Ruthenium-Stabilized Low-Coordinate Phosphorus Atoms. *p*-Cymene Ligand as Reactivity Switch

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A detailed comparative study of the structural and spectroscopic features and of the reactivity of ruthenium phosphinidene complexes (η^6-Ar)(PCy_3)Ru(PMes*) (**2a**, Ar = *p*-cymene; **2b**, Ar = benzene) has been undertaken. The structures of complexes **2a** and **2b** have been determined by single-crystal X-ray diffraction and display similar features. Both compounds possess identical chemical behavior toward Brönsted acids such as HBF_4: protonation of the phosphinidene ligand yields the new cationic complexes [(η^6-Ar)(PCy_3)Ru(PHMes*)]BF_4 (**3aBF$_4$**, Ar = *p*-cymene; **3bBF$_4$**, Ar = benzene), which exhibit an unprecedented phosphenium-bearing hydrogen substituent. **3aBF$_4$** has been characterized using X-ray diffraction techniques. The lone pair of the phosphorus atom of the phosphinidene ligand remains also accessible to the Lewis acid BH_3: the reactions of **2a** and **2b** with borane give the adducts (η^6-Ar)-(PCy_3)Ru[P(BH_3)Mes*] (**4a**, Ar = *p*-cymene; **4b**, Ar = benzene). In the presence of the larger borane BPh_3, no reaction occurs until water is introduced in the reaction vessel. This results in the generation of [(η^6-Ar)(PCy_3)Ru(PHMes*)]BPh_3OH (**3aBPh$_3$OH**, Ar = *p*-cymene; **3bBPh$_3$OH**, Ar = benzene) presumably through protonation of **2a** and **2b** by the previously unknown adduct $H_2O{\cdot}BPh_3$. Phosphinidene complexes react also with electrophilic alkylating reagents such as organic iodides provided the alkyl substituent is small. Treatment of **2a** and **2b** with 1 equiv of methyliodide leads to the alkylation at the phosphinidene center and yields the phosphenium complexes [(η^6-Ar)(PCy_3)Ru(PMeMes*)]I (**5a**, Ar = *p*-cymene; **5b**, Ar = benzene). Examination of the reactivity toward electron-rich reagents such as the alkynes RCCH (R = Me_3Si, Ph) yields unexpected results: **2a** instantaneously reacts to generate phosphaindane complexes **6** and **7**, whereas no reaction occurs when using **2b**. A detailed kinetic study provides evidence for a dissociative mechanism involving the release of the phosphine ligand in **2a** and explains its specificity. The *p*-cymene ligand in **2a** acts as a reactivity switch due to the higher steric hindrance of this arene.

Introduction

Transition metal-catalyzed carbon−heteroatom bond formation is a fundamental process in chemical synthesis.[1] Among the existing methodologies, catalyzed atom transfer plays a pivotal role and has stimulated the tremendous development of the chemistry of carbene, imido, and oxo complexes.[2] In this context, phosphinidene complexes have attracted considerable attention since their existence was evidenced.[3] In the last two decades, these efforts have resulted in significant progress exemplified by the first structural characterization of terminal phosphinidene complexes.[4] These advances have stimulated the development of strategies for the generation of phosphinidene in the coordination sphere of transition metals.[5] Thus, several pathways are currently available and have allowed preparation and full characterization of phosphinidene complexes incorporating different transition metals (Ti,[6] Zr,[7] V,[8] Ta,[9] Mo,[10] W,[11] Re,[12] Fe,[13] Ru,[14,15] Os,[13] Co,[16] Rh,[16] Ir,[17] Ni[18]). From a synthetic

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standpoint, only terminal phosphinidene complexes are of major interest since bridging phosphinidenes display little reactivity in a μ_2-, μ_3-, or μ_4-bridging modes except in rare cases.[19] Terminal phosphinidene complexes exist in two varieties, which display electrophilic Fisher-type or nucleophilic Schrock-type properties and, thus, mimic their carbene analogues. A recent computational study has shown that, in addition to the ancillary ligands on the metal, both the charge on the complex and the nature of the phosphinidene substituents can significantly influence electro- or nucleophilicity.[20]

Surprisingly, despite the considerable attention fueled by the analogy with carbene, direct involvement of phosphinidene in catalytic processes has been demonstrated in only two cases.[21] Similarly, studies concerning the synthetic potential of phosphinidene complexes are still very rare except in the case of the transient *in situ* generated complex $(CO)_5W(PPh)$. The phosphorus atom exhibits electrophilic properties, and the numerous examples of addition to olefinic and acetylenic systems have been reviewed recently.[22] In contrast, little of the chemical behavior of nucleophilic phosphinidene complexes has been explored, the most documented one being $Cp_2(PMe_3)Zr$-(PMes*) (Mes* = 2,4,6-tri-*tert*-butylphenyl). The characteristic reactions are 1,2-additions with protic reagents, [2+2] cycloadditions with alkynes leading to phosphametallacycles,[4,23,24] and the phospha-Wittig reaction with carbonyl compounds.[4,9,24] Comparatively, group 9 metal phosphinidene complexes of general formula $Cp^*(PPh_3)M(PMes^*)$ (M = Co, Rh, Ir) exhibit poor reactivity, reacting only with organic iodides. DFT calculations showed that the lower nucleophilicity of the phosphorus atom accounts largely for such a discrepancy with the reactivity of the related zirconium complexes.[16] Additionally, in the latter case, the facile dissociation of the PMe_3 ligand also appears crucial for explaining its unique reactivity.[25]

We have recently reported the synthesis and the first structural evidence for monomeric metaphosphonate by taking advantage of the high reactivity of the phosphinidene complex (η^6-*p*-cymene)(PCy_3)Ru(PMes*) (*p*-cymene = 4-methylisopropylbenzene).[26] As a part of our ongoing studies of the reactivity of phosphinidene complexes, we examined the behavior (η^6-Ar)(PCy_3)Ru(PMes*) (Ar = *p*-cymene, benzene) toward electrophilic reagents and alkynes. Surprisingly, in the latter case, the benzene ligand derived complex did not react, while total consumption of (η^6-*p*-cymene)(PCy_3)Ru(PMes*) was immediately observed. To the best of our knowledge, there is no example in the literature reporting that benzene and the *p*-cymene ligand could induce such different behaviors of the corresponding organometallic complexes. This prompted us to investigate in depth their structural and chemical features. In this paper, we describe (i) the full characterization of these phosphinidene complexes and (ii) their respective reactivity toward electrophilic and electron-rich reactants in order to identify the exact origin of this contradictory behavior. This comparative analysis addresses this issue, and we will show how subtle structural changes result in dramatic enhancement of the reactivity of such species.

Results and Discussion

Synthesis, Spectroscopic, and Structural Characterizations. The ruthenium-complexed terminal phosphinidenes were synthesized using the base-induced dehydrohalogenation−ligation sequence described by Lammerstma et al.[17] The reaction of (η^6-Ar)$(PH_2Mes^*)RuCl_2$ (**1a**, Ar = *p*-cymene; **1b**, Ar = benzene) with 2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of PCy_3 afforded (η^6-Ar)(PCy_3)Ru-(PMes*) (**2a**, Ar = *p*-cymene; **2b**, Ar = benzene) as water-stable green crystals in high yields. Their ^{31}P, ^{13}C, and ^1H NMR spectra display nearly identical signals (Scheme 1). The high-field ^{31}P NMR resonances (δ 813 for **2a** and δ 819 for **2b**) for the phosphorus atom of the phosphinidene ligand are in the typical region for terminal phosphinidene complexes.[5] The slight shielding of this chemical shift in **2a** is also observed for the PCy_3 resonance (δ 35 for **2a** and δ 38 for **2b**). This minor difference can be attributed to the slight donating effect of *p*-cymene, compared to that of the benzene ligand. A similar trend is observed for (η^6-Ar)(PPh_3)Ru(PMes*).[15,27] The η^6-Ar ligand and the Mes* moiety are in free rotation in complexes **2** since no decoalescence is observed for the aryl or the methyl protons in the ^1H NMR spectra, even at low temperature.

X-ray diffraction analyses of both complexes were then conducted. The solid-state structures of **2a** and **2b** are shown in Figure 1 and reveal very similar features. The environment of the ruthenium atom is congested, and the X-ray structure shows a long Ru−PCy_3 bond (2.386(4) Å for **2a** and 2.389(7) Å for **2b**) and a short Ru−PMes* one (2.205(3) Å for **2a** and 2.237(7) Å for **2b**). The short Ru−PMes* distances together with the acute angles Cy_3P−Ru−PMes* (85.98(14)° for **2a** and 86.7(3)° for **2b**) and Ru−P−C_{ipso}(Mes*) (110.5(4)° for **2a** and 107.6(8)° for **2b**) are characteristic for terminal bent phosphinidene complexes. Concerning these angles, the difference between **2a** and **2b** can be rationalized in terms of steric repulsion between the arene ligand and Mes* substituent. However, these variations are minor and both structures very much resemble that of (η^6-*p*-cymene)(PPh_3)Os(PMes*) and (η^6-benzene)(PPh_3)Ru(PMes*).[15]

Since the physical properties provide no clear evidence to rationalize the different behavior between **2a** and **2b**, a detailed reactivity study was undertaken in order to gain some insight.

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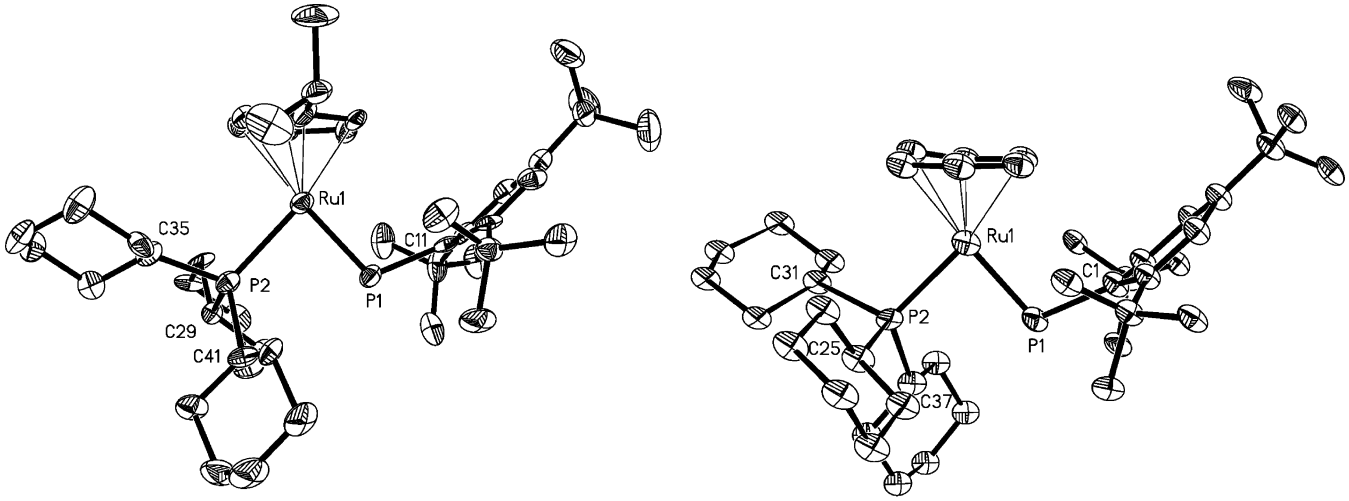
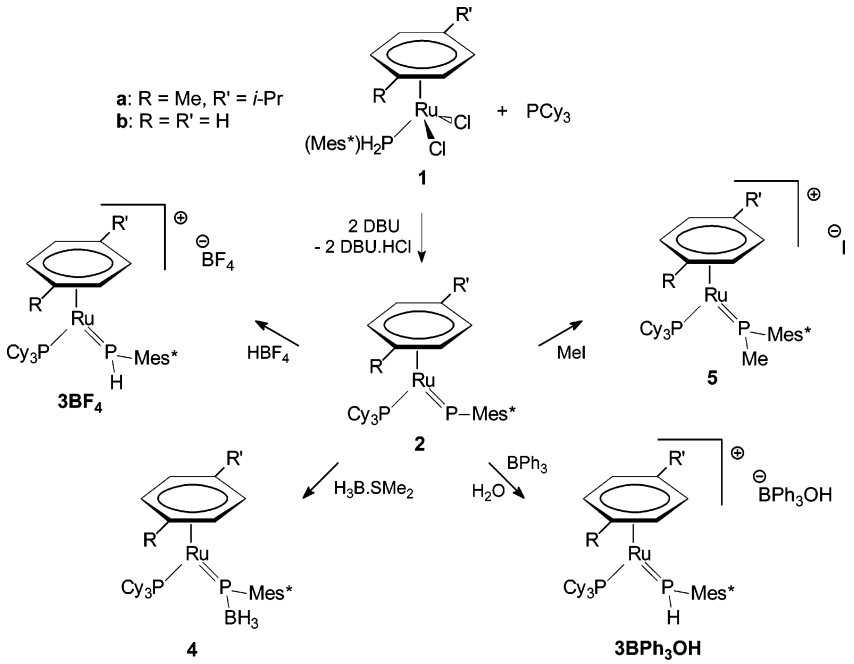


2a **2b**

Figure 1. Molecular structure of complexes **2a** and **2b** (50% probability level for the thermal ellipsoids). All H atoms have been omitted for clarity. Selected metrical parameters (Å) and angles (deg): For **2a**: Ru1−P1 2.205(3); Ru−P2 2.386(4); P1−C11 1.843(14); Ru1−centroid(arene) 1.766; P1−Ru1−P2 85.98(14); Ru1−P1−C11 110.5(4). For **2b**: Ru1−P1 2.237(7); Ru1−P2 2.389(7); P1−C1 1.91(2); Ru1−centroid(arene) 1.778; P1−Ru1−P2 86.7(3); Ru1−P1−C1 107.6(8).

