Pyridinecarboxamidato−Nickel(II) Complexes

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The synthesis, characterization, and reactivity toward ethylene of pyridinecarboxamidato complexes of nickel are reported. These compounds are isoelectronic to α-iminocarboxamidato complexes, which are useful ethylene polymerization catalysts. Addition of a benzene solution containing *N*-phenyl-2-pyridinecarboxamide and $B(C_6F_5)_3$ to bis(methallyl)nickel results in the formation of [*N*-phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2N,N]-Ni(η^3-CH_2CMeCH_2) (**3**) in 93% yield. A similar procedure using *N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamide provides [*N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamidatotris-(pentafluorophenyl)borate-κ^2N,N]Ni(η^3-CH_2CMeCH_2) (**4**) in 92% yield. The solid-state structures of **3** and **4** were determined by X-ray diffraction techniques. The intramolecular metrical parameters are consistent with substantial partial positive charge at the nickel atom. Deprotonation of *N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamide in THF with KH, followed by addition to Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3) and subsequent treatment with 2 equiv of $B(C_6F_5)_3$, produces [*N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2N,N]Ni(η^3-$CH_2C_6H_5$) (**5**). Compound **5** is obtained as a mixture of isomers. Deprotonation of *N*-(2,6-diisopropylphenyl)-6-triisopropylsilyl-2-pyridinecarboxamide, followed by addition to Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3), gives a product (**7**) which lacks a benzyl fragment. An X-ray diffraction study shows that metalation of one of the isopropyl groups and loss of the benzyl ligand takes place. The reactivity of **3**, **4**, **5**, and **7** toward ethylene is presented. Considerably more activity is obtained with **5**, probably as a result of faster initiation. The pyridine ligand leaves an open quadrant adjacent to nickel. As a result, the molecular weight of the product is not high.

Introduction

Nickel-based olefin polymerization and oligomerization catalysts[1] continue to attract considerable recent attention.[2,3] Depending on the ancillary ligand framework, these catalysts participate in chain-walking reactions,[4,5] tolerate polar functionalities,[6] and may even be used in water.[7] These properties provide materials with unique topologies,[8] could enable manufacturing alternatives for the ever-growing polyolefin industry,[9] and are complementary in many ways to those of early metal-based catalysts.[10,11]

We discovered, during our efforts at developing tandem catalytic processes,[12−14] that the reactivity of SHOP-type catalysts such as [$(C_6H_5)_2PC_6H_4C(O)O$-κ^2P,O]-Ni(η^3-CH_2CMeCH_2)[15] toward ethylene increases substantially upon addition of $B(C_6F_5)_3$. Carbonyl coordination to the borane gives the complex [$(C_6H_5)_2PC_6H_4C$-$(OB(C_6F_5)_3)O$-κ^2P,O]Ni(η^3-CH_2CMeCH_2). Adduct formation removes electron density from the nickel atom.[16]

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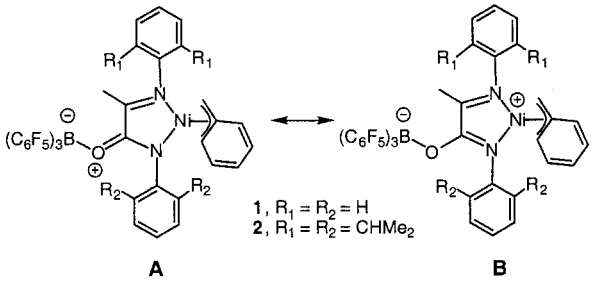
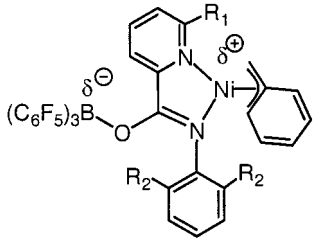
It is possible to extend this activation concept to the design of polymerization catalysts by taking into account mechanistic insight obtained from Brookhart's diimine complexes.[17] Complexes **1** and **2**, containing α-iminocarboxamide ligands, have been synthesized and their reactivity toward ethylene has been studied.[18] The two resonance structures shown below illustrate the removal of electron density from the nickel center upon Lewis acid coordination. Attaching isopropyl groups at the 2,6 positions increases the rate of propagation relative to the rate of chain transfer. Under identical reaction conditions compound **1** produces oligomers, whereas **2** provides branched polymers. The η^3-benzyl fragment was selected, instead of the more frequently used methallyl, because it leads to faster initiation rates.[19]

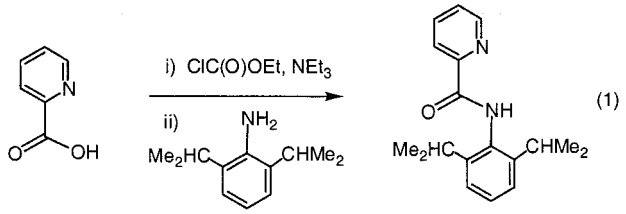


In this contribution we report on the synthesis and reactivity of pyridinecarboxamidato nickel complexes which are isoelectronic to **1** and **2**. We examine the effect on the reactivity toward ethylene of substitution at the 2,6 positions of the benzamide aryl ring as well as the 6 position of the pyridine ring. We also probe the effect of methallyl versus η^3-benzyl substitution on the rate of initiation.

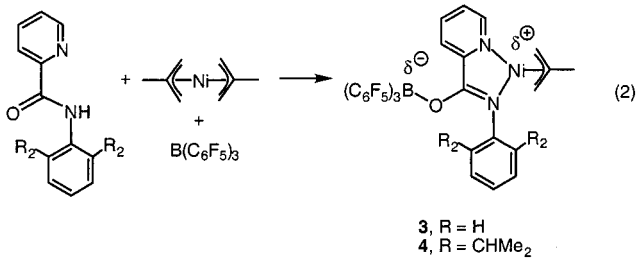


Results and Discussion

Synthesis and Characterization. Literature precedent exists for the use of *N*-phenyl-2-pyridinecarboxamide as a ligand for late transition metals.[20] The bulkier *N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamide can be obtained in multigram quantities and in excellent yield (92%) from 2-pyridinecarboxylic acid by addition of ethyl chloroformate and triethylamine, followed by 2,6-diisopropylaniline (eq 1).



