ORGANOMETALLICS

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Synthesis, Reactivity, and Coordination of Semihomologous dppf Congeners Bearing Primary Phosphine and Primary Phosphine Oxide Groups

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Cite This: *Organometallics* 2021, 40, 427–441 Read Online

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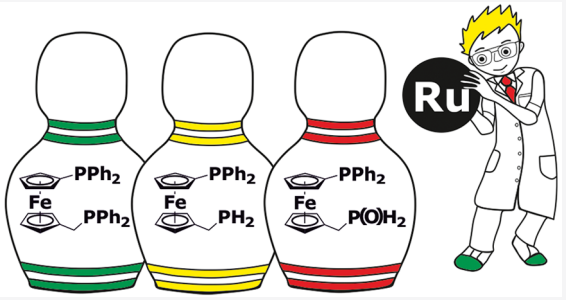
ABSTRACT: This contribution reports the synthesis of two phosphinoferrocene ligands desymmetrized by an inserted methylene spacer, viz., a bis-phosphine combining primary and tertiary phosphine moieties in its structure, $Ph_2PfcCH_2PH_2$ (**2**), and a structurally unique, stable phosphine-primary phosphine oxide $Ph_2PfcCH_2P(O)H_2$ (**7**; fc = ferrocene-1,1′-diyl). Compounds **2** and **7**, together with 1,1′-bis(diphenylphosphino)ferrocene (dppf), the bis-tertiary phosphine $Ph_2PfcCH_2PPh_2$, and the adduct $Ph_2P(BH_3)fcCH_2PH_2$ (**6**), were studied as ligands in Ru(II) complexes bearing auxiliary η^6-arene ligands and both free ligands and the isolated complexes were structurally authenticated, using spectroscopic methods and X-ray crystallography, and further investigated by cyclic voltammetry. The results suggest that distinct donor moieties in the unsymmetric ligands differentiate the otherwise identical coordinated metal centers and that the phosphine moiety in phosphine-phosphine oxide ligand **7** is preferably coordinated to Ru(II), before the phosphine oxide group, which must tautomerize into the hydroxyphosphine form prior to coordination.



INTRODUCTION

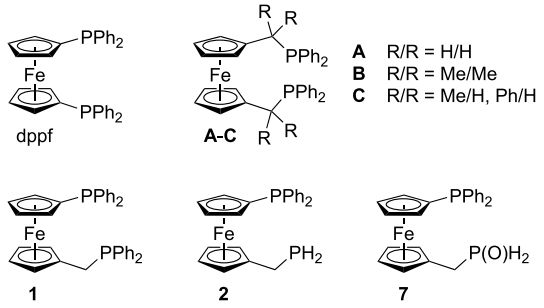
1,1′-Bis(diphenylphosphino)ferrocene (Chart 1), commonly abbreviated as dppf and first reported in 1965,[1] has become an indispensable ligand for coordination chemistry and catalysis.[2] Its enormous practical success has prompted the search for purpose-tailored dppf analogs. To date, several dppf derivatives have been reported with varied substituents at the phosphorus atoms,[3] among which 1,1′-bis(di-*tert*-butylphosphino)-ferrocene has attracted particular attention for its favorable catalytic properties.[4]

In contrast, other approaches toward dppf modification that only partly retain the parent structure have been studied less often. These approaches include replacing one phosphine moiety by another group, which provides access to a vast family of functional phosphinoferrocene ligands and organometallic synthetic building blocks,[5] or inserting a spacer into the cyclopentadienyl-phosphorus bonds. The latter approach has so far resulted in the preparation of symmetrical homologous ligands **A**[6] and **B**,[7] their analogs with chiral phospholane substituents[8] and rigid phenylene spacers,[9] and C-chiral bis-phosphines **C**[10] (Chart 1).[11]

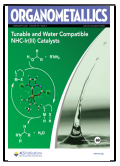
In our research, we desymmetrized the parent dppf structure by introducing a spacer group into *one* of the equivalent C(ferrocene)−P bonds and synthesized semihomologous dppf congener **1**.[12] The current data on **1** and related compounds[13] have shown that such a structural modification differentiates the two coordination sites (both sterically and electronically) and increases the structural flexibility of these ligands, thereby altering their coordination behavior with respect to the more rigid dppf.

Inspired by the structure of the simple, air-stable primary phosphine $FcCH_2PH_2$ (Fc = ferrocenyl),[14] we decided to synthesize and study a novel ferrocene bis-phosphine, **2** (Chart 1), containing tertiary and primary phosphine moieties and the flexible methylene linker. Compound **2** is a homologue of

Chart 1



Received: December 4, 2020
Published: January 22, 2021



https://dx.doi.org/10.1021/acs.organomet.0c00767
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Ph_2PfcPH_2 (fc = ferrocene-1,1′-diyl), which has been used as an intermediate in the synthesis of chiral phosphines for catalytic C−C bond hydrogenation[15] and is an isomer of the somewhat overlooked, planar-chiral 1-(diphenylphosphino)-2-(phosphinomethyl)ferrocene.[16]

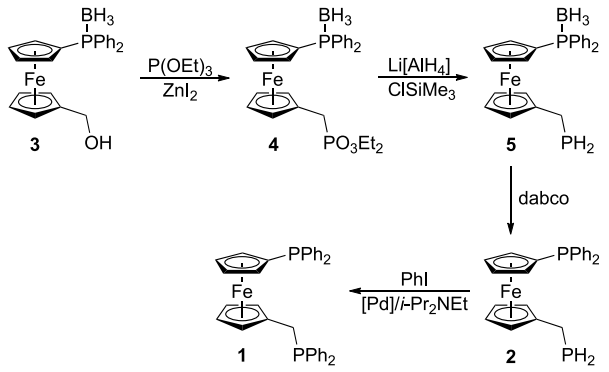
Furthermore, building upon our recent discovery that the ferrrocenymethyl group can stabilize even the hitherto elusive primary phosphine oxides,[17] we also describe the synthesis of compound **7** (Chart 1) as the first primary phosphine oxide functionalized by an additional phosphine moiety.

The coordination preferences of the newly prepared ligands are probed through reactions with Ru^{II} precursors with aromatic π-ligands and compared with those of dppf and **1**. The complexes are further studied by cyclic voltammetry and catalytically evaluated in Ru-catalyzed double bond isomerization using anethole as a model substrate and in Ru-mediated cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran.

RESULTS AND DISCUSSION

Synthesis of the Ligands. Bis-phosphine **2** was obtained by manipulating the hydroxyl group in borane-protected phosphinoalcohol **3**[13d] (Scheme 1). Specifically, the alcohol

Scheme 1. Synthesis and Arylation of Bis-phosphine 2[a]



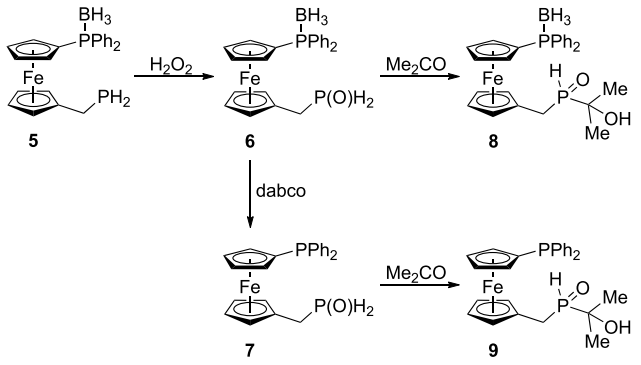
[a]Legend: dabco = 1,4-bicyclo[2.2.2]octane, [Pd] = $Pd(OAc)_2$.

was converted into phosphonic acid ester **4** via a reaction with triethyl phosphite/ZnI_2,[18] and the ester was reduced with $Li[AlH_4]/ClSiMe_3$[19] to give semiprotected bis-phosphine **5**. Subsequent deprotection with 1,4-diazabicyclo[2.2.2]octane (dabco)[20] in THF produced target compound **2** in approximately 60% yield over the three steps after a final crystallization.

Compound **2** was isolated as an air-stable and thermally robust, crystalline solid (mp 114 °C) with a characteristic yet only faint smell of phosphane. It did not react with acetone (at 40 °C; see below) but could be arylated[21] with iodobenzene in the presence of palladium(II) acetate (5 mol %) and an amine additive, giving known[12] bis-tertiary phosphine **1** in 78% yield (Scheme 1). Similar results were found when using $[Pd_2(dba)_3]$ as the catalyst (dba = dibenzylideneacetone).

To synthesize a ferrocene-based, hybrid phosphine-primary phosphine oxide ligand, we further oxidized P-protected intermediate **5** with aqueous hydrogen peroxide at 0 °C (Scheme 2). The oxidation proceeded rapidly and selectively, producing phosphine oxide **6** in 84% yield. Upon treatment with dabco, this compound was converted into phosphine oxide **7** in a virtually quantitative yield (95%). Similarly to

Scheme 2. Synthesis of Phosphine Oxides 6−9[a]



[a]Legend: dabco = 1,4-bicyclo[2.2.2]octane

$FcCH_2P(O)H_2$,[17] compounds **6** and **7** reacted with acetone at slightly elevated temperature (40 °C; the reaction proceeds even at room temperature but only slowly), providing the corresponding addition products **8** and **9** in good yields. Phosphine oxides **6**−**9** were stable under ambient conditions (we noted, however, that compounds **8** and **9** slowly and partly regenerated **6** and **7**, respectively, in a dichloromethane solution[17,22]).

^{31}P NMR spectra of **2** and **5** displayed diagnostic triplets of triplets ($^1J_{PH}$ = 194 Hz, $^2J_{PH}$ = 4−5 Hz) due to the primary phosphine moieties at $\delta_P \approx -126$ (Figure 1). The signal of the

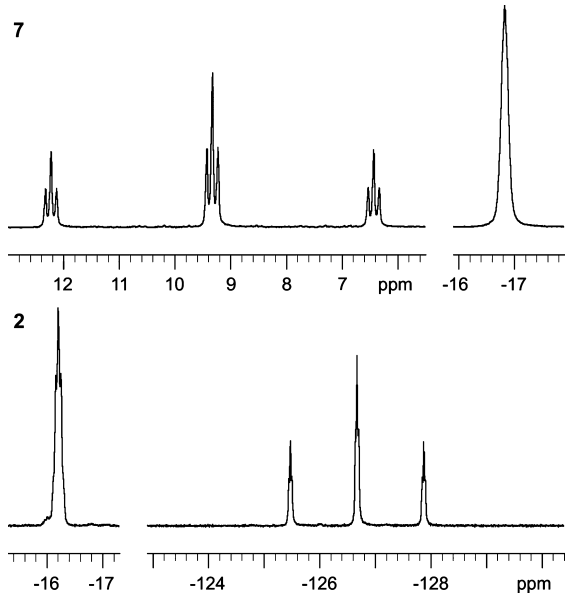


Figure 1. ^{31}P NMR spectra of **2** and **7**. Spectra are shown with identical scaling at both axes.

PPh_2 group was observed as a singlet at δ_P −16.2 for **2** and as a broad multiplet at δ_P 16.4 for BH_3-adduct **5**. Correspondingly, the PH_2 groups gave rise to doublets of multiplets at $\delta_H \approx 2.8$ in the ^1H NMR spectra, whereas the signals of the CH_2 linker were observed as doublets of triplets at $\delta_H \approx 2.3$. The presence of the PH_2 moieties was further manifested as intense bands in the ≈2300−2360 cm^{-1} range of IR spectra, attributable to P−H stretching modes.

Oxidation of the PH_2 group in **6** and **7** shifted the ^{31}P NMR signal downfield ($\delta_P \approx 9$) and increased the $^1J_{PH}$ coupling constant (≈ 470 Hz; see Figure 1). The signal of the $P(O)H_2$

https://dx.doi.org/10.1021/acs.organomet.0c00767
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hydrogens also shifted ($\delta_H \approx 6.8$), reflecting the stronger electron-withdrawing nature of the phosphinyl moiety. Even so, replacing one PH hydrogen with the 2-hydroxyprop-2-yl moiety in **8** and **9** was clearly indicated in the NMR spectra: The ^{31}P NMR spectra displayed doublets of multiplets with a large $^1J_{PH}$ coupling constant ($\approx$ 455 Hz), whereas the PH signals were observed at $\delta_H \approx 2.3$ in the ^1H NMR spectrum, split into a more complicated pattern (ddd for **8** and dt for **9**) due to the diastereotopic nature of the CH_2 hydrogens attached to the stereogenic phosphorus atom. For the same reason, two separate signals were found for the chemically equivalent methyl groups. No signals attributable to hydroxyphosphine tautomers were observed in the NMR spectra of phosphine oxides **6**–**9**.

