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A Synthetic Cycle for the Ruthenium-Promoted Formation of 1*H*-Phosphindoles from Phosphaalkynes

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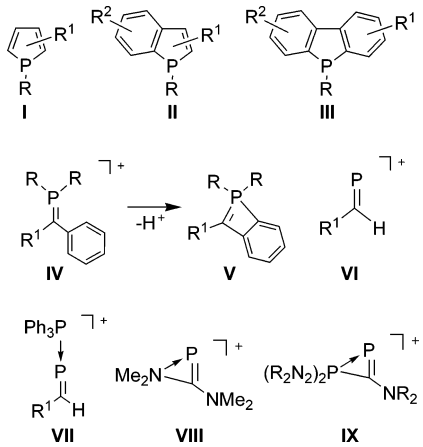
Abstract: Beginning with inexpensive and commercially available starting materials, a rational synthesis for the new phosphaalkyne $Ph_3C-C{\equiv}P$ (**1**) is presented. Coordination of **1** to group 8 transition metal centers furnishes the η^1-complexes $[MH(dppe)_2(Ph_3CC{\equiv}P)]OTf$, where M = Fe (**3**) or Ru (**4**) (dppe = bis-1,2-diphenylphosphinoethane). Treatment of **3** or **4** with a strong acid cyclizes the coordinated phosphaalkyne and is the first example of an electrophilic aromatic substitution reaction in which the electrophile is a low coordinate phosphorus. With the aid of DFT calculations, we were able to gain a more thorough understanding of the energetics and mechanism of this new cyclization reaction. Thermolysis of the iron-3,3-diphenyl-3*H*-phosphindole adduct (**6**) in CH_3CN results in quantitative formation of the free 3*H*-phosphindole (**7**). Alternatively, when ruthenium-3,3-diphenyl-3*H*-phosphindole adduct (**5**) is irradiated, a photochemical rearrangement occurs furnishing 2,3-diphenyl-1*H*-phosphindole (**9**). Mechanistic work is presented that provides an explanation for this transformation. Compounds **1**, **3**, **5**, and **9** have been characterized by single X-ray diffraction studies. Finally, a synthetic cycle for the conversion of **1** to 1*H*-phosphindole **9** has been developed that recycles the ruthenium cation $[RuH(dppe)_2]^+$.

Introduction

Heterocycles containing a low-coordinated phosphorus center[1−3] have found widespread applications ranging from ligands in transition metal complexes[4] to devices in material science.[5] Specifically, phospholes **I**, phosphindoles (benzophospholes) **II**, and dibenzophospholes **III** have been extensively studied (Chart 1). In view of the potential of these compounds, economic synthetic routes are desirable with the ultimate goal of finding catalytic pathways using readily available starting materials. Some years ago, we studied the use of highly electrophilic methylene phosphonium ions **IV**[6−8] in electrocyclic ring closure reactions leading to benzo-λ^5-phosphetes and naphtho-λ^5-phosphetes **V**.[9,10] Phosphavinylium ions **VI** are a class of highly electrophilic and reactive low-valent phosphorus compounds that are potentially suitable precursors for comparable electrocyclic ring closures. Previously, these ions have been proposed as intermediates in the protonation of phosphaalkynes under superacidic conditions.[11] Some donor-stabilized phosphavinylium ions include $Ph_3P \rightarrow P{=}C(SiMe_3)_2$ **VII**,[12] the cyclic intramolecularly stabilized aza-phosphirenylium ion **VIII** (generated in the gas-phase only), and the diphosphirenylium ion **IX**.[13,14] We report here the synthesis of phosphindoles via an electrocyclic ring closure reaction using suitable and easily accessible group 8 phosphaacetylene complexes as precursors. Although not catalytic, we developed this reaction into a complete synthetic cycle.

Chart 1



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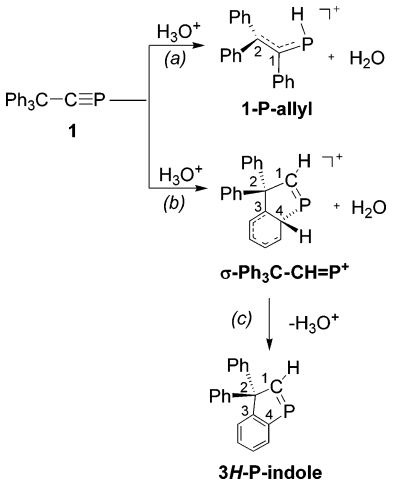
10.1021/ja0651198 CCC: $33.50

Scheme 1. Protonation of **1** Leading to **1-P-allyl** or **3*H*-P-Indole**; Structures are Computed



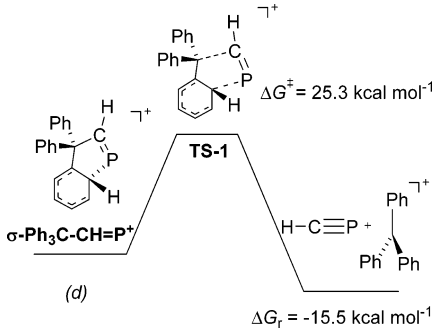
Results and Discussion

Computational Studies. The protonation of various phosphaalkynes, R−C≡P (R = H, alkyl, $SiMe_3$, F, NO_2), has been computed prior to our own work, and with the exception of H−C≡P, hydrogen-bridged species were formed; R_2N−C≡P species give P-protonated cations as minima.[11,15]

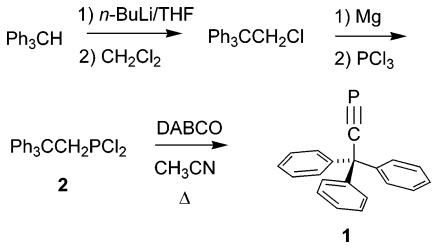
For our purposes, we chose the triphenylmethyl substituted phosphaalkyne, Ph_3C−C≡P **1**, which is especially simple to synthesize and isolate (vide infra). DFT calculations were carried out by implementing the B3LYP exchange-correlation functional[16−18] with the 6-31G* basis set using Gaussian 03.[19] The results are shown in Scheme 1 (see SI for details). Protonation of **1** at the terminal phosphorus center with H_3O^+ as acid did not lead to a stable minimum structure of $[Ph_3C-CCPH]^+$. Rather, minimization with a 2,1-phenyl shift gave a distorted 1-phosphaallyl cation, **1-P-allyl**. Reaction (a) is exothermic by $\Delta G_r^{298} = -66.6$ kcal mol^{-1} (zero-point energies and thermal corrections at 298 K were obtained from frequency calculations). C-protonation of **1**, reaction (b), is 20 kcal mol^{-1} less exothermic but leads to a cyclic structure that is best described as an intramolecular σ-complex between the phosphavinylium moiety and one phenyl group. The calculated C═P distance (1.680 Å) in ***σ*-Ph$_3$C−CH═P$^+$** is rather long when compared to the above-mentioned phosphavinylium ions (Chart 1, calculated distances <1.60 Å) and more typical of a P═C double bond. The P···C_{arene} interaction at 2.050 Å is considerably longer than usual P−C bonds (~1.86 Å, see also ref 10) but is not unusual for comparable σ-type complexes.[20] The stabilization provided by the P···C_{arene} interaction likely contributes to the elongated P═C double bond. Deprotonation of ***σ*-Ph$_3$C−CH═P$^+$** gives the 3*H*-phosphindole, **3*H*-P-indole**, but reaction (c) is endothermic by 28.9 kcal mol^{-1}.

The dissociation (d) of the triphenylmethyl (trityl) cation from ***σ*-Ph$_3$C−CH═P$^+$** is another reaction channel for this stabilized phosphavinyl cation (Scheme 2). This reaction is calculated to be exothermic by −15.5 kcal mol^{-1}, and hence, this would be an attractive new method to prepare the elusive H−C≡P.[21] However, a rather high activation barrier (25.3 kcal mol^{-1}) is predicted for this process so that 3*H*-phosphindole formation may compete with trityl cation dissociation (d). In light of these computational results, we decided to investigate synthetic methods for accessing phosphaalkyne **1**. To prevent P-protonation and rearrangement (a), we envisioned blocking this reaction pathway by complexation to an inert metal fragment. The following describes the outcome of our experimentation.