N-Phenyl-2-pyridinecarboxamide does not react directly with bis(methallyl)nickel. Apparently, the amide N-H is not sufficiently acidic to protonate the methallyl ligand.[21] However, when $B(C_6F_5)_3$, *N*-phenyl-2-pyridinecarboxamide, and bis(methallyl)nickel are all mixed simultaneously in benzene and allowed to react for 3 h, one obtains [*N*-phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2N,N]Ni(η^3-CH_2CMeCH_2) in 93% yield (compound **3** in eq 2). It is likely that in these reactions the borane precoordinates to the carbonyl, thereby lowering the pK_a of the amide site. A similar procedure using *N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamide provides [*N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2N,N]-Ni(η^3-CH_2CMeCH_2) in 92% yield (compound **4** in eq 2).



Compounds **3** and **4** have similar ^{1}H, ^{11}B, and ^{19}F NMR spectra. For example the ^{1}H NMR signals for the methylene protons appear at 2.00, 1.94, 1.71, and 1.44 ppm for **3** and 2.07, 1.88, 1.82, and 1.75 ppm for **4**. In the case of **4**, at room temperature, two methine proton resonances are observed (3.54 and 3.02 ppm), indicating that the rotations of the phenyl ring and the methallyl group are frozen with respect to the NMR time scale.[22] The two ortho carbons are also inequivalent in the ^{13}C NMR spectrum (141.11 and 140.82 ppm). For **3**, the two ortho carbon resonances are equivalent, consistent with a considerably faster rotation rate of the aryl unit.

Single crystals of **3** suitable for X-ray diffraction study were obtained by allowing a hexane and benzene solution (10:1) to stand at room temperature, and the result of these studies is shown in Figure 1. A square planar coordination geometry is observed, with the

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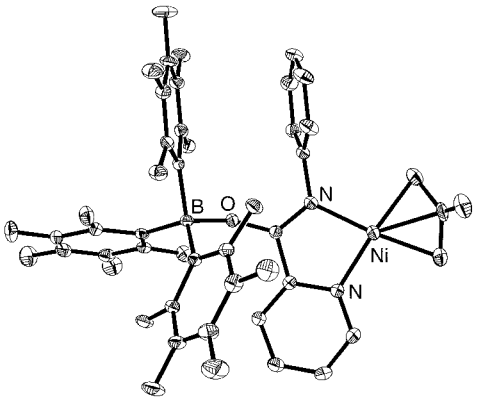


Figure 1. ORTEP drawing of **3**. Hydrogen atoms not shown for clarity.

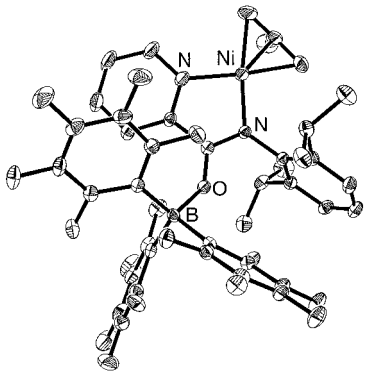


Figure 2. ORTEP drawing of **4**. Hydrogen atoms not shown for clarity.

amidato functionality coordinating via the nitrogen atom. The C−OB distance (1.300(5) Å) is longer than average C−O double bond lengths (∼1.22 Å), while the C−NNi distance (1.298(5) Å) indicates considerable partial double bond character.[23] These data confirm a strong contribution by a resonance structure similar to **B**. That the pyridine N−Ni distance is nearly identical (1.921(3) Å) to the amidato N−Ni distance (1.933(4) Å) reflects the similarity in bonding between the two nitrogen atoms. It is also interesting to note the intramolecular "stacking" between one of the pentafluorophenyl groups on boron and the phenyl group on nitrogen.[24] Interactions of this type have been observed in the solid-state structures of the adducts of $B(C_6F_5)_3$ and PhC(O)X compounds (X = OEt and NPr).[25]

Figure 2 shows the solid-state structure of **4**. The coordination sphere around nickel is similar to that observed for **3**, with nearly identical intramolecular bond distances and angles. The bulky isopropyl groups bear their influence on two noteworthy distortions. The methallyl ligand is "rotated" in such a way that the methyl group points away from the diisopropylphenyl fragment (Figure 3). One can obtain a measure of this distortion by examining the pyN−Ni−C_β−CH_3 torsional angles (ca. −78° for **3** and ca. −67° for **4**). In **4**, the C−O−B angle is larger (139.6(2)°) than in **3** (130.6(3)°)

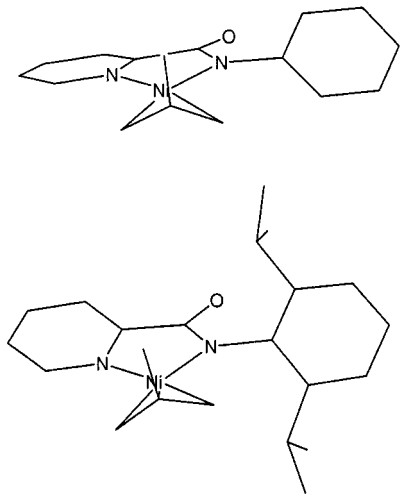
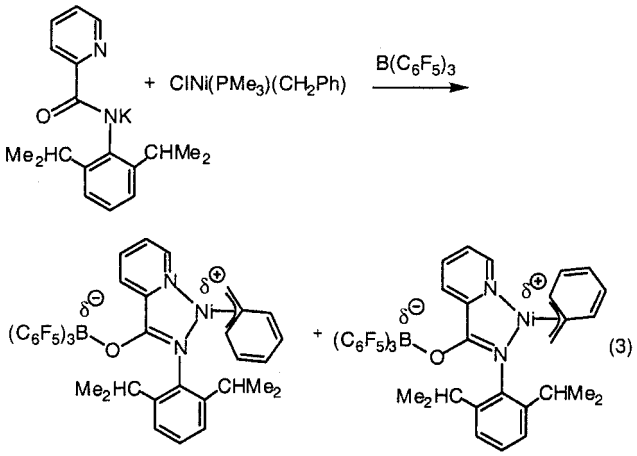


Figure 3. Comparison of the molecular structures of **3** and **4**.

to decrease steric interference between the diisopropylphenyl and $B(C_6F_5)_3$ fragments.

