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Gold Compounds Anchored to a Metalated Arene Scaffold: Synthesis, X-ray Molecular Structures, and Cycloisomerization of Enyne

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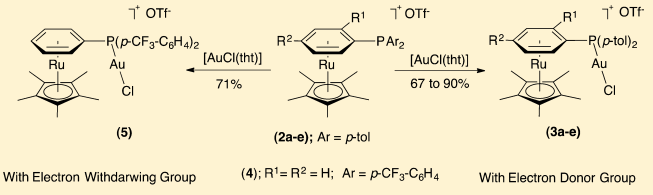
Supporting Information

ABSTRACT: A novel series of π-complexes of phosphino ligands, [Cp*Ru(η^6-arene-PAr_2)][OTf], has been prepared in which the diarylphosphine unit is attached to a metalated π-arene scaffold. These organometallic phosphino ligands display either an electron-donating methyl group ($-PAr_2 = -P(p\text{-tol})_2$) or electron-withdrawing trifluoromethyl group ($-PAr_2 = -P(p\text{-}C_6H_4CF_3)_2$). This unique class of metallo ligands was converted to heterodinuclear gold complexes upon treatment with [AuCl(tht)]. The molecular structures of [Cp*Ru(η^6-p-$CH_3C_6H_4$-P(p-tol)$_2$-Au-Cl)][OTf] and [Cp*Ru(η^6-C_6H_5-P(p-$C_6H_4CF_3$)$_2$)-Au-Cl][OTf] were ascertained by single-crystal X-ray diffraction. A comparative study of these structures with that of [Cp*Ru(η^6-C_6H_5-PPh_2-Au-Cl)][OTf] previously reported revealed important information about the electronic nature of the gold center when it is bonded to a $-PPh_2$, $-P(p\text{-tol})_2$, or $-P(p\text{-}C_6H_4CF_3)_2$ metallo ligand. DFT computations also shed light on the effect of [Cp*Ru$^+$] coordination to [AuCl(PAr_3)] precatalysts. Several complexes of the family with electron-donating and -withdrawing groups were evaluated toward cycloisomerization reactions of a classical *N*-tethered 1,6-enyne. These results are presented and discussed.



INTRODUCTION

There is a resurgence of interest in designing metallo ligands for applications in various fields of chemistry.[1] Particularly attractive is the use of phosphine−ferrocene-based metallo ligands to synthesize active catalysts which have proven to be effective in promoting high activity and enantioselectivity in a range of metal-mediated asymmetric transformations.[2] In the latter, it is believed that metallo ligands would influence both the electronic and steric properties of the active metal site. However, the development of alternative, structurally diverse metallo ligands to the well-known ferrocenyl-based compounds has received little attention.[3] Some of us have developed the synthesis of several neutral metalated π-quinones, thioquinones, and selenoquinones stabilized by "Cp*M" fragments (M = Rh, Ir).[4] These π-quinonoid species were successfully used as metallo ligands to prepare a variety of coordination assemblies and polymers with luminescent properties.[5] More recently we described the synthesis of the heterodinuclear complex L_M→Au-Cl, where a gold center is attached to a phosphino metallo ligand L_M of formula κ^1-PPh_2-[Cp*Ru(η^6-benzene)][OTf] (**2a**′-OTf) (Scheme 1). The subsequent heterobimetallic complex [Cp*Ru(η^6-C_6H_5-PPh_2-Au-Cl)][OTf] (**3a**′-OTf) was found to be active in metal-catalyzed cycloisomerization reactions and especially toward β-hydroxyallenynes.[6] Thus, we decided to extend the scope of this class of metalated phosphino ligands L_M by introducing new diarylphosphine moieties displaying electron-donating and -withdrawing groups (vide infra).

Homogeneous gold catalysis has emerged as a powerful tool for organic transformations, thus providing a variety of bond-forming reactions for the synthesis of complex chemical structures.[7] In this context, efforts have been devoted to prepare new gold complexes by tuning the electronic and/or the steric properties of the donor ligand bound to the metal center "L→Au" (L= PR_3, carbenes, cyclic and acyclic aminocarbenes, carbodiphosphoranes, etc.).[8]

We sought to change the electronic and steric properties around the gold center in hopes that this might lead to new reactive species. In this paper we extended our approach to other diarylphosphino π-complexes L_M displaying electron-donating and -withdrawing groups, which allowed us to obtain a series of heterodinuclear Ru−Au compounds. The molecular structures of two such compounds (**3b**-OTf and **5**-OTf) are reported and compared to that of a parent complex previously described (**3a**′-OTf).[6] The X-ray data provided us with valuable information about the electronic properties of the gold center within the binuclear species. The steric and electronic influences of [Cp*Ru$^+$] coordination to [AuCl(PAr_3)] have been investigated by DFT computations. Furthermore, this

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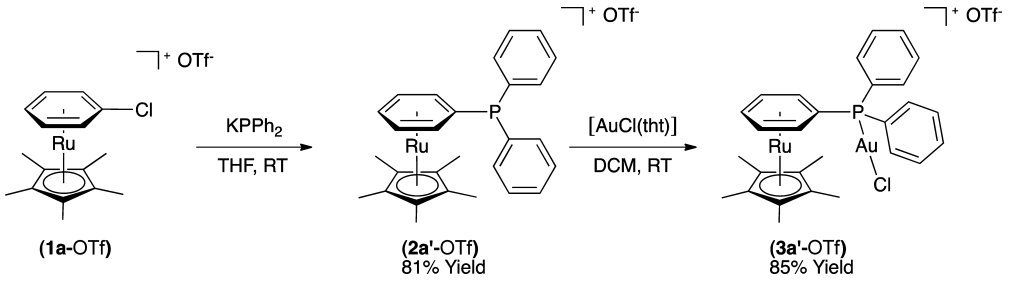
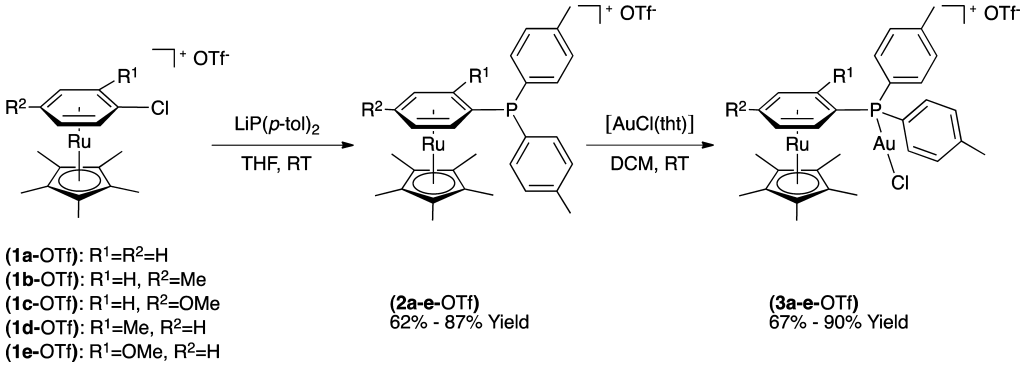
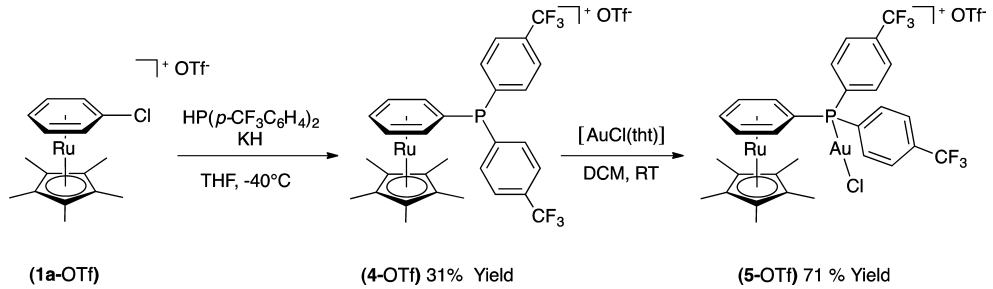
Scheme 1. Previous Work: Preparation of the Phosphino Ligand 2a′-OTf and the Related Heterobimetallic Precatalyst 3a′-OTf



Scheme 2. Preparation of a New Set of Heterodinuclear Ru−Au Complexes [Cp*Ru(η^6-arene-P(*p*-tol)$_2$)-Au-Cl][OTf] (3a−e-OTf)



Scheme 3. Preparation of a Heterodinuclear Gold Complex with Electron-Withdrawing Trifluoromethyl Groups in the Para Position (5-OTf)



family of ligands was evaluated toward the same 1,6-enyne cycloisomerization reaction in order to probe the role of the metalated phosphino ligands on the activity of the gold center and to establish a structure−reactivity relationship.

