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Cycloruthenated Complexes from Iminophosphoranes: Synthesis, Structure, and Reactivity with Internal Alkynes

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Cycloruthenated complexes [(η^6-arene)Ru(C_6H_4-2-PPh_2=NR)Cl] (arene = benzene, *p*-cymene; R = Ph, H) containing orthometalated iminophosphoranes have been obtained by transmetalation reactions from Hg(C_6H_4-2-PPh_2=NR)$_2$ derivatives to [(η^6-arene)Ru(μ-Cl)Cl]$_2$. These complexes react cleanly with internal alkynes $R_1C{\equiv}CR_2$ (R_1, R_2 = Ph, Et, CO_2Me), KPF_6, and $CuBr_2$, yielding the 1,1,2-triphenyl-3,4-di(alkyl/aryl)-2,1λ^5-benzazaphosphinin-2-ium heterocycles [C_6H_4-PPh_2-NPh-C(R_1)=C(R_2)-3,4]$^+$ as PF_6 salts. In all studied cases only the monoinsertion products have been observed. In the case of the asymmetric alkyne MeC≡CPh the insertion is regioselective, and the [C_6H_4-PPh_2-NPh-C(Me)=C(Ph)-3,4]PF_6 salt is obtained.

Introduction

The use of orthometalated complexes as synthetic tools in a variety of metal-mediated organic processes, either catalytic or stoichiometric, is well established.[1] Among different transition metals, orthopalladated complexes are by far the most used due to their versatility, stability, and availability. However, it is also well known that other transition metals can provide alternative behaviors, and, in some cases, they can even show a complementary reactivity with respect to their Pd counterparts. The synthesis of different types of heterocycles by reaction of metallacycles with alkynes[2,3] is a paradigm of this affirmation: cyclopalladated complexes can insert one, two, or three equivalents of alkynes, as a function of the orthometalated substrate and/or the substituents of the alkyne,[3a−c] while most of the cycloruthenated derivatives react with only a single equivalent, regardless of the nature of the alkyne.[3d−f]

We are interested in using iminophosphoranes as C,N-bidentate ligands for the synthesis of orthometalated complexes, because of their versatility, structural characteristics, and applications.[4] Among them, we have reported complexes of Pd(II) and Au(III) as efficient catalysts for C−C

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couplings,[4a,h] and we have studied the regioselectivity of the cyclopalladation for *N*-benzyl,[4d] *N*-benzoyl,[4b,h] and *N*-naphthyl[4j] substrates. In these studies we have determined that the orthopalladation of iminophosphoranes contaning *N*-benzyl or *N*-naphthyl substituents can be oriented toward the *N*-benzyl or the *N*-naphthyl ring at low temperature or toward the *P*-aryl rings at high temperature, while palladation of *N*-benzoyl derivatives occurs exclusively at the benzoyl ring. This control has allowed the regioselective functionalization—by iodination or CO insertion—of *N*-naphthyltri(aryl)phosphoranes, either at the *P*-aryl ring or at the *N*-naphthyl ring.[4j]

The facile insertion of CO into the Pd−C bond of these derivatives and the subsequent observed C−N bond coupling[4j] suggest that additional plausible functionalization processes could arise from the reactions of the orthopalladated iminophosphoranes with other unsaturated molecules, such as internal alkynes. However, despite multiple attempts covering a variety of experimental conditions, we have not observed the insertion of the alkyne on the Pd−C bond of the orthopalladated iminophosphoranes. In fact, the only report found in the bibliography about the insertion of alkynes in orthopalladated iminophosphoranes describes that this reaction takes place on the *N*-aryl ring of [Pd-{C_6H_4(N=PPh_3)-2}I(tmeda)],[5] and only with the electron-poor alkyne DMAD (DMAD = MeO_2C-C≡C-CO_2-Me).

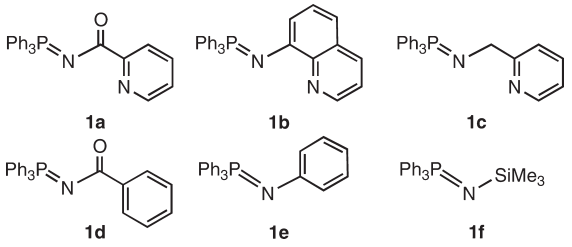
Due to this lack of reactivity, it seems reasonable to attempt the reactivity of complexes with orthometalated iminophosphoranes where the metal is no longer palladium. We have chosen ruthenium as the metal, since orthoruthenated complexes are very scarcely represented in the literature[6] and because they can show a complementary reactivity toward internal alkynes with respect to the orthopalladated analogues.[3]

In this contribution we report the synthesis of new orthoruthenated complexes derived from iminophosphoranes and their successful reactivity with internal alkynes to give 2,1λ^5-benzazaphosphinin-2-ium heterocycles.

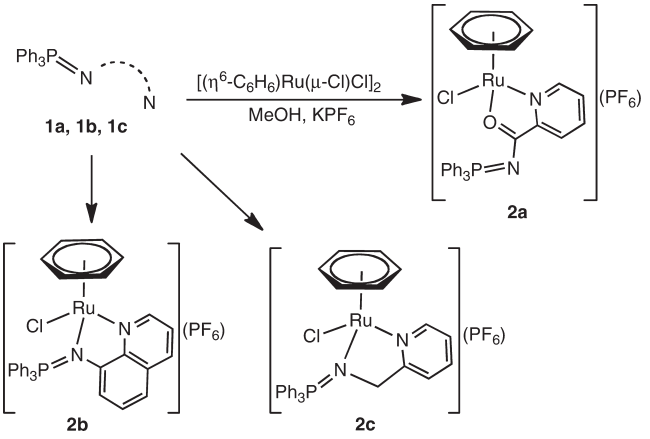
Results and Discussion

1. Synthesis of Coordination Compounds. Aiming to perform the synthesis of the orthoruthenated compounds by C−H bond activation, the reaction of the iminophosphoranes **1a**−**f**[7] (Chart 1) with the precursors [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$[8a] or [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ (*p*-cymene = 1,4-$MeC_6H_4{}^iPr$)[8b] was attempted under different experimental conditions reported in the literature.[2a,b,3d,9]

Chart 1. Iminophosphoranes Used in This Work



Scheme 1. Synthesis of the Coordination Compounds 2a−c



In the case of the potentially chelating iminophosphoranes **1a**−**c**, only the coordination compounds **2a**−**c** (Scheme 1) were identified in the reaction crudes, while products derived from a C−H bond activation were not detected even at traces level. The syntheses shown in Scheme 1 for **2a**−**c** represent the optimized conditions for their preparation. In the case of iminophosphoranes **1d**−**f** untractable black suspensions were obtained.

