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Palladium Alkynyl and Allenylidene Complexes: Very Efficient Precatalysts for C−C Coupling Reactions†

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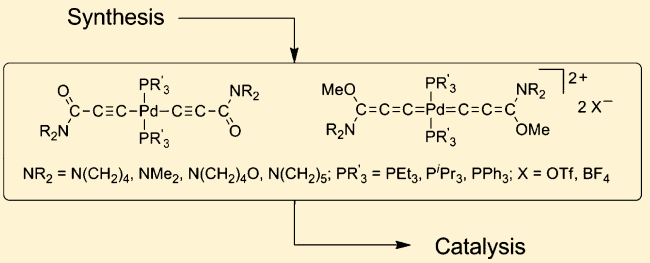
Supporting Information

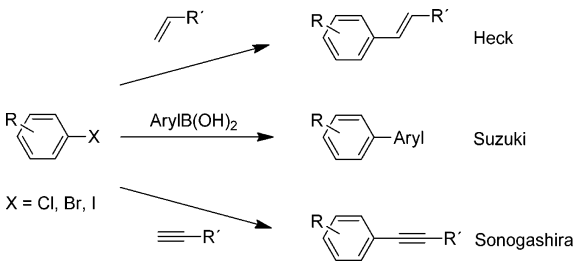
ABSTRACT: Oxidative addition of BrC≡CC(=O)O-menthyl (**1a**) to [Pd(PPh$_3$)$_4$] affords the alkynyl complex *trans*-[Br(PPh$_3$)$_2$Pd−C≡CC(=O)O-menthyl] (**2a**). Subsequent reaction of **2a** with trifluoroacetate gives *trans*-[(F$_3$CCOO)(PPh$_3$)$_2$Pd−C≡CC(=O)O-menthyl] (**3a**). Reaction of *trans*-[Br(PPh$_3$)$_2$Pd−C≡CC(=O)NC$_4$H$_8$] (**2b**) with 10 equiv of NaI gives *trans*-[I(PPh$_3$)$_2$Pd−C≡CC(=O)NC$_4$H$_8$] (**4b**). The efficiency of the new palladium complexes **3a** and **4b** as precatalysts is compared with that of recently published cationic palladium allenylidene complexes in C−C coupling reactions. Further *trans*-bis(alkynyl)palladium complexes, *trans*-[(PEt$_3$)$_2$Pd(−C≡CC{=O}NR$_2$)$_2$] (NR$_2$ = N(CH$_2$)$_4$ (**9b**), NMe$_2$ (**9c**), N(CH$_2$)$_4$O (**9d**), N(CH$_2$)$_5$ (**9e**)), *trans*-[(P^{i}Pr$_3$)$_2$Pd(−C≡CC{=O}NMe$_2$)$_2$] (**11c**), and *trans*-[(PPh$_3$)$_2$Pd(−C≡CC{=O}NR$_2$)$_2$] (NR$_2$ = N(CH$_2$)$_4$ (**13b**), NMe$_2$ (**13c**), N(CH$_2$)$_4$O (**13d**)), were synthesized by treating HC≡CC(=O)NR$_2$ with AgNO$_3$ followed by transmetalation of the alkynyl ligand from silver to [PdCl$_2$(PEt$_3$)$_2$], [PdCl$_2$(P^{i}Pr$_3$)$_2$], or [PdCl$_2$(PPh$_3$)$_2$], respectively. Methylation of complexes **9b−e** with MeOTf yields dicationic bis(allenylidene) complexes of palladium, *trans*-[(PEt$_3$)$_2$Pd{=C=C=C(OMe)NR$_2$}$_2$]$^{2+}$(OTf)$^-_2$ (NR$_2$ = N(CH$_2$)$_4$ (**10b-OTf**), NMe$_2$ (**10c-OTf**), N(CH$_2$)$_4$O (**10d-OTf**), N(CH$_2$)$_5$ (**10e-OTf**). Alkylation of complex **9e** with [Me$_3$O]BF$_4$ or [Et$_3$O]BF$_4$ gave *trans*-[(PEt$_3$)$_2$Pd{=C=C=C(OR)N(CH$_2$)$_5$}$_2$]$^{2+}$(BF$_4$)$^-_2$ (R = Me (**10e-BF$_4$**), Et (**10e′-BF$_4$**)). Complexes **11c** and **13b−d** were methylated accordingly to obtain the corresponding bis(allenylidene) complexes **12c-OTf**, **12c-BF$_4$**, **14b-OTf**, **14c-OTf**, and **14d-OTf**. The catalytic activities of the new bis(alkynyl) and bis(allenylidene) complexes were investigated and compared with those of the mono(alkynyl) and mono(allenylidene) complexes. The palladium alkynyl and allenylidene complexes are both found to be very efficient precatalysts for Heck, Suzuki, and Sonogashira reactions. Even aryl chlorides were efficiently coupled in Heck and Suzuki reactions when complex **9e** was used as precatalyst. Powder diffraction, TEM, and DLS measurements indicate that palladium nanoparticles are not formed during catalysis in the Heck reaction.



INTRODUCTION

Palladium-catalyzed carbon−carbon bond forming reactions are among the most powerful tools in modern organic chemistry.[1] While the Heck reaction usually is performed at high temperatures, other C−C coupling reactions such as the Suzuki reaction and the Sonogashira reaction (Scheme 1) can be carried out at or even below room temperature. The temperature is a very important parameter in catalytic applications. A large number of catalytically active palladium complexes have been described in the literature. Some of them, however, require high temperatures for activation and others are not very stable at high temperatures. Therefore, creating new organometallic catalyst systems is a very challenging field of research and is often a balancing act between activity and stability.

Scheme 1



The synthesis of the first allenylidene complexes [L$_n$M=C=C=C(R^1)R^2] was simultaneously reported in 1976 by Fischer et al. (M = Cr, W)[2] and Berke (M = Mn).[3] Since then allenylidene complexes of many transition metals have been prepared, including complexes of titanium, chromium, tungsten, manganese, rhenium, iron, ruthenium, osmium, rhodium, iridium, and platinum.[4] Some of these complexes have been used as catalyst precursors:[5] for instance, in ring-closing metathesis,[6] in ring-opening metathesis,[7] in dehydrogenative dimerization of tin hydrides,[8] and in selective transetherification of substituted vinyl ethers.[9] Allenylidene complexes of palladium, however, have been unknown for a long time. Only recently have the first palladium allenylidene and bis(allenylidene) complexes been synthesized and isolated.[10,11]

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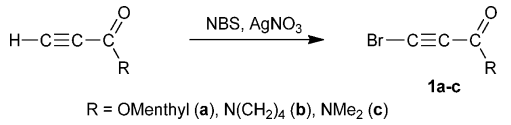
We now report on the catalytic activity of some of these palladium allenylidene complexes in C−C coupling reactions: namely Heck, Suzuki, and Sonogashira reactions. For comparison reasons new C(=O)R-substituted palladium alkynyl and allenylidene complexes as well as a broad range of bis(alkynyl) and bis(allenylidene) complexes were additionally synthesized and their catalytic activities in the same C−C coupling reactions were studied.

RESULTS AND DISCUSSION

Synthesis of Palladium Mono(alkynyl) and Mono(allenylidene) Complexes. Recently, we developed an easy to perform synthesis for O,N-substituted cationic palladium allenylidene complexes. Oxidative addition of terminally brominated *N,N*-dimethylpropiolamides **1b,c** (Scheme 2) to

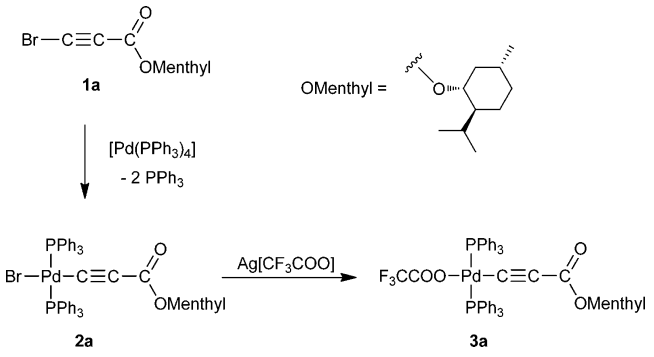
Scheme 2



$[Pd(PPh_3)_4]$ gave the stable palladium(II) alkynyl complexes *trans*-$[Br(PPh_3)_2Pd{-}C{\equiv}CC(=O)NR_2]$. Subsequent methylation with either MeOTf or $[Me_3O]BF_4$ yielded the first cationic allenylidene complexes of palladium, $[Br(PPh_3)_2Pd{=}C{=}C{=}C(OMe)NR_2]^+X^-$ (X = OTf, BF_4).[10]

Similarly, replacing brominated *N,N*-dimethylpropiolamide[12] by bromoalkyne **1a** in the oxidative addition reaction afforded the stable palladium(II) alkynyl complex **2a** in 99% yield (Scheme 3). Bromoalkyne **1a** was obtained by bromination of

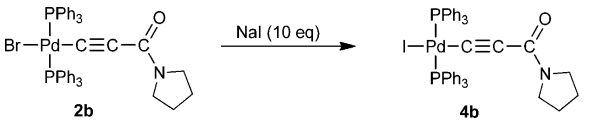
Scheme 3



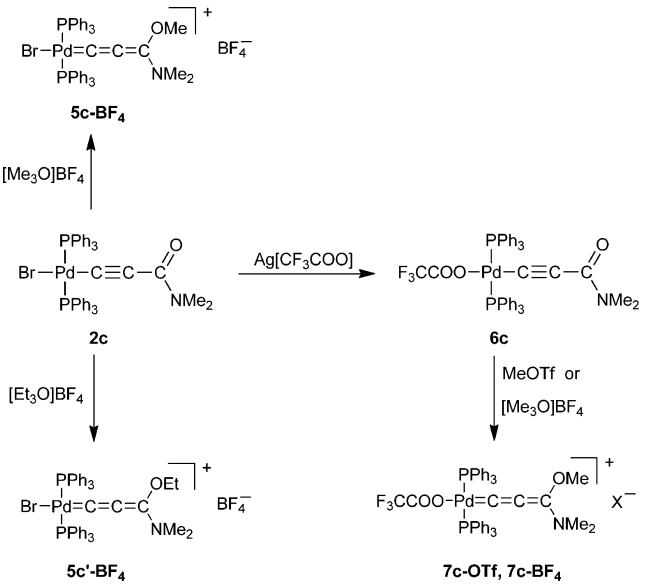
menthyl propiolate with *N*-bromosuccinimide (Scheme 2). This reaction can also be perfomed with propiolamides to obtain compounds **1b,c**. Due to the low π-donor properties of the terminal O,O-substitution pattern in **2a**, the electron density on the metal center is less than that in the recently investigated O,N-substituted alkynyl complexes **2b,c** (see Schemes 4 and 5). To further decrease the electron density at the metal, the trans-bromo ligand was replaced by electron-withdrawing trifluoroacetate. When a solution of **2a** in CH_2Cl_2 was treated with silver trifluoroacetate, AgBr quickly precipitated from the reaction mixture. The trifluoroacetato complex **3a** was isolated in 88% yield as a yellow solid after purification by column chromatography (Scheme 3).

An additional modification of the properties of the alkynyl complex was achieved by variation of the terminal substituents

Scheme 4



Scheme 5

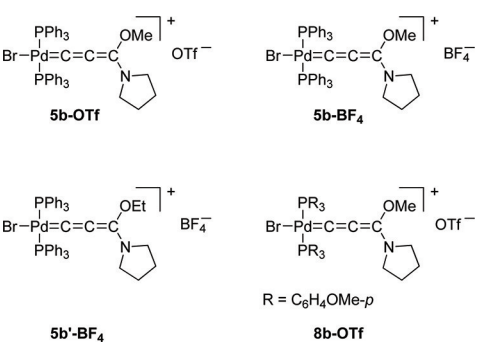


of the alkynyl ligand. A high electron density at the metal center should favor oxidative addition of aryl halides, which often constitutes the rate-limiting step in palladium-catalyzed cross-coupling reactions. Therefore, complex **2b** with an O,N instead of O,O substitution pattern was prepared. The iodo complex **4b** (Scheme 4), obtained by treating complex **2b**[10] with 10 equiv of NaI at room temperature, was isolated in 81% yield.

