Rigid *N*-Phosphino Guanidine P,N Ligands and Their Use in Nickel-Catalyzed Ethylene Oligomerization

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The rigid bidentate P,N-ligands **3a**−**d** (phosphino substituent: **a**, Ph; **b**, mes; **c**, N-*i*-Pr_2; **d**, NPh_2), each with a 7-phosphino-1,5,7-triazabicyclo[4.4.0]dec-5-ene skeleton, are readily prepared in high yields and have been used in the preparation of the nickel complexes [$NiBr_2$(**3a**−**d**)] (**4a**−**d**). The derivatives **4a**,**d** are both diamagnetic, while their counterparts **4b**,**c** are paramagnetic with values of μ_{eff}(300 K) of 2.05 and 2.10 μ_B, respectively. The structure of **4a** has been determined in the solid state by X-ray diffraction, which confirmed the κ^2P,N coordination of **3a** and the essentially square-planar geometry about Ni. In combination with $EtAlCl_2$ the Ni(II) complexes of **4b**−**d** are active ethylene oligomerization initiators (C_2H_4, 1 bar; Ni:Al = 1:14; toluene), affording varying mixtures of butenes, hexenes, and octenes (trace), depending on the nature of the P-donor, but with a reasonable selectivity toward C_4 with complex **4c**. In contrast, under identical reaction conditions complex **4a** gives rise to products resulting from a sequence of ethylene oligomerization and subsequent Friedel−Crafts alkylation of the toluene solvent. Notably, no activity toward ethylene (1 bar) was observed for **4**/MAO (Ni:Al = 1:15 or 1:500).

Introduction

Since the pioneering work of Keim and co-workers,[1] nickel(II)-based initiators have been instrumental in the development of alkene oligomerization processes. This is an area that has been driven by the industrial significance of the resulting synthetically versatile short-chain alkenes (C_4−C_{10}), used as comonomers and as precursors to plasticizers, detergents, etc.[2] Over the past decade there has been a gradual move away from the use of monoanionic heteroditopic chelate ligands (e.g., [P,O],[1,3−6] [N,O],[7] and [N,S][8]) that were used traditionally, following the discovery that neutral bidentate scaffolds afford Ni(II) initiators that efficiently oligomerize ethylene at considerably lower temperatures and pressures.[9−13] Notably, the combination of neutral chelating P,N-ligands with Ni(II) has been shown to be very effective for the catalytic oligomerization of ethylene, exploiting the electronic and steric asymmetry these ligands impose to control reactivity and selectivity.[14−21]

Despite the potential structural diversity of chelating P,N-metal scaffolds, the majority of structure/property correlation investigations for ethylene polymerization have focused on the influence of the N-donor moiety, with comparatively few studies having probed the role of the P-donor component in any systematic fashion.[16,17] Here we report the "one-pot" synthesis of a family of readily prepared P,N ligands that exploit the ease of P−N bond formation to facilitate introduction of a range of variously substituted R_2P fragments onto a bicyclic guanidine skeleton.[22] This approach gives metal scaffolds that are rigid and predisposed to afford κ^2P,N binding with an encumbered P donor and a "tied-back" imine donor, reminiscent of the steric demands imposed by the [P,O] chelates employed by Keim.

Results and Discussion

The desired *N*-phosphino guanidine P,N ligands **3a**−**d** were prepared in a two-step process from commercially available

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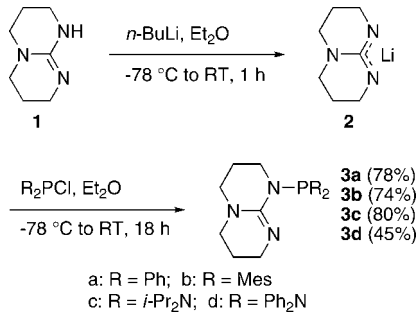
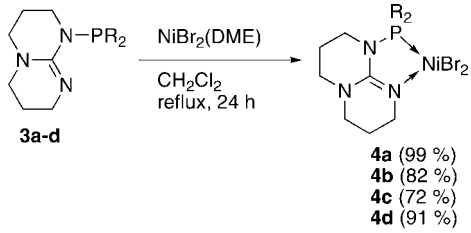
Scheme 1. Synthesis of *N*-Phosphino Guanidines 3



Scheme 2. Synthesis of Ni(II) *N*-Phosphino Guanidine Complexes 4



1,5,7-triazabicyclo[4.4.0]dec-5-ene (**1**) via the intermediate lithium salt **2** and isolated in excellent yield as moderately air stable crystalline solids (Scheme 1). Each of the ligands presents a single resonance by ^{31}P NMR spectroscopy, with chemical shifts consistent with mono- and tris-aminophosphines for **3a**,**b** and **3c**,**d**, respectively.[22]

The desired nickel(II) derivatives [$NiBr_2$(**3a**−**d**)] (**4a**−**d**) were prepared by reacting equimolar quantities of the appropriate ligand with $NiBr_2$(DME) (DME = 1,2-dimethoxyethane) in CH_2Cl_2 at reflux for 24 h (Scheme 2). During this time the complexes **4a**−**d** precipitated from the reaction medium and were obtained as air-stable red-purple solids in excellent yields. For each complex, satisfactory elemental analyses were obtained. Using mass spectrometry (FAB), an $[M - Br]^+$ ion was observed in each case, with no evidence for higher molecular weight species. All the complexes have rather low solubility in common solvents and react with DMSO to form as yet unidentified paramagnetic products.

