ChemPubSoc Europe

DOI: 10.1002/ejoc.201701259

EurJOC European Journal of Organic Chemistry

Full Paper

Pd and Au Catalysis

Stereoselective Catalytic Synthesis of Alkynylated Phosphaethenes Leading to Activation-Free Gold Catalysis

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Abstract: The π-accepting property of alkene-like phosphaethenes (–P=C<) is attractive for the development of Lewis acidic transition-metal catalysts. The stereoselective monoalkynylation of a sterically encumbered *gem*-dibromophosphaethene by a Sonogashira process has been accomplished, and the corresponding 2-alkynyl-2-bromo-1-phosphaethenes were obtained. Subsequent arylation of the 2-alkynyl-2-bromo-1-phosphaethenes by the palladium version of the Kumada–Tamao–Corriu (KTC) reaction gave the corresponding 2-alkynyl-2-aryl-1-phosphaethenes through an inversion of the configuration. The 2-alkynyl-2-aryl-1-phosphaethenes were converted into the corresponding chloro-gold(I) complexes, and screening of their catalytic activity revealed that both appropriate π-conjugative substituents and the stereochemistry were decisive for the efficiency of the gold-catalyzed reactions under activation-free conditions. Chloro-gold complexes bearing 2,2-diaryl-1-phosphaethene ligands showed moderate-to-good catalytic activity.

Introduction

Intensive research into low-coordination phosphorus chemistry has revealed that the olefin-like character of the P=C double bond, and thus extension of a π-conjugated system with a phosphaalkene (methylenephosphine) unit(s) is of interest.[1,2] The lowest-unoccupied molecular orbital (LUMO) of phosphaalkene has a very low energy, which is promising for the development of unique transition-metal catalysts with strong π-accepting character.[3,4] In the past decade we have developed chloro-gold catalysts bearing low-coordinate phosphine ligands,[5–7] because the π-accepting character is effective for inducing very soft Lewis acidic character around a gold(I) center.[8,9]

Tuning of the LUMO levels of phosphaalkenes by incorporating π-conjugated units is one of the promising approaches for the exploration of functional materials. However, appropriate extension of a π-conjugated system is often a requisite to promote desirable catalytic activity. For example, our previous study[6] revealed that the catalytic activity of bis(chloro-gold) complexes bearing 3,4-diphosphinidenecyclobutene (DPCB)[10] depended considerably on the substituents at the 1,2-positions and excessive extension of π-conjugation seemed to be disadvantageous for improving the catalytic activity (Figure 1).

Most of the DPCB-chloro-gold complexes showed high catalytic activity, but the presence of the aurophilic interaction[11] was somewhat undesirable to evaluate the effect of the phosphaethene unit on activation-free chloro-gold catalysis. We expected that mononuclear phosphaethene-gold complexes would be desirable to determine the effects of low-coordinate phosphorus on the catalytic activity.

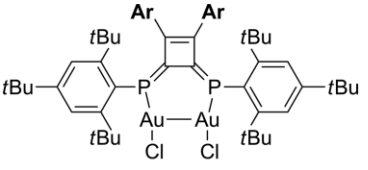
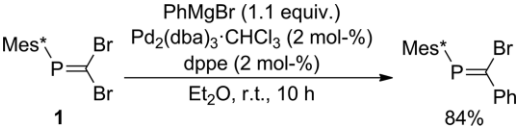


Figure 1. π-extended DPCB-chloro-gold catalysts.

Recently we reported the regioselective catalytic monoarylation of the sterically encumbered *gem*-dibromophosphaethene **1** by the palladium version of the Kumada–Tamao–Corriu (KTC) cross-coupling reaction (Scheme 1).[12] Optimization of the reaction conditions successfully diminished the undesired phosphorus version of the Fritsch–Buttenberg-Wiechell rearrangement, and the remaining bromine atom could be subsequently converted into other substituents through an inversion of the stereochemistry. The success of the KTC process to afford the 2-bromo-2-aryl-1-phosphaethenes prompted further exploration of synthetic π-extension processes by using **1**.



Scheme 1. Palladium version of the KTC coupling reaction for the monoarylation of dibromophosphaethene **1**. Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$.

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201701259.

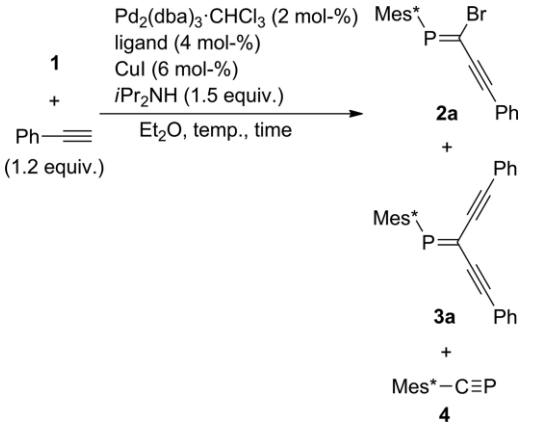
We expected that the protocol for the π-extension of **1** by palladium-catalyzed π-functionalization would be promising for exploring highly active and efficient mononuclear chloro-gold catalysts. As described above, developing catalytically active mononuclear phosphaethene-chloro-gold complexes would be desirable for analyzing the mechanisms of unique gold catalysis. After establishing the KTC process for **1**, we investigated the catalytic activity of chloro-gold complexes bearing ligated 2,2-diaryl-1-phosphaethenes [Mes*P=C(Ar^1)Ar^2; Mes* = 2,4,6-tri-*tert*-butylphenyl], which were synthesized through sequential catalytic arylation reactions from **1** (see the Supporting Information).[12,13]

In this paper, we disclose the Sonogashira process[14,15] for the regioselective catalytic alkynylation of **1** and its application in activation-free gold catalysis. In comparable previous works, Ott and co-workers intensively studied various alkynyl-substituted phosphaethenes for the development of π-extended phosphaethene derivatives.[16] In a study of alkynyl-substituted phosphaethenes, Ott et al. found that the nucleophilic substitution reaction of bromophosphaethenyllithium [Mes*P=C(Br)Li][17] with sulfonylacetylenes afforded the corresponding 2-bromo-2-alkynyl-1-phosphaethenes [Mes*P=C(Br)C≡CR], which underwent subsequent transformation and redox analyses.[18,19] In this work we have demonstrated an efficient catalytic process for the synthesis of various alkynyl-substituted 2-bromo-1-phosphaethenes by using **1**. The resultant 2-bromo-1-phosphaethen-3-ynes can be employed for the stereoselective synthesis of 2-aryl-2-alkynyl-1-phosphaethenes [Mes*P=C(Ph)C≡CR]. The catalytic activities of the chloro-gold complexes produced from the 2-aryl-2-alkynyl-1-phosphaethenes have been evaluated and are discussed. 2,2-Diaryl-1-phosphaethenes were also employed in the gold-catalyzed reactions.

Results and Discussion

The results of ligand screening for the Sonogashira coupling of **1** and phenylacetylene are presented in Table 1. Screening of the solvents and amines led to the conclusion that the use of diethyl ether and diisopropylamine was appropriate for the regioselective catalytic alkynylation of **1** (see Tables S1 and S2 in the Supporting Information). Bis(diphenylphosphanyl)methane (dppm) afforded **2a** in a moderate yield together with the bis(alkynyl) product **3a**[20] and phosphaalkyne **4** (Table 1, entry 1). Increasing the methylene chain in the $Ph_2P(CH_2)_nPPh_2$ system was not effective (entries 2–4). To our delight, 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) gave **2a**[17] in 72 % yield, and the amounts of **3a** and **4** were reduced (entry 5). 1,2-Bis(diphenylphosphanyl)benzene (dppbz) did not work well (entry 6), and 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP) promoted dual alkynylation rather than the formation of **2a** (entry 7). Bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos) afforded **2a** in a comparable yield to dppm, but the rearrangement reaction affording **4** was facilitated (entry 8). Although sterically encumbered tricyclohexylphosphine and SPhos promoted the formation of **4** rather than the alkynylation reaction (entries 9 and 10), tri(2-furyl)phosphine (TFP) gave **2a** in a moderate yield (entry 11). The reaction in the presence of dppf at a lower temperature (0 °C) gave the best result (entry 12). DPEPhos also gave improved results upon cooling (entries 13 and 14). However, we concluded that the conditions of entry 12 should be employed for further studies.

Table 1. Regioselective catalytic alkynylation of **1**.



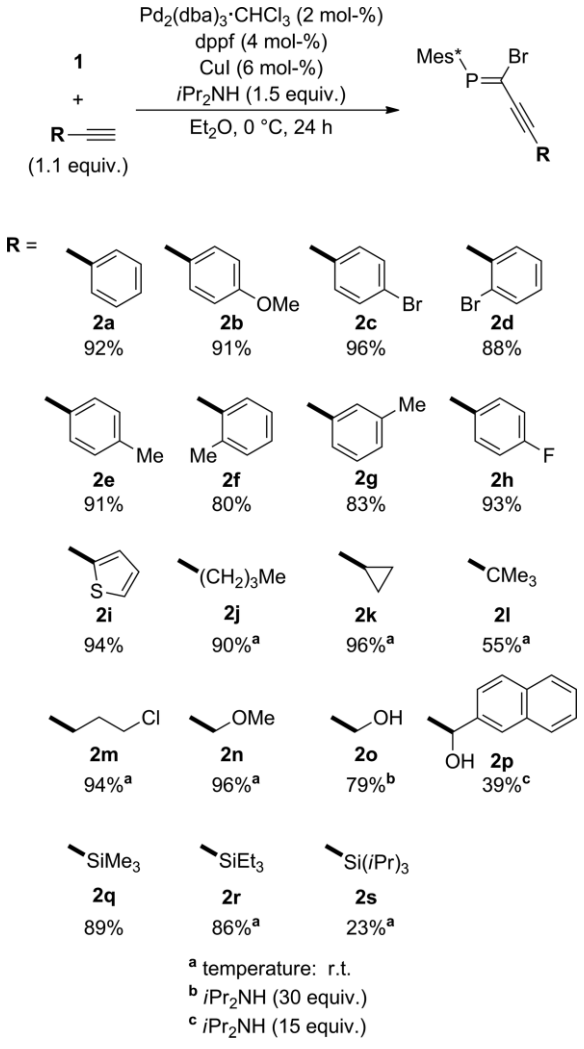
Entry	Ligand	Temp, time [°C], [h]	Yield of **2a** [%][a]	Yields of **3a**, **4**, and **1** [%][a]
1	dppm	25, 20	40	**3a**: 11, **4**: 29, **1**: 19
2	dppe	25, 20	12	**3a**: 13, **4**: 15, **1**: 57
3	dppp	25, 20	0	**3a**: 0, **4**: 3, **1**: 97
4	dppb	25, 20	29	**3a**: 7, **4**: 34, **1**: 28
5	dppf	25, 20	72	**3a**: 13, **4**: 15, **1**: 0
6	dppbz	25, 20	5	**3a**: 8, **4**: 6, **1**: 81
7	BINAP	25, 20	28	**3a**: 33, **4**: 21, **1**: 17
8	DPEPhos	25, 20	40	**3a**: 2, **4**: 41, **1**: 14
9	PCy_3[b]	25, 20	12	**3a**: 4, **4**: 40, **1**: 42
10	SPhos	25, 20	16	**3a**: 3, **4**: 57, **1**: 23
11	TFP[b]	25, 20	47	**3a**: 17, **4**: 21, **1**: 14
12	dppf[c]	0, 24	92[d]	**3a**: 0, **4**: 5, **1**: 0
13	DPEPhos	0, 8	39	**3a**: 3, **4**: 32, **1**: 25
14	DPEPhos	–40, 70	67	**3a**: 2, **4**: 6, **1**: 25

[a] Yields were determined by ^{1}H NMR spectroscopy. [b] 8 mol-% of the ligand was employed. [c] 1.1 equiv. of phenylacetylene was used. [d] Isolated yield.

