Synthesis and Reactivity of Ruthenium Arene Complexes Incorporating Novel $Ph_2PCH_2CH_2BR_2$ Ligands. Easy Access to the Four-Membered Ruthenacycle [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)]

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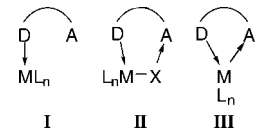
The ambiphilic ligands $Ph_2PCH_2CH_2BR_2$ (**1a**,**b**: BR_2 = BCy_2 (**a**), 9-BBN (**b**)) were readily prepared by hydroboration of vinyldiphenylphosphine. Reaction of **1a**,**b** with $[(p\text{-cymene})RuCl_2]_2$ afforded the corresponding complexes $[(p\text{-cymene})RuCl_2(Ph_2PCH_2CH_2BR_2)]$ (**2a**,**b**), in which the borane moiety remains pendant, as confirmed by an X-ray diffraction analysis of **2b**. Reaction of **2a**,**b** with $AgBF_4$ in the presence of acetonitrile leads to the formation of the corresponding cationic complexes $[(p\text{-cymene})RuCl(Ph_2PCH_2CH_2BR_2)(CH_3CN)][BF_4]$ (**3a**,**b**) without alteration of the pendant borane moiety. In contrast, treatment of **2a**,**b** with AgOAc induces CH_2-B bond cleavage and affords the four-membered ruthenacycle $[(p\text{-cymene})RuCl(\kappa^{C,P}\text{-}CH_2CH_2PPh_2)]$ (**4**), characterized by X-ray diffraction. By reaction with chlorodicyclohexylborane, **4** gives back **2a** via ring-opening σ-bond metathesis, whereas **4** reacts with chlorodiethylalane via alkylation at ruthenium with retention of the four-membered metallacycle to afford the ethyl complex $[(p\text{-cymene})RuEt(\kappa^{C,P}\text{-}CH_2CH_2PPh_2)]$ (**5**).

Introduction

Ambiphilic ligands combining donor and acceptor moieties (referred to as D and A, respectively) have attracted increasing attention over the past few years. The Lewis base moiety D is expected to coordinate to a metal center as a classical L ligand, while the Lewis acid fragment A can remain pendant[1] or, alternatively, interact with either a coligand[2] or the metal itself.[2e,3] The three coordination modes **I**−**III** can thus be distinguished (Chart 1). All of them have been evidenced spectroscopically and structurally. In particular, the D→M→A bridging coordination (mode **III**) has been exploited to gain more insight into unusual M→borane interactions,[4,5] which were first authenticated structurally in metallaboratranes.[6] In addition, the presence of pendant Lewis acid moieties (mode **I**) opens interesting perspectives in organometallic catalysis, via anchoring a substrate in the coordination sphere[1a,c,7]or activating intramolecularly a M−X bond.[8]These developments have stimulated our efforts to increase the structural variety of ambiphilic derivatives and to study the reactivity of complexes incorporating such structures.

Chart 1



Phosphine−borane (PB) derivatives have already proved very fruitful in coordination chemistry[2e−g,3] and also as metal-free systems for the reversible activation of H_2,[9] as readily tunable fluorescent systems,[10] and as direct precursors for photoisomerizable heterodienes.[11] We thus decided to retain the PB combination but to modify the linker that dictates the distance between both sites and the flexibility of the whole ligand. So

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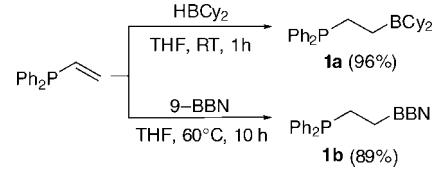
far,[12] essentially rigid aryl spacers such as *o*- and *p*-C_6H_4 groups have been studied. [2e,3,9,13–15] In comparison, alkyl spacers have only been scarcely studied,[16] and we thus became interested in incorporating a $-CH_2CH_2-$ unit as a flexible version of the *o*-C_6H_4 linker.

From a synthetic viewpoint, most of the PB and PAl systems known to date have been prepared by ionic couplings from phosphorus-containing nucleophiles and halogenoboranes or -alanes.[17,18] We thought that the hydroboration of vinylphosphines[19,20] would provide a straightforward access to the desired ligands from readily available precursors. To the best of our knowledge, $Et_2PCH_2CH_2B(OCH_2CH_2O)$, prepared by hydrophosphination of the corresponding vinylboronate,[21] was the unique precedent of a phosphine−borane featuring a $-CH_2-CH_2-$ linker.[22] Schmidbaur et al.[23] recently studied the hydroboration of alkenylphosphines with 9-BBN.[24] Accordingly, allyl- and homoallylphosphines readily afforded $P(CH_2)_nB$ (n = 3, 4) derivatives stabilized by intramolecular P→B interactions.[23] The authors mentioned that such a reaction could not be extrapolated to the vinyldiphenylphosphine.

Scheme 1. Synthesis of the Phosphine−Borane ligands 1a,b



We decided to revisit this entry route to PB ligands and report here the synthesis of the phosphine−boranes $Ph_2PCH_2CH_2BR_2$ (BR_2 = BCy_2, 9-BBN) via hydroboration and their coordination to the (*p*-cymene)$RuCl_2$ fragment. Neutral and cationic ruthenium complexes can thus be obtained with the new ligands adopting the coordination mode **I** (see Chart 1). The synthesis, characterization, and reactivity of the four-membered metallacycle [(*p*-cymene)$RuCl(\kappa^{C,P}$-$CH_2CH_2PPh_2)$] (**4**) are also described, highlighting the reversible breaking/formation of the CH_2B bond of the coordinated Ph_2P-$CH_2CH_2BR_2$ ligands.

