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Cleavage of Carbon−Carbon Bonds in Aromatic Nitriles Using Nickel(0)

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Abstract: The nickel(0) fragment [(dippe)Ni] has been found to react with a variety of aromatic nitriles. Initial π-coordination to the C═C and C≡N bonds of 2-cyanoquinoline is found to lead ultimately to C−CN oxidative addition. 3-Cyanoquinoline reacts similarly, although no η^2-CN complex is observed. 2-, 3-, And 4-cyanopyridines react initially to give η^2-nitrile complexes that then lead to quantitative formation of C−CN oxidative addition products. Benzonitrile reacts similarly but undergoes reversible insertion into the Ph−CN bond to give an equilibrium mixture of Ni(II) and Ni(0) adducts. A series of para-substituted benzonitriles has been studied in terms of both the position of the equilibrium between (dippe)Ni(η^2-arylnitrile) ⇌ (dippe)-Ni(CN)(aryl) and the rate of approach to equilibrium, and the Hammett plots indicate a buildup of negative charge at the ipso carbon both in the transition state and the Ni(II) product. Terephthalonitrile gives both η^2-nitrile and oxidative addition adducts, as well as dimetalated products. No C−C or C−N cleavage of the aromatic ring is seen with quinoline or acridine; only η^2-arene complexes are formed. The structures of many of these compounds are supported by X-ray data.

Introduction

The cleavage of a variety of strong C−X σ-bonds, including C−H, C−F, C−S, and C−C, has been accomplished using low-valent transition metals.[1] Of these, the latter remain a challenge in substrates that do not contain ring strain or proximity effects to bring about the bond cleavage. We report here an example of C−CN bond cleavage that is both efficient and, in some cases, reversible. These results are of relevance due to the fact that this type of activation and these intermediates are directly connected to the selective functionalization of a variety of organic nitriles for the production of unsymmetrical biaryls;[2] they are involved in the cycloaddition of nitriles,[3] and they have been reported more recently to be involved in the silicon-assisted C−C bond activation of nitriles.[4]

The nickel dimer $[(dippe)NiH]_2$ has been reported to be capable of cleaving the C−S bond in a variety of thiophenes, benzothiophenes, and dibenzothiophenes[5] and serves as a functional model for the hydrodesulfurization (HDS) reaction. The nickel dimer also has been shown to cleave the central carbon−carbon bond in biphenylene[6] and the C−C bond in acetylenes.[7] In these reactions, the hydrido dimer serves as a source of the nickel(0) fragment [Ni(dippe)], which undergoes oxidative addition to a variety of substrates. In an effort to expand the HDS capabilities of this complex to include HDN reactions, we examined the reactivity of $[(dippe)NiH]_2$ with quinolines and other heterocycles. Rather than observing C−N cleavage, however, we found that C−CN cleavage in substrates derivatized with an electron-withdrawing cyano group was quite facile with this complex.[8]

Results and Discussion

Reactions of Quinolines and Derivatives. Reaction of $[(dippe)NiH]_2$ with quinoline leads to a single new product (**1**), as determined by NMR spectroscopy. The ^{31}P NMR spectrum shows two broad asymmetric doublets, indicative of two types of phosphorus environments. The ^{1}H NMR spectrum shows a 1:1 ratio of dippe:quinoline resonances. Particularly, two resonances appear as multiplets at δ 4.2 and 4.7, suggesting η^2-coordination of one of the double bonds of the quinoline (eq 1). A single-crystal X-ray structure of **1** provides confirmation of this hypothesis, with the C−C double bond in the nitrogen-containing ring bound to the metal (Figure 1). The ring

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(1) For a recent review of these topics, see: *Topics in Organometallic Chemistry. Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer-Verlag: 1999; Berlin.
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(7) Muller, C.; Iverson, C.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 9718.
(8) A preliminary report of this reactivity has appeared: Garcia, J. J.; Jones, W. D. *Organometallics* **2000**, *19*, 5544.

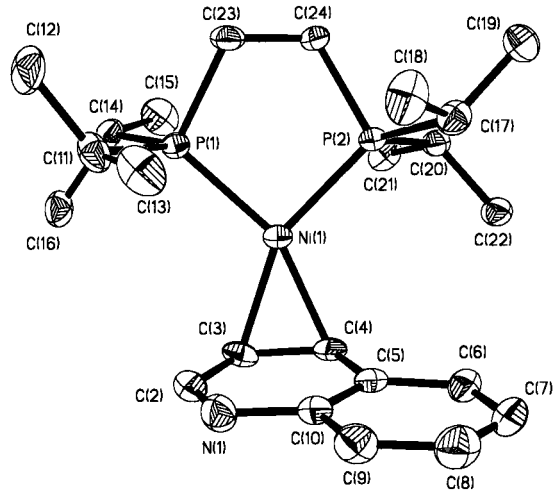
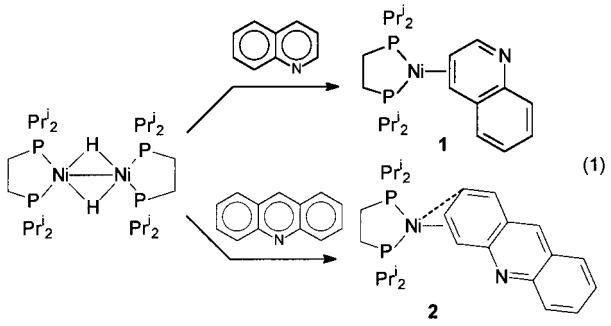


Figure 1. ORTEP drawing of (dippe)Ni(η^2-quinoline), **1**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(3), 1.969(5); Ni(1)−C(4), 1.973(5); C(3)−C(4), 1.435(6); P(1)−Ni(1)−P(2), 92.45(5).



is bound symmetrically, with nickel−carbon distances of 1.969 (5) and 1.973(5) Å for Ni1−C3 and Ni1−C4, respectively. The quinoline ring is tilted at an angle of 103.0° to the Ni1−C3−C4 plane.

A similar situation is observed in the reaction of [(dippe)-NiH]$_2$ with acridine (eq 1). The ^{31}P NMR spectrum of the product (**2**) is similar to that of the η^2-quinoline complex; however, in this case four upfield resonances are seen at δ 5.26, 5.32, 5.73, and 6.09 for the aromatic hydrogens in the ^{1}H NMR spectrum, suggesting an η^4-bound arene ring. In contrast, a single-crystal X-ray structure reveals η^2-coordination to the benzenoid ring, with the nitrogen being endo to the η^2-coordination site (Figure 2). The nickel−carbon bond distances show some evidence of metal interaction with a third carbon atom, with distances for Ni1−C2, Ni1−C3, Ni1−C4, and Ni1−C5 of 2.029(5), 1.969(5), 2.488(6), and 3.027 Å, respectively. The acridine ring is tilted at an angle of 91.4° to the Ni1−C2−C3 plane.

In an effort to compare the reactivity with substituted quinolines for C−N bond activation, [(dippe)NiH]$_2$ was reacted with 2-cyanoquinoline. At ambient temperature, a mixture of two compounds is obtained, both of which appear to be Ni(0) species. The ^{31}P NMR spectrum shows features for one compound, **3a**, which are similar to those of **1** and **2**, implying the formation of an η^2-C,C-2-cyanoquinoline complex (Scheme 1). Also the ^{1}H NMR spectrum shows two doublets for the coordinated C=C moiety at δ 5.48 and 5.66. The ^{31}P NMR spectrum of the second product, **3b**, also shows two inequivalent phosphorus nuclei with J_{P-P} consistent with a Ni(0) species (68

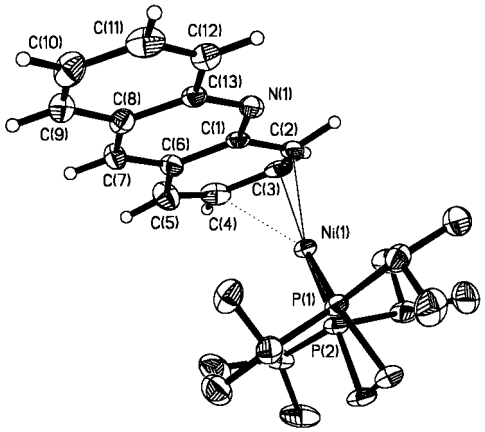
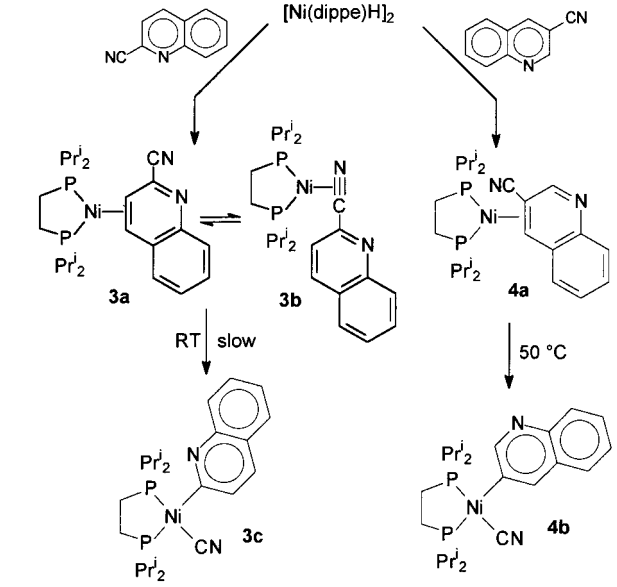


Figure 2. ORTEP drawing of (dippe)Ni(η^2-acridine), **2**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(2), 2.029(5); Ni(1)−C(3), 1.969(5); Ni(1)−C(4), 2.488-(6); Ni(1)−C(5), 3.027; C(2)−C(3), 1.424 (7); P(1)−Ni(1)−P(2), 92.13(6).