RESULTS AND DISCUSSION

Synthesis and Characterization of a Novel Family of π-Complexed Phosphino Ligands, [Cp*Ru(η^6-arene-PAr$_2$)][OTf] (2a−e-OTf), and the Related Gold Complexes [Cp*Ru(η^6-arene-PAr$_2$)-Au-Cl][OTf] (3a−e-OTf). The synthesis of the organometallic phosphino ligand **2a**′-OTf was performed as described previously[6] in two steps starting from the ruthenium precursor [Cp*Ru(CH$_3$CN)$_3$][OTf][9] and using the commercially available KPPh$_2$. In addition, we had also reported that treatment of the organometallic phosphino ligand **2a**′-OTf with 1 equiv of [AuCl(tht)] (tht = tetrahydrothiophene) in dichloromethane provided the target gold compound **3a**′-OTf in high yield (Scheme 1).[6]

We sought to prepare a variety of metalated phosphino ligands displaying electron-donating and -withdrawing groups in comparison to the previously reported ligand **2a**′-OTf. It is well-known that a small change in the nature of the phosphine ligands has an important impact on the solubility and reactivity of the target catalyst precursors. Unfortunately, all attempts to prepare the organometallic phosphine ligands with alkyl groups −PR$_2$ (R = −Cy, −Et, −Me) were unsuccessful. However, with tolyl groups, they were successfully introduced following the method reported by Gladysz and co-workers for the formation of LiP(*p*-tol)$_2$.[10]

Thus, the novel series of complexes [Cp*Ru(η^6-arene-P(*p*-tol)$_2$)][OTf] (**2a-e**-OTf) were prepared by treatment of the appropriate haloaromatic metal complex [Cp*Ru(η^6-arene-Cl)][OTf] (**1a-e**-OTf) with LiP(*p*-tol)$_2$ prepared in situ by addition of 1 equiv of a *n*-BuLi solution in *n*-hexanes to a HP(*p*-tol)$_2$ solution in *n*-hexanes (Scheme 2). All phosphine ligands of this series were isolated as white microcrystalline solids after reaction workup and were fully characterized by NMR spectroscopy and microanalytical data (see the Experimental Section). For instance, the ^{1}H NMR spectrum of [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-tol)$_2$)][OTf] (**2a**-OTf) recorded in CD$_2$Cl$_2$ shows a singlet at δ 2.00 ppm attributed to the methyl protons of the Cp* and also a singlet at δ 2.40 ppm assigned to the methyl protons of the *p*-tolyl groups while three multiplets are visible

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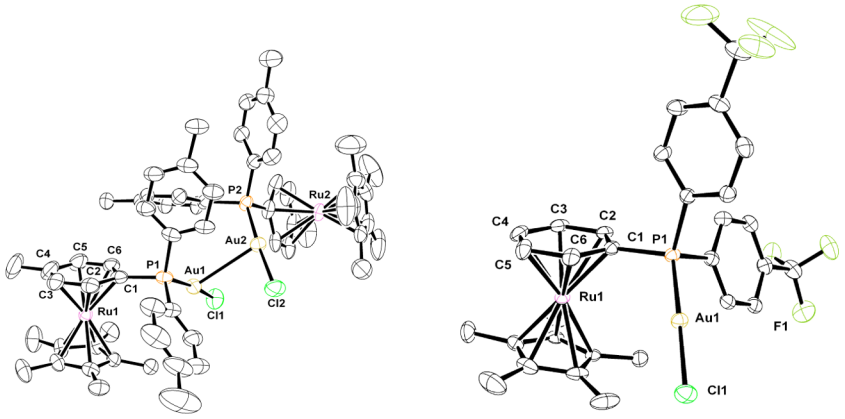

Figure 1. Molecular structures of the cationic heterodinuclear complexes (left) [Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl]$^+$ (**3b**) and (right) [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$)-Au-Cl]$^+$ (**5**) with the atom-numbering system. Complex **3b** shows dimer formation as a result of an Au1- - -Au2 interaction at 3.0809(4) Å. Hydrogen atoms are omitted for clarity.

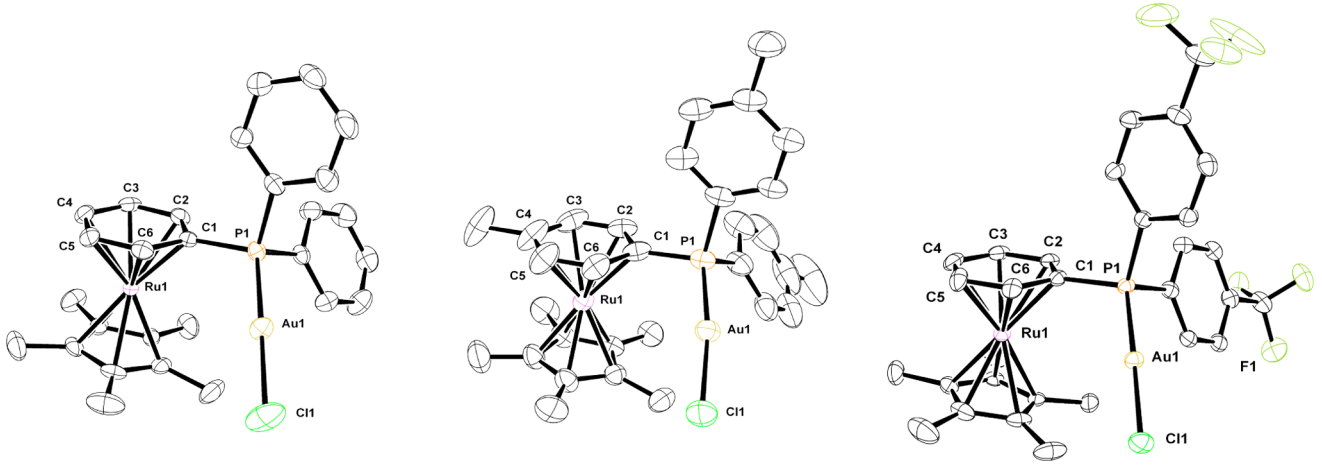

Figure 2. Molecular structures of cationic heterodinuclear complexes (left) **3a**′, (middle) **3b** (Au- - -Au interaction not shown), and (right) **5** with atom-numbering system exhibiting similar features (i.e. the AuCl moiety leans toward the "Cp*Ru" moiety due to the orientation of the diaryl phosphine groups). Hydrogen atoms are omitted for clarity.

at δ 5.45, 5.78, and 5.88 ppm, attributed to the protons of the η^6-aromatic ring. We also note the presence of a set of multiplets in the range δ 7.28−7.36 ppm attributed to the aromatic protons of the −P(*p*-tol)$_2$ moiety. Furthermore, the ^{31}P NMR spectrum recorded in CD_2Cl_2 showed a singlet at δ −16.8 ppm. Gratifyingly, after many attempts we were able to prepare a novel metalated phosphino ligand [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$][OTf] (**4**) with an electron-withdrawing group (−*p*-C$_6$H$_4$CF$_3$) bound to the phosphorus atom following a different synthetic procedure (Scheme 3).[11] Having obtained the organometallic phosphine ligands with different electron-donating and -withdrawing groups, we carried out the preparation of the related gold complexes (vide infra).

