2514 *Organometallics* **2006,** *25,* 2514−2524

Ethylene Polymerization Using Discrete Nickel(II) Iminophosphonamide Complexes

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Received December 30, 2005

The syntheses and structures of the discrete (π-allyl)nickel iminophosphonamide (PN_2) complexes **2a**−**d** from the reaction of (π-allyl)nickel bromide and the corresponding PN_2 ligands **3a**,**b** or from the reaction of (π-allyl)$_2$Ni and phosphorane **1** are reported. Complexes **2a**,**b** are characterized by having long Ni−N distances coupled with an acute bite angle for the PN_2 ligand. The π-allyl ligands in complexes **2a**−**d** are not fluxional on the NMR time scale at room temperature, although chemical exchange between the isomeric complexes **2c**,**d** occurs via PN_2 ligand reorientation. Purified complexes **2a**−**d** are not active for ethylene polymerization; it is only when complexes **2c**,**d** are generated in situ in the presence of monomer that high-M_w branched poly(ethylene) is formed. A variety of indirect evidence suggests that the active catalyst arises from the reaction of Ni(0)−alkene complexes with phosphorane **1**, either preformed or generated in situ through decomposition of (π-allyl)$_2$Ni. A bona fide $PN_2NiPh(PPh_3)$ complex, **5**, was prepared from $NiPh(PPh_3)_2Br$ and the PN_2 ligand **3a** and was structurally characterized. This complex is active for 1-hexene isomerization in the absence of an activator. During hexene isomerization, variable amounts of the paramagnetic bis(PN_2) complex **4** are produced along with ligand **3a**. In addition, the fluxional intermediate **6**, containing both a PN_2 ligand and coordinated PPh_3, is present during catalysis. Reaction of **5** with an equimolar amount of propene provides α-methylstyrene, the product of 1,2-insertion followed by β-H elimination. Complex **5** is not effective for polymerization or oligomerization of ethylene under a variety of conditions. The reactions of complex **5** with various phosphine scavengers were studied, and of these only $Rh(acac)(C_2H_4)_2$ is both effective and selective for PPh_3. Hard Lewis acids, including $AlMe_3$, $B(C_6F_5)_3$, and PMAO, have a pronounced tendency toward abstraction of the PN_2 or other anionic ligands in these unhindered complexes. All of the complexes reported in this paper are extremely active for ethylene dimerization in the presence of PMAO. In the presence of stoichiometric Rh(I), complex **5** rapidly isomerizes 1-hexene and in the presence of ethylene produces branched PE oligomers at modest activity.

Introduction

There has been considerable interest in the development of late-transition-metal complexes as catalysts for the polymerization of olefins. In particular, a variety of cationic and neutral group 10 complexes have been shown to be effective for the production of branched poly(ethylene) from ethylene monomer,[1] although the catalyst stability and thus activity at elevated temperature has proven problematic with some of these systems. Some of these catalysts have been shown to be competent for the copolymerization of ethylene with functional monomers,[2] particularly acrylates, although catalyst activity often suffers in the presence of such comonomers.

The most thoroughly studied systems from a mechanistic perspective are the cationic α-diimine complexes of Ni and Pd, for which a great deal is known about the nature of the resting states and the insertion and chain-walking isomerization rates from both an experimental[3] and theoretical[4] perspective. More recently attention has been focused on zwitterionic analogues of these complexes[5] as well as neutral Ni catalysts based on hindered salicylaldimine[6] or anilino−troponate[7] ligands. In addition, sterically hindered, cationic, chelating diphosphine complexes are competent polymerization catalysts, provided the chelate ring size is small,[8] while there has been attention

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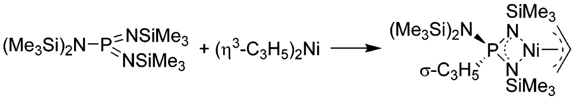
10.1021/om051103z CCC: $33.50

redevoted to neutral phosphino−enolate or analogous complexes of Ni,[9] originally investigated by Keim and co-workers.[10]

Branched poly(ethylene) is produced using these catalyst systems because chain-walking isomerization of the chain, involving a reversible β-H elimination/reinsertion sequence, competes with coordination (trapping) and insertion of monomer. It is therefore of interest to note that the occurrence of this process was first postulated in the early work of Fink and co-workers,[11] using a catalyst formulation first reported by Keim et al.[12]

This catalyst formulation was generated in situ in the presence of ethylene through the reaction of either $Ni(COD)_2$ or (π-allyl)$_2$Ni with the sterically hindered phosphorane $(Me_3Si)_2N-P(=NSiMe_3)_2$ (**1**) and provided poly(ethylene) which was said to resemble low-density poly(ethylene) in its properties.[12] In the case of (π-allyl)$_2$Ni and phosphorane **1**, the product of this reaction in the absence of monomer was shown to be the (π-allyl)Ni−iminophosphonamide (PN_2) complex **2** (eq 1). The Pd analogue of **2** was structurally characterized but was inactive for ethylene polymerization.[12]



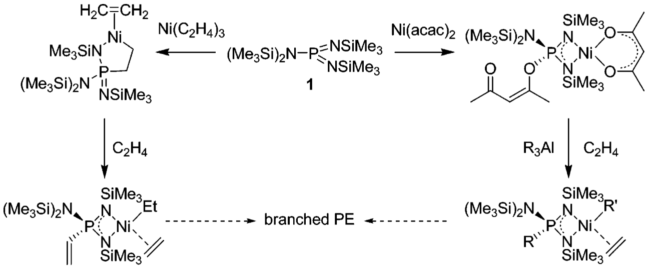
1 **2**

(1)

Subsequent work from the group of Yano in Japan established that $Ni(COD)_2$ in combination with phosphorane **1** could be activated for ethylene polymerization using an α-olefin and that the polymers formed had Me and Hx^+ branching in roughly equal amounts, as judged from their ^{13}C NMR spectra.[13] Branches of intermediate length were not detected in the ^{13}C NMR spectra, while some of the longer branches present were of sufficient length to influence the hydrodynamic radius of the polymer in solution (i.e. $g' = [\eta]_{br}/[\eta]_{lin} = 0.6-0.7$). In a subsequent patent application, Yano et al. demonstrated that the reaction of, for example, $Ni(acac)_2$ with phosphorane **1** gave rise to an active catalyst formulation in the presence of alkylaluminums; the polymers formed had similar properties.[14]

Finally, in some mechanistic work reported by the group of Fink, the reactions of both $Ni(C_2H_4)_3$ and $Ni(acac)_2$ with phosphorane **1** were examined, and the products were characterized by X-ray crystallography.[11c] In the former case, a *stable* $Ni(alkyl)(C_2H_4)$ complex was formed, while the latter reaction provided a $PN_2Ni(acac)$ complex (Scheme 1). The former compound was said to rearrange to a $PN_2Ni(C_2H_4)R$ complex in the presence of monomer, while the latter could be activated

Scheme 1



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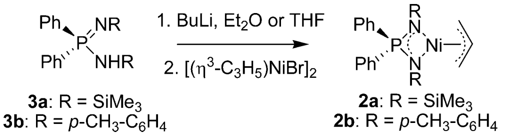
for ethylene polymerization by the addition of an alkylaluminum compound. The activity of the formulations derived from Ni(0)−alkene precursors and phosphoranes analogous to **1** were shown to be a sensitive function of both the phosphorane and Ni(0)−alkene structures.[11c]

The poly(ethylene) formed using the Keim family of catalysts is interesting from a materials perspectives—it has variable crystallinity depending on both M_w and branching but should melt-process like low-density PE. However, the activity and stability of these catalyst formulations are too low for practical use. As we had earlier developed flexible synthetic routes to PN_2 ligands and investigated the synthesis and chemistry of some group 4 PN_2 complexes,[15] including their use as ethylene polymerization catalysts,[16] we were motivated to develop syntheses of discrete $PN_2Ni(L)R$ complexes with a view to improving the catalytic activity of these interesting systems. We report here synthetic, structural, and mechanistic studies of this interesting class of polymerization catalyst.[17]

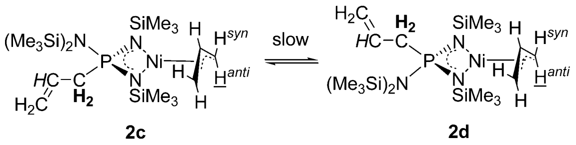
Results and Discussion

Synthesis and Structure of π-Allyl Complexes. On the basis of the early report of Keim, we initially targeted the synthesis of discrete π-allyl PN_2 complexes as catalyst precursors. Complexes **2** can be prepared in high yield through the reaction of $[(\pi\text{-allyl})NiBr]_2$ with the salt of the corresponding PN_2 ligand (eq 2) or through the reaction of $(\pi\text{-allyl})_2Ni$ with phosphorane **1**, as reported by Keim and co-workers (eq 1). Complexes **2** are reasonably air-stable, crystalline solids that can be handled in the open laboratory for short periods of time.



(2)

The complex originally reported by Keim exists as a 60:40 mixture of stereoisomers **2c**,**d** that differ in the orientation of the unsymmetrical PN_2 ligand with respect to the π-allyl group (eq 3). In solution, separate and sharp ^{1}H and ^{13}P NMR signals are seen for each isomer, indicating that isomerization is slow on the NMR time scale at room temperature. ^{1}H chemical shift assignments for each isomer could be made through a combination of 2D DQF-COSY and NOESY spectra (see the Supporting Information for details), but it was not possible to deduce the structure of the major stereoisomer from these data.