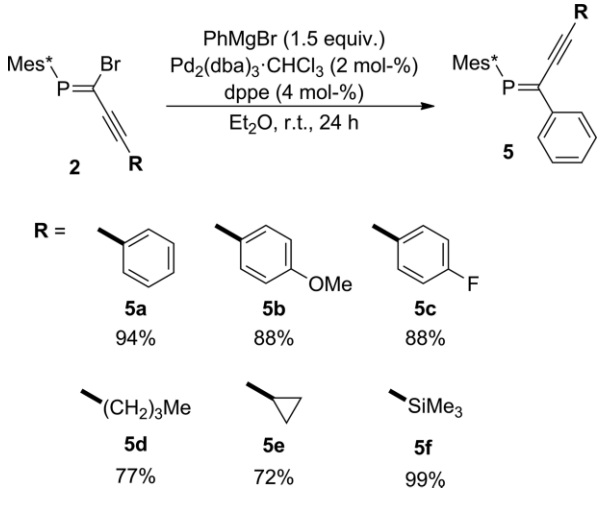
Scheme 2 shows the scope of the reaction with respect to the alkyne reagent. Alkoxy, halogen, and alkyl substituents on the phenyl group were tolerated (**2a**–**h**), as was a heteroaryl group (**2i**). The use of alkyl groups revealed weak steric effects (**2j**–**l**). Haloalkyl, alkoxymethyl, and hydroxymethyl groups did not detrimentally affect the coupling process (**2m**–**p**). Trimethyl- and triethylsilyl groups were tolerated in the alkynylation reaction (**2q**,**r**), but the triisopropylsilyl group reduced the yield (**2s**), probably due to steric encumbrance.

The bromine atom in **2** was useful for installing π-functional substituents into the compound. In this study we chose **2a**, **2b**, **2h**, **2j**, **2k**, and **2q** as reactants for the Pd-catalyzed arylation reaction (Scheme 3). All of these substrates gave the corresponding arylated products **5a**–**f** in moderate-to-good yields. The inversion of stereochemistry was characterized by NMR spectroscopy and confirmed by X-ray crystallographic analysis of the chloro-gold complexes (see below).

The stereoisomer of **5f** was prepared by the Sonogashira reaction of (*Z*)-2-bromo-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene. However, the desired product **5f′** was not ob-

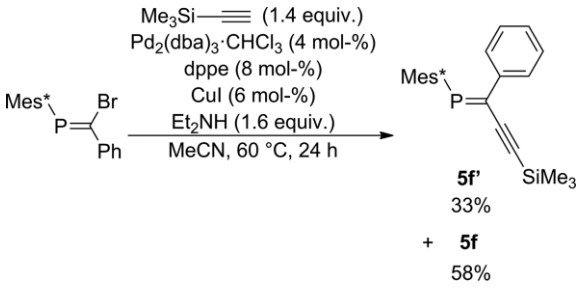


Scheme 2. Scope of the alkyne reagents in the regioselective alkynylation of **1**.



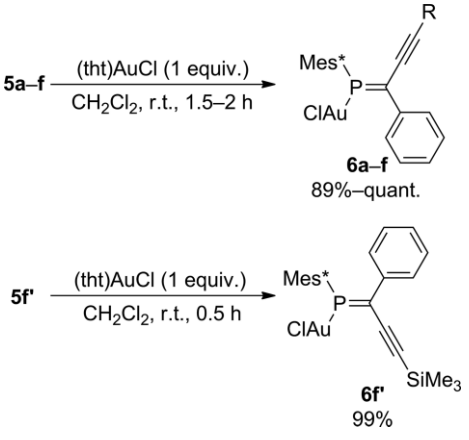
Scheme 3. Arylation of **2** by the palladium version of the KTC reaction.

tained exclusively, and considerable isomerization affording **5f** was observed (Scheme 4).[21] Fortunately, **5f′** was purified by silica gel column chromatography.



Scheme 4. Catalytic alkynylation of the sterically encumbered 2-bromo-2-phenyl-1-phosphaethene.

The sterically encumbered π-extended phosphaalkenes bearing both phenyl and alkynyl groups were screened for activation-free gold catalysis. The reactions of **5a**–**f** and **5f′** with [AuCl(tht)] (tht = tetrahydrothiophene) afforded the corresponding chloro-gold complexes **6a**–**f** and **6f′** almost quantitatively (Scheme 5). Figure 2 shows ORTEP drawings of **6f** and **6f′**. No aurophilic interaction was observed in the crystalline state.



Scheme 5. Preparation of mononuclear chloro-gold(I) complexes.

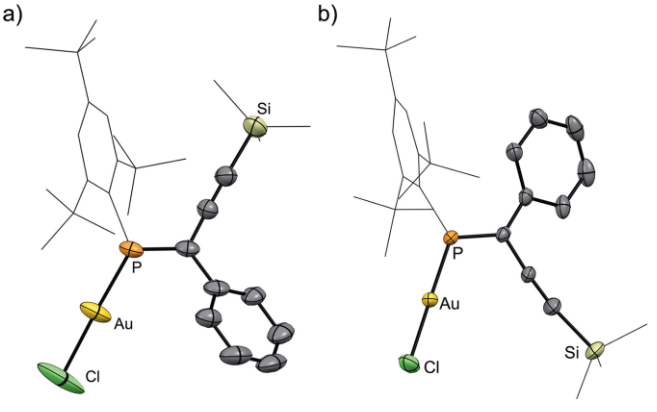
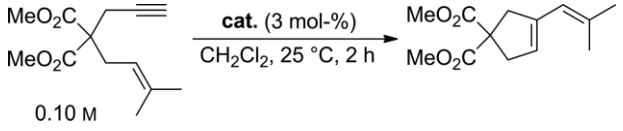


Figure 2. Molecular structures of a) **6f** and b) **6f′** (ellipsoids drawn at the 50 % probability level). Hydrogen atoms have been omitted. The *p*-*tert*-butyl and trimethylsilyl groups in **6f** are disordered, and the atoms with predominant occupancy factors are displayed.

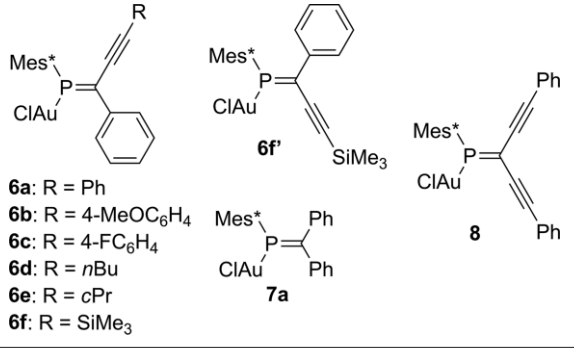
Table 2 shows the results of the gold-catalyzed cycloisomerization of a 1,6-enyne[22] in the presence of **6a**–**f**, **6′f**, and the related complexes **7a** and **8**. Although **6a** gave a poor result (Table 2, entry 1), **6b** and **6c** afforded the cyclized product in

moderate yields (entries 2 and 3). These results indicate that tuning the π-conjugated 1-phosphabut-1-en-3-yne skeleton through the phenyl group leads to an improvement in the catalytic activity. In the cycloisomerization reaction, both the π-donating methoxy group and electronegative fluorine are effective in increasing the catalytic activity of the gold center. The alkyl-substituted derivatives **6d** and **6e** afforded the cycloisomerized product in moderate-to-good yields (entries 4 and 5). To our delight, the catalytic activity of **6f** was quite high (entry 6). In comparison with **6d**, the silyl group, which has a moderately π-accepting character, is advantageous for increasing the catalytic activity. The reduction potential of **5f** is lower than that of **5d** (see Table S3 in the Supporting Information). On the other hand, the stereoisomer **6f′** showed a remarkable reduction in the catalytic activity (entry 7). Although the reason for this is unclear, steric encumbrance might affect the gold center: The X-ray structure of **6f′** has a smaller P–C–C_{sp} angle [113.6(4)°] than the P–C–C_{sp2} angle of **6f** [122.7(4)°]. Chloro-gold complexes **7a** and **8** showed good and moderate catalytic activities, respectively (entries 8 and 9). These results indicate that appropriate π-extension of the P=C skeleton and tuning of the π-conjugative substituent are requisites for efficient gold catalysis utilizing the phosphaethene ligands.

Table 2. Au-catalyzed cycloisomerization of a 1,6-enyne. SM = starting material.

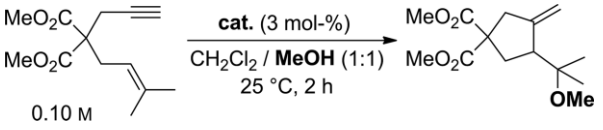


Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**6a**	15	83
2	**6b**	63	37
3	**6c**	47	52
4	**6d**	85	15
5	**6e**	61	37
6	**6f**	99	0
7	**6f′**	36	61
8	**7a**	98	0
9	**8**	80	20



The results of the catalyzed alkoxycyclization of 1,6-enyne are summarized in Table 3.[23] Although **6a**–**e** showed low activity (Table 3, entries 1–5), **6f** gave the methylenecyclopentene derivative in good yield (entry 6). Complex **6f** was not significantly affected in the catalytic process.[24] Similar to the case of the cycloisomerization reaction, **6f′** gave a poor result (entry 7), whereas complexes **7a** and **8** showed acceptable catalytic activity (entries 8 and 9). A slight decomposition of **8** to afford gold(0) particles was observed after the catalytic reaction (entry 9). The reaction with **6f** (entry 6) indicates that the combination of phenyl and an appropriate alkynyl substituent as well as the stereochemistry are important for developing useful mononuclear phosphaalkene-gold complexes for the alkoxycyclization reaction. An increase in the amount of **6f** gave the product almost quantitatively (entry 10), which indicates that the catalytic activity of **6f** is comparable to that of the DPCB-digold complex.[6]

Table 3. Au-catalyzed alkoxycyclization of a 1,6-enyne.

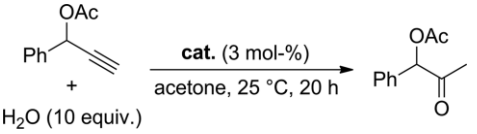


Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**6a**	10	88
2	**6b**	14	86
3	**6c**	12	88
4	**6d**	17	82
5	**6e**	11	87
6	**6f**	80	19
7	**6f′**	11	87
8	**7a**	68	31
9	**8**	68	30
10	**6f**[a]	98	trace

[a] 6 mol-% of catalyst was used.

The catalytic activities of **6**–**8** in the hydration of a propargyl acetate are presented in Table 4.[25] Following the screening of the reaction conditions it was concluded that the use of acetone as the solvent was appropriate. Although **6a** showed relatively low catalytic activity, the use of substituted phenyl groups (**6b** and **6c**) was effective in improving the yield (Table 4, entries 2 and 3). The alkyl-substituted derivatives **6d** and **6e** were found to be undesirable catalysts for the hydration reaction (entries 4 and 5). Similarly to the cyclization reactions of the 1,6-enyne, the trimethylsilyl derivative **6f** showed high catalytic ac-

Table 4. Au-catalyzed hydration of a propargyl acetate.



