DOI: 10.1002/chem.200800538

Palladium-Catalyzed Formation of Highly Substituted Naphthalenes from Arene and Alkyne Hydrocarbons

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Abstract: Several highly substituted naphthalenes **3** have been synthesized in a one-pot reaction by treatment of arenes **1** with alkynes **2** in the presence of palladium acetate and silver acetate. In this Pd-catalyzed protocol, an arene provides a benzo source for the construction of a naphthalene core through twofold aryl C−H bond activation. Reaction of triphenylphosphine with diphenylethyne (**2a**) under the catalysis of Pd^{IV} complexes produced 1,2,3,4-tetraphenylnaphthalene (**3ba**) in 62% yield. Here, triphenylphosphine undergoes one aryl C−P bond cleavage and one aryl C−H bond activation to serve as a benzo moiety. Crystal structures of cycloadducts **3ea**, **3ga**, and **3ac** have been analyzed. The twisted naphthalenes arise not only from the overcrowded substituents but also from the contribution of the CH_3–π interaction.

Keywords: alkynes • C−P cleavage • C−H activation • crystal engineering • cyclization • naphthalene • palladium

Introduction

Catalytic activation of aryl C−H bonds with subsequent C−C bond formation is one of the most attractive endeavors for synthetic chemists, because such processes provide particularly efficient tools for the construction of valuable and versatile intermediates.[1] This concept offers several advantages: simplicity, cleanliness, and atom economy.[2] Fujiwara et al. reported that Pd- and Pt-catalyzed *trans*-hydroarylations of alkynes in trifluoroacetic acid selectively form *cis*-arylalkenes.[3] In contrast, in the presence of a trialkylborane and a dinuclear palladium complex, *cis*-hydroarylations of alkynes can be achieved by following the protocol of Tsukada et al.[4] Under the catalysis of metal trifluoromethanesulfonates $[M(OTf)_n]$ ($M = In, Sc, Zr$),[5] and Au^{I}[6a,b,7] or Au^{III}[7] complexes, hydroarylation of terminal arylethynes generates 1,1-diarylalkenes. However, Au^{III}-catalyzed hydroarylation of terminal electron-deficient alkynes (e.g., alkynoates) under solvent-free conditions produces *cis*-1,2-disubstituted alkenes.[7] Intramolecular hydroarylation of alkynes can also be catalyzed by Ru^{II},[9] Pt^{II},[9,10] or Au^{I}[6a,c,10] complexes. In a similar manner, hydroarylation reactions have been applied in the synthesis of coumarins and their derivatives from aryl alkynoates[9,11] or phenols and alkynoates.[3b,12]

These previously reported methods mainly concern the monoarylation of alkynes by cleavage of one C−H bond on an arene unit, that is, one aryl moiety is attached. Recently, we observed that naphthalenes can be formed under palladium catalysis from one arene and two molecules of an alkyne. This is the first example, to the best of our knowledge, in which an arene provides a benzo unit to furnish a naphthalene core by twofold aryl C−H activation on the same arene. Therefore, we optimized the reaction conditions and tested various arenes to develop a new and simple method for the preparation of highly substituted naphthalenes.[13]

Results and Discussion

Limited systematic studies of the reaction conditions for the synthesis of 5,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3aa**) from *p*-xylene (**1a**) and diphenylacetylene (**2a**) showed that AgOAc and $Pd(OAc)_2$ played key roles in this reaction (Table 1). Two equivalents of AgOAc (relative to alkyne **2a**) had to be used for best results. $Pd(OAc)_2$ and $K_2[PdCl_6]$ both turned out to be efficient catalysts, but the former is better than the latter (compare entries 10 and 13 in Table 1). Other palladium complexes, such as $[Pd(PPh_3)_4]$ and $[PdCl_2(PPh_3)_2]$, did not provide the desired co-cycliza-

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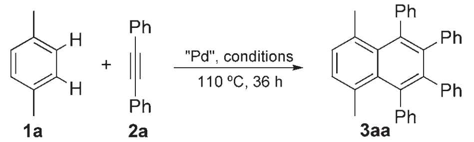
Table 1. Optimization of reaction conditions for the preparation of 5,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3aa**) from *p*-xylene (**1a**) and diphenylacetylene (**2a**).



