ORGANOMETALLICS

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Developing P-Stereogenic, Planar–Chiral P-Alkene Ligands: Monodentate, Bidentate, and Double Agostic Coordination Modes on Ru(II)

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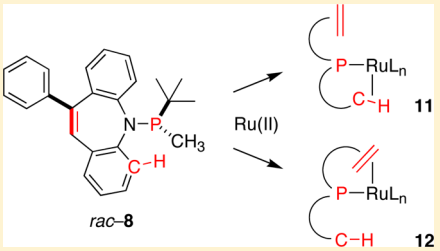
Supporting Information

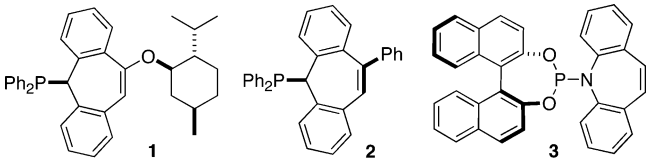
ABSTRACT: 10-Phenyl-5*H*-dibenz[*b*,*f*]azepine (**5**) is synthesized by Suzuki cross coupling of the protected bromo alkene **4** with $PhB(OH)_2$. **5** reacts with PCl_3 to afford the dichlorophosphanyl-azepine **6** in >90% yield. Alkylation of **6** with 1 equiv of *t*-BuMgBr leads, after recrystallization in Et_2O, to the diastereomerically enriched (*dr* > 98:2) chloride *rac*-**7**, which the crystal structure reveals to be the (pS,R_P)/(pR,S_P) pair. The fact that *rac*-**7** crystallizes in the Sohncke space group $P2_12_12_1$ opens up the possibility of a mechanical separation of the enantiomers. Methylation of *rac*-**7** is perfectly stereoselective with inversion of configuration at the P atom to yield the new ligand *rac*-**8** as the (*R*,*R*)/(*S*,*S*) pair. The corresponding BH_3-protected diastereomer *rac*-**9** (i.e., the (*R*,*S*)/(*S*,*R*) pair), is isolated after flash column chromatography in 73% yield. Compounds **5**–**9** are accessible in multigram quantities. X-ray crystal structures of Ru(II) complexes demonstrate the ambidentate nature of ligand *rac*-**8**: Complex **10** is exclusively P-coordinated, while in complex **11** two ligands bind Ru through their P donors and stabilize the 14-electron metal center with a double agostic interaction. In complex **12**, the ligand coordinates in a $\kappa P,\eta^2$-alkene bidentate fashion.



INTRODUCTION

Over the past decade, chiral P-alkene ligands have emerged as competent ligands for various enantioselective metal-catalyzed transformations.[1] In 2004, Grützmacher and co-workers established the first example of such a chiral P-alkene ligand built on the dibenzotropylidene scaffold by placing the chiral auxiliary (−)-menthol on the alkene function (**1**, see Table 1),[2]

Table 1. Inspiring Chiral P-Alkene Ligands Featuring the Dibenzo-Tropylidene and -Azepine Motifs



and soon thereafter, they disclosed the elegant, auxiliary-free, ligand **2**.[3] Some time ago, we developed a general method for the preparation of a library of dibenz[*b*,*f*]azepine-derived chiral P-alkene ligands.[4] In particular, (*S*)-binol-derived **3**[5] emerged as a "privileged ligand" when used in the correct stoichiometry of 2:1 with respect to the metal: $[Rh(\mathbf{3})_2]BF_4$ catalyzes the conjugate addition of arylboronic acids to enones with up to 99% *ee* for a wide range of substrates,[6] and Carreira and co-workers showed that the "chiral-at-Ir" complex $[Ir(\mathbf{3})_2Cl]$[7] catalyzes allylation reactions with exquisite enantioselectivity.[8]

The L/M stoichiometry of 2:1 does not negatively affect catalytic performance thanks to the hemilability of the alkene function. Structural studies revealed a flexible sp^3–sp^2 hybridization at the N atom in ligand **3** depending on whether the alkene coordinates to the metal (sp^3) or not (sp^2).[9] We note that substitution of the sp^3 hybridized methine in tropylidene-based architectures (which also have been shown to be hemilabile) for the hybridization-flexible N-function of the azepine moiety further "spring-loads" the alkene function and may enhance its hemilability. P-Alkene ligands with stereogenic phosphorus atoms are very rare,[10] even though P-stereogenic ligands are currently eliciting considerable attention for applications in asymmetric catalysis,[11] and to the best of our knowledge, the combination of P-stereogenicity with planar chirality in this ligand class is unprecedented. Here, we wish to communicate preliminary results of a feasibility study for the diastereoselective synthesis of dibenz[*b*,*f*]azepine based P-alkene ligands exhibiting both P-stereogenicity and planar chirality. The coordination behavior of the new ligand is assessed in Ru(II) complexes and confirms its expected ambidentate behavior as well as the ability to engage in C–H agostic interactions.[12]