The lack of C−H bond activation in substrates **1a**−**c** is probably related with the initial chelate bonding of the iminophosphoranes and the resulting *fac*-Cl,N,O or -Cl,N,N arrangements. Once chelation has been produced, the fragment PPh_3 points away from the metal, avoiding their mutual interaction and, hence, the possible C−H activation. This effect is more evident in the case of **2a**, due to the κ^2-N,O bonding mode. In fact, orthometalation of **1a** is known in the case of Pd and Pt,[4a] but the resulting ligand is κ^3-C,N,N coordinated, occupying three positions of the molecular plane. Moreover, we have shown that orthopalladated iminophosphoranes can also behave as κ^3-C,N,P tridentate ligands,[4h,j] but always the three donor atoms are coplanar with the metal. None of these conditions can be satisfied here. On the other hand, while the κ^2-N,N bonding in **2b** and **2c** is expected, the reasons for the adoption of the κ^2-N,O bonding mode are not totally clear, but can be a consequence of the oxophilic behavior of the Ru(II) center and the minimization of steric interactions between the bulky PPh_3 group and the η^6-arene fragment.

Complexes **2a**−**c** show correct elemental analyses and mass spectra for the proposed structures shown in Scheme 1. The IR of **2a** shows a strong absorption at 1534 cm^{-1}, due to the ν_{CO} stretch. This band has been shifted to lower frequency when compared with that in the free ligand **1a**

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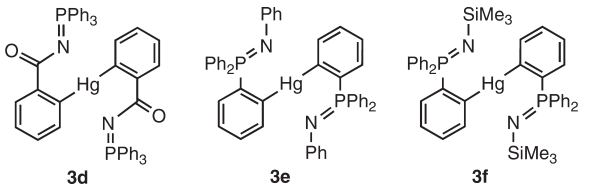
Chart 2. Hg Compounds Used As Transmetalating Reagents for the Synthesis of Ruthenacyccles

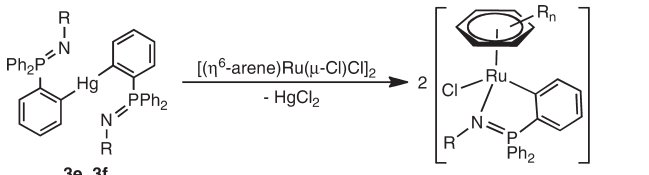


(1601 cm^{-1}),[7a] suggesting the O-bonding of the carbonyl oxygen instead of the N-bonding of the iminic N atom. The N-bonding of the iminophosphoranes in **2b** and **2c** is clearly inferred from the shift to lower wavenumbers of the band due to the ν_{PN} stretch, while, as expected, it remains essentially unchanged in **2a**. The NMR data are in good agreement with the structures depicted in Scheme 1. Key features for **2a** are the presence of a ^{31}P NMR signal with a chemical shift very close to that of the free ligand **1a** and a notable deshielding of the pyridinic H_6 proton, also with respect to **1a**. Both facts suggest that the ligand is bonded through the pyridinic N atom and the carbonyl oxygen. In the case of **2b** and **2c**, the ^{31}P NMR spectra show signals strongly shifted to low field, indicating the iminic N-bonding, this fact being in keeping with the IR data. Moreover, the downfield shifts of the ortho protons of the quinoline (H_2) and pyridine (H_6) fragments are diagnostic for their N-coordination in **2b** and **2c**. Therefore, **2a** contains an iminophosphorane κ^2-N,O chelate, a bonding mode already known and fully characterized in Pd complexes,[11] while **2b** and **2c** contain κ^2-N,N chelates. The molecular structure of **2a** has been determined by X-ray diffraction methods (see below).

2. Synthesis of Orthoruthenated Compounds. The synthesis of the cycloruthenated complexes has been successfully accomplished through transmetalation processes.[12] This strategy is commonly used as an alternative to the C−H bond activation reaction when a clear lack of reactivity of the latter is observed. Previous work in ruthenium derivatives has shown that the use of lithium species as transmetalating agents is not the best choice, because of extensive reduction and formation of black Ru, while Hg(II) or Zn(II) complexes[3d,e,13] behave as efficient transmetalating reagents under mild reaction conditions. Therefore, the Hg(II) complexes **3d**−**f** shown in Chart 2 have been prepared using literature procedures,[4k,10] and we have tested their reactivity toward Ru(II) precursors. The results are shown in Scheme 2.

The reaction of the arene derivative $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ or $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl]_2$ with **3e** and **3f** (1:1 molar ratio) in CH_2Cl_2 at room temperature affords, after elimination of the $HgCl_2$, the cycloruthenated complexes $[(\eta^6\text{-arene})Ru\{(C_6H_4)\text{-}2\text{-}Ph_2P{=}NR\text{-}\kappa\text{-}C,N\}Cl]$ (**4e**−**5f**, see Scheme 2) as stable red solids in good yields. In all cases the transmetalation occurs under very mild reaction conditions. It is noteworthy that the hydrolysis of the silyl group from **3f** occurs during the synthesis of complexes **4f** and **5f**, which contain a NH fragment bonded to the Ru center. This process is likely a consequence of the presence of traces of water. Despite many attempts to obtain the expected silyl derivatives, this small amount of water proved to be difficult to remove, and **4f** and **5f** were systematically found as the only reaction products. In complexes **4e**−**5f** the ruthenium atom is a stereogenic center. However, due to the absence of additional chiral sources during their synthesis, **4e**−**5f** are obtained as racemic mixtures.

Scheme 2. Synthesis of the Orthometalated Compounds 4e−5f



arene = C_6H_6 R = Ph **4e**, H **4f**
arene = *p*-cymene R = Ph **5e**, H **5f**

The nature of the arene does not seem to be very important for the reaction outcome, since similar yields have been obtained in the case of benzene and *p*-cymene. However, both the electronic and steric nature of the iminophosphorane exert a strong influence over the course of the reaction. On one hand, we have attempted the transmetalation using the corresponding monoaryl complexes $[ClHg(C_6H_4\text{-}2\text{-}PPh_2{=}NR)]$, but low conversions were observed, even at high temperatures, indicating that electron-rich bis-aryl species are necessary to achieve high yields. Due to these reasons, these reactions are not described here. On the other hand, the steric hindrance of the iminophosphorane is also important. For instance, the organomercury species **3d** does not react with the ruthenium precursors, even at the reflux temperature, while sterically less demanding complexes **3e** and **3f** react smoothly. Although the reasons remain speculative, it is sensible to assume that the observed results are related to the large volume of the free iminophosphonium group in **3d**. As described above, this is the argument invoked for the κ^2-N,O bonding mode observed in **2a**, and it is probably playing a similar role here.

The characterization of **4e**−**5f** is straighforward and follows the same basic key features than those described for complexes **2**. The IR spectra of **4e**−**5f** show that the bands assigned to the $\nu_{P=N}$ stretch (range 1279−1295 cm^{-1}) appear shifted to lower energies with respect to those of the free ligands (around 1325 cm^{-1}), suggesting N-bonding. The ^1H NMR spectra show the presence of signals due to the η^6-arene and C_6H_4P units. The characterization of the ruthenacycle is also evident from the observation of six well-resolved peaks on the aromatic region of the ^{13}C NMR spectra, due to the C_6H_4P unit, and from the strong downfield shifts undergone by the ^{31}P signals, appearing now in the 40−50 ppm region, with respect to the free ligands, suggesting that the P atom belongs to the metallacycle. In the case of **4f** and **5f**, the N−H unit is characterized from both the IR (ν_{NH} at about 3200 cm^{-1}) and the ^1H NMR spectra (broad singlet at 0.9 ppm for **4f** and doublet at 1.24 ppm for **5f**). The molecular structures of **4f** and **5e** have been determined by X-ray diffraction methods (see below).