Entry	Catalyst (mol %)[a]	Solvent	Additives (equiv)	Yield [%]
1	$Pd(OAc)_2$ (20)	*p*-xylene	AgOAc (2)	24
2	$Pd(OAc)_2$ (20)	*p*-xylene	AgOAc (0.4)	16
3	$[PdCl_2(PPh_3)_2]$ (20)	*p*-xylene	AgOAc (1)	trace[b]
4	$[Pd(PPh_3)_4]$ (20)	*p*-xylene	AgOAc (1)	0[c]
5	$Pd(OAc)_2$ (0)	*p*-xylene	AgOAc (1)	0[c]
6	$Pd(OAc)_2$ (20)	MeCN	AgOAc (2)	35
7	$Pd(OAc)_2$ (20)	DMF	AgOAc (2)	30
8	$Pd(OAc)_2$ (20)	MeCN	AgOAc (2)	52[d]
9	$Pd(OAc)_2$ (20)	MeCN	AgOAc (1)	29[d,e]
10	$Pd(OAc)_2$ (10)	MeCN	AgOAc (2)	55[d]
11	$Pd(OAc)_2$ (7.5)	MeCN	AgOAc (2)	60[d]
12	$Pd(OAc)_2$ (7.5)	MeCN	AgOAc (2)	56[d,f]
13	$K_2[PdCl_6]$ (10)	MeCN	AgOAc (2)	30[d]

[a] The amounts of catalysts and additives, and the chemical yields are relative to the amount of alkyne. [b] 32 % yield (relative to PPh_3 from $[PdCl_2(PPh_3)_2]$) of 1,2,3,4-tetraphenylnaphthalene (**3ba**) was isolated. [c] Most of **2a** was recovered. [d] The alkyne was added to the reaction mixture within 10 h with a syringe pump. [e] 37% of the alkyne was recovered. [f] The reaction was carried out under air for 16 h instead of under a N_2 atmosphere.

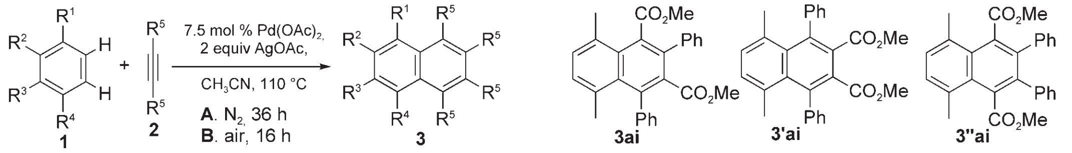
tion product **3aa**. When the reaction was carried out in either acetonitrile or *N*,*N*-dimethylformamide, **3aa** was obtained with higher purity relative to that obtained in *p*-xylene. Although the alkyne **2a** was completely consumed under these conditions, the yields were still low.[14] Fortunately, slow addition of **2a** to the reaction mixture (within 10 h) increased the yield from 35 to 52 % (compare entries 6 and 8 in Table 1). Under the optimized reaction conditions ($Pd(OAc)_2$ (7.5 mol %) and AgOAc (2 equiv) in acetonitrile at 110 °C), **3aa** could be obtained in 60 % yield (entry 11 in Table 1). In addition, the reaction time could be decreased from 36 to 16 h when the reaction was carried out under air, instead of under a nitrogen atmosphere.