Received: December 6, 2016

DOI: 10.1021/acs.organomet.6b00879
Organometallics XXXX, XXX, XXX–XXX

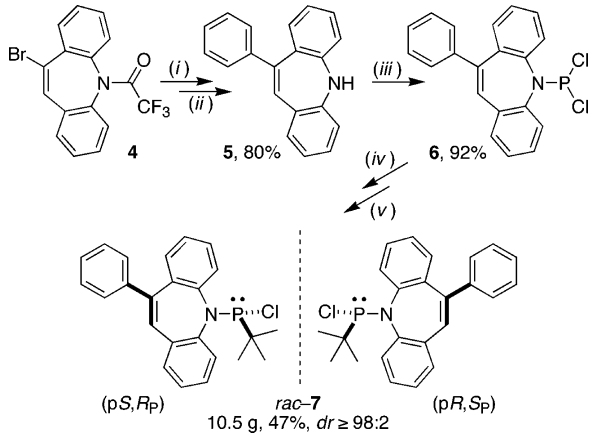
RESULTS AND DISCUSSION

At the outset of this project, easy access to multigram quantities of the phenyl-dibenz[*b*,*f*]azepine scaffold **5** was needed (see Scheme 1). The limited scalability of a published route using a ring expansion methodology[13] prompted us to develop the more versatile Suzuki coupling of phenylboronic acid with the bromo alkene precursor **4**.[14] This method affords orange crystalline **5** on a 30 g scale, which then reacts cleanly with PCl_3 in the presence of NEt_3 to yield the dichlorophosphoramide **6** on up to a 25 g scale. Alkylation of **6** with 1 equiv of *t*-BuMgCl at low temperature leads to a 2:1 diastereomeric mixture, which is characterized by the respective doublets of the *t*-Bu groups in the ^{1}H NMR spectrum centered at 0.94 ppm (major) and 1.02 ppm (minor).[15] The high solubility difference of the diastereomers in Et_2O allows for their ready separation, and washing the crude product with cold Et_2O gives *rac*-**7** in high diastereomeric purity on a 10 g scale. At 80 °C in benzene solution, however, epimerization takes place within hours to give a 50/50 mixture of diastereomers. Single crystal X-ray diffraction analysis of *rac*-**7** pinpoints the exact relative configurations of the stereogenic phosphorus center and the planar−chiral phenyl-dibenzazepine backbone (see Figure 1). The molecule crystallizes in the Sohncke space group $P2_12_12_1$ as a conglomerate, and the chiral crystal that was selected contained exclusively the (p*R*,*S*$_P$)-enantiomer. The formation of a conglomerate of enantiomorphous crystals is a rather rare occurrence[16] and means that *rac*-**7** could in principle be mechanically resolved into its enantiomers (the Pasteur method). The crystal structure evinces an *S*-configured P atom and a p*R* planar chirality,[17] which arises from the phenyl-substituted inversion-resistant *endo*-conformation of the boat-shaped azepine ring.[18] Thus, *rac*-**7** consists of equimolar amounts of (p*S*,*R*$_P$) and the pictured (p*R*,*S*$_P$) enantiomers. The N atom is roughly trigonal planar with bond angles summing nearly 360°, as is observed in other uncoordinated azepine-based P-alkenes.[4,10b]

The direct methylation of *rac*-**7** at room temperature with $LiCH_3$ (1.6 M in Et_2O) in benzene solution[19] is perfectly stereoselective and affords ligand *rac*-**8** in excellent isolated yields (see eq 1).[20] Normally, BH_3-protection of the P atom and very low reaction temperatures are required in order to achieve good stereocontrol in alkylations of chlorophosphines.[11a,21] In our case, no epimerization takes place, and the *dr* is best checked by ^{1}H NMR by comparing the integrals of the doublets of the methyl groups that resonate at 1.20 ppm (main diastereomer, $^2J_{PH}$ = 8.0 Hz) and 1.37 ppm (diastereomer impurity, $^2J_{PH}$ = 7.9 Hz). The ^{31}P{^{1}H} NMR spectrum shows a singlet resonance at 70 ppm. We infer from the crystal structures of the Ru-complexes (*vide infra*) that the nucleophilic methylation occurs with complete inversion of configuration at P, as is commonly observed in alkylations of BH_3-protected chloro-phosphines.[22] In contrast to *rac*-**7**, no epimerization of *rac*-**8** is observed upon prolonged heating at 80 °C in benzene solution. Furthermore, the BH_3-protected enantiomers of *rac*-**8** are readily separated on analytical chiral HPLC column (Chiracel OD-H, elution Δt = 4.2 min).

As mentioned above, *rac*-**7** is washed free of the other diastereomer with Et_2O thanks to very diverse solubilities. Therefore, the combined ether washings are enriched with the other diastereomer in a 4:1 ratio. This mixture cannot be effectively separated by conventional means, but, when isolated, methylated in analogy to *rac*-**7**, and protected with BH_3, the major diastereomer is readily separated by flash column chromatography to afford crystalline, air-stable *rac*-**9** in 73% isolated yield (the rest being BH_3-protected *rac*-**8**). The stereochemistry of *rac*-**9** is confirmed by its X-ray crystal structure shown in Figure 2, and as with BH_3-protected *rac*-**8**, enantiomer separation of *rac*-**9** is achieved by chiral HPLC. Finally, *rac*-**9** is deprotected quantitatively by DABCO in benzene solution at 70 °C but the separation of the BH_3·

Scheme 1. Synthesis of Diastereomerically Enriched *rac*-7 as a Conglomerate of Chiral Crystals[a]



[a](i) 1.2 equiv of $PhB(OH)_2$, 5 mol % $Pd(PPh_3)_4$, K_2CO_3, DME/H_2O; (ii) $NaOH_{aq}$, MeOH; (iii) PCl_3, NEt_3, Et_2O; (iv) *t*-BuMgCl, Et_2O, −45 °C; (v) slurrying and washing with cold Et_2O.