In addition, for the catalytic studies several allenylidene complexes (**5c-BF$_4$**, **5c′-BF$_4$**, **7c-OTf**, and **7c-BF$_4$**) and the alkynyl-(trifluoroacetato) complex **6c** were synthesized as summarized in Scheme 5. Alkylation of **2c** with $[Me_3O]BF_4$ and $[Et_3O]BF_4$ gave allenylidene complexes **5c-BF$_4$** and **5c′-BF$_4$**, respectively. Substitution of trifluorooacetate for the trans-bromo ligand in **2c** gave alkynyl complex **6c**; subsequent alkylation of **6c** with MeOTf or $[Me_3O]BF_4$ yielded the OTf^- salt **7c-OTf** and the BF_4^- salt **7c-BF$_4$**.[10]

The complexes **5b-OTf**, **5b-BF$_4$**, **5b′-BF$_4$**, and **8b-OTf** (Chart 1) were prepared by analogous alkylation procedures

Chart 1



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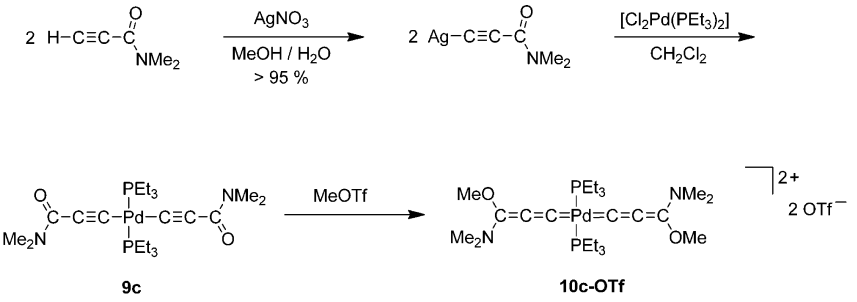
Scheme 6

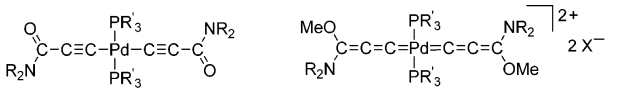


starting from *trans*-$[Br(PPh_3)_2Pd{-}C{\equiv}CC(=O)NC_4H_8]$ or *trans*-$[Br\{P(C_6H_4OMe\text{-}p)_3\}_2Pd{-}C{\equiv}CC(=O)NC_4H_8]$.[10]

Synthesis of Palladium Bis(alkynyl) and Bis(allenylidene) Complexes. In 2010 we determined that even dicationic bis(allenylidene) complexes are readily accessible by alkylation of suitable alkynyl complexes (Scheme 6). Transmetalation of the alkynyl ligand from silver[13] to palladium gives the stable palladium bis(alkynyl) complex **9c**. Subsequent alkylation with MeOTf yielded the dicationic allenylidene complex **10c-OTf**.[11]

To extend the scope of our recently established synthetic route (Scheme 6), we synthesized a broad range of new palladium bis(alkynyl) and bis(allenylidene) complexes (Chart 2).

Chart 2

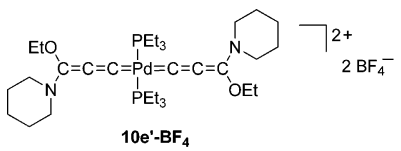


NR_2 = N(CH$_2$)$_4$ (**b**), NMe_2 (**c**), N(CH$_2$)$_4$O (**d**), N(CH$_2$)$_5$ (**e**) X = OTf, BF_4

$PR'_3 = PEt_3$:	**9b**	**10b-OTf**
	9c	**10c-OTf**
	9d	**10d-OTf**
	9e	**10e-OTf, 10e-BF$_4$**
$PR'_3 = P^iPr_3$:	**11c**	**12c-OTf, 12c-BF$_4$**
$PR'_3 = PPh_3$:	**13b**	**14b-OTf**
	13c	**14c-OTf**
	13d	**14d-OTf**

It is noteworthy to say that in addition to pyrrolidine (**b**) and dimethylamine (**c**) also morpholine (**d**) and piperidine (**e**) could be introduced as terminal N substituents, following the same synthetic route. Furthermore, a variation of the phosphine substituents from PEt_3 to P^iPr_3 and PPh_3 was successful using $[PdCl_2(P^iPr_3)_2]$ or $[PdCl_2(PPh_3)_2]$ instead of $[PdCl_2(PEt_3)_2]$ as the alkynyl acceptor. Finally, different counterions (OTf and BF_4) and O substituents (Me and Et (see Chart 3)) of the

Chart 3



10e'-BF$_4$

bis(allenylidene) complexes were obtained by applying $[Me_3O]BF_4$, $[Et_3O]BF_4$, and MeOTf as the alkylation agents.

All new complexes were characterized by spectroscopic means; the purity of the compounds was established by elemental analysis. The resonances of the alkynyl and allenylidene ligands in the ^{13}C NMR spectra compare well with those of known palladium alkynyl complexes.[10,11] In comparison to the corresponding mono(alkynyl) complexes the C1 resonances of the bis(alkynyl) complexes are observed at lower field by about 16 ppm. Variation of the phosphine ligands as well as terminal substituents affects the signals of the alkynyl ligand only marginally.

In the ^{31}P NMR spectra the single signal for the phosphine ligands shifts to higher field in the row P^iPr_3 (~46 ppm) > PPh_3 (~25 ppm) > PEt_3 (~19 ppm). The same trends are observed in the NMR spectra of the allenylidene complexes. The formation of dicationic bis(allenylidene) complexes by alkylation of bis(alkynyl) complexes is accompanied by a pronounced shift of the C1 resonances to lower field (~35 ppm) and a shift of the C2 resonance to higher field (~8 ppm).

The solid-state structures of bis(alkynyl) complexes **9e** (Figure 1) and **11c** (Figure 2) and of the dicationic bis(allenylidene) complex **10e'-BF$_4$** (Figure 3) were additionally

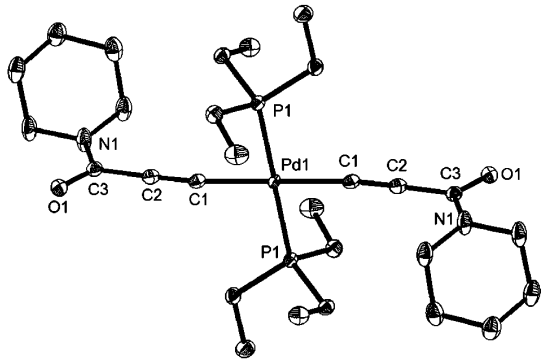


Figure 1. Structure of the bis(alkynyl) complex **9e** in the crystal state (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity).

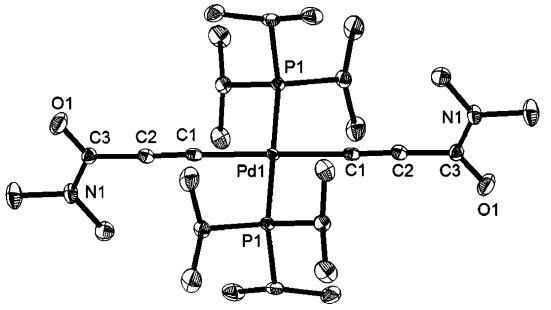


Figure 2. Structure of the bis(alkynyl) complex **11c** in the crystal state (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity).

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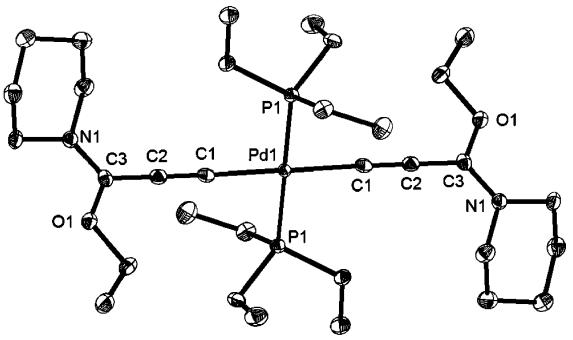

Figure 3. Structure of the bis(alkynyl) complex **10e′-BF$_4$** in the crystal state (ellipsoids drawn at the 50% probability level; hydrogen atoms and BF_4 counterions are omitted for clarity).

established by X-ray structure analysis (Tables 1 and 2). In all three complexes the metal has a square-planar coordination. As already deduced from the appearance of only one phosphorus resonance in the ^{31}P NMR spectra, the phosphine ligands are mutually trans. The Pd−C1 distances of the palladium bis(alkynyl) complexes (1.9990(16) Å (**9e**), 1.996(2) Å (**11c**)) are significantly longer than those of a corresponding palladium mono(alkynyl) complex (1.947(3) Å).[10] In both bis(alkynyl) complexes the plane formed by the atoms C3−O1−N1 (C3 plane) and the coordination plane of palladium are almost perpendicular (87.9° (**9e**), 80.6° (**11c**)). In contrast, in the palladium bis(allenylidene) complex **10e′-BF$_4$** the C3 plane is strongly tilted against the coordination plane of palladium (63.5°). In all three complexes the Pd−C3 chain is slightly bent: Pd−C1−C2 = 174.69(12) (**9e**), 176.30(19) (**11c**), 176.1(2)° (**10e′-BF$_4$**) and C1−C2−C3 = 177.30(15) (**9e**), 177.7(2) (**11c**), 171.6(2)° (**10e′-BF$_4$**). However, a modest deviation from linearity of the MCCC fragment in allenylidene complexes is often observed.[4] The Pd−C and C1−C2 distances in the dicationic allenylidene complex **10e′-BF$_4$** (1.986(2) and 1.209(3) Å) compare well with the bond lengths in the corresponding alkynyl complex **9e** (1.9990(16) and 1.208(2) Å). The four resonance forms of allenylidene complexes can explain these similarities (Scheme 7). The C2−C3 bond in **10e′-BF$_4$** (1.419(3) Å) is significantly shorter than in **9e** (1.456(2) Å). As expected, alkylation results in an elongation of the C3−O1 bond (**9e**, 1.2339(18) Å; **10e′-BF$_4$**, 1.318(3) Å) and, conversely, leads to a significant shortening of the C3−N bond (**9e**, 1.362(2) Å; **10e′-BF$_4$**, 1.308(3) Å).

