Synthesis of Water-Soluble, Aliphatic Phosphines and Their Application to Well-Defined Ruthenium Olefin Metathesis Catalysts

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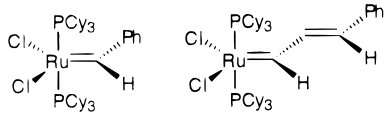
Water-soluble aliphatic phosphines $Cy_2P(CH_2)_2N(CH_3)_3^+Cl^-$ (**14**), Cy_2P[4-(*N*,*N*-dimethylpiperidinium)]$^+Cl^-$ (**15**), $Cy_2P(CH_2)_2SO_3^-Na^+$ (**16**), and $CyP[(CH_2)_2N(CH_3)_3^+Cl^-]_2$ (**17**) (Cy = cyclohexyl) were prepared from air-stable, borane-protected precursors. Spectroscopic investigations of corresponding $Pd(PR_3)_2Cl_2$ complexes were used to estimate the steric parameters of these new phosphines. Spectroscopic investigation of $Ni(CO)_3PR_3$ complexes of the new phosphines indicated that phosphines bearing quaternary amine functionalities were less electron donating than tricyclohexylphosphine, while the presence of a sulfonate group increased phosphine electron donation. Cationic phosphines **14** and **15** were used to synthesize water-soluble ruthenium carbene complexes of the type $(Cy_2PR)_2Cl_2Ru{=}CHPh$. These complexes initiate the ring-opening metathesis polymerization (ROMP) of functionalized 7-oxanorbornenes in water, methanol, and aqueous emulsions.

Introduction

In this contribution, we report the synthesis of water-soluble, aliphatic phosphines via borane-protected intermediates. These phosphines were designed to be both sterically and electronically similar to tricyclohexylphosphine, a ligand of specific importance to the activity and reactivity of ruthenium carbene complexes of the type $RuCl_2(=CHPh)(PR_3)_2$, which initiate ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) in organic solvents.[1] Ruthenium-based catalysts **1** and **2** are particularly attractive,



1 **2**

as they offer functional group tolerances and oxidative stabilities unmatched by complexes of other metals. In fact, although these catalysts are insoluble in water, our group has recently demonstrated their utilities as living polymerization catalysts in aqueous media.[2] The economic, environmental, and processing benefits of homogeneous aqueous catalysis and aqueous two-phase catalysis[3] prompted us to pursue the synthesis of well-defined, *water-soluble* ruthenium-based initiators for olefin metathesis.

The chemistry of water-soluble phosphines has received considerable attention.[3,4] Much work in this area has been devoted to the development of aromatic phosphines, such as trisulfonated triphenylphosphine (TPPTS). In contrast, relatively little effort has been directed toward the development of water-soluble aliphatic phosphines.[5] Compounds of this type are of considerable interest to our group, as the metathesis activities of the well-defined ruthenium metathesis catlaysts are generally maximized by the coordination of sterically-demanding, electron-donating phosphines to the ruthenium center.[1g] Traditionally, preparation of water-soluble aliphatic phosphines has been complicated by their increased sensitivities to oxidation and their tendency to react with other electrophiles. A synthetic approach reported by Stelzer *et al.* is based on aminoalkylation of PH_3 with ω-chloroalkylamines followed by selective N-quaternization with alkyl iodides.[5b−d] Additionally, Bartik *et al.* have prepared a series of electron-donating, water-soluble phosphines via direct *para*-sulfonation of tris(ω-phenylalkyl)phosphines of the type $P[(CH_2)_x(C_6H_5)]_3$.[5a]

The synthetic approach presented herein is mediated by borane-protected phosphorus intermediates. Phos-

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(1) (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Schwab, P. E.; France, M. B.; Grubbs, R. H.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (c) Schwab, P. E.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (e) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (f) Schwab, P. E.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (g) Dias, E. L.; Grubbs, R. H. manuscript in preparation.

(2) (a) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784. (b) Fraser, C., Grubbs, R. H. *Macromolecules* **1995**, *28*, 7248.

(3) (a) Hermann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (b) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177. (c) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43. (d) Arhancet, J. P.; Davis, M. E.; Merola, J. S. Hanson, B. E. *Nature* **1989**, *339*, 454. (e) Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* **1982**, *62*, 135. (f) Smith, R. T.; Ungar, R. K.; Baird, M. C. *Transition Met. Chem* **1982**, *7*, 288. (g) Larpent, C.; Patin, H.; Thilmont, N.; Valdor, J. F.; *Synth. Commun.* **1991**, *21* (4), 495.

(4) (a) Herd, O.; Hessler, A.; Langhans, K. P.; Stelzer, O.; Sheldrick, W. S.; Weferling, N. *J. Organomet. Chem.* **1994**, *475*, 99. (b) Herd, O.; Langhans, K. P.; Stelzer, O.; Weferling, N.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1058. (c) Herrman, W. A.; Kellnar, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103. (d) Larpent, C.; Dabard, R.; Patin, H. *Inorg. Chem.* **1987**, *26*, 2922. (e) Bartik, T.; Bartik, B.; Hanson, B. E., Glass, T.; Bebout, W. *Inorg. Chem.* **1992**, *31*, 2667.

(5) (a) Bartik, T.; Bartik, B.; Hanson, B. E., Guo, I.; Toth, I. *Organometallics***1993**, *12*, 164. (b) Bitterer, F.; Kucken, S.; Stelzer, O. *Chem. Ber.* **1995**, *128*, 275. (c) Brauer, D. J.; Fischer, J.; Kucken, S.; Langhans, K. P.; Stelzer, O.; Weferling, N. *Z. Naturforsch.* **1994**, *49b*, 1511. (d) Hessler, A.; Kucken, S.; Stelzer, O.; Blotevogelbaltronat, J.; Sheldrick, W. S. *J. Organomet. Chem.***1995**, *501*, 293.

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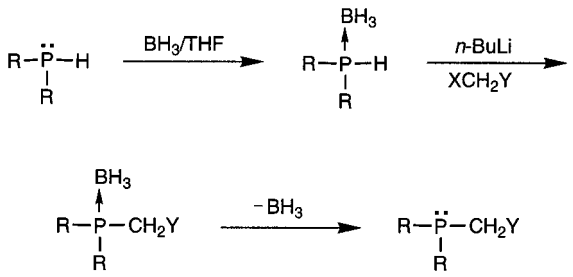
Scheme 1. Synthesis of Functionalized Phosphines via Air-Stable, Borane-Protected Intermediates



phine−borane complexes[6,7] have recently been used as intermediates in the synthesis of phosphine derivatives not accessible by other methods.[8] They are typically prepared via the reaction of a free phosphine with borane, although Imamoto *et al.* have prepared a variety of phosphine−borane complexes in a one-step synthesis from phosphine oxides.[9] Borane-protected phosphines are stable to metalation with lithium reagents and can subsequently be reacted with various electrophiles under mild conditions to yield functionalized phosphine boranes (Scheme 1). Notably, the borane group acts as both a protecting group and an activating group. In fact, hydrogen, methyl, and methylene groups adjacent to the phosphorus atom are activated toward deprotonation by strong bases.[10] The borane moiety can be removed quantitatively, and with retention of configuration, by treatment with either a large excess of a nucleophilic amine[6a] or tetrafluoroboric acid.[8c,d]

Results and Discussion

In the following sections, we discuss the synthesis of charged, water-soluble, aliphatic phosphines via borane-protected intermediates. The syntheses of cyclohexylphosphine− and dicyclohexylphosphine−borane are outlined, followed by different routes to the synthesis of mono- and difunctionalized phosphine−boranes. Phosphine deprotection schemes are addressed, and the steric and electronic parameters are determined through spectroscopic investigation of corresponding $Pd(PR_3)_2Cl_2$ and $Ni(CO)PR_3$ complexes. Two new phosphines have been applied to the synthesis of well-defined, water-soluble ruthenium carbene complexes which initiate the ROMP of functionalized 7-oxanorbornenes in protic media.

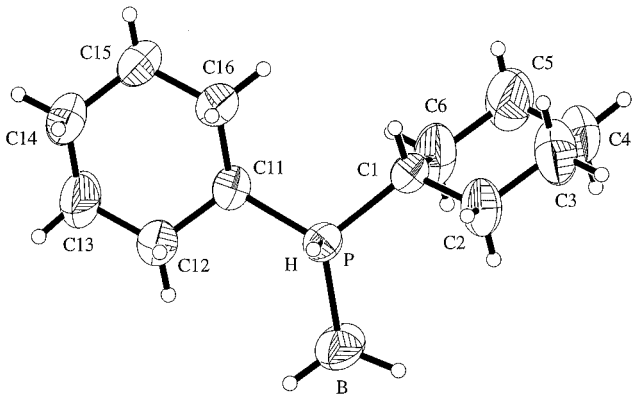
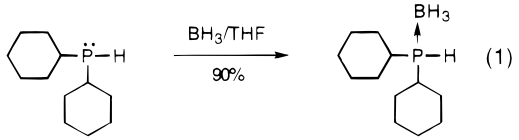


Figure 1. Molecular structure of dicyclohexylphosphine−borane (**3**).