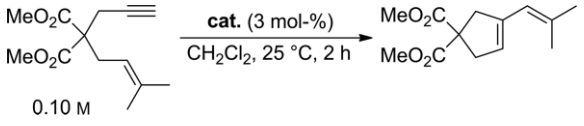
Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**6a**	40	60
2	**6b**	69	31
3	**6c**	71	29
4	**6d**	29	71
5	**6e**	22	78
6	**6f**	88	12
7	**6f′**	40	60
8	**7a**	66	34
9	**8**	30	70

tivity (entry 6) with the stereoisomer **6f′** giving an inferior result (entry 7). The catalytic activity of **7a** was comparable to those of **6b** and **6c** (entry 8), whereas **8** was ineffective in the hydration reaction (entry 9).

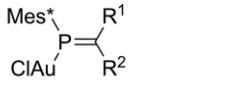
It is quite hard to identify a correlation between the catalytic activity of the gold complex and the structure of the ligand quantitatively. The estimated energy levels of the highest-occupied molecular orbitals (HOMOs) and LUMOs of **5a**–**f**, **5f′**, **7a** (w/o AuCl), and **8** (w/o AuCl) based on differential-pulse voltammetry (DPV) measurements are presented in Table S3 in the Supporting Information. Although further intensive studies are required to confirm the effective molecular design of catalysts bearing ligated phosphaethenes, we are confident that the catalytic activities of the mononuclear phosphaethene-chloro-gold complexes depend on the substituents at the sp^2-hybridized carbon atom of the P=C moiety as well as the stereochemistry of the P=C double bond.

In addition to the phosphaethene-chloro-gold complex bearing the silylethynyl and phenyl groups (**6f**) proving to be a highly active catalyst, the chloro-gold complex **7a** bearing 2,2-diphenyl-1-phosphaethene also showed promising catalytic activity. Thus, we also screened chloro-gold complexes bearing the 2,2-diaryl-1-phosphaethene ligands in the gold-catalyzed reactions. All the chloro-gold complexes bearing 2,2-diaryl-1-phosphaethene ligands **7b**–**7f** catalyzed the cycloisomerization reaction to afford the product almost quantitatively (Table 5, entries 1–5). Even the chloro-gold complex bearing 2-bromo-2-phenyl-1-phosphaethene (**7g**) showed moderate catalytic activity (entry 6). Thus, although complexes **7** were not effective for the alkoxycyclization (Table 6) and hydration reactions (Table 7), the 2,2-diaryl-1-phosphaethenes show promise for activation (co-catalyst)-free gold catalysis.

Table 5. Au-catalyzed cycloisomerization of a 1,6-enyne.



Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**7b**	98	0
2	**7c**	90	10
3	**7d**	98	0
4	**7e**	90	8
5	**7f**	97	0
6	**7g**	51	47



7b: R^1 = Ph, R^2 = 4-$MeOC_6H_4$
7c: R^1 = Ph, R^2 = 4-ClC_6H_4
7d: R^1 = R^2 = 4-PhC_6H_4
7e: R^1 = R^2 = 2-naph
7f: R^1 = R^2 = 2-thienyl
7g: R^1 = Br, R^2 = Ph

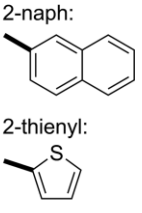
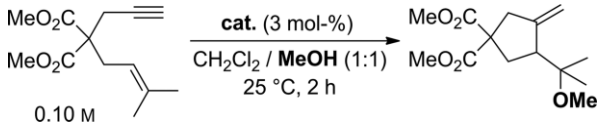
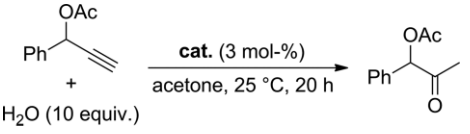


Table 6. Au-catalyzed alkoxycyclization of a 1,6-enyne.



Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**7b**	26	74
2	**7c**	14	83
3	**7d**	14	84
4	**7e**	7	91
5	**7f**	15	83
6	**7g**	15	83

Table 7. Au-catalyzed hydration of a propargyl acetate.



Entry	Catalyst	Yield [%]	Recovery of SM [%]
1	**7b**	24	76
2	**7c**	41	59
3	**7d**	32	68
4	**7e**	35	65
5	**7f**	26	74
6	**7g**	42	58

Conclusions

We have succeeded in developing the regioselective Sonogashira coupling reaction of the sterically encumbered *gem*-dibromophosphaethene **1** to afford various 2-alkynyl-2-bromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethenes **2** stereoselectively in high yields. The bromine atom in **2** was useful for subsequent catalytic arylation by the KTC procedure, and the resultant 2-alkynyl-2-phenyl-1-phosphaethenes indicated that an appropriate π-extension and the stereochemistry were significant for developing phosphaethene-chloro-gold complexes for use as catalysts. To the best of our knowledge, it is unprecedented that the stereochemistry of phosphaalkenes is decisive for the catalytic activity of transition-metal complexes. 2,2-Diaryl-1-phosphaethenes also induced moderate-to-good catalytic activity in the chloro-gold unit. Intensive studies on the reaction mechanisms and the exploration of novel gold-catalyzed transformations using the low-coordinate phosphine ligands will be carried out.

Experimental Section

General: ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded with a Bruker Avance 300 (300 MHz) spectrometer. ^1H and ^{13}C NMR chemical shifts are expressed in parts per million downfield from $CHCl_3$ as internal standard (δ_H = 7.26 ppm, δ_C = 77.16 ppm) in $CDCl_3$. ^{31}P NMR chemical shifts are expressed in parts per million downfield from 85 % H_3PO_4 as external standard (δ = 0 ppm) in $CDCl_3$. ^{19}F NMR chemical shifts are expressed in parts per million downfield from benzotrifluoride as internal standard (δ = –63.24 ppm) in

$CDCl_3$. Mass spectra were recorded with a JEOL JMS-T100LC spectrometer. Electrochemical analyses were measured on a BAS Electrochemical Analyzer Model 620Ds. All experiments were carried out under argon unless otherwise noted. The *gem*-dibromophosphaethene **1** was synthesized according to the literature.[26]

Typical Procedure for the Ethynylation of 1: A solution of 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**1**, 50 mg, 0.11 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (2.3 mg, 2 mol-%), phosphine ligand (4 mol-%), and CuI (1.3 mg, 6 mol-%) in diethyl ether (2.0 mL) was stirred for 0.5 h at room temperature. Diisopropylamine (0.17 mmol) and phenylacetylene (14.7 μL, 0.13 mmol) were added to the mixture at the corresponding reaction temperature. After stirring for 20 or 24 h at the corresponding reaction temperature, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (2 mL) and then stirred for 10 min. Then Et_2O (5 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried with Na_2SO_4, and the solvents evaporated in vacuo. The yield was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 50:1) to afford **2a**.

2a:[18] Yellow solid (48.2 mg, 92 %). R_f = 0.35 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 2 H, Ph), 7.47 (d, J = 1.1 Hz, 2 H, Mes*), 7.37–7.34 (m, 3 H, Ph), 1.55 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 151.9, 137.4 (d, $^1J_{PC}$ = 54.8 Hz, P=C), 133.3 (d, $^1J_{PC}$ = 44.3 Hz), 132.0 (d, J = 6.0 Hz), 129.2, 128.7, 122.9 (d, J = 7.5 Hz), 122.6, 97.8 (d, J_{PC} = 22.5 Hz), 92.8 (d, J_{PC} = 20.2 Hz), 38.3, 35.5, 33.2 (d, J = 6.7 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 290.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{27}H_{35}BrP$ $[M + H]^+$ 469.1660; found 469.1680. Compounds **3a** and **4** were characterized by comparison with the physical data described in previous reports.[20,27]

2b: 4-Ethynylanisole (14.5 μL, 0.12 mmol) was used as the alkyne reagent. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 10:1) to afford **2b** as a yellow solid (50.5 mg, 91 %). R_f = 0.05 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 4 H, Ar), 6.87 (d, J = 8.8 Hz, 2 H, Ar), 3.83 (s, 3 H, OMe), 1.53 (s, 18 H, *o*-*t*Bu), 1.35 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5 (d, J = 1.5 Hz), 153.7, 151.8, 137.5 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.7 (d, $^1J_{PC}$ = 42.7 Hz), 133.7 (d, J = 6.0 Hz), 122.5, 114.9 (d, J = 6.8 Hz), 114.4, 98.3 (d, J = 22.5 Hz), 91.9 (d, J = 20.2 Hz), 55.7, 38.3, 35.5, 33.2 (d, J = 6.0 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 285.1 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{28}H_{37}BrOP$ $[M + H]^+$ 501.1745; found 501.1766.

2c: 1-Bromo-4-ethynylbenzene (22.2 mg, 0.12 mmol) was used as the alkyne reagent. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2c** as a yellow solid (59.9 mg, 96 %). R_f = 0.47 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 4 H, Ar), 7.38 (d, J = 8.5 Hz, 2 H, Ar), 1.53 (s, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 152.0, 137.2 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.4 (d, J = 6.0 Hz), 132.7 (d, $^1J_{PC}$ = 43.5 Hz), 132.0, 123.6 (d, J = 3.0 Hz), 122.7, 121.8 (d, J = 8.2 Hz), 96.5 (d, J = 21.8 Hz), 93.7 (d, J = 20.3 Hz), 38.2, 35.5, 33.2 (d, J = 6.8 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 293.6 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{27}H_{34}Br_2P$ $[M + H]^+$ 547.0765; found 547.0767.

2d: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 μL, 0.33 mmol), Et_2O (4.0 mL), and 1-bromo-2-ethynylbenzene (31 μL, 0.24 mmol) were used. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 50:1) to afford **2d** as a yellow solid (107.9 mg, 88 %). R_f = 0.28 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (dd, J = 7.9, 0.8 Hz, 1 H, Ar), 7.54 (d, J = 7.7 Hz, 1 H, Ar), 7.48 (d, J = 1.1 Hz, 2 H, Ar), 7.30 (td, J = 7.5, 1.1 Hz, 1 H, Ar), 7.19 (t, J = 7.5 Hz, 1 H, Ar), 1.56 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 152.0, 137.2 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.6 (d, J = 6.0 Hz), 132.9, 132.4 (d, $^1J_{PC}$ = 44.3 Hz), 130.2 (d, J = 2.3 Hz), 127.3, 126.2 (d, J = 7.5 Hz), 125.1 (d, J = 7.5 Hz), 122.6, 96.8 (d, J = 20.2 Hz), 96.1 (d, J = 22.5 Hz), 38.3, 35.5, 33.3 (d, J = 6.7 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 295.3 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{27}H_{34}Br_2P$ $[M + H]^+$ 547.0765; found 547.0751.

2e: 4-Ethynyltoluene (15.6 μL, 0.12 mmol) was used as the coupling partner. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 40:1) to afford **2e** as a yellow solid (51.1 mg, 91 %). R_f = 0.35 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 4 H, Ar), 7.16 (d, J = 8.0 Hz, 2 H, Ar), 2.37 (s, 3 H, Me), 1.54 (s, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 151.8, 139.5, 137.5 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 132.7, 131.9 (d, J = 6.8 Hz), 129.5 (d, J = 5.3 Hz), 122.6, 119.8 (d, J = 7.5 Hz), 98.3 (d, J = 22.5 Hz), 92.3 (d, J = 20.2 Hz), 38.3, 35.5, 33.2 (d, J = 6.0 Hz), 31.7, 21.9 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 287.8 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{28}H_{37}BrP$ $[M + H]^+$ 483.1816; found 483.1837.