3. Synthesis of Heterocycles by C−C and C−N Coupling. It has been reported[3d−f] that orthoruthenated complexes derived from substituted benzylamines react with one equivalent of alkynes to give tetrahydroisoquinolinium heterocycles. The reaction occurs through coordination of the alkyne and migratory insertion into the Ru−C bond, with

(10) Synthesis of the Hg(II) derivatives. Compound **3e**: (a) Stuckwish, C. G. *J. Org. Chem.* **1976**, *41*, 1173. Compound **3f**: (b) Steiner, A.; Stalke, D. *Angew. Chem., Int. Ed.* **1995**, *34*, 1752. Compound **3d**: see ref 4k.

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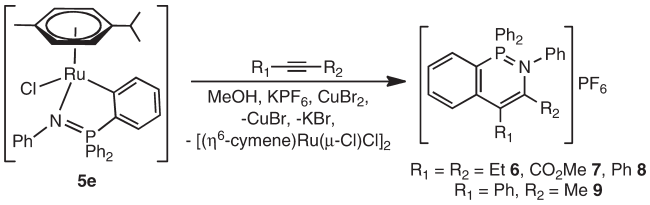
Scheme 3. Synthesis of the Heterocycles 6−9 by Alkyne Insertion into the Ru−C Bond



concomitant C−C coupling, affording a vinylic intermediate. This vinylic species underwent reductive elimination of the heterocyclic fragment through C−N coupling, affording a Ru(0) species that could be isolated.[3d,e] This Ru(0) complex contains a η^4-bonded isoquinolinium ligand, which can be released by oxidation with $CuBr_2$. Aiming to obtain new heterocycles, the reactivity of the orthoruthenated derivative **5e** (as a representative compound) toward internal alkynes with different substituents (EtC≡CEt, $MeO_2CC{\equiv}CCO_2Me$, PhC≡CPh, PhC≡CMe) has been attempted. The results are presented in Scheme 3.

The one-pot reaction of **5e** with alkynes $R_1C{\equiv}CR_2$, KPF_6, and $CuBr_2$, following previously reported procedures,[3e] affords the 1,1,2-triphenyl-3,4-di(alkyl/aryl)-2,1λ^5-benzazaphosphinin-2-ium heterocycles $[C_6H_4\text{-}PPh_2\text{-}NPh\text{-}C(R_1){=}C(R_2)\text{-}3,4]^+$ as PF_6 salts (**6**−**9**). The presence of KPF_6 is mandatory, since reactions performed in the absence of this reagent did not afford the heterocyclic species. This reflects the importance of the generation of a vacant site, by chloride abstraction, position where the alkyne could be bonded to initiate the reaction. In this respect, complex **5e** inserts only one equivalent of alkyne, even in the presence of an excess of this reagent. This means that the reaction is completely selective toward the formation of a single product, in good agreement with previous observations.[3d,e] On the other hand, attempts to isolate the putative Ru(0) intermediates were unsuccessful; therefore only the one-pot processes have been fully studied.

Compounds **6**−**9** were obtained as yellow-orange solids in moderate to good yields. There is a clear relationship between the yield of the reaction and the nature of the alkyne substituents. The reaction takes place more efficiently in the case of electron-donating substituents, and the yield decreases notably as the electron-withdrawing ability of the substituents increases: **6** (Et, 66%), **8** (Ph, 56%), **7** (CO_2Me, 33%). It has been proposed[3d−f] that the reductive elimination takes place by nucleophilic attack of the vinylic carbon to the coordinated nitrogen. Therefore, the lower yields of **7** compared with **6** can be explained due to the lower nucleophilicity of the ester-substituted vinylic carbon, compared with the alkyl-substituted vinylic carbon. These results are also in good agreement with previous observations in benzylamines.[3e] The reactions of orthoruthenated benzylamines with DMAD, or with other ester-substituted alkynes, stopped at the insertion step and further reductive elimination from the vinylic intermediate did not occur, avoiding the formation of the heterocycle.[3e] It is clear that the performance of this system based on orthoruthenated iminophosphoranes is better than that described previously with benzylamines[3e] since, even in the case of the most electron-deficient alkyne (DMAD), the reaction affords the expected heterocycle. Moreover, it is also more efficient that those based on palladium, where no reaction was observed between the orthopalladated iminophosphorane and the alkynes.

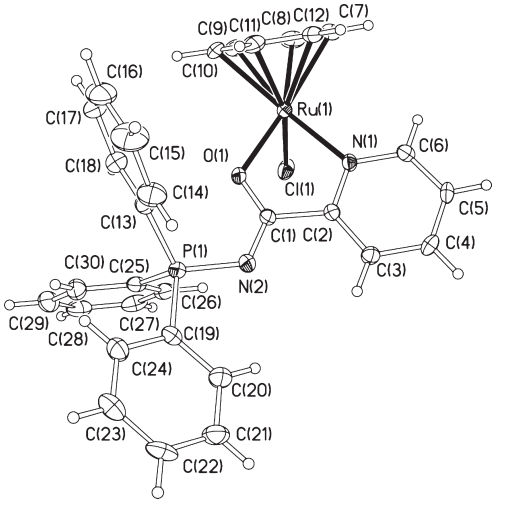


Figure 1. Molecular drawing of the cation of **2a**. The PF_6 counteranion has been removed for clarity. Selected distances [Å] and angles [deg]: Ru(1)−O(1) 2.082(2); Ru(1)−N(1) 2.090(3); Ru(1)−C(12) 2.160(3); Ru(1)−C(8) 2.165(4); Ru(1)−C(11) 2.168(3); Ru(1)−C(10) 2.172(3); Ru(1)−C(7) 2.173(3); Ru(1)−C(9) 2.182(3); Ru(1)−Cl(1) 2.3932(9); O(1)−C(1) 1.272(4); C(1)−N(2) 1.298(4); C(1)−C(2) 1.490(4); N(2)−P(1) 1.623(3); O(1)−Ru(1)−Cl(1) 85.06(7); N(1)−Ru(1)−Cl(1) 85.07(7); O(1)−Ru(1)−N(1) 77.48(9).

In the case of the asymmetric alkyne PhC≡CMe, two regioisomers are plausible. The NMR spectra of **9** show a single set of resonances in each case; therefore **9** is obtained as a single regioisomer. The ^{1}H NOESY-1D experiments performed show that the irradiation of the peak at 2.27 ppm (Me) induces a clear enhancement on the ortho protons of the N-Ph ring, giving proof of their spatial proximity. This means that the less bulky methyl group is over the C atom bonded to the nitrogen[3d] and that the attack of the alkyne to the metal takes place avoiding NPh−Ph interactions. This allows us to conclude that the origin of the regioselectivity is based on steric factors. This result is in good agreement with previous observations in ruthenacycles, although is it not possible to make general rules since many parameters are usually involved.[14] In our case, even when groups with small steric differences are considered, as in PhC≡CMe, a complete selectivity is observed.

Full characterization of the heterocyclic species **6**−**9** was carried out on the basis of their analytic and spectroscopic data. Therefore, **6**−**9** show correct elemental analyses for the proposed stoichiometry, and their MS display peaks with the correct isotopic distribution. The IR spectra show the $\nu_{P=N}$ stretch in the 1285−1310 cm^{-1} region, while in the ^{31}P NMR spectra a single peak in each case appears in the range 29.5−35.0 ppm.

