Organometallics **2003,** *22,* 2817−2819

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

Hongyi Hou, Peter K. Gantzel,† and Clifford P. Kubiak*

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

Received February 19, 2003

*Summary: The new nickel isocyanide complex [Ni(triphos)(CN-xylyl)] (**1**) has been prepared by the reaction of Ni(COD)$_2$, triphos (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine), and CN-xylyl (xylyl = 2,6-Me$_2$C$_6$H$_3$). Complex **1** adds 2 equiv of HBF$_4$ to afford a stable dicationic nickel carbene complex, [Ni(triphos)-C(H)N(H)xylyl]$^{2+}$(BF$_4$)$_2$$^-$ (**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.[1] Although palladium and platinum carbene complexes have been widely used in Heck and Suzuki type reactions,[2] nickel carbenes have been less thoroughly studied.[3] Among the nickel carbene complexes, heteroatom-stabilized (Fischer) carbenes represent the vast majority.[4] The typical route to methoxy(amino) or bis(amino) carbene complexes is nucleophilic attack of alcohols or amines on coordinated isocyanides.[5] 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.

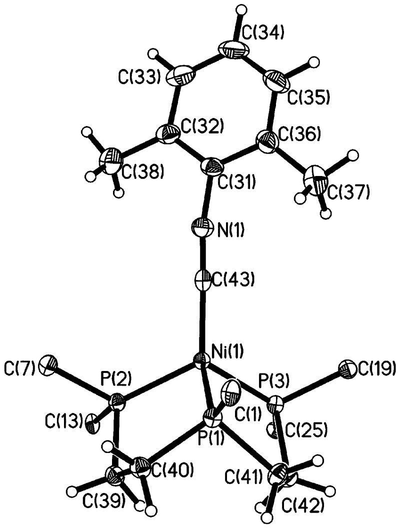


Figure 1. ORTEP drawing of [Ni(triphos)(CN-xylyl)] (**1**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)−C(43), 1.787(3); Ni(1)−P(1), 2.1405(8); Ni(1)−P(3), 2.1455(8); Ni(1)−P(2), 2.1493(8); N(1)−C(43), 1.172(3);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

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$_2$C$_6$H$_3$) to 1 equiv of Ni(COD)$_2$[6] (COD = 1,5-cyclooctadiene) at room temperature in THF.[7]

The ^{31}P{^{1}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 ν(CN) stretching band at 1992 cm^{-1}. 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

---

* To whom correspondence should be addressed. E-mail: ckubiak@ucsd.edu.

† Address correspondence pertaining to crystallographic studies to this author. E-mail: pgantzel@ucsd.edu.

(1) (a) Kücükbay, H.; Cetinkaya, B.; Salaheddine, G.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2434. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (c) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (d) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **2001**, 201. (e) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Hermann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773.

(2) (a)Herrmann, W. A.; Cornils, B. E. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany, 1996; Vol. 1; Vol. 2. (b) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93. (c) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483.

(3) (a) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976

(4) (a) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (b) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999,** *575*, 80. (c) Xu, D.; Miki, K.; Tanaka, M.; Kasai, N.; Yasuoka, N.; Wada, M. *J. Organomet. Chem.* **1989**, *371*, 267.

(5) Oguro, K.; Wada, M.; Okawara, R. *J. Chem. Soc., Chem. Commun.* **1975**, *97*, 899.

(6) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

(7) Ni(COD)$_2$ (275 mg, 1 mmol), triphos (534 mg, 1 mmol), and CN-xylyl (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$_3$NC$_{43}$H$_{42}$: 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 ν(CN) at 1992 cm^{-1}. ^{31}P{^{1}H} NMR (THF): δ 63.7(t) and 48.2(d) ppm. ^{1}H NMR (d_8-THF): δ 2.3 (s, 6H, −CH$_3$ on xylyl), 1.6, 2.1 (m, 8H, PCH$_2$CH$_2$P). Crystals of **1** were grown from THF/ether by slow diffusion of ether.

