Cleavage of Carbon−Carbon Bonds in Alkyl Cyanides Using Nickel(0)

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The reaction of the complex [(dippe)NiH]$_2$ (**1**) with a variety of alkyl cyanides afforded nickel(0) compounds of the type [(dippe)Ni(η^2-RCN)], where R = Me, Et, Pr, ^{i}Pr, ^{t}Bu, cyclopropyl, cyclobutyl, adamantyl (**2**−**9**, respectively). When compounds **2**−**9** were warmed to yield oxidative addition products, the thermal reaction proceeded only in the case of **2** to produce [(dippe)Ni(Me)(CN)] (**10**). Photochemical activation did produce oxidative addition products from compounds **2**−**8**, which rapidly evolved to the β-elimination products of the organic moiety in most cases and to the formation of [(dippe)Ni(CN)$_2$] (**11**). Reaction of **1** with acetonitrile in the presence of BPh$_3$ gives [(dippe)Ni(η^2-MeCNBPh$_3$)] (**12**), which does not undergo thermal C−CN cleavage upon heating. X-ray crystal structures are reported for **10**−**12**.

Introduction

The activation of C−C bonds under mild conditions is currently a very active area of research and remains a challenge in organometallic chemistry. A limited number of successful systems able to accomplish such cleavage have been reported.[1] While a variety of compounds containing transition metals have been studied in homogeneous reactions leading to C−C bond cleavage, the use of alkyl and aryl cyanides as substrates has been scarcely studied. Relevant examples in that field have been published by Parkin with the use of *ansa*-molybdenocenes to activate acetonitrile under photochemical conditions[2] and by Brookhart and Bergman for the recently reported silicon-assisted activation of alkyl and aryl cyanides.[3] Very few others are known for similar activations.[4] The relevance of this activation is connected to the fact that these intermediates are involved in the selective functionalization of organic nitriles in cross-coupling reactions,[5] and also they are involved in the cycloaddition of nitriles.[6] A related photochemical activation of acetonitrile by Cp(CO)$_2$Fe-(SiMe$_3$) has been recently reported.[7]

We have previously reported results concerning the C−C bond activation of aryl and heteroaryl cyanides using [(dippe)NiH]$_2$, leading to the formation of an η^2-nitrile complex of nickel(0), which then undergoes oxidative addition to form the corresponding nickel(II) complex.[8] Both types of compounds were isolated and characterized by X-ray structural determinations. We report here the extension to a variety of alkyl cyanides. Our findings indicate that the initial η^2 coordination of the nitrile moiety is favored in all cases; however, the C−CN bond cleavage can be accomplished thermally only with acetonitrile, all other larger nitriles being activated only with the use of photochemical conditions.

Results and Discussion

Reaction of [(dippe)NiH]$_2$ (1) with Acetonitrile. The reaction at room temperature of [(dippe)NiH]$_2$ with CH$_3$CN in THF yields quantitatively only one compound, with the formulation of [(dippe)Ni(η^2-CH$_3$CN)] (**2**) (Scheme 1). As observed in aromatic nitriles, the reaction afforded initially the η^2-nitrile complex. The ^{31}P NMR spectrum was useful for characterization of the Ni(0) compound, showing two slightly broadened asymmetric doublets, characteristic of two types of phosphorus environments with resonances at δ 63.4 ($^2J_{P-P} = 77$ Hz) and δ 78.7 ($^2J_{P-P} = 77$ Hz). Such J_{P-P} coupling constants are typical for similar low-valent nickel

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Scheme 1
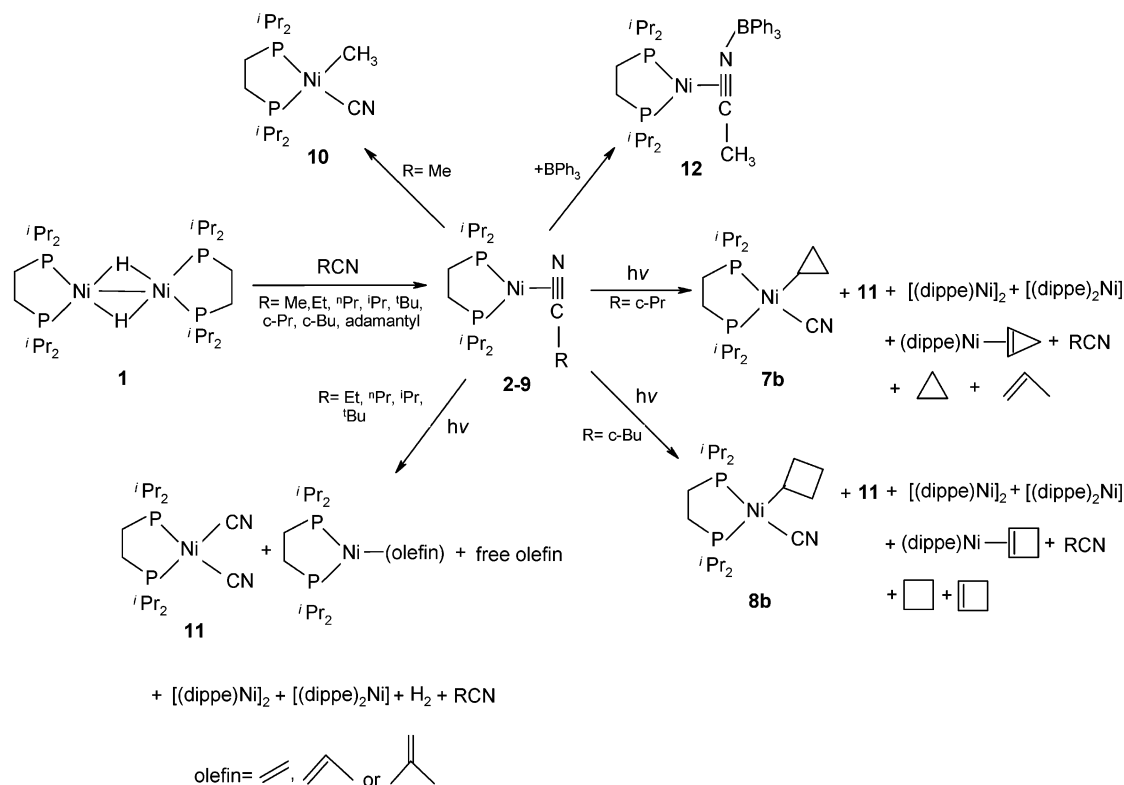
compounds.[8] The ^{1}H NMR spectrum shows two multiplets assigned to methyl resonances for the two types of isopropyl groups along with two methylene multiplets and one doublet at δ 2.42 ($^4J_{H-P} = 4.8$ Hz) for the methyl of the η^2-coordinated acetonitrile. In the ^{13}C NMR spectrum, the acetonitrile C≡N carbon is shifted downfield to δ 160.45 (dd, $^2J_{C-P} = 20, 11$ Hz), compared to δ 117.2 in the free nitrile. The signal assigned to the CH$_3$ appears at δ 15.0 ($^3J_{C-P} = 18.5, 16.5$ Hz), confirmed by a HETCOR determination.