4. X-ray Molecular Structures of 2a, 4f, and 5e. A drawing of the molecular structure of **2a** is shown in Figure 1. The Ru atom is in a pseudo-octahedral "piano-stool" environment, where the benzene ligand is the stool and the legs are the Ru−O, Ru−N, and Ru−Cl bonds. As a whole, all bond distances and angles do not show deviations from values found in the literature for structurally related complexes.

(14) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214.

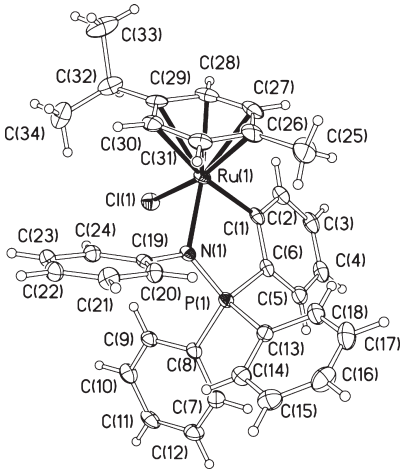


Figure 2. Molecular drawing of the cation of **5e**. Selected distances [Å] and angles [deg]: Ru(1)−C(1) 2.0574(18); Ru(1)−N(1) 2.1241(14); Ru(1)−C(27) 2.147(2); Ru(1)−C(31) 2.165(2); Ru(1)−C(28) 2.1767(19); Ru(1)−C(26) 2.184(2); Ru(1)−C(29) 2.2516(18); Ru(1)−C(30) 2.2668(18); Ru(1)−Cl(1) 2.4067(6); P(1)−N(1) 1.5980(15); C(1)−Ru(1)−N(1) 81.81(6); C(1)−Ru(1)−Cl(1) 82.91(6); N(1)−Ru(1)−Cl(1) 86.78(5).

The average Ru−C(benzene) distance is 2.170(3) Å, which is similar to that found in $[(\eta^6\text{-}C_6H_6)RuCl(C_6H_4CH_2NMe_2)]$ (2.18 Å).[3d] Both the Ru(1)−O(1) [2.082(2) Å] and the Ru(1)−N(1) [2.090(3) Å] bond distances are slightly shorter than those found in [(η^6-*p*-cymene)RuCl(N−O)]A (N−O = 2-benzoylpyridine, A = PF_6; 2-acetylpyridine, A = BPh_4),[15] while the Ru(1)−Cl(1) bond distance [2.3932(9) Å] is slightly longer than those found in the aforementioned complexes. The bond angles O(1)−Ru(1)−Cl(1) [85.06(7)°], N(1)−Ru(1)−Cl(1) [85.07(7)°], and O(1)−Ru(1)−N(1) [77.48(9)°] are identical, within experimental error, to those observed in [(η^6-*p*-cymene)RuCl(N−O)]A.[15] Internal parameters of the N,O-chelate are similar to those found in Pd complexes[11] and do not merit further comment.

Drawings of the molecular structures of **5e** and **4f** are shown in Figures 2 and 3, respectively. The two molecules are isostructural, with the Ru atom in a pseudo-octahedral "piano-stool" environment, similar to that described for **2a**. The couples of bond distances between the same atoms involving the Ru center are identical, within experimental error (for instance, **5e**: Ru(1)−C(1) 2.0574(18) Å, Ru(1)−N(1) 2.1241(14) Å, and Ru(1)−Cl(1) 2.4067(6) Å; **4f**: Ru(1)−C(7) 2.050(4) Å, Ru(1)−N(1) 2.121(3) Å, and Ru(1)−Cl(1) 2.4319(11) Å), and are also identical to those found for similar complexes.[3d,16] For instance, the experimental values found in $[(\eta^6\text{-}C_6H_6)RuCl(C_6H_4CH_2NMe_2)]$ are Ru−C [2.08(1) Å], Ru−N [2.148(8) Å], and Ru−Cl [2.430(2) Å].[3d]

Conclusion

The transmetalation reaction is an adequate synthetic procedure for the preparation of new orthoruthenated derivatives from iminophosphoranes. These cyclometalated species react with internal alkynes with a high degree of selectivity, affording new benzazaphosphinin-2-ium heterocycles, not achievable by other synthetic methods. The method is highly tolerant to the nature of the alkyne substituents and to the ligands around the Ru center, displaying a high performance in all studied cases.

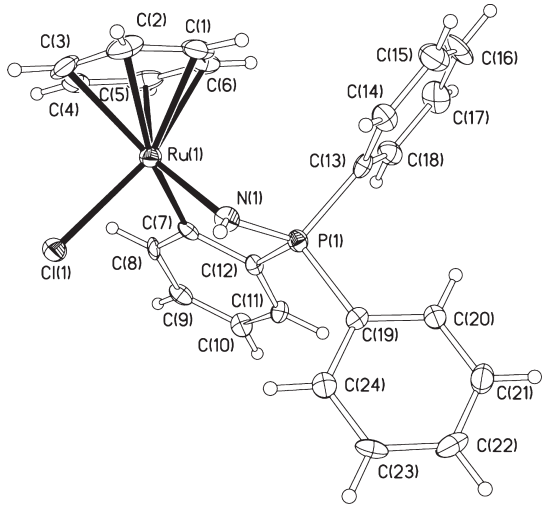


Figure 3. Molecular drawing of the cation of **4f**. Selected distances [Å] and angles [deg]: Ru(1)−C(7) 2.050(4); Ru(1)−N(1) 2.121(3); Ru(1)−C(5) 2.137(4); Ru(1)−C(6) 2.136(4); Ru(1)−C(1) 2.151(4); Ru(1)−C(4) 2.177(4); Ru(1)−C(3) 2.212(4); Ru(1)−C(2) 2.262(5); Ru(1)−Cl(1) 2.4319(11); P(1)−N(1) 1.586(4); C(7)−Ru(1)−N(1) 80.44(17); C(7)−Ru(1)−Cl(1) 87.54(11); N(1)−Ru(1)−Cl(1) 85.92(9).

Experimental Section

General Methods. Solvents were dried and distilled using standard procedures before use. Elemental analyses (CHNS) were carried out on a Perkin-Elmer 2400-B microanalyzer. Infrared spectra (4000−380 cm^{-1}) were recorded on a Perkin-Elmer Spectrum One IR spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions at 25 °C on a Bruker AV400 spectrometer (δ in ppm, J in Hz) at ^1H operating frequency of 400.13 MHz. ^1H and ^{13}C spectra were referenced using the solvent signal as internal standard, while ^{31}P spectra were externally referenced to H_3PO_4 (85%). ESI+ mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix). The iminophosphoranes $Ph_3P{=}NPh$, **1e**, and $Ph_3P{=}NSiMe_3$, **1f**, were obtained from commercial sources and were used as received. The iminophosphoranes $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$, **1a**,[7a] $Ph_3P{=}N\text{-}C_9H_6N$, **1b**,[7b] $Ph_3P{=}NCH_2\text{-}2\text{-}NC_5H_4$, **1c**,[7c] and $Ph_3P{=}NC(O)Ph$, **1d**,[7a] the ruthenium precursors $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$[8a] and [($\eta^6$-*p*-cymene)Ru($\mu$-Cl)Cl]$_2$ (*p*-cymene = 1,4-$MeC_6H_4{}^iPr$),[8b] and the mercury compounds $[Hg(C_6H_4C(O)N{=}PPh_3)_2]$, **3d**,[4k] $[Hg(C_6H_4\text{-}2\text{-}PPh_2{=}NPh)_2]$, **3e**,[10a] and $[Hg(C_6H_4\text{-}2\text{-}PPh_2{=}NSiMe_3)_2]$, **3f**,[10b] were prepared following literature procedures.

