## Efficient Synthesis of N-Aryl Nickel(II) Carbenes by Protonation of Nickel(0) Isocyanide Complexes

Hongyi Hou, Peter K. Gantzel,<sup>†</sup> and Clifford P. Kubiak\*

Department of Chemistry and Biochemistry, University of California at San Diego, 9500 Gilman Drive, La Jolla, California 92093-0358

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Summary: The new nickel isocyanide complex [Ni(triphos)(CN-xylyl)] (1) has been prepared by the reaction of Ni(COD)<sub>2</sub>, triphos (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine), and CN-xylyl (xylyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Complex 1 adds 2 equiv of HBF<sub>4</sub> to afford a stable dicationic nickel carbene complex, [Ni(triphos)-C(H)N(H)xylyl]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub><sup>-</sup> (2), in high yield. Nickel carbene 2 exhibits transfer hydrogenation of ketones.

Transition metal carbene complexes are useful catalysts and important intermediates in the synthesis of organic molecules. Carbene complexes play key roles in olefin metathesis, cyclopropanation, furan synthesis, and C-C coupling reactions.<sup>1</sup> Although palladium and platinum carbene complexes have been widely used in Heck and Suzuki type reactions,<sup>2</sup> nickel carbones have been less thoroughly studied.<sup>3</sup> Among the nickel carbene complexes, heteroatom-stabilized (Fischer) carbenes represent the vast majority.<sup>4</sup> The typical route to methoxy(amino) or bis(amino) carbene complexes is nucleophilic attack of alcohols or amines on coordinated isocyanides.<sup>5</sup> We now report the preparation of a new nickel(0) isocyanide complex, [Ni(triphos)(CN-xylyl)] (1), and its straightforward conversion to nickel carbene complexes, by protonation.

The Ni(0) isocyanide complex [Ni(triphos)(CN-xylyl)] (1) was prepared by addition of 1 equiv of triphos (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine) and 1 equiv of CN-xylyl (xylyl =  $2,6-Me_2C_6H_3$ )

**Figure 1.** ORTEP drawing of [Ni(triphos)(CN-xylyl)] (1) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)-C(43), 1.787(3); Ni(1)-P(1), 2.1405-(8); Ni(1)-P(3), 2.1455(8); Ni(1)-P(2), 2.1493(8); N(1)-C(43), 1.172(3); N(1)-C(31), 1.381(3); C(43)-Ni(1)-P(1), 121.99(8); C(43)-Ni(1)-P(3), 117.71(8); P(1)-Ni(1)-P(3), 90.49(3); C(43)-Ni(1)-P(2), 116.97(8); P(1)-Ni(1)-P(2), 89.80(3); P(3)-Ni(1)-P(2), 114.20(3); C(43)-N(1)-C(31), 168.7(3).

to 1 equiv of  $Ni(COD)_2^6$  (COD = 1,5-cyclooctadiene) at room temperature in THF.<sup>7</sup>

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** in THF consists of a triplet and a doublet centered at 63.7 and 48.2 ppm with J = 44.3 Hz and a ratio of 1:2. The IR showed an intense  $\nu$ (CN) stretching band at 1992 cm<sup>-1</sup>. In the solid state, **1** is stable indefinitely under an inert atmosphere and is stable for several hours in air. The complex is also stable in organic solvents in the absence of oxygen. The

 $<sup>\</sup>ast$  To whom correspondence should be addressed. E-mail: <code>ckubiak@ucsd.edu</code>.

 $<sup>^\</sup>dagger$  Address correspondence pertaining to crystallographic studies to this author. E-mail: pgantzel@ucsd.edu.

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<sup>(7)</sup> Ni(COD)<sub>2</sub> (275 mg, 1 mmol), triphos (534 mg, 1 mmol), and CNxylyl (131 mg, 1 mmol) were added to a 50 mL round-bottom flask. THF (25 mL) was then added to the flask. The reaction was allowed to stir for 12 h at 25 °C. The yellow solution was concentrated under vacuum, and diethyl ether was added to the residue to precipitate **1** as a bright yellow powder. The solid was collected by filtration and washed with diethyl ether three times and then dried under vacuum to obtain **1** in yields of 90%. Anal. Calcd for NiP<sub>3</sub>NC<sub>43</sub>H<sub>42</sub>: P, 12.83; C, 71.29; N, 1.93; H, 5.84. Found: P, 12.79; C, 70.95; N, 1.70; H, 5.88. IR showed intensive  $\nu$ (CN) at 1992 cm<sup>-1</sup>, <sup>31</sup>P{<sup>1</sup>H} NMR (THF):  $\delta$  63.7(t) and 48.2(d) ppm. <sup>1</sup>H NMR (*d*<sub>8</sub>-THF):  $\delta$  2.3 (s, 6H, –CH<sub>3</sub> on xylyl), 1.6, 2.1 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P). Crystals of **1** were grown from THF/ether by slow diffusion of ether.