Scheme 2. Calculated Formation of H-CP



Scheme 3. Synthesis of New Phosphaalkyne **1**



Synthesis of Phosphaalkyne 1. While the isolation of numerous hydrocarbon-substituted phosphaalkynes, R−C≡P (R = ^{t}Bu,[22] adamantyl,[23] Mes = 2,4,6-$Me_3C_6H_2$,[24] Mes* = 2,4,6-$^t Bu_3C_6H_2$[25]) has been reported since the initial discovery of H−C≡P, their preparative methods can be cumbersome; isolated yields are often low, and their stability toward oligomerization is poor. Even the syntheses of ^{t}Bu-CP and Ad-CP require multiple steps, expensive reagents, and arduous reaction conditions. The conventional synthetic method for generating R−C≡P compounds utilizes $P(SiMe_3)_3$ and relies on a base-initiated elimination of hexamethyldisiloxane from an $R(Me_3SiO)C$═$PSiMe_3$ phosphaalkene.[26−28] Our attempts to synthesize the corresponding triphenylmethyl substituted phosphaalkene from the acid chloride Ph_3CCOCl and $P(SiMe_3)_3$ were unsuccessful. Alternatively, we explored a more economical, atom-efficient route for accessing phosphaalkynes. Scheme 3 outlines our approach, which exploits PCl_3 rather than $P(SiMe_3)_3$ as an abundant source of phosphorus.[29] From inexpensive and readily available reagents, two synthetic steps were required to access

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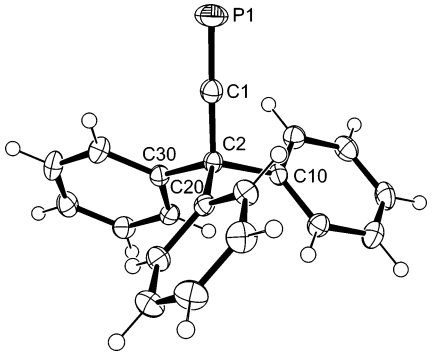

Figure 1. Structure of **1**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: P1−C1, 1.538(2); C1−C2, 1.485(2); P1−C1−C2, 178.5(2); C10−C2−C20, 111.4(1); C20−C2−C30, 110.5(1); C10−C2−C30, 110.1(1).

(2,2,2-triphenylethyl) phosphonous dichloride (**2**) in moderate yield (>58%) but on a multigram scale. Compound **2** was characterized by multinuclear NMR, IR, and mass spectroscopies, and EA.

Various reaction conditions and bases were screened in order to effect the dehydrochlorination of **2**. Treatment of **2** with anionic bases such as *tert*-butoxide or bis(trimethylsilyl)amide resulted in chloride substitution rather than deprotonation. Both *n*- and *tert*-butyl lithium reacted with **2** to give mixtures of inseparable products. Tertiary amines showed varied reactivity. While 1,9-bis(dimethylamino)-naphthalene (proton sponge) was unreactive toward **2**, the bicycloamines 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) reacted with **2** to give salts that were insoluble in nonpolar organic solvents and decomposed upon attempted isolation (similar reactivity has been reported[30,31]).

Treatment of **2** with 10 equiv of 1,8-diazabicyclo[2.2.2]octane (DABCO) in hot acetonitrile furnished one new product with a ^{31}P NMR chemical shift at $\delta = -48.2$ ppm, within the expected range for a phosphaalkyne. No intermediate species were observed when the reaction was monitored in situ by NMR spectroscopy. Identification of this product as $Ph_3CC{\equiv}P$ (**1**) was made by multinuclear NMR spectroscopies, MS, and single-crystal X-ray diffraction. Optimization of the reaction conditions allowed for the isolation of phosphaalkyne **1** on a multigram scale in approximately 64% yield.

Spectroscopic data for **1** are in accord with other known phosphaalkynes. A doublet in the ^{13}C NMR at $\delta = 177.6$ ppm ($^1J_{C-P} = 40.6$ Hz) was indicative of the alkynyl carbon. The β-carbon (C2) was found at $\delta = 64.0$ ppm ($^2J_{CP} = 18.7$ Hz) while the aryl carbon resonances were located in the region between 145 and 126 ppm. In the Raman spectrum, a strong signal at 1512 cm^{-1} was observed for the CP triple bond.

Colorless crystals suitable for X-ray diffraction were grown from a concentrated solution of **1** in toluene at −30 °C. A molecular representation of **1** is shown in Figure 1. The propeller-like orientation of the aryl substituents leaves the phosphorus−carbon triple bond unhindered. With a nearly linear P1−C2−C3 angle (178.50°) and a carbon−phosphorus bond length of 1.538 Å, the structure of **1** is similar to those of other phosphaalkynes.[32,33]

While the dehydrohalogenation reaction of **2** to synthesize **1** must be carried out under inert conditions, the product itself is stable and a sample of **1** in C_6D_6 showed no degradation after more than two weeks when exposed to air. With respect to the computed protonation reaction discussed above, reactions of **1** with various acids were studied. Remarkable was the inertness of **1** toward a 1 M solution of HCl etherate, as determined by the unchanged ^{1}H and ^{31}P NMR spectra. Reversion of **1** to the alkyl phosphonous dichloride **2** or a chloro-substituted phosphaalkene was never observed. Tosyl sulfonic acid (TsOH) was also unreactive with **1**. Protonation of **1** with stronger acids such as trifluoromethanesulfonic acid (TfOH) gave inconclusive results, even when the reaction was monitored in situ at low temperature by NMR spectroscopy. Lewis acids such as triphenyl- or perfluorophenyl borane showed no reactivity with **1**, whereas $GaCl_3$ reacted to give unidentifiable products.

Synthesis of Metal−Phosphaalkyne Complexes. The complexation of phosphaalkynes to transition metal centers is well-documented, and various coordination modes have been reported.[34,35] Typically, η^2-coordination to the metal via the phosphorus−carbon π-bond is observed.[36] Only when bulky ligands surround the metal center is the less common η^1- or σ-coordination mode (via the lone pair of electrons at phosphorus) observed.[37−40] We envisioned that by coordination of **1** to a metal, protonation would selectively occur at the carbon center, thus eliminating undesired side reactions. The choice to use the $MH(dppe)_2^+$ fragment (dppe = 1,2-bis(diphenylphosphino)ethane) was based upon the easily accessible starting materials, convenience of having numerous NMR active nuclei with which to monitor the reaction, and the sheltered pocket around the metal created by the dppe ligands which leaves one open coordination site when M has a d^6 electronic configuration. Furthermore, Nixon et al. previously employed $FeH(dppe)_2^+$ to successfully isolate an η^1-complex with ^{t}Bu-C≡P.[40,41]

Coordination of **1** to iron and ruthenium cations was straightforward. Treatment of $[MH(dppe)_2]^+$ with **1** in dichloromethane[42] furnished the desired iron(II) (**3**) and ruthenium(II) (**4**) complexes in almost quantitative yield (Scheme 4). Confirmation that the phosphaalkyne coordinated to the metal center was obtained via ^{31}P{^{1}H} NMR spectroscopy; a new quintet was observed at a higher frequency relative to free **1** [**3**: $\delta = 0.94$ ppm, (qnt, $^2J_{PP} = 35.1$ Hz). **4**: $\delta = -27.3$ ppm, (qnt, $^2J_{PP} = 27.5$ Hz)]. Further evidence for the complexation of **1** to the metal was seen by the AXY_4 splitting pattern of the hydride resonance in the ^{1}H NMR spectrum. Coupling of the hydride ligand to both the coordinated phosphaalkyne and four chemically equivalent phosphorus nuclei of the ancillary dppe ligands resulted in the observed doublet of quintets and indicated that

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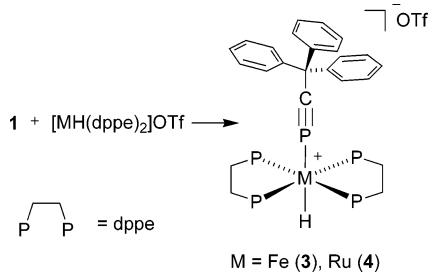
(42) The Fe(II) cation was synthesized in situ after salt metathesis with KOTf. See Experimental Section for details.