The structure of **4a** (CD_2Cl_2 solvate) was confirmed in the solid state by an X-ray diffraction study (Figure 1). This revealed an essentially square-planar geometry about nickel with only a small (ca. 3°) pseudotetrahedral twist between the NiPN and $NiBr_2$ planes. Ligand **3a** binds in a κ^2P,N fashion as expected, with a moderately acute P(1)−Ni(1)−N(1) bite angle of 85.32(8)°, which is compensated for by a slight opening of the Br(1)−Ni(1)−Br(2) angle (92.225(16)°). The electronic asymmetry imposed by ligand **3a** is reflected in a small difference between the two Ni−Br bond distances (0.02 Å), with the longer of the two being trans to phosphorus, as expected. The phosphino guanidine presents a planar CN_3 core with delocalized bonding across the N(1)C(1)N(2) moiety. The Ni(1)−N(1) bond distance (1.912(2) Å) is comparatively short (cf. 1.983(2) Å in $NiCl_2$(**1**)$_2$),[23] something that reflects the tight binding of the P,N chelate.[21] Despite repeated attempts, crystals of **4b**−**d** suitable for study by X-ray diffraction could not be obtained.

In order to probe the structures of the various Ni(II) complexes **4**, an investigation of their magnetic properties in

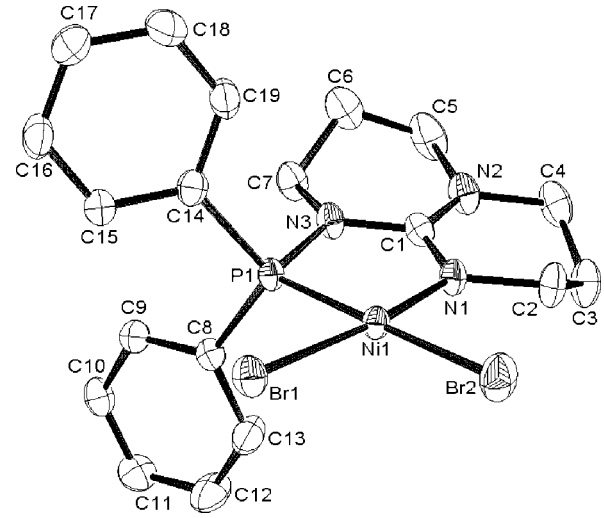


Figure 1. Molecular structure of **4a**·$^1/_2CD_2Cl_2$ (showing 50% thermal ellipsoids). The hydrogen atoms and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−P(1) = 2.1054(8), Ni(1)−N(1) = 1.912(2), Ni(1)−Br(1) = 2.3283(5), Ni(1)−Br(2) = 2.3483(5), P(1)−N(3) = 1.698(2), C(1)−N(1) = 1.322(4), C(1)−N(2) = 1.338(4), C(1)−N(3) = 1.390(4); P(1)−Ni(1)−N(1) = 85.32(8), P(1)−Ni(1)−Br(1) = 84.63(2), Br(1)−Ni(1)−Br(2) = 92.225(16), N(1)−Ni−Br(2) = 97.87(8), P(1)−Ni(1)−Br(2) = 175.66(3), N(1)−Ni(1)−Br(1) = 169.89(8), N(1)−C(1)−N(2) = 125.5(3), N(1)−C(1)−N(3) = 116.8(3), N(2)−C(1)−N(3) = 117.7(3).

the solid[24,25] and solution states[24,26] was undertaken. Complexes **4a**,**d** are both diamagnetic, consistent with the square-planar nickel geometry observed crystallographically for **4a**. In contrast, complexes **4b**,**c** are paramagnetic, with magnetic moments μ_{eff}(300 K) of 2.05 and 2.10 μ_B, respectively, in both solution and the solid state. These values are lower than the predicted spin-only magnetic moments for tetrahedral d^8 species, but are comparable to those measured for other P,N-chelated Ni(II) complexes.[27] Since the cryoscopically determined molecular weight data for **4b**,**c** are consistent with monometallic structures,[28] the anomalously low magnetic moments are believed to result from moderate distortions away from square planarity, caused by geometric and steric constraints imposed by the rigid scaffolds **3b**,**c**.[29]

Despite their rather low solubility, **4a**−**d** were all sufficiently soluble in toluene at room temperature (1×10^{-3} M solutions) to permit their screening for homogeneous ethylene oligomerization activity. Toluene solutions of each of the nickel complexes were treated with either MAO (15 or 500 equiv) or $EtAlCl_2$ (14 equiv) as activator, aged, and subsequently allowed to contact ethylene.

No reaction with ethylene (1 bar) was detected upon activating any of the complexes **4a**−**d** with MAO. However, in contrast, the initiators generated from treatment of **4b**−**d** with $EtAlCl_2$ in toluene react in a very exothermic manner, spontaneously reaching ca. 80 °C after approximately 5 min, temperatures that were maintained for the remainder of the test period (ca. 25 min) without the need for external heating. Similar aluminum

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Table 1. Ethylene Oligomerization Studies Employing Proinitiators 4a−d and $EtAlCl_2$ as Activator[a]

	mass of all products[b] (g)	C_4 [1-C_4][c] (mass %)	C_6 [1-C_6][c] (mass %)	C_8 [1-C_8][c] (mass %)	K[d]	**5**[e] (mass %)	productivity[f]	TON[g]
4a	8.9	9.0 [62.5]	1.1 [13.6]	0	0.1	89.9	6066	6345
4b	4.4	73.5 [13.3]	24.9 [2.8]	1.6 [13.6]	0.3	0	2981	3118
4c	6.3	85.4 [4.1]	14.2 [0.5]	0.4 [18.1]	0.2	0	4299	4497
4d	2.2	54.5 [5.8]	42.0 [0.52]	3.5 [18.3]	0.8	0	1513	1582

[a] Reaction conditions: **4** (5.00×10^{-5} mol), toluene (50 mL), ambient temperature, 1 bar C_2H_4 constant pressure, $EtAlCl_2$ (14 equiv), in a Schlenk, 30 min. [b] Mass [(liquid phase) − (50 mL of C_7H_8)]. [c] Determined by quantitative GC; data are an average of three runs. [d] K = hexenes (mol)/butenes (mol). [e] Friedel−Crafts alkylated products. [f] In units of g of C_2H_4 (g of Ni)$^{-1}$ h^{-1}. [g] In units of mol of C_2H_4 (mol of Ni)$^{-1}$ h^{-1}.

