## **ORGANOMETALLICS**

# Palladium End-Capped Polyynes via Oxidative Addition of 1-Haloalkynes to Pd(PPh<sub>3</sub>)<sub>4</sub>

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**Supporting Information** 

**ABSTRACT:** Reported here is the use of 1-haloacetylenes and 1-halopolyynes as synthons for the preparation of new palladium(II) endcapped polyynes. The 1-haloalkynes were obtained in a series of transformations from *para*-substituted bromoarenes that included Sonogashira coupling followed by halogenation and chain elongation via Cadiot–Chodkiewicz protocol. The key step for the synthesis of metal complexes was oxidative addition of 1-haloalkynes to Pd(PPh<sub>3</sub>)<sub>4</sub>, which allowed obtaining a series of metal compounds 1-5-C<sub>n</sub>X with carbon chains up to hexatriyne in 75–100% yield. All the compounds were characterized by NMR and HRMS or elemental analysis. The <sup>13</sup>C spectra



of the 1-haloalkynes showed interesting, although expected, shifts of the carbon chain atoms close to the halogen termini. X-ray crystal structures were obtained for three polyynes—two butadiynes ( $2-C_4[Pd]Br$  and  $3-C_4[Pd]Br$ ) and one hexatriyne ( $1-C_6[Pd]Br$ )—and the latter is the first reported X-ray crystal structure of palladium end-capped hexatriyne.

O rganic, organometallic, and metal-containing polyynes have been attracting constant interest in the scientific community for more than five decades now. Such species not only are being regarded as model compounds for the still elusive, allotropic sp-hybridized form of carbon, carbyne, but also have significant application potential. They are, for instance, used as precursors of conducting polymers.<sup>1</sup> In nanoelectronics they play a role in molecular wires and switches, and they are interesting as materials for optoelectronics due to their nonlinear optical response.<sup>2</sup> Organometallic polyynes take a significant place among all polyynes,<sup>3</sup> and to date the most intensive studies have concerned rhenium,<sup>4</sup> ruthenium,<sup>5</sup> iron,<sup>6</sup> and especially platinum<sup>7</sup> complexes.

Alkynyl palladium complexes (especially C2 species) have also been studied for many years. Such compounds are key intermediates in many coupling reactions<sup>8</sup> and have been lately recognized as active catalysts for living polymerization of isocyanides.9 Very recently, during the preparation of this article, the use of palladium end-capped butadiynes as highly active initiators for this reaction was reported.<sup>9c</sup> Moreover, organometallic polymers based on such complexes exhibit nonlinear optical, luminescence, and liquid crystalline properties that make them potentially attractive in commercial uses.<sup>10</sup> Despite this long-standing research, oligoynic palladium complexes remain rare in the literature, and only a few examples of compounds with a butadiyne carbon chain are known to date.<sup>11</sup> To the best of our knowledge, there has been no report in the literature on X-ray crystal structures of palladium end-capped polyynes longer than C<sub>4</sub>.

In order to obtain palladium end-capped polyynes, we have considered utilizing one of the known approaches used before for the synthesis of  $\sigma$ -alkynyl palladium(II) complexes. In general, there are three main synthetic pathways to such compounds, as shown in Scheme 1. The first approach, which involves dehydrohalogenation, was discovered by Hagihara and



(1)	PdX <sub>2</sub> (PR <sub>3</sub> ) <sub>2</sub>	+	R'— <del>—</del> —H	Cul, HNEt₂ ►	$R' \longrightarrow PR_3 \\ Pd-X \\ PR_3 \\ PR_3$
(2)	PdX <sub>2</sub> (PR <sub>3</sub> ) <sub>2</sub>	+	R' <del>───</del> ─ML <sub>n</sub>		$R' \longrightarrow PR_3 \\ Pd-X \\ PR_3 \\ PR_3$
(3)	Pd(PR <sub>3</sub> ) <sub>4</sub>	+	R' <del></del> X		$R' \longrightarrow PR_3 \\ Pd-X \\ PR_3 \\ PR_3$

co-workers and starts from a palladium(II) compound and a terminal alkyne, which are reacted with the use of a copper(I) halide as a catalyst and an amine as a base (method 1).<sup>12</sup> The second method is a reaction between a palladium(II) complex and a metal alkynyl (method 2). In this regard, there are protocols which use trimethylstannyl alkynyl compounds<sup>13</sup> and lithium,<sup>14</sup> silver,<sup>15</sup> or copper(I) acetylides.<sup>15c</sup> The third approach is an oxidative addition between a palladium(0) phosphine complex and 1-haloacetylene (method 3).<sup>15,16</sup> Similar approaches are used for other transition metal alkynyl and polyynyl compounds.

It is noteworthy that oxidative addition is intensely studied for organometallic palladium complexes with, for instance, aryl, vinyl, and NHC (NHC = N-heterocyclic carbene) ligands.<sup>17</sup>

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A common strategy that leads to polyynic metal complexes usually includes an attachment of an acetylene group to a metal, as the first step, followed by the carbon chain elongation.<sup>4–7</sup> This strategy did not seem rational in the case of  $\sigma$ -alkynyl palladium complexes, which are usually quite labile in solution.<sup>12a</sup> Hence, cross-coupling reactions used for a chain elongation would probably cause substantial difficulties. From this reason, we decided to first synthesize organic polyynes and then to use them for the synthesis of polyynic palladium complexes (as method 3 in Scheme 1). Such an approach, first, prevented the presence of usually less stable terminal polyynes (see method 1 in Scheme 1).<sup>18</sup> Second, such oxidative additions usually give high yields and pure products.<sup>16</sup> Third, it was possible to avoid reactive and toxic organometallic intermediates used in method 2 in Scheme 1.

In this paper we present an effective synthesis of a series of palladium end-capped polyynes and a few  $\sigma$ -ethynyl palladium complexes by oxidative addition of 1-haloalkynes to Pd(0). It is, to the best of our knowledge, the first use of 1-halopolyynes as substrates for the synthesis of metal end-capped polyynes. The crystal structures of palladium end-capped polyynes (up to hexatriyne) are also reported. All new complexes were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, IR, ESI-MS, and TGA-DTA techniques.

#### RESULTS AND DISCUSSION

**Synthesis of Palladium Complexes.** In the first thrust we have synthesized a series of 1-haloacetylenes and 1-halopolyynes, which were next used for the synthesis of respective palladium complexes.

All the syntheses started from *para*-substituted derivatives of bromobenzene to give a group of trimethylsilyl-protected polyynes with the use of the known synthetic strategy.<sup>19</sup> First, a trimethylsilylacetylene moiety was introduced via palladium-catalyzed Sonogashira coupling as shown in Scheme 2. Then, 1-bromoacetylenes 1-5-C<sub>2</sub>Br were obtained via bromination with *in situ* deprotection. Next, trimethylsilyl-protected butadiynes 1-5-C<sub>4</sub>TMS were synthesized through Cadiot–Chodkiewicz cross-coupling using trimethylsilylacetylene in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI catalyst and diisopropylamine. Hexatriyne 1-C<sub>6</sub>TMS was the only C<sub>6</sub> precursor that was successfully synthesized via C<sub>4</sub> elongation in cross-coupling reaction of 1-C<sub>2</sub>Br with HC<sub>4</sub>TMS.<sup>20</sup>

Polyynic precursors for palladium complexes were obtained by bromination or iodination of the trimethylsilyl-protected compounds with *in situ* deprotection with good to excellent yields, as shown in Scheme 2 (compound 2-C<sub>4</sub>Br was known from the literature, but we modified its synthetic pathway; see Supporting Information).<sup>21</sup> It was noticed that 1-bromo- and 1iodobutadiynes slowly decompose at room temperature, yielding insoluble black solids. In the case of hexatriyne 1- $C_6Br$  decomposition was much faster, and extra careful handling was required. Nevertheless, all the compounds can be stored at low temperatures for months.

With acetylenic and polyynic precursors in hand we carried out their reactions with  $Pd(PPh_3)_4$  in dry  $CH_2Cl_2$  at room temperature under an inert atmosphere. Palladium(0) easily underwent an oxidative addition, and target palladium(II) complexes were obtained with good to excellent yields, as shown in Scheme 3. Reaction was always nearly quantitative, but it was necessary to separate the products from triphenylphosphine, which disengaged from the metal coordination sphere. For this purpose, the products were precipitated

Scheme 2. Synthesis of 1-Halopolyyne Precursors



Scheme 3. Synthesis of Palladium Complexes



with hexanes and the solution containing triphenylphosphine was filtered off. As a consequence, some more soluble complexes (4- $C_2[Pd]Br$ , 5- $C_2[Pd]Br$ , and 2- $C_4[Pd]I$ ) were obtained with slightly lower yields.

