Polymerization of Ethylene with Cationic Palladium and Nickel Catalysts Containing Bulky Nonenolizable Imine−Phosphine Ligands

Olafs Daugulis and Maurice Brookhart*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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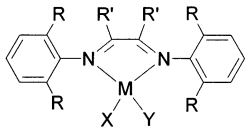
A number of bulky, nonenolizable Pd(II) and Ni(II) imine−phosphine complexes have been synthesized and tested in the ethylene polymerization. These catalysts show improved temperature stability with respect to the corresponding diimine complexes. Nickel imine−phosphine precatalysts containing *gem*-dimethyl substituent α to phosphorus display moderate activity and produce substantially higher molecular weight polyethylene compared to the corresponding enolizable complexes.

Introduction

In the late 70's and 80's several Ni(II) catalysts capable of polymerizing ethylene were described.[1] The report in 1995 of versatile, highly active Pd(II) and Ni(II) aryl-substituted α-diimine catalysts **1** sparked



M = Ni, Pd

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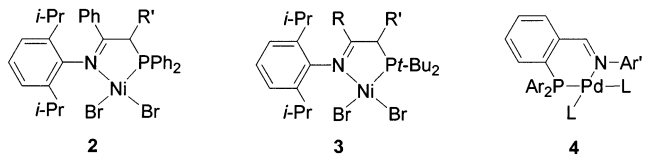
renewed interest in developing late metal catalysts for olefin polymerization.[2a] The key to producing high molecular weight polymers is clearly the incorporation of substituents in the ortho-positions of the aryl rings which provide bulk in the axial sites of the square plane and retard the rate of chain transfer.[2a] These α-diimine catalysts have been demonstrated to convert ethylene,[2a−c] α-olefins,[2a,b,d] cyclopentene,[2e] and *trans*-1,2-disubstituted olefins[2f] to high molecular weight polymers with unique microstructures as a result of migration of the metal along the polymer backbone (chain-running) in competition with monomer insertion. A limited set of polar monomers can be copolymerized with ethylene and α-olefins.[1e,2g,h]

Considerable effort has been expended to identify other Ni(II) and Pd(II) complexes bearing bulky bidentate ligands which can be similarly employed in olefin polymerizations and which expand the scope of utility of such catalysts.[1e−g,2] A particularly important goal is to identify catalysts with increased activity, lifetime, and thermal stability while maintaining the feature of chain-running that gives rise to polymers with unique microstructures. Recognizing the high stability of Pd(II) and Ni(II) phosphine complexes and the fact that bidentate complexes containing a single aryl imine arm function much like diimine systems,[3] complexes containing bidentate phosphine−imine ligands are obvious and attractive targets.

Several phosphine−imine nickel complexes have recently been described in the patent literature. In a contribution from Eastman, complexes of general type **2** were reported together with their ethylene polymerization properties upon MAO activation.[4] At 0−23 °C and 1 atm of ethylene a small amount of high molecular weight (M_w up to 400 000) polyethylene was obtained, suggesting incomplete precatalyst activation. In contributions by Guan, precatalysts of type **3** were shown to



polymerize ethylene at high temperatures (70−100 °C) to give polyethylene with a bimodal molecular weight

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(2) (a) Johnson, L. K.; Killian, C. K.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, M. A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Tempel, D. J. WO 9623010, 1996. (c) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320. (d) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664. (e) McLain, S. J.; Feldman, J.; McCord, E. F.; Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705. (f) Leatherman, M. D.; Brookhart, M. *Macromolecules* **2001**, *34*, 2748. (g) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (h) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

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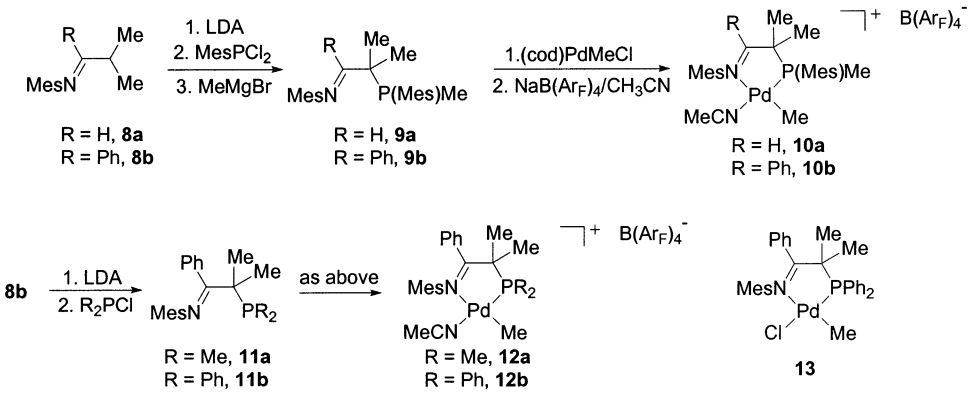
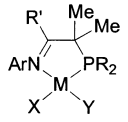
Scheme 1



distribution if activated by PMAO-IP or MAO.[5] The major fraction of the polyethylene generally had M_w in the range of a few thousands, but the minor fraction consisted of very high molecular weight polymer (M_w up to 10^6). One possible explanation of these data is that while at low pressures and temperatures used by Killian et al. the precatalyst is not completely activated, at higher temperatures used by Guan the catalyst is partially chemically modified, and this modification is responsible for the low molecular weight fraction in the polymer. Since the catalyst backbone is easily enolizable (e.g. ligands **5** and **6** exist either as enamines or imine−enamine mixtures in solution),[5,6] and complexation to a metal is expected to increase the acidity, the enolization of the catalyst backbone by the MAO activator is possible. Feringa and co-workers have described nonenolizable palladium phosphine−imine catalysts **4** that oligomerize ethylene at 100 °C.[7a]

The aim of the work reported here was to prepare Pd(II) and Ni(II) complexes from bulky phosphine−imine bidentate ligands which are nonenolizable in the hope of obtaining thermally stable polymerization catalysts which would produce high molecular weight, branched polyethylene. Since ethylene polymerization catalysts containing smaller chelate rings seem generally to be more productive,[8] the focus of this work has been on the complexes of general type **7** containing five-membered rather than six-membered chelate rings and a *gem*-dimethyl group α to phosphorus, which renders these phosphine−imine chelate ligands rigid, bulky, and nonenolizable.



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Results and Discussion

1. Synthesis of Phosphine−Imine Palladium Complexes and Their Use as Ethylene Polymerization Catalysts. Phosphine−imine ligands bearing *gem*-dimethyl groups adjacent to phosphorus were prepared using precedented procedures.[4−6] The imines **8a**,**b** were deprotonated using *t*-BuLi or LDA to form the corresponding lithium azaenolates. The reactions with phosphorus electrophiles were carried out in two ways. If the bulky mesityl (Mes) substituent was introduced on phosphorus, the azaenolate was reacted with $MesPCl_2$ followed by MeMgBr to introduce the other substituent on phosphorus yielding **9a**,**b**. Use of MesP(Me)Cl gave rise to mixtures of products presumably arising from the reaction at both carbon and nitrogen of the azaenolate.[6a,b] In the case of less hindered phenyl- and methyl-substituted compounds it was possible to react the azaenolate directly with Ph_2PCl and Me_2PCl affording **11a**,**b**. We observed that the amount of reaction at the N-terminus of the azaenolate increased with steric hindrance and decreased with increasing electrophilicity of the phosphorus electrophile. The purity and yield of the ligands was estimated from the ^{31}P NMR spectra, and after the addition of (cod)PdMeCl to crude iminophosphines the corresponding ligand−palladium methyl chloride complexes were isolated. Chloride abstraction was effected by reaction with $NaB(Ar_F)_4$ in acetonitrile/dichloromethane affording cationic acetonitrile complexes **10a**,**b** and **12a**,**b** (Scheme 1).