Pyridinecarboxamidato−nickel compounds containing the more reactive η^3-benzyl ligand, instead of methallyl, are readily obtained starting with Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3).[26] Addition of KH to a solution of *N*-(2,6-diisopropyl)phenyl-2-pyridinecarboxamide in THF results in clean deprotonation. Addition of this solution to Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3), followed by 2 equiv of $B(C_6F_5)_3$, results in the precipitation of $Me_3P-B(C_6F_5)_3$ and two compounds in a 10:1 ratio. This ratio was constant at a given temperature, regardless of reaction and workup conditions. We propose that the product is a mixture of the two isomers for [*N*-(2,6-diisopropyl)-phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)-borate-κ^2N,N]Ni(η^3-$CH_2C_6H_5$) (**5**), as shown in eq 3.[27]



5

The NMR spectroscopic features for the two isomers of **5** are similar, and only those of the major species will be discussed in detail. Signals for the aromatic hydrogens on the benzyl ligand occur in the 5.8−6.6 ppm range, consistent with η^3 coordination.[18] The two methine protons are equivalent, while the two methyl

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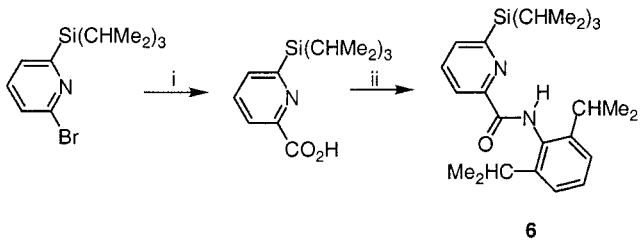
(27) Similar isomerization was observed in α-iminocarboxamide ligands: see ref 18.

Scheme 1[a]



6

[a] (i) *n*-BuLi, then CO_2; (ii) ClC(O)OEt, NEt_3, then 2,6-diisopropylaniline.

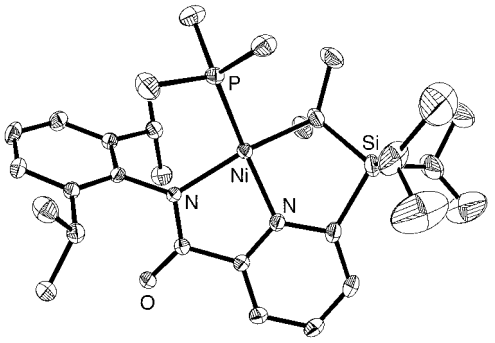
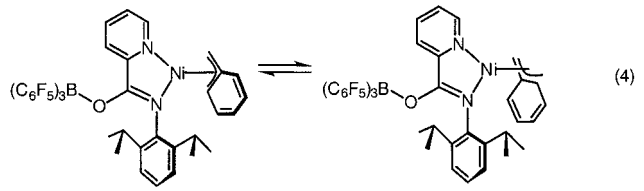


Figure 4. ORTEP drawing of **7**. Hydrogen atoms not shown for clarity.

groups on each isopropyl remain inequivalent. These data are consistent with a fast suprafacial motion of the benzyl ligand, as shown in eq 4 below.[26]



(4)

Efforts to study the effect of substitution on the pyridine ligand focused on the synthesis of *N*-(2,6-diisopropylphenyl)-6-triisopropylsilyl-2-pyridinecarboxamide (**6**). Ligand synthesis begins with the quenching of 2-lithio-6-triisopropylsilylpyridine[28] with CO_2, which gives 6-triisopropylsilyl-2-pyridinecarboxylic acid in 93% yield (Scheme 1). Addition of triethylamine and ethylchloroformate to this acid, followed by 2,6-diisopropylaniline and purification by chromatography, provides **6** in 71% yield.

Deprotonation of **6** using KH in THF, followed by addition to Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3) in toluene, results in the immediate precipitation of KCl. The ^{1}H NMR spectrum of the resulting red organometallic product shows five unique methyl resonances at 1.58 (d), 1.38 (d), 1.29 (d), 1.08 (d), and 1.04 (s) ppm in a 1:1:1:1:1 ratio. No signals due to a benzyl fragment were detected, while the ^{31}P NMR spectrum displayed a signal at −24 ppm. A single-crystal X-ray diffraction study (Figure 4) confirms loss of the benzyl ligand and metalation of one of the isopropyl groups. The product is thus compound **7**, as shown in eq 5. It is noteworthy that the carboxamide ligand continues to prefer *N*-coordination, despite the crowded ligand environment.

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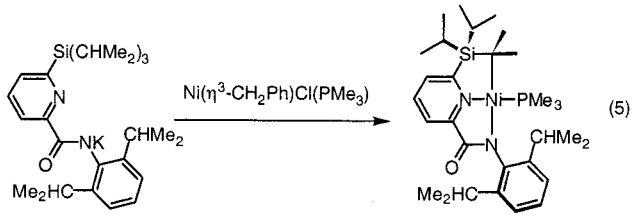
Table 1. Reactivity Studies with Ethylene[a]

entry	compound	$B(C_6F_5)_3$ (equiv)	time (h)	consumed ethylene[b] (g)	solid fraction[c] (g)
1	**3**	0	1.0	0.15	0
2	**3**	1	1.0	0.56	0
3	**3**	5	1.0	3.1	0
4	**3**	10	1.0	4.1	0
5	**4**	0	20	0.40	0.32
6	**4**	1	8	0.80	0.77
7	**4**	5	6.5	2.7	1.6
8	**4**	10	6.5	4.2	2.4
9	**5**	0	1.0	2.4	1.0
10	**5**	1	1.0	7.6	1.0
11	**5**	5	1.0	5.6	1.2
12	**7**	0	1.0	0	0
13	**7**	2	1.0	0	0
14	**7**	2 $Ni(COD)_2$	1.0	0	0
15	**7**	10	1.0	1.6	0

[a] Polymerization conditions: 25 μmol Ni, 30 mL of toluene, 100 psig ethylene. [b] Consumed ethylene monitored by a mass flow controller. [c] Precipitated polymer in acetone.



