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

Juventino J. Garcia[†] and William D. Jones*[,‡]

Facultad de Química, Universidad Nacional Autonoma de Mexico, Mexico, D.F. 04510, Mexico, and Department of Chemistry, University of Rochester, Rochester, New York 14627

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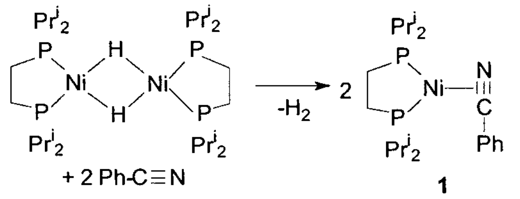
Summary: The nickel(0) fragment [(dippe)Ni] has been found to π-coordinate to the CN bond of benzonitrile and undergo reversible insertion into the Ph−CN bond.

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 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.



(1)

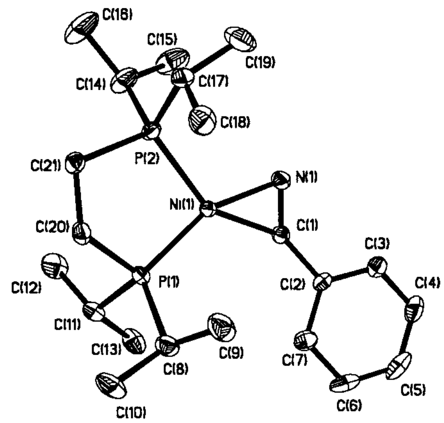


Figure 1. ORTEP drawing of (dippe)Ni(η^2-NCPh) (**1**). Ellipsoids are shown at the 30% level. Selected distances (Å) and angles (deg): N(1)−C(1) = 1.225(6), Ni(1)−N(1) = 1.908(3), Ni(1)−C(1) = 1.867(4), C(1)−C(2) = 1.475(6); N(1)−C(1)−C(2) = 136.1(4).

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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[†] Universidad Nacional Autonoma de Mexico.

[‡] University of Rochester.

(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: Berlin, 1999.

(2) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855−10856. Vicic, D. A.; Jones, W. D. *Organometallics* **1998**, *17*, 3411−3413. Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784−4794.

(3) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784−4794. Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040−4049.

(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).

(6) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040. Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4660−4668.

10.1021/om0008474 CCC: $19.00

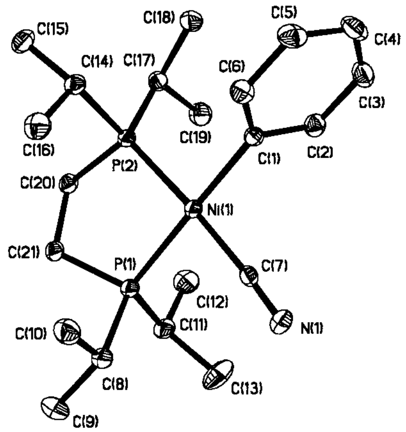
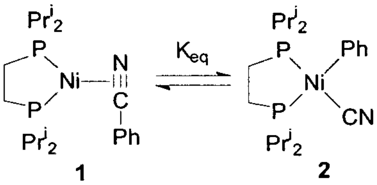


Figure 2. ORTEP drawing of (dippe)Ni(Ph)(CN) (**2**). Ellipsoids are shown at the 30% level. Selected distances (Å) and angles (deg): N(1)−C(7) = 1.148(3), Ni(1)−C(1) = 1.935(2), Ni(1)−C(7) = 1.877(3); C(1)−Ni(1)−C(7) = 89.62(10).

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** 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 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.



(2)

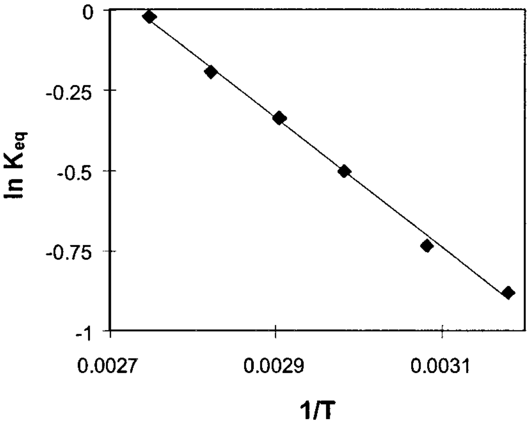


Figure 3. van't Hoff plot for the equilibrium shown in eq 2.

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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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[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).

[9] 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, A. *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.

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

[11] 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 69; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899 (http://webbook.nist.gov), 2000.

[12] 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.