C–CN Bond Activation of Aromatic Nitriles and Fluxionality of the η^2 -Arene Intermediates: Experimental and Theoretical Investigations

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Received January 1, 2010

[Ni(dippe)H]₂ has been reacted with a variety of aromatic nitriles. Both experimental and DFT calculation results have shown that an η^2 -arene complex with nickel coordinated to the C=C double bond next to the cyano substituent is the crucial intermediate leading to C–CN bond activation. Furthermore, the fluxional processes of the η^2 -arene species were investigated by low-temperature experiments as well as computational methods. In the case of dicyanobenzenes, a mechanism similar to that found for PhCN was found with the Ni(dippe) fragment rotating as it migrated around the phenyl ring through a series of η^3 -allyl-like transition states. For polycyclic aromatic nitriles, only certain η^2 -arenes were stable enough to contribute to the fluxional process, and nickel migrates via an η^4 -coordinated transition state. The transition states connecting the η^2 -nitrile complex to the η^2 -arene intermediate and the η^2 -arene precursor and the ring. In the reaction of 9-cyanoanthracene, the instability of the η^2 -arene precursor and the high-energy activation barrier resulted in the absence of the C–CN oxidative addition product. The complex with 9-cyanophenanthrene undergoes only C–CN cleavage upon photolysis.

Introduction

The cleavage of carbon–carbon σ -bonds has important applications in both organic synthesis and industrial processes.¹ However, due to the kinetic inertness and thermodynamic stability of these bonds, this type of activation remains a continuing challenge in organometallic chemistry, especially in substrates without relief of strain or aromatization providing a substantial extra driving force.² Among the exceptions, several examples of C–C bond activations in aryl cyanides by transition metals have been reported.³

The hydride-bridged nickel dimer $[Ni(dippe)(\mu-H)]_2$, in the presence of a suitable ligand, releases H₂ gas to generate a product resulting from reaction with the electron-rich

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[(dippe)Ni⁰] fragment. For example, C–C and C–S bond cleavage is seen in a variety of biphenylene and thiophene substrates.^{4,5} Our group has also investigated the reaction of aromatic nitriles using this dimer.⁶ Recent results of reactions with benzonitrile showed that while initial coordination of nickel produces an η^2 -C,N-nitrile adduct, a higher energy η^2 -arene intermediate was formed prior to C–C bond cleavage (eq 1). The fluxionality of the η^2 -arene complex was demonstrated both experimentally and computationally.⁷

ORGANOMETALLICS



In this paper, we report reactions of a variety of aromatic nitriles with [Ni(dippe)H]₂ at ambient and low temperatures. DFT methods, using [Ni(dmpe)] as a model for [Ni(dippe)],

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Figure 1. ORTEP drawing of $[Ni(dippe)H]_2$. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)-Ni(1)A, 2.3737(5); Ni(1)-H(1), 1.64(6); Ni(1)-H(2), 1.51(7); Ni(1)-P(1), 2.1291(6); Ni(1)-P(2), 2.1212(6). Selected angles (deg): P(1)-Ni(1)-P(2), 91.78(2); P(2)-Ni(1)-Ni(1)A, 136.28(2); P(2)-Ni(1)-H(1), 106(2); H(1)-Ni(1)-H(2), 76(3).

were undertaken to examine the energetics, intermediates, and reaction pathways of the C–CN bond activation. Again, it was found that formation of an η^2 -arene complex is crucial prior to C–C bond cleavage. This complex is fluxional and can exist as a stable species in reactions with polycyclic aromatic nitriles. The transition states leading to C–CN oxidative addition products showed very similar geometries to that seen for PhCN,⁷ but an additional fluxional pathway has been identified.

Results and Discussion

Structure of the [Ni(dippe)H]₂ **Complex.** The red dimer [Ni(dippe)H]₂ is readily prepared from the reaction of Ni-(dippe)Cl₂ and LiHBEt₃.⁸ Recrystallization from hexanes allowed the X-ray structure of the nickel dimer to be obtained (Figure 1). At each Ni center, two P atoms and one bridging H atom are essentially planar, with the second bridging H atom out of the plane. The twist angle between the P1-Ni1-P2 and P1A-Ni1A-P2A planes is 80° and compares with values of 80° in [Ni(dtbpe)H]₂,⁹ 63° in [Ni(dcypp)H]₂,¹⁰ and 75° in [Ni(dippp)H]₂.¹¹ The angle between the Ni1-H1-Ni1A and Ni1-H2-Ni1A planes is approximately 156°. The distance between the two Ni atoms is 2.37 Å, indicating the presence of a Ni-Ni bond between the two formally Ni¹ centers. The Ni¹-Ni¹ distances in the other hydride dimers average 2.44 Å.

Reactions with Dicyanobenzenes. The reaction of $[Ni(dippe)H]_2$ with 1,2-dicyanobenzene at -60 °C initially formed both η^2 -nitrile (A1) and η^2 -arene complexes (eq 2, A2–A5). The major product A1 showed a pair of doublets in the ³¹P{¹H} NMR spectrum at δ 62.7 and 73.5 ($J_{P-P} = 62$ Hz). The minor product showed a singlet at δ 57.0 in the ³¹P{¹H} NMR spectrum and two broad upfield peaks at δ 5.83 (2H) and 6.28 (2H) in the ¹H NMR

spectrum, assigned to the ortho and meta protons of the η^2 -C,C adduct. These observations suggest rapid equilibrations of isomers A2, A3, A4, and A5 (eq 3). As the temperature of the sample increased to -20 °C, the η^2 -arene complexes completely disappeared, leaving only A1. When the temperature reached 60 °C, a new set of doublets appeared in the ${}^{31}P{}^{1}H{}$ spectrum that belonged to the C–CN activation product A6. When the mixture was cooled back to room temperature, none of the η^2 -arene complexes were observed to reappear in the NMR spectrum (Supporting Information, Figure SI-1).



Upon adding a second equivalent of $[Ni(dippe)H]_2$ to A1, a new pair of broad doublets appeared in the ³¹P{¹H} NMR spectrum (C₆D₆) at δ 62.0 and 72.5 ($J_{P-P} = 70$ Hz), which was assigned to a bis- η^2 -nitrile complex (A7).^{6b} After sitting at room temperature for 1 h, a new species (A8) appeared in the ³¹P{¹H} NMR spectrum with characteristics of two different Ni centers, each displaying a pair of doublets, both Ni(II) (δ 63.4 and 77.5, $J_{P-P} = 25$ Hz) and Ni(0) (δ 63.1 and 74.5, $J_{P-P} = 71$ Hz) within the same molecule, indicating only one C–CN bond in A7 was cleaved (eq 4). About 50% A6 was also observed. Single-crystal structures of A6 and A8 were obtained as shown in Figure 2.



A computational study was undertaken to examine the fluxionality of the η^2 -arene complexes and the pathway leading to the C–CN oxidative addition product. The [Ni(dmpe)] fragment was used as a model of the active species [Ni(dippe)] in the experiment.¹² Initially the ground

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Figure 2. ORTEP drawing of (a) (dippe)Ni(CN)(C_6H_4CN) (**A6**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(8), 1.863(4); Ni(1)–C(1), 1.911(4); Ni(1)–P(1), 2.1915(12); Ni(1)–P(2), 2.1815(12); C(7)–N(1), 1.145(5); C(7)–C(2), 1.442(6); C(8)–N(2), 1.144(5). Selected angles (deg): P(1)–Ni(1)–P(2), 88.64(4); C(1)–Ni(1)–C(8), 88.42(16); N(2)–C(8)–Ni(1), 177.7(4); C(7)–C(2)–C(1), 119.4(3); N(1)–C(7)–C(2), 178.3(4). (b) (dippe)Ni(μ -NCPh)Ni(CN)(dippe) (**A8**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(7), 1.869(3); Ni(1)–N(1), 1.913(2); Ni(1)–P(1), 2.1673(9); Ni(1)–P(2), 2.1396(8); C(7)–N(1), 1.230(3); C(7)–C(1), 1.464(4); Ni(2)–C(2), 1.933(3); Ni(2)–C(8), 1.861(3); Ni(2)–P(3), 2.1924(8); Ni(2)–P(4), 2.1653(8); C(8)–N(2), 1.157(3). Selected angles (deg): P(1)–Ni(1)–P(2), 91.32(3); C(7)–Ni(1)–N(1), 37.93(10); C(7)–N(1)–Ni(1), 69.14(16); C(7)–C(1)–C(2), 119.2(2); C(1)–C(2)–Ni(2), 118.50(19); C(2)–Ni(2)–C(8), 88.59(11); N(2)–C(8)–Ni(2), 173.4(2); P(3)–Ni(2)–P(4), 87.98(3).



Figure 3. Energetics of C–C bond activation of 1,2-dicyanobenzene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1,2-dicyanobenzene) (PCM corrected in THF).

states were constructed on the basis of previously reported X-ray structures for Ni(dippe)(η^2 -NCPh) and Ni(dippe)-(Ph)(CN).^{6c} Local minima for all the species were located on the potential energy surface in the gas phase, and all the optimized structures and selected bond lengths are summarized in the Supporting Information (Figure 3, SI-17, and Table SI-1).