A single-crystal X-ray analysis confirmed the structure of **13** (Figure 1). As expected on electronic grounds, chloride is *trans* to the better donor phosphorus while methyl is *trans* to the poorer donor nitrogen.[9] The fact

(3) (a) Johnson, L. K.; Bennett, A. M. A.; Ittel, S. D.; Wang, L.; Parthasarathy, A.; Hauptman, E.; Simpson, R. D.; Feldman, J.; Coughlin, E. B. WO 9830609, 1998. (b) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, T. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (c) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217.

(4) Killian, C. M.; McDevitt, J. P.; Mackenzie, P. B.; Moody, L. S.; Ponasik, J. A., Jr. WO 9840420, 1998.

(5) (a) Guan, Z. WO 0059956, 2000. (b) Guan, Z.; Marshall, W. J. *Organometallics* **2002**, *21*, 3580.

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(7) (a) van den Beuken, E. K.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *Chem. Commun.* **1998**, 223. For a report of nonenolizable phosphine−imine cobalt dichloride complexes and their ethylene polymerization properties, see: (b) Tsukahara, T.; Kanno, T. JP 2000128922, 2000. Oligomerization of norbornene using palladium phosphine−imine palladium catalysts has also been reported. See: (c) Chen, Y.-C.; Chen, C.-L.; Chen, J.-T.; Liu, S.-T. *Organometallics* **2001**, *20*, 1285. Dimerization and trimerization of ethylene using phosphine−imine palladium catalysts has been described. (d) Chen, J.-T.; Liu, S.-L.; Zhao, K.-Q. *J. Chin. Chem. Soc.* **2000**, *47*, 279.

(8) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21.

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

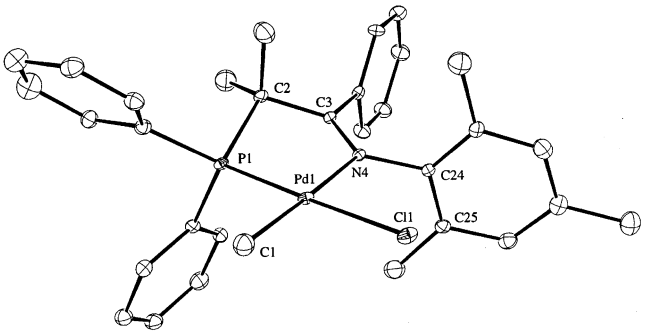


Figure 1. ORTEP view of **13**. Selected interatomic distances (Å) and angles (deg): Pd(1)−N(4) = 2.176(12), Pd(1)−P(1) = 2.206(4), Pd(1)−C(1) = 2.012(16), P(1)−C(2) = 1.880(12), N(4)−C(3) = 1.282(21); N(4)−Pd(1)−P(1)−C(2) = −25.1(8), Pd(1)−N(4)−C(24)−C(25) = 84.5(16).

Table 1. Oligomerization/Polymerization of Ethylene by 10a,b and 12a,b

entry	catalyst[a]	time, h	g of polymer	TOF, h^{-1}	M_n[b]	Br/1000 C[c]
1	**10a**	3	0.43	510	350	89
2	**10a**	15	0.97	230	350	90
3	**10b**[d]	3	0.06	70	660	116
4	**10b**[d,e]	3	0.09	110	620	113
5	**12a**	3	∼0	∼0		
6	**12b**[d,e]	3	∼0	∼0		

[a] 0.01 mmol of catalyst in 100 mL of toluene used, 400 psi ethylene, 80 °C. [b] M_n determined by ^{1}H NMR spectroscopy (see Experimental Section for details). [c] Branching per 1000 C determined by ^{1}H NMR spectroscopy (see Experimental Section for details). [d] Small amount of polyethylene obtained may cause errors in M_n and branching determination due to adventitious alkane impurities. [e] Reaction in chlorobenzene (100 mL).

that the methyl group is *cis* to the phosphorus is demonstrated also by the magnitude of Me−P coupling constants (J(Me−P), ^{1}H 2.3 Hz and ^{13}C 0 Hz; similar values were observed also for **10a**,**b**, **12a**,**b**, and the intermediate palladium methyl chloride complexes).[6c] The bond lengths in **13** are typical for palladium−diimine complexes (C(3)−N(4) 1.282(21) Å, Pd(1)−N(4) 2.176(12) Å).[10] The five-membered chelate ring adopts an envelope conformation with P(1) forming the flap of the envelope (torsion angle N(4)−Pd(1)−P(1)−C(2) = −25.1(8)°). The mesityl group is positioned almost perpendicular to the chelate ring (torsion angle Pd(1)−N(4)−C(24)−C(25) 84.5(16)°) providing efficient blocking of the axial sites on palladium from one side.

Ethylene oligomerizations with catalysts **10a**,**b** and **12a**,**b** were carried out at 400 psi and 80 °C (Table 1). Aldimine-derived catalyst **10a** was substantially more active than ketimine-containing **10b** but produced lower M_n oligomers (entry 1 vs entry 3). Catalyst **10a** has a substantial lifetime at 80 °C (entries 1 and 2). Unexpectedly, diphenyl- and dimethyl-substituted complexes **12a**,**b** produced only negligible amounts of oligomer at 80 °C. The activities of these phosphine−imine systems are low compared with those of diimine−Pd catalysts.

To further explore the surprising inactivity of **12b**, the methyl ethylene complex **14a** was prepared in the reaction of **13** with $NaB(Ar_F)_4$ in the presence of ethylene and the barrier to migratory insertion was determined. The loss of the methyl resonance in the ^{1}H NMR spectrum of **14a** was measured with respect to time in the presence of 20 equiv of ethylene yielding $k = 3 \times 10^{-6}$ s^{-1} at 23 °C, corresponding to $\Delta G^{\ddagger} = 24.8(3)$ kcal/mol. For comparison, a typical ethylene insertion barrier into a diimine−palladium methyl bond is ca. 17 kcal/mol,[2a] and the insertion barriers into diphosphine−palladium methyl bonds are 16.3−17.9 kcal/mol.[11] Clearly, complexes containing diphosphine and diimine ligands are substantially more reactive than the ones containing imine−phosphine ligands. In the imine−phosphine palladium complexes the situation is unfavorable for migratory insertion since in the more stable isomer **14a** the Pd−CH_3 bond is expected to be stronger than the Pd−CH_3 bond in **14b** while the Pd−ethylene interaction is stronger than that in **14c** (see Figure 2). Thus the stability of the methyl ethylene "unit" is greatest in **14a**. In the transition state where the Pd−CH_3 bond is largely broken and the ethylene unit is transforming to a σ bond, the unsymmetrical ligand will likely provide less stabilization than either symmetrical ligand, thus a larger ground state/transition state energy difference can be expected for the unsymmetrical bidentate ligand. A simpler but equivalent explanation arises if the migratory insertion is regarded as an attack of the nucleophilic methyl group on the electrophilic ethylene ligand. The methyl group in **14a** (*trans* to N) is less nucleophilic than the methyl group in **14b** (*trans* to P), while the ethylene unit in **14a** (*trans* to P) is less electrophilic than ethylene in **14c** (*trans* to N). This point is illustrated quantitatively in Figure 2 below. Vrieze *et al.* have used similar arguments to rationalize varying rates of CO insertion into palladium−methyl bonds.[12]

2. Syntheses and Ethylene Polymerization Properties of Phosphine−Imine Nickel Complexes. Nickel dibromide complexes of the phosphine−imines were produced by the reaction of crude imines (synthesized as above, see Scheme 1) with $NiBr_2$(DME) (Scheme 2). The precatalysts **16** were isolated as highly colored solids, insoluble in most organic solvents but moderately soluble in chlorinated hydrocarbons. For comparison the closest analogous enolizable complex **18** was also synthesized.

The dimethyl-substituted complex **16a** was used to screen the behavior and efficiency of several aluminum alkyl derived activators (Table 2). Use of ethylaluminum dichloride led to the production of butenes with $>10^6$ TO/h in a very exothermic reaction (the reactor was cooled with a −78 °C bath to maintain 19−26 °C).[13] Activation using diethylaluminum chloride resulted in the production of butenes and a trace of polymer (^{1}H analysis of crude reaction mixture). PMAO-IP afforded both butenes and polymer. Gratifyingly, use of MMAO-3A under 400 psi of ethylene at room temperature gave exclusively polymer with M_n 2 400 and 13 500 TO/h.