Table 1. Selected Bond Lengths and Angles for Dicyclohexylphosphine−Borane (3)

Bond Lengths (Å)			
P−C(1)	1.819(2)	P−B	1.919(3)
P−C(11)	1.819(2)	P−H	1.262(0)
Bond Angles (deg)			
C(1)−P−C(11)	109.15(9)	C(1)−P−B	101.4(7)
C(1)−P−B	113.97(13)	C(11)−P−H	104.3(7)
C(11)−P−B	114.27(12)	B−P−H	112.6(7)

Synthesis of Monofunctionalized Phosphines. Dicyclohexylphosphine, a highly air-sensitive liquid, reacts with BH_3·THF to yield the borane adduct **3** as an air-stable, crystalline solid (eq 1).[8c,d] Recrystallization from ether at −20 °C yielded crystals suitable for analysis by single-crystal X-ray diffraction.[11] The molecular structure of **3** is shown in Figure 1. The coordination sphere around the phosphorus atom is distorted tetrahedral; selected bond distances and angles are provided in Table 1.



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Compound **3** was metalated with *n*-BuLi in THF at −78 °C, and the generated phosphide anion was allowed to react with amine-functionalized electrophiles to yield the amine-functionalized phosphine−boranes **4** and **7** in 65% and 45% yields, respectively (Scheme 2). The synthesis of **7** using 4-chloro-*N*-methylpiperidine proceeded very slowly and in low yields, presumably due to the secondary center from which chloride displacement must occur. Piperidine tosylate **6** provided a more suitable leaving group. Compounds **4** and **7** were purified by column chromatography over silica gel. Interestingly, migration of the borane group from the phosphorus atom to the nitrogen atom of the tertiary amines was not observed under these conditions,[12] even though aliphatic amines are commonly used to deprotect phosphine boranes.

(6) For reviews on phosphine−boranes see: (a) Imamoto, T. *Pure Appl. Chem.* **1993**, *65* (4), 655. (b) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287. (c) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449. (d) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343. (e) Arbusov, B. A.; Nikonov, G. N. *Rev. Heteroatom Chem.* **1990**, *3*, 1.

(7) For spectroscopic investigations on phosphine−boranes see: (a) Power, W. P. *J. Am. Chem. Soc.* **1995**, *117*, 1800. (b) Couley, A. H.; Kemp, R. A.; Lattman, M.; McKee, M. L. *Inorg. Chem.* **1982**, *21*, 85. (c) Albanese, J. A.; Kreider, D. G.; Schaeffer, C. D.; Yoder, C. H.; Samples, M. S. *J. Org. Chem.* **1985**, *50*, 2059. (d) Young, D. E.; McAchran, G. E.; Shore, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 4390.

(8) (a) Enders, D.; Berg, T.; Raabe, G.; Runsink, J. *Helv. Chim. Acta* **1996**, *79*, 118. (b) Brenchley, G.; Fedouloff, M.; Mahon, M. F.; Molloy, K. C., Wills, M. *Tetrahedron* **1995**, *51*, 10581. (c) McKinstry, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655. (d) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319. (e) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523. (f) Oshiki, T.; Imamoto, T. *J. Am. Chem. Soc.* **1992**, *114*, 3975. (g) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357.

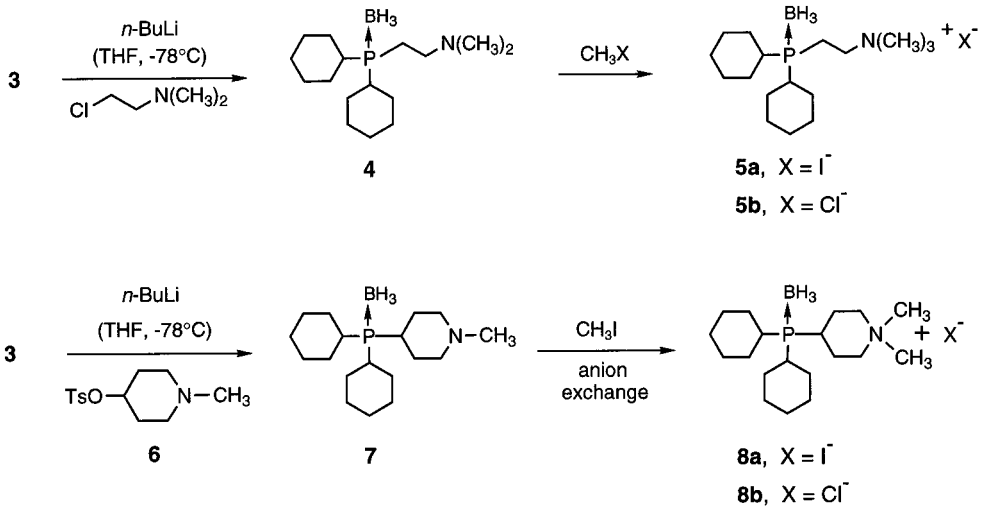
(9) (a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. (b) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301.

(10) (a) Imamoto, T.; Hikosaka, T. *J. Org. Chem.* **1994**, *59*, 6753. (b) Gourdel, Y.; Ghanimi, A.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 1011. (c) Schmidbaur, H.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 283. (d) Imamoto, T.; Oshiki, T. *Tetrahedron Lett.* **1989**, *30*, 383.

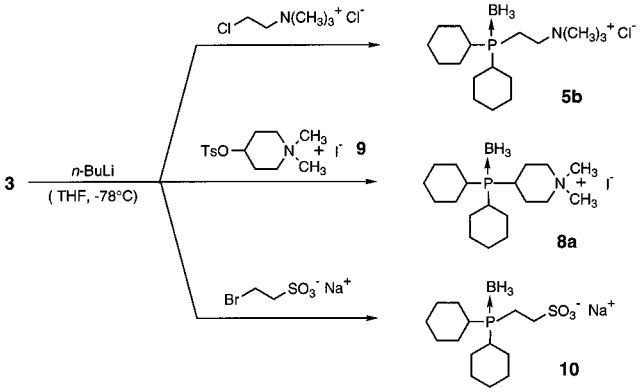
(11) Day, M. *Acta Crystallogr.*, submitted for publication.

(12) NMR-spectroscopic investigations of the crude reaction mixture showed no evidence for borane migration; additionally, no transfer of the boronato group was observed by heating **2** in THF at 60°C for 18 h.

Scheme 2. Synthesis of Monofunctionalized Phosphines



Scheme 3. Synthesis of Monofunctionalized Phosphines via Direct Functionalization with Charged Electrophiles

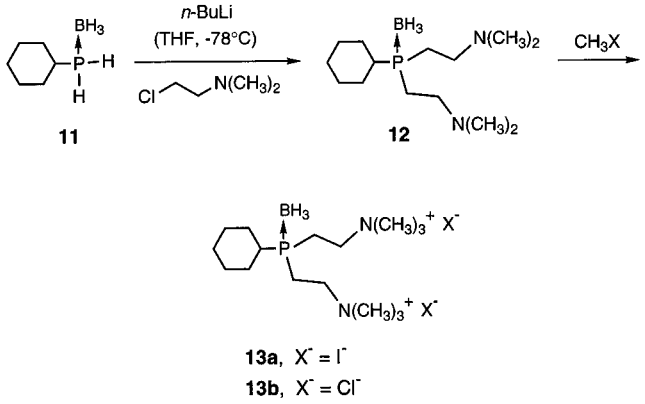


Quarternization of the amino groups of **4** and **7** with methyl iodide gave exclusively N-methylated products **5a** and **8a** in quantitative yield, further illustrating the stability of the phosphorus-boron bond (Scheme 2). Chloride salts **5b** and **8b** were also synthesized, as the iodide salts were not water soluble upon removal of the borane moiety as discussed below. The ammonium chloride **5b** was readily produced through quaternization of **4** with methyl chloride, but the piperidinium chloride **8b** could not be obtained by the same procedure due to a much slower reaction rate. Phosphine **8b** was therefore prepared from iodide **8a** employing an anion-exchange resin.

The synthesis of phosphine−boranes **5b** and **8a** was also achieved in one step by direct conversion of lithiated **3** with electrophiles bearing N-quaternized functionalities (Scheme 3). The success of this approach allowed an extension of the methodology to the synthesis of phosphine−boranes bearing anionic functionalities such as **10**, which was obtained from the corresponding bromoethanesulfonate in good yield. Purification of the ionically-functionalized phosphine−boranes was readily accomplished by crystallization.