Synthesis of [(η^6-C$_6$H$_6$)Ru((Ph$_3$P=N-CO-2-NC$_5$H$_4$)-κ-*N*, *O*)Cl](PF$_6$), 2a. A suspension of [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$ (0.130 g, 0.26 mmol), **1a** (0.200 g, 0.52 mmol), and KPF_6 (0.092 g, 0.52 mmol) in MeOH (25 mL) was stirred at room temperature for 6 h. During this time the color of the suspension evolved from red to deep yellow. After the reaction time the yellow solid was filtered, washed with MeOH (5 mL) and Et_2O (2 × 15 mL), and

(15) Zuccaccia, D.; Bellachioma, G.; Cardaci, G.; Zuccaccia, C.; Macchioni, A. *Dalton Trans.* **2006**, 1963.
(16) Attar, S.; Nelson, J. H.; Fischer, J.; de Cian, A.; Sutter, J. P.; Pfeffer, M. *Organometallics* **1995**, *14*, 4559.

dried in vacuo. Obtained: 0.243 g (63% yield). Anal. Calcd for $[C_{30}H_{25}ClF_6N_2OP_2Ru]$ (741.04): C, 48.58; H, 3.40; N, 3.78. Found: C, 48.43; H, 3.32; N, 3.53. IR: 1534 ($\nu_{C=O}$), 1297($\nu_{P=N}$) cm^{-1}. MS (FAB+): 597 (50%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 5.56 (s, 6H, η^6-C_6H_6), 7.61 (m, 6H, H_m, PPh_3), 7.71−7.96 (m, 10H, H_5, $C_5H_4N + H_p + H_o$, PPh_3), 8.02 (t, 1H, H_4, C_5H_4N, $^3J_{HH}$=7.4), 8.34 (d, 1H, H_3, C_5H_4N, $^3J_{HH}$=7.3), 9.21 (d, 1H, H_6, C_5H_4N, $^3J_{HH}$ = 5.2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 83.7 (s, η^6-C_6H_6), 127.8 (s, C_3, C_5H_4N), 129.4 (d, C_m, PPh_3, $^3J_{PC}$=13.0), 129.7 (s, C_5, C_5H_4N), 133.2 (d, C_o, PPh_3, $^2J_{PC}$=10.8), 133.9 (d, C_p, PPh_3, $^4J_{PC}$=2.9), 139.5 (s, C_4, C_5H_4N), 151.5 (s, C_2, C_5H_4N), 154.3 (s, C_6, C_5H_4N), 178.1 (s, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.72.

Synthesis of [(η^6-C_6H_6)Ru((Ph_3P=N-8-C_9H_6N)-κ-N,O)Cl]-(PF_6), 2b. [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$ (0.124 g, 0.25 mmol) was reacted with **1b** (0.200 g, 0.50 mmol) and KPF_6 (0.091 g, 0.50 mmol) in MeOH (25 mL), as reported for **2a**, to give **2b** as an orange solid. Obtained: 0.238 g (62% yield). Anal. Calcd for $[C_{33}H_{27}ClF_6N_2P_2Ru]$ (764.04): C, 51.88; H, 3.56; N, 3.67. Found: C, 51.21; H, 3.30; N, 3.51. IR: 1287 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 619 (80%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 5.18 (s, 6H, η^6-C_6H_6), 6.32 (d, 1H, H_7, C_9H_6N, $^3J_{HH}$ = 7.9), 6.84 (t, 1H, H_6, C_9H_6N, $^3J_{HH}$=7.9), 7.07 (d, 1H, H_5, C_9H_6N, $^3J_{HH}$ = 8.0), 7.55−7.68 (m, 9H, $H_m + H_p$, PPh_3), 7.75 (t, 1H, H_3, C_9H_6N, $^3J_{HH}$=8.3), 7.91 (m, 6H, H_o, PPh_3), 8.17 (d, 1H, H_4, C_9H_6N, $^3J_{HH}$ = 8.1), 9.30 (d, 1H, H_2, C_9H_6N, $^3J_{HH}$ = 5.0). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 84.5 (η^6-C_6H_6), 117.8 (C_5, C_9H_6N), 121.6 (C_7, C_9H_6N), 127.2 (C_6, C_9H_6N), 129.6 (C_m, PPh_3), 132.7 (C_3, C_9H_6N), 134.0 (C_p, PPh_3), 134.5 (C_o, PPh_3), 138.5 (C_4, C_9H_6N), 153.7 (C_2, C_9H_6N). Signals due to the quaternary C atoms were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.42.

Synthesis of [(η^6-C_6H_6)Ru((Ph_3P=N-CH_2-2-NC_5H_4)-κ-N,N)Cl](PF_6), 2c. [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$ (0.200 g, 0.40 mmol) was reacted with **1c** (0.294 g, 0.80 mmol) and KPF_6 (0.147 g, 0.80 mmol) in MeOH (25 mL), as reported for **2a**, to give **2c** as a yellow solid. Obtained: 0.384 g (66% yield). Anal. Calcd for $[C_{30}H_{27}ClF_6N_2P_2Ru]$ (727.71): C, 49.51; H, 3.74; N, 3.85. Found: C, 49.36; H, 3.62; N, 3.81. IR: 1291 ($\nu_{P=N}$) cm^{-1}. MS (FAB+): 583 (65%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 4.14 (t, 1H, CH_2, $^3J_{HP}$=17.2), 4.76 (dd, 1H, CH_2, $^3J_{HP}$=9.6, $^2J_{HH}$=17.2), 5.21 (s, 6H, η^6-C_6H_6), 7.11 (d, 1H, H_3, C_5H_4N, $^3J_{HH}$=7.6), 7.33 (t, 1H, H_5, C_5H_4N, $^3J_{HH}$=6.4), 7.48−7.52 (m, 6H, H_m, PPh_3), 7.58−7.63 (m, 9H, $H_p + H_o$, PPh_3), 7.73 (td, 1H, H_4, C_5H_4N, $^3J_{HH}$=6.4, $^4J_{HH}$=1.2), 8.91 (d, 1H, H_6, C_5H_4N, $^3J_{HH}$=5.2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 61.1 (s, CH_2), 84.8 (s, η^6-C_6H_6), 119.9 (s, C_3, C_5H_4N), 124.9 (s, C_5, C_5H_4N), 126.8 (d, C_i, PPh_3, $^1J_{PC}$=98.0), 129.1 (d, C_m, PPh_3, $^3J_{PC}$=12.4), 133.5 (d, C_p, PPh_3, $^4J_{PC}$=2.6), 134.3 (d, C_o, PPh_3, $^2J_{PC}$=10.0), 139.0 (s, C_4, C_5H_4N), 154.6 (s, C_6, C_5H_4N), 163.3 (d, C_2, C_5H_4N, $^3J_{PC}$ =8.6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.64.