(5)

7

Reactivity Studies. Table 1 summarizes the reactivity of compounds **3**, **4**, **5**, and **7** toward ethylene. Entries 1−4 show that the addition of additional $B(C_6F_5)_3$ increases the total amount of ethylene consumed by **3** over a period of 1 h. There is no change in the ^{1}H NMR spectra of **3** after the addition of 20 equiv of $B(C_6F_5)_3$ at similar concentrations ([Ni] = 0.010 M). Therefore the equilibrium constant overwhelmingly favors coordination of the borane.[29] Increased product formation is likely due to scrubbing of impurities by the additional borane. Examination of the product obtained by using **3** shows that it is a distribution of ethylene oligomers; no precipitate is observed. GC/MS analysis shows that, in addition to 1-alkenes, the product contains a substantial fraction of internal alkenes and 1-alkene dimers. The active species derived from **3** thus reacts further with the 1-alkene product.[30] One can examine the rate of ethylene consumption as a function of time by using a mass flow controller designed to keep a constant pressure. As shown in Figure 5, for the reaction in entry 4, there is a steady increase of activity for the first 30 min. After this period of time a substantial decline is observed.

Entries 5−8 in Table 1 show that the reactions with **4**/C_2H_4 differ from those with **3**/C_2H_4 in two important respects. First, substantially longer reaction times are required with **4**/C_2H_4 to obtain similar quantities of product. Figure 5 also shows the activity versus time profile for entry 8. Substantial reactivity is observed

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(30) For homogeneous catalysts that are selective for 1-alkene formation see: (a) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997** *119*, 9305. (b) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (c) Barnhart, R. W.; Bazan, G. C.; Mourney, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (d) Review: Skupinska, J. *Chem. Rev.* **1991**, *91*, 3.

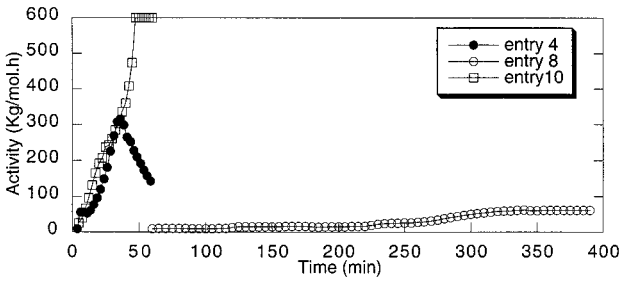

Figure 5. Ethylene consumption rate monitored by a mass flow controller.

only after ∼3.5 h, and the maximum activity is considerably lower than that observed for **3**/C_2H_4 under identical conditions. Similar observations were made for the reaction in entry 7. That a solid product is obtained with **4**/C_2H_4 is a second important difference relative to **3**/C_2H_4. This solid product was shown by ^{1}H NMR spectroscopy to be low molecular weight branched polyethylene (M_n, 860; branch number/1000C, 80).[31] Low molecular weight ethylene oligomers are also obtained. The fraction of the solid is also given in Table 1.

Comparison of **4** vs **5** (entries 9−11) reveals that the formally isoelectronic replacement of methallyl for η^3-benzyl yields a precatalyst that more quickly converts to the catalytically important species. This improved reactivity is readily evident upon comparison of the data in Figure 5. For **5**/C_2H_4, there is no induction period. Note that for entry 10, the reaction reaches an activity at 50 min of 600 kg/mol·h. This rate is the maximum flow rate that can be measured under our experimental conditions.

Finally, entries 12−15 show that compound **7** does not produce an effective catalyst. Efforts to use Ni(COD)$_2$ in the expectation that PMe_3 would be removed from **7** to give an active species were not successful.[32] Only in the presence of a large excess of $B(C_6F_5)_3$ is ethylene consumed. The product under these conditions is a distribution of low molecular weight oligomers consisting of 1-alkenes, internal alkenes, and 1-alkene dimers.

Summary Discussion

In summary, the synthesis and characterization of pyridinecarboxamidato−nickel complexes has been demonstrated. The ligand environment of these complexes provides bonding to the metal similar to the α-iminocarboxamide ligands in complexes **1** and **2**. Considerably more efficient formation of the propagating species occurs with the use of the η^3-benzyl ligand, compared to methallyl. While the pyridinecarboxamidate and α-iminocarboxamide ligands are similar in an electronic sense, the pyridine ring leaves an open quadrant adjacent to the metal center. It is not possible to obtain a similar congestion of the axial sites,[2] and a result the average molecular weight of the product obtained with **4** is considerably smaller than the product obtained with **2** under similar reaction conditions. Attempts to increase steric hindrance by addition of the bulky triisopropylsilyl group resulted in metalation of one of the isopropyl groups and a concomitant deactivation of the metal center.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques.[33] Toluene, THF, hexane, and pentane were distilled from benzophenone ketyl. *N*-Phenyl-2-pyridinecarboxamide[20] and 2-bromo-6-triisopropylpyridine[28] were synthesized according to the literature methods. Tris(pentafluorophenyl)boron was provided by Boulder and purified by sublimation. NMR spectra were obtained using a Varian Unity 400 or 500 spectrometer. ^{1}H NMR spectra were calibrated using signals from the solvent and are reported downfield from $SiMe_4$. ^{11}B NMR and ^{19}F NMR spectra were calibrated and reported downfield from external BF_3·OEt_2 and α,α,α-trifluorotoluene, respectively. Mass spectrometric analyses were obtained using a VG-70E double-focusing magnetic sector instrument operated with a OPUS/SIOS data system. Desert Analytics, Inc., Tucson, AZ, performed elemental analyses. The use of the mass flow controller has been described elsewhere.[34]