Scheme 1



Hz), but no corresponding upfield resonances for a coordinated olefin are seen in the ^{1}H NMR spectrum. Initially, more **3b** is formed than **3a**. **3b** is formulated as an η^2-nitrile complex (vide infra). Upon standing at room temperature, however, this mixture of compounds (**3a** and **3b**) slowly converts into a single new product, **3c**. Product **3c** is formulated as the Ni(II) derivative (dippe)Ni(CN)(2-quinolinyl), as the ^{31}P NMR spectrum now shows two sharp doublets with J_{P-P} = 21 Hz. A single-crystal X-ray structure of the product is shown in Figure 3. The quinoline ring is almost perpendicular to the nickel square plane (109.5°).

[(dippe)NiH]$_2$ also reacts with 3-cyanoquinoline at room temperature. In contrast to 2-cyanoquinoline, only a single species (**4a**) is seen initially (Scheme 1). **4a** shows only two ^{31}P NMR resonances as broad asymmetric doublets similar to those for **1**, **2**, and **3a**, with J_{P-P} = 55 Hz, and is consequently formulated as an η^2-C=C adduct. The ^{1}H NMR spectrum shows a single upfield singlet at δ 4.54, indicating that coordination has occurred at the cyano-substituted double bond and not at the cyano substituent. A single-crystal X-ray structure of **4a** is shown in Figure 4, confirming the coordination site. The nickel−

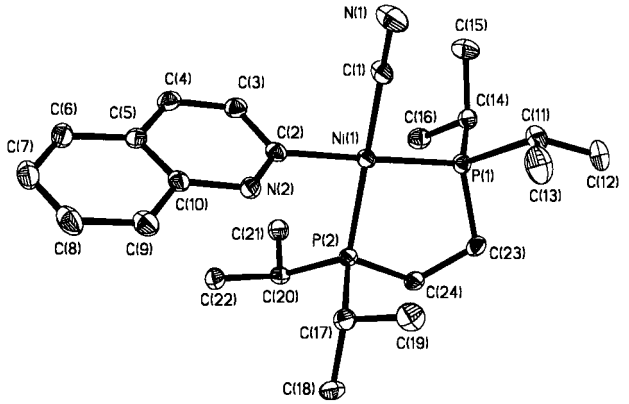


Figure 3. ORTEP drawing of (dippe)Ni(2-quinolinyl)(CN), **3c**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(2), 1.918(2); Ni(1)−C(1), 1.877(3); C(1)−N(1), 1.138-(4); P(1)−Ni(1)−P(2), 89.15(3).

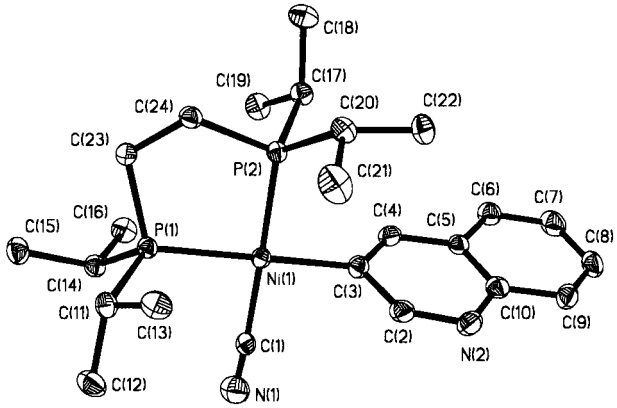


Figure 5. ORTEP drawing of (dippe)Ni(3-quinolinyl)(CN), **4b**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(3), 1.929(4); Ni(1)−C(1), 1.912(4); C(1)−N(1), 1.079-(5); P(1)−Ni(1)−P(2), 88.69(4).

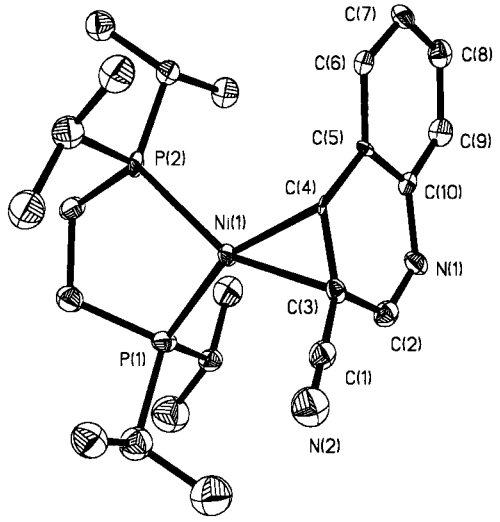


Figure 4. ORTEP drawing of (dippe)Ni(η^2-3-cyanoquinoline), **4a**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(3), 2.004(16); Ni(1)−C(4), 1.977(15); C(1)−N(2), 1.14(2); C(3)−C(4), 1.40(2); P(1)−Ni(1)−P(2), 91.8(2).

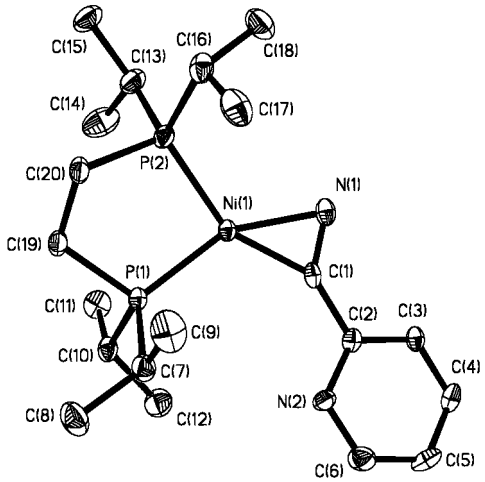


Figure 6. ORTEP drawing of (dippe)Ni(η^2-2-cyanopyridine), **5a**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−N(1), 1.935(6); Ni(1)−C(1), 1.862(7); C(1)−N(1), 1.238-(9); N(1)−C(1)−C(2), 137.0(7); P(1)−Ni(1)−P(2), 91.45(8).

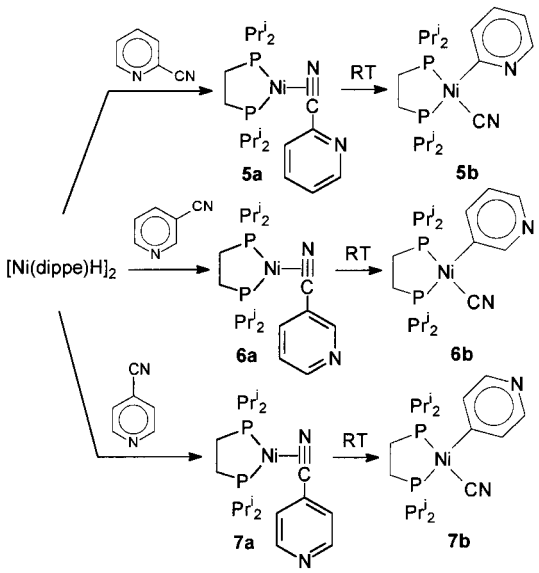
carbon distances Ni1−C3 and Ni1−C4 are 2.004(16) and 1.977-(15) Å, respectively, and the quinoline ring is tilted at an angle of 99.8° to the Ni1−C3−C4 plane.

Upon gentle heating (50 °C), **4a** is converted completely into the Ni(II) oxidative addition product (dippe)Ni(CN)(3-quinolinyl) **4b**, which precipitates from solution. The ^{31}P NMR spectrum for **4b** shows the smaller value for J_{P-P} of 26 Hz, as seen in **3c**. A single-crystal X-ray structure of **4b** is shown in Figure 5, showing a quinoline ring that is nearly perpendicular to the nickel square plane (109.0°), as in **3c**.

Reactions of Cyanopyridines. At this point, one can ask if the cleavage of aryl-CN bonds is specific to quinolines, or would monocyclic analogues also undergo similar reactions. Consequently, [(dippe)NiH]$_2$ was reacted with 2-cyanopyridine. Anticipated binding modes include coordination of the nitrile nitrogen in an η^1-fashion, coordination of the nitrile CN group in an η^2-fashion, η^2-C═C coordination of the arene, and simple dative coordination of the pyridine nitrogen. It was not obvious which of these binding modes would be preferred. By ^{31}P NMR spectroscopy, only a single Ni(0) complex was seen showing two doublets at δ 68.8 and 82.2 (J_{P-P} = 68 Hz). A single-crystal X-ray structure of the product (Figure 6) shows this preferred binding mode to be the η^2-nitrile, **5a** (Figure 6). The nitrile C≡N bond is lengthened by ∼0.1 Å upon coordination, as compared with the unperturbed aryl-CN in **4a**. The pyridine ring is coplanar with the nickel square plane geometry, but the ^{1}H NMR spectrum is consistent with rapid rotation around the C−CN bond. As with the quinoline derivatives, nickel(0) complex **5a** converts into a nickel(II) C−CN cleavage product (**5b**) upon standing (Scheme 2). While an X-ray structure of the product was not obtained, **5b** is assigned as the 2-pyridyl cyanide derivative. This formulation is consistent with the ^{13}C NMR spectrum, which contained a signal at δ 136.3 with a dd multiplicity, due to the coupling of the quaternary carbon of the cyanide group to two inequivalent phosphorus atoms, and a similar signal at δ 188.1 (dd) assigned to the carbon in position 2 of the heterocycle bound directly to the metal. The ^{31}P NMR spectrum for **5b** shows also a smaller value for J_{P-P} of 20 Hz, as seen in **4b**.

