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Synthesis of Bulky Arylphosphanes by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reaction and Their Use as Ligands

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Treatment of 1-alkynylphosphane sulfides with 1,6- or 1,7-diynes in the presence of a cationic rhodium catalyst results in a formal [2+2+2] cycloaddition reaction to afford the corresponding aromatic phosphane sulfides. The aromatic rings formed in the cycloaddition naturally bear one or two substituents at the *ortho* positions to the phosphorus atom, which creates a sterically hindered environment around the phosphorus atom. The following desulfidation of the products is facile under radical conditions or with the aid of tris(dimethylamino)phosphane, providing the corresponding bulky phosphanes. Dicyclohexyl(2,6-diphenylaryl)-phosphane, which is available through this sequence, proves to serve as an efficient ligand in palladium-catalyzed cross-coupling amination reactions.

Keywords: amination · cross-coupling · cycloaddition · phosphanes · rhodium

Introduction

In the past decade, bulky triorganophosphanes have attracted increasing attention as excellent ligands for transition-metal catalysts in preparing biologically intriguing compounds as well as functional organic materials.[1] There are two important methods for the preparation of such bulky ligands: the reactions of chlorophosphanes with bulky organometallic reagents[2] and the transition-metal-catalyzed phosphination or phosphinylation of bulky aryl halides.[3] However, the bulky organometallic reagents and bulky aryl halides are not always readily available. Conceptually new approaches to bulky phosphanes should be developed.

We have been interested in the use of 1-alkynylphosphanes as starting materials in creating new phosphanes.[4,5] During the course of our study, we have developed rhodium-catalyzed formal [2+2+2] cycloaddition reactions[6] of 1,6-diynes and 1-alkynylphosphane sulfides,[7–9] which offer a novel approach to bulky phosphanes. Herein we report the full details of this approach. The use of the bulky phosphane ligands in palladium-catalyzed reactions is also disclosed.

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Results and Discussion

Rhodium-Catalyzed Formal [2+2+2] Cycloaddition of Tethered Diynes with 1-Alkynylphosphane Sulfides

The reaction of 1,6-diyne **1a** with 1-octynyldiphenylphosphane sulfide (**2a**) was chosen as a model reaction. Treatment of **1a** with **2a** in dichloromethane in the presence of a cationic rhodium catalyst and binap at 25 °C afforded the corresponding phosphane sulfide **3a** in high yield (Table 1, entry 1). The only by-product was **4a**, derived from homocycloaddition of **1a**. Binap proved to be the choice of ligand. When dppe, dppb, dppf, or PPh_3 (2 equiv) was used, the conversion of **2a** was modest and significant amounts of **4a** were obtained (Table 1, entries 2–5). The use of 1.5 mol % of $[RhCl(cod)]_2$ and 3.0 mol % of PPh_3 resulted in the predominant formation of homo-cycloadduct **4a**, leaving most of **2a** unreacted (Table 1, entry 6). The rhodium catalysts coordinated by two phosphorus atoms were effective for the successful cross-cycloaddition. Chlorinated solvents were suitable for the reaction (Table 1, entries 7 and 8). The generation of the cationic rhodium by the action of silver tetrafluoroborate was essential. No **3a** was detected in the

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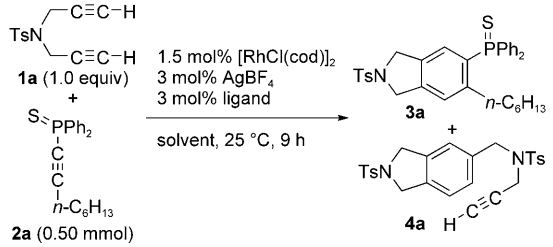
Table 1. Optimization of formal [2+2+2] cycloaddition reactions of tethered diyne **1a** with 1-octynyldiphenylphosphane sulfide (**2a**).[a]



Entry	Ligand	Solvent	**3a** [%][b]	**4a** [mmol][b]
1	binap	CH_2Cl_2	86	0.03
2	dppe	CH_2Cl_2	56	0.11
3	dppb	CH_2Cl_2	48	0.13
4	dppf	CH_2Cl_2	66	0.08
5	PPh_3[c]	CH_2Cl_2	52	0.12
6	PPh_3	CH_2Cl_2	9	0.22
7	binap	$ClCH_2CH_2Cl$	81	0.04
8	binap	toluene	61	0.10
9[d]	binap	CH_2Cl_2	<1	0.24

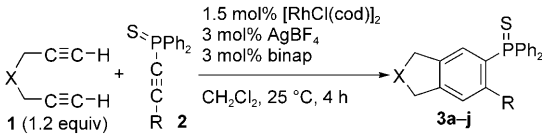
[a] Ts = *p*-$MeC_6H_4SO_2$. [b] Based on NMR analysis. [c] 6 mol%. [d] In the absence of $AgBF_4$.

absence of the silver salt, and **4a** was cleanly formed (Table 1, entry 9). The cationic rhodium center induces strong coordination of **2a**, and chlorinated solvents enhance the interaction.

