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Synthesis of the First Stable Palladium Allenylidene Complexes

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Oxidative addition of $BrC{\equiv}CC(=O)NR_2$ to $[Pd(PPh_3)_4]$ affords the *trans*-alkynylbromopalladium complexes *trans*-$[Br(PPh_3)_2Pd{-}C{\equiv}CC(=O)NR_2]$ ($NR_2 = NMe_2$ (**2a**), $N(CH_2)_4$) (**2b**)). Subsequent reaction of **2a**,**b** with P^iPr_3 in excess gives *trans*-$[Br(P^iPr_3)_2Pd{-}C{\equiv}CC(=O)NR_2]$ (**5a**,**b**). The analogous reaction of **2b** with $P(C_6H_4OMe\text{-}4)_3$ gives *trans*-$[Br(P\{C_6H_4OMe\text{-}4\}_3)_2Pd{-}C{\equiv}CC(=O)NR_2]$ (**7b**), and that of **2a** with trifluoroacetate gives *trans*-$[(F_3CCOO)(PPh_3)_2Pd{-}C{\equiv}CC(=O)NMe_2]$ (**9a**). Methylation of **2a**,**b**, **7b**, and **9a** with either MeOTf or $[Me_3O]BF_4$ and ethylation of **2a**,**b** with $[Et_3O]BF_4$ yield the first cationic allenylidene complexes of palladium, *trans*-$[R^*(PR'_3)_2Pd{-}C{\equiv}CC(OMe)NR_2]^+X^-$ ($R^* = Br, CF_3COO$; $R' = Ph, C_6H_4OMe\text{-}4, {}^iPr$; $X = OTf, BF_4$).

Introduction

The synthesis of the first allenylidene complexes, $L_nM{=}C{=}C{=}C(R^1)R^2$, was reported in 1976 simultaneously by Fischer et al. ($M = Cr, W$)[1] and Berke ($M = Mn$).[2] Fischer's synthesis involved Lewis acid induced ethanol abstraction from ethoxycarbene complexes $[(CO)_5M{=}C(OEt)(CH{=}C\text{-}(NMe_2)Ph)]$. Berke obtained the manganese allenylidene complex $[Cp(CO)_2Mn{=}C{=}C{=}C(^tBu)_2]$ on treatment of the methyl propiolate complex $[Cp(CO)_2Mn(HC{\equiv}CCOOMe)]$ with an excess of ^{t}BuLi, presumably via an alkynyl complex as an intermediate. Since then a large number of allenylidene complexes of many transition metals have been prepared, including complexes of titanium, chromium, tungsten, manganese, rhenium, iron, ruthenium, osmium, rhodium, and iridium.[3] Most syntheses now use propargylic alcohols, $HC{\equiv}CC(R)(R')OH$, as sources of the allenylidene C_3 fragment. Coordination of the propargylic alcohol to the transition metal is followed by its rearrangement into a hydroxyvinylidene ligand. On subsequent elimination of water, allenylidene ligands are formed. This strategy was originally introduced by Selegue.[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 the dehydrogenative dimerization of tin hydrides,[8] and in selective transetherification of substituted vinyl ethers.[9]

Allenylidene complexes of palladium have been unknown until now, and consequently their catalytic activity has not been studied. This is surprising, especially when considering the broad range of applications of palladium complexes in organic synthesis and catalysis.[10] Many commonly used catalysts for CC coupling reactions such as, for example, the Mizoroki−Heck reaction or the Suzuki coupling reaction are based on palladium complexes.

We now report on the synthesis and the spectroscopic properties of the first palladium allenylidene complexes from readily available *N*,*N*-dimethylpropiolamides as the C_3 source.

Results and Discussion

Initially, we envisioned the transmetalation of allenylidene ligands from chromium to palladium, since N-heterocyclic carbene ligands such as pyrazolin-3-ylidene and pyrazolidin-

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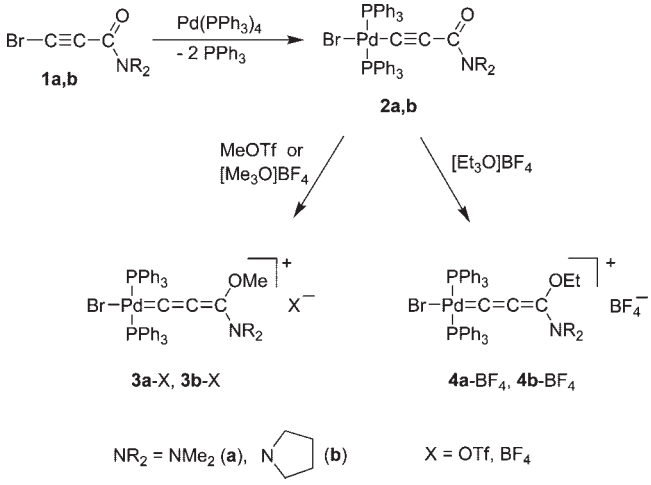
Scheme 1