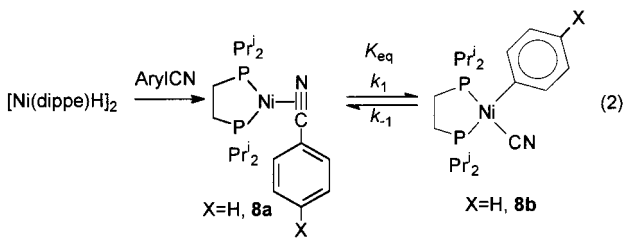
Reactions of [(dippe)NiH]$_2$ with 3-cyanopyridine and 4-cyanopyridine were also examined (Scheme 2). In each case a single nickel(0) adduct was initially observed (**6a** and **7a**, respectively). The ^{31}P NMR data for these species is consistent with their formulation as η^2-nitrile adducts. Resonances for **6a** are doublets at δ 68.6 and 80.7, with J_{P-P} of 64.5 Hz, and for

Scheme 2



7a doublets are seen at δ 67.0 and 79.0, with J_{P-P} of 63.5 Hz. These complexes then convert slowly into the nickel(II) C−CN insertion products, **6b** and **7b**, with resonances in the ^{31}P NMR spectrum at δ 75.15 and 84.0 (J_{P-P} of 24 Hz) and δ 74.75 and 84.9 (J_{P-P} of 24 Hz), respectively.

Reactions of Benzonitrile and Derivatives. Reaction of [(dippe)NiH]$_2$ with benzonitrile in THF-d_8 solution leads to rapid formation of the η^2-nitrile complex, (dippe)Ni(η^2-NCPh), **8a** (eq 2). The solution of the red dihydride complex becomes



yellow as the reaction occurs, and the product can be isolated by removal of solvent (and dihydrogen) under vacuum and recrystallization at low temperature. The ^{31}P NMR spectrum of the product displays two slightly broadened doublets (δ 66.4 and 78.6) with J_{P-P} = 68 Hz, characteristic of an asymmetric Ni(0) complex. The ^{1}H NMR spectrum shows four distinct methyl resonances for the two types of isopropyl groups along with two methylene multiplets. Three phenyl ring resonances are also observed in the aromatic region of the spectrum. The IR spectrum in THF solution shows ν_{C-N} at 1745 cm^{-1}, substantially reduced from the free ligand value of 2235 cm^{-1} due to π-back-bonding to the nitrile. In the ^{13}C NMR spectrum, the benzonitrile C≡N carbon is shifted downfield to δ 169.2 (dd, J = 29.1, 8.8 Hz), compared to δ 119 in the free nitrile. These data are consistent with an in-plane coordination of the benzonitrile ligand, and a single crystal X-ray structure confirms this geometry (Figure 7). The 3-coordinate Ni(0) complex is essentially planar, with the C and N atoms of the benzonitrile ligand lying in the plane. Other P_2Ni(0)-π-alkyne complexes are known to adopt a similar geometry.[9] The bent N1−C1−C2 angle of 150.9° indicates substantial π-back-bonding to the CN group, which adds enough d^8 Ni(II)-metallazacyclopropane

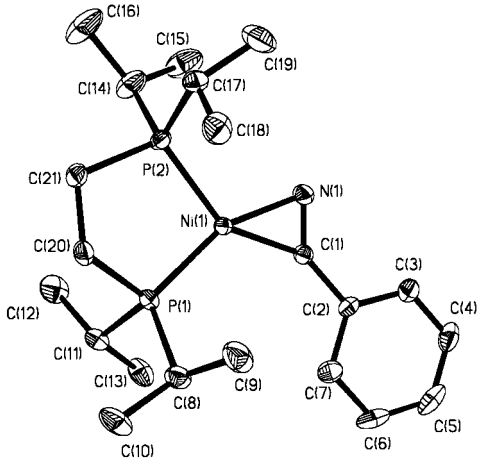


Figure 7. ORTEP drawing of (dippe)Ni(η^2-benzonitrile), **8a**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−N(1), 1.908(3); Ni(1)−C(1), 1.867(4), C(1)−N(1), 1.225-(6); N(1)−C(1)−C(2), 136.1(4); P(1)−Ni(1)−P(2), 91.54(5).

character to the complex to account for the preference for a square planar structure. The back-bonding is also evident in the lengthening of the N1−C1 bond (1.225(6) Å). The phenyl group is coplanar with the Ni1−N1−C1 plane and the square plane of the complex, despite the fact that a perpendicular arrangement might have been expected on steric grounds, suggesting an electronic preference for this geometry. The ^{1}H NMR spectrum shows no evidence, however, for hindered rotation around the aryl−CN bond.

At room temperature in THF solution, **8a** slowly converts to a new product, **8b**, as the solution turns a pale yellow. The ^{1}H and ^{31}P NMR spectra of compound **8b** display similar patterns of resonances to those observed for **8a**. The coupling constant J_{P-P} in the ^{31}P NMR spectrum of **8b** is only 20.6 Hz; however, and the IR spectrum of **8b** shows ν_{C-N} at 2108 cm^{-1}. The ^{13}C NMR spectrum shows the C≡N σ-coordinated to nickel at δ 138.1 (dd, J = 80.5, 30.2 Hz). Crystals of **8b** were isolated at room temperature, and a single-crystal X-ray structure showed the compound to be the C−C cleavage product (dippe)Ni(Ph)-(CN) (Figure 8). The C1−N1 distance is only 1.148 (3) Å and the C1−Ni−C2 bond angle is 89.6 (1)°. Note that the phenyl group now rotates to lie perpendicular to the square plane of the complex (78.7°), in contrast to **8a** but in agreement with structures **3c** and **4b**.

The formation of **8b** from **8a** does not go to completion, but rather reaches an equilibrium favoring **8b** after 1−2 days (eq 2). Indeed, upon redissolving isolated crystals of pure **8b** in THF-d_8, **8a** was seen to be regenerated at the expense of **8b**. The equilibrium constant K_{eq} was found to be ∼1 at 91 °C. The equilibrium ratio of **8a**:**8b** varied with temperature, and determination of K_{eq} over the temperature range 41−91 °C allowed for the determination of the thermodynamic parameters $\Delta H°$ = 4.00(22) kcal/mol and $\Delta S°$ = 10.9(6) eu from a van't Hoff plot (Figure 9).

The rate of approach to equilibrium was also monitored to determine the observed rate of formation of **8b** from **8a** (k_{obs}) according to eqs 2 and 3, where [**8a**]$_0$ is the initial concentration

(9) For instance see: Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Krüger, C. *Eur. J. Inorg. Chem.* **2001**, 77. Rosenthal, U.; Shulz, W.; Görls, H. *Z. Anorg. Allg. Chem.* **1987**, *550*, 169. Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1988**, *348*, 135.

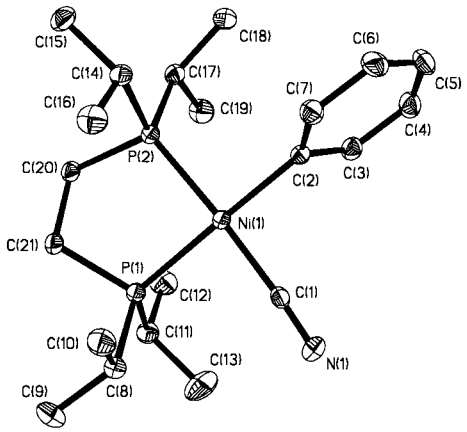


Figure 8. ORTEP drawing of (dippe)Ni(Ph)(CN), **8b**. Ellipsoids are shown at the 30% probability level. Selected distances (Å) and angles (deg): Ni(1)−C(2), 1.935(2); Ni(1)−C(1), 1.877(3); C(1)−N(1), 1.148(3), P(1)−Ni(1)−P(2), 88.56(3).