In the Ni(dmpe)(η^2 -C,N-nitrile) complex SA1, the coordinated C–N bond is longer than that in free 1,2-dicyanobenzene (1.23 Å vs 1.16 Å), and the C–C–N angle bends to 138.8°. The coordination around nickel is almost planar, with the angle between the P–Ni–P and the C–N–Ni planes being only 2.9°. The phenyl group is also coplanar with the Ni–N–C plane. The C–CN oxidative addition product SA6 has a square-planar geometry around the nickel center, and the phenyl ring is perpendicular to the P–Ni–P plane. TSA12 was located from a relaxed potential energy

surface scan by constraining the Ni-Cipso distance in SA1 to shorten and optimizing the resulting structures as the Ni-C_{ipso} distance was reduced. The structure around the energy maximum was optimized as a transition state. The intrinsic reaction coordinate calculation (IRC) starting from this transition state leads to SA1 in one direction and the η^2 -arene complex SA2 in the other, where the nickel atom is coordinated through the C=C between the two nitrile substituents. In TSA12, nickel coordinates to the nitrile carbon (Ni-CN = 2.04 Å) and weakly through its nitrogen and aryl carbon atoms (Ni–N = 2.33 Å, Ni– C_{ipso} = 2.30 Å). The Ni-C-C plane is at an angle of 61.5° to the P-Ni-P plane. The transition state (TSA26) leading to the formation of the oxidative addition product SA6 was located by a relaxed potential energy surface scan by constraining the Ni-CN distance in SA2 to shorten and optimizing the resulting structures as the distance was reduced. IRC following Article



Figure 4. ORTEP drawing of (dippe)Ni(3-cyanophenyl)(CN) (B5). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)-C(8), 1.890(2); Ni(1)-C(1), 1.927(2); Ni(1)-P(1), 2.1815(6); Ni(1)-P(2), 2.1863(6); C(7)-N(1), 1.153(3); C(8)-N(2), 1.112(3); Selected angles (deg): P(1)-Ni(1)-P(2), 89.02(2); C(8)-Ni(1)-C(1), 88.67(8); N(2)-C(8)-Ni(1), 178.3(2).

demonstrated that **TSA26** connected **SA6** to the η^2 -arene complex **SA2**. In **TSA26**, the Ni–CN bond is 0.12 Å longer than in **SA6**, while the C–CN distance is lengthened only by 0.04 Å. The C–C–N angle is 146.6°, much smaller than in **SA2** (176.6°). Also, the Ni–C–N plane rotates at an angle of 38.5° to the P–Ni–P plane (see weo's for **TSA12** and **TSA26** in the Supporting Information). Therefore, **TSA26** can be viewed as having essentially formed the Ni–CN bond while only slightly breaking the C–CN bond and is well-progressed toward the nickel(II) square-planar product.

SA2 therefore is established as the immediate precursor of the C-CN activation. Four stable, high-energy η^2 -arene complexes, SA2, SA3, SA4, and SA5, have been located on the potential energy surface. All of them have nickel metal bound to the phenyl ring through one of the C=C double bonds. The nickel-carbon bond lengths are very similar, and the angle between the plane of the phenyl ring and the P-Ni-P plane is 64.9° in SA2, 69.3° in SA3, 73.3° in SA4, and 78.9° in SA5. The transition states connecting these η^2 -arene complexes (TSA23, TSA34, TSA45) all show an η^3 -allyl-like structure with the allyl perpendicular to the P-Ni-P plane, and they are located at much lower energies than TSA12 or TSA26. The low kinetic barriers for the migration of the nickel around the phenyl ring prevent the detection of the different η^2 -arene species in the NMR spectrum even at -60 °C. The NiP₂ unit rotates as it migrates around the aromatic ring, and the two phosphorus environments exchange with each other when the nickel returns to the starting position (see movie in Supporting Information). These result in one singlet being observed in the ${}^{31}P{}^{1}H$ NMR spectrum for the η^2 -arene complexes, in contrast to what was seen for the η^2 -C,C-benzonitrile complex (two doublets in the ${}^{31}P{}^{1}H$ spectrum at low T).

[Ni(dippe)H]₂ was also reacted with 1,3-dicyanobenzene at -60 °C, and observations were made that differed slightly from those seen with 1,2-dicyanobenzene (eq 5). Two pairs of doublets were observed in the ³¹P{¹H} NMR spectrum. The major pair at δ 64.8 and 76.4 ($J_{P-P} = 62$ Hz) belonged to the η^2 -nitrile complex **B1**, and the minor pair at δ 57.0 and 61.4 ($J_{P-P} = 74$ Hz) was assigned to the fluxional η^2 -C,C-arene complexes **B2–B4** (eq 6). One set of upfield peaks was seen in the corresponding ¹H NMR spectrum for the aromatic protons. When the temperature was raised to -30 °C, the resonances of the η^2 -arene complexes disappeared (see Supporting Information, Figure SI-2). Upon heating, a new complex appeared in the ³¹P{¹H} NMR spectrum (δ 70.8 and 82.5, $J_{P-P} = 26$ Hz), corresponding to the C–CN cleavage product **B5**. After heating at 60 °C for 13 h, **B1–B4** completely converted to **B5**. A single-crystal structure of **B5** was obtained and is shown in Figure 4.



Similar to 1,2-dicyanobenzene, adding another equivalent of [Ni(dippe)H]₂ to **B1** at room temperature led to the bis- η^2 -nitrile species **B6**, with a pair of sharp doublets in the ³¹P{¹H} NMR spectrum (C₆D₆, δ 63.0 and 75.2, $J_{P-P} =$ 68 Hz). The corresponding resonances in the ¹H NMR spectrum indicated C_s symmetry in **B6**, with one meta-H (δ 7.24, t, J = 8 Hz, 1H), two ortho-H (δ 7.99, d, $J_{H-H} =$ 6 Hz, 2 H), and one ortho-H between the two cyano substituents (δ 8.79, s, 1H). Upon heating, one of the two C–CN bonds was cleaved, leading to product **B7** (eq 7). **B7** has two pairs of doublets in the ³¹P{¹H} NMR spectrum (C₆D₆, δ 63.2 and 75.3, $J_{P-P} = 68$ Hz; δ 67.3 and 76.0, $J_{P-P} =$ 17 Hz), again indicating the presence of both Ni(0) and Ni(II) coordination centers in the same molecule.



Results from the computational study are summarized in Figure 5. Again, the η^2 -arene complex **SB2** lies at the center of the C–CN activation pathway. There are two different transition states located on the potential energy surface. One is **TSB12**, which connects the η^2 -nitrile complex **SB1** and **SB2**, and the other is **TSB25**, which connects **SB2** and the oxidative addition product **SB5**. The three η^2 -arene complexes **SB2**, **SB3**, and **SB4** have comparable energies and can equilibrate through a series of η^3 -allyl-like transition states



Figure 5. Energetics of C–C bond activation of 1,3-dicyanobenzene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1,3-dicyanobenzene) (PCM corrected in THF).



Figure 6. Energetics of C–C bond activation of 1,4-dicyanobenzene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1,4-dicyanobenzene) (PCM corrected in THF).

(TSB22, TSB23, TSB34, and TSB44). The barriers for nickel metal migration around the phenyl ring are much lower than the barrier for C–CN activation; thus the η^2 -arene complexes are again fluxional. SB2, SB3, and SB4 are much less stable than SB1 or SB5, which explains the disappearance of the η^2 -arene resonances upon heating. In contrast to 1,2-dicyanobenzene, the rotational migration of the [Ni(dippe)] fragment preserves the distinct phosphorus environments (see weo in Supporting Information). Instead of a singlet as seen for A2–A5, two sharp doublets were observed in the ³¹P{¹H} NMR spectrum for B2–B4. The fluxional behavior and ³¹P{¹H} spectrum of B2–B4 are similar to those seen with benzonitrile.⁷

The reaction of $[Ni(dippe)H]_2$ with 1,4-dicyanobenzene at low temperature initially formed two Ni(0) species. At -60 °C, the major product showed one pair of doublets in the ³¹P{¹H} NMR spectrum (δ 62.8 and 74.5, $J_{P-P} =$ 62 Hz), with a single corresponding resonance at δ 7.8 in the ¹H NMR spectrum, assigned to the η^2 -nitrile complex C1 (eq 8). The singlet for the aryl protons was possibly due to accidental degeneracy of the chemically distinct protons. The minor doublets at δ 55.9 and 60.1 ($J_{P-P} = 71 \text{ Hz}$) in the ³¹P{¹H} NMR spectrum and the slightly broad upfield singlet at δ 5.9 in the ¹H NMR spectrum were assigned to the equilibrating η^2 -arene complexes C2 and C2' (eq 9). The observation of two doublets in the ${}^{31}P{}^{1}H{}$ spectrum of C2/C2' was surprising, as the rotational migration of the [Ni(dippe)] unit was expected to equilibrate the phosphorus nuclei via a symmetrical η^2 -C,C intermediate. These resonances disappeared from the NMR spectrum when the mixture was warmed to 0 °C (see Supporting Information, Figure SI-3). C-CN activation occurred upon heating, leading to the Ni(II) species C3. C1 can also react with another equivalent of [Ni- $(dippe)H]_2$ to form a bis- η^2 -nitrile compound C4, which undergoes oxidative addition reaction. The formation and

Scheme 1. Reactions of [(dippe)NiH]₂ with 1-Cyanonaphthalene, 2-Cyanonaphthalene, 1-Cyano-4-methylnaphthalene, and 1,4-Dicya-



single-crystal structures of C1, C3, and C4 were described in an earlier report.^{6b}





The results from DFT calculations (Figure 6) show that the η^2 -arene complex SC2 is connected to the η^2 -nitrile SC1 by transition state TSC12 and to the oxidative addition product SC3 by another transition state, TSC23, as with the other dicyanobenzenes. TSC12 and TSC23 have structures similar to TSA12 and TSA25. In calculating the fluxional process, if the nickel migrated via η^3 -allyl-like transition states as before, it would equilibrate the two phosphorus environments as nickel moves from one cyano-substituted double bond to the other (see Supporting Information weo). This pathway includes another η^2 -arene complex with an energy higher than SC2 by 3.3 kcal mol^{-1} , in which nickel coordinates to the central double bond and has a fluxional barrier of 12 kcal mol^{-1} (see Figure SI-4). As this pathway is in contradiction with the observed phosphorus data, another migration mode was modeled in which nickel migrates between C2 and C2' via a single η^4 -coordinated transition state, TS22'_2 (eq 9). This migration pathway has a



Figure 7. ORTEP drawing of (dippe)Ni($C_{10}H_7$)(CN) (**D13**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(1), 1.872(4); Ni(1)–C(2), 1.953(5); Ni(1)– P(1), 2.1949(12); Ni(1)–P(2), 2.1805(11); C(1)–N(1), 1.138(5). Selected angles (deg): P(1)–Ni(1)–P(2), 87.48(4); C(2)–Ni(1)– C(1), 89.27(18); N(2)–C(8)–Ni(1), 175.3(4).

lower energy barrier and does not equilibrate the phosphorus environments. (Figure 6 and weo in Supporting Information). The change from [1,2] to [1,3] shifts around the ring can be attributed to the preference for binding to a double bond substituted with a cyano group.

For the dicyanobenzenes, the C–CN bond cleavage still occurs in the same way as with benzonitrile, i.e., via an η^2 -C, C adduct. For the fluxional η^2 -arene intermediates, however, the migration mode of nickel metal varies from $\eta^2 \rightarrow [\eta^3]^{\ddagger} \rightarrow \eta^2$ to $\eta^2 \rightarrow [\eta^4]^{\ddagger} \rightarrow \eta^2$ and results in different behaviors in the low- T^{31} P NMR spectra.