Synthesis of [(η^6-C_6H_6)Ru{(C_6H_4)-2-Ph_2P=NPh-κ-C,N}Cl], 4e. To a suspension of [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$ (0.059 g, 0.12 mmol) in CH_2Cl_2 (20 mL) was added compound **3e** (0.107 g, 0.12 mmol). The resulting suspension was stirred at room temperature for 3 days, then filtered through Celite. The red solution was evaporated to small volume (≈1−2 mL). The residue was treated with Et_2O (20 mL). Subsequent stirring promoted the precipitation of a red solid, which was filtered, washed with Et_2O (15 mL), dried in vacuo, and identified as **4e**. Obtained: 0.080 g (59% yield). Anal. Calcd for $[C_{30}H_{25}ClNPRu]$ (567.02): C, 63.55; H, 4.44; N, 2.47. Found: C, 63.10; H, 4.21; N, 2.18. IR: 1287 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 567 (60%) $[M]^+$. ^1H NMR ($CDCl_3$): δ 5.17 (s, 6H, η^6-C_6H_6), 6.85−6.95 (m, 2H, $H_3 + H_4$, C_6H_4), 7.02−7.11 (m, 3H, $H_m + H_p$, NPh), 7.13 (t, 2H, H_o, NPh, $^3J_{HH}$=7.1), 7.27 (m, 1H, H_5, C_6H_4), 7.62−7.69 (m, 6H, $H_m + H_p$, PPh_2), 7.84 (m, 4H, H_o, PPh_2), 8.25 (d, 1H, H_6, C_6H_4, $^3J_{HH}$=6.9). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 85.6 (s, η^6-C_6H_6), 120.3 (d, C_i, PPh_2, $^1J_{PC}$=102.1), 123.1 (d, C_4, C_6H_4, $^3J_{PC}$=14.2), 124.4 (s, NPh), 128.2 (s, NPh), 129.2 (d, C_3, C_6H_4, $^2J_{PC}$=20.7), 129.5 (s, C_o, NPh), 130.2 (d, C_m, PPh_2, $^3J_{PC}$=13.5), 131.05 (d, C_5, C_6H_4, $^4J_{PC}$=3.1), 134.0 (d, C_o, PPh_2, $^2J_{PC}$=11.3), 135.5 (d, C_p, PPh_2, $^4J_{PC}$ = 2.9), 140.8 (d, C_6, C_6H_4, $^3J_{PC}$=14.5), 153.4 (s, C_i, NPh), 181.1 (s br, C_1, C_6H_4). The signal due to C_2 (C_6H_4) was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.51.

Synthesis of [(η^6-*p*-cymene)Ru{(C_6H_4)-2-Ph_2P=NPh-κ-C,N}Cl], 5e. Compound **5e** was prepared following the same synthetic method as that described for **4e**. Therefore [(η^6-*p*-cymene)RuCl(μ-Cl)]$_2$ (0.186 g, 0.30 mmol) was reacted with **3e** (0.273 g, 0.30 mmol) in 20 mL of CH_2Cl_2 to give **5e** as a red solid. Obtained: 0.168 g (45% yield). Anal. Calcd for $[C_{34}H_{33}ClNPRu]$ (623.13): C, 65.53; H, 5.34; N, 2.25. Found: C, 65.10; H, 5.21; N, 2.18. IR: 1284 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 623 (70%) $[M]^+$. ^1H NMR ($CDCl_3$): δ 0.98−1.04 (m, 6H, Me_2-cymene), 1.98 (s, 3H, Me-cymene), 2.66 (m, 1H, CH-cymene), 4.51, 4.60, 4.81, 4.91 (4d, 4H, C_6H_4-cymene, $^3J_{HH}$=5.6), 6.88−6.94 (m, 3H, H_p, NPh + $H_3 + H_4$, C_6H_4), 7.08 (t, 2H, H_o, NPh, $^3J_{HH}$=7.6), 7.23−7.33 (m, 3H, H_5, $C_6H_4 + H_m$, PPh), 7.36−7.41 (m, 3H, H_m, NPh, + H_p, PPh), 7.50 (m, 2H, H_m, PPh), 7.55−7.62 (m, 3H, $H_o + H_p$, PPh), 7.81 (m, 2H, H_o, PPh), 8.20 (dd, 1H, H_6, C_6H_4, $^3J_{HH}$=7.6, $^4J_{HH}$ = 2.6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.7 (s, Me-cymene), 22.2, 22.4 (2s, Me_2-cymene), 30.4 (s, CH-cymene), 77.8, 80.1, 87.4, 90.3, 97.0, 106.8 (6s, C_6H_4-cymene), 122.2 (s, C_o, NPh), 122.4 (d, C_4, C_6H_4, $^3J_{PC}$=13.7), 128.1−129.3 (ovelapped, C_p, NPh + C_m, PPh + C_p, PPh), 129.5 (d, C_3, C_6H_4, $^2J_{PC}$ = 21.4), 130.7 (s, C_5, C_6H_4), 131.8, 132.0 (overlapped, C_m, NPh + C_p, PPh), 132.2 (d, C_i, PPh_2, $^1J_{PC}$=80.0), 133.3 (d, C_o, PPh, $^2J_{PC}$=9.5), 134.3 (d, C_o, PPh, $^2J_{PC}$=10.2), 136.3 (C_2, C_6H_4, $^1J_{PC}$=140.1), 141.0 (d, C_6, C_6H_4, $^3J_{PC}$=14.7), 153.4 (s, C_i, NPh), 183.4 (d, C_1, C_6H_4, $^2J_{PC}$ = 23.3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.04.

Synthesis of [(η^6-C_6H_6)Ru{(C_6H_4)-2-Ph_2P=NH-κ-C,N}Cl], 4f. Compound **4f** was prepared following the same synthetic method as that described for **4e**. Therefore [(η^6-C_6H_6)RuCl(μ-Cl)]$_2$ (0.131 g, 0.26 mmol) was reacted with **3f** (0.236 g, 0.26 mmol) in 20 mL of CH_2Cl_2 to give **4f** as a red solid. Obtained: 0.155 g (61% yield). Anal. Calcd for $[C_{24}H_{21}ClNPRu]$ (490.93): C, 58.72; H, 4.31; N, 2.85. Found: C, 58.53; H, 4.08; N, 2.78. IR: 1295 ($\nu_{P=N}$) cm^{-1}; 3200 (ν_{N-H}) cm^{-1}. MS (MALDI+): 491 (65%) $[M]^+$. ^1H NMR ($CDCl_3$): δ 0.90 (s br, 1H, NH), 5.14 (s, 6H, η^6-C_6H_6), 6.95−6.99 (m, 2H, $H_3 + H_4$, C_6H_4), 7.26 (m, 1H, H_5, C_6H_4), 7.39 (m, 2H, H_m, PPh), 7.48−7.57 (m, 5H, $H_m + H_p + H_o$, PPh), 7.64 (m, 1H, H_p, PPh), 7.75 (m, 2H, H_o, PPh), 8.19 (dd, 1H, H_6, C_6H_4, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.0). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 84.5 (s, η^6-C_6H_6), 121.7 (d, C_4, C_6H_4, $^3J_{PC}$ = 13.8), 130.1 (d, C_m, PPh_2, $^3J_{PC}$ = 12.9), 130.8 (d, C_3, C_6H_4, $^2J_{PC}$=20.2), 131.4 (d, C_i, PPh_2, $^1J_{PC}$=88.3), 133.6 (d, C_5, C_6H_4, $^4J_{PC}$=2.9), 133.5 (d, C_o, PPh_2, $^2J_{PC}$=10.5), 135.5 (d, C_p, PPh_2, $^4J_{PC}$=2.9), 139.8 (d, C_6, C_6H_4, $^3J_{PC}$=14.0), 177.2 (d, C_1, C_6H_4, $^2J_{PC}$=21.1). The signal due to C_2 (C_6H_4) was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.19.