activator dependence has been reported for a number of related nickel-based ethylene oligomerization systems.[16,20,30,31]

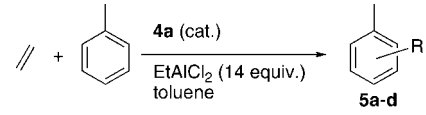
Analysis of the resulting organic products (quantitative GC/GC-MS) revealed the formation of C_4, C_6, and C_8 alkenes as isomeric mixtures of products (no polymer was obtained) with reasonably modest productivities (1513−4299 g of C_2H_4 (g of Ni)$^{-1}$ h^{-1}) that are comparable with those for other Ni/ligand-based oligomerization systems (Table 1).[27,32−36] However, the mild reaction conditions (1 bar, Ni:Al = 1:14) are a notable feature of proinitiators **4b−d**, especially as the selectivity toward butenes is retained, despite low regioselectivity.[16]

It is evident that for proinitiators **4b−d** there is a clear dependence of oligomerization productivity and selectivity upon the nature of the P-donor components. Although there is no discernible relationship between the catalytic outcomes and the basicity of the P-donor fragment,[22] proinitiator **4d**, which possesses the weakest σ-donating P-center, exhibits the lowest productivity and selectivity (Table 1), suggesting that the P,N-chelate is displaced during catalysis. In contrast, **4c** displays both the best activity and 1-C_4 selectivity; not only is its P center significantly more Lewis basic but it also provides considerable steric bulk.[22]

In contrast, exposure of toluene solutions of **4a**/$EtAlCl_2$ (Ni:Al = 1:14) to ethylene under identical conditions led to a quite different set of products. Here, only very small amounts of alkene products (<1 wt %) were observed after 30 min. Instead, GC-MS analysis revealed the presence of C_4, C_6, C_8, and C_{10} alkyl-substituted toluenes (**5a−d**), each as a mixture of regioisomers, as the only products (Table 2). Notably, in the absence of either **4a** or $EtAlCl_2$, or on replacing **4a** by $NiBr_2(PPh_3)_2$, no organic products could be detected. Furthermore, reactions of **4a**/$EtAlCl_2$/C_2H_4 undertaken in CH_2Cl_2 or chlorobenzene afforded only trace quantities of butenes and hexenes, while reactions undertaken in CH_2Cl_2 with 100 equiv of toluene present resulted in complete conversion of the aromatic hydrocarbon to **5a−d** in a ratio comparable to those observed for runs undertaken in neat toluene.

To simplify the task of identifying the organic products resulting from this transformation, a benzene solution of **4a** was treated with $EtAlCl_2$ (Ni:Al = 1:14) and allowed to contact ethylene (1 bar), as above; again, this afforded a mixture of products (GC-MS). Here, the predominant species (ca. 65%) were *o*-/*p*-$C_6H_4(C_2H_5)_2$ (**6**) and $C_6H_5(C_4H_9)$ (**7**), present in a 1:6 ratio, respectively, with the remainder being higher molecular weight alkylated phenyl products analogous to **5b−d**. Careful fractional distillation allowed **7** to be isolated, with subsequent NMR and mass spectrometric analyses identifying a mixture of *n*-butyl- and *sec*-butylbenzene (1:10 ratio, respectively) by comparison with authentic samples.

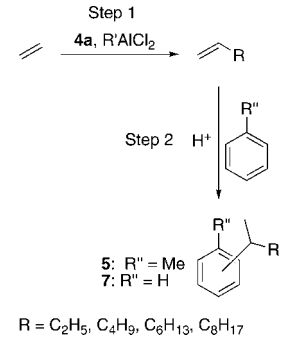
Table 2. Distribution of Friedel−Crafts Products Obtained from the Reaction between Ethylene and Toluene in the Presence of Proinitiator 4a and $EtAlCl_2$ as Activator[a]



compound	R	product distribution (%)[b]
a	C_4H_9	39.5
b	C_6H_{13}	19.7
c	C_8H_{17}	25.4
d	$C_{10}H_{21}$	14.1

[a] Reaction conditions: **4a** (5.00×10^{-5} mol), toluene (50 mL), ambient temperature, 1 bar C_2H_4 constant pressure, $EtAlCl_2$ (14 equiv), in a Schlenk, 30 min. [b] Determined by quantitative GC; data are an average of three runs.

Scheme 3. Proposed Pathway for the Formation of Compounds 5



In order to verify the origins of the ethyl groups observed in **6**, both benzene and toluene solutions of **4a** were treated with $MeAlCl_2$ (Ni:Al = 1:14) and exposed to ethylene (1 bar). In both cases, products and product ratios were obtained identical with those from the analogous reactions employing $EtAlCl_2$, ruling out direct alkylation from the alkylaluminum reagent.

Together, these observations are consistent with a two-stage process for the formation of **5** and **7** (Scheme 3). Step 1 is **4a**/R′$AlCl_2$-promoted (R′ = Me, Et) oligomerization of ethylene, generating C_4 to C_{10} alkenes (as observed with **4b−d**). Step 2 is a Friedel−Crafts alkylation of the aromatic solvent by the olefins generated in step 1, a process that accounts for the saturated side chains of the alkyl-substituted benzenes obtained and for the predominance of *sec*-butyl- over *n*-butylbenzene, a result of rearrangement of the carbocation intermediate.