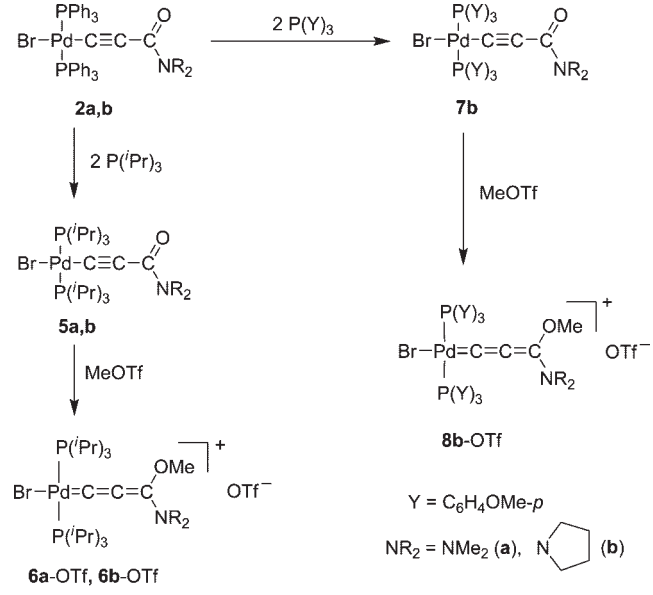


3-ylidene proved readily transferable from pentacarbonylchromium complexes to gold, palladium, and platinum in high yield.[11] The analogous transmetalation of several allenylidene ligands from chromium to tungsten likewise proceeded quickly in yields ranging from 83 to 97%.[12] However, all attempts to transfer allenylidene ligands from chromium to palladium met with failure. Therefore, the strategy had to be changed and an approach starting from alkynyl complexes was investigated.

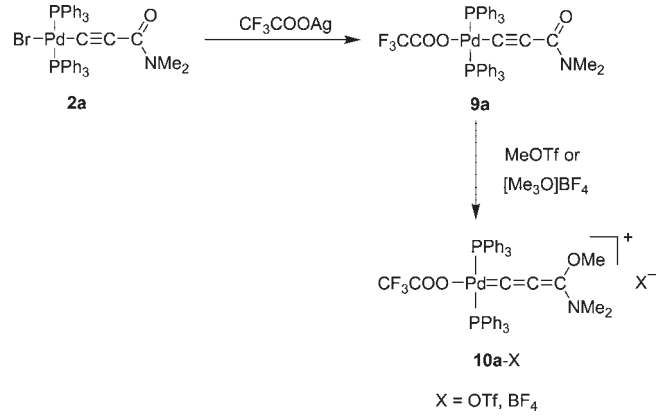
Recently, we developed an easy to perform one-pot synthesis for π-donor-substituted allenylidene pentacarbonyl complexes of chromium and tungsten. Sequential reaction of the solvent complexes $[(CO)_5M(THF)]$ (M = Cr, W) with appropriate deprotonated alkynes as the C_3 source and $[R_3O]BF_4$ as the alkylating agent afforded the corresponding amino- and alkoxyallenylidene complexes in very good yields.[13] Modification of this route turned out to also be applicable to the preparation of palladium allenylidene complexes.

Terminal halogenoalkynes are known to react with zerovalent palladium complexes by oxidative addition, affording stable palladium(II) alkynyl complexes.[14] Thus, treatment of a suspension of $[Pd(PPh_3)_4]$ in CH_2Cl_2 at ambient temperature with $BrC{\equiv}CC(=O)NMe_2$ (**1a**) afforded the neutral alkynyl complex **2a** (Scheme 1). Bromoalkyne **1a** was obtained by reaction of propynoic acid dimethylamide with *N*-bromosuccinimide (NBS). Pure alkynyl complex **2a** was isolated, after repeated crystallization from mixtures of CH_2Cl_2 and Et_2O, as a colorless solid in 85% yield. The subsequent alkylation of **2a** at −50 °C with a slight excess of MeOTf proceeded smoothly and afforded the cationic palladium allenylidene complex **3a**-OTf as a light yellow solid in 91% yield after crystallization from pentane−CH_2Cl_2 mixtures (Scheme 1). The corresponding BF_4 salt, **3a**-BF_4, was obtained when $[Me_3O]BF_4$ instead of MeOTf was used as the alkylation agent. The complexes **2b**, **3b**-OTf, **3b**-BF_4, **4a**-BF_4, and **4b**-BF_4 were synthesized accordingly.

Scheme 2



Scheme 3



Modification of the properties of the allenylidene complex can be achieved by variation of the terminal substituents of the allenylidene ligand and the coligands at palladium. The variation of the terminal substituents was achieved by starting from alkyne **1b** instead of **1a** and employing $[Et_3O]BF_4$ as the alkylation agent; otherwise the same reaction sequence was followed (Scheme 1).