The crystal structures of **2** and **9** are shown in Figure 2 (for additional diagrams and parameters, see the Supporting Information). Both compounds comprised regular ferrocene units with similar Fe–C distances (2.035(2)–2.055(2) Å for **2**; 2.028(3)–2.056(3) Å for **9**) and negligible tilting (4.86(9) and 2.1(2)°, respectively). The cyclopentadienyls in **2** adopted an approximate 1,2′-conformation[23] with the torsion angle C1–Cg1–Cg2–C6 (hencefort denoted as τ; Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1–5) and C(6–10), respectively) of −81.8(1)°. A similar, though more compact, arrangement was identified in **9** (τ = 69.7(2)°). In the crystal, the molecules of **9** assembled into infinite chains through O–H···O=P hydrogen bonds (O1···O2 = 2.645(4) Å; see the Supporting Information).

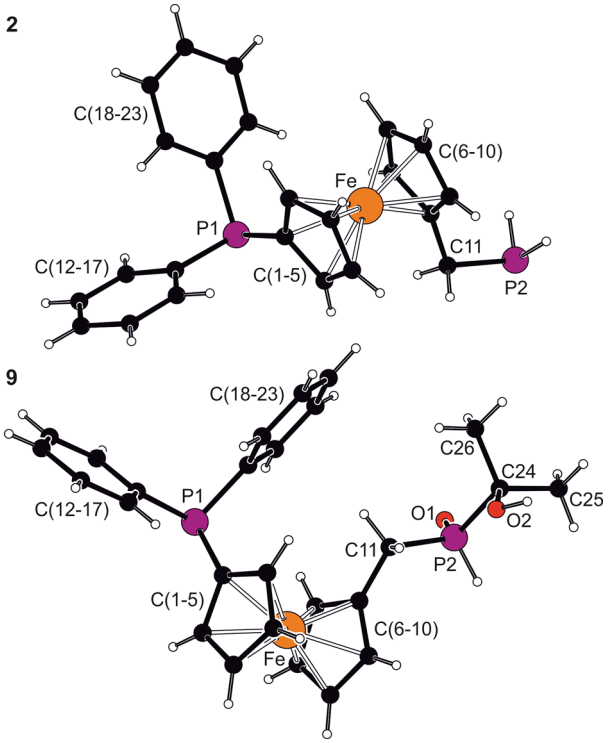
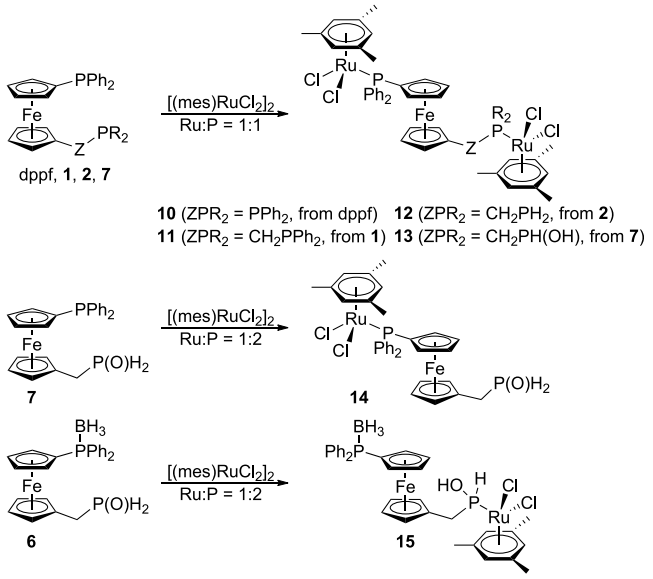


Figure 2. Molecular structures of **2** and **9**. Selected distances and angles (in Å and deg): for **2**: P1–C1 1.806(2), P1–C12 1.844(2), P1–C18 1.844(2), P2–C11 1.853(2), C6–C11–P2 114.9(1); for **9**: P1–C1 1.812(3), P1–C12 1.838(3), P1–C18 1.836(3), P2–O1 1.486(3), P2–C11 1.803(3), C6–C11–P2 111.8(2), C11–P2–O1 114.4(2). Parameters pertaining to the disordered $CH_2P(O)$ arm are given for the more populated orientation.

Synthesis of Ru(II) Complexes. The coordination behavior of compounds **1**, **2**, **6**, and **7** was evaluated through reactions with Ru(II) precursors bearing auxiliary π-ligands. The prototypical ligand dppf was also included in these studies for comparison purposes. Initially, we focused on (η^6-mes)Ru(II) complexes featuring the ligands in a P,P′-bridging mode. The reactions of $[\{(\eta^6\text{-mes})RuCl(\mu\text{-Cl})\}_2]$ (mes = mesitylene) with dppf, **1**, and **2** proceeded cleanly, producing respective diruthenium complexes **10**, **11**, and **12** as the sole products (Scheme 3).

Scheme 3. Synthesis of (η^6-mes)Ru(II) Complexes 10–15[a]



[a]mes = mesitylene.

When using hybrid ligand **7**, the reaction was accompanied by tautomerization of the primary phosphine oxide moiety, leading to phosphine-hydroxyphosphine complex **13**. Upon reducing the amount of the Ru precursor by half, the analogous reaction selectively produced phosphine complex **14** featuring uncoordinated phosphine oxide moiety. Conversely, the reaction of $[(\eta^6\text{-mes})RuCl_2]_2$ with ligand **6**, whose tertiary phosphine group was unavailable for coordination, led to hydroxyphosphine complex **15** (Scheme 3).

Generally, complexes **10**–**15** were relatively poorly soluble and exerted structural dynamics which complicated their characterization by NMR spectroscopy. The coordination of the PPh_2 moiety led to a rather uniform downfield shift of the ^{31}P NMR signal by 37–38 ppm (≈42 ppm for CH_2PPh_2 in **1**), whereas the coordination of the PH_2 group in **2** *or* tautomerization/coordination of the $P(O)H_2$ groups in **6** and **7** resulted in a considerably larger shift of approximately 107 ppm (the tautomerization was further indicated by changes in the non-decoupled ^{31}P NMR spectra, wherein the triplets due to P–H interactions in the $P(O)H_2$ groups were replaced by doublets of the PH(OH) fragments).

The molecular structures of **10**·THF·$2CH_2Cl_2$ and **12**·$2CHCl_3$ determined by X-ray crystallography (Figure 3) were generally similar to that of $[(L\text{^}L)\{(\eta^6\text{-arene})RuCl_2\}_2]$ (L^L = dppf and $fc(CH_2PPh_2)_2$)[24] and $[(\eta^6\text{-}p\text{-cymene})RuCl_2(FcCH_2PH_2\text{-}\kappa P)]$.[25] The complex molecule in the structure of **10**·THF·$2CH_2Cl_2$ was situated on the crystallographic inversion center, which rendered the ferrocene

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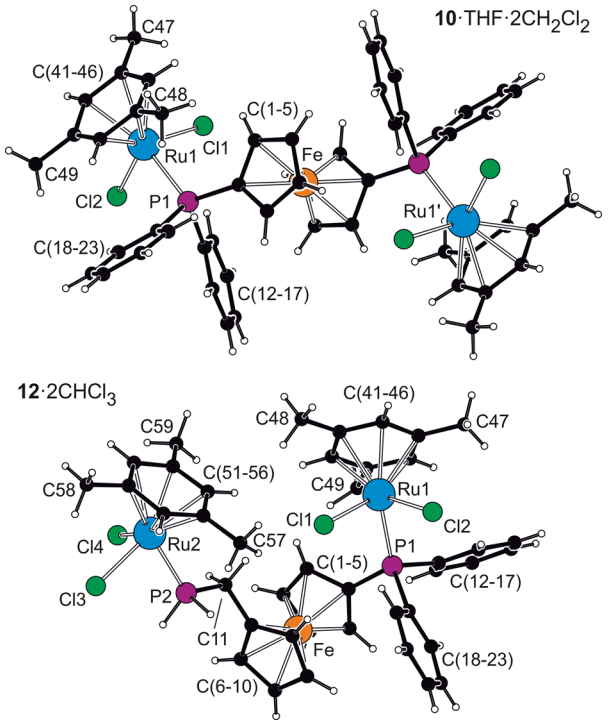


Figure 3. Views of the complex molecules in the structures of **10**·THF·$2CH_2Cl_2$ and **12**·$2CHCl_3$. Selected distances (in Å): for **10**·THF·$2CH_2Cl_2$: Ru1−P1 2.3598(5), Ru1−Cl1 2.4082(5), Ru1−Cl2 2.4113(5), Ru1−C(arene) 2.198(2)−2.270(2), Fe1−C(1−5) 2.039(2)−2.064(2); for **12**: Ru1−P1 2.3620(7), Ru1−Cl1 2.4160(7), Ru1−Cl2 2.4122(8), Ru1−C(arene) 2.205(3)−2.271(3), Ru2−P2 2.2770(7), Ru2−Cl3 2.4097(9), Ru2−Cl4 2.4027(9), Ru2−C(arene) 2.176(3)−2.263(3), Fe1−C(1−10) 2.025(3)−2.053(3).

cyclopentadienyls exactly parallel and brought their phosphine substituents and the ligated ruthenium fragments into anti positions. Ferrocene cyclopentadienyls in unsymmetric complex **12**·$2CHCl_3$ were mutually rotated by τ = 90.5(2)° and tilted by 4.4(2)°. In both complexes, the ruthenium atoms adopted the usual "piano stool" geometry, wherein the basal planes (Cl_2P) were oriented parallel to the π-coordinated arene ring (interplanar angles: 2.89(7)° for **10** and 1.6(1)° (Ru1) and 2.6(1)° (Ru2) for **12**). Notably, the Ru−PPh_2 bonds (≈2.36 Å) were significantly elongated with respect to the Ru−PH_2 bond in **12** (≈2.28 Å), most likely for steric reasons.

The structure of **15** (Figure 4) corroborated that the phosphine oxide moiety underwent tautomerization upon coordination. The P−H and P−OH bonds of the Ru-bound PH(OH) unit, located between the bulky (η^6-mes)Ru and ferrocene fragments, alternated in their positions, thereby resulting in positional disorder. The length of the Ru−P bond in **15** was very similar to the Ru−PH_2 bond distance in complex **12**, and the geometry of the fcPPh_2·BH_3 fragment matched that of dppf·$2BH_3$.[26]

Next, we focused on cationic (η^6-mes)Ru(II) complexes accommodating the studied ferrocene phosphines as chelating donors. The reaction[24a,b] of [{(η^6-mes)RuCl(μ-Cl)}$_2$] with dppf in the presence of Na[PF_6] produced [(η^6-mes)RuCl(dppf-κ^2*P*,*P*′)][PF_6] (**16**) in 89% yield (Scheme 4). Attempts to similarly prepare complexes with ligands **1** and **2** only led to equilibrium mixtures containing the respective compounds [(η^6-mes)RuCl(L^L)][PF_6], based on ^{31}P NMR analysis,[27] which could not be separated by crystallization or chromatography. Practically identical mixtures were obtained in the reaction of stoichiometric amounts of **1** or **2** with [(η^6-mes)RuCl(MeCN-κN)$_2$][PF_6] in dichloromethane (for the synthesis of the Ru-precursor, see the Supporting Information). Reactions with ligand **7** were also unsuccessful, albeit mainly due to extensive decomposition of the ligand in the reaction mixtures (compound **7** seems to decompose in the presence of the PF_6^- anion).

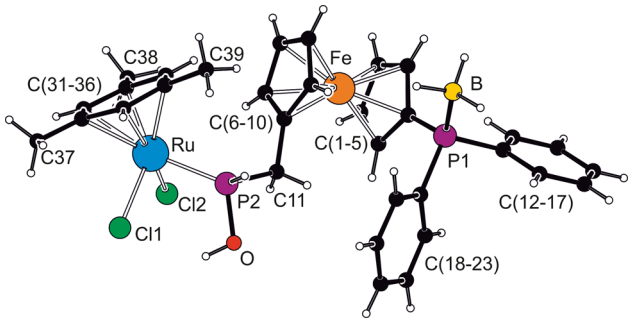
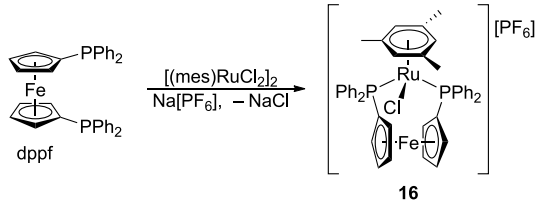


Figure 4. Molecular structure of complex **15**. Selected distances (in Å): Ru−P2 2.2815(8), Ru−Cl1 2.416(2) (dominant position), Ru−Cl2 2.4052(9), Ru−C(arene) 2.193(3)−2.275(3), P2−O 1.637(3), P1−B 1.924(4), Fe1−C(1−10) 2.025(3)−2.045(3).