Results and Discussion

Synthesis of the Ligands $Ph_2PCH_2CH_2BR_2$ (1a,b: BR_2 = BCy_2 (a), 9BBN (b)). The hydroboration of vinyldiphenylphosphine was first investigated with Cy_2BH. The reaction readily occurs at room temperature in THF and is complete within 1 h. The desired product **1a** was obtained in nearly quantitative yield as a white solid (Scheme 1). The monomeric structure of **1a** and the absence of an intramolecular P→B interaction were indicated by multinuclear NMR spectroscopy.

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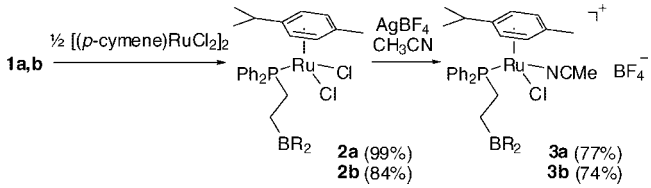
(23) Schmidbaur, H.; Sigl, M.; Schier, A. *J. Organomet. Chem.* **1997**, *529*, 323–327.

(24) Only $RPh_2P→BH_3$ adducts have been obtained so far in the reaction of $Ph_2P-(CH_2)_n-CH=CH_2$ (n = 0, 1, 2) with BH_3.[23]

Scheme 2. Synthesis of the Neutral (2a,b) and Cationic (3a,b) Ruthenium Complexes



Indeed, the ^{31}P NMR chemical shift (δ –8.9 in CD_2Cl_2) is very similar to that of Ph_2PEt (δ –11.7 in C_6D_6), and a broad signal is observed at δ +81.8 in the ^{11}B NMR spectrum, as expected for a trialkylborane. The reaction was found to be totally regioselective, the introduction of the boron atom at the terminal carbon atom being unambiguously deduced from the $^1H/^{13}C$ signals attributable to the CH_2CH_2 spacer. In our hands, 9-BBN was also found to readily react with vinyldiphenylphosphine, although more drastic conditions (10 h at 60 °C) were necessary. The resulting phosphine−borane **1b** was isolated in 89% yield. Its monomeric open structure was substantiated by the similarity of its NMR data ($\delta(^{31}P)$ −10.4, $\delta(^{11}B)$ +87.4) with those of **1a**. The absence of any P→B interaction in the PCH_2CH_2B derivatives **1a**,**b** markedly contrasts with the closed form adopted by the related $P(CH_2)_nB$ (n = 3, 4) compounds[23] and is most likely disfavored by the ring strain it would induce, although related four-membered PC_2B rings have been found to be accessible with the *o*-C_6H_4 spacer.[14,25]

Coordination of Ligands 1a,b to the [(*p*-cymene)RuCl$_2$] Fragment. X-ray Structure of [(*p*-cymene)RuCl$_2${Ph$_2$PCH$_2$CH$_2$(9-BBN)}] (2b). Very recently, we have reported the synthesis of the new NB ambiphilic ligand (2-picolyl)BCy_2 and its coordination to the (*p*-cymene)$RuCl_2$ fragment via a coordination mode of type **II** (see Chart 1).[2h] This prompted us to investigate the behavior of the PB ligands toward the same ruthenium fragment. The dimer $[(p\text{-cymene})RuCl_2]_2$ is readily cleaved by **1a**,**b** in 1 h at room temperature (Scheme 2). The resulting complexes $[(p\text{-cymene})RuCl_2(Ph_2PCH_2CH_2BR_2)]$ ($BR_2 = BCy_2$ (**2a**), 9-BBN (**2b**)) were isolated in very good yields as red solids and were fully characterized by multinuclear NMR spectroscopy and elemental analysis. The coordination of the phosphorus atom to ruthenium was indicated by the shift to lower field of the ^{31}P NMR resonances (**2a**, δ +28.9; **2b**, δ +27.2). The ^{11}B NMR signals (**2a**, δ +81.7; **2b**, δ +86.3) showed that the borane moiety does not participate in the coordination, ruling out the presence of any Ru→B or Ru−Cl→B interactions. This situation was confirmed by an X-ray diffraction study performed on **2b** (Figure 1, Table 1). Although the modest quality of the crystallographic data precludes a detailed discussion of the geometric parameters, it is clear that the borane moiety remains pendant[1,7] and that the overall structure of **2b** very much resembles those of the borane-free complexes $[(p\text{-cymene})RuCl_2(\text{phosphine})]$.[26]

This situation is in marked contrasts with the Ru−Cl→B interaction found for the related NB ligand in $[(p\text{-cymene})RuCl_2((2\text{-picolyl})BCy_2)]$.[2h] The higher rigidity and lower steric demand of the 2-picolyl moiety compared to the $Ph_2PCH_2CH_2$ group most likely explain this difference. This highlights that subtle stereoelectronic effects may have a noticeable influence on the coordination of ambiphilic ligands. From a synthetic viewpoint, the reverse sequence of coordination followed by hydroboration proved to be much less efficient. Indeed, 9-BBN does not react with $[(p\text{-cymene})RuCl_2(Ph_2PCH{=}CH_2)]$ at room temperature and only leads to complex mixtures at 70 °C.[27]

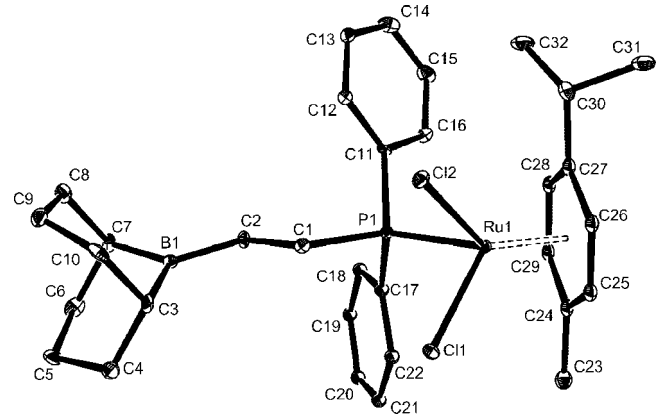


Figure 1. Molecular view of **2b** in the solid state (thermal ellipsoids at the 30% probability level), with hydrogen atoms and solvate molecules omitted. Selected bond lengths (Å) and bond angles (deg): P1–Ru1 = 2.352(2), Ru1–Cl1 = 2.4003(19), Ru1–Cl2 = 2.4106(18), P1–C1 = 1.841(7), C1–C2 = 1.526(9), C2–B1 = 1.565(11); Cl1–Ru1–Cl2 = 86.73(7), P1–Ru1–Cl1 = 87.72(7), P1–Ru1–Cl2 = 85.78(7).