To attain the target gold compound **3a**-OTf, we treated the organometallic phosphino ligand **2a**-OTf with 1 equiv of [AuCl(tht)] in dichloromethane. The reaction proceeded smoothly under argon and was left for 1 h. Workup provided a white crystalline solid in 90% yield (Scheme 2). Elemental analysis and spectroscopic data suggested the formation of [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-tol)$_2$)-Au-Cl][OTf] (**3a**-OTf). The ^{1}H NMR recorded in CD_2Cl_2 is in agreement with the proposed formula and showed signals downfield relative to the phosphine ligand **2a**-OTf. The ^{31}P NMR spectrum in CD_2Cl_2 was the most informative and showed a singlet at δ 32.5 ppm. The downfield shift of the signal is significative of the coordination of the gold center by the organometallic phosphine ligand. The related heterodinuclear gold complexes [Cp*Ru(η^6-arene-P(*p*-tol)$_2$)-Au-Cl][OTf] (**3b**−**e**-OTf) and [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$)-Au-Cl][OTf] (**5**-OTf) were also obtained as pale white solids and were fully characterized by NMR spectroscopy and elemental analysis (see the Experimental Section). In addition, the X-ray molecular structures of [Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (**3b**-OTf) and [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$)-Au-Cl][OTf] (**5**-OTf) were determined and compared to that of [Cp*Ru(η^6-C$_6$H$_5$-PPh$_2$)-Au-Cl][OTf] (**3a**′-OTf) described previously (vide infra).[6]

Molecular Structures of [Cp*Ru(η^6-C$_6$H$_5$-PPh$_2$)-Au-Cl][OTf] (3a′-OTf), [Cp*Ru(η^6-p-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (3b-OTf), and [Cp*Ru(η^6-C$_6$H$_5$P(*p*-C$_6$H$_4$CF$_3$)$_2$)-Au-Cl][OTf] (5-OTf). Convenient crystals for X-ray study of the heterodinuclear Ru−Au complexes **3b**-OTf and **5**-OTf were obtained at room temperature by vapor diffusion of diethyl ether into a dichloromethane solution. Crystal data are given in Table S1 (Supporting Information). The X-ray structure of **3b**-OTf revealed the presence of two independent heterobimetallic molecules a and b, which exhibit an Au- - -Au interaction

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Table 1. Comparative Bond Lengths (Å) and Angles (deg) for Complexes 3a′-OTf, 3b-OTf, 5-OTf, and [AuCl(PPh$_3$)]

3a′-OTf		3b-OTf		5-OTf		[AuCl(PPh$_3$)]	
Au1−P1	2.218(1)	Au1−P1	2.230(1)	Au1−P1	2.220(2)	Au−P	2.235(3)
		Au2−P2	2.230(2)	Au2−P2	2.221(2)		
Au1−Cl1	2.270(1)	Au1−Cl1	2.281(2)	Au1−Cl1	2.271(2)	Au−Cl	2.279(3)
		Au2−Cl2	2.287(2)	Au2−Cl2	2.277(2)		
Ru1−C1	2.217(3)	Ru1−C1	2.230(6)	Ru1−C1	2.240(5)		
Ru1−C2	2.205(3)	Ru1−C2	2.198(6)	Ru1−C2	2.226(6)		
Ru1−C3	2.209(3)	Ru1−C3	2.208(6)	Ru1−C3	2.200(6)		
Ru1−C4	2.212(3)	Ru1−C4	2.234(6)	Ru1−C4	2.196(6)		
Ru1−C5	2.197(3)	Ru1−C5	2.215(6)	Ru1−C5	2.204(6)		
Ru1−C6	2.200(3)	Ru1−C6	2.204(5)	Ru1−C6	2.213(5)		
P1−C1	1.817(3)	P1−C1	1.803(6)	P1−C1	1.825(5)	P−C1	1.803(13)
P1−C17	1.819(3)	P1−C18	1.795(6)	P1−C17	1.823(6)	P−C7	1.866(12)
P1−C23	1.815(4)	P1−C25	1.818(5)	P1−C24	1.821(5)	P−C13	1.792(13)
P1−Au1−Cl1	176.34(4)	P1−Au1−Cl1	171.65(6)	P1−Au1−Cl1	178.19(6)	P−Au−Cl	179.63(8)
C1−P1−C17	108.70(14)	C1−P1−C25	103.7(3)	C1−P1−C24	105.5(2)	C1−P−C7	103.3(4)
C23−P1−C1	102.60(15)	C18−P1−C1	107.8(3)	C17−P1−C1	106.7(2)	C1−P−C13	106.2(5)
C23−P1−C17	103.79(13)	C18−P1−C25	105.9(3)	C17−P1−C24	105.0(3)	C7−P−C13	105.8(4)
C1−P1−Au1	111.84(10)	C1−P1−Au1	108.08(18)	C1−P1−Au1	112.24(19)	C1−P−Au	114.8(5)
C17−P1−Au1	112.29(11)	C18−P1−Au1	115.5(2)	C17−P1−Au1	113.01(19)	C7−P−Au	113.3(5)
C23−P1−Au1	116.80(10)	C25−P1−Au1	114.99(17)	C24−P1−Au1	113.67(18)	C13−P−Au	112.5(5)

(3.0809(4) Å), resulting in the formation of a dimeric compound (Figure 1).[12]

For comparison purposes, the molecular structures of **3b**, **5**, and **3a**′ are depicted in Figure 2 and comparative bond distances and angles are given in Table 1. We notice that the "Cp*Ru" moiety is symmetrically coordinated to the η^6-phenyl group. The structures of **3b** and **5** exhibited features similar to that of **3a**′; we note for instance that the AuCl molecular brick leans in the same fashion toward the "Cp*Ru" unit. The solid-state structures of **3a**′, **3b**, and **5** showed marked differences from the known complex [AuCl(PPh$_3$)] (Figure 2).[13] At first glance and in contrast to [AuCl(PPh$_3$)], the two sides of the cationic gold complexes are no longer equivalent, at least in the solid state. Indeed, one face of this complex is closer to the "Cp*Ru", which would hinder the approach of the substrate while the other side is open; thus, one might expect a different reactivity in comparison to the parent compound [AuCl(PPh$_3$)]. Furthermore, the sum of three C−P−C angles (θ) for **3b** was found to be 317.60°, on average, comparable to that for **5** (317.28°) but slightly larger than those for **3a**′ (315.20°) and [AuCl(PPh$_3$)] (315.16°).[2b] We then evaluated the electronic properties of these organometallic ligands.[14]

The electronic properties of these metalated phosphines **2a**′, **2a**−**d**, and **4** were evaluated by converting the metalated phosphino ligands to the related selenide complexes [Cp*Ru(η^6-arene-PAr$_2$)=Se][OTf]. Subsequent measurement of $^1J_{P-Se}$ coupling constants allowed us to classify the donor capacity of these compounds as follows: **2c** > **2d** > **2b** > **2a** > **2a**′ > **4**. It is worth mentioning that electron-withdrawing groups on phosphorus cause the coupling constant to increase, while electron-donating groups provide a smaller coupling constant value (Table 2).[15]

We reasoned that the "Cp*Ru" moiety should increase the π-acidity of the phosphines. This hypothesis was first verified by DFT computations[16] using the "allyl model" reported by Toste et al. (Table 3).[17] Enhancing the π-acidity decreases the back-donation to the allyl ligand. As a result, the Au−C bond order decreases. The geometrical sequel is the increase of d2, the decrease of d3, and the increase of d4. This prediction is perfectly followed when P(p-tol)$_3$ is compared with [Cp*Ru(η^6-p-MeC$_6$H$_4$-P(p-tol)$_2$)] (**2b**). Inspection of the natural charge distributions shows that the charge on gold virtually does not change with the coordination of the "Cp*Ru" unit on the phosphine. On the other hand, the charge on the phosphine decreases upon complexation of ruthenium, as a result of charge transfer to the allyl framework. Thus, the introduction of "Cp*Ru" enhances the electrophilicity of the substrate.