Reactions of various benzene derivatives **1** with internal alkynes **2** were examined. Benzene and toluene furnished **3ba** and **3ca**, respectively, in low yields and unsatisfying purities (entries 2 and 3 in Table 2). Although dialkylbenzenes provided clean products in higher yields than benzene and toluene, trimethylbenzenes generated the cycloadducts exclusively in similar yields (Table 2). In contrast to *p*-xylene (**1a**) and 1,2,4-trimethylbenzene (**1l**), the electron-deficient 2-chloro-*p*-xylene (**1r**) showed lower reactivity in this co-cyclization reaction (entries 1, 12 and 18 in Table 2). Bromo-substituted xylenes are not suitable starting materials in this protocol. 2-Bromo-1,4-dimethylbenzene (**1s**) produced the debrominated cycloadduct **3aa** in 64 % yield (entry 19 in Table 2).[15] 2-Bromo-1,3-dimethylbenzene (**1w**) did form the bromo-substituted product **3wa**, but the conversion and yield were low (entry 23 in Table 2). Heteroatom-substituted arenes, such as aniline, pyrrole, and pyridine, did not undergo co-cyclizations with alkyne **2a**. Anisole (**1p**) and 1,2-dimethoxybenzene (**1q**) generated the corresponding products in very low yields (less than 10 %) under a nitrogen atmosphere (**A** conditions), but the yields could be improved when the reactions were carried out under air (**B** conditions). Dimethylanisoles gave better results than anisole and 1,2-dimethoxybenzene. Bulky substituents (especially *i*Pr and *t*Bu) in 1,3- and 1,4-disubstituted benzenes led to lower yields than methyl groups. Mono- and 1,2-disubstituted benzenes each yielded two regioisomeric co-cyclization products. Toluene, *o*-xylene, and anisole generated regioisomers in ratios close to 1:1 (entries 3, 11, and 16 in Table 2). However, the reaction of *o*-xylene with bis(4-*tert*-butylphenyl)ethyne (**2b**) produced **3kb-a** and **3kb-b** in an 87:13 ratio (entry 30 in Table 2). Bicyclic arenes, such as, indane (**1n**) and 1,2,3,4-tetrahydronaphthalene (**1o**), have also been utilized in this reaction, and the former provided a higher yield and regioselectivity than the latter. Remarkably, 5,6-dialkyl-1,2,3,4-tetraarylnaphthalenes were obtained as the major products from 1,2-dialkylbenzenes, whereas 1,2-dimethoxybenzene (**1q**) formed 6,7-dimethoxy-1,2,3,4-tetraphenylnaphthalene (**3qa-b**) as the almost exclusive cycloadduct.

Apparently, diarylethynes, such as 1,2-diphenylethyne (**2a**), 1,2-di(4-alkylphenyl)ethynes, and 1,2-di(4-fluorophenyl)ethyne (**2d**), are most suitable for these co-cyclizations. 4-Octyne (**2g**) and 3,3-dimethyl-1-phenyl-1-propyne (**2h**) did not yield the correspondingly substituted naphthalenes from *p*-xylene, and dimethyl acetylenedicarboxylate (**2f**) furnished tetraester **3af** in very low yield. Reaction of *p*-xylene with an asymmetric alkyne, such as, methyl phenylpropiolate (**2i**), produced naphthalene derivatives **3ai** and **3′ai** in 23 and 13 % yields, respectively. Traces of regioisomer **3″ai** can also be detected.

Highly substituted naphthalenes have been found to have twisted naphthalene cores that accommodate the steric repulsion. The usual twist angle for octasubstituted naphthalenes is approximately 20–30°.[16] X-ray quality crystals of 5-*n*-butyl-8-methyl-1,2,3,4-tetraphenylnaphthalene (**3ea**), 5,8-diisopropyl-1,2,3,4-tetraphenylnaphthalene (**3ga**) and 5,8-dimethyl-1,2,3,4-tetra(4-tolyl)naphthalene (**3ac**) were grown from CH_2Cl_2/MeOH. Compound **3ea** easily formed a large crystal in contrast to the other naphthalenes described in this article. According to crystallographic analyses, compounds **3ea**, **3ga**, and **3ac** display naphthalene cores with overall twist angles of 23.9, 22.3, and 20.7°, respectively (Table 3).[17,18] The contribution of the end-to-end twist from the tetraarylbenzo ring for **3ea** (13.1°) is slightly larger than that for **3ga** (10.7°) and **3ac** (11.2°). In addition, compounds **3ea** and **3ac** show intermolecular interactions and two naphthalene molecules form a pair through two CH_3–π interactions (Figure 1). Examples of CH_3–π interactions, such as those in calix[4]arene•toluene complexes, have been previously reported.[19] The methyl carbon atom in the central naphthalene core of **3ea** and **3ac** lies approximately 3.58 and 3.73 Å, respectively, from the tetraarylbenzo plane, depending on the conformation of the methyl group; therefore the intermolecular distance of one methyl hydrogen atom to

Table 2. Preparation of naphthalene derivatives **3** from arenes **1** and internal alkynes **2**.



