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Crowded Diphosphinomethane Ligands in Catalysis: $[(R_2PCH_2PR'_2-\kappa^2P)-NiR'']^+$ Cations for Ethylene Polymerization without Activators

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Supporting Information

ABSTRACT: The preparation of a series of nickel dichloride complexes with bulky diphosphinomethane chelate ligands $R_2PCH_2PR'_2$ is reported. Reaction with the appropriate Grignard reagent leads to the corresponding dimethyl and dibenzyl complexes. Cationic monomethyl and mono- η^3 -benzyl complexes are generated from these dialkyl complexes by protonation with $[H(OEt_2)_2]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$, while the complex $[(dtbpm-\kappa^2P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[B(3,5-(CF_3)_2C_6H_3)_4]^$ is obtained from protonation of the Ni(0) olefin complex $(dtbpm-\kappa^2P)Ni(\eta^2-trans-stilbene)$. Crystal structures of examples of dichlorides, dimethyl, dibenzyl, cationic methyl, and



cationic η^3 -benzyl complexes are reported. Solutions of the cations polymerize ethylene under mild conditions and without the necessity of an activating agent, to form polyethylene having high molecular weights and low degrees of chain branching. In comparison to the Ni methyl cations, the η^3 -benzyl cation complexes are more stable and somewhat less active but still very efficient in C₂H₄ polymerization. The effect on the resulting polyethylene of varying the substituents R, R' on the phosphine ligand has been examined, and a clear trend for longer chain PE with less branching in the presence of more bulky substituents on the diphosphine has been found. Density functional calculations have been used to examine the rapid suprafacial η^3 to η^3 haptotropic shift processes of the [(R₂PCH₂PR'₂)Ni] fragment and the $\eta^3 - \eta^1$ change of the coordination mode of the benzyl group required for polymerization in those cations.

INTRODUCTION

The immense volume and commercial value of industrial oligomer and polymer production from α -olefins, in particular from ethylene and propylene, are the impetus for continual research into new types of transition-metal catalysts with improved activities and selectivity patterns.¹ Catalyst research is increasingly guided by the detailed mechanistic understanding obtained from sophisticated experimental² and theoretical studies.^{3–5} Well-defined, single-component systems are most suitable for such studies, and metallocenes of d⁰ metals are by far the most extensively investigated homogeneous polymerization catalysts.

A groundbreaking discovery in the field of homogeneous catalysis was the report by Brookhart et al. in 1995 that squareplanar nickel and palladium alkyl cations with bulky diimine ligands can catalyze the polymerization of α -olefins.⁶ This was the first report of the use of late transition metals for polymerization rather than oligomerization as intended and observed for typical SHOP catalysts,⁷ and Brookhart-type systems have since been studied extensively, both experimentally^{8–20} and theoretically.^{21–23} The specific feature of the ligand system that leads to polymerization rather than chain termination is the pair of bulky, substituted aryl rings oriented perpendicular to, and at the front of, the ligand chelate ring. The steric bulk of these aryl rings prevents monomer association at an axial coordination site after β -H elimination from the growing chain, which could start a new polymer chain. Instead, either linear polymer chain formation or chain walking can occur via reinsertion at the other side of the double bond, leading to branched polyethylene.

During the past decade various examples of ethylene polymerizations by nickel complexes have been published.^{24–38} The nickel–indenyl systems of Zargarian polymerize ethylene when activated with PMAO, but not with other chloride abstracting agents. The BP system³⁹ is similar to Brookhart's, with a bulky, neutral bidentate ligand, which inhibits chain transfer in the same way as described above.

For quite some time research in our group has focused on the use of the sterically bulky, electron-rich ligand bis($\underline{di}(\underline{tert}$ -<u>butyl)phosphino)methane</u> (dtbpm),⁴⁰ the narrow bite angle and the steric bulk of which imposes unusual reactivity and bonding patterns upon four-membered-ring chelated metal centers.^{41–43} Relevant for the present study, neutral, threecoordinate (dtbpm- $\kappa^2 P$)Rh^I alkyl complexes (alkyl = e.g. neopentyl) stabilized by γ -agostic interactions have been prepared and investigated^{44,45} which do not polymerize ethylene. They do, however, bind C₂H₄ to form Rh(I) η^2 -ethylene complexes of highly unusual structures, being potential models for alkyl olefin intermediates preceding the olefin insertion step.⁴⁶ It was

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expected that iso(valence)electronic (dtbpm- $\kappa^2 P$)Ni^{II} alkyl cations could be active catalysts for ethylene polymerization, because the steric crowding provided by the *tert*-butyl groups, potentially also protecting against chain termination, is similar to that in Brookhart's (and the BP) systems, as shown in Figure 1.



Figure 1. Comparison of ball-and-stick (front view toward Ni) and space-filling (top view upon the chelate ring planes) representations of metal fragments taken from the X-ray structures of a typical Brookhart diazadiene Ni dichloride (with two o_io' -diisopropyl-substituted *N*-phenyl groups, top structures) and of (dtbpm- $\kappa^2 P$)NiCl₂ (bottom structures, vide infra). Only the metal centers with their chelate rings in two orientations are shown; the two chlorides have been omitted for a clearer picture in both cases.

If steric effects play the same role as in Brookhart's bulky diazadiene ligands, the positive charge of the bisphosphine Ni(II) systems should lead to distinctly higher polymerization reactivity than in the neutral rhodium(I) case because of weaker back-bonding from the metal center to coordinated olefins. We have already shown that, in contrast to smaller ligands such as dppm,⁴⁷ the use of the dtbpm ligand with Pd(II) leads to very efficient catalysts for CO/ethylene copolymerization, yielding high-molecular-weight polyketones.⁴⁸

Varying the substituents on the phosphorus atoms while retaining the small bite angle caused by the methylene bridge was expected to allow for variable steric and electronic environments at the metal center. The effect of this alteration on the resulting metal complex should be manifested in its structure and reactivity and in the physical characteristics of the polyethylene produced. Similar ligand variations have been studied in the Brookhart and the BP systems and have been found to affect the chain branching and molecular weight; it was found by Brookhart that a sterically less bulky ligand led to less branched and lower molecular weight polyethylene.⁶ In studies on the BP system, the less bulky ligands led to shorter chains but with higher levels of branching than with the bulkiest ligands studied.²⁶

In this paper we report the preparation of thermally sensitive dimethyl and dibenzyl nickel(II) complexes containing a series of bidentate, bulky, electron-rich diphosphinomethane ligands $R_2PCH_2PR'_2$. Protonation with $[H(OEt_2)_2]^+[B(3,5-(CF_3)_2-C_6H_3)_4]^-$ leads to loss of methane or toluene to give the well-defined methyl or η^3 -benzyl cations; the latter are thermally quite stable compounds. The nickel(0) stilbene complex (dtbpm- κ^2P)Ni(η^2 -trans-PhCH=CHPh), easily accessible from trans-stilbene by in situ reduction of $[(dtbpm-\kappa^2P)NiCl_2,^{41a} can also be protonated with this acid to give the benzyl-substituted$

 η^{3} -benzyl complex [(dtbpm- $\kappa^{2}P$)Ni(η^{3} -CH(CH₂Ph)Ph]⁺[B(3,5-(CF₃)₂C₆H₃)₄]⁻.

To the best of our knowledge, the solid-state structures of cationic monomethyl complexes $[(R_2PCH_2PR'_2-\kappa^2P)Ni(CH_3)-(S)]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$ (S = solvent) disclosed here are so far the only cases of isolated and structurally characterized monomethyl Ni(II) cations active in C_2H_4 polymerization, although such species have been multiply studied by NMR at low temperature in solution.

The polymerization capability for ethylene using these methyl and η^3 -benzyl cations has been tested under standardized conditions. The properties of the resulting polymers are presented and correlated with the substitution (steric bulk) of the phosphine ligands, similar to the studies with sterically varying heterocyclic imine ligands.⁵¹ The type of well-defined single-site cationic Ni polymerization catalysts described in detail here has been disclosed in 2002.52 The only closely related study of cationic η^3 -benzyl nickel compounds with diphosphine ligands as catalyst precursors for ethylene ologomerization/ polymerization by Càmpora et al. appeared 2 years later.⁵³ These authors investigated the bite-angle dependence of cationic *p*-CF₃substituted η^3 -benzyl nickel complexes carrying bisphosphines ${}^{i}Pr_{2}P(CH_{2})_{n}P^{i}Pr_{2}$ (n = 1-3) in ethylene oligo- and polymerization. Their synthesis of the $[(P-P)\kappa^2 - P)Ni(p-CF_3 - \eta^3 - benzyl)]^+$ cations is less generally applicable and straightforward than the synthesis we had reported earlier and we refer to here. A cationic η^3 -benzyl Ni diimine complex was reported in 2003⁵⁴ by Monteiro et al., which is only moderately active in ethylene polymerization when MAO is applied as an activator. A zwitterionic n^3 -benzyl Ni complex has been used by Bazan et al. for C₂H₄ polymerization.⁵⁵ Brookhart et al. have tested the dibromide (dtbpm- $\kappa^2 P$)NiBr₂ using standard activating cocatalysts, as disclosed in a patent.^{41b}

RESULTS AND DISCUSSION

Synthesis and Structures. Deep red nickel dichloride complexes of the bidentate phosphine ligands $R_2PCH_2PR'_2$ ($R = R' = {}^{t}Bu$, dtbpm; R = Ph, $R' = {}^{t}Bu$, ptbpm; R = Cy, $R' = {}^{t}Bu$, ctbpm; $R = {}^{i}Pr$, $R' = {}^{t}Bu$, iptbpm; R = R' = Cy, dcpm) can be prepared easily by direct reaction of the respective bisphosphine ligands with anhydrous NiCl₂ in refluxing ethanol (Scheme 1), as reported for dtbpm.^{41a}

Scheme 1. Synthesis of the Ni(II) Dichloride Complexes



These air-stable complexes are very soluble in halogenated hydrocarbons and slightly soluble in hot ethanol. They, and all of the other complexes prepared in this work, are diamagnetic red, orange, or yellow square-planar nickel(II) complexes.

The molecular structures of the dichloride compounds have been determined in order to study the effect of the change

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in phosphine substituents on the geometry in the solid state. Important bond distances and angles are presented in Table 1,

Table 1. Selected Bond Distances (Å) and Angles (deg) of (L)NiCl₂ in the Solid State

L	dtbpm	ctbpm ^a	iptbpm ^a	dcpm
Ni-P	2.1745(6)	2.1763(6), 2.1674(6)	2.1833(6), 2.1510(6)	2.1542(7), 2.1524(7)
Ni-Cl	2.2060(6)	2.2171(6), 2.2161(6)	2.2262(6), 2.1961(7)	2.2180(7), 2.2174(7)
P-Ni-P	77.85(3)	76.40(2)	76.09(2)	75.70(2)
P-C-P	95.1(1)	93.5(1)	93.0(1)	91.7(1)
mean deviation from P–P–Ni–	0.019	0.040	0.040	0.148

Cl–Cl plane

^{*a*}The first value of Ni–P is the distance to the phosphorus atom bearing *tert*-butyl substituents (if applicable), and the first value of Ni–Cl is that *trans* to that phosphorus atom.

and Table 2 contains important data collection and structure solution parameters for all structures other than (ptbpm- $\kappa^2 P$)-NiCl₂ (the single-crystal structure of which could not be solved satisfactorily, although the connectivity is clear from the data obtained). Full crystallographic details for the four structures are provided in the Experimental Section. The structure of (dcpm- $\kappa^2 P$)NiCl₂ has been reported independently elsewhere, ⁵⁶ in a modification without cocrystallized solvent. The structure of the solvate (dcpm- $\kappa^2 P$)NiCl₂·CHCl₃ reported here is similar to the reported structure, and details are provided for comparison.

Figure 2 shows the solid-state structure of $(dtbpm-\kappa^2 P)$ -NiCl₂·3CH₂Cl₂. Because the structures with other phosphine ligands are similar, ORTEP diagrams are given in the



Figure 2. ORTEP diagram (50% probability displacement ellipsoids) of $(dtbpm-\kappa^2 P)NiCl_2$. Hydrogen atoms and cocrystallized solvent CH₂Cl₂ have been omitted for clarity.

Supporting Information. The core of each structure is a P–P– Ni–Cl–Cl square plane, and the narrow bite angle of these methylene-bridged diphosphine ligands is manifested in P– Ni–P angles of around 76°, compared to 87° in the analogous ethylene-bridged diphosphine complex (dppe- $\kappa^2 P$)NiCl₂⁵⁷ and 91° in (dtbpe- $\kappa^2 P$)NiCl₂.⁵⁸

The core of $(dcpm-\kappa^2 P)NiCl_2 \cdot CHCl_3$ is very slightly distorted from an ideal square plane toward a tetrahedral structure; the angle between the Cl–Ni–Cl plane and the P–Ni–P plane is 14°. This is not a pyramidal distortion, as shown by the torsion angle defined by one of the phosphorus atoms, the midpoint between the two phosphorus atoms, the midpoint between the two chlorine atoms, and one of the chlorine atoms of 14°. The analogous torsion angles in the other three dichloride structures are below 4°. There is no obvious cause for

Table 2. Selected Crystal Data and Data Collection Parameters for $(dtbpm-\kappa^2 P)NiCl_2 \cdot 3CH_2Cl_2$, $(ctbpm-\kappa^2 P)NiCl_2$, $(iptbpm-\kappa^2 P)-NiCl_2$, and $(dcpm-\kappa^2 P)NiCl_2 \cdot CHCl_3$

	$(dtbpm-\kappa^2 P)NiCl_2\cdot 3CH_2Cl_2$	$(\text{ctbpm-}\kappa^2 P)\text{NiCl}_2$	(iptbpm- $\kappa^2 P$)NiCl ₂	$(dcpm-\kappa^2 P)NiCl_2 \cdot CHCl_3$
formula	$C_{20}H_{44}Cl_8NiP_2$	$C_{21}H_{42}Cl_2NiP_2$	$C_{15}H_{34}Cl_2NiP_2$	C ₂₆ H ₄₇ Cl ₅ NiP ₂
fw	688.80	486.10	405.97	657.54
color	red	red	red	red
space group (No.)	C2/c (15)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)
a (Å)	15.1240(3)	9.7401(2)	17.9811(2)	11.2757(2)
b (Å)	12.0207(3)	17.1283(4)	8.3568(1)	12.4752(2)
c (Å)	17.9892(3)	14.5481(3)	14.1060(1)	22.8363(1)
β (deg)	94.486(1)	99.398(1)	108.869(1)	102.322(1)
V (Å ³)	3260.4(1)	2394.5(1)	2005.7	3138.3
Z	4	4	4	4
$d_{\rm calcd} ({\rm g/cm^3})$	1.403	1.348	1.344	1.392
μ (Mo K α) _{calcd} (mm ⁻¹)	1.358	1.172	1.384	1.161
size (mm)	$0.31\times0.25\times0.22$	$0.40 \times 0.11 \times 0.08$	$0.27\times0.20\times0.13$	$0.40 \times 0.10 \times 0.08$
transmissn range	0.49-0.78	0.65-0.91	0.71-0.84	0.65-0.91
2θ range (deg)	4.3-55.0	3.7-50.0	2.4-51.0	3.7-51.1
no. of rflns collected	5948	20 419	14 466	22 909
no. of unique rflns	3546	4238	3459	5446
no. of rflns, $F_o^2 > 2\sigma(F_o^2)$	2977	3473	3114	4370
no. of variables	157	266	191	307
R1 ^a	0.037	0.029	0.029	0.032
wR2 ^b	0.086	0.065	0.067	0.066
GOF	1.04	1.06	1.08	1.04
max/min residual electron density (e/Å 3)	0.47 and -0.48	0.48 and -0.33	0.58 and -0.56	0.34 and -0.28

^aR1 = $\sum ||F_o| - |F_c|| / \sum ||F_o|$. ^bwR2 = $\left[\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2\right]^{1/2}$.

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this distortion, which is also observed in the reported structure without cocrystallized solvent.56 The two nickel-phosphorus distances in the complexes containing the unsymmetrical ligands ptbpm, ctbpm, and iptbpm are different; the Ni-P distance to the phosphorus atom bearing the tert-butyl groups is slightly longer than the distance to the other phosphorus atom in each structure. This may be a superposition of a steric effect, caused by the bulkiest groups on the phosphorus atom in the strained four-membered ring, and an electronic effect-the electron rich metal atom binds the less electron rich P atom more closely. The difference between the two phosphorus atoms is also apparent in the ${}^{31}P{}^{1}H$ NMR spectra of these compounds, which each display two doublets. The chemical shift of the phosphorus atom bearing two tert-butyl groups is similar in each case, at around δ –5, while the chemical shift of the other phosphorus atom varies significantly. The ${}^{2}J_{PP}$ coupling constants are similar and relatively large (ca. 140 Hz) (see Experimental Section for full characterization details).