Scheme 1



Reactivity Studies. The philicity of terminal phosphinidene complexes has been shown to depend essentially on the electronic properties of the ligands.[20] The electron-rich fragment (η^6-Ar)(PCy_3)Ru is expected to induce a significant electronic density flow from the transition metal on the phosphinidene phosphorus and, thus, to enhance nucleophilicity of the phosphinidene ligand. Consistently, the nucleophilicity of the phosphorus atom in **2** is illustrated by its reactivity toward electrophilic reagents.

Reactions with Electrophiles. First, we examined the reactivity of **2** toward Brönsted acids (Scheme 1). Protonation of the phosphinidene atom is readily achieved. However, according to the nucleophilicity of the anion, different complexes are obtained. Reaction with HCl results in the instantaneous formation of (η^6-Ar)(PCy_3)$RuCl_2$ (**1**) with the release of PH_2-Mes*. Treatment of a solution **2** with the acid HBF_4 incorporating the non-nucleophilic anion BF_4^- leads to a rapid color change from dark green to purple with formation of the new cationic complexes [(η^6-Ar)(PCy_3)Ru(PHMes*)]BF_4 (**3aBF$_4$**, Ar = *p*-cymene; **3bBF$_4$**, Ar = benzene) in high yields (Scheme 1).

The discrepancy between the reactivity of **2** with HCl and HBF_4 is reminiscent of the somewhat related imido complex (PMe_3)$_2$$ReMe_3$(NPh): reaction with HBF_4 led to protonation, while in the case of CH_3COOH a unidentate coordination mode was characterized for acetate.[28] These results can be attributed to the relative nucleophilicity of the anions: The presence of **3BF$_4$** is evident from their ^{31}P NMR spectra, which exhibit a

signal assigned to the phosphenium ligand PHMes* at δ 174 (^1J(P, H) = 336 Hz, ^2J(P, P) = 84 Hz) for **3aBF$_4$** and at δ 191 (^1J(P, H) = 343 Hz, ^2J(P, P) = 84 Hz) for **3bBF$_4$**. Of interest is that these ^{31}P chemical shifts are lower than the values typically found (200−320 ppm) for phosphenium resonances presumably because of the strong donating properties of the ruthenium fragment.[29] The ^{1}H NMR spectra display a resonance at δ 8.86 for **3aBF$_4$** and δ 9.00 for **3bBF$_4$** characteristic of the acidic proton of the PHMes* moiety, suggesting the presence of a non-negligeable partial positive charge on the phosphorus atom. Other signals are slightly shifted downfield from the corresponding resonances of **2**. Interestingly, to the best of our knowledge, **3aBF$_4$** and **3bBF$_4$** are the first P−H-functionalized cationic phosphenium complexes. Despite renewed interest in the phosphenium group as a strong π-acidic ligand in the context of the preparation of electrophilic late transition metal catalysts,[30] the range of phosphenium ligands in cationic complexes remains indeed confined quasi-exclusively to diamino, aminoalkoxy, or dialkoxy phosphenium moieties.[29] Stabilization of hydrogen-substituted phosphenium and more generally phosphenium ligands bearing weakly π- and σ-donating substituents (for instance aryl or alkyl) represents a true synthetic challenge. [(CO)$_4$Fe{P(Fc)$_2$}]AlCl$_4$ (Fc = ferrocenyl) is the only example for which no N- or O-based substituent (i.e., strongly π-donating and σ-withdrawing fragments) is borne by the two-coordinate phosphorus cation.[31] However, it could not be characterized using X-ray diffraction techniques. In this case, delocalization on the ferrocenyl susbtituent is invoked to allow stabilization. Concerning **3BF$_4$**, the unprecedented stabilization of a phosphenium ligand bearing a hydrogen substituent can be assigned to the powerful electron-rich nature of the fragment (η^6-Ar)(PCy$_3$)Ru. The decisive factor is, indeed, the π-basicity of the transition metal fragment.[29] Computational studies support that stabilization results predominantly from transition metal π-back-donation and as a minor component from π-donation from a phosphorus substituent.[29]

Single crystals of **3aBF$_4$** were grown from a toluene solution at −25 °C. The molecular representation is depicted in Figure 2 and confirmed the formulation deduced from NMR consideration. To date, a very limited number of phosphenium complexes have been structurally characterized.[29]

Similarly to what was observed in the previously reported X-ray diffraction molecular structures, the M−P(phosphenium) bond is substantially shorter (2.173(9) Å) than the M−P dative bond (2.394(8) Å).[29a] This result is consistent with double-bond character as evidenced with the similar ruthenium−phosphinidene distance found in **2a**. However, all structurally characterized cationic phosphenium complexes involve an amino or alkoxy substituent on the phosphorus atom, and thus, this prevents further relevant comparison. The metrical parameters of the fragment (η^6-Ar)(PCy$_3$)Ru of **3aBF$_4$** are very similar to those of **2a** and **2b**, but the protonation of the phosphinidene ligand results in noteworthy modifications of the P−Ru−P and Ru−P−C(Mes*) angles, which increase significantly (91.0(3)° and 132.2(10)°). The latter value compares well to that observed

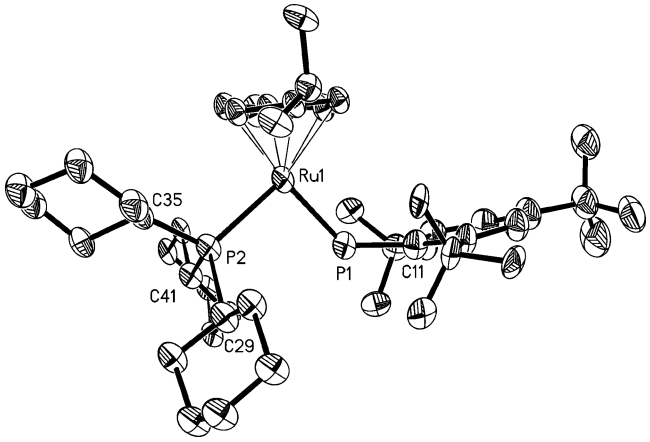


Figure 2. Molecular structure of complex **3aBF$_4$·C$_7$H$_8$** (50% probability level for the thermal ellipsoids). All H atoms, the anion, and the solvent molecule (toluene) have been omitted for clarity. Selected metrical parameters (Å) and angles (deg): Ru1−P1 2.173(9); Ru1−P2 2.394(8); P1−C11 1.79(3); Ru1−centroid(arene) 1.743; P1−Ru1−P2 91.0(3); Ru1−P1−C11 133.2(10).

in the somewhat related phosphido complex (η^5-Cp′)(PMe$_3$)$_2$-Mo(PHMes*) (Cp′ = C$_5$EtMe$_4$, Mo−P−C(Mes*) = 133.0(3)°).[32]

The lone pair of the phosphorus atom of the phosphinidene ligand remains also accessible to electrophilic alkylating reagents and Lewis acids. Treatment of **2** with an excess of BH$_3$·SMe$_2$ gives the expected adducts (η^6-Ar)(PCy$_3$)Ru[P(BH$_3$)Mes*] (**4a**, Ar = *p*-cymene; **4b**, Ar = benzene) (Scheme 1), which were characterized spectroscopically. These borane adducts decomposed on attempted recrystallization, and satisfactory elemental analysis could not be obtained. Although no ^{11}B−^{31}P coupling is observed, the ^{31}P NMR spectrum shows some line broadening and the PMes* chemical shift changes significantly on complexation (from 813 to 506 ppm for **4a** and from 819 to 521 ppm for **4b**). For comparison, on formation of the adduct PH$_2$-Mes*·BH$_3$, the ^{31}P NMR signal moves from δ −130 to −62.[27] Additionally, the ^{11}B NMR spectra display resonances in the expected range for a tetracoordinated boron atom (at δ 18.3 for **4a** and **4b**), consistent with a rehybridization at boron.

Replacing BH$_3$ by BPh$_3$ leads to interesting results. In a first stage, no reaction is observed, the size of the borane BPh$_3$ disfavoring presumably its coordination. However, in the presence of water, the color of the solution changes to purple. In the ^{1}H, ^{31}P, and ^{13}C NMR spectra, very similar resonances to those of **3BF$_4$** were observed and assigned to [(η^6-Ar)-(PCy$_3$)Ru(PHMes*)]BPh$_3$OH (**3BPh$_3$OH**) (Scheme 1). ^{11}B NMR resonances for **3aBPh$_3$OH** and **3bBPh$_3$OH** allow unequivocal identification of a tetracoordinated boron atom. Studies on properties of boranes and in particular of B(C$_6$F$_5$)$_3$ have focused much interest and have shown that water adducts may be regarded as strong Brönsted acid.[33] The pK_a for the complex (C$_6$F$_5$)$_3$B·OH$_2$ is estimated to be 8.4 in acetonitrile. Such a value indicates that (C$_6$F$_5$)$_3$B·OH$_2$ and HCl possess comparable Brönsted acidity. However, there is, to the best of our knowledge, no report concerning direct or indirect observation of the adduct Ph$_3$B·OH$_2$, which is assumed to be involved in the formation of **3BPh$_3$OH**. Interestingly, a significant difference is observed for the ^{1}H, ^{31}P, and ^{13}C NMR arene signals of **3aBPh$_3$OH** (and **3bBPh$_3$OH**) compared to those of **3aBF$_4$** (and **3bBF$_4$**). This result suggests some sort of ion-

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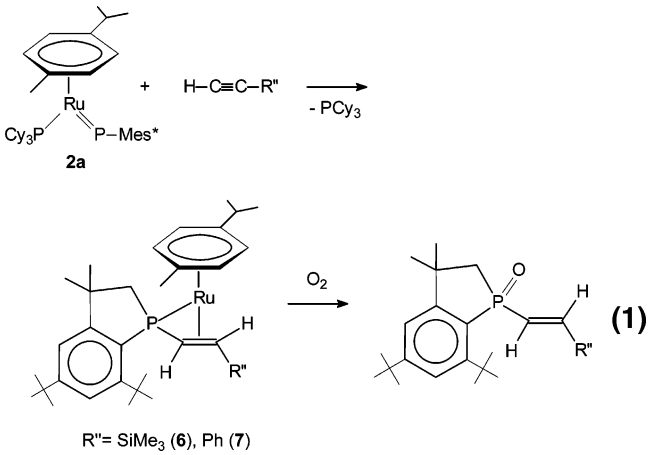
pairing interactions involving anion and η^6-Ar ligands. However, the exact origin of these phenomena remains to be clarified.