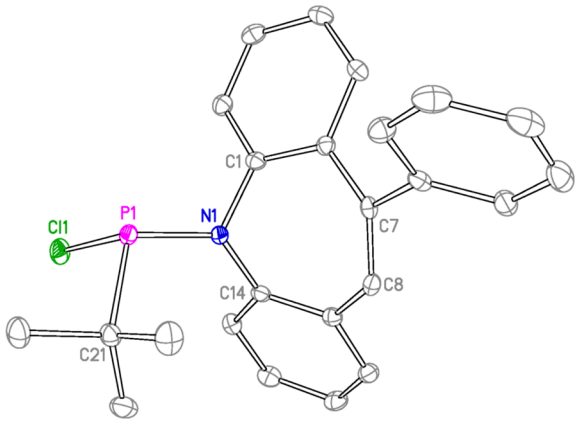
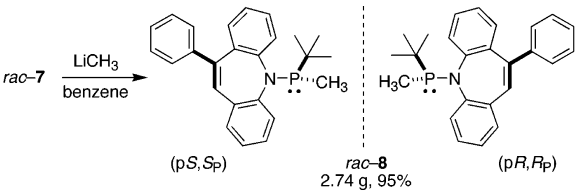


Figure 1. Molecular structure of the (p*R*,*S*$_P$)-enantiomer of *rac*-**7** in the chiral crystal plotted with 50% displacement ellipsoids. H atoms are omitted. Selected distances (Å) and angles (deg): P1−N1 1.680(2), Cl1−P1 2.1393(7), P1−C21 1.861(2), N1−C1 1.440(3), C7−C8 1.350(3), C1−N1−P1 114.7(2), C1−N1−C14 114.0(2), C14−N1−P1 130.8(2), N1−P1−Cl1 105.18(7), N1−P1−C21 107.2(1), C21−P1−Cl1 98.41(7).



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DOI: 10.1021/acs.organomet.6b00879
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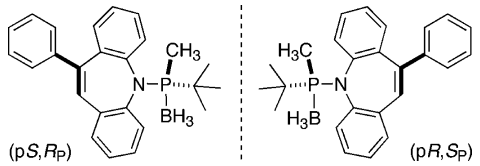


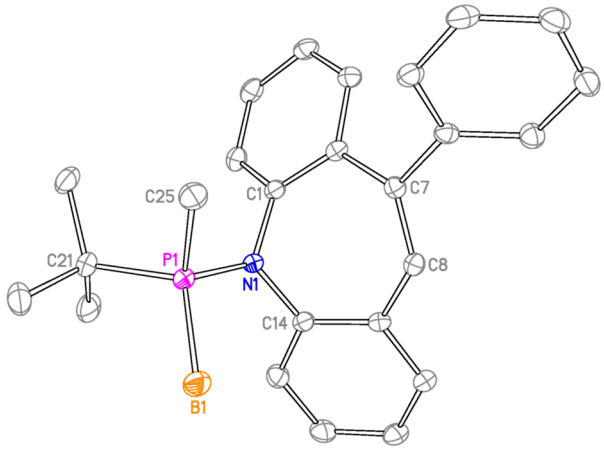


Figure 2. Molecular structure of the (pR,S_P)-enantiomer in the crystal of *rac*-**9** plotted with 50% displacement ellipsoids. H atoms are omitted. Selected distances (Å) and angles (deg): P1−N1 1.689(2), P1−B1 1.918(2), P1−C21 1.864(2), P1−C25 1.815(2), N1−C1 1.439(2), C7−C8 1.354(2), N1−P1−B1 111.06(6), C21−P1−B1 113.78(7), C1−N1−P1 122.63(8), C14−N1−P1 120.85(8), N1−P1−C21 109.94(6), N1−P1−C25 106.22(6).

DABCO adduct from the free phosphine is still a matter of optimization.[23]

Two equivalents of *rac*-**8** react with the precursor $[RuCl_2(p\text{-cymene})]_2$ in CH_2Cl_2 solution to afford 18-valence-electron complex *rac*-**10** in good isolated yield as red crystals (Scheme 2). Its crystal structure confirms the expected monodentate coordination of ligand **8** and the stereochemistry (see Figure 3). When *rac*-**10** is left undisturbed in a pentane-layered $CDCl_3$ solution, it disproportionates and precipitates as deep purple plates and orange needles, which correspond to complexes **11** and **12**, respectively. The disproportionation/crystallization appears to be quantitative, leaving behind a colorless mother

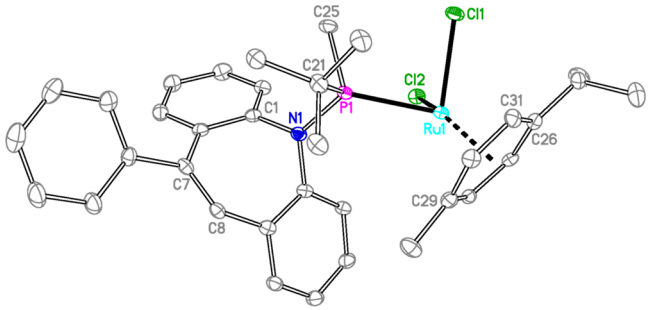
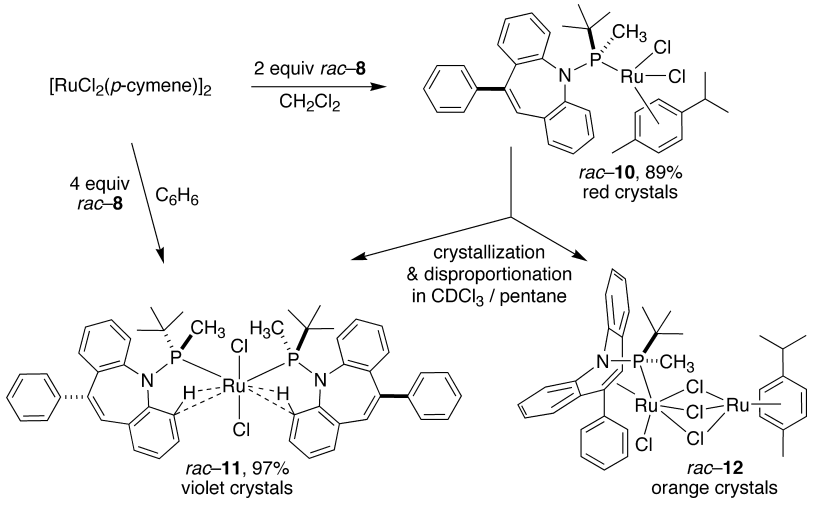