At room temperature in THF solution in the presence of additional CH$_3$CN, complex **2** slowly converts to the new product [(dippe)Ni(Me)(CN)] (**10**), as the solution changes from orange to yellow. Better yields are obtained on warming the sample up to 80 °C (5 days, 90% yield in solution by ^{31}P NMR spectroscopy). The key changes observed are as follows: the ^{31}P NMR spectrum displays a pattern of signals similar to those observed for **2**, with resonances at δ 80.65 ($^2J_{P-P} = 17.6$ Hz) and δ 81.75 ($^2J_{P-P} = 17.6$ Hz). Such J_{P-P} coupling constants are typical for nickel(II). The ^{13}C NMR spectrum shows the C≡N σ-coordinated to nickel at δ 128.4 (dd, $^2J_{C-P} = 83, 30$ Hz), and the signal assigned to the η^1-CH$_3$ appears at δ −6.4 ($^2J_{C-P} = 60.3, 26.1$ Hz). The ^{1}H NMR spectrum is consistent with the oxidative addition of the acetonitrile, where the signal assigned to the CH$_3$ is at δ 0.1 (dd, $^3J_{H-P} = 9, 4$ Hz). Complex **10** was also characterized by an X-ray structure determination, the latter confirming the proposal depicted in Scheme 1. Formation of **10** is competitive with loss of CH$_3$CN and decomposition of the [Ni(dippe)] fragment to a species tentatively assigned as [Ni$_2$(dippe)$_2$] by analogy to Pd[9] and Pt[10] analogues, so that higher yields of **10** are

obtained if a slight excess of CH$_3$CN is present. Evidence for loss of CH$_3$CN in **2** can be demonstrated by the exchange of coordinated CH$_3$CN with added CD$_3$CN. The highest yield of **10** was obtained after heating the solution for 5 days at 80 °C. When a pure sample of **10** was redissolved in THF-d_8, **2** was not seen to be regenerated at room temperature or upon warming to 100 °C for 5 days, indicating that there is not an equilibrium between **10** and **2**. Photolyzing a THF solution of **2** (λ > 300 nm) for 6 h led to the formation of a mixture of **10** and of [(dippe)Ni(CN)$_2$] (**11**). The latter was characterized by a characteristic singlet in the ^{31}P NMR spectrum at δ 91.0 and confirmed by an X-ray structure determination (vide infra).

X-ray Structure of [(dippe)Ni(CH$_3$)(CN)] (10). The complex derived from the oxidative addition of acetonitrile to the dippe−nickel moiety is depicted in Figure 1; selected bond lengths and angles are given in Table 1. The molecule shows disorder between the methyl and cyanide groups, which could be successfully modeled by placing 50% of each group in each location. While this disorder renders the distances obtained from the model inaccurate, one can clearly see that the C−C bond has been cleaved, giving the product [(dippe)Ni(CH$_3$)(CN)]. The cyanide C1−N1 distance is 1.116(12) Å, and the C1−Ni−C2 bond angle is 87.4(4)°.

Reaction of [(dippe)NiH]$_2$ (1) with Larger Alkyl Cyanides. Similar to the reaction discussed above, complex **1** reacted with a variety of alkyl cyanides other than acetonitrile, in which the size and linearity (branched or cyclic) was changed. In the case of CH$_3$-CH$_2$CN in THF the reaction yielded only one product with the formulation [(dippe)Ni(η^2-CH$_3$CH$_2$CN)] (**3**)