The yellow dimethyl and the red dibenzyl complexes can be prepared from the dichloride complexes by reaction of the appropriate Grignard reagent with the dichloride complex in cold THF or pentane (Scheme 2).





Optimal conditions for the syntheses vary according to the ligand set, and full details are provided in the Experimental Section. The stability of these compounds in solution varies from extreme thermal sensitivity, decomposing at -78 °C, to stability up to 55 °C and is clearly related to the steric bulk of the phosphine ligands, with the bulkiest ligands (dtbpm and ctbpm) leading to the least stable molecules. After extensive screening, cold THF was found to be the best solvent for the synthesis of the dimethyl complexes. The complex (dtbpm- $\kappa^2 P$)NiMe₂ reductively eliminates ethane with a half-life of less than 30 min in solution at room temperature, generating the unstable [(dtbpm- $\kappa^2 P$)Ni⁰] fragment which, in the presence of additional appropriate ligands, can be trapped and forms adducts.⁵⁹⁻⁶¹ This is consistent with the reported facile thermal elimination of neopentane and neosilane from $(dtbpm-\kappa^2 P)Pt$ -(Np)(H) and (dtbpm- $\kappa^2 P$)Pt(Ns)(H), respectively,⁶² and the elimination of ethane or $Me_3Si(CH_2)_2SiMe_3$, respectively, from (dtbpm- $\kappa^2 P$)PdMe₂ and (more facile) (dtbpm- $\kappa^2 P$)Pd(CH₂-SiMe₃)₂.⁶³ While in the cases of platinum and palladium, in the absence of other ligands the eight-membered cyclic d¹⁰-d¹⁰ dimer (μ -dtbpm)₂M₂⁶²⁻⁶⁴ is formed with bridging dtbpm ligands, in the nickel case, in the absence of additional ligands, thermal decomposition leads to precipitation of black elemental nickel and free ligand, which is observed for all of the dimethyl compounds reported here. Remarkably, in the solid state rather than in solution, the dimethyl complexes are thermally stable with

decomposition points in the range of 92-128 °C, which might be an indication of a solvent-assisted reductive elimination.

The X-ray crystal structures of the four dimethyl complexes prepared have been also determined; an ORTEP diagram of (dtbpm- $\kappa^2 P$)NiMe₂ is presented in Figure 3, while Table 3



Figure 3. ORTEP diagram (50% probability displacement ellipsoids) of (dtbpm- $\kappa^2 P$)NiMe₂. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of (L)NiMe₂ in the Solid State

L	dtbpm	ptbpm ^a	iptbpm ^a	dcpm
Ni-P	2.2382(7), 2.2377(7)	2.2298(5), 2.2056(4)	2.230(1), 2.197(1)	2.1806(6), 2.2135(6)
Ni-C(methyl)	1.957(3), 1.953(3)	1.958(2), 1.959(2)	1.968(3), 1.960(3)	1.969(2), 1.956(2)
P-Ni-P	76.93(2)	75.75(2)	75.86(2)	76.002
Р-С-Р	96.8(1)	94.57(7)	94.6(1)	93.5(1)
mean deviation from P–P–Ni–C–C plane	0.037	0.018	0.021	0.077

^aThe first value of Ni–P is the distance to the phosphorus atom bearing *tert*-butyl substituents (if applicable), and the first value of Ni–C(methyl) is that trans to that phosphorus atom.

contains selected bond distances and angles and Table 4 provides important data collection and structure solution parameters.

Again, because the structures are similar, ORTEP diagrams of the remainder of the dimethyl complexes appear in the Supporting Information. As for the dichloride complexes, the dimethyl molecules have a square-planar geometry about the nickel center. As was observed above, the greatest distortion from planarity is observed in the dcpm case; the angle between the C-Ni-C and P-Ni-P planes for $(dcpm-\kappa^2 P)NiMe_2$ is 8°, which is only a very slight distortion; the torsion angle described for the dichloride structures in this case is also 8°. The Ni-P distances for the dimethyl complexes are slightly longer than those for the dichloride complexes, while the angles around nickel are unchanged. The bond lengthening to the phosphorus atoms is obviously related to the increased electron donor properties of the methyl groups in comparison to the chloride ligands. As observed in the dichloride cases, the nickel-phosphorus distances of the molecules with unsymmetrical diphosphine ligands are somewhat different, with the distance to the phosphorus atom bearing the tert-butyl groups

Table	4.	Selected	Crystal	Data	and	Data	Collection	Parameters	for	(L)NiMe.
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L	dtbpm	ptbpm	iptbpm	dcpm
formula	C ₁₉ H ₄₄ NiP ₂	C ₂₃ H ₃₆ NiP ₂	C17H40NiP2	C27H52NiP2
fw	393.19	433.17	365.14	497.34
color	yellow	yellow	yellow	yellow
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a (Å)	17.9363(3)	18.48480(1)	18.5285(2)	11.4633(4)
b (Å)	8.5024(2)	9.85510(1)	8.0957(1)	12.6493(5)
c (Å)	14.8549(3)	13.2549(2)	14.8617(2)	19.6646(7)
β (deg)	92.437(1)	102.944(1)	110.879(1)	102.983(1)
V (Å ³)	2263.3(1)	2353.28(4)	2082.89(4)	2778.5(2)
Ζ	4	4	4	4
$d_{\rm calcd} ({\rm g/cm^3})$	1.154	1.223	1.164	1.189
μ (Mo K α) _{calcd} (mm ⁻¹)	0.996	0.965	1.077	0.825
size (mm)	$0.42 \times 0.20 \times 0.08$	$0.44\times0.34\times0.22$	$0.26 \times 0.16 \times 0.11$	$0.34 \times 0.20 \times 0.16$
transmissn range	0.68-0.92	0.68-0.82	0.77-0.89	0.77-0.88
2θ range (deg)	4.5-51.2	2.2-51.2	2.6-51.3	3.6-51.1
no. of rflns collected	16 162	17 255	14 935	20 323
no. of unique rflns	3927	4091	3614	4817
no. of rflns, $F_o^2 > 2\sigma(F_o^2)$	3049	3630	3060	4008
no. of variables	213	249	194	273
R1 ^a	0.033	0.023	0.033	0.032
wR2 ^b	0.073	0.060	0.075	0.075
GOF	1.03	1.02	1.09	1.03
max/min residual electron density (e/ų)	0.41 and -0.30	0.36 and -0.16	0.49 and -0.22	0.48 and -0.33
${}^{t}R1 = \sum F_{o} - F_{c} / \sum F_{o} . {}^{b}wR2 = [\sum w(F_{o})]$	$\int_{0}^{2} - F_{\rm c}^{2})^{2} / \sum w (F_{\rm o}^{2})^{2}]^{1/2}.$			

again being slightly longer. In addition, as observed for the dichlorides, the chemical shifts in the ³¹P{¹H} NMR spectra are very similar for those phosphorus atoms, and to the singlet of (dtbpm- $\kappa^2 P$)NiMe₂, at δ 19, but the coupling constants are much smaller (around 10 Hz).

The dibenzyl complexes are thermally less stable than the dimethyl complexes, presumably due to the increased steric bulk of two benzyl groups compared with two methyl groups around the metal center. Neither (dtbpm- $\kappa^2 P$)NiBz₂ nor (ctbpm- $\kappa^2 P$)-NiBz₂ could be prepared in THF; precipitation of black nickel was observed even at -78 °C. In those two cases, the dibenzyl complex was generated in a heterogeneous reaction in pentane at -78 °C, extracted into diethyl ether, and added directly to a flask containing $[H(OEt_2)_2]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$ to generate the benzyl cation. The steric bulk of the ligands ptbpm and iptbpm is less, and the dibenzyl complexes bearing these ligands can be prepared in THF at -35 °C and isolated by crystallization from toluene. The dibenzyl complex (dcpm- $\kappa^2 P$)NiBz₂ can be prepared in pentane at room temperature and crystallized from toluene. Thus, some measure of the relative bulkiness of the diphosphine ligands is implied by the varying decomposition reactivity of their nickel dibenzyl complexes.

The structures of (ptbpm- $\kappa^2 P$)NiBz₂ and (iptbpm- $\kappa^2 P$)NiBz₂ were determined crystallographically. ORTEP diagrams of the complexes are shown in Figures 4 and 5, while Table 5 contains selected bond distances and angles for the two complexes and Table 6 contains data collection and structure solution parameters.

Important features of these structures are that the benzylic carbon atoms do not lie in the plane of the Ni–diphosphine fragment; they are shifted toward a tetrahedral geometry, particularly in the case of (ptbpm- $\kappa^2 P$)NiBz₂, in which the P–Ni–P and C–Ni–C planes intersect at an angle of 26°. The torsion angle, described for the dichloride complexes above, in



Figure 4. ORTEP diagram (50% probability displacement ellipsoids) of (ptbpm- $\kappa^2 P$)NiBz₂. Hydrogen atoms have been omitted for clarity.



Figure 5. ORTEP diagram (50% probability displacement ellipsoids) of (iptbpm- $\kappa^2 P$)NiBz₂. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) of (ptbpm- $\kappa^2 P$)NiBz₂ and (iptbpm- $\kappa^2 P$)NiBz₂ and of the Cations of [(dtbpm- $\kappa^2 P$)Ni(Me)(THF)]⁺[BAr_f]⁻•2THF and [(ptbpm- $\kappa^2 P$)Ni(Me)(THF)]⁺[BAr_f]⁻ in the Solid State

	$(ptbpm-\kappa^2 P)$ NiBz ₂ ^a	(iptbpm- $\kappa^2 P$) NiBz ₂ ^{<i>a</i>}	$[(dtbpm- \kappa^2 P) \\ Ni(Me) \\ (THF)]^{+b}$	$[(\text{ptbpm-} \kappa^2 P) \\ \text{Ni(Me)} \\ (\text{THF})]^{+,b}$
Ni-P ^a	2.2653(7),	2.2641(8),	2.3082(9),	2.292(2),
	2.2079(7)	2.2250(8)	2.1402(9)	2.101(2)
Ni-C	1.993(2),	1.996(3),	1.941(3)	1.941(8)
	1.993(2)	1.990(3)	1.941(3)	1.941(8)
P-Ni-P	74.19(2)	75.42(3)	78.33(3)	77.01(8)
Р-С-Р	93.9(1)	95.9(1)	98.3(2)	95.9(3)
intersection of planes	26	17	11	9
mean deviation from plane	0.249	0.165	0.106	0.091
$Ni-O_{THF}$			1.989(2)	1.991(5)

^{*a*}The first value of Ni–P is the distance to the phosphorus atom bearing *tert*-butyl substituents, and the first value of Ni–C(benzyl) is that trans to that phosphorus atom. ^{*b*}The first Ni–P distance given is to the phosphorus atom trans to the methyl ligand, which in the ptbpm case is the phosphorus atom bearing the *tert*-butyl substituents.

this case measures 26° , indicating that the distortion is again not toward pyramidal. In (ptbpm- $\kappa^2 P$)NiBz₂, the phenyl residues of the benzyl ligands point in opposite directions in the solid state, presumably for steric reasons, while in (iptbpm- $\kappa^2 P$) NiBz₂ they lie on the same side of the chelate plane but point outward; again, a distortion toward tetrahedral is shown by a torsion angle of 16° between one phosphorus atom, the midpoint between the phosphorus atoms, the midpoint between the benzylic carbon atoms, and one of the benzylic carbon atoms. The nickel-phosphorus distances in both complexes are unequal, again due to the asymmetrical diphosphine ligands (Table 5). The Ni-C distances to the benzyl CH₂ carbon atoms are similar to those to the methyl carbon atoms in the structures of the dimethyl complexes. The Ni-P bond lengths are also similar to those observed in the dimethyl structures. The chemical shifts of the phosphorus atoms bearing tert-butyl groups for the dibenzyl complexes are once again observed at around δ 20, while the ${}^{2}J_{\rm PP}$ coupling constants in the complexes with asymmetric ligands are all around 30 Hz. Interestingly, the chemical shifts of the two phosphorus atoms of $(\text{ctbpm-}\kappa^2 P)$ -NiBz₂ are the same as for the free ligand ctbpm,⁶⁵ and only the large difference in coupling constants (30 vs 108 Hz) distinguishes the ³¹P{¹H} NMR spectra.

Reaction of the dimethyl or dibenzyl complexes with $[H(OEt_2)_2]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$ in diethyl ether leads to loss of one of the carbon ligands as methane or toluene, respectively, and to the formation of the yellow to orange cationic salts with the noncoordinating counterion $[B(3,5-(CF_3)_2C_6H_3)_4]^-$ (= $[BAr_f]^-$). The benzyl-substituted η^3 -benzyl cation complex $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$ was also prepared, in that case by reaction of the known Ni(0) stilbene complex $(dtbpm-\kappa^2 P)Ni(trans-PhCH=CHPh)^{41}$ with $[H(OEt_2)_2]^+[BAr_f]^-$.

In an NMR tube, addition of 1 equiv of $[H(OEt_2)_2]^+[BAr_f]^-$ to a solution of any of the dimethyl complexes at room temperature leads to quantitative formation of the corresponding cation; gas bubbles, presumably of methane, can be observed.

Table 6. Selected Crystal Data and Data Collection Parameters for (ptbpm-κ ² P)NiBz ₂ , (iptbpm-κ ² P)NiBz ₂ ,	$[(dtbpm-\kappa^2 P)]$
NiMe(THF)] ⁺ [BAr _f] ⁻ ·2THF, and [(ptbpm- $\kappa^2 P$)NiMe(THF)] ⁺ [BAr _f] ⁻ in the Solid State	

	(ptbpm- $\kappa^2 P$)NiBz ₂	$\begin{array}{c} (\text{iptbpm-} \ \kappa^2 P) \\ \text{NiBz}_2 \end{array}$	[(dtbpm- κ²P) NiMe(THF)]⁺[BAr _f]⁻-2THF	$[(ptbpm- \kappa^2 P) \\ NiMe(THF)]^+[BAr_f]^-$
formula	C ₃₅ H ₄₄ NiP ₂	$C_{29}H_{48}NiP_2$	$C_{62}H_{77}BF_{24}NiO_{3}P_{2}$	C58H53BF24NiOP2
fw	585.35	517.32	1457.70	1353.46
color	red	red	yellow	yellow-orange
space group (No.)	$P2_1/n$ (14)	$P2_1/c$ (14)	C2/c (15)	$P\overline{1}$ (2)
a (Å)	12.1364(7)	13.3737(7)	20.5704(1)	12.962(1)
b (Å)	15.6573(9)	11.5980(6)	17.3468(2)	14.146(1)
c (Å)	16.700(1)	18.7372(9)	39.5515(1)	17.793(1)
α (deg)	90	90	90	96.491(2)
β (deg)	95.757(1)	90.607(1)	100.352(1)	108.742(1)
γ (deg)	90	90	90	91.243(2)
V (Å ³)	3157.5(3)	2906.1(3)	13883.5(2)	3064.0(4)
Ζ	4	4	8	2
$d_{\rm calcd} ({\rm g/cm}^3)$	1.231	1.182	1.395	1.467
μ (Mo K α) _{calcd} (mm ⁻¹)	0.737	0.792	0.432	0.481
size (mm)	$0.17\times0.16\times0.16$	$0.50 \times 0.26 \times 0.14$	$0.44 \times 0.39 \times 0.38$	$0.38 \times 0.19 \times 0.16$
transmissn range	0.88-0.89	0.69-0.90	0.83-0.85	0.84-0.93
2θ range (deg)	3.6-51.1	3.0-51.1	2.1-51.3	3.32-45.0
no. of rflns collected	23 117	20 983	51 766	11 660
no. of unique rflns	5444	5024	12 085	7857
no. of rflns, $F_o^2 > 2\sigma(F_o^2)$	3693	4208	9277	4362
no. of variables	349	299	1048	946
R1 ^a	0.036	0.041	0.049	0.066
wR2 ^b	0.066	0.109	0.115	0.134
GOF	1.01	1.04	1.07	1.02
max/min residual electron density (e ⁻ /Å ³)	0.29 and -0.22	1.09 and -0.39	0.44 and -0.37	0.42 and -0.44

 ${}^{a}\text{R1} = \sum ||F_{o}| - |F_{c}|| / \sum ||F_{o}|. {}^{b}\text{wR2} = \left[\sum w (F_{o}^{2} - F_{c}^{2})^{2} / \sum w (F_{o}^{2})^{2}\right]^{1/2}.$

The vacant coordination site of each Ni(II) methyl cation complex is occupied by the solvent (THF in these experiments), and the two phosphorus atoms are inequivalent, resulting in two doublets in the ${}^{31}P{}^{1}H{}$ spectra for the complexes with symmetric ligands (dtbpm and dcpm). In the cases of the complexes bearing unsymmetric phosphine ligands, ptbpm and iptbpm, both possible isomers **A** and **B** of the methyl cations are formed (Figure 6), and two sets of two doublets are observed in the ${}^{31}P{}^{1}H{}$ spectra.