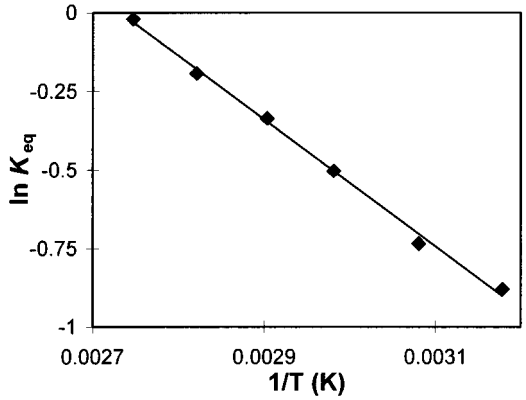


Figure 9. van't Hoff plot for the equilibrium: (dippe)Ni(η^2-benzonitrile) ⇌ (dippe)Ni(Ph)(CN).

of **8a** and $[\mathbf{8a}]_{eq}$ is the equilibrium concentration of **8a**. The expressions for the forward and reverse rate constants are shown in eqs 4 and 5.

$$[\mathbf{8b}] = ([\mathbf{8a}]_0 - [\mathbf{8a}]_{eq})(1 - e^{-k_{obs}t}) \quad (3)$$

$$k_1 = \frac{K_{eq}k_{obs}}{1 + K_{eq}} \quad (4)$$

$$k_{-1} = \frac{k_{obs}}{1 + K_{eq}} \quad (5)$$

Similar reactions were also observed with a series of para-substituted benzonitriles, *p*-XC_6H_4CN, where X = NH_2, OCH_3, CH_3, F, $COOCH_3$, CF_3, and CN (eq 2). While the last member of this series, terephthalonitrile, goes essentially to completion (K_{eq} > 1000), the other members displayed equilibrium positions and rates of approach to equilibrium that could be measured by NMR spectroscopy. Table 1 summarizes the rate and equilibrium data, as well as the Hammett σ_p values for the aromatic substituents. A plot of ln K_{eq} vs σ_p is shown in Figure 10a, and the strong correlation provides a ρ value of +6.1. This large and positive value for ρ indicates that negative charge is being stabilized on the ipso carbon of the substituted aryl group, consistent with the organometallic nature of this bond as possessing substantial $Ni^{\delta+}-C^{\delta-}$ character.

Table 1. Effect of Substituents on the Equilibrium in Eq 2 (54 °C, THF-d_8)

X	σ_p	K_{eq}	k_{obs}, min^{-1}	k_1, min^{-1}
NH_2	−0.66	0.0395	0.014 68	0.000 558
OCH_3	−0.27	0.3423	0.002 076	0.000 529
CH_3	−0.17	0.7391	0.001 492	0.000 634
H	0	1.618	0.001 141	0.000 705
F	0.06	3.878	0.000 76	0.000 604
CO_2CH_3	0.45	28.4	0.002 123	0.002 051
CF_3	0.54	57.8	0.001 393	0.001 369
CN	0.66	>1000	0.003 119	0.003 119

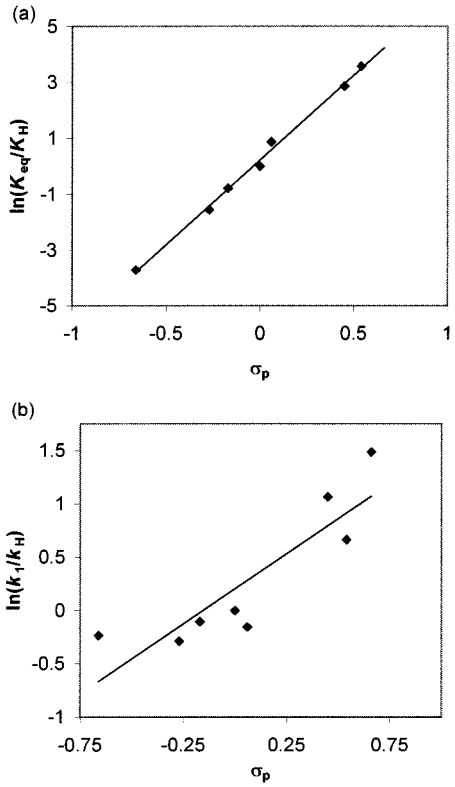


Figure 10. (a) Hammett plot for the equilibrium constants (K_{eq}) from eq 2 vs σ_P at 54 °C (X = CN omitted). (b) Hammett plot for the forward rate constants (k_1) from eq 2 vs σ_P at 54 °C.

Similarly, a plot of ln k_1 vs σ_p, also shown in Figure 10b, gives a ρ value of +1.3. While there is somewhat more scatter in this plot, the positive slope correlation is unmistakable and is consistent with the localization of charge density on the ipso carbon in the transition state for C−CN bond cleavage, although not so much as in the Ni(II) product.

Reactions of Terephthalonitrile. The dicyano substrate terephthalonitrile reacts with $[(dippe)NiH]_2$ (2:1 ratio) to give initially the Ni(0) complex, i.e., the η^2-nitrile complex (dippe)-Ni(η^2-NCC_6H_4CN), **9a** (Scheme 3). The NMR spectra of the crude reaction mixture showed no evidence for any complex other than **9a**. The ^{31}P NMR spectrum showed two doublets at δ 70.25 and 79.3, with J_{P-P} = 63 Hz. A single-crystal X-ray structure of **9a** shows the η^2-coordination mode to the CN moiety (Figure 11). The arene group can be seen to be nearly coplanar with the Ni1−C1−N1 unit, as in **8a** and **5a**. Upon standing at room temperature for 1 week, **9a** converts quantitatively into isomer **9b**, which is a nickel(II) derivative with one C−CN bond added to the metal center. Again, ^{31}P NMR spectra showed the presence of only two doublets at δ 74.1

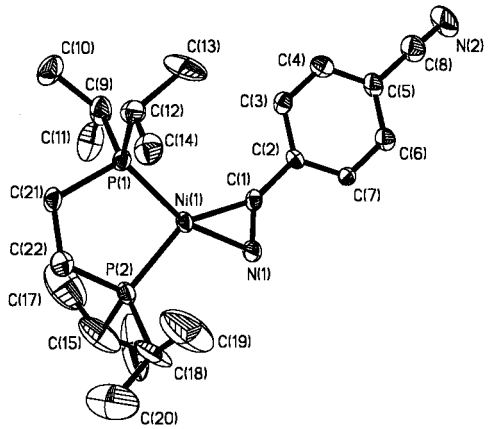
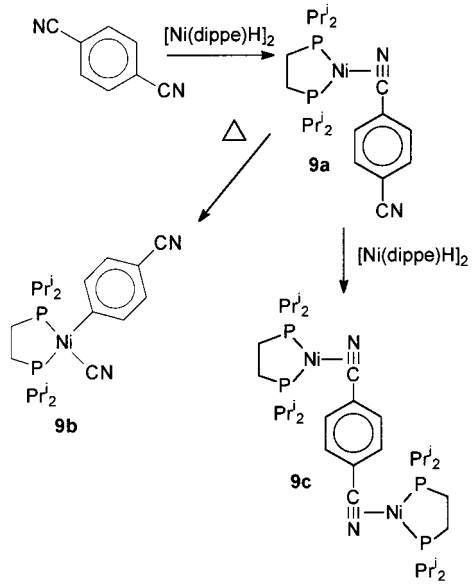


Figure 11. ORTEP drawing of (dippe)Ni(η^2-1,4-dicyanobenzene), **9a**. Ellipsoids are shown at the 30% probability level. Ni(1)−N(1), 1.905(6); Ni(1)−C(1), 1.857(7), C(1)−N(1), 1.228(9); N(2)−C(8), 1.144(10); N(1)−C(1)−C(2), 133.9(7); P(1)−Ni(1)−P(2), 91.42(8).

Scheme 3



and 83.6, with $J_{P-P} = 24.5$ Hz. The X-ray structure of **9b** shows the expected d^8 square planar geometry with the aryl group rotated perpendicular (77.3°) (Figure 12).

Alternatively, intermediate **9a** can be reacted with an additional equivalent of [(dippe)NiH]$_2$. A new product, **9c**, is observed, which is characterized as having two (dippe)Ni moieties per terephthalonitrile ligand. NMR data are consistent with a bis-η^2-nitrile compound, and ^{31}P NMR showed two doublets at δ 66.4 and 78.4, with $J_{P-P} = 68$ Hz. A single-crystal X-ray structure shows the two nitriles coordinated to a (dippe)-Ni moiety (Figure 13). As expected, C−CN cleavage can be seen as **9c** undergoes the expected oxidative addition reaction.

Comparison with Other C−CN Cleavages. While a few examples of C−CN cleavage have been reported,[10] the reversibility of this reaction is not well-documented.[11] The observation

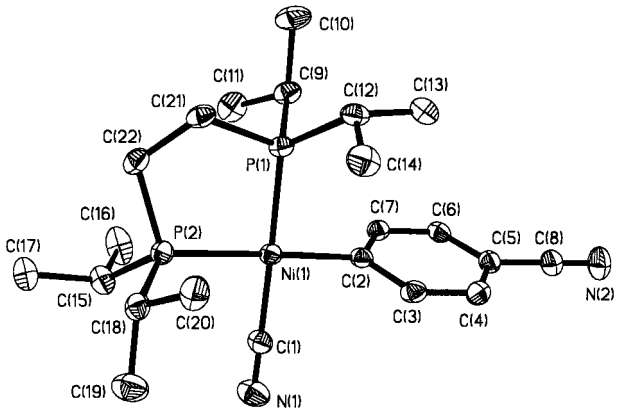


Figure 12. ORTEP drawing of (dippe)Ni(4-cyanophenyl)(CN), **9b**. Ellipsoids are shown at the 30% probability level. Ni(1)−C(1), 1.877(2); Ni(1)−C(2), 1.923(2); C(1)−N(1), 1.141(3); (C(8)−N(2), 1.148(3); P(1)−Ni(1)−P(2), 88.92(2).