Figure 3. Molecular structure of the (pS,R_P)-enantiomer[24] in the crystal of *rac*-**10** plotted with 50% displacement ellipsoids. H atoms and cocrystallized CD_2Cl_2 are omitted. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.410(2), Ru1−Cl2 2.389(1), Ru1−P1 2.405(2), Ru1−C26 2.260(4), Ru1−C29 2.278(4), Ru1−C31 2.169(4), P1−N1 1.709(4), P1−C21 1.888(4), P1−C25 1.817(4), N1−C1 1.448(5), C7−C8 1.343(6), Cl2−Ru1−Cl1 86.12(4), Cl2−Ru1−P1 83.85(4), N1−P1−Ru1 118.1(2), N1−P1−C21 106.8(2), N1−P1−C25 101.9(2), C21−P1−Ru1 116.1(2), C25−P1−Ru1 110.4(2), C25−P1−C21 101.3(2).

liquor. Complex *rac*-**11** is also accessible directly and in good yields by reacting 4 equiv of the ligand per $[RuCl_2(p\text{-cymene})]_2$ affording crystalline material with identical unit cell parameters. The crystal of *rac*-**11** constitutes a true racemate containing both enantiomeric complexes, (pR,pR,S_P,S_P)-**11** (depicted in Figure 4) and its mirror image (pS,pS,R_P,R_P)-**11**.[24] The C_2-symmetric complex bears two homochiral, P-coordinated ligands in *cis* position and two chlorides *trans* to each other, thus creating a sawhorse coordination geometry around Ru. The resulting formal 14-electron count on Ru and the *cis*-divacant octahedral coordination sphere are satisfied by a double agostic interaction of the aryl C−H bonds of the dibenzazepine moieties. The C13···Ru and C38···Ru contacts measure 2.63 and 2.59 Å, respectively.[25] The corresponding H atoms H13 and H38 are in calculated positions at 1.98 and 1.96 Å from the metal, respectively. The preference for the agostic interactions over coordination of the alkene functions of the ligands is rather unexpected and probably driven by steric constraints. This agostic interaction persists in solution and is detected by NMR spectroscopy. The resonances of the agostic H and C atoms in *rac*-**11** are correlated by a standard HMQC

Scheme 2. Syntheses of Complexes 10−12 Showing the Three Coordination Modes of Ligand 8



DOI: 10.1021/acs.organomet.6b00879
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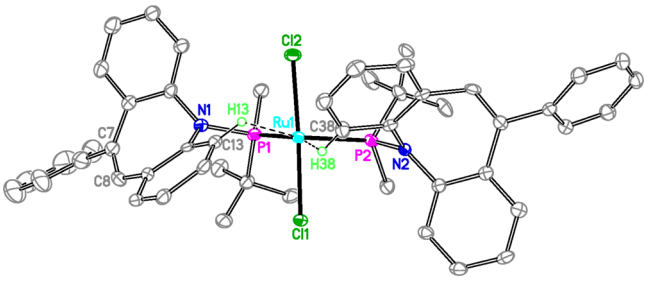

Figure 4. Molecular structure of the (p*R*,p*R*,*S*$_P$,*S*$_P$)-enantiomer[24] in the crystal of *rac*-**11** plotted with 50% displacement ellipsoids. Most H atoms are omitted. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.415(1), Ru1−Cl2 2.397(1), Ru1−P1 2.269(1), Ru1−P2 2.272(1), Ru1···C13 2.628, Ru1···C38 2.589, Ru1···H13 1.982, Ru1···H38 1.957, C7−C8 1.339(6), P1−N1 1.725(3), P2−N2 1.721(3), Cl2−Ru1−Cl1 170.81(3), P1−Ru1−P2 108.12(4), Ru1···H13−C13 123.5, Ru1···H38−C38 122.0.

experiment and show the characteristic low-frequency shifts in the ^{1}H and ^{13}C NMR spectra at δ = 6.21 and 111.46 ppm, respectively. The H resonance at 6.21 ppm is a doublet of doublets due to coupling to the P nucleus ($^2J_{H,P}$ = 10.5 Hz) and the vicinal aromatic proton ($^3J_{H,H}$ = 6.7 Hz), which causes the only crosspeak in a separate ^{1}H,^{1}H COSY experiment. In the ^{13}C{^{1}H} NMR spectrum, the resonance of the agostic C nucleus at 111.46 ppm appears as a pseudo triplet due to coupling to the P atoms with $|^2J_{C,Ptrans} + {}^2J_{C,Pcis}|$ = 6.9 Hz.[25b] In addition, the proton-coupled ^{13}C NMR spectrum shows a $^1J_{C,H}$ coupling to the agostic H atom of 140 Hz (as doublet of multiplets), which is significantly less than the usual ∼160 Hz for aromatic C−H bonds,[26] indicating that indeed this carbon atom is involved in an weak agostic interaction in solution even at room temperature.

Figure 5 reveals the chloride-bridged dinuclear structure of complex *rac*-**12**. The Ru center bearing the η^6-coordinated *p*-cymene ligand is pseudotetrahedral, while the Ru atom bearing ligand **8** is in an octahedral coordination environment. Most importantly, the structure proves the ability of this new P-alkene ligand to adopt a bidentate coordination mode and to