The reactivity of **2a** and **2b** toward electrophilic alkylating reagents such as organic iodides was also examined. Treatment of **2** with 1 equiv of methyliodide leads to the alkylation at the phosphinidene center and yields the phosphenium complexes [(η^6-Ar)(PCy_3)Ru(PMeMes*)]I (**5a**, Ar = *p*-cymene; **5b**, Ar = benzene), which can be isolated as purple solids (Scheme 1). This structural formulation is based on the ^{1}H, ^{13}C, and ^{31}P NMR spectra. The ^{31}P NMR spectra display doublets of quadruplets at δ 240 ($^2J_{PH}$ = 9.7 Hz; $^2J_{PP}$ = 82.1 Hz) and 248 ($^2J_{PH}$ = 10.2 Hz; $^2J_{PP}$ = 76.3 Hz) for the phosphenium ligand P(Me)(Mes*) in **5a** and **5b**, respectively. Accordingly, in the ^{1}H NMR spectra, the methyl signals appear as doublets (2.13 ppm, $^2J_{PH}$ = 9.7 Hz for **5a** and 2.21 ppm, $^2J_{PH}$ = 10.2 Hz for **5b**) arising from the coupling with the phosphorus nucleus. In addition, the NMR data of **5** compare well to those of complexes **3** and are consistent with the formation of cationic complexes with a phosphenium ligand.

However, interestingly the *p*-cymene ligand in **5a** no longer exhibits fluxional behavior anymore, as evidenced by the ^{1}H NMR spectrum, which shows for the aryl protons of the *p*-cymene ligand three resonances in a 2:1:1 ratio, the last two being significantly shifted upfield relative to those of **3a**$^+$. Such a behavior had been previously observed in the related metaphosphonate complex (η^6-*p*-cymene)(PCy_3)Ru((η^2-OPOMes*)[26] and for half-sandwich complexes exposed to the magnetic anisotropy cone of the phenyl substituent (known as the "β-phenyl effect").[34] Consistently, the proximity between *p*-cymene and Mes* moieties results also in restricted rotation about the P−C(Mes*) bond, as evidenced by the presence of two Mes* aryl signals in addition to two *o*-Me resonances. This result is attributed to the higher steric congestion around the ruthenium atom in **2a** compared to that in **2b**. This prompted us to study the reactivity of **2** with the larger alkyl reagent isopropyliodide. However, no reaction was observed, confirming that if there is a difference in terms of steric hindrance; both complexes remain highly encumbered, preventing in this case the electrophilic attack.

Reactions with Alkynes: Mechanistic Studies. Despite the electron-rich nature of the ruthenium fragment and the nucleophilicity of the phosphinidene ligand, **2a** reacts instantaneously with alkynes ($Me_3SiC{\equiv}CH$ and $PhC{\equiv}CH$) to afford the allylphosphaindane complexes **6** and **7** (eq 1).



The formation of **6** and **7** and the release of PCy_3 are evident from the NMR data. In the ^{1}H and ^{13}C NMR spectra of **6** and **7** signals corresponding to two nonequivalent *t*-Bu groups, four Me groups, and a new CH_2 moiety indicate unambiguously the formation of a coordinated vinylphosphine fragment.[35] Additionally, the presence of vinylic proton signals at δ ~2.4 and 3.4 coupled with a phosphorus nucleus clearly shows the formation of a coordinated vinylphosphine fragment. These assignments are in agreement with those of an analogous complex that has been recently fully characterized and showed similar NMR resonances.[15] Furthermore, **6** and **7** have been prepared separately using the method described by Lammerstma et al., that is, by reacting (η^6-*p*-cymene)(PH_2Mes*)$RuCl_2$ with 2 equiv of DBU in the presence of the corresponding alkyne.[15]

Of interest to note is that the addition of these unsymmetrical alkynes occurs regioselectively with the larger substituent R″ located *trans* to the phosphorus atom. Only one regioisomer is observed by ^{1}H NMR spectroscopy since the spectrum displays one set of resonances for Ph (or for $SiMe_3$). Oxidation of **6** allowed formation and crystallization of the oxidized version of the vinylphosphaindane ligand. Despite the poor quality of these crystals, connectivity of atoms was unambiguously established and evidenced the *trans* geometry of the phosphavinyl derivative.[36]

This result is consistent with the trend observed for the reaction of zirconocene imido[37] or phosphinidene complexes[38] with alkynes. The regioselectivity has been rationalized in terms of steric repulsion between the substituent of the phosphinidene (or imido) group and the ones of the alkyne.

In marked contrast, no reaction occurs with **2b**. Additionally, the high reactivity of **2a** is in total contradiction with the lack of reactivity of the previously reported group 8 and 9 series compounds.[15,16] Such a difference between the chemical behavior of **2a** and **2b** was very surprising, since neither the spectroscopic properties, structural characteristics, nor the preliminary reactivity studies give any insight of potentially different reactivity. This prompted us to study the details of the reaction. The phosphinidene ligand exhibits nucleophilic properties, and thus, the first step is thought to be the coordination of alkyne at the ruthenium center in order to allow the reaction to proceed. The second step of this anticipated mechanism (formation of a metallacycle) is analogous to that described in the case of a related zirconium complex,[39] then followed by an intramolecular C−H insertion of the P atom and subsequent H transfer to yield **6** or **7** (Scheme 2).

Evidently, the key step for the understanding of the specificity of our system is the generation of the complex (η^6-*p*-cymene)-(η^2-HC≡CR″)Ru(PMes*), which has, thus, focused our interest. In the two limiting cases, complexation of alkyne could occur according to an associative or a dissociative mechanism. In the latter case, phosphine dissociation to generate a 16-electron intermediate, (η^6-*p*-cymene)Ru(PMes*), is an appealing hypothesis for synthetic outcomes since it would provide an entry to the chemistry of an unsaturated phosphinidene species related to the valuable $Cp_2(PMe_3)$Zr(PMes*) complex. Involvement of (η^6-Ar)Ru(PMes*) has also been proposed to account for the formation of several complexes connected to phosphinidene

(34) Brunner, H.; Zwack, T.; Zabel, M.; Beck, W.; Böhm, A. *Organometallics* **2003**, *22*, 1741−1750.

(35) Aitken, R. A.; Clasper, P. N.; Wilson, N. J. *Tetrahedron Lett.* **1999**, *40*, 5271−5274.

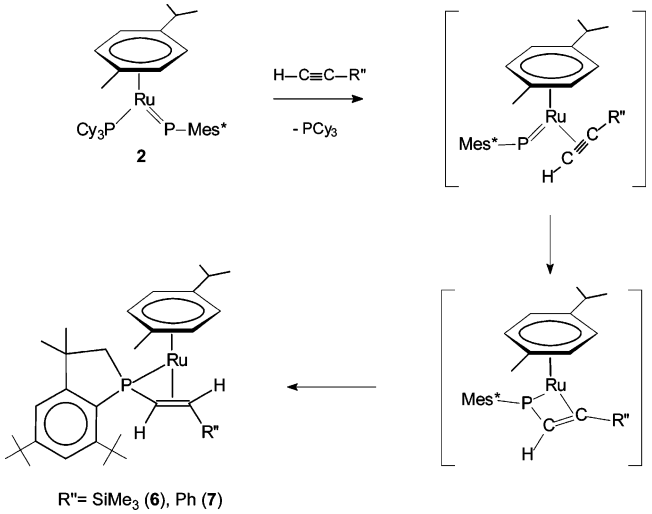
(36) Because a single crystal was of low quality, the details of the structural parameters could not be discussed, but the regiochemistry of the olefin moiety was determined to be the *E*-configuration.

(37) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *120*, 2753−2763.

(38) Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 5729−5737.

(39) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 4204−4205.

Scheme 2



species.[15] However, a recent computational study on the related group 9 metals phosphinidene complexes of general formula Cp*(PPh$_3$)M(PMes*) (M = Co, Rh, Ir) showed a high dissociation energy of the stabilizing phosphine ligand.[16] Additionally, an associative pathway should not be excluded since the freeing of a coordination site may also be achieved through ligand-induced ring slippage of η^6- to η^4-arene, as previously reported for the reaction of phosphine, phosphite, or isonitrile with a related ruthenium-naphthalene complex.[40] Finally, migration of a metal fragment off the arene centroid and more generally arene exchange have been shown to be facilitated for arene-ML$_2$ complexes.[41]

Preliminary studies proved that it was difficult to investigate mechanistic details in solution since none of the putative ruthenium intermediate could be observed by spectroscopic means. Consequently, we undertook a detailed kinetic study on phosphine complexation as a model for the alkyne coordination (Scheme 3).

This approach was successfully exploited for a phosphine/olefin substitution study on Grubbs' ruthenium-based olefin metathesis catalysts.[42] However, the rate of exchange between free phosphines and PCy$_3$ is insufficient to support spin-saturation labeling experiments as kinetic probes. Therefore, the concentration of the exchange products was monitored with time by ^{1}H NMR. This substitution reaction is reversible since the same product distribution (K) can also be established from the reaction of (η^6-*p*-cymene)(PPh$_3$)Ru(PMes*) (**8**) with PCy$_3$.

A numerical approach was used to treat the kinetic curves. The two models (see Supporting Information) corresponding

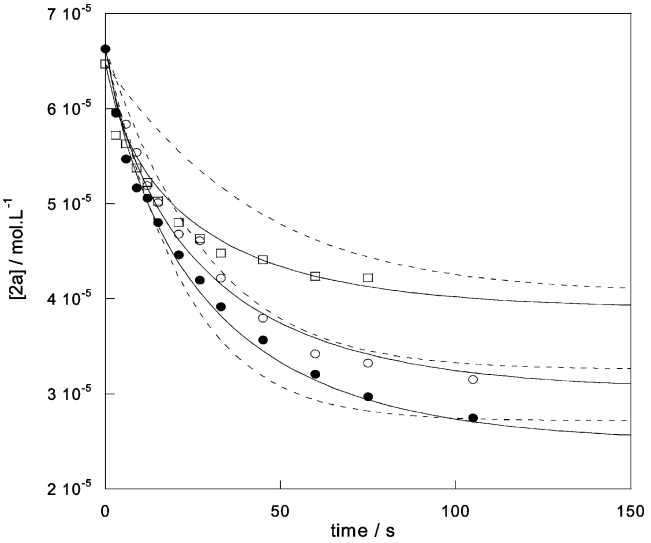


Figure 3. Plot of [**2a**] versus time at different concentrations of PPh$_3$ (□ 1 equiv, ○ 2 equiv, ● 3 equiv). Solid line: best fit obtained for the three curves simultaneously using the dissociative model. Dotted line: best fit using the associative model.

to the two proposed pathways were used to reproduce the experimental data. When only one experiment is presented to each model, the quality of the fitting obtained is equivalent and does not allow a choice between the two mechanisms. This problem was resolved by fitting simultaneously three experiments involving increasing concentrations of PPh$_3$ (1, 2, and 3 equiv). The result is in this case clearly in favor of the dissociative pathway (Figure 3).