The resulting compounds are rather unstable in solution, and it was important to avoid reaction times longer than 1 h. Otherwise dark, insoluble impurities emerged and additional signals in <sup>31</sup>P NMR spectra were observed. Although the decomposition was characteristic for all the complexes (the C<sub>2</sub> species were even more unstable due to the steric interaction between the arylalkynyl group and the bulky phosphines), the decomposition pattern was more thoroughly investigated for 1-C<sub>4</sub>[Pd]Br and 3-C<sub>4</sub>[Pd]Br in CDCl<sub>3</sub> solution, and the process was monitored by <sup>31</sup>P{H} NMR in the presence of triphenylphosphine as an external standard. Here, we noticed a simultaneous decrease of the corresponding phosphorus signals of 1-C<sub>4</sub>[Pd]Br and 3-C<sub>4</sub>[Pd]Br at 24.3 ppm and a growth of a few new peaks. In both cases, peaks at 22.6 ppm (assigned to Pd(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>),<sup>22</sup> 24.8, and 24.7 ppm appeared (see Figures 1 and 2 in the Supporting Information). Moreover, in the <sup>31</sup>P NMR spectrum of 1-C<sub>4</sub>[Pd]I we observed a signal at 24.7 ppm increasing with time and another one at 13.4 ppm, which could be assigned to Pd(PPh<sub>3</sub>)<sub>2</sub>I<sub>2</sub> (see Figure 3 in the Supporting Information).<sup>22a</sup> Several studies on intermolecular alkynyl ligand transfer in palladium(II) complexes<sup>12a,23</sup> suggest that signals with a chemical shift near 24.8 could be assigned to 1-C<sub>4</sub>[Pd]C<sub>4</sub>-1 and 3-C<sub>4</sub>[Pd]C<sub>4</sub>-3 dimers (Scheme 4). More-

### Scheme 4. Possible Decomposition Path of Palladium Complexes in CDCl<sub>3</sub>



over,  $Pd(PPh_3)_2Br_2$  was isolated from completely decomposed products (it was recrystallized and characterized by X-ray single-crystal diffraction, and the lattice parameters were nearly identical to the literature data for  $Pd(PPh_3)_2Br_2$ ).<sup>22b</sup> Palladium end-capped butadiynes are described in the literature as airstable,<sup>9c</sup> and in accordance with that we did not observe significant decomposition during short exposition of the solid samples to the air.

We have also noticed that iodides are significantly less stable in solution than bromides; therefore, mainly bromides were obtained during our studies. Also the <sup>13</sup>C NMR spectra of iodides presented a real challenge. Probably due to low stability of iodides in solution, it appeared impossible to obtain single crystals appropriate for X-ray analysis. Nevertheless, all palladium complexes, including iodides, may be stored as solids under an inert atmosphere for months.

**Characterization of Palladium Complexes.** The organic precursors and palladium complexes were characterized using <sup>1</sup>H and <sup>13</sup>C NMR, IR, and ESI-MS or elemental analysis. Additionally, <sup>31</sup>P NMR spectra and TGA-DTA measurements were performed for the complexes. The <sup>1</sup>H NMR spectra of the latter consist of multiplets from coordinated PPh<sub>3</sub> ligands, two doublets of *para*-phenylene groups and signals of the R substituent (in some cases). The length of the carbon chain has a strong influence on the proton signals of the C<sub>6</sub>H<sub>4</sub> group, as shown in Figure 1 for the aromatic part of the <sup>1</sup>H NMR spectrum of 1-C<sub>n</sub>[Pd]Br complexes. These differences are probably the result of an interactions through space between protons of the benzonitrile group and the triphenylphosphine ligands that are coordinated to the palladium.

As shown above, proton spectra of 1-haloalkynes and palladium complexes are usually quite simple and do not bring much structural information. Much more interesting are the carbon spectra. In Table 1 the chemical shifts of acetylene carbons for compounds with butadiynyl and hexatriynyl chains are collected. It is noteworthy that for 1-haloalkynes the signals of the carbon atoms directly attached to the halogen atom are strongly upfield shifted, far from typical chemical shifts for acetylenes. Here, they fall into the range from 6.5 (1-C<sub>4</sub>I) to 7.1 ppm (2-C<sub>4</sub>I) for iodides and from 46.6 (5-C<sub>4</sub>Br) to 48.2 (2-C<sub>4</sub>Br) ppm for bromides and these values are consistent with



**Figure 1.** Partial <sup>1</sup>H NMR spectrum (300 K, CDCl<sub>3</sub>, 500 MHz) of 1-C<sub>2</sub>[Pd]Br (top),  $1-C_4$ [Pd]Br (middle), and  $1-C_6$ [Pd]Br (bottom). Signals of the PPh<sub>3</sub> group, black; signals of benzonitrile group, red.

the literature.<sup>24,4b</sup> Unfortunately, we did not see any interesting correlation between the chain length and the position of the signals in <sup>1</sup>H, <sup>13</sup>C, or <sup>31</sup>P NMR spectra (also in the complexes).

The situation essentially changes after incorporation of palladium into the carbon-halogen bond. Then, the first carbon in the chain becomes shifted downfield with a chemical shift between 105.3  $(1-C_6[Pd]Br)$  and 110.8 ppm  $(2-C_4[Pd]I)$ . Moreover, the first three carbon atoms become triplets due to the coupling with phosphorus atoms of triphenylphosphines. The J(C,P) coupling constants were 14.8, 7.0, and 2.1 Hz for the first, second, and the third carbon atom, respectively. The acetylenic range of the <sup>13</sup>C NMR spectrum for 1-C<sub>6</sub>[Pd]Br is shown in Figure 2. Signals of phosphine ipso, ortho, and meta carbons are "virtual triplets" with J(CP) coupling constants of 25.0, 6.3, and 5.3 Hz, respectively. Such coupling is known as "virtual coupling" and is often observed for trans square planar diphosphine complexes.<sup>25</sup> The presence of only one singlet in <sup>31</sup>P NMR spectra confirms square planar geometry and trans configuration of the palladium complexes. The chemical shift for these complexes is between 22.3 and 25.0 ppm and is typical for trans  $\sigma$ -alkynyl complexes of palladium with triphenylphosphine.<sup>16e</sup>

IR stretching bands for palladium complexes and the 1-haloalkynes are within the typical acetylenic range (see Table 1). For 1-5-C<sub>2</sub>[Pd]Br compounds the data are in good agreement with those for the known  $\sigma$ -alkynyl palladium complexes.<sup>16e</sup> Luckily, it appeared rather easy to perform HRMS characterization of the palladium complexes with the use of an ESI ion source. The signals from  $[M - X]^+$  with a characteristic palladium isotope pattern could easily be observed. These fragment ions formed by the loss of halogen anions from the intact complex under the measurement conditions.

Thermal stability of palladium complexes was next investigated using the TGA-DTA technique. Compounds 1– 5-C<sub>4</sub>[Pd]X and 1-C<sub>6</sub>[Pd]Br appeared surprisingly stable in the solid state. Measurements performed under a N<sub>2</sub> atmosphere proved that the most stable complexes from the ones discussed (1-C<sub>4</sub>[Pd]Br: 206 °C, 1-C<sub>6</sub>[Pd]Br: 207 °C, 2-C<sub>4</sub>[Pd]Br: 208 °C) decomposed at temperatures above 200 °C (see Table 4 in the Supporting Information). The C<sub>2</sub> compounds are less thermally stable probably due to the more crowded environment around the metal center. Table 1. <sup>13</sup>C NMR and IR Data for Butadiynyl and Hexatriynyl Palladium Complexes and the Corresponding Precursors<sup>*a,b*</sup>

R = 1, -CN; 2, -NO<sub>2</sub>; 3, -C(O)Me; 4, -C(O)H; 5, -C(O)Ph Y = Br. I or Pd(PPh<sub>2</sub>)X

 $C_5$ ,  $C_6$  only for 1-C<sub>6</sub>Br and 1-C<sub>6</sub>[Pd]Br

palladium complexes							substrates								
	C1 <sup>c</sup>	$C2^d$	C3 <sup>e</sup>	C4	C5	C6	$\nu (C \equiv C)^{f}$		C1	C2	C3	C4	C5	C6	$\nu (C \equiv C)^f$
1-C <sub>4</sub> [Pd]Br	107.4	92.1	82.2	69.8			2187, 2065	1-C <sub>4</sub> Br	47.4	65.0	78.5	72.0			2221, 2131
2-C <sub>4</sub> [Pd]Br	108.7	92.1	83.4	69.8			2187, 2072	$2-C_4Br$	48.2	65.0	79.3	71.8			2218, 2111
3-C <sub>4</sub> [Pd]Br	105.9	92.4	81.2	70.8			2184, 2069	3-C <sub>4</sub> Br	46.7	65.3	77.5	73.1			2218, 2128
4-C <sub>4</sub> [Pd]Br	107.0	92.4	82.1	70.8			2184, 2069	4-C <sub>4</sub> Br	47.2	65.2	78.1	72.9			2217, 2128
5-C <sub>4</sub> [Pd]Br	105.7	92.5	81.0	70.9			2184, 2070	5-C <sub>4</sub> Br	46.6	65.3	77.2	73.2			2219, 2136
1-C <sub>4</sub> [Pd]I	109.6	90.7	82.1	70.1			2184, 2062	$1-C_4I$	6.5	79.1	78.0	71.7			2203, 2105
2-C <sub>4</sub> [Pd]I	110.8	90.8	83.3	70.0			2183, 2068	$2-C_4I$	7.1	79.8	78.0	71.4			2203, 2106
1-C <sub>6</sub> [Pd]Br	105.3	92.3	72.6	55.4	80.7	71.9	2163, 2138, 2038	$1-C_6Br$	44.8	66.0	58.3	69.5	78.3	73.6	2178, 2092

<sup>*a*</sup>All chemical shifts given in ppm. <sup>*b*</sup>All NMR spectra were measured in CDCl<sub>3</sub>. <sup>*c*</sup>Triplet, J(C,P) = 14.8 Hz. <sup>*d*</sup>Triplet, J(C,P) = 7.0 Hz. <sup>*e*</sup>Triplet, J(C,P) = 2.1 Hz. <sup>*f*</sup>All wave numbers are given in [cm<sup>-1</sup>].