Scheme 4. Coordination of **1** to Fe and Ru Cations



the phosphaalkyne was coordinated trans to the hydride [**3**: $\delta = -12.03$ ppm; **4**: $\delta = -9.44$ ppm]. The magnitude of the trans H−P coupling was significantly larger for ruthenium complex **4** (*trans*-$^2J_{HP} = 129.6$ Hz) compared to iron complex **3** (*trans*-$^2J_{HP} = 58.6$ Hz); the latter being comparable to the value reported for $[FeH(dppe)_2(^tBu\text{-}C{\equiv}P)]^+$.[40] The cis couplings showed the opposite behavior and are larger for **3** (*cis*-$^2J_{HP} = 52.8$ Hz) when compared to **4** (*cis*-$^2J_{HP} = 17.4$ Hz).

Both solids could be crystallized from CH_2Cl_2 layered with hexane or THF layer with toluene at room temperature. Yellow crystals of **3** suitable for X-ray analysis were obtained from a supersaturated toluene solution. A molecular representation is depicted in Figure 2. The results of the study confirm an η^1-coordination of **1** to iron. The Fe−P1 (phosphaalkyne) bond length of 2.165(6) Å is slightly longer than in the analogous $[FeH(dppe)_2(^tBu\text{-}C{\equiv}P)]^+$ complex.[40] The P≡C bond (1.535(2) Å) does not change significantly upon coordination to iron. A slight bend in the P−C−C bond angle of coordinated **1** is observed in the solid state, although the overall geometry remains linear.

Complexes **3** and **4** were both found to be stable toward water. Iron complex **3** reacted with TfOH or MeOTf to give large amounts of unidentifiable paramagnetic products (vide infra). The reactivity of ruthenium complex **4**, however, was more easily monitored due to the preferred low spin d^6 electronic configuration. Therefore, our initial focus was on this complex.

Phosphindole Synthesis. The reaction of **4** with strong acids such as TfOH or TsOH at low temperature in CD_2Cl_2 resulted in the formation of one new product, compound **5**. A quintet at $\delta = 232$ ppm accompanied by a doublet at $\delta = 62$ ppm was observed by $^{31}P\{^1H\}$ NMR spectroscopy. In the ^1H-coupled ^{31}P NMR spectrum, the signal at $\delta = 232$ became a complex multiplet with coupling to at least three hydrogen nuclei. The ^1H NMR spectrum of this new product exhibited equally complex resonances. While a doublet of quintets at $\delta = -8.57$ ppm indicated a hydride ligand cis to two dppe ligands and trans to one additional phosphorus nucleus, numerous other resonances ranging from $\delta = 8.2$ to 5.32 ppm did not give a clear indication of the new product.

Multinuclear 2-D NMR experiments (HMQC, TOCSY, NOESY) were used to elucidate the structure of **5**. From the $^1H-^{31}P$ HMQC correlation experiment, strong coupling was observed between the doublet at $\delta(^1H) = 8.2$ ppm and the multiplet at $\delta(^{31}P) = 232$ ppm with $J_{HP} = 26.8$ Hz. Three aryl proton resonances at $\delta = 6.65$, 6.00, and 5.38 ppm were also found to have cross-peaks with the signal at $\delta(^{31}P) = 232$ ppm. On the basis of the $^1H-^{13}C$ correlation experiment, it was determined that the proton resonating at $\delta = 8.2$ ppm was bonded to a carbon found at $\delta = 172.4$ ppm ($J_{C-P} = 36.5$ Hz).

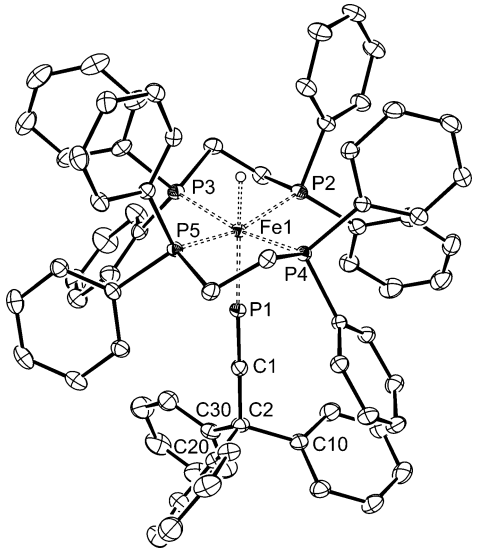


Figure 2. Structure of the cationic portion of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [deg]: P1−C1, 1.535(2); C1−C2, 1.495(3); Fe1−P1, 2.1645(6); Fe1−P2, 2.2704(6); Fe1−P3, 2.2902(6); Fe1−P4, 2.2792(6); Fe1−P5, 2.2683(6); P1−C1−C2, 174.6(2); C1−P1−Fe1, 172.95(9) C1−C2−C20, 107.6(2); C20−C2−C30, 110.9(2); C10−C2−C30, 108.7(2); P1−Fe1−P2, 97.57(2); P1−Fe1−P3, 96.95(2); P1−Fe1−P4, 95.05(2); P1−Fe1−P5, 97.15(2); P2−Fe1−P3, 84.45(2); P3−Fe1−P5, 93.74(2); P5−Fe1−P4, 83.71(2); P4−Fe1−P2, 95.01(2).

Additional 2-D NMR experiments suggested that two aryl rings of the coordinated phosphaalkyne ligand remained equivalent while the third was significantly perturbed compared to **4** and also lacked a fifth proton. All the NMR data suggested the formation of a new phosphaalkene heterocycle in which one aryl ring of the Ph_3C group underwent an electrophilic aromatic cyclization reaction to furnish a coordinated 3,3-diphenyl-3*H*-phosphindole (**7**) in nearly quantitative yield.

By slow evaporation of a THF/toluene solution of **5**, crystals suitable for X-ray analysis were obtained. The results confirm the structure of the new heterocyclic ligand coordinated to ruthenium (Figure 3). The trigonal planar geometry around the coordinated phosphorus is expected for such a phosphindole. Selected bond lengths and angles are given in the caption.[43]

In view of the computational results discussed above, we propose that the formation of **5** occurs upon protonation at the alkynyl carbon C2, to give a highly electrophilic Ru-complexed phosphavinylium ion (Scheme 5). As seen in the free ion ***σ*-$Ph_3C-CH{=}P^+$**, stabilization of this intermediate phosphavinylium cation complex by π-arene interaction leads to an electrophilic aromatic cyclization reaction. This reaction resembles the Bischler-Napieralski ring closure, in which the carbon atom of a nitrilium group is attacked by an internal nucleophile.[44]

Attempts were made to isolate the free 3*H*-phosphindole **7**. Thermolysis of an acetonitrile solution of **5** gave no reaction even with added chloride until above 120 °C, at which point much decomposition occurred. However, photolysis of **5** in a solution of CH_3CN using a medium pressure Hg lamp gave cleanly the acetonitrile adduct $[RuH(dppe)_2(CH_3CN)]^+$ (**8**) and a new phosphorus product (**9**) with a ^{31}P NMR chemical shift

(43) An uncoordinated 3,3-dimethyl-3*H*-phosphindole was reportedly synthesized by gas-phase pyrolysis. See: Aitken, R. A.; Clasper, P. N.; Wilson, N. J. *Tetrahedron Lett.* **1999**, *40*, 5271.
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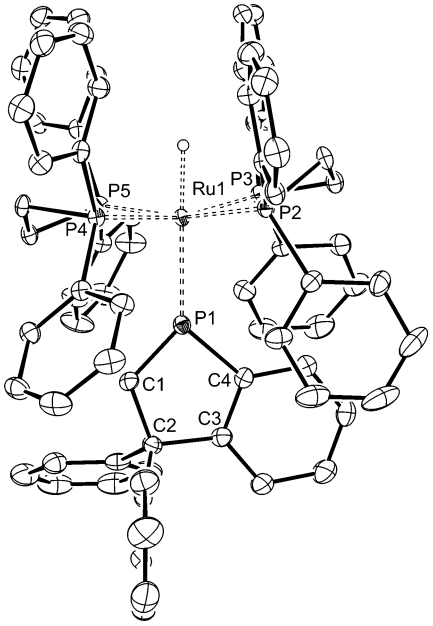
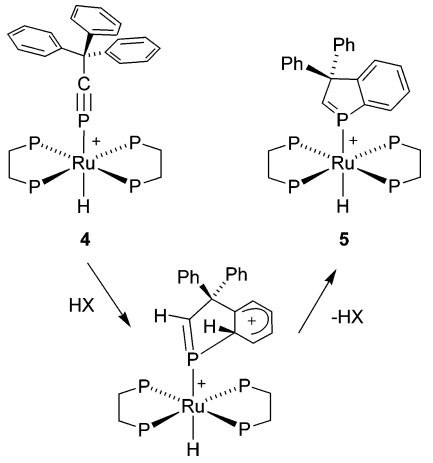
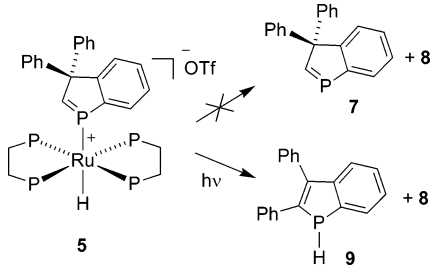