(3)

Protons in *italics*, **bold** or underline are resolved and show observable EXSY correlation

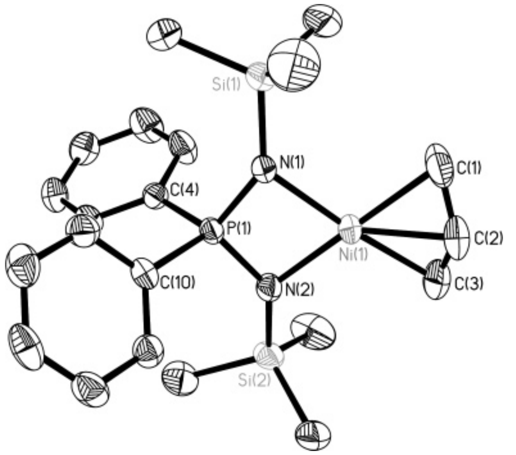


Figure 1. Molecular structure of complex **2a**, depicted with 50% thermal ellipsoids and with hydrogen atoms omitted.

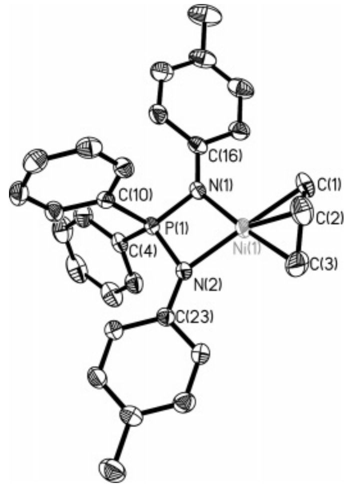


Figure 2. Molecular structure of complex **2b**, depicted with 50% thermal ellipsoids and with hydrogen atoms omitted.

The 2D NOESY spectra were informative with respect to the nature of an exchange process involving these two isomers (eq 3). In particular, while in-phase exchange correlation was seen between the resolved P−σ-allyl protons (both CH_2 and CH), and the *anti*-π-allyl protons (H^{anti}) of the two different isomers, there was no evidence for exchange between the *anti*-π-allyl and/or *syn*-π-allyl protons on the same/different isomers, despite the use of a variety of mixing times.

We thus conclude that the π-allyl ligand is not fluxional (involving a conventional $\pi-\sigma-\pi$ allyl isomerization mechanism) on the NMR time scale and that the observed exchange process arises from either rotation of the PN_2 ligand about the Ni- - -P axis (as is observed for early-metal PN_2 complexes)[15−16] or from reversible dissociation into an η^1 form. Given the long Ni- - -N distances observed in the solid-state structure of these complexes (vide infra), the latter hypothesis is more reasonable for these late-metal systems.

Complexes **2a**,**b** were characterized further by X-ray crystallography, and molecular structure plots appear in Figures 1 and 2, respectively, while Tables 1 and 2 contain selected crystallographic data and selected metrical data, respectively.

Both of these complexes display similar structural characteristics—they differ principally in that the PN_2Ni ring is slightly puckered in the case of **2b**. In both cases, the π-C_3H_5 group is disordered in the solid state ("up−down" disorder with respect to the PN_2 ligand), but with grossly unequal occupancies such that the disorder could not be accurately modeled.

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Table 1. Selected Crystallographic and Refinement Data for PN_2Ni Complexes[a]

	2a	**2b**	**5**
emp formula	$C_{21}H_{33}N_2NiPSi_2$	$C_{29}H_{29}N_2NiP$	$C_{42}H_{48}N_2NiP_2Si_2$
formula wt	459.35	495.22	757.65
T (K)	180(1)	180(1)	150(1)
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
unit cell dimens			
a (Å)	14.6477(7)	8.7003(3)	12.3383(8)
b (Å)	9.5088(4)	10.5517(4)	13.5161(9)
c (Å)	18.5319(9)	14.7301(6)	23.308(2)
α (deg)		106.076(1)	
β (deg)	110.413(1)	102.483(1)	
γ (deg)		98.836(1)	
V (Å^3)	2419.07(19)	1235.39(8)	3887.0(4)
Z	4	2	4
ρ(calcd) (Mg/m^3)	1.261	1.331	1.295
abs coeff (mm^{-1})	0.976	0.869	0.675
F(000)	976	520	1600
cryst size (mm^3)	0.32 × 0.23 × 0.22	0.37 × 0.34 × 0.31	0.34 × 0.30 × 0.24
θ range (deg)	1.48−28.28	1.50−30.00	1.74−27.88
no. of rflns coll	26 195	15 544	21 869
no. of indep rflns	6014 (R(int) = 0.0693)	7207 (R(int) = 0.0273)	9250 (R(int) = 0.0316)
completeness in θ, %	100.0	99.8	100.0
max/min transmissn	0.843/0.754	0.818/0.714	0.857/0.798
no. of data/restraints/params	6014/0/250	7207/0/301	9250/0/448
GOF (F^2)	1.821	2.621	1.301
R ($I > 2\sigma(I)$)	R1 = 0.0488 wR2 = 0.0871	R1 = 0.0369 wR2 = 0.0857	R1 = 0.0311 wR2 = 0.0539
R (all data)	R1 = 0.0581 wR2 = 0.0888	R1 = 0.0399 wR2 = 0.0862	R1 = 0.0353 wR2 = 0.0546
diff peak/hole (e Å^{-3})	0.754/−0.549	0.987/−0.667	0.312/−0.252

[a] Data were collected using Mo Kα radiation with $\lambda = 0.710\,73$ Å. A face-indexed analytical absorption correction was applied. Refinement was full-matrix least squares based on F^2.

Table 2. Selected Bond Lengths and Angles for $NiPN_2$ Complexes with Estimated Standard Deviations in Parentheses

complex **2a**		complex **2b**		complex **5**	
		Bond Lengths (Å)			
Ni(1)−N(1)	1.973(2)	Ni(1)−N(1)	1.941(1)	Ni(1)−N(1)	2.055(2)
Ni(1)−N(2)	1.968(2)	Ni(1)−N(2)	1.959(1)	Ni(1)−N(2)	1.976(1)
P(1)−N(1)	1.594(2)	P(1)−N(1)	1.610(1)	P(1)−N(1)	1.599(1)
P(1)−N(2)	1.599(2)	P(1)−N(2)	1.618(1)	P(1)−N(2)	1.596(2)
P(1)−C(4)	1.819(2)	P(1)−C(4)	1.809(2)	P(1)−C(13)	1.816(2)
P(1)−C(10)	1.819(2)	P(1)−C(10)	1.806(1)	P(1)−C(19)	1.826(2)
Si(1)−N(1)	1.707(2)	N(1)−C(16)	1.402(2)	Si(1)−N(1)	1.732(2)
Si(2)−N(2)	1.715(2)	N(2)−C(23)	1.401(2)	Si(2)−N(2)	1.725(1)
Ni(1)−C(1)	2.011(2)	Ni(1)−C(1)	1.991(2)	Ni(1)−C(1)	1.885(2)
Ni(1)−C(2)	1.946(2)	Ni(1)−C(2)	1.943(2)	Ni(1)−P(2)	2.157(1)
Ni(1)−C(3)	1.989(2)	Ni(1)−C(3)	1.999(2)		
C(1)−C(2)	1.332(4)	C(1)−C(2)	1.352(3)		
C(2)−C(3)	1.370(4)	C(2)−C(3)	1.371(3)		
		Bond Angles (deg)			
N(2)−Ni(1)−N(1)	78.1(1)	N(1)−Ni(1)−N(2)	75.9(1)	N(2)−Ni(1)−N(1)	76.9(1)
N(1)−P(1)−N(2)	102.0(1)	N(1)−P(1)−N(2)	96.0(1)	N(1)−P(1)−N(2)	103.3(1)
P(1)−N(1)−Ni(1)	89.9(1)	P(1)−N(1)−Ni(1)	92.9(1)	P(1)−N(1)−Ni(1)	88.4(1)
P(1)−N(2)−Ni(1)	90.0(1)	P(1)−N(2)−Ni(1)	92.0(1)	P(1)−N(2)−Ni(1)	91.3(1)
C(4)−P(1)−C(10)	102.9(1)	C(10)−P(1)−C(4)	106.7(1)	C(13)−P(1)−C(19)	106.3(1)
C(1)−Ni(1)−C(3)	73.2(1)	C(1)−Ni(1)−C(3)	72.4(1)	C(1)−Ni(1)−P(2)	87.6(1)
N(1)−Ni(1)−C(1)	103.9 (1)	N(1)−Ni(1)−C(1)	102.9 (1)	C(1)−Ni(1)−N(2)	93.9(1)
N(2)−Ni(1)−C(3)	104.4(1)	N(2)−Ni(1)−C(3)	108.8 (1)	N(1)−Ni(1)−P(2)	101.6(1)
C(1)−C(2)−C(3)	123.9(1)	C(1)−C(2)−C(3)	119.8(2)		

The Ni- - -C distances are in the range expected for neutral (π-allyl)nickel complexes, especially those featuring anionic amido-/imino-based ligands.[18] The π-allyl ligand is bonded to the metal center such that the Ni(1)−C(2) distances of 1.946(2) and 1.943(2) Å in **2a**,**b**, respectively, are significantly shorter than either of the distances to the terminal C atoms (Ni(1)−C(1) = 2.011(2), 1.991(2) Å; Ni(1)−C(3) = 1.989(2), 1.999(2) Å). This type of distortion, which is fairly pronounced in this case, is common in electron-rich (π-allyl)Ni complexes.[18,19] It can be attributed to π back-bonding between a filled metal d_{xz} orbital and the highest energy π-MO of the allyl ligand, where the largest orbital coefficient is located at C(2).[20]

Bonding within the π-allyl ligand appears somewhat localized, with C(1)−C(2) = 1.332(4), 1.352(3) Å being significantly shorter than C(2)−C(3) = 1.370(4), 1.371(3) Å. Since there is

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limited or at least no systematic variation in the corresponding Ni- - -C distances, this may reflect the positional disorder primarily associated with C(2), which has the largest thermal parameters of the three atoms.