The use of $[IrCl(cod)]_2$ or [Cp*RuCl(cod)], with or without the silver salt, failed to afford **3a**, yielding **4a** instead. The reaction of 1-octynyldiphenylphosphane with **1a** led to no conversion. The trivalent phosphane coordinates to the rhodium center so strongly that the catalyst becomes deactivated. The reaction of 1-octynyldiphenylphosphane oxide with **1a** provided the corresponding product in 40% yield along with **4a**.[9] The sulfide moiety of **2a** properly assists the reaction of a rhodacyclopentadiene intermediate with **2a** in the catalytic cycle.[10]

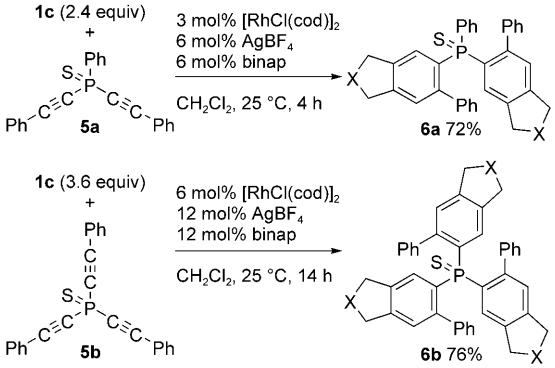
Table 2 summarizes the reactions of tethered terminal diynes **1** and 1-alkynylphosphane sulfides **2**. Diyne **1c**, derived from dimethyl malonate, reacted efficiently with **2a** to furnish the corresponding triarylphosphane sulfide **3c** in the highest yield of isolated product of 97% (Table 2, entry 3). Tetramethylene-tethered 1,7-octadiyne (**1e**) underwent the cross-cycloaddition more smoothly than trimethylene-tethered 1,6-heptadiyne (**1d**, Table 2, entries 4 and 5).

Table 2. Rhodium-catalyzed formal [2+2+2] cycloaddition reactions for synthesizing (mono-*ortho*-substituted aryl)diphenylphosphane sulfides **3a–j**.



Entry	**1**	X	**2**	R	**3**	Yield [%]
1	**1a**	*p*-$MeC_6H_4SO_2N$	**2a**	*n*-C_6H_{13}	**3a**	71
2	**1b**	O	**2a**	*n*-C_6H_{13}	**3b**	77
3	**1c**	$C(CO_2Me)_2$	**2a**	*n*-C_6H_{13}	**3c**	97
4	**1d**	CH_2	**2a**	*n*-C_6H_{13}	**3d**	60
5	**1e**	CH_2CH_2	**2a**	*n*-C_6H_{13}	**3e**	93
6	**1c**	$C(CO_2Me)_2$	**2b**	Ph	**3f**	85
7	**1c**	$C(CO_2Me)_2$	**2c**	*i*Pr	**3g**	83
8	**1c**	$C(CO_2Me)_2$	**2d**	*t*Bu	**3h**	74
9	**1c**	$C(CO_2Me)_2$	**2e**	*o*-$MeOC_6H_4$	**3i**	85
10	**1c**	$C(CO_2Me)_2$	**2f**	Me_3Si	**3j**	80

The scope of 1-alkynylphosphane sulfides was satisfactory (Table 2, entries 6–10). A variety of substituents, that is, phenyl, isopropyl, *tert*-butyl, *o*-methoxyphenyl, and trimethylsilyl groups, on the acetylenic terminus of **2** were compatible. Double and triple cycloaddition took place upon treatment of dialkynylphenylphosphane sulfide **5a** and trialkynylphosphane sulfide **5b** with **1c** with the rhodium catalyst (Scheme 1).



Scheme 1. Rhodium-catalyzed multiple formal cycloaddition [X = C-$(COOMe)_2$].

Although diynes having internal acetylenic moieties failed to react at 25 °C, the reactions proceeded in 1,2-dichloroethane at reflux to yield the corresponding products (Table 3). The newly formed aromatic rings of the products inherently have two substituents at the *ortho* positions to the phosphorus atom. Synthesis of (2,6-disubstituted aryl)-phosphanes is not easy.[2,3] We indeed performed the reaction of 2,6-diphenylphenyllithium with chlorodiphenylphos-

Abstract in Japanese:

1-アルキニルホスフィンスルフィドと 1,6-あるいは 1,7-ジインの混合物に対して、カチオン性ロジウム錯体触媒を作用させると、形式的な[2+2+2]環化付加反応が進行し、対応する芳香族ホスフィンスルフィドが生成する。本反応で生じるベンゼン環にはリン原子のオルト位に一つあるいは二つの置換基が必然的に存在することになり、リン原子周りに立体障害が生じる。得られたホスフィンスルフィドをラジカル条件下あるいはトリス（ジメチルアミノ）ホスフィンを用いて還元すると、対応するかさ高いホスフィンが収率よく得られる。なかでも、ジシクロヘキシル（2,6-ジフェニルアリール）ホスフィンはパラジウム触媒を用いるハロゲン化アリールのアミノ化において優れた配位子として機能する。

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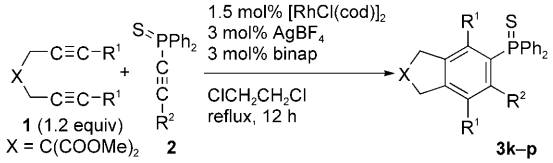
Table 3. Rhodium-catalyzed formal [2+2+2] cycloaddition reactions for synthesizing (di-*ortho*-substituted aryl)diphenylphosphane sulfides **3k–p**.



