Mono- and Dipalladium Movement on the π-Conjugated Five-Carbon Chain

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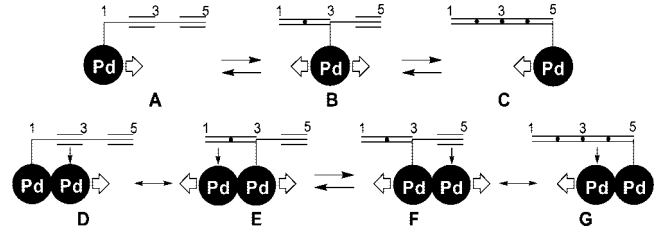
We prepared new mono- and dipalladium complexes containing a highly conjugated pentadiynyl ligand where the palladium movement to the C5 position with the bonding rearrangement provided the first cumulenyl-type complexes.

Introduction

The 1,3-metal shift on an allyl, a propargyl, and an allenyl ligand is very common for both transition metals and typical metals.[1] Usually, the metal moves reversibly on three carbons and the position of the metal is governed by the thermodynamic stability of the complex. We reported the synthesis of mono- and dinuclear palladium complexes containing a propargyl/allenyl ligand.[2] Dinuclear complexes reveal the unique μ-η^3-coordination of the Pd−Pd unit to three carbons. In an extension of these studies, we focused on the metal dynamics of the more expanded sp-hybridized polyyne system pentadiyne.[3] In this system metal movements of a longer distance (**A**−**C**) as well as novel dimetal movements (**D**−**G**) are possible, which may be referred to as metal trains on a rail such as those found in new switchable-type devices (Chart 1).[4] Notably, Pd movement to the C5 position with the bonding rearrangement may afford first cumulenyl-type complexes **C** and **G**. Herein, we report the synthesis of palladium complexes bearing a pentadiynyl ligand and the controlling of the palladium movement on the π-conjugated five-carbon chain.

Chart 1. Palladium Movements on Five-Carbon Chain



Results and Discussion

The reactions of pentadiynyl halide **1a** with $Pd(PPh_3)_2$ complex generated from 0.5 equiv of $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) and 2 equiv of PPh_3 in $CDCl_3$ at room temperature gave a mixture of complexes η^1-(penta-2,4-diyn-1-yl)- and η^1-(penta-1,2-dien-4-yn-3-yl)palladium (**2a**, **3a**) in a ratio of 44:56 (Table 1, entry 1). Elemental analysis on the mixture shows that the expected composition and NMR spectral data of **2a** and **3a** are very close to those of the reported η^1-propargyl- and η^1-allenylpalladium complexes.[2a,5] To the best of our knowledge, reported η^1-pentadiynyl transition-metal complexes have been limited to Mo and Fe, where 1,3-metal shift on the diynyl ligand has not been observed.[6] Similarly bromide analogues **2b** and **3b** were obtained (entry 2). In contrast, the methyl-substituted pentadiynyl chlorides **1c** or **1d** afforded only η^1-(penta-1,2-dien-4-yn-3-yl)palladium **3c** or **3d** quantitatively (entries 3 and 4). Further isomerization to the cumulenyl-type complexes **4** did not occur even at 50 °C in $CDCl_3$ for 12 h. The structure of **3a** was confirmed by X-ray crystallography (Figure 1). X-ray study shows that the five carbons in the allenyl-yne unit and the terminal phenyl ring in complex **3a** exist approximately on one plane, which suggests the presence of an extended π orbital at the C2−C11 moiety.

The reaction of **1a** or **1d** with 2 equiv of $Pd(PPh_3)$ complex generated from 1 equiv of $Pd_2(dba)_3$ and 2 equiv of PPh_3 in $CDCl_3$ at room temperature gave dipalladium complex **5a** or **5d** as the sole product (Scheme 1). The structure of **5d** was confirmed by X-ray crystallography (Figure 2). The spectral data are completely consistent with those of the reported μ-η^3-propargyl/allenyldipalladium complexes.[2c] These palladium complexes did not isomerize to the cumulenyl complexes **6** even at 50 °C in $CDCl_3$ for 12 h.