Table 2. Important Bond Distances (Å) and Angles (deg) in 9e, 11c, and 10e′-BF$_4$

	9e	11c	10e′-BF$_4$
Pd−C1	1.9990(16)	1.996(2)	1.986(2)
Pd−P	2.3009(8)	2.3306(6)	2.3315(8)
C1−C2	1.208(2)	1.212(3)	1.209(3)
C2−C3	1.456(2)	1.455(3)	1.419(3)
C3−N	1.362(2)	1.352(3)	1.308(3)
C3−O	1.2339(18)	1.235(3)	1.318(3)
Pd−C1−C2	174.69(12)	176.30(19)	176.1(2)
C1−C2−C3	177.30(15)	177.7(2)	171.6(2)

Table 1. Crystallographic Data and Refinement Methods for 9e, 11c, and 10e′-BF$_4$

	9e	11c·2CH$_2$Cl$_2$	10e′-BF$_4$
empirical formula	$C_{28}H_{50}N_2O_2P_2Pd$	$C_{30}H_{58}Cl_4N_2O_2P_2Pd$	$C_{32}H_{60}B_2F_8N_2O_2P_2Pd$
M_r	615.04	788.92	846.78
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	7.8879(16)	11.614(2)	10.590(2)
b (Å)	9.0249(18)	10.940(2)	15.586(3)
c (Å)	11.313(2)	16.303(6)	15.350(5)
α (deg)	96.64(3)	90	90
β (deg)	105.58(3)	112.50(2)	129.296(19)
γ (deg)	96.99(3)	90	90
V (Å^3)	760.7(3)	1913.7(9)	1960.7(8)
Z	2	2	2
cryst size (mm^3)	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.50 × 0.45 × 0.40
ρ_{calcd} (g cm^{-3})	1.343	1.369	1.434
μ (mm^{-1})	0.741	0.876	0.624
F(000)	324	824	880
T (K)	100(2)	100(2)	100(2)
max 2θ (deg)	53.40	53.56	53.58
index ranges	$-9 \le h \le 9$	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-11 \le k \le 11$	$-13 \le k \le 13$	$-19 \le k \le 17$
	$-14 \le l \le 14$	$-20 \le l \le 20$	$-19 \le l \le 19$
no. of data	10 741	26 492	25 256
no. of unique data	3174	4056	4165
R(int)	0.0400	0.0493	0.0402
no. of params	160	187	223
goodness of fit on F^2	1.088	1.146	1.017
R1, wR2 ($I > 2\sigma(I)$)	0.0187, 0.0464	0.0293, 0.0639	0.0311, 0.0691
R1, wR2 (all data)	0.0203, 0.0469	0.0348, 0.0654	0.0387, 0.0717
largest diff peak/hole (e Å^{-3})	0.328, −0.560	0.576, −0.599	0.787, −0.718

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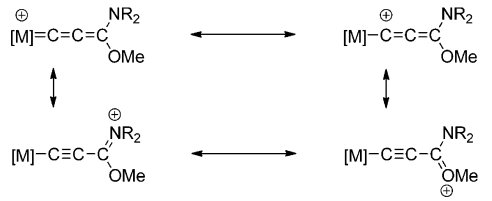
Scheme 7

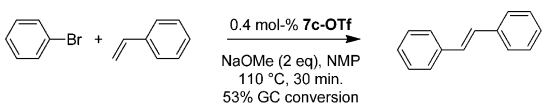


The conclusions drawn from the solid-state structures are supported by the spectroscopic data. The formation of the dicationic bis(allenylidene) complexes by alkylation of the bis(alkynyl) complexes was accompanied by just a slight shift of the ν(CCC) vibration to lower energy (~6 cm^{-1}). The positions of the ν(CCC) vibration are dependent on the phosphine ligands. With diminishing alkalinity of the phosphine ligands we observe a shift to higher energy (P^iPr_3 > PEt_3 > PPh_3).

Catalytic Investigations. Initial reactivity experiments indicated that these alkynyl as well as the allenylidene complexes are active catalyst precursors in carbon−carbon coupling reactions. Therefore, the catalytic properties of the palladium complexes presented were investigated in detail. The activity in different types of C−C coupling reactions—Heck, Suzuki and Sonogashira reactions—was explored. The neutral alkynyl complexes and the cationic allenylidene complexes span a rather broad range of electron density at the metal. Consequently, significant differences in relative activity for alkynyl and allenylidene complexes were observed in the three types of carbon−carbon bond forming reactions.

Heck Coupling. First, we decided to test our complexes in a Heck reaction[14] to test not only their activity as precatalysts but also their stability at the elevated temperatures needed for this type of reaction. After some initial attempts bromobenzene (1 equiv) could be successfully coupled with styrene (1.5 equiv) at 130 °C using 0.4 mol % of complex **7c-OTf**. To optimize the reaction we screened 14 common bases (NaOAc, K_2CO_3, Na_2CO_3, NaO^{t}Bu, KO^{t}Bu, K_3PO_4, Cs_2CO_3, NEt_3, KOH, NaOH, $NaNH_2$, NaOMe, LiOAc, Na_2HPO_4) and found NaOMe to give the highest conversion. Due to this optimization the reaction temperature could be decreased to 110 °C and within 30 min 53% of the bromobenzene was converted to stilbene using NaOMe as base, NMP as solvent, and 0.4 mol % of **7c-OTf** as precatalyst (Scheme 8). It is

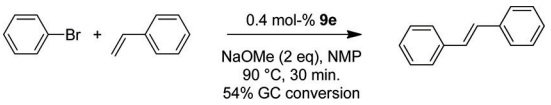
Scheme 8



noteworthy that a full conversion can be achieved by extending the reaction time. In order to be able to detect higher or lower conversions, we adjusted the reaction time to get approximately 50% conversion.

The reaction could not be improved by variation of the solvent. In other high-boiling solvents such as DMA and DMSO no conversion of the bromobenzene took place and in 1,4-dioxane a conversion of only 1.5% of the starting material was observed. Under these optimized conditions we tried to lower the reaction temperature to 90 °C; however, no conversion of the bromobenzene was observed when **7c-OTf** was used as precatalyst. However, the bis(alkynyl) complex **9e** showed catalytic activity at this, for Heck type reactions, fairly low temperature (Scheme 9). The lower temperature allowed

Scheme 9



us to use other solvents such as ethanol (36% conversion) and an ethanol/water mixture (24% conversion). These results indicate a high stability of the bis(alkynyl) complex **9e**, even in aqueous media. However, due to the highest conversion we used NMP for our further investigations.

In the following study a reaction temperature of 110 °C was chosen for mono(alkynyl) and mono(allenylidene) complexes and 90 °C for bis(alkynyl) and bis(allenylidene) complexes. The activity as precatalyst of the various cationic mono(allenylidene) complexes varied only slightly (50−68%); the neutral mono(alkynyl) complexes **3a** and **4b**, however, gave significantly slower conversions (Table 3). The efficiency as

Table 3. Influence of Alkynyl and Allenylidene Complexes on the Heck Coupling of Bromobenzene with Styrene[a]

entry	complex	conversn[b]
1	**3a**	26
2	**4b**	23
3	**5c-BF$_4$**	64
4	**5c′-BF$_4$**	58
5	**7c-OTf**	50
6	**7c-BF$_4$**	68
7	**5b-BF$_4$**	51
8	**8b-OTf**	66
9[c]	**9b**	6
10[c]	**9e**	54
11[c]	**14c-OTf**	12

[a]Reaction conditions: 0.25 mmol of bromobenzene, 0.375 mmol of styrene, 0.4 mol % of the Pd complex, 0.5 mmol of NaOMe, and 1 mL of NMP; 110 °C; 0.5 h. [b]GC conversion (%) of bromobenzene using *n*-dodecane as internal standard. [c]At 90 °C.

precatalyst turned out to be dependent on the anion (compare entries 5 and 6); the BF_4 salt gave a somewhat higher conversion than the CF_3SO_3 salt. Changing the ligand in the trans-position from trifluoroacetate (entry 6) to the less electron-withdrawing bromo ligand (entry 3) did not affect the catalytic activity. Variation of the substituent at the allenylidene ligand (OMe versus OEt, NMe_2 versus $N(CH_2)_4$) influenced the activity only marginally. The same was true for replacing PPh_3 by the more basic phosphine $P(C_6H_4OMe\text{-}p)_3$ and simultaneously BF_4^- by OTf^- (increase in activity by about 30%; see entries 7 and 8). At lower temperature (90 °C), in addition to complex **9e** only complexes **9b** and **14c-OTf** showed catalytic activity (Table 3). A significant difference in activity was obtained within these complexes, with **9e** being the most active precatalyst under the applied conditions.

With the highly active precatalyst **9e** it was even possible to perform the Heck coupling reaction of 4-chloroacetophenone with styrene (ratio 1:1.5; Scheme 10). With NaOMe as the base and *N*-methyl-2-pyrrolidone as the solvent over 18 h at 140 °C, 76% GC conversion of 4-chloroacetophenone was

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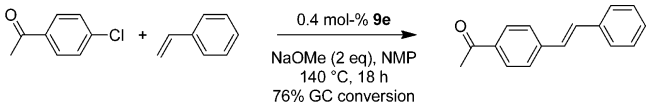
Scheme 10



obtained. Under these calm reaction conditions for none of the commercially available complexes $[PdCl_2(PEt_3)_2]$, $[PdCl_2(P^iPr_3)_2]$, and $[PdCl_2(PPh_3)_2]$ was a coupling reaction observed.

At the elevated temperatures (>100 °C) usually required for catalyzing Heck coupling reactions, palladium nanoparticles could be formed by decomposition of the Pd complexes. Palladium nanoparticles have been suggested to be the catalytically active species in palladium-catalyzed coupling reactions.[15] To determine whether or not such palladium nanoparticles are formed from palladium allenylidene precatalysts, the coupling of bromobenzene with styrene catalyzed by complex **8b-OTf** (Table 3, entry 8) was studied in detail. First we repeated this reaction but with a drop of mercury added and the solution was vigorously stirred. This test has often been successful in demonstrating the presence of homogeneous catalysts when no poisoning of the catalyst was observed. In our case the reaction got significantly poisoned by mercury, which indicates that a heterogeneous or (not very well protected by the ligands) homogeneous Pd(0) species is present in the catalytic cycle.[16] To further study the presence of Pd nanoparticles, we extended the reaction time from 30 min to 3 h to get full conversion of the starting material. In this reaction the desired product (*trans*-stilbene) was formed in 92% yield along with 8% of 1,1-diphenylethene as a side product. After it was cooled to ambient temperature, the reaction mixture was dried in air and the resulting solid was analyzed by powder XRD (see Figure 4). The observed reflections compare well to those

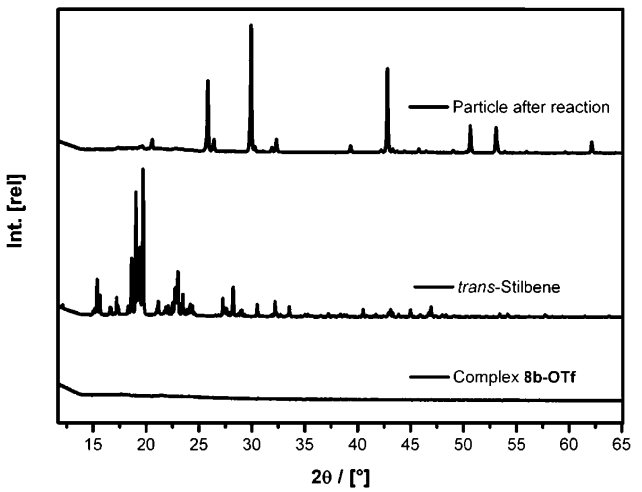


Figure 4. Powder XRD patterns of complex **8b-OTf**, *trans*-stilbene, and the reaction mixture after catalysis.

obtained from palladium and palladium oxide particles. From the comparison of the XRD pattern with those of XRD powder patterns of *trans*-stilbene and complex **8b-OTf** it followed that the observed reflections were due neither to *trans*-stilbene nor to complex **8b-OTf**.

The size of palladium particles is important for their catalytic activity. Usually, the size of the catalytically active palladium nanoparticles is in the diameter range 2−20 nm. Therefore, the size distribution of the palladium and palladium oxide particles in the reaction mixture was determined by dynamic light scattering. As shown in Figure 5, the diameter of the particles

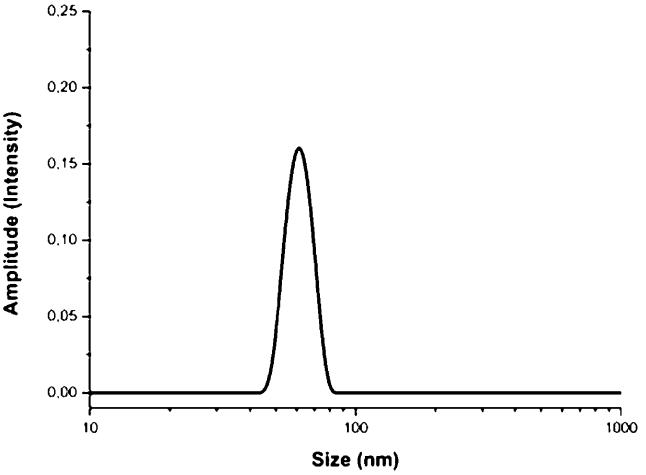
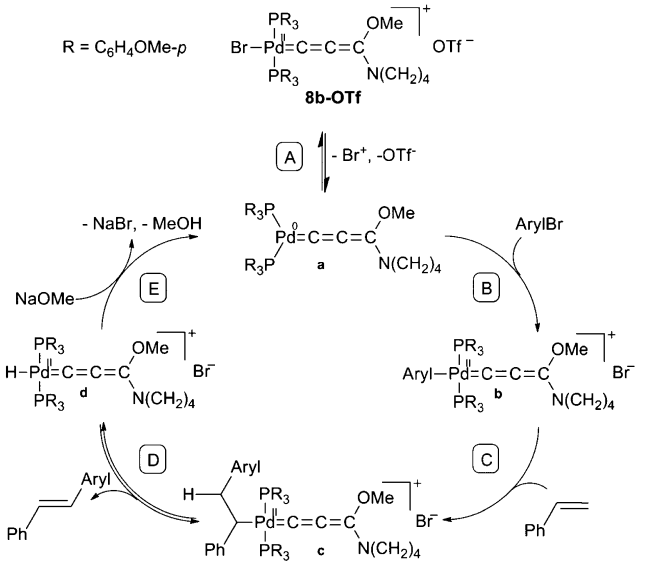


Figure 5. Size distribution of particles after catalysis measured by dynamic light scattering (DLS).

formed in the reaction catalyzed by complex **8b-OTf** was about 60−70 nm. This suggested that these particles were not the catalytically active species. Also, we could not identify any particles smaller than 50 nm by transition electron microscopy (TEM). On the basis of these results it is likely that a molecular species formed from the allenylidene precursor complex is the catalytically active species.