(10) (a) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88. (b) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.

(11) Ledford, J.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 5266.

(12) Dekker, G. P. C. M.; Buijs, A.; Elsevier: C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.

(13) This behavior is reminiscent of Wilke-type systems $R_3PNi(allyl)^+$. See ref 1a.

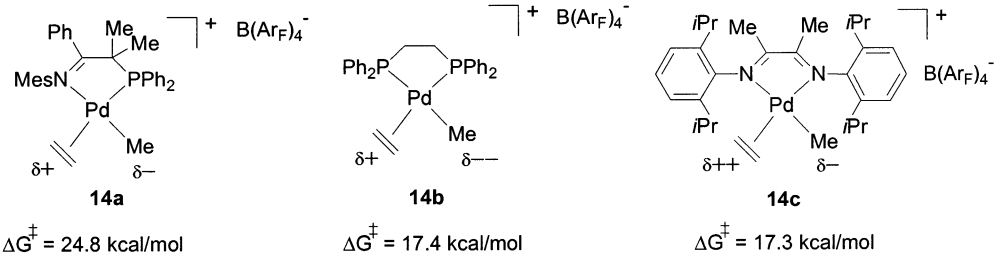
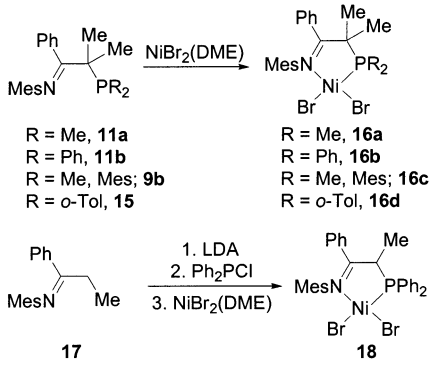


Figure 2. Comparison of migratory insertion barriers.

Scheme 2



Given the molecular weight and reactivity dependences observed in the case of palladium complexes it was hoped that mesityl-substituted precatalyst **16c** would be more reactive than dimethyl-substituted complex **16a** and give high molecular weight product. Unexpectedly, only a small amount of polymer with a bimodal molecular weight distribution (M_p = 37 200; 3 100) was obtained (Table 3). On the other hand, diphenyl-substituted precatalyst **16b** was found to be more effective − in 1 h at 29 °C and 400 psi of ethylene with MMAO-3A activation 4.1 g (29 ,300 TO/h) of a clear, extremely tough, elastomeric material with M_n = 72 000, M_w = 133 000 was obtained (0.005 mmol of precatalyst was used). No significant amount of lower molecular weight material was observed in the reaction and the GPC trace showed a single monomodal peak. In a 3-h run under similar conditions 10.0 g (24 000 TO/h) of polymer was obtained. Lower productivity in this case is clearly due to mass-transport problems: the contents of the reactor had gelled due to polymer occluding all solvent. At 100 psi of ethylene, the TOF dropped to 14 000 h^{-1}. Interestingly, also tetraethyldialumoxane could be used as an activator, albeit with some loss of activity (15 000 TO/h *vs* 29 000 TO/h using MMAO-3A). At 60 °C (MMAO-3A activator) no significant difference of activity between 30 min and 1.5 h was observed, suggesting long catalyst lifetime under these conditions. For comparison, diimine-Ni catalysts have a half-life of less than 1 h at that temperature.[2c] At 80 °C catalyst starts to decompose, but it still has a reasonable lifetime. A trace of butenes was observed in the crude NMR of the 80 °C polymerization mixture. As expected, the molecular weight decreases with increasing temperature (M_w = 290 000 at 0 °C, 140 000 at 29 °C, 52 000 at 60 °C, 19 000 at 80 °C), while branching slightly increases (56 br/1000 C at 0 °C to 74 br/1000 C at 80 °C). Increase of steric bulk at phosphorus (**16d**) gave rise to lower molecular weight material (M_w = 75 000 vs 140 000 for diphenyl-substituted precatalyst at room temperature). A control experiment using the closest analogous enolizable precatalyst at 60 °C revealed that the nonenolizable backbone is essential for obtaining high molecular weight polymer. Precatalyst **18**, lacking one methyl group in the backbone, produced polymer with M_w = 2 400 compared to M_w = 50 000 for the nonenolizable complex **16b** containing a *gem*-dimethyl group. Additionally, a small amount (*ca.* 0.15 g) of polymer precipitated from the reaction mixture, and a fraction of this precipitate was insoluble in bromobenzene at 130 °C, suggesting the possibility of a minor very high molecular weight fraction as observed by Guan.[5]

Analysis of the nature of the branching was carried out using ^{13}C spectroscopy (Table 4).[14] The polymer formed by **16b** at 29 °C has almost exclusively methyl branches, while 80 °C material contains a substantial amount of higher branches. Polymer formed by **16d** at 60 °C contains an abnormal amount of higher branches. In general, polyethylenes obtained using catalysts **16** are substantially more branched than polymers obtained by diimine−nickel catalysts under similar conditons.[2c] The total number of branches calculated from ^{13}C spectral analysis agrees with the branching number obtained from the ^1H spectra.

Summary

A number of Pd and Ni imine−phosphine catalysts possessing nonenolizable ligand backbone have been synthesized and tested in the polymerization of ethylene. These catalysts show improved temperature stability with respect to the corresponding diimine complexes. At 80 °C the palladium catalysts oligomerize ethylene giving branched oligomers with M_n up to 660. The ethylene insertion barrier into the palladium−methyl bond of **14a** was shown to be 24.8(3) kcal/mol, which is *ca.* 8 kcal/mol higher than the corresponding insertion barriers in palladium−diimine and palladium−diphosphine complexes.[15] This shows a possible disadvantage

(14) Cotts, M. P.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *19*, 6945.

(15) For diimine−palladium and nickel alkyl ethylene complexes, the difference in migratory insertion barriers is 4−5 kcal/mol. In the case of phosphine−imine complexes, the difference is >8 kcal/mol between **14a** and its Ni cogener (TOF of 30 000 at 29 °C corresponds to $\Delta G^{\ddagger}$ = 16.4 kcal/mol assuming the alkyl olefin resting state for precatalyst **16b**). One possible explanation for the unexpectedly low barrier in the Ni complex is that *cis*/*trans* isomerization occurs from the more stable isomer (Ni cogener of **14a**) to the less stable isomer with ethylene *trans* to nitrogen and the migrating alkyl group *trans* to phosphorus. In the less stable isomer the migratory insertion is expected to proceed with a much lower barrier. Provided *cis*/*trans* isomerization is fast relative to insertion, the observed rate constant for insertion via minor isomer will be $K_{eq}k_{ins(minor)}$, which may exceed $k_{ins(major)}$. A computational study in the salicylaldiminato Ni(II) system has predicted a similar behavior. See: Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741.

Table 2. Activator Studies Using 16a (0.018 mmol) in Chlorobenzene (100 mL) at 30−35 °C, 400 psi of Ethylene Pressure

entry	activator/equiv	time, h	product	TOF, h^{-1}	M_n[a]	Br/1000 C[a]
1[b]	$EtAlCl_2$/400	0.3	butenes	10^6		
2	Et_2AlCl/300	0.5	butenes	nd		
3	PMAO-IP/750	1	butenes + PE	nd	nd	nd
4	MMAO-3A/370	1	PE, 6.8 g	13500	2400	65
5	MMAO-3A/370	5	PE, 18.0 g	7100	2800	66

[a] Branching/1000 C and M_n determined by ^1H NMR spectroscopy (see Experimental Section for details). [b] 0.0046 mmol of catalyst used, 19−26 °C, 200 psi of ethylene; TON determined by ^1H NMR analysis of crude reaction mixture.