Reaction with Cyanonaphthalenes and Derivatives. To compare the reactivity of polycyclic aromatic nitriles for



Figure 8. Energetics of C–C bond activation of 1-cyanonaphthalene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1-cyanonaphthalene) (PCM corrected in THF).



Figure 9. ORTEP drawing of (dippe)Ni($C_{10}H_7$)(CN) (E13). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(1), 1.8779(16); Ni(1)–C(3), 1.922(5); Ni(1)–P(1), 2.2018(4); Ni(1)–P(2), 2.1809(4); C(1)–N(1), 1.139(2). Selected angles (deg): P(1)–Ni(1)–P(2), 88.919(15); C(3)–Ni(1)–C(1), 86.3(2); N(2)–C(8)–Ni(1), 178.76(16).

C-CN bond activation, [Ni(dippe)H]₂ was reacted with cyanonaphthalenes and derivatives. The reaction with 1-cyanonaphthalene at ambient temperature gave a mixture of two Ni(0) species (Scheme 1). In the ${}^{31}P{}^{1}H{}$ NMR spectrum, one had features of the η^2 -nitrile complex (D1), with two doublets at δ 62.0 and 73.8 ($J_{P-P} = 65$ Hz). The other showed two inequivalent resonances (δ 57.4 and 60.7, $J_{\rm P-P} = 61$ Hz) with three corresponding upfield resonances in the ¹H spectrum at δ 4.66, 5.93, and 6.15, implying the coordination of nickel to the substituted ring. Unlike the η^2 -arene species of the dicyanobenzenes, the latter complex is relatively stable. Upon heating or standing at room temperature, these two Ni(0) complexes slowly converted into a new product, D13, which displayed two sharp doublets in the ³¹P{¹H} NMR spectrum with $J_{P-P} = 20$ Hz and was formulated as the C-CN bond oxidative addition product (dippe)Ni(CN)(1-naphthyl) (see Figures SI-5 and SI-6). A single-crystal X-ray structure of D13 is shown in Figure 7. The coordination geometry around nickel is essentially

square planar, and the naphthalene ring is almost perpendicular to the nickel square plane (86.8°).

A DFT calculation was conducted in order to investigate the C–CN activation pathway (Figure 8). Both the η^2 -nitrile complex (SD1) and the oxidative addition product (SD13) were optimized as ground states. The potential energy surface scan from SD1 leads to the transition state TSD13, with similar coordination geometry to that seen in the dicyanobenzenes (TSA12, TSB12, and TSC12). Another transition state, TSD313, was located by a potential energy surface scan starting from SD13. The IRC calculations from TSD13 and TSD313 both led to the η^2 -arene species SD3, with nickel coordinated to the C1–C2 double bond. Ten other possible η^2 -arene complexes were modeled (SD2, SD4-12) (Figure 8). On the basis of the energies, only two isomers, SD3 and SD5, are stable enough to be observed in the experiment. There can be a fast equilibration between SD3 and SD5 (eq 10) via the η^4 -arene transition state TSD35 with a low kinetic barrier of about 7 kcal/mol. While the fluxional process results in a shift of all three proton resonances upfield, it does not render equivalent the two phosphorus environments (see Supporting Information for weo), consistent with the observation of two doublets at ambient temperature in the ${}^{31}P{}^{1}H$ NMR spectrum. A similar rearrangement via an η^4 -transition state was proposed for the complexes Ni(dippe)(η^2 -naphthalene)¹³ and Ni(PBuⁿ₃)₂(η^2 -anthracene).¹⁴



A similar situation was observed in the reaction of [Ni-(dippe)H]₂ with 2-cyanonaphthalene (Scheme 1). The ³¹P NMR spectrum of the two products indicates the presence of

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Figure 10. Energetics of C–C bond activation of 2-cyanonaphthalene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 2-cyanonaphthalene) (PCM corrected in THF).

 η^2 -nitrile and η^2 -arene complexes (see Figures SI-7 and SI-8). Upon heating, (dippe)Ni(CN)(2-naphthyl) (E13) appeared, and its single-crystal structure is shown in Figure 9. DFT computational results (Figure 10) again indicate that among all of the possible η^2 -arene species (SE3–12), only the fast equilibration between SE3 and SE5 would be observed in the NMR spectra. SE3 is the intermediate in the C–CN activation process, connecting both to the η^2 -nitrile SE1 and the oxidative addition product SE13. On the basis of the energies, the oxidative addition product SE13 would be thermodynamically preferred, and this matches the experimental observations.

To study the effect of substituents on the cyanonaphthalene, [(dippe)NiH]₂ has been reacted with 1-cyano-4-methylnaphthalene and 1,4-dicyanonaphthalene (Scheme 1). For the reaction with 1-cyano-4-methylnaphthalene, experimental results are very similar to those seen with 1-cyano- and 2-cyanonaphthalenes (Figures SI-9 and SI-10). The DFT calculations (Figure 11) show that with an electron-donating substituent in the para-position to the CN group, the energies of another two η^2 -arene species (SF8 and SF10), in which nickel coordinates to the unsubstituted ring, are now comparable to SF3 and SF5. The kinetic barrier for equilibration between the latter two via an η^4 transition state is much lower. The transition state leading to the sp³ C_{ipso}-CH₃ bond cleavage (TSF514) is about 16 kcal/ mol higher in energy than that of the C-CN bond activation (TSF313), and the Ni(II) species SF14 is about 24 kcal/mol higher in energy than SF15. Thus C-CN bond activation is highly preferred both kinetically and thermodynamically over C-CH₃ bond activation. A single-crystal structure of F13 was obtained, as shown in Figure 12.

One obvious difference in the reaction with 1,4-dicyanonaphthalene is that the η^2 -nitrile complex (G1) can barely be seen even at low temperature (Scheme 1, Figures SI-11 and SI-12). Upon heating, G1 is completely converted to the η^2 -arene species G3 (Figure 13a). G3 displays two sharp doublets in the ³¹P{¹H} NMR spectrum, indicating two inequivalent phosphorus environments and an upfield singlet at δ 5.90 (2 H) in the ¹H NMR spectrum. Upon heating to 70 °C, the ³¹P{¹H} spectrum showed the characteristics of coalescence, which might be due to the PNiP fragment rotating around the C=C double bond, which would equilibrate the two phosphorus environments. When the sample was cooled back to room temperature, the resonances of G3 appeared as two sharp doublets again. With continued heating at 75 °C, the C-CN activation product G13 started to appear. Upon heating to 80 °C for 36 h, small yellow crystals of G13 formed, and the structure is shown in Figure 13b.

The bis- η^2 -nitrile complex **G14** could also be formed by adding another equivalent of [Ni(dippe)H]₂ to **G3**, with a single new pair of doublets in the ³¹P{¹H} NMR spectrum (C₆D₆) at δ 52.7 and 65.2 (dd, $J_{P-P} = 56, 13$ Hz), indicative of two equivalent Ni(dippe) fragments coordinated to Ni(0), each with two distinct phosphorus environments. The coupling constants suggest that the nickel might coordinate to the C=C double bond next to the cyano substituent from either face of the dicyanonaphthalene molecule, as shown below. **G14** turned out to be very stable, and no C-CN cleavage was observed upon heating or irradiation ($\lambda > 300$ nm). A similar bifacial coordination has been seen in [Cp*Rh(PMe₃)]₂(μ - η^2 : η^2 -naphthalene)¹⁵ and [Ni(dtbpe)]₂(μ - η^2 : η^2 -benzene).¹⁶



DFT calculations (Figure 14) show that the η^2 -arene complex SG3 has lower energy than the η^2 -nitrile species SG1, but higher energy than the oxidative addition product

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Figure 11. Energetics of C-C bond activation of 1-cyano-4-methylnaphthalene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1-cyano-4-methylnaphthalene) (PCM corrected in THF).



Figure 12. ORTEP drawing of Ni(dippe)(CN)(4-Me-1-Naphthyl), F13. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)-C(1), 1.935(3); Ni(1)-C(12), 1.892(5); Ni(1)-P(1), 2.1952(11); Ni(1)-P(2), 2.1777(12); C(12)-N(1), 1.111(6). Selected angles (deg): P(1)-Ni(1)-P(2), 88.15(5); C(12)-Ni(1)-C(1), 89.39(16); N(1)-C(12)-Ni(1), 176.5(4).

SG13, which explains that in the experiment the η^2 -arene was initially the major product, while G13 was thermodynamically preferred. All of the η^2 -arene species are at high energies except for SG3 and SG5, which can rapidly equilibrate via the η^4 -arene transition state TSG35 without interchanging the two phosphorus environments. The equilibration also results in a C_s symmetry intermediate η^4 -arene complex and results in symmetric aromatic proton resonances in the ¹H NMR spectrum. A simulation of the PNiP fragment rotation in SG3 has also been conducted, and the kinetic barrier is very similar to that in the experiment (see Supporting Information, Figure SI-13 and weo), providing evidence that the coalescence arises from rotation of the C=C bond around the nickel. **Reaction with Cyanoanthracene and Cyanophenanthrene.** The reaction of $[Ni(dippe)H]_2$ with 9-cyanoanthracene initially formed two Ni(0) species (Scheme 2). In this case, similar to 1,4-dicyanonapthalene, the major product was the η^2 -arene species H4, displaying two doublets in the ³¹P{¹H} NMR spectrum at δ 52.5 and 71.5 with $J_{P-P} = 44$ Hz, similar to the η^2 -acridine complex reported previously.^{6b} The corresponding ¹H NMR spectrum showed four upfield proton resonances at δ 5.34, 5.58, 5.65, and 5.80, suggesting an η^4 -bound arene ring. However, the single-crystal X-ray structure, shown in Figure 15, reveals η^2 -coodination. The minor product was the Ni(0) adduct with the nitrile, H1. No C–CN activation was observed upon heating or upon irradiation ($\lambda > 300$ nm).

The computational investigation results are shown in Figure 16. The η^2 -arene complex SH4 is about 3 kcal/mol lower in energy than the η^2 -nitrile species SH1, which explains the small amount of the latter observed in the experiment even at low temperature (Figures SI-14 and SI-15). SH2 is the η^2 -arene intermediate preceding the C–CN activation. However, SH2 is much less stable compared to SH4 (>7 kcal/ mol). The transition state TSH210 leading to C-CN cleavage is 3 kcal/mol higher in energy than the free fragments (Ni(dmpe) + 9-cyanoanthracene). Thus it is highly possible that the complex decomposes rather than undergo C-CN bond activation. The instabilities of both the intermediate SH2 and transition state TSH210 result in the absence of the oxidative addition product SH10 in the experiment. The fast equilibration between SH4 and SH6 via TSH46 results in all four aromatic protons being shifted upfield in ¹H NMR spectrum. In accord with SH4 being more stable than SH6, crystallization of H4/H6 gives crystals of only H4, as shown in Figure 15. The high energy of TSH210 for C-CN cleavage suggests that substrate dissociation may occur in preference to C-CN cleavage.