Entry	Arene	R^1	R^2	R^3	R^4	Alkyne	R^5	Conditions	Product	Yield [%][a]	Procedure
1	**1a**	Me	H	H	Me	**2a**	Ph	**A**	**3aa**	60	GP1
2	**1b**	H	H	H	H	**2a**	Ph	**A**	**3ba**	17	GP1
3	**1c**	Me	H	H	H	**2a**	Ph	**A**	**3ca-a**	15[b]	GP1
		H	Me	H	H		Ph		**3ca-b**		
4	**1d**	Et	H	H	Et	**2a**	Ph	**A**	**3da**	35[c]	GP1
5	**1e**	*n*Bu	H	H	Me	**2a**	Ph	**A**	**3ea**	27[c]	GP1
6	**1f**	*i*Pr	H	H	Me	**2a**	Ph	**A**	**3fa**	37	GP1
7	**1g**	*i*Pr	H	H	*i*Pr	**2a**	Ph	**A**	**3ga**	17[c]	GP1
8	**1h**	*t*Bu	H	H	Me	**2a**	Ph	**A/B**	**3ha**	6	GP1
9	**1i**	Me	H	Me	H	**2a**	Ph	**A**	**3ia**	43(35[c])	GP1
10	**1j**	*i*Pr	H	*i*Pr	H	**2a**	Ph	**A**	**3ja**	31	GP1
11	**1k**	Me	Me	H	H	**2a**	Ph	**A**	**3ka-a**	51[d]	GP1
		H	Me	Me	H		Ph		**3ka-b**		
12	**1l**	Me	Me	H	Me	**2a**	Ph	**A**	**3la**	50	GP1
13	**1m**	Me	Me	Me	H	**2a**	Ph	**A**	**3ma**	52	GP1
14	**1n**	−(CH$_2$)$_3$−		H	H	**2a**	Ph	**A**	**3na-a**	55[e]	GP1
		H	−(CH$_2$)$_3$−		H		Ph		**3na-b**		
15	**1o**	−(CH$_2$)$_4$−		H	H	**2a**	Ph	**A**	**3oa-a**	28[f]	GP1
		H	−(CH$_2$)$_4$−		H		Ph		**3oa-b**		
16	**1p**	OMe	H	H	H	**2a**	Ph	**B**	**3pa-a**	40[g]	GP1
		H	OMe	H	H		Ph		**3pa-b**		
17	**1q**	OMe	OMe	H	H	**2a**	Ph	**B**	**3qa-a**	16[h]	GP1
		H	OMe	OMe	H		Ph		**3qa-b**		
18	**1r**	Me	Cl	H	Me	**2a**	Ph	**B**	**3ra**	16	GP1
19	**1s**	Me	Br	H	Me	**2a**	Ph	**B**	**3sa**	1 (+64[i])	GP1
20	**1t**	OMe	Me	H	Me	**2a**	Ph	**B**	**3ta**	47	GP1
21	**1u**	OMe	H	Me	Me	**2a**	Ph	**B**	**3ua**	48	GP1
22	**1v**	Me	OMe	Me	H	**2a**	Ph	**B**	**3va**	52	GP1
23	**1w**	Me	Br	Me	H	**2a**	Ph	**B**	**3wa**	16[j]	GP1
24	**1a**	Me	H	H	Me	**2b**	4-*t*Bu-Ph	**A**	**3ab**	38	GP2
25	**1a**	Me	H	H	Me	**2c**	4-tol	**A**	**3ac**	47	GP2
26	**1a**	Me	H	H	Me	**2d**	4-F-Ph	**A**	**3ad**	62	GP1
27	**1a**	Me	H	H	Me	**2e**	4-OMe-Ph	**A**	**3ae**	14	GP2
28	**1a**	Me	H	H	Me	**2f**	CO$_2$Me	**A**	**3af**	10[k]	GP1
29	**1a**	Me	H	H	Me	**2g**	*n*Pr	**A**	**3ag**	–[l]	GP1
30	**1k**	Me	Me	H	H	**2b**	4-*t*Bu-Ph	**A**	**3kb-a**	48[m]	GP2
		H	Me	Me	H		4-*t*Bu-Ph		**3kb-b**		