10.1021/om030108y CCC: $25.00
Publication on Web 06/03/2003

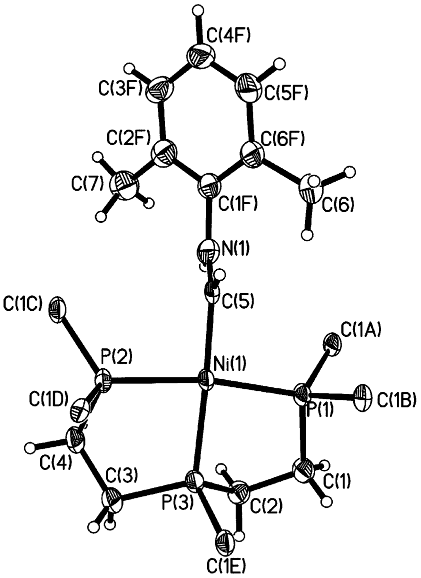


Figure 2. ORTEP drawing of [Ni(triphos)C(H)N(H)-xylyl]$^{2+}$(BF$_4$)$_2$$^-$ (**2**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)−C(5), 1.860(4); Ni(1)−P(3), 2.1871(10); Ni(1)−P(2), 2.1927(9); Ni(1)−P(1), 2.1943(10); 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).

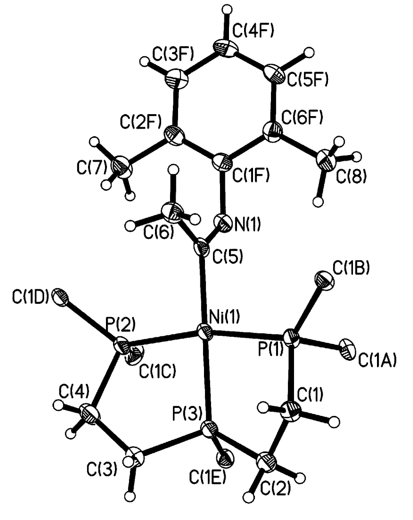
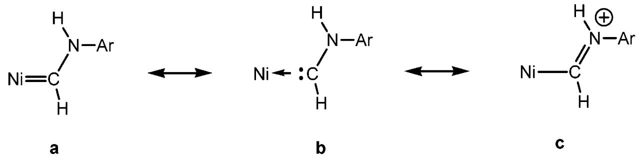
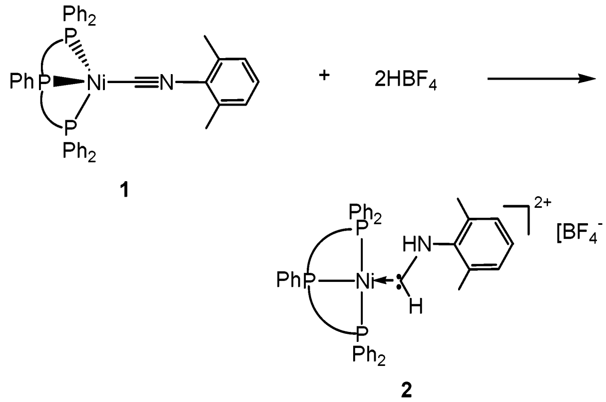


Figure 3. ORTEP drawing of [Ni(triphos)C(CH$_3$)=Nxylyl]$^+$(I)$^-$ (**3**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)−C(5), 1.926(3); Ni(1)−P(3), 2.2088(9); Ni(1)−P(2), 2.1807(9); Ni(1)−P(1), 2.1804(9); N(1)−C(5), 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).

Scheme 1



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).[8] Treatment of **1** with 2 equiv of HBF$_4$ affords the stable cationic nickel aminocarbene complex [Ni(triphos)C(H)N(H)xylyl]$^{2+}$(BF$_4$)$_2$$^-$ (**2**) in 85% yield, eq 1.[9] The ^{31}P{^{1}H} NMR spectrum of **2** in CD$_2$Cl$_2$ 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.