In 2000 Amatore and Jutand showed that $[Pd^{II}Cl_2(PPh_3)_2]$ is reduced to $[Pd^0Cl(PPh_3)_2]^-$ rather then the often expected $[Pd^0(PPh_3)_2]$.[17] On the basis of this mechanism we postulate that a neutral Pd(0) spezies **a** is formed from the cationic Pd allenylidene complex **8b-OTf**, as despicted in Scheme 11.

Scheme 11. Postulated Mechanism for the Heck Reaction Catalyzed with Precatalyst 8b-OTf



How this reduction (step A) exactly occurs remains unclear. However, we expect the base to play a crucial role. In step B

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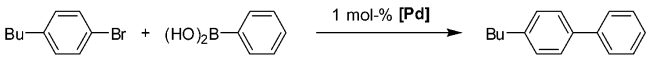
oxidative addition occurs, forming first a five-coordinate species, which then converts to complex **b** in the preferred square-planar geometry. Syn addition of an alkene (step C) gives complex **c**, and β-hydride elimination (step D) forms complex **d**. In this step the product is released. Finally the base reduces the hydrido complex and the catalytic cycle is closed. In conclusion, we think that formation of the catalyst from the precatalyst (step A) is the main reason for different activities within the series of complexes (Table 3). However, this mechanism is only a postulation, and to draw a final conclusion about the nature of the catalytically active species a more detailed mechanistic study, including a three-phase test and supporting theoretical calculations, will be needed.

Suzuki Coupling. The Suzuki coupling[18] of 1-bromo-4-butylbenzene with phenylboronic acid (ratio 1:1.5; Scheme 12)

Scheme 12



was likewise studied in detail. The para-substituted bromo(butyl)benzene was chosen, since the heterocoupling product, the homocoupling product of the phenylboronic acid (often observed as the product of a side reaction), and reduction products of the bromobenzene are easily differentiated.

Initially, 1 mol % of complex **7c-OTf** as catalyst precursor, 2 equiv of potassium phosphate as base, and THF as solvent were employed. At 50 °C the reaction was complete within approximately 24 h. No reaction was observed without base and without palladium catalyst. Decreasing the loading of complex **7c-OTf** to 0.1 or 0.01 mol % resulted in a reduction of the conversion to 58% or 33%, respectively. Analogously to the Heck reaction described before, the Suzuki coupling proved to be considerably base-dependent (Table 4). The highest

Table 4. Influence of the Base on the Suzuki Coupling of 1-Bromo-4-Butylbenzene with Phenylboronic Acid[a]

entry	base	conversn[b]
1	K_3PO_4	53
2	K_2CO_3	34
3	Na_2CO_3	3
4	LiO^tBu	0
5	NaO^tBu	93
6	KO^tBu	18
7	KOEt	20
8	Cs_2CO_3	94
9	$LiNEt_2$	8
10	LDA	15
11	$LiN(TMS)_2$	0
12	$NaN(TMS)_2$	0
13	$KN(TMS)_2$	0
14	$NaNH_2$	8

[a]Reaction conditions: 0.1 mmol of 1-bromo-4-butylbenzene, 0.15 mmol of phenylboronic acid, 1 mol % of complex **7c-OTf**, 0.2 mmol of base, and 1 mL of THF; 50 °C; 4 h. [b]GC conversion (%) of 1-bromo-4-butylbenzene using *n*-dodecane as internal standard.

conversions were obtained after 4 h at 50 °C with NaO^tBu (93%) and Cs_2CO_3 (94%) (entries 5 and 8) as the base. Under analogous conditions potassium phosphate gave 53% conversion.

Table 5 summarizes the activities of various alkynyl and allenylidene complexes after the reaction time has been reduced

Table 5. Influence of the Pd Complex on the Suzuki Coupling of 1-Bromo-4-Butylbenzene with Phenylboronic Acid[a]

entry	complex	conversn[b]
1	**3a**	92
2	**4b**	33
3	**5c-BF_4**	100
4	**5c′-BF_4**	60
5	**7c-OTf**	64
6	**7c-BF_4**	74
7	**5b-OTf**	71
8	**5b-BF_4**	97
9	**5b′-BF_4**	70
10	**8b-OTf**	26

[a]Reaction conditions: 0.1 mmol of 1-bromo-4-butylbenzene, 0.15 mmol of phenylboronic acid, 1 mol % of the Pd complex, 0.2 mmol of Cs_2CO_3, and 1 mL of THF; 50 °C; 1 h. [b]GC conversion (%) of 1-bromo-4-butylbenzene using *n*-dodecane as internal standard.

from 4 to 1 h. The differences in activity and the influence of the substituents and ligands were more pronounced than in the Heck reactions described before. As with the Heck coupling, the anion in the allenylidene complexes exerted a small influence, the OTf salts being slightly less active than the BF_4 salts (entries 5 and 7 versus 6 and 8). Whereas replacing OMe by OEt (entries 3 vs 4 and 8 vs 9) led to a significant decrease in activity, the influence of substitution of NMe_2 for $N(CH_2)_4$ was almost negligible.

When the trifluoroacetato ligand in a trans position was replaced by the less electron-withdrawing bromo ligand, an increase in activity was observed (entries 3 and 6). In contrast, replacing PPh_3 by the more basic $P(C_6H_4OMe)_3$ in a cis position and thus increasing the electron density at palladium caused a drop in activity (complexes **5b-OTf** and **8b-OTf**, entries 7 and 10).

Surprisingly different are the results obtained with alkynyl complexes. In both neutral alkynyl complexes the palladium atom is more electron rich than in the cationic allenylidene complexes. Complex **4b**, having a π-electron-donating iodide in a trans position and the better π-donating pyrrolidinyl substituent, gave a much lower conversion than complex **3a** (CF_3COO^- in trans position and O-menthyl as substituent at C_γ). Since a high electron density on the metal center should favor the oxidative addition step of the catalytic cycle, these results suggest that the oxidative addition is not the rate-limiting step in the catalytic cycle of the Suzuki coupling with alkynyl or allenylidene complexes.

Under the aforementioned conditions (1 mol % of complex, NaO^tBu, THF, 50 °C, 4 h) no coupling product was formed when bis(alkynyl) complex **9e** was used as the precatalyst. Even with the more reactive iodobenzene we had to increase the temperature from 50 to 70 °C to get a 30% conversion (after 4 h) using NaO^tBu as base and THF as solvent. Under the same conditions a change of solvent from THF to EtOH resulted in a significant increase of reactivity. Full conversion (100%) was observed in EtOH and also in the solvent mixtures THF/EtOH and EtOH/water, while in some common solvents (NMP, hexane, DMF, DMSO, 1,4-dioxane, toluene, acetonitrile, benzene) no conversion of the starting material was observed. For our further studies we used the EtOH/water mixture as a "green" solvent. Under these optimized solvent conditions we got a 73% conversion of 1-bromo-4-butylbenzene with

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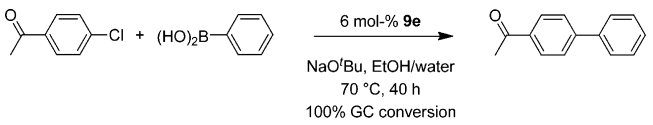
phenylboronic acid using **9e** as precatalyst (1 mol % of complex, NaO^{t}Bu, EtOH/water, 50 °C, 4 h).

With complex **9e** it was even possible to perform the Suzuki coupling reaction of 4-chloroacetophenone with phenylboronic acid (ratio 1:1.5; Scheme 13). With NaO^{t}Bu as the base and

Scheme 13

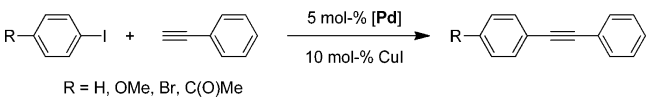


EtOH/H_2O (1:1) as the solvent over 22 h at 70 °C a 51% GC conversion of 4-chloroacetophenone was obtained. After the reaction time was increased from 22 to 40 h and the catalyst loading from 3 to 6%, full conversion of the aryl chloride was observed. Under these calm reaction conditions for none of the commercially available complexes $[PdCl_2(PEt_3)_2]$, $[PdCl_2(P^iPr_3)_2]$, and $[PdCl_2(PPh_3)_2]$ was a coupling reaction observed.

Furthermore, we repeated the Suzuki coupling reaction with complex **7c-OTf**, except with a drop of mercury added and vigorous stirring of the solution. Analogously to the Heck reaction, the Suzuki reaction was significantly poisoned by mercury.

Sonogashira Coupling. The coupling of iodobenzene with phenylacetylene (ratio 1:1.2; R = H; Scheme 14), employing

Scheme 14



5 mol % of complex **7c-OTf** as catalyst precursor, 10 mol % of copper iodide as cocatalyst in THF, and 2 equiv of triethylamine as base, went to completion at ambient temperature within less than 3 h. In contrast, no reaction took place without base and without palladium complex.

Secondary and tertiary amines are commonly used as bases for Sonogashira coupling reactions.[19] However, in some cases the conversion could be significantly increased by changing the base.[20] The screening of some bases (Table 6) confirmed

Table 6. Influence of the Base on the Sonogashira Coupling of Iodobenzene with Phenylacetylene[a]

entry	base	conversn[b]
1	K_2CO_3	47
2	Cs_2CO_3	6
3	NEt_3	67
4	KOH	8

[a]Reaction conditions: 0.1 mmol of iodobenzene, 0.12 mmol of phenylacetylene, 5 mol % of complex **5b-OTf**, 10 mol % of CuI, 0.2 mmol of base, and 1 mL of THF; room temperature; 1 h. [b]GC conversion (%) of iodobenzene using *n*-dodecane as internal standard.

that the coupling of iodobenzene with phenylacetylene is significantly base dependent. For our catalyst system, NEt_3 gave the best results.

In addition to bases, the solvent likewise considerably influences the activity of the complexes. In the screening of

Table 7. Influence of the Solvent on the Sonogashira Coupling of Iodobenzene with Phenylacetylene[a]

entry	solvent	conversn[b]
1	THF	71
2	DMF	32
3	DMSO	99
4	acetonitrile	21
5	toluene	9
6	propylene carbonate	99
7	diethyl carbonate	89
8	dimethyl carbonate	44

[a]Reaction conditions: 0.1 mmol of iodobenzene, 0.12 mmol of phenylacetylene, 5 mol % of complex **5b-OTf**, 10 mol % of CuI, 0.2 mmol of NEt_3, and 1 mL of solvent; room temperature; 1 h. [b]GC conversion (%) of iodobenzene using *n*-dodecane as internal standard.

eight solvents (Table 7), DMSO and propylene carbonate gave the best results.