2f: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 μL, 0.33 mmol), Et_2O (4.0 mL), and 2-ethynyltoluene (31 μL, 0.24 mmol) were used. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 50:1) to afford **2f** as a yellow solid (86.5 mg, 80 %). R_f = 0.33 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.47 (m, 3 H, Ar), 7.31–7.15 (m, 3 H, Ar), 2.50 (s, 3 H, Me), 1.56 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 151.9, 142.0, 141.0 (d, J = 6.0 Hz), 137.4 (d, $^1J_{PC}$ = 54.7 Hz, P=C), 133.3, 132.1 (d, J = 6.0 Hz), 129.9 (d, J = 2.3 Hz), 129.3 (d, J = 2.3 Hz), 125.9, 122.6, 97.2 (d, J = 22.5 Hz), 96.8 (d, J = 20.2 Hz), 38.3, 35.5, 33.3 (d, J = 6.7 Hz), 31.7, 21.1 (d, J = 5.3 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 287.9 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{28}H_{37}BrP$ $[M + H]^+$ 483.1816; found 483.1814.

2g: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 μL, 0.33 mmol), Et_2O (4.0 mL), and 3-ethynyltoluene (31 μL, 0.24 mmol) were used. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 50:1) to afford **2g** as a yellow solid (89.5 mg, 83 %). R_f = 0.30 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J = 1.2 Hz, 2 H, Ar), 7.37 (s, 2 H, Ar), 7.25–7.18 (m, 2 H, Ar), 2.36 (s, 3 H, Me), 1.56 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 151.9, 138.3, 137.4 (d, $^1J_{PC}$ = 54.8 Hz, P=C), 133.3, 132.6 (d, J = 6.0 Hz), 130.2 (d, $^1J_{PC}$ = 36.7 Hz), 130.1 (d, J = 2.3 Hz), 129.1 (d, J = 6.0 Hz), 128.6 (d, J = 6.7 Hz), 122.6, 98.2 (d, J = 23.3 Hz), 92.5 (d, J = 20.2 Hz), 38.3, 35.5, 33.2 (d, J = 6.0 Hz), 31.7, 21.5 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 289.5 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{28}H_{37}BrP$ $[M + H]^+$ 483.1816; found 483.1808.

2h: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 μL, 0.33 mmol), Et_2O (4.0 mL), and 1-ethynyl-4-fluorobenzene (28 μL, 0.24 mmol) were used. The crude mixture was purified by silica gel column chromatography (hexane) to afford **3n** as a yellow solid (101.5 mg, 93 %). R_f = 0.37 (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.48 (m, 4 H, Ar), 7.07 (t, J = 8.7 Hz, 2 H, Ar), 1.56 (s, 18 H, *o*-*t*Bu), 1.39 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2 (d, J = 249.8 Hz), 153.7, 151.9, 137.3 (d, $^1J_{PC}$ = 54.7 Hz, P=C), 134.9

(d, J = 9.0 Hz), 134.0 (dd, J = 8.3, 6.0 Hz), 133.0 (d, $^1J_{PC}$ = 44.3 Hz), 122.6, 116.1 (d, J = 21.8 Hz), 96.6 (d, J = 22.5 Hz), 92.4 (d, J = 20.2 Hz), 38.2, 35.5, 33.2 (d, J = 6.7 Hz), 31.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –109.7 (s, 1 F) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 290.9 (d, $^8J_{FP}$ = 5.0 Hz) ppm. HRMS (APCI-TOF): calcd. for $C_{27}H_{34}BrFP$ $[M + H]^+$ 487.1566; found 487.1566.

2i: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL), and 2-ethynylthiophene (25 µL, 0.24 mmol) were used. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2i** as a yellow solid (99.8 mg, 94 %). R_f = 0.29 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (s, 2 H, Ar), 7.46–7.32 (m, 2 H, Ar), 7.03 (dd, J = 5.1, 3.8 Hz, 1 H, Ar), 1.55 (s, 18 H, o-tBu), 1.38 (s, 9 H, p-tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 151.9, 137.2 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.3 (d, J = 6.8 Hz), 132.4 (d, $^1J_{PC}$ = 43.5 Hz), 129.0 (d, J = 3.0 Hz), 127.7 (d, J = 2.3 Hz), 122.9 (d, J = 8.2 Hz), 122.6, 96.2 (d, J = 20.2 Hz), 91.0 (d, J = 22.5 Hz), 38.2, 35.5, 33.2 (d, J = 6.7 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 290.9 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{25}H_{33}BrPS$ $[M + H]^+$ 475.1224; found 475.1211.

2j: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL), and 1-hexyne (28 µL, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2i** as a yellow oil (90.3 mg, 90 %). R_f = 0.43 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 1.2 Hz, 2 H, Mes*), 2.52 (td, J = 9.6, 7.0 Hz, 2 H, CH_2), 1.64–1.42 (m, 22 H, CH_2, o-tBu), 1.35 (s, 9 H, p-tBu), 0.96 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.7, 137.6 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 135.0 (d, $^1J_{PC}$ = 42.7 Hz), 122.5, 100.7 (d, J = 22.5 Hz), 84.3 (d, J = 21.7 Hz), 38.2, 35.4, 33.2 (d, J = 6.7 Hz), 31.7, 30.9 (d, J = 4.5 Hz), 22.5, 20.4 (d, J = 4.5 Hz), 14.0 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 281.7 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{25}H_{39}BrP$ $[M + H]^+$ 449.1973; found 449.1959.

2k: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL), and cyclopropylacetylene (21 µL, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane dichloromethane = 50:1) to afford **2k** as a yellow solid (92.8 mg, 96 %). R_f = 0.37 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.3 Hz, 2 H, Mes*), 1.60–1.57 (m, 1 H, CH), 1.51 (s, 18 H, o-tBu), 1.35 (s, 9 H, p-tBu), 0.96–0.88 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (d, J = 0.7 Hz), 151.7, 137.5 (d, $^1J_{PC}$ = 54.7 Hz, P=C), 134.9 (d, $^1J_{PC}$ = 42.7 Hz), 122.5, 103.9 (d, J = 21.8 Hz), 79.7 (d, J = 21.0 Hz), 38.2, 35.4, 33.2 (d, J = 6.8 Hz), 31.7, 9.9 (d, J = 3.8 Hz), 1.4 (d, J = 6.0 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 282.0 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{24}H_{35}BrP$ $[M + H]^+$ 433.1660; found 433.1650.

2l: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL) and 3,3-dimethyl-1-butyne (30 µL, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2l** as a colorless solid (55.2 mg, 55 %). R_f = 0.50 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, J = 1.4 Hz, 2 H, Mes*), 1.50 (s, 18 H, o-tBu), 1.34 (s, 9 H, tBu), 1.31 (s, 9 H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (d, J = 0.7 Hz), 151.6, 137.8 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 135.1 (d, $^1J_{PC}$ = 42.7 Hz), 122.5, 108.0 (d, J = 22.5 Hz), 82.9 (d, J = 21.0 Hz), 38.2, 35.4, 33.2 (d, J = 6.7 Hz), 31.7, 31.1 (d, J = 4.5 Hz), 29.0 (d, J = 4.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 280.2 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{25}H_{39}BrP$ $[M + H]^+$ 449.1973; found 449.1980.

2m: 5-Chloro-1-pentyne (13 µL, 0.12 mmol) was used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 10:1) to afford **2m** as a yellow oil (49.3 mg, 94 %). R_f = 0.26 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.3 Hz, 2 H, Mes*), 3.68 (t, J = 6.4 Hz, 2 H, CH_2), 2.71 (td, J = 9.5, 6.9 Hz, 2 H, CH_2), 2.07 (quint., J = 6.6 Hz, 2 H, CH_2), 1.50 (s, 18 H, o-tBu), 1.34 (s, 9 H, p-tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.8, 137.3 (d, $^1J_{PC}$ = 54.8 Hz, P=C), 134.1 (d, $^1J_{PC}$ = 43.5 Hz), 122.5, 97.9 (d, J = 22.5 Hz), 84.9 (d, J = 21.7 Hz), 44.0, 38.2, 35.4, 33.2 (d, J = 6.8 Hz), 31.7, 31.6 (d, J = 4.5 Hz), 18.1 (d, J = 5.3 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 285.5 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{24}H_{36}BrClP$ $[M + H]^+$ 469.1427; found 469.1425.

2n: Methyl propargyl ether (10 µL, 0.12 mmol) was used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 1:1) to afford **2n** as a yellow oil (46.8 mg, 96 %). R_f = 0.17 (hexane/ethyl acetate = 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.4 Hz, 2 H, Mes*), 4.38 (d, J = 8.2 Hz, 2 H, CH_2), 3.44 (s, 3 H, OMe), 1.49 (s, 18 H, o-tBu), 1.34 (s, 9 H, p-tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (d, J = 1.5 Hz), 152.0, 137.0 (d, $^1J_{PC}$ = 54.7 Hz, P=C), 132.6 (d, $^1J_{PC}$ = 43.5 Hz), 122.6, 93.4 (d, J = 21.7 Hz), 89.1 (d, J = 21.0 Hz), 61.0 (d, J = 5.3 Hz), 58.3, 38.2, 35.5, 33.2 (d, J = 6.8 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 294.3 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{23}H_{35}BrOP$ $[M + H]^+$ 437.1609; found 437.1604.

2o: iPr$_2$NH (470 µL, 3.3 mmol) and 2-propyn-1-ol (6.5 µL, 0.12 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 1:1) to afford **2o** as a yellow solid (37.5 mg, 79 %). R_f = 0.16 (hexane/dichloromethane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.3 Hz, 2 H, Mes*), 4.56 (d, J = 8.3 Hz, 2 H, CH_2), 2.18 (s, 1 H, OH), 1.49 (s, 18 H, o-tBu), 1.34 (s, 9 H, p-tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 152.0, 136.9 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 132.5 (d, $^1J_{PC}$ = 43.5 Hz), 122.6, 95.5 (d, J = 22.5 Hz), 88.3 (d, J = 21.0 Hz), 52.2 (d, J = 5.3 Hz), 38.2, 35.5, 33.2 (d, J = 6.0 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 294.8 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{22}H_{33}BrOP$ $[M + H]^+$ 423.1452; found 423.1463.

2p: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (470 µL, 3.3 mmol), Et_2O (4.0 mL) and 1-(naphthalen-1-yl)prop-2-yn-1-ol (44.7 mg, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 1:1) to afford **2p** as a yellow solid (47.8 mg, 39 %). R_f = 0.27 (hexane/dichloromethane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (s, 1 H, Ar), 7.96–7.83 (m, 3 H, Ar), 7.70 (dd, J = 8.5, 1.7 Hz, 1 H, Ar), 7.51 (dt, J = 9.9, 3.6 Hz, 2 H, Ar), 7.45 (d, J = 1.1 Hz, 2 H, Mes*), 5.92 (d, J = 7.7 Hz, 1 H, CH), 2.18 (s, 1 H, OH), 1.52 (s, 18 H, o-tBu), 1.36 (s, 9 H, p-tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7 (d, J = 1.5 Hz), 152.0, 137.7 (d, J = 3.0 Hz), 136.9 (d, $^1J_{PC}$ = 54.7 Hz, P=C), 133.7, 133.5, 132.2 (d, $^1J_{PC}$ = 44.3 Hz), 129.0, 128.6, 128.0, 126.8, 126.7, 126.1, 125.1, 122.7, 96.5 (d, J = 22.5 Hz), 89.5 (d, J = 21.8 Hz), 65.8 (d, J = 4.5 Hz), 38.2, 35.5, 33.2 (d, J = 6.8 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 295.9 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{32}H_{37}BrP$ $[M – OH]^+$ 531.1816; found 531.1823.