(1)

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),[8] 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^2 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 π-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,[10] which gives a nickel

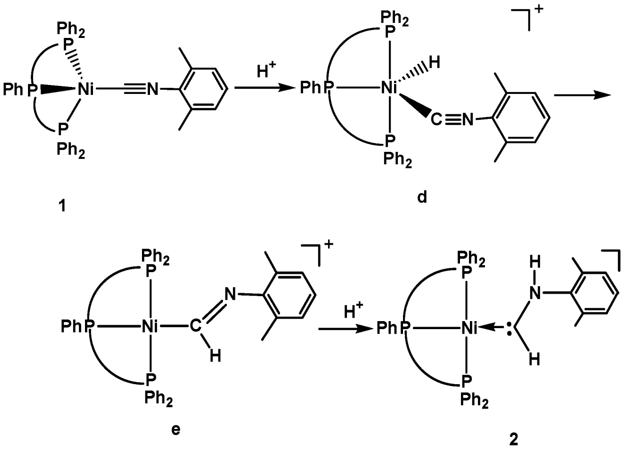
---

(8) Dean, J. A. *Lange's Handbook of Chemistry*; McGraw-Hill Handbooks: New York, 1999.

(9) [Ni(triphos)(CN-xylyl)] (**1**) (181 mg, 0.25 mmol) was dissolved in 10 mL of THF. A HBF$_4$/ether solution (69 μL, 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$_3$NC$_{43}$H$_{44}$B$_2$F$_8$: 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 ν(CN) at 1558 cm^{-1}. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ 104.2(t) and 53.1(d) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.5 (s, 6H, −CH$_3$ on xylyl), 3.6, 3.2, 2.7 (m, 8H, PCH$_2$CH$_2$P), 12.1 (m, 1H, −NH), 10.0 (ddt, 1H, : CH−N $J_{\mathrm{P(trans)-H}}$ = 19.6 Hz, $J_{\mathrm{H(N)-H}}$ = 6.8 Hz, $J_{\mathrm{P(cis)-H}}$ = 2.4 Hz). gHMQC technique showed the C(carbene) δ 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**.

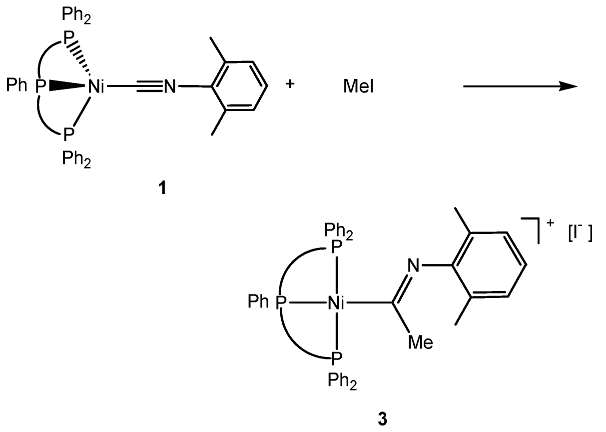
(10) (a) James, T. L.; Cai, L.; Muetterties, M. C.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 4148. (b) Miedaner, A.; Dubois, D. L.; Curtis, C. J. *Organometallics* **1993**, *12*, 299. (c) McEwen, G. K.; Rix, C. J.; Traynor, M. F.; Verkade, J. G. *Inorg. Chem.* **1974**, *13*, 2800. (d) Schunn, R. A. *Inorg. Chem.* **1970**, *9*, 394.