Figure 2. Partial  ${}^{13}$ C NMR spectrum (acetylenic range) of  $1-C_6$ [Pd]Br in CDCl<sub>3</sub> (300 K, 151 MHz).

X-ray Crystallography of Palladium Complexes. All single crystals appropriate for X-ray analysis were obtained using liquid diffusion techniques. Crystals of  $2-C_2[Pd]Br$ ,  $2-C_4[Pd]Br$ ,  $3-C_4[Pd]Br$ , and  $1-C_6[Pd]Br$  were crystallized from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexanes. In the case of  $1-C_2[Pd]Br$  a mixture of hexanes and toluene proved the most effective. All the complexes are unstable in solution, and crystals could be obtained only when the crystallization process was finished in up to 2 days. Otherwise, only crystals of the decomposition product (Pd(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>) were observed.

All complexes crystallize in the monoclinic system in the  $P2_1$ (2-C<sub>2</sub>[Pd]Br),  $P2_1/n$  (2-C<sub>4</sub>[Pd]Br, 3-C<sub>4</sub>[Pd]Br), or  $P2_1/c$  (1-C<sub>6</sub>[Pd]Br) space group with Z = 4, except for 1-C<sub>2</sub>[Pd]Br, which crystallizes in the triclinic system,  $P\overline{1}$  space group, with Z= 2. For 1-C<sub>2</sub>[Pd]Br, there are two molecules in the asymmetric unit. The details of all X-ray single-crystal diffraction experiments are given in Table 1 in the Supporting Information, and molecular structures are shown in Figures 3-5.

In all palladium complexes the metal atom is fourcoordinated and adopts a slightly distorted square planar geometry (see Table 2 in the Supporting Information). Selected bond lengths are shown in Table 2. Pd–C1 bond lengths in  $1-C_2$ [Pd]Br (1.935(4) Å),  $2-C_2$ [Pd]Br (1.969(6) and



**Figure 3.** Anisotropic displacement ellipsoid plot of  $1-C_2[Pd]Br$  (left) and  $2-C_2[Pd]Br$  (right; one molecule of the two from the asymmetric unit). Hydrogen atoms and toluene molecule (for  $1-C_2[Pd]Br$ ) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.



Figure 4. Anisotropic displacement ellipsoid plot of  $2-C_4$ [Pd]Br (left) and  $3-C_4$ [Pd]Br (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

1.966(8) Å), and 3-C<sub>4</sub>[Pd]Br (1.940(4) Å) are in a lower region of a typical range for neutral  $\sigma$ -alkynyl palladium complexes (usually 1.94–2.07 Å)<sup>16a,e,26</sup> and are in accordance with the data for known butadiynyl complexes.<sup>9c</sup> The analogous distance for 2-C<sub>4</sub>[Pd]Br (1.927(5) Å) and 1-C<sub>6</sub>[Pd]Br (1.931(5) Å) is slightly lower and can be compared to that



Figure 5. Anisotropic displacement ellipsoid plot of 1-C<sub>6</sub>[Pd]Br. Hydrogen atoms and CH<sub>2</sub>Cl<sub>2</sub> molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

in some palladium allenylidene complexes (1.925(3) Å).<sup>16a</sup> The length of the C1-C2 bond for the polyynic structures (1.22-1.23 Å) is similar to that for the recently reported butadiynyl palladium complexes with chloride and triethyl phosphines (1.20-1.21 Å).

The geometry of butadiyne and hexatriyne chains is noticeably deviated from linearity. Surprisingly, the distortion of the chain in  $1-C_6[Pd]Br$  (contraction 0.19%) is smaller than that for 2-C<sub>4</sub>-[Pd]Br and 3-C<sub>4</sub>[Pd]Br (contraction 0.50% and 0.45%, respectively). The chain contraction that additionally includes first atoms of the end-groups is higher and amounts to 1.03% for 2-C<sub>4</sub>[Pd]Br, 0.98% for 3-C<sub>4</sub>[Pd]Br, and 0.35% for 1- $C_6[Pd]Br$ . These values are rather high for such short carbon rods and usually can be observed for longer polyynes.<sup>3</sup> As mentioned above, the lengths of the triple bonds in the carbon chains usually exceed 1.22 Å (except of 2-C<sub>2</sub>[Pd]Br) and are rather in the range typical for carbon rods longer than hexatriyne.<sup>3</sup>

In all the structures we observed a residual electron density peak between C1 and C2 carbon atoms, which was refined as bromine from the small amount of  $Pd(PPh_3)_2Br_2$  (3–6%). As already mentioned,  $Pd(PPh_3)Br_2$  is one of the decomposition products of the palladium complexes, and its presence had been previously confirmed by <sup>31</sup>P NMR. Small amounts of this compound form during crystallization and cocrystallize with the described complexes.

contr.<sup>b</sup> Pd-CAr

0.98% 0.35%

1.03%

0.50% 0.45% 0.19%

1.436(4)

1.430(5)

1.435(5)

1.210(5)

1.344(5)

1.222(5)

1.362(5)1.377(6)

1.227(6)

1.940(4)1.931(5)

2.335(1)

2.348(1)2.328(2)

2.450(1)

3-C4[Pd]Br 1-C6[Pd]Br

2.457(1)

2.338(1)

2.330(2)

1.225(7)

1.374(6)

1.221(6)

1.198(5)1.204(4) <sup>a</sup>Contraction C1-Cx =  $(C1-Cx \text{ sum of bond lengths} - C1-Cx \text{ distance})/C1-Cx \text{ sum of bond lengths} \times 100\%$ . <sup>b</sup>Contraction Pd-C<sub>Ar</sub> =  $(Pd-C_{Ar} \text{ sum of bond lengths} - Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ sum of bond lengths} = Pd-C_{Ar} \text{ distance})/Pd-C_{Ar} \text{ dist$ 

of bond lengths X 100%; <sup>c</sup>Two molecules in the asymmetric unit.

Table 2. Selected Bond Lengths  $\begin{bmatrix} \hat{A} \end{bmatrix}$  in Palladium Complexes

Although butadiynes hold a great potential for 1,4topochemical polymerization,<sup>1,27</sup> we have decided to analyze the packing for the only the  $C_6$  carbon chain in hexatriyne 1- $C_6[Pd]Br$ . Since the compound crystallizes in the  $P2_1/c$  space group, the molecules form two sets of parallel chains (in headto-tail orientation). The closest chain-chain separation was analyzed, which is understood as the closest carbon-carbon distance from two neighboring carbon chains. As revealed by thorough analysis (see Figure 6), the closest distance between



**Figure 6.** Packing diagram for  $1-C_6$  [Pd]Br with the shortest chainchain distances. The distances (Å) are C6–C4(i) 4.725; C5–C5(i) 4.667. Symmetry operations for related atoms are (i) 2-x, -y, 1-z; (ii) 1-x, -y, 1-z.

two carbon atoms from parallel chains of  $1-C_6[Pd]Br$  is 4.667 Å, which is larger than the sum of the van der Waals radii (3.56 Å). Such a great value excludes (despite the geometry) the possibility of any 1,*n*-topochemical polymerization.

Also in the case of butadiynes  $2-C_4$ [Pd]Br and  $3-C_4$ [Pd]Br the analogous distances were similarly high and amounted to 4.603 and 4.700 Å, respectively. Such high separation of polyyne chains may explain high thermal stability observed for butadiynes and hexatriyne.

#### SUMMARY

In summary, we have shown the new synthetic approach to the organometallic polyynes. The use of Cadiot-Chodkiewicz cross-coupling and halogenations with in situ deprotection allowed obtaining a series of 1-halobutadiynes and 1bromohexatriyne. The use of these 1-halopolynes in the highly atom economic reaction with the tetrakis(triphenylphosphine)palladium(0) complex yielded a series of palladium end-capped carbon rods up to the hexatriyne  $(1-\overline{C}_6[Pd]Br)$ . The trans configuration of the resulting compounds was confirmed by NMR and X-ray diffraction studies. X-ray crystal structures were determined for two  $\sigma$ -ethynyl palladium complexes (1-C<sub>2</sub>[Pd]Br, 2-C<sub>2</sub>[Pd]Br), two palladium end-capped butadiynes  $(2-C_4[Pd]Br, 3-C_4[Pd]Br)$ , and one palladium end-capped hexatriyne ( $1-C_6[Pd]Br$ ). To the best our knowledge, the latter is the first reported X-ray crystal structures of palladium endcapped hexatriyne. Chains in  $2-C_4[Pd]Br$  and  $3-C_4[Pd]Br$ exhibited unexpectedly large distortions from linearity. Our present work focuses on the use of the oxidative addition as the method for the synthesis of longer organometallic polyynes, and the versatility of this protocol will be expanded.

#### EXPERIMENTAL SECTION

For full details, including copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra and X-ray crystallography details, see the Supporting Information.