Although the origins of this unusual preference toward aromatic alkylation behavior with **4a**/$EtAlCl_2$ remain unclear,

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a number of scenarios are possible. The most likely is that the oligomerization initiator generated from the reaction between **4a** and the aluminum alkyl is extremely active, but with a very short lifetime. This would generate significant concentrations of short-chain alkenes rapidly at the start of a run, prior to the loss of the active Ni species. Subsequently, the unsaturated hydrocarbons undergo slower Friedel−Crafts alkylation. Notably, it has been disclosed previously that ethyl- and butyl-substituted benzenes are alkylated by ethylene in the presence of catalytic quantities of $MoCl_5/EtAlCl_2/ROH$ ($Mo:Al:H^+ = 1:4:3$), through what is assumed to be a similar pathway.[37]

Conclusion

The readily prepared, easily derivatized *N*-phosphino guanidines are attractive scaffolds for Ni(II), with the resulting complexes being active ethylene oligomerization initiators in the presence of $EtAlCl_2$ whose selectivity may be be altered through variation of the steric and electronic demands of the P-donor component. Notably, these initiators operate at ambient temperature and 1 bar of ethylene, using a low Ni:Al ratio (1:14), a feature of particular current industrial relevance. In contrast, in either benzene or toluene, the Ph_2P-substituted system in combination with $EtAlCl_2$ (Ni:Al = 1:14) gives rise to an unusual ethylene oligomerization/Friedel−Crafts alkylation reaction sequence. This is believed to occur due to the formation of a highly active yet very short-lived Ni-based initiator that generates higher alkenes, which act as substrates for a classical Al-catalyzed alkylation of the aromatic solvents. Studies are ongoing to enhance the selectivity of proinitiators **4b−d** and to better understand the origins of the Friedel−Crafts chemistry.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive materials were performed under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox (Saffron Scientific) (unless stated otherwise). Solvents were freshly distilled under nitrogen from sodium/benzophenone (diethyl ether, toluene, DME), from calcium hydride (dichloromethane), from sodium (hexane), or from P_2O_5 (CD_2Cl_2, C_6D_6, and $CDCl_3$) and degassed prior to use. Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded on Bruker AM 250, AMX 300, and AMX 400 spectrometers; chemical shifts were referenced to residual protio impurities in the deuterated solvent (^1H), to the deuterated solvent (^{13}C), or to external aqueous 85% H_3PO_4 (^{31}P). Chemical shifts are reported in ppm and coupling constants in Hz. All spectra were obtained at ambient probe temperature (298 K) unless stated otherwise. For ^1H NMR spectra, ^{31}P-coupled resonances were verified by obtaining $^1H\{^{31}P\}$ spectra. ^{13}C NMR spectra were assigned with the aid of DEPT 135. Infrared spectra were recorded (Nujol mulls (KBr windows), KBr disks, or solution (KBr windows)) on a Perkin-Elmer 1600 spectrophotometer; Nujol was dried over sodium wire. FAB (3-nitrobenzyl alcohol matrix) and EI mass spectra were recorded on a Kratos Concept 1H instrument and are reported in *m/z*. GC-MS measurements were performed either using a Perkin-Elmer Autosystem XL GC (PE-5MS 30 m coil, internal diameter 0.25 mm, film thickness 0.25 μm) coupled to a Perkin-Elmer Turbomass mass spectrometer or using a Thermo Finnegan Trace instrument (Agilent HP-5MS 30 m column, internal diameter 0.25 mm, film thickness 0.25 μm). $NiBr_2$(DME), DABCO, $EtAlCl_2$ (1 M, toluene), and PCl_3 were purchased from Aldrich and used as received. $(Pr^i_2N)_2PCl$ was prepared according to the literature.[38] Ethylene was obtained from BOC. Gases were passed through a drying column (silica/$CaCO_3/P_2O_5$) prior to use. Melting points were obtained in sealed glass tubes under nitrogen, using a Gallenkamp melting point apparatus, and are uncorrected.

Bis(diphenylamino)chlorophosphine ($(Ph_2N)_2PCl$). A three-necked round-bottom flask fitted with a reflux condenser and pressure-equalizing dropping funnel was charged with DABCO (13.55 g, 0.121 mol) and placed under vacuum. After back-filling with N_2, PCl_3 (10 mL, 0.115 mol) and DME (50 mL) were added and the vessel was stirred and cooled to 0 °C. The dropping funnel was charged with a DME (150 mL) solution of Ph_2NH (39.76 g, 0.235 mol), which was added dropwise over 2 h to the cooled reaction vessel. A further aliquot of DME (50 mL) was washed through the dropping funnel, before replacing it with a stopper. The reaction vessel was warmed to room temperature over 4 h and then heated at reflux for 6 days to give a yellow solution with a voluminous white precipitate. The solution was filtered using a glass frit and the precipitate washed with DME (50 mL). The DME was removed in vacuo to leave a brown oil. Unreacted/excess DABCO, Ph_2NH, and some $(Ph_2N)PCl_2$ were removed under high vacuum (0.01 mmHg) at 150 °C. The resulting viscous orange oil was shown by $^{31}P\{^1H\}$ NMR spectroscopy to be a mixture of $(Ph_2N)PCl_2$ (11%) and $(Ph_2N)_2PCl$ (89%) (76.99 g, 72%, combined yield). Further attempts at purification failed to separate the two products. Data for the desired product only: ^1H NMR (250.13 MHz, $CDCl_3$) δ 7.10 (8H, m, *o*-C_6H_5), 7.00 (4H, m, *p*-C_6H_5), 6.87 (8H, m, *m*-C_6H_5); $^{13}C\{^1H\}$ (62.90 MHz, $CDCl_3$) δ 145.35 (d, $^2J_{PC} = 10.2$, *i*-C_6H_5), 129.24 (s, *m*-C_6H_5), 126.30 (d, $^3J_{PC} = 8.6$, *o*-C_6H_5), 125.15 (s, *p*-C_6H_5); $^{31}P\{^1H\}$ (101.26 MHz, $CDCl_3$) δ +123.1 (s); MS (EI+) 402 M^+, 234 $(M - NPh_2)^+$, 198 $(M - NPh_2 - Cl)^+$.