Synthesis of [(η^6-*p*-cymene)Ru{(C_6H_4)-2-Ph_2P=NH-κ-C,N}Cl], 5f. Compound **5f** was prepared following the same synthetic method as that described for **4e**. Therefore [(η^6-*p*-cymene)RuCl(μ-Cl)]$_2$ (0.168 g, 0.27 mmol) was reacted with **3f** (0.245 g, 0.27 mmol) in 20 mL of CH_2Cl_2 to give **5f** as a red solid. Obtained: 0.130 g (44% yield). Anal. Calcd for $[C_{28}H_{29}ClNPRu]$ (547.02): C, 61.48; H, 5.34; N, 2.56. Found: C, 61.13; H, 5.17; N, 2.39. IR: 1279 ($\nu_{P=N}$) cm^{-1}; 3140 (ν_{N-H}) cm^{-1}. MS (MALDI+): 547 (45%) $[M]^+$. ^1H NMR ($CDCl_3$): δ 1.05−1.11 (m, 6H, Me_2-cymene), 1.24 (d, 1H, NH, $^2J_{HP}$=6.9), 1.74 (s, 3H, Me-cymene), 2.55 (m, 1H, CH-cymene), 4.48, 4.96, 5.12, 5.29 (4s br, 4H, C_6H_4-cymene), 6.94−7.00 (m, 2H, $H_3 + H_4$, C_6H_4), 7.23−7.83 (m, 11H, H_5, $C_6H_4 + H_m + H_p + H_o$, PPh_2), 8.16 (dd, 1H, H_6, C_6H_4, $^3J_{HH}$=7.7, $^4J_{HH}$=1.0). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.46.

Synthesis of [$C_6H_4PPh_2$NPh-C(Et)=C(Et)-3,4](PF_6), 6. To a solution of complex **5e** (0.138 g, 0.22 mmol) in MeOH (20 mL)) were added KPF_6 (0.050 g, 0.27 mmol) and 3-hexyne (31 μL, 0.27 mmol, and the resulting red solution was stirred at room temperature for 1 h. After this time $CuBr_2$ (0.110 g, 0.50 mmol)

was added, and a black suspension was formed in a few seconds. The stirring was maintained at the same temperature for 15 h. After the reaction time the solvent was evaporated to dryness, and the black residue was extracted twice with CH_2Cl_2 (2 × 20 mL). The solid was discarded, and the clear filtered yellow solution was evaporated to a small volume (≈1 mL) and treated with Et_2O (15 mL), promoting the precipitation of **6** as a yellow solid. This solid was filtered, washed with additional Et_2O (10 mL), and dried in vacuo. Obtained: 0.085 g (66% yield). Anal. Calcd for $[C_{30}H_{29}F_6NP_2]$ (579.50): C 62.18; H, 5.04; N, 2.42. Found: C 62.35; H, 4.80; N, 2.37. IR: 1302 ($\nu_{P=N}$) cm^{-1}. MS (MALDI +): 434 (100%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 0.97 (t, 3H, Me, $^3J_{HH}$=7.0), 1.04 (t, 3H, Me, $^3J_{HH}$=6.9), 2.40 (q, 2H, CH_2, $^3J_{HH}$=7.0), 2.77 (q, 2H, CH_2, $^3J_{HH}$=7.0), 7.04 (m, 2H, H_o, NPh), 7.24−7.27 (m, 4H, H_m + H_p, NPh + H_3, C_6H_4), 7.42 (m, 1H, H_4, C_6H_4), 7.60−7.70 (m, 8H, H_m + H_o, PPh_2), 7.84−7.93 (m, 3H, H_6, C_6H_4 + H_p, PPh_2), 7.99 (m, 1H, H_5, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.9 (s, Me), 22.7 (s, CH_2), 14.7 (s, Me), 24.5 (s, CH_2), 96.8, 102.2 (2s, C═C), 112.9 (d, C_i, PPh_2, $^1J_{PC}$ = 100.5), 116.9 (d, C_1, C_6H_4, $^1J_{PC}$ = 104.0), 126.1 (d, C_3, C_6H_4, $^3J_{PC}$ = 9.8), 127.2 (d, C_2, C_6H_4, $^2J_{PC}$ =10.0), 128.7 (s, C_p, NPh), 129.3 (d, C_o, NPh, $^3J_{PC}$ = 1.3), 129.6 (d, C_6, C_6H_4, $^2J_{PC}$=13.9), 130.4 (s, C_m, NPh), 130.9 (d, C_m, PPh_2, $^3J_{PC}$ = 13.6), 131.8 (d, C_5, C_6H_4, $^3J_{PC}$ = 11.2), 135.2 (d, C_o, PPh_2, $^2J_{PC}$=11.6), 136.2 (d, C_4, C_6H_4, $^4J_{PC}$ = 2.0), 136.6 (d, C_p, PPh_2, $^4J_{PC}$ = 2.7), 139.3 (s, C_i, NPh). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.01.

Synthesis of $[C_6H_4PPh_2NPh\text{-}C(CO_2Me)═C(CO_2Me)\text{-}3,4](PF_6)$, 7. Compound **7** was prepared following the same experimental procedure as that described for **6**. Therefore, **5e** (0.150 g, 0.24 mmol) was reacted with $MeO_2C\text{-}C≡C\text{-}CO_2Me$ (35 μL, 0.28 mmol), KPF_6 (0.053 g, 0.28 mmol), and $CuBr_2$ (0.118 g, 0.53 mmol) in MeOH (30 mL) to give **7** as a yellow solid. Obtained: 0.051 g (33% yield). Anal. Calcd for $[C_{30}H_{25}F_6NO_4P_2]$ (639.46): C, 56.35; H, 3.94; N, 2.19. Found: C, 56.50; H, 3.75; N, 2.10. IR: 1670 ($\nu_{C=O}$), 1631($\nu_{C=O}$), 1287 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 494 (100%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 3.21 (s, 3H, OMe), 3.37 (s, 3H, OMe), 6.91 (d, 2H, H_o, NPh, $^3J_{HH}$ = 7.6), 7.03−7.07 (m, 2H, H_p, NPh + H_3, C_6H_4), 7.21−7.28 (m, 3H, H_m, NPh + H_4, C_6H_4), 7.35 (d, 1H, H_6, C_6H_4, $^3J_{HH}$=7.0), 7.71−7.50 (m, 7H, H_5, C_6H_4 + H_m + H_p, PPh_2), 7.64−7.74 (m, 4H, H_o, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.0 (s, OMe), 52.0 (s, OMe), 120.6 (s, C_4, C_6H_4), 120.9 (s, C_o, NPh), 124.2 (s, C_p, NPh), 126.9 (d, C_6, C_6H_4, $^2J_{PC}$ = 13.0), 128.2 (d, C_m, PPh_2, $^3J_{PC}$ = 11.0), 129.1 (s, C_m, NPh), 131.4 (d, C_p, PPh_2, $^4J_{PC}$=2.8), 132.2 (d, C_o, PPh_2, $^2J_{PC}$=9.6), 133.2 (d, C_3, C_6H_4, $^3J_{PC}$=10.0), 133.9−134.2 (m, C_i, PPh_2 + C_i, C_6H_4), 135.0 (d, C_5, C_6H_4, $^3J_{PC}$ =12.0), 139.8 (d, C_2, C_6H_4, $^2J_{PC}$=8.0), 139.9, 147.1 (2s, C═C), 164.1, 169.0 (2s, C═O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.52.