Table 3. Polymerization of Ethylene by 16a−d and 17 in Chlorobenzene[a] at 400 psi

entry	catalyst	time, h	temp, °C	g of PE	TOF, h^{-1}	M_w	Br/1000 C[b]	PDI
1[c]	**16b**	4	0	1.9	3 400	290 000	56	2.2
2	**16b**	1	29	4.1	29 000	133 000	62	1.9
3	**16b**	3	29	10.0	24 000	140 000	64	1.9
4	**16b**	0.5	60	2.4	34 000	52 000	69	1.9
5	**16b**	1.5	60	6.6	31 000	52 000	70	2.0
6	**16b**	0.5	80	2.6	37 000	19 000	71	1.5
7	**16b**	1.5	80	4.4	21 000	19 000	74	1.6
8[d]	**16b**	1	29	2.1	15 000	143 000	63	1.9
9[e]	**16b**	1	29	2.0	14 000	104 000	65	2.0
10[c,f,g]	**16c**	0.5	60	0.24	1 700	37 000; 3 100[h]	57	ND
11[f,g]	**16d**	1.1	29	6.3	20 000	75 000	67	1.8
12[c,f]	**16d**	0.6	60	7.4	44 000	17 000	71	2.2
13	**18**	1.5	60	7.0	33 000	2 400	94	2.1

[a] 0.005 mmol of precatalyst in 200 mL of chlorobenzene, MMAO-3A activator, Al/Ni ratio 1800. [b] Branching/1000 C determined by ^1H NMR spectroscopy (see Experimental Section for details). [c] 100 mL of solvent used. [d] Tetraethyldialumoxane activator (1800 equiv). [e] 100 psi of ethylene pressure. [f] 0.01 mmol of precatalyst used. [g] Al/Ni ratio 660. [h] Bimodal molecular weight distribution; M_p (peak molecular weights) reported.

Table 4. Analysis of Polyethylene Branching Using ^{13}C Spectroscopy

catalyst	Me[a]	Et	Pr	*n*Bu	*s*Bu[b]	Am	higher	br/1000 C[c]
16b[d]	55.5	2.4	>1	>1	>1	>1	>1	58
% Me[e]	95.9	4.1						
16b[f]	50.2	7.1	3.9	4.1	1.5	2.3	7.2	75
% Me[e]	67.1	9.5	5.2	5.5	3.1	9.6		
16d[g]	33.9	7.5	1.6	4.9	2.1	1.7	17.1	67
% Me[e]	50.6	11.2	2.4	7.3	2.5	25.5		

[a] Number of corresponding branches per 1000 C. [b] A *s*Bu branch is counted as one Me and one Et branch. [c] Total number of methyl branches per 1000 C. [d] Entry 3 from Table 3. [e] Percent of the methyl groups in the given branch with respect to total Me. [f] Entry 6 from Table 3. [g] Entry 12 from Table 3.

in using chelating ligands with two electronically inequivalent groups, whereby a reaction intermediate is sufficiently stabilized in the ground state to substantially retard the rate of migratory insertion.

Nickel imine−phosphine precatalysts containing *gem*-dimethyl substituent α to phosphorus display moderate activity and produce substantially higher molecular weight polyethylene compared to the corresponding enolizable complexes. A control experiment using non-enolizable precatalyst **16b** and enolizable precatalyst **18** revealed that under the same conditions the former produces more than 20 times higher molecular weight polyethylene than the latter, even though they differ only by a single methyl group in the backbone. Future studies will focus on copolymerizations of ethylene with α-olefins and polar comonomers using catalyst **16b**, as well as the variations in reactivity through the modification of imine moiety. Mechanistic studies of the nickel phosphine−imine catalysts are underway.

Experimental Section

General Considerations. All the operations related to catalysts or phosphines were carried out under an argon atmosphere using standard Schlenk techniques. The ^1H, ^{31}P, and ^{13}C spectra were recorded using Bruker 300 or 400 MHz spectrometers and referenced against residual solvent peaks (^1H, ^{13}C) or H_3PO_4 (^{31}P). Flash chromatography was performed using 60 Å silica gel (SAI). Room-temperature GPC measurements were performed on a Waters Alliance HPLC Separations Module equipped with Waters Styragel HR2, HR4, and HR5 columns in series and a Waters 2410 Differential Refractometer RI (refractive index) detector relative to polystyrene standards. Samples consisted of ∼1 mg of polymer in 1 mL of degassed THF. High-temperature (135 °C) GPC was performed by DuPont Analytical (Wilmington, DE) in 1,2,4-trichlorobenzene using a Waters HPLC equipped with Shodex columns. A calibration curve was established with polystyrene standards and universal calibration was applied using Mark−Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Differential scanning calorimetry was recorded on a Seiko Instruments DSC 220 calibrated with the melting transition of indium. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. ^{13}C NMR analyses of polymers were carried out under the conditions reported by the DuPont group.[14]

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum transferred from P_2O_5 and degassed by repeated freeze−pump−thaw cycles. The following starting materials were made using literature procedures: mesityldichlorophosphine,[16] $NiBr_2$(DME),[17] and (cod)PdMeCl.[18] $NaB(Ar_F)_4$ was purchased from Boulder Scientific. PMAO-IP and MMAO-3A were purchased from Akzo Nobel. Alkylaluminum chlorides and tetraethyldialumoxane were purchased from Aldrich.

Analysis of Polymer Molecular Weight and Branching by ^1H NMR Spectroscopy. The following labels are used for

(16) Sakaki, J.-i.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta* **1993**, *76*, 2654.
(17) Ward, L. G. L. *Inorg. Synth.* **1971**, *13*, 154.
(18) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

denoting different types of hydrogen signals in the polymer spectrum ($CDCl_3$ solvent): H1 (vinylidene end group, C═C**H**$_2$, br s, 4.7 ppm); H2 (1,2-disubstituted olefin, C**H**═C**H**, m, 5.3−5.4 ppm); H3 (trisubstituted olefin C═C**H**, m, 5.18 ppm); H4 (α-olefin, **H**$_2$C═C**H**, m, 5.85, 5.0, 4.9 ppm); H5 (alkyl methyl, alk-C**H**$_3$, m, 0.77−0.95 ppm); H6 (allylic methyl, C═C−C**H**$_3$, m, 1.6 ppm); H7 (alkyl methylene and methine, alk-C**H** and alk-C**H**$_2$, m, ca. 1.0−1.45 ppm); H8 (allylic methylene or methine, C═C−C**H**$_2$ and C═C−C**H**, m, 1.85−2.05 ppm). In the following formulas H*n* values refer to integral values.

$$N_{av} = (2/V) \times (A) + 2$$

where N_{av} = average number of carbons in polymer chain

$$V = \mathrm{H1} + \mathrm{H2} + 2\mathrm{H3} + (2/3)\mathrm{H4}$$

and

$$A = (\mathrm{H5} + \mathrm{H6} + \mathrm{H7} + \mathrm{H8} - \mathrm{H1} - \mathrm{H2} - 3\mathrm{H3} - (1/3)\mathrm{H4})/2$$

$$M_n = N_{av} \times 14.01$$

$$N_{br} = (1000/N_{av}) \times (Y - X)$$

where N_{br} = number of methyl branches per 1000 C, $Y = ((\mathrm{H5} + \mathrm{H6})/3) \times (2/V)$, $X = ((\mathrm{H1}/2) + \mathrm{H2} + 2\mathrm{H3} + (\mathrm{H4}/3)) \times (2/V)$. The formula is not exact since the signal of secondary homoallylic hydrogen overlaps with the signal of H6.

Spectral Data for the B(Ar$_F$)$_4$ Counterion. The following ^{1}H and ^{13}C spectroscopic assignments of the B(Ar$_F$)$_4$ counterion were invariant for different complexes and temperatures and are not reported in the spectroscopic data for each of the cationic complexes. **B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4^-$ (B(Ar$_F$)$_4$).** ^{1}H NMR (CD_2Cl_2): 7.74 (br s, 8H), 7.57 (s, 4H). ^{13}C{^{1}H} NMR (CD_2Cl_2) 162.2 (q, J_{C-B} = 37.4 Hz), 135.2, 129.3 (q, J_{C-F} = 31.3 Hz), 125.0 (q, J_{C-F} = 272.5 Hz), 117.9.