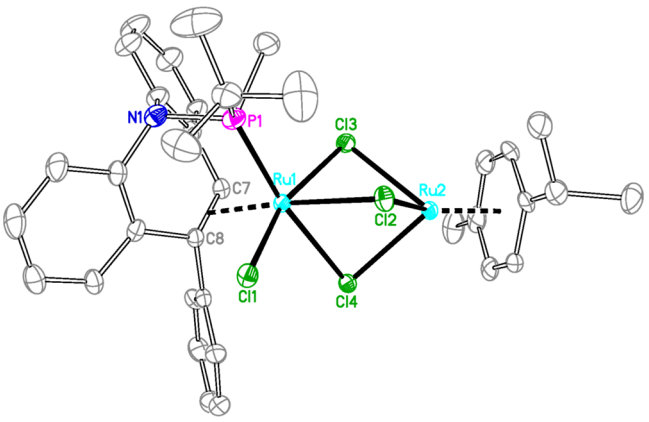

Figure 5. Molecular structure of the (p*S*,*R*$_P$)-enantiomer[24] of *rac*-**12** in the crystal plotted with 50% displacement ellipsoids. H atoms and cocrystallized $CDCl_3$ are omitted. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.374(2), Ru1−Cl2 2.451(2), Ru1−Cl3 2.450(2), Ru1−Cl4 2.579(1), Ru1−P1 2.233(2), Ru1−C7 2.191(4), Ru1−C8 2.247(4), C7−C8 1.426(5), P1−N1 1.739(4), P1−Ru1−C8 93.7(2), C7−Ru1−P1 86.4(2).

remain configurationally stable upon metal coordination (i.e., no epimerization due to inversion of the planar chirality upon coordination takes place). The C7−C8 bond distance of the coordinated alkene is strongly elongated to 1.426(5) Å when compared to 1.343(6) and 1.339(6) Å of the uncoordinated alkene functions in complexes **10** and **11**, respectively (*vide supra*). This π back-bonding effect is also visible in the slight pyramidylization of the phenyl-substituted atom C8 (sum of bond angles to the other C atoms: 352°). As previously observed in crystal structures where ligands of type **3** are in a bidentate coordination mode, here also the N atom adopts a distinctly trigonal pyramidal conformation (sp^3 hybridized) with bond angles totalling 337°, contrasting its planar geometry in **7**, **9**, and **11**.[4,6,7,9b]

To summarize, novel P-stereogenic, planar−chiral P-alkene ligands **8** and BH_3-protected **9** are accessible in multigram scales and in diastereomerically pure forms. We note that these are the first examples of P-alkene ligands that combine point and planar chirality. The exclusive formation of the stereochemically stable *endo*-conformers means that an asymmetric synthesis is now in reach. The intermediate P-stereogenic chloride *rac*-**7** crystallizes solvent-free in a chiral space group and thus may, in principle, be mechanically resolved. This would make both enantiomers of ligand **8** accessible because the methylation of *rac*-**7** is perfectly stereoselective. The prerequisite for a successful implementation of this route is the ability to grow large enough single crystals of *rac*-**7**, and currently, we are working on this and other asymmetric methods to obtain ligands **8** and **9** in optically pure form. Importantly, the borane-protected enantiomers of **8** and **9** are readily separated by enantioselective HPLC. Preliminary complexation experiments of ligand **8** with Ru(II) prove the stereochemical rigidity of the planar−chiral dibenzazepine backbone and display three coordination modes. Whereas the monodentate P-coordination versus bidentate P-alkene coordination indicates a hemilabile alkene function reminiscent of similar P-alkene systems, the direct observation of a bidentate P−C−H agostic coordination mode in this class of chiral P-alkene ligands is unprecedented. Results and applications of the optically pure variants of ligands **8** and **9** in asymmetric catalysis will be communicated in due course.

EXPERIMENTAL SECTION

All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glovebox techniques. THF, Et_2O, and benzene were distilled from purple Na/Ph_2CO solutions; toluene from Na; pentane, C_6D_6, and THF-D_8 from Na_2K alloy; CH_3CN, CH_2Cl_2, and CD_2Cl_2 from CaH_2; and NEt_3 and 1,4-dioxane from K. CD_3CN and $CDCl_3$ were degassed with three freeze−pump−thaw cycles and then kept in a glovebox over activated molecular sieves (3 and 4 Å, respectively). Sealed bottles of DME (TCI, >99%), BH_3·THF (Sigma-Aldrich, 1.0 M in THF), and PCl_3 (Aldrich, 99%) were opened in the glovebox and used as received. MeLi (Sigma-Aldrich, 1.6 M in Et_2O) was filtered (GF/B glass fiber) and titrated before use. **4**,[14] $Pd(PPh_3)_4$,[27] *t*-BuMgCl solution in Et_2O,[28] and $[RuCl_2(p\text{-cymene})]_2$[29] were prepared according to published procedures. Elemental analyses were performed on a Euro EA 3000 analyzer, and air-sensitive samples were handled and prepared in a glovebox. NMR spectra were recorded on Jeol EX 270, ECP 400 or ECX 400 instruments operating at 269.71, 399.78, and 400.18 MHz for ^{1}H; at 67.82, 100.52, and 100.62 MHz for ^{13}C; and at 161.83 and 162.00 MHz for ^{31}P, respectively. Chemical shifts are given in ppm and are reported relative to residual solvent peaks as secondary standard.[30] The Delta NMR Processing and Control Software was used to process and visualize the NMR data.[31]

