Electrophilic Metal Precursors and a *β*-Diimine Ligand for Nickel(II)- and Palladium(II)-Catalyzed Ethylene Polymerization†

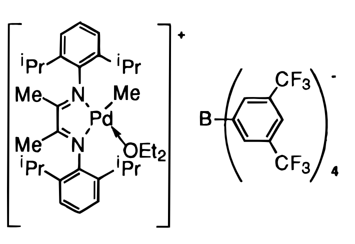
Jerald Feldman,* Stephan J. McLain, Anju Parthasarathy, William J. Marshall, Joseph C. Calabrese, and Samuel D. Arthur

Central Research & Development, Experimental Station, DuPont Company, Wilmington, Delaware 19880-0328

Received November 14, 1996⊗

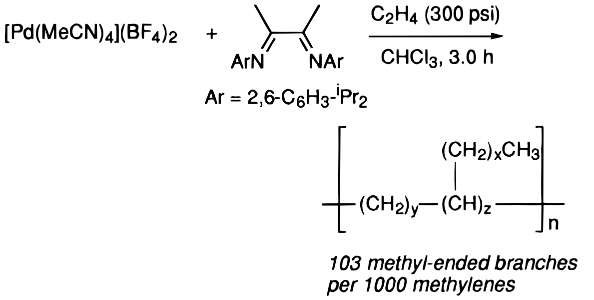
Summary: The α-diimine ligand ArN=C(Me)C(Me)=NAr (Ar = 2,6-C_6H_3-$^iPr_2$) reacts with $Pd(OAc)_2$ in the presence of HBF_4·Et_2O, or $[Pd(MeCN)_4](BF_4)_2$ in the absence of acid, to give ethylene polymerization catalysts. The reactions of a related β-diimine ligand with $[Pd(MeCN)_4](BF_4)_2$ and (1,2-dimethoxyethane)$NiBr_2$, and the polymerization activity of catalysts derived from it, are discussed.

The discovery of a new class of Ni(II) and Pd(II) catalysts for the polymerization of ethylene and α-olefins was reported recently by Brookhart and co-workers.[1] Complex **1** is an example of such a catalyst; **1** incorporates a sterically hindered α-diimine ligand, which allows it to polymerize ethylene and α-olefins to high molecular weight. In the course of our studies on these systems, we have found some new precursors and ligands for diimine-based Ni(II)- and Pd(II)-catalyzed ethylene polymerization. Our results are detailed here.



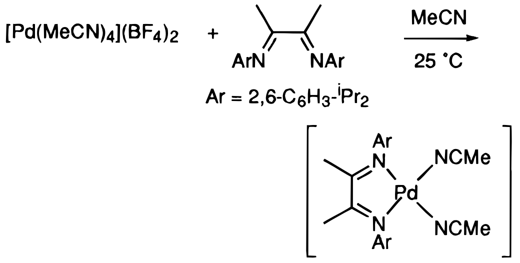
1

We have found that catalytically active Pd species can be generated *in situ* from simple precursors, e.g., weakly ligated Pd(II) dications. Reaction of $[Pd(MeCN)_4](BF_4)_2$[2] with ArN=C(Me)C(Me)=NAr (Ar = 2,6-C_6H_3-$^iPr_2$) under 300 psi of ethylene in chloroform results in formation of amorphous polyethylene (eq 1).[3] The polymer is highly branched, and the branching level and distribution are identical to those obtained when the well-defined initiator **1** is used as catalyst (103 methyl-ended branches per 1000 methylene units).[1] The total turnover number based on Pd is 7700 in 3.0 h, which is comparable to the activity exhibited by **1** and suggests that most of the Pd present eventually forms active catalyst. Molecular weight determination by GPC (trichlorobenzene vs linear polyethylene) gave values of $M_n = 10\,800$, $M_w = 21\,200$, and $M_w/M_n = 2.0$; these are about an order of magnitude lower than those typically observed with **1**, a reflection of the different anions present $\{BF_4^-$ vs $B[(3,5\text{-}C_6H_3\text{-}(CF_3)_2]_4^-\}$.[4] An active ethylene polymerization catalyst can also be generated from $Pd(OAc)_2$ plus HBF_4·Et_2O in the presence of ArN=C(Me)C(Me)=NAr.[3] Again, highly branched polyethylene is produced (1200 turnovers in 1.5 h).[5] The above reactions also proceed in methylene chloride[6] and in aromatic solvents.