For attaining the coordination of the C5 atom to the palladium unit, the steric repulsion between the substituent at the acetylene

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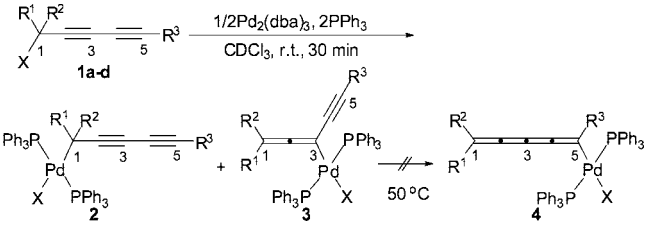
Table 1. Reaction of Pentadiynyl Halides with $Pd(PPh_3)_2$



entry	**1**	R^1	R^2	R^3	X	yield (%)[a]	complex	**2**	:	**3**	:	**4**
1	**1a**	H	H	Ph	Cl	77	**2a** + **3a**	44	:	56	:	0
2	**1b**	H	H	Ph	Br	74	**2b** + **3b**	46	:	54	:	0
3	**1c**	Me	H	Ph	Cl	quant.	**3c**	0	:	100	:	0
4	**1d**	Me	Me	TES[b]	Cl	quant.	**3d**	0	:	100	:	0

[a] Determined by ^{1}H NMR spectroscopy. [b] TES = Et_3Si.

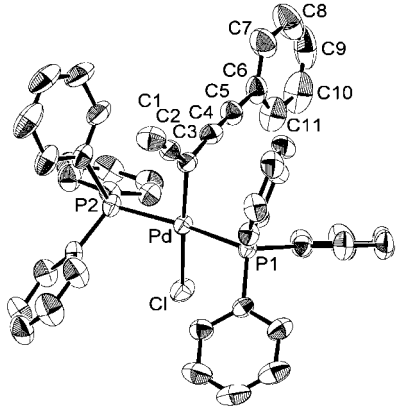
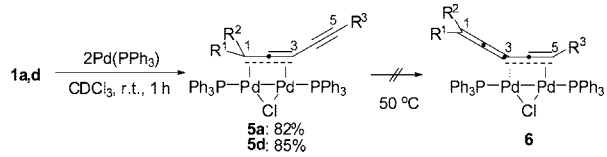


Figure 1. Molecular structure of **3a** drawn with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−C(2) = 1.312(9), C(2)−C(3) = 1.286(7), C(3)−C(4) = 1.430(8), C(4)−C(5) = 1.199(9), C(3)−Pd = 2.025(4), C(1)−C(2)−C(3) = 178.9(6), C(2)−C(3)−C(4) = 126.4(4), C(3)−C(4)−C(5) = 174.5(5).

Scheme 1. Reaction of Pentadiynyl Chlorides with $2Pd(PPh_3)$



terminal and the phosphine Ph group seems too large, so we planned to reduce the steric repulsion in order to cause the Pd unit to migrate. However no diynyl halide without protection at the acetylene terminal is available due to its low stability. Thus we first prepared the triethylsilyl (TES)-protected complex **5d** from the comparably stable **1d**[7] and then examined the desilylation to reduce the steric repulsion. We found that the treatment of silyl-substituted propargyl/allenyldipalladium complex **5e**[2c] with silica gel provided the desilylated complex **5e-H** (Scheme 2). However TES group of **5d** could not be removed under similar conditions.

More surprisingly, when we treated **5d** with HCl (generated from a reaction of H_2O with Me_3SiCl *in situ*), desilylation reaction did not take place, but an unexpected product **7** from triprotonation at the C2 and C5 carbons was obtained (Scheme 3). Unfortunately, reaction intermediates were not detected even

(7) Triethylsilyl-protected pentadiynyl alcohol, which is a pre-material of **1d**, was prepared according to the literature procedure; see: Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002**, *67*, 6841–6844.

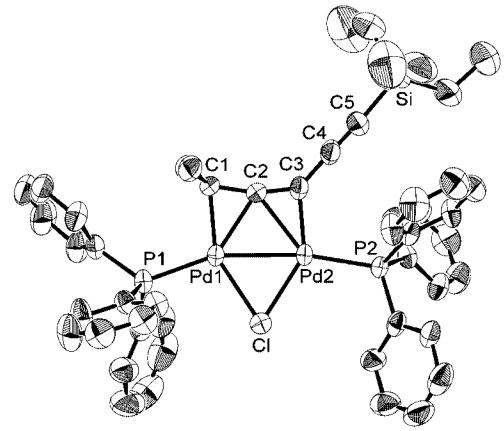
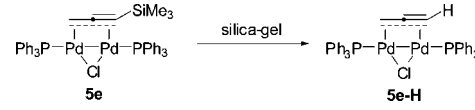


Figure 2. Molecular structure of **5d** drawn with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−C(2) = 1.408(9), C(2)−C(3) = 1.274(9), C(3)−C(4) = 1.419(10), C(4)−C(5) = 1.177(11), Pd(1)−Pd(2) = 2.6443(5), Pd(1)−C(1) = 2.083(6), Pd(1)−C(2) = 2.229(7), Pd(2)−C(2) = 2.339(6), Pd(2)−C(3) = 2.000(6), C(1)−C(2)−C(3) = 165.2(7).