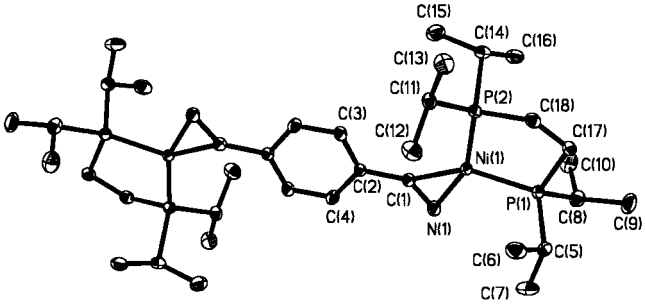


Figure 13. ORTEP drawing of [(dippe)Ni]$_2$(η^2,η^2-1,4-dicyanobenzene), **9c**. Ellipsoids are shown at the 30% probability level. Ni(1)−N(1), 1.918(3); Ni(1)−C(1), 1.853(3), C(1)−N(1), 1.225(4); N(2)−C(8), 1.148(3); N(1)−C(1)−C(2), 136.4(3); P(1)−Ni(1)−P(2), 91.70(4).

of C−CN cleavage is particularly impressive, considering the strength of the C−CN bond in benzonitrile (132.7 kcal/mol).[12] η^2-Coordination of nitriles is also known.[13]

Two recent reports following our communication of the ready formation and interconversion of **8a** and **8b** are worth mentioning. First, Miller has found that reaction of benzonitriles with alkoxy-modified Grignard reagents in the presence of catalytic Ni(PMe$_3$)$_2$Cl$_2$ leads to the formation of biaryl products in high yields.[2] This type of metal-catalyzed cross coupling is unprecedented and is likely to proceed through a nickel-based C−CN cleavage. The present system might prove useful for similar couplings. Second, Brookhart and Bergman have observed the

(10) For the cleavage of C−CN bonds, see: Abba, M.; Yamamoto, T. *J. Organomet. Chem.* **1997**, *532*, 267. Favero, G.; Movillo, A.; Turco, A. *J. Organomet. Chem.* **1983**, *241*, 251. Morvillo, A.; Turco, *J. Organomet. Chem.* **1981**, *208*, 103. Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403. Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543. Burmeister, J. L.; Edwards, L. M. *J. Chem. Soc. (A)* **1971**, 1663.

(11) For the formation of C−CN bonds, see: (a) Favero, G.; Gaddi, M.; Morvillo, A.; Turco, A. *J. Organomet. Chem.* **1978**, *149*, 395. (b) Cassar, L. *J. Organomet. Chem.* **1973**, *54*, C57. (c) Tsuji, Y.; Kusui, T.; Kojima, T.; Sugiura, Y.; Yamada, N.; Tanaka, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 4835. (d) Luo, F.-H.; Chu, C.-I.; Cheng, C.-H. *Organometallics* **1998**, *17*, 1025. (e) Huang, J.; Haar, C. M.; Nolan, S. P.; Marcone, J. E.; Moloy, K. G. *Organometallics* **1999**, *18*, 297. (f) Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8527.

(12) Calculated using ΔH_f data from: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899 (http://webbook.nist.gov), February 2000.

(13) For η^2-nitriles, see: Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178. Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650. Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1986**, *5*, 1913. Zecchin, S.; Zotti, G.; Pilloni, G. *Inorg. Chim. Acta* **1979**, *33*, L117. Storhoff, B.; Infante, A. J. *Inorg. Chem.* **1974**, *13*, 3043. Payne, D. H.; Frye, H. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 505. Bland, W. J.; Kemmitt, R. D. W.; Moore, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1292. Krogmann, K.; Mattes, R. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1046. Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017.

stoichiometric cleavage of aromatic and aliphatic C−CN bonds using a metal−silyl complex.[4] Initial formation of an iminoacyl intermediate via migration of silicon to nitrogen is believed to precede isonitrile deinsertion. This result suggests that other Lewis acids might be capable of affecting C−CN cleavage.[11e,f] Finally, control of the reversible formation of C−CN bonds might lead to improved regioselectivity in the hydrocyanation of olefins.

Conclusions

We have demonstrated that a simple Ni(0) fragment can cleave the C−CN bonds of a variety of arylnitriles and heterocyclic nitriles under very mild conditions. The C−C bond cleavage proceeds via η^2-coordination of nitriles and is reversible. The position of the equilibrium can be altered by variation of the substituents on the arene. The polar character of the Ni−C bond was demonstrated through equilibrium and kinetic studies using substituted benzonitriles. Further studies are currently underway for the expansion of this reactivity to alkyl cyanides.

Experimental Section

All reactions were carried out using standard Schlenk and glovebox techniques, under nitrogen. Solvents were dried and distilled before use. 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 used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were determined on a Bruker AMX400 or AVANCE400 spectrometers in THF-d_8, unless otherwise stated. ^{1}H and ^{13}C chemical shifts (δ) are relative to the deuterated solvent resonances, and ^{31}P NMR spectra are relative to external 85% H_3PO_4. Infrared spectra were obtained using a Perkin-Elmer 1600 FT spectrophotometer. Desert Analytics, USA, and USAI−UNAM carried out elemental analyses. [(dippe)NiH]$_2$ was synthesized according to the previously reported procedure.[14] Quinoline, acridine, 2-cyanoquinoline, 3-cyanoquinoline, benzonitrile, and 1,4-terephthalonitrile were purchased from Aldrich; 2-cyanopyridine and 4-cyanopyridine were purchased from Fluka; liquid ligands were distilled and dried over molecular sieves before use; solid ligands 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. Microsoft Excel was used for all data analysis. Errors are indicated as standard deviations of least squares linear fits.

Preparation of [(dippe)Ni(η^2-quinoline)], 1. Quinoline (102.7 μL, 0.86 mmol) was added to a THF solution (10 mL) of the nickel dimer [(dippe)NiH]$_2$ (0.28 g, 0.43 mmol) at room temperature in the glovebox. After mixing, a strong effervescence was observed for 3 min. The solution was then stirred for 30 min, venting all the released gas (H_2) to the box. The reaction mixture was evaporated to dryness and dried under vacuum for 6 h. The residue was recrystallized from hexanes and further dried for 2 h. Yield: 90% of yellow crystals. Anal. Calcd for $C_{23}H_{39}NP_2Ni$: C 61.35, H 8.73, N 3.12. Found: C 61.27, H 8.57, N 3.09. NMR spectra in THF-d_8, ^{1}H: δ (ppm) 0.9−1.3 (m, 24H), 1.5−1.8 (m, 4H), 2.0−2.15 (m, 4H), 4.2 (m, br, 1H), 4.7 (d, br, 1H), 6.81 (m, br, 1H), 6.86 (m, br, 1H), 6.99 (m, br, 1H), 7.19 (m, br, 1H), 8.26 (m, br, 1H). ^{31}P: δ (ppm) 65.3 (d, *J* 68.5 Hz), 66.6 (d, *J* 68.5 Hz).

Preparation of [(dippe)Ni(η^2-acridine)], 2. Complex **2** was prepared from [(dippe)NiH]$_2$ (0.26 g, 0.4 mmol) and acridine (0.1447 g, 0.8 mmol) following the same procedure and purification methods as described above for complex **1**. Yield: 85%. Anal. Calcd for $C_{27}H_{41}NP_2Ni$: C 64.82, H 8.26, N 2.79. Found: C 64.51, H 8.30, N 2.81. NMR spectra in THF-d_8, ^{1}H: δ (ppm) 0.6−1.1 (m, 24H), 1.45−1.6 (m, 4H), 1.9−2.1 (m, 4H), 5.26 (m, br, 1H), 5.32 (m, br, 1H), 5.73 (m, br, 1H), 6.09 (m, br, 1H), 7.01 (m, br, 1H), 7.18 (m, br, 2H), 7.31 (d, 1H), 7.48 (d, 1H). ^{31}P: δ (ppm) 60.9 (d, *J* 50 Hz), 75.3 (d, *J* 50 Hz).

Preparation of [(dippe)Ni(η^2-C,C-2-CN-quinoline)] (3a), [(dippe)-Ni(η^2-C,N-2-CN-quinoline)] (3b), and [(dippe)Ni(CN)(2-quinolinyl)] (3c). Complex **3a** was prepared from [(dippe)NiH]$_2$ (0.22 g, 0.34 mmol) and 2-cyanoquinoline (0.1066 g, 0.69 mmol). The reagents were mixed at room temperature, adding the 2-cyanoquinoline to a THF solution (10 mL) of the nickel dimer. After mixing a strong effervescence was observed during 3 min and the solution was constantly stirred for 15 min, venting all the released gas to the box. The solution was then evaporated to dryness and dried for 2 h. The residue was recrystallized from hexanes and further dried for 2 h, during the crystallization and drying the sample was kept in a dry ice/acetone cold bath. If the reaction mixture is left in solution at room temperature, a precipitate for complex **3c** is observed at 2 h of reaction, after 12 h such a precipitate becomes rather abundant, the precipitate was filtered and washed with hexanes (2 × 10 mL). Yield: 88%. Anal. Calcd for $C_{24}H_{38}N_2P_2Ni$ (**3c**): C 60.65, H 8.05, N 5.89. Found: C 60.83, H 8.31, N 5.83. IR ν (CN) 2106 cm^{-1}. NMR spectra for **3b** in THF-d_8, ^{1}H: δ (ppm) 0.87−1.32 (m, 24 H), 1.7−1.74 (m, 4H), 2.15−2.16 (m, 2H), 2.17−2.4 (m, 2H), 7.50 (m, 1H), 7.65 (m, 1H), 7.84 (d, *J* 7.6 Hz, 1H), 7.9 (d, *J* 8.4 Hz, 1H), 8.01 (d, *J* 8.4 Hz, 1H), 8.15 (d, *J* 8.4 Hz, 1H). ^{31}P: δ (ppm) 68.9 (d, *J* 68 Hz), 82.75 (d, *J* 68 Hz). NMR for **3a** in THF-d_8, ^{1}H: δ (ppm) 5.48 (d, *J* 8 Hz, 1H), 5.66 (d, *J* 8 Hz, 1H), 6.85 (m, 1H), 6.96 (m, 1H), 7.3 (m, 1H), 8.2 (m, 1H). NMR spectra for **3c** in THF-d_8, ^{1}H: δ (ppm) 0.9−0.97 (m, 6H), 1.1−1.15 (m, 6H), 1.26−1.32 (m, 6H), 1.45−1.51 (m, 6H), 1.65−1.82 (m, 4H), 2.1−2.14 (m, 2H), 2.38−2.41 (m, 2H), 7.31 (m, 1H), 7.49−7.57 (m, 2H), 7.64 (d, *J* 8 Hz, 1H), 7.70 (d, *J* 8.4 Hz, 1H), 7.91 (d, *J* 8.4 Hz, 1H). ^{13}C: δ (ppm) 17.98 (s, CH_3), 18.9 (s, CH_3), 19.14 (s, br, CH_3), 19.80 (dd, CH_2), 19.99 (s, br, CH_3), 22.33 (dd, CH_2), 24.15 (d, CH), 25.3 (d, CH), 123.8 (s, CH), 125.9 (s, C), 127.9 (s, CH), 128.2 (s, CH), 128.3 (s, br, CH), 128.5 (s, CH), 132.25 (d, CH, J_{P-C} 10 Hz), 140.5 (dd, J_{P-C} 70.4 Hz, 20.1 Hz, CN), 148.65 (d, J_{P-C} 10 Hz, CH), 192.0 (dd, J_{P-C} 90.5 Hz, 30.0 Hz, C). ^{31}P: δ (ppm) 73.7 (d, *J* 21 Hz), 80.27 (d, *J* 21 Hz).