Synthesis of $[C_6H_4PPh_2NPh\text{-}C(Ph)═C(Ph)\text{-}3,4](PF_6)$ 8. Compound **8** was prepared following the same experimental procedure as that described for **6**. Therefore, **5e** (0.171 g, 0.27 mmol) was reacted with diphenylacetylene (Ph-C≡C-Ph) (0.06 g, 0.33 mmol), KPF_6 (0.06 g, 0.33 mmol), and $CuBr_2$ (0.135 g, 0.60 mmol) in MeOH (30 mL) to give **8** as an orange solid. Obtained: 0.103 g (56% yield). Anal. Calcd for $[C_{38}H_{29}F_6NP_2]$ (675.58): C, 67.56; H, 4.33; N, 2.07. Found: C, 67.44; H, 4.24; N, 1.99. IR: 1308 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 530 (100%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 5.37 (m, 2H, Ph), 5.50 (m, 2H, Ph), 6.94−7.07 (m, 9H, 1H, Ph + 8H, Ar), 7.20 (m, 1H, C_6H_4), 7.33−7.58 (m, 9H, 2H, C_6H_4 + 7H, Ar), 7.58−7.88 (m, 6H, 1H, C_6H_4 + 5H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.7 (d, C_i, PPh_2, $^1J_{PC}$ = 100.4), 117.6 (d, C_1, C_6H_4, $^1J_{PC}$ = 103.6), 120.3 (s, Ar), 124.5 (s, Ar), 127.1 (s, Ar), 127.6 (d, Ar, J_{PC}=1.5), 127.8 (s, Ar), 127.8 (s, Ar), 128.4−128.6 (2 CH overlapped, C_6H_4 + Ar), 129.0 (d, Ar, J_{PC}=27.5), 129.6 (d, Ar, J_{PC}=2.1), 130.6 (d, C_m, PPh_2, $^3J_{PC}$=13.0), 130.9 (s, Ar), 131.3 (d, C_6H_4, J_{PC}=11.1), 131.4 (s, Ar), 131.9 (s, Ar), 132.1 (d, C_6H_4, J_{PC} = 9.8), 133.1 (s, Ar), 134.6 (C_o, PPh_2, $^2J_{PC}$=11.0), 135.7 (d, C_6H_4, J_{PC}=2.0), 136.7 (d, C_p, PPh_2, $^4J_{PC}$=2.7). Signals due to the carbons C═C, C_1, NPh, C_i, Ph, and C_2, C_6H_4 were not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.97.

Synthesis of $[C_6H_4PPh_2NPh\text{-}C(Me)═C(Ph)\text{-}3,4](PF_6)$, 9. Compound **9** was prepared following the same experimental procedure as that described for **6**. Therefore, **5e** (0.171 g, 0.27 mmol) was reacted with 1-phenyl-1-propyne (Ph-C≡C-Me) (41 μL, 0.33 mmol), KPF_6 (0.06 g, 0.33 mmol), and $CuBr_2$ (0.135 g, 0.60 mmol) in MeOH (30 mL) to give **9** as an orange solid. Obtained: 0.096 g (58% yield). Anal. Calcd for $[C_{33}H_{27}F_6NP_2]$ (613.51): C, 64.60; H, 4.44; N, 2.28. Found: C, 64.90; H, 4.31; N, 2.17. IR: 1295 ($\nu_{P=N}$) cm^{-1}. MS (MALDI+): 468 (100%) $[M - PF_6]^+$. ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H, Me), 6.94−7.03 (m, 5H, NPh), 7.23−7.33 (m, 5H, Ph), 7.53 (m, 1H, H_5, C_6H_4), 7.76−7.88 (m, 11H, H_6, C_6H_4 + H_m + H_p + H_o, PPh_2), 8.04−8.10 (m, 2H, H_3 + H_4, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.3 (s, Me), 111.7 (d, C_i, PPh_2, $^1J_{PC}$ = 99.3), 117.1 (d, C_1, C_6H_4, $^1J_{PC}$=104.1), 120.8 (d, C_2, C_6H_4, $^2J_{PC}$=9.1), 126.9 (d, C_3, C_6H_4, $^3J_{PC}$=9.7), 127.8 (d, C_m, NPh, $^3J_{PC}$=1.6), 128.6 (s, Ph), 129.1 (d, C_o, NPh, $^3J_{PC}$ = 2.2), 129.3 (s, C_p, NPh), 129.5 (d, C_o, Ph, $^5J_{PC}$=1.2), 129.9 (d, C_6, C_6H_4, $^2J_{PC}$=13.7), 130.7 (d, C_m, PPh_2, $^3J_{PC}$=13.7), 130.9 (s, Ph), 131.3 (d, C_5, C_6H_4, $^3J_{PC}$=11.4), 133.9 (d, C═C, $^3J_{PC}$=4.7), 134.7 (d, C_o, PPh_2, $^2J_{PC}$=11.7), 136.1 (d, C_4, C_6H_4, $^4J_{PC}$=2.2), 136.5 (d, C_p, PPh_2, $^4J_{PC}$=2.9), 137.1 (d, C_1, Ph, $^4J_{PC}$ = 1.6), 137.4 (s, C═C), 140.6 (d, C_i, NPh, $^2J_{PC}$ = 5.3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.86.

X-ray Crystallography. Crystals of adequate quality for X-ray measurements were grown by slow diffusion of Et_2O into CH_2Cl_2 solutions of the crude products at 25 °C. A single crystal of each compound was mounted at the end of a quartz fiber in a random orientation, covered with magic oil, and placed under the cold stream of nitrogen. Data collection was performed at room temperature or low temperature (150 K) on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected in each case based on three ω-scan or φ-scan runs. The diffraction frames were integrated using the program CrysAlis RED,[17] and the integrated intensities were corrected for absorption with SADABS.[18] The structures were solved and developed by Patterson and Fourier methods.[19] The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[20]

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Supporting Information Available: CIF files giving complete data collection parameters for **2a**, **5e**, and **4f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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