2q: (Trimethylsilyl)acetylene (17 µL, 0.12 mmol) was used as coupling partner. The crude mixture was purified by silica gel column

chromatography (hexane) to afford **2q** as a yellow solid (46.0 mg, 89 %). R_f = 0.23 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, J = 1.1 Hz, 2 H, Mes*), 1.53 (s, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu), 0.28 (s, 9 H, SiMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (d, J = 0.7 Hz), 151.9, 137.2 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.2 (d, $^1J_{PC}$ = 44.3 Hz), 122.6, 106.4 (d, J = 19.5 Hz), 104.0 (d, J = 20.2 Hz), 38.2, 35.5, 33.2 (d, J = 6.7 Hz), 31.7, 0.3 (d, J = 1.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 294.8 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{24}H_{39}BrPSi$ $[M + H]^+$ 465.1742; found 465.1758.

2r: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL), and (triethylsilyl)acetylene (44 µL, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2r** as a yellow oil (97.4 mg, 86 %). R_f = 0.50 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 1.1 Hz, 2 H, Mes*), 1.52 (s, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu), 1.06 (t, J = 7.8 Hz, 9 H, CH_3), 0.71 (q, J = 7.9 Hz, 6 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.8, 137.3 (d, $^1J_{PC}$ = 55.5 Hz, P=C), 133.3 (d, $^1J_{PC}$ = 44.3 Hz), 122.6, 108.0 (d, J = 20.2 Hz), 102.1 (d, J = 20.3 Hz), 38.2, 35.4, 33.2 (d, J = 6.8 Hz), 31.7, 7.8, 4.7 (d, J = 1.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 293.7 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{27}H_{45}BrPSi$ $[M + H]^+$ 507.2212; found 507.2224.

2s: Compound **1** (100 mg, 0.22 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (4.6 mg, 2 mol-%), dppf (4.9 mg, 4 mol-%), CuI (2.5 mg, 6 mol-%), iPr$_2$NH (47 µL, 0.33 mmol), Et_2O (4.0 mL), and (triisopropylsilyl)acetylene (55 µL, 0.24 mmol) were used. The reaction was conducted at room temperature. The crude mixture was purified by silica gel column chromatography (hexane) to afford **2s** as a yellow oil (28.1 mg, 23 %). R_f = 0.56 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 1.3 Hz, 2 H, Mes*), 1.50 (s, 18 H, *o*-*t*Bu), 1.34 (s, 9 H, *p*-*t*Bu), 1.12–1.11 (m, 21 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.8, 137.4 (d, $^1J_{PC}$ = 56.3 Hz, P=C), 133.4 (d, $^1J_{PC}$ = 43.5 Hz), 122.6, 109.0 (d, J = 19.5 Hz), 101.6 (d, J = 20.3 Hz), 38.2, 35.5, 33.2 (d, J = 6.8 Hz), 31.7, 19.0, 11.7 (d, J = 1.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 292.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{30}H_{51}BrPSi$ $[M + H]^+$ 549.2681; found 549.2676.

Synthesis of 3a:[20] A mixture of **2a** (200 mg, 0.43 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (17.6 mg, 4 mol-%), dppe (13.6 mg, 8 mol-%), and CuI (4.9 mg, 6 mol-%) in MeCN (4 mL) was stirred for 0.5 h at room temperature under argon. Et_2NH (71 µL, 0.68 mmol) and phenylacetylene (66 µL, 0.60 mmol) were added to the mixture at room temperature. After stirring for 24 h at 60 °C, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (2 mL) and stirred for 10 min. Then Et_2O (5 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with brine (5 mL), dried with Na_2SO_4, and the solvents evaporated in vacuo. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 20:1) to afford **3a** as a yellow solid (130.3 mg, 62 %). R_f = 0.42 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.58 (m, 2 H, Ph), 7.51 (s, 2 H, Ph), 7.36–7.34 (m, 3 H, Ph), 7.23–7.14 (m, 3 H, Ph), 6.91 (d, J = 7.3 Hz, 2 H, Mes*), 1.56 (s, 18 H, *o*-*t*Bu), 1.34 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.7, 151.0, 141.9 (d, $^1J_{PC}$ = 34.5 Hz), 135.8 (d, $^1J_{PC}$ = 56.3 Hz, P=C), 132.0 (d, J = 6.0 Hz), 131.7 (d, J = 3.8 Hz), 128.8 (d, J = 1.5 Hz), 128.7, 128.3, 123.7 (d, J = 6.8 Hz), 123.5 (d, J = 5.3 Hz), 122.6, 103.5 (d, J = 9.7 Hz), 96.5 (d, J = 17.2 Hz), 90.5 (d, J = 26.2 Hz), 89.6 (d, J = 20.3 Hz), 38.6, 35.4, 33.5 (d, J = 6.0 Hz), 31.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 331.5 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{35}H_{40}P$ $[M + H]^+$ 491.2868; found 491.2869.

Typical Procedure for the Kumada–Tamao–Corriu (KTC)-Type Arylation of 2: A mixture of **2**, $[Pd_2(dba)_3]$·$CHCl_3$ (2–4 mol-%), and phosphine ligand (4–8 mol-%) in Et_2O was stirred for 0.5 h at room temperature under argon. ArMgBr (THF solution) was added at room temperature. After stirring for 24 h at room temperature, the mixture was quenched with 1 M $HCl_{aq.}$ (1.0 mL) and then Et_2O (5.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 5.0 mL). The combined organic layers were washed with brine (10 mL), dried with Na_2SO_4, and the solvents evaporated. The crude mixture was purified by silica gel column chromatography.

5a: Phenylmagnesium bromide (0.16 mmol, 1.0 M in THF) was added to a mixture of **2a** (50 mg, 0.11 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (2.2 mg, 2 mol-%), and dppe (1.7 mg, 4 mol-%) in Et_2O (2 mL) under argon. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 50:1) to afford **5a** as a yellow solid (50.0 mg, 94 %). R_f = 0.27 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03–7.99 (m, 2 H, Ph), 7.56 (d, J = 0.9 Hz, 2 H, Mes*), 7.46–7.38 (m, 3 H, Ph), 7.26–7.17 (m, 3 H, Ph), 6.96–6.94 (m, 2 H, Ph), 1.58 (s, 18 H, *o*-*t*Bu), 1.39 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5 (d, $^1J_{PC}$ = 41.3 Hz), 154.8, 150.5, 140.9 (d, J = 21.7 Hz), 137.1 (d, $^1J_{PC}$ = 54.0 Hz, P=C), 131.6 (d, J = 3.8 Hz), 128.9, 128.9 (d, J = 5.2 Hz), 128.4, 128.3, 125.8 (d, J = 20.2 Hz), 124.1 (d, J = 5.3 Hz), 122.6, 107.7 (d, J = 9.7 Hz), 90.9 (d, J = 21.8 Hz), 38.6, 35.4, 33.4 (d, J = 6.8 Hz), 31.8 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 290.7 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{33}H_{40}P$ $[M + H]^+$ 467.2868; found 467.2888.

5b: Phenylmagnesium bromide (1.4 mmol, 1.0 M in THF) was added to a mixture of **2b** (480.7 mg, 0.96 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (19.9 mg, 2 mol-%), and dppe (15.3 mg, 4 mol-%) in Et_2O (12 mL) under argon . The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 10:1) to afford **5b** as a yellow solid (422.4 mg, 88 %). R_f = 0.19 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16–8.13 (m, 2 H, Ar), 7.71 (s, 2 H, Mes*), 7.56–7.47 (m, 3 H, Ar), 7.02 (d, J = 8.7 Hz, 2 H, Ar), 6.86 (d, J = 8.9 Hz, 2 H, Ar), 3.87 (s, 3 H, OMe), 1.72 (s, 18 H, *o*-*t*Bu), 1.55 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9 (d, $^1J_{PC}$ = 41.2 Hz), 159.9 (d, J = 2.3 Hz), 154.8, 150.3, 140.9 (d, J = 21.8 Hz), 137.4 (d, $^1J_{PC}$ = 54.0 Hz, P=C), 133.2 (d, J = 3.8 Hz), 128.9, 128.8, 125.8 (d, J = 21.0 Hz), 122.5, 116.4 (d, J = 4.5 Hz), 114.0, 108.3 (d, J = 9.7 Hz), 90.3 (d, J = 21.7 Hz), 55.5, 38.6, 35.4, 33.4 (d, J = 6.7 Hz), 31.8 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 285.1 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{34}H_{42}OP$ $[M + H]^+$ 497.2973; found 497.2959.

5c: Phenylmagnesium bromide (1.5 mmol, 1.0 M in THF) was added to a mixture of **2h** (479.0 mg, 0.98 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (20.3 mg, 2 mol-%), and dppe (15.7 mg, 4 mol-%) in Et_2O (12 mL) under argon. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 30:1) to afford **5c** as a yellow solid (418.7 mg, 88 %). R_f = 0.52 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12–8.08 (m, 2 H, Ar), 7.67 (s, 2 H, Mes*), 7.54–7.46 (m, 3 H, Ar), 7.02–6.99 (m, 4 H, Ar), 1.68 (s, 18 H, *o*-*t*Bu), 1.49 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9 (d, $^1J_{PC}$ = 41.2 Hz), 159.9 (d, J = 2.3 Hz), 154.8, 150.3, 140.9 (d, J = 21.8 Hz), 137.4 (d, $^1J_{PC}$ = 54.0 Hz, P=C), 133.2 (d, J = 3.8 Hz), 128.9, 128.8, 125.8 (d, J = 21.0 Hz), 122.5, 116.4 (d, J = 4.5 Hz), 114.0, 108.3 (d, J = 9.7 Hz), 90.3 (d, J = 21.7 Hz), 55.5, 38.6, 35.4, 33.4 (d, J = 6.7 Hz), 31.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.7 (br. s, 1 F) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 290.6 (d, $^8J_{FP}$ = 5.0 Hz) ppm. HRMS (APCI-TOF): calcd. for $C_{33}H_{39}FP$ $[M + H]^+$ 485.2773; found 485.2774.

5d: Phenylmagnesium bromide (1.4 mmol, 1.0 M in THF) was added to a mixture of **2j** (412.9 mg, 0.92 mmol), $[Pd_2(dba)_3]$·$CHCl_3$ (19.0 mg, 2 mol-%), and dppe (14.6 mg, 4 mol-%) in Et_2O (12 mL)

under argon. The crude mixture was purified by silica gel column chromatography (hexane) to afford **5d** as a yellow oil (315.1 mg, 77 %). R_f = 0.40 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 2 H, Ph), 7.56 (d, J = 0.9 Hz, 2 H, Mes*), 7.44–7.37 (m, 3 H, Ph), 2.08 (dd, J = 12.2, 6.8 Hz, 2 H, CH_2), 1.61 (s, 18 H, *o*-*t*Bu), 1.45 (s, 9 H, *p*-*t*Bu), 1.31–1.27 (m, 4 H), 0.91 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8 (d, $^1J_{PC}$ = 40.5 Hz), 154.3, 150.0, 141.5 (d, J = 21.8 Hz), 137.8 (d, $^1J_{PC}$ = 53.2 Hz, P=C), 128.7 (d, J = 1.5 Hz), 128.6 (d, J = 6.0 Hz), 125.7 (d, J = 21.0 Hz), 122.4, 110.2 (d, J = 8.2 Hz), 81.9 (d, J = 21.7 Hz), 38.5, 35.4 33.3 (d, J = 6.7 Hz), 31.8, 30.9 (d, J = 3.0 Hz), 22.3, 20.1 (d, J = 3.0 Hz), 13.9 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 284.3 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{31}H_{44}P$ [M + H]$^+$ 447.3181; found 447.3191.