The most characteristic features of these structures are the long Ni- - -N distances of 1.941(1)−1.973(2) Å, which approach or even exceed the sum of the single-bond covalent radii of Ni and N (1.96 Å).[21] The P- - -N distances show minor variation in these two structures (1.594(2)−1.618(1) Å), with those of **2a** being on average significantly shorter than those in **2b**. These values are intermediate in length between P−N and P═N bonds in P(V) compounds.[22]

In addition, the PN_2 ligand engages the metal in **2a**,**b** with characteristically narrow bite angles of 78.1(1) and 75.9(1)°, respectively, while the endocyclic angles at P, and to a lesser extent N, show significant variation (N(1)−P(1)−N(2) = 102.0(1), 96.0(1)°; P(1)−N(1)−Ni(1) = 89.9(1), 92.9(1)°; P(1)−N(2)−Ni(1) = 90.0(1), 92.0(1)°). As would be expected, the variation in the N(1)−P(1)−N(2) angles is compensated by changes to the exocyclic C(4)−P(1)−C(10) angles of 102.9(1) and 106.7(1)°, respectively.

The picture that emerges from a consideration of these two structures is one where the π-allyl moiety is functioning as a weak π-acceptor ligand while the PN_2 ligand is weakly bound to Ni in comparison. Since the PN_2 ligand is a three-electron σ-donor, with four π electrons largely localized on the N atoms and minimal π-acceptor properties, one would expect the bonding between Ni and N to be somewhat repulsive. The bindings of these two ligands to the metal appear to be important in a consideration of the chemical reactivity of these complexes.

Attempted Ethylene Polymerization. When pure, *none* of these π-allyl complexes are active for ethylene polymerization under a variety of conditions of T and P reported by Keim.[12,23] Instead, high-M_w ($M_w \approx 10^5-10^6$ with PDI $\approx 2-3$ based on SEC-MALLS) poly(ethylene) ($T_m = 98$ °C) is produced, albeit at low activity (~10^3 g pf PE/((mol of Ni) h)), only when phosphorane **1** and (π-allyl)$_2$Ni are combined in a reactor previously saturated with ethylene at 450 psig and 25 °C.[12,17] The material is branched (ca. 30−40 total branches/1000 C atoms) and has a microstructure consistent with that reported by Yano and co-workers,[13,14] which will be discussed in more detail elsewhere.[24]

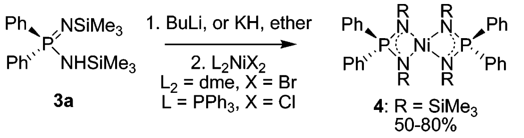
These two findings taken together suggest that it is either an impurity formed and/or intercepted by ethylene during chemical reaction of the precursor components or possibly an impurity already present in either starting material that is responsible for catalysis under these conditions. We note that the crude reaction mixtures formed from (π-allyl)$_2$Ni and phosphorane **1** in the absence of monomer are inactive for ethylene polymerization—in fact, this reaction is quite clean on the basis of NMR analysis if freshly prepared (π-allyl)$_2$Ni is employed.

A variety of evidence suggests that the culprit is in fact (π-allyl)$_2$Ni, which is known to be thermally unstable in solution or even in the solid state.[25] In particular, the use of the more thermally stable and easily purified (π-methallyl)$_2$Ni[26] as a catalyst precursor does not give rise to a very active catalyst, even though it reacts analogously (though more slowly) with phosphorane **1** to furnish a (π-methallyl)$NiPN_2$ complex.[27] Also, though not systematically studied, “aged” solutions of (π-allyl)$_2$Ni which had clearly started to deposit Ni(0) gave rise to more active formulations than did those that were freshly prepared and used.[27]

It is known that in the presence of donors (e.g. CO, PR_3, alkenes) (π-allyl)$_2$Ni decomposes in solution via reductive elimination of 1,5-hexadiene to form Ni(0);[25] a Ni(0)-hexadiene complex[28] is a likely intermediate in this process. Given that $Ni(COD)_2$ or other Ni(0)−alkene complexes and phosphorane **1** also give rise to (more) active catalyst formulations,[11−13] it seems reasonable to conclude that this same reaction is also responsible for polymerization activity when one starts with the (π-allyl)$_2$Ni precursor.

Since it was unclear from these studies what was the active species in ethylene polymerization involving phosphorane **1** and Ni(0) or Ni(II) precursors, we elected to prepare a bona fide $(PN_2)NiR(L)$ complex and study its chemistry.

Synthesis, Structure, and Chemistry of a Discrete $PN_2Ni(PPh_3)Ph$ Complex. Mono- and bis-PN_2 complexes of Ni have been reported in the literature. Both were formed in low yield from the reaction of sterically hindered PN_2 salts and Ni halides in ethereal solution.[29] In our hands and using an Li or K salt of ligand **3a**, we have discovered that this reaction proceeds in higher yield and generally affords the deep blue and paramagnetic bis(PN_2) complex **4** as the sole product, regardless of stoichiometry or mode of addition (eq 4). The same result was observed when using *trans*-$NiCl_2(PPh_3)_2$ as a reagent, suggesting than the intermediate mono$(PN_2)Ni(L)Cl$ complex must be more reactive toward further substitution than the starting material.



(4)

In view of this, the use of a preformed $L_2NiR(X)$ precursor appeared necessary, and the metathetical reaction of $(Ph_3P)_2$-

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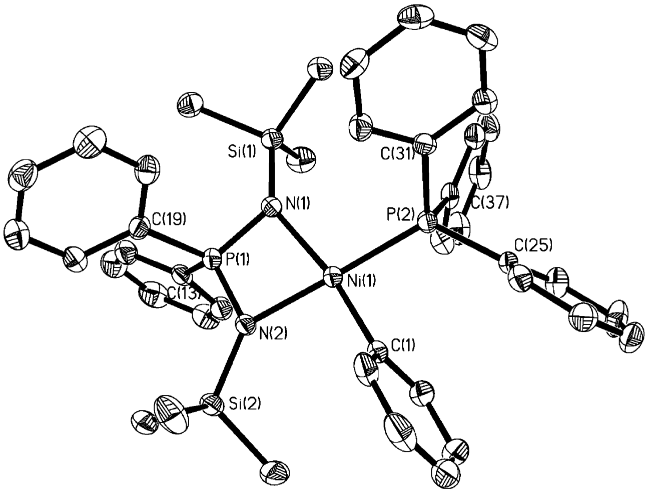
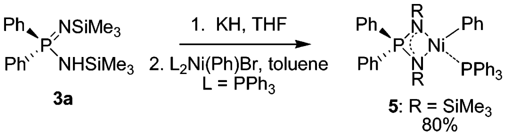


Figure 3. Molecular structure of complex **5** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted.

NiPh(Br) with the K salt of ligand **3a** proceeded uneventfully in high yield to furnish the expected PN_2 complex **5** (eq 5).



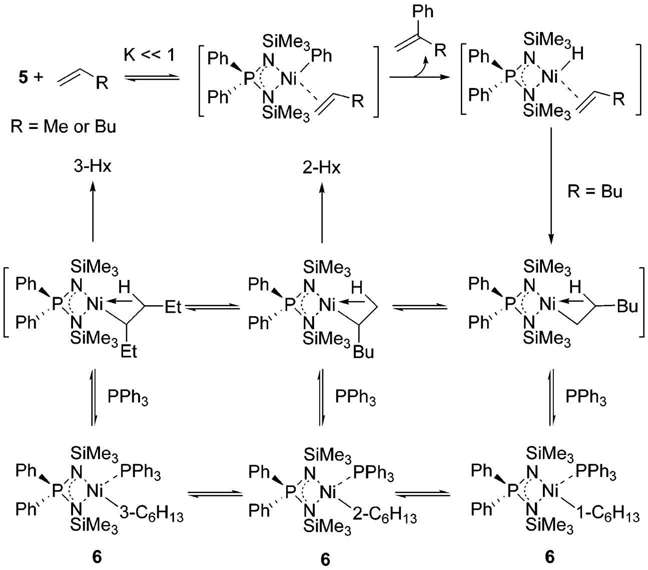
(5)

This complex is again crystalline and reasonably air stable in the solid state. Its molecular structure is depicted in Figure 3, while selected crystallographic and refinement data and selected metrical data appear in Tables 1 and 2, respectively. In comparison with the other structures reported here, the Ni(1)−N(1) and Ni(1)−N(2) distances of 2.055(2) and 1.976(1) Å, respectively, are even longer in this structure and show the expected variation with the trans influence of the remaining ligands. The P- - -N distances are essentially equivalent to those observed in the structure of **2a**. The bite angle of the PN_2 ligand at 76.9(1)° is intermediate between that seen in **2a**,**b**, while the endocyclic angles at P and N largely resemble those in the structure of complex **2a**. The coordination geometry about Ni is rigorously planar, with an angle between Ni−Ph and Ni- - -PPh_3 of 87.6(1)°.