Scheme 4. Synthesis of Complex 16



The crystal structure of **16**·CH_2Cl_2 (Figure 5) was unexceptional in view of the data reported for [(η^6-arene)RuCl(dppf-κ^2*P*,*P*′)][PF_6], where arene = C_6Me_6[24a,b] and *p*-cymene.[28] The complex cation had a three-legged piano stool structure symmetrically capped with the η^6-benzene ring (Ru1−C(41−46) = 2.251(3)−2.310(3) Å). The Ru−Cl and Ru−P distances were similar to those determined for **10**·

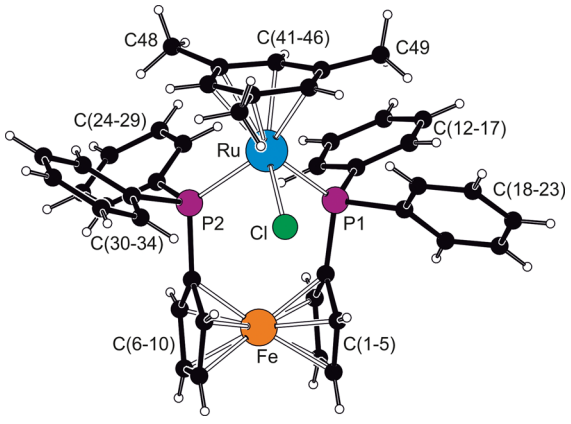


Figure 5. View of the complex cation in the structure of **16**·CH_2Cl_2. Selected distances and angles (in Å and deg): Ru−P1 2.3636(9), Ru−P2 2.3619(9), Ru−Cl 2.4030(8), P1−Ru−P2 95.10(3), Cl−Ru−P1/2 81.21(3)/88.64(3), Fe−C(1−10) 2.024(3)−2.062(3); the angle subtended by the C(41−46) and the {P1,P2,Cl} basal plane is 3.9(1)°.

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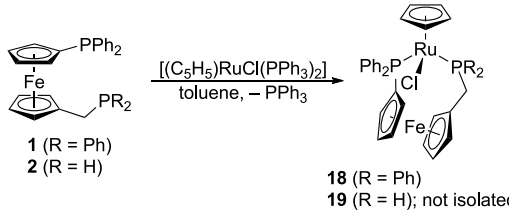
$2CH_2Cl_2$·THF and did not differ much even from each other. Nevertheless, an asymmetry arose around the Ru atom, most likely resulting from the dissimilar steric demands of the Ru-bound ligands, with the largest interligand angle associated with the chelating dppf ligand. Because of chelate coordination, the ferrocene cyclopentadienyls were practically eclipsed (τ = 6.0(2)°) and, additionally, exerted negligible tilting (2.1(2)°).

To eliminate the problem with compound isolation, we replaced the (η^6-mes)Ru(II) moiety by the iso-π-electronic fragment (η^5-C_5H_5)Ru(II) toward synthesizing charge-neutral compounds analogous to the known dppf complex [(η^5-C_5H_5)RuCl(dppf-κ^2P,P')] (**17**).[29] Indeed, a modified method for preparing **17** based on thermally assisted replacement of triphenylphosphine ligands in [(η^5-C_5H_5)RuCl(PPh_3)$_2$] employing bis-phosphine **1** produced the corresponding chelate complex [(η^5-C_5H_5)RuCl(**1**-κ^2P,P')] (**18**), which was isolated as a rusty brown, air-stable solid in a 82% yield (Scheme 5).

Scheme 5. Synthesis of (η^5-C_5H_5)Ru(II) Complexes 18 and 19



Regrettably, repeated attempts to similarly prepare complex [(η^5-C_5H_5)RuCl(**2**-κ^2P,P')] (**19**) were unsuccessful. The reactions of bis-phosphine **2** with [(η^5-C_5H_5)RuCl(PPh_3)$_2$] or, alternatively, [(η^5-C_5H_5)RuCl(cod)] (cod = η^2:η^2-cycloocta-1,5-diene) afforded mixtures in which complex **19** was detected as the main product[30] but could not be isolated in pure form. Even more complicated reaction mixtures were obtained when sequentially adding **2** and (Bu_4N)Cl as a chloride source (1 equiv of each) to [(η^5-C_5H_5)Ru(MeCN-κN)$_3$][PF_6] in dichloromethane. Analogous reactions with **7** were hampered by the decomposition of the ligand in the reaction mixtures at elevated temperatures or in the presence of PF_6^-.

The formation of complexes **18** and **19** was clearly indicated by ^{31}P NMR spectra showing a pair of doublets due to interacting nonequivalent Ru-bound phosphorus atoms. In addition, ^{1}H and ^{13}C NMR spectra of isolated complex **18** displayed eight resonances for the diastereotopic ferrocene CH groups (the Ru atom in **18** becomes a stereogenic center). Although we could not isolate pure bulk samples of **19**, we serendipitously obtained a few single crystals of this compound (as solvate **19**·CH_2Cl_2) and were thus able to structurally authenticate both **18** and **19** by X-ray diffraction analysis (Figure 6).

Complexes **18** and **19** adopted the typical piano stool structures similar to those of **16** and **17** (the Ru–C distances in **18** and **19** were slightly shorter than in arene complex **16**, presumably strengthened by a stronger interaction with the anionic cyclopentadienyl ligand). In both compounds, the Ru–P bond involving the ferrocene-bound PPh_2 group was longer than the Ru–P bond with the CH_2PR_2 (R = H and Ph) moiety. Both homologated ligands **1** and **2** forced wider bite angles than did dppf in **17** (95.01(4)°).[31] The dihedral angles between the ferrocene cyclopentadienyl rings were 2.4(2)° in

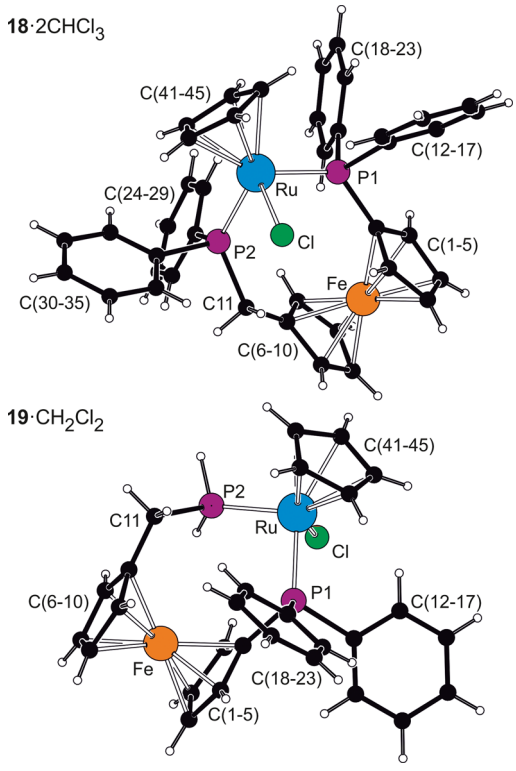


Figure 6. Views of the complex molecules in the structures of **18**·$2CHCl_3$ and **19**·CH_2Cl_2. Selected distances and angles (in Å and deg): for **18**: Ru–P1 2.311(1), Ru–P2 2.296(1), Ru–Cl 2.4473(9), P1–Ru–P2 101.66(4), Cl–Ru1–P1/2 89.28(2)/85.53(2), Ru–C(41–45) 2.187(5)–2.218(4), Fe–C(1–10) 2.040(3)–2.057(5); for **19**: Ru–P1 2.2858(8), Ru1–P2 2.2698(5), Ru–Cl 2.4439(6), P1–Ru–P2 96.19(6), Cl–Ru1–P1/2 89.28(2)/85.53(2), Ru–C(41–45) 2.179(2)–2.225(2), Fe–(C1–10) 2.046(2)–2.074(2).

18 and 5.6(1)° in **19**, and the rings appeared rotated from an ideal eclipsed conformation by −37.8(3)° in **18** and by 20.6(1)° in **19**.

Electrochemistry. The electrochemical behavior of the phosphine ligands and their neutral (η^6-mes)Ru(II) complexes that form a more complete series was investigated by cyclic voltammetry at a glassy carbon disc electrode in dichloromethane containing $Bu_4N[PF_6]$ as the supporting electrolyte, with particular focus on the anodic region where the oxidation of the metal centers was expected.

In line with previous reports,[32] dppf underwent an oxidation at 0.18 V versus ferrocene/ferrocenium reference (Figure 7). This redox process, attributable to the ferrocene/ferrocenium couple, was followed by chemical reactions that made it quasireversible within the usual time scale of cyclic voltammetry: Relatively faster scanning rendered the oxidation virtually reversible, whereas slower scan rates or scanning toward more positive potentials made it practically irreversible (additional ill-defined oxidative waves due to newly formed species could be observed at higher potentials; see Figure 7). The redox response[33] of semihomologous bis-phosphine **1** was practically identical except that the redox wave was shifted to less positive potentials (E = 0.08 V) because the influence of one of the electron-withdrawing phosphine moieties was lessened by the nonconjugated methylene spacer (σ_p for PPh_2 is 0.19).[34]

For bis-phosphine **2**, the ferrocene-centered oxidation was essentially reversible at a 0.10 V s^{-1} scan rate and occurred at E

https://dx.doi.org/10.1021/acs.organomet.0c00767
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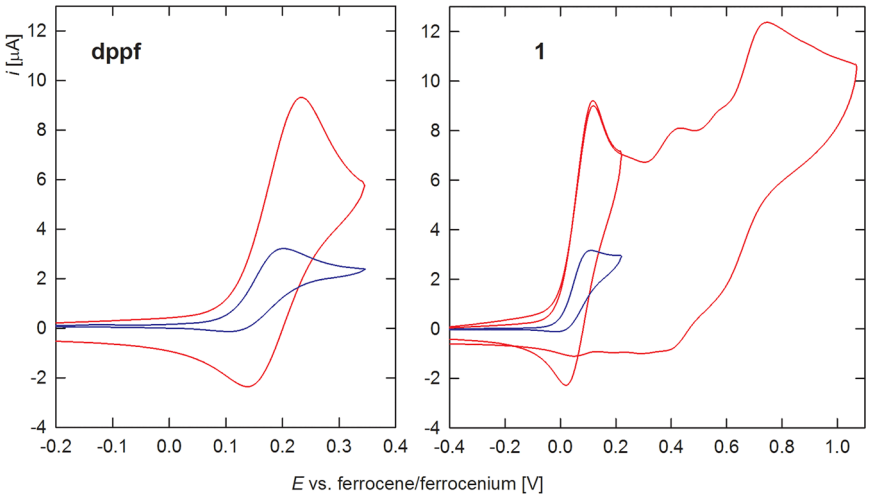

Figure 7. Cyclic voltammograms of dppf and **1**. The voltammograms recorded at a scan rate of 0.10 V s^{-1} are shown in red, and those at 0.010 V s^{-1} are shown in blue. The ratio of the anodic peak currents determined at 0.10 and 0.010 V s^{-1} scan rates, $i_{pa}(0.10)/i_{pa}(0.010)$, was 2.9 for both compounds (the theoretical value is $\sqrt{10} \approx 3.16$).

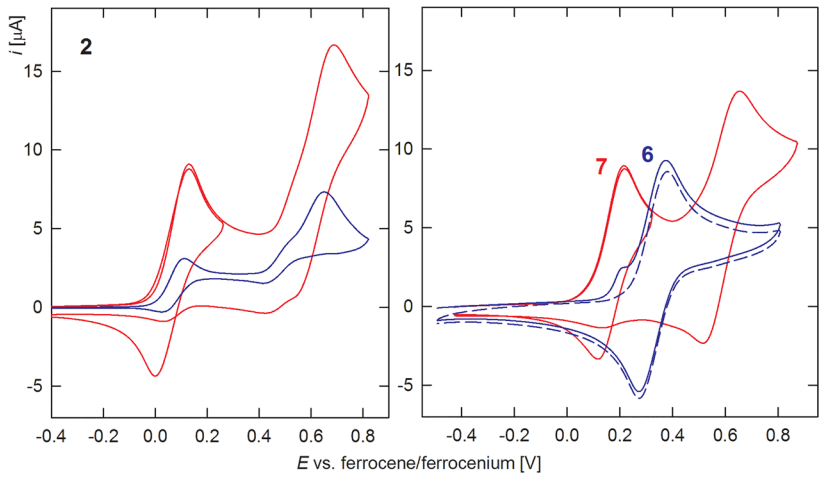

Figure 8. (left) Cyclic voltammograms of **2**. The voltammograms recorded in dichloromethane at a scan rate 0.10 V s^{-1} are shown in red, and those recorded at 0.010 V s^{-1} are shown in blue. (right) Cyclic voltammograms of **6** (blue) and **7** (red). The second scan is shown as a dashed line.

= 0.08 V, thus reflecting the presence of the methylene linker that minimizes the influence of the attached moiety (PPh_2 vs PH_2; Figure 7). At more positive potentials, an additional redox event was observed, consisting of two closely spaced, irreversible oxidations that convoluted into a composite wave peaking at $E \approx 0.70$ V and associated with a counter wave at approximately 0.43 V (peak potentials at 0.10 V s^{-1} are given). The cyclic voltammogram of phosphine oxide **7** also displayed two redox changes in the anodic region (Figure 8). Initially, the compound underwent a reversible oxidation presumably located at the ferrocene core. The redox wave occurred at more positive potentials ($E = 0.17$ V) with respect to that of **2**, in line with the electron-withdrawing nature of the $CH_2P(O)H_2$ moiety. The second oxidation at $E = 0.59$ V was also reversible but affected the preceding redox step during reverse scan. Finally, adduct **6** showed a single reversible oxidation in the accessible potential range (Figure 7). The position of the wave ($E = 0.32$ V) suggested further electron density removal from the ferrocene core associated with P → B donation. In its anodic branch, the redox wave was preceded by a prepeak, which disappeared (or decreased in intensity) upon repeated scanning and was explained by adsorption phenomena.