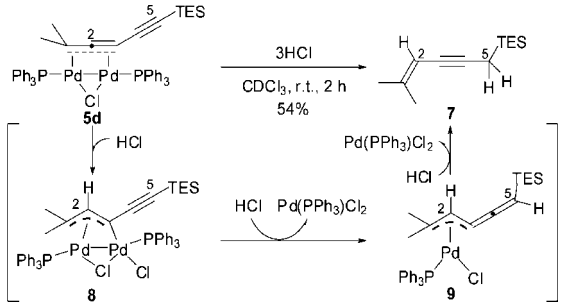
Scheme 2. Desilylation of 5e with Silica Gel



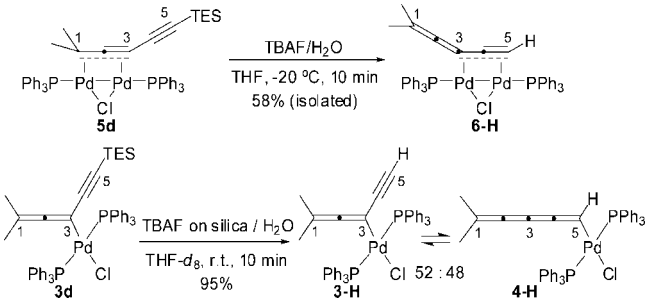
when smaller amounts of HCl were added. We previously found that the protonation of μ-η^3-propargyl/allenyldipalladium with HCl gave μ-vinylcarbenedipalladium,[2c] so the corresponding complex **8** may be produced first. A second protonation may occur at the C5 carbon to give η^3-allylmonopalladium **9**, followed by protonation again at the C5 carbon to provide **7**. The reaction of **3d** with HCl produced the dien-yne compound (Me_2C═C═CHC≡CTES). Therefore the triprotonation is based on the dipalladium coordination.

Finally, the TES group could be removed by adding tetrabutylammonium fluoride (TBAF) (Scheme 4). In the reaction of **5d** the ^{1}H NMR spectrum shows a new double-doublet signal at 5.93 ppm with 31.5 and 2.8 Hz coupling constants (J_{HP}), which is very close to the methyne proton signal of the reported μ-η^3-propargyl/allenyldipalladium complex **5e-H**.[2c] The P−P coupling constant is extremely large (74.4 Hz), which indicates that the four atoms P−Pd−Pd−P exist almost in a straight line.[2c] In ^{13}C NMR C−P couplings are observed on three signals at 73.00, 76.98, and 87.37 ppm, which are assigned to the μ-η^3-coodinating carbons, while a free cumulenyl carbon (C2) observed at 187.68 ppm also shows a C−P coupling. The methyl

Scheme 3. Reaction of 5d with HCl



Scheme 4. Desilylation of 5d and 3d Using TBAF



proton and carbon resonances of **5d** have phosphorus couplings: ^{1}H NMR δ 1.08 (d, $^4J_{HP}$ = 4.3 Hz, $(CH_3)_2CCC$); ^{13}C NMR δ 25.38 (d, $^3J_{CP}$ = 4.8 Hz, $(CH_3)_2CCC$). For **6-H** the corresponding phosphorus couplings disappear. These spectral data and elemental analysis may correspond with a novel cumulenyldipalladium complex, **6-H**. Other isomers were not observed in this reaction, so the Pd−Pd unit might move on the five-carbon unit as soon as the silyl-stopper is taken off. On the contrary, the similar desilylation reaction of **3d** gave the mixture of dien-yn-yl complex **3-H** and tetraenyl complex **4-H**, which is the first example of η^1-cumulenyl metal complexes (**3-H**:**4-H** = 52:48). These complexes gradually decompose in a solution without changing the ratio, which indicates that monopalladium moves reversibly between the C3 and C5 carbons. 1,3-Metal shift on the propargyl/allenyl transition-metal complexes has been discussed including the mechanistic aspects in both metal complexes[8] and catalytic reactions.[9] To the best of our knowledge, this is the first report of the dimetal movement on a five-carbon unit, so-called (1–3),(3–5)-dimetal shift.