Figure 6. The two possible stereoisomers **A** and **B** of [(L)NiMe- $(THF)]^+$ formed from protonation of the corresponding dimethyl complex in THF with L = ptbpm (R = tBu, R' = Ph) and L = iptbpm (R = tBu, R' = iPr).

Spectra were assigned by two-dimensional NMR spectroscopy, by redissolution of structurally determined crystals, and by comparison between the compounds (complete spectral data and assignments are given in the Experimental Section). Not surprisingly, the two isomers are not produced in a 1:1 ratio. In the case of ptbpm, a ratio of 1.7:1 of the two isomers was formed (determined by integration of ³¹P{¹H} NMR spectra), with isomer A in slight excess. In the case of iptbpm, the ratio of the two isomers was almost 1:6, with the favored isomer being that with the methyl ligand trans to the tert-butyl-substituted phosphorus atom, isomer B. This assignment is based on comparison with the ${}^{31}P{}^{1}H$ spectra of the benzyl cations described below. It is not clear why this isomer should be favored to such a large extent. The isomers A and B do not interconvert on the NMR time scale at room temperature, as evidenced by sharp signals in the NMR spectra for each isomer, although dissociation of the solvent ligand is expected to be facile. This is not surprising, because the inversion of a T-shaped three-coordinate d⁸ metal complex through a Y-shaped geometry is electronically disfavored.43 The predominance of B could be caused by kinetic control through the protolysis reaction.

Ligands such as PPh₃, for example, readily displace THF from $[(L)NiMe(THF)]^+$, and the X-ray structure of $[(dtbpm-\kappa^2 P)NiMe(PPh)_3]^+$ is displayed in the Supporting Information.

The methyl cation salts are extremely air sensitive. Nonetheless, it was possible to determine crystallographically the solid-state structures of two of these compounds as the first representatives of this class. An ORTEP diagram of the cation of $[(dtpm-\kappa^2 P)Ni(Me)(THF)]^+[BAr_f]^-\cdot 2THF$ is shown in Figure 7, while Table 5 contains important bond distances and angles of that structure as well as those for $[(ptpm-\kappa^2 P)Ni-(Me)(THF)]^+[BAr_f]^-$, an ORTEP diagram of which is included in the Supporting Information.

The isomer of the cation $[(\text{ptbpm}-\kappa^2 P)\text{NiMe}(\text{THF})]^+$ for which the structure could be determined is that with the *tert*butyl groups on the phosphorus atom trans to the methyl ligand, isomer **B**, which is the minor isomer formed from the synthesis but crystallizes preferentially. Important data collection and structure solution parameters for both structures are provided in Table 6. The bond distances about the metal in



Figure 7. ORTEP diagram (50% probability displacement ellipsoids) of the cation of $[(dtbpm-\kappa^2 P)Ni(Me)(THF)]^+[BAr_f]^-\cdot 2THF$. Hydrogen atoms and a noncoordinated THF have been omitted for clarity.

the cations are, as expected, somewhat shorter than for their dimethyl precursors. The distortion away from planarity for the methyl cations is greater than in the dimethyl complexes but much less than in the dibenzyl complexes.

The η^3 -benzyl cations are far more stable, both oxidatively and thermally, than the methyl cations, due to the η^3 -coordination mode of the benzyl ligand. These orange salts can be handled briefly in air in the solid state and melt at over 150 °C. As in the case of the methyl cations, the two possible isomers for each of the compounds with unsymmetric diphosphine ligands depicted in Figure 8 are formed. In all cases, they are



Figure 8. The two possible isomers C and D of $[(L)Ni(\eta^3-Bz)]^+$ formed from protonation of the corresponding dibenzyl complex for L = ptbpm, ctbpm, and iptbpm (R = tBu).

observed in the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra in approximately equal amounts.

These isomers are not expected to interconvert for the same reasons the methyl cations do not.⁴³ Isomer C is analogous to the methyl cation isomer A, because the benzylic carbon is cis to the *tert*-butyl-substituted phosphorus atom, while isomer D is similarly analogous to isomer B. Suprafacial haptotropic fluxionality of the benzyl ligand, shown in Scheme 3, is fast on the NMR time scale, as evidenced by the observation of only one set of phenyl resonances in the ¹H and ¹³C{¹H} NMR spectra of the benzyl cations.

A transition state for this process was calculated using density functional theory (B3LYP/SDD,6-31G(d)) for a simplified model having dhpm (=H₂PCH₂PH₂) as the diphosphine ligand. The energy of the transition state is only 5.0 kJ/mol higher than that of the two degenerate (enantiomeric) η^3 ground states; thus, it is not surprising that the process is fast on the NMR time scale and could not be frozen out. This is comparable with the value calculated for the neutral rhodium system [(H₂PCH₂PH₂K²-P)Rh(η^3 -Bz)] (B3LYP/LANL2DZ) of 6.7 kJ/mol.^{66a} In the unsubstituted

Scheme 3. Schematic Illustration of the Suprafacial Haptotropic η^3 to η^3 Shift of the Benzyl Ligand, Keeping the Two P Atoms Inequivalent (for both R = R' and R \neq R')



benzyl systems and for R = R', the geometries before and after suprafacial shift are identical. It should be noted, however, that for frontier orbital overlap reasons the two P atoms do not interchange during this dynamic process: i.e., the benzyl ligand displays a symmetric spectrum, while the ³¹P signals remain as two doublets even for the symmetrical diphosphinomethanes. The metal fragment undergoes what has been called a "windshieldwiper motion".

In monocationic η^3 -benzyl complexes such as $[(\text{dtbpm}-\kappa^2 P)-\text{Ni}(\eta^3\text{-benzyl})]^+$ or one of its congeners carrying other diphosphinomethanes, the Ni fragment can be formally counted either as a neutral d¹⁰ ML₂ unit interacting with a benzyl cation or a dicationic d⁸ ML₂ moiety interacting with a benzyl anion. In either representation, the dominant frontier MO interaction is between the π_4 -MO of the benzyl unit (empty or filled) and the b₂-type MO of the bisphosphine Ni fragment (filled or empty), as shown in Scheme 4.^{66b}

Scheme 4. Dominant Frontier MO Interaction between a Bent Bisphosphine Ni Fragment (Arbitrarily Taken as a Dicationic d⁸ ML₂) and a Benzyl Anion Unit



In the η^3 to η^3 metal shift process, the change of the overlap situation while passing the C_s transition state is indicated in Scheme 5. In the transition state, there is still appreciable frontier MO overlap, provided the metal moves without interchange of P_a and P_b .

In the protonated stilbene system, this suprafacial shift of the benzylic part of the ligand leads to a syn and anti conformation Scheme 5. Overlap Situation between the b_2 -Type Frontier MO of a Ni Bisphosphine and the Relevant Frontier MO π_4 of the Benzyl Ligand along the η^3 to η^3 Rearrangement Pathway, Viewed from the Side of the Ni Fragment



of the benzyl residue with respect to the metal. The syn geometry is observed in the crystal structure (see below).

The crystal structures of the two symmetric benzyl cations as well as that of $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^$ have been determined by X-ray crystallography. Figure 9 shows



Figure 9. ORTEP diagram (50% probability displacement ellipsoids) of the cation of $[(dtbpm-\kappa^2 P)NiBz]^+[BAr_f]^-$ ·THF. Hydrogen atoms have been omitted.

an ORTEP diagram of the cation of $[(dtbpm-\kappa^2 P)Ni(\eta^3-Bz)]^+$ $[BAr_f]^-$ ·THF and Figure 10 one isomer of the cation of



Figure 10. ORTEP diagram (50% probability displacement ellipsoids) of the cation of $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$. Hydrogen atoms have been omitted.

 $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$, and Table 7 contains selected bond distances and angles of the three structures. Table 8 provides important data collection and structure solution parameters.

Details of the crystallographic studies as well as an ORTEP diagram of the cation of $[(dcpm-\kappa^2 P)Ni(\eta^3-Bz)]^+[BAr_f]^-\bullet THF$ are presented in the Supporting Information. The crystal structures of $[(ptbpm-\kappa^2 P)Ni(\eta^3-Bz)]^+[BAr_f]^-$ and $[(ctbpm-\kappa^2 P)-Ni(\eta^3-Bz)]^+[BAr_f]^-$ were also determined but are severely disordered; thus, no bond distances could be extracted. The whole

Table 7. Selected Bond Distances (Å) and Angles (deg) of the Molecular Structures of the Cations of $[(dtbpm-\kappa^2 P)-NiBz]^+[BAr_f]^-$ THF, $[(dcpm-\kappa^2 P)NiBz]^+[BAr_f]^-$, and $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$ in the Solid State

	[(dtbpm- κ²P)NiBz]+	[(dcpm- <i>k</i> (2 unique	² P)NiBz] ⁺ molecules)	$\begin{matrix} [(\text{dtbpm-}\kappa^2 P) \\ \text{Ni}(\eta^3\text{-}\text{CH-} \\ (\text{CH}_2\text{Ph})\text{Ph}]^{+a} \end{matrix}$	toluene ⁶⁷
Ni-P ^b	2.254(1), 2.181(1)	2.205(2), 2.152(2)	2.242(3), 2.141(2)	2.276(1), 2.205(1)	
Ni-C1	1.999(6)	2.001(8)	2.06(1)	2.009(3)	
Ni-C2	2.055(4)	2.017(7)	2.054(8)	2.062(3)	
Ni-C3	2.183(6)	2.169(7)	2.136(8)	2.202(3)	
P-Ni-P	79.24(5)	77.79(7)	77.44(8)	78.9(1)	
Р-С-Р	98.4(2)	95.0(3)	96.1(3)	99.3(1)	
C1-C2	1.430(9)	1.42(1)	1.49(1)	1.444(5)	1.5024(17)
C2-C3	1.403(8)	1.41(1)	1.35(1)	1.408(5)	1.3929(18)
C3-C4	1.39(1)	1.40(1)	1.40(1)	1.431(5)	1.389(2)
C4-C5	1.33(1)	1.35(1)	1.37(1)	1.368(7)	1.380(2)
C5-C6	1.42(1)	1.42(1)	1.44(1)	1.384(7)	1.3795(19)
C6-C7	1.37(1)	1.37(1)	1.35(1)	1.346(6)	1.3861(18)
C7–C2	1.417(8)	1.44(1)	1.41(1)	1.422(5)	1.3906(16)

^{*a*}The labeling of the carbon atoms in this structure is different, but the distances around the equivalent positions of the benzyl ligand have been given: i.e. C1 = C37, C2 = C36, C3 = C35, C4 = C34, C5 = C33, C6 = C32, C7 = C31. ^{*b*}The first Ni–P distance given is to the phosphorus atom trans to the benzylic carbon, while the second Ni–P distance is to the phosphorus atom trans to the ring.

cation in each case is disordered over two orientations, with the bulky alkyl residues of the diphosphine ligand being in the same region for both orientations, while the nickel atom and the benzyl groups are located on both sides of this region, resulting in a crystallographic mixture of the two isomers.

The Ni-P and Ni-C bond distances in the benzyl cations are within the normal range, as observed in the structures of the dibenzyl complexes. The bond distances in the phenyl rings of the benzyl ligands are unequal, indicating some loss of aromaticity. The contribution of the cyclohexadiene resonance structure F depicted in Scheme 6 is apparent in the pattern of lengthening and shortening of bonds. Thus, the bonds C^3-C^4 , $C^{5}-C^{6}$, and $C^{7}-C^{2}$ in a benzyl ligand are expected to lengthen and the bonds C^1-C^2 , C^4-C^5 , and C^6-C^7 are expected to shorten relative to toluene. This is observed (see Table 7), especially for the dtbpm structure. The electron density of the bond C2–C3 is directly involved in binding to the metal, which is expected to increase the bond distance. The bond length is observed (at 1.403 Å) to be slightly longer than the related bonds in toluene⁶⁷ (1.393 Å) in each structure. The resolution of the dcpm structure is not as good, but the trend is nonetheless present.

Ethylene Polymerization. Pressurizing a solution of the cation $[(dtbpm-\kappa^2 P)Ni(Me)(THF)]^+[BAr_f]^-$ in diethyl ether at 0 °C with 7 bar of ethylene causes the solution to become cloudy within minutes as a white precipitate is formed. The polymer can be isolated and has been characterized by differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). The molecular weight curve is narrow, showing the single-site nature of the catalyst, and the mean molecular weight of 470 000 g/mol corresponds to a long-chain polymer. The melting point of 136 °C is typical for a long, unbranched polyethylene chain; the low degree of branching

Table 8. Selected Crystal Data and Data Collection Parameters for $[(dtbpm-\kappa^2 P)NiBz]^+[BAr_f]^-$ ·THF, $[(dcpm-\kappa^2 P)NiBz]^+[BAr_f]^-$, and $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$

	$[(dtbpm-\kappa^2 P)$ NiBz] ⁺ [BAr _f] ⁻ ·THF	[(dcpm-κ ² P) NiBz] ⁺ [BAr _f] ⁻	$[(dtbpm-\kappa^2 P) \\ Ni(\eta^3-CH- (CH_2Ph)Ph)]^+- \\ [BAr_f]^-$
formula	$\mathrm{C_{60}H_{65}BF_{24}NiOP_2}$	$\mathrm{C}_{64}\mathrm{H}_{65}\mathrm{BF}_{24}\mathrm{NiP}_{2}$	$\mathrm{C}_{63}\mathrm{H}_{63}\mathrm{BF}_{24}\mathrm{NiP}_{2}$
fw	1389.58	1421.62	1407.59
color	orange	orange	red
space group (No.)	$P2_1(4)$	P1 (2)	$P2_1/c$ (14)
a (Å)	13.3717(2)	17.6494(1)	12.7881(3)
b (Å)	17.6205(2)	19.3171(2)	18.7788(4)
c (Å)	13.7480(2)	21.0416(3)	27.1176(6)
α (deg)	90	113.020(1)	90
β (deg)	98.526(1)	92.120(1)	93.422(1)
γ (deg)	90	94.502(1)	90
V (Å ³)	3203.45(8)	6564.3(1)	6500.5(3)
Ζ	2	4	4
$d_{\rm calcd}~({\rm g/cm^3})$	1.441	1.438	1.438
$\mu \ (\mathrm{mm}^{-1})$	0.462	0.451	0.455
size (mm)	$0.26\times0.17\times0.14$	$0.52\times0.25\times0.25$	$0.45\times0.29\times0.25$
transmissn range	0.89-0.94	0.80-0.90	0.82-0.89
2θ range (deg)	3.8-55.0	2.4-46.5	2.6-51.2
no. of rflns collected	32 890	35 555	29 792
no. of unique rflns	14 525	18 629	11 007
no. of rflns, $F_o^2 > 2\sigma(F_o^2)$	9945	11 643	8170
no. of variables	910	1823	1040
R1 ^a	0.062	0.088	0.041
wR2 ^b	0.115	0.212	0.089
GOF	1.09	1.07	1.03
max/min residual electron density (e ⁻ /Å ³)	0.39 and -0.26	1.11 and -0.41	0.31 and -0.30
${}^{a}\mathrm{R1} = \sum F_{\mathrm{o}} - F_{\mathrm{o}} $	$F_{\rm c} /\sum F_{\rm o} $. ^b wR2 =	$= \left[\sum w(F_{o}^{2} - F_{c}^{2})\right]$	$(F_o^2)^2 / \sum w (F_o^2)^2]^{1/2}.$

Scheme 6. Resonance Forms of the Benzyl Ligand Showing Aromatic and Nonaromatic Contributing Structures^a



(6.2 methyl branches/1000 carbon atoms as determined by IR) is presumably because the insertion step is more rapid than potential chain-walking steps.

The other methyl cations were generated in situ by dissolution of the respective dimethyl complex and 1 equiv of $[H(OEt_2)_2]^+[BAr_f]^-$ in diethyl ether at room temperature. This is more practical due to the extreme thermal, oxygen, and water sensitivity of the methyl cations. In each case, polymerization begins immediately upon pressurization with

ethylene (10 bar) and leads to a white powder of polyethylene being precipitated. The melting points and molecular weights of the polymers produced by the different ligand systems are shown in Table 9. In each case, single-site catalysis is observed at 25 $^{\circ}$ C.