DOI: 10.1021/acs.organomet.6b00879
Organometallics XXXX, XXX, XXX−XXX

10-Phenyl-5*H*-dibenz[*b*,*f*]azepine (5). **4** (56.57 g, 160.5 mmol) was dissolved in DME (1 L) in a Schlenk flask and degassed by vacuum/N_2 cycles. The brown solution was then transferred via cannula into a 2 L Schlenk flask, which had previously been loaded inside a glovebox with freshly prepared $Pd(PPh_3)_4$ (9.27 g, 8.02 mmol) and phenylboronic acid (23.56 g, 192.6 mmol). A degassed aqueous solution of K_2CO_3 (30.44 g, 216.6 mmol, 300 mL H_2O) was added, and the reaction mixture was heated to reflux overnight. After the reaction was allowed to cool down, the orange organic layer was extracted with CH_2Cl_2 (3 × 400 mL). Pd black was removed by filtration over Celite and the organic phase dried over Mg_2SO_4. Rotary evaporation of the solvent afforded an orange solid, which was suspended in MeOH (4 × 200 mL) and 1 equiv of 1.0 M aqueous NaOH. The reaction mixture was refluxed for 3 h. After cooling to RT, the mixture was extracted with Et_2O (800 mL), the Et_2O phase washed with brine (2 × 400 mL) and H_2O (2 × 400 mL), filtered over Celite, and dried over Mg_2SO_4. Evaporation of the solvent and recrystallization from boiling MeOH yielded yellow crystals (35.5 g, 82%). Anal. Calcd for $C_{20}H_{15}N$: C 89.19, H 5.61, N 5.20. Found: C 89.11, H 5.53, N 5.01. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.42−7.32 (m, 5H), 7.18−7.09 (m, 3H), 6.98−6.93 (m, 1H), 6.85−6.82 (m, 1H), 6.79−6.9 (m, 4H), 5.16 (s, 1H). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$, δ) 119.3, 120.4, 123.1, 123.3, 127.4, 128.2, 128.9, 129.5, 130.0, 130.4, 131.4, 132.1, 143.9, 144.1, 149.1, 150.0. For further drying, the product was transferred to a glovebox, slurried in dry pentane (300 mL), filtered, and dried *in vacuo*.

***N*-(Dichlorophosphanyl)-10-phenyl-dibenz[*b*,*f*]azepine (6).** PCl_3 (20.63 g, 150.2 mmol) was added rapidly to a solution of **5** (20.24 g, 75.12 mmol) and NEt_3 (30.4 g, 300 mmol) in Et_2O (700 mL). The formation of a white precipitate was immediately observed. After stirring for 3 days, the volatiles were removed under reduced pressure. The product was extracted with toluene (400 mL) and separated from NH_4Cl by filtration (GF/B glass fiber filter). The solvent was removed under reduced pressure and the resulting solid slurried in cold *n*-pentane (1 L), filtered, and further washed with cold pentane until it was off-white. HV-drying yielded a white solid (25.6 g, 92%). Anal. Calcd for $C_{20}H_{14}Cl_2NP{\cdot}0.05C_7H_8{\cdot}0.05C_5H_{12}$: C, 65.12; H, 3.75; N, 3.75. Found: C, 65.43; H, 3.86; N, 4.09. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.67 (d, J = 12 Hz, 1H), 7.53−7.33 (m, 10H), 7.23 (t, J = 8 Hz, 1H), 7.11−7.07 (m; 2H) ppm. The spectrum shows the presence of ca. 5 mol % of cocrystallized toluene and pentane. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ) 149.5 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ) 143.65, 143.06, 143.02, 142.90, 142.85, 137.47, 137.44, 136.12, 136.08, 130.82, 129.88 (d, $^2J_{C,P}$ = 3 Hz), 129.27, 129.18, 129.00, 128.85, 128.07, 128.00 (d, $^2J_{C,P}$ = 3 Hz), 127.67, 127.62, 127.54, 126.83, 126.67.

***N*-(*tert*-Butylchlorophosphanyl)-10-phenyl-dibenzo[*b*,*f*]-azepine (*rac*-7).** A solution of *t*-BuMgCl in Et_2O (52.4 mL, 57.1 mmol, 1.09 M) was added dropwise over 20 min to a stirred slurry of **6** (21.21 g, 57.12 mmol) in Et_2O (600 mL), which was kept at −45 °C. The reaction mixture was allowed to warm slowly to −15 °C, and then the cooling bath was removed and stirring was continued for 45 min at RT. The reaction mixture was evaporated to dryness and the product separated from $MgCl_2$ by extraction with benzene (200 mL, filtration over GF/B glass fiber filter). The clear yellow filtrate was stripped to a yellowish powder under HV, slurried in 180 mL of Et_2O at −10 °C for 1 h, then cooled further down to −30 °C for 3 h, rapidly filtered while cold, and washed with small portions of cold Et_2O (2 × 20 mL). The product was isolated as a white powder after drying in HV (10.5 g, 47%). Anal. Calcd for $C_{24}H_{23}ClNP$: C, 73.56; H, 5.92; N, 3.57. Found: C, 74.08; H, 5.92; N, 3.53. Diffraction-quality single crystals were grown from a saturated Et_2O solution. ^{1}H NMR (400 MHz, C_6D_6, δ) 8.14 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.27−7.25 (m, 2H), 7.17−7.11 (m, 3H), 7.06−6.99 (m, 3H) 6.96 (s, 1H), 6.92−6.88 (m, 2H), 6.74 (t, J = 7.9 Hz, 1H), 0.94 (d, 9H, $^3J_{H,P}$ = 14.6 Hz, $PC(CH_3)_3$). The spectrum indicates a diastereomeric purity of >98:2. ^{31}P NMR (162 MHz, C_6D_6, not decoupled, δ) 153.74 (pseudo-octet, $^3J_{H,P}$ = 14.6 Hz). $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6, δ) 149.83 (d, $^2J_{C,P}$ = 25.8 Hz), 145.77 (d, $^2J_{C,P}$ = 10.9 Hz), 143.81, 143.42, 136.33 (d, $^3J_{C,P}$ = 5.4 Hz), 134.59, 130.18, 130.01, 129.52, 129.11, 128.99, 128.81, 128.42, 127.92, 126.70 (d, $^3J_{C,P}$ = 4.6 Hz), 126.25, 126.21, 126.06, 126.00, 125.98, 37.31 (d, $^1J_{C,P}$ = 37 Hz, $PC(CH_3)_3$), 25.73 (d, $^2J_{C,P}$ = 21.8 Hz, $PC(CH_3)_3$). The combined washings are enriched with the other diastereomer in a 4:1 ratio.

