Reversible Cleavage of Carbon−Carbon Bonds in Benzonitrile Using Nickel(0)

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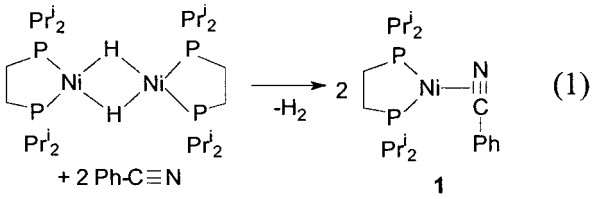
Summary: The nickel(0) fragment [(dippe)Ni] has been found to π-coordinate to the CN bond of benzonitrile and undergo reversible insertion into the Ph−CN bond.

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 last bond remains 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 reversible.

The nickel dimer $[(dippe)NiH]_2$ has been reported to be capable of cleaving the C−S bond in a variety of thiophenes[2] and the C−C bond in biphenylene.[3] The hydrido dimer serves as a source of the nickel(0) fragment [Ni(dippe)], which undergoes oxidative addition to a variety of substrates. We have discovered that the reaction of $[(dippe)NiH]_2$ with benzonitrile in THF-d_8 solution leads to the rapid formation of the η^2-nitrile complex (dippe)Ni(η^2-NCPh) (**1**). The solution of the



wine red dihydride complex becomes yellow as the reaction occurs, and the product can be isolated by crystallization at low temperature. The ^{31}P NMR spectrum (162 MHz) 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 and three resonances for the phenyl ring.[4] The IR spectrum in THF solution shows ν_{C-N} at 1745 cm^{-1}, reduced from the free ligand value of 2235 cm^{-1}. The ^{13}C NMR spectrum shows a downfield

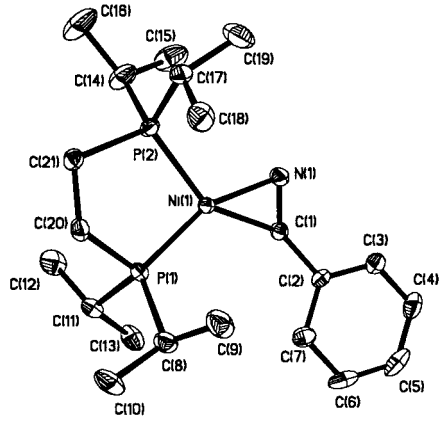


Figure 1. ORTEP drawing of (dippe)Ni(η^2-NCPh) (**1**). Ellipsoids are shown at the 30% level. Selected distances (Å) and angles (deg): N(1)−C(1) = 1.225(6), Ni(1)−N(1) = 1.908(3), Ni(1)−C(1) = 1.867(4), C(1)−C(2) = 1.475(6); N(1)−C(1)−C(2) = 136.1(4).

shift of the benzonitrile C≡N carbon 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.

Crystals of **1** were formed by cooling a solution to −30 °C, and the single-crystal X-ray structure was determined at −80 °C (Figure 1).[5] The three-coordinate Ni(0) complex is essentially planar, with the C and N atoms of the benzonitrile ligand completing the corners of the square plane. Other P_2Ni^0−π-alkyne complexes are known to adopt a similar geometry.[6] The N1−C1−C2 angle of 150.9° is indicative of a significant amount of π-back-bonding to the CN group and, as such, adds enough d^8 Ni(II) metallaazacyclopropane 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). Also to be noted is that the phenyl group is coplanar with the Ni1−N1−C1 plane and the square plane of the complex, suggesting an electronic preference for this

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(4) For **1**: ^{1}H NMR (THF-d_8) δ 1.05−1.18 (m, 20 H), 1.23−1.29 (dd, 4 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 NMR (THF-d_8) δ 66.4 (d, J = 68 Hz), 78.6 (d, J = 68 Hz).

(5) Crystal data for the X-ray structural determination of **1**: $C_{21}H_{37}NP_2Ni$, M_r = 424.17, hexagonal, $a = b$ = 11.3315(4) Å, c = 30.9995(14) Å, V = 3447.1(2) Å^3, T = 193 K, space group $P6_5$ (No. 170), Z = 6, μ(Mo Kα) = 0.988 mm^{-1}, 15 786 reflections measured, 3294 unique (R_{int} = 0.0464), which were used in calculations. The final wR2(F^2) value was 0.0919 (R1 = 0.0412, all data).