Overall, the initial oxidation of the studied phosphine ligands can be ascribed to oxidation of the ferrocene unit, as expected because the HOMO orbital of dppf is prevalently localized at the ferrocene core.[35] In some cases, the reversibility of the ferrocene/ferrocenium redox transition is affected by follow-up reactions in which the electro-generated product is converted into other species (typically redox-active) and can be linked to electron density relocations within the conjugated ferrocene−phosphine system.[36] The subsequent oxidative steps are difficult to explain because they are often of a composite nature and can be affected by chemical processes coupled with the preceding redox step.

Complex **10**, combining redox sites of two types (i.e., the ferrocene unit and two equivalent (η^6-arene)Ru(II) fragments), underwent two successive oxidations.[37] The first reversible oxidation, which occurred at $E = 0.16$ V due to the ferrocene ligand, was followed by an irreversible oxidation at 0.75 V (peak potential at 0.10 V s^{-1} is given), corresponding to a simultaneous one-electron irreversible oxidation of the two chemically equivalent Ru(II) centers. Similar behavior was reported for the analogous (η^6-arene)Ru(II) complexes featuring dppf and **A** as the bridging ligands[24a,b] and was

https://dx.doi.org/10.1021/acs.organomet.0c00767
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also observed for **11**–**13** (Figure 9). The ferrocene units in **11**, **12**, and **13** were oxidized reversibly at E = 0.06, 0.11, and 0.11

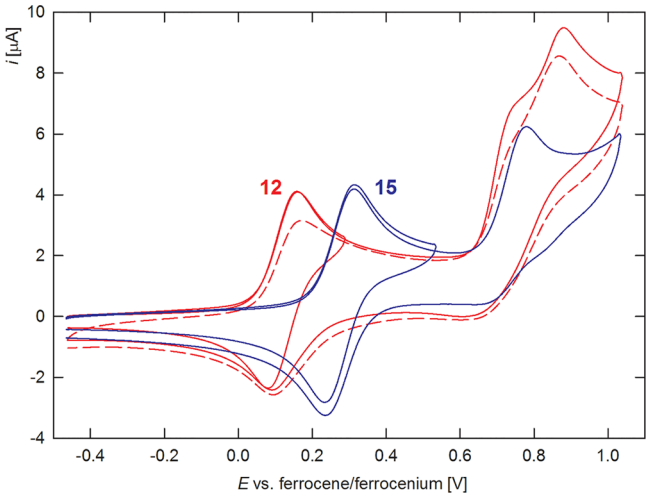
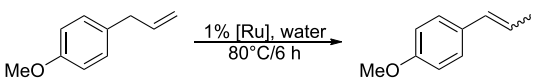


Figure 9. Cyclic voltammograms of **12** (red) and **15** (blue) as recorded in dichloromethane at scan rate 0.10 V s^{-1}. The second scan is shown by dashed line.

V, respectively, whereas the two nonequivalent Ru(II) centers, distinguished by the asymmetric bis-phosphine ligands, were oxidized in two closely separated irreversible redox steps in the 0.70–0.87 V range. Similar to the respective free ligand, the first oxidation of complex **15** was shifted to 0.27 V, reflecting the presence of the BH_3 unit (see above), followed by an additional one-electron irreversible oxidation of the Ru^{II} center at 0.77 V (peak potential determined at 0.10 V s^{-1}). Complex **14** could not be analyzed due to its instability in the presence of the PF_6^- anion.

Catalytic Testing. Considering the wide applications of ruthenium compounds in transition metal catalysis,[38] we evaluated the diruthenium(II) complexes, choosing two reactions that manipulate unsaturated C–C bonds and focusing on the possible influence of the different P-donor moieties. The first series of experiments was performed using a model catalytic double bond isomerization of estragole (**20**) to anethole (**21**; see Table 1),[39] in which the beneficial effect of the P–OH moiety has been recently established.[40] The reaction was performed in water[41] using potassium carbonate as a base in the presence of 1 mol % Ru (i.e., 0.5 mol %

Table 1. Ru-Catalyzed Isomerization of Estragole in Water[a]



20 **21**

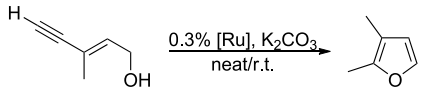
catalyst	conversion (%)	E/Z
10	97	90/10
11	85	78/22
12	68	76/24
13	25	70/30
17	<5	
18	<5	

[a]Reaction conditions: 1 mol % [Ru], K_2CO_3 (6 mol %), and estragole (2.0 mmol) were reacted in 1 mL of water at 80 °C for 6 h. The conversion was determined by ^{1}H NMR spectroscopy.

dirutenium complex). The results outlined in Table 1 indicate the superior performance of the (η^6-mes)Ru(II) complexes, which can be related to their easier catalytic activation, presumably by removal of the Ru-bound chloride ligand that provides a vacant coordination at Ru. Among the arene complexes, the compound with tertiary phosphine ligands performed better than "hydroxyphosphine" complex **13**, and the most active dppf-based catalyst (**10**) also showed the highest selectivity to (*E*)-alkene.

The other testing reaction was the cycloisomerization of (*Z*)-3-methylpent-2-en-4-yn-1-ol (**22**) into 2,3-dimethylfuran (**23**; Table 2).[42] In these experiments, the Ru catalyst (0.3 mol

Table 2. Ru-Catalyzed Cyclization of Enynol 22



22 **23**

catalyst	yield of **23** (%)	catalyst	yield of **23** (%)
10	76	**13**	78
11	81	**17**	0
12	80	**18**	0

[a]Neat substrate **22** and Ru-catalysts (0.3 mol %) were reacted at room temperature (23–25 °C) in the air for 18 h. The yield was determined by ^{1}H NMR spectroscopy.

%) was added directly to the neat substrate, and the reaction was allowed to proceed in the air for 18 h. To our delight, arene complexes **10**–**13** were catalytically active, even at room temperature, without requiring a high temperature to initiate the cyclization reaction, in contrast to other Ru catalysts.[42,43] However, the product yields achieved with **10**–**13** varied only slightly. The (η^5-C_5H_5)Ru(II) complexes, **17** and **18**, showed no appreciable activity.

CONCLUSION

The findings of this study further demonstrate that the "homologation" approach is a viable route toward new unsymmetric ligands with modified steric and electronic properties. Newly prepared bis-phosphine **2**, combining primary and tertiary phosphine moieties in its structure, and phosphine-phosphine oxide **7**, which is the first phosphine ligand bearing an additional *primary* phosphine oxide moiety, are remarkably stable and hence suitable for further synthesis (this was already exemplified by the **2** → **1** conversion reported herein) and for other applications (e.g., catalytic). Moreover, both structural and electrochemical data indicate that the two different donor moieties available in these ligands differentiate the coordinated metal fragments, which can further affect catalytic applications of these ligands.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses were performed in argon or nitrogen atmosphere using standard Schlenk techniques and oven-dried glassware. Compounds **3**,[13d] [(η^5-C_5H_5)RuCl(PPh_3)$_2$],[44] [(η^5-C_5H_5)Ru(MeCN-κN)$_3$][PF_6],[45] and [(η^5-C_5H_5)RuCl(cod)][46] (cod = η^2:η^2-cycloocta-1,5-diene) were prepared according to literature procedures. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich or Alfa-Aesar) and used as received. Anhydrous dichloromethane, tetrahydrofuran and methanol used for syntheses were prepared using a PureSolv MD5 solvent purification system (Innovative Technology). Acetonitrile and toluene were dried over anhydrous potassium carbonate and sodium metal, respectively,

https://dx.doi.org/10.1021/acs.organomet.0c00767
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and distilled prior to use. Solvents used for crystallizations and for chromatography (reagent-grade; Lach-Ner, Czech Republic) were utilized without additional purification.

NMR spectra were recorded at 25 °C on a Varian Unity Inova 400 spectrometer operating at 400, 101, and 162 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ in ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) and to external 85% aqueous H_3PO_4 (^{31}P). FTIR spectra were acquired with a Thermo Nicolet 6700 instrument over the 400−4000 cm^{-1} range. Electrospray ionization (ESI) mass spectra were recorded on a Compact QTOF-MS spectrometer (Bruker Daltonics). Elemental analyses were conducted using a PE 2400 Series II CHNS/O Elemental Analyzer (PerkinElmer). The amount of residual solvent(s) was verified by NMR analysis.

Electrochemical measurements were recorded using a mAUTOLAB III multipurpose apparatus (Eco Chemie, Netherlands) at room temperature and a standard three-electrode cell equipped with a glassy carbon disc (2 mm diameter) working electrode, a platinum sheet auxiliary electrode, and a double-junction Ag/AgCl (3 M KCl) reference electrode. The compounds were dissolved in anhydrous dichloromethane to give a solution containing 1 mM analyte and 0.1 M $Bu_4N[PF_6]$ (Fluka, puriss grade for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon before the measurements and then kept under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[47]

Synthesis of 1-(Diphenylphosphino)-1′-[(diethoxyphosphinyl)methyl]ferrocene−borane (1:1) (4). A reaction flask equipped with a large stirring bar was charged with alcohol **3** (4.14 g, 10.0 mmol), zinc(II) iodide (3.50 g, 11.0 mmol), and triethyl phosphite (17 mL, 100 mol) under argon (the content of the reaction flask gently warmed upon mixing). The resulting mixture was stirred at room temperature overnight and then diluted with chloroform (180 mL) and 3 M aqueous hydrochloric acid (80 mL). The organic layer was separated, washed with brine (200 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The oily residue was kept under oil pump vacuum (3×10^{-3} Torr at 50 °C) to remove the excess of triethyl phosphite and subsequently purified by column chromatography (silica gel, ethyl acetate). A second orange band was collected, which afforded ester **4** after evaporation. Yield: 4.48 g (84%), orange oil. The compound may be contaminated with up to 10% of diethyl phosphite. However, this impurity does not hamper the subsequent reduction, after which it can be easily removed during the crystallization step.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8−1.7 (br m, 3H, BH_3), 1.25 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, Me), 2.59 (d, $^{2}J_{PH}$ = 19.7 Hz, 2H, CH_2P), 3.96 (qd, J = 7.1, 0.9 Hz, 4H, CH_2O), 4.02 (vt, J' = 2.0 Hz, 2H, fc), 4.25 (d vt, J' = 1.0, 1.1 Hz, 2H, fc), 4.32 (vq, J' = 2.0 Hz, 2H, fc), 4.48 (d vt, J' = 1.1, 0.7 Hz, 2H, fc), 7.38−7.50 (m, 6H, PPh_2), 7.55−7.61 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 16.43 (d, $^{3}J_{PC}$ = 6 Hz, Me), 27.33 (d, $^{1}J_{PC}$ = 139 Hz, CH_2P), 61.93 (d, $^{2}J_{PC}$ = 7 Hz, CH_2O), 69.22 (d, J_{PC} = 68 Hz, C^{ipso} of fc), 69.78 (s, CH of fc), 71.22 (d,J_{PC} = 4 Hz, CH of fc), 72.81 (d, J_{PC} = 7 Hz, CH of fc), 73.73 (d, J_{PC} = 10 Hz, CH of fc), 79.77 (d,J_{PC} = 3 Hz, C^{ipso} of fc), 128.44 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.92 (d, J_{PC} = 3 Hz, CH of PPh_2), 131.53 (s, C^{ipso} of PPh_2), 132.62 (d, J_{PC} = 10 Hz, CH of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 16.4 (br s, PPh_2BH_3), 25.3 (s, $PO(OEt)_2$). IR (Nujol) ν_{max}: 3075 w, 3056 w, 2724 w, 2349 s, 2344 s, 2255 m, 1701 m, 1588 w, 1572 w, 1483 w, 1438 s, 1415 w, 1311 w, 1251 s, 1237 m, 1217 m, 1205 w, 1182 m, 1174 m, 1130 m, 1110 s, 1059 s, 1029 s, 959 s, 928 m, 896 w, 865 m, 841 m, 823 m, 814 m, 800 m, 784 m, 764 m, 744 s, 670 s, 669 w, 639 s, 624 s, 610 s, 531 m, 495 s, 476 s, 467 m, 439 m cm^{-1}. ESI-HRMS (m/z): calcd for $C_{27}H_{32}BFeO_3P_2$ ([M − H]$^{+}$), 533.1269. Found, 533.1262. Anal. Calcd for $C_{27}H_{33}BFeO_3P_2$ (534.2): C, 60.71; H, 6.23. Found: C, 60.58; H, 6.07.