General Polymerization Procedure. Polymerizations using Pd catalysts and **16a** were carried out in a mechanically stirred 300-mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple in the reaction mixture. The reactor was charged with toluene or chlorobenzene (100 mL) and heated for 1 h at 150 °C. After cooling to room temperature the solvent was poured out and the reactor heated under vacuum at 150 °C for 1 h. The reactor was filled with Ar, cooled to room temperature, pressurized to 200 psi of ethylene, and vented three times. A solution of the catalyst in 100 mL of the appropriate solvent was added to the reactor via cannula followed by activator if applicable. After that the reactor was pressurized with ethylene and the reaction mixture stirred for the appropriate time. Polymerizations using Ni catalysts other than **16a** and entries 10 and 12 in Table 3 (100 mL of solvent used in these cases) were carried out in a 600-mL Parr reactor equipped with water cooling and an electric heating mantle controlled by a thermocouple in the reaction mixture in 200 mL of solvent. After venting, the reaction mixture was worked up in one of three ways: (A) the reaction mixture was evaporated and the distillate checked for oligomers by GC (no oligomers up to C_{10} were observed; used for polymerizations catalyzed by palladium complexes); (B) the reaction mixture was extracted with 10% HCl (occasionally chloroform was added to make the separations better) and evaporated (used for polymerizations catalyzed by **16a**, **16b** at 60 and 80 °C, **16c**, **16d**, **18**); and (C) the reaction mixture was poured into methanol and stirred for 1 h and the precipitate washed with a 1:1 mixture of methanol and 10% aqueous HCl, and then with methanol (used for 0 and 29 °C polymerizations catalyzed by **16b**). On some occasions, the methanol/water layer was evaporated and the residue checked by NMR. No significant quantity of oligomers was detected. In all cases ^{1}H NMR spectra of the crude reaction mixtures were acquired to check for butenes. Higher molecular weight polymers were dried in a vacuum oven at 75 °C.

The following polymer T_m values were determined (entry number in Table 3; T_m, °C): 1, 74; 3, 64; 4, 59 (shoulder at 43); 8, 69; 9, 59; and 12, 11 (shoulder at 38).

Isobutyraldehyde 2,4,6-Trimethylphenylimine (8a). 2,4,6-Trimethylaniline (4.2 mL, 30 mmol, Aldrich) was mixed with isobutyric aldehyde (5.5 mL, 60 mmol, Aldrich), chloroform (50 mL), *p*-toluenesulfonic acid (0.29 g, 1.5 mmol, Aldrich), and $MgSO_4$ (*ca.* 10 g). The reaction mixture was stirred at room temperature for 22 h. After filtration and washing of $MgSO_4$ with chloroform (20 mL) molecular sieves (3 Å) were added and stirring was continued for an additional 24 h. The solvent and excess aldehyde were evaporated and the residue was distilled at reduced pressure collecting three fractions: (1) 68−74 °C/0.5 mm, mixture of product/amine; (2) 74−76 °C/0.5 mm, product; and (3) 76−78 °C/0.5 mm, product. Fractions 2 and 3 were combined to give 3.0 g (52.9%) of the imine. The compound is unstable at room temperature and has to be stored at −30 °C. ^{1}H NMR ($CDCl_3$) 7.52 (d, 1H, J = 4.8 Hz), 6.84 (br s, 2H), 2.70 (d of septets, 1H, J = 4.8, 6.9 Hz), 2.26 (s, 3H), 2.05 (s, 6H), 1.22 (d, 6 H, J = 6.9 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): 172.7, 148.7, 132.6, 128.7, 126.8, 35.0, 20.8, 19.2, 18.1.

Isobutyrophenone 2,4,6-Trimethylphenylimine (8b). 2,4,6-Trimethylaniline (16.9 mL, 120 mmol, Aldrich) was mixed with isobutyrophenone (12.0 mL, 80 mmol, Acros) and *p*-TsOH (1.5 g, 8.0 mmol, Aldrich). The resulting mixture was heated for 10 h at 220 °C in a flask equipped with a Dean−Stark trap. Vacuum distillation afforded two fractions: (1) unreacted starting materials, 40−48 °C/0.3 mm; and (2) product as a yellow oil, 98−108 °C/0.1 mm (6.2 g, 29.2%). ^{1}H NMR (tetrachloroethane-d_2, 383 K) 7.29 (s, 5H), 6.77 (s, 2H), 3.13 (septet, 1H, J = 6.8 Hz), 2.26 (s, 3H), 2.05 (s, 6H), 1.34 (d, 6 H, J = 6.8 Hz). ^{13}C{^{1}H} NMR (tetrachloroethane-d_2, 403 K): 174.1 (br), 145.6 (br), 138.8 (br), 130.9 (br), 128.1, 128.0, 127.4, 126.6, 124.8 (br), 36.3 (br), 20.3, 20.1, 17.6. Anal. Calcd for $C_{19}H_{23}N$: C 85.98, H 8.74, N 5.28. Found: C 85.95, H 8.87, N 5.42.

[(MesN═CHCMe$_2$PMesMe)Pd(NCMe)Me]$^+$ B(Ar$_F$)$_4^-$ (10a). To a solution of isobutyraldehyde 2,4,6-trimethylphenylimine (0.378 g, 2.0 mmol) in diethyl ether (5 mL) was added *t*-BuLi (1.25 mL of a 1.7 M solution in pentane, 2.1 mmol, Aldrich) at −78 °C. The solution was stirred for 10 min at −78 °C, warmed to room temperature, and stirred for 20 min. The yellow solution of azaenolate was added dropwise to a solution of mesityldichlorophosphine (0.37 mL, 2.1 mmol) in THF (5 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (+101.5 ppm). The reaction mixture was recooled to −78 °C and MeMgBr (0.71 mL of a 3.1 M solution in ether, 2.2 mmol, Strem) was added in one portion. After warming to room temperature the mixture was stirred for 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (−18.0 ppm) together with starting material (+101.5 ppm). The reaction mixture was recooled to −78 °C and additional MeMgBr (1 mL, 3.1 mmol) was added. After warming to room temperature the mixture was stirred for 12 h. ^{31}P NMR (crude reaction mixture) showed the complete consumption of the starting material. TMSCl (0.5 mL) was added to quench the excess MeMgBr, the solution was stirred for 30 min at room temperature and evaporated, and the residue was extracted with hexanes (4 × 10 mL). The hexane extracts were evaporated to give the iminephosphine ligand as a yellowish oil. To the crude ligand was added (cod)PdMeCl (0.26 g, 0.98 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at room temperature and evaporated, and the residue was purified by extraction with hexanes (3 × 10 mL). **9a***PdMeCl was obtained as a light yellow, hexane-insoluble powder, 0.37 g (36.3%). ^{1}H NMR ($CDCl_3$, 330 K) 7.40

(d, 1H, J = 26.0 Hz), 6.95 (d, 2H, J = 3.2 Hz), 6.85 (s, 2H), 2.91 (br s, 6H), 2.30 (s, 3H), 2.26 (s, 3H), 2.23 (d, 3H, J = 9.1 Hz), 2.21 (s, 6H), 1.66 (d, 3H, J = 10.1 Hz), 1.19 (d, 3H, J = 11.9 Hz), 0.54 (Pd−Me, d, 3H, J = 3.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +31.2 ppm (s).

To the mixture of **9a***PdMeCl (0.10 g, 0.196 mmol) and $NaB(Ar_F)_4$ (0.174 g, 0.196 mmol) was added dry acetonitrile (1 mL) and CH_2Cl_2 (2 mL). The mixture was stirred for 12 h at room temperature, cannula filtered to remove NaCl, evaporated, and coevaporated with hexanes (3 mL). The product was obtained as a light yellow foam (0.240 g, 88.8%). ^1H NMR (CD_2Cl_2) 7.54 (d, 1H, J = 27.1 Hz), 7.03 (d, 2H, J = 3.7 Hz), 6.96 (s, 2H), 3.10 (br s, 3H), 2.55 (br s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.24 (d, 3H, J = 9.9 Hz), 2.19 (s, 6H), 1.74 (br s, 3H), 1.70 (d, 3H, J = 11.3 Hz), 1.21 (d, 3H, J = 13.1 Hz), 0.32 (Pd−Me, d, 3H, J = 2.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +34.4 ppm (s). Anal. Calcd for $C_{58}H_{50}BF_{24}N_2PPd$: C 50.50, H 3.65, N 2.03. Found: C 50.75, H 3.85, N 1.90.