5e: Phenylmagnesium bromide (1.4 mmol, 1.0 M in THF) was added to a mixture of **2k** (405.1 mg, 0.93 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (19.3 mg, 2 mol-%), and dppe (14.9 mg, 4 mol-%) in Et_2O (12 mL) under argon. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 30:1) to afford **5c** as a yellow solid (288.0 mg, 72 %). R_f = 0.45 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03–7.99 (m, 2 H, Ph), 7.61 (d, J = 0.7 Hz, 2 H, Mes*), 7.48–7.40 (m, 3 H, Ph), 1.64 (s, 18 H, *o*-*t*Bu), 1.51 (s, 9 H, *p*-*t*Bu), 1.28–1.19 (m, 1 H, CH), 0.75–0.68 (m, 2 H, CH_2), 0.26 (td, J = 6.5, 3.8 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2 (d, $^1J_{PC}$ = 40.5 Hz), 154.1, 150.1, 141.3 (d, J = 22.5 Hz), 137.4 (d, $^1J_{PC}$ = 54.0 Hz, P=C), 128.7, 128.7 (d, J = 8.2 Hz), 125.7 (d, J = 21.0 Hz), 122.5, 114.0 (d, J = 9.0 Hz), 78.0 (d, J = 21.8 Hz), 38.6, 35.4, 33.2 (d, J = 6.8 Hz), 31.8, 9.7 (d, J = 2.3 Hz), 1.5 (d, J = 3.8 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 280.6 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{30}H_{40}P$ [M + H]$^+$ 431.2868; found 431.2884.

5f: Phenylmagnesium bromide (0.16 mmol, 1.0 M in THF) was added to a mixture of **2q** (50 mg, 0.11 mmol), $[Pd_2(dba)_3]$•$CHCl_3$ (2.2 mg, 2 mol-%), and dppe (1.7 mg, 4 mol-%) in Et_2O (2 mL) under argon. The crude mixture was purified by silica gel column chromatography (hexane) to afford **5f** as a yellow solid (49.2 mg, 99 %). R_f = 0.42 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97–7.93 (m, 2 H, Ph), 7.56 (d, J = 1.0 Hz, 2 H, Mes*), 7.44–7.36 (m, 3 H, Ph), 1.57 (s, 18 H, *o*-*t*Bu), 1.42 (s, 9 H, *p*-*t*Bu), –0.01 (s, 9 H, SiMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.3 (d, $^1J_{PC}$ = 41.2 Hz), 154.0 (d, J = 1.5 Hz), 150.3, 140.7 (d, J = 21.7 Hz), 136.6 (d, $^1J_{PC}$ = 54.0 Hz, P=C), 128.8 (d, J = 6.0 Hz), 125.5, 125.5, 122.9, 112.5 (d, J = 9.0 Hz), 105.0 (d, J = 20.2 Hz), 38.6, 35.4, 33.2 (d, J = 6.7 Hz), 31.8, 0.1 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 297.0 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{30}H_{44}PSi$ [M + H]$^+$ 463.2950; found 463.2967.

5f′: A mixture of (*Z*)-2-Bromo-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [Mes*P=C(Br)Ph; 300 mg, 0.67 mmol],[12] $[Pd_2(dba)_3]$•$CHCl_3$ (27.9 mg, 4 mol-%), dppe (21.5 mg, 8 mol-%), and CuI (7.7 mg, 6 mol-%) in MeCN (6 mL) was stirred for 0.5 h at room temperature under argon. Et_2NH (112 µL, 1.1 mmol) and (trimethylsilyl)acetylene (133 µL, 0.94 mmol) were added to the mixture at room temperature. After stirring for 24 h at 60 °C, the reaction mixture was quenched with a saturated aqueous ammonium chloride solution (2 mL) and stirred for 10 min. Then Et_2O (5 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried with Na_2SO_4, and the solvents evaporated in vacuo. The crude mixture was purified by silica gel column chromatography (hexane/dichloromethane = 40:1) to afford **5f′** as a yellow solid (102.4 mg, 33 %) accompanied by the stereoisomer **5f** (180.8 mg, 58 % yield). R_f = 0.37 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 0.5 Hz, 2 H, Mes*), 7.03 (dd, J = 7.6, 5.8 Hz, 1 H, Ph), 6.92 (t, J = 7.6 Hz, 2 H, Ph), 6.62 (dd, J = 7.3, 1.3 Hz, 2 H, Ph), 1.44 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu), 0.30 (s, 9 H, SiMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2 (d, $^1J_{PC}$ = 41.3 Hz), 154.6, 151.8, 139.6 (d, J = 17.2 Hz), 134.8 (d, $^1J_{PC}$ = 66.0 Hz, P=C), 128.2 (d, J = 6.8 Hz), 127.8 (d, J = 4.5 Hz), 127.8 (d, J = 3.0 Hz), 122.8, 108.8 (d, J = 27.8 Hz), 101.5 (d, J = 19.5 Hz), 38.4, 35.4, 33.2 (d, J = 7.5 Hz), 31.8, 0.5 (d, J = 2.3 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 282.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{30}H_{44}PSi$ [M + H]$^+$ 463.2950; found 463.2962.

Typical Procedure for the Preparation of Chloro-gold(I) Complexes: A mixture of the corresponding phosphaethene (0.15–0.25 mmol) and [(tht)AuCl] (1 equiv.) in DCM (2–3 mL) under argon was stirred for 1.5–2 h at room temperature. After evaporation under reduced pressure, the resultant residue was washed with hexane (5 mL) to afford the corresponding phosphaethene gold(I) chloride complex.

6a: A mixture of **5a** (100 mg, 0.21 mmol) and [(tht)AuCl] (68.7 mg, 0.21 mmol) in DCM (3 mL) under argon was stirred for 1.75 h at room temperature. Yellow solid (149.9 mg, quant.). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.14–8.09 (m, 2 H, Ph), 7.70 (d, J = 3.9 Hz, 2 H, Mes*), 7.55–7.47 (m, 3 H, Ph), 7.36–7.22 (m, 3 H, Ph), 6.96–6.92 (m, 2 H, Ph), 1.74 (d, J = 1.1 Hz, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 157.5, 155.1 (d, J = 2.3 Hz), 154.7 (d, $^1J_{PC}$ = 80.3 Hz, P=C), 138.5 (d, J = 4.5 Hz), 132.2 (d, J = 7.5 Hz), 131.4 (d, J = 5.2 Hz), 130.3 (d, J = 3.0 Hz), 129.9 (d, J = 3.0 Hz), 129.2 (d, J = 2.3 Hz), 127.8 (d, J = 18.0 Hz), 125.5 (d, J = 34.5 Hz), 124.8 (d, J = 9.7 Hz), 123.0 (d, J = 9.7 Hz), 113.4 (d, J = 19.5 Hz), 90.7 (d, J = 21.0 Hz), 39.9 (d, J = 1.5 Hz), 36.2, 34.9, 31.7 ppm. ^{31}P NMR (125 MHz, CD_2Cl_2): δ = 213.2 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{33}H_{39}AuClNaP$ [M + Na]$^+$ 721.2041; found 721.2034.

6b: A mixture of **5b** (100 mg, 0.20 mmol) and [(tht)AuCl] (64.5 mg, 0.20 mmol) in DCM (3 mL) under argon was stirred for 2 h at room temperature. Orange solid (158.2 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.05 (m, 2 H, Ar), 7.67 (d, J = 3.8 Hz, 2 H, Mes*), 7.50–7.43 (m, 3 H, Ar), 6.83 (dd, J = 8.9, 1.8 Hz, 2 H, Ar), 6.73 (d, J = 8.9 Hz, 2 H, Ar), 3.79 (s, 3 H, OMe), 1.72 (d, J = 1.0 Hz, 18 H, *o*-*t*Bu), 1.39 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.0 (d, J = 3.7 Hz), 157.1, 154.7 (d, $^1J_{PC}$ = 80.2 Hz, P=C), 154.2 (d, J = 3.0 Hz), 137.9 (d, J = 5.2 Hz), 133.5 (d, J = 7.5 Hz), 130.8 (d, J = 6.0 Hz), 129.4 (d, J = 3.0 Hz), 127.1 (d, J = 18.8 Hz), 125.2 (d, $^1J_{PC}$ = 34.5 Hz), 124.1 (d, J = 9.7 Hz), 114.6 (d, J = 9.0 Hz), 114.4 (d, J = 2.3 Hz), 114.1 (d, J = 18.8 Hz), 90.0 (d, J = 20.3 Hz), 55.7, 39.5 (d, J = 1.5 Hz), 35.7, 34.5, 31.4 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 206.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{68}H_{82}AuO_2P_2$ [M_2 – $AuCl_2$]$^+$ 1189.5456; found 1189.5457.

6c: A mixture of **5c** (100 mg, 0.21 mmol) and [(tht)AuCl] (66.2 mg, 0.21 mmol) in DCM (3 mL) under argon was stirred for 1.5 h at room temperature. Yellow solid (150.8 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09–8.05 (m, 2 H, Ar), 7.66 (d, J = 3.9 Hz, 2 H, Mes*), 7.51–7.43 (m, 3 H, Ar), 6.94–6.85 (m, 4 H, Ar), 1.71 (d, J = 1.1 Hz, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.4 (dd, J = 251.3, 4.5 Hz, P=C), 157.1, 154.4 (d, J = 2.2 Hz), 153.3, 137.6 (d, J = 5.2 Hz), 133.7 (t, J = 7.9 Hz), 131.0 (d, J = 6.0 Hz), 129.4 (d, J = 3.0 Hz), 127.1 (d, J = 18.0 Hz), 125.0 (d, $^1J_{PC}$ = 34.5 Hz), 124.1 (d, J = 9.7 Hz), 118.6 (dd, J = 9.0, 3.0 Hz), 116.1 (dd, J = 22.5, 2.3 Hz), 111.6 (d, J = 18.8 Hz), 89.9 (d, J = 21.0 Hz), 39.5 (d, J = 1.5 Hz), 35.7, 34.5, 31.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.0 (br. s, 1 F) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 212.1 (d, $^8J_{FP}$ = 6.2 Hz) ppm. HRMS (APCI-TOF): calcd. for $C_{33}H_{38}AuFP$ [M – Cl]$^+$ 681.2361; found 681.2378.