The structure of this compound can be compared to that of a neutral (α-imino-amido)Ni(PMe_3)CH_2Ph complex reported by Bazan and co-workers.[5g] In that structure, which adopts a coordination geometry intermediate between square planar and tetrahedral, the Ni−N distance involving the imine N is 2.001(3) Å, while that involving the amido N is 1.936(2) Å. Suffice it to say that the Ni- - -N distances in complex **5** are significantly longer than the average of these two distances (1.968(3) Å), highlighting the repulsive nature of the Ni−N interactions in this structure.

Complex **5** is fluxional in solution with a single resonance for the N−$SiMe_3$ groups at 25 °C. However, on cooling, decoalescence occurs and two signals in a 1:1 ratio are observed at low *T*, consistent with the inequivalence of these groups in the solid-state structure (see the Supporting Information). Analysis of the line shapes over a 100 °C *T* range using the program DNMR 4.0[30] provides $\Delta H^{\ddagger} = 10.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.7 \pm 0.5$ eu, respectively. The entropy of activation, though negative, is not particularly diagnostic of the mechanism, given that its value is close to zero.

Scheme 2



The rate of this exchange process was unaffected in the presence of free PPh_3. This observation allows us to rule out a phosphine substitution mechanism for the dynamic behavior seen.[31] Instead, we believe, as with the π-allyl complexes **2c**,**d**, that reversible dissociation of the hemilabile PN_2 ligand or rotation of this ligand about the Ni- - -P vector is responsible for fluxional behavior.

Complex **5** catalyzes the isomerization of 1-hexene (1-Hx) to a mixture of 2- and 3-hexene at room temperature. Under pseudo-first-order conditions ($[1\text{-Hx}]_0 = 5.9$ M; $[\mathbf{5}] = 0.051$ M), isomerization of 1-Hx occurs with an initial TOF of 5.7 h^{-1} at 25 °C, while the initial rate of reaction of complex **5** with 1-Hx has $k_{\text{obs}} = 6.4 \times 10^{-4}$ s^{-1} $= k[1\text{-Hx}]_0$. Monitoring of this reaction by ^{31}P NMR spectroscopy (Figure 4) revealed the gradual consumption of both signals due to **5** and the appearance of a signal at ca. 0 ppm which corresponds to that of ligand **3a**. It is also evident from this figure that an intermediate is formed which has both a PN_2 ligand and coordinated PPh_3, although the signals are line-broadened in comparison to those of the starting material. In the ^{1}H NMR spectrum, signals due to ligand **3a** grow in over time at the expense of those of **5**, while variable amounts of the paramagnetic complex **4** also appear during this period.[32] A series of multiplets are seen in the region of 2−3 ppm during catalysis, although the signals are line-broadened.

Our interpretation of these results is that intermediates **6**, featuring a 1-, 2- or 3-hexyl group, and coordinated PPh_3, are formed by reversible insertion/elimination into a PN_2Ni−H bond, where the latter, unobserved species (no Ni−H resonances were detected despite the use of a 40 ppm sweep width) is formed from initial insertion of hexene into Ni−Ph followed by β-elimination (Scheme 2). That the latter step actually occurs was revealed by a NMR experiment involving the reaction of **5** with ca. 1.0 equiv of propene at 25 °C; the expected product, α-methylstyrene (Scheme 2, R = Me), could be isolated by vacuum transfer of the volatile materials following consumption of **5**.

The formation of **3a** by reductive elimination from a PN_2-Ni−H complex is expected on the basis of recent mechanistic work from both the Grubbs and Brookhart groups on related

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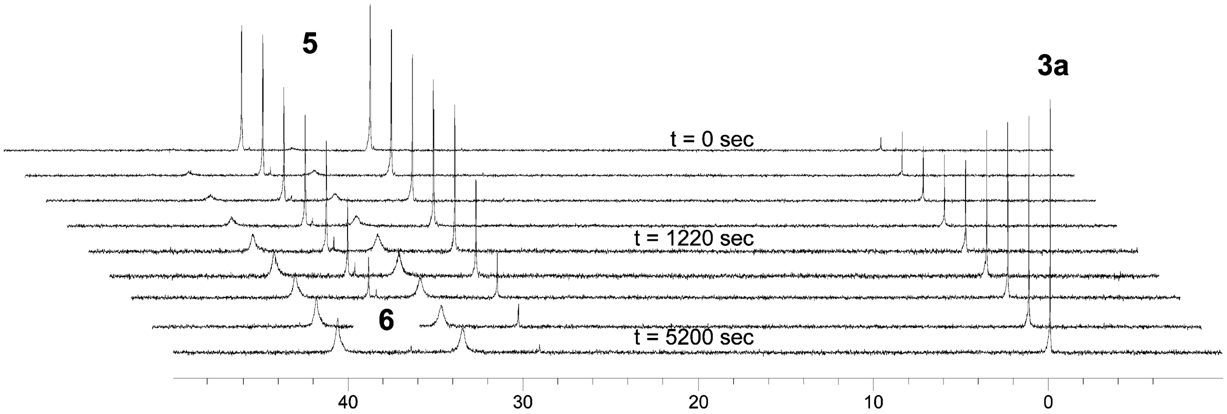
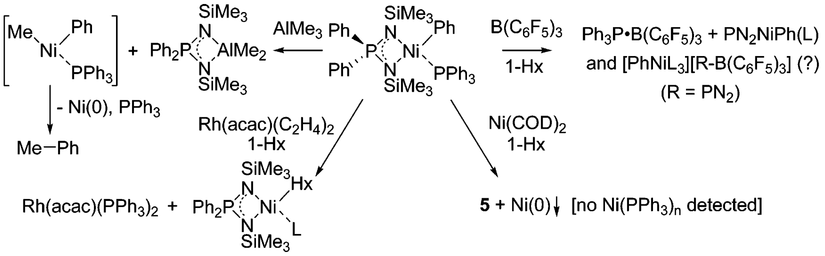


Figure 4. ^{31}P NMR spectra (121 MHz, C_6D_6) of a mixture of complex **5** and 1-hexene at 25 °C over a period of 1.44 h.

Scheme 3



neutral Ni catalysts.[6−7] The formation of the bis(PN_2) complex **4** could arise from subsequent ligand substitution of **5** or **6**, according to the mechanism proposed in the literature for this process.

Complex **5** was inactive for ethylene polymerization under a variety of conditions at typical reactor concentrations ([Ni] = 1−4 mM). We attribute this negative finding to the generally unfavorable equilibrium for displacement of phosphine by alkene (vide supra) coupled with the low equilibrium solubility of ethylene in solution at various values of *P* and *T*. In view of this, our attention was focused on the efficacy of various phosphine scavengers for activation of this compound.

Summarized in Scheme 3 are the reactions of compound **5** with a variety of scavengers. These NMR experiments were usually conducted in the presence of 1-Hx so as to judge whether enhancement of catalysis was observed. Perhaps unsurprisingly, the reaction of **5** with $AlMe_3$ results in effective scavenging of the PN_2 ligand, forming the known compound $Ph_2P(NSiMe_3)_2$-$AlMe_2$[33] and toluene (see the Supporting Information). The latter compound presumably is formed from reductive elimination of the unstable $(Ph_3P)NiPh(Me)$ complex formed. 1-Hx is not isomerized in the presence of $AlMe_3$ and complex **5**.

The use of $B(C_6F_5)_3$ as scavenger in the absence of 1-Hx led to formation of the expected phosphine−borane.[34] However, in addition, major amounts of a unidentified $Ni^{II}(PPh_3)_3$ complex were generated, as judged from the appearance of an AA′X spin system in the ^{31}P NMR spectrum of the mixture (see the Supporting Information). The corresponding ^{19}F NMR spectrum (see the Supporting Information) revealed a mixture of mainly unreacted borane (which was in exchange with phosphine−borane) and evidence for PN_2 (or perhaps even Ni−Ph) abstraction, as signals due to a tetrahedral borate moiety were present. In the presence of 1-hexene, isomerization to 2- and 3-hexene was somewhat faster; here, however, there was evidence for formation of species bearing Ni−C_6F_5 groups probably arising via abstraction of an anionic ligand by borane followed by back-transfer of a C_6F_5 group[35] (see the Supporting Information).

Clearly, the activation chemistry exhibited by this scavenger is complicated and quite unselective; however, when complex **5** was activated with 1.0 equiv of $B(C_6F_5)_3$ in the presence of ethylene (150 psig, 25 °C), rapid (ca. 10^5 g of C_2H_4/((mol of Ni) h)) though short-lived (<10 min) consumption of monomer was observed. No polymer was formed, but a mixture of 1- and 2-butenes was produced; the interpretation of this result is not clear, as many Ni(II) alkyls are known to be effective for ethylene dimerization.

