

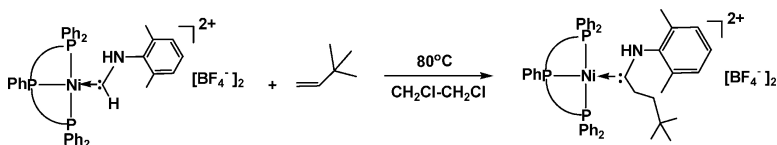
Communication

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J. Am. Chem. Soc., **2003**, 125 (32), 9564-9565 • DOI: 10.1021/ja030108p • Publication Date (Web): 22 July 2003

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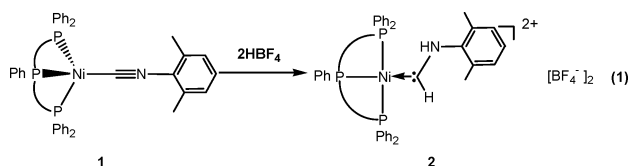
Hydrocarbation Chemistry Proceeding from Nickel Carbenes

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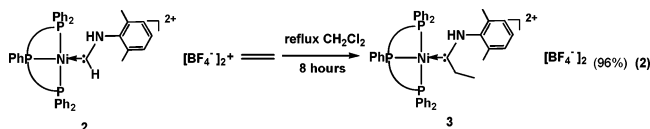
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Transition metal-mediated carbon–carbon bond formations have provided important new synthetic routes to many organic compounds.^{1,2} In many cases, mechanistic studies demonstrate that metal carbene complexes are intermediates.³ We recently reported an efficient route to *N*-aryl nickel (II) carbenes by protonation of the corresponding nickel (0) isocyanide complexes, eq 1.⁴



Nearly 20 years ago, Casey and co-workers reported a new class of carbon–carbon bond-forming reactions “hydrocarbations” because they involved the direct C–H bond addition across the C=C double bond of alkenes.⁵ They showed that a cationic bridging iron-methylidyne complex undergoes this type of reaction with alkenes with anti-Markovnikov regioselectivity.⁶ To our knowledge, no additional examples of hydrocarbations have been subsequently reported. In principle, hydrocarbation, together with hydroboration⁷ and hydrozirconation,⁸ represents a potentially general reaction type for adding carbon-to-hydrogen bonds to alkenes. Here we report our ongoing studies of the cationic nickel aminocarbene complex **2**,⁴ its hydrocarbation chemistry with alkenes, and mechanistic studies.

Refluxing a solution of **2** in methylene chloride at 40 °C under an ethylene atmosphere for 8 h results in complete conversion to the ethylcarbene complex **3** [Ni(triphos)C(CH₂CH₃)N(H)xylyl]²⁺(BF₄⁻)₂, (triphos = Bis(2-diphenylphosphinoethyl)phenylphosphine) eq 2. Recrystallization of the product from methylene chloride/ether gave single crystals of **3** suitable for X-ray crystallography, Figure 1.



The coordination geometry about the nickel center is approximately square planar, as expected for a 16e⁻ Ni (II) complex. The C(5)–N(1) bond distance (1.302 (3) Å) is shorter than a typical C–N single bond (1.472 (5) Å) but longer than the C–N triple bond of isocyanides (1.157 (5) Å). The three substituents on the carbene carbon C(5) are coplanar, consistent with sp² character of the carbon atom. The nickel–carbon bond distance of **3**, *d*(Ni1–C5) = 1.901 (2) Å is 0.114 Å longer than the Ni–C distance of isocyanide complex **1**, and 0.041 Å longer than the Ni–C distance of **2**. The metrical parameters therefore show significant iminium alkyl character (c), similar to that observed in parent carbene, **2** (Scheme 1).⁴

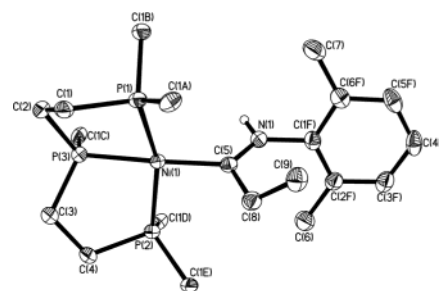
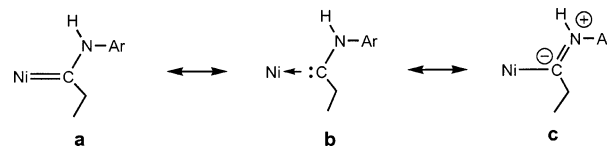
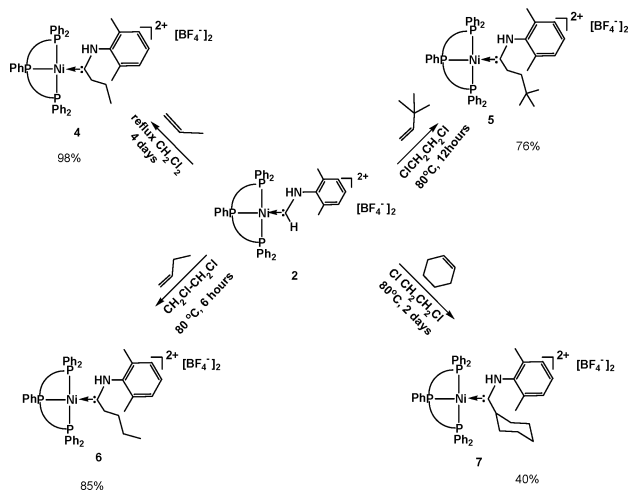