Table 1. Crystallographic Data for Complexes 2b and 4

	2b	4
empirical formula	$C_{32}H_{42}BCl_2PRu \cdot CH_2Cl_2$	$C_{24}H_{28}ClPRu$
formula wt	725.33	483.95
cryst syst	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
a, Å	17.312(4)	7.9420(4)
b, Å	13.681(3)	11.1756(5)
c, Å	28.015(6)	13.0715(6)
α, deg	90	77.024(4)
β, deg	90	73.311(4)
γ, deg	90	82.677(4)
V, Å^3	6635(3)	1080.47(9)
Z	8	2
calcd density, Mg/m^3	1.452	1.488
abs coeff, mm^{-1}	0.865	0.93
no. of rflns collected	41 322	11 845
no. of indep rflns	6774	6909
R1 ($I > 2\sigma(I)$)	0.0766	0.0316
wR2	0.1300	0.0545
$(\Delta/r)_{max}$ (e Å^{-3})	2.334 and −0.815	0.945 and −0.937

Chloride Abstraction and Access to the Four-Membered Ruthenacycle [(*p*-cymene)RuCl($\kappa^{C,P}$-CH$_2$CH$_2$PPh$_2$)] (4). A rich chemistry has been gained from chloride abstraction of $[(p\text{-cymene})RuCl_2(L)]$ derivatives with some interesting catalytic applications.[28] Our first attempt to prepare cationic complexes by treating **2a**,**b** with silver tetrafluoroborate was successful. The reactions were performed at room temperature in dichlo-

(25) Note also that the (2-picolyl)(dicyclohexyl)borane was found to adopt a head-to-tail dimeric structure in the solid state (as the result of intermolecular N→B interactions) and to equilibrate in solution with a strained monomeric structure (intramolecular N→B interaction).[2h]

(26) For selected examples, see: (a) Gupta, D. K.; Sahay, A. N.; Pandey, D. S.; Jha, N. K.; Sharma, P.; Espinosa, G.; Cabrera, A.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **1998**, *568*, 13–20. (b) McQuade, P.; Rath, N. P.; Barton, L. *Inorg. Chem.* **1999**, *38*, 5468–5470. (c) Chaplin, A. B.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2005**, 4762–4774.

(27) A previous example of hydroboration of alkenylphosphines in the coordination sphere of a metal was reported to only give complex mixtures: Coles, S. J.; Faulds, P.; Hurthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234–240.

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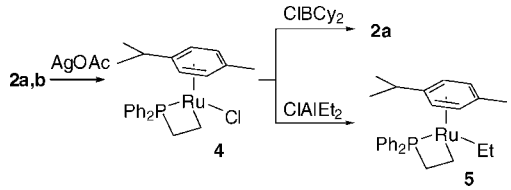
Scheme 3. Synthesis and Reactivity of the Four-Membered Ruthenacycle 4



romethane in the presence of a slight excess of acetonitrile to stabilize the ruthenium center by reaching a 18-electron configuration. After standard workup, the cationic complexes [(*p*-cymene)RuCl($Ph_2PCH_2CH_2BR_2$)(CH_3CN)][BF_4] (**3a**,**b**) were isolated in good yields as yellow powders. As expected,[29] formation of the cationic complexes is accompanied by a low-field ^{31}P NMR shift of about 5 ppm. The coordination of one molecule of acetonitrile to the ruthenium center was clearly apparent from the ^1H and ^{13}C NMR signals observed for the CH_3CN coligand ($\delta(^1H)$ ~2.4, $\delta(^{13}C)$ ~4 ppm). In addition, the four distinct signals observed for the aromatic protons of the *p*-cymene were consistent with the presence of a stereogenic Ru center.[30] Lastly, the broad signals observed at ~85 ppm in the ^{11}B NMR spectra unambiguously indicated the retention of the pendant borane moiety.

Interestingly, chloride abstraction turned to be very much dependent on the nature of the silver salt. When the basic salt AgOAc was used in place of $AgBF_4$, the ruthenium complexes **2a**,**b** afforded the new complex [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (**4**), isolated as a yellow powder in 61% yield. **4** is formulated as a four-membered metallacycle on the basis of NMR and X-ray data (Scheme 3, Table 1). The ^{31}P NMR signal for **4** (δ −21.6) is shielded to higher field by about 50 ppm compared to those of the neutral precursors. The absence of any ^{11}B NMR signal indicates the elimination of the borane group, in agreement with the formation of the unique complex **4**, whatever the borane substituent of the starting complex. The signal observed at δ −3.6 (J_{PC} = 53 Hz) in the ^{13}C NMR spectrum of **4** suggests the formation of an original four-membered ruthenacycle. Indeed, a few related ruthenacycles have been reported,[31] and all of them exhibit a ^{13}C NMR signal near 0 ppm for the CH_2Ru unit.[31b–e] Single crystals of complex **4** were grown upon allowing a THF/pentane solution to stand at 4 °C for several days, and its structure was confirmed by an X-ray diffraction analysis (Figure 2). In the solid state, the four-membered ring noticeably deviates from planarity (P−C−C−Ru torsion angle of 23.1°). The P−Ru−C bond angle is the most acute among the endocyclic angles (66.7°), and the P−Ru and C−Ru bond lengths are 2.2821(6) and 2.146(2) Å, respectively. Overall, the geometric parameters measured for **4** fall in the middle range of those found in the few structurally characterized four-membered ruthenacycles.[31d–g]

The formation of **4** may result from the initial addition of the acetate to the boron atom, leading to an ate complex,