Figure 3. Structure of the cationic portion of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [deg]: P1−C1, 1.664(4); C1−C2, 1.519(5); C2−C3, 1.525(6); C3−C4, 1.392(6); C4−P1, 1.819(4); Ru1−P1, 2.327(2); Ru1−P2, 2.351(1); Ru1−P3, 2.369(1); Ru1−P4, 2.370(1); Ru1−P5, 2.372(1); P1−C1−C2, 116.5(3); C1−C2−C3, 105.1(3); C2−C3−C4, 114.9(4); C3−C4−P1, 111.1(3); C4−P1−C1, 92.4(2); P1−Ru1−P2, 99.38(4); P1−Ru1−P3, 97.38(4); P1−Ru1−P4, 94.90(4); P1−Ru1−P5, 92.07(4); P2−Ru1−P3, 83.29(5); P3−Ru1−P5, 95.09(5); P5−Ru1−P4, 82.64(5); P4−Ru1−P2, 96.51(5).

Scheme 5. Proposed Mechanism for Electrophilic Aromatic Cyclization Reaction



Scheme 6. Release of 1*H*-Phosphindole from Ruthenium Complex **5**



of $\delta = -50$ ppm after only 15 min (Scheme 6). In the ^{1}H-coupled ^{31}P NMR spectrum, this signal appeared as a doublet with a large $^1J_{H-P} = 205.5$ Hz. Separation of product **9** from the ruthenium cation **8** was achieved by simply removing the volatile materials under reduced pressure followed by extraction with diethyl ether. Using 2-D NMR spectroscopy, the structure of **9** was determined to be the rearranged 1*H*-phosphindole, rather than the 3*H*-phosphindole **7**, which would arise from simple cleavage of the Ru−P bond. To confirm the identity of **9**, single crystals suitable for X-ray analysis were grown from a concentrated solution in diethyl ether at −30 °C. As predicted from NMR spectroscopic data, the structure of 2,3-diphenyl-1*H*-phosphindole (**9**) was confirmed by a single-crystal X-ray diffraction study and, to the best of our knowledge, is the first structurally characterized 1*H*-phosphindole (Figure 4).

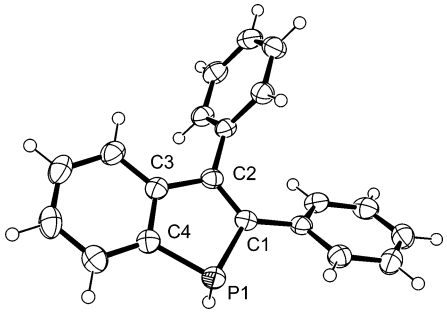
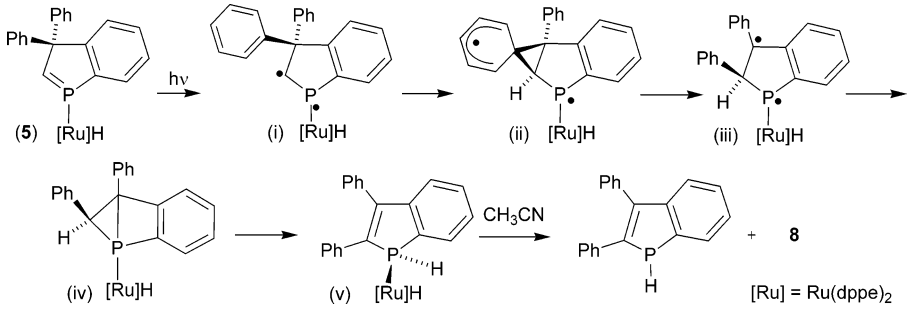


Figure 4. Structure of **9**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: P1−C1, 1.830(2); C1−C2, 1.357(2); C2−C3, 1.467(2); C3−C4, 1.410(3); C4−P1, 1.808(2); P1−C1−C2, 111.5(1); C1−C2−C3, 113.9(2); C2−C3−C4, 113.5(2); C3−C4−P1, 110.3 (1); C4−P1−C1, 90.36(8).

Note that, in the course of the remarkable 3*H*-phosphindole → 1*H*-phosphindole transformation, the C=P bond, the C-bonded hydrogen center, and one phenyl group are shifted. What role does the Ru center play in this process and is this exclusively a photochemical reaction? To address these questions, isolation of the uncomplexed 3*H*-phosphindole **7** was required. Therefore, we repeated the protonation reaction of iron phosphaalkyne complex **3** with TfOH in CH_2Cl_2 at −78 °C. After removal of large amounts of paramagnetic material via filtration through basic alumina, we were able to isolate the desired iron−phosphindole adduct [FeH(dppe)$_2$(**7**)]OTf (**6**) in 44% yield. Heating a CH_3CN solution of **6** to 75 °C gave the desired 3*H*-phosphindole **7** and [FeH(dppe)$_2$(CH_3CN)][OTf] in quantitative yield after 18 h. In comparison to the Ru analogue, this cleavage reaction was permissible due to the higher lability of first row transition metal complexes.

With pure 3,3-diphenyl-3*H*-phosphindole **7** in hand, we investigated its photochemical reactivity. Irradiation of a CH_2Cl_2 solution of **7** for 10 min furnished a mixture of products, including 1*H*-phosphindole **9** in less than 30% yield. This result contrasts with the nearly quantitative photochemical reaction of ruthenium adduct **5**. Furthermore, irradiation of **7** in the presence of 10 equiv of sensitizer (anthracene or benzophenone) did not result in higher conversion to **9**. Finally, when **7** was added to a CD_3CN solution of [RuH(dppe)$_2$]OTf, only the solvated ruthenium cation [RuH(dppe)$_2$(CD_3CN)]$^+$ and free **7** were observed by NMR spectroscopy. Displacement of CD_3CN from ruthenium by **7** to furnish **5** did not occur. Irradiation of this solution for 10 min resulted in partial consumption of **7**. Clean formation of **9** was *not* observed. Had irradiation of this mixture resulted in complete conversion of free 3*H*-phosphindole **7** to 1*H*-phosphindole **9**, we would have concluded that in the original photochemical reaction (1) displacement of **7** from

Scheme 7. Proposed Photochemical Rearrangement of 3*H*- to 1*H*-Phosphindole via Phenyl Migration



$[RuH(dppe)_2(\mathbf{7})]^+$ occurred followed by (2) rearrangement of uncoordinated **7** to give **9** via a *photoinduced energy transfer from ruthenium*. Since very little rearranged product was observed when $[RuH(dppe)_2(CD_3CN)]^+$ and **7** were irradiated, we conclude that the photochemical rearrangement occurs when the phosphindole is coordinated to ruthenium.

Our proposed mechanism for this rearrangement is based on the known photoreactivity of 4,4-diphenylcyclohexanones, extensively studied by Zimmerman and co-workers (Scheme 7).[45−48] Upon irradiation of **5**, the diradical is formed (i). Migration of the adjacent phenyl ring (ii) gives the more stable dibenzyl radical (iii). Collapse of the radical generates a phosphirane (iv), which then ring opens simultaneously with the 5,1-*H*-sigmatropic shift (v). (Phosphirane → vinyl phosphine conversion has precedent, albeit at elevated temperatures.[49−51] It is plausible that the metal center lowers the activation energy for such a process or that it occurs from a photoexcited state.) Last, displacement of **7** from the ruthenium cation with solvent furnishes the observed 1*H*-phosphindole and the solvated species $[RuH(dppe)_2(CH_3CN)]^+$.