Dimesitylphosphine Oxide ($Mes_2P(=O)H$). We used a modified literature procedure:[39] to a cooled (0 °C), stirred solution of PCl_3 (8.5 mL, 9.70×10^{-2} mol) in diethyl ether (600 mL) was added a solution of MesMgBr (1.0 M, diethyl ether, 200 mL, 0.200 mol) dropwise over 2 h. The resultant mixture was stirred and warmed to room temperature and then heated at reflux overnight. After the mixture was recooled (0 °C), deoxygenated, distilled water (150 mL) was added dropwise with vigorous stirring and the mixture warmed to room temperature overnight. The diethyl ether was removed in vacuo and the aqueous solution extracted with deoxygenated DCM and then dried over $MgSO_4$. The DCM was removed in vacuo to leave a yellow solid, which was then dissolved in hot toluene and the solution filtered. Prolonged cooling at −30 °C gave the product as white crystals (14.31 g, 52%). ^1H NMR (250.13 MHz, $CDCl_3$): δ 8.55 (1H, d, $^1J_{PH} = 476.1$, P*H*), 6.86 (4H, d, $^4J_{PH} = 3.9$, $C_6H_2(CH_3)_3$), 2.40 (12H, s, *o*-$C_6H_2(CH_3)_3$), 2.29 (6H, s, *p*-$C_6H_2(CH_3)_3$). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ 142.11 (d, $^4J_{PC} = 2.5$, *p*-$C_6H_2(CH_3)_3$), 141.92 (d, $^2J_{PC} = 10.2$, *o*-$C_6H_2(CH_3)_3$), 130.67 (d, $^3J_{PC} = 10.7$, *m*-$C_6H_2(CH_3)_3$), 126.59 (d, $^1J_{PC} = 100.2$, *i*-$C_6H_2(CH_3)_3$), 21.35 (d, $^5J_{PC} = 1.0$, *p*-$C_6H_2(CH_3)_3$), 20.97 (d, $^3J_{PC} = 8.1$, *o*-$C_6H_2(CH_3)_3$). ^{31}P NMR (101.26 MHz, $CDCl_3$): δ 10.0 (d, $^1J_{PH} = 476$). MS (FAB+): 287 $(MH)^+$, 167 $(M - Mes)^+$, 119 Mes^+. Anal. Calcd for $C_{18}H_{23}OP$: C, 75.50; H, 8.09. Found: C, 75.40; H, 8.21.

Dimesitylchlorophosphine (Mes_2PCl). We used a modified literature procedure:[39] in a thick-walled Young's tap ampule, $Mes_2P(O)H$ (14.31 g, 5.00×10^{-2} mol) was dissolved in neat PCl_3 (85 mL), the system was heated to 60 °C, and the ampule was sealed. After 3 weeks of stirring at this temperature the solution was cooled and filtered through a glass frit to remove the orange solid that had formed. Excess PCl_3 was then removed in vacuo to leave a yellow oil. Repeated addition of diethyl ether (3 × 20 mL) and removal in vacuo, followed by exposure to vacuum for 12 h,

(37) Olechowski, J. R. (Cities Service Company) U.S. Patent 3,720,725, 1973.

(38) King, R. B.; Sadanani, N. D. *Synth. React. Org. Met.-Org. Chem.* **1985**, *15*, 149–153.

(39) Bokanov, A. I.; Rozanel'skaya, N. A.; Steanov, B. I. *J. Gen. Chem. USSR* **1978**, *48*, 1732–1733.

left the product as a pale yellow solid (13.07 g, 86%). ^{1}H NMR (301.24 MHz, C_6D_6): δ 6.60 (4H, d, $^4J_{PH}$ = 3.2, $C_6H_2(CH_3)_3$), 2.38 (12H, d, $^4J_{PH}$ = 2.0, *o*-$C_6H_2(CH_3)_3$), 2.01 (6H, s, *p*-$C_6H_2(CH_3)_3$). ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ 142.28 (d, $^2J_{PC}$ = 18.3, *o*-$C_6H_2(CH_3)_3$), 140.05 (s, *p*-$C_6H_2(CH_3)_3$), 133.61 (d, $^1J_{PC}$ = 46.3, *i*-$C_6H_2(CH_3)_3$), 131.10 (d, $^3J_{PC}$ = 2.0, *m*-$C_6H_2(CH_3)_3$), 23.31 (d, $^3J_{PC}$ = 15.8, *o*-$C_6H_2(CH_3)_3$), 21.20 (s, *p*-$C_6H_2(CH_3)_3$). ^{31}P{^{1}H} NMR (101.26 MHz, C_6D_6): δ 85.0 (s). MS (FAB+): 269 (M − Cl)$^+$. Anal. Calcd for $C_{18}H_{22}PCl$: C, 70.93; H, 7.27. Found: C, 68.67; H, 7.99.