In the reaction with 9-cyanophenanthrene on the other hand, both the η^2 -nitrile (I1) and η^2 -arene (I2) complexes were observed at low temperature (Scheme 2, Figure SI-16).



Figure 13. (a) ORTEP drawing of Ni(dippe)($1,2-\eta^2-1,4$ -dicyanonaphthalene) (**G3**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(1), 1.9794(11); Ni(1)–C(2), 1.9765(12); Ni(1)–P(1), 2.1866(4); Ni(1)–P(2), 2.1807(4); C(1)–C(11), 1.4404(16); C(11)–N(1), 1.1557(16); C(1)–C(2), 1.4556(16); C(2)–C(3), 1.4221(17); C(3)–C(4), 1.3704(18); C(4)–C(12), 1.4336(17); C(12)–N(2), 1.1522(17). Selected angles (deg): P(1)–Ni(1)–P(2), 92.092(15); C(2)–Ni(1)–C(1), 43.18(5); C(1)–C(11)–N(1), 178.43(14); C(4)–C(12)–N(2), 178.85(15). (b) ORTEP drawing of Ni(dippe)(CN)(4-CN-naphthyl) (**G13**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(1), 1.933(3); Ni(1)–C(12), 1.877(3); Ni(1)–P(1), 2.1847(8); Ni(1)–P(2), 2.1915(9); C(12)–N(2), 1.137(4). Selected angles (deg): P(1)–Ni(1)–P(2), 88.32(3); C(12)–Ni(1)–C(1), 88.95(12); N(2)–C(12)–Ni(1), 177.9(4); C(4)–C(11)–N(1), 178.6(4).



Figure 14. Energetics of C–C bond activation of 1,4-dicyanonaphthalene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 1,4-dicyanonaphthalene) (PCM corrected in THF).

The former has two doublets in the ³¹P{¹H} NMR spectrum at δ 61.7 and 72.5 with $J_{P-P} = 68$ Hz. The latter shows a pair of doublets at δ 55.6 and 62.6 with smaller coupling constant ($J_{P-P} = 58$ Hz). In the corresponding ¹H NMR spectrum, the resonances for the η^2 -arene species are shifted upfield compared to the η^2 -nitrile species. When the temperature was increased to 30 °C, the η^2 -nitrile complex **I1** completely converted into the η^2 -arene complex **I2**. A single-crystal X-ray structure for the η^2 -arene complex was obtained (Figure 17), which showed nickel coordinating to the C=C double bond next to the cyano substituent. Upon heating to 120 °C for 1 week in THF, no C-CN cleavage was observed. Upon irradiation for 30 min, the oxidative addition product **I18** appeared in the ³¹P{¹H} NMR spectrum, with two sharp doublets at δ 65.8 and 75.7 with $J_{P-P} = 21$ Hz. After irradiation for 36 h, only about 27% of **I18** was formed, and upon heating at 120 °C for 1 h, it was completely converted back to **I2**.

Results from DFT calculations are summarized in Figure 18. The η^2 -nitrile species **SI1** is about 1.4 kcal/mol higher in energy than the η^2 -arene species **SI2**. While both adducts could be observed at low temperature, upon warming, **SI2** is calculated to be preferred thermodyanically, consistent with the experimental observations. All other possible η^2 -arene





Figure 15. ORTEP drawing of $C_{29}H_{41}NNiP_2$ (**H4**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)–C(1), 2.0285(16); Ni(1)–C(2), 1.9634(16); Ni(1)– P(1), 2.1631(5); Ni(1)–P(2), 2.1697(5); C(1)–C(2), 1.449(3); C(2)–C(3), 1.428(3); C(3)–C(4), 1.362(3); C(4)–C(12), 1.449(2); C(1)–C(11), 1.446(2); C(11)–C(12), 1.449(2). Selected angles (deg): P(1)–Ni(1)–P(2), 92.10(2); C(2)–Ni(1)– C(1), 42.52(7); N(1)–C(15)–C(9), 178.8(2).

complexes (SI3-17) are much higher in energy than SI2 and would not be expected to be observed in the NMR spectrum. As for the 9-cyanoanthracene reaction, TSI218 for C-CN cleavage is also at high energy, and dissociation may occur in preference to C-CN activation.

In reactions of the Ni(dippe) fragment with polycyclic aromatic nitriles, the η^2 -arene complexes with nickel coordinated via the C=C double bond containing a cyano substituent were in every case the intermediates leading to C-CN bond cleavage. Among all possible structures, only certain η^2 -arenes were stable enough to be observed, and some were even more stable than the η^2 -nitrile species. The fluxional processes result from a [1,3] migration around the end of the fused polycyclic aromatic ring via an η^4 transition state. This same preference for the formation of η^2 -complexes in which the loss of resonance energy is minimized was seen in studies of Cp*Rh(PMe_3)-(polycyclic arene) complexes¹⁷ and other P₂Ni(arene) complexes.¹⁸

Conclusion

The reaction of [Ni(dippe)H]₂ with cyanobenzenes, cyanonapthalene, and derivatives at low temperature leads to the formation of both η^2 -nitrile and η^2 -arene complexes. Both converted to C-CN activation products upon heating. Due to the high polarity of the C-CN bond cleavage products, solvent effects were taken into consideration in all DFT calculations in terms of the PCM correction, and the results show excellent agreement with the experimental observations. The transition state for the C-CN cleavage was located on the potential energy surface and found to connect with the η^2 -arene complex with nickel coordinated to the C=C double bond next to the cyano substituent. In the case of 9-cyanoanthracene and 9-cyanophenanthrene, η^2 -arene species were more stable than η^2 -nitrile complexes. No C-CN cleavage was observed in the reaction with 9-cyanoanthracene, ascribed to the inability to coordinate to the tetrasubstituted double bond adjacent to the nitrile. The fluxionalities of the η^2 -arene complexes were due to lowenergy barriers for migration of the [Ni(dippe)] fragment around the aromatic ring via a series of η^3 - or η^4 -coordinated transition states.

Experimental Section

General Procedures. All reactions were carried out using standard Schlenk and glovebox techniques under nitrogen. Solvents were dried and distilled before use from sodium/ benzophenone ketyl or directly taken from an Innovative Technologies MD-6 solvent purification system. Deuterated solvents (Cambridge Isotope Laboratories) for NMR experiments were dried over sodium/benzophenone ketyl and distilled under vacuum. All other chemicals and filter aids were reagent grade and were used as received. ¹H and ³¹P{¹H} NMR spectra were determined on AVANCE400 spectrometers in THF- d_8 or toluene- d_8 ; chemical shifts (δ) are relative to the deuterated solvent residual protons, and ${}^{31}P{}^{1}H{}$ NMR spectra are relative to external 85% H₃PO₄. The synthesis of [Ni(dippe)H]₂ was carried out using the previously reported procedure.¹⁹ 1,2-, 1,3-, and 1,4-Dicyanobenzene, 1- and 2-cyanonaphthalene, 9-cyanoanthracene, and 9-cyanophenanthrene were purchased from Aldrich. 1,4-Dicyanonapthalene was obtained from Alfa Aesar, and 1-cyano-4-methylnaphthalene was obtained from Matrix Scientific. All were dried under vacuum before use.

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Figure 16. Energetics of C–C bond activation of 9-cyanoanthracene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 9-cyanoanthracene) (PCM corrected in THF).



Figure 17. ORTEP drawing of $C_{29}H_{41}NNiP_2$ (**12**). Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ni(1)-C(1), 1.9666(15); Ni(1)-C(2), 1.9608(14); Ni(1)-P(1), 2.1785(10); Ni(1)-P(2), 2.1708(11); C(1)-C(2), 1.452(2); C(1)-C(14), 1.465(2); C(1)-C(15), 1.468(3); C(15)-N(1), 1.152(3); C(2)-C(3). Selected angles (deg): P(1)-Ni(1)-P(2), 90.34(9); C(2)-Ni(1)-C(1), 43.41(6); N(1)-C(15)-C(1), 178.7(3).

Computational Details. When available, known experimental structures for the complexes were used as the starting point for the calculations. To simplify these calculations, the i-Pr groups were substituted by methyl groups. This simplification is assumed to have no steric outcome on the calculations, as established in earlier studies of both dmpe and dippe ligands on nickel.⁷ The gas-phase structures were fully optimized in redundant internal coordinates,²⁰ with density functional theory (DFT) and a wave function incorporating Becke's three-parameter hybrid functional (B3),²¹ along with the Lee–Yang–Parr

correlation functional (LYP).²² All calculations were performed using the Gaussian03 package.²³ The Ni and P atoms were represented with the effective core pseudopotentials of the Stuttgart group and the associated basis sets improved with a set of f-polarization functions for Ni ($\alpha = 3.130$)²⁴ and a set of d-polarization functions for P ($\alpha = 0.387$).²⁵ The remaining atoms (C, H, and N) were represented with 6-31G(d,p)²⁶ basis sets. The geometry optimizations were performed without any symmetry constraints, and the local minima and the transition states were checked by frequency calculations. For each transition-state structure, the intrinsic reaction coordinate (IRC) routes were calculated in both directions toward the corresponding minima. For some of the transition states, the IRC calculations failed to reach the energy minima on the potential energy surface; therefore, in those cases geometry optimizations were carried out as a continuation of the IRC path. Because of the polarity of the structures, the solvent effects on their relative stabilities were evaluated by calculating the free energies of solvation in terms of the polarizable continuum model (PCM). The self-consistent reaction field calculations using the PCM-UA0 solvation model²⁷ were carried out for the gas-phase-optimized structures. The dielectric constant in the PCM calculations was set to $\varepsilon = 7.58$ to simulate THF as the solvent media used in the experimental study. Gibbs free energies have been calculated at 298.15 K and 1 atm. The Ortep32 package was used to display the molecular structures.