**General Procedures.** All reactions were conducted under  $N_2$  with the use of standard Schlenk techniques. Glassware was predried at 120 °C. Solvents were treated as follows: hexanes and toluene were distilled from Na, THF was distilled from Na/benzophenone,  $CH_2Cl_2$ was distilled from  $P_2O_5$ , and  $CH_3CN$  (HPLC grade) was used as received.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker 300, Avance 500, and Avance III 600 MHz spectrometers. For all the <sup>1</sup>H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks (CDCl<sub>3</sub>, <sup>1</sup>H: 7.26 ppm, <sup>13</sup>C: 77.2 ppm). For the <sup>31</sup>P NMR spectra, H<sub>3</sub>PO<sub>4</sub>(aq) (85%) was used as an external standard (0 ppm). Coupling constants are given in Hz. HRMS spectra were recorded using Bruker Apex Ultra FT-ICR and MicOTOF-Q spectrometers with an ESI ion source. IR spectra were recorded using a Bruker 66/s FTIR spectrometer. TGA-DTA data were collected using a Setaram SETSYS 16/18 thermal analyzer. Microanalysis was conducted with an Elementar CHNS Vario EL III analyzer.

Details of X-ray Data Collection and Reduction. X-ray diffraction data were collected with KUMA KM4 CCD ( $\omega$  scan technique) diffractometers with an Oxford Cryosystem-Cryostream cooler at 100 K.<sup>28</sup> The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on  $F^2$  by use of the SHELXTL package.<sup>29</sup> Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.

Synthesis. General Procedure for the Halogenation of Trimethylsilyl-Protected Polyynes. To a solution of polyyne in acetonitrile with an addition of H<sub>2</sub>O under a nitrogen atmosphere and in the dark was added AgF, and the mixture was stirred for 20 min. Next NBS or NIS was introduced, and the mixture was stirred for several hours. Acetonitrile was removed under reduced pressure. Et<sub>2</sub>O and H<sub>2</sub>O (v/v 1:1) was added to the residue. The organic layer was separated, washed with H<sub>2</sub>O ( $3 \times 25$  mL), and dried over MgSO<sub>4</sub>. Crude product was purified using a short silica gel plug (10 cm, DCM/ hexanes; v/v; 1:1) to yield the product.

**4-(Bromobutadiynyl)benzonitrile**, NCC<sub>6</sub>H<sub>4</sub>(C≡C)<sub>2</sub>Br (1-C<sub>4</sub>Br). 4-((Trimethylsilyl)butadiynyl)benzonitrile (0.098 g, 0.44 mmol), acetonitrile (25 mL), H<sub>2</sub>O (0.020 mL, 1.1 mmol), AgF (0.056 g, 0.44 mmol), and NBS (0.095 g, 0.53 mmol) were reacted according to the general procedure for 20 h. Workup gave a beige solid of 1-C<sub>4</sub>Br in 95% yield (0.097 g, 0.42 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm): δ = 7.63−7.60 (m, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 7.59−7.56 (m, 2H; *m*-C<sub>6</sub>H<sub>4</sub>), 1<sup>3</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm): δ = 133.5 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 132.3 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 126.3 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 118.3 (1C; CN), 112.9 (1C; *p*-C<sub>6</sub>H<sub>4</sub>), 78.5 (1C; C≡CC≡CBr), 72.0 (1C; C≡CC≡CBr), 65.0 (1C; C≡CC≡CBr), 47.7 (1C; C≡CC≡CBr). HRMS(ESI): *m/z* calcd for C<sub>11</sub>H<sub>5</sub>BrN 229.9600 [M + H]<sup>+</sup>; found 229.9610. IR (Nujol mull; cm<sup>-1</sup>): ν = 2233 (C≡N), 2221 (C≡C), 2131 (C≡C).

**4-(Bromobutadiynyl)acetophenone,** CH<sub>3</sub>(**O**)CC<sub>6</sub>H<sub>4</sub>(**C**≡**C**)<sub>2</sub>Br (**3-C**<sub>4</sub>Br). 4-((Trimethylsilyl)butadiynyl)acetophenone (0.074 g, 0.31 mmol), acetonitrile (10 mL), H<sub>2</sub>O (0.011 mL, 0.06 mmol), AgF (0.039 g, 0.31 mmol), and NBS (0.066 g, 0.37 mmol) were reacted according to the general procedure for 20 h. Workup gave a yellow solid of **3-**C<sub>4</sub>Br in 90% yield (0.070 g, 0.28 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm): *δ* = 7.90 (d, *J*(H,H) = 8.4 Hz, 2H; *m*-C<sub>6</sub>H<sub>4</sub>), 7.58 (d, *J*(H,H) = 8.4 Hz, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 2.60 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm): *δ* = 197.3 (1C; CO), 137.3 (1C; *p*-C<sub>6</sub>H<sub>4</sub>), 133.2 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 128.4 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 126.1 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 77.5 (1C; C≡CC≡CBr), 73.1 (1C; C≡CC≡CBr), 65.3 (1C; C≡CC≡CBr), 46.7 (1C; C≡CC≡CBr), 26.8 (1C; CH<sub>3</sub>). HRMS(ESI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub>BrO 246.9753 [M + H]<sup>+</sup>; found 246.9763. IR (Nujol mull; cm<sup>-1</sup>): *ν* = 2218 (C≡C), 2131 (C≡C), 1668 (C=O). **4-(Bromobutadiynyl)benzaldehyde**, **H(O)CC<sub>6</sub>H<sub>4</sub>(C≡C)<sub>2</sub>Br (4-C<sub>4</sub>Br)**. 4-((Trimethylsilyl)butadiynyl)benzaldehyde (0.350 g, 1.35 mmol), acetonitrile (40 mL), H<sub>2</sub>O (0.050 mL, 2.8 mmol), AgF (0.171 g, 1.35 mmol), and NBS (0.316 g, 1.76 mmol) were reacted according to the general procedure for 18 h. Workup gave a beige solid of 4-C<sub>4</sub>Br in 88% yield (0.278 g, 1.19 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm): δ = 10.01 (s, 1H; CHO), 7.83 (d, *J*(H,H) = 8.3 Hz, 2H; *m*-C<sub>6</sub>H<sub>4</sub>), 7.64 (d, *J*(H,H) = 8.3 Hz, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 13.6 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 129.7 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 127.5 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 78.1 (1C; C≡CC≡CBr), 72.9 (1C; C≡CC≡CBr), 65.2 (1C; C≡CC≡CBr), 47.2 (1C; C≡CC≡CBr). Anal. Calcd (%) for C<sub>11</sub>H<sub>5</sub>OBr: C 56.69, H 2.16. Found: C 56.74, H 1.96. HRMS(ESI): *m/z* calcd for C<sub>11</sub>H<sub>6</sub>BrO 232.9597 [M + H]<sup>+</sup>; found 232.9605. IR (Nujol mull; cm<sup>-1</sup>): *ν* = 2217 (C≡C), 2128 (C≡C), 1699 (C=O).

4-(Bromobutadiynyl)benzophenone,  $C_6H_5(O)CC_6H_4(C \equiv$ C)<sub>2</sub>Br (5-C<sub>4</sub>Br). 4-((Trimethylsilil)butadiynyl)benzophenone (0.369 g, 1.22 mmol), acetonitrile (50 mL), H<sub>2</sub>O (0.055 mL, 3.1 mmol), AgF (0.155 g, 1.22 mmol), and NBS (0.260 g, 1.46 mmol) were reacted according to the general procedure for 3.5 h. Workup (chromatography on silica gel 10 cm, DCM/hexanes; v/v; 2:1) gave 5-C<sub>4</sub>Br as a brown solid in 89% yield (0.334 g, 1.08 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta = 7.79 - 7.74$  (m, 4H; m-C<sub>6</sub>H<sub>4</sub>, o-C<sub>6</sub>H<sub>5</sub>), 7.62-7.57 (m, 3H, o-C<sub>6</sub>H<sub>4</sub>, p-C<sub>6</sub>H<sub>5</sub>), 7.51-7.46 (m, 2H; m-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 195.8 (1C; CO), 138.0 (1C; p-C<sub>6</sub>H<sub>4</sub>), 137.3 (1C; i-C<sub>6</sub>H<sub>5</sub>), 132.9 (1C; p-C<sub>6</sub>H<sub>5</sub>), 132.8 (2C; o-C<sub>6</sub>H<sub>4</sub>), 130.1 (4C; m-C<sub>6</sub>H<sub>4</sub>, o-C<sub>6</sub>H<sub>5</sub>), 128.6 (2C; m-C<sub>6</sub>H<sub>5</sub>), 125.4 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 77.2 (1C; C≡CC≡CBr), 73.2 (1C; C≡CC≡CBr), 65.3 (1C; C $\equiv$ CC $\equiv$ CBr), 46.6 (1C; C $\equiv$ CC $\equiv$ CBr). HRMS(ESI): m/zcalcd for C<sub>17</sub>H<sub>9</sub>BrONa 330.9729 [M + Na]<sup>+</sup>; found 330.9718. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2219$  (C $\equiv$ C), 2136 (C $\equiv$ C), 1652 (C $\equiv$ O).