In all subsequent reactions, DMSO was used as the solvent. For a comparison of the relative activities of the various complexes, the reaction time was reduced to 30 min. The relative activities of the alkynyl and allenylidene complexes in Sonogashira coupling reactions (Table 8) deviated strongly

Table 8. Influence of the Pd Complex on the Sonogashira Coupling of Iodobenzene with Phenylacetylene[a]

entry	complex	conversn[b]
1	**3a**	96
2	**4b**	100
3	**5c-BF$_4$**	10
4	**5c′-BF$_4$**	1
5	**7c-OTf**	72
6	**7c-BF$_4$**	88
7	**5b-OTf**	48
8	**5b-BF$_4$**	85
9	**5b′-BF$_4$**	79

[a]Reaction conditions: 0.1 mmol of iodobenzene, 0.12 mmol of phenylacetylene, 5 mol % of Pd complex, 10 mol % of CuI, 0.2 mmol of NEt_3, and 1 mL of DMSO; room temperature; 30 min. [b]GC conversion (%) of iodobenzene using *n*-dodecane as internal standard.

from those in Heck (Table 3) and Suzuki reactions (Table 5). Whereas in Heck reactions the alkynyl complexes **3a** and **4b** were the least active catalyst precursors, they turned out to be the most active complexes in Sonogashira reactions. Both complexes gave full or nearly full conversion of iodobenzene and phenylacetylene to diphenylacetylene. Within the series of allenylidene complexes, **5c-BF$_4$** and **5c′-BF$_4$** showed the least activity (in contrast to the case for Suzuki reactions). Again, a moderate dependence on the anion was observed, BF_4 salts giving slightly better results than OTf salts. Catalysis of the Sonogahira reaction by nanoparticles formed by decomposition of the alkynyl or allenylidene complexes seems unlikely, since all Sonogahira reactions were performed at room temperature. Under the reaction conditions employed, all complexes were stable, even at elevated temperatures. Furthermore, TEM measurements did not indicate formation of any nanoparticles.

When different substituted aryl iodides were employed in the reaction with phenylacetylene, full or nearly full conversions

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were observed within 1 h, although the catalyst loading was reduced from 5 to 3 mol %. Only 4-iodoanisole gave a somewhat lower conversion (80%). The reaction of 4-bromo-1-iodobenzene with phenylacetylene yielded only (4-bromophenyl)phenylacetylene. The corresponding (4-iodophenyl)phenylacetylene was not formed, presumably due to the lower reactivity of aryl bromides in comparison to aryl iodides. The heterocoupling products (Table 9) were obtained

Table 9. Influence of the Para Substituent R on the Sonogashira Coupling of the Aryl Iodides R-C_6H_4-I-*p* with Phenylacetylene[a]

entry	R	conversn[b]	yield[b]
1	H	100	95
2	$COCH_3$	99	94
3	OMe	80	75
4	Br	100	95

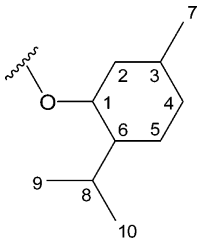
[a]Reaction conditions: 0.1 mmol of aryliodide, 0.12 mmol of phenylacetylene, 3 mol-% of complex **4b**, 10 mol-% of CuI, 0.2 mmol of NEt_3 and 1 mL of DMSO; room temp.; 1 h. [b]GC conversion (%) of the aryliodide and GC yield (%) of diarylacetylene using *n*-dodecane as internal standard.

in very high yield. Formation of homocoupling products of in situ formed copper acetylide species (Glaser coupling) could not be detected.

In summary, the new neutral alkynyl as well as the cationic allenylidene complexes of palladium are very active catalyst precursors for several carbon−carbon bond-forming reactions. These complexes are readily available by straightforward syntheses and are remarkably stable. The relative reactivity varies considerably, depending on the type of carbon−carbon coupling reaction. In general, in comparison to the alkynyl complexes **3a** and **4b** allenylidene complexes turned out to be (a) more active catalyst precursors in Heck reactions and (b) somewhat less active in Sonagashira reactions. In Suzuki C−C coupling reactions the differences in activity between alkynyl and allenylidene complexes are small; however, the activity significantly depends on the substitution pattern. The high activity allows for rather modest reaction temperatures: for instance, room temperature in Sonogashira reactions. In Heck and Suzuki reactions even aryl chlorides are efficiently coupled when complex **9e** was used as precatalyst. Under these calm reaction conditions for none of the commercially available complexes $[PdCl_2(PEt_3)_2]$, $[PdCl_2(P^iPr_3)_2]$, and $[PdCl_2(PPh_3)_2]$ was a coupling reaction observed.

EXPERIMENTAL SECTION

General Considerations. All operations were performed under an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (petroleum ether, hexane), or sodium (THF, Et_2O). The silica gel used for chromatography (Baker, silica for flash chromatography) was nitrogen-saturated. The yields refer to analytically pure compounds and were not optimized. The propiolamides,[12] the bromoalkynes **1b,c**, the complexes **2b,c**, **5c-BF_4**, **5c′-BF_4**, **6c**, **7c-OTf**, **7c-BF_4**, **5b-OTf**, **5b-BF_4**, **5b′-BF_4**, and **8b-OTf**,[10] the silver acetylides,[13] complexes **9b,c**, **10b-OTf**, and **10c-OTf**,[11] and $[Me_3O]BF_4$ and $[Et_3O]BF_4$[21] were prepared according to literature procedures. All other chemicals were commercial products and were used as supplied. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with Bruker Avance 400 and Varian Inova 400 spectrometers at ambient temperature. Chemical shifts are relative to the residual solvent peaks or tetramethylsilane (^1H, ^{13}C) or 100% H_3PO_4 (^{31}P). For the menthyl group the following labeling scheme was used:



IR spectra were obtained on a Biorad FTS 60 instrument and MS on a Finnigan MAT 312 instrument . Elemental analysis was carried out on Heraeus Elementar vario EL and Elementar vario MICRO Cube instruments. The UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. GC/MS analyses were made on an Agilent Technologies 5975C MSD interfaced to an Agilent Technologies 7890A series GC.

1-Bromo-(−)-menthyl Propiolate (1a). A solution of 10 mmol of menthyl propiolate in 40 mL of acetone was treated at ambient temperature with 2.16 g (12 mmol) of *N*-bromosuccinimide and 150 mg (0.9 mmol) of $AgNO_3$. After 80 min the reaction mixture was poured onto 200 mL of ice water. The aqueous phase was extracted three times with 50 mL portions of ethyl acetate. The combined organic extracts were dried over $MgSO_4$. The solid was filtered off and the solvent removed in vacuo. The crude product was filtered over a short plug of silica using CH_2Cl_2 as the eluent. Removal of the solvent in vacuo gave **1a** as a white solid. Yield: 2.56 g (89%). Mp: 85 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 4.71 (td, $^3J_{HH}$ = 11.1 Hz, $^4J_{HH}$ = 4.3 Hz, 1 H, H^1), 1.95 (m, 2 H, H^2), 1.83 (m, 2 H, H^4), 1.62 (m, 1 H, H^8), 1.36 (m, 1 H, H^6), 0.99 (m, 2 H, H^5), 0.96 (m, 1 H, H^3), 0.85−0.83 (m, 6 H, H^9, H^{10}), 0.69 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, H^7) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 177.5 (C(=O)O), 152.1 (BrC≡C), 76.8 (C^1), 46.7 (C^6), 40.4 (C^2), 34.0 (C^4), 31.2 (C^3), 29.5 (C^8), 26.0 (C^5), 23.2 (BrC≡*C*), 21.8 (C^{10}), 20.6 (C^9), 16.1 (C^7) ppm. IR (CH_2Cl_2): ν(C≡C) 2198 cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 287 (1) [M^+], 207 (1) [(M − Br)$^+$], 138 (100) [(M − Br − C≡CC(=O)O − H)$^+$], 123 (59) [(M − Br − C≡CC(=O)O − H − CH_3)$^+$], 95 (76) [(M − Br − C≡CC(=O)O − H − C_3H_7)$^+$]. Anal. Calcd for $C_{13}H_{19}BrO_2$ (287.20): C, 54.37; H, 6.67. Found: C, 54.09; H, 6.71.

***trans*-Bromo(3-((−)-menthoxy)-3-oxy-1-propynyl)bis-(triphenylphosphine)palladium(II) (2a).** A suspension of 1.16 g (1.0 mmol) of $[Pd(PPh_3)_4]$ in 25 mL of CH_2Cl_2 was treated with 0.43 g (1.5 mmol) of **1a** at ambient temperature. The mixture was stirred for 30 min. Then the solvent was removed in vacuo and the crude product was purified by column chromatography using a petroleum ether/CH_2Cl_2 mixture as the eluent. Removal of the solvent gave **2a** as a yellow solid. Yield: 0.91 g (99%). Mp: 174 °C dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.73−7.68 (m, 12 H, *o*-CH), 7.49−7.40 (m, 18 H, *m*,*p*-CH), 4.30 (td, $^3J_{HH}$ = 10.9 Hz, $^4J_{HH}$ = 4.7 Hz, 1 H, H^1), 1.63 (m, 2 H, H^2), 1.56 (m, 2 H, H^4), 1.47 (m, 1 H, H^8), 1.34 (m, 1 H, H^6), 1.13 (m, 2 H, H^5), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^9), 0.80 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^{10}), 0.70 (m, 1 H, H^3), 0.57 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^7) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 152.7 (*C*(O)OR), 135.2 (t, $^2J_{PC}$ = 6.4 Hz, *o*-C), 131.0 (*p*-C), 128.4 (t, $^3J_{PC}$ = 5.6 Hz, *m*-C), 74.0 (C^1), 47.0 (C^6), 41.3 (C^2), 34.5 (C^4), 31.7 (C^3), 25.7 (C^8), 23.3 (C^5), 22.1 (C^{10}), 20.9 (C^9), 16.0 (C^7) ppm; not observed Pd−C≡*C*, *i*-C. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 24.6 ppm. IR (CH_2Cl_2): ν(C≡C) 2115 cm^{-1}; ν(CO) 1677 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 301 (4.279). FAB-MS: *m*/*z* (%) 837 (4) [(M − Br)$^+$], 633 (22) [(M − C≡CC(=O)O-menthyl − Ph)$^+$], 367 (30) [(M − Br − C≡CC(=O)O-menthyl − PPh_3)$^+$]. Anal. Calcd for $C_{49}H_{49}BrO_2P_2Pd$ (918.20): C, 64.10; H, 5.38. Found: C, 64.03; H, 5.41.

***trans*-(3-(−)-Menthoxy-3-oxy-1-propynyl)trifluoroacetato-{bis(triphenylphosphine)}palladium(II) (3a).** A suspension of 0.63 g (0.69 mmol) of **2a** and 0.15 g (0.69 mmol) of $Ag[CF_3CO_2]$ in 30 mL of dry CH_2Cl_2 was stirred for 30 min at room temperature. The precipitate (AgBr) that formed was filtered off. The solvent of the crude reaction mixture was removed in vacuo. The crude product was

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purified by column chromatography on silica using a CH_2Cl_2/acetone mixture as eluent. Removal of the solvent in vacuo gave **3a** as a yellow solid. Yield: 0.58 g (88%). Mp: 85 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73−7.63 (m, 12 H, *o*-CH), 7.45−7.35 (m, 18 H, *m,p*-CH), 4.22 (td, $^3J_{HH}$ = 10.9 Hz, $^4J_{HH}$ = 4.7 Hz, 1 H, H^1), 1.62 (m, 5 H, H^2, H^4, H^8), 1.35 (m, 1 H, H^6), 1.14 (m, 2 H, H^5), 0.79 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^9), 0.70 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^{10}), 0.54 (m, 1 H, H^3), 0.45 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, H^7) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 134.6 (t, $^2J_{PC}$ = 6.7 Hz, *o*-C), 130.8 (*p*-C), 129.0 (t, $^1J_{PC}$ = 25.5 Hz, *ipso*-C), 128.4 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 74.0 (C^1), 46.8 (C^6), 40.7 (C^2), 34.1 (C^4), 31.2 (C^3), 25.5 (C^8), 23.1 (C^5), 22.0 (C^{10}), 20.8 (C^9), 16.1 (C^7) ppm; not observed Pd−*C*≡*CC*, F_3CCO. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 23.5 ppm. IR (CH_2Cl_2): ν(C≡C) 2123 cm^{-1}; ν(CO) 1680 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 299 (4.417). FAB-MS: *m/z* (%) 838 (54) [(M − CF_3COO)$^+$], 760 (8) [(M − CF_3COO − Ph)$^+$], 655 (45) [(M − PPh_3)$^+$], 552 (18) [(M − CF_3COO − Ph − C≡CC(=O)O-menthyl)$^+$], 470 (100) [(M − PPh_3 − C(=O)O-menthyl)$^+$]. Anal. Calcd for $C_{51}H_{49}F_3O_4P_2Pd$ (951.31): C, 64.39; H, 5.19. Found: C, 64.38; H, 5.58.