Figure 1. ORTEP diagram of **3**. Phenyl rings on the phosphorus atoms are not included. Selected bond distances (Å) and angles (deg) are as follows: Ni(1)–C(5), 1.901(2); N(1)–C(5), 1.302(3); N(1)–C(1F), 1.452(3); C(5)–C(8), 1.512(4); C(5)–N(1)–C(1F), 128.4(2); N(1)–C(5)–Ni(1), 120.70(19); C(8)–C(5)–Ni(1), 120.22(18); N(1)–C(5)–C(8), 119.0(2).

Scheme 1



Scheme 2. Hydrocarbation of Alkenes with Complex 2



Complex **2** reacts with cyclohexene, propene, 1-butene, and 3,3-dimethyl 1-butene quantitatively and regioselectively to give the anti-Markovnikov hydrocarbation products (Scheme 2). Thus, the regiochemistry is the same as that of hydroboration reactions and the hydrocarbation reactions reported by Casey.⁶ The structures of propyl carbene complex [Ni(triphos)C(CH₂CH₂CH₃)N(H)xylyl]²⁺(BF₄⁻)₂ (**4**), isohexyl carbene [Ni(triphos)C(CH₂CH₂C(CH₃)₃)N(H)xylyl]²⁺(BF₄⁻)₂ (**5**) and cyclohexyl carbene [Ni(triphos)-C(C₆H₁₁)N(H)xylyl]²⁺(BF₄⁻)₂ (**7**) are further established by X-ray crystallography, Figures 2, 3.⁹

Mechanistic studies suggest the importance of a “hydride” pathway over “alkene” (metallocycle formation or carbocation)

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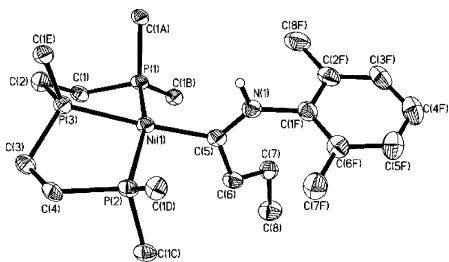


Figure 2. ORTEP diagram of **4**. Phenyl rings on the phosphorus atoms are not included. Selected bond distances (Å) and angles (deg) are as follows: Ni(1)–C(5), 1.914(4); N(1)–C(5), 1.305(5); N(1)–C(1F), 1.458(5); C(5)–C(6), 1.500(5); C(5)–N(1)–C(1F), 130.2(3); N(1)–C(5)–Ni(1), 120.3(3); C(6)–C(5)–Ni(1), 120.6(3); N(1)–C(5)–C(6), 119.1(3).

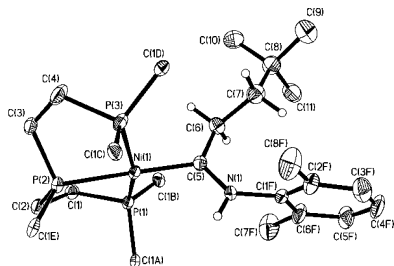
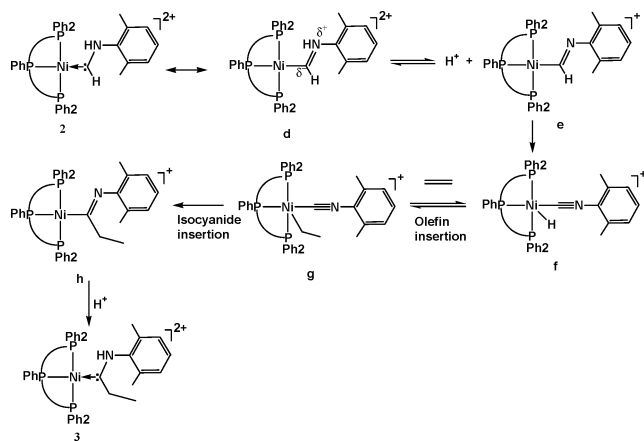


Figure 3. ORTEP diagram of **5**. Phenyl rings on the phosphorus atoms are not included. Selected bond distances (Å) and angles (deg) are as follows: Ni(1)–C(5), 1.908(6); N(1)–C(5), 1.318(8); N(1)–C(1F), 1.461(8); C(5)–C(6), 1.503(8); C(5)–N(1)–C(1F), 132.3(5); N(1)–C(5)–Ni(1), 120.0(4); C(6)–C(5)–Ni(1), 120.7(4); N(1)–C(5)–C(6), 119.2(5).