Preparation of [(dippe)Ni(η^2-C,C-3-CN-quinoline)] (4a) and [(dippe)Ni(CN)(3-quinolinyl)] (4b). Complex **4a** was prepared from [(dippe)NiH]$_2$ (0.192 g, 0.29 mmol) and 3-cyanoquinoline (0.0920 g, 0.59 mmol), following a similar procedure as described for **3a**. Analogously, complex **4a** reacts further in solution to give complex **4b**; however, improved yields for **4b** were obtained if the reaction was gently warmed to 50 °C for 12 h. Yield: 80%. Anal. Calcd for $C_{24}H_{38}N_2P_2Ni$ (**4a** and **4b**): C 60.65, H 8.05, N 5.89. Found (respectively): C 60.28, H 8.13, N 5.93, and C 60.56, H 8.10, N 5.81. NMR spectra for **4a** in THF-d_8, ^{1}H: δ (ppm) 0.18−0.24 (m, 6H) 0.9−0.1.2 (m, 12H), 1.3−1.34 (m, 6H), 1.52−1.69 (m, 4H), 2.03−2.1 (m, 4H), 4.54 (s, br, 1H), 6.93−6.98 (m, 2H), 7.07 (m, 1H), 7.23 (m, 1H), 8.13 (s, br, 1H). ^{31}P: δ (ppm) 64.9 (d, *J* 55 Hz), 69.9 (d, *J* 55 Hz). NMR spectra for **4b** in THF-d_8, ^{1}H: δ (ppm) 0.88−0.97 (m, 6H), 1.11−1.16 (m, 6H), 1.27−1.32 (m, 6H), 1.46−1.52 (m, 6H), 1.79−2.0 (m, 4H), 2.07−2.2 (m, 2H), 2.40−2.46 (m, 2H), 7.38 (m, 1H), 7.46 (m, 1H), 7.60 (d, *J* 8 Hz, 1H), 7.88 (d, *J* 8.4 Hz, 1H), 8.03 (d, *J* 4.8 Hz, 1H), 9.02 (s, br, 1H). ^{13}C: δ (ppm) 17.7−20.9 (m, CH_3), 22.33 (m, CH_2), 24.5 (m, CH), 25.7 (m, CH), 125.1−128.8 (m), 129.1 (s), 129.7 (s, CH), 138.8 (dd, J_{P-C} 75.5 Hz, 27 Hz, C), 142.5 (s), 143.1 (s), 145.8 (s), 152.0 (dd, J_{P-C} 70.5 Hz, 30.0 Hz, CN), 157.5 (s), 158.4 (s). ^{31}P: δ (ppm) 74.6 (d, *J* 26 Hz), 84.1 (d, *J* 26 Hz).

Preparation of [(dippe)Ni(η^2-C,N-2-CN-pyridine)] (5a) and [(dippe)Ni(CN)(2-pyridyl)] (5b). Both compounds were prepared as described above for **3a** and **3c**, respectively, from [(dippe)NiH]$_2$ (0.1953 g, 0.30 mmol) and 2-cyanopyridine (0.0631 g, 0.606 mmol). Analogously, complex **5a** reacts further in solution to give complex **5b**. Better yields for **5b** were obtained if the reaction was gently warmed to 50 °C for 12 h. Yield: 86%. Anal. Calcd for $C_{20}H_{36}N_2P_2Ni$ (**5a** and **5b**): C 56.50, H 8.53, N 6.58. Found (respectively): C 56.45, H 8.50, N

(14) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855.

6.47, and C 56.60, H 8.48, N 6.34. NMR spectra for **5a** in THF-d_8, ^{1}H: δ (ppm) 1.0−1.30 (m, 24H), 1.62−1.67 (m, 4H), 2.1−2.21 (m, 4H), 7.2 (m, 1H), 7.65 (m, 1H), 7.74 (d, *J* 8 Hz, 1H), 8.57 (d, *J* 4 Hz, 1H). ^{31}P: δ (ppm) 68.6 (d, *J* 68 Hz), 82.3 (d, *J* 68 Hz). NMR spectra for **5b** in THF-d_8, ^{1}H: δ (ppm) 0.87−0.98 (m, 6H), 1.11−1.15 (m, 6H), 1.24−1.32 (m, 6H), 1.41−1.48 (m, 6H), 1.70−1.9 (m, 4H), 2.14−2.2 (m, 2H), 2.30−2.42 (m, 2H), 6.52 (m, 1H), 6.94 (m, 1H), 7.47 (d, *J* 8 Hz, 1H), 8.31 (d, *J* 4 Hz, 1H). ^{13}C: δ (ppm) 13.4 (s, CH_3), 16.96 (s, CH_3), 18.0 (s, CH_3), 18.26 (s, CH_3), 19.23 (s, CH_3), 23.3−25.4 (m), 115.98 (s, CH), 129.3 (s, CH), 135.2 (d, *J* 9 Hz, CH), 136.3 (dd, *J* 75 Hz, *J* 30 Hz, CN), 188.1 (dd, *J* 94 Hz, *J* 29 Hz, C). ^{31}P: δ (ppm) 72.5 (d, *J* 20 Hz), 79.6 (d, *J* 20 Hz).

Preparation of [(dippe)Ni(η^2-C,N-3-CN-pyridine)] (6a) and [(dippe)Ni(CN)(3-pyridyl)] (6b). Both compounds were prepared as described above for **3a** and **3c,** respectively, from [(dippe)NiH]$_2$ (0.1676 g, 0.260 mmol) and 3-cyanopyridine (0.0542 g, 0.520 mmol). Analogously, complex **6a** reacts further in solution to give complex **6b**. Better yields for **6b** were obtained when the reaction was gently warmed to 50 °C for 12 h. Yield: 80%. Anal. Calcd for $C_{20}H_{36}N_2P_2Ni$ (**6a** and **6b**): C 56.50, H 8.53, N 6.58. Found (respectively): C 56.60, H 8.61, N 6.43, and C 56.28, H 8.72, N 6.32. NMR spectra for **6a** in THF-d_8, ^{1}H: δ (ppm) 1.0−1.17 (m, 18H), 1.23−1.3 (m, 6H), 1.63−1.72 (m, 4H), 2.09−2.20 (m, 4H), 7.3 (m, 1H), 7.95 (d, *J* 8 Hz, 1H), 8.48 (d, *J* 4 Hz, 1H), 8.91 (s, 1H). ^{31}P: δ (ppm) 68.6 (d, *J* 65 Hz), 80.7 (d, *J* 65 Hz). NMR spectra for **6b** in THF-d_8, ^{1}H: δ (ppm) 0.88−0.95 (m, 6H), 1.06−1.15 (m, 6H), 1.20−1.29 (m, 6H), 1.39−1.46 (m, 6H), 1.73−1.92 (m, 4H), 2.04−2.14 (m, 2H), 2.36−2.42 (m, 2H), 6.80 (m, 1H), 7.58 (m, br, 1H), 7.89 (d, *J* 4 Hz, 1H), 8.48 (s, 1H). ^{13}C (ppm) 18.1 (s, CH_3), 19.22 (s, CH_3), 19.4 (s, CH_3), 20.3 (s, CH_3), 22.5−23.1 (m, CH), 24.68−26.4 (m, CH_2), 123.1 (s, CH), 136.6 (m, br, CN), 143.7 (s, CH), 145.2 (s, CH), 154.7 (dd, *J* 70 Hz, *J* 30 Hz, C), 157.1 (s, CH). ^{31}P: δ (ppm) 75.15 (d, *J* 24 Hz), 85.0 (d, *J* 24 Hz).