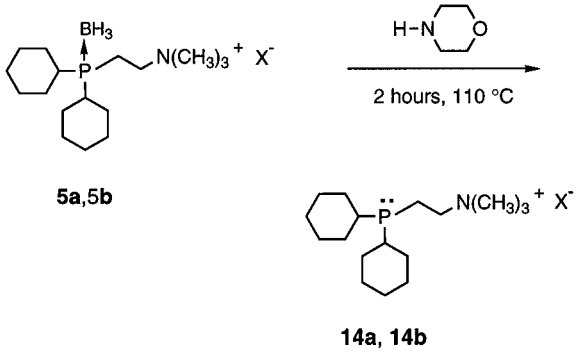
Synthesis of Difunctionalized Phosphines. The methodology outlined above was extended to the synthesis of difunctionalized phosphine−boranes derived from cyclohexylphosphine−borane (Scheme 4). Cyclohexylphosphine−borane **11** was obtained in quantitative yield by the reaction of cyclohexylphosphine with BH_3−THF. Phosphine−borane **11** was then metalated with 2 equiv of *n*-BuLi in THF at −78 °C and treated with 2-chloro-*N*,*N*-dimethylaminoethane to yield the diamine **12** in 40% yield. Conversion of **12** with methyl iodide or methyl chloride yielded the quaternized, difunctionalized phosphine−boranes **13a** and **13b**, respectively. Attempts to prepare difunctionalized species by employing charged electrophiles failed due to difficulty in selectively isolating the difunctionalized phosphine boranes from the product mixture.

Scheme 4. Synthesis of Difunctionalized Phosphines



Phosphine Deprotection: Removal of the Boronato Group. The removal of the boronato protecting group has previously been accomplished by treatment with a large excess of a strongly nucleophilic amine,[6a,8g] such as diethylamine or morpholine, or by treatment with tetrafluoroboric acid.[8c,d] The latter method was not suitable in this current study, as subsequent product purification necessitates an aqueous workup. Our attempts to deprotect the phosphine−boranes with excess diethylamine resulted in incomplete conversion and multiple products. Treatment of phosphine−boranes **5**, **8**, **10**, and **13** with morpholine at 110 °C for 2 h, however, resulted in quantitative deprotection as monitored by ^{1}H NMR (Scheme 5). In some cases, isolated yields were slightly lower due to efforts to quantitatively remove morpholine−borane. This was especially true for the sulfonated phosphine **16** which was isolated in 18% yield, though NMR spectroscopy unequivocally demonstrated complete deprotection. The deprotected

Scheme 5. Morpholine-Mediated Phosphine Deprotection



phosphines are crystalline solids which slowly oxidize in nondegased solvents or upon exposure to air.

Interestingly, the counterions of the cationic phosphines **14** and **15** were discovered to play a crucial role in the water-solubility of these phosphines. Phosphines **14a** and **15a**, which have iodide counterions, are soluble only in methanol while the corresponding chlorides **14b** and **15b** are completely soluble in both methanol and water. The solubility of difunctionalized phosphine **17** is not subject to this counterion influence, as both the iodide and chloride derivatives are totally water soluble. Sulfonated phosphine **16** is completely soluble in both methanol and water.

Determination of Phosphine Steric Parameters. The steric bulk of phosphines is typically expressed in terms of cone angles, usually the Tolman cone angle, θ_{Tol}, originally derived from space-filling models,[13] or the Musco cone angle, θ_{Mus}, derived from phosphine X-ray diffraction data.[14] Space-filling molecular models were not employed in this study to mechanically estimate the cone angles of the new phosphines, as uncertainty existed regarding the steric demands of the charged moieties and the spatial requirements of the counterions. We elected to estimate the cone angles of our new phosphines by preparing corresponding *trans*-$Pd(PR_3)_2Cl_2$ complexes, as an empirical linear relationship has been demonstrated between the ^{31}P NMR chemical shift and both θ_{Tol} and θ_{Mus}.[15] Accordingly, *trans*-$Pd(PR_3)_2Cl_2$ complexes of phosphines **14b**, **15b**, **16**, and **17b** were prepared by the reaction of *cis*-/*trans*-$Pd(PhCN)_2Cl_2$ with 2 equiv of phosphine (eq 2).[3a,15,16]

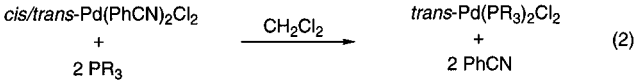


Table 2. ^{31}P NMR Chemical Shifts for *trans*-$Pd(PR_3)_2Cl_2$ Complexes[a]

phosphine	chem shift (ppm)	phosphine	chem shift (ppm)
PCy_3	25.12	**14**	26.90
12b	25.16	**15b**	18.08
13b	26.67		

[a] Spectra recorded in CH_2Cl_2, referenced to H_3PO_4.

The ^{31}P NMR spectrum for each complex was recorded directly *in situ*. Each spectrum consisted of a sharp singlet, and neither uncoordinated phosphine nor the sterically-discouraged *cis*-$Pd(PR_3)_2Cl_2$ complexes[15,16] were observed. Table 2 provides the spectral data obtained for the palladium complexes of the new phosphines. The reference value for *trans*-$Pd(PCy_3)_2Cl_2$ has been recorded for comparison.

While investigating these palladium complexes, we noted a substantial difference between our experimental data and the value previously reported for the tricyclohexylphosphine complex. We determined the ^{31}P NMR chemical shift for *trans*-$(PCy_3)_2PdCl_2$ to be 25.12 ppm, and a similar value of 25.4 ppm was reported recently.[17] These values differ significantly from the previously reported value of 58.4 ppm and cannot be extrapolated to the correct cone angle of 170° via the relationship described above.[15] Since this correlation could not be used reliably to determine the cone angle for PCy_3, it was not employed to numerically derive cone angles for our phosphines. However, the ^{31}P NMR chemical shift values were used for a qualitative comparison of these phosphines with PCy_3. The ^{31}P NMR chemical shift values for the *trans*-$Pd(PR_3)_2Cl_2$ complexes of the dicyclohexyl-derived phosphines **14b**, **15b**, and **16** are within ±1.5 ppm of the value for *trans*-$Pd(PCy_3)_2Cl_2$. This suggests that these new phosphines are sterically similar to PCy_3. By analogy, the difunctionalized phosphine **17b** has a chemical shift which is 7 ppm upfield from that of PCy_3 and may possibly be sterically less-demanding. However, as the ^{31}P NMR chemical shifts our $Pd(PR_3)_2Cl_2$ complexes may be affected by the charged nature of the substituents and the presence of Cl^- ions in solution, assignment of cone angles for these new phosphines should be made with discretion.

Determination of Phosphine Electronic Parameters. Phosphine ligands may also be organized in an electronic series based on the carbonyl stretching frequencies of monosubstituted nickel carbonyl complexes of the type $Ni(CO)_3PR_3$.[5a,13,18] Tolman has defined the phosphine electronic parameter, χ, as

$$\chi_{PR_3} = \nu(CO)(A_{1(PR_3Ni(CO)_3)}) - \nu(CO)(A_{1(P(tBu)_3Ni(CO)_3)})$$

where the A_1 carbonyl stretching mode, ν(CO), is measured in CH_2Cl_2.[13] By this relationship, the value of χ decreases as the electron-donating character of a

(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(14) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41.
(15) Bartik, T.; Himmler, T. *J. Organomet. Chem.* **1985**, *293*, 343.
(16) (a) Grim, S. O.; Keiter, R. L. *Inorg. Chim. Acta* **1970**, *4*, 56. (b) Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871.
(17) Grushin, V. V.; Bensimon, C.; Alper, H. *Inorg. Chem.* **1994**, *33*, 4804.
(18) Strohmeir, W.; Müller, F. J. *Chem. Ber.* **1967**, *100*, 2812.

Table 3. FTIR Stretching Frequencies, ν_{A_1}, and Electronic Parameters, χ, for $Ni(CO)_3PR_3$ Complexes[a]

phosphine	ν_{A_1} (cm^{-1})	χ (cm^{-1})	phosphine	ν_{A_1} (cm^{-1})	χ (cm^{-1})
14	2054.0	−2.1	PEt_3	2061.7	5.6
P(*t*-Bu)$_3$	2056.1	0.0	**12b**	2065.3	9.2
PCy_3	2056.4	0.3	PPh_3	2068.9	12.8
P(*i*-Pr)$_3$	2059.2	3.1	**15b**	2071.9	15.8
13b	2061.1	5.0			

[a] Spectra recorded in CH_2Cl_2 on CsF_2 plates.

phosphine approaches the electron-donating character of P(*t*-Bu)$_3$. Alkylphosphines readily form monosubstituted complexes with $Ni(CO)_4$ under mild reaction conditions.[5a,18] Accordingly, the $Ni(CO)_3PR_3$ complexes of phosphines **14b**, **15b**, **16**, and **17b** were prepared by the reaction of $Ni(CO)_4$ with 1 equiv of phosphine in CH_2Cl_2 at room temperature (eq 3).