[*N*-Phenyl-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2 *N,N*](η^3-methallyl)nickel (3). *N*-Phenyl-2-pyridinecarboxamide (0.198 g, 1.00 mmol) and tris(pentafluorophenyl)boron (0.512 mg, 1.00 mg) were weighed into a vial and dissolved in benzene (4.0 g). Bis(methallyl)nikel-(II) (0.173 mg, 1.05 mmol) in benzene (2.0 g) was added at room temperature, and the solution was stirred for 3 h. Removal of solvent under vacuum gave a yellow oily residue, which solidified by trituration with pentane (4 g) overnight. The yellow powder was isolated by filtration, washed with pentane (∼10 g), and placed under vacuum overnight. The product is obtained as a yellow powder in 93% yield. ^{1}H NMR spectroscopy showed that 0.37 molecules of pentane were retained for each molecule of **3**. Single crystals for elemental analysis and X-ray diffraction studies were grown from hexane and benzene (∼10:1) at room temperature overnight. Half a molecule of hexane was incorporated for each molecule of **3** in the crystal lattice. ^{1}H NMR (400 MHz, C_6D_6): δ 7.71 (d, J = 8.0 Hz, 1 H, py-H^3), 7.03 (t, J = 8.0 Hz, 2 H, ph-H^{2,6}), 7.00−6.83 (m, 4 H, py-H^3, ph-H$^{3-5}$), 6.65 (td, J = 8.0, 1.6 Hz, 1 H, py-H^4), 6.06 (ddd, J = 8.0, 5.2, 1.2 Hz, 1 H, py-H^5), 2.00 (d, J = 2.8 Hz, 1 H, methallyl-CH_2), 1.94 (dd, J = 2.8, 1.2 Hz, 1 H, methallyl-CH_2), 1.71 (s, 1 H, methallyl-CH_2), 1.58 (s, 3 H, methallyl-CH_3), 1.44 (s, 1 H, methallyl-CH_2). ^{13}C NMR (100 MHz, C_6D_6): δ 166.92 (carbonyl), 152.13 (py-C^2), 151.98 (py-C^6), 149 (dm, J = 250 Hz, *p*-*C*F), 147.73 (ph-C^1), 140 (dm, J = 240 Hz, *o*-*C*F), 138.81 (py-C^4), 138 (dm, J = 260 Hz, *m*-*C*F), 130.64 (ph-C^4), 128.88 (ph-C^{3,5}), 127.90 (py-C^5), 126.46 (py-C^3), 126.21 (methallyl-*C*CH$_3$), 123.70 (ph-C^{2,6}), 121 (m, *i*-B*C*), 61.63 (methallyl-*C*H$_2$), 54.19 (methallyl-*C*H$_2$), 23.09 (methallyl-*C*H$_3$). ^{19}F NMR (C_6D_6, 376 MHz): δ −75.7 (br, *o*-F), −101.3 (t, J = 20 Hz, *p*-F), −107.2 (td, J = 20, 4 Hz, *m*-F). ^{11}B NMR (toluene, 128 MHz): δ −0.75. Anal. Calcd ($C_{34}H_{16}B_1F_{15}N_2O_1Ni$·$C_3H_7$): C, 51.3; H, 2.68; N, 3.27. Found: C, 51.0; H, 2.58; N, 3.27.

***N*-(2,5-Diisopropylphenyl)-2-pyridinecarboxamide.** 2-Pyridinecarboxylic acid (3.1 g, 25 mmol) was dissolved in THF (100 mL) and cooled to −15 °C. Triethylamine (3.5 mL, 25 mmol) and ethyl chloroformate (2.4 mL, 25 mmol) were then added successively. The resulting suspension was stirred for 30 min, and 2,6-(diisopropyl)aniline (4.43 g, 25 mmol) was added. The reaction mixture was warmed to room temperature slowly and stirred for 4 h, whereupon evolution of CO_2 gas

(31) This number is not corrected for end group contribution.

(32) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

(33) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, D.C., 1987.

(34) Bazan, G. C.; Rogers, J. S.; Fang, C. C. *Organometallics* **2001**, *20*, 2059.

was detected. The mixture was filtered and washed with THF. The solvent was removed to give an oily residue, which was purified by passing through a short silica gel column using methylene chloride. The oily compound solidifies from hexane at room temperature. Overall yield was 92% (6.52 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (br, 1 H, NH), 8.66 (ddd, J = 4.8, 1.6, 1.2 Hz, 1 H, py-H^6), 8.31 (dt, J = 7.6, 1.2 Hz, 1 H, py-H^3), 7.92 (td, J = 7.6, 1.6 Hz, 1 H, py-H^4) 7.51 (ddd, J = 7.6, 4.8, 1.2 Hz, py-H^5), 7.33 (t, J = 8.0 Hz, 1 H, ph-H^4), 7.23 (d, J = 8.0 Hz, 2 H, ph-H^{3,5}), 3.15 (septet, J = 13.6 Hz, 2 H, *i*Pr−C*H*), 1.23 (d, J = 13.6 Hz, 6 H, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.71 (carbonyl), 149.99 (py-C^2), 148.41 (py-C^6), 146.43 (ph-C^{2,6}), 137.73 (py-C^4), 131.38 (ph-C^1), 128.41 (py-C^5), 126.60 (py-C^3), 123.67 (ph-C^{3,5}), 122.84 (ph-C^4), 29.12 (*i*Pr-*C*H), 23.86 (*i*Pr-*C*H$_3$). IR (neat): 3350, 3294 (br, NH), 1688 (carbonyl) cm^{-1}. HRMS-EI *m*/*z* M$^+$ calcd ($C_{15}H_{22}N_2O_1$), 282.1705; found, 282.1718.