Table 2. ^{31}P NMR Data (δ in ppm and J in Hz) for PPh$_3$ and Metalated Phosphino Ligands (P(III)) and the Selenide Derivatives (P(V)) in CD_2Cl_2

phosphino ligand	δ(P(III))	selenide derivative δ(P(V))	$^1J_{P-Se}$
[Cp*Ru(η^6-C$_6$H$_5$-PPh$_2$)]$^+$ (**2a**′)	−13.3	35.9 (**2a**′=Se)	775
[Cp*Ru(η^6-C$_6$H$_5$-P(p-tol)$_2$)]$^+$ (**2a**)	−16.8	35.0 (**2a**=Se)	772
[Cp*Ru(η^6-p-MeC$_6$H$_4$-P(p-tol)$_2$)]$^+$ (**2b**)	−17.3	33.7 (**2b**=Se)	771
[Cp*Ru(η^6-p-MeOC$_6$H$_4$-P(p-tol)$_2$)]$^+$ (**2c**)	−16.9	33.3 (**2c**=Se)	768
[Cp*Ru(η^6-o-MeC$_6$H$_4$-P(p-tol)$_2$)]$^+$ (**2d**)	−22.4	31.2 (**2d**=Se)	769
[Cp*Ru(η^6-C$_6$H$_5$-P(p-C$_6$H$_4$CF$_3$)$_2$)]$^+$ (**4**)	−14.9	36.7 (**4**=Se)	796
PPh$_3$	−7.9	35.9 (Ph$_3$P=Se)	724

The increase of the d1 value also suggests that the steric demand around the Au−P bond increases significantly upon complexation of "Cp*Ru". To gain more insight into this issue, we looked at the percent buried volume[18] for **2a**′, **2b**, and **4** using the X-ray structures of **3a**′, **3b**, and **5** (Table 4). Clearly, the complexation of "Cp*Ru" to PPh$_3$ results in a more crowded environment around gold, the %V_{bur} value increasing from 34.8 to 42.9 (entries 1 and 2). The same is true for P(p-tol)$_3$ and the corresponding metalated phosphine (entries 3 and 4). In fact, the values for phosphines **2a**′, **2b**, and **4** are comparable with those of P(t-Bu)$_3$ or P(o-tol)$_3$, which are the most sterically demanding phosphines after P(Mes)$_3$ (entries

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Table 3. Geometrical Features and Natural Charges of Gold Complexes Optimized by M06 Computations

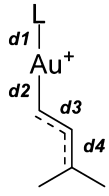
	L	*d1* (Å)	*d2* (Å)	*d3* (Å)	*d4* (Å)	q_{allyl} (*e*)	q_{Au} (*e*)	q_L (*e*)
	P(*p*-tol)$_3$	2.396	2.046	1.388	1.394	0.30	0.31	0.39
	[Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P*p*-tol$_2$)]$^+$ (**2b**)	2.408	2.051	1.381	1.403	0.35	0.31	0.34

Table 4. %V_{bur} Values of Some Ligands

entry	L	%V_{bur} in L-Au-Cl for M−P length at 2.00 Å
1	P(Ph)$_3$	34.8[a]
2	[Cp*Ru(η^6-C$_6$H$_5$-PPh$_2$)]$^+$ (**2a′**)	42.9[b] (*43.8*)[c]
3	P(*p*-tol)$_3$	34.2[a]
4	[Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)]$^+$ (**2b**)	43.1[b] (*43.4*)[c]
5	P(*t*-Bu)$_3$	43.9[a]
6	P(*o*-tol)$_3$	44.8[a]
7	P(Mes)$_3$	50.5[a]
8	[Cp*Ru(η^6-C$_6$H$_5$-P(*p*-tol)$_2$)]$^+$ (**2a**)	(*43.5*)[c]
9	[Cp*Ru(η^6-*o*-MeC$_6$H$_4$-P(*p*-tol)$_2$)]$^+$ (**2d**)	(*46.7*)[c]
10	[Cp*Ru(η^6-*p*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)]$^+$ (**2c**)	(*44.2*)[c]
11	[Cp*Ru(η^6-*o*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)]$^+$ (**2e**)	(*47.2*)[c]
12	[Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$)] (**4**)	43.4[b] (*44.6*)[c]

[a]Values obtained from ref 17. [b]Values obtained from X-ray structures. [c]Values obtained from the calculated gold complexes of Table 3.

5−7). The rest of the %V_{bur} values were obtained from calculated geometries, since the X-ray structures of the corresponding gold chlorides are not available. Along the series of metalated phosphines (entries 2, 4, and 8−12), the largest %V_{bur} values are observed with ortho-substituted aryl groups (entries 9 and 11).

Comparison of the Heterobimetallic Gold Compounds 3a′-OTf, 3a−e-OTf, and 5-OTf in Catalysis. The catalytic activity of the heterodinuclear gold complexes [Cp*Ru(η^6-arene-PAr$_2$)-Au-Cl][OTf] was then tested in the cycloisomerization reaction of *N*-tethered 1,6-enyne **6** and compared to the commercially available homologous mononuclear phosphine gold compounds [AuCl(PAr$_3$)], in order to probe any platform effect on the selectivity and/or the reactivity (Figure 3).[19,20] When **6** was submitted to [Cp*Ru(η^6-C$_6$H$_5$-PPh$_2$)-Au-Cl][OTf] (**3a′**-OTf; 5 mol %), in the presence of AgSbF$_6$ (7 mol %) in dichloromethane at room temperature, the related bicyclic product **7** was cleanly and selectively formed, but in a slower fashion than when [AuCl(PPh$_3$)] was used, with concomitant catalyst degradation (Figure 3-1, yellow curve).[21] After 75 min, 79% conversion (**7**/(**6** + **7**) ratio) was observed for **3a′**-OTf vs 84% for [AuCl(PPh$_3$)], and the corresponding bicycle **7** was isolated in 67% and 76% yields, respectively. As **3a′**-OTf was not stable enough, we switched to [AuCl(P(*p*-Tol)$_3$)] bimetallic analogues. By using the [Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl] catalyst **3b**-OTf, not only was the stability improved but also the reactivity increased and a positive platform effect was observed (Figure 3-2, blue curve). Indeed, after 75 min, the conversion reached 98% with **3b**-OTf vs 84% for its mononuclear counterpart [AuCl(P(*p*-tol)$_3$)], and the heterocyclic product **7** was isolated in 92% vs 73% yield, respectively.