7-(Diphenylphosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene (3a). To a stirred, cooled (−78 °C) suspension of **1** (5.10 g, 3.66×10^{-2} mol) in Et_2O (200 mL) was added *n*-BuLi (1.6 M, hexanes, 22.9 mL, 3.66×10^{-2} mol). The vessel was warmed to room temperature over 1 h, affording a white suspension. After the mixture was recooled (−78 °C), Ph_2PCl (6.6 mL, 3.66×10^{-2} mol) in Et_2O (80 mL) was added and the mixture stirred at −78 °C for 1 h before being warmed to room temperature and then stirred for 18 h. Removal of solvents in vacuo followed by addition of toluene and filtration through a glass frit gave a transparent yellow solution. Concentration and crystallization at −30 °C gave colorless crystals of **3a** (9.23 g, 78%, mp 120−123 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 7.36 (10H, m, C_6H_5), 3.44 (2H, t, $^3J_{HH}$ = 5.7, CH_2), 3.16 (2H, t, $^3J_{HH}$ = 6.1, CH_2), 3.08 (2H, t, $^3J_{HH}$ = 6.4, CH_2), 2.99 (2H, t, $^3J_{HH}$ = 5.7, CH_2), 1.86 (2H, ps-quin, $^3J_{HH}$ = 5.9, CH_2), 1.69 (2H, ps-quin, $^3J_{HH}$ = 5.3, CH_2). ^{13}C{^{1}H} NMR (75.78 MHz, $CDCl_3$): δ 151.9 (d, $^2J_{PC}$ = 20.5, *C*=N), 138.2 (d, $^1J_{PC}$ = 20.5, *i*-C_6H_5), 132.3 (d, $^2J_{PC}$ = 21.0, *o*-C_6H_5), 128.5 (s, *p*-C_6H_5), 128.2 (d, $^3J_{PC}$ = 5.5, *m*-C_6H_5), 48.8 (s, CH_2), 48.6 (s, CH_2), 44.2 (s, CH_2), 42.9 (d, $^2J_{PC}$ = 10.0, CH_2), 24.2 (s, CH_2), 23.1 (s, CH_2). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): δ 41.6 (s). MS (FAB+): 322 (M − H)$^+$, 247 (MH − Ph)$^+$, 186 (MH − TBD)$^+$. Anal. Calcd for $C_{19}H_{22}N_3P$: C, 70.57; H, 6.86; N, 12.99. Found: C, 70.44; H, 6.95; N, 12.43.

7-(Dimesitylphosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene (3b). To a stirred, cooled (−78 °C) suspension of **1** (2.74 g, 1.97×10^{-2} mol) in diethyl ether (100 mL) was added *n*-BuLi (2.0 M, pentane, 9.9 mL, 1.97×10^{-2} mol), and the vessel was warmed to room temperature over 1 h. After the mixture was recooled (−78 °C), an ethereal solution (50 mL) of Mes_2PCl (6.00 g, 1.97×10^{-2} mol) was added via cannula. The mixture was stirred at −78 °C for 1 h before being warmed to room temperature and then stirred for 18 h, resulting in a pale yellow solution with a white precipitate. Removal of solvent in vacuo left a beige powder. Addition and subsequent removal of DCM (50 mL) gave a beige foam, which was dissolved in toluene and filtered through a glass frit to give an orange solution. Concentration and crystallization at −30 °C gave colorless crystals of **3b** (5.94 g, 74%, mp 189−190 °C). ^{1}H NMR (301.24 MHz, $CDCl_3$): δ 6.73 (4H, d, $^4J_{PH}$ = 2.9, *m*-$C_6H_2(CH_3)_3$), 3.42 (2H, t, $^3J_{HH}$ = 5.5, CH_2), 3.13 (2H, t, $^3J_{HH}$ = 6.0, CH_2), 3.05 (4H, ps-t, $^3J_{HH}$ = 6.0, CH_2), 2.22 (6H, s, *p*-$C_6H_2(CH_3)_3$), 2.16 (12H, d, $^4J_{PH}$ = 1.2, *o*-$C_6H_2(CH_3)_3$), 1.81 (2H, ps-quin, $^3J_{HH}$ = 5.7, CH_2), 1.60 (2H, ps-quin, $^3J_{HH}$ = 6.0, CH_2). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 151.56 (d, $^2J_{PC}$ = 21.5, *C*=N), 141.32 (d, $^2J_{PC}$ = 19.0, *o*-$C_6H_2(CH_3)_3$), 137.41 (s, *p*-$C_6H_2(CH_3)_3$), 134.14 (d, $^1J_{PC}$ = 33.1, *i*-$C_6H_2(CH_3)_3$), 129.86 (d, $^3J_{PC}$ = 2.1, *m*-$C_6H_2(CH_3)_3$), 48.85 (d, $^4J_{PC}$ = 1.8, CH_2), 48.45 (s, CH_2), 44.53 (d, $^2J_{PC}$ = 12.2, CH_2), 44.16 (d, $^4J_{PC}$ = 1.5, CH_2), 24.16 (s, CH_2), 23.35 (s, CH_2), 22.07 (d, $^3J_{PC}$ = 16.6, *o*-$C_6H_2(CH_3)_3$), 20.88 (s, *p*-$C_6H_2(CH_3)_3$). ^{31}P{^{1}H} NMR (121.94 MHz, $CDCl_3$): δ 27.7 (s). MS (FAB+): 408 (MH)$^+$, 392 (M − Me)$^+$, 288 (M − Mes)$^+$, 269 (M − TBD)$^+$. IR (KBr, $CDCl_3$ solution): ν(C=N) cannot be assigned unambiguously. Anal. Calcd for $C_{25}H_{34}N_3P$: C, 73.68; H, 8.41; N, 10.31%. Found: C, 73.78; H, 8.52; N, 10.19.