[*N*-(2,6-Diisopropylphenyl)-2-pyridinecarboxamidatotris(pentafluorophenyl)borate-κ^2 *N,N*](η^3-methallyl)nickel (4). This compound was prepared using a procedure similar to the synthesis of **3** from *N*-(2.6-diisopropylphenyl)-2-pyridinecarboxamide. This reaction works best when 1.2 equiv of ligand is used, instead of 1.0 equiv. The product is obtained as a yellow powder in 93% yield. Single crystals for elemental analysis and X-ray diffraction studies were grown from pentane and benzene (∼1:3) at room temperature 2 days. Two and a half benzene molecules were incorporated in the single crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 7.41 (d, J = 8.0 Hz, 1 H, py-H^3), 7.18 (t, J = 8.0 Hz, 1 H, ph-H^4), 7.13 (dd, J = 5.2, 1.2 Hz, py-H^6), 6.97 (d, J = 8.0 Hz, 1 H, ph-H^{3or5}), 6.96 (d, J = 8.0 Hz, ph-H^{3or5}), 6.27 (td, J = 8.0, 1 Hz, 1.2 H, py-H^4), 6.00 (ddd, J = 8.0, 5.2, 1.2 Hz, 1 H, py-H^5) 3.54 (septet, J = 6.8 Hz, 1 H, *i*Pr-C*H*), 3.02 (septet, J = 6.8 Hz, 1 H, *i*Pr−C*H*), 2.07 (d, J = 2.8 Hz, 1 H, methallyl-CH_2), 1.88 (t, J = 2.4, 1 H, methallyl-CH_2), 1.82 (d, J = 2.0 Hz, 1 H, methallyl-CH_2), 1.75 (s, 1 H, methallyl-CH_2), 1.56 (s, 3 H, methallyl-CH_3), 1.17 (d, J = 6.8 Hz, 3 H, *i*Pr-CH_3), 1.09 (d, J = 6.8 Hz, 3 H, *i*Pr-CH_3), 1.07 (d, J = 6.8 Hz, 3 H, *i*Pr-CH_3), 1.05 (d, J = 6.8 Hz, 3 H, *i*Pr-CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 166.08 (carbonyl), 152.18 (py-C^6), 150.71 (py-C^2), 149 (dm, J = 250 Hz, *p*-*C*F), 142.58 (ph-C^1), 141.11, 140.82 (ph-C^{2,6}), 140 (dm, J = 240 Hz, *o*-*C*F), 138 (dm, J = 260 Hz, *m*-*C*F), 137.58 (py-C^4), 131.43 (py-C^5), 127.61 (ph-C^{3,5}), 126.61 (methallyl-*C*CH$_3$), 126.26, 124.00 (py-C^3, ph-C^4), 121 (m, *i*-B*C*), 58.37, 56.70 (methallyl-*C*H$_2$), 28.85, 28.56 (*i*Pr-*C*H), 25.53, 25.22 (*i*Pr-CH_3), 23.95, 23.17 (*i*Pr-*C*H$_3$), 22.74 (methallyl-*C*H$_3$). ^{19}F NMR (C_6D_6, 376 MHz): δ −75.3 (br, *o*-F), −100.1 (br, *p*-F), −106.8 (br, *m*-F). ^{11}B NMR (toluene, 128 MHz): δ −0.34. Anal. Calcd ($C_{40}H_{28}B_1F_{15}N_2O_1$-Ni·$C_{15}H_{15}$): C, 59.9; H, 3.94; N, 2.54. Found: C, 60.1; H, 4.02; N, 2.76.

[*N*-(2,6-Diisopropylphenyl)-2-pyridinecarboxamidatotris(pentafluorophenyl)-borate-κ^2*N,N*](η^3-benzyl)nickel (5). *N*-(2.6-Diisopropyl)phenyl-2-pyridinecarboxamide (0.282 g, 1.00 mmol) and KH (0.040 g, 1.0 equiv) were weighed in a vial inside a glovebox. THF (6.0 g) was added at room temperature, and the mixture was stirred overnight. After cooling to −30 °C, the solution was added to a solution of Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3) (261 mg, 1.0 mmol) in THF (10 g) which had been cooled to −30 °C. The solvent was removed slowly under vacuum for 30 min. The residue was extracted with toluene (30 mL), and the solvent was then removed to give a red solid. A cooled solution (−30 °C) of tris(pentafluorophenyl)-boron (1.024 g, 2.0 equiv) in toluene (15 g) was added to the red solid, and the solution was stirred for 30 min at room temperature. The byproduct, $(C_6F_5)_3B-PMe_3$, was filtered off. The solvent was removed under vacuum. Crystallization from toluene and pentane (∼3:1) overnight at −30 °C gave an orange solid (0.810 g, 86%). ^{1}H NMR spectra showed that the product is a mixture of two isomers (10:1 ratio). The peaks of the minor isomer are reported in italics. ^{1}H NMR (400 MHz, C_6D_6): δ 7.26 (d, J = 8.0 Hz, 1 H, py-H^3), 7.22 (t, J = 8.0 Hz, 1 H, ph-H^4), 7.09 (t, J = 8.0 Hz, 1 H, benzyl-ph-H^4), 7.04, *6.91* (d, J = 8.0 Hz, 2 H, ph-H^{3,5}), 6.65 (dd, J = 5.2, 0.8 Hz, py-H^6), 6.64 (t, J = 8.0, 2 H, benzyl-ph-H^{3,5}), 6.13, *6.21* (td, J = 8.0, 1.6 Hz, 1 H, py-H^4), 5.94−5.89 (br, 2 H, benzyl-ph-H^{2,6}), 5.89 (ddd, J = 8.0, 5.2, 1.2 Hz, 1 H, py-H^5), 3.52, *3.19* (septet, J = 6.8 Hz, 2 H, *i*Pr-C*H*), 1.33, *1.49* (s, 2 H, benzyl-CH_2), 1.26, *0.98* (d, J = 6.8 Hz, 6 H, *i*Pr-CH_3), 1.13, *0.88* (d, J = 6.8 Hz, 6 H, *i*Pr-C*H*3). ^{13}C NMR (100 MHz, C_6D_6): δ 166.62 (carbonyl), 164.81, 143.16, 140.94, 137.49, 135.06, 128.51, 128.28, 127.66, 127.17, 126.36, 124.23, 117.47, 37.56 (benzyl-*C*H$_2$), 28.83 (*i*Pr-*C*H), 25.43, 23.67 (*i*Pr-*C*H). ^{11}B NMR (toluene, 128 MHz): δ −0.66. Anal. Calcd ($C_{43}H_{28}B_1F_{15}N_2O_1Ni$): C, 54.8; H, 3.00; N, 2.97. Found: C, 54.9; H, 3.03; N, 2.57.