The metal-bound C_α atom and the terminal C_γ atom in allenylidene complexes are electrophilic centers (see resonance forms II and III in Scheme 4).[3] Therefore, nucleophilic additions to these centers might compete with substitution of halides for the bromide ligand or of phosphines for the PPh_3 ligands. To avoid such side reactions at the allenylidene ligand, the alkynyl complexes **2a**,**b** were chosen as the starting compounds for the modification of the coligand set in allenylidene complexes.

Treatment of a solution of **2a**,**b** in CH_2Cl_2 with 2.2 equiv of the more nucleophilic phosphines P^iPr_3 and $P(C_6H_4OMe\text{-}4)_3$ led to quantitative exchange of both PPh_3 ligands. Complexes **5a**,**b** and **7b** were obtained as colorless or pale yellow solids after several recrystallization cycles from Et_2O in 70−74% yield. These alkynyl complexes were subsequently converted into cationic allenylidene complexes by alkylation with MeOTf. The resulting allenylidene complexes were then isolated in 98% (**6a**-OTf), 97% (**6b**-OTf), and 91% yield (**8b**-OTf) (Scheme 2).

When $Ag^+[CF_3COO]^-$ was added to a solution of **2a** in CH_2Cl_2, AgBr instantaneously precipitated and the trifluoroac-

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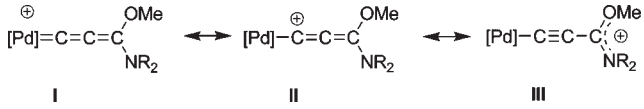
Scheme 4



etato complex **9a** was isolated as a colorless solid in 96% yield. Alkylation of **9a** with MeOTf or $[Me_3O]BF_4$ finally afforded the allenylidene complexes **10a**-OTf and **10a**-BF_4 in 90% and 86% yields, respectively (Scheme 3).

All new alkynyl and allenylidene complexes were characterized by spectroscopic means and by elemental analysis. The structures of **5b** and **10a**-BF_4 were additionally established by X-ray diffraction studies.

From the observation of only one singlet in the ^{31}P NMR spectra it followed that the two phosphine ligands are mutually trans. There was no indication of the presence of a cis isomer. Two singlets for the two N-bound methyl groups in the NMR spectra of all alkynyl complexes indicated a rather high barrier to rotation around the C(sp^2)−N bond. From the coalescence of the two signals of complex **2a** in $C_2D_2Cl_4$ at 115 °C an energy barrier of $\Delta G^{\ddagger} = 76.1 \pm 0.4$ kJ/mol was calculated. The barrier is slightly lower than that in free propiolamides (RC≡CC(=O)NMe_2, R = H, Me, Ph: 79.6−82.1 kcal/mol),[15] indicating minor back-donation from palladium to the alkynyl ligand and almost negligible interaction of the metal with the C(=O)NMe_2 fragment. The resonances of the alkynyl ligand in the ^{13}C NMR spectra compared well with those of known palladium alkynyl complexes.[14d] As expected, increasing the electron density at palladium in the series **9a**, **2a**, **7b** led to a shift of the ^{13}C resonance of the metal-bound alkynyl C_α atom to lower field. The resonances of C_β and C_γ were unaffected by varying the substitution pattern of the metal center.

The formation of the cationic allenylidene complexes by alkylation of the alkynyl complexes was accompanied by a pronounced shift of the C_α resonance to lower field by about 45 ppm, a shift of the C_β resonance to higher field ($\Delta\delta \approx 11$ ppm) and a shift of the ν(CC) vibration to lower energy by 10−15 cm^{-1}. The resonances of the C_γ atom and the N−CH_3 groups were again almost unaffected by the alkylation. Similar trends have been observed on alkylation of alkynylpentacarbonylchromate complexes to give neutral allenylidene complexes.[12] The extent of these shifts and the observation of two resonances for the dimethylamino substituent in the ^1H and ^{13}C NMR spectra demonstrate the importance of the zwitterionic resonance forms II and III for the overall bond description of these cationic allenylidene complexes (Scheme 4).[12] As in **2a**, **5a**, **7b**, and **9a**, both phosphine ligands are mutually trans, as indicated by the presence of only one signal for both phosphorus nuclei in the ^{31}P NMR spectra.

A comparison of the spectroscopic data of these cationic palladium allenylidene complexes with those of the related neutral complexes [$(CO)_5$M=C=C=C(NMe_2)OMe] (M = Cr, W) reveals that in cationic palladium allenylidene complexes the alkynyl character (see III in Scheme 4) is significantly more pronounced than in the corresponding group 6 complexes, as evidenced by the ν(CC) vibration at higher energy by about 70−90 cm^{-1}.