Preparation of [(dippe)Ni(η^2-C,N-4-CN-pyridine)] (7a) and [(dippe)Ni(CN)(4-pyridyl)] (7b). Both compounds were prepared as described above for **3a** and **3c,** respectively, from [(dippe)NiH]$_2$ (0.2097 g, 0.325 mmol) and 4-cyanopyridine (0.0678 g, 0.651 mmol). Analogously, complex **7a** reacts further in solution to give complex **7b**. Best yields for **7b** were obtained when the reaction was gently warmed to 50 °C for 12 h. Yield: 80%. Anal. Calcd for $C_{20}H_{36}N_2P_2Ni$ (**7a** and **7b**): C 56.50, H 8.53, N 6.58. Found (respectively): C 56.33, H 8.42, N 6.62, and C 56.61, H 8.46, N 6.18. NMR spectra for **7a** in THF-d_8, ^{1}H: δ (ppm) 1.0−1.16 (m, 18H), 1.23−1.31 (m, 6H), 1.62−1.77 (m, 4H), 2.03−2.21 (m, 4H), 7.45 (d, *J* 4 Hz, 2H), 8.54 (d, *J* 4 Hz, 2H). ^{31}P: δ (ppm) 67.0 (d, *J* 63 Hz), 79.0 (d, *J* 63 Hz). NMR spectra for **7b** in THF-d_8, ^{1}H: δ (ppm) 0.92−1.0 (m, 6H), 1.09−1.15 (m, 6H), 1.22−1.28 (m, 6H), 1.35−1.43 (m, 6H), 1.68−1.90 (m, 4H), 2.04−2.14 (m, 2H), 2.34−2.40 (m, 2H), 7.37 (m, br, 2H), 7.83 (m, br, 2H). ^{13}C: δ (ppm) 18.1 (s, CH_3), 19.21 (s, CH_3), 19.4 (s, CH_3), 20.3 (s, CH_3), 22.5−23.0 (m, CH), 24.82−26.4 (m, CH_2), 123.1 (s, CH), 135.3 (s, CH), 136.4 (m, br, CN), 145.9 (s, CH), 177.0 (dd, *J* 70 Hz, *J* 30 Hz, C). ^{31}P: δ (ppm) 74.75 (d, *J* 24 Hz), 84.9 (d, *J* 24 Hz).

Preparation of [(dippe)Ni(η^2-C,N-benzonitrile)] (8a) and [(dippe)-Ni(CN)(phenyl)] (8b). Both compounds were prepared as described above for **3a** and **3c**, respectively, from **1** (0.180 g, 0.279 mmol) and benzonitrile (0.0576 g, 0.558 mmol). Analogously, complex **8a** reacts further in solution to give complex **8b**. Best yields for **8b** were obtained when the reaction was gently warmed to 50 °C for 3 days. Yield: 85%. Anal. Calcd for $C_{21}H_{37}NP_2Ni$ (**8a** and **8b**): C 59.46, H 8.79, N 3.30. Found (respectively): C 59.36, H 8.97, N 3.30, and C 59.46, H 8.90, N 3.40. NMR spectra for **8a** in THF-d_8, ^{1}H: δ (ppm) 1.05−1.18 (m, 18 H), 1.23−1.29 (dd, 6 H), 1.61−1.72 (m, 4 H), 2.09−2.17 (m, 4 H), 7.27 (q, *J* = 7.1 Hz, 2 H), 7.32 (t, *J* = 7.0 Hz, 1 H), 7.72 (d, *J* = 7.0 Hz, 2 H). ^{31}P: δ (ppm) 66.4 (d, *J* = 68 Hz), 78.6 (d, *J* = 68 Hz). ^{31}P: δ (ppm) 66.4 (d, *J* = 68 Hz), 78.6 (d, *J* = 68 Hz). NMR spectra for **8b** in THF-d_8, ^{1}H: δ (ppm) 0.92 (dd, *J* = 14.7, 7.2 Hz, 6 H), 1.14 (dd, *J* = 13.7, 7.1 Hz, 6 H), 1.27 (dd, *J* = 13.3, 6.8 Hz, 6 H), 1.45 (dd, *J* = 15.7, 7.2 Hz, 6 H), 1.69−1.89 (m, 4 H), 2.06−2.14 (m, 2 H), 2.37−2.43 (m, 2 H), 6.67 (t, *J* = 7.1 Hz, 1 H), 6.87 (pt, *J* = 7.1 Hz, 2 H), 7.34 (pt, *J* = 5.6 Hz, 2 H). ^{31}P: δ (ppm) 71.2 (d, *J* = 20.6 Hz), 81.7 (d, *J* = 20.6 Hz).

Reaction of [(dippe)NiH]$_2$ with 1,4-Terephthalonitrile. The reaction of [(dippe)NiH]$_2$ (0.1010 g, 0.156 mmol) and 1,4-terephthalonitrile (0.0401 g, 0.313 mmol) produced almost quantitatively the complex [(dippe)Ni(η^2-C,N-1,4-(CN)$_2$-benzene)], **9a**. Similar to the above-described reactions, on warming a solution of this compound to 50 °C for 12 h, complex [(dippe)Ni(CN)(4-CN-phenyl)], **9b**, was obtained. The use of [(dippe)NiH]$_2$ (0.0950 g, 0.147 mmol) and 1,4-terephthalonitrile (0.0188 g, 0.147 mmol) allowed the production of complex [(dippe)Ni]$_2$(η^2,η^2-C,N-1,4-(CN)$_2$-benzene)], **9c**. Total yield: 90%. NMR spectra for **9a** in THF-d_8, ^{1}H: δ (ppm) 1.05−1.18 (m, 18 H), 1.23−1.29 (m, 6H), 1.65−1.73 (m, 4 H), 2.06−2.22 (m, 4 H), 7.69 (d, *J* 8 Hz, 2 H), 7.75 (d, *J* 8.0 Hz, 2 H). ^{31}P: δ (ppm) 67.5 (d, *J* 63 Hz), 79.3 (d, *J* 63 Hz). NMR spectra for **9b** in THF-d_8, ^{1}H: δ (ppm) 0.92 (m, 6 H), 1.13 (m, 6 H), 1.27 (m, 6 H), 1.44 (m, 6 H), 1.72−1.82 (m, 4 H), 2.06−2.10 (m, 2 H), 2.38−2.41 (m, 2 H), 7.14 (d, *J* 8 Hz, 2 H), 7.6 (d, br, *J* 8 Hz, 2 H). ^{31}P: δ (ppm) 73.1 (d, *J* 24.5 Hz), 83.6 (d, *J* 24.5 Hz). NMR spectra for **9c** in THF-d_8, ^{31}P: δ (ppm) 66.4 (d, *J* 68 Hz), 78.7 (d, *J* 68 Hz).

Hammett Studies. In the glovebox, a colorless solution of ArCN (Ar = 4-RC$_6$H$_4$; R = NH_2, OCH_3, CH_3, H, F, $COOCH_3$, CF_3, or CN; 39 μmol) in THF was added to a dark red solution of [(dippe)Ni(H)]$_2$ (12.0 mg, 18.6 μmol) in THF in an NMR tube. The reaction mixture immediately turned golden-brown, and H_2 gas evolved. To remove H_2, the solvent was evaporated in vacuo, leaving a brown, oily residue that was dried for 5 h and then redissolved in THF-d_8. A ^{31}P NMR spectrum showed complete conversion to the η^2-CN Ni(0) complex but no formation of the Ni(II) C−CN cleavage product. The sample was then heated to 54 °C, and conversion of the Ni(0) to the Ni(II) complex was monitored by ^{31}P NMR over a period of 1−3 days, until an equilibrium mixture of Ni(0) and Ni(II) was obtained. K_{eq} = [Ni(II)]/[Ni(0)] was calculated from the average integrations of several ^{31}P NMR spectra of the equilibrium mixture. The first-order rate constant, k_{obs} (min^{-1}), was obtained by fitting a plot of [Ni(II)] vs time to the equation $C = (C_{final} - C_{initial})(1 - e^{-k_{obs}t})$, where C = [Ni(II)], using Microsoft Excel. The forward rate constant, k_1 (min^{-1}), was calculated via the equation $k_1 = k_{obs}/[1 + (1/K_{eq})]$. Hammett plots of $\ln(K_{eq}/K_0)$ vs σ_p and $\ln(k_1/k_0)$ vs σ_p were generated using the values K_0 and k_0 derived for R = H.

(dippe)Ni(ArCN); Ar = C$_6$H$_5$. Vide supra.

(dippe)Ni(Ar)(CN); Ar = C$_6$H$_5$. Vide supra.