***N*-(*tert*-Butyl(methyl)phosphanyl)-10-phenyl-dibenzo[*b*,*f*]-azepine (*rac*-8).** A solution of MeLi in Et_2O (5.2 mL, 8.0 mmol, 1.54 M) was added dropwise via syringe to a stirred solution of *rac*-**7** (3.050 g, 7.783 mmol) in C_6H_6 (78 mL). The solution was stirred for 20 h after which time it turned turbid. The reaction mixture was centrifuged (15 min, 4500 rpm) and the supernatant solution decanted off, discarding the remaining solid. Evaporation of the volatiles yielded an off-white powder that was washed by slurrying in pentane (20 mL) for 24 h, cooled to −33 °C, and filtered while still cold. HV drying afforded 2.74 g (95%) of a white powder. Anal. Calcd for $C_{25}H_{26}NP$: C, 80.84; H, 7.06; N, 3.77. Found: C, 81.19; H, 7.11; N, 3.77. ^{1}H NMR (400 MHz, C_6D_6, δ) 7.53−7.50 (m, 2H), 7.36 (d, J = 7.9 Hz, 1H), 7.23−7.02 (m, 9H), 6.94 (t, J = 7.2 Hz, 1H), 6.80 (t, J = 7.9 Hz, 1H), 1.37 (d, J = 7.9 Hz, 3H), 1.20 (d, $^2J_{H,P}$ = 8.0 Hz, 3H, PCH_3), 1.02 (d, $^3J_{H,P}$ = 7.9 Hz, 9H, $PC(CH_3)_3$). ^{31}P NMR (162 MHz, C_6D_6, H-coupled, δ) 70.31−69.88 (m). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, δ) 150.15 (d, $^2J_{C,P}$ = 13.0 Hz), 149.43 (d, J = 3.0 Hz), 143.75, 143.61, 139.04, 136.30, 136.28, 130.57, 129.25, 129.13, 129.01, 128.81, 128.70, 128.43, 125.12, 124.83, 32.65 (d, $^1J_{C,P}$ = 20.4 Hz, $PC(CH_3)_3$), 26.46 (d, $^2J_{C,P}$ = 16.9 Hz, $PC(CH_3)_3$), 12.02 (d, $^1J_{C,P}$ = 25.8 Hz, PCH_3). BH_3 protection was performed by adding BH_3·THF (2.82 mL, 1.0 M in THF) to a solution of *rac*-**8** (1.05 g, 2.82 mmol) in THF. After stirring for 1 h, the solvent was removed under HV to afford 1.08 g (quantitative yield) of a snow-white glassy solid. ^{1}H NMR (270 MHz, $CDCl_3$, δ) 7.70−7.53 (m, 3H), 7.55−7.28 (m, 7H), 7.28−7.22 (m, 1H), 7.16−7.05 (m, 2H), 7.02−6.93 (m, 1H), 1.28 (d, $^2J_{H,P}$ = 8.37 Hz, 3H, PCH_3), 1.18 (d, $^3J_{H,P}$ = 14.15 Hz, 9H, $PC(CH_3)_3$), 1.2−0.1 (m, 3H). ^{31} P NMR (162 MHz, $CDCl_3$, δ) 82.8−83.4 (m). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$, δ) 145.7 (d, $^2J_{C,P}$ = 4.64 Hz), 144.1, 143.3, 142.8, 138.3, 137.2, 130.3, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.4, 127.8, 126.6, 126.2, 33.0 (d, $^1J_{C,P}$ = 33.2 Hz, $PC(CH_3)_3$), 26.2, 9.9 (d, $^1J_{C,P}$ = 37.8 Hz, PCH_3). Analytical chiral HPLC separation was performed on a Chiracel OD-H column (99:1 hexane/*i*-PrOH, 0.7 mL/min): t_{R1} = 9.00 min, t_{R2} = 13.24 min.

***N*-(Boranato-*tert*-butyl(methyl)phosphanyl)-10-phenyl-dibenzo[*b*,*f*]azepine (*rac*-9).** First, 3.04 g (7.76 mmol) of the isolated ether washings of *rac*-**7** (*vide supra*) that are enriched with the opposite diasteromer in a *ca*. 4:1 ratio were methylated according to the procedure described for *rac*-**8** and then treated with BH_3 (7.8 mL, 1.0 M solution in THF) at RT for 1 h. The solution was evaporated to a yellowish glassy solid (2.88 g). Then, 1.00 g thereof was submitted to flash column chromatography (hexane/NEt_3 9:1) to yield 586 mg (73% with respect to the major diastereomer) of *rac*-**9** in 98% diasteromeric purity. Anal. Calcd for $C_{25}H_{29}BNP$: C, 77.93; H, 7.59; N, 3.64. Found: C, 77.75; H, 7.63; N, 3.53. ^{1}H NMR (270 MHz, $CDCl_3$, δ) 7.61−7.55 (m, 1H), 7.55−7.47 (m, 1H), 7.46−7.30 (m, 7H), 7.26−7.21 (m, 1H), 7.20 (s, 1H), 7.17−7.07 (m, 1H), 7.06 (m, 1H), 1.54 (d, $^2J_{H,P}$ = 8.37 Hz, 3H, PCH_3), 1.11 (d, $^3J_{H,P}$ = 14.23 Hz, 9H, $PC(CH_3)_3$), 1.1−0.1 (m, 3H). ^{31}P NMR (162 MHz, $CDCl_3$, δ) 81.4−82.8 (m). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, δ) 150.15 (d, $^2J_{C,P}$ = 13.0 Hz), 149.43 (d, $^2J_{C,P}$ = 3.0 Hz), 143.75, 143.61, 139.04, 136.30, 136.28, 130.57, 129.25, 129.13, 129.01, 128.81, 128.70, 128.43, 125.12, 124.83, 32.65 (d, $^1J_{C,P}$ = 20.4 Hz, $PC(CH_3)_3$), 26.46 (d, $^2J_{C,P}$ = 16.9 Hz, $PC(CH_3)_3$), 12.02 (d, $^1J_{C,P}$ = 25.8 Hz, PCH_3). Diffraction-quality single crystals of *rac*-**9** were obtained from a saturated 9:1 hexane/NEt_3 solution. Analytical chiral HPLC separation was performed on a Chiracel OD-H column (99:1 hexane/*i*-PrOH, 0.7 mL/min): t_{R1} = 12.95 min, t_{R2} = 13.85 min.