(1)

We synthesized $\{[\eta^2\text{-ArN=C(Me)C(Me)=NAr]Pd(MeCN)_2}\}(BF_4)_2$ (**2**) by the reaction shown in eq 2.[7]



(2)

2

Complex **2** is also a catalyst for ethylene polymerization, but it is much less active than the system formed *in situ* in eq 1 (1100 turnovers in 9 h at 400 psi of C_2H_4).[3,8] A plausible explanation is that **2** reacts less rapidly to give an initiating species than $[Pd(MeCN)_4](BF_4)_2$.

---

† Contribution no. 7507.

⊗ Abstract published in *Advance ACS Abstracts*, March 15, 1997.

[1] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

[2] (a) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898. (b) Sen, A.; Lai, T.; Thomas, R. R. *J. Organomet. Chem.* **1988**, *358*, 567.

[3] Experimental details are given in the Supporting Information.

[4] With well-defined catalysts analogous to **1**, polymer molecular weight is inversely related to the coordinating ability of the anion: McLain, S. J.; Feldman, J. unpublished results. BF_4^- is a relatively coordinating anion: Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[5] $M_n = 30\,500$ and $M_w = 43\,000$ ($M_w/M_n = 1.4$) vs linear polyethylene; polymer contained 100 methyl-ended branches per 1000 methylene units.

[6] An experiment identical to that shown in eq 1,[3] but run in CH_2Cl_2, gave 6970 turnovers in 3.0 h ($M_n = 12\,300$; $M_w = 23\,500$ ($M_w/M_n = 1.9$) vs linear polyethylene in trichlorobenzene.

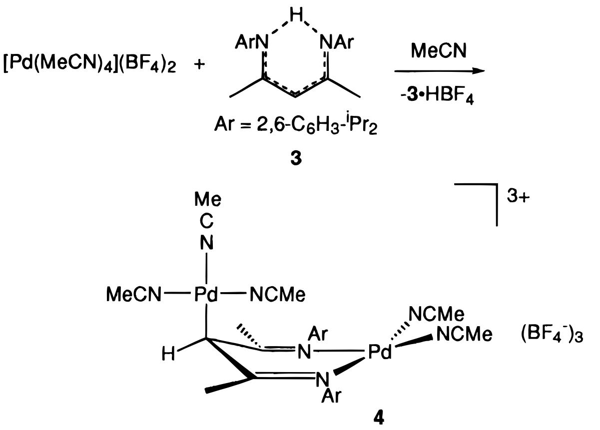
[7] The X-ray crystal structure of **2** is included as Supporting Information. Selected data for **2**: ^1H NMR (CD_2Cl_2, 25 °C) δ 7.51 (t, 2H, H_p), 7.34 (d, 4H, H_m), 3.22 (sept, 4H, C*H*Me_2), 2.52 (s, 6H, N=CMe), 1.95 (s, 6H, N≡CMe), 1.49 (d, 12H, CHMe*Me′*), 1.31 (d, 12H, CH*Me*Me′). Analytical and X-ray samples were crystallized by slow diffusion of pentane into an acetonitrile solution of **2**, giving the bis(MeCN) solvate. Anal. Calcd for $C_{36}H_{52}B_2F_8N_6Pd$: C, 50.94; H, 6.17; N, 9.90. Found: C, 50.52; H, 6.17; N, 9.59.