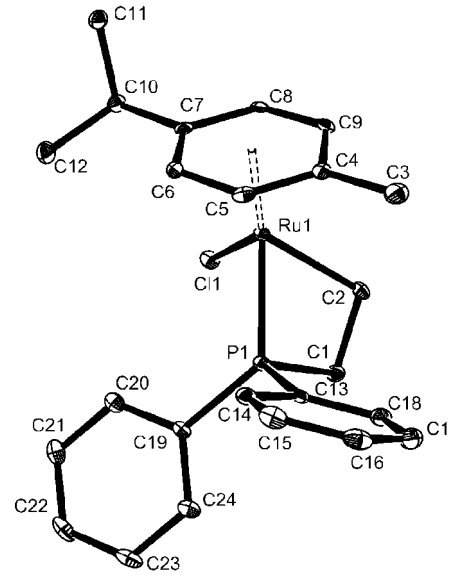


Figure 2. Molecular view of **4** in the solid state (thermal ellipsoids at the 30% probability level), with hydrogen atoms omitted. Selected bond lengths (Å) and bond angles (deg): P1–Ru1 = 2.2821(6), Ru1–Cl1 = 2.4271(5), Ru1–C2 = 2.146(2), P1–C1 = 1.811(2), C1–C2 = 1.539(3); Cl1–Ru1–C2 = 85.17(6), P1–Ru1–Cl1 = 88.66(2), P1–Ru1–C2 = 66.75(6), Ru1–C2–C1 = 103.23(13), P1–C1–C2 = 93.05(13), C1–P1–Ru1 = 89.98(7).

followed by nucleophilic attack of the terminal CH_2 group to the ruthenium center, the elimination of the chlorine being assisted by the silver cation.[32] Two alternative sequences are also plausible: (i) halide abstraction followed by nucleophilic attack by acetate at boron and zwitterion pair collapse with loss of R_2BOAc or (ii) halide abstraction, followed by acetate coordination to ruthenium and intramolecular R_2BOAc elimination. Known four-membered ruthenacycles were typically obtained from highly unsaturated complexes via C−H activation of an *i*Pr or *t*Bu group at phosphorus. The formation of **4** provides an alternative route relying on the activation of the borane moiety of an ambiphilic ligand. In this regard, it is noteworthy that **4** was not observed when the related borane-free complex [(*p*-cymene)$RuCl_2(Ph_2PEt)$] was reacted with AgOAc.

Reactivity of the Four-Membered Ruthenacycle 4. The behavior of the ruthenacycle **4** toward Lewis acids was studied. Chlorodicyclohexylborane was found to slowly react in THF at room temperature to quantitatively give back the neutral complex **2a**. The ring opening of the ruthenacycle provides a new synthetic route to PCH_2CH_2B complexes and most probably proceeds via σ-bond metathesis. Alternatively, one may consider the electrophilic addition of the chloroborane with cleavage of the Ru−C bond and subsequent transfer of the chloride from boron to ruthenium.

As a first evaluation of the influence of the Lewis acid, an NMR in situ experiment was performed by adding chlorodiethylalane to the ruthenacycle **4** in THF-d_8. In this case, complete conversion of **4** required heating at 50 °C for 24 h. ^{31}P NMR monitoring revealed the formation of the new complex **5** with retention of the four-membered ruthenacycle ($\delta(^{31}P)$ −13.3). On the basis of multinuclear NMR data, **5** can be formulated as the ethyl complex [(*p*-cymene)RuEt($\kappa^{C,P}$-CH_2-

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(32) Somewhat related processes have been reported by Tilley and Fontaine for the rearrangement of [$PhB(CH_2P$-*i*-$Pr_2)_3Rh(PMe_3)_2$] and [Cp*$RhMe_2(Me_2PCH_2AlMe_2)$], respectively. See: Turculet, L.; Feldman, J. D.; Tilley, D. *Organometallics* **2004**, *23*, 2488–2502, and ref 8b.

CH_2PPh_2)]. Retention of the four-membered ruthenacycle is indicated by the diagnostic signal observed in ^{13}C NMR for the CH_2Ru unit (δ −9.6, J_{PC} = 52 Hz). Substitution of the chlorine atom at ruthenium by an ethyl group is apparent from ^1H and ^{13}C NMR data and is further corroborated by 2D experiments and 1D TOCSY {^{31}P}. The reaction with the chloroalane proceeds via a RuCl/AlEt redistribution process, leading to alkylation at ruthenium with retention of the four-membered metallacycle. At this stage, it is difficult to precisely identify the factors that explain the different behavior observed toward $ClBCy_2$ and $ClAlEt_2$, since the nature of both the group 13 element and the alkyl substituents may play a role.

Conclusion

Two representative ambiphilic PB ligands incorporating a flexible $-CH_2CH_2-$ linker have been prepared by simple hydroboration of a vinylphosphine. Their coordination to the (*p*-cymene)$RuCl_2$ fragment provides rare examples of complexes featuring pendant Lewis acids, in marked contrast with what we have recently observed when using NB ligands (2-picolylboranes). By using $AgBF_4$ as chloride abstractor, the corresponding cationic species **3a**,**b** were obtained without alteration of the pendant borane moieties. In contrast, AgOAc promotes the activation of the CH_2-B bond of the coordinated PB ligands, leading to the original four-membered ruthenacycle **4**. Interestingly, **4** displays a versatile reactivity toward Lewis acids: (i) with $ClBCy_2$, the ambiphilic PB ligand is reformed in the coordination sphere of the metal and the neutral complex **2a** is recovered; (ii) with $ClAlEt_2$, alkylation at ruthenium with retention of the ruthenacycle is achieved.