Structure of [Ni(dippe)H]₂. [Ni(dippe)H]₂ was synthesized according to the previously reported procedure.¹⁹ The initial dark red, oily residue was dissolved in hexanes and slowly evaporated under vacuum, yielding thin, dark red plates. NMR spectra for [Ni(dippe)H]₂ in THF- d_8 (25 °C), ¹H: δ –9.89 (quintet, 2 H, bridging H), 1.25 (d, J_{H-H} = 36 Hz, 48 H, CH Me_2), 1.61 (s, 8 H, CH₂), 2.03 (s, 8 H, CHMe₂); ³¹P{H}: δ 73.45 (s); ¹³C: δ 19.53 (s, CH Me_2), 20.32 (s, CH₂), 23.08 (m, CHMe₂). Anal. Calcd for C₂₈H₆₆Ni₂P₄: C, 52.21; H, 10.33. Found: C, 52.20; H, 10.45.

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Figure 18. Energetics of C-C bond activation of 9-cyanophenanthrene by [Ni(dmpe)] (free energies in kcal mol⁻¹) relative to the total energies of fragments ([Ni(dmpe)] and 9-cyanophenanthrene) (PCM corrected in THF).

Reaction of $[Ni(dippe)H]_2$ with 1,2-Dicyanobenzene. [Ni-(dippe)H]_2 (10 mg, 0.016 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 1,2-dicyanobenzene (4.0 mg, 0.031 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 60 °C in the NMR probe. NMR spectra for A1 in THF- d_8 (-60 °C), ¹H: δ 7.46 (t, $J_{H-H} = 8$ Hz, 1 H, meta-H), 7.67 (t, $J_{H-H} = 8$ Hz, 1 H, meta-H), 7.65 (d, $J_{H-H} = 8$ Hz, 1 H, ortho-H), 7.76 (d, $J_{P-H} = 8$ Hz, 1 H, ortho-H); ³¹P{H}: δ 62.7 (d, $J_{P-P} = 62$ Hz), 73.5 (d, $J_{P-P} = 62$ Hz); NMR spectra for A2-5 in THF- d_8 (-60 °C), ¹H: δ 6.28 (d, $J_{P-H} = 7$ Hz, 2 H, meta-H), 5.83 (d, $J_{P-H} = 7$ Hz, 2 H, ortho-H); ³¹P{H}: δ 57.0 (s). See Supporting Information for stacked plots of VT spectra.

Isolation of (dippe)Ni(CN)(C₆H₄CN), A6. [Ni(dippe)H]₂ (10.2 mg, 0.016 mmol) was dissolved in toluene; then 1,2-dicyanobenzene (4.5 mg, 0.034 mmol) was added. After heating at 100 °C for 1 h, all species converted to A6 completely. Yelloworange crystals were obtained by vapor diffusion of a toluene solution with hexanes under an N2 atmosphere at room temperature. NMR spectra for A6 in THF- d_8 (25 °C), ¹H: δ 0.55 (dd, $J = 7.2, 14.4 \text{ Hz}, 3 \text{ H}, \text{CH}_3), 1.11 \text{ (dd}, J = 6.8, 11.2 \text{ Hz}, 3 \text{ H},$ CH₃), 1.23-1.29 (m, 6 H, CH₃), 1.33-1.45 (m, 9 H, CH₃), 1.52 $(dd, J = 7.2, 15.6 \text{ Hz}), 1.73 - 1.88 \text{ (m, 4 H, CH}_2), 2.0 - 2.06 \text{ (m, })$ 1 H, CH), 2.30 (m, 1 H, CH), 2.39 (m, 1 H, CH), 2.54 (m, 1 H, CH), 6.83 (t, J = 7.6 Hz, 1 H, meta-H), 7.07 (t, J = 7.6 Hz, 1 H, meta-H), 7.29 (1 H, ortho-H), 7.46 (t, J = 6 Hz, 1 H, ortho-H); ³¹P{H}: δ 67.1 (d, $J_{P-P} = 25$ Hz), 79.1 (d, $J_{P-P} = 25$ Hz); ¹³C: δ 16.88 (d, J = 5.1 Hz, CH₃), 17.75 (s, CH₃), 18.67 (d, J = 2.1Hz, CH₃), 19.17 (d, J = 2.6 Hz, CH₃), 19.59 (s, CH₃), 20.23 (d, J = 2.3 Hz, CH₃), 20.48 (s, CH₃), 20.51 (dd, J = 14.3, 20.1 Hz, CH_2), 21.27 (d, J = 3.9 Hz, CH_3), 22.37 (dd, J = 18.9, 24.1 Hz, CH₂), 22.86 (s, CH), 23.09 (s, CH), 26.84 (s, CH), 27.07 (d, J = 3.0 Hz, CH), 122.8 (s, CN), 122.9 (s, CH), 123.5 (s, C), 129.6 (d, J = 2.8 Hz, CH), 132.7 (s, CH), 133.2 (dd, J = 30.6, 74.0 Hz, CN), 138.3 (s, CH), 169.8 (dd, J = 27.6, 72.6 Hz, C). Anal. Calcd for C₂₂H₃₆N₂NiP₂: C, 58.83; H, 8.08; N, 6.24. Found: C, 58.55; H, 8.18; N, 6.14.

Isolation of (dippe)Ni(μ - η^2 -N,C: η^1 -C-C₆H₄CN)Ni(CN)(dippe), A8. [Ni(dippe)H]₂ (10.0 mg, 0.016 mmol) was dissolved in toluene; then 1,2-dicyanobenzene (2.5 mg, 0.017 mmol) was added. **A8** was observed to form at room temperature, along with **A6**. Yelloworange crystals were obtained by vapor diffusion of a toluene solution with hexanes under an N₂ atmosphere at room temperature. There is also one Ni(dippe)(CN)(C₆H₄CN) molecule and a toluene solvent molecule cocrystallized in the unit cell. NMR spectra for **A8** in C₆D₆ (25 °C), ¹H: δ 7.30 (s, br, 1 H), 7.66–7.70 (m, 2 H), 7.79 (m, 1 H); ³¹P{H}: δ 63.4 and 77.5 (d, *J*_{P-P} = 25 Hz), 63.1 and 74.5 (d, *J*_{P-P} = 71 Hz). Anal. Calcd for C_{61.5}H₁₀₈N₄Ni₃P₆ (corrected with 0.5 toluene): C, 58.37; H, 8.60; N, 4.43. Found: C, 58.62; H, 8.56; N, 4.24.

Reaction of [Ni(dippe)H]₂ with 1,3-Dicyanobenzene (1:2 ratio). $[Ni(dippe)H]_2$ (10 mg, 0.016 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 1,3-dicyanobenzene (4.2 mg, 0.032 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ${}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 60 °C in the NMR probe. NMR spectra for **B1** in THF- d_8 (-60 °C), ¹H: δ 7.60 (t, $J_{H-H} = 8$ Hz, 1 H, meta-H), 7.79 (d, $J_{\rm H-H}$ = 8 Hz, 1, ortho-H), 7.97 (d, $J_{\rm H-H} = 8$ Hz, 1 = H, ortho-H), 8.00 (s, 1 H, ortho-H); ³¹P{H}: δ 64.8 (d, $J_{P-P} = 62$ Hz), 76.4 (d, $J_{P-P} = 62$ Hz); NMR spectra for **B2–4** in THF- d_8 (–60 °C); ¹H: δ 7.1 (d, J_{P-H} = 4 Hz, 1 H, meta-H) (other peaks are overlapped by other protons); ${}^{31}P{H}$: δ 57.0 (d, $J_{P-P} = 74$ Hz), 61.4 (d, $J_{P-P} = 74$ Hz). After heating at 60 °C for 13 h, the oxidative addition product **B5** was the only product left. NMR spectra for **B5** in THF- d_8 (25 °C), ¹H: δ 0.93 $(dd, J = 7, 16 Hz, 6 H, CH_3), 1.12 (dd, J = 7, 14 Hz, 6 H, CH_3),$ 1.25 (dd, J = 7, 14 Hz, 6 H, CH₃), 1.42 (dd, J = 7, 16 Hz, 6 H, CH₃), 1.73–1.92 (m, 4 H, CH₂), 2.05 (m, 2 H, CH), 2.39 (m, 2 H, CH), 7.0 (m, 2 H), 7.64 (m, 2 H); ${}^{31}P{H}$: δ 68.0 (d, $J_{P-P} = 24$ Hz), 78.9 (d, $J_{P-P} = 24$ Hz); ${}^{13}C$: δ 18.18 (s, CH₃), 19.12 (s, CH_3), 19.4 (d, J = 1.5 Hz, CH_3), 20.32 (d, J = 2.9 Hz, CH_3), $20.47 (dd, J = 14.6, 21.0 Hz, CH_2), 22.76 (dd, J = 19.7, 23.7 Hz)$ CH₂), 24.82-26.33 (m, CH), 111.3 (s, br, CN), 120.8 (s, C), 126.0 (s, CH), 126.5 (s, CH), 135.0 (br, CN), 140.5 (s, CH), 142.5 (s, CH), 163.2 (dd, J = 28.3, 74.0 Hz, C). Anal. Calcd for C22H36N2NiP2: C, 58.83; H, 8.08; N, 6.24. Found: C, 58.58; H, 7.86; N, 5.98.

Reaction of [Ni(dippe)H]₂ with 1,3-Dicyanobenzene (1:1 ratio). [Ni(dippe)H]₂ (13.8 mg, 0.021 mmol) was dissolved in C_6D_6 at

room temperature; then 1,3-dicyanobenzene (3.0 mg, 0.023 mmol) was added. ¹H and ³¹P NMR spectra were recorded at 25 °C in the NMR probe showing B6. NMR spectra for B6 in THF- d_8 (25 °C), ¹H: δ 1.05 (dd, J = 6.8, 15.6 Hz, 12 H, CH₃), 1.09-1.17 (overlapped, 24 H, CH₃), 1.27 (dd, J = 7.2, 14.8 Hz, 12 H, CH₃), 1.66 (m, CH₂, 8H), 2.16 (m, 8 H, CH), 7.32 (t, J = 7.6 Hz, 1 H, meta-H), 7.61 (d, $J_{H-H} = 8.0$ Hz, 2 H, ortho-H), 8.12 (s, 1 H, ortho-H); ³¹P{H}: δ 61.0 (d, $J_{P-P} = 69$ Hz), 73.1 (d, $J_{\rm P-P} = 69 \,\rm Hz$); ¹³C: δ 19.04 (s, CH₃), 19.34 (d, $J = 2.6 \,\rm Hz$, CH₃), 19.84 (d, J = 7.6 Hz, CH₃), 20.50 (d, J = 9.0 Hz, CH₃), 20.88 $(dd, J = 14.9, 19.1 Hz, CH_2), 23.13 (t, J = 27.3 Hz, CH_2), 25.46$ (dd, J = 3.4, 13.4 Hz, CH), 26.38 (dd, J = 5.1, 17.4 Hz, CH),128.4 (s, CH), 130.0 (s, C), 130.1 (d, J = 2.5 Hz, CH), 131.7 (s, CH), 168.7 (dd, J = 8.5, 28.6 Hz, CN). Upon heating at 100 °C for 1 h, the C-CN cleavage product B7 appeared, but the major products were from decomposition. NMR spectra for B7 in C_6D_6 (25 °C), ¹H: δ 7.05 (t, J = 7 Hz, 1 H), 7.15 (m, overlapped, 2 H), 8.04 (d, J = 7 Hz, 1 H); ³¹P{H}: δ 63.2 (d, $J_{P-P} = 68$ Hz), 75.3 (d, $J_{P-P} = 68$ Hz), 67.3 (d, $J_{P-P} = 16$ Hz), 76.0 (d, $J_{P-P} = 16$ Hz) 17 Hz). The crystallization of B7 was unsuccessful because of decomposition and B5 easily deposited from the solution.