4-((Trimethylsilyl)hexatriynyl)benzonitrile, NCC<sub>6</sub>H<sub>4</sub>(C $\equiv$ C)<sub>3</sub>Si(CH<sub>3</sub>)<sub>3</sub> (1-C<sub>6</sub>TMS). To a solution of 4-(bromoethynyl)benzonitrile (0.670 g, 3.25 mmol) and (trimethylsilyl)butadiyne (0.609 g, 4.98 mmol) in dry, oxygen-free THF (20 mL) were added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.114 g, 0.163 mmol) and CuI (0.031 g, 0.163 mmol) under a nitrogen atmosphere. Next diisopropylamine (1.15 mL, 8.13 mmol) was slowly added, and the mixture was stirred at room temperature for 40 min. Product was purified using flash chromatography (silica gel, DCM/hexanes, v/v, 1:1). Yield: 0.401 g (50%, 1.62 mmol), beige solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta = 7.65 - 7.56$  (m, 4H; C<sub>6</sub>H<sub>4</sub>), 0.23 (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 133.6 (2C; m-C<sub>6</sub>H<sub>4</sub>), 132.3 (2C; o-C<sub>6</sub>H<sub>4</sub>), 126.1 (1C; i-C<sub>6</sub>H<sub>4</sub>), 118.2 (1C; CN), 113.1 (1C; p- $C_6H_4$ ), 91.0 (1C; C=CC=CCi), 87.8 (1C; C=CC=CC CSi), 78.5 (1C; C≡CC≡CC≡CSi), 74.6 (1C; C≡CC≡CC≡CSi), 69.2 (1C; C≡CC≡CC≡CSi), 60.8 (1C; C≡CC≡CC≡CSi), -0.4  $(3C; Si(CH_3)_3)$ . Anal. Calcd (%) for  $C_{16}H_{13}NSi$ : C 77.69, H 5.30, N 5.66. Found: C 77.50, H 5.27, N 5.62. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  = 2226 (C=N), 2180 (C=C), 2161 (C=C), 2074 (C=C),

**4-(Bromohexatriynyl)benzonitrile,** NCC<sub>6</sub>H<sub>4</sub>(C≡C)<sub>3</sub>Br (1-C<sub>6</sub>Br). 4-((Trimethylsilyl)hexatriynyl)benzonitrile (0.140 g, 0.566 mmol), acetonitrile (10 mL), H<sub>2</sub>O (0.025 mL, 1.4 mmol), AgF (0.072 g, 0.57 mmol), and NBS (0.131 g, 0.728 mmol) were reacted according to the general procedure for 35 min. Workup gave 1-C<sub>6</sub>Br as a yellow solid in 95% yield (0.137 g, 0.539 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> 7.26 ppm): δ = 7.65−7.57 (m, 4H; *o*,*m*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm): δ = 133.7 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 132.3 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 125.8 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 118.2 (1C; CN), 113.3 (1C; *p*-C<sub>6</sub>H<sub>4</sub>), 78.3 (1C; C≡CC≡CC≡CBr), 73.6 (1C; C≡CC≡CC≡CBr), 69.5 (1C; C≡CC≡CC≡CBr), 66.0 (1C; C≡CC≡CC≡CBr), 58.3 (1C; C≡CC≡CC≡CBr), 44.8 (1C; C≡CC≡CC≡CBr). HRMS(ESI): *m*/*z* calcd for C<sub>13</sub>H<sub>3</sub>BrN 253.9600 [M + H]<sup>+</sup>; found 253.9604. IR (Nujol mull; cm<sup>-1</sup>): *ν* = 2229 (C≡N), 2178 (C≡C), 2092 (C≡C).

4-(lodobutadiynyl)benzonitrile, NCC<sub>6</sub>H<sub>4</sub>(C $\equiv$ C)<sub>2</sub>I (1-C<sub>4</sub>I). 4-((Trimethylsilyl)butadiynyl)benzonitrile (0.174 g, 0.780 mmol), acetonitrile (30 mL), H<sub>2</sub>O (0.028 mL, 1.6 mmol), AgF (0.099 g, 0.788 mmol), and NIS (0.217 g, 0.934 mmol) were reacted according to the general procedure for 4 h. Workup gave 1-C<sub>4</sub>I as a yellow solid in 69% yield (0.150 g, 0.541 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.62–7.60 (m, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 7.58–7.55 (m, 2H; *m*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 133.7 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 132.3 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 126.1 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 118.3 (1C; C $\equiv$ N), 113.0 (1C; *p*-C<sub>6</sub>H<sub>4</sub>), 79.1 (1C; C $\equiv$ CC $\equiv$ CI), 78.0 (1C; C $\equiv$ CC $\equiv$ CI), 71.7 (1C; C $\equiv$ CC $\equiv$ CI), 6.5 (1C; C $\equiv$ CC $\equiv$ CI). HRMS(ESI): *m/z* calcd for C<sub>11</sub>H<sub>5</sub>IN 277.9461 [M + H]<sup>+</sup>; found 277.9476. IR (KBr; cm<sup>-1</sup>):  $\nu$  = 2233 (C $\equiv$ N), 2203 (C $\equiv$ C), 2105 (C $\equiv$ C).

**4-(Iodobutadiynyl)nitrobenzene**, **O<sub>2</sub>NC**<sub>6</sub>**H**<sub>4</sub>(**C**≡**C**)<sub>2</sub>**I** (2-C<sub>4</sub>**I**). 4-((Trimethylsilyl)butadiynyl)-4-nitrobenzene (0.315 g, 1.30 mmol), acetonitrile (40 mL), H<sub>2</sub>O (0.046 mL, 2.6 mmol), AgF (0.164 g, 1.30 mmol), and NIS (0.340 g, 1.47 mmol) were reacted according to the general procedure for 1 h. Workup gave 2-C<sub>4</sub>I as a yellow solid in 81% yield (0.313 g, 1.05 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 8.21–8.18 (m, 2H; *m*-C<sub>6</sub>H<sub>4</sub>), 7.65–7.62 (m, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 134.0 (2C; *o*-C<sub>6</sub>H<sub>4</sub>), 128.1 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 123.8 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 79.8 (1C; C≡CC≡CI), 78.0 (1C; C≡CC≡CI), 71.4 (1C; C≡CC≡CI), 71.1 (1C; C≡CC≡CI), 78.0 (1C; C≡CC≡CI), 71.4 (1C; C≡CC≡CI), 71.1 (1C; C≡CC≡CI), 2106 (C≡C), 1591 (NO<sub>2</sub>), 1340 (NO<sub>2</sub>).

General Procedure for Synthesis of Palladium Complexes. Pd(PPh<sub>3</sub>)<sub>4</sub> was dissolved in dry DCM under a N<sub>2</sub> atmosphere. Next 1haloacetylene or 1-halopolyyne was added, and the mixture was stirred for 1 h at rt. After this time the solution was concentrated under reduced pressure, and hexanes was added to precipitate the yellowish palladium complex. The crude product was filtered off and dissolved in a small amount of DCM. Next hexanes was added, and the yellow solid was filtered off and dried under reduced pressure to give the final palladium complex as a yellowish solid.

Bromo((4-cyanophenyl)ethynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>(C=CC<sub>6</sub>H<sub>4</sub>CN)] (1-C<sub>2</sub>[Pd]Br). Pd-(PPh<sub>3</sub>)<sub>4</sub> (0.136 g, 0.118 mmol), 4-(bromoethynyl)benzonitrile (0.024 g, 0.12 mmol), and DCM (10 mL) were reacted and worked up according to the general procedure. Yield: 0.080 g (81%, 0.096 mmol). Mp with decomposition: 170 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta = 7.78 - 7.70$  (m, 12H; o-C<sub>6</sub>H<sub>5</sub>), 7.44-7.34 (m, 18H; m,p- $C_6H_5$ , 7.12 (d, J(H,H) = 9.0 Hz, 2H;  $m-C_6H_4$ ), 6.12 (d, J(H,H) = 9.0Hz, 2H; o-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 135.2  $(t, J(C,P) = 6.3 \text{ Hz}, 12C; o-C_6H_5), 133.2 (1C; i-C_6H_4), 131.5 (t, I)$  $J(C_{1}P) = 25.1 \text{ Hz}, 6C; i-C_{6}H_{5}), 131.1 (2C; o- \text{ or } m-C_{6}H_{4}), 131.0 (2C;$ o- or  $m-C_6H_4$ ), 130.6 (6C;  $p-C_6H_5$ ), 128.2 (t, J(C,P) = 5.3 Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 119.5 (1C; CN), 109.9 (t, J(C,P) = 6.8 Hz, 1C; PdC $\equiv$ C), 109.0 (1C; PdC=C), 108.1 (1C; p-C<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 25.0 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for C<sub>45</sub>H<sub>34</sub>NP<sub>2</sub>Pd 756.1212 [M - Br]<sup>+</sup>; found 756.1208. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2224$  (C $\equiv$ N), 2114 (C $\equiv$ C).