The solid-state structures of the alkynyl complex **5b** (Figure 1) and of the cationic allenylidene complex **10a**-BF_4 (Figure 2)

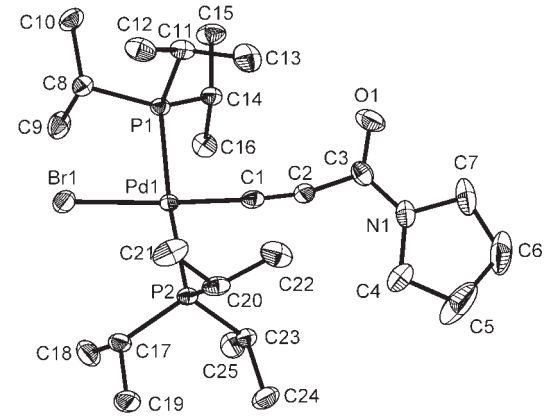


Figure 1. Structure of the alkynyl complex **5b** in the crystal (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Important distances (Å) and angles (deg): Pd(1)−C(1) = 1.947(3), Pd(1)−Br(1) = 2.4629(8), Pd(1)−P(1) = 2.3581(9), Pd(1)−P(2) = 2.3500(9), C(1)−C(2) = 1.209(5), C(2)−C(3) = 1.454(4), C(3)−O(1) = 1.244(4), C(3)−N(1) = 1.331(4), N(1)−C(4) = 1.466(5); C(1)−Pd(1)−Br(1) = 176.41(9), Pd(1)−C(1)−C(2) = 175.6(3), C(1)−C(2)−C(3) = 168.1(3), C(2)−C(3)−O(1) = 120.5(3), C(2)−C(3)−N(1) = 117.5(3).

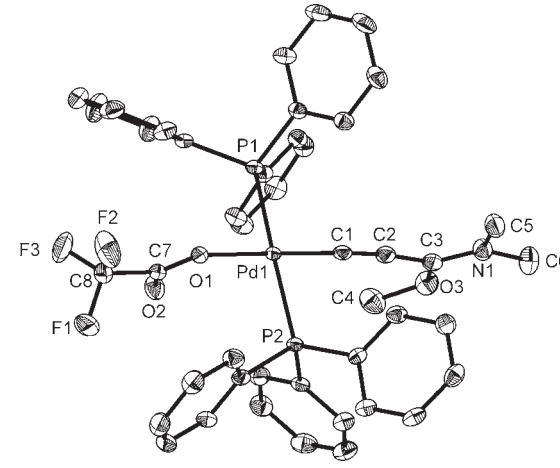


Figure 2. Structure of the cation of complex **10a**-BF_4 in the crystal (ellipsoids drawn at the 50% probability level; hydrogen atoms, two molecules of methylene chloride, and the anion BF_4^- omitted for clarity). Important distances (Å) and angles (deg): Pd(1)−C(1) = 1.925(3), Pd(1)−O(1) = 2.067(2), Pd(1)−P(1) = 2.3338(9), Pd(1)−P(2) = 2.3303(9), C(1)−C(2) = 1.217(4), C(2)−C(3) = 1.420(4), C(3)−N(1) = 1.296(4), C(3)−O(3) = 1.330(4), O(3)−C(4) = 1.446(4), O(1)−C(7) = 1.267(3), O(2)−C(7) = 1.223(4); C(1)−Pd(1)−O(1) = 178.69(9), Pd(1)−C(1)−C(2) = 176.7(2), C(1)−C(2)−C(3) = 172.6(3), C(2)−C(3)−N(1) = 123.0(3), C(2)−C(3)−O(3) = 120.8(3), N(1)−C(3)−O(3) = 116.2(3).

were determined by X-ray diffraction studies. The complex **10a**-BF_4 crystallizes from dichloromethane with two molecules of CH_2Cl_2; the BF_4^- anion is slightly disordered. In both complexes the palladium atom engages in square-planar coordination. In **5b** the plane formed by the atoms C(3), O(1), and N(1) and the coordination plane of palladium are almost coplanar (torsion angle O(1)−C(3)−Pd(1)−P(1) = 12.0°). In contrast, the allenylidene plane (formed by the atoms C(3), N(1), and O(3)) and the trifluoracetate plane in **10a**-BF_4 are perpendicular (89.6 and 87.9°, respectively) to the coordination plane of palladium. In both complexes the Pd−C_3 chain is slightly bent: Pd−C(1)−C(2) = 175.6(3)° (**5b**) and 176.7(2)° (**10a**-BF_4), C(1)−C(2)−C(3) = 168.1(3)° (**5b**) and 172.6(3)° (**10a**-BF_4). However, a modest

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deviation from linearity of the MC_3 fragment in allenylidene complexes is often observed.[3]

The Pd−C bond (1.925(3) Å) in the allenylidene complex **10a**-BF_4 is close to the shorter limit of observed Pd−C bond lengths and is shorter than the Pd−C bond in the related cationic N-heterocyclic carbene (NHC) complexes *trans*-$[L(PR_3)_2Pd(NHC)]^+$ (1.97−2.01 Å)[16] or in the neutral alkynyl complexes *trans*-$[L(PR_3)_2Pd{-}C{\equiv}CR]$ (1.947(3) Å in **5b**; range usually observed 1.95−2.07 Å[14d,17]). Similarly to other neutral π-donor-substituted allenylidene complexes of chromium and tungsten[11−13,18] the C(1)−C(2) bond is very short (1.217(4) Å) and only slightly longer than in the alkynyl complex **5b** (1.209(5) Å). Conversely, the C(2)−C(3) bond in **10a**-BF_4 (1.420(4) Å) is rather long and is even longer than that in $[(CO)_5Cr{=}C{=}C{=}C(O\text{-adamantyl})NMe_2]$ (1.366(7) Å)[18] but, as expected, is shorter than in **5b** (1.454(4) Å). The terminal bonds of the chain, C(3)−O(3) and C(3)−N(3), however, compare well with those in related complexes.