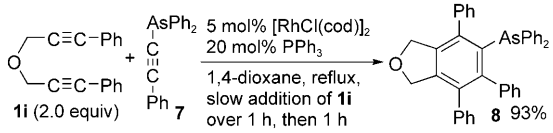
Entry	**1**	R^1	**2**	R^2	**3**	Yield [%]
1	**1f**	Me	**2a**	n-C_6H_{13}	**3k**	87[a]
2	**1g**	Ph	**2a**	n-C_6H_{13}	**3l**	90[a]
3	**1g**	Ph	**2b**	Ph	**3m**	65
4	**1h**	*i*Pr	**2c**	*i*Pr	**3n**	70[b]
5	**1h**	*i*Pr	**2g**	2-MeO-1-naphthyl	**3o**	77[b]
6	**1h**	*i*Pr	**2g**	2-MeO-1-naphthyl	**3o**	77[c] (40% *ee*)
7	**1h**	*i*Pr	**2g**	2-MeO-1-naphthyl	**3o**	72[d] (55% *ee*)
8	**1i**[e]	Ph	**2b**	Ph	**3p**	67[b]

[a] Performed for 4 h. [b] $[RhCl(cod)]_2$ (5 mol%), $AgBF_4$ (10 mol%), binap (10 mol%). [c] $[RhCl(cod)]_2$ (5 mol%), $AgBF_4$ (10 mol%), (*R*)-binap (10 mol%). [d] $[RhCl(cod)]_2$ (5 mol%), $AgBF_4$ (10 mol%), (*R*)-tol-binap (10 mol%). [e] X is O instead of $C(COOMe)_2$.

phane in THF at 25°C. However, the corresponding bulky phosphane, diphenyl(2,6-diphenylphenyl)phosphane, was obtained in only 22% yield, along with a significant amount of *m*-terphenyl.

Interestingly, the reaction of **1h** with diphenyl[(2-methoxy-1-naphthyl)ethynyl]phosphane sulfide (**2g**) afforded phosphane sulfide **3o** having a chiral axis (Table 3, entry 5). It is worth noting the use of (*R*)-binap and (*R*)-tol-binap led to chiral induction, affording **3o** with 40% *ee* and 55% *ee* (Table 3, entries 6 and 7).[9]

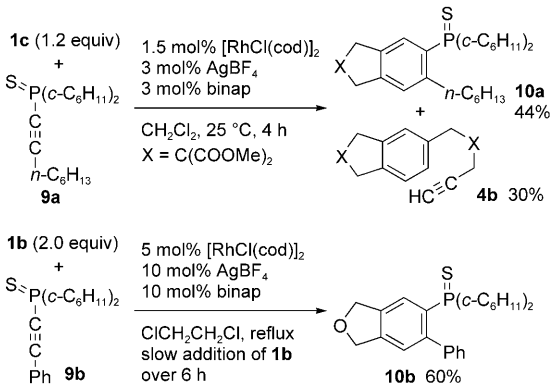
Bulky triarylarsine **8** was synthesized under different conditions (Scheme 2). It is noteworthy that trivalent diphenyl-



Scheme 2. Rhodium-catalyzed cycloaddition yielding a bulky triarylarsine.

(phenylethynyl)arsine (**7**), instead of the corresponding pentavalent derivatives such as arsine sulfide, could be used as the substrate. The reaction proceeded in the absence of $AgBF_4$. Binap was not essential, and triphenylphosphane served well. Importantly, **1i** should be added slowly over 1 h to attain a high yield. After extensive screening, the reaction was most efficient in 1,4-dioxane.

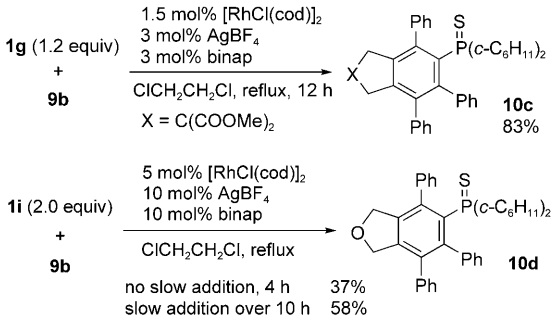
1-Alkynyldicyclohexylphosphane sulfides **9a** and **9b** were less reactive than the corresponding diphenyl analogues **2a** and **2b**. Because of the low reactivity of **9**, homo-cycloaddition of tethered terminal diynes **1** predominated. For instance, the reaction of terminal diyne **1c** with **9a** provided the desired product **10a** in 44% yield with concomitant formation of **4b** (30% yield based on **1c**; Scheme 3). Attempts



Scheme 3. Reactions of tethered terminal diynes with 1-alkynyldicyclohexylphosphane sulfides **9**.

to improve the yield of **10a** failed. The reaction of dipropargyl ether (**1b**) with **9b** requires a higher temperature as well as slow addition of **1b**.