Table 9. Comparison of Melting Points of Polyethylene Produced by Methyl Cations Generated in Situ from (L)NiMe₂ and $[H(OEt_2)_2]^+[BAr_f]^-$ at 25 °C and 10 bar in Diethyl Ether

L	melting pt of polymer ($^{\circ}C$)	$M_{\rm w} \left({ m g/mol} ight)$
dtbpm	134.3	101 316
ptbpm	124.5	28 904
iptbpm	120.4	11 939
dcpm	109.5	5885

GPC analysis (Figure 11) also shows the polymer characteristics as a function of the bisphosphine ligand systems and the monomodal nature of the polyethylene formed.

The trend in melting points of the polyethylene reflects the trend in molecular weights; only dtbpm as auxiliary ligand leads to long-chain polyethylene. The difference is presumably due to the steric effects of the substituents on the diphosphine ligand, which shield the growing polymer chain from termination in a manner similar to that proposed by Brookhart.^{6,8}

The benzyl cations were expected to be more stable and more easily handled, which indeed they are, in comparison with the corresponding methyl cations. For an η^3 -benzyl complex to polymerize ethylene, however, the ligand must change coordination mode to η^1 , in order to generate a vacant coordination site for ethylene to bind (Scheme 7). This process has been studied theoretically using density functional theory. Despite extensive searching, no minimum was found for an η^1 -coordinated benzyl in the absence of another ligand. This contrasts with the situation for the analogous, neutral rhodium complex, for which a minimum was found for (dtbpm- $\kappa^2 P$)-Rh(η^1 -CH₂C₆H₅), 47.7 kJ/mol higher in energy than the η^3 ground state.⁶⁶ We note that the neutral ethylene adduct (dtbpm- $\kappa^2 P$)Rh(CH₂^tBu- κC)(η^2 -C₂H₄) could be isolated but does not have the expected square-planar structure.⁴⁶





These results support the hypothesis that the coordination change in the nickel cation only occurs in the presence of the incoming ligand, which effectively pushes the phenyl ring of the benzyl ligand out of the coordination sphere. The energy for coordination of ethylene to the η^3 -benzyl complex to form an η^1 -benzyl ethylene complex as shown in Scheme 7 was calculated to be endothermic by 30.1 kJ/mol.⁶⁸

Three polymerization experiments were conducted with the stilbenyl cation $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$ at different temperatures with 7 bar of ethylene pressure.

Table 10. Polymerization Activity of [(dtbpm- $\kappa^2 P$)Ni-(η^3 -CH(CH₂Ph)Ph]⁺[BAr_f]⁻ with 7 bar of Ethylene at 0 °C in Et₂O

concn (mmol/L)	solvent	temp (°C)	yield (mg)	activity (kg/((mol of Ni) h))	TON
4.4	Et_2O	28	205	3.4	121
2.7	Et_2O	44	665	18.5	660
2.6	THF	70	1300	36.8	1314

Table 10 summarizes the results of those experiments, and Figure 11 displays the GPC traces of polyethylenes obtained with cationic benzyl complexes and dtbpm, itbpm, ptbpm, and dcpm as ligands.

In the case of $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^$ at the two lower temperatures (28 and 44 °C), unreacted $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$ was observed by ${}^{31}P{}^{1}H$ NMR spectroscopy in the solution after the polymerization reaction, and the solutions were still active in catalysis



Figure 11. GPC traces of polymers produced from the methyl cations generated in situ from $(L)NiMe_2$ and $[H(OEt_2)_2]^+[BAr_f]^-$ at 25 °C and 10 bar in diethyl ether (L = dcpm, itbpm, ptbpm, dtbpm).

when further ethylene was added. At 70 °C, this was no longer the case, which implies that all of the η^3 ligand moves to η^1 coordination at that temperature and pressure. The reaction at higher temperature also resulted in the production of liquid oligomers (butene to decene), which were identified by GC/ MS but not included in the yield. The polymer produced at 44 °C was analyzed and has an average molecular weight of 182 137 g/mol and one methyl branch per 1000 carbon atoms. The molecular weight curve could be deconvoluted into two components, each with a narrow distribution, and averaged masses of 104 664 and 253 441 g/mol.

Polymerization with the series of benzyl cations $[(L)NiBz]^+$ $[BAr_f]^-$ was tested at 40 °C and 10 bar of ethylene pressure in

Table 11. Polymerization Activity of $[(L)NiBz]^+[BAr_f]^-$ at 40 °C with 10 bar of Ethylene in Et₂O

L	concn (mmol/L)	time (h)	yield (mg)	activity (kg/(mol h))
dtbpm	0.50	6	84	5.6
ptbpm	1.08	3	355	22
ctbpm	2.63	3	200	5.1
iptbpm	1.34	2	157	11.6
dcpm	1.04	3.5	129	7.8

 Et_2O , and the results are summarized in Table 11. See also the GPC traces in Figure 12.

Unreacted benzyl cations can be observed by ³¹P{¹H} NMR spectroscopy after the reaction. In a separate experiment, a solution of a benzyl cation in an NMR tube was placed under 1 bar of ethylene pressure at -78 °C and gradually warmed to room temperature. Although the precipitation of a white solid was observed in the NMR tube, no change in the ³¹P{¹H} NMR spectrum was observed. These results indicate that not all of the catalyst is active up to 40 °C, presumably due to the barrier to associative $\eta^3 - \eta^1$ conversion described above, implying that the activity of each catalytic center is higher than is indicated by the data. For comparison of the polymers produced by the catalysis, the experiment was repeated at room temperature for each cation. Table 12 shows the characteristics of the resulting polymers.

Table 12. Physical Properties of Polyethylene Produced at Room Temperature (25 °C) by $[(L)NiBz]^+[BAr_f]^-$ with 10 bar of Ethylene in Et₂O

L	melting pt (°C)	mol wt (g/mol)	total Me branches per 1000 C atoms
dtbpm	137.7	167 917	1
ptbpm	126.0	12 303	4.6
ctbpm	133.5	30 260	2.8
iptbpm	129.2	26 177	2.6
dcpm	125.1	10 825	6

Clearly, the sterically bulky dtbpm, while leading to slower catalysis, also gives much longer chains with less branching than the other diphosphine ligands. Note that the unsymmetric ligands nonetheless gave single-site catalysis, presumably because the growing polymer chain moves from one side of the ligand to the other at each insertion step.

The trend in molecular weight for the polymers produced by the benzyl cations parallels the trend observed for the much more active methyl cations, except that the ordering of the ligands ptbpm and iptbpm is inverted. However, unlike in Brookhart's system, the bulkier ligands lead to not only longer chains but also less branching.^{6,7}

Copolymerization of ethylene with 1-hexene is possible. If $[(dtbpm-\kappa^2 P)Ni(Me)(Solv)]^+[BAr_f]^-$ is used as a catalyst in Et₂O at ambient temperature, the polymerization activity amounts to 62.5 kg/(mol h). It should be noted that is close to twice as efficient as ethylene polymerization, a phenomenon which has been observed before.⁶⁹ The melting point of the copolymer is 125.4 °C, significantly lower than without 1-hexene. GPC shows an M_w value of 144 000 with PDI = 2.73, indicating again single-site catalysis. ¹³C NMR analysis reveals that 1-hexene is incorporated into the polyethylene chain with around 81 molecules per 1000 C atoms (2 mol %) and that the expected *n*-butyl side chains are formed. A typical ¹³C NMR spectrum is given in the Supporting Information.

It should also be mentioned parenthetically that the Ni dichlorides, if activated with MAO (1:1000), are polymerization catalysts if at 70 °C an ethylene pressure of 40 bar is used. Lower pressures and temperatures only lead to oily oligomers. For (dtbpm- $\kappa^2 P$)NiCl₂ polyethylene is produced with



Figure 12. GPC traces of polymers produced from the η^3 -benzyl cations at room temperature with 10 bar of ethylene in Et₂O and dtbpm, itbpm, ptbpm, and dcpm as ligands. See Table 12 for characterization.

 $M_{\rm w} = 170\ 000\ {\rm g/mol}$ but a PDI of 16.8, because there is a second, small low-molecular-weight minimum visible by GPC. As mentioned earlier and disclosed in their patent,^{41b} Brookhart et al. have tested the dibromide (dtbpm- $\kappa^2 P$)NiBr₂ with MMAO (26–28 °C, 6.9 bar), obtaining a wax-type polymer ($M_{\rm w} = 7860$, $M_{\rm n} = 3410$, PDI = 2.3).

CONCLUSIONS

Stable dichloro nickel(II) complexes bearing bulky methylenebridged diphosphine ligands (diphosphinomethanes) of the type R₂PCH₂PR'₂ are readily prepared. They physically resemble the archetypal nickel complexes with ethylene- or propylenebridged diphosphine ligands. These dichlorides can be transformed to thermally rather sensitive but fully characterized dimethyl or dibenzyl derivatives, which by protonolysis and methane or toluene loss, respectively, lead to highly sensitive cationic monomethyl and much more stable, fluxional cationic mono- η^3 -benzyl complexes. In reactions with ethylene, the new nickel methyl cations bearing these bulky diphosphine ligands, as either isolated compounds or generated in situ, are very active ethylene polymerization catalysts. Rather than oligomers, solid polyethylene is produced at room temperature and low pressure, in the absence of an activating agent. The solid-state structure of highly active THF ligated cationic monomethyl complexes of Ni(II) could be determined. For the cationic η^3 -benzyl complexes bearing the members of the sterically crowded diphosphinomethane series we also find high catalytic activity for polyethylene formation without a need for activators. The change from η^3 -benzyl to η^1 -benzyl coordination, necessary for initiating the polymer formation, does not occur by itself but is induced by ethylene association. As shown for an η^2 -stilbene complex of a diphosphine-ligated Ni(0), cationic η^3 -benzyl type Ni(II) catalysts can also be easily prepared by protonation of appropriate Ni(0) olefin complexes. As to the dependence of catalyst activity and polymer structure on diphosphinomethane ligand structure, the greater the steric bulk of the diphosphine, the longer the polymer chains that are produced but the lower the catalytic activity.

A density functional study of the complete catalytic cycle has been performed, which will be published separately.⁶⁸

EXPERIMENTAL SECTION

General Comments. All reactions and product manipulations were carried out under dry argon using standard Schlenk and glovebox (Braun instruments) techniques unless otherwise indicated. Dry, oxygen-free solvents were employed throughout, except where noted. The elemental analyses were performed by the Mikroanalytisches Laboratorium der Chemischen Institute of Heidelberg University. The following compounds were prepared by literature procedures: (dtbpm- $\kappa^2 P$)NiCl₂,^{41a} [H(OEt₂)₂]⁺[BAr_f]⁻⁷⁰ and the ligands dtbpm, ptbpm, ctbpm, iptbpm, and dcpm.⁶⁵ Methyl and benzyl Grignard reagents were purchased as THF and diethyl ether solutions, respectively, from Fluka, and their concentrations were determined by titration. Anhydrous nickel dichloride was purchased from Fluka and used without further purification. Ethylene for polymerization was of grade 2.7 and was not further purified before use.

(ptbpm- $\kappa^2 P$)NiCl₂. In a manner analogous to that reported for (dtbpm- $\kappa^2 P$)NiCl₂, anhydrous NiCl₂ (0.37 g, 2.83 mmol) was weighed into a Schlenk flask equipped with a magnetic stirrer and the ligand ptbpm (1.00 g, 2.90 mmol) was weighed into a separate Schlenk flask. Ethanol was added to both flasks (30 mL), which were then both warmed to reflux. The colorless ctbpm solution was transferred via cannula through the reflux condenser into the nickel dichloride solution, and the yellow slurry immediately became pale orange. The mixture was heated to reflux for 2.5 h, during which time the color

darkened significantly. The reaction flask was then sealed under nitrogen and cooled to -20 °C overnight, which led to the precipitation of a large quantity of a deep red solid. The product was extracted into CH₂Cl₂, filtered, and recrystallized at -60 °C.

Yield: 0.83 g (60%). Mp: 280 °C dec. Anal. Calcd for $C_{21}H_{30}NiCl_2$: C, 53.2; H, 6.38; P, 13.1; Cl, 15.0. Found: C, 53.1; H, 6.16; P, 12.8; Cl, 14.7. ¹H NMR (CD₂Cl₂, 298 K, 300 MHz): δ 1.50 (d, 18H, ³J_{HP} = 15.6 Hz, C(CH₃)₃), 2.85 (t, 2H, ²J_{HP} = 8.9 Hz, PCH₂P), 7.52 (m, 6H, *m/p*-C₆H₅), 8.22 (q, 4H, *o*-C₆H₅). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, 202.5 MHz): δ -53.5 (d, ²J_{PP} = 166.5 Hz, PPh₂), -4.4 (d, ²J_{PP} = 166.5 Hz, P(C(CH₃)₃)₂. ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 125.8 MHz): δ 24.2 (d, ¹J_{CP} = 19.2 Hz, PCH₂P), 28.2 (d, ²J_{CP} = 3.0 Hz, C(CH₃)₃), 37.2 (d, ¹J_{CP} = 8.1 Hz, C(CH₃)₃), 128.0 (d, ¹J_{CP} = 42.4 Hz, *i*-C₆H₅), 129.4 (d, ²J_{CP} = 11.1 Hz, *o*-C₆H₅), 132.3 (s, *p*-C₆H₅), 133.2 (d, ³J_{CP} = 10.1 Hz, *m*-C₆H₅). MS (FD+): *m/z* 472.0 [M]⁺ with correct isotope pattern. IR (KBr): ν [cm⁻¹] 3048 w, 2966 m, 2947 m, 2899 w, 2366 w, 1686 m, 1542 w, 1467 s, 1434 s, 1374 m, 1336 m, 1258 w, 1177 m, 1097 s, 1021 m, 809 w, 744 s, 720 s, 690 s, 523 m, 486 m, 476 m.

(ctbpm- κ^2 P)NiCl₂. This was prepared in a manner analogous to that for (ptbpm- κ^2 P)NiCl₂ with a yield of 1.38 g (98%). Mp: 319–320 °C. Anal. Calcd for C₂₁H₄₂NiCl₂: C, 51.9; H, 8.71; P, 12.7. Found: C, 51.7; H, 8.55; P, 12.7. ¹H NMR (CD₂Cl₂, 298 K, 500 MHz): δ 1.40 (m, 10H, C₆H₁₁), 1.57 (d, 18H, ³J_{HP} = 15 Hz, C(CH₃)₃), 1.75 (m, 2H, C₆H₁₁), 1.85 (m, 4H, C₆H₁₁), 2.19 (t, 2H, ²J_{HP} = 9 Hz, PCH₂P), 2.42 (m, 6H, C₆H₁₁). ³¹P{¹H} NMR (CD₂Cl₂, 298 K, 202.5 MHz): δ -30.41 (d, ²J_{PP} = 140 Hz, PCY₂), -6.11 (d, ²J_{PP} = 140 Hz, P(C(CH₃)₃)₂). ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 125.8 MHz): δ 15.51 (overlapping dd, ¹J_{CP} = 20 Hz, PCH₂P), 25.9 (s, *p*-C₆H₁₁), 26.9 (d, ²J_{CP} = 11.5 Hz, *o*-C₆H₁₁), 27.5 (d, ²J_{CP} = 11.5 Hz, *o*-C₆H₁₁), 28.4 (d, ³J_{CP} = 4 Hz, *m*-C₆H₁₁), 29.1 (s, C(CH₃)₃), 29.5 (d, ³J_{CP} = 4 Hz, *m*/C(CH₃)₃). MS (FAB): *m*/z 935.3 [2M - Cl]⁺, 486.2 [M]⁺, 449.2 [M - Cl]⁺ with correct isotope patterns. IR (KBr): *ν* [cm⁻¹] 2930 s, 2853 s, 1473 m, 1447 m, 1392 w, 1373 m, 1341 w, 1273 w, 1209 w, 1178 m, 1120 w, 1081 m, 1019 m, 889 m, 852 w, 809 m, 754 m, 718 w, 682 m, 466 w.