The parameters extracted from the fitting procedure are (i) the dissociation rate of PCy$_3$ ($k_1 = 3.3 \times 10^{-2}$ s^{-1}) and (ii) that of PPh$_3$ ($k_{-2} = 8.5 \times 10^{-3}$ mol^{-1}·L·s); (iii) without further information on the intermediate concentration the constants k_{-1} and k_2 cannot be reached, but their ratio can ($k_{-1}/k_2 = 9$). These results show that rate constants involving PCy$_3$ are larger than those of PPh$_3$: dissociation of PCy$_3$ from (η^6-*p*-cymene)(PCy$_3$)-Ru(PMes*) (**2a**) is faster than that of PPh$_3$ from (η^6-*p*-cymene)-(PPh$_3$)Ru(PMes*) (**8**), and trapping of PCy$_3$ by the intermediate **A** is also quicker than that of PPh$_3$. This result was unanticipated since a less electron-donating phosphine is generally expected to be more labile.[42] Addressing the relative importance of steric and electronic factors for tertiary phosphine ligands has attracted much recent attention due to their ubiquitous involvement in organometallic chemistry. In order to gain insight into the relative influence of these factors, experiments were conduced for a series of phosphines. For this study, the kinetic curves

Scheme 3. [a] Dissociative Pathway; [b] Associative Pathway

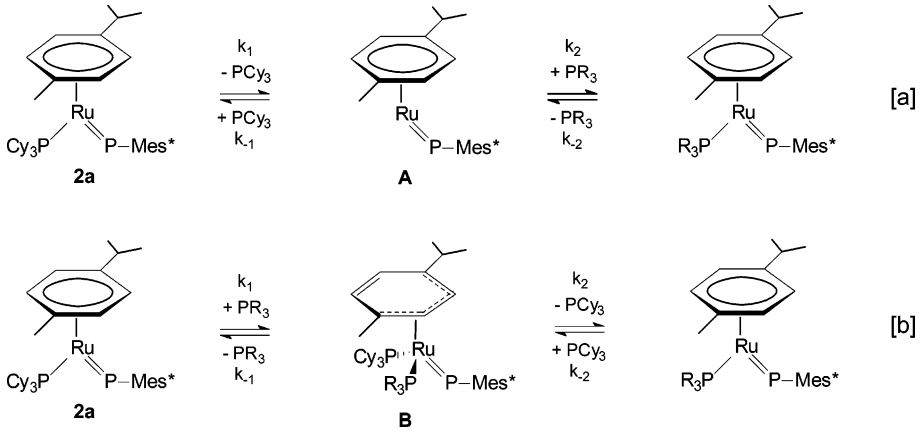


Table 1. Kinetic Parameters Extracted from Phosphine Exchange Reaction

entry	PR_3	K	k_{-1}/k_2 coord	k_1/k_{-2} dissos	k_{-2} ($mol^{-1}\cdot L\cdot s$)	pK_a[a]	ν_{CO}[b] (cm^{-1})	θ[c] (deg)
1	$P(NC_4H_4)_3$	78	0.9	72.6	4.60×10^{-4}	n.d.	2090.4[d]	145[d]
2	$P(p\text{-}ClC_6H_4)_3$	0.85	1.6	1.4	2.42×10^{-2}	1.03	2072.8	145
3	PPh_3	0.44	9.0	3.9	8.51×10^{-3}	2.73	2068.9	145
4	$P(p\text{-}MeOC_6H_4)_3$	0.24	13.1	3.2	1.06×10^{-2}	4.59	2066.1	145
5	$P(m\text{-}MeC_6H_4)_3$	0.86	6.8	7.8	4.26×10^{-3}	3.30	2067.2	165
6	$P(o\text{-}MeC_6H_4)_3$	0				3.08	2066.6	194
7	$P(o\text{-}MeOC_6H_4)_3$	0				~8.8[e]	n.d.	205[f]

[a] pK_a of the corresponding conjugate acid.[43] [b] ν_{CO}: carbonyl stretching frequency in the corresponding $Ni(CO)_3L$ complex in CH_2Cl_2.[43] [c] Tolman cone angle.[43] [d] Electronic and steric properties are discussed in ref 44. [e] Electronic properties of $P(o\text{-}MeOC_6H_4)_3$ were found to be comparable to those of $P(i\text{-}Pr)_3$.[45a] [f] Reference 45b.

were treated with the dissociative model, the values of k_1 and k_{-1} were fixed to those obtained previously, and k_2 and k_{-2} were provided by fitting. Rate constants of susbstitution reactions and steric (Tolman cone angle) and electronic characteristics[43] are gathered in Table 1. Considering isosteric phosphines ($P(NC_4H_4)_3$,[44] $P(p\text{-}ClC_6H_4)_3$, PPh_3, $P(p\text{-}MeOC_6H_4)_3$, entries 1 to 4), the less basic the phosphine, the more the equilibrium is driven toward the formation of the new complexes (η^6-*p*-cymene)(PR_3)Ru(PMes*) (*K* increases). On the other hand, examination of the ratio between coordination rate constants (k_{-1}/k_2) establishes a clear trend: the donor properties of PR_3 slow down its trapping by **A**. As a consequence, changing the phosphine from $P(NC_4H_4)_3$ to $P(p\text{-}MeOC_6H_4)_3$ leads indeed to an approximately 15-fold decrease in the coordination rate. The effect of electronic properties on the dissociation rate constants (k_1/k_{-2}) looks less obvious to rationalize in the cases of the three arylphosphines (entries 2−4) since the variations are relatively weak. A similar observation was made by Grubbs et al. (during the study of phosphine dissociation in ruthenium olefin metathesis catalysts), who stressed the point that no linear correlation between phosphine pK_a and its dissociation rate constant exists.[42] However, it is interesting to note that in the case of $P(NC_4H_4)_3$ the dissociation is significantly disfavored (20-fold, entry 1).

Concerning the influence of steric effects, the phosphine PCy_3 in **2a** exchanges only with smaller phosphines, evidencing the dominant role of the congestion of the added phosphine. This is in particular illustrated by the absence of reaction of **2a** with $P(o\text{-}MeC_6H_4)_3$ or $P(o\text{-}MeOC_6H_4)_3$,[45] although their electronic properties should promote coordination (because they are less basic) and disfavor decoordination.[46] Interestingly, this positive influence of a large phosphine was unexpected since the reactivity of Cp*(PR_3)Rh(PMes*) has been shown to increase by reducing the size of its stabilizing ligand PR_3.[16]

Two important ligand effects in this system involve an acceleration of the critical step of phosphine dissociation: the donating and the hindering characteristics of the PR_3 ligand. In other words, the presence of a strongly π-acidic phosphine $P(NC_4H_4)_3$ led to an important stabilization of the phosphinidene complex **12**. As an illustration, only 10% of conversion of phenylacetylene into **7** is observed when reacting **12** at 50 °C for 3 days. The inertness of **12** is consistent with a DFT study on group 9 transition metal phosphinidene complexes, which stressed a significant increase of the bond dissociation energy of the highly π-acidic carbonyl ligand compared to that of phosphine.[16] However, the dominant effect is unambiguously steric. This result is in perfect agreement with the observation that reaction of alkynes occurs exclusively in the presence of the more hindered arene, which plays the role of reactivity switch.

Conclusion

In summary, ruthenium phosphinidene complexes (η^6-Ar)-(PCy_3)Ru(PMes*) that differ only in the substituent borne by the arene ligand were prepared and showed dramatically different chemical behavior toward alkynes: introduction of alkyl groups on the arene ligand, i.e., changing the arene ligand from benzene to *p*-cymene, allowed the reaction with alkyne to proceed. A detailed comparative study of the structural and spectroscopic features of both complexes did not allow the identification of the origin of this phenomenon. Reactivity studies of (η^6-Ar)(PCy_3)Ru(PMes*) with HBF_4 and MeI have afforded unprecedented cationic phosphenium complexes and have provided a first insight for addressing this issue: in the case of [(η^6-Ar)(PCy_3)Ru(PMeMes*)]I, the free rotation of the Mes* substituent and Ar ligand was stopped only in the case of the more crowded arene ligand, suggesting that alkyl groups of *p*-cymene could be not as innocent as initially anticipated. Careful examination of the mechanism of reaction of phosphinidene complexes with alkyne and in particular of the first step (phosphine dissociation) brought evidence for the involvement of both electronic and steric factors. We have demonstrated that in contrast with common expectations the lability of the phosphine increased with its donor properties. However, the dominant factor proved to be steric, the specificity of (η^6-*p*-cymene)(PCy_3)Ru(PMes*) being directly related to the critical PCy_3 dissociation step, which occurs only when the arene is *p*-cymene. Thus, the reactivity arises from the repulsion of the sterically demanding phosphine ligand with the alkyl groups of the arene ligand.

Increasing steric congestion about reactive centers is a well-known strategy for kinetic stabilization or for controlling chemo-,[47] regio-,[48] or enantioselectivity.[49] Nevertheless, to the

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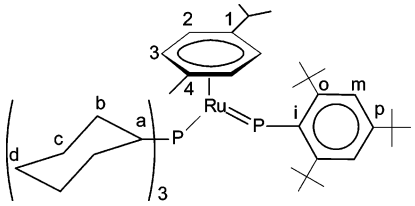
(41) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499−525.
(42) Sandford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.
(43) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. For PCy_3, the pK_a of the corresponding conjugate acid is 9.7; the carbonyl stretching frequency in the corresponding $Ni(CO)_3L$ complex in CH_2Cl_2 is 2056.4 cm^{-1}, and Tolman cone angle (θ) is 170°.
(44) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696−7710.
(45) (a) Pruchnick, F. P.; Smolenski, P.; Wajda-Hermanowicz, K. *J. Organomet. Chem.* **1998**, *570*, 63−69. (b) Suomalainen, P.; Laitinen, R.; Jääskeläinen, S.; Haukka, M.; Pursiainen, J. T.; Pakkanen, T. A. *J. Mol. Catal. A* **2002**, *179*, 93−100.
(46) We have checked that the two complexes (η^6-*p*-cymene)[P(*o*-$MeOC_6H_4)_3$]Ru(PMes*) and (η^6-*p*-cymene)[P(*o*-$MeC_6H_4)_3$]Ru(PMes*) could be prepared separately and, thus, that these phosphines are not too large to prevent their formation.
(47) Ananikov, V. P.; Szilagyi, R.; Morokuma, K.; Musaev, D. G. *Organometallics* **2005**, *24*, 1938−1946.

best of our knowledge, it is the first evidence reporting that such a subtle change induces a reactivity switch. This study provides a rare example for which the "catch 22" situation of kinetic stabilization versus reactivity[4] vanishes: hindering of the large phosphine results on one hand in the stabilization of the metal−phosphinidene bond and, on the other hand, in the enhancement of the elimination rate of the phosphine that enables the coordination of reactants. The reactivity of (η^6-Ar)-(PCy_3)Ru(PMes*) and of $Cp_2(PMe_3)Zr$(PMes*) arise, thus, from the same facile dissociation of the stabilizing ligand. In the latter case, the pronounced oxo- and halophilicity of zirconium[4] has been used elegantly to produce new sophisticated phosphorus-based molecules from carbonyl or dichloride compounds. Concerning (η^6-Ar)(PCy_3)Ru(PMes*), the functional group tolerance of ruthenium[50] could also be exploited to complement the scope of these reactions and to open up new perspectives for synthetic applications of these nucleophilic phosphinidene species.

Experimental Section

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. All reagents were purchased from Aldrich and were used without further purification. NMR spectra were recorded in C_6D_6 on Bruker AC 200 or ARX 400 instruments. Infrared spectra were recorded with a Perkin-Elmer 1600 FT spectrometer. Elemental analyses were done by the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. ^{1}H and ^{13}C{^{1}H} NMR assignments were confirmed by ^{1}H COSY, HSQC (^{1}H−^{13}C), and HMQC (^{1}H−^{13}C) experiments. (η^6-*p*-Cymene)(PCy_3)$RuCl_2$, (η^6-benzene)(PCy_3)$RuCl_2$, (η^6-*p*-cymene)(PPh_3)$RuCl_2$, (η^6-*p*-cymene)-[P(*p*-$ClC_6H_4)_3$]$RuCl_2$, (η^6-*p*-cymene)[P(*p*-$MeC_6H_4)_3$]$RuCl_2$, (η^6-*p*-cymene)[P(*p*-$MeOC_6H_4)_3$]$RuCl_2$, (η^6-*p*-cymene)[P($NC_4H_4)_3$]$RuCl_2$, (η^6-*p*-cymene)[P(*m*-$MeC_6H_4)_3$]$RuCl_2$, and (η^6-*p*-cymene)[P(*o*-$MeOC_6H_4)_3$]$RuCl_2$ were prepared according to literature procedures.[51] Atom labeling used in the NMR assignments of **2**−**13** is given below (for example **2a**):