In conclusion, we prepared new mono- and dipalladium complexes containing a pentadiynyl ligand and found palladium movement on the conjugated five-carbon unit.

Experimental Section

General Procedures. Most of the commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry N_2 by use of standard vacuum line techniques. ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer. The H and C contents were determined from an elemental analysis using a Perkin-Elmer 2900II CHNS/O analyzer. Melting points were determined on a Yanaco MP-500D micro melting point apparatus. 5-Phenylpenta-2,4-diyn-1-ol[10] and 6-phenylhexa-3,5-diyn-2-ol[11] were prepared according to the published methods.

Preparation of (5-Chloropenta-1,3-diynyl)benzene/ClCH$_2$C≡CC≡CPh (1a). To a solution of 1.00 g (6.40 mmol) of 5-phenylpenta-2,4-diyn-1-ol and 1.70 g (6.48 mmol) of Ph_3P in 300 mL of dry THF was added 0.855 g (6.40 mmol) of NCS under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. The mixture was diluted with hexane and passed through a pad of silica gel to remove the precipitated Ph_3PO. The obtained residue was purified by a silica gel column (silica gel 60N, hexane/Et_2O, 9:1) to give 860 mg (77% isolated yield) of **1a** as a yellow oil. HRMS calcd for $C_{11}H_7Cl$: 174.0236. Found: 174.0228. ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 4.29 (s, 2H), 7.33 (dd, $^3J_{HH}$ = 7.3 Hz, 7.3 Hz, 2H), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.50 (d, $^3J_{HH}$ = 7.3 Hz, 2H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 30.8, 71.0, 72.9, 76.5, 79.5, 121.1, 128.4, 129.5, 132.6.

Preparation of (5-Bromopenta-1,3-diynyl)benzene/BrCH$_2$C≡CC≡CPh (1b). Bromination of 5-phenylpenta-2,4-diyn-1-ol using NBS gave **1b** (69% isolated yield, yellow oil). HRMS calcd for $C_{11}H_7Br$: 217.9731. Found: 217.9605. ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 4.06 (s, 2H), 7.34 (dd, $^3J_{HH}$ = 7.3 Hz, 7.3 Hz, 2H), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 7.3 Hz, 2H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 14.6, 71.3, 73.1, 76.8, 79.8, 121.0, 128.3, 129.4, 132.5.

Preparation of (5-Chlorohexa-1,3-diynyl)benzene/ClCH(Me)C≡CC≡CPh (1c). Chlorination of 6-phenylhexa-3,5-diyn-2-ol gave **1c** (70% isolated yield, yellow oil). HRMS Calcd for $C_{12}H_9Cl$: 188.0393. Found: 188.0395. ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 1.83 (d,$^3J_{HH}$ = 6.8 Hz, 3H), 4.80 (q, $^3J_{HH}$ = 6.8 Hz, 1H), 7.36 (dd, $^3J_{HH}$ = 7.3 Hz, 7.3 Hz, 2H), 7.41 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.52 (d, $^2J_{HH}$ = 7.3 Hz, 2H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 26.1, 44.0, 70.0, 72.8, 80.0, 80.7, 121.1, 128.4, 129.5, 132.6.

Preparation of (5-Chloro-5-methylhexa-1,3-diynyl)triethylsilane/ClCMe$_2$C≡CC≡CSiEt$_3$ (1d). The preparation of **1d** was carried out similarly to the literature procedure.[12] CuCl (0.10 g, 1.01 mmol) was added to a 30% *n*-$BuNH_2$ (42.1 mL) aqueous solution at room temperature, which resulted in the formation of a blue solution immediately. A few crystals of hydroxylamine hydrochloride were added to discharge the blue color. Triethyl(ethynyl)silane (8.5 g, 60.6 mmol) was added to the solution at room temperature, forming a yellow acetylide suspension, which was immediately cooled with an ice–water mixture. 1-Bromo-3-chloro-3-methylbut-1-yne (9.19 g, 50.5 mmol) was added at once, and the ice bath was removed. More crystals of hydroxylamine hydrochloride were added throughout the reaction as necessary to prevent the solution from turning blue. After several additions of hydroxylamine hydrochloride crystals, the reaction mixture had a rusty color. After 30 min, the reaction was complete according to TLC. The product was repeatedly extracted with diethyl ether, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product could be purified by a silica gel column (silica gel 60N, hexane only) to give 5.91 g (49% isolated yield) of **1d** as a colorless oil. HRMS calcd for $C_{13}H_{21}ClSi$: 240.1101. Found: 240.1102. ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 0.62 (q, $^3J_{HH}$ = 7.9 Hz, 6H), 0.99 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 1.86 (s, 6H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 4.1, 7.3, 34.3, 57.4, 69.0, 78.3, 87.7, 87.8.