(iptbpm-κ²*P*)NiCl₂. This was prepared in a manner analogous to that for (ptbpm-κ²*P*)NiCl₂ with a yield of 47%. Mp: 309 °C dec. Anal. Calcd for C₁₃H₃₄P₂NiCl₂: C, 44.4; H, 8.44; Cl, 17.5; P, 15.3. Found: C, 44.2; H, 8.20; Cl, 17.5; P, 15.3. ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.37 (dd, 6H, ³*J*_{PH} = 15.4 Hz, ³*J*_{HH} = 7.2 Hz, CH(CH₃)₂), 1.49 (dd, 6H, ³*J*_{PH} = 17.0 Hz, ³*J*_{HH} = 7.2 Hz, CH(CH₃)₂), 1.58 (d, 18H, ³*J*_{PH} = 15.1 Hz, C(CH₃)₃), 2.21 (t, 2H, ²*J*_{PH} = 9.2 Hz, PCH₂P), 2.73 (6-line m, 2H, CH(CH₃)₂). ³¹P{¹H} NMR (122 MHz, CD₂Cl₂, 298 K): δ -5.2 (d, ²*J*_{PP} = 140.8 Hz, P(C(CH₃)₃)₂), -21.7 (d, ²*J*_{PP} = 140.8 Hz, P(ⁱPr)₂). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 298 K): δ 16.6 (overlapping dd, ²*J*_{CP} = 19.3 Hz, PCH₂P), 18.1 (s, CH(CH₃)₂), 19.7 (s, CH(CH₃)₂), 25.6 (d, ²*J*_{CP} = 16.0 Hz, CH(CH₃)₂), 29.4 (d, ²*J*_{CP} = 2.2 Hz, C(CH₃)₃), 37.4 (d, ¹*J*_{CP} = 8.7 Hz, C(CH₃)₃). MS (FAB): *m/z* 773.2 [2M - Cl]⁺, 404.1 [M]⁺, 369.1 [M - Cl]⁺ with correct isotope patterns. IR (KBr): ν [cm⁻¹] 2959 m, 2871 m, 2359 w, 2340 w, 1634 w, 1470 s, 1374 m, 1258 w, 1179 m, 1091 m, 1050 m, 1023 m, 887 w, 811 w, 767 m, 708 m, 696 m, 574 w, 482 w.

(dcpm- $\kappa^2 P$)NiCl₂. This was prepared in a manner analogous to that for (ptbpm- $\kappa^2 P$)NiCl₂ in 70% yield. Mp: 347 °C dec. Anal. Calcd for C₂₅H₄₆P₂NiCl₂: C, 55.79; H, 8.62; Cl, 13.18; P, 11.51. Found: C, 55.62; H, 8.74; Cl, 13.19; P, 11.54. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 1.2–2.6 (m, C₆H₁₁ and PCH₂P). ³¹P{¹H} NMR (122 MHz, CDCl₃, 298 K): δ –24.06; note that this differs from the reported value of δ –32.5.^{56 13}C{¹H} NMR (75 MHz, CDCl₃, 298 K): δ 13.6 (t, ¹J_{PC} = 20.3 Hz, PCH₂P), 25.7 (C₆H₁₁), 26.6 (C₆H₁₁), 27.0 (C₆H₁₁), 27.8 (C₆H₁₁), 29.0 (C₆H₁₁), 34.9 (C₆H₁₁). MS (FAB): *m/z* 536 [M]⁺, 501 [M – Cl]⁺ with correct isotope patterns. IR (KBr): ν [cm⁻¹] 2921 s 2854 s, 2358 w, 1449 m, 1326 w, 1294 w, 1264 w, 1204 w, 1179 w, 1111 w, 1069 m, 1046 w, 1026 w, 996 w, 915 w, 885 w, 850 w, 820 w, 774 w, 746 w, 708 w, 684 w, 655 w, 530 w, 510 w, 462 w.

(dtbpm- $\kappa^2 P$)NiMe₂. In a Schlenk tube, 1.0 g (2.31 mmol) of (dtbpm- $\kappa^2 P$)NiCl₂ was suspended in 25 mL of THF and the suspension stirred overnight at room temperature. The mixture was then cooled to -78 °C, and a dropping addition funnel was added to

the flask. The methyl Grignard solution (1.6 mL of 2.9 M in THF, 4.64 mmol) was diluted with 25 mL of THF, transferred to the addition funnel, and then added to the cooled suspension over 4 h with stirring. After the addition was complete, the suspension was stirred at -20 °C for 1 h. The solvent was then removed under dynamic vacuum, and the yellow-gray residue was extracted into toluene (3 × 10 mL) and filtered through Celite. The filtrate was cooled to -30 °C to avoid decomposition. The volume of toluene was reduced by half at 0 °C under dynamic vacuum and cooled to -30 °C, which resulted in the precipitation of yellow crystals. These were washed with cold toluene and dried under vacuum. A second crop of crystals was also obtained from the mother liquor. The compound is thermally sensitive in solution and in the solid state, with a half-life at room temperature of less than 1 h in solution and 1 week in the solid state.

Yield: 560 mg (62%). Mp: 92–94 °C dec. Anal. Calcd for C₁₉H₄₄-NiP₂: C, 58.1; H, 11.2; Ni, 14.9; P, 15.8. Found: C, 57.7; H, 11.3; Ni, 15.0; P, 15.3. ¹H NMR (270 MHz, C₆D₆, 278 K): δ 0.57 ("t", 6H, ³J_{cis-PH} + ³J_{trans-PH} = 7.32 Hz, Ni(CH₃)₂), 1.25 ("t", 36H, ³J_{PH} + ⁵J_{PH} = 11.7 Hz, C(CH₃)₃), 2.15 (t, 2H, ²J_{PH} = 6.35 Hz, PCH₂P). ³¹P{¹H} NMR (109 MHz, toluene-d₈, 273 K): δ 17.9 (s). ¹³C{¹H} NMR (75.5 MHz, toluene-d₈, 273 K): δ 0.16 (d, ²J_{PC} = 59.7 Hz, Ni(CH₃)₂), 25.2 (t, ¹J_{PC} = 4.85 Hz, PCH₂P), 31.1 ("t", ²J_{PC} + ⁴J_{PC} = 2.29 Hz, C(CH₃)₃), 35.1 (dd, ³J_{PC} = 1.84 Hz, C(CH₃)₃). IR (KBr): ν [cm⁻¹]: 2990 vs, 2950 vs, 2865 vs, 1636 vs, 1479 s, 1390 m, 1365 m, 1260 w, 1165 s, 1104 m, 1019 m, 934 w, 813 s, 736 m, 676 m, 567 m.

(ptbpm- $\kappa^2 P$)NiMe₂. In a Schlenk flask, 1 g (2.1 mmol) (ptbpm- $\kappa^2 P$)NiCl₂ was suspended in 25 mL of THF and the suspension cooled to -35 °C. In a dropping addition funnel, 1.77 mL (4.2 mmol) of methyl Grignard solution (2.38 M in THF) was diluted with 25 mL of THF and added to the suspension at -35 °C, which resulted in a yellow solution. The solvent was removed under vacuum at room temperature, and the product was extracted into diethyl ether and decanted from the MgCl₂. Upon cooling to -40 °C, a small amount of precipitate formed (MgCl₂) and the solution was once more decanted. The volume was reduced to 15 mL under dynamic vacuum and the product crystallized at -40 °C. The crystals were collected and washed twice with cold diethyl ether to remove the faint black discoloration.

Yield: 720 mg (79%) Mp: 104 °C dec. Anal. Calcd for $C_{23}H_{36}P_2Ni$: C, 63.77; H, 8.38; P, 14.30. Found: C, 62.96; H, 8.16; P, 14.02. ¹H NMR (300 MHz, d_8 -toluene, 298 K): δ 0.83 (dd, 3H, ${}^{3}J_{cisPH} = 4.4$ Hz, ${}^{3}J_{trans-PH} = 10.9$ Hz, NiCH₃), 0.94 (dd, 3H, ${}^{3}J_{cisPH} = 3.7$ Hz, ${}^{3}J_{trans-PH} = 11.7$ Hz, NiCH₃), 1.32 (d, 18H, ${}^{3}J_{PH} = 12.4$ Hz, C(CH₃)₃), 2.79 (°t", 2H, ${}^{2}J_{PH} = 4.4$ Hz, ${}^{2}J_{PH} = 10.9$ Hz, PCH₂P), 7.26 (m, o/p-C₆H₃), 8.02 (t, ${}^{3}J_{HH} = 7.86$ Hz, m-C₆H₅). ${}^{31}P{}^{1}H$ NMR (122 MHz, d_8 -toluene, 298 K): δ -20.5 (d, ${}^{2}J_{PP} = 8.9$ Hz, PPh₂), 19.6 (d, ${}^{2}J_{PP} = 8.9$ Hz, P(C(CH₃)₃)₂). ${}^{13}C{}^{1}H$ NMR (75 MHz, d_8 -THF, 298 K): δ 1.1 (dd, ${}^{2}J_{cis-PC} = 13.81$ Hz, ${}^{2}J_{trans-PC} = 80.3$ Hz, NiCH₃), 2.3 (dd, ${}^{2}J_{cis-PC} = 15.2$ Hz, ${}^{2}J_{trans-PC} = 73.35$ Hz, NiCH₃), 29.2 (d, ${}^{2}J_{PC} = 5.5$ Hz, C(CH₃)₃), 30.5 (dd, ${}^{1}J_{PC} = 9.69$ Hz, ${}^{1}J_{PC} = 17.99$ Hz, PCH₂P), 34.1 (dd, ${}^{1}J_{PC} = 9.00$ Hz, ${}^{3}J_{PC} = 3.46$ Hz, o-C₆H₅), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}CCH_{3}$), 134.9 (dd, ${}^{1}J_{PC} = 16.51$ Hz, ${}^{3}J_{PC} = 9.69$ Hz, ${}^{i}C-6H_{5}$). IR (KBr): ν [cm⁻¹] 3054 w, 2953 s, 2899 s, 2867 m, 2361 w, 2342 w, 1636 w, 1592 w, 1473 m, 1437 m, 1369 w, 1168 s, 1125 s, 1096 s, 1024 s, 936 m, 814 m, 739 m, 721 s, 697 s, 510 m.

(iptbpm- $\kappa^2 P$)NiMe₂. In a Schlenk flask, 395 mg (0.97 mmol) of (iptbpm- $\kappa^2 P$)NiCl₂ was suspended in 20 mL of THF and the suspension cooled to -35 °C. At this temperature, a solution of 0.65 mL (1.95 mmol) methyl Grignard (3 M in THF), diluted with 10 mL of THF, was added over several hours. The suspension dissolved to an orange solution, which was stirred for 30 min at -10 °C, following which the solvent was completely removed under dynamic vacuum. The solid was extracted into diethyl ether, filtered through Celite, and then cooled to -40 °C to crystallize. X-ray-quality crystals were obtained. A second crop of crystals was obtained by reducing the volume of the mother liquor.

Yield: 300 mg (85%) Mp: 110 °C dec. Anal. Calcd for $C_{17}H_{40}P_2Ni$: C, 55.92; H, 11.04; P, 16.97. Found: C, 55.00; H, 11.19; P, 16.46. ¹H NMR (300 MHz, C_6D_6 , 298 K): δ 0.50 ("t", 3H, ³J_{PH} = 4.8 Hz, NiCH₃), 0.54 ("t", 3H, ³J_{PH} = 4.53 Hz, NiCH₃), 1.06 (dd, 6H, ³J_{PH} = 12.81 Hz, ${}^{3}J_{\text{HH}} = 7.18$ Hz, $\text{CH}(\text{CH}_{3})_{2}$), 1.07 (dd, 6H, ${}^{3}J_{\text{PH}} = 12.99$ Hz, ${}^{3}J_{\text{HH}} = 7.35$ Hz, $\text{CH}(\text{CH}_{3})_{2}$), 1.20 (d, 18H, ${}^{3}J_{\text{PH}} = 12.0$ Hz, $\text{C}(\text{CH}_{3})_{3}$), 1.85 ("t", 2H, ${}^{2}J_{\text{PH}} = 7.14$ Hz, PCH_{2}P), 1.98 (m, 2H, $\text{CH}(\text{CH}_{3})_{2}$). ${}^{31}\text{P}\{^{1}\text{H}\}$ NMR (122 MHz, $C_{6}D_{6}$, 298 K): δ 1.0 (d, ${}^{2}J_{\text{PP}} = 13.36$ Hz, $\text{P}({}^{\text{i}}\text{Pr})_{2}$, 19.1 (d, ${}^{2}J_{\text{PP}} = 13.36$ Hz, $\text{P}(\text{C}(\text{CH}_{3})_{3})_{2}$). ${}^{13}\text{C}\{^{1}\text{H}\}$ NMR (75 MHz, $C_{6}D_{6}$, 298 K): δ 0.0 (dd, ${}^{2}J_{\text{cis-PC}} = 6.63$ Hz, ${}^{2}J_{\text{rans-PC}} = 9.50$ Hz, NiCH₃), 0.6 (dd, ${}^{2}J_{\text{cis-PC}} = 4.03$ Hz, ${}^{2}J_{\text{rans-PC}} = 8.63$ Hz, NiCH₃), 19.5 (d, ${}^{2}J_{\text{PC}} = 17.86$ Hz, $\text{CH}(\text{CH}_{3})_{2}$), 22.1 ("t", ${}^{1}J_{\text{PC}} = 6.05$ Hz, PCH_{2}P), 24.5 (dd, ${}^{1}J_{\text{PC}} = 4.61$ Hz, ${}^{3}J_{\text{PC}} = 1.15$ Hz, $\text{CH}(\text{CH}_{3})_{2}$), 29.6 (d, ${}^{2}J_{\text{PC}} = 3.46$ Hz, $\text{C}(\text{CH}_{3})_{3}$), 34.6 (dd, ${}^{1}J_{\text{PC}} = 4.60$ Hz, ${}^{3}J_{\text{PC}} = 2.30$ Hz, $\text{C}(\text{CH}_{3})_{3}$). IR (KBr): ν [cm⁻¹] = 2951 s, 2867 s, 1469 s, 1386 w, 1367 m, 1178 m, 1093 m, 1043 w, 1020 m, 939 w, 884 w, 912 m, 746 m, 688 m, 593 w, 485 w.

(dcpm- $\kappa^2 P$)NiMe₂. The dichloride (dcpm- $\kappa^2 P$)NiCl₂ (523 mg, 0.88 mmol) was weighed into a Schlenk tube, dissolved in 30 mL of THF, and cooled to -50 °C, and 0.61 mL (1.76 mmol) of a methyl Grignard solution (2.9 M in THF) was added with stirring. The reaction mixture was stirred for 1 h at -40 °C, during which time the solution remained red. Gradual warming to +10 °C led to a color change to yellow. The solvent was then removed under dynamic vacuum, leaving a pale yellow solid, which was extracted into toluene (3 × 10 mL) and filtered through Celite. The volume was reduced by half under dynamic vacuum, and the yellow-brown solution was cooled to -78 °C. This led to X-ray-quality crystals, which were washed with cold pentane and dried under vacuum.

Yield: 363 mg (83%). Mp: 128 °C dec. Anal. Calcd for $C_{27}H_{52}P_2N_i$: C, 65.21; H, 10.54; P, 12.46. Found: C, 65.28; H, 10.70; P, 12.21. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 0.68 (dd, 6H, ³J_{cis-PH} = 4.2 Hz, ³J_{trans-PH} = 11.1 Hz, Ni(CH₃)₂), 1.1–2.4 (m, 44H, C₆H₁₁). ³¹P{¹H} NMR (122 MHz, C₆D₆, 298 K): δ -4.50 (s). ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): δ 0.26 (dd, ²J_{trans-PC} = 75 Hz, ²J_{cis-PC} = 15.5 Hz, Ni(CH₃)₂), 20.69 (t, ¹J_{PC} = 12.2 Hz, PCH₂P), 26.57 (s, C₆H₁₁), 27.44 (d, ²J_{PC} = 8.8 Hz, o-C₆H₁₁), 27.62 (d, ²J_{PC} = 11.0 Hz, o-C₆H₁₁), 29.29 (s, C₆H₁₁), 29.63 (d, ³J_{PC} = 3.3 Hz, m-C₆H₁₁), 35.15 (d, ¹J_{PC} = 11 Hz, *i*-C₆H₁₁). IR (KBr): ν [cm⁻¹] = 2919 s, 2849 s, 1447 m, 1341 w, 1265 w, 1176 w, 1103 w, 1066 w, 997 w, 915 w, 890 w, 850 w, 819 w, 755 w.

[(dtbpm- $\kappa^2 P$)NiMe(THF)]⁺[BAr_f]⁻. The isolated dimethyl complex (dtbpm- $\kappa^2 P$)NiMe₂ (15 mg, 38.1 μ mol) was weighed into a Schlenk flask with 38.6 mg (38.1 μ mol) of [H(OEt₂)₂]⁺[BAr_f]⁻. At room temperature, 5 mL of diethyl ether and 1 mL of THF were added and the mixture was stirred. Gas evolution was observed. After 10 min the solvent volume was reduced to ca. 1 mL under dynamic vacuum and 5 mL of pentane was carefully added. Within 2 h, yellow crystals formed on the walls of the flask. These crystals were of X-ray quality.