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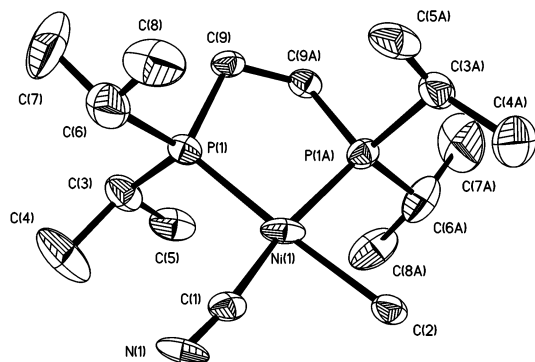
Figure 1. Molecular structure of complex **10** with thermal ellipsoids at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 10−12

atoms	10	11	12
	Distances		
Ni(1)−C(1)	1.804(12)	1.900(3)	1.837(3)
Ni(1)−P(1)	2.1714(10)	2.1787(9)	2.1403(8)
C(1)−N(1)	1.116(12)	1.109(3)	1.236(4)
Ni(1)−X[a]	2.122(13)	1.900(3)	1.904(2)
	Angles		
P(1)−Ni(1)−P(1A)[b]	88.40(5)	88.38(5)	91.23(3)
C(1)−Ni(1)−X[a]	87.4(4)	90.46(15)	38.53(11)
P(1)−Ni(1)−C(1)	101.0(3)	90.88(8)	108.66(10)
P(1A)[b]−Ni(1)−X[a]	83.8(3)	90.88(8)	121.27(7)

[a] For **10**, X = C(2); for **11**, X = C1(A); for **12**, X = N(1). [b] P(2) for **12**.

(Scheme 1). The reaction afforded initially the η^2-nitrile complex. The ^{31}P NMR spectrum was helpful to characterize the corresponding Ni(0) compound, showing two slightly broadened doublets, indicative of two types of phosphorus environments with resonances at δ 64.5 ($^2J_{P-P}$ = 76 Hz) and δ 79.4 ($^2J_{P-P}$ = 76 Hz). No other compound was detected by ^{31}P NMR spectroscopy in the crude reaction mixture. As with acetonitrile, the ^{1}H NMR spectrum shows four distinct methyl resonances for the two types of isopropyl groups along with two methylene multiplets. Two multiplets at δ 1.56 and 2.75 ($^4J_{H-P}$ = 4.0 Hz) are observed for the ethyl moiety of the η^2-coordinated propionitrile. In the ^{13}C NMR spectrum, the acetonitrile C≡N carbon is shifted downfield to δ 167.0 (dd, $^2J_{C-P}$ = 30, 11 Hz), compared to δ 121.0 in the free nitrile. Further warming of the reaction mixture up to 80 °C for 48 h did not produce any other complex or isomeric form that could be detected by NMR spectroscopy. Heating to higher temperatures led to decomposition to [(dippe)$_2$Ni],[11] metallic nickel, and free nitrile.

Photolyzing a THF solution of **3** (λ > 300 nm) for 23 h led to the formation of a yellow precipitate characterized as [(dippe)Ni(CN)$_2$] (**11**), confirmed by an X-ray structure determination (vide infra), and [(dippe)Ni(η^2-C$_2$H$_4$)] (62%) that remains in solution. The latter was characterized as a singlet in the ^{31}P NMR spectrum at δ 72.76 and by comparison with an authentic sample.[12] Also seen are singlets for [(dippe)$_2$Ni$_2$] (33%) and [(dippe)$_2$Ni] (5%) at δ 62.6 (s) and 53.99 (s), respectively.[13] The ^{1}H NMR spectrum of the volatiles from the

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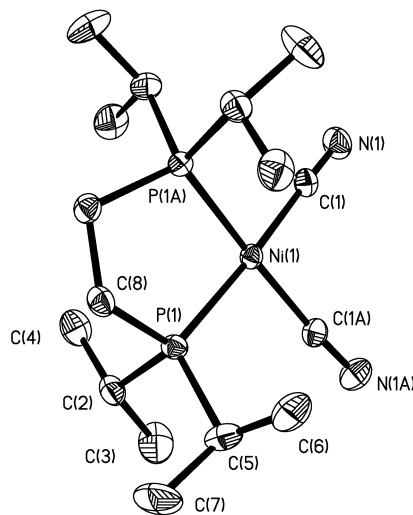(12) Pörschke, K. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 12, 1288.

Figure 2. Molecular structure of complex **11** with thermal ellipsoids at the 30% probability level.

reaction mixture confirmed the presence of CH$_2$=CH$_2$ and H$_2$ as singlets at δ 5.36 and 4.55, respectively.

As mentioned above, **11** can be formed thermally in low yields for **2** but in higher yields in the independent photolytic activation of **2** or **3** (also for **4−8**, vide infra) and can be envisaged as a disproportion product derived from compounds of the type [(dippe)Ni(R)(CN)] and [(dippe)Ni(H)(CN)]. However, the latter intermediate seems to be unlikely, at least in the case of R = Me, due to the absence of β-hydrogens, but it nevertheless is seen upon photolysis of **2**. Compound **11** is depicted in Figure 2; selected bond lengths and angles are given in Table 1. The X-ray structure confirmed the compound as containing two CN ligands: [(dippe)Ni(CN)$_2$]. The cyanide C1−N1 distance is 1.140(3) Å, and the C1−Ni−C1A bond angle is 90.03(15)°.