Preparation of η^1-(Penta-2,4-diyn-1-yl)palladium Complex/(PPh$_3$)$_2$ClPdCH$_2$C≡CC≡CPh (2a) and η^1-(Penta-1,2-dien-4-yn-3-yl)palladium Complex/[CH$_2$=C=C(C≡CPh)]PdCl(PPh$_3$)$_2$ (3a). To a dry THF solution (50 mL) of 772 mg (0.668 mmol) of $Pd(PPh_3)_4$ was added 129 mg (0.739 mmol) of (5-chloropenta-1,3-diynyl)benzene **1a** under nitrogen atmosphere. After 15 min at room temperature, the volume of the solvent was reduced to half by a rotary evaporator. After the addition of 600 mL of pentane, the

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yellow precipitate obtained was collected on a glass filter and washed with diethyl ether and pentane. The yellow mixture of **2a** and **3a** was dried under vacuum in 69% isolated yield (369 mg). In the case of the NMR study, to a $CDCl_3$ solution (0.6 mL) of 3.5 mg (0.020 mmol) of diynylchloride **1a** were added 10.4 mg (0.010 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ and 10.5 mg (0.040 mmol) of PPh_3 under nitrogen atmosphere. The reaction was monitored by ^1H and ^{31}P NMR. After 30 min at room temperature, **2a** and **3a** were yielded (77%, **2a**:**3a** = 44:56); mp 148.8–151.5 °C (dec). Anal. Calcd for $C_{47}H_{37}ClP_2Pd \cdot CH_2Cl_2$: C 64.79, H 4.41. Found: C 64.53, H 4.39. **2a**: ^1H NMR (500.16 MHz, $CDCl_3$) δ 1.32 (t, $^3J_{HP}$ = 6.4 Hz, 2H), 7.32–7.38 (m, 9H), 7.40–7.46 (m, 14H), 7.77–7.82 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 26.9 (s). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 5.71, 70.0, 83.5 (t, $^3J_{CP}$ = 2.5 Hz), 94.3, 124.9. **3a**: ^1H NMR (500.16 MHz, $CDCl_3$) δ 3.31 (t, $^5J_{HP}$ = 2.8 Hz, 2H), 6.96–6.99 (m, 2H), 7.18–7.21 (m, 3H), 7.32–7.38 (m, 6H), 7.40–7.46 (m, 12H), 7.77–7.82 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 23.1 (s). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 67.1, 86.4 (t, $^3J_{CP}$ = 2.4 Hz), 88.7, 123.3, 205.4 (t, $^3J_{CP}$ = 4.1 Hz). Crystal data for **3a**: M = 890.54, yellow, monoclinic, a = 12.987(4) Å, b =17.217(5) Å, c = 19.018(5) Å, α = 90.0000°, β = 100.673(11)°, γ = 90.0000°, V = 4179(2) Å^3, Z = 4, D_{calcd} = 1.415 g/cm^3, T = 243.1 K, $R(R_w)$ = 0.0682 (0.0829), CCDC file number 281584.