With a view to focusing on softer Lewis acids,[36] the reactions of complex **5** with 1-hexene in the presence of both $Ni(COD)_2$ (which is a source of 16e Ni^0L_3) and $Rh(acac)(C_2H_4)_2$ were investigated. In the former case, there was no evidence for enhanced isomerization of 1-Hx and the only obvious chemical reaction involved plating out of Ni(0). In the latter case, the rate of 1-Hx isomerization was dramatically enhanced, while the formation of $Rh(acac)(PPh_3)_2$ was evident in the ^{31}P NMR spectrum of the mixture (see the Supporting Information). Even

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(31) The signal due to free PPh_3 was line-broadened due to exchange, while both signals due to **5** are sharp in the ^{31}P NMR spectra of these mixtures (see the Supporting Information). We believe this arises from rapid, though unfavorable, association of PPh_3 to form a five-coordinate square-pyramidal complex wherein the two PPh_3 ligands are apical and equatorial and only the apical PPh_3 is able to undergo rapid (but degenerate) dissociation. Thus, free PPh_3 is not in exchange with bound PPh_3 in complex **5**. This process would have to be independent of that which exchanges the $NSiMe_3$ groups to account for the observed behavior.

(32) The ^{31}P NMR shift of complex **4** is paramagnetically shifted to very high field (ca. −1500 to −2000 ppm[29]) and is not detected in these experiments.

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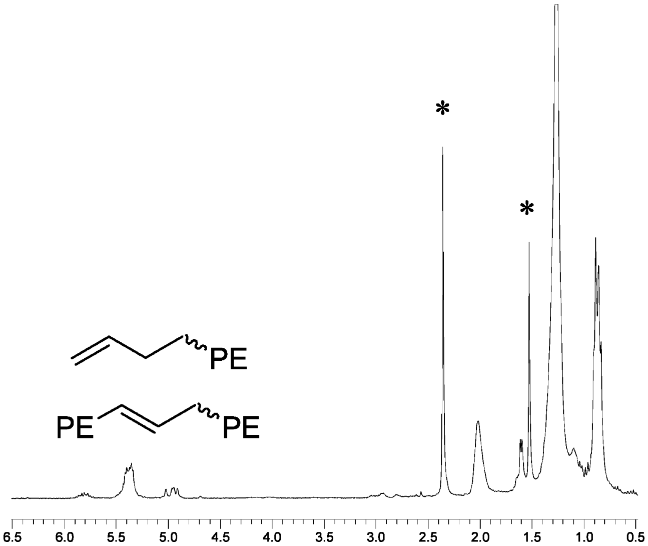

Figure 5. ^1H NMR spectrum (300 MHz, C_6D_6) of ethylene oligomers prepared using complex **5** (2.0 mM) and $Rh(acac)(C_2H_4)_2$ (1.0 mM) at 25 °C and 150 psig of C_2H_4. The sample is contaminated with toluene and dissolved water (indicated by asterisks).

under these concentrated conditions, $[Ni] = 2[Rh] = 0.025$ M with $[1\text{-Hx}] \approx 0.25$ M, complete consumption of complex **5** required about 30 min at 25 °C, highlighting the sluggishness of the initial phosphine displacement reaction.

Thus, only Rh(I) appears selective (and effective) for phosphine abstraction. In the presence of stoichiometric $Rh(acac)(C_2H_4)_2$, at 25 °C and 150 psig of C_2H_4, complex **5** (2 mM) slowly oligomerized ethylene ($A \approx 10^2-10^3$ g of PE/((mol of Ni) h)) to form branched material, whose ^1H NMR spectrum (Figure 5) revealed signals due to terminal vinyl and internal vinylene protons and enhanced intensity for terminal Me groups. By comparison of the integrated intensities of these signals to those of the main chain protons, it was determined that $M_n = 530$ ($X_n = 19$) with a branching frequency corresponding to 80 Me groups/1000 C atoms (or ~3 Me groups per chain in this case).

It is thus clear that a bona fide $PN_2NiR(L)$ complex is competent for ethylene oligomerization and that the microstructure of the oligomers formed correspond to those observed using catalysts derived from phosphorane **1** and Ni(0) or Ni(II) precursors. The differences are that the discrete PN_2 complex is less active (by about an order of magnitude) and provides much lower M_w material with a higher branching frequency. Of course, all three of these differences may be related to the presence of phosphine in this reaction (phosphine inhibits the activity of the Keim-based catalysts[27]), although it seems reasonable to expect that the less hindered nature of this discrete complex is also a contributing factor.[3,4]

Finally, in view of recent reports describing the generation of high-activity ethylene oligomerization catalysts from the reaction of isoelectronic Ni(II)−amidinate complexes and excess methylaluminoxane (PMAO),[37] we briefly investigated the behavior of all of the complexes reported here under similar conditions. Complexes **2a−d**, **4**, and especially **5** are all very active catalysts for ethylene dimerization, with activities of 10^6-10^7 g of C_2H_4/((mol of Ni) h) at 150 psig of C_2H_4 and 200:1 Al:Ni at 25 °C. There is no evidence for formation of any high-M_w material in these reactions (branched or otherwise), and the selectivity for butene (1-butene and *cis-*/*trans-*2-butene) generally exceeds 90%.

In our view, given the earlier work of Keim, Fink, and Yano, as well as our own studies reported here, this chemistry is *not characteristic* of a bona fide (η^2-PN_2)NiR complex. In fact, in view of the very clean reaction of $AlMe_3$ with complex **5** (vide supra), we suspect that PMAO reacts with these complexes through PN_2 ligand abstraction, perhaps coupled with ionization, to furnish L_nNiR^+ species (e.g. $L = PPh_3$, η^1-$[R_3Al{-}N(SiMe_3){-}PR'_2{=}N(SiMe_3)]^-$). It would be expected that such complexes are active and selective for ethylene dimerization, providing neutral (or anionic) L is unhindered.

Conclusions

(π-allyl)Ni(PN_2) complexes do not appear to be viable catalyst precursors for ethylene polymerization, even though they are the major product formed on reaction of phosphorane **1** with $(\pi\text{-allyl})_2Ni$. Instead, it seems likely that thermal or ethylene-mediated decomposition of the latter material forms Ni(0)−alkene complexes in situ and that these give rise to the active catalyst by analogy to work using preformed Ni(0)−alkene complexes.[11−14]

On the other hand, a bona fide $PN_2NiR(PPh_3)$ complex can be activated for ethylene polymerization using a *selective* phosphine scavenger. Under these conditions, it produces branched, oligo(ethylene) materials that closely resemble those formed using the phosphorane/Ni(0) or Ni(II) formulations. In view of this result, as well as prior mechanistic work,[11] it thus is clear that the active species involved in the formation of branched PE is a sterically hindered $PN_2NiR(L)$ complex. Our synthetic studies thus set the stage for further development of these interesting catalysts.

Finally, we briefly note that activation of late-metal systems with PMAO (or related hard Lewis acids such as AlR_3) may not always have the intended effect of scavenging soft donor ligands such as phosphine. In the present case, it is quite clear that a sterically unhindered, and weakly bound, hard Lewis base (i.e. the PN_2 ligand) is more susceptible to abstraction by alkylaluminum compounds.

Experimental Section

All materials were obtained from Aldrich Chemical Co. or Strem Chemical Co. Ltd. and purified as required, unless otherwise noted. All synthetic procedures were conducted under a N_2 atmosphere using Schlenk techniques or in a MBraun MB-150 glovebox. Tetrahydrofuran, diethyl ether, toluene, hexane, and dichloromethane were purified by passage through activated La Roche A-2 alumina and Engelhard CU-0226s Q-5 columns.[38]

Routine ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on Varian Mercury or Gemini 300 MHz instruments. Tetrahydrofuran-d_8 was dried over molecular sieves. Benzene-d_6, toluene-d_8, and bromobenzene-d_5 were distilled from Na or Na/K alloy prior to use. Acetonitrile-d_3, methylene-d_2 chloride, and chloroform-d were distilled from P_2O_5 and stored over 4 Å mole sieves. ^1H NMR spectra were referenced with respect to residual protonated solvent, while ^{13}C NMR spectra were referenced with respect to deuterated solvent. ^{19}F NMR spectra were referenced with respect to tetrafluoro-*p*-xylene (TFX: δ −145.69 in toluene-d_8). ^{31}P NMR spectra were referenced to a phosphoric acid external standard. Variable-temperature experiments were performed using a Varian

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Inova 400 MHz instrument. The spectrometer thermocouple was calibrated to within 5% of the actual temperature using a sample of MeOH. IR spectra were obtained on a DigiLab Excalibur FTS 3000 spectrometer and were not calibrated. Elemental analyses were performed by either Oneida Research Services or Galbraith Laboratories.

Tris(perfluorophenyl)borane was predried in a hexane solution containing activated 4 Å molecular sieves and recrystallized from hexane at −30 °C. The compounds Ni(COD)$_2$,[39] (η^3-C_3H_5)$_2$Ni,[25] [η^3-(2-Me)C_3H_4]$_2$Ni,[26] [(η^3-C_3H_5)NiBr]$_2$,[25] [($Me_3Si)_2N{-}P({=}NSiMe_3)_2$] (**1**),[40] [$Ph_2P(NHTol)({=}NTol)$] (**3b**),[15] and $(PPh_3)_2Ni(Ph)Br$[41] were prepared according to literature procedures.