We then investigated the influence of the substituent at the arene platform. As indicated by the J_{Se-P} NMR constants (Table 2), **2a−e**-OTf ligands possess comparable π-acidic properties within the family; therefore, a similar behavior in catalysis was expected. Indeed, when the [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl] catalyst **3c**-OTf was used, an equivalent reactivity was observed (Figure 4, black curve). A similar result was observed with the [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-tol)$_2$)-Au-Cl][OTf] catalyst **3a**-OTf, bearing no substituent at the platform (Figure 4, red curve), thus underlying the scant influence of the platform's para substitution with respect to the stability and the reactivity of the catalyst. However, the steric properties should not be neglected, as highlighted by ortho-substituted catalysts **3d**-OTf and **3e**-OTf, possessing the largest %V_{bur} values of the tested series (Table 4). Moving the methyl substituent from the para to the ortho position (**3d**-OTf) indeed slowed down the reaction (green curve), and when an *o*-methoxy group was introduced (**3e**-OTf), no conversion was observed, presumably because of the degradation of the cationic catalyst in solution (brown curve).

As a π-acidic bimetallic catalyst had better activity than its homologous mononuclear phosphine gold compound, we then tested [Cp*Ru(η^6-C$_6$H$_5$-P(*p*-C$_6$H$_4$CF$_3$)$_2$)-Au-Cl][OTf] (**5**-OTf), bearing two electron-withdrawing groups (*p*-C$_6$H$_4$CF$_3$) bound to the phosphorus atom. The latter should be more π-acidic than the previous **3a−e**-OTf family, with regard to the Se−P coupling constant in **4**═Se (798 Hz vs 768−772 Hz for **2a−e**═Se phosphines; see Table 2). Treatment of enyne **6** by **5**-OTf catalyst (5 mol %) in the presence of AgSbF$_6$ (7 mol %) (CH$_2$Cl$_2$, room temperature) led indeed to the fastest reaction and full conversion was obtained after 45 min (Figure 5, purple curve).

CONCLUDING REMARKS

In conclusion, we have reported a novel approach to prepare metalated phosphino ligands [Cp*Ru(η^6-arene-P(*p*-Ar)$_2$)]$^+$ (**2a−e** and **4**) displaying electron-donating and -withdrawing groups, which can be converted to the unique types of heterobimetallic cationic gold complexes **3a′**, **3a−e**, and **5**, where the −PAr$_2$-Au-Cl unit is now attached to the metalated π-arene platform [Cp*Ru(η^6-arene)][OTf]. The structures of three compounds of this family were further ascertained by

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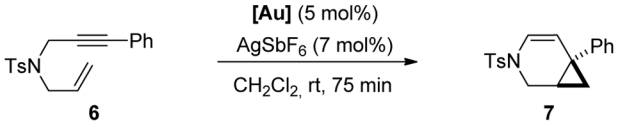

[Au]	conversion [7/(7+6)]	corrected isolated yield[a]
3a'-OTf	79%	67%
[PPh_3AuCl]	84%	76%
3b-OTf	98%	92%
[$P(p\text{-}MeC_6H_4)_3AuCl$]	80%	73%

a) as **7** and **6** co-elute, a corrected yield was calculated from the isolated **7**+**6** mixture

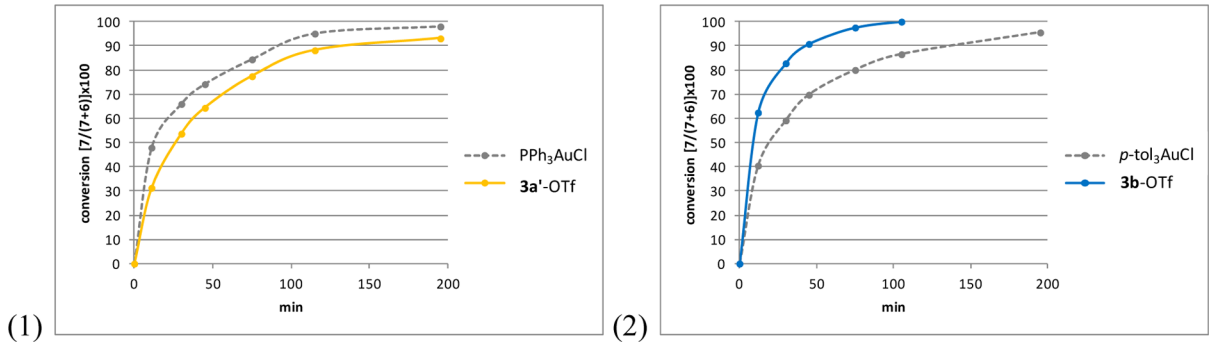

Figure 3. Comparison of **3a**′-OTf (1) and **3b**-OTf (2) with their homologous mononuclear triarylphosphine gold complexes, in the cycloisomerization of *N*-tethered 1,6-enyne **6**.

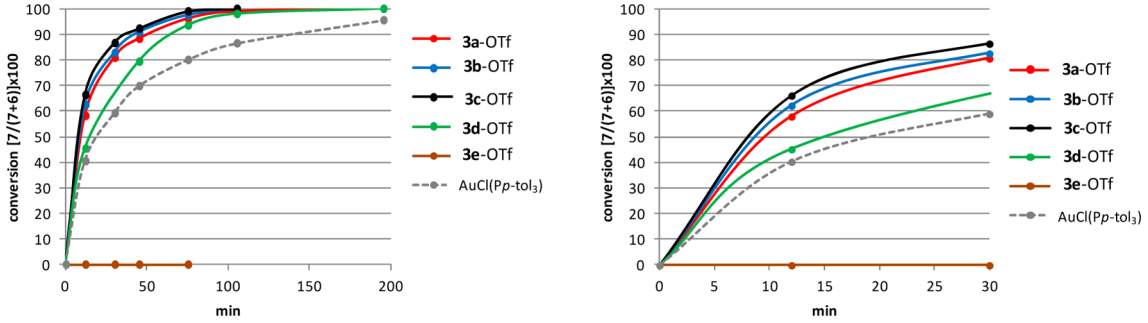

Figure 4. Influence of the platform substitution on the cycloisomerization of *N*-tethered 1,6-enyne **6**.

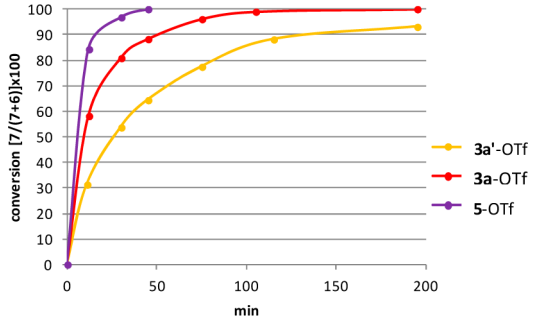

Figure 5. Influence of substitution of the aryls bound to the phosphorus atom on the cycloisomerization of *N*-tethered 1,6-enyne **6**.

single-crystal X-ray crystallography. The catalytic properties of these heterodinuclear gold compounds were investigated toward cycloisomerization of an *N*-tethered 1,6-enyne to give selectively the related bicyclic product. In this reaction, the π-acidic properties of our new metallo ligands were highly interesting, notably in complex **5**, which generates a powerful catalyst in the presence of a silver salt. These results open the way to the preparation of optically enriched binuclear catalysts, displaying both planar chirality and high π-acidity, toward enantioselective cycloisomerization reactions.[26]

EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H NMR spectra were recorded at 300 or 400 MHz in CD_2Cl_2, and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CD_2Cl_2 δ 5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration. ^{13}C NMR spectra were recorded at 75 or 100 MHz in CD_2Cl_2, and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CD_2Cl_2 δ 54.0 ppm). ^{31}P NMR spectra were recorded at 121 MHz in CD_2Cl_2 with chemical shifts in ppm referenced to H_3PO_4 as external standard. Glassware was oven-dried prior to use. All reactions were carried out using Schlenk techniques for the complex synthesis and under an argon atmosphere for the catalysis. THF and diethyl ether were distilled from sodium–benzophenone. CH_2Cl_2 was distilled from CaH_2. Other reagents were obtained from commercial suppliers and used as received. TLC