S0276-7333(96)00968-5 CCC: $14.00

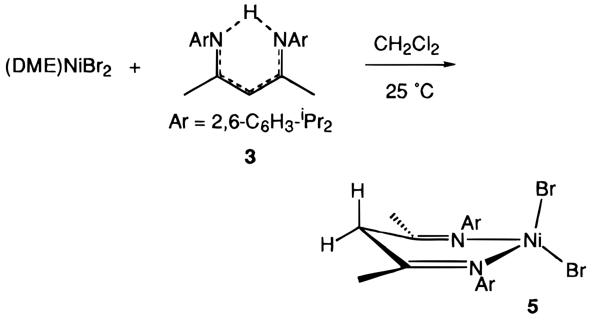
The mechanism by which the above systems initiate is presently unclear. Sen and others have demonstrated that electrophilic precursors such as $[Pd(MeCN)_4](BF_4)_2$ and related Pd(II) complexes [e.g., $(dppe)Pd(BF_4)_2$] are catalysts for the addition polymerization of norbornene and styrene and for the oligomerization of ethylene and α-olefins.[2b,9] Propagation via cationic mechanisms has often been suggested for these reactions.[2b,9a–f] However, Risse et al. have shown that norbornene polymerization catalyzed by $[Pd(MeCN)_4](BF_4)_2$ almost certainly proceeds by an insertion mechanism.[10] Although the mechanism for catalyst initiation in norbornene polymerization is still uncertain,[9j] water appears to be necessary in the $[Pd(MeCN)_4](BF_4)_2$-catalyzed polymerization of 2,3-diester derivatives of norbornadiene in acetonitrile, suggesting initiation by Wacker-type nucleophilic attack by water on a coordinated olefin to give a Pd σ-alkyl complex.[11] We have not ruled out initiation by adventitious nucleophile in our system. However, we note that the polymerization reaction shown in eq 1 gives essentially identical yields in ethanol-stabilized, reagent grade chloroform and in amylene-stabilized chloroform dried by distillation from P_2O_5.[12]

Regardless of the actual mechanism for catalyst initiation, the ethylene polymerizations described here clearly proceed by an insertion mechanism. We propose that, in oligomerizations of ethylene catalyzed by $[Pd(MeCN)_4](BF_4)_2$ and other dicationic Pd(II) complexes, propagation also proceeds by an insertion mechanism; the catalysts described here *polymerize* ethylene because they incorporate a sterically hindered α-diimine ligand.[13]

We prepared an analogous, sterically hindered β-diimine ligand and examined its reactions with Pd(II) and Ni(II) catalyst precursors (eqs 3 and 4). NMR data for **3** are consistent with the symmetrical, hydrogen-bridged "β-iminoamine" structure shown.[14] Although complexes incorporating anionic ligands of this type have been reported,[14–16] examples in which the ligand is bound as a neutral donor appear to be rare.[16] Reaction between **3** and $[Pd(MeCN)_4](BF_4)_2$ in acetonitrile at 25 °C gives **3**·HBF_4 (identified by ^1H NMR spectroscopy) and complex **4** (eq 3). Despite repeated attempts, we were unable to obtain crystals of **4** in pure form free from coprecipitated **3**·HBF_4. Nevertheless, we were able to identify **4** on the basis of X-ray crystallography;[17] the structure of the trication and selected distances and bond angles are shown in Figure 1. The complex, which crystallizes as the tris(acetonitrile) solvate, has an unusual structure: the central carbon atom of the β-diimine ligand is σ-bound to a $Pd(MeCN)_3{}^+$ fragment, while the nitrogen atoms are bound to a $Pd(MeCN)_2{}^{2+}$ fragment. Bond distances within the six-membered chelate ring are consistent with the localized diimine structure drawn in eq 4; the ring itself adopts a boat conformation. Most likely, **4** arises from initial formation of **3**•HBF_4 and $[(\eta^2\text{-ArNC(Me)=CHC(Me)=NAr})Pd(MeCN)_2]^+$, followed by electrophilic attack on C_β of the latter by a second equivalent of $[Pd(MeCN)_4]^{2+}$.



(3)



(4)

Unlike the analogous reaction of α-diimines, reaction between **3** and $[Pd(MeCN)_4](BF_4)_2$ under 1000 psi of ethylene at 25 °C in $CDCl_3$ resulted in primarily the formation of butenes, and at most a trace of polymer. Whether this is due to the sensitivity of the β-CH_2 group toward activation or an intrinsic problem with this nonrigid chelate ring system is not yet known. Attempts to prepare well-defined Pd catalysts (cf. complex **1**) from ligand **3** have thus far been unsuccessful.

A β-diimine complex of Ni(II) was prepared as shown in eq 4. Purple complex **5** is paramagnetic and displays

---

(8) M_n = 24 000 and M_w = 43 100 (M_w/M_n = 1.8) vs linear polyethylene; polymer contained 94 methyl-ended branches per 1000 methylene units.