[(MesN=CPhCMe$_2$PMesMe)Pd(NCMe)Me]$^+$ B(Ar$_F$)$_4^-$ (10b). To a solution of isobutyrophenone 2,4,6-trimethylphenylimine (0.53 g, 2.0 mmol) in diethyl ether (5 mL) was added *t*-BuLi (1.25 mL of a 1.7 M solution in pentane, 2.1 mmol, Aldrich) at −78 °C. The solution was stirred for 10 min at −78 °C, warmed to room temperature, and stirred for 20 min. The red-brown solution of azaenolate was added dropwise to a solution of mesityldichlorophosphine (0.37 mL, 2.1 mmol) in THF (5 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (+103.7 ppm). The reaction mixture was recooled to −78 °C and MeMgBr (1.4 mL of a 3.1 M solution in ether, 4.3 mmol, Strem) was added in one portion. After warming to room temperature the mixture was stirred for 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (−20.3 ppm). TMSCl (0.5 mL) was added to decompose the excess MeMgBr, and the solution was stirred for 30 min at room temperature and evaporated. The residue was extracted with hexanes (4 × 10 mL). The hexane extracts were evaporated to give crude ligand as a yellow oil. To the crude ligand was added (cod)PdMeCl (0.416 g, 1.57 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at room temperature and evaporated, and the residue was purified by extraction with hexanes (3 × 10 mL). **9b***PdMeCl was obtained as a white, hexane-insoluble powder, 0.94 g (80.2%). ^1H NMR ($CDCl_3$) 7.25−7.14 (m, 3H), 7.02−6.91 (m, 4H), 6.58 (s, 2H), 2.95 (br s, 6H), 2.37 (d, 3H, J = 8.9 Hz), 2.30 (s, 3H), 2.27 (s, 3H), 2.22 (s, 3H), 2.07 (s, 3H), 1.42 (d, 3H, J = 10.2 J), 1.37 (d, 3H, J = 13.5 Hz), 0.54 (Pd−Me; d, 3H, J = 2.9 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +41.6 ppm (s).

The synthesis of cationic acetonitrile complex **10b** was performed as in the case of **10a**, using **9b***PdMeCl (0.10 g, 0.171 mmol) and $NaB(Ar_F)_4$ (0.151 g, 0.171 mmol), and a reaction time of 14 h. Product was obtained as a white powder, 0.228 g (91.6%). ^1H NMR (CD_2Cl_2) 7.37−7.25 (m, 3H), 7.07−6.99 (m, 4H), 6.74 (s, 2H), 2.88 (br s, 6H), 2.37 (d, 3H, J = 9.7 Hz), 2.32 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H), 2.14 (s, 3H), 1.72 (s, 3H), 1.67 (s, 3H), 1.48 (d, 3H, J = 11.5 Hz), 1.37 (d, 3H, J = 14.4 Hz), 0.32 (Pd−Me, d, 3H, J = 1.8 Hz).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): +42.2 ppm (s). Anal. Calcd for $C_{64}H_{54}BF_{24}N_2PPd$: C 52.82, H 3.74, N 1.92. Found: C 52.81, H 3.95, N 1.82.

[(MesN=CPhCMe$_2$PMe$_2$)Pd(NCMe)Me]$^+$ B(Ar$_F$)$_4^-$ (12a). To a solution of isobutyrophenone 2,4,6-trimethylphenylimine (0.265 g, 1.0 mmol) in diethyl ether (3 mL) was added *t*-BuLi (0.62 mL of a 1.7 M solution in pentane, 1.05 mmol, Aldrich) at −78 °C. The solution was stirred for 10 min at −78 °C, warmed to room temperature, and stirred for 30 min. The red-brown solution of azaenolate was added dropwise to a solution of dimethylchlorophosphine (0.083 mL, 1.05 mmol, Strem) in THF (2 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (−27.9 ppm). The reaction mixture was evaporated and the residue extracted with toluene and filtered through a plug of Celite to remove inorganic salts. After evaporation of the solvent crude ligand was obtained as a yellowish oil. To the crude ligand was added (cod)PdMeCl (0.195 g, 0.74 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at room temperature, filtered, and evaporated. The residue was purified by flash chromatography on silica gel (3.3 × 2.3 cm) in CH_2Cl_2 followed by ethyl acetate. Fractions containing the product were evaporated and triturated with ethyl acetate (10 mL) to give **11a***PdMeCl (0.202 g, 41.9%) as a white powder. ^1H NMR ($CDCl_3$) 7.29−7.19 (m, 3H), 7.04−6.96 (m, 2H), 6.60 (s, 2H), 2.22 (s, 6H), 2.08 (s, 3H), 1.56 (d, 6H, J = 9.9 Hz), 1.49 (d, 6H, J = 12.6 Hz), 0.67 (Pd−Me, d, 3H, J = 3.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +45.6 ppm (s). Anal. Calcd for $C_{22}H_{31}ClNPPd$: C 54.78, H 6.48, N 2.90. Found: C 54.67, H 6.48, N 2.84.

The synthesis of the cationic acetonitrile complex **12a** was performed as in the case of **10a**, using **11a***PdMeCl (0.08 g, 0.166 mmol) and $NaB(Ar_F)_4$ (0.147 g, 0.166 mmol), and a reaction time of 2 h. Product was obtained as a white powder, 0.211 g (94.1%). ^1H NMR (CD_2Cl_2) 7.40−7.27 (m, 3H), 7.07−7.00 (m, 2H), 6.74 (s, 2H), 2.19 (s, 6H), 2.14 (s, 3H), 1.68 (s, 3H), 1.60 (d, 6H, J = 10.7 Hz), 1.49 (d, 6H, J = 13.5 Hz), 0.44 (Pd−Me, d, 3H, J = 2.0 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +48.8 ppm (s). Anal. Calcd for $C_{56}H_{46}BF_{24}N_2PPd$: C 49.78, H 3.43, N 2.07. Found: C 50.11, H 3.44, N 2.11.

[MesN=CPhCMe$_2$PPh$_2$]PdMeCl (13). The reaction was carried out as in the case of **12a** on a 2 mmol scale using chlorodiphenylphosphine (0.38 mL, 2.1 mmol, Aldrich) instead of chlorodimethylphosphine. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of the product (+13.4 ppm). The reaction mixture was evaporated and the residue extracted with toluene and filtered through a plug of Celite to remove inorganic salts. After evaporation of the solvent crude ligand was obtained as a yellowish oil. To the crude ligand was added (cod)PdMeCl (0.270 g, 1.02 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 12 h at room temperature. After evaporation the residue was extracted with hexanes (2 × 10 mL) and dried to give **13** (0.202 g, 41.9%) as a light yellow, hexane-insoluble powder. X-ray quality crystals were obtained by recrystallization from acetonitrile at −30 °C. ^1H NMR (CD_2Cl_2): 7.86−7.74 (m, 4H), 7.67−7.50 (m, 6H), 7.36−7.24 (m, 3H), 7.18−7.07 (m, 2H), 6.64 (s, 2H), 2.14 (s, 9H), 1.43 (d, 6H, J = 12.8 Hz), 0.65 (Pd−Me, d, 3H, J = 2.3 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 185.1 (d, J_{C-P} = 8.9 Hz), 144.5, 135.4 (d, J_{C-P} = 6.9 Hz), 135.0 (d, J_{C-P} = 11.2 Hz), 134.9, 132.0 (d, J_{C-P} = 2.5 Hz), 130.1, 129.4 (d, J_{C-P} = 10.5 Hz), 128.8, 128.7, 128.6, 127.5 (d, J_{C-P} = 44.9 Hz), 125.8, 53.6 (d, J_{C-P} = 25.8 Hz), 26.1 (d, J_{C-P} = 1.7 Hz), 21.0, 19.8, −3.8 (Pd−Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +71.2 ppm (s). Anal. Calcd for $C_{32}H_{35}ClNPPd$: C 63.37, H 5.82, N 2.31. Found: C 63.62, H 5.97, N 2.31.