The reaction of internal diyne **1g** with dicyclohexyl(phenylethynyl)phosphane sulfide (**9b**) was successful without using a slow addition technique to yield highly crowded **10c** in high yield (Scheme 4). Internal diyne **1g** was not prone to



Scheme 4. Reactions of tethered internal diynes with dicyclohexyl(phenylethynyl)phosphane sulfide (**9b**).

undergo homo-cycloaddition, owing to the steric hindrance around the acetylenic moieties. On the other hand, when oxygen-tethered internal diyne **1i** was used as the substrate, slow addition of **1i** was essential to attain a satisfactory result. Thus, oxygen-tethered **1i** proved to be less reactive than malonate-tethered **1g** in the cross-cycloaddition.

Desulfidation of the Phosphane Sulfides

The phosphane sulfides thus obtained should be readily reduced to the parent phosphane. To this end, the desulfidation reaction developed by Chatgilialoglu proved to be facile, clean, and high-yielding (Table 4).[11] For instance, treatment of **3c** with tris(trimethylsilyl)silane (TTMSS) in the presence of a radical initiator in benzene at reflux afforded the reduced product **11a** in 97% yield. Reduction of more bulky triarylphosphane sulfides, **3m**, **3n**, **3o**, **3p**, and **6b**, proceeded smoothly. Dicyclohexyl-substituted bulky phosphane sulfides **10b** and **10c** readily underwent the de-

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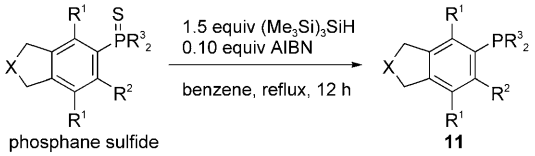
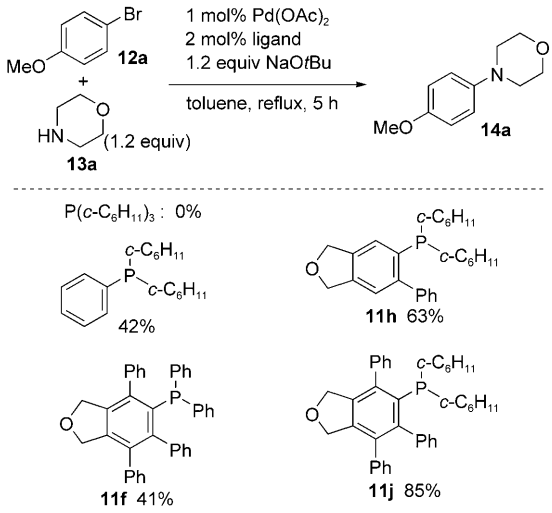
Table 4. Radical desulfidation of phosphane sulfides.



Entry	Phosphane sulfide	Phosphane	Yield [%]
1	**3c**	**11a**	97
2	**3f**	**11b**	91
3	**3m**	**11c**	84
4	**3n**	**11d**	49[a] (100[b])
5	**3o**	**11e**	78
6	**3p**	**11f**	77
7	**6b**	**11g**	91
8	**10b**	**11h**	82
9	**10c**	**11i**	80

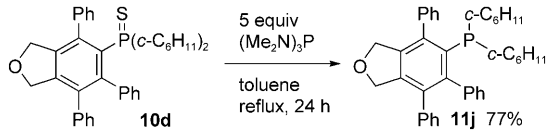
[a] The low yield was due to the instability in air. [b] Determined by ^{31}P NMR analysis of the crude product.



Scheme 6. Ligand screening in palladium-catalyzed amination.

sulfidation. Except for triisopropyl-substituted **11d**, the phosphanes obtained were stable in air. The purification of the trivalent phosphanes on silica gel could be performed without any special care.

Desulfidation with tris(dimethylamino)phosphane was found to be an alternative method (Scheme 5).[12] Treatment of phosphane sulfide **10d** with a large excess of tris(dimethylamino)phosphane in boiling toluene for 24 h provided the corresponding trivalent phosphane **11j** in 77% yield.



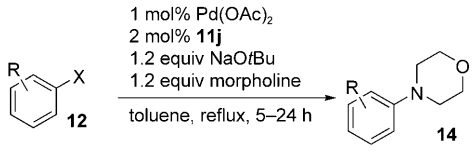
Scheme 5. Desulfidation with $(Me_2N)_3P$.