(9) (a) Sen, A.; Lai, T. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Sen, A.; Lai, T. *Organometallics* **1982**, *1*, 415. (c) Lai, T.; Sen, A. *Organometallics* **1984**, *3*, 866. (d) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421. (e) Sen, A.; Jiang, Z. *Organometallics* **1993**, *12*, 1406. (f) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661. (g) Mehler, C.; Risse, W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 255. (h) Mehler, C.; Risse, W. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 455. (i) Breunig, S.; Risse, W. *Makromol. Chem.* **1992**, *193*, 2915. (j) Mehler, C.; Risse, W. *Macromolecules* **1992**, *25*, 4226.

(10) An insertion mechanism is indicated by the regioselectivity of the polymerization.[9g,j] The recent preparation of well-defined Pd(II) alkyl and allyl catalysts for norbornene/norbornadiene polymerizations also suggests an insertion type mechanism: (a) Safir, A. L.; Novak, B. M. *Macromolecules* **1995**, *28*, 5396. (b) Safir, A. L.; Novak, B. M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1994**, *35*, 901. (c) Goodall, B. L.; Benedikt, G. M.; McIntosh, L. H.; Barnes, D. A. U.S. Patent 5,468,819, Nov 21, 1995. (d) Reinmuth, A.; Mathew, J. P.; Melia, J.; Risse, W. *Makromol. Chem., Rapid Commun.* **1996**, *17*, 173.

(11) Novak, B. M.; Safir, A. L. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1996**, *37*, 335.

(12) Addition of 100 μL of water to the reaction shown in eq 1 causes catalyst activity to *decrease* (2625 turnovers in 3 h) and dramatically reduces polymer molecular weight (M_n = 670). Thus, water appears to serve as a chain transfer agent. We further conclude that, if adventitious water is playing a role in catalyst initiation, it need be present in only trace amounts.

(13) When less sterically hindered α-diimine ligands are employed, oligomers result; e.g., reaction of $[Pd(MeCN)_4](BF_4)_2$ with $(2\text{-R-}C_6H_4)N{=}CMeCMe{=}N(2\text{-R-}C_6H_4)$ under 300 psi of C_2H_4 in $CDCl_3$ gave branched oligomers (R = ^{t}Bu, M_n = 203; R = Ph, M_n = 128).

(14) Full details are given in the Supporting Information. Ligands of this type have been prepared previously: Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408.

(15) (a) Holm, R. H; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241. (b) Healy, P. C.; Bendall, M. R.; Doddrell, D. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 727.

(16) Honeybourne, C. L.; Webb, G. A. *Chem. Commun.* **1968**, 739.

(17) Crystal data for **4**·$(MeCN)_3$: $Pd_2F_{12}N_{10}C_{45}B_3H_{65}$, triclinic, $P1$ (No. 2); a = 11.853(2), b = 13.734(4), and c = 18.883(5) Å; α = 100.75(2), β = 92.92(2), and γ = 114.33(2)° from 25 reflections; T = −70 °C, V = 2723.5 Å^3, Z = 2, D_c = 1.487 g/cm^3. A yellow wedge, ~0.32 mm × 0.27 mm × 0.34 mm, obtained by slow diffusion of petroleum ether into MeCN at 25 °C, was used for the data collection; 10 320 reflections were collected in the range 2.2° ≤ 2θ ≤ 50.0°, with scan width 1.20−2.30°ω and scan speed 1.70−6.70 deg/min. Final R = 0.040, R_w = 0.037, error of fit = 1.15, max Δ/σ = 0.24.