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measurements were performed on silica gel plates visualized either with a UV lamp (254 nm). Flash chromatography was performed on silica gel (230−400 mesh). Infrared spectra were measured using a Tensor 27 (ATR diamond) Bruker spectrometer. IR data are reported as characteristic bands (cm^{-1}). The syntheses of **1a−e**-OTf, **2a**′-OTf, and **3a**′-OTf have already been reported in the literature.[6,9]

Synthesis of [Cp*Ru(η^6-C_6H_5-P(*p*-tol)$_2$)][OTf] (2a-OTf). A solution of LiP(*p*-tol)$_2$ in hexanes (0.8 mL, 0.40 mmol) was prepared in a Schlenk tube under argon by addition of ″BuLi (1.6 M in hexanes) to HP(*p*-tol)$_2$ (10 wt % in hexanes) at room temperature, and the mixture was stirred for 15 min. This yellow mixture was added at once to a solution of compound **1a** (200 mg, 0.40 mmol) dissolved in tetrahydrofuran (20 mL) under argon, and the resulting orange solution was stirred for 1 h. The solution was then evaporated to dryness, dissolved in CH_2Cl_2, and passed through Celite to eliminate the salt (LiCl) that formed during the reaction. Precipitation from CH_2Cl_2/diethyl ether gave a white solid. Yield: 77%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.36 (m, H arene, 4H), 7.28 (m, H arene, 4H), 5.88 (m, H π-arene, 1H), 5.78 (m, H π-arene, 2H), 5.45 (m, H π-arene, 2H), 2.40 (s, 2Me, 6H), 2.00 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 141.2, 134.5, 134.2, 130.1 (C arene), 98.1, 96.9, 88.3, 87.4, 87.0 (C π-arene), 21.0 (5 CH_3, Cp*), 10.6, 10.1 (2 CH_3, *p*-tol). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −16.8. Anal. Calcd for $C_{31}H_{34}F_3O_3PRuS$ (675.70 g mol^{-1}): C, 55.10; H, 5.07. Found: C, 55.18; H, 5.15.

Synthesis of [Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)][OTf] (2b-OTf). This compound was prepared in a way similar to that for **2a**-OTf. Yield: 87%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.37 (m, H arene, 4H), 7.28 (m, H arene, 4H), 5.63 (m, H π-arene, 2H), 5.42 (m, H π-arene, 2H), 2.41 (s, 2*p*-CH_3 arene, 6H), 2.25 (s, *p*-CH_3 π-arene, 3H), 1.96 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 141.2, 134.5, 134.2, 130.1 (C arene), 100.4, 96.2, 88.3, 88.1, 87.8 (C π-arene), 21.0 (5 CH_3, Cp*), 17.9, 10.6, 10.1 (3 CH_3, *p*-tol). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −17.3. Anal. Calcd for $C_{32}H_{36}F_3O_3PRuS$ (689.73 g mol^{-1}): C, 55.72, H 5.26. Found: C, 55.80; H, 5.32.

Synthesis of [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)][OTf] (2c-OTf). This complex was prepared in a fashion similar to that for **2a**-OTf. Yield: 62%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.36 (m, H arene, 4H), 7.28 (m, H arene, 4H), 5.81 (m, H π-arene, 2H), 5.38 (m, H π-arene, 2H), 3.86 (s, *p*-OCH_3 π-arene, 3H), 2.40 (s, 2 *p*-CH_3 arene, 6H), 1.97 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 141.0, 134.4, 134.1, 130.0 (C arene), 97.2, 96.1, 87.2, 87.1, 75.7 (C π-arene), 57.5 (*p*-OCH_3), 21.0 (5 CH_3, Cp*), 10.4, 10.3 (2 CH_3, *p*-tol). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −16.9. Anal. Calcd for $C_{32}H_{36}F_3O_4PRuS$ (705.73 g mol^{-1}): C, 54.46; H, 5.14. Found: C, 54.58; H, 5.12.

Synthesis of [Cp*Ru(η^6-*o*-MeC$_6$H$_4$-P(*p*-tol)$_2$)][OTf] (2d-OTf). This complex was prepared in a fashion similar to that for **2a**-OTf. Yield: 75%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.36 (m, H arene, 4H), 7.21 (m, H arene, 4H), 5.87 (m, H π-arene, 1H), 5.69 (m, H π-arene, 2H), 5.13 (m, H π-arene, 1H), 2.42 (s, *p*-CH_3 arene, 3H), 2.38 (s, *p*-CH_3 arene, 3H), 2.00 (s, *o*-CH_3 π-arene, 3H), 1.96 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 141.4, 134.7, 134.0, 130.0 (C arene), 100.9, 96.5, 88.4, 88.1, 87.2 (C π-arene), 21.0 (5 CH_3, Cp*), 17.2, 10.4, 10.1 (3 CH_3, *p*-tol). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −22.4. Anal. Calcd for $C_{32}H_{36}F_3O_3PRuS$ (689.73 g mol^{-1}): C, 55.72; H, 5.26. Found: C, 55.77; H, 5.34.

Synthesis of [Cp*Ru(η^6-*o*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)][OTf] (2e-OTf). This complex was prepared in a fashion similar to that for **2a**-OTf. Yield: 74%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.42 (m, 10H, H arene), 5.84 (m, 2H, *J* = 1.8 Hz, *J* = 5.9 Hz, H π-arene), 5.57 (dd, 2H, *J* = 0.8 Hz, *J* = 5.9 Hz, H π-arene), 1.95 (s, Cp*, 15H), 1.76 (d, 6H, *J* = 0.8 Hz, *o*-CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 141.4, 135.7, 135.5, 130.1 (C arene), 97.8, 95.8, 88.0, 86.3, 74.2 (C π-arene), 57.2 (*p*-OCH_3), 21.9 (5 CH_3, Cp*), 10.5, 10.4 (2 CH_3, *p*-tol). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −12.0. Anal. Calcd for $C_{32}H_{36}F_3O_4PRuS$ (705.73 g mol^{-1}): C, 54.46; H, 5.14. Found: C, 54.61; H, 5.21.

Synthesis of [Cp*Ru(η^6-C_6H_5-P(*p*-tol)$_2$)-Au-Cl][OTf] (3a-OTf). **2a**-OTf (315 mg, 0.49 mmol) was dissolved in CH_2Cl_2 (30 mL) under argon, and [AuCl(tht)] (156 mg, 0.49 mmol) was added to the solution. The reaction mixture was stirred for 1 h at room temperature. After that, the solution was passed through Celite. A white crystalline solid was obtained after precipitation from CH_2Cl_2−diethyl ether. Yield: 90%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.49 (m, H arene, 4H), 7.40 (m, H arene, 4H), 6.18 (m, H π-arene, 1H), 6.12 (m, H π-arene, 2H), 6.00 (m, H π-arene, 2H), 2.46 (s, 2 *p*-Me, 6H), 2.04 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 134.2 (d, C2 arene, J_{C-P} = 14.6 Hz), 133.1 (d, C4 arene, J_{C-P} = 2.7 Hz), 129.5 (d, C3 arene, J_{C-P} = 12,3 Hz), 125.9 (d, C1 arene, J_{C-P} = 62.5 Hz), 91.8 (d, C1 π-arene, J_{C-P} = 53.0 Hz), 88.7 (d, C4 π-arene, J_{C-P} = 1.1 Hz), 88.4 (d, C2 π-arene, J_{C-P} = 13.2 Hz), 87.5 (d, C3 π-arene, J_{C-P} = 7.4 Hz), 11.3 (s, 5 CH_3, Cp*). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 32.5. Anal. Calcd for $C_{31}H_{34}AuClF_3O_3PRuS$ (908.12 g mol^{-1}): C, 41.00; H, 3.77. Found: C, 41.08; H, 3.86.