By the very same procedure used for **3**, complex **1** reacted with other RCN species, where R = Pr, ^{i}Pr, ^{t}Bu, cyclopropyl, cyclobutyl, adamantyl, in THF to yield quantitatively only one product with the formulation [(dippe)Ni(η^2-RCN)] (**4−9**) (Scheme 1). Since the reaction afforded the η^2-nitrile complex initially, the ^{31}P NMR spectrum was the main diagnostic tool used to identify the product as the corresponding Ni(0) compound, showing two slightly broadened doublets, indicative of two types of phosphorus environments with resonances at δ ~64 and ~78. In all cases the values of the J_{P-P} coupling constants (73 Hz average) are in agreement with the characteristic values found in nickel(0) complexes, as quoted above for **2** and **3**. No other compound was detected by ^{31}P NMR spectroscopy in the crude reaction mixture. As for **2** and **3**, further warming of compounds **4−9** to 90 °C for 48 h did not produce any other complex that could be detected by NMR spectroscopy, only decomposition to [(dippe)$_2$Ni], metallic nickel, and the corresponding free nitrile.

Photolyzing THF solutions of **4−6** (λ > 300 nm) for 24 h to several days led to the slow precipitation of [(dippe)Ni(CN)$_2$] (**11**) as yellow crystals and to the formation of the corresponding [(dippe)Ni(η^2-C$_2$H$_3$R')] that remains in solution, along with small quantities

(13) The formation of both compounds was also observed on warming the THF solutions of **1** for long periods of time, leading also to the reductive elimination of H$_2$.
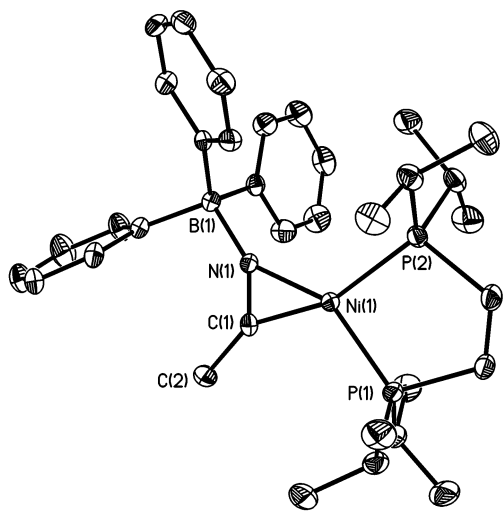
Figure 3. Molecular structure of complex **12** with thermal ellipsoids at the 30% probability level.

of free olefin, free nitrile, [(dippe)₂Ni₂], and traces of [(dippe)₂Ni]. The ¹H NMR spectra of the volatiles from each reaction mixture confirmed the presence of the corresponding olefin, free nitrile, and H₂. Note, however, that irradiation of the cyclopropyl cyanide derivative **7** gave the cyclopropyl cyanide complex **7b**, some **11**, and some of the Ni(0) decomposition product as well as free nitrile, propene, and cyclopropane. Irradiation of the cyclobutyl cyanide derivative **8** likewise gave the cyclobutyl cyanide complex **8b** along with the cyclobutene complex, free cyclobutene, **11**, and cyclobutane. In sharp contrast, the adamantyl complex **9** was both thermally and photochemically stable under the reaction conditions used. Small amounts of [(dippe)₂Ni₂] and [(dippe)₂-Ni] formed after 3 days of irradiation.

Reaction with Acetonitrile in the Presence of BPh₃. It has been reported that Lewis acids such as BPh₃ accelerate and favor the cleavage of C−CN bonds in allyl cyanides.[14] Therefore, a solution of acetonitrile and BPh₃ in THF-d_8 was added to a solution of **1**. Over the course of several minutes, the solution turned yellow-brown, and a ³¹P NMR spectrum showed the formation of a new complex with two doublets at δ 81.7 ($^2J_{P-P}$ = 43 Hz) and 61.7 ($^2J_{P-P}$ = 43 Hz) as the major product (∼75%). The ¹H NMR spectrum shows a doublet at δ 1.95 for the methyl group of the nitrile. This product is assigned as the BPh₃ adduct [(dippe)Ni(η^2-MeCN-BPh₃)] (**12**), in analogy to other similar adducts with allyl cyanide.[14] Heating this solution to 100 °C overnight shows only the clean presence of **12**, indicating that the Lewis acid inhibits C−CN cleavage; such an inhibition of oxidative addition, leading to the opposite effect (i.e., to the reductive elimination of RCN promoted by Lewis acids), has been reported in related palladium compounds.[15] A single-crystal X-ray structure of **12** was obtained (Figure 3), showing the η^2 coordination as proposed for **2** prior to binding of the Lewis acid. The C−N bond is lengthened from 1.153 Å in acetonitrile[16]

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to 1.236(4) Å in **12**. The N−C−CH₃ angle bends from linear to 136.8(3)°. The Ni(1)−N(1) distance is almost 0.1 Å longer than the Ni(1)−C(1) distance, perhaps reflecting the sterics associated with the bulky BPh₃ group. The C(1)−C(2) distance of 1.501(4) Å is only slightly longer than that in free acetonitrile (1.465 Å).[16]

Conclusions

We have shown that the complex [(dippe)NiH]₂ is an effective precursor of a Ni(0) species that can cleave C−CN bonds of a variety of alkyl cyanides under relatively simple and mild conditions. Such cleavage was mediated by η^2-coordinated nitriles and is irreversible. For the smaller substrate acetonitrile, such activation proceeds both thermally and photochemically; for larger nitriles the process does not proceed thermally but does occur under photochemical conditions. As the size of the alkyl cyanide was increased, the C−CN activation decreased dramatically, with the Ni(0) complex derived from adamantyl cyanide being the most stable. Lewis acid binding was actually found to inhibit C−CN cleavage. Studies are currently underway to extend the scope of this reaction.