Synthesis of 1-(Diphenylphosphino)-1′-(phosphinomethyl)ferrocene−borane (1:1) (5). Neat trimethyl-chlorosilane (3.8 mL, 30 mmol) was slowly introduced to a suspension of Li[AlH_4] (1.14 g, 30 mmol) in dry THF (150 mL) while stirring and cooling on ice. The resulting mixture was stirred for 10 min before adding a solution of ester **4** (3.20 g, 6.0 mmol in 100 mL of THF). After completing the addition, the cooling bath was removed, and the reaction mixture was stirred at room temperature overnight. Then, the reaction flask was cooled in an ice bath, and methanol (200 mL) was cautiously added to terminate the reaction. The resulting mixture was evaporated under vacuum, leaving an orange residue, which was taken up with hexane (300 mL), filtered, and evaporated. The residue was redissolved in chloroform, filtered, and evaporated to give pure phosphine **5** as an orange oil. Yield: 2.53 g (98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8−1.7 (br m, 3H, BH_3), 2.27 (td, $^{3}J_{HH}$ = 7.5 Hz, $^{2}J_{PH}$ = 4.6 Hz, 2H, CH_2), 2.78 (dm, $^{1}J_{PH}$ = 194.0 Hz, 2H, PH_2), 3.99 (vt, J' = 1.8 Hz, 2H, fc), 4.08 (vt, J' = 1.8 Hz, 2H, fc), 4.35 (vq, J' = 2.0 Hz, 2H, fc), 4.48−4.50 (m, 2H, fc), 7.38−7.49 (m, 6H, PPh_2), 7.55−7.62 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 13.86 (d, J_{PC} = 9 Hz, CH_2), 68.85 (d, J_{PC} = 69 Hz, C^{ipso} of fc), 69.26 (s, CH of fc), 69.60 (d, J_{PC} = 3 Hz, CH of fc), 72.64 (d, J_{PC} = 8 Hz, CH of fc), 73.58 (d, J_{PC} = 10 Hz, CH of fc), 90.84 (d, J_{PC} = 3 Hz, C^{ipso} of fc), 128.40 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.86 (d, J_{PC} = 2 Hz, CH of PPh_2), 131.38 (d, $^{1}J_{PC}$ = 59 Hz, C^{ipso} of PPh_2), 132.64 (d, J_{PC} = 10 Hz, CH of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −125.9 (s, PH_2), 16.4 (br d, J = 74 Hz, PPh_2BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ −125.9 (tt, $^{1}J_{PH}$ = 194 Hz, $^{2}J_{PH}$ = 5 Hz, PH_2), 16.4 (br m, PPh_2BH_3). IR (Nujol) ν_{max}: 3078 m, 3056 m, 2366 s, 2336 s, 2293 w, 1981 w, 1792 w, 1749 w, 1734 w, 1717 w, 1697 w, 1684 w, 1670 w, 1653w, 1647 w, 1636 w, 1584 w, 1576 w, 1559 w, 1540 w, 1521 w, 1507 w, 1457 s, 1435 s, 1418 w, 1313 m, 1198 w, 1182 m, 1174 m, 1134 m, 1109 s, 1059 s, 1027 s, 998 w, 928 m, 896 w, 830 s, 759 m, 741 s, 701 s, 669 m, 637 s, 622 m, 610 m, 531 m, 496 s, 466 s, 439 m, 419 w cm^{-1}. ESI-MS (m/z): 429 ([M − H]$^{+}$). Anal. Calcd for $C_{23}H_{22}FeP_2$ (430.0): C, 64.24; H, 5.86. Found: C, 64.25; H, 5.67.

Synthesis of 1-(Diphenylphosphino)-1′-(phosphinomethyl)ferrocene (2). A reaction flask was charged with adduct **5** (2.58 g, 6.0 mmol) and 1,4-diazabicyclo[2.2.2]octane (1.35 g, 12.0 mmol). Dry tetrahydrofuran (50 mL) was introduced under argon, and the resulting solution was stirred at 45 °C overnight. Subsequent evaporation produced an orange residue, which was purified by chromatography over silica gel, eluting with diethyl ether−hexane (1:1). A single broad orange band was collected and evaporated, affording **2** as an orange solid. The compound was further crystallized from hot heptane. Yield: 1.80 g (72%), orange crystalline solid. Mp 114 °C (heptane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (td, $^{3}J_{HH}$ = 7.3 Hz, $^{2}J_{PH}$ = 4.7 Hz, 2H, CH_2), 2.82 (dm, $^{1}J_{PH}$ = 194.2 Hz, 2H, PH_2), 4.00 (vt, J' = 1.8 Hz, 2H, fc), 4.03 (vt, J' = 1.7 Hz, 2H, fc), 4.04 (vq, J' = 1.8 Hz, 2H, fc), 4.34 (vt, J' = 1.7 Hz, 2H, fc), 7.28−7.40 (m, 10H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 14.07 (d, $^{1}J_{PC}$ = 9 Hz, CH_2), 68.61 (s, CH of fc), 68.77 (d, J_{PC} = 2 Hz, CH of fc), 71.62 (d, J_{PC} = 4 Hz, CH of fc), 73.62 (d, J_{PC} = 15 Hz, CH of fc), 75.79 (d, J_{PC} = 5 Hz, C^{ipso} of fc), 89.89 (d, J_{PC} = 3 Hz, C^{ipso} of fc), 128.10 (d, J_{PC} = 7 Hz, CH of PPh_2), 128.48 (s, CH of PPh_2), 133.49 (d, J_{PC} = 19 Hz, CH of PPh_2), 139.07 (d, $^{1}J_{PC}$ = 19 Hz, C^{ipso} of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −126.7 (s, PH_2), −16.2 (s, PPh_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ −126.7 (tt, $^{1}J_{PH}$ = 194 Hz, $^{2}J_{PH}$ = 4 Hz, PH_2), −16.2 (m, PPh_2). IR (Nujol) ν_{max}: 3097 w, 3083 w, 3069 w, 3054 w, 3041 w, 3030 w, 3015 w, 2726 w, 2359 w, 2303 s, 2296 s, 1974 w, 1901 w, 1829 w, 1767 w, 1733 w, 1679 m, 1646 m, 1584 s, 1569 w, 1775 s, 1433 s, 1414 w, 1395 w, 1381 m, 1325 w, 1312 m, 1305 m, 1279 w, 1236 m, 1210 w, 1193 m, 1163 s, 1124 m, 1091 m, 1078 w, 1036 s, 1026 s, 998 m, 977 w, 936 w, 924 w, 916 w, 863 w, 856 m, 827 s, 812 s, 749 s, 699 s, 668 w, 661 w cm^{-1}. ESI-HRMS: calcd for $C_{23}H_{23}FeOP_2$ ([M + H + O]$^{+}$), 433.0568. Found, 433.0565. Anal. Calcd for $C_{23}H_{22}FeP_2$ (416.2): C, 66.37; H, 5.33. Found: C, 66.40; H, 5.27.

Synthesis of 1-(Diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene (1). An oven-dried Schlenk flask was charged (in this order) with phosphine **2** (205 mg, 0.5 mmol), iodobenzene (204 mg, 1.0 mmol), *N*,*N*-diisopropylethylamine (162 mg, 1.25 mmol), and palladium(II) acetate (5.6 mg, 25 μmol) under argon. Dry acetonitrile (5 mL) was

https://dx.doi.org/10.1021/acs.organomet.0c00767
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introduced, and the reaction mixture was stirred at 80 °C overnight. Then, the mixture was cooled to room temperature and evaporated under vacuum with chromatographic silica gel. The crude, preadsorbed product was transferred onto the top of a chromatographic column and eluted with a diethyl ether−hexane mixture (1:1). A single orange band was collected and evaporated, leaving phosphine **1** as orange oil, which solidifies when stored in a fridge. Yield: 220 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.86 (s, 2H, CH_2), 3.84 (vt, J' = 1.8 Hz, 2H, fc), 3.89 (vt, J' = 1.8 Hz, 2H, fc), 4.01 (vq, J' = 1.9 Hz, 2H, fc), 4.32 (vt, J' = 1.8 Hz, 2H, fc), 7.24−7.37 (m, 20H, PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −16.2 (s, PPh_2), −11.4 (s, CH_2PPh_2). The data match those in the literature.[12a]

Synthesis of 1-(Diphenylphosphino)-1′-(phosphinylmethyl)ferrocene−borane (1:1) (6). In air, phosphine **5** (0.70 g, 3.0 mmol) was dissolved in a mixture of methanol (20 mL) and dichloromethane (30 mL), and the reaction flask, equipped with stirring bar, was cooled in an ice bath. Hydrogen peroxide solution (3 mL of 30% aqueous solution, 58 mmol) was added over 5 min while stirring, and the resulting mixture was stirred and cooled for another 5 min. Then, the excess of hydrogen peroxide was destroyed by *slowly* adding saturated aqueous sodium thiosulfate (30 mL). ***Caution!****Rapid addition can result in overheating of the reaction mixture and decomposition!* The mixture was transferred to a separatory funnel and diluted with dichloromethane (20 mL) and brine (30 mL). The organic phase was separated, and the aqueous residue was extracted with dichloromethane (20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under vacuum. The crude product was purified by flash chromatography over silica gel eluting with a dichloromethane−methanol mixture (10:1). Evaporation of the first orange band afforded phosphine oxide **6** as a yellow solid. Yield: 613 g (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8−1.7 (br m, 3H, BH_3), 2.78 (dt, $^2J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 4.6 Hz, 2H, CH_2), 4.09 (t, J' = 1.9 Hz, 2H, fc), 4.19 (dt, J' = 0.9, 1.9 Hz, 2H, fc), 4.38 (q, J' = 1.8 Hz, 2H, fc), 4.56 (dt, J' = 1.1, 1.9 Hz, 2H, fc), 6.79 (dt, $^1J_{PH}$ = 470.0 Hz, $^3J_{HH}$ = 4.6 Hz, 2H, $P(O)H_2$), 7.40−7.52 (m, 6H, PPh_2), 7.56−7.62 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 28.20 (d, $^1J_{PC}$ = 62 Hz, CH_2), 69.72 (d, J_{PC} = 68 Hz, C^{ipso} of fc), 70.25 (s, CH of fc), 70.84 (d, J_{PC} = 4 Hz, CH of fc), 72.74 (d, J_{PC} = 8 Hz, CH of fc), 73.98 (d, J_{PC} = 9 Hz, CH of fc), 128.54 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.97 (d, $^1J_{PC}$ = 60 Hz, C^{ipso} of PPh_2), 131.12 (d, J_{PC} = 2 Hz, CH of PPh_2), 132.62 (d, J_{PC} = 10 Hz, CH of PPh_2); the signal due to C^{ipso} of fc is obscured by the solvent resonance. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 8.5 (s, $P(O)H_2$), 16.2 (br m, PPh_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.5 (tt, $^1J_{PH}$ = 470 Hz, $^2J_{PH}$ = 16 Hz, $P(O)H_2$), 16.2 (br m, PPh_2). IR (DRIFTS) ν_{max}: 3074 m, 2383 s, 2344 s, 2247 w, 1587 w, 1485 m, 1466 m, 1434 s, 1387 w, 1363 w, 1363 w, 1311 w, 1250 w, 1220 s, 1201 s, 1182 s, 1172 s, 1129 m, 1109 s, 1060 s, 1025 s, 999 m, 924 w, 911 w, 870 w, 861 w, 837 s, 822 w, 810 w, 779 w, 762 w, 743 s, 700 s, 639 m, 624 s, 612 m, 531 m, 511 m, 496 s, 473 s, 441 w cm^{-1}. ESI-MS (m/z): 469 ([M + Na]$^+$), 915 ([2 M + Na]$^+$). Anal. Calcd for $C_{23}H_{25}BFeOP_2$ (446.0): C, 61.93; H, 5.65. Found: C, 61.74; H, 5.61.