$$Ni(CO)_4 + PR_3 \xrightarrow{CH_2Cl_2} Ni(CO)_3PR_3 + CO \qquad (3)$$

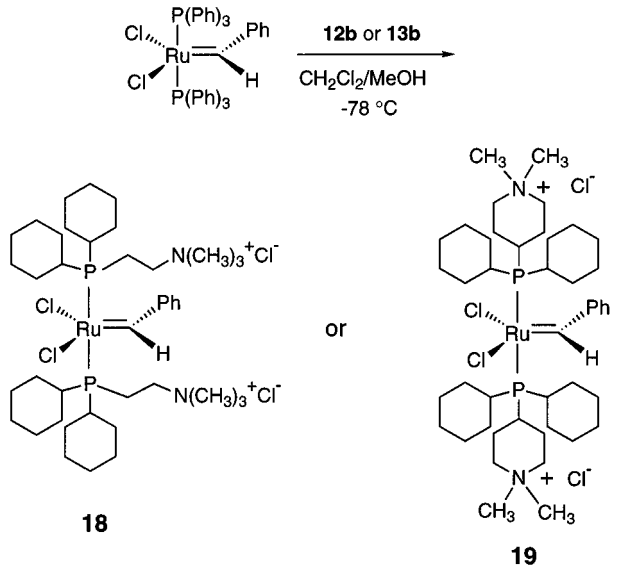
The nickel complexes were not isolated but were recognized by their characteristic carbonyl stretching modes in the infrared spectrum. ^{31}P NMR spectra for each complex consisted of a sharp singlet with no evidence of uncoordinated phosphine or polysubstituted species. The spectral data and χ values for all new phosphines are presented in Table 3, as well as parameters for several other representative phosphines.[13]

From the data in Table 3, it is evident that phosphine electron-donating capability is strongly influenced by the nature of the functional group. Anionic phosphine **16** is more electron-donating than both PCy_3 and P(*t*-Bu)$_3$, whereas the cationic phospines **14b**, **15b**, and **17b** are significantly less electron-donating. In fact, the difunctionalized phosphine **17b** has a χ value which exceeds that of PPh_3. Presumably, the negatively-charged sulfonate group inductively increases the electron density on phosphorus atom, whereas the positively-charged quaternary ammonium functionalities withdraw electron density by the same mechanism. This hypothesis is supported by the observation that the electronic parameter for **17b**, which contains two quaternary groups, is nearly twice the value of the electronic parameter for **14b**, containing only one. Additionally, the quaternary functionality on **15b** is further from the phosphorus center. Consequently, **15b** is more electron-donating than **14b** or **17b**, although this method has been used only once to determine electronic contributions of charged substituents on phosphorus.[5a]

Synthesis and Properties of Water-Soluble Ruthenium Carbene Complexes. Ruthenium carbene complexes **18** and **19** were prepared by phosphine exchange of **14b** and **15b** with $RuCl_2(=CHPh)(PPh_3)_2$[19] or via a one-pot procedure using $RuCl_2(PPh_3)_3$ and phenyldiazomethane, modified slightly from the procedure for the synthesis of **1** (Scheme 6).[19] Complex **18** was obtained in 67% yield as a purple microcrystalline solid after repeated precipitation from CH_2Cl_2/pentane and CH_2Cl_2. Complex **19** was obtained in 54% yield as a purple microcrystalline solids after repeated precipitation from CH_2Cl_2/pentane and CH_2Cl_2/THF.

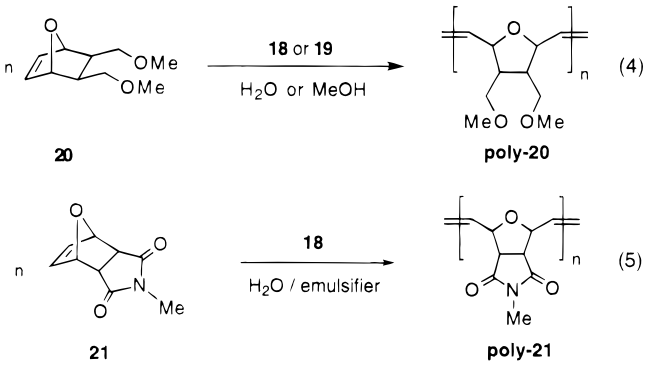
(19) As **1** is a much faster initiating species for ROMP than **2** in organic media (see ref 1c), we designed these complexes incorporating the benzylidene moiety.

Scheme 6. Synthesis of Water-Soluble Ruthenium Carbene Complexes



The ruthenium carbene complexes **18** and **19** are completely soluble in both water and methanol. While the stability of the complexes in methanolic solution extends over a period of weeks, decomposition is observed after 2 days in water.[20] Both complexes are completely insoluble in solvents such as benzene, THF, acetone, and ethanol. Although complex **19** is soluble in CH_2Cl_2, it decomposes over a period of hours in solution.

Preliminary experiments have demonstrated that **18** and **19** serve as efficient initiators for the ROMP[21] of several functionalized 7-oxanorbornene derivatives **20** and **21** in water, methanol, and aqueous emulsions (eqs 4 and 5). Polydispersities for the corresponding poly-



mers are typically low (1.1−1.3) although we occasionally observed bimodal molecular weight distributions. Ongoing investigations into the metathesis activity of these water-soluble complexes will be addressed in forthcoming contributions.

Conclusions

In this contribution, we have reported a new synthetic approach to bulky, aliphatic, water-soluble phosphines

(20) Interestingly, the carbene protons in these complexes exchange rapidly with deuterons in D_2O and, on a slower time scale, methanol-d_4 solution. The mechanism for this exchange is under investigation.

(21) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Schrock, R. R. In *Ring-Opening Polymerization;* Brunelle, D. J., Ed.; Hanser: Munich, Vienna, New York, 1993; p 129.

via air-stable, borane-protected intermediates. Judicious choice of electrophile provides ready access to a variety of neutral and cationically- and anionically-functionalized phosphine−boranes, and subsequent treatment with morpholine resulted in quantitative removal of the boronato group. The cone angles of the new phosphines were estimated using ^{31}P NMR chemical shifts of the corresponding $Pd(PR_3)_2Cl_2$ complexes. Infrared spectroscopic investigations of corresponding $Ni(CO)_3PR_3$ complexes indicate that the phosphines bearing positively-charged functionalities are less electron-donating than tricyclohexylphosphine, while the presence of a sulfonate group increases electron-donating character. Dicyclohexylphosphine derivatives **14** and **15** have been applied to the synthesis of water-soluble ruthenium carbene complexes **18** and **19** which initiate the ROMP of functionalized 7-oxanorbornenes in protic media. The potential of these complexes to initiate the polymerization of a variety of water-soluble monomers is currently under investigation.

Experimental Section

General Considerations. All manipulations involving free phosphines were performed in a nitrogen-filled drybox or by using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H NMR (300.1 MHz) and ^{13}C NMR (75.49 MHz) spectra were recorded on a GE QE-300 spectrometer; ^{31}P NMR (161.9 MHz) spectra were recorded on a JEOL GX-400 spectrometer. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for proton spectra or to phosphoric acid for phosphorus spectra. FTIR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer using cesium fluoride salt plates. Column chromatography was performed with E. Merck 230−400 ASTM mesh, 0.040−0.063 mm particle size, silica gel 60.

Materials. Dichloromethane, tetrahydrofuran, and pentane were purified by passage through solvent purification columns containing activated alumina. Pyridine was distilled from calcium hydride. Methanol and morpholine were degassed by stirring under vacuum for 15 min prior to use. Deionized water used for the polymerizations was degassed by purging with argon and then stirring under vacuum prior to use. Dicyclohexylphosphine, cyclohexylphosphine, bis(benzonitrile)palladium dichloride, and nickel tetracarbonyl were purchased from Strem Chemicals, Inc. Amberlite IRA-400-(Cl) ion exchange resin was obtained from Sigma-Aldrich. Tris(triphenylphosphine)ruthenium dichloride,[22] phenyldiazomethane,[23] $RuCl_2(=CHPh)(PPh_3)_2$,[1c] and norbornenes **20**[23] and **21**[24] were prepared as previously reported. All other reagents were reagent grade and used without further purification.

Dicyclohexylphosphine−Borane, $Cy_2PH(BH_3)$ (3). Dicyclohexylphosphine (19.7 g, 0.99 mol) in THF (100 mL) was placed into a Schlenk flask equipped with a stirbar, capped with a rubber septum, and purged with argon. The solution was cooled to 0 °C, and BH_3·THF (100 mL of a 1.0 M solution in THF, 0.1 mol, 1.01 equiv) was slowly added *via* cannula. The colorless solution was stirred for 2 h at 0 °C and then allowed to warm to room temperature. Evaporation of the solvent resulted in a crystalline white solid, which was recrystallized from pentane. Yield: 18.9 g (90%) as white needles. ^{1}H NMR (δ, CD_3OD): 4.11 (app dsx, $^3J_{HH}$ = 5.93 Hz, J_{HP} = 359.0 Hz, 1H), 1.95−1.71 (m, 10H), 1.45−1.23 (m, 12H), 0.23 (br q, 96.60 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 28.73, 28.47, 28.01, 27.07, 26.03, 25.87, 25.70, 25.30. ^{31}P NMR (δ, CD_3OD): 17.50 (br m). Anal. Calcd for $C_{12}H_{26}BP$ (M_r = 212.13): C, 67.95; H, 12.35. Found: C, 68.23; H, 11.86.