**Figure 2.** ORTEP drawing of  $[Ni(triphos)C(H)N(H)-xylyl]^{2+}(BF_4)_2^{-}(2)$  with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)-C(5), 1.860(4); Ni-(1)-P(3), 2.1871(10); Ni(1)-P(2), 2.1927(9); Ni(1)-P(1), 2.1943(10); N(1)-C(5), 1.268(5); N(1)-C(1F), 1.427(4); C(5)-Ni(1)-P(3), 176.62(11); C(5)-Ni(1)-P(2), 93.55(10); P(3)-Ni(1)-P(2), 84.40(4); P(3)-Ni(1)-P(1), 85.58(4); C(5)-Ni(1)-P(1), 96.21(10); P(2)-Ni(1)-P(1), 168.68(4); C(5)-N(1)-C(1F), 126.7(3); N(1)-C(5)-Ni(1), 131.5(3).



**Figure 3.** ORTEP drawing of  $[Ni(triphos)C(CH_3)=$ Nxylyl]<sup>+</sup>(I)<sup>-</sup> (**3**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)–C(5), 1.926(3); Ni-(1)–P(3), 2.2088(9); Ni(1)–P(2), 2.1807(9); Ni(1)–P(1), 2.1804(9); N(1)–C(5), 1.273(4); N(1)–C(1F), 1.434(3); C(5)– Ni(1)–P(3), 177.83(10); C(5)–Ni(1)–P(2), 95.94(9); P(3)– Ni(1)–P(2), 83.27(3); P(3)–Ni(1)–P(1), 84.67(3); C(5)– Ni(1)–P(1), 96.23(9); P(2)–Ni(1)–P(1), 167.52(4); C(5)– N(1)–C(1F), 121.7(3); N(1)–C(5)–Ni(1), 119. 2(3).

coordination geometry about Ni in **1** is a distorted tetrahedron, as expected for an  $18e^-$  Ni(0) complex. The C(43)-N(1) bond distance [1.172(3) Å] is slightly longer than that for the free isocyanide (1.157(5) Å).<sup>8</sup> Treat-



ment of **1** with 2 equiv of HBF<sub>4</sub> affords the stable cationic nickel aminocarbene complex [Ni(triphos)C-(H)N(H)xylyl]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub><sup>-</sup> (**2**) in 85% yield, eq 1.<sup>9</sup> The <sup>31</sup>P- $\{^{1}H\}$  NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub> consists of a triplet and a doublet centered at 104.2 and 53.1 ppm with J = 34.4 Hz and a ratio of 1:2.



Protonation of **1** to afford **2** results in oxidation of Ni(0) to Ni(II). This is evident in the change of coordination geometry from tetrahedral in **1** to square planar in **2**. The C(5)–N(1) bond distance (1.268(5) Å) is shorter than a typical C–N single bond (1.472(5) Å),<sup>8</sup> but longer than the C–N triple bond of isocyanides(1.157(5) Å). The three substituents on the carbene carbon C5 are coplanar, consistent with the sp<sup>2</sup> character of the carbon atom. The nickel–carbon bond distance of **2**, d(Ni1–C5) = 1.860(4) Å, is 0.07 Å longer than the Ni–C distance of **1**. Overall, the metrical parameters fall into a range that reflects essentially no  $\pi$ -carbene (**a**) character and significant iminium formyl character (**c**) (Scheme 1).

Our results show that protonation of 1 is a facile means to prepare stable cationic nickel carbene complexes in good yield. A proposed mechanism is based on initial metal protonation,<sup>10</sup> which gives a nickel

<sup>(8)</sup> Dean, J. A. Lange's Handbook of Chemistry, McGraw-Hill Handbooks: New York, 1999.

<sup>(9) [</sup>Ni(triphos)(CN-xylyl)] (1) (181 mg, 0.25 mmol) was dissolved in 10 mL of THF. A HBF<sub>4</sub>/ether solution (69  $\mu$ L, wt % 54, d 1.18, 0.5 mmol) was then added to the solution. The reaction mixture was allowed to stir for 3 h, during which time the pale yellow solid **2** precipitated. **2** was collected by filtration and washed with THF three times and then dried under vacuum. Yield: 85%. Anal. Calcd for NiP<sub>3</sub>-NC<sub>43</sub>H<sub>44</sub>B<sub>2</sub>F<sub>8</sub>: P, 10.32; C, 57.38; N, 1.56; H, 4.93. Found: P, 10.03; C, 57.00; N, 1.26; H, 4.95. IR showed a medium  $\nu$ (CN) at 1558 cm<sup>-1</sup>. <sup>31</sup>P-{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  104.2(t) and 53.1(d) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.5 (s, 6H, -CH<sub>3</sub> on xylyl), 3.6, 3.2, 2.7 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P), 12.1 (m, 1H, -NH), 10.0 (ddt, 1H, : CH-N  $J_{P(trans)-H} = 19.6$  Hz,  $J_{H(N)-H} = 6.8$ Hz,  $J_{P(cis)-H} = 2.4$  Hz). gHMQC technique showed the C(carbene)  $\delta$ 246.5 ppm through the correlation with the proton attached on the carbon at 10.0 ppm. Single crystals of **2** were obtained by slow diffusion of diethyl ether into a methylene chloride solution of **2**.