Palladium-Catalyzed Reactions with Bulky Phosphane Ligands Prepared by the Cycloaddition/Desulfidation Sequence

To evaluate the performance of the bulky phosphane ligands prepared by the method presented herein, we examined the palladium-catalyzed amination of aryl halides[13] with the bulky ligands. As a model reaction, we chose the reaction of 4-bromoanisole (**12a**) with morpholine (**13a**) with the aid of palladium acetate, ligand, and sodium *tert*-butoxide (Scheme 6). Although tricyclohexylphosphane was completely ineffective, dicyclohexylphenylphosphane promoted the amination to yield the corresponding aniline **14a** in 42% yield. Interestingly, introducing one or two phenyl groups at the *ortho* positions to the phosphorus atom improved the yield of **14a**. (2-Phenylaryl)phosphane **11h** was more effective than dicyclohexylphenylphosphane, and (2,6-diphenylaryl)phosphane **11j** was more effective than **11h**. Bulky triarylphosphane **11f** was inferior to aryldicyclohexylphosphane **11j**. The electron-rich and bulky nature of **11j** enhances the activity of the palladium catalyst.

The scope of aryl halides was examined by using **11j** as the ligand (Table 5). The amination of 4-bromotoluene proceeded smoothly (Table 5, entry 1). The reaction of 4-bromo-*N*,*N*-dimethylaniline was less efficient (Table 5, entry 2). Unfortunately, the reactions of bromobenzene (Table 5, entry 3), electron-deficient aryl bromide (entry 4), and *ortho*-substituted 2-bromotoluene (entry 5) suffered from low yields, albeit with full conversion. Aryl chloride also underwent the amination with moderate efficiency (Table 5, entry 6).

Table 5. Scope of aryl halides in palladium-catalyzed amination with morpholine by using **11j** as ligand.



Entry	R	X	*t* [h]	**14**	Yield [%]
1	4-Me	Br	5	**14b**	83
2	4-Me_2N	Br	24	**14c**	67
3	H	Br	5	**14d**	28
4	4-CF_3	Br	5	**14e**	32
5	2-Me	Br	5	**14f**	35
6	4-MeO	Cl	17	**14a**	55

The scope of amine is summarized in Scheme 7. Besides morpholine, the reaction of *N*-methylaniline proceeded smoothly, yielding **15b** in 76% yield. Piperidine was less reactive, and 2.5 mol% of the palladium catalyst was necessary to achieve a satisfactory yield. Dibutylamine was less reactive, and the product **15c** was obtained in only 34% yield in the reaction at a high temperature.

Palladium-catalyzed amination with primary amines was successful when tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$], **11j**, and 1,2-dimethoxyethane were used (Scheme 8). Except for *tert*-butylamine, the reactions afford-

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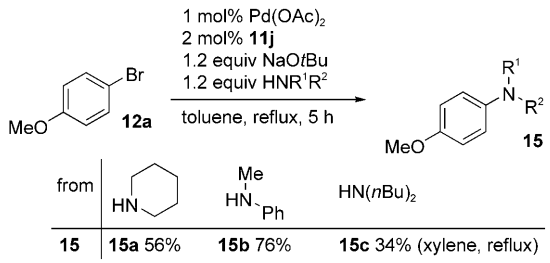
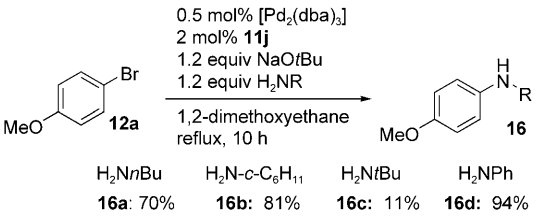


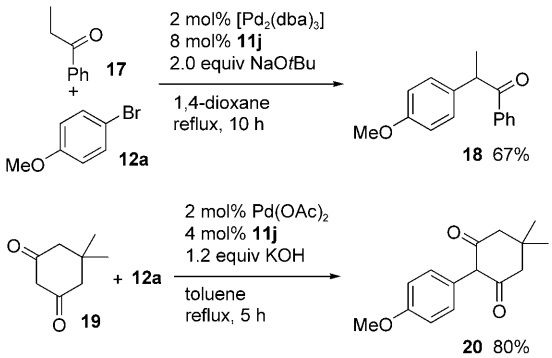
Scheme 7. Scope of secondary amines in palladium-catalyzed amination by using **11j** as ligand.



Scheme 8. Scope of primary amines in palladium-catalyzed amination by using **11j** as ligand.

ed the corresponding anilines in high yields. In the reaction of butylamine, diarylated product *N*,*N*-bis(4-methoxyphenyl)butylamine was formed in 9% yield, in addition to **16a**; compact butylamine is capable of undergoing the second arylation.

Ligand **11j** was effective not only in the amination reaction but also in the palladium-catalyzed arylation of ketones[14] (Scheme 9). Treatment of ethyl phenyl ketone (**17**) with **12a** in the presence of sodium *tert*-butoxide and catalytic amounts of $[Pd_2(dba)_3]$ and **11j** in refluxing dioxane provided **18** in good yield. The palladium-catalyzed arylation reaction of 1,3-diketone **19** with **12a** in the presence of potassium hydroxide in refluxing toluene afforded **20** in high yield. Ketone **19** readily tautomerizes into the corresponding highly stable enol form, which is unreactive under the conventional palladium-catalyzed arylation conditions. Sterically demanding ligand **11j** allowed **19** to react, probably because **11j** enhances the reductive elimination step of



Scheme 9. Palladium-catalyzed α-arylation of ketones by using **11j** as ligand.

the catalytic cycle. It is worth noting that the reaction of 1,3-diketone **19** with **12a** did not proceed at all even with the aid of XPhos,[15] which showed the highest performance in the palladium-catalyzed arylation of 1,3-dicarbonyl compounds.