Scheme 2



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.[11]



(2)

Initial studies of the reactivity of carbene **2** reveal unprecedented types of carbene reactivity including transfer hydrogenation and hydrocarbation of alkenes.[12] 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.[13] Results of our studies of the hydrocarbation chemistry of carbene **2** will be communicated separately.[14]

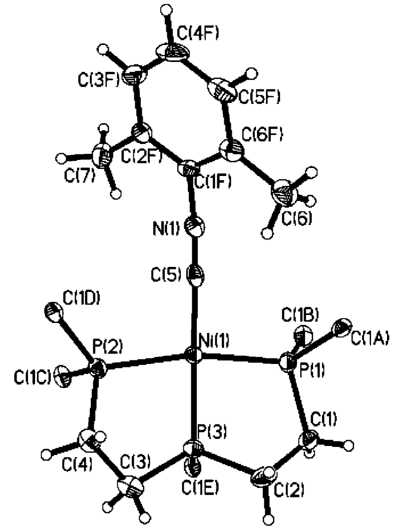
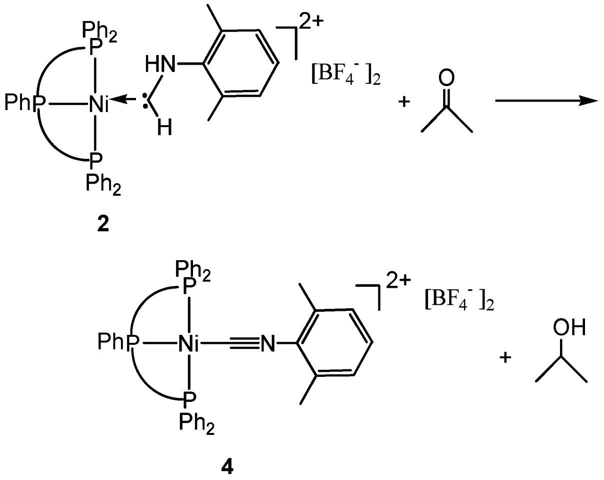


Figure 4. ORTEP drawing of [Ni(triphos)CN-xylyl]$^{2+}$-(BF$_4$)$_2$$^-$ (**4**) with 50% probability ellipsoids. Phenyl rings on the phosphorus are not included. Selected bond distances (Å) and angles (deg): Ni(1)−C(5), 1.843(4); Ni(1)−P(3), 2.1639(11); Ni(1)−P(2), 2.2172(11); Ni(1)−P(1), 2.2220-(11); 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).



(3)

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

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.

OM030108Y

---

(11) [Ni(triphos)(CN-xylyl)] (**1**) (91 mg, 0.125 mmol) was dissolved in 5 mL of toluene. MeI (7.8 μL, 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$_3$NC$_{44}$H$_{45}$I·C$_7$H$_8$: 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 ν(CN) at 1556 cm^{-1}. ^{31}P{^{1}H} NMR (CH$_2$-Cl$_2$): δ 86.6 and 35.3 ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.4 (s, 6H, −CH$_3$ on xylyl), 3.1, 2.6, 2.2 (m, 8H, PCH$_2$CH$_2$P), 1.7 (d, 3H, −CH$_3$). gHMBC technique showed the C(Ni−C) δ 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**.

(12) (a) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950. (b) 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.

(13) [Ni(triphos)C(H)N(H)xylyl]$^{2+}$(BF$_4$)$_2$$^-$ (**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 ν(CN) stretching band at 2174 cm^{-1}. Anal. Calcd for NiP$_3$-NC$_{43}$H$_{42}$B$_2$F$_8$: C, 57.51; N, 1.56; H, 4.71. Found: C, 57.24; N, 1.61; H, 4.63. ^{31}P{^{1}H} NMR (acetone): δ 120.1(t) and 61.8(d) ppm. ^{1}H NMR (d_6-acetone): δ 1.8 (s, 6H, −CH$_3$ on xylyl). Crystals of **4** were grown from acetone/ether by slow diffusion of ether.

(14) Hou, H.; Gantzel, P. K.; Kubiak, C. P. *J. Am. Chem. Soc.*, submitted.