***trans*-Iodo(3-(*N,N*-tetramethyleneamino)-3-oxy-1-propynyl)bis(triphenylphosphine)palladium(II) (4b).** A solution of 0.41 g (0.49 mmol) of **2b** and 0.74 g (4.9 mmol) of NaI in 30 mL of dry CH_2Cl_2 was stirred for 5 h at room temperature. The precipitate was filtered off. The solvent of the crude reaction mixture was removed in vacuo. The crude product was purified by column chromatography on silica using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent in vacuo gave **4b** as a yellow solid. Yield: 0.35 g (81%). Mp: 145 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72−7.70 (m, 12 H, *o*-CH), 7.39−7.26 (m, 18 H, *m,p*-CH), 3.03 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, NCH_2), 2.23 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, NCH_2), 1.57 (m, 2 H, CH_2), 1.38 (m, 2 H, CH_2) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 152.8 (*C*(O)NC_4H_8), 135.4 (m, *o*-C), 132.6 (*p*-C), 130.9 (t, $^1J_{PC}$ = 19.6 Hz, *i*-C), 128.3 (t, $^3J_{PC}$ = 5.4 Hz, *m*-C), 108.2 (br, Pd−*C*≡C), 104.0 (br, Pd−C≡*C*), 47.2 (NCH_2), 44.5 (NCH_2), 25.4 (CH_2), 25.0 (CH_2) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 22.1 ppm. IR (CH_2Cl_2): ν(C≡C) 2114 cm^{-1}; ν(CO) 1677 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 297 (4.302). FAB-MS: *m/z* (%) 880 (71) [M$^+$], 751 (82) [(M − I − 2H)$^+$], 491 (72) [(M − I − PPh_3)$^+$]. Anal. Calcd for $C_{43}H_{38}INOP_2Pd$ (880.05): C, 58.69; H, 4.35; N, 1.59. Found: C, 58.69; H, 4.74; N, 1.48.

***trans*-Bis(3-(*N*-morpholino)-3-oxy-1-propynyl)bis(triethylphosphine)palladium(II) (9d).** A suspension of 0.25 g (1.0 mmol) (3-(*N*-morpholino)-3-oxy-1-propynyl)silver(I) in 20 mL of CH_2Cl_2 was treated with 0.16 g (0.4 mmol) of [$PdCl_2(PEt_3)_2$] at ambient temperature. The mixture was stirred for 14 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **9d** as a beige solid. Yield: 0.14 g (58%). Mp: 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82−3.58 (m, 16 H, $N(CH_2)_4O$), 1.95 (m, 12 H, PCH_2CH_3), 1.14 (m, 18 H, PCH_2CH_3), ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 154.3 (s, C_γ), 120.7 (t, $^2J_{PC}$ = 16.5 Hz, C_α), 104.2 (t, $^3J_{PC}$ = 3.3 Hz, C_β), 67.0 (s, NCH_2CH_2O), 66.7 (s, NCH_2CH_2O), 47.2 (s, NCH_2), 41.6 (s, NCH_2), 16.9 (t, $^1J_{PC}$ = 14.6 Hz, PCH_2CH_3), 8.5 (s, PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 19.6 ppm. IR (CH_2Cl_2): ν(C≡C) 2090 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 237 (4.783). FAB-MS: *m/z* (%) 619 (100) [M$^+$], 503 (15) [(M − PEt_3)$^+$], 363 (38) [(M − PEt_3 − CCC(=O)$N(CH_2)_4O$)$^+$]. Anal. Calcd for $C_{26}H_{46}N_2O_4P_2Pd$ (619.02): C, 50.45; H, 7.49; N, 4.53. Found: C, 50.40; H, 7.09; N, 4.66.

***trans*-Bis(3-oxy-3-(pentamethyleneamino)-1-propynyl)bis(triethylphosphine)palladium(II) (9e).** A suspension of 0.24 g (1.0 mmol) of (3-oxy-3-(pentamethylenamino)-1-propynyl)silver(I) in 20 mL of CH_2Cl_2 was treated with 0.16 g (0.4 mmol) of [$PdCl_2(PEt_3)_2$] at ambient temperature. The mixture was stirred for 16 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **9e** as a beige solid. Yield: 0.19 g (78%). Mp: 140 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (t, *J* = 5.3 Hz, 4 H, $NCH_2CH_2CH_2$), 3.52 (t, *J* = 5.3 Hz, 4 H, $NCH_2CH_2CH_2$), 1.95 (m, 12 H, PCH_2CH_3), 1.60−1.49 (m, 12 H, $NCH_2CH_2CH_2$), 1.13 (m, 18 H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 154.1 (s, C_γ), 118.8 (t, $^2J_{PC}$ = 16.7 Hz, C_α), 104.5 (t, $^3J_{PC}$ = 3.2 Hz, C_β), 47.9 (s, $NCH_2CH_2CH_2$), 41.7 (s, $NCH_2CH_2CH_2$), 26.5 (s, $NCH_2CH_2CH_2$), 25.5 (s, $NCH_2CH_2CH_2$), 24.8 (s, $NCH_2CH_2CH_2$), 16.8 (t, $^1J_{PC}$ = 14.4 Hz, PCH_2CH_3), 8.4 (s, PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 19.6 ppm. IR (CH_2Cl_2): ν(C≡C) 2089 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 235 (4.623). FAB-MS: *m/z* (%) 615 (100) [M$^+$], 497 (14) [(M − PEt_3)$^+$], 363 (29) [(M − PEt_3 − CCC(=O)$N(CH_2)_5$)$^+$]. Anal. Calcd for $C_{28}H_{50}N_2O_2P_2Pd$ (615.08): C, 54.68; H, 8.19; N, 4.55. Found: C, 54.50; H, 8.25; N, 4.56%.

***trans*-[Bis(3-(*N*-morpholino)-3-methoxy-1,2-propadienylidene)bis(triethylphosphine)palladium(II)] Trifluoromethanesulfonate (10d-OTf).** A solution of 0.60 g (0.1 mmol) of **9d** in 10 mL of CH_2Cl_2 was treated with 0.24 μL (0.2 mmol) of MeOTf at ambient temperature. The mixture was stirred for 2.5 h. Removal of the solvent gave **10d-OTf** as a yellow solid. Yield: 0.20 g (99%). Mp: 93 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.29 (s, 6 H, OCH_3), 4.01 (t, *J* = 4.8, 4 H, $N(CH_2CH_2)_2O$), 3.91−3.81 (m, 12 H, $N(CH_2CH_2)_2O$), 2.05−1.94 (m, 12 H, PCH_2CH_3), 1.26−1.14 (m, 18 H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 156.6 (t, $^2J_{PC}$ = 15.3 Hz, C_α), 153.6 (s, C_γ), 121.5 (q, J_{CF} = 322.4 Hz, SO_3CF_3), 97.3 (t, $^3J_{PC}$ = 3.4 Hz, C_β), 66.2 (s, $N(CH_2CH_2)_2O$), 65.8 (s, $N(CH_2CH_2)_2O$), 62.5 (s, OCH_3), 51.1 (s, NCH_2), 46.9 (s, NCH_2), 17.6 (t, $^1J_{PC}$ = 15.0 Hz, PCH_2CH_3), 8.85 (s, PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 22.0 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.8 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2082 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 281 (4.578). Anal. Calcd for $C_{30}H_{52}F_6N_2O_{10}P_2PdS_2$ (947.23): C, 38.04; H, 5.53; N, 2.96. Found: C, 37.84; H, 5.82; N, 2.84.

***trans*-[Bis(3-(pentamethyleneamino)-3-methoxy-1,2-propadienylidene)bis(triethylphosphine)palladium(II)] Trifluoromethanesulfonate (10e-OTf).** A solution of 0.05 g (0.1 mmol) of **9e** in 10 mL of CH_2Cl_2 was treated with 0.22 μL (0.2 mmol) of MeOTf at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **10e-OTf** as a yellow solid. Yield: 0.08 g (100%). Mp: 97 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.24 (s, 6 H, OCH_3), 3.99 (s, 4 H, $N(CH_2CH_2)_2CH_2$), 3.81 (s, 4 H, $N(CH_2CH_2)_2CH_2$), 2.05−1.93 (m, 12 H, PCH_2CH_3), 1.76 (s, 12 H, $N(CH_2CH_2)_2CH_2$), 1.27−1.11 (m, 18 H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 154.4 (t, $^2J_{PC}$ = 15.6 Hz, C_α), 152.6 (s, C_γ), 99.5 (t, $^3J_{PC}$ = 3.0 Hz, C_β), 61.9 (s, OCH_3), 52.9 (s, $N(CH_2CH_2)_2CH_2$), 47.7 (s, $N(CH_2CH_2)_2CH_2$), 26.6 (s, $N(CH_2CH_2)_2CH_2$), 25.8 (s, $N(CH_2CH_2)_2CH_2$), 23.7 (s, $N(CH_2CH_2)_2CH_2$), 17.6 (t, $^1J_{PC}$ = 14.8 Hz, PCH_2CH_3), 8.88 (s, PCH_2CH_3) ppm; not observed SO_3CF_3. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.7 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.9 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2083 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 275 (4.830). FAB-MS: *m/z* (%) 629 (100) [(M − $2BF_4$ − CH_3)$^+$], 374 (50) [(M − $2BF_4$ − $2PEt_3$)$^+$]. Anal. Calcd for $C_{32}H_{56}F_6N_2O_8P_2PdS_2$ (943.28): C, 35.09; H, 5.22; N, 2.34. Found: C, 35.19; H, 5.46; N, 2.78.

***trans*-[Bis(3-(pentamethyleneamino)-3-methoxy-1,2-propadienylidene)bis(triethylphosphine)palladium(II)] Tetrafluoroborate (10e-BF_4).** A solution of 0.19 g (0.3 mmol) of **9e** in 10 mL of CH_2Cl_2 was treated with 0.11 g (0.8 mmol) of $[Me_3O]BF_4$ at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **10e-BF_4** as a yellow solid. Yield: 0.25 g (98%). Mp: 120 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.20 (s, 6 H, OCH_3), 3.94 (s, 4 H, $N(CH_2CH_2)_2CH_2$), 3.76 (s, $N(CH_2CH_2)_2CH_2$), 1.98−1.89 (m, 12 H, PCH_2CH_3), 1.78−1.64 (m, 12 H, $N(CH_2CH_2)_2CH_2$), 1.21−1.09 (m, 18 H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 154.1 (t, $^2J_{PC}$ = 15.7 Hz, C_α), 152.3 (s, C_γ), 96.8 (t, $^3J_{PC}$ = 3.2 Hz, C_β), 61.9 (s, OCH_3), 52.3 (s, $N(CH_2CH_2)_2CH_2$), 47.3 (s, $N(CH_2CH_2)_2CH_2$), 26.3 (s, $N(CH_2CH_2)_2CH_2$), 25.5 (s, $N(CH_2CH_2)_2CH_2$), 23.4 (s, $N(CH_2CH_2)_2CH_2$), 17.3 (t, $^1J_{PC}$ = 15.1 Hz, PCH_2CH_3), 8.56 (s, PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.6 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −152.5 (BF_4), −152.5 (BF_4) ppm. IR (CH_2Cl_2): ν(CCC) 2083 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 276 (4.532). FAB-MS: *m/z* (%) 629

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(76) [(M − 2OTf − CH_3)$^+$], 528 (64) [(M − 2OTf − PEt_3)$^+$], 408 (100) [(M − 2OTf − 2PEt_3)$^+$]. Anal. Calcd for $C_{30}H_{56}B_2F_8N_2O_2P_2Pd{\cdot}0.9CH_2Cl_2$ (818.75): C, 41.85; H, 6.57; N, 3.17. Found: C, 41.96; H, 6.25; N, 3.39.