(η^6-*p*-Cymene)(PCy_3)Ru(PMes*) (2a). To a red slurry of (η^6-*p*-cymene)(PH_2Mes*)$RuCl_2$ (0.601 g; 1.03 mmol) and PCy_3 (0.274 g; 0.98 mmol) in toluene (10 mL) was added DBU (0.29 mL; 1.97 mmol). The mixture was stirred for 1 h at room temperature to afford a dark green solution. The toluene was removed *in vacuo* and the dark green solid then extracted with pentane (10 mL) and filtered to remove DBU·HCl. Removal of the pentane to a minimal volume and cooling to −25 °C gave 0.780 g of a crystalline solid in 80% yield. Mp: 168 °C dec. ^{31}P NMR (81.0 MHz): δ 35.27 (d, $^2J_{PP}$ = 15.3 Hz, PCy_3); 812.94 (d, $^2J_{PP}$ = 15.3 Hz, PMes*). ^{1}H NMR (400.1 MHz): δ 1.05 (d, $^3J_{HH}$ = 6.6 Hz, 6H, C_1−CH−(CH_3)$_2$); 1.31 (m, 12H, C_cH_2); 1.57 (s, 9H, C_p−C−(CH_3)$_3$); 1.74 (s, 18H, C_o−C−(CH_3)$_3$); 1.76 (s, 3H, C_4−CH_3); 1.93 (m, 6H, C_dH_2); 2.11 (m, 12H, C_bH_2); 2.56 (m, 4H, C_1−CH−(CH_3)$_2$ and C_aH); 4.71 (AB, $^3J_{HH}$ = 5.9 Hz, 2H, C_3H); 4.79 (AB, $^3J_{HH}$ = 5.9 Hz, 2H, C_2H); 7.56 (d, $^4J_{HP}$ = 3.9 Hz, 2H, C_mH). ^{13}C{^{1}H} NMR (100.6 MHz): δ 18.74 (C_4−CH_3); 24.42 (C_1−CH−(CH_3)$_2$); 27.37 (C_d); 28.35 (d, $^3J_{CP}$ = 9.2 Hz, C_c); 30.33 (C_b); 31.29 (C_1−CH−(CH_3)$_2$); 31.95 (C_p−C−(CH_3)$_3$); 32.80 (C_o−C−(CH_3)$_3$); 34.93 (C_p−C−(CH_3)$_3$); 36.84 (C_a); 38.77 (C_o−C−(CH_3)$_3$); 81.46 (C_3); 86.07 (C_2); 89.58 (C_4); 103.53 (C_1); 119.09 (C_m); 145.35 (C_p); 145.99 (C_o); 176.52 (C_i determined using 2D NMR experiments). Anal. Calcd for $C_{46}H_{76}P_2Ru$: C, 69.75; H, 9.67. Found: C, 69.65; H, 9.47.

(η^6-Benzene)(PCy_3)Ru(PMes*) (2b). A similar procedure to that described for **2a** was used. (η^6-Benzene)(PH_2Mes*)$RuCl_2$ (0.321 g; 0.61 mmol) and PCy_3 (0.164 g; 0.59 mmol) gave **2b** as a green solid (0.187 g, 42%). Crystallization from pentane at −25 °C gave green crystals suitable for X-ray analysis. Mp: 180 °C dec. ^{31}P NMR (81.0 MHz): δ 38.09 (d, $^2J_{PP}$ = 7.6 Hz, PCy_3); 819.06 (d, $^2J_{PP}$ = 7.6 Hz, PMes*). ^{1}H NMR (200.1 MHz): δ 1.31 (m, 12H, C_cH_2); 1.57 (s, 9H, C_p−C−(CH_3)$_3$); 1.69 (s, 18H, C_o−C−(CH_3)$_3$); 1.83 (m, 12H, C_bH_2); 2.07 (m, 6H, C_dH_2); 2.58 (m, 3H, C_aH); 4.69 (s, 6H, $CH_{benzene}$); 7.56 (s, 2H, C_mH). ^{13}C{^{1}H} NMR (50.3 MHz): δ 27.41 (C_d); 28.32 (d, $^3J_{CP}$ = 10.2 Hz, C_c); 30.46 (C_b); 31.88 (C_p−C−(CH_3)$_3$); 32.35 (C_o−C−(CH_3)$_3$); 34.93 (C_p−C−(CH_3)$_3$); 36.26 (dd, $^1J_{CP}$ = 19.4 Hz, $^3J_{CP}$ = 5.5 Hz, C_a); 38.14 (C_o−C−(CH_3)$_3$); 81.90 ($C_{benzene}$); 119.69 (C_m); 145.69 (C_p); 145.95 (C_o). Anal. Calcd for $C_{42}H_{68}P_2Ru$: C, 68.54; H, 9.31. Found: C, 67.89; H, 9.05.

[(η^6-*p*-Cymene)(PCy_3)Ru(PHMes*)]BF_4 (3aBF$_4$). To a green solution of **2a** (0.135 g, 0.17 mmol) in toluene (5 mL) was added 0.18 mmol of HBF_4 (54 wt % in Et_2O). The solution turned immediately to violet, and the mixture was stirred for 10 min at room temperature. The volatiles were removed *in vacuo*, leaving a violet residue. Trituration with pentane afforded pure **3aBF$_4$** as a violet powder (0.131 g, 88%). Crystallization from toluene at −25 °C gave green crystals suitable for X-ray analysis. Mp: 117 °C. ^{31}P NMR (81.0 MHz): δ 45.39 (dd, $^2J_{PP}$ = 83.9 Hz, $^3J_{PH}$ = 18.9 Hz, PCy_3); 173.94 (dd, $^1J_{PH}$ = 335.7 Hz, $^2J_{PP}$ = 83.9 Hz, PHMes*). ^{1}H NMR (400.1 MHz): δ 1.07 (d, $^3J_{HH}$ = 6.5 Hz, 6H, C_1−CH−(CH_3)$_2$); 1.36 (m, 12H, C_cH_2); 1.46 (s, 9H, C_p−C−(CH_3)$_3$); 1.51 (s, 18H, C_o−C−(CH_3)$_3$); 1.76 (s, 3H, C_4−CH_3); 1.95 (m, 6H, C_dH_2); 2.25 (m, 12H, C_bH_2); 2.77 (m, 3H, C_aH); 3.03 (m, 1H, C_1−CH−(CH_3)$_2$); 5.32 (AB, $^3J_{HH}$ = 4.7 Hz, 2H, C_3H); 5.79 (AB, $^3J_{HH}$ = 4.7 Hz, 2H, C_2H); 7.61 (s, 2H, C_mH); 8.86 (dd, $^1J_{HP}$ = 335.7 Hz, $^3J_{HP}$ = 18.9 Hz, PHMes*). ^{13}C{^{1}H} NMR (100.6 MHz): δ 18.00 (C_4−CH_3); 23.74 (C_1−CH−(CH_3)$_2$); 26.97 (C_d); 27.47 (d, $^3J_{CP}$ = 9.2 Hz, C_c); 30.39 (C_b); 31.34 (C_p−C−(CH_3)$_3$); 31.51 (C_1−CH−(CH_3)$_2$); 32.70 (C_o−C−(CH_3)$_3$); 33.71 (d, $^1J_{CP}$ = 7.4 Hz, C_a); 35.46 (C_p−C−(CH_3)$_3$); 38.88 (C_o−C−(CH_3)$_3$); 84.87 (C_3); 89.45 (C_2); 100.31 (C_4); 113.03 (C_1); 122.81 (d, $^3J_{CP}$ = 8.3 Hz, C_m); 152.70 (C_o); 153.00 (C_p); 166.03 (C_i). ^{19}F NMR (188.3 MHz): δ −73.40 (s). ^{11}B NMR (96.3 MHz): δ −0.12 (br s). Anal. Calcd for $C_{46}H_{77}BF_4P_2Ru$: C, 62.79; H, 8.82. Found: C, 62.31; H, 8.58.

[(η^6-Benzene)(PCy_3)Ru(PHMes*)]BF_4 (3bBF$_4$). A similar procedure to that described for **3aBF$_4$** was used. **2b** (0.125 g; 0.17 mmol) and HBF_4 (0.18 mmol, 54 wt % in Et_2O) gave **3bBF$_4$** as a violet solid (0.113 g, 81%). Mp: 126 °C. ^{31}P NMR (81.0 MHz): δ 48.31 (dd, $^2J_{PP}$ = 83.9 Hz, $^3J_{PH}$ = 16.7 Hz, PCy_3); 190.93 (dd, $^1J_{PH}$ = 343.3 Hz, $^2J_{PP}$ = 83.9 Hz, PHMes*). ^{1}H NMR (300.1 MHz): δ 1.41 (m, 12H, C_cH_2); 1.44 (s, 9H, C_p−C−(CH_3)$_3$); 1.52 (s, 18H, C_o−C−(CH_3)$_3$); 1.82 (m, 6H, C_dH_2); 2.02 (m, 12H, C_bH_2); 2.53 (m, 3H, C_aH); 5.30 (s, 6H, $CH_{benzene}$); 7.53 (s, 2H, C_mH); 9.00 (dd, $^1J_{HP}$ = 343.3 Hz, $^3J_{HP}$ = 16.7 Hz, 1H, PH). ^{13}C{^{1}H} NMR (75.5 MHz): δ 26.56 (C_d); 27.25 (d, $^3J_{CP}$ = 10.5 Hz, C_c); 30.10 (C_b); 31.41 (C_p−C−(CH_3)$_3$); 32.34 (C_o−C−(CH_3)$_3$); 33.82 (d, $^1J_{CP}$ = 7.2 Hz, C_a); 36.45 (C_p−C−(CH_3)$_3$); 38.27 (C_o−C−(CH_3)$_3$); 87.06

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($C_{benzene}$); 122.27 (d, $^3J_{CP}$ = 7.8 Hz, C_m); 152.39 (C_o); 152.95 (C_p); 165.76 (C_i). ^{19}F NMR (188.3 MHz): δ −71.90 (s). ^{11}B NMR (96.3 MHz): δ −0.18 (br s). Anal. Calcd for $C_{42}H_{69}BF_4P_2Ru$: C, 61.23; H, 8.44. Found: C, 60.99; H, 8.62.

[(η^6-*p*-Cymene)(PCy_3)Ru(PHMes*)]BPh_3OH (3aBPh$_3$OH). To a green solution of **2a** (0.244 g, 0.31 mmol) in toluene (10 mL) was added 0.074 g of BPh_3 (0.31 mmol). In the presence of water (6 μL, 0.31 mmol), the solution turned slowly to violet, and the mixture was stirred for 24 h at room temperature. The volatiles were removed *in vacuo*, leaving a violet residue. Trituration with pentane afforded pure **3aBPh$_3$OH** as a violet powder (0.288 g, 87%). Mp: 198 °C. ^{31}P NMR (81.015 MHz): δ 45.15 (dd; $^2J_{PP}$ = 83.9 Hz; $^3J_{HP}$ = 19.0 Hz; PCy_3); 186.32 (dd; $^1J_{PH}$ = 341.1 Hz; $^2J_{PP}$ = 83.9 Hz; PHMes*). ^{1}H NMR (200.132 MHz): δ 1.00 (d; $^3J_{HH}$ = 6.7 Hz; 6H; C_1−CH−(CH_3)$_2$); 1.26 (m; 12H; C_cH_2); 1.37 (s; 9H; C_p−C−(CH_3)$_3$); 148 (s; 18H; C_o−C−(CH_3)$_3$); 1.70 (s; 3H; C_4−CH_3); 1.83 (m; 6H; C_dH_2); 2.24 (m; 12H; C_bH_2); 2.74 (m; 4H; C_aH and C_1−CH−(CH_3)$_2$); 4.81 (m; 4H; C_2H and C_3H); 6.98 (m; 9H; C_bH_{Ph} and C_dH_{Ph}); 7.44 (s; 2H; C_mH); 7.71 (m; 6H; C_cH_{Ph}); 9.00 (dd; $^1J_{HP}$ = 341.1 Hz; $^3J_{HP}$ = 19.0 Hz; 1H; PH). ^{13}C{^{1}H} NMR (50.323 MHz): δ 18.19 (s; C_4−CH_3); 23.58 (s; C_1−CH−(CH_3)$_2$); 26.37 (s; C_d); 27.51 (d; $^3J_{CP}$ = 11.1 Hz; C_c); 30.01 (s; C_b); 30.94 (s; C_1−CH−(CH_3)$_2$); 31.20 (s; C_p−C−(CH_3)$_3$); 32.64 (s; C_o−C−(CH_3)$_3$); 34.22 (d; $^1J_{CP}$ = 50.9 Hz; C_a); 35.28 (s; C_p−C−(CH_3)$_3$); 38.70 (s; C_o−C−(CH_3)$_3$); 83.76 (s; C_3); 87.99 (s; C_2); 99.45 (d; $^2J_{CP}$ = 3.4 Hz; C_4); 112.66 (d; $^2J_{CP}$ = 2.8 Hz; C_1); 122.34 (d; $^3J_{CP}$ = 8.3 Hz; C_m); 127.25 (s; C_{bPh}); 128.29 (s; C_{aPh}); 131.96 (s; C_{dPh}); 134.90 (s; C_{cPh}); 152.40 (s; C_o); 153.06 (s; C_p); 159.05 (s; C_i). ^{11}B NMR (96.29 MHz): δ 1.43 (br s). Anal. Calcd for $C_{64}H_{93}BOP_2Ru$: C, 73.05; H, 8.91. Found: C, 73.26; H, 9.02.