Synthesis of 1-(Diphenylphosphino)-1′-(phosphinylmethyl)ferrocene (7). Compound **6** (89.2 mg, 0.20 mmol), 1,4-diazabicyclo[2.2.2]octane (26.9, 0.24 mmol), and tetrahydrofuran (5 mL) were mixed in a reaction flask under argon, and the mixture was stirred at 50 °C overnight. Subsequent evaporation afforded an orange residue, which was purified by chromatography over silica gel, eluting with a dichloromethane−methanol mixture (10:1). The first orange band was collected and evaporated to give phosphine **7** as orange oil, which gradually solidified. Yield: 82 mg (95%). Mp 107 °C (amorphous sample).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (dt, $^2J_{PH}$ = 16.2 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, CH_2), 4.08−4.11 (m, 6H, fc), 4.40 (vt, J' = 1.8 Hz, 2H, fc), 6.77 (dt, $^1J_{PH}$ = 469.3 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, $P(O)H_2$), 7.31−7.40 (m, 10H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 28.24 (d, $^1J_{PC}$ = 62 Hz, CH_2), 69.04 (d, J_{PC} = 84 Hz, C^{ipso} of fc), 69.74 (s, CH of fc), 70.03 (d, J_{PC} = 4 Hz, CH of fc), 71.79 (d, J_{PC} = 4 Hz, CH of fc), 73.99 (d, J_{PC} = 15 Hz, CH of fc), 75.91 (s, C^{ipso} of fc), 128.25 (d, J_{PC} = 7 Hz, CH of PPh_2), 128.75 (s, CH of PPh_2), 133.51 (d, J_{PC} = 20 Hz, CH of PPh_2), 138.75 (d, $^1J_{PC}$ = 9 Hz, C^{ipso} of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −16.8 (s, PPh_2), 9.3 (s, $P(O)H_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −16.8 (s, $PPh_2{\cdot}BH_3$), 9.3 (tt, $^1J_{PH}$ = 469 Hz, $^2J_{PH}$ = 16 Hz, $P(O)H_2$). IR (Nujol) ν_{max}: 3089 w, 3073 m, 3051 m, 2669 w, 2347 m, 2324 m, 1719 w, 1583 w, 1568 w, 1435 s, 1239 w, 1214 s, 1201 s, 1115 m, 1096 m, 1028 s, 1018 m, 998 w, 975 w, 914 w, 847 w, 834 m, 818 m, 752 s, 729 m, 700 s, 632 w, 489 s, 455 w, 437 w cm^{-1}. ESI-MS (m/z): 455 ([M + Na]$^+$), 887 ([2 M + Na]$^+$). Anal. Calcd for $C_{23}H_{22}FeOP_2{\cdot}0.1CH_2Cl_2$ (440.7): C, 62.96; H, 5.08. Found: C, 62.93; H, 5.04.

Synthesis of 1-(Diphenylphosphino)-1′-{[(2-hydroxyprop-2-yl)phosphinyl]methyl}ferrocene−borane (1:1) (8). A solution of phosphine **6** (223 mg, 0.50 mmol) in reagent-grade acetone (5 mL) was heated at 40 °C under argon overnight. The resulting mixture was evaporated, and the crude product was purified by chromatography over silica gel with a dichloromethane−methanol mixture (10:1) as the eluent. Subsequent evaporation produced **8** as an orange powder. Yield: 218 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8−1.7 (br s, 3H, BH_3), 1.35 (d, $^3J_{PH}$ = 14.7 Hz, 3H, Me), 1.37 (d, $^3J_{PH}$ = 14.9 Hz, 3H, Me), 2.65−2.82 (m, 2H, CH_2), 3.79 (br s, 1H, OH), 4.03 (d vt, J' = 1.3, 2.6 Hz, 1H, fc), 4.05 (d vt, J' = 1.4, 2.5 Hz, 1H, fc), 4.25−4.28 (m, 2H, fc), 4.33−4.36 (m, 2H, fc), 4.52−4.54 (m, 2H, fc), 6.33 (ddd, $^1J_{PH}$ = 454.9 Hz, J_{HH} = 5.1, 1.9 Hz, 1H, PH), 7.38−7.50 (m, 6H, PPh_2), 7.54−7.62 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 23.85 (d, $^2J_{PC}$ = 8 Hz, Me), 24.59 (d, $^2J_{PC}$ = 9 Hz, Me), 25.65 (d, $^1J_{PC}$ = 56 Hz, CH_2), 69.11 (s, C−OH), 69.84 (d, J_{PC} = 9 Hz, C^{ipso} of fc), 69.91 (s, CH of fc), 70.06 (s, CH of fc), 70.91 (d, J_{PC} = 3 Hz, CH of fc), 71.21 (d, J_{PC} = 3 Hz, CH of fc), 72.80 (d, J_{PC} = 7 Hz, CH of fc), 72.88 (d, J_{PC} = 7 Hz, CH of fc), 73.70 (d, J_{PC} = 9 Hz, CH of fc), 74.10 (d, J_{PC} = 10 Hz, CH of fc), 79.91 (d, J_{PC} = 4 Hz, C^{ipso} of fc), 128.49 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.50 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.98 (d, J_{PC} = 2 Hz, CH of PPh_2), 131.02 (d, $^1J_{PC}$ = 59 Hz, C^{ipso} of PPh_2), 131.05 (d, J_{PC} = 2 Hz, CH of PPh_2), 131.13 (d, $^1J_{PC}$ = 59 Hz, C^{ipso} of PPh_2), 132.60 (d, J_{PC} = 9 Hz, CH of PPh_2), 132.62 (d, J_{PC} = 9 Hz, CH of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 16.3 (br s, PPh_2BH_3), 46.0 (s, P(O)H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.3 (br m, PPh_2BH_3), 46.0 (dm, $^1J_{PH}$ = 455 Hz, P(O)H). IR (Nujol) ν_{max}: 3177 br m, 2332 m, 1629 w, 1309 w, 1202 s, 1172 m, 1157 w, 1135 m, 1109 m, 1059 m, 1029 m, 998 w, 974 w, 942 m, 929 m, 836 m, 819 m, 804 m, 764 m, 739 s, 702 s, 638 m, 608 m, 531 w, 499 m, 471 m, 442 w cm^{-1}. ESI-MS (m/z): 527 ([M + Na]$^+$), 1031 ([2 M + Na]$^+$). Anal. Calcd for $C_{26}H_{31}BFeO_2P_2{\cdot}0.25CH_2Cl_2$ (525.4): C, 60.01; H, 6.04. Found: C, 59.84; H, 5.95.

Synthesis of 1-(Diphenylphosphino)-1′-{[(2-hydroxyprop-2-yl)phosphinyl]methyl}ferrocene (9). Phosphine **7** (173 mg, 0.40 mmol) was dissolved in reagent-grade acetone (5 mL), and the solution was stirred at 40 °C under argon overnight. The mixture was cooled to room temperature and evaporated under vacuum, leaving a crude product, which was purified over silica gel using a dichloromethane−methanol mixture (10:1) as the eluent. Evaporation of the second orange band afforded **9** as an orange solid. Yield: 155 mg (79%). Crystals suitable for structure determination were obtained by recrystallization from ethyl acetate/hexane.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, $^3J_{PH}$ = 12.9 Hz, 3H, Me), 1.38 (d, $^3J_{PH}$ = 13.0 Hz, 3H, Me), 2.72 (d, $^3J_{HH}$ = 3.5 Hz, 1H, CH_2), 2.75 (d, $^3J_{HH}$ = 3.5 Hz, 1H, CH_2), 3.25 (d, $^3J_{PH}$ = 3.8 Hz, 1H, OH), 4.04−4.08 (m, 4H, fc), 4.15 (vd, J' = 1.4 Hz, 1H, fc), 4.20 (vd, J' = 1.3 Hz, 1H, fc), 4.37 (vt, J' = 1.8 Hz, 2H, fc), 6.35 (dt, $^1J_{PH}$ = 454.1 Hz, $^3J_{HH}$ = 3.5 Hz, 1H, PH), 7.30−7.39 (m, 10H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 23.87 (d, $^2J_{PH}$ = 7 Hz, Me), 24.75 (d, $^2J_{PH}$ = 8 Hz, Me), 26.26 (d, $^1J_{PH}$ = 53 Hz, CH_2), 69.40 (s, CH of fc), 69.69 (s, CH of fc), 70.08 (br s, CH of fc), 70.47 (br s, CH of fc), 71.89 (br s, 2CH of fc), 73.90 (d, J_{PC} = 11 Hz, CH of fc), 74.04 (d, J_{PC} = 11 Hz, CH of fc), 78.87 (br s, C^{ipso} of fc), 128.22 (s, CH of PPh_2), 128.65 (s, CH of PPh_2), 133.57 (d, J_{PH} = 17 Hz, CH of PPh_2), 138.91 (s, C^{ipso} of PPh_2). Signals due to C−OH and C^{ipso} fc were not observed, presumably due to overlaps. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −16.8 (s, PPh_2), 45.9 (s, P(O)H). ^{31}P NMR (162 MHz,

https://dx.doi.org/10.1021/acs.organomet.0c00767
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$CDCl_3$): δ 16.8 (s, PPh_2), 45.9 (d of septets, $^1J_{PH}$ = 454 Hz, $^2J_{PH}$ = 13 Hz, P(O)H). IR (Nujol) ν_{max}: 3146 br s, 3066 m, 2326 s, 2170 w, 2066 w, 1435 s, 1210 w, 1192 m, 1119 s, 1097 m, 1030 m, 999 w, 975 m, 925 w, 908 m, 846 m, 804 s, 751 s, 743 s, 699 s, 568 w, 527 w, 503 s, 484 m, 462 w cm^{-1}. ESI-MS (m/z): 529 ($[M + O + Na]^+$), 1003 ($[2 M + Na]^+$). Anal. Calcd for $C_{26}H_{28}FeO_2P_2 \cdot 0.2CH_2Cl_2$ (507.3): C, 62.03; H, 5.64. Found: C, 62.01; H, 5.41.

Synthesis of [μ-1κP:2$\kappa P'$-1,1′-Bis(diphenylphosphino)-ferrocene]bis[dichloro(η^6-mesitylene)ruthenium(II)] (10). [{(η^6-Mesitylene)RuCl(μ-Cl)}$_2$] (58 mg, 0.10 mmol) and dppf (55 mg, 0.10 mmol) were dissolved in dichloromethane (40 mL) under argon, and the solution was stirred overnight. Subsequent evaporation afforded analytically pure complex **10** as a red solid in quantitative yield. Crystals suitable for structure determination were grown from a dichloromethane/hexane mixture. The yield of crystalline material was 58 mg (50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 18H, Me), 4.10 (very br s, 8H, CH of fc), 4.40 (s, 6H, C_6H_3), 7.27−7.37 (m, 12H, PPh_2), 7.63−7.72 (m, 8H, PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 20.7 (s). IR (Nujol) ν_{max}: 3567 br m, 3053 s, 1992 w, 1586 w, 1570 w, 1559 w, 1540 m, 1528 m, 1507 w, 1482 m, 1265 m, 1190 m, 1092 m, 1073 m, 1026 s, 879 w, 839 s, 751 s, 728 m, 698 s, 669 w, 623 w, 570 w, 542 s, 523 s, 487 m, 471 s, 445 m cm^{-1}. ESI-MS (m/z): 811 ($[M - (mes)RuCl_2 - Cl)]^+$). Anal. Calcd for $C_{52}H_{52}Cl_4FeRu_2P_2 \cdot 1.5CH_2Cl_2$ (1266.1): C, 50.75; H, 4.38. Found: C, 50.86; H, 4.29.

Synthesis of {μ-1κP:2$\kappa P'$-1-(Diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene}bis[dichloro(η^6-mesitylene)ruthenium(II)] (11). [{(η^6-Mesitylene)RuCl(μ-Cl)}$_2$] (41 mg, 0.070 mmol) and phosphine **1** (40 mg, 0.070 mmol) were dissolved in dichloromethane (20 mL) under argon, and the mixture was stirred overnight. Subsequent evaporation produced a red solid, which was redissolved in dichloromethane (3 mL), precipitated with pentane, and isolated by suction. Yield of 11:64 mg (68%), red solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (s, 9H, Me), 1.89 (s, 9H, Me), 3.02 (br s, 2H, fc), 3.34 (br s, 2H, fc), 3.54 (br d, $^2J_{PH}$ = 7.1 Hz, 2H, CH_2), 4.33 (br vq, J' = 1.2 Hz, 2H, fc), 4.42 (br s, 2H, fc), 4.44 (s, 3H, C_6H_3), 4.65 (s, 3H, C_6H_3), 7.24−7.36 (m, 10H, PPh_2), 7.38−7.44 (m, 2H, PPh_2), 7.60−7.68 (m, 4H, PPh_2), 7.68−7.76 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 18.23 (s, Me), 18.36 (s, Me), 26.89 (d, $^1J_{PC}$ = 24 Hz, CH_2), 71.41 (s, CH of fc), 71.86 (s, CH of fc), 72.01 (d, J_{PC} = 8 Hz, CH of fc), 75.27 (br s, CH of fc), 82.24 (d, J_{PC} = 8.5 Hz, C^{ipso} of fc), 86.17 (d, J_{PC} = 4 Hz, CH of C_6H_3), 87.20 (d, J_{PC} = 3 Hz, CH of C_6H_3), 100.90 (d, J_{PC} = 3 Hz, C^{ipso} of C_6H_3), 102.86 (d, J_{PC} = 2 Hz, C^{ipso} of C_6H_3), 126.96 (d, J_{PC} = 10 Hz, CH of PPh_2), 127.73 (d, J_{PC} = 9 Hz, CH of PPh_2), 129.69 (br s, CH of PPh_2), 130.46 (d, J_{PC} = 2 Hz, CH of PPh_2), 130.73 (d, J_{PC} = 42 Hz, C^{ipso} of PPh_2), 133.88 (d, J_{PC} = 9 Hz, CH of PPh_2), 134.25 (br d, J_{PC} = 6 Hz, CH of PPh_2). The signals due to C^{ipso} of fc and PPh_2 were not observed, presumably due to overlaps. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 21.8 (s, PPh_2), 30.4 (s, CH_2PPh_2). IR (Nujol) ν_{max}: 2726 w, 1992 w, 1541 w, 1507 w, 1299 m, 1096 m, 1030 m, 922 w, 841 s, 746 m, 698 m, 669 w, 558 m, 537 w, 497 m cm^{-1}. ESI-MSI (m/z): 789 ($[M - (mes)RuCl_2 - HCl - Cl]^+$). Anal. Calcd for $C_{54}H_{54}Cl_4FeRu_2P_2 \cdot 0.5CH_2Cl_2$ (1195.2): C, 53.76; H, 4.64. Found: C, 53.73; H, 4.55.