Experimental Section

All reactions were carried out using standard Schlenk and glovebox techniques, under nitrogen. Solvents were dried and distilled before use from sodium/benzophenone ketyl. Also, deuterated solvents (Cambridge Isotope Laboratories) for NMR experiments were distilled from sodium/benzophenone ketyl and stored over 3 Å molecular sieves. All other chemicals, filter aids, and chromatographic materials were reagent grade and were used as received. ¹H, ¹³C, and ³¹P NMR spectra were determined on Bruker AMX400 and AVANCE400 spectrometers in THF-d_8 unless otherwise stated; chemical shifts (δ) are relative to the deuterated solvent residual protons, and ³¹P NMR spectra are relative to external 85% H₃PO₄. Photolysis experiments were done using an Ace-Hanovia UV lamp, Model 6515, or an Oriel 200 W Hg/Xe lamp. Desert Analytics and USAI-UNAM carried out elemental analyses. The synthesis of [(dippe)NiH]₂ was carried out using the previously reported procedure.[11a] All nitriles used were purchased from Aldrich; liquid substrates were distilled and dried over molecular sieves, and solid substrates were dried under high vacuum for 12 h. A Siemens SMART system with a CCD area detector was used for X-ray structure determinations. All complexes were purified by crystallization or column chromatography.

Preparation of [(dippe)Ni(η^2-CH₃CN)] (2) and [(dippe)-Ni(Me)(CN)] (10). Complex **2** was prepared from [(dippe)-NiH]₂ (0.12 g, 0.18 mmol) and acetonitrile (19.5 µL, 0.37 mmol). The reagents were mixed at room temperature, with the acetonitrile being added to a THF solution (10 mL) of the nickel dimer. After mixing, a strong effervescence was observed over 3 min and the solution was constantly stirred for 15 min, with all of the released gas (H₂) being vented to the drybox. The solvent was then evaporated to dryness and the residue recrystallized from hexanes and dried for 2 h under vacuum. During the crystallization and drying process, the sample was kept in a dry ice/acetone cold bath to prevent further reaction. Compound **2** was obtained in 90% yield. If the reaction mixture is left in solution at room temperature, complex **10** begins to form after 2 h of reaction. After 72 h complex **10** is abundant, but still a mixture of **2** and **10** is seen in solution. Both are separated by chromatography on a neutral alumina column, with hexanes as eluent; complex **2** eluted before **10**. Yield: 68% for **10**. Anal. Calcd for **2**, C₁₆H₃₅NNiP₂: C, 53.07; H, 9.7; N,

3.86. Found: C, 53.0; H, 9.7; N, 3.9. Anal. Calcd for **10**, $C_{16}H_{35}$-NNiP$_2$: C, 53.07; H, 9.7; N, 3.86. Found: C, 52.9; H, 9.6; N, 3.83. NMR spectra for **2** (THF-d_8): ^{1}H, δ 1.0−1.12 (m, 12H, CH$_3$), 1.14−1.25 (m, 12 H, CH$_3$), 1.5−1.65 (m, 4 H, CH$_2$), 2.0−2.15 (m, 4 H, CH), 2.42 (d, $^4J_{H-P}$ = 4.8 Hz, 3 H, CH$_3$CN); ^{13}C-$\{^1H\}$, δ 15.0 (dd, $^3J_{C-P}$ = 18.5, 16.5 Hz, CH$_3$), 19.5−20.5 (m, CH$_3$), 21.4 (m, CH$_2$), 23.3 (m, CH$_2$), 25.5−26.2 (m, CH), 160.45 (dd, $^2J_{C-P}$ = 20, 11 Hz, CN); ^{31}P$\{^1H\}$, δ 63.4 ($^2J_{P-P}$ = 77 Hz), 78.7 ($^2J_{P-P}$ = 77 Hz). NMR spectra for **10** in THF-d_8: ^{1}H, δ 0.1 (dd, $^3J_{H-P}$ = 9, 4 Hz, 3 H, CH$_3$), 1.15−1.40 (m, 24 H, CH$_3$), 1.61−1.87 (m, 4 H, CH$_2$), 2.24−2.40 (m, 4 H, CH); ^{13}C$\{^1H\}$, δ −6.4 (dd, $^2J_{C-P}$ = 60.3, 26.1 Hz, CH$_3$), 19.5−20.5 (m, CH$_3$), 23.0−24.0 (m, CH$_2$), 25.8−26.4 (m, CH), 128.4 (dd, $^2J_{C-P}$ = 83, 30 Hz, CN); ^{31}P$\{^1H\}$, δ 80.65 ($^2J_{P-P}$ = 17.6 Hz), 81.75 ($^2J_{P-P}$ = 17.6 Hz). Small quantities of a byproduct assigned as [(dippe)$_2$Ni$_2$] (δ 62.6, s) can be seen in the ^{31}P NMR spectrum crude reaction mixture. Preparations employing an excess of CH$_3$CN contain less of this byproduct.

Preparation of [(dippe)Ni(η^2-CH$_3$CH$_2$CN)] (3). This compound was prepared by a procedure similar to that described above, using **1** (0.212 g, 0.329 mmol) dissolved in THF (10 mL) and adding propionitrile (47 μL, 0.660 mmol). Yield: 75%. Anal. Calcd for $C_{17}H_{37}$NNiP$_2$: C, 54.28; H, 9.9; N, 3.72. Found: C, 54.3; H, 9.8; N, 3.6. NMR spectra for **3** in THF-d_8: ^{1}H, δ 1.0−1.25 (m, 27 H, CH$_3$), 1.5−1.65 (m, 4 H, CH$_2$), 2.0−2.1 (m, 4 H, CH), 2.75 (m, 2 H, CH$_2$CN); ^{31}P$\{^1H\}$, δ 64.5 ($^2J_{P-P}$ = 76 Hz); 79.4 ($^2J_{P-P}$ = 76 Hz). Irradiation for 5 h gives **11** as sparingly soluble crystals and (dippe)Ni(C$_2$H$_4$) (δ 72.76, s), along with [(dippe)$_2$Ni$_2$] (δ 62.6, s) and [(dippe)$_2$Ni] (δ 53.99, s) in a 12:6:1 ratio.