In summary, the first isolable palladium allenylidene complexes are accessible by a straightforward two-step synthesis from readily available bromoalkynes. The new complexes are remarkably stable. For instance, after heating for 14 h at 160 °C the intensity of the ν(CC) vibration in the IR spectra of **3a**-OTf only decreased to a minor degree, thus confirming the stability of the new allenylidene complexes. They exhibit all characteristic features of π-donor-substituted allenylidene complexes.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane), and sodium (Et_2O). The yields refer to analytically pure compounds and are not optimized. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Jeol JNX 400, a Varian Inova 400, or a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts are reported relative to the residual solvent peaks or tetramethylsilane (^{1}H, ^{13}C) and 100% H_3PO_4 (^{31}P). Other instrumentation: IR, Biorad FTS 60; MS, Finnigan MAT 312; elemental analysis, Heraeus Elementar Vario EL. *N*,*N*-Dimethylpropiolamide[19] and $[Pd(PPh_3)_4]$[20] were synthesized according to literature procedures. All other reagents were used as obtained from commercial suppliers.

1-Bromo-*N*,*N*-dimethylpropiolamide (1a). A solution of 0.97 g (10 mmol) of *N*,*N*-dimethylpropiolamide in 40 mL of acetone was treated at ambient temperature with 2.16 g (12 mmol) of NBS and 150 mg (0.9 mmol) of $AgNO_3$. After 60 min the reaction mixture was poured onto 200 mL of ice water. The aqueous phase was extracted three times with 30 mL portions of ethyl acetate. The combined organic extracts were dried over $MgSO_4$. The solid was then filtered off and the solvent removed in vacuo. The crude product was filtered over a short plug of silica using CH_2Cl_2/acetone (5:1) as the eluant. Removal of the solvent gave 1.36 g (7.9 mmol; 79%) of **1** as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (s, 3H, NCH_3), 3.12 (s, 3H, NCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 34.0 (NCH_3), 38.0 (NCH_3), 55.2 (C≡*C*Br), 73.4 (*C*≡CBr), 153.0 (*C*(O)NMe_2). IR (CH_2Cl_2): ν(C≡C) 2198 cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 176 (48) [M^+], 161 (100) [$(M - CH_3)^+$]. Anal. Calcd for C_5H_6BrNO (176.01): C, 34.12; H, 3.44; N, 7.96. Found: C, 34.09; H, 3.51; N, 8.05.

1-Bromo-*N*,*N*-tetramethylenepropiolamide (1b). The synthesis of **1b** was carried out analogously to **1a**. The crude product was purified by column chromatography using CH_2Cl_2 as solvent. Yield: 1.72 g (8.51 mmol; 85%) of **1b** as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (m, 4H, CH_2CH_2), 3.44 (t, J = 7.0 Hz, 2H, NCH_2), 3.61 (t, J = 7.0 Hz, 2H, NCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6 (CH_2), 25.3 (CH_2), 45.4 (NCH_2), 48.0 (NCH_2), 53.8 (C≡*C*Br), 74.6 (*C*≡CBr), 177.4 (C(O)NC_4H_8). IR (CH_2Cl_2): ν(CCC) 2196 cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 202 (79) [M^+], 146 (22) [$(M - C_4H_8)^+$], 132 (100) [$(M - NC_4H_8)^+$], 122 (29) [$(M - Br)^+$], 99 (100) [$(M - Br - C{\equiv}C)^+$]. Anal. Calcd for C_7H_8BrNO (202.05): C, 41.61; H, 3.99; N, 6.93. Found: C, 42.46; H, 4.37; N, 8.21.