Synthesis of [μ-1κP:2$\kappa P'$-1-(Diphenylphosphino)-1′-(phosphinomethyl)ferrocene]bis[dichloro(η^6-mesitylene)-ruthenium(II)] (12). [{(η^6-Mesitylene)RuCl(μ-Cl)}$_2$] (32 mg, 0.10 mmol) and phosphine **2** (58 mg, 0.10 mmol) were dissolved in dry dichloromethane (40 mL), and the resulting solution was stirred overnight. The reaction mixture was evaporated, and the residue was crystallized from chloroform/hexane. The resulting crystals were isolated by suction and dried under vacuum. Yield: 64 mg (64%), red crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 9H, Me), 2.17 (d, J_{PH} = 1.0 Hz, 9H, Me), 3.12 (br s, 2H, CH_2), 3.52 (br s, 2H, fc), 3.89 (br s, 2H, fc), 4.46 (br s, 2H, fc), 4.50 (br s, 3H of C_6H_3 and 2H of fc), 4.60 (dt, $^1J_{PH}$ = 361.5 Hz, $^3J_{PH}$ = 6.6 Hz, 2H, PH_2), 4.98 (s, 3H, C_6H_3), 7.32−7.43 (m, 6H, PPh_2), 7.77−7.85 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 18.24 (d, J_{PC} = 1 Hz, Me), 19.00 (d, J_{PC} = 1 Hz, Me), 19.26 (d, $^1J_{PC}$ = 19 Hz, CH_2), 70.40 (s, CH of fc), 70.97 (s, CH of fc), 71.05 (s, CH of fc), 76.38 (d, J_{PC} = 25 Hz, C^{ipso} of fc), 82.06 (d, J_{PC} = 5 Hz, CH of C_6H_3), 85.98 (d, J_{PC} = 6 Hz, CH of fc), 86.57 (d, J_{PC} = 4 Hz, CH of C_6H_3), 103.02 (br s, C^{ipso} of C_6H_3), 104.48 (d, J_{PC} = 2 Hz, C^{ipso} of C_6H_3), 127.27 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.91 (d, J_{PC} = 2 Hz, CH of PPh_2), 133.95 (br s, CH of PPh_2). The signals due to C^{ipso} of fc and PPh_2 were not observed. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −19.4 (s, PH_2), 20.8 (s, PPh_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ −19.4 (t, $^1J_{PH}$ = 361 Hz, PH_2), 20.8 (s, PPh_2). IR (Nujol) ν_{max}: 1933 w, 1526 m, 1298 m, 1192 w, 1161 m, 1085 m, 1031 s, 930 m, 884 s, 837 m, 814 w, 760 s, 749 m, 698 s, 543 m, 524 m, 490 m, 469 m, 444 w, 426 w cm^{-1}. ESI-MS (m/z): 669 ($[(M - RuCl_2(mes) - 2Cl + OMe]^+$). Anal. Calcd for $C_{41}H_{46}Cl_4FeP_2Ru_2 \cdot 0.25CHCl_3$ (1030.4): C, 48.08; H, 4.52. Found: C, 48.49; H, 4.44.

Synthesis of {μ-1κP:2$\kappa P'$-1-(Diphenylphosphino)-1′-[(hydroxyphosphino)methyl]ferrocene}bis[dichloro(η^6-mesitylene)ruthenium(II)] (13). Ligand **7** (43 mg, 0.10 mmol) and [{(η^6-mesitylene)RuCl(μ-Cl)}$_2$] (58 mg, 0.10 mmol) were dissolved in dichloromethane (10 mL), and the resulting mixture was stirred overnight. Subsequent evaporation afforded pure complex **13** as a red solid in an essentially quantitative yield (102 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 9H, Me), 2.08 (d, J_{PC} = 0.8 Hz, 9H, Me), 3.22−3.50 (m, 2H, CH_2), 3.41 (br s, 1H, fc), 3.69 (br s, 1H, fc), 4.00 (br s, 2H, fc), 4.45−4.55 (m, 7H, 3H of C_6H_3 and 4H of fc), 4.88 (s, 3H, C_6H_3), 6.80 (dt, $^1J_{PH}$ = 377.9 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, PH), 7.34−7.42 (m, 6H, PPh_2), 7.74−7.87 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 18.26 (s, Me), 18.73 (s, Me), 30.35 (br s, CH_2), 70.29 (s, CH of fc), 70.91 (s, CH of fc), 71.26 (s, CH of fc), 71.62 (s, CH of fc), 72.89 (s, C^{ipso} of fc), 82.20 (s, C^{ipso} of fc), 82.77 (s, CH of C_6H_3), 86.55 (s, CH of C_6H_3), 103.05 (s, C^{ipso} of C_6H_3), 105.85 (s, C^{ipso} of C_6H_3), 127.15 (d, J_{PC} = 16 Hz, CH of PPh_2), 127.38 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.94 (d, J_{PC} = 9.0 Hz, CH of PPh_2), 133.97 (br d, $^1J_{PH}$ = 112 Hz, C^{ipso} of PPh_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 20.7 (s, PPh_2), 117.1 (br s, P(OH)H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.7 (s, PPh_2), 117.1 (d, $^1J_{PH}$ = 378 Hz, P(OH)H). IR (Nujol) ν_{max}: 1524 m, 1094 m, 1031 m, 931 w, 878 s, 836 w, 748 m, 699 m, 543 m, 523 m, 487 m, 471 m, 434 w cm^{-1}. ESI-MS (m/z): 945 ($[M - HCl - Cl]^+$), 1237 ($[M + RuCl_2(mes) - HCl - Cl]^+$). Anal. Calcd for $C_{41}H_{46}Cl_4FeOP_2Ru_2$ (1016.5): C, 48.44; H, 4.56. Found: C, 48.16; H, 4.58.

Synthesis of {1-(Diphenylphosphino-κP)-1′-[(phosphinyl)-methyl]ferrocene}[dichloro(η^6-mesitylene)ruthenium(II)] (14). Phosphine **7** (95 mg, 0.22 mmol) and [{(η^6-mesitylene)RuCl(μ-Cl)}$_2$] (64 mg, 0.11 mmol) were dissolved in dichloromethane (15 mL). The resulting mixture was stirred overnight and then evaporated, leaving complex **14** as an orange powdery solid in a quantitate yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (br s, 9H, Me), 2.96 (br d, $^2J_{PH}$ = 16.0 Hz, 2H, CH_2), 3.58 (br s, 2H, fc), 3.86 (br s, 2H, fc), 4.44 (br s, 2H, fc), 4.54 (br s, 5H, 3H of C_6H_3 and 2H of fc), 6.79 (dt, $^1J_{PH}$ = 470 Hz, $^3J_{PH}$ = 4.5 Hz, 2H, $P(O)H_2$), 7.35−7.45 (m, 6H, PPh_2), 7.78−7.85 (m, 4H, PPh_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 18.23 (s, Me), 28.04 (d, $^1J_{PC}$ = 62 Hz, CH_2), 70.73 (s, CH of fc), 70.83 (br s, 2 × CH of fc), 71.70 (s, CH of fc), 77.22 (s, CH of fc), 86.98 (s, CH of C_6H_3), 102.56 (s, C^{ipso} of C_6H_3), 127.05 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.01 (d, J_{PC} = 2 Hz, CH of PPh_2), 133.88 (br s, CH of PPh_2). The signals due to C^{ipso} of fc and PPh_2 were not observed. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 9.4 (s, $P(O)H_2$), 21.1 (br s, PPh_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.4 (tt, $^1J_{PH}$ = 470 Hz, $^2J_{PH}$ = 16 Hz, $P(O)H_2$), 21.1 (br s, PPh_2). IR (Nujol) ν_{max}: 1541 w, 1250 w, 1221 w, 1193 w, 1027 s, 835 w, 822 w, 762 w, 746 w, 697 w, 545 m, 523 w, 483 w, 474 w, 458 w, 444 w, 420 w cm^{-1}. ESI-MS (m/z): 685 ($[M - 2Cl + OMe]^+$), 1369 ($[2M - HCl-3Cl + 2OMe]^+$). Anal. Calcd for $C_{32}H_{34}Cl_2FeOP_2Ru \cdot 0.2CH_2Cl_2$ (741.4): C, 52.17; H, 4.68. Found: C, 52.30; H, 4.64.

Synthesis of {1-(Diphenylphosphino)-1′-[(hydroxy-phosphino-κP)methyl]ferrocene}[dichloro(η^6-mesitylene)-ruthenium(II)]−borane (1:1) (15). Complex **6** (67 mg, 0.15 mmol) and [{(η^6-mesitylene)RuCl(μ-Cl)}$_2$] (44 mg, 0.075 mmol) were

https://dx.doi.org/10.1021/acs.organomet.0c00767
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dissolved in dichloromethane (10 mL), and the resulting solution was stirred overnight. Subsequent evaporation left complex **15** as a red-orange powder in quantitative yield. Crystals used for structure determination were obtained from chloroform/hexane.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8−1.7 (br s, 3H, BH_3), 2.05 (d, J_{PH} = 1.2 Hz, 9H, Me), 2.95−3.04 (m, 1H, CH_2), 3.27−3.34 (m, 1H, CH_2), 4.10 (d vt, J = 1.3, 2.4 Hz, 1H, fc), 4.19 (d vt, J = 1.3, 2.4 Hz, 1H, fc), 4.30−4.32 (m, 3H, fc), 4.40−4.42 (m, 1H, fc), 4.52−4.54 (m, 2H, fc), 4.79 (s, 3H, C_6H_3), 6.77 (dtd, $^1J_{PH}$ = 375.3 Hz, $^3J_{HH}$ = 5.5, 1.4 Hz, 1H, PH), 7.39−7.66 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 18.71 (d, J_{PC} = 1 Hz, Me), 29.53 (d, $^1J_{PC}$ = 38 Hz, CH_2), 69.58 (d, J_{PC} = 68 Hz, C^{ipso} of fc), 69.75 (s, CH of fc), 70.34 (s, CH of fc), 71.27 (d, J_{PC} = 2 H, CH of fc), 71.88 (d, J_{PC} = 2 H, CH of fc), 73.00 (d, J_{PC} = 8 H, CH of fc), 73.21(d, J_{PC} = 7 H, CH of fc), 73.90 (s, CH of fc), 74.00 (d, J_{PC} = 2 H, CH of fc), 81.09 (d, J_{PC} = 3 Hz, C^{ipso} of fc), 82.53 (d, J_{PC} = 5 Hz, CH of C_6H_3), 106.19 (d, J_{PC} = 2 Hz, C^{ipso} of C_6H_3), 128.50 (d, J_{PC} = 2 Hz, CH of PPh_2), 128.61 (d, J_{PC} = 2 Hz, CH of PPh_2), 130.72 (d, $^1J_{PC}$ = 60 Hz, C^{ipso} of PPh_2), 131.00 (d, J_{PC} = 2 Hz, CH of PPh_2), 131.09 (d, $^1J_{PC}$ = 60 Hz, C^{ipso} of PPh_2), 131.33 (d, J_{PC} = 2 Hz, CH of PPh_2), 132.44 (d, J_{PC} = 9 Hz, CH of PPh_2), 132.74 (d, J_{PC} = 9 Hz, CH of PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 16.3 (br s, PPh_2BH_3), 115.3 (s, P(OH)H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.3 (br s, PPh_2BH_3), 115.3 (ddd, $^1J_{PH}$ = 375 Hz, $^2J_{PH}$ = 18, 8 Hz, P(OH)H). IR (nujol) ν_{max}: 3180 br m, 3079 m, 3053 m, 2914 w, 2379 m, 2341 m, 2326 m, 1572 w, 1528 m, 1483 w, 1455 w, 1436 m, 1399 w, 1383 w, 1371 m, 1311 w, 1298 w, 1266 w, 1240 w, 1185 w, 1173 s, 1127 m, 1108 s, 1053 s, 1030 s, 999 m, 986 m, 961 m, 923 s, 872 s, 840 m, 829 m, 806 w, 753 m, 737 s, 700 s, 638 m, 624 m, 530 m, 500 s, 477 m, 442 m, 404 m cm^{-1}. ESI-MS (m/z): 958 ([M + $RuCl_2$(mes) − HCl − Cl]$^+$). Anal. Calcd for $C_{32}H_{37}BCl_2FeOP_2Ru$ (738.2): C, 52.06; H, 5.05. Found: C, 51.82; H, 4.99.