(dippe)Ni(ArCN); Ar = 4-NH$_2$C$_6$H$_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 75.9 (d, $^2J_{P-P}$ = 71.6 Hz), 63.7 (d, $^2J_{P-P}$ = 71.6 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.49 (d, *J* = 8.0 Hz, 2 H, ArCN), 6.53 (d, *J* = 7.6 Hz, 2 H, ArCN), 4.72 (br s, 2 H, NH_2), 2.14 (m, 4 H, ^{i}Pr CH), 1.64 (m, 4 H, PCH_2), 1.24 (dd, *J* = 7.2 Hz, 14.8 Hz, 6 H, ^{i}Pr CH_3), 1.11 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-NH$_2$C$_6$H$_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 79.3 (d, $^2J_{P-P}$ = 20.7 Hz), 68.8 (d, $^2J_{P-P}$ = 20.7 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 6.96 (br m, 2 H, Ar), 6.39 (br m, 2 H, Ar), 4.42 (br s, 2 H, NH_2), 2.38 (m, 2 H, ^{i}Pr CH), 2.1−2.2, one resonance under Ni(0) resonance (m, 2 H, ^{i}Pr CH),1.85 (m, 4 H, PCH_2), 1.44 (dd, *J* = 7.0 Hz, 15.4 Hz, 6 H, ^{i}Pr CH_3), 1.1−1.3, two resonances under Ni(0) resonances (dd, 6 H each, ^{i}Pr CH_3), 0.96 (dd, *J* = 7.2 Hz, 15.2 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-OCH$_3$C$_6$H$_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 76.4 (d, $^2J_{P-P}$ = 69.1 Hz), 64.2 (d, $^2J_{P-P}$ = 69.1 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.68 (d, *J* = 8.4 Hz, 2 H, ArCN), 6.89 (d, *J* = 8.4 Hz, 2 H, ArCN), 3.79 (s, 3 H, OCH_3), 2.14 (m, 4 H, ^{i}Pr CH), 1.66 (m, 4 H, PCH_2), 1.25 (dd, *J* = 7.2 Hz, 14.8 Hz, 6 H, ^{i}Pr CH_3), 1.11 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-OCH$_3$C$_6$H$_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 79.8 (d, $^2J_{P-P}$ = 21.5 Hz), 69.4 (d, $^2J_{P-P}$ = 21.5 Hz).

^{1}H NMR (400 MHz, THF-d_8): δ = 7.17 (m, 2 H, Ar), 6.60 (d, J = 7.6 Hz, 2 H, Ar), 3.63 (s, 3 H, OCH_3), 2.39 (m, 2 H, ^{i}Pr CH), 2.22 (m, 2 H, ^{i}Pr CH), 1.84 (m, 4 H, PCH_2), 1.45 (dd, J = 6.8 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3), 1.1−1.3, two resonances under Ni(0) resonances (dd, 6 H each, ^{i}Pr CH_3), 0.94 (dd, J = 7.2 Hz, 15.2 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-$CH_3C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 76.4 (d, $^2J_{P-P}$ = 68.9 Hz), 64.2 (d, $^2J_{P-P}$ = 68.9 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.61 (d, J = 8.0 Hz, 2 H, ArCN), 7.14 (d, J = 7.6 Hz, 2 H, ArCN), 2.33 (s, 3 H, CH_3), 2.15 (m, 4 H, ^{i}Pr CH), 1.66 (m, 4 H, PCH_2), 1.26 (dd, J = 7.2 Hz, 14.8 Hz, 6 H, ^{i}Pr CH_3), 1.11 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-$CH_3C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 79.6 (d, $^2J_{P-P}$ = 20.4 Hz), 69.3 (d, $^2J_{P-P}$ = 20.4 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.21 (m, 2 H, Ar), 6.75 (d, J = 6.8 Hz, 2 H, Ar), 2.40 (m, 2 H, ^{i}Pr CH), 2.16 (s, 3 H, CH_3), 2.14 (m, 2 H, ^{i}Pr CH),1.84 (m, 4 H, PCH_2), 1.45 (dd, J = 6.8 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3), 1.26 (dd, J = 6.8 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3), 1.13 (dd, J = 6.7 Hz, 13.7 Hz, 6 H, ^{i}Pr CH_3), 0.93 (dd, J = 7.2 Hz, 15.2 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-FC_6H_4. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 76.9 (d, $^2J_{P-P}$ = 66.3 Hz), 64.8 (d, $^2J_{P-P}$ = 66.3 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.74 (m, 2 H, ArCN), 7.08 (t, J = 8.6 Hz, 2 H, ArCN), 2.15 (m, 4 H, ^{i}Pr CH), 1.68 (m, 4 H, PCH_2), 1.26 (dd, J = 7.2 Hz, 14.8 Hz, 6 H, ^{i}Pr CH_3), 1.12 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-FC_6H_4. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 80.6 (d, $^2J_{P-P}$ = 23.0 Hz), 70.0 (d, $^2J_{P-P}$ = 23.0 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.28 (m, 2 H, Ar), 6.71 (t, J = 8.8 Hz, 2 H, Ar), 2.40 (m, 2 H, ^{i}Pr CH), 2.14 (m, 2 H, ^{i}Pr CH),1.84 (m, 4 H, PCH_2), 1.45 (dd, J = 7.0 Hz, 15.8 Hz, 6 H, ^{i}Pr CH_3), 1.27 (dd, J = 7.0 Hz, 13.4 Hz, 6 H, ^{i}Pr CH_3), 1.14 (dd, J = 7.0 Hz, 13.8 Hz, 6 H, ^{i}Pr CH_3), 0.95 (dd, J = 7.4 Hz, 15.4 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-$CH_3O(CO)C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 76.9 (d, $^2J_{P-P}$ = 65.5 Hz), 65.0 (d, $^2J_{P-P}$ = 65.5 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.99 (d, J = 8.0 Hz, 2 H, ArCN), 7.72 (d, J = 8.0 Hz, 2 H, ArCN), 3.86 (s, 3 H, OMe), 2.15 (m, 4 H, ^{i}Pr CH), 1.69 (m, 4 H, PCH_2), 1.27 (dd, J = 7.0 Hz, 15.0 Hz, 6 H, ^{i}Pr CH_3), 1.11 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-$CH_3O(CO)C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 80.6 (d, $^2J_{P-P}$ = 22.6 Hz), 70.3 (d, $^2J_{P-P}$ = 22.6 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.54 (d, J = 2.8 Hz, 4 H, Ar), 3.75 (s, 3 H, OCH_3), 2.41 (m, 2 H, ^{i}Pr CH), 2.10 (m, 2 H, ^{i}Pr CH),1.80 (m, 4 H, PCH_2), 1.45 (dd, J = 7.2 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3), 1.28 (dd, J = 7.2 Hz, 13.6 Hz, 6 H, ^{i}Pr CH_3), 1.14 (dd, J = 7.0 Hz, 13.8 Hz, 6 H, ^{i}Pr CH_3), 0.96 (dd, J = 7.4 Hz, 15.4 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-$CF_3C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 77.2 (d, $^2J_{P-P}$ = 64.3 Hz), 65.2 (d, $^2J_{P-P}$ = 64.3 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.83 (d, J = 8.0 Hz, 2 H, ArCN), 7.67 (d, J = 8.4 Hz, 2 H, ArCN), 2.15 (m, 4 H, ^{i}Pr CH), 1.69 (m, 4 H, PCH_2), 1.27 (dd, J = 7.0 Hz, 15.0 Hz, 6 H, ^{i}Pr CH_3), 1.12 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-$CF_3C_6H_4$. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 81.0 (d, $^2J_{P-P}$ = 23.0 Hz), 70.6 (d, $^2J_{P-P}$ = 23.0 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.59 (m, 2 H, Ar), 71.5 (d, J = 7.7 Hz, 2 H, Ar), 2.42 (m, 2 H, ^{i}Pr CH), 2.10 (m, 2 H, ^{i}Pr CH),1.84 (m, 4 H, PCH_2), 1.46 (dd, J = 7.2 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3), 1.29 (dd, J = 7.0 Hz, 13.4 Hz, 6 H, ^{i}Pr CH_3), 1.15 (dd, J = 7.0 Hz, 13.8 Hz, 6 H, ^{i}Pr CH_3), 0.95 (dd, J = 7.2 Hz, 15.6 Hz, 6 H, ^{i}Pr CH_3).

(dippe)Ni(ArCN); Ar = 4-CNC_6H_4. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 77.3 (d, $^2J_{P-P}$ = 63.3 Hz), 65.5 (d, $^2J_{P-P}$ = 63.3 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.75 (d, J = 8.0 Hz, 2 H, ArCN), 7.69 (d, J = 8.0 Hz, 2 H, ArCN), 2.14 (m, 4 H, ^{i}Pr CH), 1.70 (m, 4 H, PCH_2), 1.26 (dd, J = 7.2 Hz, 14.8 Hz, 6 H, ^{i}Pr CH_3), 1.10 (m, 18 H, ^{i}Pr CH_3).

(dippe)Ni(Ar)(CN); Ar = 4-CNC_6H_4. ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 81.5 (d, $^2J_{P-P}$ = 23.8 Hz), 70.9 (d, $^2J_{P-P}$ = 23.8 Hz). ^{1}H NMR (400 MHz, THF-d_8): δ = 7.61 (m, 2 H, Ar), 7.14 (d, J = 7.6 Hz, 2 H, Ar), 2.42 (m, 2 H, ^{i}Pr CH), 2.09 (m, 2 H, ^{i}Pr CH),1.84 (m, 4 H, PCH_2), 1.45 (dd, J = 7.4 Hz, 15.8 Hz, 6 H, ^{i}Pr CH_3), 1.28 (dd, J = 6.8 Hz, 13.6 Hz, 6 H, ^{i}Pr CH_3), 1.14 (dd, J = 7.0 Hz, 13.8 Hz, 6 H, ^{i}Pr CH_3), 0.96 (dd, J = 7.4 Hz, 15.4 Hz, 6 H, ^{i}Pr CH_3).

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Supporting Information Available: Includes experimental details for X-ray structures, tables of X-ray data, and thermodynamic and kinetic plots for the studied reactions.This material is available free of charge via the Internet at http://pubs.acs.org.

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