6-Triisopropylsilyl-2-pyridinecarboxylic Acid. A solution of *n*BuLi (1.5 M, 2.5 mL, 3.8 mmol) was added dropwise to a solution of 2-bromo-6-triisopropylpyridine (1.0 g, 3.2 mmol) in THF (10 mL) at −78 °C. The resulting orange solution was stirred at −78 °C for 10 min and then warmed to −45 °C for 15 min. After recooling to −78 °C, the solution was poured onto solid CO_2 via cannula. After stirring for 1 h at room temperature, the mixture was poured into a separatory funnel containing aqueous concentrated NH_4Cl (50 mL). The product was extracted twice with diethyl ether (30 mL). The combined organic fractions were dried over $MgSO_4$, and the solvent was removed to give a white crystalline solid (0.83 g, 93%). The compound was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.2 Hz, 1 H, py-H^3), 7.88 (t, J = 7.2 Hz, 1 H, py-H^4), 7.76 (d, J = 7.2 Hz, 1 H, py-H^5), 1.51 (septet, J = 7.6 Hz, 3 H, *i*Pr-C*H*), 1.01 (d, J = 7.6 Hz, 18 H, *i*Pr-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.81 (carbonyl), 136.30, 134.86, 122.51 (py-C^{3,4,5}), 18.66 (*i*Pr-*C*H$_3$), 10.91 (*i*Pr-*C*H). IR (neat): 3250 (br, OH), 1775 (carbonyl) cm^{-1}. HRMS-EI *m*/*z* M$^+$ calcd ($C_{15}H_{25}N_1O_2Si_1$), 279.1655; found, 279.1658.

***N*-(2,6-Diisopropylphenyl)-6-triisopropylsilyl-2-pyridinecarboxamide (6).** Triethylamine (0.42 mL, 3.0 mmol) and ethyl chloroformate (0.29 mL, 3.0 mmol) were added successively at −15 °C to a solution of 6-triisopropylsilyl-2-pyridinecarboxylic acid (0.83 g, 3.0 mmol). The mixture was stirred for 15 min at −15 °C, at which time a white precipitate (presumably HCl·NEt_3) formed. 2,6-Diisopropylaniline (0.53 g, 3.0 mmol) was added and the cooling bath removed. After stirring at room temperature for 4 h, the mixture was filtered and the solvent was removed to give a residue. Purification was accomplished by column chromatography on silica gel with hexane and ether (5:1). The compound solidified upon standing at room temperature. Overall yield was 0.93 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (br s, 1 H, N*H*), 8.22 (dd, J = 7.6, 1.2 Hz, 1 H, py-H^3), 7.83 (t, J = 7.6 Hz, 1 H, py-H^4), 7.69 (dd, J = 7.6, 1.2 Hz, 1 H, py-H^5), 7.34 (dd, J = 8.0, 6.8 Hz, 1 H, ph-H^4), 7.25 (d, J = 7.6 Hz, 2 H, ph-H^{3,5}), 3.17 (septet, J = 6.8 Hz, 2 H, *i*Pr-C*H*), 1.53 (septet, J = 7.6 Hz, 3 H, SiC*H*), 1.22 (d, J = 6.8 Hz, 12 H, SiCHCH_3) 1.23 (d, J = 7.6 Hz, 18 H, *i*Pr-CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 164.18, 163.87 (carbonyl, py-C^6), 149.72 (py-*C*^{2}), 146.41 (ph-*C*^{2}), 135.38, 133.47, 121.49 (py-C^{3,4,5}), 131.79 (ph-*C*^{1}), 128.35 (ph-*C*^{4}), 123.69 (ph-*C*^{3,5}), 29.15 (*i*Pr-*C*H), 23.75 (*i*Pr-*C*H$_3$), 18.68 (SiCH*C*H$_3$), 10.06 (Si*C*H). IR (neat): 3350 (br, NH), 1694 (carbonyl) cm^{-1}. HRMS-EI *m*/*z* M$^+$ calcd ($C_{27}H_{42}N_2O_1Si_1$), 438.3066; found, 438.3058.

[*N*-(2,6-diisopropylphenyl)-6-(triisopropylsilyl-κC2)-pyridinecarboxamidato-κ*N,N*](trimethylphosphine)-nickel (7). *N*-(2,6-Diisopropylphenyl)-6-(triisopropylsilyl)-2-pyridinecarboxamide (78.9 mg, 0.180 mmol) and KH (22 mg, 3.0 equiv) were weighed in a vial inside a glovebox. THF (1.0 g) was added, and the mixture was stirred for 3 h at room temperature. NMR spectra indicate at this stage the clean formation of the potassium salt. ^{1}H NMR (400 MHz, THF-d_6): δ 8.44 (d, J = 8.0 Hz, 1 H, py-H^3), 7.55 (t, J = 7.6 Hz, 1 H, py-H^4), 7.44 (d, J = 7.6 Hz, 1 H, py-H^5), 7.06 (d, J = 7.6 Hz, 2 H, ph-H^{3,5}), 6.89 (t, J = 7.6 Hz, 1 H, ph-H^4), 3.24 (septet, J = 6.8 Hz, 2 H, *i*Pr-C*H*), 1.32 (septet, J = 7.6 Hz, 3 H, SiC*H*), 1.20−1.05 (m, 30 H, *i*Pr-CH_3, SiCHCH_3). ^{13}C NMR (100 MHz,