η^1-(Penta-2,4-diyn-1-yl)palladium Complex/$(PPh_3)_2BrPd$-$CH_2C{\equiv}CC{\equiv}CPh$ (2b) and η^1-(Penta-1,2-dien-4-yn-3-yl)palladium Complex/$[CH_2{=}C{=}C(C{\equiv}CPh)]PdBr(PPh_3)_2$ (3b): 71% isolated yield (74% NMR yield, **2b**:**3b** = 46:54); mp 137.8–139.4 °C (dec). Anal. Calcd for $C_{47}H_{37}BrP_2Pd$: C 66.41, H 4.39. Found: C 66.56, H 4.55. **2b**: ^1H NMR (500.16 MHz, $CDCl_3$) δ 1.51 (t, $^3J_{HP}$ = 5.9 Hz, 2H), 7.28–7.57 (m, 23H), 7.65–7.81 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 26.8 (s). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 8.77, 70.7, 86.0, 94.8, 124.9. **3b**: ^1H NMR (500.16 MHz, $CDCl_3$) δ 3.37 (t, $^5J_{HP}$ = 2.8 Hz, 2H), 6.96–6.98 (m, 2H), 7.17–7.22 (m, 3H), 7.28–7.57 (m, 18H), 7.65–7.81 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 23.1 (s). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 67.2, 86.1, 88.3, 123.3, 205.2 (t, $^3J_{CP}$ = 4.9 Hz).

η^1-(Penta-1,2-dien-4-yn-3-yl)palladium Complex/$[MeCH{=}C{=}C(C{\equiv}CPh)]PdCl(PPh_3)_2$ (3c): 72% isolated yield (>99% NMR yield); mp 145.1–147.6 °C (dec). Anal. Calcd for $C_{48}H_{39}ClP_2Pd$: C 70.34, H 4.80. Found: C 70.36, H 4.81. ^1H NMR (500.16 MHz, $CDCl_3$): δ 0.87 (d, $^3J_{HH}$ = 7.0 Hz, 3H), 3.86 (q, $^3J_{HH}$ = 7.0 Hz, 1H), 6.93–6.96 (m, 2H), 7.16–7.20 (m, 3H), 7.34–7.44 (m, 12H), 7.61–7.65 (m, 6H), 7.77–7.81 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 20.0 (brs), 20.4 (brs). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 12.4, 79.9, 82.6, 87.3, 93.2, 202.7 (t, $^3J_{CP}$ = 3.9 Hz).

η^1-(Penta-1,2-dien-4-yn-3-yl)palladium Complex/$[Me_2C{=}C{=}C(C{\equiv}CSiEt_3)]PdCl(PPh_3)_2$ (3d): 73% isolated yield (>99% NMR yield); mp 141.2–143.9 °C (dec). Anal. Calcd for $C_{49}H_{51}ClP_2PdSi$: C 67.50, H 5.90. Found: C 67.45, H 5.87. ^1H NMR (500.16 MHz, $CDCl_3$): δ 0.86 (t, $^3J_{HH}$ = 7.8 Hz, 9H), 0.71 (s, 6H), 0.40 (q, $^3J_{HH}$ = 7.8 Hz, 6H), 7.33–7.41 (m, 18H), 7.71–7.76 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 21.34 (s). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 4.5, 7.6, 18.9, 79.5, 91.2, 95.6, 104.4 (t, $^4J_{CP}$ = 3.4 Hz), 200.0 (t, $^3J_{CP}$ = 3.8 Hz).

Preparation of Ph-Ethynyl-Dipalladium Complex/$(PPh_3)_2$-$ClPd_2[CH_2CC(C{\equiv}CPh)]$ (5a). To a dry CH_2Cl_2 solution (5.0 mL) of 120 mg (0.116 mmol) of $Pd_2(dba)_3CHCl_3$ and 68.7 mg (0.262 mmol) of PPh_3 was added 22.0 mg (0.126 mmol) of diynylchloride **1a** under nitrogen atmosphere. After 1 h at room temperature, the reaction mixture was purified by a silica gel column (Wakogel C-200, CH_2Cl_2, R_f = 0.83), and the first yellow-orange eluent was concentrated to give **5a** (58.8 mg) in 56% isolated yield. The same reaction was carried out in an NMR tube (82% NMR yield, after 1 h); mp 166.4–167.5 °C (dec). Anal. Calcd for $C_{47}H_{37}ClP_2Pd_2 \cdot 2/3CH_2Cl_2$: C 60.83, H 4.11. Found: C 60.83, H 4.13. ^1H NMR (500.16 MHz, $CDCl_3$): δ 2.18 (d, $^3J_{HP}$ = 5.5 Hz, 2H), 6.77 (d, $^2J_{HH}$ = 7.3 Hz, 2H), 7.09 (dd, $^2J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 7.3 Hz, 2H), 7.16 (t, $^2J_{HH}$ = 7.3 Hz, 1H), 7.30–7.37 (m, 9H), 7.39–7.43 (m, 9H), 7.63–7.71 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 27.7 (d, $^3J_{PP}$ = 83.0 Hz), 32.1 (d, $^3J_{PP}$ = 83.0 Hz). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 9.34 (d, $^2J_{CP}$ = 2.5 Hz), 81.3 (d, $^3J_{CP}$ = 19.9 Hz), 98.6 (d, $^2J_{CP}$ = 1.7 Hz), 109.6 (dd, $^{2,2}J_{CP}$ = 12.4, 3.3 Hz), 123.8.