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hydride complex (**d**). Subsequent insertion of the isocyanide ligand to give a nickel imino formyl complex (**e**) followed by N-protonation gives **2** (Scheme 2).

The corresponding MeI alkylation reaction adds some support to this mechanism. Reaction of 1 equiv of MeI with **1** stops at the imino acyl step to give [Ni(triphos)- $C(CH_3)=Nxylyl|^+(I)^-$  (**3**) as the final product, eq 2.<sup>11</sup>



Initial studies of the reactivity of carbene **2** reveal unprecedented types of carbene reactivity including transfer hydrogenation and hydrocarbation of alkenes.<sup>12</sup> Treatment of **2** with excess acetone leads to the transformation of **2** to  $[Ni(triphos)(CN-xylyl)]^{2+}(BF_4)_2^{-}$  (**4**) and the transfer hydrogenation product 2-propanol, eq 3.<sup>13</sup> Results of our studies of the hydrocarbation chemistry of carbene **2** will be communicated separately.<sup>14</sup>



**Figure 4.** ORTEP drawing of  $[Ni(triphos)CN-xyly]^{2+}(BF_4)_2^-$  (**4**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)-C(5), 1.843(4); Ni(1)-P(3), 2.1639(11); Ni(1)-P(2), 2.2172(11); Ni(1)-P(1), 2.2220-(11); N(1)-C(5), 1.163(5); N(1)-C(1F), 1.402(5); C(5)-Ni(1)-P(3), 173.06(13); C(5)-Ni(1)-P(2), 96.20(12); P(3)-Ni(1)-P(2), 83.34(4); P(3)-Ni(1)-P(1), 84.52(4); C(5)-Ni(1)-P(1), 95.85(12); P(2)-Ni(1)-P(1), 167.86(4); C(5)-N(1)-C(1F), 172.5(4); N(1)-C(5)-Ni(1), 170.7(4).



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**Supporting Information Available:** Tables of crystallographic data collection and refinement parameters, positional and thermal parameters, and bond distances and angles for **1**, **2**, **3**, and **4** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(11) [</sup>Ni(triphos)(CN-xylyl)] (1) (91 mg, 0.125 mmol) was dissolved in 5 mL of toluene. MeI (7.8  $\mu$ L, 0.125 mmol) was then added to the solution. The reaction was allowed to stir for 12 h, during which time the yellow solid **3** precipitated. **3** was collected by filtration and washed with ether three times and then dried under vacuum. Yield: 83%. Anal. Calcd for NiP<sub>3</sub>NC<sub>44</sub>H<sub>45</sub>I·C<sub>7</sub>H<sub>8</sub>: C, 63.91; N, 1.46; H, 5.57. Found: C, 63.33; N, 1.05; H, 5.52. (Because of the low stability of **3**, analysis was carried out multiple times. A trace amount of toluene was found in the NMR spectrum, so the analytical data showed a partial amount of toluene.) IR showed an intense  $\nu$ (CN) at 1556 cm<sup>-1</sup>, <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>-Cl<sub>2</sub>):  $\delta$  86.6 and 35.3 ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.4 (s, 6H, –CH<sub>3</sub> on xylyl), 3.1, 2.6, 2.2 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P), 1.7 (d, 3H, –CH<sub>3</sub>). gHMBC technique showed the C(Ni–C)  $\delta$  190.2 ppm through the correlation with the proton of the methyl group (1.7 ppm) attached on the carbon. Single crystals of **3** were obtained by slow diffusion of diethyl ether into a THF solution of **3**.

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<sup>(13) [</sup>Ni(triphos)C(H)N(H)xylyl]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub><sup>-</sup> (2) (200 mg, 0.22 mmol) was dissolved in 10 mL of acetone. The reaction was allowed to stir at 45 °C for 1 day. 2-Propanol was detected by GC in the reaction mixture. The yellow solution was concentrated under vacuum, and diethyl ether was added to the residue to precipitate **4** as yellow powder. The solid was collected by filtration and washed with diethyl ether three times and then dried under vacuum to obtain **4** in yields of 80%. IR showed an intense  $\nu$ (CN) stretching band at 2174 cm<sup>-1</sup>. Anal. Calcd for NiP<sub>3</sub>-NC<sub>43</sub>H<sub>42</sub>B<sub>2</sub>F<sub>8</sub>: C, 57.51; N, 1.56; H, 4.71. Found: C, 57.24; N, 1.61; H, 4.63. <sup>31</sup>P{<sup>1</sup>H} NMR (acetone):  $\delta$  120.1(t) and 61.8(d) ppm. <sup>1</sup>H NMR ( $d_6$ -acetone):  $\delta$  1.8 (s, 6H,  $-CH_3$  on xylyl). Crystals of **4** were grown from acetone/ether by slow diffusion of ether.

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