be preferred if the metal is very electron rich as it is in $Ni(PCy_3)_2$ or $Ni(PEt_3)_3$, see: ref 35 and 36. Reductive elimination of PhCN from $PhNi(PCy_3)_2CN$ can be induced by adding $P(OEt)_3$ as described in ref 37.

(51) The first step of butadiene hydrocyanation for example produces 3-pentenenitrile and 2-methyl-3-butenenitrile. The reversibility of oxidative addition makes it possible to equilibrate these isomers.

(52) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(53) Drinkard, W. C.; Lindsey, R. V. U.S. Patent 3 496 215, 1970.

(54) Kobler, H.; Schuster, K.-H.; Simchen, G. *Justus Liebigs Ann. Chem.* **1978**, 1946.

(55) Brannock, K. C.; Burpitt, R. D. *J. Org. Chem.* **1965**, 30, 2564.

(56) MacPeek, D. L.; Starcher, P. S.; Phillips, B. *J. Am. Chem. Soc.* **1959**, *81*, 680.

(57) Kieczykowski, G. R.; Schlessinger, R. H.; Sulsky, R. B. *Tetrahedron Lett.* **1975**, *52*, 4650.

of P(O-*p*-tolyl)$_3$, 1.47 g (1.0 mmol) of Ni[P(O-*p*-tolyl)$_3$]$_4$, and 0.28 g (2.0 mmol) of ZnCl$_2$. Stirring was started, and the reaction temperature was adjusted to 68 °C. About 5 mL of HCN was placed in the bubbler and a nitrogen flow rate of 1.37 mL/h was started, which corresponded to 0.6 mmol of HCN/min. After 3 h, the HCN feed was stopped and the reaction mixture was cooled to room temperature. A GC analysis gave the following area percentages: ADN:MGN:ESN:T3PN:C3PN:4PN:T2PN:C2PN = 34.79:6.98:0.77:31.14:5.20:1.64:0.51:0.94. The conversion of PN's to DN's was approximately 52%, and the ratio of ADN/ADN + MGN + ESN was 0.815.

^{1}H NMR Measurements of the Addition of HCN to (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$. In a typical experiment, 0.6 g (0.54 mmol) of Ni[P(O-*p*-tolyl)$_3$]$_3$ and 0.4 mL of toluene-d_8 were mixed in a 5-mm rubber-stoppered NMR tube. After the nickel catalyst was dissolved, the tube contents were cooled to −77 °C using a dry ice–acetone bath. Next, 8 mL (0.36 mmol) of ethylene gas was added to the tube with a gas-tight syringe, followed by 25 μL (1.2 mmol) of liquid HCN added by means of a chilled (0 °C) microliter syringe. ^{1}H NMR spectra were then recorded as a function of time and temperature by using a Nicolet NT 360 WB spectrometer.

Acknowledgment. We are indebted to M. F. Wilson for running the experiment in which DCN was added to ethylene to show scrambling of deuterium between α- and β-positions and to F. G. Kitson for GC/MS of the reaction products.

Note Added in Proof. The intermediate EtNiL$_2$CN [L = P(O-*o*-tolyl)$_3$] was shown to have a cis square-planar stereochemistry by the observation of a doublet (J_{PC} = 35 Hz) for the *CH$_2$Ni at δ 11.6 in the ^{13}C{^{1}H} spectrum generated from HCN and mono ^{13}C-labeled (*C$_2$H$_4$)NiL$_2$ in toluene-d_8 at −50 °C. The doublet structure is attributed to coupling of the methylene carbon to the unique phosphorus trans to it; coupling to the cis-phosphorus is not observed. The methyl carbon at δ 14.1 shows no P–C coupling.

Identical ^{13}C resonances are observed on adding *C$_2$H$_4$ to HNiL$_3$CN at −50 °C. Monotoring the product *C$_2$H$_5$CN (at δ 10.2) at −50 °C shows that its rate of formation *is the same* whether one adds HCN to (C$_2$H$_4$)NiL$_2$ or C$_2$H$_4$ to HNiL$_3$CN. This suggests that carbon–carbon coupling during the hydrocyanation of monoenes occurs in *cis*-RNiL$_2$CN, rather than in RNiL$_3$CN as shown in Figures 1–3.