Yield: 45.8 mg (71%) (quantitative by NMR) Mp: 125 °C dec. Anal. Calcd for C₅₄H₆₁P₂NiOBF₂₄: C, 49.38; H, 4.68; P, 4.72. Found: C, 49.50; H, 4.55; P, 4.79. ¹H NMR (500 MHz, d_8 -THF, 298 K): δ -0.33 (dd, 3H, ${}^{3}J_{PH} = 3.00$ Hz, ${}^{3}J_{PH} = 4.35$ Hz, NiCH₃), 1.53 (d, 18H, ${}^{3}J_{\rm PH} = 13.05$ Hz, C(CH₃)₃), 1.61 (d, 18H, ${}^{3}J_{\rm PH} = 14.05$ Hz, C(CH₃)₃), 2.72 (dd, 2H, ${}^{2}J_{\rm PH}$ = 10 Hz, ${}^{2}J_{\rm PH}$ = 6.4 Hz, PCH₂P), 7.58 (s, 4H, $p-C_6H_3(CF_3)_2$, 7.80 (s, 8H, $o-C_6H_3(CF_3)_2$). ³¹P{¹H} NMR (300 MHz, d_8 -THF, 298 K): δ 9.7 (d, ${}^2J_{PP}$ = 22.1 Hz), 37.8 (d, ${}^2J_{PP}$ = 22.1 Hz). ¹³C{¹H} NMR (126 MHz, d_8 -THF, 298 K): δ –9.37 (dd, ² J_{PC} = 40.1 Hz, ${}^{2}J_{PC} = 59.4$ Hz, NiCH₃), 22.62 (dd, ${}^{1}J_{PC} = 10.4$ Hz, ${}^{1}J_{PC} = 13.7$ Hz, PCH₂P), 31.19 (d, ${}^{2}J_{PC} = 6.1$ Hz, C(CH₃)₃), 31.34 (d, ${}^{2}J_{PC} = 2.8$ Hz, C(CH₃)₃), 36.47 (dd, ${}^{1}J_{PC} = 3.8$ Hz, ${}^{3}J_{PC} = 1.4$ Hz, C(CH₃)₃), 38.72 (dd, ${}^{1}J_{PC}$ = 13.7 Hz, ${}^{3}J_{PC}$ = 5.2 Hz, C(CH₃)₃), 118.35 (m, p- $C_6H_3(CF_3)_2$), 125.68 (q, ${}^1J_{CF}$ = 272.3 Hz, CF₃), 130.32 (qm, ${}^2J_{CF}$ = 31.6 Hz, $M - C_6H_3(CF_3)_2$), 135.88 (s, $o-C_6H_3(CF_3)_2$), 163.13 (q, ${}^{1}J_{BC} = 49.5 \text{ Hz}, i \cdot C_{6}H_{3}(CF_{3})_{2}$). MS (FAB): m/z 377.2 [(dtbpm)-NiMe]⁺, 1617.5 $[2*[(dtbpm)NiMe]^+ + [BAr_f]^-]^+$ with correct isotope patterns. IR (KBr): ν [cm⁻¹] 2965 w, 1612 w, 1481 w, 1356 s, 1167 s, 1135 s, 1026 w, 887 w, 839 w, 808 w, 715 m, 683 m, 670 m.

[(ptbpm- $\kappa^2 P$)NiMe(THF- d_8)]⁺[BAr_f]⁻. The isolated dimethyl complex (ptbpm)NiMe₂ (5.7 mg, 13.2 μ mol) and 13.3 mg (13.2 μ mol) of [H(OEt₂)₂]⁺[BAr_f]⁻ were weighed into an NMR tube and dissolved in 0.4 mL of d_8 -THF. Gas evolution was observed, and the

solution became yellow-orange. Ratio of isomers: 1.7:1 A:B (Figure 6) on the basis of an integration of the ${}^{31}P\{^{1}H\}$ NMR spectrum.

¹H NMR (300 MHz, *d*₈-THF, 298 K): δ –0.15 (dd, 3H, ${}^{3}J_{PH} = 4.52$ Hz, ${}^{3}J_{PH} = 2.83$ Hz, NiCH₃), –0.08 (dd, 3H, ${}^{3}J_{PH} = 5.27$ Hz, ${}^{3}J_{PH} = 2.45$ Hz, NiCH₃), 1.39 (d, 18H, ${}^{3}J_{PH} = 13.75$ Hz, C(CH₃)₃), 1.47 (d, 18H, ${}^{3}J_{PH} = 14.69$ Hz, C(CH₃)₃), 7.57 (s, 8H, *p*-C₆H₃(CF₃)₂), 7.60 (m, 12H, *o*,*p*-C₆H₅), 7.79 (s, 16H, *o*-C₆H₃(CF₃)₂), 7.90 (m, 8H, *m*-C₆H₅). ${}^{31}P{}^{1}H$ NMR (122 MHz, *d*₈-THF, 298 K): δ –29.2 (d, ${}^{2}J_{PP} = 26.6$ Hz, PPh₂, **A**), 4.9 (d, ${}^{2}J_{PP} = 28.8$ Hz, PPh₂, **B**), 17.2 (d, ${}^{2}J_{PP} = 28.9$ Hz, P(C(CH₃)₃)₂, **B**), 43.3 (d, ${}^{2}J_{PP} = 26.5$ Hz, P(C(CH₃)₃)₂, **A**).

[(iptbpm- $\kappa^2 P$)NiMe(THF- d_8)]⁺[BAr_f]⁻. The reaction was conducted in a manner exactly analogous to that for the ptbpm analogue. Isomer **B** is formed in a 6-fold excess (determined by ³¹P{¹H} NMR spectroscopy).

¹H NMR (300 MHz, d_8 -THF, 298 K): δ –0.39 (dd, 3H, ${}^{3}J_{PH}$ = 2.60 Hz, ${}^{3}J_{PH}$ = 4.34 Hz, NiCH₃, **B**), –0.31 (br s, NiCH₃, A), 1.30 (dd, 6H, ${}^{2}J_{HH}$ = 7.06 Hz, ${}^{3}J_{PH}$ = 15.04 Hz, CH(CH₃)₂), 1.46 (d, 18H, ${}^{3}J_{PH}$ = 13.54 Hz, C(CH₃)₃), 2.4 (m, 2H, PCH₂P), 2.6 (m, 2H, CH(CH₃)₂). ³¹P{¹H} NMR (122 MHz, d_8 -THF, 298 K): δ –9.6 (d, ${}^{2}J_{PP}$ = 20.9 Hz, P(ⁱPr)₂, **A**), 14.1 (d, ${}^{2}J_{PP}$ = 21.4 Hz, P(ⁱPr)₂, **B**), 27.7 (d, ${}^{2}J_{PP}$ = 21.3 Hz, P(C(CH₃)₃)₂, **B**), 41.3 (d, ${}^{2}J_{PP}$ = 20.9 Hz, P(C(CH₃)₃)₂, **A**).

 $[(dcpm-\kappa^2 P)NiMe(THF)]^+[BAr_f]^-$. The reaction was conducted in a manner identical to that for the ptbpm analogue.

¹H NMR (300 MHz, *d*₈-THF, 298 K): *δ* –0.44 (dd, 3H, ³*J*_{PH} = 2.64 Hz, ³*J*_{PH} = 4.52 Hz, NiCH₃), 1.20 – 2.41 (br m, 44H, C₆H₁₁), 2.46 (dd, 2H, ²*J*_{PH} = 8.10 Hz, ²*J*_{PH} = 11.11 Hz, PCH₂P), 7.57 (s, 4H, *p*-C₆H₃(CF₃)₂), 7.79 (s, 8H, *o*-C₆H₃(CF₃)₂). ³¹P{¹H} NMR (122 MHz, *d*₈-THF, 298 K): *δ* –13.1 (d, ²*J*_{PP} = 34.0 Hz), 23.0 (d, ²*J*_{PP} = 34.0 Hz).

(dtbpm- $\kappa^2 P$)NiBz₂. The dichloride complex (dtbpm- $\kappa^2 P$)NiCl₂ (60 mg, 138.6 μ mol) was suspended in 15 mL of pentane and cooled to -40 °C, the benzyl Grignard solution (0.28 mL of 1.0 M in diethyl ether, 280 μ mol) was added, and the reaction mixture was stirred for 4 h at that temperature. The pentane solution became pale red. The solvent was decanted, and the solid product was washed twice with pentane. Finally, the product was extracted into diethyl ether, and the extract was filtered through a cold Celite pad and used directly in the synthesis of [(dtbpm- $\kappa^2 P$)NiBz]+[BAr_f]⁻. The ³¹P{¹H} NMR spectrum of a part of the product was collected after filtration, upon removing the diethyl ether under vacuum. No yield was determined because of the product's high instability.

³¹P{¹H} NMR (122 MHz, d_8 -THF, 228 K): δ 11.1 (s).

(ptbpm- $\kappa^2 P$)NiBz₂. The dichloride complex (ptbpm- $\kappa^2 P$)NiCl₂ (200 mg, 0.42 mmol) was suspended in 10 mL of THF and cooled to -25 °C. Over a period of 45 min, 0.84 mL (0.84 mmol) of a benzyl Grignard solution (1 M in diethyl ether) diluted with 10 mL of THF was added. The reaction mixture was then stirred for another 45 min at that temperature, following which the THF was removed under dynamic vacuum and the product was extracted into toluene. Filtration through Celite led to a red solution. The volume of toluene was reduced by half under dynamic vacuum, and the solution was cooled to -40 °C, which resulted in crystallization of the product. The crystals were washed in pentane and dried under vacuum.

Yield: 152 mg (62%). Mp: 49 °C dec. Anal. Calcd for $C_{35}H_{44}P_2Ni$: C, 71.82; H, 7.58; P, 10.58. Found: C, 71.64; H, 7.73; P, 10.34. ¹H NMR (300 MHz, C_6D_6 , 298 K): δ 1.06 (d, 18H, ³J_{PH} = 12.5 Hz, C(CH₃)₃), 2.39 (dd, 2H, ²J_{PH} = 8.16 Hz, ²J_{PH} = 6.66 Hz, PCH₂P), 2.89 (s, 4H, CH₂C₆H₅), 7.10 (br m, 16H, C₆H₅), 7.55 (m, 4H, C₆H₅). ³¹P{¹H} NMR (122 MHz, C₆D₆, 298 K): δ –11.5 (d, ²J_{PP} = 28.6 Hz, PPh₂), 22.3 (d, ²J_{PP} = 28.6 Hz, P(C(CH₃)₃)₂).

(ctbpm- $\kappa^2 P$)NiBz₂. The dichloride complex (ctbpm- $\kappa^2 P$)NiCl₂ (0.44 g, 0.9 mmol) was weighed in the box into a round-bottomed flask equipped with a magnetic stirrer. Pentane (40 mL) was added, and the slurry was cooled to -60 °C. Benzyl Grignard (2.6 mL of 0.71 M solution in diethyl ether, 1.8 mmol) was added, and the slurry was stirred at a temperature between -60 and -40 °C for 4 h. During this time, the solid observed on the walls of the flask changed from red to orange in color. After 4 h, stirring was stopped and the slurry was allowed to settle for 1 h. Decantation was attempted; however, a significant amount of solid was transferred as well. The residue was dried in vacuo and then extracted into diethyl ether, and the resulting orange solution was cooled to -78 °C and used in the subsequent reaction. A small fraction of the solid was extracted into $C_6 D_6$, and the $^1\mathrm{H}$ and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra were measured. The product was not isolated, and no yield was determined.

¹H NMR ($C_6D_{6^{\prime}}$ 300K, 300 MHz): δ 1.17 (m, 8H, C_6H_{11}), 1.28 (d, 18H, ${}^{3}J_{HP} = 12$ Hz, $C(CH_3)_3$), 1.7 (br m, 8H, C_6H_{11}), 1.81 ("t", 2H, ${}^{2}J_{HP} = 7$ Hz, PCH₂P), 1.95 (br, C_6H_{11}), 2.03 (br, C_6H_{11}), 2.70 (s, 4H, $CH_2C_6H_5$), 7.12 (t, 2H, ${}^{3}J_{HH} = 7.14$ Hz, C_6H_5), 7.31 (m, 4H, C_6H_5), 7.58 (d, 4H, ${}^{3}J_{HH} = 7.35$ Hz, C_6H_5). ${}^{31}P{}^{1}H{}$ NMR ($C_6D_{6^{\prime}}$ 300K, 121.5 MHz): δ -6.24 (d, ${}^{2}J_{PP} = 30$ Hz, PCy₂), 18.8 (d, ${}^{2}J_{PP} = 30$ Hz, P(C(CH₃)₃).

(iptbpm- $\kappa^2 P$)NiBz₂. The dichloride complex (iptbpm- $\kappa^2 P$)NiCl₂ (164 mg, 0.405 mmol) was suspended in 10 mL of THF and cooled to -25 °C. While the suspension was stirred, 2 equiv of a benzyl Grignard solution (0.81 mL of a 1.0 M solution in diethyl ether diluted with 10 mL of THF) was added. The solution became red. After addition of the Grignard reagent the reaction was stirred at the same temperature for a further 30 min. The solvent was then removed under dynamic vacuum, and the residue was extracted into toluene and the extract filtered through Celite. Careful addition of pentane and cooling to -40 °C led to the precipitation of the product.

Yield: 119.2 mg (57%). Mp: 83 °C dec. Anal. Calcd for $C_{29}H_{48}P_2Ni$: C, 67.33; H, 9.35. Found: C, 67.20; H, 9.37. ¹H NMR (300 MHz, C_6D_6 , 298 K): δ 0.91 (dd, 6H, ${}^{3}J_{PH}$ = 11.7 Hz, ${}^{2}J_{HH}$ = 7.1 Hz, CH- $(CH_{3})_{2}$), 1.05 (dd, 6H, ${}^{3}J_{PH} = 14.0$ Hz, ${}^{2}J_{HH} = 7.2$ Hz, $CH(CH_{3})_{2}$), 1.20 (d, 18H, ${}^{3}J_{PH} = 12.0$ Hz, C(CH₃)₃), 1.66 (t, 2H, ${}^{2}J_{PH} = 7.2$ Hz, PCH₂P) 1.82 (dsept, 2H, ${}^{2}J_{PH} = 2.4$ Hz, ${}^{2}J_{HH} = 7.2$ Hz, $CH(CH_{3})_{2}$), 7.07 (t, 2H, ${}^{3}J_{HH} = 7.2$ Hz, $p-C_{6}H_{5}$), 7.26 ("t", 4H, ${}^{3}J_{HH} = 7.5$ Hz, m- $\begin{array}{l} C_{6}H_{5}), \ 7.52 \ (d, \ 4H, \ ^{3}J_{HH} = 7.5 \ Hz, \ o-C_{6}H_{5}), \ ^{31}P_{1}^{1}H_{1} \ NMR \ (122 \ MHz, \ C_{6}D_{6}, \ 298 \ K): \ \delta \ 1.71 \ (d, \ ^{2}J_{PP} = 27.8 \ Hz, \ P(^{P}P_{2}), \ 17.60 \ (d, \ ^{2}J_{PP} = 27.8 \ Hz, \ P(C(CH_{3})_{3})_{2}). \ ^{13}C_{1}^{1}H_{1} \ NMR \ (75 \ MHz, \ C_{6}D_{6}, \ 298 \ N) \ (75 \ MHz, \ C_{6}D_{6}, \ N) \ (75 \ MHz, \ N) \ (75 \ MLz, \ N)$ K): δ 18.9 (s, CH(CH₃)₂), 20.6 (s, CH(CH₃)₂), 24.7 (d, ¹J_{PC} = 8.3 Hz, $CH(CH_3)$), 29.9 (d, ${}^{2}J_{PC}$ = 5.5 Hz, $C(CH_3)_3$), 30.15 (m, N = 13.2 Hz, PCH₂P), 34.8 (dd, ${}^{2}J_{PC} = 7.3$ Hz, ${}^{2}J_{PC} = 5.3$ Hz, $CH_{2}C_{6}H_{5}$), 38.2 (s, C(CH₃)₃), 121.18 (s, o-C₆H₅), 126.22 (s, p-C₆H₅), 128.74 (s, m- C_6H_5), 154.5 (s, *i*- C_6H_5). MS (FAB): m/z 516 [M]⁺ (isotope pattern not completely correct due to overlap), 425 $[M + H - toluene]^+$ (correct isotope pattern). IR (KBr): ν [cm⁻¹] 3061 w, 3027 m, 2957 s. 2869 s, 1602 w, 1494 w, 1468 m, 1454 m, 1385 m, 1365 m, 1262 m, 1178 s, 1163 s, 1095 s, 1022 m, 941 m, 885 w, 815 s, 794 w, 752 s, 698 s, 641 w, 591 w, 520 w, 483 w.