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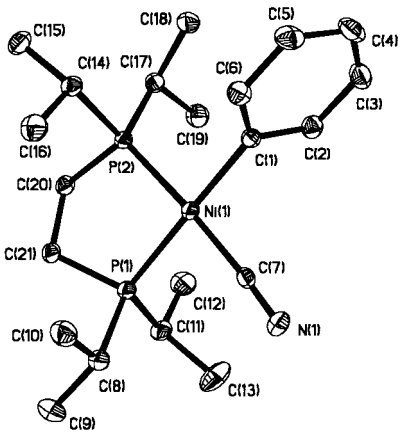
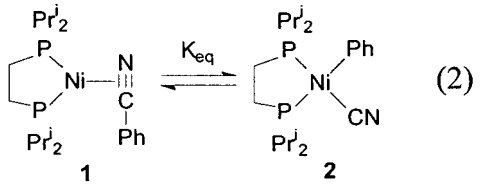


Figure 2. ORTEP drawing of (dippe)Ni(Ph)(CN) (**2**). Ellipsoids are shown at the 30% level. Selected distances (Å) and angles (deg): N(1)−C(7) = 1.148(3), Ni(1)−C(1) = 1.935(2), Ni(1)−C(7) = 1.877(3); C(1)−Ni(1)−C(7) = 89.62(10).

geometry. The ^{1}H NMR spectrum, however, shows no evidence for hindered rotation around the C1−C2 bond.

If a THF solution of **1** is allowed to stand at room temperature, a new product is observed to grow in over several days as the solution turns a pale yellow. The new product **2** has symmetry similar to that of **1**, as the ^{1}H and ^{31}P NMR spectra also display similar patterns of resonances.[7] The coupling constant J_{P-P} in the ^{31}P NMR spectrum is now only 20.6 Hz, and the IR spectrum of **2** shows ν_{C-N} at 2108 cm^{-1}. The ^{13}C NMR spectrum shows the C≡N π-coordinated to nickel at δ 138.1 (dd, J = 80.5, 30.2 Hz). Crystals of **2** 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 2).[8] The C7−N1 distance is only 1.148(3) Å, and the C1−Ni−C7 bond angle is 89.6(1)°. Note that the phenyl group now rotates to be perpendicular to the square plane of the complex.

Interestingly, the formation of **2** from **1** did not go to completion. This observation suggested that perhaps the reaction was reversible and equilibrium had been reached (eq 2). Indeed, when isolated crystals of pure **2**



(2)

were redissolved in THF-d_8, **1** was seen to be regenerated at the expense of **2**. The equilibrium constant K_{eq} was found to be ∼1 at 91 °C. The ratio of **1** to **2** was found to vary with temperature, and determination of

(7) For **2**: ^{1}H NMR (THF-d_8) δ 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 NMR (THF-d_8) δ 71.2 (d, J = 20.6 Hz), 81.7 (d, J = 20.6 Hz).

(8) Crystal data for the X-ray structural determination of **2**: $C_{21}H_{37}NP_2Ni$, M_r = 424.17, orthorhombic, a = 15.9459(6) Å, b = 14.2501(6) Å, c = 19.9039(8) Å, V = 4522.8(3) Å^3, T = 193 K, space group *Pbca* (No. 61), Z = 8, μ(Mo Kα) = 1.004 mm^{-1}, 19 318 reflections measured, 3253 unique (R_{int} = 0.0409), which were used in calculations. The final wR2(F^2) value was 0.0675 (R1 = 0.0450, all data).

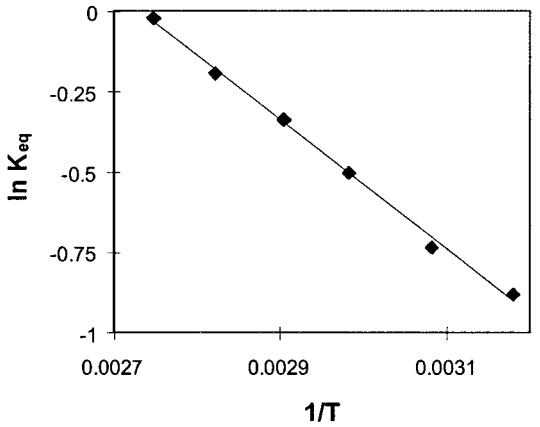


Figure 3. van't Hoff plot for the equilibrium shown in eq 2.

K_{eq} over the temperature range 41−91 °C allowed for the extraction 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 3). While a few examples of C−CN cleavage have been reported,[9] the reversibility of this reaction is not well-documented.[10] The present observations are particularly impressive, considering the strength of the C−CN bond in benzonitrile (132.7 kcal/mol).[11] η^2-Coordination of nitriles is also known.[12] Control of the reversibility might lead to improved regioselectivity in the hydrocyanation of olefins.

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Supporting Information Available: Tables giving crystallographic data, intramolecular distances and angles, and positional and thermal parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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