Registry No. Ni[P(O-*o*-tolyl)$_3$]$_3$, 28829-00-7; Ni[P(O-*p*-tolyl)$_3$]$_3$, 87482-65-3; HNi[P(O-*o*-tolyl)$_3$]$_3$CN, 59220-71-2; (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$, 31666-47-4; Ni[P(O-*o*-tolyl)$_3$]$_4$, 36841-11-9; EtNi[P(O-*o*-tolyl)$_3$]$_2$CN, 87482-66-4; HNi[P(O-*o*-tolyl)$_3$]$_3$CN·BPh$_3$, 87482-67-5; HNi[P(O-*o*-tolyl)$_3$]$_3$CN·B(*o*-tolyl)$_3$, 87482-68-6; PhNi(PPh$_3$)$_2$CN, 87482-69-7; AlCl$_3$, 7446-70-0; ZnCl$_2$, 7646-85-7; BPh$_3$, 960-71-4; B(*o*-tolyl)$_3$, 42270-57-5; BCy$_3$, 1088-01-3; B(OPh)$_3$, 1095-03-0; C$_2$F$_4$, 116-14-3; HCN, 74-90-8; C$_2$H$_4$, 74-85-1; (CH$_3$)$_3$CCH$_2$CH$_2$CN, 15673-05-9; ADN, 111-69-3; MGN, 28906-50-5; 2PN, 13284-42-9; C3PN, 16545-78-1; T3PN, 16529-66-1; 4PN, 592-51-8; ESN, 17611-82-4; acrylonitrile, 107-13-1; propionitrile, 107-12-0; propylene, 115-07-1; *n*-butyronitrile, 109-74-0; isobutyronitrile, 78-82-0; *tert*-butylethylene, 558-37-2; styrene, 100-42-5; 3-phenylpropionitrile, 645-59-0; 2-phenylpropionitrile, 1823-91-2; butadiene, 106-99-0; 2-methyl-3-butenenitrile, 16529-56-9; 1,3-hexadiene, 592-48-3; 1,5-hexadiene, 592-42-7; heptenenitrile, 87482-64-2.

Supplementary Material Available: Data illustrating the calculation of the relative rate constants k_i (Figure 4) from the relative substrate and product concentrations at steady state and at t = 0, starting with pure 4PN (2 pages). Ordering information is given on any current masthead page.

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[58] The actual isomer ratios of the 3PN used were T3PN:C3PN:4PN:T2PN:C2PN = 0.92:0.04:0.03:0.002:0.008.

Synthesis and Structure of Triphenylphosphonium Bis(diphenylstibino)methylide: A Conformational Study

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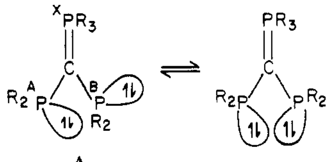
The title compound was prepared in a high-yield one-pot synthesis from chlorodiphenylstibine and triphenylphosphonium methylide. Methyltriphenylphosphonium chloride is the only transylidation byproduct. The structure of the new ylide was determined by X-ray diffraction methods (monoclinic, space group $P2_1/n$, Z = 4, a = 1094.7 (2) pm, b = 1451.4 (2) pm, c = 2276.8 (4) pm, β = 90.67 (1)°). In the crystal, the molecule adopts the conformation B (R = C$_6$H$_5$) with the lone pairs of electrons at the antimony atoms oriented in the plane of the heavy atoms (P1, Sb1, Sb2) which also includes the ylidic carbon atom C1. The conformation is analogous to that found recently for the phosphorus compound A (R = C$_6$H$_5$) both in the crystal and in solution. The pronounced conformational preference is discussed in terms of lone pair repulsion and of electrostatic and steric forces. Parallels in the structures of diphosphinoamines and -methanides are pointed out, along with their relevance for coordination chemistry.

Introduction

In a study of the structure and bonding in phosphino-substituted ylides A,[1] an important class of powerful ligands,[1-5] a striking preference for a rotational orientation of the lone pairs at the trivalent phosphorus atoms (^{A}P, ^{B}P) was detected recently. Conformation A was found to prevail in solution, as shown by variable-temperature ^{31}P nuclear magnetic resonance spectroscopy. For R = C$_6$H$_5$



A A′

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