We calculated the structures of the 1*H*-phosphindole, 2*H*-phosphindole, and 3*H*-phosphindole using DFT theory (B3LYP/6-31+G*), and the results are shown in Figure 5.[52,53] The agreement between the experimental structure of **9** and the computed parent 1*H*-phosphindole is very good with the exception of the P1−C4 bond, which is about 0.03 Å shorter in **9**. Also, the agreement between the structural parameters of the coordinated 3,3-diphenyl-3*H*-phosphindole in **4** and the parent 3*H*-phosphindole is satisfactory. As expected, benz-annulation of the phosphole changes the stability order from: 2*H*-phosphole > 1*H*-phosphole > 3*H*-phosphole[53] to 1*H*-phosphindole (0.0 kcal mol^{-1}) > 3*H*-phosphindole (1.1 kcal mol^{-1}) > 2*H*-phosphindole (14.3 kcal mol^{-1}). The latter is especially high in energy because of severe perturbation of the π-system of the benzo group by the exocyclic C═C and C═P moieties in the five-membered ring. From these calculations, it appears that the photochemical "Phospha-Zimmerman rearrangement" is nearly thermoneutral.

Last, we investigated whether the transformation of $Ph_3CC{\equiv}P$ to **7** or **9** could be achieved catalytically. While this has not yet been realized, some preliminary results are notable: (1) A stoichiometric amount of acid is required for the cyclization reaction of ruthenium adduct **4** to the cyclized product **5**. (2) Irradiation of pure ruthenium−phosphindole adduct **5** in CH_2Cl_2 with added $Ph_3CC{\equiv}P$ furnishes 1*H*-phosphindole **9** and ruthenium−phosphaalkyne **4** quantitatively. (3) When a CH_3CN (or CD_3CN) solution of $Ph_3CC{\equiv}P$, TsOH, and ruthenium−acetonitrile adduct **8** is allowed to mix at ambient temperature for 2 days (or at 60 °C for 12 h), the cyclized product **5** is formed in quantitative yield.[54] (4) If this same sample containing **5** and acid is then irradiated, only decomposition occurs. The acid must first be removed from the reaction mixture before irradiation. (5) Other soft Lewis acids (e.g., Ni^{2+}, Pd^{2+}, Cu^+, Ag^+, Au^+) either have shown no reactivity toward **1** or result in decomposition of all starting materials with or without added acid. Formally, however, the synthesis of **9** has been achieved through

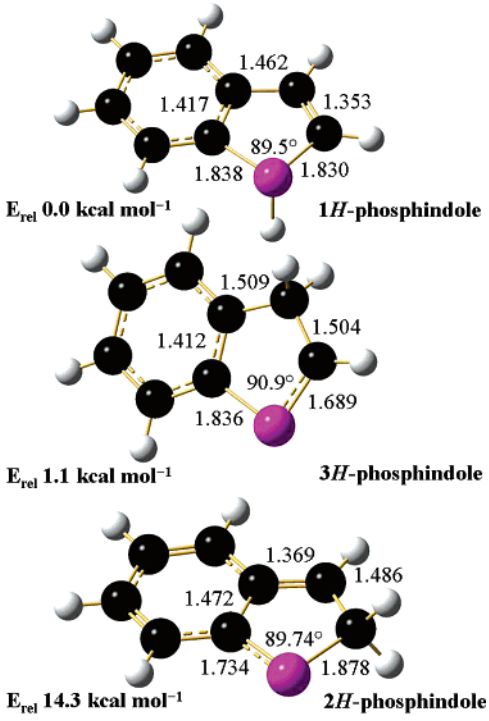


Figure 5. Computed structures and relative energies of 1*H*-phosphindole, 3*H*-phosphindole, and 2*H*-phosphindole obtained from DFT using the B3LYP functional at the 6-31+G* level of theory.

(45) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036.
(46) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033.
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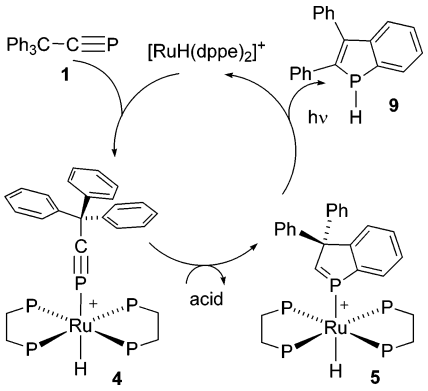
(51) Haber, S.; Lefloch, P.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1799.
(52) Computations of phospholes at the MP2/6-31G* level gave the stability order: 2*H*-phosphole (0.0 kcal mol^{-1}) > 3*H*-phosphole (3.7 kcal mol^{-1}) > 1*H*-phosphole (6.5 kcal mol^{-1}). See: Bachrach, S. M. *J. Org. Chem.* **1993**, *58*, 5414.
(53) Using B3LYP/6-31G*, we satisfactorily reproduced previous results obtained for the comparable series of phospholes at the B3LYP/aug-cc-pVTZ level. For these nonbenzannulated heterocycles, the stability order follows: 2*H*-phosphole (0.0 *(0.0)* kcal mol^{-1}) > 1*H*-phosphole [2.7 *(2.2)* kcal mol^{-1}] > 3*H*-phosphole (4.2 *(3.9)* kcal mol^{-1}); values in italics at B3LYP/aug-cc-pVTZ. See: Ozimi_ski, W. P.; Dobrowolski, J. C. *Chem. Phys.* **2005**, *313*, 123.

Scheme 8. Synthetic Cycle for the Conversion of Phosphaalkyne **1** to 1*H*-Phosphindole **9**



a synthetic cycle by treating the isolated acetonitrile adduct **8** with $Ph_3CC{\equiv}P$ in CH_2Cl_2 followed by addition of TfOH at low temperature to give 3*H*-phosphindole adduct **5**. After removal of the volatile materials under reduced pressure and a quick wash of the solid with diethyl ether, photolysis of **5** in CH_3CN furnished **8** and free heterocycle **9** in greater than 90% yield (Scheme 8). Theoretically, this cycle could be repeated indefinitely.

Conclusion

A straightforward synthesis of the sterically protected triphenylmethyl substituted phosphaalkyne $Ph_3CC{\equiv}P$ has been presented. This crystalline compound was reacted with two group 8 organometallic cations to furnish the η^1-coordinated complexes $[MH(dppe)_2(Ph_3CC{\equiv}P)]OTf$, where M = Fe (**3**) or Ru (**4**). Both of these compounds reacted with strong acids to give the first example of an electrophilic aromatic substitution reaction in which the electrophile originated from a phosphaalkyne. Irradiation or thermolysis of the metal complexes yielded the free phosphindole heterocycle, and in the former case, a photochemical rearrangement occurred providing access to the 1*H*-phosphole in nearly quantitative yield. With the aid of DFT calculations, we were able to gain a more thorough understanding of the energetics and mechanism of this new cyclization reaction.

The phosphorus electrophilic aromatic cyclization reaction and the photochemical "Phospha-Zimmerman reaction" presented in this article provide yet other examples of the carbon−phosphorus analogy. The diagonal relationship between these two elements demonstrates once again that "classic" organic chemistry is not only reserved for carbon but can be extended to other main group elements, especially phosphorus in its low valence states. The potential of synthesizing other phosphorus heterocycles from phosphaalkynes is yet to be realized, and efforts into this field are sure to be rewarding.

Experimental Section

General. All experiments were performed using standard Schlenk and vacuum line techniques or in a Braun glovebox under an inert atmosphere of Ar in 20-mL scintillation vials unless otherwise noted. Glassware was dried at 120 °C overnight prior to use. All reagents were used as received from commercial suppliers unless otherwise noted. All solvents were distilled under Ar from the appropriate drying agent and stored over 3 Å molecular sieves prior to use. Deuterated solvents were purchased from Euriso-top, degassed and distilled from the proper drying agent, and stored over 3 Å sieves. Silica gel, alumina, and diatomaceous earth (Celite) used for chromatography or filtrations were dried under vacuum at 240 °C for 2 days and stored in the glovebox.

All NMR spectra were recorded on Bruker Avance spectrometers. Chemical shifts (δ) are expressed in parts per million (ppm). ^{1}H NMR spectra were recorded at 500, 400, 300, or 250 MHz, and chemical shifts were referenced to the residual protiated solvent peak. ^{13}C NMR spectra are proton-decoupled and were recorded at 75.5 MHz; chemical shifts were referenced to the solvent. ^{19}F NMR spectra were recorded at 188 MHz, and chemical shifts are reported relative to an external standard of $CFCl_3$. ^{31}P NMR spectra were recorded at 121.5 or 101.3 MHz; chemical shifts were referenced to an external standard of H_3PO_4. Coupling constants J are given in hertz as absolute values, unless specifically stated. Where a first-order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, qnt, or m for singlets, doublets, triplets, quartets, quintets, or multiplets, unless otherwise specified.

IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR Raman spectrometer with KBr beam splitter (range 500−4000 cm^{-1}) using the ATR technique. The absorption bands are described as follows: very strong (vs), strong (s), medium (m), weak (w), or broad (br). Mass spectra were recorded on a Finnigan MAT SSQ 7000 mass spectrometer. Melting points were determined with a Büchi melting point apparatus and are not corrected. Samples were prepared in open glass capillaries.

The following compounds were synthesized according to literature procedure: Ph_3CCH_2Cl,[55] $FeHCl(dppe)_2$,[56] $RuH_2(dppe)_2$, and $[RuH(dppe)_2][BF_4]$.[57] $[RuH(dppe)_2][OTf]$ was made via anion metathesis of $[RuH(dppe)_2][BF_4]$ in THF using KOTf (1.2 mol equiv) followed by filtration through diatomaceous earth to remove the precipitated KBF_4.

(2,2,2-Triphenylethyl)phosphonous Dichloride (2). Following a literature procedure, 1-chloro-2,2,2-triphenylethane (14.0 g, 0.0478 mol) was converted to the Grignard reagent using freshly ground Mg turnings (ca. 10 g) in THF.[55] The Grignard was cannula transferred to a solution of PCl_3 (12.6 mL, 0.144 mol) in THF (75 mL) cooled to −15 °C over 1 h. The resulting mixture was allowed to warm to room temperature over 4 h. The volatile materials were removed under reduced pressure, giving a grayish-black solid. The product was extracted with diethyl ether (ca. 300 mL) and filtered through diatomaceous earth on a medium-pore fitted glass frit. The volatile materials were removed under reduced pressure to give a yellow solid. The solid was dissolved in hot toluene (ca. 50 mL) and cooled to −20 °C for crystallization. After 1 day, white microcrystals grew. The mother liquor was removed via cannula and saved for further crops. The crystals were washed with cold toluene, combining the toluene with the mother liquor. Excess solvent was removed under reduced pressure. Crop 1 yield: 6.31 g (36.6%). Further crops were obtained from the combined mother liquors. Total yield: 10.0 g (57.5%). Mp 122−124 °C. ^{1}H NMR (C_6D_6): δ 7.22 (d, ^3J = 7.2 Hz, 6H), 7.06 (m, 9H), 3.88 (d, $^2J_{HP}$ = 4.12 Hz, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.1 (d, $^3J_{CP}$ = 3.8 Hz, C_{ipso}), 129.2 (d, J_{CP} = 3.8 Hz, C_{aryl}), 128.7 (C_{aryl}), 127.1 (C_{aryl}), 58.7 (d, $^1J_{C-P}$ = 52.9 Hz, $-CH_2-PCl_2$), 56.7 (d, $^2J_{CP}$ = 17.7 Hz, $Ph_3C-CH_2PCl_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 185.8. IR (solid ATR): 3055 (w), 3018 (w), 1490 (s), 1440 (s), 1406 (m), 1189 (m), 1158 (m), 1085 (m), 1032 (m), 1001, 767 (s), 752 (s), 696 (s). Anal. Calcd for $C_{20}H_{17}Cl_2P$: C, 66.87; H, 4.77. Found: C, 67.04; H, 5.06. EI HRMS: m/z calcd for $C_{20}H_{17}Cl_2P$, 358.04449 $[M]^+$; found, 358.0443.

(54) The analogous reaction with $[FeH(dppe)_2(CH_3CN)]^+$ does not work.

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(56) Giannoccaro, P.; Sacco, A.; Ittel, S. D.; Cushing, M. A., Jr. *Inorg. Synth.* **1977**, *17*, 69.
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2,2,2-Triphenylmethylphosphaalkyne (1). A 300-mL flask equipped with a resealable Teflon stopper and a stir bar was charged with **2** (2.9 g, 8.1 mmol) and CH_3CN (150 mL). The solution was heated to just below reflux (ca. 75 °C). A 150-mL flask equipped with a resealable Teflon stopper was charged with DABCO (9.8 g, 81 mmol) and CH_3CN (50 mL). Both Teflon stoppers were replaced with rubber septa. The solution of DABCO was heated until all DABCO dissolved. The DABCO solution was then slowly added to the solution of **2** at 75 °C via cannula, over 30 min. *Reversing the addition resulted in large amounts of unidentified side products.* Upon addition of DABCO, the solution turned yellow and generated a white vapor. After stirring the solution at 75 °C for 4 h, the volatile materials were removed under reduced pressure to leave an orange-yellow solid. Toluene (50 mL) and a saturated, O_2-free aqueous solution of NH_4Cl (50 mL) were added. After 4 × 15 mL toluene extractions, the toluene extracts were combined and the volatile materials were removed under reduced pressure. The crude product was redissolved in toluene (ca. 20 mL) and filtered through a pad of basic alumina (I) on a medium-pore fitted glass frit eluting with 40 mL of toluene. The solvent was concentrated to ca. 10 mL and cooled to −30 °C for crystallization. Faint yellow microcrystals grew after 1 day. The mother liquor was decanted away from the solid and saved. The solid was washed with cold toluene (2 × 5 mL) and then cold Et_2O (3 × 5 mL), combining the washes with the mother liquor. Excess solvent was removed from the solid under reduced pressure to furnish analytically pure material. Yield: 1.98 g (39.6.9%). Additional crops were isolated from the mother liquor. Combined yields were typically > 60%. Mp 130−132 °C. ^{1}H NMR (C_6D_6): δ 7.40 (dd, J = 7.5, 1.5 Hz, 6H), 7.04 (m, 9H). ^{1}H NMR (THF-d_8): δ 7.30−7.20 (m, 15H). ^{13}C{^{1}H} NMR (THF-d_8): δ 177.6 (d, $^1J_{C-P}$ = 40.6 Hz), 145.2 (d, $^3J_{CP}$ = 5.9 Hz), 129.5, 128.2, 127.2, 64.0 (d, $^2J_{CP}$ = 18.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −48.1. ^{31}P{^{1}H} NMR (THF-d_8): δ −47.8. IR (solid ATR): 3029 (w), 3056 (w), 1593 (m, P≡C), 1489 (s), 1443 (s), 1181 (w), 1158 (w), 1080 (m), 1030 (m), 1002 (w), 763 (m), 746 (vs), 695 (vs), 635 (s). Anal. Calcd for $C_{20}H_{15}P$: C, 83.90; H, 5.28. Found: C, 83.90; H, 5.38. EI HRMS: *m*/*z* calcd for $C_{20}H_{15}P$, 286.09114 $[M]^+$; found, 286.0905. Crystals suitable for X-ray analysis were grown from a toluene solution at −30 °C.

[FeH(dppe)$_2$(Ph$_3$CC≡P)]OTf (3). A 200-mL Schlenk flask was charged with $FeHCl(dppe)_2$ (0.811 g, 0.91 mmol), KOTf (0.206 g, 1.09 mmol), **1** (0.313 g, 1.09 mmol), and 60 mL of dichloromethane. The dark purple-red solution was stirred for 18 h, at which point it turned orange. The organic layer was washed with three 20 mL portions of O_2-free water and then dried with $MgSO_4$. After filtration, the volatile materials were removed under reduced pressure. The resulting red solid was washed with diethyl ether (3 × 15 mL), and excess solvent was removed under reduced pressure. Yield: 1.09 (91.2%). Mp 201−204 °C. ^{1}H NMR (CD_2Cl_2): δ 7.4−7.2 (m, 33H), 7.1−6.95 (m, 14H), 6.93 (t, J_{H-H} = 7.5 Hz, 8H), 2.45 (b, 4H), 2.12 (b, 4H), −12.03 (dqnt, *trans*-$^2J_{PH}$ = 58.2 Hz, *cis*-$^2J_{PH}$ = 52.8 Hz, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 173.3 (d, $^1J_{C-P}$ = 136.1 Hz), 145.8 (d, $^3J_{CP}$ = 9.8 Hz), 135.0 (m), 134.5 (m) 133.1, 131.1, 130.7, 130.4, 129.3, 128.4, 128.1, 128.0, 126.9, 66.4 (d, $^2J_{CP}$ = 9.9 Hz), 32.6 (qnt, $^1J_{C-P} \approx$ 12 Hz). ^{19}F NMR (CD_2Cl_2): δ −78.5. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 78.8 (d, $^2J_{PP}$ = 35.1 Hz), 0.94 (qnt, $^2J_{PP}$ = 35.1 Hz). IR (solid ATR): 3059 (w), 2977 (w), 1486 (m), 1433 (m), 1265 (vs), 1143 (m), 1031 (s), 1001 (m), 882 (m), 741 (s), 691 (vs), 635 (vs). X-ray quality crystals were grown from a solution of **3** in CH_2Cl_2 layered with hexane. Anal. Calcd for $C_{77}H_{74}F_3FeO_4P_5S$ (with 1 equiv of Et_2O): C, 67.84; H, 5.42. Found: C, 67.25; H, 5.22.