Reaction of [Ni(dippe)H]₂ with 1,4-Dicyanobenzene. [Ni- $(dippe)H_2$ (9.6 mg, 0.015 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 1,4-dicyanobenzene (4.0 mg, 0.030 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 60 \degree C in the NMR probe. NMR spectra for **C1** in THF- d_8 (-60 °C), ¹H: δ 7.81 (s, ⁴H, ortho-H); ³¹P{H}: δ 62.8 (d, $J_{P-P} = 62$ Hz), 74.5 (d, $J_{P-P} = 62$ Hz); NMR spectra for C2 in THF- d_8 (-60 °C), ¹H: δ 5.91 (s, br, 4 H, ortho-H); ³¹P{H}: δ 55.9 (d, $J_{P-P} = 71$ Hz), 60.1 (d, $J_{P-P} = 72$ Hz). NMR spectra for C1 in THF- d_8 (25 °C), ¹H: δ 1.05–1.18 (m, 18 H), 1.23-1.29 (m, 6 H), 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); ³¹P{H}: δ 67.5 (d, J = 63 Hz), 79.3 (d, J = 63 Hz). NMR spectra for C3 in THF-*d*₈ (25 °C), ¹H: δ 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 = 8Hz, 2 H); ${}^{31}P{H}$: δ (ppm) 73.1 (d, J = 24 Hz), 83.6 (d, J = 24Hz). NMR spectra for C4 in THF- d_8 (25 °C), ³¹P{H}: δ (ppm) 66.4 (d, J = 68 Hz), 78.7 (d, J = 68 Hz). ^{5b}C1–C4 were reported previously.6b IR data for C4 were recorded in the solid state $(\nu_{\rm CN} = 1739 \text{ cm}^{-1})$ and in THF solution $(\nu_{\rm CN} = 1738 \text{ cm}^{-1})$, indicating the same structure as seen in the X-ray study.6b

Reaction of [Ni(dippe)H]₂ with 1-Cyanonaphthalene. [Ni(dippe)H]₂ (9.8 mg, 0.015 mmol) was dissolved in THF-*d*₈, transferred into an NMR tube capped with a septum, and cooled to $-78 \,^{\circ}$ C in a dry ice/ acetone bath. Then 1-cyanonaphthalene (4.9 mg, 0.031 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 80 °C in the NMR probe. NMR spectra for **D1** in THF-*d*₈ ($-60 \,^{\circ}$ C), ¹H: δ 7.50 (m, 3 H), 7.54 (t, $J = 8 \,\text{Hz}, 1 \,\text{H})$, 7.86 (t, $J = 8 \,\text{Hz}, 2 \,\text{H})$, 9.51 (d, $J_{P-H} = 8 \,\text{Hz}, 1 \,\text{H})$; ³¹P{H}: δ 61.5 (d, $J_{P-P} = 68 \,\text{Hz})$, 72.6 (d, $J_{P-P} = 68 \,\text{Hz})$. NMR spectra for **D3/D5** in THF-*d*₈ ($-60 \,^{\circ}$ C), ¹H: δ 4.66 (dd, J = 5, 10 Hz, 1 H), 5.93 (d, $J = 8 \,\text{Hz}, 1 \,\text{H})$, 6.15 (dd, $J = 6, 8 \,\text{Hz}, 1 \,\text{H})$, 6.84 (t, $J = 8 \,\text{Hz}, 1 \,\text{H})$, 6.92 (d, $J = 8 \,\text{Hz}, 1 \,\text{H})$, 7.02 (t, $J = 8 \,\text{Hz}, 1 \,\text{H})$, 7.91 (d, $J = 7 \,\text{Hz}, 1 \,\text{H}$); ³¹P{H}: δ 57.4 (d, $J_{P-P} = 60 \,\text{Hz})$.

Isolation of Ni(dippe)(1-naphthyl)(CN). The mixture from the above reaction, upon standing at room temperature, eventually converted to a new species, which is the oxidative addition product Ni(dippe)(1-naphthyl)(CN), **D13**. Yellow crystals were obtained by vapor diffusion of a benzene solution with hexanes under an N₂ atmosphere at room temperature. NMR spectra for **D13** in THF- d_8 (25 °C), ¹H: δ 0.051 (dd, J = 7, 14 Hz, 3 H, CH₃), 0.927 (dd, J = 7, 16 Hz, 3 H, CH₃), 1.050 (dd, J = 7, 12 Hz, 3 H, CH₃), 1.29 (dd, J = 7, 12 Hz, 3 H, CH₃), 1.34 (dd, J = 7, 16 Hz,

3 H, CH₃), 1.37 (dd, J = 7, 14 Hz, 3 H, CH₃), 1.48 (dd, J = 7, 16 Hz, 3 H, CH₃), 1.57 (dd, J = 7, 15 Hz, 3 H, CH₃), 2.29–2.58 (m, 8 H, CH and CH₂), 7.04 (t, J = 7 Hz, 1 H), 7.24–7.29 (m, 3 H), 7.39 (t, J = 6 Hz, 1 H), 7.54 (d, J = 8 Hz, 1 H), 8.54 (d, J = 8 Hz, 1 H); ³¹P{H}: δ 64.9 (d, $J_{P-P} = 20$ Hz), 75.0 (d, $J_{P-P} = 20$ Hz).; ¹³C: δ 16.75 (s, CH₃), 17.02 (s, CH₃), 18.78 (s, CH₃), 18.92 (s, CH₃), 19.91 (s, CH₃), 20.44 (s, CH₂), 22.43 (s, CH₂), 22.55 (s, CH), 22.78 (s, CH), 122.6 (s, CH), 123.2 (s, CH), 124.9 (s, CH), 125.3 (s, C), 126.2 (s, CH), 128.7 (s, CH), 129.9 (s, CH), 133.8 (s, C), 135.0 (s, CN), 135.5 (s, CH), 143.9 (s, C). Anal. Calcd for C₂₅H₃₉NNiP₂: C, 63.32; H, 8.29; N, 2.95. Found: C, 62.85; H, 8.32; N, 2.97.

Reaction of [Ni(dippe)H]₂ with 2-Cyanonaphthalene. [Ni(dippe)H]₂ (9.8 mg, 0.015 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to $-78 \,^{\circ}$ C in a dry ice/acetone bath. Then 2-cyanonaphthalene (4.9 mg, 0.031 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 80 °C in the NMR probe. NMR spectra for E1 in THF- d_8 ($-60 \,^{\circ}$ C), ¹H: δ 7.46 (m, 2 H), 7.84 (d, $J = 8 \,\text{Hz}, 2 \,\text{H}$), 7.91 (d, $J = 8 \,\text{Hz}, 2 \,\text{H}$), 8.14 (s, 1 H); ³¹P{H}: δ 62.0 (d, $J_{P-P} = 65 \,\text{Hz}$), 73.8 (d, $J_{P-P} = 65 \,\text{Hz}$). NMR spectra for E3/5 in THF- d_8 ($-60 \,^{\circ}$ C), ¹H: δ 6.12 (dd, $J = 9 \,\text{Hz}, 1 \,\text{H}$), 6.82 (t, $J = 8 \,\text{Hz}, 1 \,\text{H}$), 6.84 (s, 1 H), 6.96 (t, $J = 6 \,\text{Hz}, 1 \,\text{H}$), 7.27 (t, $J = 8 \,\text{Hz}, 1 \,\text{H}$), 7.84 (t, 1 H); ³¹P{H}: δ 55.0 (d, $J_{P-P} = 61 \,\text{Hz}$), 64.1 (d, $J_{P-P} = 61 \,\text{Hz}$).

Isolation of Ni(dippe)(2-naphthyl)(CN). The mixture from the above reaction, upon standing at room temperature, eventually converted to a new species, which was the oxidative addition product Ni(dippe)(2-naphthyl)(CN), E13. Yellow crystals were obtained by vapor diffusion of a THF solution with hexanes under an N2 atmosphere at room temperature. NMR spectra for **E13** in THF- d_8 (25 °C), ¹H: δ 0.933 (dd, J = 7, 15 Hz, 6 H, CH₃), 1.13 (dd, J = 7, 14 Hz, 6 H, CH₃), 1.21 (dd, J = 7, 14 Hz, 6 H, CH_3), 1.30 (dd, J = 7, 13 Hz, 6 H, CH_3), 1.74–1.89 (m, 4 H, CH₂), 2.10 (m, 2 H, CH), 2.43 (m, 2 H, CH), 7.12 (t, J = 7 Hz, 1 H), 7.20 (t, J = 7 Hz, 1 H), 7.39 (d, J = 8 Hz, 1 H), 7.50 (d, J = 8 Hz, 1 H), 7.57 (d, J = 8 Hz, 1 H), 7.65 (m, 1 H), 7.71 (d, J = 6 Hz, 1 H); ³¹P{H}: δ 67.0 (d, $J_{P-P} = 22$ Hz), 77.1 (d, $J_{P-P} = 21$ Hz).; ¹³C: δ 17.70 (s, CH₃), 18.72 (s, CH₃), 19.07 (s, CH_3), 19.92 (d, J = 3.2 Hz, CH_3), 22.49 (t, J = 21.7 Hz, CH_2), 25.58 (s, CH), 25.79 (s, CH), 122.8 (s, CH), 124.1 (s, C), 124.5 (s, CH), 126.2 (s, CH), 127.8 (s, CH), 128.5 (s, CH), 131.5 (s, C), 134.0 (s, CN), 135.1 (s, CH), 136.6 (s, CH), 142.2 (m, C). Anal. Calcd for C₂₅H₃₉NNiP₂: C, 63.32; H, 8.29; N, 2.95. Found: C, 63.08; H, 8.11; N, 2.80.