[(η^6-Benzene)(PCy_3)Ru(PHMes*)]BPh_3OH (3bBPh$_3$OH). A similar procedure to that described for **3aBPh$_3$OH** was used. **2b** (0.057 g, 0.08 mmol), BPh_3 (0.019 g, 0.08 mmol), and H_2O (2 μL, 0.08 mmol) gave **3bBPh$_3$OH** as a violet solid (0.063 g, 83%). Mp: 167 °C. ^{31}P NMR (81.015 MHz): δ 48.07 (d; $^2J_{PP}$ = 83.9 Hz; $^3J_{HP}$ = 18.7 Hz; PCy_3); 199.13 (dd; $^1J_{PH}$ = 350.0 Hz; $^2J_{PP}$ = 83.9 Hz; PHMes*). ^{1}H NMR (300.13 MHz): δ 1.27 (m; 12H; C_cH_2); 1.38 (s; 9H; C_p−C−(CH_3)$_3$); 1.45 (s; 18H; C_o−C−(CH_3)$_3$); 1.75 (m; 6H; C_dH_2); 2.21 (m; 12H; C_bH_2); 2.75 (m; 3H; C_aH); 4.85 (s; 6H; $CH_{benzene}$); 7.02 (m; 9H; C_bH_{Ph} et C_dH_{Ph}); 7.42 (s; 2H; C_mH); 7.94 (m; 6H; C_cH_{Ph}); 8.99 (dd; $^1J_{HP}$ = 350.0 Hz; $^3J_{HP}$ = 18.7 Hz; 1H; PH). ^{13}C{^{1}H} NMR (75.468 MHz): δ 26.40 (s; C_d); 27.51 (d; $^3J_{CP}$ = 11.2 Hz; C_c); 30.14 (s; C_b); 31.17 (s; C_p−C−(CH_3)$_3$); 32.45 (s; C_o−C−(CH_3)$_3$); 33.86 (d; $^1J_{CP}$ = 48.5 Hz; C_a); 35.28 (s; C_p−C−(CH_3)$_3$); 38.47 (s; C_o−C−(CH_3)$_3$); 86.64 (s; $C_{benzene}$); 122.51 (d; $^3J_{CP}$ = 8.8 Hz; C_m); 127.15 (s; C_{bPh}); 128.28 (s; C_{aPh}); 132.65 (s; C_{dPh}); 135.02 (s; C_{cPh}); 152.32 (s; C_o); 153.55 (s; C_p); 160.77 (s; C_i). ^{11}B NMR (96.29 MHz): δ 1.52 (s). Anal. Calcd for $C_{60}H_{75}BOP_2Ru$: C, 73.08; H, 7.67. Found: C, 73.14; H, 8.00.

(η^6-*p*-Cymene)(PCy_3)Ru[P(BH_3)Mes*] (4a). To a green solution of **2a** (0.087 g, 0.11 mmol) in toluene (5 mL) was added an excess of BH_3·SMe_2 (1.1 mmol, 2 M in toluene). The solution turned slowly to violet, and the mixture was stirred for 15 min at room temperature. The volatiles were removed *in vacuo*, and pure **4a** was obtained as an oily violet residue (0.080 g, 90%). ^{31}P NMR (81.0 MHz): δ 48.69 (d, $^2J_{PP}$ = 68.7 Hz, PCy_3); 506.27 (d, $^2J_{PP}$ = 68.7 Hz, P(BH_3)). ^{1}H NMR (200.1 MHz): δ 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 6H, C_1−CH−(CH_3)$_2$); 1.35 (m, 12H, C_cH_2); 1.46 (s, 9H, C_p−C−(CH_3)$_3$); 1.54 (m, 12H, C_bH_2); 1.83 (s, 18H, C_o−C−(CH_3)$_3$); 2.02 (s, 3H, C_4−CH_3); 2.16 (m, 6H, C_dH_2); 2.70 (m, 4H, C_aH and C_1−CH−(CH_3)$_2$); 4.55 (m, 4H, C_2H and C_3H); 7.65 (s, 2H, C_mH). ^{13}C{^{1}H} NMR (75.5 MHz): δ 19.23 (C_4−CH_3); 25.68 (C_1−CH−(CH_3)$_2$); 28.28 (C_d); 30.49 (br s; C_c); 30.77 (C_b); 31.09 (C_1−CH−(CH_3)$_2$); 31.45 (C_p−C−(CH_3)$_3$); 33.51 (C_o−C−(CH_3)$_3$); 34.90 (C_p−C−(CH_3)$_3$); 35.31 (br s; C_a); 40.11 (C_o−C−(CH_3)$_3$); 81.01 (C_3); 85.63 (C_2); 89.12 (C_4); 103.05 (C_1); 119.25 (C_m); 144.85 (C_p); 145.51 (C_o). ^{11}B NMR (96.3 MHz): δ 18.33 (br s).

(η^6-Benzene)(PCy_3)Ru[P(BH_3)Mes*] (4b). A similar procedure to that described for **4a** was used. **2b** (0.089 g, 0.11 mmol) and BH_3·SMe_2 (1.1 mmol, 2 M in toluene) gave **4b** as an oily violet residue (0.069 g, 83%). ^{31}P NMR (81.0 MHz): δ 48.40 (d, $^2J_{PP}$ = 68.7 Hz, PCy_3); 521.06 (d, $^2J_{PP}$ = 68.7 Hz, P(BH_3)). ^{1}H NMR (200.1 MHz): δ 1.33 (m, 12H, C_cH_2); 1.47 (s, 9H, C_p−C−(CH_3)$_3$); 1.59 (m, 12H, C_bH_2); 1.71 (s, 18H, C_o−C−(CH_3)$_3$); 1.99 (m, 6H, C_dH_2); 2.56 (m, 3H, C_aH); 4.64 (s, 6H, $CH_{benzene}$); 7.54 (s, 2H, C_mH). ^{13}C{^{1}H} NMR (75.5 MHz): δ 27.20 (C_d); 29.12 (br s, C_c); 29.80 (C_b); 30.22 (C_p−C−(CH_3)$_3$); 31.41 (C_o−C−(CH_3)$_3$); 33.90 (br s, C_a); 37.01 (C_p−C−(CH_3)$_3$); 41.04 (C_o−C−(CH_3)$_3$); 80.43 ($C_{benzene}$); 118.26 (C_m); 144.53 (C_p); 146.05 (C_o). ^{11}B NMR (96.3 MHz): δ 18.29 (br s).

[(η^6-*p*-Cymene)(PCy_3)Ru(PMeMes*)]I (5a). To a green solution of **2a** (0.658 g, 0.83 mmol) in toluene (10 mL) was added MeI (0.052 mL, 0.83 mmol). The solution turned slowly to violet, and the mixture was stirred for 1 h at room temperature. The volatiles were removed *in vacuo*. Trituration with pentane afforded pure **5a** as a violet powder (0.737 g, 95%). Mp: 160 °C. ^{31}P NMR (81.0 MHz): δ 48.80 (d, $^2J_{PP}$ = 82.1 Hz, PCy_3); 240.38 (dq, $^2J_{PP}$ = 82.1 Hz, $^2J_{PH}$ = 9.7 Hz, PMeMes*). ^{1}H NMR (200.1 MHz): δ 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C_1−CH−CH_3); 1.32 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C_1−CH−CH_3); 1.43 (s, 9H, C_p−C−(CH_3)$_3$); 1.46 (s, 9H, C_o−C−(CH_3)$_3$); 1.52 (s, 9H, C_o−C−(CH_3)$_3$); 1.56 (s, 3H, C_4−CH_3); 1.86 (m, 12H, C_cH_2); 2.13 (d, $^2J_{HP}$ = 9.7 Hz, 3H, P−CH_3); 2.26 (m, 6H, C_dH_2); 2.56 (m, 12H, C_bH_2); 3.27 (m, 4H, C_aH and C_1−CH−(CH_3)$_2$); 3.73 (s, 1H, C_2H); 4.77 (s, 1H, C_3H); 5.43 (s, 2H, C_2H and C_3H); 7.54 (s, 1H, C_mH); 7.65 (s, 1H, C_mH). ^{13}C{^{1}H} NMR (50.3 MHz): δ 18.60 (C_4−CH_3); 21.48 (C_1−CH−(CH_3)$_2$); 26.31 (C_d); 27.65 (d, $^3J_{CP}$ = 9.2 Hz, C_c); 30.25 (C_b); 30.58 (C_1−CH−(CH_3)$_2$); 31.09 (C_o−C−(CH_3)$_3$); 31.26 (C_p−C−(CH_3)$_3$); 32.41 (d, $^1J_{CP}$ = 7.4 Hz, C_a); 34.64 (br s, P−CH_3); 35.10 (C_p−C−(CH_3)$_3$); 39.67 (C_o−C−(CH_3)$_3$); 79.54 (C_3); 83.99 (C_2); 100.97 (d, $^2J_{CP}$ = 6.5 Hz, C_4); 112.96 (d, $^2J_{CP}$ = 5.6 Hz, C_1); 123.56 (d, $^3J_{CP}$ = 7.4 Hz, C_m); 144.94 (d, $^2J_{CP}$ = 13.9 Hz, C_o); 149.36 (C_p); 152.16 (d, $^2J_{CP}$ = 2.0 Hz, C_o); 166.82 (C_i). Anal. Calcd for $C_{47}H_{79}IP_2Ru$: C, 60.44; H, 8.53. Found: C, 59.95; H, 8.17.

[(η^6-Benzene)(PCy_3)Ru(PMeMes*)]I (5b). A similar procedure to that described for **5a** was used. **2b** (0.610 g; 0.83 mmol) and MeI (0.052 mL, 0.83 mmol) gave **5b** as a violet solid (0.641 g, 88%). Mp: 144 °C. ^{31}P NMR (81.0 MHz): δ 51.89 (d, $^2J_{PP}$ = 76.3 Hz, PCy_3); 248.19 (dd, $^2J_{PH}$ = 10.2 Hz, $^2J_{PP}$ = 76.3 Hz, PMeMes*). ^{1}H NMR (200.1 MHz): δ 1.36 (s, 9H, C_p−C−(CH_3)$_3$); 1.56 (s, 18H, C_o−C−(CH_3)$_3$); 1.85 (m, 12H, C_cH_2); 2.21 (d, $^2J_{HP}$ = 10.2 Hz, 3H, P−CH_3); 2.33 (m, 6H, C_dH_2); 3.14 (m, 12H, C_bH_2); 3.67 (m, 3H, C_aH); 5.31 (s, 6H, $CH_{benzene}$); 7.51 (s, 2H, C_mH). ^{13}C-{^{1}H} NMR (50.3 MHz): δ 26.44 (C_d); 27.77 (d, $^3J_{CP}$ = 10.2 Hz, C_c); 30.36 (C_b); 31.11 (C_p−C−(CH_3)$_3$); 31.52 (C_o−C−(CH_3)$_3$); 34.29 (br s, P−CH_3); 34.75 (d, $^1J_{CP}$ = 3.7 Hz, C_a); 35.17 (s, C_p−C−(CH_3)$_3$); 39.31 (s, C_o−C−(CH_3)$_3$); 87.42 (d, $^2J_{CP}$ = 3.7 Hz, $C_{benzene}$); 123.52 (d, $^3J_{CP}$ = 8.3 Hz, C_m); 146.12 (d, $^2J_{CP}$ = 15.7 Hz, C_o); 149.95 (C_p); 152.47 (d, $^2J_{CP}$ = 2.0 Hz, C_o); 166.56 (d, $^1J_{CP}$ = 44.4 Hz, C_i). Anal. Calcd for $C_{43}H_{71}IP_2Ru$: C, 58.83; H, 8.15. Found: C, 58.42; H, 8.07.