[RuH(dppe)$_2$(Ph$_3$CC≡P)]OTf (4). A 20-mL vial equipped with a stir bar was charged with $[RuH(dppe)_2]OTf$ (0.200 g, 0.19 mmol) and THF (10 mL). To the resulting orange suspension was added **1** (0.057 g, 0.200 mmol), and the mixture was stirred. After 10 min, the solution was filtered through diatomaceous earth eluting with THF. The solution was concentrated to approximately 8 mL, layered with 8 mL of toluene, and let evaporate slowly. After 1 day, large crystals grew. The mother liquor was removed via pipet, and the solid was washed with cold THF. Excess solvent was removed under reduced pressure, furnishing analytically pure colorless crystalline material. Yield: 0.237 g (93.3%). Mp > 180 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.31−7.20 (m, 33H) 7.00 (m, 16H), 6.57 (d, J = 6.9 Hz, 6H), 2.48 (br, 4H), 2.13 (br, 4H), −9.44 (dqnt, *trans*-$^2J_{HP}$ = 129.6, *cis*-$^2J_{HP}$ = 17.4 Hz, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 171.3 (d, $^1J_{C-P}$ = 122.8 Hz) 145.5 (d, $^1J_{C-P}$ = 10.5 Hz), 134.2 (m), 134.0 (m) 132.9, 132.7, 130.6, 129.2, 128.7, 128.3, 128.0, 126.5, 65.5 (d, $^3J_{CP}$ = 12.3 Hz), 31.2 (qnt, $^1J_{C-P}$ = 12.6 Hz) (one aryl carbon signal could not be resolved). ^{19}F NMR (CD_2Cl_2): δ −78.5. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 60.2 (d, $^2J_{PP}$ = 27.5 Hz), −27.3 (qnt, $^2J_{PP}$ = 27.5 Hz). IR (solid ATR): 3057 (w), 1486 (m), 1435 (s), 1266 (vs), 1224 (s), 1151 (s), 1092 (s), 1030 (vs), 1000 (m), 878 (m), 819 (m), 742 (s), 692 (vs), 674 (s), 636 (vs). Anal. Calcd for $C_{73}H_{64}F_3O_3P_5RuS$: C, 65.71; H, 4.83. Found: C, 65.86; H, 5.02.

(The BF_4 salt could be made in a similar fashion starting from $[RuH(dppe)_2]BF_4$. Mp 195 °C.)

[RuH(dppe)$_2$(3,3-diphenylphosphindole)]OTf (5). A 100-mL Schlenk flask equipped with a stir bar was charged with **4** (0.257 g, 0.200 mmol) and CH_2Cl_2 (ca. 25 mL). The solution was cooled to ca. −78 °C, and TfOH (20 μL, 0.22 mmol) was added via a gastight syringe. The resulting yellow solution was allowed to warm slowly to ambient temperature. After being stirred for 18 h, the volatile materials were removed under reduced pressure. The crude product was washed with diethyl ether (3 × 20 mL), and excess solvent was removed under reduced pressure. The solid was dissolved in CH_2Cl_2 (20 mL) and cannula filtered to a narrow (ca. 4 cm diameter) Schlenk tube. The volume was reduced to ca. 10 mL and then carefully layered with hexane (ca. 20 mL). After 2 days, medium-sized colorless needles grew. The mother liquor was removed via cannula, and excess solvent was removed under reduced pressure. Yield: 0.241 g (89.3%). Mp 208 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.19 (d, $^2J_{HP}$ = 26.4 Hz, 1H), 7.49−7.0 (m, 34H), 6.82−6.21 (m, 17H), 6.63 (t, J_{HH} = 7.4 Hz, 1H), 5.99 (dt, J_{HH} = 7.4, 2.1 Hz, 1H), 5.32 (t, J_{HH} = 7.8 Hz, 1H), 3.02 (b, 4H), 2.51 (b, 4H), −8.56 (dqnt, $^2J_{HP}$ = 87.2, 19.8 Hz, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 172.4 (d, $^1J_{C-P}$ = 36.3 Hz), 152.7 (d, $^3J_{CP}$ = 5.6 Hz), 144.1 (d, J_{CP} = 10.3 Hz), 139.1 (d, $^1J_{C-P}$ = 17.8 Hz), 135.9 (b), 134.8 (b), 132.7 (s), 132.2 (s), 130.2 (s), 128.8 (d, $^2J_{CP}$ = 14.3 Hz), 128.6 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.2 (s), 126.4 (d, $^4J_{CP}$ = 5.4 Hz), 126.0 (d, $^3J_{CP}$ = 7.0 Hz), 124.8 (d, $^3J_{CP}$ = 10.8 Hz), 72.5 (d, $^2J_{CP}$ = 9.4 Hz), 33.5 (m, $^1J_{C-P} \approx$ 13 Hz). ^{19}F NMR (CD_2Cl_2): δ −78.8. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 232.0 (qnt, $^2J_{PP}$ = 24.5 Hz), 63.1 (d, $^2J_{PP}$ = 24.5 Hz). IR (solid ATR): 3053 (w), 1485 (m), 1434 (s), 1260 (vs), 1222 (m), 1188 (m), 1148 (m), 1091 (s), 1029 (vs), 873 (w), 812 (m), 741 (s), 693 (vs), 670 (s), 635 (vs). Anal. Calcd for $C_{73}H_{64}F_3O_3P_5RuS$: C, 65.71; H, 4.83. Found: C, 65.50; H, 5.01. Crystals suitable for X-ray analysis were grown by slow evaporation of a THF/toluene solution of **5**.

[FeH(dppe)$_2$(3,3-diphenylphosphindole)]OTf (6). A 100-mL Schlenk flask equipped with a stir bar was charged with **3** (0.290 g, 0.223 mmol) and CH_2Cl_2 (ca. 30 mL). The solution was cooled to ca. −78 °C, and TfOH (20 μL) was added via a gastight syringe. The resulting solution was slowly warmed to ambient temperature over 3 h. The volatile materials were removed under reduced pressure, and the residue was washed with diethyl ether (3 × 20 mL) to ensure all TfOH was removed. The yellow solid was dissolved in THF (ca. 10 mL) and filtered through a small plug of basic alumina (ca. 2 cm in a pasture pipet), which removed the paramagnetic materials, into a 20-mL scintillation vial. To the yellow THF solution was added toluene (5 mL), and the solution was allowed to slowly evaporate at room temperature. After 1 day, bright, clear yellow crystals grew. The mother liquor was removed via pipet and saved for further crops. The crystals were washed with diethyl ether, and excess solvent was removed under reduced pressure. Combined yield: 0.129 g (44.5%). Mp 230−232 °C.