$Cy_2P(BH_3)CH_2CH_2N(CH_3)_2$ (4). **3** (4 g, 18.90 mmol) in THF (100 mL) was placed into a Schlenk flask and purged with argon. The solution was cooled to −78 °C, and *n*-butyllithium (12.4 mL of a 1.6 M solution in hexane, 19.80 mmol, 1.05 equiv) was added dropwise *via* syringe over a period of 10 min. The colorless reaction mixture was stirred for 2 h while slowly warming to room temperature. Upon cooling of the solution to −78°C, 2-chloro-*N*,*N*-dimethylaminoethane (2.44 g, 22.70 mmol, 1.20 equiv) in THF (50 mL) was slowly added *via* syringe. The reaction mixture was kept for 2 h at −78 °C and then stirred at room temperature overnight. Evaporation of the solvent gave a white solid which was subjected to column chromatography (silica gel/methanol, R_f = 0.25) to yield 3.48g (65%) of a white solid. ^{1}H NMR (δ, CD_3OD): 2.43 (d t, J_{HH} = 4.50 Hz, J^3_{HP} = 12.0 Hz, 2H), 2.27 (s, 6H), 1.85−1.65 (m, 10H), 1.61−1.54 (m, 4H), 1.35−1.16 (m, 10H), 0.24 (br q, 87.30 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 53.76, 53.72, 43.55, 31.71, 31.28, 26.64, 26.58, 26.43, 26.38, 25.79, 16.49, 16.08. ^{31}P NMR (δ, CD_3OD): 24.56 (br m). Anal. Calcd for $C_{16}H_{35}BNP$ (M_r = 283.26): C, 67.85; H, 12.45; N, 4.94. Found: C, 67.88; H, 12.45; N, 5.04.

$Cy_2P(BH_3)CH_2CH_2N(CH_3)_3^+I^-$ (5a). **4** (1.50 g, 5.30 mmol) was dissolved in ether (60 mL) followed by addition of methyl iodide (1.88 g, 13.24 mmol, 2.5 equiv). The reaction mixture was stirred for 4 h at room temperature, during which a white solid precipitated. The precipitate was collected by filtration, washed with ether, and dried *in vacuo* to yield 2.17 g (97%) of a white solid. ^{1}H NMR (δ, CD_3OD): 3.57 (d t, J_{HH} = 4.40 Hz, $^3J_{HP}$ = 12.9 Hz, 2H), 3.18 (s, 9H), 2.17 (m, 2H), 1.95−1.72 (m, 12H), 1.43−1.20 (m, 10H), 0.30 (b q, J_{HP} = 93.9 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 62.09, 51.73, 31.65, 31.22, 26.25, 26.22, 26.13, 26.10, 25.32, 13.00, 12.62. ^{31}P NMR (δ, CD_3OD): 27.61 (br m). Anal. Calcd for $C_{17}H_{38}BINP$ (M_r = 425.20): C, 48.02; H, 9.00; N, 3.29. Found: C, 47.66; H, 8.78; N, 3.20.

$Cy_2P(BH_3)CH_2CH_2N(CH_3)_3^+Cl^-$ (5b). Method I. By Methylation of 4 with Methyl Chloride. **4** (1.50 g, 5.30 mmol) was dissolved in ether (60 mL) followed by addition of methyl chloride (53 mL of a 1.0 M solution in CH_2Cl_2, 10 equiv). The mixture was stirred for 72 h, during which a white solid precipitated. The solvent was removed, and the resulting white residue was washed with ether and dried *in vacuo* to yield 1.68 g (96%) of a white solid.

Method II. By Conversion of 3 with (2-Chloroethyl)-trimethylammonium Chloride. Lithiation of **3** (4 g, 18.9 mmol) with *n*-butyllithium (12.4 mL of a 1.6 M solution in hexane, 19.80 mmol, 1.05 equiv) was achieved as described above. Upon cooling of the solution to −78 °C, (2-chloroethyl)-trimethylammonium chloride (3.59 g, 22.70 mmol, 1.20 equiv) was added in small portions against a counterstream of argon. The white suspension was allowed to warm to room temperature and then stirred at 60 °C for 6 h. Removal of the solvent under reduced pressure yielded a white solid which was extracted with $CHCl_3$ (250 mL). The solvent was evaporated, and the resulting residue was repeatedly washed with ether (500 mL) to give 3.41 g (54%) of a white solid. ^{1}H NMR (δ, D_2O): 3.52 (d t, J_{HH} = 4.40 Hz, $^3J_{HP}$ = 12.0 Hz, 2H), 3.13 (s, 9H), 2.17 (m, 2H), 1.97−1.67 (m, 12H), 1.28−1.18 (m, 10H), 0.25 (b q, J_{HP} = 97.5 Hz, 3H). ^{13}C NMR (δ, D_2O): 62.10, 52.34, 31.11, 30.66, 26.25, 26.08, 25.94, 25.28, 12.71, 12.31. ^{31}P NMR (δ, D_2O): 24.80 (br m). Anal. Calcd for $C_{17}H_{38}BClNP$ (M_r = 333.75): C, 61.19; H, 11.47; N, 4.20. Found: C, 60.73; H, 11.28; N, 3.97.

4-(*p*-Toluenesulfonyl)-*N*-methylpiperidine (6). *p*-Toluenesulfonyl chloride (25.0 g, 131.0 mmol, 1.16 equiv) was

(22) Stephenson, T. A.; Wilkinson, G. J. *Inorg. Nucl. Chem.* **1966**, *28*, 945.
(23) (a) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (b) Yates, P.; Shapiro, B. L. *J. Org. Chem.* **1958**, *23*, 759.
(24) (a) Brion, F. *Tetrahedron Lett.* **1982**, *23*, 5299. (b) Dauben, W. G.; Krabbenhoft, H. O. *J. Am. Chem. Soc.* **1976**, *98*, 1992. (c) Nelson, W. L.; Allen, D. R. *Heterocycl. Chem.* **1972**, *9*, 561.
(25) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 3345.

slowly added to a solution of 4-hydroxy-*N*-methylpiperidine (13.0 g, 113.0 mmol) and 4-(dimethylamino)pyridine (150 mg, 1.23 mmol) in 250 mL of dry pyridine at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h, during which the solution turned dark red and an orange precipitate formed. Ether (500 mL) was added to complete the precipitation. The red supernatant was decanted, and the orange precipitate was repeatedly washed with ether (1500 mL) until the washings became colorless. A saturated aqueous solution of sodium bicarbonate (500 mL) was added to the residue, and the resulting dark red slurry was extracted with ether (4 × 300 mL). The combined ether layers were washed with saturated aqueous sodium bicarbonate solution and water and dried over $MgSO_4$, and the solvent was evaporated *in vacuo* to yield 17.8 g (59%) of a viscous orange oil. This compound decomposed over several days upon solidification and was therefore used immediately after preparation. ^{1}H NMR (δ, CD_3OD): 7.80 (d, J_{HH} = 7.80 Hz, 2H), 7.43 (d, J_{HH} = 7.80 Hz, 2H), 4.55 (m, 1H), 2.56 (m, 2H), 2.44 (s, 3H), 2.29 (m, 2H), 2.23 (s, 3H), 1.85−1.69 (m, 4H). ^{13}C NMR (δ, CD_3OD): 144.74, 134.09, 129.48, 127.12, 77.10, 51.12, 44.35, 30.45, 20.00. Anal. Calcd for $C_{13}H_{19}BNO_3S$ (M_r = 269.38): C, 57.98; H, 7.11; N, 5.20. Found: C, 57.74; H, 7.08; N, 5.10.

$Cy_2P(BH_3)$(*N*-methylpiperidine) (7). Lithiation of **3** (3.2 g, 15.1 mmol) with *n*-butyllithium (10.0 mL of a 1.6 M solution in hexane, 16.0 mmol, 1.06 equiv) was performed as described above. Upon cooling of the solutin to −78 °C, **6** (2.0 g, 7.42 mmol, 0.5 equiv) in THF (50 mL) was slowly added *via* syringe. The reaction mixture was maintained at −78 °C for 2 h and then stirred at 60 °C for 6 h. Upon evaporation of the solvent ether (50 mL) and saturated aqueous sodium bicarbonate solution (50 mL) were added. The organic phase was separated and the aqueous phase extracted with ether (2 × 100 mL). Evaporation of the combined organic layers gave a white solid which was subjected to column chromatography (silica gel/methanol, R_f = 0.22) to yield 1.25 g (54%) of a white solid. ^{1}H NMR (δ, CD_3OD): 2.97−2.94 (m, 2H), 2.25 (s, 3H), 2.03−1.74 (m, 19H), 1.44−1.27 (m, 10H), 0.25 (b q, J_{HP} = 89.0 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 55.57, 55.42, 44.72, 30.70, 30.29, 28.03, 27.61, 27.30, 26.63, 26.49, 26.40, 25.64. Anal. Calcd for $C_{18}H_{37}BNP$ (M_r = 309.29): C, 69.91; H, 12.06; N, 4.53. Found: C, 70.08; H, 11.99; N, 4.36.

$Cy_2P(BH_3)$(*N*,*N*-dimethylpiperidinium iodide) (8a). Method I. By methylation of 7 with Methyl Iodide. This was done analogous to the method for **5a** to yield a white solid (98%).