[a] The amounts of catalysts, additives and chemical yields are relative to alkyne **2**. Alkyne was added to the reaction mixture within 10 h from a syringe pump. The ratios of regioisomers were according to the ^{1}H NMR spectra. [b] **3ca-a**/**3ca-b** 56:44. [c] 10 mol% Pd(OAc)$_2$ was used. [d] **3ka-a**/**3ka-b** 64:36. [e] **3na-a**/**3na-b** $>$ 95:5. [f] **3oa-a**/**3oa-b** 75:25. [g] **3pa-a**/**3pa-b** 45:55. [h] **3qa-a**/**3qa-b** $<$5:95. [i] Additionally, 64% of **3aa** was isolated. [j] 40% of **2a** was recovered. [k] Including 2% of hexamethyl benzenehexacarboxlate. [l] A complex mixture. [m] **3kb-a**/**3kb-b** 87:13.

the tetraphenylbenzo plane in **3ea** should be between 2.52 and 2.97 Å,[20] which is in the range of the standard mean value for an interaction of the CH$_3$–arene type.[21] The degree of twisting of the tetraarylbenzo ring relates to the strength of the CH$_3$–π interaction, and it makes **3ea** more twisted than the other two examples. Besides the main contribution from the steric repulsion, van der Waals attraction is also a factor that leads to naphthalene core distortion from the preferred geometry.

The formation of naphthalene **3aa** most probably starts with an electrophilic palladation of *p*-xylene (**1a**) to yield the arylpalladium acetate **7** (route **A** in Scheme 1).[1c,22] *syn*-Addition of the Ar−Pd bond in **7** to the triple bond of diphenylacetylene (**2a**) would yield the vinylpalladium species **9**, and this would be followed by the insertion of another molecule of **2a** to afford the arylbutadienylpalladium intermediate **8**. In a side reaction, aryl-1,2-diphenylethylene **10** could be formed by protonlysis/depalladation due to the presence of acetic acid,[1c,3] but **10** was not observed as a byproduct. Intramolecular electrophilic palladation of **8** would lead to palladabenzocycloheptatriene **4**, which subsequently would undergo reductive elimination to yield naphthalene **3aa**. An alternative formation of the key intermediate **8** could start with the reaction of Pd(OAc)$_2$ with two molecules of alkyne **2a** to give 1-palladacyclopentadiene **5** (route **B** in Scheme 1).[23,24] Palladacycle **5** can produce hexasubstituted benzene **6** by insertion of another alkyne **2a**, and reductive elimination. However, because *p*-xylene (**1a**) is ap-

Table 3. Crystal data for compounds **3ea**, **3ga**, and **3ac**.

	3ea	**3ga**	**3ac**
formula	$C_{39}H_{36}$	$C_{40}H_{36}$	$C_{40}H_{36}$
T [K]	296(2)	273(2)	296(2)
crystal system	triclinic	monoclinic	monoclinic
space group	P_1	$P2_1/n$	$P2_1/n$
a [Å]	8.2578(18)	15.3046(4)	12.2147(10)
b [Å]	14.048(3)	11.7211(3)	10.8707(9)
c [Å]	14.451(3)	16.5363(6)	24.577(2)
α [°]	64.265(4)	90	90
β [°]	86.469(4)	95.1640(10)	103.471(3)
γ [°]	74.429(4)	90	90
V [Å^3]	1451.8(5)	2954.35(13)	3173.6(5)
Z	2	4	4
crystal size [mm^3]	$0.40\times0.15\times0.10$	$0.30\times0.20\times0.10$	$0.25\times0.10\times0.08$
R-factor [%]	4.00	5.99	6.03
distance of sp^3-C–π interaction [Å]	3.58	–	3.73
end-to-end twist [°]:			
overall naphthalene	23.9	22.3	20.7
tetraarylbenzo ring	13.1	10.7	11.2