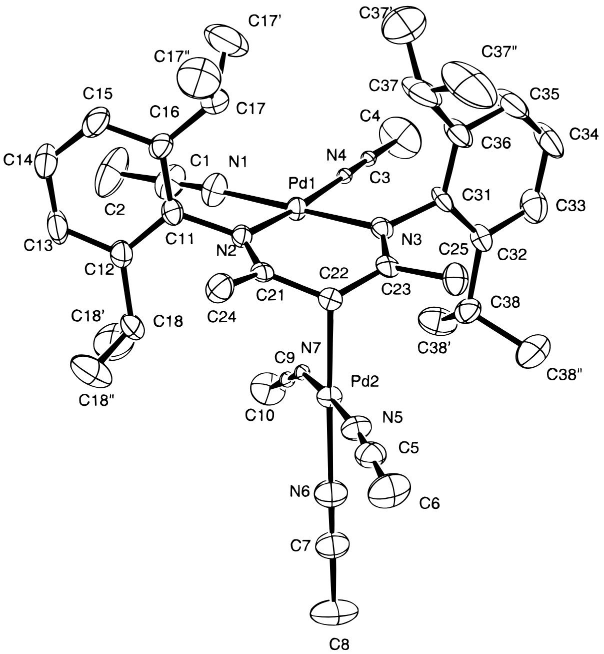
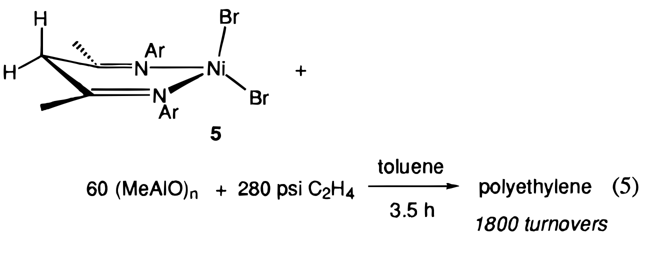


Figure 1. Molecular structure of the trication in **4**. Acetonitriles of crystallization are omitted. Selected bond lengths (Å) and angles (deg): Pd1−N1 = 2.006(4), Pd1−N4 = 2.010(4), Pd1−N2 = 2.009(4), Pd1−N3 = 1.997(4), C21−N2 = 1.274(5), C23−N3 = 1.294(5), C21−C22 = 1.477(6), C22−C23 = 1.469(6), Pd2−C22 = 2.084(4), N2−Pd1−N3 = 92.1(2), Pd2−N7−C9 = 158.5(4).

a contact-shifted ^{1}H NMR spectrum with relatively narrow line widths at room temperature.[18] The X-ray crystal structure of **5** is shown in Figure 2a.[19] The Ni(II) atom adopts a pseudotetrahedral coordination geometry; the ligand is bound as the β-diimine tautomer. As in complex **4**, the six-membered chelate ring sits in a boat conformation (Figure 2b).

Complex **5** is a precursor for ethylene polymerization (eq 5).[3] The polymerization reaction differs from that catalyzed by the analogous α-diimine complex [ArN═C(Me)C(Me)═NAr]NiBr$_2$ in two significant ways: the polyethylene produced is more crystalline (linear)[20] and complex **5** is a less active catalyst precursor (1800 turnovers in 3.5 h).[1a] This may be related to the larger chelate ring size in complex **5**; a similar decrease in activity in going from a five- to a six-membered chelate ring has been noted with SHOP catalysts for ethylene oligomerization.[21]



$$60\ (\mathrm{MeAlO})_n + 280\ \mathrm{psi}\ \mathrm{C_2H_4} \xrightarrow[3.5\ \mathrm{h}]{\text{toluene}} \text{polyethylene} \quad (5)$$