Scheme 3. Hydride Pathway of Hydrocarbation



pathways. This mechanism is briefly summarized here (Scheme 3). From the preparation of **2**, one would expect very acidic protons on both the carbene carbon and the nitrogen. The crystal structure of **2** further indicates significant iminium formyl ground-state character of **2**.⁴ α -Hydrogen elimination is the microscopic reverse of hydride insertion/imino formyl formation and would give the

nickel (II) hydride complex (**f**). Subsequent olefin insertion and isocyanide insertion gives hydrocarbation product **3**.

The hydride mechanism is supported by the following observations: Isotope labeling experiments by using d_4 -ethylene or $[\text{Ni}(\text{triphos})\text{C}(\text{D})\text{N}(\text{D})\text{xylyl}]^{2+}(\text{CF}_3\text{SO}_3^-)_2$ showed deuterium at both the methylene group and the methyl group of the α -ethyl carbene **3**.¹⁰ The alkene pathways (either form metallocycle or carbocation) would not give a mixed result.

When ethylene was bubbled into the hydrocarbation product of propene $[\text{Ni}(\text{triphos})\text{C}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{N}(\text{H})\text{xylyl}]^{2+}(\text{BF}_4^-)_2$ (**4**), there was no alkyl exchange after refluxing for several days. The corresponding ethyl complex reaction with propene showed no alkyl exchange either. This result rules out a reversible alkene pathway as the source of H/D scrambling.

Upon addition of weak, noncoordinating bases such as 2,6-lutidine to methylene chloride solutions of **2**, the formation of nickel hydride complex **f** was detected by ¹H NMR showing the hydride peak (dt) centered at -11.5 ppm, while IR showed $\nu(\text{CN})$ for the isocyanide ligand at 2129 cm^{-1} . Deliberate formation of hydride intermediate **f** greatly accelerates the rate of formation of hydrocarbation product.

These results demonstrate a surprisingly ‘classical’ organometallic mechanism for a decidedly ‘nonclassical’ class of carbon–carbon bond-forming ‘hydrocarbation’ reactions.

Acknowledgment. We gratefully acknowledge the DOE (DE-FG03-99ER14992) for support.

Supporting Information Available: Tables of crystallographic data collection and refinement parameters, position and thermal parameters, bond distances and angles for **3**, **4**, **5**, and **7** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Sausalito, California, 1999. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, California, 1987.
- (2) Söderberg, Björn C. G. *Coord. Chem. Rev.* **2002**, *224*, 171.
- (3) (a) Ivin, J. J. *Olefin Metathesis*; Academic Press: New York, 1983. (b) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: New York, 1984. (c) Doyle, Michael P. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I. Ed.; Wiley-VCH: New York, 2000; p 191.
- (4) Hou, H.; Gantzel, P. K.; Kubiak, C. P. *Organometallics* **2003**, *22*, 2817.
- (5) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950.
- (6) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043.
- (7) (a) Brown, H. C.; Ramachandran, P. V. *Pure Appl. Chem.* **1994**, *66*, 201. (b) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.
- (8) (a) Wipf, P.; Takahashi, H.; Zhuang, N. *Pure Appl. Chem.* **1998**, *70*, 1077. (b) Kalesse, M. *Acros Org. Acta* **1995**, *1*, 29.
- (9) For crystal structure of complex **7**, see Supporting Information.
- (10) The reaction of **2** with d_4 -ethylene gives 60% $[\text{Ni}(\text{triphos})\text{C}(\text{CD}_2\text{CD}_2\text{H})\text{N}(\text{H})\text{xylyl}]^{2+}(\text{BF}_4^-)_2$ and 40% $[\text{Ni}(\text{triphos})\text{C}(\text{CDHCD}_3)\text{N}(\text{H})\text{xylyl}]^{2+}(\text{BF}_4^-)_2$, while reaction of $[\text{Ni}(\text{triphos})\text{C}(\text{D})\text{N}(\text{D})\text{xylyl}]^{2+}(\text{CF}_3\text{SO}_3^-)_2$ with ethylene gives 74% $[\text{Ni}(\text{triphos})(\text{CH}_2\text{CH}_2\text{D})\text{N}(\text{D})\text{xylyl}]^{2+}(\text{CF}_3\text{SO}_3^-)_2$ and 26% $[\text{Ni}(\text{triphos})(\text{CHDCH}_3)\text{N}(\text{D})\text{xylyl}]^{2+}(\text{CF}_3\text{SO}_3^-)_2$.

JA030108P