Synthesis of [Cp*Ru(η^6-*p*-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (3b-OTf). **3b**-OTf was prepared from the metalated phosphino ligand **2b**-OTf in a way similar to that described for **3a**-OTf. Yield: 92%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.51 (m, H arene, 4H), 7.39 (m, H arene, 4H), 6.00 (m, H π-arene, 4H), 2.47 (s, 2 *p*-CH_3 arene, 6H), 2.37 (s, *p*-CH_3 π-arene, 3H), 1.98 (s, Cp*, 15H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ (ppm) 135.4 (d, J_{C-P} = 14.6 Hz, CH arene), 134.1 (CH arene), 130.6 (d, J_{C-P} = 12.3 Hz, CH arene), 127.3 (d, J_{C-P} = 62.7 Hz, C*q* arene), 103.8 (CH π-arene), 98.9 (C*q* Cp*), 92.1 (d, J_{C-P} = 53.8 Hz, C*q* π-arene), 89.6 (d, J_{C-P} = 13.6 Hz, CH π-arene), 89.4 (d, J_{C-P} = 7.7 Hz, CH π-arene), 18.7 (*p*-CH_3 π-arene) 11.7 (5 CH_3, Cp*). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 31.9. Anal. Calcd for $C_{32}H_{36}AuClF_3O_3PRuS$ (922,15 g mol^{-1}): C, 41.68; H, 3.93. Found: C, 41.60; H, 3.83.

Synthesis of [Cp*Ru(η^6-*p*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (3c-OTf). **3c−OTf** was prepared from the metalated phosphino ligand **2c**-OTf in a fashion similar to that described for **3a**-OTf. Yield: 80%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.52 (m, H arene, 4H), 7.40 (m, H arene, 4H), 6.09 (m, H π-arene, 2H), 6.03 (m, H π-arene, 2H), 3.86 (s, OCH_3, 3H), 2.46 (s, 2 Me, 6H) 1.97 (s, Cp*, 15H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ (ppm) 135.3 (d, J_{C-P} = 14.6 Hz. CH arene), 134.1 (CH arene), 130.6 (d, J_{C-P}= 12.3 Hz, CH arene), 127.6 (d, J_{C-P} = 62.7 Hz, C*q* arene), 98.6 (C*q* Cp*), 89.7 (d, J_{C-P} = 54.8 Hz, C*q* arene), 88.9 (d, J_{C-P} = 14.9 Hz, C*q* arene), 87.8 (C*q* π-arene), 77.1 (d, J_{C-P} = 8.6 Hz, CH π-arene), 58.6 (*p*-OCH_3 π-arene), 11.7 (5 CH_3, Cp*). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 31.7. Anal. Calcd for $C_{32}H_{36}AuClF_3O_4PRuS$ (938.15 g mol^{-1}): C, 40.97; H, 3.87. Found: C, 41.04; H, 3.85.

Synthesis of [Cp*Ru(η^6-*o*-MeC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (3d-OTf). **3d**-OTf was prepared from the metalated phosphino ligand **2d**-OTf in a fashion similar to that described for **3a**-OTf. Yield: 67%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.36−7.55 (m, H arene, 8H), 6.17 (m, H π-arene, 1H), 6.02 (m, H π-arene, 1H), 5.80 (m, H π-arene, 1H), 5.21 (m, H π-arene, 1H), 2.49 (s, *p*-CH_3 arene, 3H), 2.45 (s, *p*-CH_3 arene, 3H), 2.38 (s, *o*-CH_3 π-arene, 3H), 2.09 (s, Cp*, 15H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ (ppm) 145.5 (C*q* arene), 136.2, 136.0, 135.1, 134.9, 131.9, 131.7 (8 CH arene), 99.2 (C*q* π-arene), 98.8 (C*q* Cp*), 91.9, 90.4, 89.3, 87.6 (4 CH π-arene), 22.4 (*o*-CH_3 π-arene), 19.8 (*p*-CH_3 arene), 19.7 (*p*-CH_3 arene), 12.0 (5 CH_3, Cp*). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 24.9. Anal. Calcd for $C_{32}H_{36}AuClF_3O_3PRuS$ (922,15 g mol^{-1}): C, 41.68; H, 3.93. Found: C, 41.80; H, 3.90.

Synthesis of [Cp*Ru(η^6-*o*-MeOC$_6$H$_4$-P(*p*-tol)$_2$)-Au-Cl][OTf] (3e-OTf). **3e**-OTf was prepared from the metalated phosphino ligand **2e**-OTf in a fashion similar to that described for **3a**-OTf. Yield: 87%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.71 (d, *J* = 14.1 Hz, H arene, 2H), 7.69 (d, *J* = 14.1 Hz, H arene, 2H), 7.61 (m, H arene, 2H), 7.53 (m, H arene, 4H), 6.10 (dt, *J* = 2.4 Hz, *J* = 5.9 Hz, H π-arene, 1H), 5.81 (dd, *J* = 1.5 Hz, *J* = 5.9 Hz, H π-arene, 1H), 2.06 (s, Cp*, 15H), 1.89 (s, *o*-CH_3 π-arene, 6H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ (ppm) 135.7 (d, J_{C-P} = 14.6 Hz, CH arene), 134.1 (CH arene), 130.8 (d, J_{C-P} = 12,7 Hz, CH arene), 129.1 (d, J_{C-P} = 62.4 Hz, C*q* arene), 101.5 (d, J_{C-P} = 8.8 Hz, CH π-arene), 98.2 (C*q* Cp*), 96.6 (d, J_{C-P} = 47.1 Hz, C*q* arene), 91.7 (d, J_{C-P} = 4.4 Hz, CH arene), 91.2 (CH π-arene), 22.4 (d, J_{C-P} = 6.3 Hz, *o*-CH_3 π-arene), 11.4 (5 CH_3, Cp*). ^{31}P NMR (121

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MHz, CD_2Cl_2): δ (ppm) 30.42. Anal. Calcd for $C_{32}H_{36}AuClF_3O_3PRuS$ (938,15 g mol^{-1}): C, 40.97; H, 3.54. Found: C, 41.10; H, 3.60.

Synthesis of [Cp*Ru(η⁶-C₆H₅-P(*p*-C₆H₄CF₃)₂)][OTf] (4-OTf). $HP(p\text{-}C_6H_4CF_3)_2$ (250 mg, 0.77 mmol) was dissolved in tetrahydrofuran (2 mL) in a Schlenk tube under argon and then transferred at −40 °C to another Schlenk tube containing a KH (46 mg, 1.5 equiv) suspension in tetrahydrofuran (2 mL); this mixture was stirred under argon for 2 h at −40 °C. This deep red solution was added at once to a solution of compound **1a** (250 mg, 0.50 mmol) dissolved in tetrahydrofuran (20 mL) under argon; the resulting orange solution was stirred for $1^1/_2$ h at −40 °C and then was warmed slowly to room temperature. The solution was then evaporated to dryness, the residue was dissolved in CH_2Cl_2, and this solution was passed through Celite. Precipitation from CH_2Cl_2/diethyl ether gave a white solid. Yield: 33%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.76 (m, H arene, 4H), 7.61 (m, H arene, 4H), 6.05 (m, H π-arene, 1H), 5.96 (m, H π-arene, 2H), 5.51 (m, H π-arene, 2H), 2.03 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 135.4, 135.2, (2 CF_3), 126.7, 126.6, 126.6, 126.5 (12 C arene), 97.9, 88.5, 88.4, 88.3, 87.9, 87.8 (6 C π-arene), 11.1 (5 CH_3, Cp*). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) −14.9. ^{19}F NMR (120 MHz, CD_2Cl_2): δ (ppm) −63.5 $(-C_6H_4CF_3)_2$, −78.9 $(SO_3^-CF_3)$. Anal. Calcd for $C_{31}H_{28}F_9O_3PRuS$ (783.65 g mol^{-1}): C, 47.51; H, 3.60. Found: C, 47.86; H, 3.68.