Conclusions

The combination of the rhodium-catalyzed formal cycloaddition of diynes with 1-alkynylphosphane sulfides and subsequent desulfidation of the cycloadducts thus represents a conceptually novel access to bulky phosphanes. The phosphanes obtained could serve as useful ligands in palladium-catalyzed reactions, and will find many applications in organic synthesis.

Experimental Section

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ or C_6D_6 with tetramethylsilane as an internal standard. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ or C_6D_6 with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P{=}O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Determination of enantiomeric excess was performed with a Shimadzu LCMS-2010A. A syringe pump (Harvard Apparatus) was used for slow addition. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. $[RhCl(cod)]_2$ was obtained from Wako Pure Chemical. $AgBF_4$ and binap were purchased from Aldrich. Tris(trimethylsilyl)silane was obtained from TCI and was stored under argon. $Pd(OAc)_2$ and $[Pd_2(dba)_3]$ were obtained from TCI and Aldrich, respectively. Dichloromethane was dried over molecular sieves 4 Å. Benzene and toluene were dried over slices of sodium. 1-Alkynylphosphane sulfides **2** were synthesized by adding sulfur (3 equiv) to solutions of 1-alkynylphosphanes[4a] in THF at ambient temperature. Tethered diynes **1b**, **1d**, and **1e** are commercially available from Aldrich. Other diynes **1a**,[16] **1c**,[17] **1f**,[17] **1g**,[17] and **1h**[17] were prepared in the conventional ways. Compound **1i** was prepared by the conventional Williamson synthesis. Hexane and ethyl acetate were used for silica gel column chromatography.

Typical procedure for rhodium-catalyzed cycloaddition of tethered diynes with 1-alkynyldiphenylphosphane sulfide (Tables 1–3 and Schemes 1 and 2): Synthesis of **3c** is representative. $[RhCl(cod)]_2$ (3.7 mg, 0.0075 mmol), $AgBF_4$ (2.9 mg, 0.015 mmol), and binap (9.3 mg, 0.015 mmol) were placed in a 20-mL reaction flask under argon. Dichloromethane (4.0 mL), 1-octynyldiphenylphosphane sulfide (**2a**, 0.16 g, 0.50 mmol), and 4,4-di(methoxycarbonyl)-1,6-heptadiyne (**1c**, 0.13 g, 0.60 mmol) were sequentially added. The resulting solution was stirred for 4 h at 25 °C. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **3c** (0.26 g, 0.49 mmol, 97%) as a white solid.

Typical procedure for rhodium-catalyzed cycloaddition of tethered internal diynes with 1-alkynyldicyclohexylphosphane sulfide (Schemes 3 and 4): Synthesis of **10d** is representative. $[RhCl(cod)]_2$ (21 mg, 0.043 mmol),

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$AgBF_4$ (17 mg, 0.085 mmol), and binap (53 mg, 0.085 mmol) were placed in a 20-mL reaction flask under argon. 1,2-Dichloroethane (3.0 mL) and dicyclohexyl(phenylethynyl)phosphane sulfide (**9b**, 0.28 g, 0.85 mmol) were sequentially added. The resulting solution was heated at reflux, and a solution of diyne **1i** (0.42 g, 1.7 mmol) in 1,2-dichloroethane (2.0 mL) was added slowly over 10 h. After the addition was completed, the whole mixture was stirred for an additional 2 h at reflux. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification yielded **10d** (0.28 g, 0.49 mmol, 58%), which was contaminated with a small amount of the homo-cycloadduct of **1i**. Phosphane sulfide **10d** was subjected to the desulfidation shown in Scheme 5.

Typical procedure for $(Me_3Si)_3SiH$-mediated radical desulfidation reaction (Table 4): The reduction of **3m** to **11c** is representative. AIBN (1.6 mg, 0.010 mmol) and **3m** (0.068 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)-silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. The crude product was purified on silica gel to provide **11c** (0.054 g, 0.084 mmol, 84%) as a white solid.

Typical procedure for $(Me_2N)_3P$-mediated desulfidation reaction (Scheme 5): Under an atmosphere of argon, **10d** (0.28 g, 0.49 mmol) was dissolved in toluene (5 mL). A solution of tris(dimethylamino)phosphane (1.0 mol L^{-1} toluene solution, 3.3 mL, 3.3 mmol) was added. The resulting mixture was heated at reflux for 24 h. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification afforded **11j** (0.21 g, 0.38 mmol, 77%).