Ongoing efforts aim at further expanding the variety of ambiphilic compounds and at gaining more insights into the behavior of Lewis acids in the coordination sphere of transition metals.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk or glovebox techniques under an argon atmosphere. NMR spectra were recorded on Bruker ARX 250, DPX 300, Avance 300, Avance 400 and Avance 500 spectrometers. ^{11}B, ^{31}P, ^1H, and ^{13}C chemical shifts are expressed with a positive sign, in parts per million, relative to external $BF_3 \cdot Et_2O$, 85% H_3PO_4, and residual ^1H and ^{13}C solvent signals, respectively. Unless otherwise stated, NMR spectra were recorded at 293 K. Elemental analyses were performed at the LCC on a Perkin-Elmer 2400 (II) elemental analyzer. In the cases of **1a**,**b**, V_2O_5 was introduced into the samples for better combustion.

Materials and Methods. CH_2Cl_2, pentane, and CH_3CN were dried over CaH_2, and THF was dried over sodium/benzophenone and distilled prior to use. All organic reagents were obtained from commercial sources and used as received, [(*p*-cymene)$RuCl_2$]$_2$,[33] dicyclohexylborane,[34] and 9-borabicyclo[3.3.1]nonane[35] were prepared according to literature procedures.

Preparation of $Ph_2PCH_2CH_2BCy_2$ (1a). Vinyldiphenylphosphine (947 mg, 97%, 4.33 mmol), and dicyclohexylborane (795 mg, 4.47 mmol) were stirred in THF (10 mL) for 1 h at room temperature. The solvent was then removed under vacuum, affording $Ph_2PCH_2CH_2BCy_2$ as a white solid. Extraction with 20 mL of pentane was performed. Filtration and evaporation under vacuum led to a white finely divided solid. The solid is extremely hygroscopic, but the purity could be easily checked by multinuclear NMR (NMR tube prepared in a drybox). Yield: 1.63 g (96%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ −8.91. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.46 (m, 4H, H_{Ph}), 7.37 (m, 6H, H_{Ph}), 2.08 (m, 2H, H_2CP), 1.12–1.77 (m, 24H, H_2CB and H_{Cy}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): C_{Ph} not observed, δ 132.74 (d, $J_{C,P}$ = 29.2 Hz, CH_{Ph}), 128.38 (s, CH_{Ph}), 128.28 (d, $J_{C,P}$ = 6.4 Hz, CH_{Ph}), 35.74 (s broad, BCH), 27.53 (s, CH_{2Cy}), 27.12 (s, CH_{2Cy}), 27.03 (s, CH_{2Cy}), 21.32 (d, $^1J_{C,P}$ = 13.4 Hz, H_2CP), 19.69 (s broad, H_2CB). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ 81.8. Anal. Calcd for $C_{26}H_{36}PB$: C, 80.00; H, 9.30. Found: C, 80.74; H, 8.69.

Preparation of $Ph_2PCH_2CH_2$(9-BBN) (1b). Vinyldiphenylphosphine (707 mg, 97%, 3.23 mmol) and 9-borabicyclo[3.3.1]nonane (396 mg, 3.24 mmol) were stirred in THF (20 mL) for 10 h at 60 °C. The solvent was then removed under vacuum, affording $Ph_2PCH_2CH_2$(9-BBN) as a white solid. The solid was washed with 5 mL of pentane and dried under vacuum. The finely divided solid is extremely hygroscopic, but the purity could be easily checked by multinuclear NMR (NMR tube prepared in a drybox).Yield: 958 mg (89%). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ −10.44. ^1H NMR (250 MHz, CD_2Cl_2): δ 7.49 (m, 4H, H_{Ph}), 7.36 (m, 6H, H_{Ph}), 2.29 (m, 2H, H_2CP), 1.25–1.92 (m, 16H, H_2CB and $H_{9\text{-BBN}}$). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2): C_{Ph} not observed, δ 132.71 (d, $J_{C,P}$ = 18.2, CH_{Ph}), 128.36 (s, CH_{Ph}), 128.31 (d, $J_{C,P}$ = 10.0 Hz, CH_{Ph}), 33.20 (s, $H_2C_{9\text{-BBN}}$), 31.17 (s broad, $HC_{9\text{-BBN}}$), 23.23 (s broad, H_2CB and H_2C_{9BBN}), 22.08 (d, $^1J_{C,P}$ = 11.3 Hz, H_2CP). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ 87.4. Anal. Calcd for $C_{22}H_{28}PB$: C, 79.06; H, 8.44. Found: C, 78.26; H, 8.98.

Preparation of [(*p*-cymene)$RuCl_2$($Ph_2PCH_2CH_2BCy_2$)] (2a). [(*p*-cymene)$RuCl_2$)]$_2$ (683 mg, 1.12 mmol) and $Ph_2PCH_2CH_2BCy_2$ (885 mg, 2.27 mmol) were stirred in CH_2Cl_2 (15 mL) for 1 h. The solvent was then removed under vacuum, and the red solid that was obtained was washed with pentane. Yield: 1.55 g (99%). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 28.92. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.92 (m, 4H, H_{Ph}), 7.54 (m, 6H, H_{Ph}), 5.26 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, $H_{p\text{-cym}}$), 5.10 (d, $^3J_{H,H}$ = 6.0 Hz, 2H, $H_{p\text{-cym}}$), 2.50 (m, 3H, $HC_{i\text{-Pr}}$ and H_2CP), 1.88 (s, 3H, H_3C), 0.84 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, $H_3C_{i\text{-Pr}}$), 0.88–1.70 (m, 24H, H_2CB and H_{Cy}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 133.55 (d, $J_{C,P}$ = 8.3 Hz, CH_{Ph}), 132.73 (d, $^1J_{C,P}$ = 41.5 Hz, C_{Ph}), 130.34 (d, $J_{C,P}$ = 2.3 Hz, CH_{Ph}), 128.04 (d, $J_{C,P}$ = 9.1 Hz, CH_{Ph}), 107.33 (s, $C_{p\text{-cym}}$), 93.46 (s, $C_{p\text{-cym}}$), 90.53 (s, $CH_{p\text{-cym}}$), 85.50 (s, $CH_{p\text{-cym}}$), 35.61 (s, BCH), 29.96 (s, $HC_{i\text{-Pr}}$), 27.32 (s, H_2C_{Cy}), 26.93 (s, H_2C_{Cy}), 21.03 (s, $H_3C_{i\text{-Pr}}$), 17.43 (d, $^1J_{C,P}$ = 24.7 Hz, H_2CP), 17.07 (s, H_3C), 16.21 (s broad, H_2CB). $^{11}B\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 81.7. Anal. Calcd for $C_{36}H_{50}RuCl_2PB$: C, 62.07; H, 7.25. Found: C, 61.52; H, 6.65.