(dcpm- $\kappa^2 P$)NiBz₂. The dichloride complex (dcpm- $\kappa^2 P$)NiCl₂ (200 mg, 0.37 mmol) was suspended in pentane (10 mL). At room temperature, 0.74 mL (0.74 mmol) of a benzyl Grignard solution (1 M in diethyl ether) was added. After 30 min, the solution was pale red, and the solid had changed color slightly. The product was extracted into toluene and the extract filtered through Celite. Pentane was carefully added to the flask and the product crystallized at -40 °C.

Yield: 175.2 mg (73%). Mp: 96 °C dec. Anal. Calcd for $C_{39}H_{60}P_2$ Ni: C, 72.1; H, 9.31; P, 9.54. Found: C, 72.3; H, 9.48; P, 9.39. ¹H NMR (S00 MHz, C_6D_6 , 298 K): δ 1.16 (m, 16H, C_6H_{11}), 1.36 (m, 8H, C_6H_{11}), 1.74 (m, 16H, C_6H_{11}), 2.10 (m, 6H, C_6H_{11} and PCH₂P), 2.69 (s, 4H, $CH_2C_6H_5$), 7.04 (t, 2H, ³ J_{HH} = 7.35 Hz, p- C_6H_5), 7.24 ("t", 4H, ³ J_{HH} = 7.70 Hz, m- C_6H_5), 7.49 (d, 4H, ³ J_{HH} = 7.70 Hz, o- C_6H_5). ³¹P NMR (122 MHz, C_6D_6 , 298 K): δ -4.13 (s). ¹³C NMR (126 MHz, C_6D_6 , 298 K): δ 17.03 (t, ¹ J_{PC} = 14.2 Hz, PCH₂P), 26.73 (s, C_6H_{11}), 27.59 (s, C_6H_{11}), 27.80 (m, C_6H_{11}), 29.28 (s, C_6H_{11}), 30.41 (s, C_6H_{11}), 34.83 (m, $CH_2C_6H_5$), 120.95 (s, o- C_6H_5). 128.94 (s, m- C_6H_5), 129.47 (s, p- C_6H_5), 155.35 (s, *i*- C_6H_5). MS (FAB): m/z 557 [M + H - toluene]⁺ with correct isotope pattern. IR (KBr): ν [cm⁻¹] 3061 w, 3027 w, 2927 s, 2825 m, 2361 s, 2342 m, 1449 w, 1262 m, 1217 w, 1161 m, 1098 s, 1022 s, 889 w, 855 w, 800 s, 698 m, 669 w.

[(dtbpm- $\kappa^2 P$)Ni(η^3 -CH(CH₂Ph)Ph)]⁺[BAr_f]⁻. In a Schlenk flask, 200 mg (0.37 mmol) of (η^2 -trans-stilbene)[(dtbpm- $\kappa^2 P$)Ni⁰] and 372.5 mg (0.37 mmol) of [H(OEt₂)₂]⁺[BAr_f]⁻ were dissolved at 0 °C in 20 mL of diethyl ether. After the mixture was stirred for 25 min, 20 mL of pentane was added, which led to the precipitation of a pale brown solid. The solution was removed via cannula, and the solid was washed twice with pentane (5 mL each) and dried under vacuum.

Yield: 476 mg (0.34 mmol, 91%). Mp: 158 °C dec. Anal. Calcd for C43H63P2NiBF24: C, 53.76; H, 4.51; P, 4.40. Found: C, 53.67; H, 4.60; P, 4.31. ¹H NMR (500 MHz, d_6 -acetone, 298 K): δ 1.26 (d, 9H, ³ J_{PH} = 13.8 Hz, C(CH₃)₃), 1.43 (d, 9H, ${}^{3}J_{PH}$ = 13.8 Hz, C(CH₃)₃), 1.61 (d, 9H, ${}^{3}J_{PH}$ = 14.2 Hz, C(CH₃)₃), 1.63 (d, 9H, ${}^{3}J_{PH}$ = 14.2 Hz, C(CH₃)₃), 3.13 (m, 2H, CH₂C₆H₅), 3.27 (m, 2H, PCH₂P), 3.83 (m, 1H, NiCHCH₂), 6.86 (d, 1H, o-C₆H₅ on Ni), 7.13 (m, N = 44.9 Hz, 6H, C_6H_5 and $o-C_6H_5$ on Ni), 7.52 ("t", ${}^3J_{HH} = 7.5$ Hz, 1H, $m-C_6H_5$ on Ni), 7.52 (s, 4H, $p-C_6H_3(CF_3)_2$), 7.58 ("t", ${}^3J_{HH} = 7.5$ Hz, 1H, $m-C_6H_5$ on Ni), 7.74 (m, 1H, p-C₆H₅ on Ni), 7.79 (s, 8H, o-C₆H₃(CF₃)₂). ³¹P{¹H} NMR (122 MHz, d_8 -THF, 298 K): δ 16.8 (d, ² J_{PP} = 20.9 Hz), 29.6 (d, ${}^{2}J_{PP}$ = 20.9 Hz). ${}^{13}C{}^{1}H$ NMR (75 MHz, d_{8} -THF, 298 K): δ 24.8 (m, PCH₂P), 30.7-31.6 (m, C(CH₃)₃), 37.0 (m, C(CH₃)₃), 37.7 (s, NiCHCH₂C₆H₅), 38.6 (m, C(CH₃)₃), 53.9 (d, ${}^{2}J_{PC}$ = 26.1 Hz, NiCH), 109.1 (m, o-C₆H₅ on Ni), 118.1 (s, p-C₆H₃(CF₃)₂), 125.4 (q, ${}^{1}J_{CF} = 273$ Hz, CF₃), 127.2 (s, o-C₆H₅), 128.6 (s, m-C₆H₅), 129.3 (s, $p-C_6H_5$), 129.9 (q, ${}^2J_{CF}$ = 31 Hz, $M - C_6H_3(CF_3)_2$), 135.5 (s, $o-C_6H_3$ - $(CF_3)_2$, 136.2 (s, *m*-C₆H₅ on Ni), 136.8 (s, *m*-C₆H₅ on Ni), 162.7 (q, ${}^{1}J_{CB} = 50 \text{ Hz}, i-C_{6}H_{3}(CF_{3})_{2}]. \text{ MS (FAB): } m/z = 543.4 \text{ [cation]}^{+} \text{ with}$ correct isotope pattern. IR (KBr): ν [cm⁻¹] 2966 w, 1611 w, 1473 w, 1355 m, 1279 s, 1163 m, 1128 s, 885 w, 839 w, 744 w, 716 w, 682 w, 669 w.

[(dtbpm- $\kappa^2 P$)NiBz]⁺[BAr_i]⁻. The synthesis proceeded directly from the preparation of the dibenzyl complex, which was extracted into diethyl ether (6 × 3 mL) at -78 °C. The ethereal solution was filtered through Celite directly onto 100 mg (99 μ mol) of [H(OEt₂)₂]⁺-[BAr_f]⁻ at 0 °C, which led to an orange solution. During the reaction, a small amount of an unidentified colorless solid precipitated. The orange solution was then warmed to room temperature and decanted from the precipitate. The volume of solvent was reduced under dynamic vacuum, and addition of pentane led to the precipitation of the orange product, which was recrystallized from ether/pentane.

Yield: 46 mg (25%). Mp: 195 °C. Anal. Calcd for C₅₆H₅₇F₂₄P₂NiB: C, 51.05; H, 4.36; P, 4.70. Found: C, 50.98; H, 4.19; P, 4.73. ¹H NMR (300 MHz, d_6 -acetone, 298 K): δ 1.33 (d, 18H, ${}^{3}J_{PH}$ = 13.9 Hz, $C(CH_3)_3)$, 1.58 (d, 18H, ${}^{3}J_{PH} = 14.5$ Hz, $C(CH_3)_3)$, 2.60 (dd, 2H, ${}^{2}J_{PH} = 6.0 \text{ Hz}, {}^{2}J_{PH} = 3.2 \text{ Hz}, \text{ PCH}_{2}\text{P}), 3.39 \text{ (dd, 2H, }{}^{3}J_{PH} = 9.21 \text{ Hz}, {}^{3}J_{PH} = 1.5 \text{ Hz}, \text{ CH}_{2}\text{C}_{6}\text{H}_{5}), 6.77 \text{ (d, 2H, }{}^{3}J_{HH} = 6.8 \text{ Hz}, o-\text{C}_{6}\text{H}_{5}), 7.52 \text{ Hz}$ (t, 1H, ${}^{3}J_{\text{HH}} = 7.35$, p-C₆H₅), 7.66 (s, 4H, p-C₆H₃(CF₃)₂), 7.77 (m, 10H, $o-C_6H_3(CF_3)_2 + m-C_6H_5$). ³¹P{¹H} NMR (122 MHz, C₆D₆, 298 K): δ 20.0 (d, ²J_{PP} = 13.0 Hz), 36.0 (d, ²J_{PP} = 13.0 Hz). ¹³C{¹H} NMR (126 MHz, d_6 -acetone, 298 K): $\delta = 26.61$ (t, ${}^{1}J_{PC} = 13.7$ Hz, PCH₂P), 31.11 (d, ${}^{2}J_{PC} = 2.4$ Hz, $C(CH_{3})_{3}$), 31.19 (d, ${}^{2}J_{PC} = 7.6$ Hz, $C(CH_{3})_{3}$), 37.02 (d, ${}^{1}J_{PC} = 5.2$ Hz, $C(CH_{3})_{3}$), 37.49 (d, ${}^{1}J_{PC} = 10.4$ Hz, ${}^{3}J_{PC} = 10.4$ Hz, ${}^$ 4.7 Hz, $C(CH_3)_3$, 54.88 (m, N = 75.5 Hz, $CH_2C_6H_5$), 114.17 (d, ${}^3J_{PC}$ = 4.7 Hz, o- C_6H_5), 118.48 (s, p- $C_6H_3(CF_3)_2$), 125.42 (q, ${}^1J_{CF}$ = 271.82 Hz, CF₃), 128.66 (p-C₆H₅), 129.98 (qm, ${}^{2}J_{CF}$ = 31 Hz, m- $C_6H_3(CF_3)_2$), 135.58 (s, o- $C_6H_3(CF_3)_2$), 136.64 (d, J = 1.9 Hz, m- C_6H_5), 162.64 (q, ${}^{1}J_{CB}$ = 49.9 Hz, *i*- $C_6H_3(CF_3)_2$). MS (FAB): m/z453.2 [cation⁺] with correct isotope pattern. IR (KBr): ν [cm⁻¹] 2966 w, 1611 w, 1476 w, 1355 m, 1277 s, 1168 m, 1131 s, 888 w, 839 w, 807 w, 757 w, 745 w, 716 w, 682 m, 670 m.

[(ptbpm-\kappa^2 P)NiBz]⁺**[BAr**_f]⁻. The dibenzyl complex (ptbpm- $\kappa^2 P$)-NiBz₂ (24 mg, 41 μ mol) was dissolved in 5 mL of diethyl ether, and [H(OEt₂)₂)⁺[BAr_f]⁻ (41.5 mg, 41 μ mol) in 5 mL of diethyl ether was added. The red solution was stirred for 1 h, and the volume of solvent was reduced by half under dynamic vacuum. Addition of pentane led to the precipitation of the product, which was then recrystallized, from 2 mL of diethyl ether.

Yield: 47 mg (84%). Mp: 171 °C dec. Ratio of isomers C:D = 1.6:1 (from integration of the ³¹P resonances) (Figure 8). Anal. Calcd for $C_{60}H_{49}F_{24}P_2BNi: C, 53.09; H, 3.64; P, 4.56.$ Found: C, 53.24; H, 3.78; P, 4.49. ¹H NMR (500 MHz, d_6 -acetone, 298 K): δ 1.19 (d, 18H, ³J_{PH} = 14.9 Hz, C(CH₃)₃, D), 1.41 (d, 18H, ³J_{PH} = 15.2 Hz, C(CH₃)₃, C), 2.89 (dd, 2H, ²J_{PH} = 7.0 Hz, ²J_{PH} = 1.55 Hz, PCH₂P, C), 2.92 (dd, 2H, ²J_{PH} = 6.1 Hz, ²J_{PH} = 1.85 Hz, PCH₂P, D), 3.76 (dd, 2H, ³J_{PH} = 11.3 Hz, ³J_{PH} = 7.9 Hz, CH₂C₆H₅, D), 3.80 (t, 2H, ³J_{PH} = 9.4 Hz, CH₂C₆H₅, C), 6.88 (d, 4H, ³J_{HH} = 6.3 Hz, o-C₆H₅ on P, D), 6.93 (d, 4H, ³J_{HH} = 7.15 Hz, o-C₆H₅ on P, C), 7.49 (m, 1H, p-C₆H₅ on Ni, C),

7.51 (m, 4H, p-C₆H₅ on P, C + D), 7.62 (m, 1H, p-C₆H₅ on Ni, D), 7.63 (m, 8H, m-C₆H₅ on P, C + D), 7.66 (s, 8H, p-C₆H₃(CF₃)₂, C + D), 7.78 (s, 16H, o-C₆H₃(CF₃)₂, C + D), 7.84 (m, 4H, m-C₆H₅ on Ni, C + D), 7.90 (m, 8H, m-C₆H₅ on P, C + D). ³¹P{¹H} NMR (300 MHz, d_6 -acetone, 298 K): δ –18.1 (d, ${}^2J_{PP}$ = 33.5 Hz, PPh₂, C), –6.1 (d, ${}^2J_{PP}$ = 30.4 Hz, PC(CH₃)₃)₂, (d, ${}^2J_{PP}$ = 30.4 Hz, PC(CH₃)₃)₂. **D**), 43.0 (d, ${}^{2}J_{PP}$ = 33.5 Hz, P(C(CH₃)₃)₂, **C**). ${}^{13}C{}^{1}H$ NMR (126 MHz, d_6 -acetone, 298 K): δ 29.02 (d, ${}^2J_{CP}$ = 4.7 Hz, C(CH₃)₃, C), 29.14 (d, ${}^{2}J_{CP}$ = 5.5 Hz, C(CH₃)₃, D), 29.75 (m, CH₂C₆H₅, C + D), 35.96 ("t", ${}^{1}J_{CP}$ = 6.13 Hz, C(CH₃)₃, C + D), 37.19 (dd, ${}^{2}J_{trans-CP}$ = 33.9 Hz, ${}^{2}J_{cis-CP} = 3.3$ Hz, PCH₂P, C), 39.57 (d, ${}^{2}J_{trans-CP} = 25.5$ Hz, PCH₂P, **D**), 114.12 (dd, ${}^{2}J_{trans-CP} = 6.1$ Hz, ${}^{2}J_{cis-CP} = 1.4$ Hz, o-Ph-C, **D**), 114.77 $(dd, {}^{2}J_{trans-CP} = 5.6 \text{ Hz}, {}^{2}J_{trans-CP} = 1.9 \text{ Hz}, o-C_{6}H_{5}, C), 117.93 (m, i C_6H_5$), 118.65 (m, p- $C_6H_3(CF_3)_2$), 118.68 (m, i- C_6H_5), 125.80 (q, ${}^{1}J_{CF} = 272.3 \text{ Hz}, \text{ CF}_{3}$, 130.2 (qm, ${}^{2}J_{CF} = 31.6 \text{ Hz}, m-C_{6}H_{3}(CF_{3})_{2}$), 130.48 (s, p-C₆H₅), 130.56 (s, p-C₆H₅), 130.74 (s, m-C₆H₅), 130.83 (s, $m-C_6H_5$), 133.20 (d, ${}^{4}J_{CP} = 1.8$ Hz, $p-C_6H_5$ on Ni), 133.47 (d, ${}^{4}J_{CP} =$ 2.8 Hz, p-C₆H₅ on Ni), 133.93 (d, ${}^{2}J_{CP}$ = 3.8 Hz, o-C₆H₅), 134,03 (d, $^{2}J_{CP} = 3.8 \text{ Hz}, o-C_{6}H_{5}), 135.76 \text{ (s, } o-C_{6}H_{3}(CF_{3})_{2}), 137.34 \text{ (br, } m-C_{6}H_{5})$ on Ni), 137.75 (d, ${}^{3}J_{CP}$ = 1.9 Hz, *m*-C₆H₅ on Ni), 162.81 (q, ${}^{1}J_{BC}$ = 49.5 Hz, *i*-C₆H₃(CF₃)₂), *i*-C of benzyl not observed. IR (KBr): ν [cm⁻¹] 2966 w, 1611 w, 1470 w, 1439 w, 1355 s, 1279 s, 1124 s, 1019 w, 929 w, 887 m, 838 m, 808 w, 762 w, 744 w, 715 m, 682 m, 669 m, 521 w, 485 w. MS (FAB): m/z 493.2 [cation]⁺ with correct isotope pattern.