Typical procedure for palladium-catalyzed cross-coupling reaction (Table 5, Schemes 6–9): The reaction of 4-bromoanisole with morpholine (Scheme 6) is representative. Palladium acetate (0.4 mg, 0.002 mmol), **11j** (2.2 mg, 0.004 mmol), and sodium *tert*-butoxide (23 mg, 0.24 mmol) were placed in a 20-mL reaction flask filled with argon. Toluene (2.0 mL), 4-bromoanisole (**12a**, 37 mg, 0.20 mmol), and morpholine (**13a**, 21 mg, 0.24 mmol) were sequentially added. The resulting mixture was heated at reflux for 5 h. After the mixture was cooled to room temperature, water (10 mL) was added. Extractive workup with ethyl acetate followed by silica gel column purification provided **14a** (33 mg, 0.17 mmol, 85%) as a yellowish white solid.

Compounds **1h**, **2**, **3a–o**, **5**, **6**, **9**, **10a**, **10c**, **11a–e**, **11g**, and **11i** were characterized in a previous report.[7] Compounds **1a**,[16] **1c**,[18] **1f**,[17] **1g**,[19] **1i**,[20] **4**,[21] **14a**,[22] **14b**,[22] **14c**,[23] **14d**,[22] **14f**,[22] **15b**,[22] **16a**,[24] **16b**,[22] **16d**,[24] and **18**[25] showed the identical spectra as reported in the literature. Phosphane sulfides **3p**, **10b**, and **10d** were characterized as the corresponding phosphanes after desulfidation.

7: Diphenyl(phenylethynyl)arsine: IR (nujol): $\tilde{\nu}$ = 2924, 2854, 2160, 1433, 760, 741, 691 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.31–7.37 (m, 9H), 7.53–7.55 (m, 2H), 7.66–7.69 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 87.48, 106.76, 123.24, 128.52, 128.89, 128.96, 129.01, 132.14, 132.77, 136.32 ppm. Elemental analysis (%) calcd for $C_{20}H_{15}As$: C 72.73, H 4.58; found: C 72.95, H 4.42; m.p. 37.6–39.0 °C.

8: Diphenyl(1,3-dihydro-4,6,7-triphenyl-5-isobenzofuranyl)arsine: IR (nujol): $\tilde{\nu}$ = 2924, 2854, 1685, 1653, 1559, 1457, 1437, 1375, 665 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 4.79–4.80 (m, 2H), 4.98–4.99 (m, 2H), 6.80–7.14 ppm (m, 25H); ^{13}C NMR ($CDCl_3$): δ = 74.70, 74.74, 126.55, 126.73, 126.92, 127.09, 127.27, 127.86, 127.92, 127.97, 128.85, 129.44, 131.35, 133.21 (merged signal), 135.35, 137.93, 139.17, 139.42, 139.97, 140.45, 140.98, 141.87, 147.62 ppm. Elemental analysis (%) calcd for $C_{38}H_{29}AsO$: C 79.16, H 5.07; found: C 78.93, H 5.01; m.p. 148.7–150.0 °C.

11f: Diphenyl(1,3-dihydro-4,6,7-triphenyl-5-isobenzofuranyl)phosphane: IR (nujol): $\tilde{\nu}$ = 2925, 2854, 1448, 1378, 1359, 1066, 1046, 1036, 898, 877, 850, 770, 710, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 4.73 (s, 2H), 5.00 (s, 2H), 6.76–7.14 ppm (m, 25H); ^{13}C NMR ($CDCl_3$): δ = 74.76, 74.82, 126.47, 126.72 (d, J = 7.3 Hz), 126.97, 127.11, 127.84 (d, J = 11.0 Hz), 127.85, 127.86, 128.51, 129.38, 130.94 (d, J = 2.9 Hz), 132.38 (d, J = 19.6 Hz), 132.93 (d, J = 21.0 Hz), 135.82, 135.86, 137.43 (d, J = 14.4 Hz), 139.37, 139.78 (d, J = 2.4 Hz), 139.85 (d, J = 2.8 Hz), 140.27, 140.45 (d, J = 8.1 Hz), 142.29 (d, J = 9.1 Hz), 148.87 ppm (d, J = 27.1 Hz); ^{31}P NMR ($CDCl_3$): δ = −8.56 ppm. HRMS (EI): m/z calcd for $C_{38}H_{29}OP$: 532.1956; obsd: 532.1951 (Δ = −0.5 ppm); m.p. 95.0–97.9 °C.

11h: Dicyclohexyl(1,3-dihydro-6-phenyl-5-isobenzofuranyl)phosphane: IR (nujol): $\tilde{\nu}$ = 2924, 2854, 1458, 1437, 1375, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.02–1.25 (m, 10H), 1.55–1.82 (m, 12H), 5.14 (s, 2H), 5.20 (s, 2H), 7.15 (d, J = 3.5 Hz, 1H), 7.24–7.26 (m, 2H), 7.32–7.38 (m, 3H), 7.46 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 26.60, 27.38 (d, J = 4.8 Hz), 27.46 (d, J = 9.0 Hz), 29.43 (d, J = 9.0 Hz), 30.56 (d, J = 17.1 Hz), 34.92 (d, J = 14.3 Hz), 73.65, 73.67, 122.93 (d, J = 5.8 Hz), 125.15 (d, J = 3.3 Hz), 127.00, 127.57, 130.90 (d, J = 3.9 Hz), 133.56 (d, J = 22.0 Hz), 137.80, 139.91, 143.06 (d, J = 6.3 Hz), 150.15 ppm (d, J = 29.1 Hz); ^{31}P NMR ($CDCl_3$): δ = −14.48 ppm. Elemental analysis (%) calcd for $C_{26}H_{33}OP$: C 79.55, H 8.47; found: C 79.29, H 8.46; m.p. 145.0–147.9 °C.