6d: A mixture of **5d** (112.2 mg, 0.25 mmol) and [(tht)AuCl] (80.5 mg, 0.25 mmol) in DCM (3 mL) under argon was stirred for 2 h at room temperature. Yellow solid (162.6 mg, 95 %). ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 8.00–7.96 (m, 2 H, Ph), 7.59 (d, J = 3.8 Hz, 2 H, Mes*), 7.45–7.38 (m, 3 H, Ph), 2.04 (quint., J = 6.4 Hz, 2 H, CH_2), 1.68 (d, J = 0.9 Hz, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu), 1.20–1.16 (m, 4 H, CH_2), 0.80 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6, 156.0 (d, $^1J_{PC}$ = 81.0 Hz, P=C), 154.1 (d, J = 3.0 Hz), 138.4 (d, J = 5.2 Hz), 130.7 (d, J = 6.0 Hz), 129.2 (d, J = 3.0 Hz), 127.1 (d, J = 18.8 Hz), 125.2 (d, J = 36.0 Hz), 124.0 (d, J = 9.7 Hz), 116.1 (d, J = 18.8 Hz), 81.5 (d, J = 20.3 Hz), 39.3 (d, J = 1.5 Hz), 35.6, 34.4, 31.4, 30.4 (d, J = 6.7 Hz), 22.1, 20.3 (d, J = 6.7 Hz), 13.7 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 210.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{32}H_{47}AuOP$ [M + MeOH – Cl]$^+$ 675.3030; found 675.3063.

6e: A mixture of **5e** (100 mg, 0.23 mmol) and [(tht)AuCl] (74.4 mg, 0.23 mmol) in DCM (3 mL) under argon was stirred for 2 h at room temperature. Yellow solid (153.1 mg, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.96 (m, 2 H, Ph), 7.61 (d, J = 3.8 Hz, 2 H, Mes*), 7.45–7.37 (m, 3 H, Ph), 1.67 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu), 1.24–1.13 (m, 1 H, CH), 0.73 (td, J = 7.0, 4.1 Hz, 2 H, CH_2), 0.17 (td, J = 6.7, 4.2 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 155.9 (d, $^1J_{PC}$ = 81.0 Hz, P=C), 154.1 (d, J = 3.0 Hz), 138.2 (d, J = 5.3 Hz), 130.7 (d, J = 6.0 Hz), 129.2 (d, J = 3.0 Hz), 127.0 (d, J = 18.0 Hz), 125.2 (d, J = 35.2 Hz), 124.0 (d, J = 9.7 Hz), 120.4 (d, J = 18.0 Hz), 77.4 (d, J = 20.2 Hz), 39.4 (d, J = 1.5 Hz), 35.6, 34.3, 31.4, 10.2 (d, J = 5.3 Hz), 1.7 (d, J = 7.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 207.2 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{31}H_{43}AuOP$ [M + MeOH – Cl]$^+$ 659.2717; found 659.2747.

6f: A mixture of **5f** (99.9 mg, 0.22 mmol) and [(tht)AuCl] (69.2 mg, 0.22 mmol) in DCM (2 mL) under argon was stirred for 1.5 h at room temperature. Yellow solid (134.2 mg, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03–7.99 (m, 2 H, Ph), 7.63 (d, J = 3.9 Hz, 2 H, Mes*), 7.48–7.40 (m, 3 H, Ph), 1.69 (d, J = 1.1 Hz, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu), –0.07 (s, 9 H, SiMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 154.3 (d, J = 3.0 Hz), 153.3 (d, $^1J_{PC}$ = 80.2 Hz, P=C), 137.7 (d, J = 3.7 Hz), 130.9 (d, J = 6.0 Hz), 129.4 (d, J = 3.0 Hz), 127.1 (d, J = 18.8 Hz), 124.8 (d, J = 34.5 Hz), 124.4 (d, J = 10.5 Hz), 119.5 (d, J = 16.5 Hz), 103.5 (d, J = 18.8 Hz), 39.6 (d, J = 1.5 Hz), 35.9, 34.5, 31.5, –0.3 (d, J = 3.0 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 219.4 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{31}H_{47}AuOPSi$ [M + MeOH – Cl]$^+$ 691.2799; found 691.2791.

6f′: A mixture of **5f′** (75.3 mg, 0.16 mmol) and [(tht)AuCl] (52.2 mg, 0.16 mmol) in DCM (2 mL) under argon was stirred for 0.5 h at room temperature. Yellow solid (111.7 mg, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, J = 3.6 Hz, 2 H, Mes*), 7.18–7.12 (m, 1 H, Ph), 6.97 (t, J = 7.8 Hz, 2 H, Ph), 6.61–6.58 (m, 2 H, Ph), 1.57 (d, J = 1.0 Hz, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu), 0.34 (s, 9 H, SiMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 155.9 (d, J = 2.3 Hz), 151.5 (d, $^1J_{PC}$ = 80.3 Hz, P=C), 137.1 (d, J = 14.2 Hz), 129.8 (d, J = 6.8 Hz), 128.5 (d, J = 4.5 Hz), 128.3 (d, J = 12.7 Hz), 124.4 (d, J = 9.0 Hz), 123.3 (d, J = 19.5 Hz), 110.6 (d, J = 24.7 Hz), 105.5 (d, J = 2.3 Hz), 39.3 (d, J = 0.7 Hz), 35.8, 34.2 (d, J = 0.7 Hz), 31.5, 0.0 (d, J = 3.0 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 209.5 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{31}H_{47}AuOPSi$ [M + MeOH – Cl]$^+$ 691.2799; found 691.2775.

7a: A mixture of 2,2-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (65.2 mg, 0.15 mmol) and [(tht)AuCl] (47.2 mg, 0.15 mmol) in DCM (2 mL) under argon was stirred for 2 h at room temperature. Light-purple solid (98.6 mg, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H, Ph), 7.46–7.38 (m, 5 H), 7.08 (dt, J = 10.6, 3.3 Hz, 1 H, Ph), 6.93–6.87 (m, 2 H, Ph), 6.41–6.37 (m, 2 H, Ph), 1.63 (s, 18 H, *o*-*t*Bu), 1.34 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2 (d, $^1J_{PC}$ = 74.3 Hz, P=C), 157.1 (d, J = 1.5 Hz), 155.1 (d, J = 3.0 Hz), 142.4 (d, J = 10.5 Hz), 140.5 (d, J = 11.3 Hz), 130.0 (d, J = 4.5 Hz), 129.8, 129.6 (d, J = 2.2 Hz), 129.5, 129.1, 129.1 (d, J = 1.5 Hz), 128.1 (d, J = 3.0 Hz), 124.0 (d, J = 9.7 Hz), 39.4 (d, J = 1.5 Hz), 35.6, 34.5 (d, J = 0.7 Hz), 31.5 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 177.7 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{32}H_{43}AuOP$ [M + MeOH – Cl]$^+$ 671.2717; found 671.2706.

7b: A mixture of (*E*)-2-(4-methoxyphenyl)-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene[12] (147.6 mg, 0.31 mmol) and [(tht)AuCl] (100.1 mg, 0.31 mmol) in DCM (5 mL) under argon was stirred for 1 h at room temperature. Colorless solid (217.5 mg, 98.8 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (dd, J = 8.7, 3.2 Hz, 2 H, Ar), 7.38 (d, J = 3.6 Hz, 2 H, Ar), 7.06 (td, J = 7.4, 3.2 Hz, 1 H, Ar), 6.92–6.86 (m, 4 H, Ar), 6.43 (dd, J = 7.9, 2.4 Hz, 2 H, Ar), 3.83 (s, 3 H, OMe), 1.61 (s, 18 H, *o*-*t*Bu), 1.31 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1 (d, $^1J_{PC}$ = 74.2 Hz, P=C), 161.1 (d, J = 3.8 Hz), 156.9 (d, J = 1.5 Hz), 154.5 (d, J = 2.3 Hz), 140.4 (d, J = 9.7 Hz), 134.5 (d, J = 10.5 Hz), 130.9 (d, J = 18.0 Hz), 129.4 (d, J = 12.0 Hz), 128.7 (d, J = 5.3 Hz), 127.7 (d, J = 3.0 Hz), 123.6 (d, J = 25.5 Hz), 123.5 (d, J = 9.0 Hz), 114.1 (d, J = 2.3 Hz), 55.5, 39.1 (d, J = 1.5 Hz), 35.3, 34.3 (d, J = 0.7 Hz), 31.2 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 171.3 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{32}H_{41}AuClNaOP$ [M + Na]$^+$ 727.2147; found 727.2161.

7c: A mixture of (*E*)-2-(4-chlorophenyl)-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (169.8 mg, 0.36 mmol; see the Supporting Information) and [(tht)AuCl] (114.1 mg, 0.36 mmol) in DCM (3 mL) under argon was stirred for 1.5 h at room temperature. Light-purple solid (223.8 mg, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.42 (m, 4 H, Ar), 7.37 (dd, J = 8.5, 1.6 Hz, 2 H, Mes*), 7.09 (dt, J = 10.6, 3.2 Hz, 1 H, Ar), 6.91 (quint., J = 4.3 Hz, 2 H, Ar), 6.39–6.35 (m, 2 H, Ar), 1.61 (s, 18 H, *o*-*t*Bu), 1.33 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5 (d, $^1J_{PC}$ = 74.2 Hz, P=C), 157.2 (d, J = 1.5 Hz), 155.2 (d, J = 3.0 Hz), 140.8 (d, J = 10.5 Hz), 140.2 (d, J = 11.3 Hz), 136.1 (d, J = 5.2 Hz), 130.9 (d, J = 18.0 Hz), 129.5 (d, J = 12.8 Hz), 129.3, 129.3 (d, J = 7.5 Hz), 128.1 (d, J = 3.7 Hz), 124.0 (d, J = 9.0 Hz), 123.3 (d, J = 26.2 Hz), 39.3 (d, J = 1.5 Hz), 35.6, 34.5 (d, J = 1.5 Hz), 31.4 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 179.6 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{32}H_{42}AuClOP$ [M + MeOH – Cl]$^+$ 705.2327; found 705.2340.

7d: A mixture of 2,2-bis(1,1′-biphenyl-4-yl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (100 mg, 0.17 mmol, see the Supporting Information) and [(tht)AuCl] (53.9 mg, 0.17 mmol) in DCM (3 mL) under argon was stirred for 1.5 h at room temperature. Yellow solid (146.7 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 6 H, Ar), 7.52–7.43 (m, 6 H, Ar), 7.41–7.34 (m, 4 H, Ar), 7.21 (dd, J = 8.6, 1.6 Hz, 2 H, Mes*), 6.55 (dd, J = 8.6, 3.5 Hz, 2 H, Ar), 1.70 (s, 18 H, *o*-*t*Bu), 1.39 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.3 (d, $^1J_{PC}$ = 74.3 Hz, P=C), 157.2 (d, J = 0.7 Hz), 155.1 (d, J = 3.0 Hz), 142.9 (d, J = 4.5 Hz), 141.5, 141.4 (d, J = 12.0 Hz), 141.2, 140.4 (d, J = 1.5 Hz), 139.8 (d, J = 1.5 Hz), 139.6, 139.5, 130.3 (d, J = 8.2 Hz), 130.1 (d, J = 3.0 Hz), 129.2, 128.1 (d, J = 9.0 Hz), 127.7 (d, J = 2.3 Hz), 127.4 (d, J = 1.5 Hz), 127.0 (d, J = 0.8 Hz), 126.5 (d, J = 3.7 Hz), 124.0 (d, J = 24.7 Hz), 124.0 (d, J = 9.0 Hz), 39.4 (d, J = 1.5 Hz), 35.6, 34.5 (d, J = 0.7 Hz), 31.5 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 176.2 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{86}H_{94}AuP_2$ [2M + Au]$^+$ 1385.6496; found 1385.6500.