[(MesN=CPhCMe$_2$PPh$_2$)Pd(NCMe)Me]$^+$ B(Ar$_F$)$_4^-$ (12b). The synthesis of the cationic acetonitrile complex **12b** was performed as in the case of **10a**, using **13** (0.10 g, 0.165 mmol) and $NaB(Ar_F)_4$ (0.146 g, 0.165 mmol), and a reaction time of 12 h. Product was obtained as a white powder, 0.210 g (94.1%). ^1H NMR (CD_2Cl_2): 7.75−7.59 (m, 10H), 7.41−7.32 (m, 3H), 7.22−7.15 (m, 2H), 6.75 (s, 2H), 2.19 (s, 6H), 2.15 (s, 3H), 1.66 (s, 3H), 1.47 (d, 6H, J = 13.7 Hz), 0.59 (Pd−Me, d, 3H, J = 1.1 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 187.2 (d, J_{C-P} = 7.5 Hz), 143.7, 136.6, 134.8 (d, J_{C-P} = 10.8 Hz), 133.8 (d, J_{C-P} = 7.0 Hz), 133.2 (d, J_{C-P} = 2.8 Hz), 131.2, 130.0 (d, J_{C-P} = 11.1 Hz), 129.5, 129.4, 128.6, 126.0, 125.2 (d, J_{C-P} = 51.4 Hz), 118.7, 55.4 (d, J_{C-P} = 29.1 Hz), 26.1 (d, J_{C-P} = 1.0 Hz), 20.7, 19.5, 1.8, −2.6 (Pd−Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +71.5 ppm (s). Anal. Calcd for $C_{66}H_{50}BF_{24}N_2PPd$: C 53.73, H 3.42, N 1.90. Found: C 53.77, H 3.49, N 1.84.

Generation of [(MesN=CPhCMe$_2$PPh$_2$)Pd(ethylene)-Me]$^+$ B(Ar$_F$)$_4^-$ (14a), Measurement of Ethylene Insertion Barrier. Solid **13** (0.0068 g, 0.01 mmol) was mixed with NaB(Ar$_F$)$_4$ (0.012 g, 0.014 mmol) in a Teflon-lined screw-cap NMR tube. After cooling to −78 °C ethylene gas (1 mL, 0.045 mmol) was added, followed by CD_2Cl_2 (0.7 mL) and more ethylene (4 mL, 0.18 mmol). After that, the NMR tube was shaken a few times and kept at −30 °C for 48 h. Then the NMR tube was warmed to room temperature (+23 °C) and the disappearance of methyl peak (0.69 ppm, d, J = 2.2 Hz at +23 °C) of the formed methyl ethylene complex was observed vs. time by NMR, affording $k = 3 \times 10^{-6}$ s^{-1}, corresponding to $\Delta G^{\ddagger} = 24.8$-(3) kcal/mol.

Spectral data for **14**: ^{1}H NMR (CD_2Cl_2, 233 K, 1 equiv of free ethylene present): 7.69−7.49 (m, 10H), 7.44−7.30 (m, 3H), 7.23−7.11 (m, 2H), 6.74 (s, 2H), 4.98 (s, 4H; complexed ethylene; free ethylene appears at 5.38 ppm), 2.11 (s, 3H), 2.04 (s, 6H), 1.50 (d, 6H, J = 13.9 Hz), 0.64 (Pd−Me s, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K): 188.3 (d, J_{C-P} = 7.6 Hz), 141.7, 137.0, 134.3 (d, J_{C-P} = 10.7 Hz), 133.5 (d, J_{C-P} = 6.7 Hz), 132.9 (d, J_{C-P} = 2.1 Hz), 131.0, 129.9 (d, J_{C-P} = 10.7 Hz), 129.8, 129.1, 127.4, 125.4, 123.6 (d, J_{C-P} = 48.3 Hz), 111.9, 111.8, 54.0 (d, J_{C-P} = 26.5 Hz), 25.9, 20.6, 19.1, 2.6 (Pd−Me). ^{31}P{^{1}H} NMR (233 K, CD_2Cl_2) +67.5.

[MesN=CPhCMe$_2$PMe$_2$]NiBr$_2$ (16a). To crude ligand (obtained as in the case of **12a** using 1 mmol of imine) was added $NiBr_2$(DME) (0.240 g, 0.78 mmol) and CH_2Cl_2 (5 mL). The dark purple solution was stirred for 1 h at room temperature, the solution was evaporated, and the residue was washed with hexanes (3 × 10 mL). A purple solid (0.42 g, 99.0% based on Ni) was obtained.

[MesN=CPhCMe$_2$PPh$_2$]NiBr$_2$ (16b). To a solution of diisopropylamine (0.34 mL, 2.4 mmol, Aldrich) in diethyl ether (7 mL) was added *n*-BuLi (1.4 mL of a 1.6 M solution in hexanes, 2.2 mmol, Aldrich) at 0 °C. The reaction mixture was stirred at room temperature for 10 min. The solution of LDA was added to the solution of **8b** (0.53 g, 2.0 mmol) in diethyl ether (10 mL) at −78 °C. The solution was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for 1.5 h. After recooling to −78 °C Ph_2PCl (0.40 mL, 2.2 mmol, Acros) was added to the solution of the azaenolate at −78 °C. The yellow solution was stirred for 30 min at −78 °C, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of one major product (+13.5) and residual chlorodiphenylphosphine (+88.1 ppm). The residue was filtered through a 3 × 2.2 cm pad of silica gel in diethyl ether (40 mL) followed by THF (20 mL). The solvent was evaporated to give crude ligand as a yellow oil. To crude ligand was added $NiBr_2$(DME) (0.310 g, 1.0 mmol) and CH_2Cl_2 (10 mL). The dark purple-brown solution was stirred for 2 h at room temperature, the solution was evaporated, and the residue was washed with diethyl ether (2 × 20 mL) and hexanes (3 × 10 mL). A dark red-brown solid (0.650 g, quantitative based on Ni) was obtained. The reaction is cleaner and higher yielding if LDA instead of *t*-BuLi is used to deprotonate the imine. No signal in the ^{31}P spectrum was observed. ^{1}H NMR (CD_2Cl_2): 8.71 (br s, 4H), 7.80 (s, 2H), 7.39−7.18 (m, 7H), 7.10 (br d, 2H, J = 7.3 Hz), 6.39 (br t, 2H, J = 7.3 Hz), 4.76 (s, 3 H), 4.30 (s, 6 H), 2.53 (s, 6 H). Anal. Calcd for $C_{31}H_{32}Br_2NNiP$: C 55.73, H 4.83, N 2.10. Found: C 55.81, H 4.93, N 2.15.