TES-Ethynyl-Dipalladium Complex/$(PPh_3)_2ClPd_2[Me_2CCC$-$(C{\equiv}CSiEt_3)]$ (5d): 61% isolated yield (85% NMR yield); mp 160.3–166.9 °C (dec). Anal. Calcd for $C_{49}H_{51}ClP_2Pd_2Si$: C 60.16, H 5.25. Found: C 60.19, H 5.16. ^1H NMR (500.16 MHz, $CDCl_3$): δ 0.29 (q, $^3J_{HH}$ = 7.8 Hz, 6H), 0.73 (t, $^3J_{HH}$ = 7.8 Hz, 9H), 1.08 (d, $^4J_{HP}$ = 4.3 Hz, 6H), 7.33–7.39 (m, 18H), 7.64–7.73 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 25.27 (d, $^3J_{PP}$ = 60.5 Hz), 33.64 (d, $^3J_{PP}$ = 60.5 Hz). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 4.06, 7.38, 25.38 (d, $^3J_{CP}$ = 4.8 Hz), 34.47, 79.37, 97.20 (d, $^2J_{CP}$ = 18.23 Hz), 104.38, 110.54 (dd, $^{2,2}J_{CP}$ = 16.79, 8.16 Hz). Crystal data for **5d**: M = 978.23, yellow, triclinic, a = 9.161(4) Å, b =15.238(6) Å, c = 18.554(9) Å, α = 94.636(18)°, β = 97.931(18)°, γ = 91.766(15)°, V = 2554.8(19) Å^3, Z = 2, D_{calcd} = 1.272 g/cm^3, T = 296.1 K, $R(R_w)$ = 0.0775 (0.0652), CCDC file number 281585.

Reaction of 5d with HCl. To a solution of 9.8 mg (0.010 mmol) of **5d** in 0.6 mL of $CDCl_3$ were added ca. 1 μL of H_2O and 3.8 mg (0.035 mmol) of $(CH_3)_3SiCl$ under nitrogen atmosphere. The mixture changed to a yellow suspension within 10 min. The reaction was monitored by ^1H and ^{31}P NMR. After 2 h at room temperature, ene-yne compound **7** was yielded (54%). HRMS calcd for $C_{13}H_{24}Si$: 208.1647. Found: 208.1646. ^1H NMR (500.16 MHz, $CDCl_3$): δ 0.64 (q, $^3J_{HH}$ = 7.9 Hz, 6H), 0.97 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 1.64 (d, $^5J_{HH}$ = 1.8 Hz, 2H), 1.76 (s, 3H), 1.85 (s, 3H), 5.23–5.22 (m, 1H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 2.67, 3.18, 7.28, 20.60, 24.56, 89.76, 106.07, 106.11, 145.21.

Reaction of 3d with HCl. To a solution of 8.7 mg (0.010 mmol) of **3d** in 0.6 mL of $CDCl_3$ were added ca. 1 μL of H_2O and 1.2 mg (0.011 mmol) of $(CH_3)_3SiCl$ under nitrogen atmosphere. The mixture changed to a yellow suspension within 10 min. The reaction was monitored by ^1H and ^{31}P NMR. After 30 min at room temperature, a diene-yne compound was yielded (89%). HRMS calcd for $C_{13}H_{22}Si$: 206.1491. Found: 206.1490. ^1H NMR (500.16 MHz, $CDCl_3$): δ 0.66 (q, $^3J_{HH}$ = 7.9 Hz, 6H), 0.98 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 1.88 (d, $^5J_{HH}$ = 3.1 Hz, 6H), 5.64 (sept, $^5J_{HH}$ = 3.1 Hz, 1H).