***N,N′*-Bis(trimethylsilyl)diphenyliminophosphonamide (3a).** $Ph_2P(NHTMS)({=}NTMS)$ was prepared using a modified literature preparation.[42] Diphenylphosphine (6.6 g, 30 mmol) was dissolved in 75 mL of hexane. Trimethylsilyl azide (8 g, 72 mmol) was added and the solution heated under reflux for 12 h. The solution was pumped to dryness and the product distilled at 60−100 °C at 0.001 mmHg. The product (11.4 g, 90%) was a clear colorless liquid. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ 0.19 (s, 9H, NHSiCH_3), 0.36 (s, 9H, NSiCH_3), 1.88 (bs, 1H, NH), 7.04−7.10 (m, 6H, *p*-/*m*-Ar), 7.67−7.75 (m, 4H, *o*-Ar). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 0.70.

Potassium *N,N′*-Bis(trimethylsilyl)diphenyliminophosphonamide. The potassium salt of **3a** was prepared by slow dropwise addition of **3a** (6.0 g, 16.6 mmol) to a stirred suspension of KH (1.4 g, 35 mmol) in 25 mL of THF with stirring continued for 1 h. *Caution!* Addition of **3a** must be done slowly to prevent rapid H_2 formation. The resulting solution was filtered through Celite and dried under vacuum. The product was recrystallized from toluene (8 mL) layered with hexane (20 mL). [K][$Ph_2P(NTMS)_2$] formed colorless crystals (4.92 g, 75%). More material could be isolated from the supernatant. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ 0.06 (s, 18H, SiCH_3), 7.78 (m, 4H, *o*-Ar), 7.20 (m, 6H, *p*-/*m*-Ar). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 5.67. This material was used directly for the preparation of complex **5**.

(η^3-Allyl)[diphenylbis((trimethylsilyl)imino)phosphorato]nickel (2a). Ligand **3a** (708 mg, 1.97 mmol) in 10 mL of THF was cooled to −80 °C, and 1 equiv of ^{n}BuLi in hexanes (2.62 M, 0.752 mL, 1.97 mmol) was added by syringe. This solution was warmed to 20 °C. In a separate flask [(η^3-C_3H_5)NiBr]$_2$ (353 mg, 0.982 mmol) was dissolved in 10 mL of THF. The ligand solution was cooled to −80 °C, and the [(η^3-C_3H_5)NiBr]$_2$ solution was added via cannula. The resulting red solution was pumped to dryness and the residue dissolved in hexane. The product was filtered through Celite and crystallized by slow evaporation to yield dark red crystals (720 mg, 80%). ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ 0.04 (s, 18H, SiCH_3), 1.67 (dd, J = 12.9 Hz, 2H, *anti* 1-/3-allyl CH_2), 2.86 (dd J = 7.5 Hz, 2H, *syn* 1-/3-allyl CH_2), 5.01 (tt, J = 6.0 Hz, 1H, allyl CH), 7.04 (m, 3H, *p*-/*m*-Ar), 7.12 (m, 3H, *p*-/*m*-Ar), 7.79 (m, 2H, *o*-Ar), 8.06 (m, 2H, *o*-Ar). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 40.1. IR (KBr, cm^{-1}): 2948 (m), 2892 (sh), 2360 (m), 2341 (sh), 1587 (w), 1498 (m), 1481 (sh), 1434 (s), 1398 (sh), 1245 (s), 1139 (s), 1101 (sh), 854 (s), 831 (sh), 520 (m). Anal. Calcd for $C_{21}H_{33}N_2NiPSi_2$: C, 54.91; H, 7.24. Found: C, 54.62; H, 7.14.

A red crystal of **2a** with dimensions 0.33 × 0.23 × 0.22 mm was coated in PEK and mounted on a glass fiber, which was placed under a stream of nitrogen on the goniometer head of a Bruker Apex CCD diffractometer. The full sphere of data was collected to 28.28° (θ) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 180 K. The reflections were collected using ω scans. Unit cell dimensions were based on data collected using SMART and indexed using the SAINT algorithm. The total number of reflections collected was 6014 between 1.73 and 28.8° in θ. Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares refinement on F^2. Allylic hydrogen atoms were found and refined from a Fourier difference map. The remaining hydrogens were fitted with a riding model. The final cycles of refinement converged with $R = 0.0488$ and $R_w = 0.0871$.

(η^3-Allyl)[diphenylbis(4-methylphenyl)phosphorato]nickel (2b). Ligand **3b** (1.00 g, 2.31 mmol) in 10 mL of THF was cooled to −80 °C, and 1 equiv of ^{n}BuLi in hexanes (1.85 M, 1.25 mL, 2.31 mmol) was added by syringe. This solution was warmed to 20 °C. In a separate flask [(η^3-C_3H_5)NiBr]$_2$ (539 mg, 1.15 mmol) was dissolved in 10 mL of THF. The ligand solution was cooled to −80 °C, and the [(η^3-C_3H_5)NiBr]$_2$ solution was added via cannula. The resulting red solution was pumped to dryness and the residue dissolved in toluene. The product was filtered through Celite and the solvent evaporated. Compound **2b** was isolated as red crystals (842 mg, 74%) by crystallization from CH_2Cl_2 at −30 °C. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ 1.94 (dd, J = 13.2 Hz, 2H, *anti* 1-/3-allyl CH_2), 2.07 (s, 6H, ArCH_3), 2.92 (dd, J = 7.9 Hz, 2H, *syn* 1-/3-allyl CH_2), 5.26 (tt, J = 6.5 Hz, 1H, allyl CH), 6.82 (m, 6H, *o*-/*m*-*Ar*CH$_3$), 7.00 (m, 6H, *p*-/*m*-Ar), 7.91 (m, 2H, *o*-Ar), 8.10 (m, 2H, *o*-Ar). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 41.7. IR (KBr, cm^{-1}): 3019 (w), 2913 (w), 1606 (s), 1504 (s), 1434 (sh), 1286 (s), 1267 (sh), 1176 (m), 1105 (s), 997 (s), 906 (m), 815 (s), 688 (s), 597 (m), 507 (s). Anal. Calcd for $C_{29}H_{33}N_2NiP$: C, 69.76; H, 6.66. Found: C, 70.04; H, 5.99.

A red crystal of **2b** with dimensions 0.37 × 0.34 × 0.31 mm was coated in PEK and mounted on a glass fiber which was placed under a stream of nitrogen on the goniometer head of a Bruker Apex CCD diffractometer. The full sphere of data was collected to 30.30° (θ) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 180 K. The reflections were collected using ω scans. Unit cell dimensions were collected in SMART and indexed in SAINT. The total number of reflections collected was 7207 between 1.50 and 28.8° (θ). Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares refinement on F^2. Allylic hydrogen atoms were found and refined from a Fourier difference map. The remaining hydrogens were fitted with a riding model. The final cycles of refinement converged with $R = 0.0369$ and $R_w = 0.0857$.

(η^3-Allyl)[(σ-allyl)(bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorato]nickel (2c,d). A modified procedure, based on that reported by Keim,[12] was used to prepare compounds **2c**,**d**. Compound **1** (1.00 g, 2.73 mmol) was dissolved in 4.5 mL of hexane. In a separate flask 1 equiv of (η^3-C_3H_5)$_2$Ni was dissolved in 4.5 mL of hexane. The two solutions were mixed to form a deep red solution, which upon evacuation at 0.01 mmHg yielded an orange powder (1.5 g, 95%) of **2c**,**d**. ^{1}H and ^{31}P NMR spectra agreed with those reported in the literature.[12] Deep red crystals were grown from evaporation of a hexane solution. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): major isomer, δ 0.21 (s, 18H, NSiCH_3), 0.52 (s, 18H, N(SiCH_3)$_2$), 1.49 (dd, J = 12.7 Hz, 2H, *anti* 1-/3-allyl CH_2), 2.51 (ddt, J = 14.3, 6.6, 1.7 Hz., 2H, PCH_2), 2.81 (dd, J = 12.7 Hz, 2H, *syn* 1-/3-allyl CH_2), 5.05−4.85 (tt, J = 6.7, 12.7 Hz, 1H, allyl CH), 5.05−4.85 (dt, 1H, P-allyl cis CH_2), 5.24−5.16 (dt, 1H, P-allyl trans CH_2), 6.13 (m, 1H, P-allyl CH); minor isomer, δ 0.22 (s, 18H, NSiCH_3), 0.40 (s, 18H, N(SiCH_3)$_2$), 1.59 (dd, J = 12.7 Hz, 2H, *anti* 1-/3-allyl CH_2), 2.72 (ddt, J = 14.3, 7.0, 1.3 Hz., 2H, PCH_2), 2.78 (dd, J = 7.0 Hz, 2H, *syn* 1-/3-allyl CH_2),

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5.05−4.85 (m, 1H, allyl C*H*), 5.24−5.16 (dt, 1H, P-allyl cis CH_2), 5.34 (dt, 1H, P-allyl trans CH_2), 6.71 (m, 1H, P-allyl C*H*). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): major isomer, δ 34.26 (s, 1P, *P*); minor isomer, 33.25 (s, 1P, *P*). By integration of the ^{31}P spectrum, the ratio of major to minor isomer was 1.5:1.