[(ctbpm-\kappa^2 P)NiBz]⁺[BAr_f]⁻. The cold ethereal extract from the synthesis of (ctbpm- $\kappa^2 P$)NiBz₂ was filtered directly into a flask containing solid [H(OEt₂)₂]⁺[BAr_f]⁻, which was precooled to -78 °C. The color of the solution lightened, and after all of the ether solution had been added some unidentified white precipitate was observed in the bottom of the flask. The solution was warmed to room temperature at that point and filtered into a clean Schlenk flask. The volume of solvent was reduced under dynamic vacuum, and the dark orange solution was cooled to -60 °C. A small amount of flaky solid precipitated. Yield: 0.4 g, 32% based on (ctbpm- $\kappa^2 P$)NiCl₂. Mp: 190–195 °C. The NMR spectra contain the two isomers C and D in a 1:1.25 ratio (Figure 8).

¹H NMR (THF-*d*₈, 300 K, 300 MHz): δ 1.23 (d, ³*J*_{HP} = 14.2 Hz, 18H, C(CH₃)₃, **D**), 1.36 (br, 12H, C₆H₁₁), 1.46 (d, ³*J*_{HP} = 14.6 Hz, 18H, C(CH₃)₃, **C**), 1.60 (br, 2H, C₆H₁₁), 1.91 (br, 8H, C₆H₁₁), 2.05 (br, 4H, C₆H₁₁), 2.26 (br, 2H, C₆H₁₁), 2.43 (d, ³*J*_{HP} = 5.9 Hz, 2H, CH₂C₆H₅, **D**), 2.49 (d, ³*J*_{HP} = 5.9 Hz, 2H, CH₂C₆H₅, **C**), 2.95 ("t", 4H, ²*J*_{HP} = 8.7 Hz, PCH₂P, **C** + **D**), 6.50 (d, 2H, ³*J*_{HH} = 7.3 Hz, C₆H₅, **D**), 6.54 (d, 2H, ³*J*_{HH} = 7.3 Hz, C₆H₅, **C**), 7.40 (m, 4H, C₆H₅, **C** + **D**), 7.57 (8H, *p*-C₆H₃(CF₃)₂, **C** + **D**), 7.67 (pseudo q, 4H, C₆H₅, **C** + **D**), 7.79 (16H, *o*-C₆H₃(CF₃)₂, **C** + **D**). ³¹P{¹H} NMR (THF-*d*₈, 300 K, 121.5 MHz): δ -7.6 (d, ²*J*_{PP} = 23 Hz, PCy₂, **C**), 9.5 (d, ²*J*_{PP} = 21 Hz, PCy₂, **D**), 24.2 (d, ²*J*_{PP} = 21 Hz, P(C(CH₃)₃)₂, **D**), 40.0 (d, ²*J*_{PP} = 23 Hz, P(C(CH₃)₃)₂, **C**).

[(iptbpm-\kappa^2 P)NiBz]⁺**[BAr**_f]⁻. The dibenzyl complex (iptbpm- $\kappa^2 P$)-NiBz₂ (60 mg, 116 μ mol) was weighed into a Schlenk tube with [H(OEt₂)₂]⁺[BAr_f]⁻ (117.5 mg, 116 μ mol) and dissolved in 15 mL of diethyl ether. The solution became red and was stirred for an hour at room temperature. The volume of solvent was then reduced by half under dynamic vacuum. Addition of pentane (10 mL) led to precipitation of the product, which was then recrystallized from diethyl ether and washed with pentane.

Yield: 93 mg (72%). Mp: 208 °C dec. Isomer ratio: 1:1.5 = C:D (Figure 8). Anal. Calcd for $C_{46}H_{47}F_{24}P_2$ NiB: C, 50.30; H, 4.14; P, 4.80. Found: C, 50.60; H, 4.18; P, 4.91. ¹H NMR (300 MHz, d_6 -acetone, 298 K): δ 1.09 (dd, 6H, $^{3}J_{PH}$ = 15.4 Hz, $^{3}J_{HH}$ = 7.26 Hz, CH(CH₃)₂, C), 1.19 (dd, 6H, $^{3}J_{PH}$ = 16.2 Hz, $^{3}J_{HH}$ = 7.26 Hz, CH(CH₃)₂, C), 1.27 (d, $^{3}J_{PH}$ = 14.4 Hz, 18H, C(CH₃)₃, D), 1.37 (dd, 6H, $^{3}J_{PH}$ = 2.3 Hz, $^{3}J_{HH}$ = 7.26 Hz, CH(CH₃)₂, D), 1.43 (dd, 6H, $^{3}J_{PH}$ = 2.8 Hz, $^{3}J_{HH}$ = 7.23 Hz, CH(CH₃)₂, D), 1.49 (d, 18H, $^{3}J_{PH}$ = 14.9 Hz, C(CH₃)₃, C), 2.35 (m, 2H, CH(CH₃)₂, C), 2.72 (m, 2H, CH(CH₃)₂, D), 2.57 (dd, 2H, $^{2}J_{PH}$ = 6.0 Hz, $^{2}J_{PH}$ = 2.25 Hz, PCH₂P, D), 2.60 (dd, 2H, $^{2}J_{PH}$ = 6.4 Hz, $^{2}J_{PH}$ = 2.1 Hz, PCH₂P, C), 3.10 (t, 2H, $^{3}J_{PH}$ = 8.1 Hz, CH₂C₆H₅, D), 3.11 (t, 2H, $^{3}J_{PH}$ = 9.2 Hz, CH₂C₆H₅, C), 6.63 (d, 1H, $^{3}J_{HH}$ = 7.4 Hz, o-C₆H₅, D), 6.69 (d, 1H, $^{3}J_{HH}$ = 7.2 Hz, o-C₆H₅, C),

7.45 (m, 1H, C₆H₅), 7.66 (s, 8H, *p*-C₆H₃(CF₃)₂, C + D), 7.73 (m, 1H, C₆H₅), 7.78 (s, 16H, *o*-C₆H₃(CF₃)₂, C + D). ${}^{31}P{}^{1}H{}$ NMR (122) MHz, C_6D_6 , 298 K): δ 1.4 (d, ${}^2J_{PP}$ = 24.7 Hz, $P({}^{i}Pr)_{2}$, C), 18.4 (d, ${}^2J_{PP}$ = 23.2 Hz, $P({}^{i}Pr)_{2}$, D), 24.1 (d, ${}^2J_{PP}$ = 22.9 Hz, $P(C(CH_3)_3)_2$, D), 40.0 (d, ${}^{2}J_{PP}$ = 24.6 Hz, P(C(CH₃)₃)₂, C). ${}^{13}C{}^{1}H$ NMR (126 MHz, d_8 -THF, 298 K): δ 19.35 (d, ${}^2J_{PC}$ = 10.8 Hz, CH(CH₃)₂), 19.54 (d, ${}^{2}J_{PC} = 6.6$ Hz, CH(CH₃)₂), 22.58 (d, ${}^{1}J_{PC} = 17.4$ Hz, CH(CH₃)₂), 22.87 (d, ${}^{1}J_{PC}$ = 17.7 Hz, CH(CH₃)₂), 27.14 (dd, ${}^{1}J_{PC}$ = 16.5 Hz, ${}^{1}J_{PC}$ = 6.1 Hz, PCH₂P), 29.40 (d, ${}^{2}J_{PC}$ = 4.7 Hz, C(CH₃)₃), 29.51 (d, ${}^{2}J_{PC}$ = 5.6 Hz, C(CH₃)₃), 35.17 (dd, ${}^{1}J_{PC}$ = 25.0 Hz, ${}^{3}J_{PC}$ = 4.3 Hz, C(CH₃)₃), 35.97 (dd, ${}^{1}J_{PC}$ = 24.0 Hz, ${}^{3}J_{PC}$ = 4.2 Hz, C(CH₃)₃), 36.39 (dd, ${}^{2}J_{PC}$ = 4.2 Hz, ${}^{2}J_{PC}$ = 5.7 Hz, $CH_{2}C_{6}H_{5}$), 36.79 (dd, ${}^{2}J_{PC}$ = 5.7 Hz, ${}^{2}J_{PC}$ = 9.9 Hz, $CH_2C_6H_5$), 113.74 (d, ${}^2J_{PC}$ = 5.6 Hz, o- C_6H_5), 114.08 (d, ${}^2J_{PC}$ = 5.2 Hz, o-C₆H₅), 117.32 (m, i-C₆H₅), 117.77 (m, i-C₆H₅), 118.40 (m, p-C₆H₃(CF₃)₂), 125.72 (q, ${}^{1}J_{CF} = 272.2$ Hz, CF₃), 128.54 (m, p-C₆H₅), 128.84 (m, p-C₆H₅), 130.24 (qm, ${}^{2}J_{CF} = 31.6$ Hz, m-C₆H₃-(CF₃)₂), 135.81 (s, o-C₆H₃(CF₃)₂), 136.72 (s, m-C₆H₅), 136.94 (s, m- C_6H_5), 163.02 (q, ${}^1J_{BC}$ = 49.9 Hz, *i*- $C_6H_3(CF_3)_2$). IR (KBr): ν [cm⁻¹] 2968 w, 1611w, 1473 w, 1355 s, 1279 s, 1164 s, 1127 s, 888 m, 839 w, 760 w, 744 w, 715 m, 682 m, 670 m.

[(dcpm- $\kappa^2 P$)NiBz]⁺[BAr_f]⁻. The dibenzyl complex (dcpm- $\kappa^2 P$)NiBz₂ (20 mg, 30.8 μmol) was suspended in 10 mL of diethyl ether and the suspension cooled to -60 °C, and [H(OEt₂)₂]⁺[BAr_f]⁻ (31.2 mg, 30.8 mol) dissolved in 5 mLof diethyl ether was added. The reaction mixture was gradually warmed to room temperature, and no visible reaction occurred. After stirring for 24 h at room temperature, the solution was orange, and addition of pentane led to crystallization of the product, which was recrystallized from diethyl ether/pentane.

Yield: 24 mg (55%). Mp: 167 °C dec. Anal. Calcd for $C_{64}H_{65}$ - $P_2F_{24}BNi: C, 54.07; H, 4.61; P, 4.36. Found: C, 53.86; H, 4.96; P, 4.38. ¹H NMR (500 MHz, CD₂Cl₂, 298 K): <math>\delta$ 1.0–2.1 (m, 44H, C₆H₁₁), 2.30 (d, 2H, ³J_{PH} = 4.7 Hz, CH₂C₆H₅), 2.59 (t, 2H, ²J_{PH} = 9.0 Hz, PCH₂P), 6.33 (d, 2H, ³J_{HH} = 7.3 Hz, o-C₆H₅), 7.30 (m, 1H, p-C₆H₅), 7.56 (s, 4H, p-C₆H₃(CF₃)₂), 7.61 (t, 2H, ³J_{HH} = 7.7 Hz, m-C₆H₅), 7.72 (s, 8H, o-C₆H₃(CF₃)₂), ³¹P{¹H} NMR (122 MHz, d₆-acetone, 298 K): δ -3.5 (d, ²J_{PP} = 37.9 Hz), 12.6 (d, ²J_{PP} = 37.9 Hz). ¹³C{¹H} NMR (75 MHz, d₆-acetone, 298 K): δ 19.56 (t, ¹J_{PC} = 20.9 Hz, PCH₂P), 25.20 (s, C₆H₁₁), 25.34 (br, C₆H₁₁), 26.40 (m, C₆H₁₁), 28.55 (m, C₆H₁₁), 33.80 (dd, ¹J_{PC} = 12.6 Hz, ³J_{PC} = 4.4 Hz, CH-(CH₂)₅), 34.94 (dd, ²J_{PC} = 24.7 Hz, ²J_{PC} = 3.3 Hz, CH₂C₆H₅), 35.45 (dd, ¹J_{PC} = 16.5 Hz, ³J_{PC} = 5.5 Hz, *i*-C₆H₁₁), 112.22 (d, ²J_{PC} = 7.7 Hz, *o*-C₆H₅), 117.12 (m, *i*-C₆H₅), 117.45 (m, *p*-C₆H₃(CF₃)₂), 126.82 (m, *p*-C₆H₅), 134.57 (s, *o*-C₆H₃(CF₃)₂), 135.68 (s, *m*-C₆H₅).

Polymerization of Ethylene. In a typical experiment, [(dtbpm- $\kappa^2 P$)NiMe(THF)]⁺[BAr_f]⁻ (5.0 mg) was weighed into a 10 mL thickwalled glass autoclave (provided by BASF, pressure tolerance ≤ 10 bar) equipped with a magnetic stirrer, and diethyl ether (5 mL) was added. The autoclave was then cooled to 0 °C with stirring and pressurized with ethylene (7 bar). After approximately 15 min, the orange solution became cloudy and the pressure dropped slightly. Repressurization with ethylene to maintain a pressure of 7 bar was required four times in the first 1 h but not thereafter. After 3 h, the reaction was stopped and the ethylene pressure released. The polyethylene was collected by filtration, washed many times with acetone and diethyl ether, and dried at 80 °C, resulting in an off-white powder.

For ethylene polymerization reactions at pressures higher than 10 bar steel autoclaves of appropriate size were used.

Crystallographic Studies. General Considerations. For each compound studied by X-ray diffraction, a crystal was mounted on a glass fiber with perfluoropolyether. All measurements were made on a Bruker SMART diffractometer with graphite-monochromated Mo K α radiation using a CCD detector. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of reflections from 45 0.3° frames collected for 10 s each. Frames corresponding to a sphere of data were then collected using the ω -scan technique; in each case, 20 s exposures of 0.3° in ω were taken. The reflections were integrated using SAINT,⁷¹ and equivalent reflections were merged. An absorption correction was applied to each structure using SADABS,⁷² and the data were corrected for Lorentz and polarization effects. The space groups were determined by the systematic

absences of *hkl* values using XPREP.⁷³ The structures were solved by direct methods unless otherwise specified and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and not refined unless otherwise specified. The final cycle of full-matrix least-squares refinement was based on all reflections, and converged. The function minimized was $\sum w((F_o)^2 - (F_c)^2)^2$. All calculations were performed using the SHELXTL crystallographic software package of Bruker.⁷⁴ All of the complexes containing the BAr_f anion have some disordered CF₃ groups, which have been modeled using sensible geometric contrainsts. Further details are only provided for structures for which other techniques were used or disorder was modeled.

 $(dtbpm-\kappa^2 P)NiCl_2 \cdot 3CH_2Cl_2$. The structure was solved by Patterson methods. The nickel atom lies on a special position, as does the carbon atom of one CH_2Cl_2 ; therefore, the asymmetric unit consists of half the molecule and one and a half methylene chloride units. One of the methylene chloride units is disordered, and the disorder has been modeled as two positions.

 $(ctbpm-\kappa^2 P)NiCl_2$. There is some disorder in the cyclohexyl rings; however, the second chair position is not completely visible in the difference map.

 $(ptbpm-\kappa^2 P)NiMe_2$. The methyl protons were refined. One reflection was omitted from the refinement as it was in the beam stop.

 $[(dtbpm-\kappa^2 P)NiMe(THF)]^+[BAr_f]^-\cdot 2THF.$ The geometries of the two THF molecules of crystallization were coupled for refinement.

 $[(ptbpm-\kappa^2 P)NiMe(THF)]^+[BAr_f]^-$. The structure was solved with ESEL-1 and transformed into $P\overline{1}$.

 $[(dcpm-\kappa^2 P)NiBz]^+[BAr_f]^-\cdot THF$. The two unique molecules in the asymmetric unit have been refined as separate blocks.

 $[(dtbpm-\kappa^2 P)Ni(\eta^3-CH(CH_2Ph)Ph]^+[BAr_f]^-$. The structure was solved using Patterson methods. The hydrogen atoms were observed in the difference map; those bound to dtbpm were included in calculated positions, while the remainder of the hydrogens were freely refined.

GPC Analysis. The polyethylene samples obtained were analyzed by high-temperature GPC, using a Waters-150C instrument with an IR detector device (λ 3.5 mm). The solvent used was 1,2,4-trichlorobenzene at 135 °C. Calibration was achieved by using linear polyethylene standards with narrow and broad molecular weight distribution.

Calculations. The DFT calculations were carried out using the B3LYP functional in the Gaussian 98 package.⁷⁵ Basis sets used were SDD on Ni and 6-31G(d) for the remainder of the heavy atoms.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving ORTEP representations of the Ni complexes mentioned in the paper but not displayed as figures, a ¹³C NMR spectrum of a copolymer obtained from ethylene and 1-hexene, and crystallographic data for all complexes studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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NOTE ADDED AFTER ASAP PUBLICATION

In the version of this paper published December 27, 2011, the author name Paul Jakob was given incorrectly. The version of this paper that appears on the web as of January 9, 2012, has the name given correctly.