***trans*-[Bis(3-(pentamethyleneamino)-3-ethoxy-1,2-propadienylidene)bis(triethylphosphine)palladium(II)] Tetrafluoroborate (10e′-BF_4).** A solution of 0.19 g (0.3 mmol) of **9e** in 10 mL of CH_2Cl_2 was treated with 0.12 g (0.6 mmol) of $[Et_3O]BF_4$ at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **10e′-BF_4** as a yellow solid. Yield: 0.25 g (97%). Mp: 130 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.58 (q, 6 H, J = 7.0, OCH_2CH_3), 3.94 (s, 4 H, $N(CH_2CH_2)_2CH_2$), 3.76 (s, $N(CH_2CH_2)_2CH_2$), 2.00−1.87 (m, 12 H, PCH_2CH_3), 1.75−1.65 (m, 12 H, $N(CH_2CH_2)_2CH_2$), 1.41 (t, 6 H, J = 7.5, OCH_2CH_3), 1.20−1.10 (m, 18 H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 152.7 (t, $^2J_{PC}$ = 15.6 Hz, C_α), 151.4 (s, C_γ), 97.0 (t, $^3J_{PC}$ = 3.0 Hz, C_β), 72.5 (s, OCH_2CH_3), 52.1 (s, $N(CH_2CH_2)_2CH_2$), 47.2 (s, $N(CH_2CH_2)_2CH_2$), 26.3 (s, $N(CH_2CH_2)_2CH_2$), 25.5 (s, $N(CH_2CH_2)_2CH_2$), 23.4 (s, $N(CH_2CH_2)_2CH_2$), 17.3 (t, $^1J_{PC}$ = 15.1 Hz, PCH_2CH_3), 14.6 (s, OCH_2CH_3), 8.52 (s, PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.6 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −152.5 (BF_4), −152.5 (BF_4) ppm. IR (CH_2Cl_2): ν(CCC) 2083 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 275 (4.935). FAB-MS: m/z (%) 643 (75) [(M − 2BF_4 − CH_3)$^+$], 553 (60) [(M − 2BF_4 − PEt_3)$^+$], 435 (100) [(M − 2BF_4 − 2PEt_3)$^+$]. Anal. Calcd for $C_{32}H_{60}B_2F_8N_2O_2P_2Pd{\cdot}0.66CH_2Cl_2$ (836.81): C, 43.43; H, 6.84; N, 3.10. Found: C, 43.51; H, 6.88; N, 3.36.

***trans*-Bis(3-(dimethylamino)-3-oxy-1-propynyl)bis-(triisopropylphosphine)palladium(II) (11c).** A suspension of 0.51 g (2.5 mmol) of (3-(dimethylamino)-3-oxy-1-propynyl)silver(I) in 40 mL of CH_2Cl_2 was treated with 0.62 g (1.2 mmol) of $[PdCl_2(P^iPr_3)_2]$ at ambient temperature. The mixture was stirred for 25 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **11c** as a white solid. Yield: 0.31 g (40%). Mp: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (s, 6 H, NCH_3), 2.84 (s, 6 H, NCH_3), 2.75 (m, 6 H, $CH(CH_3)_2$), 1.32 (m, 36 H, $CH(CH_3)_2$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.8 (s, C_γ), 121.4 (t, $^2J_{PC}$ = 14.5 Hz, C_α), 106.9 (t, $^3J_{PC}$ = 2.6 Hz, C_β), 38.1 (s, NCH_3), 33.7 (s, NCH_3), 25.1 (t, $^1J_{PC}$ = 11.3 Hz, $CH(CH_3)_2$), 20.1 (s, $CH(CH_3)_2$) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 46.1 ppm. IR (CH_2Cl_2): ν(C≡C) 2086 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 236 (4.150). FAB-MS: m/z (%) 620 (100) [M$^+$], 459 (13) [(M − P^iPr_3)$^+$], 364 (37) [(M − P^iPr_3 − $CCC(=O)NMe_2$)$^+$]. Anal. Calcd for $C_{28}H_{54}N_2O_2P_2Pd$ (619.11): C, 54.32; H, 8.79; N, 4.52. Found: C, 54.08; H, 8.87; N, 4.70.

***trans*-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienylidene)bis(triisopropylphosphine)palladium(II)] Trifluoromethanesulfonate (12c-OTf).** A solution of 0.05 g (0.1 mmol) **11c** in 10 mL of CH_2Cl_2 was treated with 0.20 μL (0.2 mmol) of MeOTf at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **12c-OTf** as a white solid. Yield: 0.08 g (99%). Mp: 210 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.21 (s, 6 H, OCH_3), 3.46 (s, 6 H, NCH_3), 3.28 (s, 6 H, NCH_3), 2.74 (m, 6 H, $CH(CH_3)_2$), 1.40 (m, 36 H, $CH(CH_3)_2$) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 157.1 (t, $^2J_{PC}$ = 13.4 Hz, C_α), 154.4 (s, C_γ), 121.6 (q, J_{CF} = 322.9 Hz, SO_3CF_3), 99.5 (t, $^3J_{PC}$ = 2.3 Hz, C_β), 62.1 (s, OCH_3), 42.5 (s, NMe_2), 38.7 (s, NMe_2), 26.3 (t, $^1J_{PC}$ = 11.8 Hz, $CH(CH_3)_2$), 20.4 (s, $CH(CH_3)_2$) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 50.3 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.7 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2080 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 274 (3.504). FAB-MS: m/z (%) 638 (100) [(M − 2OTf − Me)$^+$], 488 (14) [(M − 2OTf − P^iPr_3)$^+$], 473 (28) [(M − 2OTf − P^iPr_3 − Me)$^+$], 380 (30) [(M − 2OTf − P^iPr_3 − C=C=C(OMe)NMe_2)$^+$]. Anal. Calcd for $C_{32}H_{60}F_6N_2O_8P_2PdS_2$ (947.32): C, 40.57; H, 6.38; N, 2.96. Found: C, 40.52; H, 6.38; N, 3.06.

***trans*-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienylidene)bis(triisopropylphosphine)palladium(II)] Tetrafluoroborate (12c-BF_4).** A solution of 0.10 g (0.2 mmol) of **11c** in 10 mL of CH_2Cl_2 was treated with 0.05 g (0.3 mmol) of $[Me_3O]BF_4$ at ambient temperature. The mixture was stirred for 2 h. Removal of the solvent gave **12c-BF_4** as a white solid. Yield: 0.10 g (75%). Mp: 200 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.13 (s, 6 H, OCH_3), 3.38 (s, 6 H, NCH_3), 3.19 (s, 6 H, NCH_3), 2.67 (m, 6 H, $CH(CH_3)_2$), 1.31 (m, 36 H, $CH(CH_3)_2$) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 155.8 (t, $^2J_{PC}$ = 13.4 Hz, C_α), 153.0 (s, C_γ), 98.1 (s, C_β), 60.8 (s, OCH_3), 41.2 (s, NMe_2), 37.3 (s, NMe_2), 25.0 (t, $^1J_{PC}$ = 12.0 Hz, $CH(CH_3)_2$), 19.1 (s, $CH(CH_3)_2$) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 50.1 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −153.54 (BF_4), −153.59 (BF_4) ppm. IR (CH_2Cl_2): ν(CCC) 2080 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 236 (4.139). FAB-MS: m/z (%) 649 (5) [(M − 2BF_4)$^+$], 634 (50) [(M − 2BF_4 − CH_3)$^+$], 475 (9) [(M − 2BF_4 − CH_3 − P^iPr_3)$^+$], 429 (100) [(M − 2BF_4 − 2OCH_3 − P^iPr_3)$^+$]. Anal. Calcd for $C_{30}H_{60}B_2F_8N_2O_2P_2Pd$ (822.79): C, 43.79; H, 7.35; N, 3.40. Found: C, 43.63; H, 7.32; N, 3.56.

***trans*-Bis(3-(tetramethyleneamino)-3-oxy-1-propynyl)bis-(triphenylphosphine)palladium(II) (13b).** A suspension of 0.23 g (1.0 mmol) of (3-(tetramethyleneamino)-3-oxy-1-propynyl)silver(I) in 20 mL of CH_2Cl_2 was treated with 0.28 g (0.4 mmol) of $[PdCl_2(PPh_3)_2]$ at ambient temperature. The mixture was stirred for 60 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **13b** as a beige solid. Yield: 0.28 g (80%). Mp: 145 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (m, 12 H, *o*-CH), 7.37 (m, 18 H, *m,p*-CH), 3.09 (t, J = 6.9 Hz, 4 H, NCH_2), 2.40 (t, J = 6.9 Hz, 4 H, NCH_2), 1.59 (p, J = 6.9 Hz, 4 H, NCH_2CH_2), 1.41 (p, J = 6.9 Hz, 4 H, NCH_2CH_2) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 153.5 (s, C_γ), 134.9 (t, $^2J_{PC}$ = 6.5 Hz, *o*-C), 131.5 (t, $^1J_{PC}$ = 25.4 Hz, *i*-C), 130.4 (s, *p*-C), 128.0 (t, $^3J_{PC}$ = 5.4 Hz, *m*-C), 118.8 (t, $^2J_{PC}$ = 16.4 Hz, C_α), 109.3 (t, $^3J_{PC}$ = 3.7 Hz, C_β), 47.1 (s, NCH_2), 44.2 (s, NCH_2), 25.1 (s, NCH_2CH_2), 24.7 (s, NCH_2CH_2) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 25.7 ppm. IR (CH_2Cl_2): ν(C≡C) 2101 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 274 (3.597). FAB-MS: m/z (%) 876 (86) [M$^+$], 613 (25) [(M − PPh_3)$^+$], 369 (100) [(M − PPh_3 − 2CCC(=O)NMe_2)$^+$]. Anal. Calcd for $C_{50}H_{46}N_2O_2P_2Pd \cdot CH_2Cl_2$ (875.28): C, 66.09; H, 5.16; N, 3.05. Found: C, 66.45; H, 5.27; N, 3.21.

***trans*-Bis(3-(dimethylamino)-3-oxy-1-propynyl)bis-(triphenylphosphine)palladium(II) (13c).** A suspension of 0.20 g (1.0 mmol) (3-(dimethylamino)-3-oxy-1-propynyl)silver(I) in 20 mL of CH_2Cl_2 was treated with 0.28 g (0.4 mmol) of $[PdCl_2(PPh_3)_2]$ at ambient temperature. The mixture was stirred for 20 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **13c** as a white solid. Yield: 0.10 g (30%). Mp: 150 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (m, 12 H, *o*-CH), 7.37 (m, 18 H, *m,p*-CH), 2.58 (s, 6 H, NCH_3), 2.22 (s, 6 H, NCH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.3 (s, C_γ), 134.9 (t, $^2J_{PC}$ = 6.5 Hz, *o*-C), 132.2 (s, *p*-C), 131.5 (t, $^1J_{PC}$ = 25.3 Hz, *i*-C), 128.1 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 119.8 (t, $^2J_{PC}$ = 16.1 Hz, C_α), 107.9 (s, C_β), 37.6 (s, NCH_3), 33.3 (s, NCH_3) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 25.4 ppm. IR (CH_2Cl_2): ν(C≡C) 2095 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 275 (3.714). FAB-MS: m/z (%) 824 (48) [M$^+$], 726 (32) [(M − CCC(=O)NMe_2)$^+$], 464 (32) [(M − PPh_3 − CCC(=O)NMe_2)$^+$], 371 (100) [(M − PPh_3 − 2CCC(=O)NMe_2)$^+$]. Anal. Calcd for $C_{46}H_{42}N_2O_2P_2Pd{\cdot}0.25CH_2Cl_2$ (823.21): C, 65.78; H, 5.07; N, 3.32. Found: C, 66.11; H, 5.08; N, 3.45.