Table 2. Crystallographic Parameters[a]

	3	4	7
formula	$C_{34}H_{16}BF_{15}N_2Ni_O$	$C_{110}H_{86}B_2F_{30}N_4Ni_2O_2$	$C_{30}H_{49}N_2NiOPSi$
fw	823.01	2204.87	571.48
a, Å	11.130(2)	12.732(2)	19.317(9)
b, Å	12.247(2)	13.421(2)	16.997(8)
c, Å	14.698(2)	16.698(2)	20.064(9)
α, deg	71.396(2)	71.222(2)	90
β, deg	68.835(2)	72.959(2)	101.925(8)
γ, deg	73.809(2)	73.756(2)	90
V, Å^3	1740.0(5)	2528.2(6)	6446(5)
space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
d(calc), g cm^{-1}	1.571	1.448	1.178
Z	2	1	8
μ, mm^{-1}	0.669	0.481	0.712
no. of data collected	15 391	26 351	33 018
no. of unique data	6110	11 277	7472
no. of variables	515	681	338
R (%)	6.80	4.76	4.45
R_w (%)	19.3	9.97	10.8
goodness of fit	1.401	0.936	1.026

[a] All data collected at 150 K with Mo Kα radiation, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\sigma(F)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$.

$CDCl_3$): *δ* 165.50, 162.51, 162.07, 153.59, 141.14, 133.82, 131.41, 125.53, 122.85, 120.92, 29.31 (*i*Pr-*C*H), 23.85 (*i*Pr-*C*H$_3$), 19.38 (SiCH*C*H$_3$), 12.51 (Si*C*H). The excess KH was filtered off, and to the filtrate was added a solution of Ni(η^3-$CH_2C_6H_5$)-Cl(PMe_3) (47 mg, 0.18 mmol) in THF (2.0 g) at room temperature. KCl precipitated immediately upon mixing the two solutions. The mixture was stirred for an additional 5 h. The solvent was removed by vacuum, and the product was extracted using pentane. The compound was purified by recrystallization from a concentrated pentane solution at room temperature and was obtained as dark red crystals in 50% yield. The crystals are analytically pure and suitable for X-ray diffraction studies. ^{1}H NMR (400 MHz, C_6D_6): *δ* 8.04 (ddd, *J* = 7.2, 2.0, 0.8 Hz, 1 H, py-H^3), 7.21 (s, 3 H, ph-H$^{2-4}$), 7.03 (t, *J* = 7.2 Hz, 1 H, py-H^4), 6.99 (ddd, *J* = 7.2, 2.0, 0.8 Hz, 1 H, py-H^5), 4.46 (septet, *J* = 6.8 Hz, 2 H, *i*Pr-C*H*), 1.58 (d, *J* = 6.8 Hz, 6 H, *i*Pr-C*H*$_3$), 1.38 (d, *J* = 6.8 Hz, 6 H, *i*Pr-C*H*$_3$), 1.29 (d, *J* = 6.8 Hz, 6 H, SiCHC*H*$_3$), 1.20−1.10 (m, 2 H, SiC*H*), 1.08 (d, *J* = 6.8 Hz, 6 H, SiCHC*H*$_3$) 1.04 (s, 6 H, NiCC*H*$_3$), 0.59 (d, *J* = 8.4 Hz, 9 H, PC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 169.96 (carbonyl), 165.35 (py-C^6), 155.33 (ph-C^1) 148.60 (py-*C*^{2}), 145.08 (ph-*C*^{2}), 136.34, 132.07 (d, *J* = 2.3 Hz), 125.10 (py-C^{3,4,5}), 123.58 (ph-*C*$^{3.5}$), 123.48 (ph-*C*^{4}), 30.06 (*i*Pr-*C*H), 29.29 (d, *J* = 5.4 Hz, Ni*C*), 26.29, 23.44 (*i*Pr-*C*H$_3$), 20.40, 19.91 (SiCH*C*H$_3$), 15.71 (d, *J* = 25 Hz, NiC*C*H$_3$), 12.25 (Si*C*H). ^{31}P NMR (162 MHz, C_6D_6): *δ* −24.03 ppm. Anal. Calcd: C, 63.0; H, 8.66; N, 4,90. Found: C, 63.1; H, 8.65; N, 5.10.

General Polymerization Procedure. In a typical reaction, 25 *μ*mol of catalyst (**3**, **4**, **5**, or **7**) and optionally a certain amount of $B(C_6F_5)_3$ was (were) weighed into a 50 mL Erlenmeyer flask containing a stirring bar in a glovebox. To the above flask was added 30 mL of toluene. The flask was then placed inside a Parr bomb reactor. The bomb was assembled and brought out of the glovebox. The ethylene was fed continuously under a pressure of 100 psig without temperature control. The ethylene flow rate was monitored by a mass flow controller. The reaction was quenched by release of ethylene pressure, and the solution was analyzed by GC−MS. The reaction mixture was poured into a flask containing 100 mL of acetone, and the precipitated polyethylene was collected by filtration. The catalytic activities are summarized in Table 1.

Crystallography. Crystals were mounted onto a thin glass fiber with paratone-8277 and immediately placed in a cold nitrogen stream at 150 K on a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation) operating at 45 kV and 40 mA. A full sphere of intensity data for each structure was collected in 2252 frames with a scan width of 0.30° and an exposure time of 30 s. The number of reflections used for the least-squares refinement of unit cell parameters (at 150 K) was 6649, 7176, and 8192 for **3**, **4**, and **7**, respectively. The empirical absorption corrections based on the equivalent reflections were performed using the program SADABS. The structures were solved by direct methods followed by successive difference Fourier methods. Full-matrix refinements were against F^2. Hydrogen atoms were calculated at idealized positions, and their atomic positions were refined as riding atoms of their parent carbon atoms. The crystal data and refinement results are summarized in Table 2.

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Supporting Information Available: Complete details for crystallographic studies of **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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