Phenyl(triphenylphosphine)[diphenylbis((trimethylsilyl)imino)phosphorato]nickel (5). [K][$Ph_2P({=}NTMS)_2$] (1.06 g, 2.53 mmol) in 5 mL of toluene was mixed with a dispersion of $(PPh_3)_2Ni(Ph)Br$ (1.87 g, 2.53 mmol) in 15 mL of toluene for 2 h. The resulting deep red solution was filtered through Celite, and the solvent was reduced to ca. 13 mL in vacuo. Upon layering with hexane, the concentrate yielded dark red cubic crystals (1.6 g, 83%). ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ −0.29 (s, 18H, SiCH_3), 6.48−6.53 (m, 3H, *m*-/*p*-*Ar*Ni), 7.99−7.01 (m, 9H, *m*-/*p*-P*Ar*$_3$), 7.21−7.31 (m, 6H, *m*-/*p*-*Ar*(PN$_2$)), 7.44−7.48 (m, 2H, *o*-*Ar*Ni), 7.84−7.90 (m, 6H, *o*-P*Ar*$_3$), 8.16−8.22 (m, 4H, *o*-*Ar*(PN$_2$)). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 37.3 (s, 1P, *P*N$_2$), 29.2 (s, 1P, *P*Ph$_3$). IR (KBr, cm^{-1}): 3031 (s), 2890 (s), 2678 (w), 2582 (w), 2316 (w), 1957 (s), 1887 (sh), 1668 (w), 1558 (s), 1434 (s), 1243 (s), 1083 (s), 831 (m). Anal. Calcd for $C_{42}H_{48}N_2NiP_2Si_2$: C, 66.58; H, 6.38. Found: C, 66.37; H, 6.21.

A red crystal of **5** with dimensions 0.37 × 0.30 × 0.24 mm was coated in PEK and mounted on a glass fiber which was placed under a stream of nitrogen on the goniometer head of a Bruker Apex CCD diffractometer. The full sphere of data was collected to 27.88° (θ) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 150 K. The reflections were collected using ω scans. Unit cell dimensions were collected in SMART and indexed in SAINT. The total number of reflections collected was 9250 between 1.74 and 27.88° (θ). Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package. The structure was solved by direct methods and refined by full-matrix least-squares refinement on F^2. All hydrogens were fitted with a riding model. The final cycles of refinement converged with $R = 0.0331$ and $R_w = 0.0539$.

Synthesis of Bis[diphenylbis((trimethylsilyl)imino)phosphorato]nickel (4). The synthesis of the paramagnetic complex **4** used a procedure modified from that reported by the Kuchen group.[29b] (Dimethoxyethane)nickel bromide (140 mg, 0.18 mmol) and [K][$Ph_2P({=}NTMS)_2$] (54 mg, 0.36 mmol) were mixed in 3 mL of THF, and this mixture was stirred for 12 h. The THF was evaporated from the resultant bright blue solution, and the residue was dissolved in a 1:1 (v:v) hexane−toluene solvent. This was filtered through Celite and the solvent evaporated in vacuo. The blue crystalline product (72 mg, 55%) was recrystallized from warm hexane. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ −6.72 (bs, 8H, *o*-*Ar*), −0.29 (bs, 4H, *p*-*Ar*), 7.12 (bs, 8H, *m*-*Ar*), 13.91 (bs, 36H, SiCH_3).

1:1 Reaction of [Li][$Ph_2P({=}NTMS)_2$] and (DME)NiBr$_2$. In 10 mL of ether ligand **3a** (300 mg, 0.832 mmol) was dissolved. The solution was cooled to −80 °C, 1 equiv of BuLi (in hexanes; 2.61 M, 0.319 mL, 0.832 mmol) was added, and the solution was warmed to 20 °C. Meanwhile a dispersion of (DME)NiBr$_2$ (265 mg, 0.832 mmol) in 10 mL of ether was cooled to −80 °C. The ligand solution was then transferred by cannula into the (DME)NiBr$_2$ dispersion, and the mixture was warmed to 20 °C. The solution turned deep blue, and blue crystals began to form. ^{1}H NMR spectroscopy indicates that the principal product was $Ph_2P({=}NTMS)_2)_2Ni$.

Reaction of Complex 5 with 1-Hexene. In a septum-equipped 5 mm NMR tube, **5** (23 mg, 31 μmol) and 170 μL of toluene-d_8 were added. After dissolution, the solution was cooled to −80 °C and 300 μL of 1-hexene was added. The cool NMR tube was agitated and lowered into a precooled (−60 °C) NMR probe. The reaction was monitored by slowly warming the probe to 25 °C. ^{1}H and ^{31}P NMR spectra were recorded at 10, 0, −20, −40, and −60 °C, but no obvious change was evident. Once the solution was warmed to 25 °C, ^{1}H and ^{31}P NMR spectra were recorded over an 80 min period. During this time the red solution turned brown and ^{1}H NMR resonances due to 2-/3-hexene appeared. Selected spectra are shown in Figure 4 or in the Supporting Information, and the data were analyzed, assuming pseudo-first-order kinetics for the disappearance of **5** and the consumption of 1-hexene.

Reaction of Complex 5 with Propene. A stock solution of TFX (1.0 M) in toluene-d_8 was made. In a septum-equipped 5 mm NMR tube, **5** (25 mg, 34 μmol) and 500 mg (ca. 530 μL) of the stock solution were added. In a separate 5 mm septum-capped NMR tube, 495 mg (ca. 525 μL) of the stock solution was added and saturated with propene at 7 psig ($[C_3H_6] = 0.34$ M). The solution of **5** was cooled to −80 °C, and 1.8 equiv (100 μL) of the propene solution was added. The cool NMR tube was agitated and lowered into a precooled (−30 °C) NMR probe. The reaction was monitored with controlled warming of the probe to 25 °C. All volatile products of this reaction were vacuum-transferred into a clean 5 mm NMR tube using an NMR tube manifold. ^{1}H NMR spectra of the resulting clear solution indicated the presence of α-methylstyrene (see the Supporting Information).

Reaction of Complex 5 with Al(CH$_3$)$_3$. In a 5 mm NMR tube, **5** (11.5 mg, 15.2 μmol) was dissolved in 309 μL of benzene-d_6. In a separate vial, Al(CH$_3$)$_3$ (20 mg, 280 μmol) was dissolved in 1.05 mL of benzene-d_6. To the solution of **5** was added 55 mg (1 equiv) of the Al(CH$_3$)$_3$ solution. The solution turned black, and Ni(0) precipitated. The ^{1}H NMR spectrum of the products were consistent with a mixture of toluene and ($Ph_2P(NTMS)_2$)AlMe$_2$, an authentic sample of which was prepared as described below.

[*N*,*N*′-Bis(trimethylsilyl)diphenyliminophosphonamido]dimethylaluminum. The compound was synthesized by dissolving **3a** (0.673 g, 1.87 mmol) in 3 mL of hexane and adding 1.5 equiv of Al(CH$_3$)$_3$.[33] Once the exothermic reaction mixture was allowed to bubble and was cooled to 20 °C, the solvent and residual Al(CH$_3$)$_3$ were removed by vacuum evaporation. Adding ca. 0.4 mL of hexane and cooling to −30 °C for 12 h yielded colorless crystals of $Ph_2P(NTMS)_2AlMe_2$ (700 mg, 90%), whose spectral data agreed with those reported in the literature.[33] ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ −0.06 (s, 18H, SiCH_3), −0.09 (s, 6H, AlCH_3), 7.71−7.81 (m, 4H, *o*-Ar), 6.99−7.12 (m, 6H, *p*-/*m*-Ar). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): δ 30.49.

Reaction of Complex 5 with B(C$_6$F$_5$)$_3$. In a 5 mm NMR tube, **5** (11.5 mg, 15.2 μmol) was dissolved in 309 μL of benzene-d_6. In a separate vial, B(C$_6$F$_5$)$_3$ (40 mg, 280 μmol) was dissolved in 1.05 mL of benzene-d_6. To the solution of **5** was added 194 mg (1 equiv) of the B(C$_6$F$_5$)$_3$ solution. The solution darkened, and a mixture of products was observed in the ^{1}H, ^{31}P, and ^{19}F NMR spectra. These are included in the Supporting Information.

Reaction of Complex 5 with B(C$_6$F$_5$)$_3$ and 1-Hexene. In a 5 mm NMR tube, **5** (22 mg, 29 μmol) was dissolved in 358 μL of benzene-d_6 and 200 μL of 1-hexene. In a separate vial, B(C$_6$F$_5$)$_3$ (10 mg, 70 μmol) was dissolved in 421 μL of benzene-d_6. To the solution of **5** was added 300 μL (53 μmol) of the B(C$_6$F$_5$)$_3$ solution by syringe in 100 μL increments. The solution darkened, and a mixture of products was observed in the ^{1}H, ^{31}P, and ^{19}F NMR spectra. Isomerization of 1-hexene commenced immediately on adding the first aliquot of borane.