Reaction of [Ni(dippe)H]₂ with 1-Cyano-4-methylnaphthalene. $[Ni(dippe)H]_2$ (10.2 mg, 0.016 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 1-cyano-4methylcyanonaphthalene (5.3 mg, 0.031 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 60 °C in the NMR probe. NMR spectra for F1 in THF- d_8 (-60 °C), ¹H: δ 2.75 (s, $3 \text{ H}, \text{CH}_3\text{-}\text{arene}), 7.39 \text{ (d}, J = 7 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (m}, 2 \text{ H}), 7.82 \text{ (d},$ J = 7 Hz, 1 H), 8.01 (d, J = 8 Hz, 1 H), 9.61 (d, J = 8 Hz, 1 H); ${}^{31}P{H}: \delta 61.4 (d, J_{P-P} = 70 \text{ Hz}), 72.7 (d, J_{P-P} = 70 \text{ Hz}); \text{NMR}$ spectra for **F3/5** in THF- d_8 (-60 °C), ¹H: δ 2.93 (s, 3 H, CH₃arene), 6.27 (d, J = 5 Hz, 1 H), 6.90 (t, J = 8 Hz, 1 H), 7.07 (m, 2 H), 7.61 (d, J = 8 Hz, 1 H), 8.18 (t, J = 9 Hz, 1 H); ³¹P{H}: δ 56.1 (d, $J_{P-P} = 62$ Hz), 60.2 (d, $J_{P-P} = 62$ Hz). Upon heating, F13 appeared as well as decomposition. After one week at room temperature, single crystals of F13 were formed in THF- d_8 solution. Yellow needle-shaped crystals could also be obtained by vapor diffusion of a THF solution with hexanes under an N₂ atmosphere at room temperature. NMR spectra for F13 in THF- d_8 (25 °C) ¹H: δ 0.059 (dd, J = 7.2, 14 Hz, 3 H, CH₃), 0.9391 (dd, J = 7.2, 16 Hz, 3 H, CH₃), 1.05 (dd, J =6.8, 11.2 Hz, 3 H, CH₃), 1.29 (dd, *J* = 7.2, 12.4 Hz, 3 H, CH₃), 1.35 (dd, J = 7.2, 16 Hz, 3 H, CH₃), 1.40 (dd, J = 7.2, 14 Hz, 3 H, CH₃), 1.48 (dd, J = 7.2, 16 Hz, 3 H, CH₃), 1.58 (dd, J = 7.6, 15.2 Hz, 3 H, CH₃), 1.65–1.79 (m, 4 H, CH₂), 2.35–2.58 (m, 4 H, CH), 2.53 (s, 3 H, CH₃(naphthalene)), 6.94 (d, J = 6.8 Hz, 1 H), 7.24–7.28 (m, 3 H), 7.77 (m, 1 H), 8.60 (m, 1 H); ³¹P{H}: δ 64.8 (d, $J_{P-P} = 20$ Hz), 75.1 (d, $J_{P-P} = 20$ Hz); ¹³C: δ 16.70 (d, J = 5.1 Hz, CH₃), 17.04 (s, CH₃), 18.82 (d, J = 14.5 Hz, CH₃), 19.29 (s, CH₃), 19.85 (s, CH₃), 20.43 (d, J = 13.5 Hz, CH₃), 21.22 (d, J = 3.9 Hz, CH₃), 20.36–20.69 (m, CH₂), 22.44 (t, J = 21.6Hz, CH₂), 22.49 (s, CH), 22.73 (s, CH), 26.55–26.68 (m, CH₃), 26.88 (s, nap-CH₃), 123.0 (s, CH), 124.6 (s, CH), 124.8 (s, CH), 126.7 (s, C), 127.5 (s, C), 129.1 (s, CH), 129.2 (s, CH), 133.6 (s, C), 134.3 (s, CN), 136.1 (s, CH), 143.9 (s, C). Anal. Calcd for C₂₆H₄₁NNiP₂: C, 63.96; H, 8.46; N, 2.87. Found: C, 63.86; H, 8.50; N, 2.86.

Reaction of [Ni(dippe)H]₂ with 1,4-Dicyanonaphthalene. [Ni- $(dippe)H]_2$ (10.2 mg, 0.016 mmol) was dissolved in THF- d_8 , transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 1,4-dicyanonaphthalene (5.6 mg, 0.031 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 70 °C in the NMR probe. NMR spectra for G1 in THF- d_8 (-60 °C), ³¹P{H}: δ 64.5 (d, J_{P-P} = 64 Hz), 75.0 (d, $J_{P-P} = 64$ Hz). NMR spectra for G3/5 in THF d_8 (-60 °C), ¹H: δ 0.79 (dd, J = 7, 16 Hz, 6 H, CH₃), 0.94 (dd, $J = 7, 13 \text{ Hz}, 6 \text{ H}, \text{CH}_3), 1.06 - 1.14 (12 \text{ H}, \text{CH}_3), 1.59 (m, 2 \text{ H}, 1.59 \text{ H})$ CH₂), 1.90 (m, 2 H, CH₂), 2.14 (m, 2 H, CH), 5.90 (s, 2 H), 7.12 (m, 2 H), 7.38 (m, 2 H); ${}^{31}P{H}$: δ 59.3 (d, J_{P-P} = 47 Hz), 62.8 (d, $J_{\rm P-P}$ = 46 Hz). Yellow crystals were obtained by vapor diffusion of a toluene solution with hexanes under an N₂ atmosphere at room temperature. NMR spectra for G3/5 in THF- d_8 (25 °C), ¹H: δ 0.879 (dd, J = 6.8, 15.2 Hz, 6 H, CH₃), 0.973 (dd, J = 7.2, 13.2 Hz, 6 H, CH₃), 1.11-1.21 (m, 12 H, CH₃), 1.56-1.66 (m, 4 H, CH₂), 1.83 (m, 2 H, CH), 2.13 (m, 2 H, CH), 5.83 (s, 2 H, ortho-H), 7.11 (m, 2 H), 7.44 (m, 2 H); ${}^{31}P{H}$; δ 61.2 (d, $J_{P-P} = 48$ Hz), 63.4 (d, $J_{P-P} = 48$ Hz); ${}^{13}C$; δ 18.93 (s, CH₃), 19.30 (s, CH_3), 19.52 (d, J = 5.3 Hz, CH_3), 19.96 (d, J = 5.5 Hz, CH_3), $20.85 (dd, J = 14.9, 22.4 Hz, CH_2), 21.99 (dd, J = 15.8, 38.7 Hz,$ CH_2), 25.30–25.71 (m, CH), 66.38 (d, J = 11.7 Hz, C), 96.76 (d, J = 3.6 Hz, CH), 121.6 (s, CN), 124.8 (s, CH), 126.7 (s, CH), 132.8 (s, C). Anal. Calcd for C₂₆H₃₈N₂NiP₂: C, 62.55; H, 7.67; N, 5.61. Found: C, 62.68; H, 7.55; N, 5.44. Upon heating a THF solution of G1 + G3 - 5 to 80 °C for 36 h, G13 formed and was crystallized from solution. NMR spectra for G13 in THF- d_8 $(25 \,^{\circ}\text{C})$, ¹H: $\delta 0.096 \,(\text{dd}, J = 7.2, 14.4 \,\text{Hz}, 3 \,\text{H}, \text{CH}_3)$, 0.968 (dd, $J = 7.2, 16.0 \text{ Hz}, 3 \text{ H}, \text{CH}_3), 1.07 (\text{dd}, J = 7.2, 12 \text{ Hz}, 3 \text{ H}, \text{CH}_3),$ $1.31 (dd, J = 7.2, 13.2 Hz, 3 H, CH_3), 1.37 (dd, J = 7.2, 16.8 Hz,$ $3 H, CH_3$, 1.41 (dd, J = 7.2, 14.4 Hz, $3 H, CH_3$), 1.49 (dd, J =7.2, 16 Hz, 3 H, CH₃), 1.58 (dd, *J* = 7.2, 15.2 Hz, 3 H, CH₃), 2.04 (m, 2H, CH₂), 2.40 (m, 2H, CH₂), 2.49-2.58 (m, 4 H, CH), 7.44–7.53 (overlapped, 3 H), 7.64 (m, 1 H), 7.99 (d, J = 8 Hz, 1 H), 8.69 (d, J = 8 Hz, 1 H); ${}^{31}P{H}$: $\delta 68.3$ (d, $J_{P-P} = 24$ Hz), 78.7 (d, $J_{P-P} = 24 \text{ Hz}$); ¹³C: δ 16.72 (d, J = 5 Hz, CH₃), 17.15 (s, CH₃), 18.79 (s, CH₃), 18.95 (s, CH₃), 19.82 (s, CH₂), 20.40 (s, CH_3), 20.50 (s, CH_3), 20.63 (s, CH_2), 21.15 (d, J = 5 Hz, CH_3), 22.33 (m, CH₂), 22.81 (s, CH), 23.04 (s, CH), 26.79 (s, CH), 26.93 (s, CH), 104.5 (s, C), 119.8 (s, C), 125.0 (s, CH), 125.9 (s, CH), 127.8 (s, CH), 128.5 (s, C), 129.8 (s, CH), 132.1 (s, C), 133.4 (s, CH), 136.6 (s, CH), 143.1 (s, C). Anal. Calcd for C₂₆H₃₈N₂NiP₂: C, 62.55; H, 7.67; N, 5.61. Found: C, 62.29; H, 7.85; N, 5.43.