Method II. By Conversion of 3 with 9. Lithiation of **3** (6.50 g, 30.6 mmol) with *n*-butyllithium (20.0 mL of a 1.6 M solution in hexane, 32.0 mmol, 1.05 equiv) was performed as described above. Upon cooling of the solution to −78 °C, **9** (12.0 g, 29.0 mmol, 0.95 equiv) was added in small portions against a counterstream of argon. The white suspension was allowed to warm to room temperature and was then stirred at 65 °C for 18 h. Removal of the solvent under reduced pressure yielded a white solid which was dissolved in hot methanol (150 mL). Ether (ca. 300 mL) was added until precipitation started. Precipitation was completed at −50 °C, and the obtained white crystalline solid was reprecipated by the same procedure to yield 5.9 g (45%). ^{1}H NMR (δ, CD_3OD): 3.60−3.40 (m, 4H), 3.20 (s, 3H), 3.10 (s, 3H), 2.37−1.76 (m, 17H), 1.46−1.30 (m, 10H), 0.31 (b q, J_{HP} = 108.0 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 61.67, 61.53, 55.41, 45.91, 31.16, 30.75, 27.41, 26.59, 26.45, 25.49, 24.32, 23.91, 21.28. ^{31}P NMR (δ, CD_3OD): 30.81 (br m). Anal. Calcd for $C_{19}H_{40}BINP$ (M_r = 451.24): C, 50.58; H, 8.94; N, 3.10. Found: C, 50.58; H, 8.89; N, 3.16.

$Cy_2P(BH_3)$(*N*,*N*-dimethylpiperidinium chloride) (8b). **8a** (1.57 g, 3.32 mmol) and Amberlite IRA-400(Cl) ion-exchange resin (30 g) were stirred in methanol/water (1/1, 100 mL) for 12 h. The resin was removed by filtration, and the procedure was repeated three times. In the last cycle hydrochloric acid (1.5 mL of a 2.0 M solution) was added. Evaporation of the filtrate yielded 1.07 g (86%) of a white solid. ^{1}H NMR (δ, D_2O): 3.55−3.28 (m, 4H), 3.14 (s, 3H), 3.05 (s, 3H), 2.31−1.67 (m, 17H), 1.35−1.16 (m, 10H), 0.26 (b q, J_{HP} = 115.5 Hz, 3H). ^{13}C NMR (δ, D_2O): 62.48, 62.35, 56.58, 46.99, 31.30, 30.68, 27.52, 26.60, 26.46, 25.68, 24.28, 23.68, 21.58. ^{31}P NMR (δ, D_2O): 27.51 (br m). Anal. Calcd for $C_{19}H_{40}BClNP$ (M_r = 359.78): C, 63.43; H, 11.20; N, 3.89. Found: C, 60.29; H, 11.17; N, 3.88.

4-(*p*-Toluenesulfonyl)-*N*,*N*-dimethylpiperidinium iodide (9). **6** (13.5 g, 50.1 mmol) was dissolved in ether (200 mL) followed by addition of methyl iodide (17.4 g, 122.6 mmol, 2.45 equiv). The mixture was stirred for 12 h at room temperature, during which a white solid precipitated. The precipitate was collected by filtration, washed with ether and dried *in vacuo* to yield 19.85 g (96%) of a white crystalline solid. ^{1}H NMR (δ, CD_3OD): 7.88 (d, J_{HH} = 8.10 Hz, 2H), 7.49 (d, J_{HH} = 8.10 Hz, 2H), 4.86 (m, 1H), 3.57 (app t, J_{HH} = 5.85 Hz, 4H), 3.28 (s, 3H), 3.22 (s, 3H), 2.46 (s, 3H), 2.27 (m, 2H), 2.05 (m, 2H). ^{13}C NMR (δ, CD_3OD): 145.36, 133.09, 129.83, 127.40, 72.01, 58.05, 52.77, 49.37, 25.38, 20.13. Anal. Calcd for $C_{14}H_{22}BNIO_3S$ (M_r = 411.32): C, 40.86; H, 5.39; N, 3.40. Found: C, 41.01; H, 5.49; N, 3.47.

$Cy_2P(BH_3)CH_2CH_2SO_3^-Na^+$ (10). Lithiation of **3** (7.00 g, 33.0 mmol) with *n*-butyllithium (21.7 mL of a 1.6 M solution in hexane, 34.7 mmol, 1.05 equiv) was performed as described above. Upon cooling of the solutin to −78 °C, sodium 2-bromoethanesulfonate (8.0 g, 37.9 mmol, 1.14 equiv) was added in small portions against a counterstream of argon. The white suspension was allowed to warm to room temperature and then stirred at 65 °C for 12 h. Removal of the solvent under reduced pressure yielded a white solid which was extracted with CH_2Cl_2 (200 mL). The extract was reduced to a volume of 50 mL, and ether (ca. 250 mL) was added until precipitation started. The precipitation was completed at −50 °C, and the resulting white crystalline solid was reprecipated by the same procedure to yield 7.57 g (67%). ^{1}H NMR (δ, CD_3OD): 2.90 (dt, J_{HH} = 5.10 Hz, $^3J_{HP}$ = 12.6 Hz, 2H), 2.04 (m, 2H), 1.85−1.70 (m, 12H), 1.41−1.26 (m, 10H), 0.25 (b q, J_{HP} = 105.0 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 45.82, 31.49, 31.05, 26.36, 26.27, 26.14, 26.04, 25.48, 14.45, 14.04. ^{31}P NMR (δ, CD_3OD): 2.78 (br m). Anal. Calcd for $C_{14}H_{29}BO_3PSNa$ (M_r = 342.25): C, 49.14; H, 8.54. Found: C, 48.67; H, 8.23.

Cyclohexylphosphine−Borane, $CyPH_2(BH_3)$ (11). Cyclohexylphosphine (10.8 g, 0.093 mol) in THF (30 mL) was placed into a Schlenk flask equipped with a stirbar, capped with a rubber septum, and purged with argon. The solution was cooled to −20 °C, and BH_3·THF (100 mL of a 1.0 M solution in THF, 0.1 mol, 1.07 equiv) was slowly added *via* the double-ended needle technique. The colorless solution was stirred for 2 h at −20 °C and then allowed to warm to room temperature. Evaporation of the solvent resulted in 12.1 g (100%) of a colorless slightly viscous liquid. ^{1}H and ^{13}C NMR showed the desired product in >95% purity. Slow evolution of gas bubbles indicated gradual decomposition, and this compound was therefore used immediately and without further purification. ^{1}H NMR (δ, CD_3OD): 4.38 (m, J_{HP} = 359.4 Hz, 2H), 1.97−1.72 (m, 6H), 1.37−1.25 (m, 5H), 0.53 (b q, J_{HP} = 93.7 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 35.39, 35.30, 29.62, 25.81, 25.66, 25.05.

$CyP(BH_3)(CH_2CH_2N(CH_3)_2)_2$ (12). Cyclohexylphosphine−borane (5.0 g, 38.47 mmol) in THF (100 mL) was placed into a Schlenk flask and purged with argon. The solution was cooled to −78 °C, and *n*-butyllithium (50.5 mL of a 1.6 M solution in hexane, 80.8 mmol, 2.1 equiv) was slowly added *via* syringe. The colorless solution was allowed to warm to room temperature over 2 h with stirring. Upon cooling of the solution to −78 °C, 2-chloro-*N*,*N*-dimethylaminoethane (8.68 g, 80.8 mmol, 2.4 equiv) in THF (100 mL) was slowly added *via* syringe. The reaction mixture was kept for 2 h at −78 °C and then stirred at room temperature overnight. Evaporation of the solvent gave a white solid which was subjected to column chromatography (silica gel/methanol, R_f = 0.05) to yield 4.18

g (40%) of a colorless viscous material, which solidified overnight. ^{1}H NMR (δ, CD_3OD): 2.54 (d t, J_{HH} = 6.05 Hz, $^3J_{HP}$ = 10.5 Hz, 4H), 2.27 (s, 12H), 1.89−1.70 (m, 10H), 1.35−1.25 (m, 5H), 0.31 (b q, J_{HP} = 86.6 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 52.53, 43.27, 32.54, 32.08, 26.11, 25.96, 25.73, 25.38, 18.36, 17.92. ^{31}P NMR (δ, CD_3OD): 18.79 (br m). Anal. Calcd for $C_{14}H_{34}BN_2P$ (M_r = 272.23): C, 61.77; H, 12.59; N, 10.29. Found: C, 61.38; H, 12.79; N, 9.89.

$CyP(BH_3)(CH_2CH_2N(CH_3)_3^+I^-)_2$ (13a). This was made by methylation of **12** with methyl iodide analogous to **5a** to yield a white solid (97%). ^{1}H NMR (δ, CD_3OD): 3.82−3.58 (m, 4H), 3.23 (s, 18H), 2.48−2.35 (m, 4H), 1.99−1.75 (m, 6H), 1.45−1.30 (m, 5H), 0.38 (b q, J_{HP} = 114.0 Hz, 3H). ^{13}C NMR (δ, CD_3OD): 60.90, 51.82, 32.62, 32.18, 25.92, 25.76, 25.55, 25.07, 15.33, 14.93. ^{31}P NMR (δ, CD_3OD): 24.36 (br m). Anal. Calcd for $C_{16}H_{40}BI_2N_2P$ (M_r = 556.11): C, 34.56; H, 7.25; N, 5.04. Found: C, 34.28; H, 7.41; N, 4.97.