Reaction of Complex 5 with Ni(COD)$_2$ and 1-Hexene. In a septum-capped 5 mm NMR tube, **5** (15 mg, 20 μmol) was dissolved in 689 μL of benzene-d_6. In a separate vial, Ni(COD)$_2$ (5 mg, 54 μmol) was dissolved in 100 μL of 1-hexene and 100 μL of benzene-d_6. The two solutions were mixed by syringe. The solution turned black, and Ni(0) precipitated. ^{1}H and ^{31}P NMR spectra were taken during the conversion of 1-hexene to 2-/3-hexenes. The ^{1}H NMR spectral line broadened as Ni(0) formed, but there were no Ni(0) phosphine complexes detected, and the rate of hexene isomerization was unaffected.

Reaction of Complex 5 with Rh(acac)(C$_2$H$_4$)$_2$ and 1-Hexene. In a Teflon valve capped 5 mm NMR tube, Rh(acac)(C$_2$H$_4$)$_2$ (14 mg, 54 μmol) was dissolved in 557 μL of benzene-d_6 and 14 μL of 1-hexene (89 μmol). A ^{1}H NMR spectrum was taken of this starting solution, to confirm the absence of 2-/3-hexenes. To this solution was added 0.5 equiv of solid complex **5** (19 mg, 25 μmol). After dissolution, ^{1}H and ^{31}P NMR spectra were taken, and formation of 2-/3-hexene was observed. Spectra are summarized in the Supporting Information.

(η^3-2-Methallyl)[(σ-2-methallyl)(bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorato]nickel. Compound **1** (25 mg, 68 μmol) was dissolved in 570 μL of benzene-d_6 in a 5 mm septum-equipped NMR tube. To this solution was added (η^3-(2-CH_3)C_3H_5)$_2$-Ni (11.5 mg, 68 μmol). The yellow solution deepened in color as the reaction progressed over 2 h. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): major isomer, δ 0.23 (s, 18H, NSiCH_3), 0.56 (s, 18H, N(SiCH_3)$_2$), 1.44 (s, 2H, *anti* 1-/3-methallyl CH_2), 2.00 (s, 3H, P-methallyl CH_3), 2.23 (m, 3H, methallyl CH_3), 2.58 (s, 2H, *syn* 1-/3-methallyl CH_2), 2.60 (d, $J = 11$, 2H, P-CH_2), 4.86 (m, 2H, P-methallyl CH_2); minor isomer, δ 0.23 (s, 18H, NSiCH_3), 0.41 (s, 18H, N(SiCH_3)$_2$), 1.49 (s, 2H, *anti* 1-/3-methallyl CH_2), 2.04 (s, 3H, P-methallyl CH_3), 2.62 (m, 3H, methallyl CH_3), 2.62 (s, 2H, *syn* 1-/3-methallyl CH_2), 2.80 (d, $J = 15$ Hz., 2H, P-CH_2), 5.05 (m, 2H, P-methallyl CH_2). ^{31}P NMR (121.4 MHz, benzene-d_6, 298 K): major isomer, δ 34.26 (s, 1P, *P*); minor isomer, 31.04 (s, 1P, *P*). By ^{31}P integration, the ratio of major to minor isomer was 1.2:1.

Polymerization Procedure. Detailed procedures for polymerization are given in the literature.[43] Polymerizations were conducted in a 300 mL stainless steel autoclave. The autoclave was dried in a 120 °C oven overnight and then brought directly into a glovebox, and scrubbing agent (if used), catalyst (if not added by syringe), magnetic stir bar, and solvent were added.

The solvent toluene and monomer ethylene were purified as described elsewhere.[43] The total impurity level in the reactor was determined by saturating 100 mL of toluene with ethylene at 28 psig and 25 °C with stirring. After venting excess monomer inside a glovebox, titration of a 16 g aliquot with 160 μL of a 21 mM standard solution of potassium and benzophenone in xylenes−tetraglyme[44] gave a total impurity level of 90 μM (expressed as [H_2O]).

Attempted Reactions of 2a−d with Ethylene. In a 300 mL reaction vessel within a glovebox, **2c**,**d** (200 mg, 400 μmol) and 100 mL of toluene were added to make a 4 mM solution. A magnetic stir bar was added to aid agitation. The reactor was sealed and removed from the glovebox. While stirring, 450 psig of ethylene was added for 4 h at 30 °C. The same reaction was also performed at 70 °C. No ethylene consumption was observed using a calibrated mass flow meter, and no polymer was formed.

Screening of complexes **2a**,**b** was performed in the same manner and concentrations were as described for complexes **2c**,**d** at 30 °C. No ethylene consumption was detected, and no polymer was formed.

In Situ Generation of 2c,d in the Presence of Ethylene. In a 300 mL reaction vessel within a glovebox, phosphorane **1** (111 mg, 400 μmol) and 100 mL of toluene were added to make a 4 mM solution. A magnetic stir bar was added to aid agitation. The reactor was sealed and removed from the glovebox. While the mixture was stirred, 450 psig of ethylene was added at 30 °C. In a 25 mL stainless steel sample vessel were placed Ni(η^3-(C_3H_5))$_2$ (56 mg, 400 μmol) and 5 mL of toluene. The solution of Ni(η^3-(C_3H_5)) was injected, and the reactor contents were allowed to react at 17 °C. The resulting solution was degassed and solvent evaporated. Polymer was washed with acidic methanol and dried in a vacuum oven for 12 h. This polymerization yielded 1.3 g of polyethylene over 4 h. The activity is calculated on the basis of the dry mass of the polymer. Details of the polymer microstructure and related polymerization experiments will be reported elsewhere.[17,24]

In Situ Generation of (TMS$_2$N)(σ-(2-CH$_3$)C$_3$H$_5$)P(N-TMS)$_2$Ni-(η^3-(2-CH$_3$)C$_3$H$_5$) in the Presence of Ethylene. This reaction was preformed in the same manner described for **1** and Ni(η^3-(C_3H_5)$_2$. In this case Ni[η^3-(2-CH_3)(C_3H_4)]$_2$ was used in place of Ni(η^3-(C_3H_5))$_2$. This polymerization yielded 190 mg of polyethylene after 2 h.

Activation of Ni Complexes with PMAO. A solution of the Ni complex (**2a**−**d**, **4,** or **5** in 100 mL of toluene, 0.1 mM) and PMAO (0.02 M) was prepared and transferred to a 300 mL autoclave fitted with a glass insert in the glovebox. The autoclave was sealed, connected to a gas manifold, briefly evacuated, and then refilled with ethylene at 150 psig and 25 °C. Rapid monomer consumption was noted using a calibrated mass flow meter (corresponding $A > 10^6$ g of C_2H_4/((mol of Ni) h)), and a significant exotherm (>10 °C) generally ensued. After 1 h, the autoclave was vented to the atmosphere, and an aliquot of the clear orange solution removed and filtered through a short plug of silica to remove catalyst and aluminoxane, washing with toluene. Analysis of the eluant by GC revealed the presence of dissolved ethylene and a mixture of 1- and 2-butenes.

Reaction of 5 with B(C$_6$F$_5$)$_3$ and Ethylene. In a 300 mL reaction vessel within a glovebox, **5** (155 mg, 200 μmol) and 10 mL of toluene were added to make a 23 mM solution. A magnetic stir bar was added to aid agitation. In a Teflon cup which was wired to the thermowell of the autoclave was placed B(C_6F_5)$_3$ (104 mg, 200 μmol). The reactor was sealed and removed from the glovebox. With stirring, 300 psig (~0.2 M) of ethylene was added at 30 °C. Addition of borane was performed by inverting the sealed reactor (and thus the Teflon cup containing B(C_6F_5)$_3$), and the contents were allowed to react at 30 °C for 0.75 h. The soluble material was analyzed by GC-MS after passing through a short plug of silica to remove catalyst. Activity was calculated on the basis of the total integral of the mass flow curve vs time. 1- and 2-butene were produced, but no polymer was formed.

Reaction of 5 with Ni(COD)$_2$ and Ethylene. This reaction was performed in the same manner as above, using Ni(COD)$_2$ instead of B(C_6F_5)$_3$. No ethylene consumption was observed, and no polymer was formed.

Reaction of 5 with Rh(acac)(C$_2$H$_4$)$_2$ and Ethylene. Twenty milligrams (77 μmol) of Rh(acac)(C_2H_4)$_2$, a magnetic stir bar, and 0.95 mL of benzene-d_6 were added to a vial. After dissolution, 30 mg (40 μmol) of **5** was added and dissolved over 8 min. Thereafter 150 psig of ethylene was added for 1 h inside a 300 mL autoclave at 20 °C. The solution was degassed and transferred to a 5 mm NMR tube. ^{1}H and ^{31}P NMR spectra were subsequently recorded. The activity of polymerization was based on the integrated mass of polymer, as determined from the ^{1}H NMR spectrum.

Acknowledgment. We thank the University of Akron for financial support of this work. R.L.S. acknowledges the Eastman Chemical Co. for a scholarship. J.C. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial stipend support. We thank Prof. Todd B. Marder (University of Durham) for helpful discussions concerning the fluxional behavior of complex **5**.

Supporting Information Available: Figures giving NMR spectra of reactions discussed in the text and crystallographic data given as CIF files for complexes **2a**,**b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051103Z

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(43) Bravakis, A.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000−1009.

(44) It should be noted that at these concentrations and using an excess of potassium to prepare this stock solution, the principal species present is the purple benzhydrole dianion. See: Wooster, C. B. *J. Am. Chem. Soc.* **1928**, *50*, 1388−1394.