Bromo((4-nitrophenyl)ethynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>(C=CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)] (2-C<sub>2</sub>[Pd]Br). Pd-(PPh<sub>3</sub>)<sub>4</sub> (0.122 g, 0.106 mmol), 4-(bromoethynyl)nitrobenzene (0.024 g, 0.11 mmol), and DCM (10 mL) were reacted and worked up according to the general procedure. Yield: 0.080 g (88%, 0.093 mmol). Decomposition: 172 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.77-7.70 (m, 14H; o-C<sub>6</sub>H<sub>5</sub>, m-C<sub>6</sub>H<sub>4</sub>), 7.45-7.34 (m, 18H; m,p- $C_6H_5$ ), 6.15 (d, J(H,H) = 9.0 Hz, 2H;  $o - C_6H_4$ ). <sup>13</sup>C NMR (126 MHz,  $CDCl_{3}$  77.2 ppm):  $\delta = 144.9 (1C; p-C_6H_4), 135.2 (t, J(C,P) = 6.3 Hz, 120)$ 12C;  $o - C_6 H_5$ ), 134.4 (1C;  $i - C_6 H_4$ ), 131.4 (t, J(C,P) = 25.1 Hz, 6C;  $i - C_6 H_5$ )  $C_6H_5$ ), 131.0 (2C; o- $C_6H_4$ ), 130.6 (6C; p- $C_6H_5$ ), 128.2 (t, J(C,P) =5.3 Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 122.9 (2C; m-C<sub>6</sub>H<sub>4</sub>), 111.7 (t, J(C,P) = 14.5 Hz, 1C; PdC≡C), 109.9 (t, *J*(C,P) = 7.1 Hz, 1C; PdC≡C). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 25.0 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for  $C_{44}H_{34}NO_2P_2Pd$  776.1110 [M - Br]<sup>+</sup>; found 776.1103. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2119$  (C=C), 1510 (NO<sub>2</sub>), 1338 (NO<sub>2</sub>).

Bromo((4-acetylphenyl)ethynyl)bis(triphenylphosphine)palladium, *trans*-[PdBr(PPh<sub>3</sub>)<sub>2</sub>( $C \equiv CC_6H_4C(O)CH_3$ ]] (3-C<sub>2</sub>[Pd]Br). Pd(PPh<sub>3</sub>)<sub>4</sub> (0.147 g, 0.127 mmol), 4-(bromoethynyl)acetophenone (0.028 g, 0.13 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.097 g (87%, 0.11 mmol). Mp with decomposition: 152 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.80–7.71 (m, 12H; o-C<sub>6</sub>H<sub>5</sub>), 7.47 (d, *J*(H,H) = 8.3 Hz, 2H; *m*-C<sub>6</sub>H<sub>4</sub>), 7.44–7.33 (m, 18H; *m*,*p*-C<sub>6</sub>H<sub>5</sub>), 6.15 (d, *J*(H,H) = 8.3 Hz, 2H; o-C<sub>6</sub>H<sub>4</sub>), 2.45 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 197.6 (1C; CO), 135.2 (t, *J*(C,P) = 6.3 Hz, 12C; o-C<sub>6</sub>H<sub>5</sub>), 133.8 (1C; *p*-C<sub>6</sub>H<sub>4</sub>), 132.6 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 131.6 (t, *J*(C,P) = 25.0 Hz, 6C; *i*-C<sub>6</sub>H<sub>5</sub>), 130.7 (2C; o-C<sub>6</sub>H<sub>4</sub>), 130.5 (6C; *p*-C<sub>6</sub>H<sub>5</sub>), 128.2 (t, *J*(C,P) = 5.3 Hz, 12C; *m*-C<sub>6</sub>H<sub>5</sub>), 127.5 (2C; *m*-C<sub>6</sub>H<sub>4</sub>), 110.7 (t, *J*(C,P) = 6.7 Hz, 1C; PdC=C), 106.8 (t, *J*(C,P) = 14.0 Hz, 1C; PdC=C), 26.5 (1C; CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.9 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): *m*/z calcd for C<sub>46</sub>H<sub>37</sub>OP<sub>2</sub>Pd 773.1366 [M - Br]<sup>+</sup>; found 773.1367. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  = 2116 (C=C), 1679 cm<sup>-1</sup> (C=O).

Bromo((4-formylphenyl)ethynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>( $C \equiv CC_6H_4C(O)H)$ ] (4-C<sub>2</sub>[Pd]Br).  $Pd(PPh_3)_4$  (0.216 g, 0.187 mmol), 4-(bromoethynyl)benzaldehyde (0.039 g, 0.19 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.094 g (59%, 0.11 mmol). Mp with decomposition: 102 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 9.78 (s, 1H; CHO), 7.82-7.65 (m, 12H; o-C<sub>6</sub>H<sub>5</sub>), 7.45-7.31 (m, 20H;  $m,p-C_6H_5$ ,  $m-C_6H_4$ ), 6.21 (d, J(H,H) = 8.0 Hz, 2H;  $o-C_6H_4$ ). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 191.7 (1C; CHO), 135.2 (t, J(C,P) = 6.3 Hz, 12C;  $o - C_6H_5$ ), 134.0 (1C;  $i - C_6H_4$ ), 133.2 (1C;  $p - C_6H_4$ ), 133.  $C_6H_4$ ), 131.5 (t,  $J(C_P) = 25.0$  Hz, 6C;  $i-C_6H_5$ ), 131.1 (2C;  $o-C_6H_4$ ), 130.6 (6C;  $p-C_6H_5$ ), 128.9 (2C;  $m-C_6H_4$ ), 128.2 (t,  $J(C_1P) = 5.3$  Hz, 12C; m-C<sub>6</sub> $\hat{H}_5$ ), 110.8 (d, J(C,P) = 6.7 Hz, 1C; PdC $\equiv C$ ), 108.8 (1C; PdC  $\equiv$  C). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 25.0 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for C<sub>45</sub>H<sub>35</sub>OP<sub>2</sub>Pd 759.1209  $[M - Br]^+$ ; found 759.1199. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  = 2111 (C≡C), 1693 (C=O).

Bromo((4-benzoylphenyl)ethynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>(C $\equiv$ CC<sub>6</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>5</sub>)] (5- $C_2[Pd]Br$ ).  $Pd(PPh_3)_4$  (0.197 g, 0.170 mmol), 4-(bromoethynyl)benzophenone (0.049 g, 0.17 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.117 g (75%, 0.128 mmol). Decomposition: 177 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.82-7.69 (m, 12H; o-PC<sub>6</sub>H<sub>5</sub>), 7.67-7.64 (m, 2H; o-C<sub>6</sub>H<sub>5</sub>), 7.56-7.51 (m, 1H; p-C<sub>6</sub>H<sub>5</sub>), 7.46-7.33 (m, 22H; m,p-PC<sub>6</sub>H<sub>5</sub>, m-C<sub>6</sub>H<sub>5</sub>, m- $C_6H_4$ ), 6.17 (d, J(H,H) = 8.2 Hz, 2H;  $o-C_6H_4$ ).<sup>13</sup>C NMR (126 MHz,  $CDCl_{3}$ , 77.2 ppm):  $\delta$  = 196.3 (1C; CO), 138.2 (1C; *i*-C<sub>6</sub>H<sub>5</sub>), 135.2 (t,  $J(C,P) = 6.3 \text{ Hz}, 12C; o-PC_6H_5), 134.0 (1C; p-C_6H_4), 132.1 (1C; p-C_6H_4)$  $C_6H_5$ , 131.6 (t, J(C,P) = 25.1 Hz, 6C; *i*-PC<sub>6</sub>H<sub>5</sub>), 130.5 (6C; *p*-PC<sub>6</sub>H<sub>5</sub>), 130.4 (2C; o-C<sub>6</sub>H<sub>4</sub>), 129.9 (2C; o-C<sub>6</sub>H<sub>5</sub>), 129.6 (2C; m- $C_6H_4$ ), 128.6 (1C; *i*- $C_6H_4$ ), 128.3 (2C; *m*- $C_6H_5$ ), 128.2 (t, *J*(C,P) = 5.3 Hz, 12C; m-PC<sub>6</sub>H<sub>5</sub>), 110.8 (t, J(C,P) = 6.8 Hz, 1C; PdC $\equiv C$ ), 108.8 (t, J(C,P) = 14.3 Hz, 1C; PdC=C). <sup>31</sup>P NMR (203 MHz,  $CDCl_{3}$ , external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 25.0 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for C<sub>51</sub>H<sub>39</sub>OP<sub>2</sub>Pd 835.1523 [M – Br]<sup>+</sup>; found 835.1518. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2114$  (C $\equiv$ C), 1657 (C $\equiv$ O).

Bromo((4-cyanophenyl)butadiynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>(( $C \equiv C$ )<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN)] (1-C<sub>4</sub>[Pd]Br).  $Pd(PPh_3)_4$  (0.225 g, 0.195 mmol), 4-(bromobutadiynyl)benzonitrile (0.045 g, 0.196 mmol), and DCM (15 mL) were reacted according to the general procedure. Yield: 0.157 g (93%, 0.182 mmol). Decomposition: 206 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm): δ = 7.75-7.69 (m, 12H; o-C<sub>6</sub>H<sub>5</sub>), 7.46 (d, J(H,H) = 8.6 Hz, 2H; m- $C_6H_4$ ), 7.44–7.37 (m, 18H; m,p- $C_6H_5$ ), 7.22 (d, J(H,H) = 8.6 Hz, 2H;  $o-C_6H_4$ ). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 135.2 (t,  $J(C,P) = 6.3 \text{ Hz}, 12\text{C}; o-C_6\text{H}_5), 132.5 (2\text{C}; m-C_6\text{H}_4), 131.9 (2\text{C}; o-C_6\text{H}_5), 132.5 (2\text{C}; m-C_6\text{H}_4), 131.9 (2\text{C}; o-C_6\text{H}_5), 132.5 (2\text{C}; m-C_6\text{H}_5), 132.5 (2\text{C};$  $C_6H_4$ ), 131.0 (t,  $J(C_1P) = 25.0$  Hz, 6C;  $i-C_6H_5$ ), 130.7 (6C;  $p-C_6H_5$ ), 129.4 (1C; *i*-C<sub>6</sub>H<sub>4</sub>), 128.3 (t, J(C,P) = 5.3 Hz, 12C; *m*-C<sub>6</sub>H<sub>5</sub>), 118.9 (1C; CN), 110.5 (1C;  $p-C_6H_4$ ), 107.4 (t, J(C,P) = 14.5 Hz, 1C;  $PdC \equiv CC \equiv C$ ), 92.1 (t, J(C,P) = 7.0 Hz, 1C;  $PdC \equiv CC \equiv C$ ), 82.2 (1C; PdC≡CC≡C), 69.8 (1C; PdC≡CC≡C). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for C<sub>47</sub>H<sub>34</sub>NP<sub>2</sub>Pd 780.1213 [M - Br]<sup>+</sup>; found 780.1202. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2225$  (C $\equiv$ N), 2187 (C $\equiv$ C), 2065 (C $\equiv$ C).