7e: A mixture of 2,2-di-2-naphthyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (100 mg, 0.18 mmol; see the Supporting Information) and [(tht)AuCl] (59.1 mg, 0.18 mmol) in DCM (3 mL) under argon was stirred for 2 h at room temperature. Yellow solid (136.0 mg, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, J = 2.9 Hz, 1 H, Ar), 7.97 (dd, J = 6.1, 4.1 Hz, 1 H, Ar), 7.89–7.83 (m, 2 H, Ar), 7.65 (d, J = 8.0 Hz, 1 H, Ar), 7.58–7.55 (m, 2 H, Ar), 7.47–7.35 (m, 7 H, Ar), 7.10–7.09 (m, 1 H, Ar), 6.58 (dt, J = 8.7, 2.1 Hz, 1 H, Ar), 1.71 (d, J = 0.6 Hz, 18 H, *o*-*t*Bu), 1.28 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0 (d, $^1J_{PC}$ = 74.2 Hz, P=C), 157.2 (d, J =

1.5 Hz), 155.0 (d, *J* = 3.0 Hz), 139.7 (d, *J* = 9.7 Hz), 137.8 (d, *J* = 12.0 Hz), 134.0 (d, *J* = 3.8 Hz), 133.3 (d, *J* = 3.0 Hz), 133.0 (d, *J* = 3.7 Hz), 132.7 (d, *J* = 3.7 Hz), 130.1 (d, *J* = 15.0 Hz), 129.2 (d, *J* = 15.0 Hz), 129.0 (d, *J* = 3.7 Hz), 128.9, 128.2 (d, *J* = 2.3 Hz), 127.7, 127.6 (d, *J* = 2.3 Hz), 127.4 (d, *J* = 0.8 Hz), 127.2, 126.9 (d, *J* = 8.2 Hz), 126.7, 126.7 (d, *J* = 1.5 Hz), 124.1 (d, *J* = 24.0 Hz), 124.1 (d, *J* = 9.8 Hz), 39.5 (d, *J* = 1.5 Hz), 35.6, 34.7 (d, *J* = 0.8 Hz), 31.4 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 178.8 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{39}H_{43}AuClNaP$ $[M + Na]^+$ 797.2354; found 797.2363.

7f: A mixture of 2,2-bis(thiophen-2-yl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (61.3 mg, 0.13 mmol; see the Supporting Information) and [(tht)AuCl] (43.2 mg, 0.13 mmol) in DCM (4 mL) under argon was stirred for 2 h at room temperature. Yellow solid (96.2 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 3.7 Hz, 2 H, Mes*), 7.53–7.48 (m, 2 H, Ar), 7.27–7.23 (m, 1 H, Ar), 7.13–7.10 (m, 1 H, Ar), 6.73–6.70 (m, 1 H, Ar), 6.26–6.23 (m, 1 H, Ar), 1.64 (d, *J* = 1.0 Hz, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.5 (s), 156.6 (d, $^1J_{PC}$ = 76.5 Hz, P=C), 156.0 (d, *J* = 3.0 Hz), 144.2 (d, *J* = 13.5 Hz), 142.4 (d, *J* = 11.3 Hz), 131.3 (d, *J* = 10.5 Hz), 131.2 (d, *J* = 17.3 Hz), 130.3 (d, *J* = 17.3 Hz), 129.0 (d, *J* = 6.0 Hz), 128.0 (d, *J* = 3.7 Hz), 127.4 (d, *J* = 6.7 Hz), 124.8 (d, *J* = 9.0 Hz), 123.4 (d, *J* = 22.5 Hz), 39.4 (d, *J* = 1.5 Hz), 35.8, 34.1 (d, *J* = 1.5 Hz), 31.6 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 166.9 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{28}H_{39}AuOPS_2$ $[M + MeOH - Cl]^+$ 683.1845; found 683.1857.

7g: A mixture of (*Z*)-2-bromo-2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene[12] (95 mg, 0.21 mmol) and [(tht)AuCl] (68.2 mg, 0.21 mmol) in DCM (3 mL) under argon was stirred for 1.5 h at room temperature. Light-purple solid (90.6 mg, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 2 H, Ar), 7.60 (d, *J* = 4.1 Hz, 2 H, Mes*), 7.47–7.39 (m, 3 H, Ar), 1.69 (s, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6 (d, $^1J_{PC}$ = 71.3 Hz, P=C), 156.2 (d, *J* = 1.5 Hz), 155.4 (d, *J* = 2.3 Hz), 140.1 (d, *J* = 7.5 Hz), 131.6 (d, *J* = 4.5 Hz), 129.3 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 17.2 Hz), 125.2 (d, *J* = 34.5 Hz), 124.3 (d, *J* = 10.5 Hz), 39.3 (d, *J* = 1.5 Hz), 35.8, 34.2 (d, *J* = 0.8 Hz), 31.4 ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 197.1 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{25}H_{34}AuBrClNaP$ $[M + Na]^+$ 699.0833; found 699.0861.

8: A mixture of phosphaethene **3a** (99.4 mg, 0.20 mmol) and [(tht)AuCl] (64.9 mg, 0.20 mmol) in DCM (3 mL) under argon was stirred for 1.5 h at room temperature. Yellow solid (136.9 mg, 93 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.72–7.66 (m, 4 H, Ar), 7.46–7.40 (m, 3 H, Ar), 7.35 (td, *J* = 7.2, 1.2 Hz, 1 H, Ar), 7.25 (t, *J* = 7.5 Hz, 2 H, Ar), 6.96 (dd, *J* = 6.6, 1.2 Hz, 2 H, Ar), 1.72 (d, *J* = 1.3 Hz, 18 H, *o*-*t*Bu), 1.36 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 157.5, 155.4 (d, *J* = 3.0 Hz), 134.8 (d, $^1J_{PC}$ = 87.8 Hz, P=C), 132.4 (d, *J* = 9.0 Hz), 131.9 (d, *J* = 7.5 Hz), 130.2 (d, *J* = 3.7 Hz), 130.2 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 2.3 Hz), 128.8 (d, *J* = 1.5 Hz), 124.2 (d, *J* = 9.0 Hz), 123.3 (d, *J* = 27.0 Hz), 122.4 (d, *J* = 11.2 Hz), 122.1 (d, *J* = 9.0 Hz), 108.7 (d, *J* = 19.5 Hz), 101.5 (d, *J* = 26.2 Hz), 88.8, 87.8 (d, *J* = 22.5 Hz), 39.4 (d, *J* = 1.5 Hz), 35.8, 34.4, 31.3 ppm. ^{31}P NMR (125 MHz, CD_2Cl_2): δ = 248.9 (s) ppm. HRMS (APCI-TOF): calcd. for $C_{36}H_{43}AuOP$ $[M + MeOH - Cl]^+$ 719.2717; found 719.2687.

Experimental Procedure for the Cycloisomerization Reaction: A solution of the 1,6-enyne (25.3 mg, 0.10 mmol) in dichloromethane (1 mL) was added to the corresponding phosphaethene-gold(I) complex (3 mol-%) under argon at 25 °C. After stirring for 2 h, the homogeneous reaction mixture was directly loaded on to a silica gel column and eluted with hexane/ethyl acetate (6:1) to give the cyclopentene derivative.

Experimental Procedure of the Alkoxycyclization Reaction: A solution of the 1,6-enyne (25.3 mg, 0.10 mmol) in DCM (0.5 mL) and methanol (0.5 mL) was added to the corresponding phosphaethene-gold(I) complex (3 mol-%) under argon at 25 °C. After stirring for 2 h, the reaction mixture was directly loaded on to a silica gel column and eluted with hexane/ethyl acetate (6:1) to give the methylenecyclopentane derivative.

Experimental Procedure for the Hydration Reaction: A solution of propargyl acetate (17.4 mg, 0.10 mmol) in acetone (1 mL) and H_2O (1.0 mmol) was added to the corresponding phosphaethene-gold(I) complex (3 mol-%) under argon at 25 °C. After stirring for 20 h the yield was determined by ^{1}H NMR analysis (1,1,2,2-tetrachloroethane was used as the internal standard).

X-ray Crystallography: X-ray diffraction data were collected with a Rigaku RAXIS-Rapid diffractometer. The structures were solved by direct methods (SHELXL-2014).[28] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[29]

X-ray Crystallographic Data for 6f: $C_{30}H_{43}AuClPSi$, yellow prisms (CH_2Cl_2/MeCN, 298 K), M_r = 695.12, crystal dimensions = 0.190 × 0.160 × 0.130 mm^3, monoclinic, space group $P2_1/c$ (#14), a = 10.7590(8), b = 16.9199(9), c = 17.5286(10) Å, β = 94.428(2)°, V = 3181.4(3) Å^3, Z = 4, λ = 0.71075 Å, $\varrho_{calcd.}$ = 1.451 g cm^{-3}, μ(Mo-K_α) = 4.812 mm^{-1}, F(000) = 1392, 49923 total reflections ($2\theta_{max}$ = 54.96°), index ranges = $-13 \le h \le 13$, $-21 \le k \le 21$, $-22 \le l \le 20$, 7278 unique reflections (R_{int} = 0.0771), $R1$ = 0.0499 [$I > 2\sigma(I)$], 0.0760 (all data), $wR2$ = 0.1339 [$I > 2\sigma(I)$], 0.1695 (all data), S = 1.094 (353 parameters).

X-ray Crystallographic Data for 6f': $C_{30}H_{43}AuClPSi$, yellow prisms (CH_2Cl_2/MeCN, 298 K), M_r = 695.12, crystal dimensions = 0.210 × 0.200 × 0.180 mm^3, monoclinic, space group $P2_1/n$ (#14), a = 12.7601(3), b = 16.212.8(6), c = 16.5283(4) Å, β = 112.6970(10)°, V = 3154.52(16) Å^3, Z = 4, λ = 0.71075 Å, $\varrho_{calcd.}$ = 1.464 g cm^{-3}, μ(Mo-K_α) = 4.853 mm^{-1}, F(000) = 1392, 30194 total reflections ($2\theta_{max}$ = 54.96°), index ranges = $-16 \le h \le 16$, $-21 \le k \le 21$, $-21 \le l \le 202$, 7199 unique reflections (R_{int} = 0.0430), $R1$ = 0.0298 [$I > 2\sigma(I)$], 0.0388 (all data), $wR2$ = 0.0974 [$I > 2\sigma(I)$], 0.1275 (all data), S = 0.992 (649 parameters).

CCDC 1572055 (for **6f**) and 1572056 (for **6f'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan through a Grant-in-Aid for Scientific Research [Nos. JP25288033 and JP15H00923 (Stimuli-responsive Chemical Species for the Creation of Functional Molecules, No. 2408)], the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (grant # 2015-23), and Nissan Chemicals Co. Ltd.

Keywords: Phosphaalkenes · Cross-coupling · Palladium · Gold · Stereochemistry

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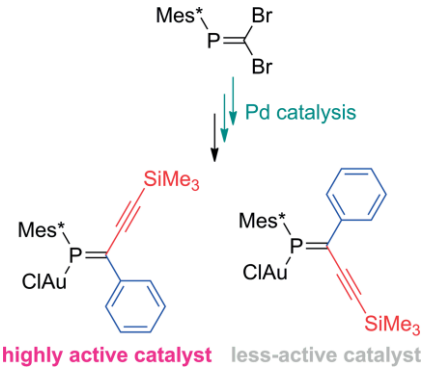
Received: September 7, 2017

Pd and Au Catalysis



The stereoselective monoalkynylation of a sterically encumbered *gem*-dibromophosphaethene has been accomplished, and subsequent arylation gave the corresponding 2-alkynyl-2-aryl-1-phosphaethenes. A study of the chloro-gold complexes bearing the 2-alkynyl-2-aryl-1-phosphaethenes revealed that an appropriate π-extension and the stereochemistry are decisive for gold catalysis.

DOI: 10.1002/ejoc.201701259