***trans*-Bromobis(triphenylphosphine)(3-dimethylamino-3-oxy-1-propynyl)palladium(II) (2a).** A suspension of 1.16 g (1 mmol) of $[Pd(PPh_3)_4]$ in 30 mL of CH_2Cl_2 was treated with 0.26 g (1.5 mmol) of **1a** at ambient temperature. The mixture was stirred for 30 min, upon which it becomes a clear yellow solution. Then, 100 mL of dry Et_2O was added. The light yellow precipitate was filtered off and washed repeatedly with Et_2O (3 × 30 mL) and pentane (2 × 50 mL). Repeated crystallization of the crude product from CH_2Cl_2/Et_2O gave 0.69 g (0.85 mmol; 85%) of pure **2a** as an off-white powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.19 (s, 3H, NCH_3), 2.49 (s, 3H, NCH_3), 7.38−7.47 (m, 18H, ArH), 7.68−7.73 (m, 12H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 33.2 (NCH_3), 37.6 (NCH_3), 104.1 (t, $^2J_{PC}$ = 10.8 Hz, Pd−*C*≡C), 107.7 (Pd−C≡*C*), 128.4 (t, $^3J_{PC}$ = 4.8 Hz, *m*-C), 130.9 (*p*-C), 131.4 (t, $^1J_{PC}$ = 25.0 Hz, *i*-C), 135.3 (t, $^2J_{PC}$ = 6.7 Hz, *o*-C), 154.4 (*C*(O)NMe_2). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 24.7. IR (CH_2Cl_2): ν(C≡C) 2109 cm^{-1}; ν(CO) 1609 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 240 (4.489), 305 (4.314). FAB-MS: *m*/*z* (%) 725 (28) [$(M - Br)^+$]. Anal. Calcd for $C_{41}H_{36}BrNOP_2Pd \cdot CH_2Cl_2$ (807.01): C, 56.56; H, 4.29; N, 1.57. Found: C, 57.09; H, 4.60; N, 1.55.

***trans*-Bromobis(triphenylphosphine)(3-*N*,*N*-tetramethyleneamino-3-oxy-1-propynyl)palladium(II) (2b).** A suspension of 1.16 g (1 mmol) of $[Pd(PPh_3)_4]$ in 30 mL of dry CH_2Cl_2 was treated with 0.30 g (1.5 mmol) of **1b** at ambient temperature. The mixture was stirred for a further 30 min, upon which it became a clear yellow solution. The solvent was removed in vacuo, and the crude product was purified by column chromatography using petroleum ether/CH_2Cl_2/acetone mixtures. Yield: 0.71 g (0.85 mmol; 85%) of **2b** as a pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 2.26 (t, J = 7.0 Hz, 2H, NCH_2), 3.03 (t, J = 7.0 Hz, 2H, NCH_2), 7.34−7.40 (m, 18 H, ArH), 7.67−7.72 (m, 12 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6 (CH_2) 25.0 (CH_2), 44.2 (NCH_2), 46.9 (NCH_2), 105.0 (t, $^3J_{PC}$ = 5.8 Hz, Pd−C≡*C*), 107.1 (t, $^2J_{PC}$ = 13.4 Hz, Pd−*C*≡C), 128.0 (t, $^3J_{PC}$ = 4.8 Hz, *m*-C), 130.4 (*p*-C), 130.9 (t, $^1J_{PC}$ = 24.9 Hz, *i*-C), 135,0 (t, $^2J_{PC}$ = 6.7 Hz, *o*-C), 152.9 (*C*(O)NC_4H_8). ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.7. IR (CH_2Cl_2): ν(CCC) 2115 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 302 (4.373). FAB-MS: *m*/*z* (%) 834 (7) [M^+], 751 (8) [$(M - Br - 2H)^+$], 489 (16) [$(M - Br - 2H - PPh_3)^+$], 367 (41) [$(M - Br - 2H - PPh_3 - C_7H_8NO)^+$]. Anal. Calcd for $C_{43}H_{38}BrNOP_2Pd$ (833.04): C, 62.00; H, 4.60; N, 1.68. Found: C, 61.86; H, 4.63; N, 1.57.

***trans*-Bromobis(triphenylphosphine)(3-dimethylamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (3a-OTf).** A solution of 0.5 g (0.62 mmol) of **2a** in 30 mL of CH_2Cl_2 was treated dropwise with 0.07 mL (0.62 mmol) of MeOTf at −50

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°C. After 10 min at −50 °C, the solution was warmed to ambient temperature. The progress of the reaction was followed by IR spectroscopy. When all of the starting material was consumed, the solvent was removed in vacuo. The remaining residue was washed twice with 30 mL of Et_2O and recrystallized from mixtures of CH_2Cl_2 and pentane. Pure **3a**-OTf (0.55 g, 0.56 mmol; 91%) was obtained as a light yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.23 (s, 3H, NCH_3), 3.40 (s, 3H, NCH_3), 3.74 (s, 3H, OCH_3), 7.03−7.11 (m, 18H, ArH), 7.21−7.25 (m, 12H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 35.1 (NCH_3), 40.3 (NCH_3), 61.7 (OCH_3), 96.1 (C_β), 120.9 (q, $^1J_{CF}$ = 316.4 Hz, CF_3), 128.9 (t, $^3J_{PC}$ = 5.8 Hz, *m*-C), 129.9 (t, $^1J_{PC}$ = 25.3 Hz, *i*-C), 132.2 (*p*-C), 135.4 (t, $^2J_{PC}$ = 6.0 Hz, *o*-C), 150.9 (t, $^3J_{PC}$ = 5.5 Hz, C_α), 154.1 (C_γ). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 24.5. IR (THF): ν(CCC) 2099 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max}, nm (log ϵ) 236 (4.563), 298 (4.361). FAB-MS: *m*/*z* (%) 821 (56) [(M − CF_3SO_3)$^+$], 560 (48) [(M − CF_3SO_3 − PPh_3)$^+$]. Anal. Calcd for $C_{43}H_{39}BrF_3NO_4P_2PdS$ (971.11): C, 53.18; H, 4.05; N, 1.44. Found: C, 53.49; H, 4.46; N, 1.34.