Bromo((4-nitrophenyl)butadiynyl)bis(triphenylphosphine)palladium, *trans*-[PdBr(PPh<sub>3</sub>)<sub>2</sub>(( $C \equiv C_2C_6H_4NO_2$ )] (2-C<sub>4</sub>[Pd]Br). Pd(PPh<sub>3</sub>)<sub>4</sub> (0.230 g, 0.199 mmol), 4-(bromobutadiynyl)nitrobenzene (0.050 g, 2.0 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.144 g (82%, 0.163 mmol). Decomposition: 208 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 8.05 (d, *J*(H,H) = 9.0 Hz, 2H; *o*-C<sub>6</sub>H<sub>4</sub>), 7.76–7.69 (m, 12H; *o*-C<sub>6</sub>H<sub>5</sub>), 7.47–7.36 (m, 18H; *m*,*p*-C<sub>6</sub>H<sub>5</sub>), 7.27 (d, *J*(H,H) = 9.0 Hz, 2H; *m*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 146.4 (1C; *p*-C<sub>6</sub>H<sub>5</sub>), 135.2 (t, *J*(C,P) = 6.2 Hz, 12C; *o*-C<sub>6</sub>H<sub>5</sub>), 132.7 (2C; *o*-C<sub>6</sub>H<sub>5</sub>), 131.6 (1C; *i*-C<sub>6</sub>H<sub>5</sub>), 131.0 (t, *J*(C,P) = 25.2 Hz, 6C; *i*-C<sub>6</sub>H<sub>5</sub>), 130.7 (6C; *p*-C<sub>6</sub>H<sub>5</sub>), 128.3 (t, *J*(C,P) = 5.4 Hz, 12C; *m*-C<sub>6</sub>H<sub>5</sub>), 123.6 (2C; *m*-C<sub>6</sub>H<sub>5</sub>), 108.7 (t, *J*(C,P) = 14.5 Hz, 1C; PdC≡CC≡C), 92.1 (t, *J*(C,P) = 6.8 Hz, 1C; PdC≡CC≡C), 83.4 (1C; PdC≡CC≡C), 69.8 (1C; PdC≡CC≡C). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.4 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): *m*/*z* calcd for C<sub>46</sub>H<sub>34</sub>NO<sub>2</sub>P<sub>2</sub>Pd 800.1111 [M - Br<sup>-</sup>]<sup>+</sup>; found 800.1113. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  = 2187 (C≡C), 2072 (C≡C), 1514 (NO<sub>2</sub>), 1338 (NO<sub>2</sub>).

Bromo((4-acetylphenyl)butadiynyl)bis(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>((C $\equiv$ C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C(O)CH<sub>3</sub>)] (3- $C_4[Pd]Br$ ). Pd(PPh<sub>3</sub>)<sub>4</sub> (0.110 g, 0.095 mmol), 4-(bromobutadiynyl)acetophenone (0.025 g, 0.10 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.073 g (87%, 0.083 mmol). Decomposition: 198 °C. <sup>1</sup>H NMR (600 MHz,  $CDCl_3$ , 7.26 ppm):  $\delta$  = 7.78 (d, J(H,H) = 8.8 Hz, 2H;  $m \cdot C_6H_4$ ), 7.75–7.71 (m, 12H;  $o \cdot C_6H_5$ ), 7.45–7.37 (m, 18H;  $m,p-C_6H_5$ ), 7.24 (d, J(H,H) = 8.8 Hz, 2H; o- $C_6H_4$ ), 2.54 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$ = 191.4 (1C; C(O)CH<sub>3</sub>), 135.6 (1C; C<sub>6</sub>H<sub>4</sub>), 135.2 (t, J(C,P) = 6.3Hz, 12C; o-C<sub>6</sub>H<sub>5</sub>), 132.2 (2C; C<sub>6</sub>H<sub>4</sub>), 131.1 (t, J(C,P) = 25.0 Hz, 6C;  $i-C_6H_5$ , 130.7 (6C;  $p-C_6H_5$ ), 129.4 (1C;  $C_6H_4$ ), 128.2 (t, J(C,P) = 5.4Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 128.1 (2C; C<sub>6</sub>H<sub>4</sub>), 105.9 (t, J(C,P) = 14.5 Hz, 1C;  $PdC \equiv CC \equiv C$ ), 92.4 (t, I(C,P) = 7.0 Hz, 1C;  $PdC \equiv CC \equiv C$ ), 81.2 (1C; PdC≡CC≡C), 70.8 (1C; PdC≡CC≡C), 26.7 (1C; CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): *m/z* calcd for C<sub>48</sub>H<sub>37</sub>OP<sub>2</sub>Pd 797.1366 [M -Br]<sup>+</sup>; found 797.1352. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2184$  (C $\equiv$ C), 2069 (C≡C), 1683 (C=O).

Bromo((4-formylphenyl)butadiynyl)bis-(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>((C $\equiv$ C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C(O)H)] (4-C<sub>4</sub>[Pd]Br). Pd(PPh<sub>3</sub>)<sub>4</sub> (0.120 g, 0.104 mmol), 4-(bromobutadiynyl)benzaldehyde (0.025 g, 0.107 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.089 g (96%, 0.10 mmol). Decomposition: 198 °C. <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ , 7.26 ppm):  $\delta = 9.93$  (s, 1H; CHO), 7.76–7.68 (m, 14H; o- $C_6H_5$ , m- $C_6H_4$ ), 7.46–7.37 (m, 18H; m,p- $C_6H_5$ ), 7.30 (d, J(H,H) = 8.1 Hz, 2H; *o*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (partial, 126 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta = 191.5 (1C; CO), 135.2 (t, J(C,P) = 6.3 Hz, 12C; o-C_6H_5), 134.8$ (1C;  $C_6H_4$ ), 132.6 (2C;  $C_6H_4$ ), 131.1 (t, J(C,P) = 25.0 Hz, 6C; i- $C_6H_5$ ), 130.7 (6C; p- $C_6H_5$ ), 129.5 (2C;  $C_6H_4$ ), 128.3 (t, J(C,P) = 5.4Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 107.0 (t, J(C,P) = 14.4 Hz, 1C; PdC $\equiv$ CC $\equiv$ C), 92.4 (t, J(C,P) = 6.4 Hz, 1C; PdC $\equiv$ CC $\equiv$ C), 82.1 (1C; PdC $\equiv$ CC $\equiv$ C), 70.8 (1C; PdC=CC=C). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for  $C_{47}H_{35}OP_2Pd$  783.1209  $[M - Br]^+$ ; found 783.1197. IR (Nujol mull;  $cm^{-1}$ ):  $\nu = 2184$  (C=C), 2069 (C=C), 1702 (C=O).

Bromo((4-benzoylphenyl)butadiynyl)bis-(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>((C=  $C_{2}C_{6}H_{4}C(O)C_{6}H_{5}$ ] (5- $C_{4}$ [Pd]Br).  $Pd(PPh_{3})_{4}$  (0.185 g, 0.160 mmol), 4-(bromobutadiynyl)acetophenone (0.055 g, 0.178 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.128 g (85%, 0.136 mmol). Decomposition: 156 °C. <sup>1</sup>H NMR (600 MHz,  $CDCl_3$ , 7.26 ppm):  $\delta = 7.76 - 7.70$  (m, 14H;  $o - PC_6H_5$ , o - 7.70 (m, 14H;  $\sigma - PC_6H_5$ ).  $C_6H_5$ ), 7.65 (d, J(H,H) = 8.6 Hz, 2H;  $m-C_6H_4$ ), 7.59–7.55 (m, 1H; p- $C_6H_5$ ), 7.48–7.39 (m, 20H; m,p-PC<sub>6</sub>H<sub>5</sub>, m-C<sub>6</sub>H<sub>5</sub>), 7.27 (d, J(H,H) = 8.6 Hz, 2H;  $o - C_6 H_4$ ). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta =$ 196.0 (1C; CO), 137.8 (1C; p-C<sub>6</sub>H<sub>4</sub>), 136.0 (1C; i-C<sub>6</sub>H<sub>5</sub>), 135.2 (t,  $J(C,P) = 6.3 \text{ Hz}, 12C; o-PC_6H_5), 132.6 (1C; p-C_6H_5), 131.9 (2C; o-PC_6H_5), 132.6 (2C; o-PC_6H_5), 132.6$  $C_6H_4$ ), 131.1 (t,  $J(C_P) = 25.0$  Hz, 6C; *i*-PC<sub>6</sub>H<sub>5</sub>), 130.7 (6C; *p*-PC<sub>6</sub>H<sub>5</sub>), 130.1 (2C; m-C<sub>6</sub>H<sub>4</sub>), 130.0 (2C; o-C<sub>6</sub>H<sub>5</sub>), 128.8 (2C; i- $C_6H_4$ ), 128.5 (1C; m- $C_6H_5$ ), 128.3 (t, J(C,P) = 5.3 Hz, 12C; m- $PC_6H_5$ ), 105.7 (t, J(C,P) = 14.5 Hz, 1C;  $PdC \equiv CC \equiv C$ ), 92.5 (t,  $J(C,P) = 6.8 \text{ Hz}, 1C; PdC \equiv CC \equiv C), 81.0 (1C; PdC \equiv CC \equiv C), 70.9$ (1C; PdC $\equiv$ CC $\equiv$ C). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0

ppm):  $\delta$  = 24.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): *m/z* calcd for C<sub>53</sub>H<sub>39</sub>OP<sub>2</sub>Pd 859.1524 [M - Br]<sup>+</sup>; found 859.1542. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  = 2184 (C $\equiv$ C), 2070 (C $\equiv$ C), 1655 (C=O).