1800 turnovers

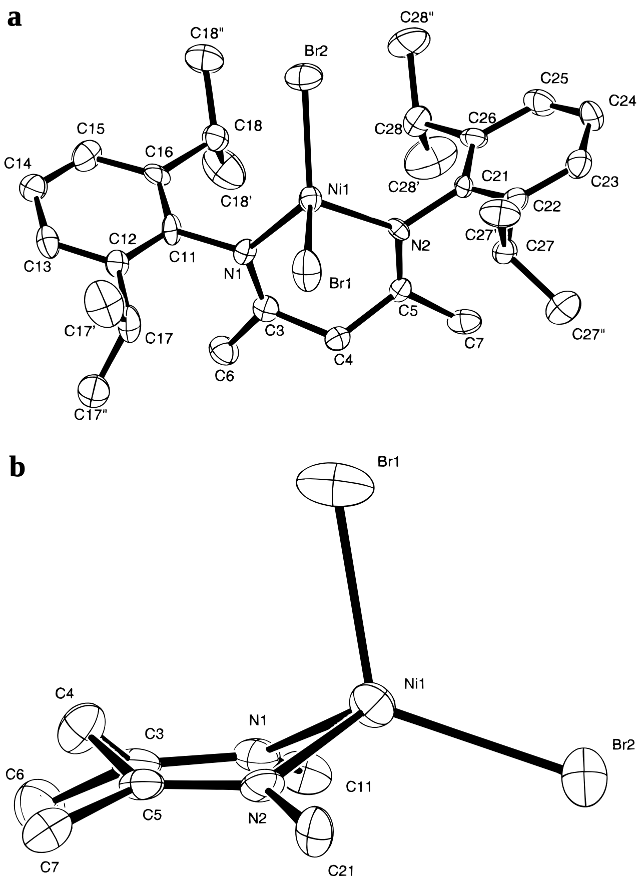


Figure 2. (a) Molecular structure of **5**. Methylene chloride of crystallization is omitted. Selected bond lengths (Å) and angles (deg): Ni−Br1 = 2.376(1), Ni−Br2 = 2.352(1), Ni−N1 = 2.010(5), Ni−N2 = 2.022(5), N1−C3 = 1.280(8), N2−C5 = 1.269(8), C3−C4 = 1.513(9), C4−C5 = 1.500(9), Br1−Ni−Br2 = 118.54(5), Br1−Ni−N1 = 102.0(2), Br1−Ni−N2 = 105.6(1), Br2−Ni−N2 = 112.1(2), Br2−Ni−N1 = 121.3(2), Ni1−Ni−N2 = 93.7(2). (b) View of the chelate ring in **5**. The Ar rings are omitted for clarity.

In conclusion, our results suggest that new catalyst precursors and ligands for diimine-based Ni(II)- and Pd(II)-catalyzed olefin polymerization await discovery. Our ongoing efforts in this area will be reported in due course.

Acknowledgment. We thank Dr. Lynda K. Johnson, Dr. Chris M. Killian, and Prof. Maurice Brookhart for sharing their results prior to publication, Matt Schiffhauer, Alicia Glatfelter, and Pete Butera for skilled technical assistance, and Dr. Steven D. Ittel for helpful discussions.

Supporting Information Available: Text giving details of the synthesis of **2**, **3**, and **5** and ^{1}H NMR characterization of the products formed in the reaction between [Pd(MeCN)$_4$](BF$_4$)$_2$ and **3** and tables giving data for the X-ray analyses of **2**, **4**, and **5** (31 pages). Ordering information is given on any current masthead page.

OM960968X

---

[18] Selected data for **5**: ^{1}H NMR (CDCl$_3$, 25 °C) δ 22.3 (s, 4H, H$_m$), 9.2 (br, 4H, C*H*Me$_2$), 3.5 (s, 12H, CH*Me*Me′), 2.4 (s, 12H, CHMe*Me′*), 1.1 (mult, 2H, β-CH$_2$), −16.3 (s, 2H, H$_p$), −21.8 (s, 6H, α-Me). Anal. Calcd for C$_{29}$H$_{42}$Br$_2$N$_2$Ni: C, 54.67; H, 6.64; N, 4.40. Found: C, 54.38; H, 6.74; N, 4.29.

[19] Crystal data for **5**·CH$_2$Cl$_2$: Br$_2$NiCl$_2$N$_2$C$_{30}$H$_{44}$, monoclinic, $P2_1/n$ (No. 14); $a = 19.347(3)$, $b = 8.018(1)$, and $c = 21.532(1)$ Å, $\beta = 101.10(1)°$ from 50 reflections; $T = -100$ °C, $V = 3277.6$ Å^3, $Z = 4$, D$_c$ = 1.463 g/cm^3. A purple rod, ~0.26 mm × 0.24 mm × 0.53 mm, obtained from CH$_2$Cl$_2$/pentane at −40 °C, was used for the data collection; 6665 reflections were collected in the range $4.0° \leq 2\theta \leq 50.0°$ with scan width 2.80°ω and scan speed 2.90−19.50 deg/min. Final $R = 0.050$, $R_w = 0.038$, error of fit = 1.06, max $\Delta/\sigma = 0.00$.

[20] $T_m = 120.2$ °C; $\Delta H_f = 155$ J/g.

[21] Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21.