Synthesis of [1,1′-Bis(diphenylphosphino)ferrocene-κ^2P,P']-[chloro(η^6-mesitylene)ruthenium(II)] hexafluorophosphate (16). dppf (55 mg, 0.10 mmol), [{(η^6-mesitylene)RuCl(μ-Cl)}$_2$] (29 mg, 0.05 mmol), and sodium hexafluorophosphate (84 mg, 0.5 mmol) were mixed in methanol and dichloromethane (10 mL each) under argon, and the suspension was stirred overnight and then evaporated. The solid residue was extracted with dichloromethane (15 mL), and the extract was filtered (PTFE syringe filter, 45 μm pore size). The filtrate was evaporated, and the crude solid was further purified by chromatography over a short silica gel column, eluting with a dichloromethane−methanol mixture (10:1). Finally, the product was dissolved in dichloromethane (approximately 5 mL) and precipitated with cold pentane (ca. 40 mL). Separated solid was isolated by suction and dried under vacuum. Yield of **16**: 85 mg (89%), orange powdery solid. Crystals suitable for structure determination were obtained by liquid-phase diffusion of hexane into a dichloromethane solution of the complex.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 9H, Me), 4.00−4.01 (m, 2H, fc), 4.09−4.11 (m, 2H, fc), 4.31−4.33 (m, 2H, fc), 4.85 (s, 3H, C_6H_3), 5.10−5.11 (m, 2H, fc), 7.40−7.50 (m, 6H, PPh_2), 7.52−7.60 (m, 4H, PPh_2), 7.64−7.72 (m, 6H, PPh_2), 7.86−7.94 (m, 4H, PPh_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 19.38 (s, Me), 68.74 (t, J_{PC} = 3 Hz, CH of fc), 73.82 (t, J_{PC} = 3 Hz, CH of fc), 74.77 (t, J_{PC} = 2 Hz, CH of fc), 79.17 (t, J_{PC} = 5 Hz, CH of fc), 84.38 (t, $^1J_{PC}$ = 28 Hz, C^{ipso} of fc), 92.65 (t, J_{PC} = 3 Hz, CH of C_6H_3), 114.28 (t, J_{PC} = 2 Hz, C^{ipso} of C_6H_3), 128.20 (t, J_{PC} = 5 Hz, CH of PPh_2), 128.25 (t, J_{PC} = 5 Hz, CH of PPh_2), 130.48 (t, J_{PC} = 24 Hz, C^{ipso} of PPh_2), 130.84 (s, CH of PPh_2), 132.47 (s, CH of PPh_2), 132.91 (t, J_{PC} = 4 Hz, CH of PPh_2), 135.83 (t, J_{PC} = 6 Hz, CH of PPh_2), 137.81 (t, $^1J_{PC}$ = 24 Hz, C^{ipso} of PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −143.9 (hept, $^1J_{PF}$ = 713 Hz, PF_6), 35.6 (s, PPh_2). IR (Nujol) ν_{max}: 1541 w, 1298 m, 1090 m, 1035 m, 842 v s, 743 m, 703 s, 631 w, 558 s, 546 w, 517 s, 508 m, 479 m, 440 w cm^{-1}. ESI-MS (m/z): 811 ([M − PF_6]$^+$). Anal. Calcd for $C_{43}H_{40}ClF_6FeRuP_3$ (956.1): C, 54.02; H, 4.22. Found: C, 54.08; H, 4.32.

Synthesis of [1,1′-Bis(diphenylphosphino)ferrocene κ^2P,P']-chloro(η^5-cyclopentadienyl)ruthenium(II) (17). The procedure was adopted from ref 29. Chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) (80 mg, 0.11 mmol) and dppf (61 mg, 0.11 mmol) were mixed in toluene (20 mL) under argon, and the mixture was heated at reflux for 24 h. After cooling, the solvent was evaporated under vacuum, and the residue was triturated with diethyl ether (50 mL). The remaining solid was filtered off, washed with diethyl ether (50 mL), and dried under vacuum to produce complex **17** as an orange solid. Yield: 61 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (v td, J' = 1.3 Hz, 2H, fc), 4.11 (s, 5H, C_5H_5), 4.24 (br s, 2H, fc), 4.32 (br s, 2H, fc), 5.19 (br s, 2H, fc), 7.27−7.44 (m, 16H, PPh_2), 7.76−7.83 (m, 4H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 45.7 (s). The data match those in the original report.[29]

Synthesis of {1-(Diphenylphosphino)-1′-[(diphenylphosphino)methyl]ferrocene-κ^2P,P'}chloro(η^5-cyclopentadienyl)ruthenium(II) (18). Analogously to the previous synthesis, chloro(cyclopentadienyl)bis(triphenylphosphine)-ruthenium(II) (72.5 mg, 0.10 mmol) and **1** (59 mg, 0.10 mmol) were mixed in anhydrous toluene (8 mL), and the mixture was heated under gentle reflux (in an oil bath) for 6 h. The clear reaction mixture was cooled, diluted with hexane (12 mL), and filtered through a PTFE syringe filter (0.45 μm pore size). The filtrate was evaporated, and the residue was redissolved in chloroform (2.5 mL) and crystallized by layering with hexane (5 mL). The crystals, which separated during several days, were filtered off, washed with pentane, and dried under vacuum. Yield of **18**·1.8$CHCl_3$: 81 mg (82%), orange-brown crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.11 (br m, 1H, fc), 3.37 (ddd, J = 15.5, 13.8, 1.2 Hz, 1H, CH_2), 3.94−3.96 (m, 1H, fc), 3.95 (s, 5H, C_5H_5), 3.91−4.00 (m, 1H, fc), 4.12−4.13 (m, 3H, fc), 4.22−4.24 (m, 1H, fc), 4.34 (dd, J = 16.0, 7.5 Hz, 1H, CH_2), 5.51−5.52 (m, 1H, fc), 7.12−7.92 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 26.53 (d, $^1J_{PC}$ = 20 Hz, CH_2), 67.84 (s, CH of fc), 68.38 (s, CH of fc), 69.45 (s, CH of fc), 69.78 (d, J_{PC} = 4 Hz, CH of fc), 70.39 (d, J_{PC} = 3 Hz, CH of fc), 71.51 (d, J_{PC} = 10 Hz, CH of fc), 72.66 (d, J_{PC} = 7 Hz, CH of fc), 76.43 (d, J_{PC} = 16 Hz, CH of fc), 81.33 (t, J_{PC} = 2 Hz, C_5H_5), 82.12 (s, C^{ipso} of fc), 84.43 (d, J_{PC} = 35 Hz, C^{ipso} of fc), 127.38 (d, J_{PC} = 9 Hz, CH of PPh_2), 127.56 (d, J_{PC} = 9 Hz, 2CH of PPh_2), 128.12 (s, 2CH of PPh_2), 128.21 (s, CH of PPh_2), 128.55 (s, CH of PPh_2), 129.96 (br d, J_{PC} = 7 Hz, CH of PPh_2), 130.25 (br s, CH of PPh_2), 132.05 (d, J_{PC} = 9 Hz, CH of PPh_2), 134.04 (d, J_{PC} = 11 Hz, CH of PPh_2), 134.97 (d, J_{PC} = 12 Hz, CH of PPh_2), 135.94 (br d, J_{PC} = 37 Hz, C^{ipso} of PPh_2), 140.63 (d, J_{PC} = 44 Hz, C^{ipso} of PPh_2), 143.21 (dd, J_{PC} = 38, 4 Hz, C^{ipso} of PPh_2), 141.15 (br d, J_{PC} = 40 Hz, C^{ipso} of PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.7 (d, $^2J_{PP}$ = 34 Hz, PPh_2), 34.6 (d, $^2J_{PP}$ = 35 Hz, PPh_2). IR (DRIFTS) ν_{max}: 3078 m, 3053 m, 3002 w, 2879 w, 1586 w, 1480 m, 1432 s, 1411 m, 1309 w, 1222 w, 1186 w, 1165 m, 1094 s, 1070 m, 1046 w, 1031 s, 1000 m, 920 w, 860 w, 827 s, 806 m, 794 m, 743 s, 696 s, 662 m, 629 w, 618 w, 602 w, 542 s, 523 s, 513 s, 494 s, 479 s, 462 s, 444 s, 427 s cm^{-1}. ESI-MS (m/z): 735 ([M − Cl]$^+$). Anal. Calcd for $C_{40}H_{35}ClFeRuP_2$·1.8$CHCl_3$ (984.9): C, 50.97; H, 3.77. Found: C, 50.82; H, 3.82.

Catalytic Estragole to Anethole Isomerization. A Schlenk tube was charged with the catalyst (0.010 mmol, 1.0 mol % of [Ru]), potassium carbonate (8.0 mg, 0.060 mmol), and estragole (296 mg, 2.0 mmol) and flushed with nitrogen. Degassed deionized water was introduced (1 mL), and the flask was stoppered and transferred into an oil bath maintained at 80 °C. After heating for 6 h, the reaction mixture was cooled to room temperature and diluted with diethyl ether (15 mL) and brine (15 mL). The organic layer was separated, and the aqueous residue was extracted with ether (15 mL). The combined organic layers were dried over $MgSO_4$ and evaporated. The conversion and (E/Z) ratios were determined by ^{1}H NMR.

(E)-1-(4-Methoxyphenyl)prop-1-ene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (d, $^3J_{HH}$ = 7.2 Hz, 3H, Me), 3.82 (s, 3H, OMe), 6.06−6.14 (m, 1H, CHCH), 6.34 (d, $^3J_{HH}$ = 11.6 Hz, 1H, CHCH) 6.84 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4), 7.27 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4).

(Z)-1-(4-Methoxyphenyl)prop-1-ene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (d, $^3J_{HH}$ = 7.2 Hz, 3H, Me), 3.77 (s, 3H, OMe), 5.66−5.71 (m, 1H, CHCH), 6.36 (d, $^3J_{HH}$ = 11.6 Hz, 1H, CHCH),

https://dx.doi.org/10.1021/acs.organomet.0c00767
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6.87 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4), 7.23 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4). The spectroscopic data are in accordance with the literature.[48]

Catalytic Cycloisomerization of (*Z*)-3-Methylpent-2-en-4-yn-1-ol into 2,3-Dimethylfuran. A vial was charged with a stirring bar, catalyst (4.5 μmol, 0.3 mmol % [Ru]), (*Z*)-3-methylpent-2-en-4-yn-1-ol (90%; 288 mg, 3.0 mmol), and anisole (324 mg, 3.0 mmol) as an inert standard and sealed. The mixture was stirred 18 h at room temperature under ambient atmosphere and then analyzed by ^{1}H NMR. The (*E*)-isomer of the starting enynol remains unchanged in the reaction mixture.

2,3-Dimethylfuran. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (br s, 3H, Me), 2.19 (br s, 3H, Me), 6.15 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH), 7.20 (d, $^3J_{HH}$ = 1.8 Hz, 1H, CH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.82 (Me), 11.27 (Me), 112.78 (CH), 113.74 (C^{ipso}), 139.56 (CH), 147.36 (C^{ipso}). The NMR data match those in the literature.[49]

X-ray Crystallography. Diffraction data ($\pm h \pm k \pm l$, θ_{max} = 27.5°) were collected with a Bruker Apex II CCD (**2**, **9**, and **18**) or a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON detector (all other compounds), both equipped with a Cryostream Cooler (Oxford Cryosystems), using Mo Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXT-2014[50] or SIR-97)[51] and then refined by full-matrix least-squares routine based on F^2 (SHELXL-2014).[52] Non-hydrogen atoms were refined with anisotropic displacement parameters. The PH hydrogens were identified on the difference electron density maps and refined as riding atoms with U_{iso}(H) set to 1.2U_{eq}(P). Hydrogens residing on carbon atoms were included in their theoretical positions and refined similarly. The phosphorus atom P2 in the structure of **9** is disordered over two positions and was modeled accordingly. In the structure of **15**, the H and OH groups bonding to phosphorus atom P2 alternated in their positions with practically equal occupancies (the compound is thus racemic), which also affected one of the Ru-bound chlorine atoms. The positions of the disordered hydrogen atoms were based not only on the difference Fourier maps but also on their surroundings and crystal packing (mainly hydrogen bonding interactions). Finally, the solvent molecules in the structure of **10**·THF·$2CH_2Cl_2$ were extensively disordered and could not be satisfactorily included in the structure model. Hence, their contribution to the overall scattering was numerically eliminated using PLATON SQUEEZE.[53] Relevant crystallographic data and refinement parameters are presented in Table S1.

All geometric data and structural diagrams were obtained using a recent version of the PLATON program.[54] The numerical values were rounded to one decimal place with respect to their estimated standard deviations (ESDs). Parameters pertaining to atoms in geometrically constrained positions (hydrogens) are given without ESDs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00767.

Synthesis and crystal structure of [(η^6-mesitylene)RuCl-(MeCN-κ*N*)$_2$][PF_6], additional structural diagrams, a summary of crystallographic parameters, and copies of the NMR spectra (PDF)

Accession Codes

CCDC 2047814−2047822 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Grant Agency of Charles University (project no. 920119) and by the Charles University Research Centre program (project UNCE/SCI/014).

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https://dx.doi.org/10.1021/acs.organomet.0c00767
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