(η^6-*p*-Cymene)Ru[η^3-P(CH=CHSiMe_3)Mes*] (6). To a green solution of **2a** (0.214 g, 0.27 mmol) in toluene (10 mL) was added $Me_3SiC{\equiv}CH$ (0.040 mL, 0.29 mmol). The solution turned to orange, and the mixture was stirred for 1 h at room temperature. The volatiles were removed *in vacuo*. The residue was extracted with pentane, filtered, and concentrated. Upon standing at −20 °C, **6** was obtained as a pure orange solid (0.156 g, 95%). Mp: 82 °C. ^{31}P NMR (81.0 MHz): δ −2.76 (m). ^{1}H NMR (400.1 MHz): δ 0.23 (s, 9H, Si(CH_3)$_3$); 1.17 (s, 3H, P−CH_2−C−CH_3); 1.25 (s, 3H, P−CH_2−C−CH_3); 1.27 (br s, 2H, P−CH_2); 1.32 (s, 9H, C_p−C−(CH_3)$_3$); 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C_1−CH−CH_3); 1.38 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C_1−CH−CH_3); 1.79 (s, 9H, C_o−C−(CH_3)$_3$); 2.10 (s, 3H, C_4−CH_3); 2.42 (d, $^3J_{HH}$ = 7.4 Hz, 1H, P−CH=CH); 2.66

(dd, $^2J_{HP}$ = 21.8 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, P−C*H*═CH); 3.44 (m, 1H, C_1−C*H*−$(CH_3)_2$); 4.28 (d, $^3J_{HP}$ = 5.5 Hz, 1H, C_2H); 5.01 (d, $^3J_{HP}$ = 5.1 Hz, 1H, C_3H); 5.09 (d, $^3J_{HP}$ = 5.7 Hz, 1H, C_2H); 5.79 (d, $^3J_{HP}$ = 5.5 Hz, 1H, C_3H); 7.22 (d, $^4J_{HH}$ = 1.8 Hz, 1H, C_mH); 7.56 (dd, $^4J_{HP}$ = 4.9 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, C_mH). $^{13}C\{^1H\}$ NMR (100.6 MHz): δ 0.34 ($Si(CH_3)_3$); 19.34 (C_4−*C*H_3); 25.83 (C_1−CH−*C*H_3); 26.36 (C_1−CH−*C*H_3); 28.66 (P−CH_2−C−*C*H_3); 30.55 (d, $^3J_{CP}$ = 9.3 Hz, P−CH_2−C−*C*H_3); 31.34 (C_1−*C*H−$(CH_3)_2$); 31.51 (C_p−C−*C*$H_3)_3$); 32.52 (C_o−C−*C*$H_3)_3$); 33.18 (P−CH═*C*H); 34.50 (d, $^1J_{CP}$ = 17.6 Hz, P−CH_2); 35.15 (C_p−*C*−$(CH_3)_3$); 37.78 (d, $^1J_{CP}$ = 10.2 Hz, P−*C*H═CH); 37.94 (C_o−*C*−$(CH_3)_3$); 41.42 (d, $^2J_{CP}$ = 6.5 Hz, C_o−*C*−$(CH_3)_2$); 72.71 (d, $^2J_{CP}$ = 9.3 Hz, C_2); 74.64 (C_3); 81.35 (C_3); 82.85 (C_2); 99.02 (d, $^2J_{CP}$ = 4.6 Hz, C_4); 110.25 (C_1); 118.25 (d, $^3J_{CP}$ = 7.4 Hz, C_m); 121.95 (d, $^3J_{CP}$ = 8.3 Hz, C_m); 126.05 (d, $^1J_{CP}$ = 32.4 Hz, C_i); 153.13 (d, $^4J_{CP}$ = 1.9 Hz, C_p); 153.77 (d, $^2J_{CP}$ = 9.3 Hz, *C*$_o$−C−$(CH_3)_3$); 159.73 (d, $^2J_{CP}$ = 12.0 Hz, *C*$_o$−C−$(CH_3)_2$). Anal. Calcd for $C_{33}H_{53}PRuSi$: C, 64.99; H, 8.76. Found: C, 64.78; H, 8.69.

Upon exposure to air, complex **6** is oxidized and converted into the corresponding phosphine oxide. ^{31}P NMR (81.0 MHz): δ 33.24 (t, $^2J_{HP}$ = 14.4 Hz). ^1H NMR (400.1 MHz): δ 0.14 (s, 9H, Si−$(CH_3)_3$); 1.34 (s, 9H, C_p−C−$(CH_3)_3$); 1.52 (s, 6H, P−CH_2−C−C*H*$_3$); 1.58 (s, 9H, C_o−C−$(CH_3)_3$); 2.19 (d, $^2J_{HP}$ = 14.4 Hz, 2H, P−CH_2); 6.84 (dd, $^3J_{HH}$ = 19.8 Hz, $^2J_{HP}$ = 31.3 Hz, 1H, P−C*H*═CH); 7.28−7.54 (m, 3H, C_mH and P−CH═C*H*).

(η^6-*p*-Cymene)Ru[η^3-P(CH═CHPh)Mes*] (7). A similar procedure to that described for **6** was used. **2a** (0.412 g; 0.52 mmol) and PhC≡CH (0.059 mL, 0.54 mmol) gave **7** as a red-orange solid (0.306 g, 96%). Mp: 192 °C. ^{31}P NMR (81.0 MHz): δ −10.40 (m). ^1H NMR (400.1 MHz): δ 1.28 (s, 3H, P−CH_2−C−C*H*$_3$); 1.37 (s, 3H, P−CH_2−C−C*H*$_3$); 1.42 (s, 9H, C_p−C−$(CH_3)_3$); 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C_1−CH−C*H*$_3$); 1.44 (d, $^3J_{HH}$ = 6.9 Hz, 3H; C_1−CH−C*H*$_3$); 1.46 (br s, 2H, P−CH_2); 1.97 (s, 9H, C_o−C−$(CH_3)_3$); 2.14 (s, 3H, C_4−CH_3); 2.79 (m, 1H, C_1−C*H*−$(CH_3)_2$); 3.03 (dd, $^2J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, P−C*H*═CH); 3.23 (d, $^3J_{HP}$ = 5.5 Hz, 1H, C_3H); 3.26 (d, $^3J_{HH}$ = 5.4 Hz, 1H, P−CH═C*H*); 4.90 (d, $^3J_{HP}$ = 4.4 Hz, 1H, C_2H); 5.21 (d, $^3J_{HP}$ = 5.5 Hz, 1H, C_3H); 5.42 (d, $^3J_{HP}$ = 5.5 Hz, 1H, C_2H); 7.24 (m, 2H, C_cH); 7.46 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C_mH); 7.48 (s, 3H, C_bH and C_dH); 7.86 (dd, $^4J_{HP}$ = 4.9 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, C_mH). $^{13}C\{^1H\}$ NMR (100.6 MHz): δ 19.82 (C_4−*C*H_3); 25.55 (C_1−CH−*C*H_3); 26.09 (C_1−CH−*C*H_3); 29.20 (P−CH_2−C−*C*H_3); 30.37 (d, $^3J_{CP}$ = 9.1 Hz, P−CH_2−C−*C*H_3); 31.44 (C_p−C−*C*$H_3)_3$); 32.51 (C_1−*C*H−$(CH_3)_2$); 33.29 (C_o−C−*C*$H_3)_3$); 33.51 (P−CH═*C*H); 35.12 (C_p−*C*−$(CH_3)_3$); 35.67 (d, $^1J_{CP}$ = 17.5 Hz, P−CH_2); 37.13 (d, $^1J_{CP}$ = 8.2 Hz, P−*C*H═CH); 37.99 (C_o−*C*−$(CH_3)_3$); 41.73 (d, $^2J_{CP}$ = 6.5 Hz, C_o−*C*−$(CH_3)_2$); 76.68 (C_2); 80.80 (d, $^2J_{CP}$ = 5.3 Hz, C_3); 81.50 (d, $^2J_{CP}$ = 5.3 Hz, C_3); 82.69 (C_2); 98.06 (d, $^2J_{CP}$ = 4.2 Hz, C_4); 110.02 (C_1); 118.25 (d, $^3J_{CP}$ = 8.3 Hz, C_m); 122.11 (d, $^3J_{CP}$ = 8.4 Hz, C_m); 122.98 (C_c); 125.97 (C_b); 128.31 (C_d); 152.09 (d, $^2J_{CP}$ = 16.2 Hz, C_a); 153.36 (C_p); 154.24 (d, $^2J_{CP}$ = 9.6 Hz, *C*$_o$−C−$(CH_3)_3$); 160.46 (d, $^2J_{CP}$ = 12.5 Hz, *C*$_o$−C−$(CH_3)_2$). Anal. Calcd for $C_{36}H_{49}PRu$: C, 70.44; H, 8.05. Found: C, 70.51; H, 8.09.

Upon exposure to air, complex **7** is oxidized and converted into the corresponding phosphine oxide. ^{31}P NMR (81.0 MHz): δ 32.46 (t, $^2J_{HP}$ = 14.0 Hz). ^1H NMR (400.1 MHz): δ 1.33 (s, 9H, C_p−C−$(CH_3)_3$); 1.51 (s, 6H, P−CH_2−C−C*H*$_3$); 1.58 (s, 9H, C_o−C−$(CH_3)_3$); 2.23 (d, $^2J_{HP}$ = 14.0 Hz, 2H, P−CH_2); 6.84 (dd, $^3J_{HH}$ = 20.2 Hz, $^2J_{HP}$ = 30.8 Hz, 1H, P−C*H*═CH); 7.16−7.72 (m, 8H, C_mH and Ph and P−CH═C*H*).

(η^6-*p*-Cymene)(PPh_3)Ru(PMes*) (8). A similar procedure to that described for **2a** was used. (η^6-*p*-Cymene)(PPh_3)$RuCl_2$ (0.102 g; 0.16 mmol), Mes*PH_2 (0.042 g; 0.150 mmol), and DBU (0.041 mL; 0.29 mmol) gave **8** as a green solid (0.117 g, 94%). Mp: 120 °C dec. ^{31}P NMR (81.0 MHz): δ 38.75 (d, $^2J_{PP}$ = 45.8 Hz, PPh_3); 835.36 (d, $^2J_{PP}$ = 45.8 Hz, PMes*). ^1H NMR (400.1 MHz): δ 0.93 (d, $^3J_{HH}$ = 6.6 Hz, 6H, C_1−CH−$(CH_3)_2$); 1.54 (s, 9H, C_p−C−$(CH_3)_3$); 1.63 (s, 18H, C_o−C−$(CH_3)_3$); 1.77 (s, 3H, C_4−CH_3); 2.42 (m, 1H, C_1−C*H*−$(CH_3)_2$); 4.58 (AB, $^3J_{HH}$ = 6.1 Hz, 2H, C_3H); 4.61 (AB, $^3J_{HH}$ = 6.1 Hz, 2H, C_2H); 7.12 (br s, 9H, C_bH and C_dH); 7.54 (br s, 2H, C_mH); 7.94 (m, 6H, C_cH). $^{13}C\{^1H\}$ NMR (100.6 MHz): δ 18.94 (C_4−*C*H_3); 24.36 (C_1−CH−(*C*$H_3)_2$); 30.79 (C_1−*C*H−$(CH_3)_2$); 31.95 (C_p−C−(*C*$H_3)_3$); 32.84 (d, $^4J_{CP}$ = 6.4 Hz, C_o−C−(*C*$H_3)_3$); 34.91 (C_p−*C*−$(CH_3)_3$); 38.66 (C_o−*C*−$(CH_3)_3$); 84.65 (d, $^2J_{CP}$ = 2.8 Hz, C_2); 87.22 (d, $^2J_{CP}$ = 2.8 Hz, C_3); 91.47 (C_4); 105.02 (C_1); 119.39 (C_m); 127.73 (C_b); 129.14 (C_d); 135.30 (d, $^3J_{CP}$ = 11.1 Hz, C_c); 139.64 (d, $^1J_{CP}$ = 38.8 Hz, C_a); 145.67 (C_p); 145.85 (C_o); 183.59 (C_i). Anal. Calcd for $C_{46}H_{58}P_2Ru$: C, 71.38; H, 7.55. Found: C, 71.48; H, 7.73.