7-(Bis(diisopropylamino)phosphino)-1,5,7-triazabicyclo[4.4.0]-dec-5-ene (3c). To a stirred, cooled (−78 °C) suspension of **1** (4.15 g, 2.98×10^{-2} mol) in diethyl ether (100 mL) was added dropwise *n*-BuLi (1.6 M, hexanes, 18.6 mL, 2.98×10^{-2} mol), and the vessel was warmed to room temperature for 1 h, to give an opaque white solution. After the solution was recooled (−78 °C), an ethereal solution (100 mL) of $(i\text{-}Pr_2N)_2PCl$ (7.95 g, 2.98×10^{-2} mol) was added via cannula. The mixture was stirred at −78 °C for 1 h before being warmed to room temperature and then stirred for 18 h, resulting in a pale yellow solution with a white precipitate. Removal of solvent in vacuo left a white powder. Addition and subsequent removal of DCM (50 mL) gave a white solid. Addition of toluene gave a pale yellow solution and white precipitate, which was removed by glass frit filtration. Concentration and crystallization at −30 °C gave colorless crystals of **3c** (8.77 g, 80%, mp 90−92 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 3.26 (8H, m, CH_2 + $NCH(CH_3)_2$), 3.02 (4H, m, CH_2), 1.80 (2H, ps-quin, $^3J_{HH}$ = 6.0, CH_2), 1.71 (2H, ps-quin, $^3J_{HH}$ = 5.7, CH_2), 1.18 (12H, d, $^3J_{HH}$ = 6.6, $NCH(CH_3)_2$), 1.13 (12H, d, $^3J_{HH}$ = 6.7, $NCH(CH_3)_2$); ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ 149.86 (d, $^2J_{PC}$ = 14.2, *C*=N), 48.78 (s, CH_2), 48.44 (s, CH_2), 46.88 (d, $^2J_{PC}$ = 15.3, $NCH(CH_3)_2$), 43.42 (s, CH_2), 41.36 (d, $^2J_{PC}$ = 3.6, CH_2), 24.51 (d, $^3J_{PC}$ = 6.6, $NCH(CH_3)_2$), 24.30 (s, CH_2), 23.44 (d, $^3J_{PC}$ = 7.1, $NCH(CH_3)_2$), 23.30 (s, CH_2). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): δ 89.6 (s). MS (FAB+): 370 (MH)$^+$, 269 (M − N-*i*-Pr_2)$^+$, 231 (M − TBD)$^+$. MS (EI): 369 (M)$^+$, 326 (M − *i*-Pr)$^+$, 269 (M − N-*i*-Pr_2)$^+$. IR (KBr, $CDCl_3$ solution): ν(C=N) cannot be assigned unambiguously. Anal. Calcd for $C_{19}H_{40}N_5P$: C, 61.76; H, 10.91; N, 18.95. Found: C, 61.69; H, 10.99; N, 19.03.

7-(Bis(diphenylamino)phosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene (3d). To a stirred, cooled (−78 °C) suspension of **1** (6.90 g, 4.96×10^{-2} mol) in diethyl ether (100 mL) was added dropwise *n*-BuLi (2.0 M, pentane, 24.8 mL, 4.96×10^{-2} mol), and the vessel was warmed to room temperature for 1 h. After the mixture was recooled (−78 °C), an ethereal solution (100 mL) of $(Ph_2N)_2PCl$ (15.33 g, 3.80×10^{-2} mol) and $(Ph_2N)PCl_2$ (1.56 g, 5.78×10^{-3} mol) (total 16.89 g of mixture) was added via cannula. The mixture was stirred at −78 °C for 1 h before being warmed to room temperature and then stirred for 18 h, resulting in an orange solution with a white precipitate. Removal of solvent in vacuo left a pale orange powder. Addition and subsequent removal of DCM (50 mL) gave a brown oil. Addition of toluene (100 mL) gave an orange solution and a white precipitate, which was removed by filtration. The precipitate was washed with DCM (30 mL) and filtered. The toluene and DCM solutions were combined, and the solvent was removed. The resultant orange solid was dissolved in a minimum amount of DCM; recrystallization at −30 °C gave colorless crystals of **3d** (7.93 g, 45%, mp 181−184 °C). ^{1}H NMR (250.13 MHz, C_6D_6): δ 7.44 (16H, m, *o*- + *m*-C_6H_5), 7.23 (4H, m, *p*-C_6H_5), 3.80 (2H, t, $^3J_{HH}$ = 5.6, CH_2), 3.18 (2H, t, $^3J_{HH}$ = 5.8, CH_2), 2.91 (2H, t, $^3J_{HH}$ = 6.0, CH_2), 2.65 (2H, t, $^3J_{HH}$ = 6.1, CH_2), 1.86 (2H, ps-quin, $^3J_{HH}$ = 5.8, CH_2), 1.50 (2H, ps-quin, $^3J_{HH}$ = 5.9, CH_2). ^{13}C{^{1}H} NMR (75.75 MHz, C_6D_6): δ 149.18 (d, $^2J_{PC}$ = 16.9, *C*=N), 148.19 (d, $^2J_{PC}$ = 11.4, *i*-C_6H_5), 129.52 (s, *m*-C_6H_5), 125.78 (d, $^3J_{PC}$ = 9.0, *o*-C_6H_5), 123.77 (s, *p*-C_6H_5), 48.53 (s, CH_2), 48.03 (s, CH_2), 44.66 (d, $^4J_{PC}$ = 3.0, CH_2), 41.13 (d, $^2J_{PC}$ = 6.6, CH_2), 24.03 (s, CH_2), 23.89 (s, CH_2). ^{31}P{^{1}H} NMR (101.26 MHz, C_6D_6): δ 92.3 (s). MS (FAB+): 506 (MH)$^+$, 367 (M − **1** − H)$^+$, 337 (M − NPh_2)$^+$. IR (KBr, C_6D_6 solution): ν(C=N) cannot be assigned unambiguously. Anal. Calcd for $C_{31}H_{32}N_5P$: C, 73.64; H, 6.38; N, 13.85. Found: C, 73.76; H, 6.29; N, 13.75.

[7-(Diphenylphosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene]-nickel Dibromide (4a). To a mixture of **3a** (311 mg, 9.61×10^{-4} mol) and $NiBr_2$(DME) (288 mg, 9.33×10^{-4} mol) was added cold (−78 °C) CH_2Cl_2 (200 mL). The solution was warmed to room temperature and then heated at reflux for 24 h. The resulting purple precipitate was recovered by filtration, washed with Et_2O (4 × 50 mL), and dried in vacuo to afford **4a** as a dark purple powder (499 mg, 99%, mp 220 °C dec). Deep red crystals, suitable for an X-ray structure determination, were grown from a CD_2Cl_2 solution layered

with hexane. MS (FAB+): 461 $(M - Br)^+$. IR (KBr): ν(CN) 1587 cm^{-1}. Anal. Calcd for $C_{19}H_{22}N_3PBr_2Ni$: C, 42.11; H, 4.09; N, 7.75. Found: C, 42.21; H, 4.17; N, 7.83.