***trans*-Bromobis(triphenylphosphine)(3-dimethylamino-3-methoxy-1,2-propadienylidene)palladium(II) Tetrafluoroborate (3a-BF_4).** The synthesis of **3a**-BF_4 from 1.0 g (1.24 mmol) of **2a** and 0.25 g (1.70 mmol, 1.4 equiv) of $[Me_3O]BF_4$ in 60 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.70 g (0.77 mmol; 62%) of **3a**-BF_4 as a yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.69 (s, 3 H, NCH_3), 2.91 (s, 3 H, NCH_3), 3.31 (s, 3 H, OCH_3), 7.45−7.56 (m, 18 H, ArH), 7.66−7.71 (m, 12 H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 37.7 (NCH_3), 41.7 (NCH_3), 61.3 (OCH_3), 128.8 (t, $^3J_{PC}$ = 5.6 Hz, *m*-C), 130.2 (t, $^1J_{PC}$ = 25.7 Hz, *i*-C), 131.8 (*p*-C), 135.1 (t, $^2J_{PC}$ = 6.4 Hz, *o*-C); C_α, C_β, C_γ not observed. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 24.7. IR (CH_2Cl_2): ν(CCC) 2098 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 298 (4.368). FAB-MS: *m*/*z* (%) 822 (72) [(M − BF_4)$^+$], 560 (37) [(M − BF_4 − PPh_3)$^+$]. Anal. Calcd for $C_{42}H_{39}BBrF_4NOP_2Pd \cdot 0.5CH_2Cl_2$ (908.85): C, 53.66; H, 4.24; N, 1.47. Found: C, 53.83; H, 4.51; N, 1.49.

***trans*-Bromobis(triphenylphosphine)(3-*N*,*N*-tetramethyleneamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (3b-OTf).** The synthesis of **3b**-OTf from 0.32 g (0.38 mmol) of **2b** and 0.04 mL (0.38 mmol) of MeOTf in 20 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.82 g (0.82 mmol; 97%) of **3b**-OTf as a yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.70 (m, 2 H, CH_2), 1.87 (m, 2 H, CH_2), 2.68(t, *J* = 7.0 Hz, 2 H, NCH_2), 3.27 (s, 3 H, OCH_3), 3.34 (t, *J* = 7.0 Hz, 2 H, NCH_2), 7.42−7.50 (m, 18 H, ArH), 7.63−7.67 (m, 12 H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 24.2 (CH_2), 24.4 (CH_2), 48.9 (NCH_2), 51.4 (NCH_2), 60.4 (OCH_3), 93.8 (C_β), 128.5 (t, $^3J_{PC}$ = 5.6 Hz, *m*-C), 129.8 (t, $^1J_{PC}$ = 25.9 Hz, *i*-C), 131.4 (*p*-C), 134.7 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 147.8 (C_α), 150.9 (C_γ). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.9. IR (CH_2Cl_2): ν(CCC) 2100 cm^{-1}; ν(CO) 1612 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 296 (4.437). FAB-MS: *m*/*z* (%) 847 (32) [(M − OTf)$^+$], 586 (20) [(M − OTf − PPh_3)$^+$], 505 (11) [(M − OTf − PPh_3 − Br)$^+$], 323 (59) [(M − OTf − 2 PPh_3)$^+$]. Anal. Calcd for $C_{45}H_{41}BrF_3NO_4P_2PdS$ (997.15): C, 54.20; H, 4.14; N, 1.40. Found: C, 54.16; H, 4.19; N, 1.36.

***trans*-Bromobis(triphenylphosphine)(3-*N*,*N*-tetramethyleneamino-3-methoxy-1,2-propadienylidene)palladium(II) Tetrafluoroborate (3b-BF_4).** The synthesis of **3b**-BF_4 from 0.48 g (0.58 mmol) of **2b** and 0.10 g (0.69 mmol, 1.2 equiv) of $[Me_3O]BF_4$ in 30 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.52 g (0.56 mmol; 97%) of **3b**-BF_4 as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (m, 2 H, CH_2), 1.86 (m, 2 H, CH_2), 2.67 (t, *J* = 7.0 Hz, 2 H, NCH_2), 3.24 (s, 3 H, OCH_3), 3.34 (t, *J* = 7.0 Hz, 2 H, NCH_2), 7.37−7.51 (m, 18 H, ArH), 7.63−7.70 (m, 12 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5 (CH_2), 24.7 (CH_2), 49.2 (NCH_2), 51.7 (NCH_2), 60.7 (OCH_3), 94.3 (C_β), 128.8 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 130.1 (t, $^1J_{PC}$ = 26.0 Hz, *i*-C), 131.7 (*p*-C), 135.1 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 151.2 (C_α), 154.1 (C_γ). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 25.0. IR (CH_2Cl_2): ν(CCC) 2101 cm^{-1}; ν(CO) 1609 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 300 (4.376). FAB-MS: *m*/*z* (%) 847 (19) [(M − BF_4)$^+$], 586 (16) [(M − BF_4 − PPh_3)$^+$], 505 (9) [(M − BF_4 − PPh_3 − Br)$^+$], 324 (40) [(M − BF_4 − 2 PPh_3)$^+$]. Anal. Calcd for $C_{44}H_{41}BBrF_4NOP_2Pd \cdot 0.5CH_2Cl_2$ (934.89): C, 54.69; H, 4.33; N, 1.43. Found: C, 54.52; H, 4.51; N, 1.35.