(η^6-*p*-Cymene)[P(*p*-$ClC_6H_4)_3$]Ru(PMes*) (9). An NMR tube was charged with **2a** (0.022 g, 0.28 mmol) and P(*p*-$ClC_6H_4)_3$ (0.010 g, 0.28 mmol) in C_6D_6 (0.5 mL). The tube was maintained at 45 °C and monitored by ^1H NMR. Data for (η^6-*p*-cymene)[P(*p*-$ClC_6H_4)_3$]Ru(PMes*) (**9**). ^{31}P NMR (81.0 MHz): δ 37.15 (d, $^2J_{PP}$ = 45.8 Hz, P(*p*-$ClC_6H_4)_3$); 843.17 (d, $^2J_{PP}$ = 45.8 Hz, PMes*). ^1H NMR (200.1 MHz): δ 0.86 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C_1−CH−(C*H*$_3)_2$); 1.51 (s, 9H, C_p−C−$(CH_3)_3$); 1.57 (s, 18H, C_o−C−$(CH_3)_3$); 1.88 (s, 3H, C_4−CH_3); 2.32 (m, 1H, C_1−C*H*−$(CH_3)_2$); 4.48 (AB, $^3J_{HH}$ = 6.4 Hz, 2H, C_3H); 4.52 (AB, $^3J_{HH}$ = 6.4 Hz, 2H, C_2H); 7.19 (d, $^3J_{HP}$ = 7.4 Hz, 6H, C_bH); 7.55 (s, 2H, C_mH); 7.62 (br s, 6H, C_cH).

(η^6-*p*-Cymene)[P(*p*-$MeC_6H_4)_3$]Ru(PMes*) (10). An NMR tube was charged with **2a** (0.025 g, 0.32 mmol) and P(*p*-tolyl)$_3$ (0.010 g, 0.32 mmol) in C_6D_6 (0.5 mL). The tube was maintained at 45 °C and monitored by ^1H NMR. Data for (η^6-*p*-cymene)[P(*p*-$MeC_6H_4)_3$]Ru(PMes*) (**10**). ^{31}P NMR (81.0 MHz): δ 36.40 (d, $^2J_{PP}$ = 45.8 Hz, P(*p*-tolyl)$_3$), 831.97 (d, $^2J_{PP}$ = 45.8 Hz, PMes*). ^1H NMR (200.1 MHz): δ 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C_1−CH−(C*H*$_3)_2$); 1.56 (s, 9H, C_p−C−$(CH_3)_3$); 1.67 (s, 18H, C_o−C−$(CH_3)_3$); 1.83 (s, 3H, C_4−CH_3); 2.10 (s, 9H, C_d−CH_3); 2.57 (m, 1H, C_1−C*H*−$(CH_3)_2$); 4.62 (AB, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H); 4.66 (AB, $^3J_{HH}$ = 6.6 Hz, 2H, C_2H); 7.06 (d, $^3J_{HP}$ = 7.2 Hz, 6H, C_bH); 7.55 (s, 2H, C_mH); 7.92 (br s, 6H, C_cH).

(η^6-*p*-Cymene)[P(*p*-$MeOC_6H_4)_3$]Ru(PMes*) (11). An NMR tube was charged with **2a** (0.025 g, 0.32 mmol) and P(*p*-$MeOC_6H_4)_3$ (0.011 g, 0.32 mmol) in C_6D_6 (0.5 mL). The tube was maintained at 45 °C and monitored by ^1H NMR. Data for (η^6-*p*-cymene)[P(*p*-$MeOC_6H_4)_3$]Ru(PMes*) (**11**). ^{31}P NMR (81.0 MHz): δ 34.51 (d, $^2J_{PP}$ = 45.8 Hz, P(*p*-$MeOC_6H_4)_3$); 830.36 (d, $^2J_{PP}$ = 45.8 Hz, PMes*). ^1H NMR (200.1 MHz): δ 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C_1−CH−(C*H*$_3)_2$); 1.55 (s, 9H, C_p−C−$(CH_3)_3$); 1.67 (s, 18H, C_o−C−$(CH_3)_3$); 1.84 (s, 3H, C_4−CH_3); 2.54 (m, 1H, C_1−C*H*−$(CH_3)_2$); 3.30 (s, 9H, C_d−OCH_3); 4.61 (AB, $^3J_{HH}$ = 6.2 Hz, 2H, C_3H); 4.69 (AB, $^3J_{HH}$ = 6.2 Hz, 2H, C_2H); 6.86 (d, $^3J_{HP}$ = 7.8 Hz, 6H, C_bH); 7.54 (s, 2H, C_mH); 7.92 (br s, 6H, C_cH).

(η^6-*p*-Cymene)[P($NC_4H_4)_3$]Ru(PMes*) (12). A similar procedure to that described for **2a** was used. (η^6-*p*-Cymene)[P($NC_4H_4)_3$]-$RuCl_2$ (0.436 g; 0.72 mmol), Mes*PH_2 (0.194 g; 0.70 mmol), and DBU (0.210 mL; 1.4 mmol) gave **12** as a green solid (0.412 g, 80%). Mp: 131 °C. ^{31}P NMR (81.0 MHz): δ 95.16 (d, $^2J_{PP}$ = 15.3 Hz, P($NC_4H_4)_3$); 886.77 (d, $^2J_{PP}$ = 15.3 Hz, PMes*). ^1H NMR (200.1 MHz): δ 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C_1−CH−C*H*$_3$); 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C_1−CH−C*H*$_3$); 1.30 (s, 3H, C_4−CH_3); 1.48 (s, 9H, C_p−C−$(CH_3)_3$); 1.56 (s, 18H, C_o−C−$(CH_3)_3$); 2.64 (m, $^3J_{HH}$ = 6.8 Hz, 1H, C_1−C*H*−$(CH_3)_2$); 4.67 (AB, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H); 4.79 (AB, $^3J_{HH}$ = 6.6 Hz, 2H, C_2H); 6.33 (br s, 6H, C_cH); 7.18 (br s, 6H, C_bH); 7.54 (d, $^4J_{HH}$ = 2.0 Hz, 2H, C_mH). $^{13}C\{^1H\}$ NMR (50.3 MHz): δ 19.16 (C_4−*C*H_3); 24.12 (C_1−CH−*C*H_3); 24.36 (C_1−CH−*C*H_3); 30.81 (C_1−*C*H−$(CH_3)_2$); 31.53 (C_p−C−(*C*$H_3)_3$); 31.82 (C_o−C−(*C*$H_3)_3$); 34.87 (C_p−*C*−$(CH_3)_3$); 38.57 (C_o−*C*−$(CH_3)_3$); 89.29 (d, $^2J_{CP}$ = 4.6 Hz, C_3); 91.56 (d, $^2J_{CP}$ = 3.7 Hz, C_2); 97.85 (C_4); 110.69 (C_1); 111.82 (d, $^3J_{CP}$ = 5.6 Hz, C_c); 119.64 (C_m); 125.50 (d, $^2J_{CP}$ = 8.3 Hz, C_b); 146.14 (C_p); 146.73

(C_o); 154.43 (d, $^1J_{CP}$ = 7.4 Hz, C_i). Anal. Calcd for $C_{40}H_{55}N_3P_2Ru$: C, 64.84; H, 7.48. Found: C, 65.01; H, 7.52.

(η^6-*p*-Cymene)[P(*m*-MeC$_6$H$_4$)$_3$]Ru(PMes*) (13). A similar procedure to that described for **2a** was used. (η^6-*p*-Cymene)[P(*m*-$MeC_6H_4)_3$]$RuCl_2$ (0.253 g; 0.37 mmol), Mes*PH_2 (0.092 g; 0.33 mmol), and DBU (0.099 mL; 0.66 mmol) gave **13** as a green solid (0.246 g, 92%). Mp: 137 °C. ^{31}P NMR (81.0 MHz): δ 38.78 (d, $^2J_{PP}$ = 45.8 Hz, P(*m*-tolyl)$_3$); 832.77 (d, $^2J_{PP}$ = 45.8 Hz, PMes*). ^{1}H NMR (400.1 MHz): δ 0.99 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $C_1-CH-(CH_3)_2$); 1.55 (s, 9H, $C_p-C-(CH_3)_3$); 1.63 (s, 18H, $C_o-C-(CH_3)_3$); 1.82 (s, 3H, C_4-CH_3); 2.15 (s, 9H, C_c-CH_3); 2.59 (m, 1H, $C_1-CH-(CH_3)_2$); 4.59 (AB, $^3J_{HH}$ = 6.4 Hz, 2H; C_3H); 4.71 (AB, $^3J_{HH}$ = 6.4 Hz, 2H, C_2H); 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 3H, C_dH); 7.10 (t, $^3J_{HH}$ = 7.7 Hz, 3H, C_eH); 7.52 (s, 2H, C_mH); 7.71 (t, $^3J_{HP}$ = 8.4 Hz, 3H, C_fH); 7.97 (d, $^3J_{HP}$ = 10.6 Hz, 3H, C_bH). ^{13}C{^{1}H} NMR (100.6 MHz): δ 18.98 (C_4-CH_3); 21.68 (C_c-CH_3); 24.40 ($C_1-CH-CH_3$); 30.88 ($C_1-CH-(CH_3)_2$); 31.97 ($C_p-C-(CH_3)_3$); 32.78 ($C_o-C-(CH_3)_3$); 34.91 ($C_p-C-(CH_3)_3$); 38.71 ($C_o-C-(CH_3)_3$); 84.62 (d, $^2J_{CP}$ = 2.0 Hz, C_3); 87.30 (d, $^2J_{CP}$ = 2.0 Hz, C_2); 91.03 (C_4); 104.67 (C_1); 119.22 (C_m); 127.60 (d, $^3J_{CP}$ = 9.4 Hz, C_e); 129.92 (C_d); 132.10 (d, $^2J_{CP}$ = 9.2 Hz, C_f); 136.34 (d, $^2J_{CP}$ = 13.9 Hz, C_b); 137.04 (d, $^3J_{CP}$ = 10.2 Hz, C_c); 139.67 (d, $^1J_{CP}$ = 37.9 Hz, C_a); 145.50 (C_p); 145.85 (C_o); 154.44 (d, $^1J_{CP}$ = 6.5 Hz, C_i). Anal. Calcd for $C_{49}H_{64}P_2Ru$: C, 72.12; H, 7.91. Found: C, 71.98; H, 7.83.

Kinetic Measurements for Phosphine Substitution Reactions. NMR tubes (5 mm) were charged with appropriate amounts of complexes and phosphines, and C_6D_6 was added to a total volume of 0.5 mL. The tube was maintained at 45 °C and monitored by ^{1}H NMR.

X-ray Diffraction Structure Analysis. Data for all structures presented in this paper were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods,[52] and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2.[53] Very small crystals of poor quality are responsible for insufficient reflections and the low quality of the structure analysis.

2a: $C_{46}H_{76}P_2Ru$, M = 792.08, monoclinic, $P2_1/c$, a = 10.359(5) Å, b = 22.300(10) Å, c = 19.612(8) Å, β = 102.577(11)°, V = 4422(3) Å^3, Z = 4, T = 193(2) K; 17 133 reflections (5318 independent, R_{int} = 0.3085) were collected. Largest electron density residue: 0.598 e Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.0909 and wR_2 = 0.2229 (all data) with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

2b: $C_{42}H_{68}P_2Ru$, M = 735.97, triclinic, $P\bar{1}$, a = 10.385(13) Å, b = 15.164(18) Å, c = 15.641(19) Å, α = 61.91(2)°, β = 73.53(2)°, γ = 78.16(2)°, V = 2076(4) Å^3, Z = 2, T = 133(2) K; 5831 reflections (3286 independent, R_{int} = 0.3049) were collected. Largest electron density residue: 1.372 e Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.1005 and wR_2 = 0.2578 (all data).

3aBF$_4$·C$_7$H$_8$: $C_{53}H_{81}BF_4P_2Ru$, M = 968.00, triclinic, $P\bar{1}$, a = 10.669(11) Å, b = 13.778(13) Å, c = 18.348(18) Å, α = 90.85(2)°, β = 95.22(2)°, γ = 99.50(2)°, V = 2648(4) Å^3, Z = 2, T = 173(2) K; 9216 reflections (5434 independent, R_{int} = 0.4753) were collected. Largest electron density residue: 0.620 e Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.1102 and wR_2 = 0.2964 (all data).

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Supporting Information Available: Kinetic modeling, Complete crystallographic data for compounds **2a**, **2b**, and **3aBF$_4$** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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