Preparation of [(*p*-cymene)$RuCl_2${$Ph_2PCH_2CH_2$(9-BBN)}] (2b). [(*p*-cymene)$RuCl_2$]$_2$ (524 mg, 0.86 mmol) and $Ph_2PCH_2CH_2$(9-BBN) (572 mg, 1.71 mmol) were stirred in CH_2Cl_2 (15 mL) for 1 h. The solvent was then removed under vacuum, and the red solid that was obtained was washed with pentane. Yield: 920 mg (84%). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 27.23. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.91 (m, 4H, H_{Ph}), 7.53 (m, 6H, H_{Ph}), 5.27 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, $H_{p\text{-cym}}$), 5.11 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, $H_{p\text{-cym}}$), 2.73 (pseudoquad, $^2J_{H,P}$ = $^3J_{H,H}$ = 8.0 Hz, 2H, H_2CP), 2.50 (sept, $^3J_{H,H}$ = 7.2 Hz, 1H, $HC_{i\text{-Pr}}$), 1.90 (s, 3H, H_3C), 1.18 (m, 2H, H_2CB), 0.85 (d, $^3J_{H,H}$ = 7.2 Hz, 6H, $H_3C_{i\text{-Pr}}$), 0.90–1.77 (m, 14H, $H_{9\text{-BBN}}$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 133.68 (d, $J_{C,P}$ = 8.3 Hz, CH_{Ph}), 132.95 (d, $^1J_{C,P}$ = 41.8 Hz, C_{Ph}), 130.32 (d, $J_{C,P}$ = 2.3 Hz, CH_{Ph}), 128.12 (d, $J_{C,P}$ = 9.2 Hz, CH_{Ph}), 107.40 (s,$C_{p\text{-cym}}$), 93.54 (s, $C_{p\text{-cym}}$), 90.48 (s, $CH_{p\text{-cym}}$), 85.58 (s, $CH_{p\text{-cym}}$), 33.04 (s, $H_2C_{9\text{-BBN}}$), 31.04 (s, $HC_{9\text{-BBN}}$), 29.99 (s, HC_i-Pr), 23.04 (s, $H_2C_{9\text{-BBN}}$), 21.06 (s, $H_3C_{i\text{-Pr}}$), 20.28 (s, H_2CB), 18.24 (d, $^1J_{C,P}$ = 26.7 Hz, H_2CP), 17.10 (s, H_3C). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ 86.3. Anal. Calcd for $C_{33}H_{44}RuCl_4PB$ (consistent with one molecule of

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(35) Soderquist, J. A.; Negron, A. *Org. Synth.* **1992**, *70*, 169–176.

CH_2Cl_2 for each molecule of [(*p*-cymene)$RuCl_2${$Ph_2PCH_2CH_2B$(9-BBN)}] present in the crystalline state): C, 54.64; H, 6.13. Found: C, 54.64; H, 5.70.

Preparation of [(*p*-cymene)RuCl($Ph_2PCH_2CH_2BCy_2$)(CH_3-CN)][BF_4] (3a). To a mixture of [(*p*-cymene)$RuCl_2$(Ph_2PCH_2-CH_2BCy_2)] (466 mg, 0.67 mmol) and silver tetrafluoroborate (136 mg, 0.70 mmol), protected from the light, was added a solution of acetonitrile (45 mg, 1.10 mmol) in CH_2Cl_2 (10 mL). A precipitate quickly appeared, while the initially red solution turned orange. The mixture was stirred for 1 h and then filtered, and the solvent was removed under vacuum. The resulting yellow solid was washed with pentane and dried in vacuo. Yield: 408 mg (77%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 32.87. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.75 (m, 4H, H_{Ph}), 7.63 (m, 6H, H_{Ph}), 5.74 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $H_{p\text{-cym}}$), 5.56 (d, $^3J_{H,H}$ = 5.6 Hz, 1H, $H_{p\text{-cym}}$), 5.27 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$), 5.09 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$), 2.62 (sept, $^3J_{H,H}$ = 7.2 Hz, 1H, $HC_{i\text{-Pr}}$), 2.55 (m broad, 2H, H_2CP), 2.42 (s, 3H, H_3CCN), 2.00 (s, 3H, H_3C), 1.15 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, $H_3C_{i\text{-Pr}}$), 1.06 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, $H_3C_{i\text{-Pr}}$), 0.93−1.69 (m, 24H, H_2CB and H_{Cy}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): C_{Ph} and *C*N (acetonitrile) not observed, δ 133.70 (d, $J_{C,P}$ = 9.2 Hz, *C*H_{Ph}), 132.21 (d, $J_{C,P}$ = 8.3 Hz, *C*H_{Ph}), 131.62 (d, $J_{C,P}$ = 2.2 Hz, *C*H_{Ph}), 131.40 (d, $J_{C,P}$ = 2.4 Hz, *C*H_{Ph}), 129.07 (d, $J_{C,P}$ = 5.9 Hz, *C*H_{Ph}), 128.97 (d, $J_{C,P}$ = 6.2 Hz, *C*H_{Ph}), 112.94 (s, $C_{p\text{-cym}}$), 99.52 (s, $C_{p\text{-cym}}$), 92.39 (s, *C*$H_{p\text{-cym}}$), 91.08 (s, *C*$H_{p\text{-cym}}$), 90.54 (s, *C*$H_{p\text{-cym}}$), 86.78 (s, *C*$H_{p\text{-cym}}$), 35.63 (s, B*C*H), 30.77 (s, H*C*$_{i\text{-Pr}}$), 27.34 (s, H_2C_{Cy}), 26.88 (s, H_2C_{Cy}). 26.85 (s, H_2C_{Cy}), 21.58 (s, $H_3C_{i\text{-Pr}}$), 21.49 (d, $^1J_{C,P}$ = 26.2 Hz, H_2*C*P), 21.29 (s, $H_3C_{i\text{-Pr}}$), 17.82 (s, H_3*C*), 17.54 (s, H_2*C*B), 3.98 (s, H_3*C*CN). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ 82.9. Anal. Calcd for $C_{38}H_{53}RuClNPB_2F_4$: C, 57.85; H, 6.77; N: 1.78. Found: C, 57.30; H, 6.13; N: 1.65.