Reaction of $[Ni(dippe)H]_2$ with 1,4-Dicyanonaphthalene (1:1 ratio). $[Ni(dippe)H]_2$ (11.4 mg, 0.018 mmol) was dissolved in THF- d_8 at room temperature; then 1,4-dicyanonaphthalene (2.6 mg, 0.014 mmol) was added. ¹H and ³¹P NMR spectra were recorded at 25 °C. NMR spectra for G14 in THF- d_8 (25 °C), ¹H: δ 0.495 (dd, J = 7, 15 Hz, 6 H, CH₃), 0.798 (dd, J = 7, 10 Hz, 6 H, CH₃), 1.02–1.30 (overlapped, 36 H, CH₃), 1.43–1.55 (m, 8 H, CH₂), 1.57–1.62 (m, 2 H, CH), 2.01 (m, 4 H, CH), 2.10 (m, 2 H, CH), 2.26 (m, 2 H, CH), 3.88 (d, J = 6 Hz, 2 H, ortho-H),

6.75 (m, 2 H), 7.32 (m, 2 H); ${}^{31}P{H}$: δ 50.7 (dd, $J_{P-P} = 57$, 12 Hz), 63.2 (dd, $J_{P-P} = 57$, 12 Hz); ${}^{13}C$: δ 17.64 (d, J = 4.3 Hz, CH₃), 18.05 (s, CH₃), 19.39 (s, CH₃), 19.28–19.39 (m, CH₃), 19.98–20.15 (m, CH₃), 20.69 (d, J = 7.6 Hz, CH₃), 20.91–21.39 (m, CH₂), 21.90 (d, J = 7.5 Hz, CH₃), 21.82–22.18 (m, CH₂), 24.63 (m, CH), 26.86–27.01 (m, CH), 34.75 (d, J = 17.3 Hz, C), 55.32 (d, J = 20.7 Hz, CH), 123.7 (s, CH), 125.0 (s, br, CN), 125.5 (s, CH), 133.6 (s, C).

Reaction of [Ni(dippe)H]₂ with 9-Cyanoanthracene. [Ni-(dippe)H]₂ (11.0 mg, 0.017 mmol) was dissolved in THF-d₈, transferred into an NMR tube capped with a septum, and cooled to -78 °C in a dry ice/acetone bath. Then 9-cyanoanthracene (7.2 mg, 0.034 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 80 °C in the NMR probe. NMR spectra for H1 in THF- d_8 (-60 °C), ³¹P{H}: δ 61.4 (d, J_{P-P} = 70 Hz), 69.5 (d, $J_{P-P} = 70$ Hz). NMR spectra for H4/6 in THF $d_8 (-60 \text{ °C})$, ¹H: δ 5.34 (t, J = 6 Hz, 1 H), 5.58 (t, J = 6 Hz, 1 H), 5.65 (s, br, 1 H), 5.80 (s, br, 1 H), 6.93 (s, br, 1 H), 6.98 (t, J = 8 Hz, 1 H), 7.13 (t, J = 8 Hz, 1 H), 7.26 (d, J = 8 Hz, 1 H), 7.47 (d, J = 8 Hz, 1 H); ³¹P{H}: δ 52.5 (d, $J_{P-P} = 33$ Hz), 71.5 (d, $J_{\rm P-P}$ = 33 Hz). The mixture was dissolved in benzene and allowed to slowly evaporate under a nitrogen atmosphere, producing dark purple crystals. NMR spectra for H4 in THF d_8 (25 °C), ¹H: δ 0.611 (dd, J = 7.2, 15.2 Hz, 3 H, CH₃), 0.915-1.18 (m, 21 H, CH₃), 1.47-1.57 (m, 4 H, CH₂), 1.703-1.79 (m, 2 H, CH), 1.94-2.03 (m, 2 H, CH), 5.49 (s, 1 H), 5.60 (s, 1 H), 5.72 (s, 1 H), 5.88 (s, 1 H), 7.03 (t, J = 7.2 Hz, 1 H) 7.08 (s, 1 H), 7.17 (t, J = 7.2 Hz, 1 H), 7.32 (t, J = 8 Hz, 1 H), 7.62 (d, J = 8.4 Hz, 1 H); ³¹P{H}: δ 53.1 (d, $J_{P-P} = 42$ Hz), 69.1 (d, $J_{P-P} = 42$ Hz); ¹³C: δ 18.61 (s, CH₃), 18.95 (s, CH₃), 19.03 (s, CH₃), 19.36 (s, CH₃), 19.73 (s, CH₃), 19.81 (s, CH₃), 19.88 (s, CH_3), 20.14 (d, J = 6.6 Hz, CH_3), 21.39–22.28 (m, CH_2), 24.83-26.74 (m, CH), 73.12 (d, J = 11.1 Hz, CH), 78.28 (d, J = 5.8 Hz, CH), 94.15 (d, J = 8.2 Hz, CH), 94.89 (s, CN), 97.35 (s, CH), 119.8 (s, C), 120.2 (s, CH), 123.8 (s, CH), 124.4 (s, CH), 125.9 (s, CH), 127.2 (s, CH), 132.4 (s, C), 133.3 (s, C), 138.6 (s, C), 147.5 (s, C). Anal. Calcd for C₂₅H₃₉NNiP₂: C, 66.44; H, 7.88; N, 2.67. Found: C, 66.09; H, 7.18; N, 3.14.

Reaction of [Ni(dippe)H]₂ with 9-Cyanophenanthrene. [Ni-(dippe)H]₂ (10.6 mg, 0.016 mmol) was dissolved in THF-d₈, transferred into an NMR tube capped with a septum, and cooled to -78 °C in dry ice/acetone bath. Then 9-cyanonphenanthrene (6.2 mg, 0.030 mmol, dissolved in 0.02 mL of THF) was added while the tube was still in the bath. ¹H and ³¹P NMR spectra were recorded once every 10 °C as the reaction mixture was warmed from -60 to 60 °C in the NMR probe. NMR spectra for I1 in THF- d_8 (-60 °C), ¹H: δ 7.61 (d, J = 7 Hz, 1 H), 7.69 (m, 3 H), 7.99 (d, J = 8 Hz, 1 H), 8.26 (s, 1 H), 8.84 (m, 2 H), 9.76 (s, br, 1 H); ³¹P{H}: δ 61.7 (d, $J_{P-P} = 68$ Hz), 72.5 (d, $J_{\rm P-P} = 68$ Hz); NMR spectra for I2 in THF- d_8 (-60 °C), ¹H: δ 7.01 (m, 2 H), 7.07 (t, J = 7 Hz, 1 H), 7.20 (t, J = 8 Hz, 1 H), 7.37 (d, J = 8 Hz, 1 H), 7.74 (d, J = 8 Hz, 1 H), 7.83 (m, 2 H), 7.99 (d, J = 8 Hz, 1 H); ³¹P{H}: δ 55.6 (d, $J_{P-P} = 57$ Hz), 62.6 (d, $J_{\rm P-P}$ = 58 Hz). Single crystals of **I2** were obtained by vapor diffusion of a toluene solution with pentane under an N₂ atmosphere at room temperature. NMR spectra for I2 in THF- d_8 (25 °C), ¹H: $\delta 0.209 \text{ (dd, } J = 6.8, 16.4 \text{ Hz}, 3 \text{ H}, \text{CH}_3), 0.350 \text{ (dd, }$ $J = 7.2, 15.6 \text{ Hz}, 3 \text{ H}, \text{CH}_3), 0.754 \text{ (dd}, J = 7.2, 10.8 \text{ Hz}, 3 \text{ H},$ CH_3), 0.858 (dd, J = 7.2, 10 Hz, 3 H, CH_3), 1.08–1.21 (m, 6 H, CH₃), 1.33-1.39 (m, 6 H, CH₃), 1.41-1.66 (m, 6 H, CH and CH₂), 2.03–2.08 (m, 2 H, CH₂), 4.67 (t, J = 5.6 Hz, 1 H), 7.0 (q, J = 8, 16.8 Hz, 2 H), 7.08 (t, J = 7.2 Hz, 1 H), 7.20 (t, J = 7.6 Hz), 7.08 (t, J = 7.6 Hz)1 H) 7.40 (d, J = 7.6 Hz, 1 H), 7.82 (d, J = 5.6 Hz, 2 H), 7.88 (d, J = 8 Hz, 1 H); ³¹P{H}: δ 55.2 (d, $J_{P-P} = 59$ Hz), 61.8 (d, $J_{P-P} = 59 \text{ Hz}$; ¹³C: δ 17.18 (d, J = 5.1 Hz, CH₃), 17.89 (s, CH₃), 19.34 (d, J = 5.8 Hz, CH₃), 19.78 (d, J = 7.4 Hz, CH₃), 19.95–20.13 (m, CH₃), 20.97 (d, J = 6.2 Hz, CH₃), 21.27 (dd, J = 3.8, 27.4 Hz, CH), 20.94-21.59 (m, CH₂), 24.14 (dd, J)

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J = 3.7, 15.8 Hz, CH, 26.63-26.92 (m, CH, 34.74 (d, J = 18.5 Hz, C), 50.68 (d, J = 21.8 Hz, CH), 122.9 (s, CH), 123.0 (s, CH), 123.1 (s, CH), 123.3 (s, CH), 123.9 (s, br, CN), 126.2 (s, CH), 126.5 (s, CH), 127.8 (d, J = 3.2 Hz, CH), 128.4 (s, CH), 128.6 (s, CH), 130.3 (d, J = 2.5 Hz, C), 135.8 (d, J = 3.6 Hz, C), 140.0 (d, J = 4.5 Hz, C). Irradiation of the sample for 36 h producted ~27% **118**. NMR spectra for **118** in THF-*d*₈ (25 °C), ¹H: δ 0.034 (dd, $J = 7, 14 \text{ Hz}, 3 \text{ H, CH}_3$), 7.33 (m, 1 H), 7.42 (m, 1 H), 7.53 (t, J = 7 Hz, 2 H), 7.71 (s, 1 H), 7.59 (t, J = 7 Hz, 2 H), 8.72 (d, J = 8 Hz, 1 H); ³¹P{H}: δ 52.7 (dd, $J_{P-P} = 56, 13 \text{ Hz}$), 65.2 (dd, $J_{P-P} = 56, 13 \text{ Hz}$). Anal. Calcd for C₂₉H₄₁NNiP₂: C, 66.44; H, 7.88; N, 2.67. Found: C, 66.25; H, 7.76; N, 2.65.

Acknowledgment. We would like to acknowledge the U.S. Department of Energy, Office of Basic Energy Sciences, grant DE-FG02-86ER13569, for financial support.

Supporting Information Available: NMR spectra at ambient temperature, VT NMR spectra, tables and pictures of calculated stable structures and transition states, and Cartesian coordinates of the optimized geometries from DFT calculations are available. Movies showing the fluxional processes and C–CN cleavage reactions. Full details of the X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org. The structures are available from the Cambridge Crystallographic Database as CCDC 759830–759839 and 772709.