Table 1. Crystal Data and Structural Refinement for **1**, **3**, **5**, and **9**

compound	1	3	5	9
empirical formula	$C_{20}H_{15}P$	$C_{87}H_{80}F_3FeO_3P_5S$	$C_{80}H_{72}F_3O_3P_5RuS$	$C_{20}H_{15}P$
M	286.29	1473.28	1426.36	286.29
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*P*21/*c* (no. 14)	*P*21/*c* (no. 14)
a/Å	16.759(1)	13.901(1)	17.285(7)	6.033(1)
b/Å	10.517(1)	16.803(1)	17.059(7)	13.668(1)
c/Å	19.233(1)	17.014(1)	23.96(1)	17.873(2)
α/deg		83.666(1)		
β/deg	113.844(1)	69.925(1)(2)	101.116(8)	91.428(2)
γ/deg		84.126(1)		
V/Å^3	3100.6(3)	3700.9(3)	6932(5)	1473.4(2)
μ/mm^{-1}	0.168	0.399	0.429	0.176
D_{calcd}/g cm^{-3}	1.227	1.322	1.367	1.291
crystal dimensions/mm^3	0.51 × 0.33 × 0.29	0.32 × 0.28 × 0.17	0.30 × 0.20 × 0.13	0.39 × 0.29 × 0.07
Z	8	2	4	4
T/K	150	200	200	200
$2\theta_{max}$/deg	56.68	56.56	52.84	56.62
reflns measured	13988	38833	36429	16620
reflns unique	3857 (R_{int} = 0.0249)	18240 (R_{int} = 0.0310)	13977 (R_{int} = 0.0682)	3648 (R_{int} = 0.0300)
parameters/restraints	190/0	904/33	831/42	194/1
*R*1 [$I \geq 2\sigma(I)$]	0.0613	0.0518	0.0469	0.0588
w*R*2 (all data)	0.1513	0.1310	0.1329	0.1476
max/min res electron density/e Å^{-3}	0.558/−0.305	0.554/−0.379	0.604/−0.832	0.441/−0.225

^{1}H NMR (CD_2Cl_2): δ 8.50 (d, $^2J_{HP}$ = 26.7 Hz, 1H), 7.45 (m, 6H), 7.34 (br, 8H), 7.26 (m, 4H), 7.12 (m, 8H), 6.83 (br, 8H), 6.79 (m, 8H), 6.67 (t, J_{HH} = 7.5 Hz, 1H), 6.03 (dt, J_{HH} = 7.5, 1.8 Hz, 1H), 5.32 (t, J_{HH} = 7.5 Hz, 1H), 3.08 (br, 4H), 2.55 (br, 4H), −10.9 (qntd, *cis*-$^2J_{HP}$ = 51.9, *trans*-$^2J_{HP}$ = 31.5 Hz, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 178.9 (d, $^1J_{C-P}$ = 38.5 Hz), 152.3 (d, $^3J_{CP}$ = 6.4 Hz), 144.3 (d, J_{CP} = 10.0 Hz), 140.4 (d, $^1J_{C-P}$ = 20.0 Hz), 136.6 (br), 135.3 (br), 133.0, 132.7, 130.1, 129.2 (d, $^2J_{CP}$ = 13.8 Hz), 128.7, 128.3, 128.1, 127.8, 127.2, 126.2, 126.1 (d, $^4J_{CP}$ = 7.5 Hz), 124.8 (d, $^3J_{CP}$ = 9.9 Hz), 72.5 (d, $^2J_{CP}$ = 8.5 Hz), 34.1 (m, $^1J_{C-P} \approx$ 11 Hz). ^{19}F NMR (CD_2Cl_2): δ −78.8. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 250.3 (qnt, $^2J_{PP}$ = 31.5 Hz), 80.3 (br). IR (solid ATR): 3055 (w), 1456 (m), 1434 (m), 1279 (m), 1261 (s), 1223 (m), 1150 (s), 1091 (m), 1066 (m), 1031 (s), 916 (w), 874 (w), 811 (m), 758 (m), 742 (s), 694 (s). Anal. Calcd for $C_{77}H_{71}F_3FeO_4P_5S$ (1 equiv of THF): C, 67.99; H, 5.26. Found: C, 67.67; H, 5.46.

3*H*-3,3-Diphenylphosphindole (7). In a resealable Schlenk flask equipped with a stir bar, **6** (0.125 g, 0.096 mmol) was dissolved in CH_3CN and heated to 75 °C. After 18 h, the volatile materials were removed under reduced pressure, and the orange residue was extracted with diethyl ether (5 × 3 mL). The ether was filtered though a small plug of diatomaceous earth into a 20-mL scintillation vial. The volatile materials were removed under reduced pressure, leaving a yellow solid. By NMR, the product was greater than 90% pure. Yield: 0.025 g (93%). ^{1}H NMR (CD_2Cl_2): δ 8.84 (d, $^2J_{HP}$ = 34.3 Hz, 1H), 7.88 (m, 1H), 7.38−7.16 (m, 13H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 191.9 (d, J_{CP} = 33.1 Hz), 154.7 (d, J_{CP} = 2.9 Hz), 146.2 (d, J_{CP} = 35.3 Hz), 143.6 (d, J_{CP} = 6.2 Hz), 130.5 (d, J_{CP} = 22.6 Hz), 128.4, 128.1 (d, J_{CP} = 2.9 Hz), 127.8, 127.4 (d, J_{CP} = 8.6 Hz), 127.0, 126.3 (d, J_{CP} = 2.6 Hz), 76.1 (d, J_{CP} = 14.0 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 222.7 (dd, J_{PH} = 34.2, 5.1 Hz). IR (solid ATR): 3058 (m), 1491 (s), 1442 (s), 1262 (w), 1155 (m), 1124 (w), 1086 (m), 1031 (m), 945 (w), 911 (m), 781 (s), 750 (vs), 696 (vs).

1*H*-2,3-Diphenylphosphindole (9). A 100-mL Schlenk tube equipped with a stir bar was charged with **5** (0.750 g, 0.541 mmol), **1** (0.155 g, 0.541 mmol), and CH_2Cl_2 (25 mL). The Schlenk tube was immersed in an ice bath, and the solution was irradiated using a Hg vapor arc lamp (150 W), which was also cooled in the ice bath. After 1 h, the volatile materials were removed under reduced pressure, leaving a yellow-green solid. The solid was collected on a medium-pore fitted glass frit and washed with diethyl ether (3 × 8 mL) to leave phosphaalkyne adduct **4**. The ether washes were combined, and the volatile materials were removed under reduced pressure to furnish a brightly colored yellow-green residue. While the yield of the photolysis reaction was essentially quantitative by NMR spectroscopy, isolation of pure **9** in high yield was unsuccessful. When the isolated material was redissolved in nonpolar solvents such as C_6D_6 or diethyl ether, an unidentifiable white insoluble material remained. However, in the solid state at −30 °C **9** appeared stable toward decomposition for at least one month. Crystals suitable for X-ray analysis were grown from a diethyl ether solution of **9** at −30 °C. Mp 195−201 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.86 (m, 1H), 7.4−7.16 (m, 13H), 5.40 (d, $^1J_{H-P}$ = 207.6 Hz, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.7 (d, J_{CP} = 2.9 Hz), 146.1 (d, J_{CP} = 6.9 Hz), 141.0 (d, J_{CP} = 5.6 Hz), 137.5, 137.3, 137.1, 136.7 (d, J_{CP} = 1.8 Hz), 129.8 (d, J_{CP} = 1.8 Hz), 129.4 (d, J_{CP} = 8.7 Hz), 129.3 (d, J_{CP} = 20.0 Hz), 128.6, 128.1, 127.7, 127.5, 126.9 (d, J_{CP} = 1.2 Hz), 125.6 (d, J_{CP} = 8.2 Hz), 123.9 (d, J_{CP} = 0.5 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −51.1 (d, J_{P-H} = 207 Hz). IR (solid ATR): 3055 (w), 2963 (w), 1490 (m), 1442 (s), 1260 (s), 1077 (vs-br), 1030 (vs-br), 798 (vs), 760 (vs), 747 (vs), 693 (vs). EI HRMS: *m*/*z* calcd for $C_{20}H_{15}P$, 286.09114 $[M]^+$; found, 286.0905.

X-ray Crystallography. Crystals suitable for X-ray analysis were mounted in degassed perfluoropolyalkyether on top of a glass fiber and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection for the X-ray structure determinations was performed on Bruker SMART Apex diffractometer system with CCD area detector by using graphite-monochromated Mo Kα (0.71073 Å) radiation and a low-temperature device. All calculations were performed by using the SHELXTL (version 6.12) and SHELXL-97 program packages.[58] The structures were solved by direct methods and successive interpretation of the difference Fourier map, followed by full matrix least-squares refinement (against F^2). Moreover, an empirical absorption correction using SADABS (version 2.03) was applied to all structures. All non-hydrogen atoms were refined anisotropically. The locations of the hydrides were fixed at metal hydrogen bond distances of 1.47 Å [Fe1−H1 (**3**)] and 1.59 Å [Ru1−H1 (**5**)].

(58) (a) *SHELXTL*, version 6.12; Bruker AXS: Madison, WI, 2002. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

The toluene molecules included in the crystal lattices of (**3**) and (**5**) are highly disordered on two positions, and a large number [33 for (**3**) and 42 for (**5**)] of restraints had to be used to achieve a satisfactory w*R*2. Table 1 shows crystal data and structural refinement for **1**, **3**, **5**, and **9**.

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Supporting Information Available: CIF files. Details of computational results. Complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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