$CyP(BH_3)(CH_2CH_2N(CH_3)_3^+Cl^-)_2$ (13b). This was made by methylation of **12** with methyl chloride analogous to **5b** to yield a white solid (96%). NMR data are identical to those of **13a**. Anal. Calcd for $C_{16}H_{40}BCl_2N_2P$ (M_r = 373.21): C, 51.50; H, 10.80; N, 7.51. Found: C, 51.78; H, 10.53; N, 7.38.

$Cy_2PCH_2CH_2N(CH_3)_3^+I^-$ (14a). **5a** (1.50 g, 3.53 mmol) in morpholine (30 mL) was placed into a Schlenk flask and purged with argon. The reaction mixture was stirred for 2 h at 110 °C and then cooled to room temperature. Evaporation of the solvent gave a gummy white residue which was dissolved in a small amount of methanol (3 mL) and reprecipitated by addition of cold THF (25 mL). The supernatant was removed *via* canula filtration, and the precipitate was washed with a small amount of THF (5 m) and dried *in vacuo* to yield 1.05 g (72%) of a white crystalline solid. ^{1}H NMR (δ, CD_3OD): 3.44 (d t, J_{HH} = 4.30 Hz, $^3J_{HP}$ = 14.1 Hz, 2H), 3.15 (s, 9H), 1.89−1.64 (m, 14H), 1.40−1.19 (m, 10H). ^{13}C NMR (δ, CD_3OD): 66.37, 65.84, 51.29, 32.81, 32.64, 29.67, 29.47, 28.52, 28.41, 26.64, 26.56, 26.47, 25.77, 14.59, 14.31. ^{31}P NMR (δ, CD_3OD): −5.92 (s). Anal. Calcd for $C_{17}H_{35}INP$ (M_r = 411.36): C, 49.64; H, 8.57; N, 3.40. Found: C, 49.69; H, 8.41; N, 3.26.

$Cy_2PCH_2CH_2N(CH_3)_3^+Cl^-$ (14b). The reaction was performed in a similar fashion to **15a**. **6b** (1.50 g, 4.49 mmol) in morpholine (30 mL) was placed into a Schlenk flask and purged with argon. The reaction mixture was stirred for 2 h at 110 °C. Upon cooling of the mixture, precipitation of a white solid started around 65 °C. The reaction mixture was cooled to room temperature and THF (50 mL) was added to complete precipitation. The supernatant was removed *via* canula filtration, and the white precipitate was washed with a small amount of THF and dried *in vacuo* to yield 1.21 g (84%). ^{1}H NMR (δ, D_2O): 3.47 (d t, J_{HH} = 4.20 Hz, $^3J_{HP}$ = 8.4 Hz, 2H), 3.18 (s, 9H), 1.95 (s, 2H), 1.88−1.72 (m, 12H), 1.35−1.12 (m, 10H). ^{13}C NMR (δ, D_2O): 66.24, 65.77,52.24, 32.20, 32.10, 29.69, 29.51, 28.51, 28.43, 26.70, 26.55, 26.45, 25.84, 14.21, 13.99. ^{31}P NMR (δ, D_2O): −6.53 (s). Anal. Calcd for $C_{17}H_{35}ClNP$ (M_r = 319.91): C, 63.83; H, 11.03; N, 4.37. Found: C, 63.57; H, 11.17; N, 4.32.

Cy_2P(*N,N*-dimethylpiperidinium iodide) (15a). This compound was made by conversion of **8a** with morpholine analogous to **14a** to yield a white solid (73%). ^{1}H NMR δ (CD_3OD): 3.55−3.45 (m, 4H), 3.19 (s, 3H), 3.10 (s, 3H), 1.95−1.71 (m, 17H), 1.40−1.26 (m, 10H). ^{13}C NMR (δ, CD_3OD): 62.49, 62.37, 55.32, 46.48, 31.71, 31.50, 30.69, 30.62, 30.54, 30.47, 26.95, 26.82, 25.79, 24.60, 24.40. ^{31}P NMR (δ, CD_3OD): 9.67 (s). Anal. Calcd for $C_{19}H_{37}INP$ (M_r = 437.40): C, 52.18; H, 8.53; N, 3.20. Found: C, 51.97; H, 8.71; N, 3.11.

Cy_2P(*N,N*-dimethylpiperidinium chloride) (15b). This compound was made by conversion of **8a** with morpholine analogous to **14a** to yield a crystalline white solid (73%). ^{1}H NMR δ (D_2O): 3.5−3.25 (m, 4H), 3.11 (s, 3H), 3.03 (s, 3H), 2.03−1.59 (m, 17H), 1.30−1.20 (m, 10H). ^{13}C NMR (δ, D_2O): 62.72, 62.60, 56.16, 46.91, 30.80, 30.69, 30.42, 30.37, 30.31, 30.24, 26.92, 26.79, 2(.85, 25.26, 25.06, 24.31, 24.14. ^{31}P NMR (δ, D_2O): 8.97 (s). Anal. Calcd for $C_{19}H_{37}ClNP$ (M_r = 345.95): C, 65.78; H, 10.75; N, 4.04. Found: C, 65.25; H, 10.81; N, 3.90.

Sodium 2-(Dicyclohexylphosphino)ethanesulfonate, $Cy_2PCH_2CH_2SO_3^-Na^+$ (16). This compound was made by conversion of **10** with morpholine analogous to **14a** to yield a white solid (15%). ^{1}H NMR (δ, CD_3OD): 2.84 (dt, J_{HH} = 4.75 Hz, $^3J_{HP}$ = 12.9 Hz, 2H), 1.91−1.84 (m, 2H), 1.84−1.54 (m, 12H), 1.33−1.16 (m, 10H). ^{13}C NMR (δ, CD_3OD): 50.25, 49.95, 32.94, 32.78, 29.92, 29.73, 28.44, 28.34, 26.73, 26.59, 26.53, 25.91, 15.80, 15.57. ^{31}P NMR (δ, D_2O): −2.91 (s). Anal. Calcd for $C_{14}H_{26}O_3PSNa$ (M_r = 328.41): C, 51.21; H, 7.98. Found: C, 50.77; H, 8.23.

$CyP(CH_2CH_2N(CH_3)_3^+I^-)_2$ (17a). This compound was made by conversion of **13a** with morpholine analogous to **14a** to yield a white solid (88%). ^{1}H NMR (δ, CD_3OD): 3.60−3.48 (m, 4H), 3.16 (s, 18H), 2.06−1.99 (m, 4H), 1.86−1.65 (m, 6H), 1.40−1.21 (m, 5H). ^{13}C NMR (δ, CD_3OD): 64.69, 64.39, 34.44, 28.93, 28.81, 26.64, 26.54, 25.89, 17.37, 17.17. ^{31}P NMR (δ, CD_3OD): −20.42 (s). Anal. Calcd for $C_{16}H_{37}I_2N_2P$ (M_r = 542.28): C, 35.44; H, 6.88; N, 5.17. Found: C, 35.23; H, 6.97; N, 5.01.

$CyP(CH_2CH_2N(CH_3)_3^+Cl^-)_2$, (17b). This compound was made by conversion of **13b** with morpholine analogous to **14b** to yield a white solid (91%). NMR data are identical to those of **17a**. Anal. Calcd for $C_{16}H_{37}Cl_2N_2P$ (M_r = 359.374): C, 53.48; H, 10.38; N, 7.80. Found: C, 51.79; H, 10.77; N, 7.65.