Synthesis of [Cp*Ru(η⁶-C₆H₅-P(*p*-C₆H₄CF₃)₂)-Au-Cl][OTf] (5-OTf). **5**-OTf was prepared from the metalated phosphino ligand **4**-OTf in a way similar to that described for **3a**-OTf. Yield: 71%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.87 (m, H arene, 4H), 7.81 (m, H arene, 4H), 6.17 (m, H π-arene, 5H), 2.00 (s, Cp*, 15H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 135.8, 135.6, 130.1, 127.4, 127.3, 127.2 (12 C arene), 99.7, 89.5, 89.4, 89.2, 88.6, 88.5 (6 C π-arene), 11.6 (s, 5 CH_3, Cp*). ^{31}P NMR (161 MHz, CD_2Cl_2): δ (ppm) 34.5. ^{19}F NMR (120 MHz, CD_2Cl_2): δ (ppm) −63.8 $(-C_6H_4CF_3)_2$, −78.8 $(SO_3^-CF_3)$. Anal. Calcd for $C_{31}H_{28}AuClF_9O_3PRuS.CH_2Cl_2$ (1099.93 g mol^{-1}): C, 34.91; H, 2.75. Found: C, 34.54; H, 2.52.

General Procedure for the Preparation of the Selenide Phosphino Ligands. The phosphine selenide derivatives were prepared according to a published procedure.[15b] Degassed methanol solutions (5 mL) containing KSeCN (3.2 mg, 0.022 mmol) and the desired phosphino ligand (0.020 mmol) were prepared and stirred at room temperature under argon for 30 min. The solutions were evaporated to dryness, the solid residues were extracted with dichloromethane, and the extracts were filtered through Celite. The reactions were quantitative and provided stable white powders, as demonstrated by ^{1}H NMR of some representative compounds **2a**−**c**=Se-OTf.

*[Cp*Ru(η⁶-C₆H₅-P(p-tol)₂)Se][OTf] (**2a**=Se-OTf).* ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.59 (m, H arene, 4H), 7.29 (m, H arene, 4H), 6.33 (m, H π-arene, 1H), 6.12 (m, H π-arene, 2H), 5.86 (m, H π-arene, 2H), 2.45 (s, 2 *p*-Me, 6H), 2.02 (s, Cp*, 15H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 35.0 ($^1J_{P-Se}$ = 772 Hz).

*[Cp*Ru(η⁶-p-MeC₆H₄-P(p-tol)₂)Se][OTf] (**2b**=Se-OTf).* ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.62 (m, H arene, 4H), 7.36 (m, H arene, 4H), 6.36 (m, H π-arene, 2H), 5.99 (m, H π-arene, 2H), 2.45 (s, 2 *p*-CH_3 arene, 6H), 2.39 (s, *p*-CH_3 π-arene, 3H), 1.97 (s, Cp*, 15H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 33.7 ($^1J_{P-Se}$ = 771 Hz).

*[Cp*Ru(η⁶-p-MeOC₆H₄-P(p-tol)₂)Se][OTf] (**2c**=Se-OTf).* ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.62 (m, H arene, 4H), 7.35 (m, H arene, 4H), 6.40 (m, H π-arene, 2H), 6.07 (m, H π-arene, 2H), 3.88 (s, *p*-OCH_3 π-arene, 3H), 2.45 (s, 2 *p*-CH_3 arene, 6H), 2.01 (s, Cp*, 15H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 33.3 ($^1J_{P-Se}$ = 768 Hz).

*[Cp*Ru(η⁶-o-MeC₆H₄-P(p-tol)₂)Se][OTf] (**2d**=Se-OTf).* ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 31.2 ($^1J_{P-Se}$ = 769 Hz).

*[Cp*Ru(η⁶-C₆H₅-P(p-C₆H₄CF₃)₂Se][OTf] (**4**=Se-OTf).* ^{31}P NMR (121 MHz, CD_2Cl_2): δ (ppm) 36.7 ($^1J_{P-Se}$ = 796 Hz).

Catalysis. The preparation of *N*-tethered 1,6-enyne **6** has already been described.[22]

General Procedure for Kinetic Studies. To a prestirred (10 min) solution of **3**-OTf (0.005 mmol, 0.05 equiv) and $AgSbF_6$ (2.4 mg, 0.007 mmol, 0.07 equiv) in CH_2Cl_2 (10 mL, *c* 0.01 M) at room temperature was added 1,6-enyne **6** (32.5 mg, 0.1 mmol, 1 equiv) in one portion. At a selected time, a sample (1 mL) was taken from the reaction mixture and filtered through a short pad of silica (Et_2O). After concentration under reduced pressure and subsequent ^{1}H NMR of the crude material, the conversion (7/(**6** + 7) ratio) was determined.

General Procedure for Isolated Yield. To a prestirred (10 min) solution of the gold complex (0.005 mmol, 0.05 equiv) and $AgSbF_6$ (2.4 mg, 0.007 mmol, 0.07 equiv) in CH_2Cl_2 (10 mL, *c* 0.01 M) at room temperature was added 1,6-enyne **6** (32.5 mg, 0.1 mmol, 1 equiv) in one portion. After 75 min at room temperature, the reaction mixture was filtered through a short plug of silica (Et_2O) and then concentrated under reduced pressure. Analysis of the crude material by ^{1}H NMR indicated the conversion (7/(**6** + 7) ratio). After purification by flash chromatography (pentane/Et_2O gradient: 95/5 to 90/10) an inseparable mixture of bicyclic **7** and enyne **6** was isolated, as a white solid. *The spectral data are in agreement with those reported in the literature.*[22]

***3a′*-OTf:** 27.7 mg, 79% conversion (crude), 67% corrected yield (7/**6** = 79/21, ^{1}H NMR ratio).

[AuCl(PPh₃)]: 29.6 mg, 84% conversion (crude), 76% corrected yield (7/**6** = 84/16, ^{1}H NMR ratio).

***3b*-OTf:** 30.4 mg, 98% conversion (crude), 92% corrected yield (7/**6** = 98/2, ^{1}H NMR ratio).

[AuCl(P(p-tol)₃)]: 28.5 mg, 80% conversion (crude), 73% corrected yield (7/**6** = 83/17, ^{1}H NMR ratio).

X-ray Structural Determination of [Cp*Ru(η⁶-*p*-MeC₆H₄-P-*p*-tol₂)-Au-Cl][OTf] (3b-OTf) and [Cp*Ru(η⁶-C₆H₅-P(*p*-C₆H₄CF₃)₂)-Au-Cl][OTf] (5-OTf). Data were collected on a Bruker Kappa-APEXII instrument. Unit cell parameter determinations, data collection strategies, and integration were carried out with the Bruker APEX2 suite of programs. A multiscan absorption correction was applied.[23]The structures were solved by direct methods using SIR92[24] and SHELXS-86,[25] respectively, and refined anisotropically by full-matrix least-squares methods using SHELXL-97.[25]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 and CIF files including X-ray crystallographic data for **3b**-OTf and **5**-OTf. This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

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