[7-(Dimesitylphosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene]-nickel Dibromide (4b). To a mixture of **3b** (235 mg, 5.77×10^{-4} mol) and $NiBr_2$(DME) (173 mg, 5.61×10^{-4} mol) was added cold (−78 °C) CH_2Cl_2 (200 mL). The mixture was stirred and warmed to room temperature over 18 h and then heated to reflux for 24 h. The resultant purple solution was filtered through a glass frit, and the volatiles were removed in vacuo to leave **4b** as a purple powder, which was washed with diethyl ether (4 × 20 mL) and dried in vacuo (287 mg, 82%). MS (FAB^+): 546 $(M - Br)^+$, 465 $(M - 2Br)^+$. IR (KBr, CH_2Cl_2 solution): ν(C═N) 1595 cm^{-1}. Anal. Calcd for $C_{25}H_{34}N_3PBr_2Ni$: C, 47.96; H, 5.47; N, 6.71. Found: C, 47.98; H, 5.33; N, 6.61.

[7-(Bis(diisopropylamino)phosphino-1,5,7-triazabicyclo[4.4.0]-dec-5-ene]nickel Dibromide (4c). To a mixture of **3c** (273 mg, 7.38×10^{-4} mol) and $NiBr_2$(DME) (221 mg, 7.16×10^{-4} mol) was added cold (−78 °C) CH_2Cl_2 (200 mL). The mixture was stirred and warmed to room temperature over 18 h, and then heated to reflux for 24 h. The resultant purple solution was filtered through a glass frit, and the volatiles were removed in vacuo to leave **4c** as a lilac powder, which was washed with pentane (5 × 30 mL) and dried in vacuo (303 mg, 72%). MS (FAB+): 508 $(M - Br)^+$, 427 $(M - 2Br)^+$, 408 $(M - Br - N\text{-}i\text{-}Pr_2)^+$. IR (KBr, CH_2Cl_2 solution): ν(C═N) 1591 cm^{-1}. Anal. Calcd for $C_{19}H_{40}N_5PBr_2Ni$: C, 38.81; H, 6.86; N, 11.91. Found: C, 38.74; H, 7.01; N, 12.06.

[7-(Bis(diphenylamino)phosphino)-1,5,7-triazabicyclo[4.4.0]dec-5-ene]nickel Dibromide (4d). A mixture of **3d** (255 mg, 5.04×10^{-4} mol) and $NiBr_2$(DME) (151 mg, 4.89×10^{-4} mol) was transferred to a Schlenk line. The vessel was cooled to −78 °C, and the solids were stirred, as DCM (60 mL) was added dropwise. The mixture was stirred and warmed to room temperature over 18 h and then heated to reflux for 24 h. The product **3d** precipitated as a purple powder and was recovered via filtration. Washing with diethyl ether (5 × 50 mL) and drying in vacuo left a light purple powder (321 mg, 91%). MS (FAB+): 644 $(M - Br)^+$, 562 $(M - 2Br)^+$. IR (KBr, CH_2Cl_2 solution): ν(C═N) 1600 cm^{-1}. Anal. Calcd for $C_{31}H_{32}N_5PBr_2Ni$: C, 51.42; H, 4.45; N, 9.67. Found: C, 51.52; H, 4.51; N, 9.61.

Generalized Catalyst Testing Procedure. In order to provide ready/reliable comparison of the catalytic outcomes, the catalyst test procedure adopted is a modification of that described by Braunstein and co-workers.[40] A large Schlenk equipped with an efficient magnetic stirrer bar was charged with **4** (5.00×10^{-5} mol) and dry toluene (50 mL) under nitrogen, prior to addition of $EtAlCl_2$ (1 M, toluene; Ni:Al = 1:14) via syringe. This solution was aged at room temperature for a period of 10 min, during which time it was degassed and left under a partial vacuum. Subsequently, it was allowed to contact ethylene (1 bar), with rapid stirring, for a period of 30 min. At the end of the run, the Schlenk was cooled in an ice bath and the reaction quenched by slow addition of HCl (1 M, 10 mL); nonane (1 mL) was added as an internal GC standard. Aliquots of the resulting organic phase were rapidly transferred to precooled GC vials and sealed; GC analyses were undertaken immediately.

X-ray Data Collection, Structure Solution and Refinement for 4a. X-ray diffraction data were collected on a Bruker Apex 2K CCD area detector diffractometer equipped with an Oxford Cryostream N_2 cooling device. Data collection and reduction were conducted using the SMART and SAINT programs, respectively.[41] All further calculations were performed using the SHELXTL package[42] and programs therein. The structure was solved using Patterson methods and was refined using full-matrix least squares based on F^2. An empirical absorption correction was applied to all data using SADABS.[43] All non-hydrogen atoms were refined anisotropically, and then hydrogen atoms were included at idealized positions and refined as rigid groups. Crystal data: $C_{19.50}H_{22}DBr_2ClN_3NiP$, $M_r = 584.36$, monoclinic, $a = 24.4597(15)$ Å, $b = 13.0822(8)$ Å, $c = 17.0457(11)$ Å, $\beta = 127.244(1)°$, $V = 4342.1(5)$ $Å^3$, $Z = 8$, μ(Mo Kα) = 4.782 mm^{-1}, $T = 150(2)$ K, crystal size 0.49 × 0.29 × 0.21 mm^3, space group $C2/c$, 16 335 reflections collected, 4264 independent reflections ($R_{int} = 0.0338$), R1 = 0.0346 and wR2 = 0.0986 for $I > 2\sigma(I)$, R1 = 0.0396 and wR2 = 0.1002 for all data. CCDC reference number 653161 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data<u>r</u>equest/cif.

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Supporting Information Available: A CIF file giving crystal data for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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