Preparation of [(*p*-cymene)RuCl{$Ph_2PCH_2CH_2$(9-BBN)}(CH_3-CN)][BF_4] (3b). To a mixture of **2b** (292 mg, 0.46 mmol) and silver tetrafluoroborate (90 mg, 0.46 mmol), protected from the light, was added a solution of acetonitrile (23 mg, 0.56 mmol) in CH_2Cl_2 (15 mL). A precipitate quickly appeared, while the initially red solution turned orange. The mixture was stirred for 1 h and then filtered, and the solvent was removed under vacuum. The resulting yellow solid was washed with pentane and dried under vacuum. Yield: 251 mg (74%). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 32.24. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.76 (m, 4H, H_{Ph}), 7.62 (m, 6H, H_{Ph}), 5.70 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$), 5.53 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$), 5.31 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$), 5.14 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, $H_{p\text{-cym}}$) 2.72 (m, 2H, H_2CP), 2.61 (sept, $^3J_{H,H}$ = 6.9 Hz, 1H, $HC_{i\text{-Pr}}$), 2.40 (s, 3H, H_3CCN), 2.00 (s, H_3C), 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, $H_3C_{i\text{-Pr}}$), 1.07 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, $H_3C_{i\text{-Pr}}$), 1.19–1.84 (m, 16H, H_2CB and $H_{9\text{-BBN}}$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): C_{Ph}, H_2*C*B, and *C*N (acetonitrile) not observed, δ 133.60 (d, $J_{C,P}$ = 9.1 Hz, *C*H_{Ph}), 132.31 (d, $J_{C,P}$ = 8.3 Hz, *C*H_{Ph}), 131.53 (d, $J_{C,P}$ = 3.0 Hz, *C*H_{Ph}), 131.38 (d, $J_{C,P}$ = 2.3 Hz, *C*H_{Ph}), 129.11 (d, $J_{C,P}$ = 1.5 Hz, *C*H_{Ph}), 128.98 (d, $J_{C,P}$ = 2.3 Hz, *C*H_{Ph}), 112.81 (s, $C_{p\text{-cym}}$), 99.58 (s, $C_{p\text{-cym}}$), 92.47 (s, *C*$H_{p\text{-cym}}$), 90.83 (s, *C*$H_{p\text{-cym}}$), 90.30 (s, *C*$H_{p\text{-cym}}$), 87.15 (s, *C*$H_{p\text{-cym}}$), 33.02 (s, $H_2C_{9\text{-BBN}}$), 31.12 (s, H*C*$_{9\text{-BBN}}$), 30.78 (s, H*C*$_{i\text{-Pr}}$), 23.00 (s, $H_2C_{9\text{-BBN}}$), 21.92 (d, $^1J_{C,P}$ = 27.3 Hz, H_2*C*P), 21.58 (s, $H_3C_{i\text{-Pr}}$), 21.33 (s, $H_3C_{i\text{-Pr}}$), 17.81 (s, H_3*C*), 3.94 (s, H_3*C*CN). $^{11}B\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 87.6.

Preparation of [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (4). In a glovebox, to a solution of [(*p*-cymene)$RuCl_2${$Ph_2PCH_2CH_2$(9-BBN)}] (500 mg, 0.79 mmol) in THF (10 mL), stirred and protected from the light, was slowly added silver acetate (131 mg, 0.78 mmol). The mixture was stirred for 2 h, during which time the initially red solution turned yellow and a precipitate appeared. The solution was then filtered and evaporated to dryness, and the remaining oil was filtered over a small alumina column with CH_2Cl_2 as eluant. The yellow fractions were collected, and the solvent was removed under vacuum, yielding a yellow oil which could be obtained as a solid by trituration in pentane. Crystals suitable for X-ray crystallography were obtained by keeping a saturated solution of [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (**4**) in a THF/pentane mixture at 4 °C for several days. Yield: 230 mg (60%). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −21.61. ^1H NMR (250 MHz, $CDCl_3$): δ 7.69 (m, 2H, H_{Ph}), 7.42 (m, 8H, H_{Ph}), 5.02 (d, $^3J_{H,H}$ = 5.5 Hz, 1H, $H_{p\text{-cym}}$), 4.94 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, $H_{p\text{-cym}}$), 4.91 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, $H_{p\text{-cym}}$), 4.32 (d, $^3J_{H,H}$ = 5.5 Hz, 1H, $H_{p\text{-cym}}$), 3.85 (m, 1H, *H*CHP), 3.48 (m, 1H, *H*CHP), 2.73 (sept, $^3J_{H,H}$ = 7.0 Hz, 1H, H*C*$_{i\text{-Pr}}$), 2.14 (m, 1H, *H*CHRu), 1.96 (m, 4H *H*CHRu and H_3C), 1.27 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, $H_3C_{i\text{-Pr}}$), 1.24 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, $H_3C_{i\text{-Pr}}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): C_{Ph} not observed, δ 133.84 (d, $J_{C,P}$ = 11.0 Hz, *C*H_{Ph}), 130.64 (d, $J_{C,P}$ = 9.7 Hz, *C*H_{Ph}), 130.24 (s, *C*H_{Ph}), 129.17 (s, *C*H_{Ph}), 128.47 (d, $J_{C,P}$ = 9.2 Hz, *C*H_{Ph}), 128.07 (d, $J_{C,P}$ = 9.9 Hz, *C*H_{Ph}), 112.44 (s, $C_{p\text{-cym}}$), 97.54 (s, $C_{p\text{-cym}}$), 87.12 (s, *C*$H_{p\text{-cym}}$), 85.35 (s, *C*$H_{p\text{-cym}}$), 83.38 (s, *C*$H_{p\text{-cym}}$), 81.87 (s, *C*$H_{p\text{-cym}}$), 37.21 (d, $^1J_{C,P}$ = 32.8 Hz, H_2*C*P), 31.10 (s, H*C*$_{i\text{-Pr}}$), 23.79 (s, $H_3C_{i\text{-Pr}}$), 22.42 (s, $H_3C_{i\text{-Pr}}$), 18.06 (H_3*C*), −3.56 (d, $^2J_{C,P}$ = 53.2 Hz, H_2*C*Ru). Anal. Calcd for $C_{24}H_{28}RuClP$: C, 59.56; H, 5.84. Found: C, 59.12; H, 5.60.