***trans*-Bis(3-(*N*-morpholino)-3-oxy-1-propynyl)bis-(triphenylphosphine)palladium(II) (13d).** A suspension of 0.12 g (0.5 mmol) of (3-(*N*-morpholino)-3-oxy-1-propynyl)silver(I) in 10 mL of CH_2Cl_2 was treated with 0.16 g (0.2 mmol) of $[PdCl_2(PPh_3)_2]$ at ambient temperature. The mixture was stirred for 14 h. After filtration through Celite the solvent was removed in vacuo. The residue was chromatographed on silica at −20 °C using a CH_2Cl_2/acetone mixture as the eluent. Removal of the solvent gave **13d** as a white solid. Yield: 0.17 g (82%). Mp: 170 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 12 H, *o*-CH), 7.40 (m, 18 H, *m,p*-CH), 3.36 (t, J = 4.7 Hz, 4 H, NCH_2CH_2O), 3.26 (p, J = 4.7 Hz, 4 H, NCH_2CH_2O), 3.01 (t, J = 4.7 Hz, 4 H, NCH_2), 2.71 (t, J = 4.7 Hz, 4 H, NCH_2), ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 153.7 (s, C_γ), 134.9 (t, $^2J_{PC}$ = 6.5 Hz, *o*-C), 131.4 (t, $^1J_{PC}$ = 25.2 Hz, *i*-C), 130.6

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(s, *p*-C), 128.2 (t, $^3J_{PC}$ = 5.7 Hz, *m*-C), 121.3 (t, $^2J_{PC}$ = 16.3 Hz, C_α), 106.9 (t, $^3J_{PC}$ = 3.9 Hz, C_β), 66.8 (s, NCH_2CH_2O), 66.5 (s, NCH_2CH_2O), 46.2 (s, NCH_2), 41.2 (s, NCH_2) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$): δ 25.5 ppm. IR (CH_2Cl_2): ν(C≡C) 2099 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 274 (3.486). FAB-MS: *m*/*z* (%) 908 (50) [M$^+$], 645 (16) [(M − PPh_3)$^+$], 509 (24) [(M − PPh_3 − $CCC(=O)NMe_2$)$^+$]. Anal. Calcd for $C_{50}H_{46}N_2O_4P_2Pd{\cdot}0.25CH_2Cl_2$ (907.28): C, 65.00; H, 5.05; N, 3.02. Found: C, 65.16; H, 5.12; N, 3.09.

***trans*-[Bis(3-(tetramethylenamino)-3-methoxy-1,2-propadienylidene)bis(triphenylphosphine)palladium(II)] Trifluoromethanesulfonate (14b-OTf).** A solution of 0.10 g (0.1 mmol) of **13b** in 10 mL of CH_2Cl_2 was treated with 0.25 μL (0.2 mmol) of MeOTf at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **14b-OTf** as a beige solid. Yield: 0.13 g (98%). Mp: 175 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70 (m, 12 H, *o*-CH), 7.56 (m, 18 H, *m*,*p*-CH), 3.39 (s, 6 H, OCH_3), 3.35 (t, *J* = 7.2 Hz, 4 H, NCH_2), 2.79 (t, *J* = 6.9 Hz, 4 H, NCH_2), 1.89 (p, *J* = 7.2 Hz, 4 H, NCH_2CH_2), 1.76 (p, *J* = 7.2 Hz, 4 H, NCH_2CH_2) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 154.8 (t, $^2J_{PC}$ = 15.0 Hz, C_α), 151.5 (s, C_γ), 134.9 (t, $^2J_{PC}$ = 6.5 Hz, *o*-C), 132.4 (s, *p*-C), 129.9 (t, $^1J_{PC}$ = 26.0 Hz, *i*-C), 129.4 (t, $^3J_{PC}$ = 5.7 Hz, *m*-C), 121.5 (q, J_{CF} = 307.6 Hz, SO_3CF_3), 98.81 (t, $^3J_{PC}$ = 4.0 Hz, C_β), 61.3 (s, OCH_3), 52.2 (s, NCH_2), 49.3 (s, NCH_2), 24.8 (s, NCH_2CH_2), 24.6 (s, NCH_2CH_2) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 25.7 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.7 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2096 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 281 (4.646). FAB-MS: *m*/*z* (%) 892 (8) [(M − 2OTf − Me)$^+$], 791 (91) [(M − 2OTf − 2Me − $N(CH_2)_4$)$^+$], 645 (14) [(M − 2OTf − PPh_3)$^+$], 380 (100) [(M − 2OTf − 2PPh_3)$^+$]. Anal. Calcd for $C_{54}H_{52}F_6N_2O_8P_2PdS_2{\cdot}2CH_2Cl_2$ (1203.49): C, 48.98; H, 4.11; N, 2.04. Found: C, 49.33; H, 3.58; N, 2.35.

***trans*-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienylidene)bis(triphenylphosphine)palladium(II)] Trifluoromethanesulfonate (14c-OTf).** A solution of 0.09 g (0.1 mmol) of **13c** in 10 mL of CH_2Cl_2 was treated with 0.25 μL (0.2 mmol) of MeOTf at ambient temperature. The mixture was stirred for 1 h. Removal of the solvent gave **14c-OTf** as a beige solid. Yield: 0.11 g (98%). Mp: 160 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70 (m, 12 H, *o*-CH), 7.56 (m, 18 H, *m*,*p*-CH), 3.36 (s, 6 H, OMe), 2.96 (s, 6 H, NCH_3), 2.72 (s, 6 H, NCH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 155.9 (t, $^2J_{PC}$ = 15.3 Hz, C_α), 154.2 (s, C_γ), 135.0 (t, $^2J_{PC}$ = 6.4 Hz, *o*-C), 132.7 (s, *p*-C), 130.0 (t, $^1J_{PC}$ = 26.5 Hz, *i*-C), 129.6 (t, $^3J_{PC}$ = 5.7 Hz, *m*-C), 121.6 (q, J_{CF} = 321.7 Hz, SO_3CF_3), 98.0 (t, $^3J_{PC}$ = 4.0 Hz, C_β), 62.9 (s, OCH_3), 42.2 (s, NCH_3), 38.1 (s, NCH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 25.4 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.7 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2094 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 227 (4.619). FAB-MS: *m*/*z* (%) 738 (100) [(M − 2OTf − C═C═C(OMe)NMe_2)$^+$], 630 (29) [(M − 2OTf − 2C═C═C(OMe)NMe_2)$^+$], 479 (43) [(M − 2OTf − PPh_3 − C═C═C(OMe)NMe_2)$^+$], 372 (71) [(M − 2OTf − PPh_3 − 2C═C═C(OMe)NMe_2)$^+$]. Anal. Calcd for $C_{50}H48F_6N_2O_8P_2PdS_2{\cdot}0.5CH_2Cl_2$ (1151.41): C, 50.81; H, 4.14; N, 2.35. Found: C, 50.73; H, 4.28; N, 2.39.

***trans*-[Bis(3-(*N*-morpholino)-3-methoxy-1,2-propadienylidene)bis(triphenylphosphine)palladium(II)] Trifluoromethanesulfonate (14d-OTf).** A solution of 0.17 g (0.2 mmol) of **13d** in 10 mL of CH_2Cl_2 was treated with 0.44 μL (0.4 mmol) of MeOTf at ambient temperature. The mixture was stirred for 2 h. Removal of the solvent gave **14d-OTf** as a beige solid. Yield: 0.22 g (99%). Mp: 170 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72 (m, 12 H, *o*-CH), 7.58 (m, 18 H, *m*,*p*-CH), 3.55 (t, *J* = 4.8 Hz, 4 H, NCH_2CH_2O), 3.51 (t, *J* = 4.8 Hz, 4 H, NCH_2CH_2O), 3.44 (s, 6 H, OCH_3), 3.36 (t, *J* = 4.8 Hz, 4H, NCH_2), 3.12 (t, *J* = 4.8 Hz, 4H, NCH_2) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 157.5 (t, $^2J_{PC}$ = 15.1 Hz, C_α), 152.8 (s, C_γ), 135.0 (t, $^2J_{PC}$ = 6.7 Hz, *o*-C), 132.7 (s, *p*-C), 130.0 (t, $^1J_{PC}$ = 26.7 Hz, *i*-C), 129.7 (t, $^3J_{PC}$ = 5.5 Hz, *m*-C), 121.6 (q, J_{CF} = 321.5 Hz, SO_3CF_3), 97.5 (t, $^3J_{PC}$ = 3.9 Hz, C_β), 66.4 (s, NCH_2CH_2O), 65.9 (s, NCH_2CH_2O), 62.1 (s, OCH_3), 50.5 (s, NCH_2), 46.5 (s, NCH_2) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 25.2 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −78.7 (SO_3CF_3) ppm. IR (CH_2Cl_2): ν(CCC) 2092 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ε) 283 (4.904). FAB-MS: *m*/*z* (%) 922 (38) [(M − 2OTf − Me)$^+$], 822 (100) [(M − 2OTf − 2Me − $N(CH_2CH_2)_2O$)$^+$], 674 (31) [(M − 2OTf − PPh_3)$^+$], 414 (94) [(M − 2OTf − 2PPh_3)$^+$]. Anal. Calcd for $C_{54}H_{52}F_6N_2O_{10}P_2PdS_2{\cdot}1.5CH_2Cl_2$ (1235.49): C, 51.33; H, 4.27; N, 2.16. Found: C, 51.35; H, 4.30; N, 2.22.

Heck Coupling. In a typical run, a test tube containing a stirring bar was charged with sodium methoxide (41.0 mg, 0.50 mmol) and the palladium catalyst (0.001 mmol, 0.4 mol %). The test tube fitted with a screw cap having a pierceable Teflon septum was then evacuated and refilled with nitrogen. NMP (1 mL), bromobenzene (26.3 μL, 0.25 mmol), and styrene (42.9 μL, 0.375 mmol) were then added via syringe. The mixture was heated at 110 °C. After 0.5 h the solution was quenched with water, diluted with ethyl acetate, and analyzed by GC using *n*-dodecane as the internal standard.

Suzuki Coupling. In a typical run, a test tube containing a stirring bar was charged with phenylboronic acid (18.3 mg, 0.15 mmol), cesium carbonate (65.2 mg, 0.20 mmol), and the palladium catalyst (0.001 mmol, 1 mol %). The test tube fitted with a screw cap having a pierceable Teflon septum was evacuated and then refilled with nitrogen. THF (1 mL) and 1-bromo-4-butylbenzene (17.6 μL, 0.10 mmol) were added via syringe. The mixture was heated to 50 °C. After 1 h the solution was quenched with water, diluted with ethyl acetate, and analyzed by GC using *n*-dodecane as internal standard.

Sonogashira Coupling. In a typical run, a test tube containing a stirring bar was charged with CuI (0.01 mmol, 10 mol %) and the palladium catalyst (0.005 mmol, 5 mol %). The test tube fitted with a screw cap having a pierceable Teflon septum was evacuated and then refilled with nitrogen. DMSO (1 mL), phenyl iodide (11.2 μL, 0.10 mmol), phenylacetylene (13.2 μL, 0.12 mmol), and triethylamine (20.8 μL, 0.15 mmol) were added via syringe. The mixture was stirred at room temperature. After 1 h the solution was quenched with water, diluted with ethyl acetate, and analyzed by GC using *n*-dodecane as internal standard.

X-ray Structural Analysis of 9e, 11c, and 10e′-BF_4. Single crystals suitable for an X-ray structural analysis of **9e**, **11c**, and **10e′-BF_4** were grown from CH_2Cl_2/hexane, CH_2Cl_2/petroleum ether, and CH_2Cl_2/Et_2O, respectively. The measurements were performed at 100(2) K with a crystal mounted on a glass fiber on a Stoe IPDS II diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.710 73 Å). The structures were solved by direct methods using the SHELX-97 program package.[22] The positions of the hydrogen atoms were calculated by assuming an ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as the riding model. All other atoms were refined anisotropically.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for the complexes **9e**, **11c**, and **10e′-BF_4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOTES

Dedication

[†]Dedicated to Helmut Fischer.

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