$RuCl_2$(=CHPh)[$Cy_2PCH_2CH_2N(CH_3)_3^+Cl^-$]$_2$ (18). $RuCl_2$(=CHPh)(PPh_3)$_2$ (1.20 g, 1.53 mmol) was placed in a Schlenk flask equipped with a stirbar, capped with a rubber septum, and purged with argon. CH_2Cl_2 (15.0 mL) was added, and the dark green solution was cooled to −78 °C. **14a** (1.0 g, 3.13 mmol, 2.05 equiv) was dissolved in methanol (10 mL) under argon, cooled to −78 °C, and slowly added to the Schlenk flask *via* syringe. The reaction mixture was stirred at −78 °C for 30 min while a color change to dark red was observed. Stirring was continued for 30 min as the reaction warmed to room temperature. Removal of the solvent *in vacuo* yielded a dark purple solid. The solid material was dissolved in CH_2Cl_2 (10 mL) and stirred, and pentane (100 mL) was added to precipitate a purple solid. The brownish red supernatant was removed and discarded *via* cannula filtration, and this procedure was repeated until the supernatant became colorless. By this stage, the solid product was insoluble in CH_2Cl_2 and was further treated with neat CH_2Cl_2, until the washings became colorless. The product was dissolved in methanol (15 mL) and cannula filtered from an insoluble dark purple material, and solvent was removed *in vacuo* to yield the desired product as a purple solid (0.680 g, 67.4%). ^{1}H NMR (δ, D_2O): 19.76 (s, carbene-H), 8.45 (d, J = 7.5 Hz, *o*-H of C_6H_5), 7.82 (t, J = 7.5 Hz, *p*-H of C_6H_5), 7.57 (t, J = 7.5 Hz, *m*-H of C_6H_5), 3.13 (b m, N−CH_2), 2.96 (s, N−CH_3), 2.36 (b m), 2.00 (b m), 1.85−1.66 (m), 1.53−1.15 (m). ^{13}C NMR (δ, D_2O): 151.70, 132.14, 130.48, 130.11, 62.17, 52.28, 33.20, 33.07, 32.94, 28.86, 28.56, 28.34, 26.76, 26.59, 26.55, 26.39, 25.55, 25.46, 25.31, 12.26, 12.17. ^{31}P NMR (δ, D_2O): 29.38 (s). ^{1}H NMR (δ, CD_3OD): 19.95 (s, carbene-H), 8.55 (d, J = 7.8 Hz, *o*-H of C_6H_5), 7.81 (t, J = 7.8 Hz, *p*-H of C_6H_5), 7.57 (t, J = 7.8 Hz, *m*-H of C_6H_5), 3.20 (b m, N−CH_2), 3.06 (s, N-CH_3), 2.42 (b m), 2.08 (b m), 1.90−1.75 (m), 1.57−1.25 (m). ^{13}C NMR (δ, CD_3OD): 152.20, 131.13, 130.25, 129.65, 61.96, 51.54, 33.29, 33.15, 33.01, 28.80, 28.43, 26.80, 26.72, 26.60, 26.53, 25.35, 12.14, 12.04, 11.92. ^{31}P NMR (δ, CD_3OD): 31.21 (s). Anal. Calcd for $C_{41}H_{76}N_2Cl_4P_2Ru$ (M_r = 901.87): C, 54.60; H, 8.49; N, 3.11. Found: C, 54.48; H, 8.61; N, 3.34. Although the [M^+] peak was not observed in the FAB mass spectrum, the observed isotopic abundance for corresponding [M + H − Cl^-] peaks identically matched the predicted isotope pattern for the [M + H − Cl^-] fragment of the title compound.

$RuCl_2$(=CHPh)[Cy_2P(*N,N*-dimethylpiperidinium chloride)]$_2$ (19). $RuCl_2(PPh_3)_3$ (1.38 g, 1.44 mmol) was placed in a Schlenk flask and purged with argon. CH_2Cl_2 (15.0 mL) was

added, and the dark red solution was cooled to −78 °C. Phenyldiazomethane (0.340 g, 2.88 mmol, 2.0 equiv) was quickly weighed under air, dissolved in pentane (1.0 mL), cooled to −78 °C, and added to the Schlenk flask *via* pipet under an argon purge. Upon addition of the diazo compound, an instantaneous color change from dark red to dark green was observed. The reaction was stirred for 5 min, and a solution of **15a** (1.10 g, 3.18 mmol, 2.2 equiv) in methanol (10 mL) was added *via* syringe. The solution became dark-red, and stirring was continued for 30 min as the reaction warmed to room temperature. Solvent was removed *in vacuo* and dried overnight to yield a burgundy solid. The solid material was dissolved in CH_2Cl_2 (15 mL) and stirred, and pentane (100 mL) was added to precipitate a burgundy solid. Pentane should be added quickly, as **19** slowly decomposes in CH_2Cl_2. The dark red supernatant was removed and discarded *via* cannula filtration, and the product was reprecipitated until the supernatant was colorless. The solid was dissolved in CH_2Cl_2 (10 mL), precipitated by addition of THF (150 mL), and cannula filtered. This process was continued until the supernatant was colorless. The product was dissolved in methanol (10 mL) and cannula filtered from insoluble material, and solvent was removed *in vacuo* to yield the desired product as a burgundy solid (0.740 g, 54%). ^{1}H NMR (δ, D_2O) δ 8.44 (d, J = 7.5 Hz, *o*-H of C_6H_5), 7.77 (t, J = 7.5 Hz, *p*-H of C_6H_5), 7.47 (t, J = 7.5 Hz, *m*-H of C_6H_5), 3.58−3.52 (m, P−CH), 3.35−3.13 (m, N−CH_2), 3.08 (s, N−CH_3), 2.97 (s, N−CH_3), 2.75−2.70 (m), 2.58−2.50 (m), 2.10−1.99 (m), 1.80−1.55 (m), 1.30−1.10 (m). ^{13}C NMR (δ, D_2O): 292.6, 152.41, 130.61, 129.09, 62.44, 52.26, 32.67, 32.55, 32.42, 29.48, 29.29, 27.82, 27.70, 27.58, 26.98, 26.79, 26.85, 26.90, 25.60, 22.80. ^{31}P NMR (δ, D_2O): 35.3 (s). Anal. Calcd for $C_{45}H_{80}N_2Cl_4P_2Ru$ (M_r = 953.99): C, 56.66; H, 8.45; N, 2.93. Found: C, 56.51; H, 8.08; N, 2.91.

General Procedure for the Preparation of $(PR_3)_2PdCl_2$ Complexes (PR_3 = 14a, 15a, 16, 17a). In a nitrogen-filled drybox, *cis,trans*-bis(benzonitrile)palladium dichloride (14.60 mg, 0.038 mmol) was dissolved in CH_2Cl_2 (0.25 mL) to yield an orange solution. Phosphine (2.0 equiv) was dissolved in CH_2Cl_2 (0.25 mL) to yield a colorless solution. The two solutions were mixed together to yield a clear, bright yellow solution. After 5−6 min, small amounts of precipitate were noted. Two drops of methanol were added to redissolve the precipitate, and ^{31}P NMR spectra were recorded directly on this solution.

***trans*-[$Cy_2PCH_2CH_2N(CH_3)_3^+Cl^-]_2PdCl_2$.** ^{31}P NMR ($\delta$)SPCLN CH_2Cl_2, 25.16 (s) ppm; D_2O, 25.20 (s) ppm.

***trans*-[Cy_2P(*N,N*-dimethylpiperidinium chloride)]$_2PdCl_2$.** ^{31}P NMR (δ)SPCLN CH_2Cl_2, 26.67 (s) ppm; D_2O, 27.08 (s) ppm.

***trans*-[$Cy_2PCH_2CH_2SO_3^-Na^+]_2PdCl_2$.** ^{31}P NMR ($\delta$, CH_2Cl_2): 26.90 (s) ppm.

***trans*-[$CyP(CH_2CH_2N(CH_3)_3^+Cl^-)_2]_2PdCl_2$.** ^{31}P NMR ($\delta$, CH_2Cl_2): 18.08 (s) ppm.

General Procedure for the Preparation of $Ni(CO)_3(PR_3)$ Complexes (PR_3 = 14a, 15a, 16, 17a). In a nitrogen-filled drybox, phosphine was weighed into a 1 dram vial and dissolved in CH_2Cl_2 (3.0 mL). Two drops of methanol were added to aid solubility. $Ni(CO)_4$ (0.178 mmol, 1.0 equiv) was added neat to this solution via syringe and immediate bubbling was observed. (*Note: Extreme care should be exercised when handling $Ni(CO)_4$, as it is extremely toxic!*) The reaction was sealed with a Teflon-lined cap and allowed to sit for 10 min. ^{31}P NMR spectra were recorded directly on this solution. Two drops of this solution were further dissolved in CH_2Cl_2 (1.0 mL) for FTIR analysis using a stop-flow injection cell.

[$Cy_2PCH_2CH_2N(CH_3)_3^+Cl^-$]$Ni(CO)_3$. ^{31}P NMR ($\delta$, CH_2Cl_2): 37.41 (s) ppm. IR (CH_2Cl_2): ν(CO) 2065.3 (w), 1991.5 cm^{-1}.

[Cy_2P(*N,N*-dimethylpiperidinium chloride)]$Ni(CO)_3$. ^{31}P NMR (δ, CH_2Cl_2): 47.37 (s) ppm. IR (CH_2Cl_2): ν(CO) 2061.1 (w), 1987.5 cm^{-1}.

[$Cy_2PCH_2CH_2SO_3^-Na^+$]$Ni(CO)_3$. ^{31}P NMR (δ, CH_2Cl_2): 35.59 (s) ppm. IR (CH_2Cl_2): ν(CO) 2054.0 (w), 1983.6 cm^{-1}.

[$CyP(CH_2CH_2N(CH_3)_3^+Cl^-)_2$]$Ni(CO)_3$. ^{31}P NMR ($\delta$, CH_2Cl_2): 24.99 (s) ppm. IR (CH_2Cl_2): ν(CO) 2071.9 (w), 2001.5 cm^{-1}.

General Polymerization Procedure. Typical polymerization reactions were conducted in the following manner. In a nitrogen-filled drybox, monomer was added to a septum-capped vial equipped with a Teflon-coated stirbar. For emulsion-type polymerizations, dodecyltrimethylammonium bromide was added. Catalyst was added to a second vial and capped with a rubber septum. Outside the drybox, water or methanol was added to each vial *via* a gastight syringe, and the polymerization was initiated by adding the catalyst solution to the vial containing the monomer. Polymerizations were terminated either by adding an excess of ethyl vinyl ether or by removing solvent under vacuum prior to analysis.

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