***rac*-[$RuCl_2(\eta^6$-*p*-cymene)(8)] (*rac*-10).** A solution of **8** (184.8 mg, 0.4975 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of $[RuCl_2(p\text{-cymene})]_2$ (152.3 mg, 0.2487 mmol) in CH_2Cl_2 (1.5 mL). The resulting deep red solution was stirred for 1 h. The solvent was then removed under HV and the red solid washed with pentane (3 × 5 mL), recrystallized from CH_2Cl_2/pentane, and dried *in vacuo* to produce a red crystalline solid (302 mg, 89%). Anal. Calcd for $(C_{35}H_{40}Cl_2NPRu)$ $(CH_2Cl_2)_{1.3}$: C, 55.18; H, 5.44; N, 1.77. Found: C,

DOI: 10.1021/acs.organomet.6b00879
Organometallics XXXX, XXX, XXX−XXX

55.07; H, 5.40; N, 1.79. ^{1}H NMR (400 MHz, CD_2Cl_2, δ) 8.23 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 6.8 Hz, 2H), 7.55−7.30 (m, 7H), 7.26 (m, 1H), 7.12−7.0 (m, 2H), 5.54 (d, J = 6.0 Hz, 1H), 5.49 (d, J = 6.1 Hz, 1H), 5.37 (d, J = 6.1 Hz, 1H), 4.49 (d, J = 6.0 Hz, 1H), 2.97 (spt, $^3J_{H,H}$ = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 1.77 (s, 3H), 1.68 (d, $^1J_{H,P}$ = 8.4 Hz, 3H, PCH$_3$), 1.38 (d, $^3J_{H,H}$ = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.33 (d, $^3J_{H,H}$ = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.15 (d, $^1J_{H,P}$ = 14.4 Hz, 9H, PC(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, δ) 97.0 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ) 146.8 (d, $^2J_{C,P}$ = 10.2 Hz), 146.40 (d, $^2J_{C,P}$ = 3.7 Hz), 143.7, 142.0, 137.3, 137.1, 130.9, 130.8, 130.2, 129.8, 129.4, 129.2, 129.1, 128.6, 128.5, 128.0, 125.6, 125.5, 110.2, 100.2, 90.1 (d, $^2J_{C,P}$ = 5.9 Hz, PC$_{cymene}$), 84.8 (d, $^2J_{C,P}$ = 3.7 Hz, PC$_{cymene}$), 84.5, 41.5 (d, $^1J_{C,P}$ = 16.9 Hz, PC(CH$_3$)$_3$), 30.4, 27.7 (d, $^1J_{C,P}$ = 5.9 Hz, PCH$_3$), 23.1, 21.1, 17.7.

***rac*-[RuCl$_2$(8)$_2$] (*rac*-11).** Benzene (3 mL) was added to a mixture of **8** (372.0 mg, 1.001 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ (153.1 mg, 0.2500 mmol) in a vial, which was sealed and heated to 75 °C for 16 h without stirring. The resulting crystalline purple precipitate was filtered (GF/B filter) and washed with benzene (1 × 2 mL) and pentane (2 × 3 mL). After HV drying a microcrystalline deep purple solid was obtained (446 mg, 97%). Anal. Calcd for $C_{50}H_{52}Cl_2N_2P_2Ru$: C, 65.64; H, 5.73; N, 3.06. Found: C, 66.02; H, 5.64; N, 2.92. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.14 (t, J = 6.7 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.65−7.20 (m, 20H), 7.10−6.96 (m, 4H), 6.21 (dd, $^2J_{H,P}$ = 10.5 Hz and $^3J_{H,H}$ = 6.7 Hz, 2H), 1.88 (d, $^2J_{H,P}$ = 8.0 Hz, 6H, PCH$_3$), 1.15 (d, $^2J_{H,P}$ = 15.1 Hz, 18H, PC(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ) 124.6 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ) 154.6 (pseudo t, $^3J_{C,P}$ = 5.2 Hz), 146.5, 144.5, 142.9, 137.9, 135.0, 133.5, 131.3, 130.7, 130.6, 130.0, 129.0, 128.7, 128.1, 125.9, 111.4, (pseudo t, $^3J_{C,P}$ = 6.9 Hz, agostic C), 43.7 (m, PC(CH$_3$)$_3$), 27.6, 13.8 (m, PCH$_3$).

Single Crystals of *rac*-11 and *rac*-12. A solution of **8** (25 mg) in $CDCl_3$ (0.5 mL) in an NMR tube was layered with pentane (1.5 mL) and left standing undisturbed for several days. This caused the quantitative precipitation of a mixture of purple plates (*rac*-**11**) and orange needles (*rac*-**12**), which both were suitable for X-ray crystal structure analyses.

Crystallographic Information. CCDC-1518576 (*rac*-**7**), CCDC-1518577 (*rac*-**9**), CCDC-1518578 (*rac*-**10**), CCDC-1518579 (*rac*-**11**), and CCDC-1518580 (*rac*-**12**) can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00879.

Crystallographic information file for compounds *rac*-**7**, *rac*-**9**, *rac*-**10**, *rac*-**11**, and *rac*-**12** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Ms. Christina Wronna for carrying out the elemental analyses , Prof. Reto Dorta and Dr. Michele Gatti for their valuable contributions regarding the synthesis of **5** and Friedrich−Alexander University for financial support.

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DOI: 10.1021/acs.organomet.6b00879
Organometallics XXXX, XXX, XXX−XXX