Reaction of [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (4) with $ClBCy_2$. A solution of chlorodicyclohexylborane (12.9 mg, 0.061 mmol) in THF-d_8 (ca. 0.5 mL) was added to **4** (25.0 mg, 0.052 mmol) in a NMR tube, affording [(*p*-cymene)$RuCl_2$($Ph_2PCH_2CH_2BCy_2$)] (**2a**) quantitatively (according to ^{31}P, ^1H, and ^{13}C NMR) over one night.

Reaction of [(*p*-cymene)RuCl($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (4) with $ClAlEt_2$. A solution of chlorodiethylalane (5.5 mg, 0.046 mmol) in THF-d_8 (ca. 0.5 mL) was added to **4** (20.3 mg, 0.042 mmol) in a NMR tube, affording [(*p*-cymene)Ru(CH_2CH_3)($\kappa^{C,P}$-$CH_2CH_2PPh_2$)] (**5**) over 1 day at 50 °C. Attempts to isolate complex **5** in pure form have so far been unsuccessful, and the complex was therefore only characterized in situ. $^{31}P\{^1H\}$ NMR (121 MHz, THF-d_8): δ −13.35. ^1H NMR (300 MHz, THF-d_8): δ 7.30 (m, 10H, H_{Ph}), 4.94 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, $H_{p\text{-cym}}$), 4.77 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, $H_{p\text{-cym}}$), 4.72 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, $H_{p\text{-cym}}$), 4.60 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, $H_{p\text{-cym}}$), 3.87 (m, 1H, *H*CHP), 3.38 (m, 1H, *H*CHP), 2.53 (sept, $^3J_{H,H}$ = 6.9 Hz, 1H, H*C*$_{i\text{-Pr}}$), 2.00 (s, 3H, $H_3C_{p\text{-cym}}$), 1.57 (m, 2H, *H*CH(CH_2P) and *H*CH_{Et}), 1.40 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, H_3C_{Et}), 1.19 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, $H_3C_{i\text{-Pr}}$), 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, $H_3C_{i\text{-Pr}}$), 0.74 (m, 1H, *H*CH(CH_2P)), 0.55 (m, 1H, *H*CH_{Et}). $^{13}C\{^1H\}$ NMR (75 MHz, THF-d_8): C_{Ph} not observed, δ 132.86 (d, $J_{C,P}$ = 11.0 Hz, *C*H_{Ph}), 130.39 (d, $J_{C,P}$ = 9.5 Hz, *C*H_{Ph}), 129.03 (d, $J_{C,P}$ = 2.2 Hz, *C*H_{Ph}), 127.96 (d, $J_{C,P}$ = 2.2 Hz, *C*H_{Ph}), 127.71 (d, $J_{C,P}$ = 5.4 Hz, *C*H_{Ph}), 127.59 (d, $J_{C,P}$ = 5.8 Hz, *C*H_{Ph}), 106.53 (d, $J_{C,P}$ = 4.4 Hz, $C_{p\text{-cym}}$), 98.06 (d, $J_{C,P}$ = 3.4 Hz, $C_{p\text{-cym}}$), 87.19 (d, $J_{C,P}$ = 1.8 Hz, *C*$H_{p\text{-cym}}$), 86.32 (d, $J_{C,P}$ = 1.3 Hz, *C*$H_{p\text{-cym}}$), 83.87 (d, $J_{C,P}$ = 4.5 Hz, *C*$H_{p\text{-cym}}$), 83.54 (d, $J_{C,P}$ = 5.7 Hz, *C*$H_{p\text{-cym}}$), 38.84 (d, $J_{C,P}$ = 33.5 Hz, H_2*C*P), 31.39 (s, H*C*$_{i\text{-Pr}}$), 22.95 (s, $H_3C_{i\text{-Pr}}$), 22.86 (d, $J_{C,P}$ = 4.0 Hz, H_3C_{Et}), 22.79 (s, $H_3C_{i\text{-Pr}}$), 18.04 (s, $H_3C_{p\text{-cym}}$), 5.31 (d, $J_{C,P}$ = 15.1 Hz, H_2C_{Et}), −9.62 (d, $J_{C,P}$ = 52.5 Hz, $H_2C(CH_2P)$).

Crystal Structure Determination of Complexes 2b and 4. Data were collected at low temperature (110 K) on an Xcalibur Oxford Diffraction diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters were obtained by means of a least-squares refinement. The structures have been solved by direct methods using SIR92[36] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97,[37] included in the software package WinGX version 1.63.[38] The atomic scattering factors were taken from ref 39. All hydrogen atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically

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refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Molecular drawing was performed with the program ORTEP32[40] with 30% probability displacement ellipsoids for non-hydrogen atoms.

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Supporting Information Available: CIF files giving crystallographic data for complexes **2b** and **4**. This material is available free of charge via the World Wide Web at http://pubs.acs.org.

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