11j: Dicyclohexyl(1,3-dihydro-4,6,7-triphenyl-5-isobenzofuranyl)phosphane: IR (nujol): $\tilde{\nu}$ = 2924, 2853, 1654, 1601, 1448, 1377, 1053, 904, 776, 760, 710, 702 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.88–1.69 (m, 22H), 4.75–4.76 (m, 2H), 4.92–4.93 (m, 2H), 6.95–6.97 (m, 4H), 7.07–7.13 (m, 6H), 7.13–7.26 (m, 2H), 7.39–7.45 (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 26.41, 27.05 (d, J = 13.4 Hz), 27.18 (d, J = 8.1 Hz), 31.84 (d, J = 9.1 Hz), 32.98 (d, J = 25.3 Hz), 35.83 (d, J = 15.3 Hz), 74.81, 74.85, 126.34, 126.52, 126.81, 127.41, 127.74, 128.12, 129.20, 129.38, 131.76, 133.28 (d, J = 29.6 Hz), 135.68 (d, J = 3.4 Hz), 138.51 (d, J = 3.3 Hz), 138.92 (merged signal), 139.80 (merged signal), 141.24 ppm (merged signal); ^{31}P NMR ($CDCl_3$): δ = 0.37 ppm. HRMS (EI): m/z calcd for $C_{38}H_{41}OP$: 544.2895; obsd: 544.2896 (Δ = +0.1 ppm); m.p. 179.4–184.0 °C.

14e: *N*-(4-Trifluoromethylphenyl)morpholine: IR (nujol): $\tilde{\nu}$ = 2924, 2855, 1615, 1527, 1453, 1378, 1328, 1308, 1268, 1239, 1206, 1162, 1105, 1073, 1053, 926, 828 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.24 (t, J = 5.0 Hz, 4H), 3.87 (t, J = 5.5 Hz, 4H), 6.92 (d, J = 9.0 Hz, 2H), 7.50 ppm (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 48.37, 66.86, 114.53, 121.22 (q, J = 32.5 Hz), 124.87 (q, J = 269.7 Hz), 126.66 (q, J = 3.8 Hz), 153.55 ppm. HRMS (EI): m/z calcd for $C_{11}H_{12}F_3NO$: 231.0871; obsd: 231.0874 (Δ = +0.3 ppm); m.p. 66.7–67.0 °C.

15a: *N*-(4-Methoxyphenyl)piperidine: IR (nujol): $\tilde{\nu}$ = 2935, 2854, 2832, 2794, 1511, 1465, 1452, 1442, 1384, 1293, 1275, 1233, 1217, 1181, 1042, 910, 824, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.52–1.56 (m, 2H), 1.70–1.74 (m, 4H), 3.02 (t, J = 5.5 Hz, 4H), 3.76 (s, 3H), 6.81–6.84 (m, 2H), 6.90–6.93 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 24.39, 26.34, 52.51, 55.76, 114.50, 118.96, 147.14, 153.73 ppm. HRMS (EI): m/z calcd for $C_{12}H_{17}NO$: 191.1310; obsd: 191.1311 (Δ = +0.1 ppm).

16c: *N-tert*-Butyl-4-methoxyaniline: IR (nujol): $\tilde{\nu}$ = 2923, 2854, 1609, 1559, 1507, 1457, 1377, 1366, 1042, 665, 406 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.23 (s, 9H), 1.25 (s, 1H), 3.77 (s, 3H), 6.76–6.82 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 29.92, 30.31, 55.74, 109.97, 114.27 (merged signal), 123.11 ppm. HRMS (EI): m/z calcd for $C_{11}H_{17}NO$: 179.1310; obsd: 179.1307 (Δ = −0.3 ppm); m.p. 67.7–70.2 °C.

20: 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3-cyclohexanedione: IR (nujol): $\tilde{\nu}$ = 2925, 2855, 2622, 1560, 1513, 1458, 1377, 1313, 1285, 1251, 1175, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.16 (s, 6H), 2.37 (s, 2H), 2.47 (s, 2H), 3.82 (s, 3H), 5.97–6.01 (br s, 1H), 6.97–6.99 (m, 2H), 7.11–7.13 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 28.58, 31.96, 41.84, 51.00, 55.50, 115.10, 116.63, 122.67, 132.02, 197.09 ppm. HRMS (EI): m/z calcd for $C_{15}H_{18}O_3$: 246.1256; obsd: 246.1251 (Δ = −0.5 ppm); m.p. 136.5–140.2 °C.

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