Preparation of [(dippe)Ni(η^2-CH$_3$CH$_2$CH$_2$CN)] (4). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.156 g, 0.242 mmol) dissolved in THF (10 mL) and adding butyronitrile (42 μL, 0.484 mmol). Yield: 77%. Anal. Calcd for $C_{18}H_{39}$NNiP$_2$: C, 55.41; H, 10.1; N, 3.59. Found: C, 55.35; H, 10.0; N, 3.56. NMR spectra for **4** in THF-d_8: ^{1}H, δ 1.0−1.30 (m, 27 H, CH$_3$), 1.5−1.65 (m, 4 H, P(CH$_2$)$_2$P), 1.70−1.8 (m, 2 H, CH$_2$), 2.0−2.15 (m, 4 H, CH), 2.76 (m, 2 H, CH$_2$CN); ^{31}P$\{^1H\}$, δ 64.3 ($^2J_{P-P}$ = 76 Hz), 78.8 ($^2J_{P-P}$ = 76 Hz). Upon photolysis for 12 h, the ^{31}P NMR spectrum shows the formation of [(dippe)Ni(η^2-propene)] (δ 72.85, d, J = 71 Hz; δ 67.38, d, J = 71 Hz), [(dippe)$_2$Ni$_2$], and [(dippe)$_2$Ni] in a 6:5:0.1 ratio. The ^{1}H NMR spectrum shows both free propene and PrCN. H$_2$ is seen at δ 4.54. **11** is observed as sparingly soluble crystals.

Preparation of [(dippe)Ni(η^2-(CH$_3$)$_2$CHCN)] (5). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.191 g, 0.296 mmol) dissolved in THF (10 mL) and adding isobutyronitrile (54 μL, 0.593 mmol). Yield: 79%. Anal. Calcd for $C_{18}H_{39}$NNiP$_2$: C, 55.41; H, 10.1; N, 3.59. Found: C, 55.43; H, 10.1; N, 3.65. NMR spectra for **5** in THF-d_8: ^{1}H, δ 1.0−1.29 (m, 30 H, CH$_3$), 1.54−1.65 (m, 4 H, P(CH$_2$)$_2$P), 2.0−2.1 (m, 4 H, CH), 2.92 (m, 1 H, CHCN); ^{31}P$\{^1H\}$, δ 64.4 ($^2J_{P-P}$ = 73 Hz), 78.6 ($^2J_{P-P}$ = 73 Hz). Upon photolysis for 23 h, the ^{31}P NMR spectrum showed the presence of [(dippe)Ni(η^2-propene)], [(dippe)$_2$Ni$_2$], and [(dippe)$_2$-Ni] in a 1:1.5:0.1 ratio. The ^{1}H NMR spectrum shows both free ^{i}PrCN and traces of propene. **11** was observed as sparingly soluble crystals.

Preparation of [(dippe)Ni(η^2-(CH$_3$)$_3$CCN)] (6). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.116 g, 0.180 mmol) dissolved in THF (10 mL) and adding trimethylacetonitrile (40 μL, 0.36 mmol). Yield: 76%. Anal. Calcd for $C_{19}H_{41}$NNiP$_2$: C, 56.46; H, 10.2; N, 3.46. Found: C, 56.33; H, 10.1; N, 3.40. NMR spectra for **6** in THF-d_8: ^{1}H, δ 1.0−1.25 (m, 33 H, CH$_3$), 1.56−1.64 (m, 4 H, CH$_2$), 2.0−2.1 (m, 4 H, CH); ^{31}P$\{^1H\}$, δ 64.4 ($^2J_{P-P}$ = 71 Hz), 77.4 ($^2J_{P-P}$ = 71 Hz). Upon photolysis for 12 h, the ^{31}P NMR spectrum showed the presence of unreacted [(dippe)-Ni(η^2-CN^{t}Bu)], [(dippe)$_2$Ni$_2$], [(dippe)Ni(η^2-isobutylene)] (δ 72.0, br, s), and [(dippe)$_2$Ni] in a 1:3:0.1:0.1 ratio. The ^{1}H NMR

spectrum shows both free ^{t}BuCN and isobutylene. **11** was observed as sparingly soluble crystals.