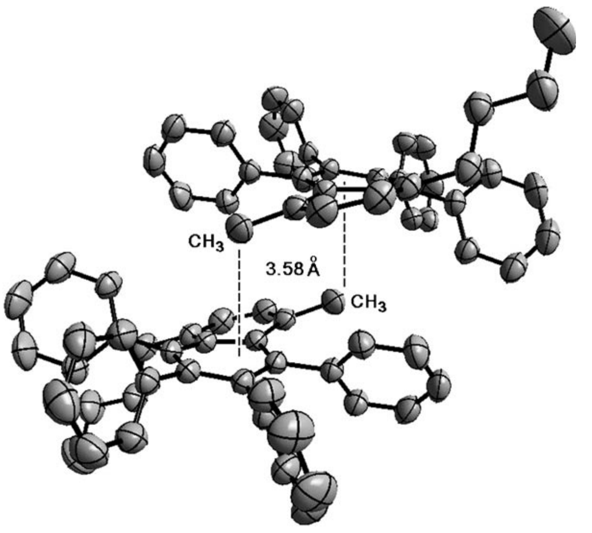
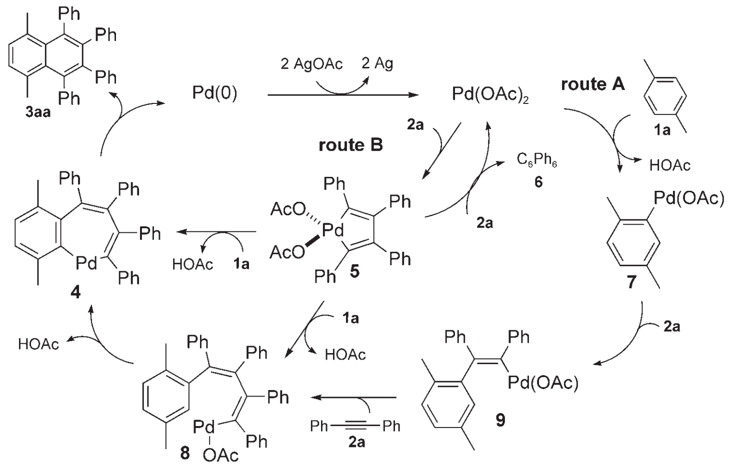


Figure 1. Intermolecular CH_3–π interactions of 5-n-butyl-8-methyl-1,2,3,4-tetraphenylnaphthalene (**3ea**).

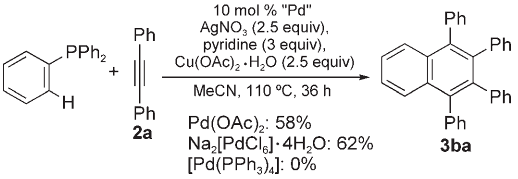


Scheme 1. Proposed mechanism for the formation of **3aa** from alkyne **2a** and p-xylene **1a**.

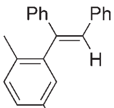
plied in large excess with respect to alkyne **2a** in this reaction,[25] the 1-palladacyclopentadiene **5** has a better chance to react with **1a** and yields **4** or **8**. The palladium(0) species produced in the reduction/elimination is eventually reoxidized by the additional silver acetate to generate $Pd(OAc)_2$. In addition, a control experiment suggested that route **B** is more reasonable. When a reaction was carried out in the absence of p-xylene, 1,2,3,4-tetraphenyltriphenylene (**11**) was isolated in 8% yield.[26] Compound **11** should be formed from hexaphenylbenzene (**6**)[27] by cyclodehydrogenation.[28]

A small amount of 1,2,3,4-tetraphenylnaphthalene (**3ba**) was obtained upon treatment of **1a** with the alkyne **2a** in the presence of $[PdCl_2(PPh_3)_2]$ (entry 3 in Table 1). Since **3ba** in this reaction could only have been formed from **2a** and the triphenylphosphine in $[PdCl_2(PPh_3)_2]$, the possibility of preparing **3ba** directly from PPh_3 was studied (Scheme 2).[29–31] A limited survey of the reaction conditions showed that the combinations of $AgNO_3$, $Cu(OAc)_2{\cdot}H_2O$, and $Pd(OAc)_2$ gave **3ba** in 43% yield. Finally, when PPh_3 and **2a** were added slowly to the mentioned catalytic system with a syringe pump, a satisfying result (58% yield) was achieved. The plausible reasons might be:

1) $Pd(OAc)_2$ is an efficient reagent for cleaving aryl C–P bonds.[32]
2) Less triphenylphosphine oxide is formed.[33,34]



Scheme 2. Preparation of 1,2,3,4-tetraphenylnaphthalene (**3ba**) from triphenylphosphine and diphenylacetylene (**2a**).