Bromo((4-cyanophenyl)hexatriynyl)bis-(triphenylphosphine)palladium, trans-[PdBr(PPh<sub>3</sub>)<sub>2</sub>((C≡ C)<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN)] (1-C<sub>6</sub>[Pd]Br). Pd(PPh<sub>3</sub>)<sub>4</sub> (0.205 g, 0.177 mmol), 4-(bromohexatriynyl)benzonitrile (0.045 g, 0.177 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.155 g (99%, 0.175 mmol). Decomposition: 207 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 7.72–7.67 (m, 12H; o-C<sub>6</sub>H<sub>5</sub>), 7.53 (d, J(H,H) = 8.4 Hz, 2H;  $m \cdot C_6H_4$ ), 7.48–7.43 (m, 8H;  $p \cdot C_6H_5$ ,  $o \cdot C_6H_4$ ), 7.43–7.38 (m, 12H;  $m \cdot C_6H_5$ ). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 77.2 ppm):  $\delta$  = 135.1 (t, J(C,P) = 6.3 Hz, 12C;  $o-C_6H_5$ ), 133.2 (2C;  $m-C_6H_4$ ), 132.1  $(2C; o-C_6H_4)$ , 130.8 (m, 12C;  $p-C_6H_5$ ,  $i-C_6H_5$ ), 128.3 (t,  $J(C_P) = 5.4$ Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 127.7 (1C; i-C<sub>6</sub>H<sub>4</sub>), 118.6 (1C; CN), 111.8 (1C;  $p-C_6H_4$ ), 105.3 (t, J(C,P) = 14.8 Hz, 1C; PdC=CC=CC=C), 92.3  $(t, J(C,P) = 7.0 \text{ Hz}, 1C; PdC \equiv CC \equiv CC \equiv C), 80.7 (1C; PdC \equiv$  $CC \equiv CC \equiv C$ ), 72.6 (t, J(C,P) = 2.1 Hz, 1C;  $PdC \equiv CC \equiv CC \equiv C$ ), 71.9 (1C; PdC=CC=CC=C), 55.4 (1C; PdC=CC=CC=C). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 24.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): *m/z* calcd for C<sub>49</sub>H<sub>34</sub>NP<sub>2</sub>Pd 804.1213 [M -Br]<sup>+</sup>; found 804.1203. IR (Nujol mull; cm<sup>-1</sup>):  $\nu = 2227$  (C $\equiv$ N), 2163 (C≡C), 2138 (C≡C), 2038 (C≡C).

lodo((4-cyanophenyl)butadiynyl))bis(triphenyphosphine)palladium, trans-[PdI(PPh<sub>3</sub>)<sub>2</sub>((C=C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN)] (1-C<sub>4</sub>[Pd]I). Pd-(PPh<sub>3</sub>)<sub>4</sub> (0.126 g, 0.109 mmol), 4-(iodobutadiynyl)benzonitrile (0.030 g, 0.11 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.097 g (quantitatively, 0.11 mmol). Decomposition: 186 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$ = 7.75-7.70 (m, 12H;  $o-C_6H_5$ ), 7.46-7.37 (m, 20H;  $p,m-C_6H_5$ ,  $o-C_6H_5$ ),  $r-C_6H_5$ ,  $r-C_6H_5$ ,  $r-C_6H_5$ ,  $r-C_6H_5$ ),  $r-C_6H_5$ ,  $r-C_6H_5$ , r-C $C_6H_4$ ), 7.21 (d, J(H,H) = 8.5 Hz, 2H;  $m-C_6H_4$ ). <sup>13</sup>C NMR (151 MHz,  $CDCl_{3}$ , 77.2 ppm):  $\delta$  = 135.2 (t, J(C,P) = 6.3 Hz, 12C; o-C<sub>6</sub>H<sub>5</sub>), 132.5  $(2C; m-C_6H_4)$ , 132.1 (t, J(C,P) = 25.7 Hz, 6C;  $i-C_6H_5$ ), 131.9 (2C;  $o-C_6H_5$ )  $C_6H_4$ ), 130.7 (6C; *p*- $C_6H_5$ ), 129.4 (1C; *i*- $C_6H_4$ ), 128.2 (t, *J*(C,P) = 5.4 Hz, 12C; m-C<sub>6</sub>H<sub>5</sub>), 118.9 (1C; CN), 110.4 (1C; p-C<sub>6</sub>H<sub>4</sub>), 109.6 (t, J(C,P) = 14.2 Hz, 1C; C C C C d), 90.7 (t, J(C,P) = 6.8 Hz, 1C; C≡CC≡CPd), 82.1 (t, J(C,P) = 1.9 Hz, 1C; C≡CC≡CPd), 70.1 ppm (1C; C=CC=CPd). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta$  = 22.3 (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for  $C_{47}H_{34}NP_{2}Pd$  780.1213 [M – I]<sup>+</sup>; found 780.1195. IR (Nujol mull;  $cm^{-1}$ ):  $\nu = 2226$  (C $\equiv$ N), 2184 (C $\equiv$ C), 2062 (C $\equiv$ C).

lodo((4-nitrophenyl)butadiynyl)bis(triphenyphosphine)palladium, trans-[Pdl(PPh<sub>3</sub>)<sub>2</sub>((C=C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)] (2-C<sub>4</sub>[Pd]I). Pd-(PPh<sub>3</sub>)<sub>4</sub> (0.128 g, 0.110 mmol), 4-(iodobutadiynyl)benzonitrile (0.033 g, 0.110 mmol), and DCM (10 mL) were reacted according to the general procedure. Yield: 0.078 g (76%, 0.084 mmol). Decomposition: 197 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 7.26 ppm):  $\delta$  = 8.05 (d, J(H,H)  $= 9.0 \text{ Hz}, 2\text{H}; m-C_6\text{H}_4), 7.75-7.69 \text{ (m, 12H; } o-C_6\text{H}_5), 7.46-7.36 \text{ (m, 12H; } o-C_6\text{H}_5)$ 18H;  $p_{,m}$ -C<sub>6</sub>H<sub>5</sub>), 7.26 (d, J(H,H) = 9.0 Hz, 2H; o-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub> 77.2 ppm):  $\delta$  = 146.4 (1C; p-C<sub>6</sub>H<sub>4</sub>), 135.2 (t,  $J(C,P) = 6.2 \text{ Hz}, 12C; o-C_6H_5), 132.6 (2C; o-C_6H_4), 132.1 (t, J(C,P) =$ 25.7 Hz, 6C; i-C<sub>6</sub>H<sub>5</sub>), 131.6 (1C; i-C<sub>6</sub>H<sub>4</sub>), 130.7 (6C; p-C<sub>6</sub>H<sub>5</sub>), 128.2  $(t, J(C,P) = 5.4 \text{ Hz}, 12\text{C}; m-C_6\text{H}_5), 123.6 (2\text{C}; m-C_6\text{H}_4), 110.8 (t, T)$  $J(C,P) = 14.3 \text{ Hz}, 1C; C \equiv CC \equiv CPd), 90.8 (t, J(C,P) = 6.8 \text{ Hz}, 1C;$ C≡CC≡CPd), 83.3 (t, J(C,P) = 2.5 Hz, 1C; C≡CC≡CPd), 70.0 (1C; C=CC=CPd). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, external H<sub>3</sub>PO<sub>4</sub> 0 ppm):  $\delta = 22.3$  (s, 2P; PPh<sub>3</sub>). HRMS(ESI): m/z calcd for C46H34INO2P2Pd 800.1111 [M - I]+; found 800.1091. IR (Nujol mull; cm<sup>-1</sup>):  $\nu$  =2183 (C=C), 2068 (C=C), 1590 (NO<sub>2</sub>), 1337  $(NO_{2})$ .

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Additional experimental procedures, X-ray crystallography details, and CIF files for  $1-C_2[Pd]Br$ ,  $2-C_2[Pd]Br$ ,  $2-C_4[Pd]Br$ ,  $3-C_4[Pd]Br$ ), and  $1-C_6[Pd]Br$ , and copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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