Preparation of [(dippe)Ni(η^2-(CH$_2$)$_2$CHCN)] (7). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.10 g, 0.155 mmol) dissolved in THF (10 mL) and adding cyclopropyl cyanide (23 μL, 0.31 mmol). Yield: 65%. Anal. Calcd for $C_{18}H_{37}$NNiP$_2$: C, 55.7; H, 9.6; N, 3.6. Found: C, 55.6; H, 9.7; N, 3.55. NMR spectra for **7** in THF-d_8: ^{1}H, δ 0.81−0.88 (m, 4 H, CH$_2$), 1.0−1.21 (m, 24 H, CH$_3$), 1.55−1.63 (m, 4H, P(CH$_2$)$_2$P), 2.0−2.1 (m, 5 H, CH and CHCN); ^{13}C$\{^1H\}$, δ 7.0 (s, CH$_2$), 7.8 (m, CH), 19.5−20.5 (m, CH$_3$), 21.4 (m, CH$_2$), 23.3 (m, CH$_2$), 25.5−26.2 (m, CH), 170.3 (dd, $^2J_{C-P}$ = 27, 9 Hz, CN); ^{31}P$\{^1H\}$, δ 64.4 ($^2J_{P-P}$ = 73 Hz), 77.4 ($^2J_{P-P}$ = 73 Hz). Upon photolysis for 12 h, the ^{31}P NMR spectrum showed the presence of [(dippe)Ni(CN)(cyclopropyl] (δ 81.96, d, $^2J_{P-P}$ = 22 Hz; δ 80.34, d, $^2J_{P-P}$ = 22 Hz), **7b**, [(dippe)Ni(η^2-cyclopropene)] (δ 71.0, s), and [(dippe)$_2$Ni$_2$] in a 10:1:3 ratio, along with a trace of [(dippe)$_2$Ni] ($\sim$1%). The ^{1}H NMR spectrum shows free c-PrCN as well as some propene and cyclopropane. **11** was observed as sparingly soluble crystals.

Preparation of [(dippe)Ni(η^2-(CH$_2$)$_3$CHCN)] (8). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.11 g, 0.170 mmol) dissolved in THF (10 mL) and adding cyclobutyl cyanide (32 μL, 0.341 mmol). Yield: 76%. Anal. Calcd for $C_{19}H_{39}$NNiP$_2$: C, 56.74; H, 9.77; N, 3.48. Found: C, 56.6; H, 9.7; N, 3.5. NMR spectra for **8** in THF-d_8: ^{1}H, δ 1.0−1.23 (m, 24 H, CH$_3$), 1.56−1.62 (m, 4 H, P(CH$_2$)$_2$P), 2.0−2.1 (m, 4 H, CH), 2.27−2.33 (m, 6 H, CH$_2$), 3.5−3.57 (m, 1 H, CHCN); ^{31}P$\{^1H\}$, δ 64.4 ($^2J_{P-P}$ = 73 Hz), 77.4 ($^2J_{P-P}$ = 73 Hz). Upon photolysis for 12 h, the ^{31}P NMR spectrum showed the presence of [(dippe)Ni(CN)(cyclobutyl] (δ 79.33, d, $^2J_{P-P}$ = 12 Hz; δ 78.31, d, $^2J_{P-P}$ = 12 Hz), **8b**, [(dippe)Ni(η^2-cyclobutene) (δ 71.21, s), and [(dippe)$_2$Ni$_2$] in a 5:4:5 ratio, along with a trace of [(dippe)$_2$Ni] ($\sim$1%). The ^{1}H NMR spectrum shows both cyclobutene (δ 5.97, s; δ 2.54, s) and cyclobutane (δ 1.96, s) in a 1:3 ratio. **11** was observed as sparingly soluble crystals.

Preparation of [(dippe)Ni(η^2-(C$_{10}$H$_{15}$)CN)] (9). This compound was prepared by a procedure similar to that described above for **2**, using **1** (0.136 g, 0.211 mmol) dissolved in THF (10 mL) and adding adamantyl cyanide (0.0749 g, 0.464 mmol). Yield: 90%. Anal. Calcd for $C_{25}H_{47}$NNiP$_2$: C, 62.26; H, 9.82; N, 2.90. Found: C, 62.31; H, 9.9; N, 3.0. NMR spectra for **9** in THF-d_8: ^{1}H, δ 1.0−1.21 (m, 24 H, CH$_3$), 1.55−1.63 (m, 4 H, P(CH$_2$)$_2$P), 1.72−1.8 (m, 6 H), 1.96−2.15 (m, 13 H); ^{13}C$\{^1H\}$, δ 19.21 (s, CH$_3$), 19.51 (s, CH$_3$), 20.0−21.0 (m, CH$_2$), 26.5−27.0 (m, CH), 30.0 (s, CH$_2$), 35.6 (m, C), 37.9 (s, CH), 43.8 (s, CH$_2$), 175.1 (dd, $^2J_{C-P}$ = 30, 10 Hz, CN); ^{31}P$\{^1H\}$, δ 64.4 ($^2J_{P-P}$ = 72 Hz), 77.7 ($^2J_{P-P}$ = 72 Hz). Upon photolysis for 4 days, about half of the complex is gone and free RCN is seen by ^{1}H NMR spectroscopy. Both [Ni$_2$(dippe)$_2$] and [Ni-(dippe)$_2$] are seen by ^{31}P NMR spectroscopy at δ 62.6 (s) and 53.99 (s), respectively, in a 6:1 ratio.