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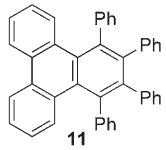

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Interestingly, $Na_2[PdCl_6]{\cdot}4H_2O$ provided **3ba** in up to 62% yield, whereas $[Pd(PPh_3)_4]$ did not afford the desired product. Although the mechanism of this reaction is not clear, $[Ag(PPh_3)_n]NO_3$ ($n=1$ or 2) could be an intermediate because $AgNO_3$ has a superior reactivity towards PPh_3.[35] In our catalytic system, heating $[Ag(PPh_3)_2]NO_3$ with alkyne **2a** furnished **3ba** in 48% yield (based on PPh_3).[36] In addition, this is the first example of a phenyl group in PPh_3 that serves as a benzo moiety for the construction of a naphthalene core by one aryl C–P bond cleavage and one aryl C–H bond activation.

Conclusion

A new and simple method for the preparation of oligosubstituted naphthalene derivatives in a one-pot operation from internal alkynes and an arene or one molecule of triphenylphosphine has been developed. Although the yields obtained with these two protocols are not excellent, the simplicity of the method provides a major advantage. Further studies of photophysical properties of oligoaryl-substituted naphthalenes **3**,[37] and exploration of mechanistic and synthetic aspects in the construction of complex aromatic compounds are in progress.

Experimental Section

General information: ^{1}H and ^{13}C NMR spectra: Bruker 300 (300 and 75.5 MHz). MS: Bruker Daltonics Apex II30. X-ray crystal structure determination: The data were collected on a Stoe-Siemens-AED diffractometer. Melting points were determined with a Büchi melting point apparatus B545 and are uncorrected. Elemental analysis: Laboratory for elemental analyses at National Cheng Kung University. Spectroscopic and analytical data for new compounds, which are not mentioned in Experimental Section, are presented as the Supporting Information.

Preparation of 1,2,3,4-Tetraphenylnaphthalene (3ba) from PPh_3 and alkyne 2a: A solution of **2a** (326 mg, 1.83 mmol) and PPh_3 (160 mg, 0.61 mmol) in CH_3CN (2.5 mL) was added over 10 h with a syringe pump to a vigorously stirred mixture of $AgNO_3$ (324 mg, 1.91 mmol), $Cu(OAc)_2{\cdot}H_2O$ (381 mg, 1.91 mmol), $Na_2PdCl_6{\cdot}4H_2O$ (33.4 mg, 76.0 μmol), pyridine (181 mg, 2.29 mmol), PPh_3 (40.0 mg, 0.15 mmol) , and alkyne **2a** (82.0 mg, 0.46 mmol) in CH_3CN (2 mL) at 110 °C under nitrogen. The suspension was kept at the same temperature for an additional 26 h. After the reaction mixture had been cooled to room temperature, it was filtered over Celite and the filtrate was concentrated. The residue was subjected to chromatography on SiO_2 (hexane/CH_2Cl_2 7:1 to 3:1) to afford **3ba** (205 mg, 62 % (based on PPh_3)) as a pale yellow solid. In addition, 133 mg of **2a** was recovered. Colorless crystals could be obtained by crystallization from CH_2Cl_2/MeOH. M.p. 203–204 °C; the ^{1}H NMR spectrum was identical to that reported in the literature.[38]

General procedures for preparation of naphthalenes from an arene 1 and an alkyne 2:

Variation 1 (GP1): For an alkyne ***2*** *(i.e.* ***2a***, ***2d***, ***2f***, ***2g*** *and* ***2i****) with good solubility in CH_3CN—5,7-dimethyl-1,2,3,4-tetraphenylnaphthalene (****3ia****)*: A solution of alkyne **2a** (270 mg, 1.51 mmol) in CH_3CN (2 mL) was added over 10 h with a syringe pump to a vigorously stirred suspension of AgOAc (500 mg, 3.00 mmol) and $Pd(OAc)_2$ (25.6 mg, 0.11 mmol) in *m*-xylene (**3i**) (2 mL) at 110 °C under nitrogen. The mixture was kept at the same temperature for an additional 26 h. After the reaction mixture had been cooled to room temperature, it was filtered over Celite and the filtrate was concentrated. The residue was subjected to chromatography on SiO_2 (hexane/CH_2Cl_2 10:1 to 6:1) to afford **3ia** (149 mg, 43 % (based on **2a**)) as a pale yellow solid. Colorless crystals were obtained by crystallization from CH_2Cl_2/MeOH. M.p. 254–255 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.92$ (s, 3 H), 2.31 (s, 3 H), 6.71–6.83 (m, 10 H), 7.05–7.30 ppm (m, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): $\delta = 21.4$ (+), 25.1 (+), 124.9 (+), 125.1 (+), 125.2 (+), 126.1 (+), 126.2×2 (+), 126.4 (+), 126.7 (+), 127.4 (+), 129.1 (C_{quat}), 131.1 (+), 131.3 (+), 131.4 (+), 131.6 (+), 132.7 (+), 133.6 (C_{quat}), 134.9 (C_{quat}), 135.6 (C_{quat}), 137.9 (C_{quat}), 138.4 (C_{quat}), 138.5 (C_{quat}), 139.5 (C_{quat}), 140.4 (C_{quat}), 140.8×2 (C_{quat}), 143.0 ppm (C_{quat}); MS (70 eV): *m/z* (%): 460 (100) $[M]^+$, 194 (17), 176 (15); elemental analysis calcd (%) for $C_{36}H_{28}$ (460.6): C 93.87, H 6.13; found: C 93.65, H 6.03; HRMS (EI) *m/z*: calcd for $C_{36}H_{28}$: 460.2191; found: 460.2192 $[M]^+$.

Variation 2 (GP2): For an alkyne ***2*** *(i.e.,* ***2b***, ***2c***, *and* ***2d****) with poor solubility in CH_3CN—5,8-dimethyl-1,2,3,4-tetra(4-tolyl)naphthalene* (**3ac**): A solution of alkyne **2c** (311 mg, 1.51 mmol) in *p*-xylene (2 mL) was added over 10 h with a syringe pump to a vigorously stirred suspension of AgOAc (500 mg, 3.00 mmol) and $Pd(OAc)_2$ (25.6 mg, 0.11 mmol) in CH_3CN (2 mL) at 110 °C under nitrogen. The mixture was kept at the same temperature for an additional 26 h. After cooling to room temperature, filtration over Celite and concentration of the filtrate, the residue was subjected to chromatography on SiO_2 (hexane/CH_2Cl_2 from 10:1 to 6:1) to afford **3ac** (182 mg, 47 % (based on **2c**)) as a pale yellow solid. Colorless crystals were obtained by crystallization from CH_2Cl_2/MeOH. M.p. 226–227 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.83$ (s, 6 H), 2.07 (s, 6 H), 2.24 (s, 6 H), 6.52–6.61 (m, 8 H), 6.85–6.93 (m, 8 H), 7.04 ppm (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT): $\delta = 21.0$ (+), 21.2 (+), 25.1 (+), 126.9 (+), 127.5 (+), 129.4 (+), 131.1 (+), 131.6 (+), 133.2 (C_{quat}), 133.8 (C_{quat}), 134.0 (C_{quat}), 135.2 (C_{quat}), 137.9 (C_{quat}), 138.0 (C_{quat}), 139.5 (C_{quat}), 140.3 ppm (C_{quat}); MS (EI, 70 eV): *m/z* (%): 516 (100) $[M]^+$, 501 (25), 486 (10); elemental analysis calcd (%) for $C_{40}H_{36}$ (516.7): C 92.98, H 7.02; found: C 92.72, H 7.02.

Acknowledgements

This work was supported by the National Science Council of Taiwan (NSC 96-2113M-006-008-MY2). We also thank Prof. S.-L. Wang and Ms. C.-Y. Chen (National Tsing-Hua University, Taiwan) for the X-ray structure analyses. The authors are indebted to Prof. A. de Meijere (University of Göttingen, Germany) for his useful suggestions and concerning the final manuscript.

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[36] Reaction of $[Ag(PPh_3)_2]NO_3$ with alkyne **2a** in our catalytic system $Cu(OAc)_2 \cdot H_2O$ (2 equiv), $Na_2[PdCl_6] \cdot 4H_2O$ (8 mol%), $AgNO_3$ (1.2 equiv), and pyridine (2.4 equiv) in CH_3CN at 110°C for 36 h gave **3ba** in 48% yield (based on PPh_3; 96% yield based on $[Ag(PPh_3)_2]NO_3$). In the absence of the additional $AgNO_3$, **3ba** (24%) can also be isolated.

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Received: March 24, 2008