Desilylation of 5d with TBAF. A 50 mL three-necked flask equipped with a magnetic bar was charged with 97.8 mg (0.100 mmol) of **5d** and 20.0 mL of THF. The flask was degassed with nitrogen and placed into a cooling bath at −40 °C. After the solution was stirred vigorously for 5 min, 110 μL (0.110 mmol) of TBAF (in 1 M THF) was added to it, and the temperature was allowed to rise at −20 °C (it took 30 min). Then 2.0 mL of H_2O was added dropwise to the solution, and the resulting mixture was stirred for 10 min at −20 °C. The reaction mixture was extracted with CH_2Cl_2, and the combined organic layers were washed with brine and dried over anhydrous Mg_2SO_4. Removal of the solvents under vacuum afforded a residue that was chromatographed on silica gel (Wakogel C200) with benzene; **6-H** was yielded (58%). In the case of the NMR study, to a solution of 4.9 mg (0.0050 mmol) of **5d** in 0.5 mL of THF-d_8 was added 4.4 mg (0.0055 mmol) of TBAF (on silica gel, 1.0–1.5 mmol F/g resin) under nitrogen atmosphere. The reaction was monitored by ^1H and ^{31}P NMR. After 30 min at room temperature, **6-H** was yielded (62%); mp 129.7–132.0 °C (dec). Anal. Calcd for $C_{43}H_{37}ClP_2Pd_2$: C 59.78, H 4.32. Found: C 59.76, H 4.38. ^1H NMR (500.16 MHz, $CDCl_3$): δ 1.13 (s, 6H), 5.93 (dd, $^{3,4}J_{HP}$ = 31.5, 2.8 Hz, 1H), 7.34–7.42 (m, 18H), 7.56–7.63 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 31.24 (d, $^3J_{PP}$ = 74.4 Hz), 32.66 (d, $^3J_{PP}$ = 74.4 Hz). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 18.75, 73.00 (d, $^2J_{CP}$ = 3.8 Hz), 76.98 (dd, $^{2,2}J_{CP}$ = 8.6, 4.8 Hz), 87.37 (dd, $^{2,3}J_{CP}$ = 6.2, 6.2 Hz), 99.01, 187.68 (d, $^3J_{CP}$ = 13.4 Hz).

Desilylation of 3d with TBAF. A 5 mL two-necked flask equipped with a magnetic bar was charged with 43.6 mg (0.050 mmol) of **3d** and 1.0 mL of THF. The flask was degassed with nitrogen. After the solution was stirred vigorously for 20 min, 80.0 mg (0.080–0.12 mmol) of TBAF (on silica gel, 1.0–1.5 mmol F/g resin) under nitrogen atmosphere was added to it. Then 0.1 mL of H_2O was added to the solution. The reaction mixture was filtered and added to pentane (200 mL) to give a light brown precipitate. After washing with diethyl ether and pentane, the precipitate was dried under vacuum to give a mixture of complexes **3-H** and **4-H** (3.8 mg, 10%). Because of their instability, complexes **3-H** and **4-H** could be characterized only spectroscopically. In the case of the NMR study, to a solution of 43.6 mg (0.050 mmol) of **3d** in 0.5 mL of THF-d_8 was added 80.0 mg (0.080–0.12 mmol) of TBAF (on silica gel, 1.0–1.5 mmol F/g resin) under nitrogen atmosphere. The reaction was monitored by ^{1}H and ^{31}P NMR. After 10 min at room temperature, **3-H** and **4-H** were yielded (95%) in a ratio of 52:48; mp 121.7–124.3 °C (dec). **3-H**: ^{1}H NMR (500.16 MHz, THF-d_8) δ 0.8 (s, 6H), 3.0 (s, 1H), 7.30–7.39 (m, 18H), 7.68–7.77 (m, 12H). ^{31}P NMR (202.46 MHz, THF-d_8): δ 19.0 (s). ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 0.8 (s, 6H), 2.7 (s, 1H), 7.34–7.41 (m, 18H), 7.65–7.77 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 22.6 (s). **4-H**: ^{1}H NMR (500.16 MHz, THF-d_8) δ 1.7 (s, 6H), 5.6 (brs, 1H), 7.30–7.39 (m, 18H), 7.68–7.77 (m, 12H). ^{31}P NMR (202.46 MHz, THF-d_8): δ 19.1 (s). ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 1.7 (s, 6H), 5.6 (m, 1H), 7.34–7.41 (m, 18H), 7.65–7.77 (m, 12H). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 22.7 (s).

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Supporting Information Available: Cif files giving X-ray crystallographic data and PXRD patterns for complexes **3a** and **5d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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