Preparation of [(dippe)Ni(η^2-CH$_3$CN−BPh$_3$)] (12). A solution of CH$_3$CN (2.2 μL, 0.042 mmol) and BPh$_3$ (8.9 mg, 0.037 mmol) in $\sim$0.5 mL of THF-d_8 was added to a solution of [(dippe)NiH]$_2$ (11.9 mg, 0.019 mmol) in $\sim$0.5 mL of THF-d_8. After about 1 min, the solution became yellow-brown, as a gas (H$_2$) was evolved. A ^{31}P NMR spectrum showed **12** as the major product ($\sim$75%). The solution was heated to 100 °C overnight. The ^{31}P NMR spectrum now showed **12** in $\sim$98% yield, giving a 90% final isolated yield. Anal. Calcd for $C_{34}H_{50}$BNP$_2$Ni: C, 67.59; H, 8.34; N, 2.32. Found: C, 67.43; H, 8.38; N, 2.61. NMR spectra for **12** in THF-d_8: ^{1}H, δ 0.755 (dd, $^3J_{H-P}$ = 15.8, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH$_3$), 0.907 (dd, $^3J_{H-P}$ = 12.6, $^3J_{H-H}$ = 7.0 Hz, 6 H, CH$_3$), 1.156 (dd, $^3J_{H-P}$ = 12.6, $^3J_{H-H}$ = 7.1 Hz, 6 H, CH$_3$), 1.199 (dd, $^3J_{H-P}$ = 17.4, $^3J_{H-H}$ = 7.1 Hz, 6 H, CH$_3$), 1.70 (m, 4 H, P(CH$_2$)$_2$P), 1.943 (d, $^4J_{H-P}$ = 5.1 Hz, 3 H, CH$_3$CN), 2.15 (m, 4 H, CH), 6.922 (t, $^3J_{H-H}$ = 6.8 Hz, 3 H, p-H), 7.010 (t, $^3J_{H-H}$

Table 2. Summary of Crystallographic Results for 10−12

	10	**11**	**12**
formula	$C_{16}H_{35}NNiP_2$	$C_{16}H_{32}N_2NiP_2$	$C_{34.5}H_{50}BN_2P_2Ni$
fw	359.08	373.09	624.22
cryst size/mm	$0.10 \times 0.16 \times 0.25$	$0.2 \times 0.2 \times 0.05$	$0.20 \times 0.28 \times 0.32$
color, shape	yellow, irreg block	yellow, prism	colorless
d(calcd)/Mg m^{-3}	1.204	1.251	1.140
cryst syst	tetragonal	tetragonal	monoclinic
space group	$I\bar{4}c2$	$I\bar{4}c2$	$P2_1/c$
a/Å	14.6416(5)	14.3969(5)	8.9614(6)
b/Å	14.6416(5)	14.3969(5)	21.0752(13)
c/Å	18.4819(9)	19.0492(9)	19.6719(12)
α/deg	90	90	90
β/deg	90	90	101.8490(10)
γ/deg	90	90	90
V/Å^3	3962.1(3)	3948.3(3)	3636.1(4)
Z	8	8	4
μ/mm^{-1}	1.133	1.141	0.645
θ range/deg	1.97−23.26	2.00−23.23	1.93−28.27
no. of rflns collected	8716	8670	23720
no. of indep rflns (R_{int}/%)	1433 (3.2)	1430 (3.5)	8749 (3.7)
abs cor	SADABS	SADABS	SADABS
range of trans factors	0.749−0.928	0.801−0.928	0.767−0.928
refinement method	FLSQ on F^2	FLSQ on F^2	FLSQ on F^2
no. of data/restraints/params	1433/0/111	1430/0/96	8749/0/367
GOF on F^2	1.018	1.025	1.035
R indices ($I > 2\sigma(I)$)/%	R1 = 0.0325, wR2 = 0.0858	R1 = 0.0276, wR2 = 0.0562	R1 = 0.0544, wR2 = 0.1499
R indices (all data)/%	R1 = 0.0356, wR2 = 0.0878	R1 = 0.0339, wR2 = 0.0579	R1 = 0.0857, wR2 = 0.1620
largest diff peak and hole/e Å^{-3}	0.216 and −0.171	0.208 and −0.198	0.846 and −0.399

= 7.2 Hz, 6 H, *m*-H), 7.315 (d, $^3J_{H-H}$ = 8.3 Hz, 6 H, *o*-H); ^{31}P-{^{1}H}, δ 81.7 ($^2J_{P-P}$ = 43 Hz), 61.7 ($^2J_{P-P}$ = 43 Hz).

Photolysis experiments. A typical experiment was performed using THF solutions of 100 mg of each complex in 5 mm sealed NMR tubes, and the reaction was followed by ^{1}H and ^{31}P NMR. These experiments were carried out on compounds **2−9** under nitrogen, at room temperature (λ > 300 nm), with results as described in the text.

Crystallographic Studies. Single crystals suitable for X-ray studies were obtained for compounds **10−12** by cooling concentrated solutions of each compound at −30 °C in a drybox. The crystals were mounted under Paratone 8277 on glass fibers and immediately placed under a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.54°) for all of the crystals. The total data collection time was approximately 12 h for 30 s/frame exposures. Frames were integrated with the Siemens SAINT program to 0.75 Å for all of the data sets. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three-dimensional centroids of >5000 reflections.[17] Data were corrected for absorption using the program SADABS.[18] Space group assignments were made on the basis of systematic

absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least squares on F^2.[19] For both of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions, giving data to parameter ratios of greater than 10:1. Compound **10** showed a disorder between the methyl and cyanide groups, which could be successfully modeled by placing 50% of each group in each location. The crystal of compound **12** also contained a disordered CH_3CN molecule situated on a center of symmetry that was modeled approximately as an "N−C−N" moiety. Further experimental details of the X-ray diffraction studies are provided in Table 2. Positional parameters for all atoms, anisotropic thermal parameters, and all bond lengths and angles, as well as fixed hydrogen positional parameters, are given in the Supporting Information for all of the structures.

Supporting Information Available: Tables giving complete crystallographic data for **10−12**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed value.

(18) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.
(19) Using the SHELX95 package, R1 = $(\sum ||F_o| - |F_c||)/\sum |F_o|$ and wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f^0(\text{Maximum of 0 or } F_o^2) + (1 - f)F_c^2]$.