[MesN=CPhCMe$_2$PMesMe]NiBr$_2$ (16c). Lithium azaenolate was prepared as in the case of **12a** using 2 mmol of the imine. The red-brown solution of azaenolate was added dropwise to a solution of dichloromethylphosphine (0.2 mL, 2.2 mmol, Strem) in THF (5 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (+101.5 ppm) in addition to starting materials (+194.5, +190.7 ppm). The solvent was evaporated under vacuum to remove excess $MePCl_2$ and THF (5 mL) was added. The reaction mixture was recooled to −78 °C and mesitylmagnesium bromide (4 mL of a 1 M solution in ether, 4 mmol, Aldrich) was added in one portion. After warming to room temperature the mixture was stirred for 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a single major product (−20.1 ppm). Acetic acid (3 drops) was added to decompose the excess Grignard reagent and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered through a 3 × 2.2 cm plug of silica gel under Ar, eluting with CH_2Cl_2 (30 mL) followed by diethyl ether (20 mL). The solvent was evaporated to give crude ligand as a yellow oil. To the crude ligand was added $NiBr_2$(DME) (0.124 g, 0.40 mmol) and CH_2Cl_2 (10 mL). The dark purple solution was stirred for 1 h at room temperature and evaporated and the residue was washed with diethyl ether (2 × 20 mL) and hexanes (20 mL). A violet solid (0.26 g, quantitative based on Ni) was obtained. No signal in the ^{31}P spectrum was observed. ^{1}H NMR (CD_2Cl_2): 7.29−7.14 (m, 5H), 6.97 (br d, 1H, J = 6.0 Hz), 6.82 (br d, 1H, J = 6.0 Hz), 6.75 (s, 1H), 6.56 (s, 1H), 4.65 (br s, 6 H), 3.18 (s, 3 H), 3.16 (s, 3 H), 2.37 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 1.37 (s, 6H). Anal. Calcd for $C_{29}H_{36}Br_2NNiP$: C 53.74, H 5.60, N 2.16. Found: C 53.90, H 5.89, N 2.21.

Di(2-methylphenyl)halophosphine.[19] A solution of $ZnCl_2$ (7.0 g, 101 mmol, Aldrich; fused under vacuum) in THF (70 mL) was added to *o*-tolylmagnesium bromide (50 mL of a 2.0 M solution in diethyl ether; 100 mmol, Aldrich) at 0 °C. The solution was warmed to room temperature and added dropwise to a solution of PCl_3 (4.3 mL, 49 mmol, Aldrich) in THF (30 mL) at −78 °C. The solution was stirred for 10 min at −78 °C, warmed to room temperature, and stirred for 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of di(2-methylphenyl)chlorophosphine and di(2-methylphenyl)-bromophosphine (+74.1; +66.3 ppm, 1/0.75 ratio). The solvent was evaporated, hexanes (200 mL) was added to the residue, and the solution was filtered through Celite followed by washing of the precipitate with toluene (50 mL) and hexanes (4 × 50 mL). Evaporation of the solvent followed by distillation under reduced pressure afforded the product (bp 125−131 °C/0.2 mm, 8.3 g, 62.0%) as a yellowish solid, 1/0.75 ratio of P−Cl/P−Br.

[MesN=CPhCMe$_2$P(*o*-Tol)$_2$]NiBr$_2$ (16d). Lithium azaenolate was prepared as in the case of **12a** using 2 mmol of the imine. The red-brown solution of azaenolate was added dropwise to a solution of di(2-methylphenyl)halophosphine (0.56 g, 2.1 mmol; 1/0.75 R_2PCl/R_2PBr) in THF (5 mL) at −78 °C. The mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for an additional 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of a major product (−11.5 ppm) in addition to several impurities. The solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered through a 3 × 2.2 cm plug of silica gel under Ar, eluting with toluene (30 mL) followed by CH_2Cl_2 (20 mL). The solvent was evaporated to give crude ligand as a yellow oil. To the crude ligand was added $NiBr_2$(DME) (0.123 g, 0.4 mmol) and CH_2Cl_2 (7 mL). The dark brown-violet solution was stirred for 2.5 h at room temperature and evaporated and the residue was washed with diethyl ether (3 × 10 mL) and hexanes (10 mL). A brown solid (0.196 g, 70.4% based on Ni) was obtained. Anal. Calcd for $C_{33}H_{36}Br_2NNiP$: C 56.93, H 5.21, N 2.01. Found: C 56.95, H 5.49, N 1.92.

Propiophenone 2,4,6-Trimethylphenylimine (17). 2,4,6-Trimethylaniline (11.5 mL, 82 mmol, Aldrich) was mixed with propiophenone (10 mL, 74.5 mmol, Aldrich) and *p*-TsOH (1.4 g, 7.3 mmol, Aldrich). The resulting mixture was heated for 2 h at 200 °C under a weak stream of Ar to remove formed H_2O.

(19) Dang, T. P.; Poulin, J.-C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105.

Table 5. Crystallographic Data Collection Parameters for 13

formula	$C_{34}H_{38}PN_2PdCl$
mol wt	647.51
cryst syst	orthorhombic
space group	$Pc2_1n$
a, Å	9.5956(9)
b, Å	13.1193(13)
c, Å	25.1307(25)
V, Å^3	3163.6(5)
Z	4
density calcd, Mg/m^3	1.359
F(000)	1333.55
cryst dimens, mm	0.30 × 0.25 × 0.10
temp, °C	−100
radiation (λ, Å)	0.71073
2θ range, deg	5.00−50.00
μ, mm^{-1}	0.75
total no. of reflns	5673
total no. of unique reflns	3892
no. of obsd data ($I > 3.0\sigma(I)$)	2971
no. of refined params	352
R_F, %	0.061
R_W, %	0.078
GOF	1.2490

After cooling to room temperature the reaction mixture was poured into hexanes (100 mL) and filtered, and the precipitate was washed with additional hexanes (2 × 100 mL) followed by the evaporation of the filtrate. The residue was filtered through a 9 × 4.1 cm plug of silica gel in hexanes/ether 10/1 (300 mL collected). After evaporation of the solvent the unreacted starting materials were distilled off under vacuum (45−50 °C/0.4 mm). The residue was crystallized from methanol at −30 °C. Product was isolated as large orange-yellow crystals, 4.8 g, (25.6%). ^{1}H NMR ($CDCl_3$): 8.00−7.94 (m, 2H), 7.51−7.45 (m, 3H), 6.89 (s, 2H), 2.50 (q, 2H, J = 7.7 Hz), 2.31 (s, 3H), 2.04 (s, 6 H), 0.98 (t, 3 H, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$): 170.8, 146.4, 138.2, 131.9, 130.3, 128.7, 128.6, 127.7, 125.6, 23.9, 20.9, 18.2, 11.6. Anal. Calcd for $C_{18}H_{21}N$: C 86.00, H 8.42, N 5.57. Found: C 85.79, H 8.41, N 5.56.

[MesN=CPhCHMePPh$_2$]NiBr$_2$ (18). To a solution of diisopropylamine (0.17 mL, 1.2 mmol, Aldrich) in diethyl ether (5 mL) was added *n*-BuLi (0.7 mL of a 1.6 M solution in hexanes, 1.1 mmol, Aldrich) at 0 °C. The reaction mixture was stirred at room temperature for 10 min. The solution of LDA was added to the solution of **17** (0.251 g, 1.0 mmol) in diethyl ether (5 mL) at −78 °C. The solution was stirred at −78 °C for 20 min, warmed to room temperature, and stirred for 1 h. After recooling to −78 °C Ph_2PCl (0.25 mL, 1.4 mmol, Acros) was added to the solution of the azaenolate at −78 °C. The yellow solution was stirred for 15 min at −78 °C, warmed to room temperature, and stirred for an additional hour. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of one major product (−1.3 ppm) and residual chlorodiphenylphosphine (+83.1 ppm). The residue was filtered through a 3 × 2.2 cm pad of silica gel in diethyl ether (40 mL) followed by THF (20 mL). The solvent was evaporated to give crude ligand as a yellow oil. To the crude ligand was added $NiBr_2$(DME) (0.155 g, 0.5 mmol) and CH_2Cl_2 (5 mL). The dark purple-brown solution was stirred for 2 h at room temperature, solution was evaporated, and the residue was washed with diethyl ether (2 × 20 mL) and hexanes (3 × 10 mL). A gray-brown solid (0.263 g, 80.4% based on Ni) was obtained. Anal. Calcd for $C_{30}H_{30}Br_2NNiP$: C 55.09, H 4.62, N 2.14. Found: C 55.36, H 4.72, N 2.08.

X-ray Crystal Structure (13). Diffraction data were collected on a Bruker SMART diffractometer using the ω-scan mode. Refinement was carried out with the full-matrix least-squares method based on F (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection are given in Table 5.

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Supporting Information Available: X-ray crystallography data for **13** and a graph for the determination of the rate of migratory insertion. This material is available free of charge via the Internet at http://pubs.acs.org.

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