***trans*-Bromobis(triphenylphosphine)(3-dimethylamino-3-ethoxy-1,2-propadienylidene)palladium(II) Tetrafluoroborate (4a-BF_4).** The synthesis of **4a**-BF_4 from 91 mg (0.11 mmol) of **2a** and 21 mg (0.11 mmol) of $[Et_3O]BF_4$ in 5 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 77 mg (0.08 mmol; 76%) of **4a**-BF_4 as a yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.01 (t, *J* = 7.0 Hz, 2 H, CH_3), 2.69 (s, 3 H, NCH_3), 2.90 (s, 3 H, NCH_3), 3.54 (q, *J* = 7.0 Hz, 2 H, CH_2), 7.45−7.56 (m, 18 H, ArH), 7.67−7.72 (m, 12 H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.3 (OCH_2CH_3), 37.5 (NCH_3), 41.4 (NCH_3), 71.9 (OCH_2CH_3), 93.1 (t, $^3J_{PC}$ = 4.8 Hz, C_β), 128.8 (t, $^3J_{PC}$ = 5.8 Hz, *m*-C), 130.1 (t, $^1J_{PC}$ = 25.9 Hz, *i*-C), 131.7 (*p*-C), 135.0 (t, $^2J_{PC}$ = 5.8 Hz, *o*-C), 149.3 (t, $^2J_{PC}$ = 12.5 Hz, C_α), 152.9 (C_γ). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 24.8. IR (CH_2Cl_2): ν(CCC) 2099 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 300 (4.335). FAB-MS: *m*/*z* (%) 834 (44) [(M − BF_4)$^+$], 573 (18) [(M − BF_4 − PPh_3)$^+$]. Anal. Calcd for $C_{43}H_{41}BBrF_4NOP_2Pd$ (922.88): C, 55.96; H, 4.48; N, 1.52. Found: C, 56.02; H, 4.50; N, 1.44.

***trans*-Bromobis(triphenylphosphine)(3-*N*,*N*-tetramethyleneamino-3-ethoxy-1,2-propadienylidene)palladium(II) Tetrafluoroborate (4b-BF_4).** The synthesis of **4b**-BF_4 from 0.81 g (0.97 mmol) of **2b** and 0.18 g (0.97 mmol) of $[Et_3O]BF_4$ in 30 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.92 g (0.96 mmol; 99%) of **4b**-BF_4 as a yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.95 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.86 (m, 2 H, CH_2), 2.67 (t, *J* = 7.0 Hz, 2 H, NCH_2), 3.31 (t, *J* = 7.0 Hz, 2 H, NCH_2), 3.48 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 7.42−7.50 (m, 18 H, ArH), 7.62−7.67 (m, 12 H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.2 (OCH_2CH_3), 24.1 (CH_2), 24.3 (CH_2), 48.8 (NCH_2), 51.3 (NCH_2), 70.7 (OCH_2CH_3), 94.1 (C_β), 128.4 (t, $^3J_{PC}$ = 5.7 Hz, *m*-C), 129.8 (t, $^1J_{PC}$ = 26.0 Hz, *i*-C), 131.4 (*p*-C), 134.7 (t, $^2J_{PC}$ = 5.7 Hz, *o*-C), 145.8 (C_α), 150.1 ($C\gamma$). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 21.8. IR (CH_2Cl_2): ν(CCC) 2101 cm^{-1}; ν(CO) 1604 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 297 (4.462). FAB-MS: *m*/*z* (%) 861 (50) [(M − BF_4)$^+$], 600 (37) [(M − BF_4 − PPh_3)$^+$]. Anal. Calcd for $C_{45}H_{43}BBrF_4NOP_2Pd$ (948.92): C, 56.96; H, 4.57; N, 1.48. Found: C, 56.83; H, 4.53; N, 1.55.

***trans*-Bromobis(triisopropylphosphine)(3-dimethylamino-3-oxy-1-propynyl)palladium(II) (5a).** At ambient temperature, a solution of 0.55 g (0.68 mmol) of **2a** in 30 mL of CH_2Cl_2 was treated with 0.29 mL (1.50 mmol, 2.2 equiv) of P^iPr_3. The progress of the reaction was monitored by IR spectroscopy. When all of the starting material was consumed (60 min), the solvent was removed in vacuo and the crude product purified by column chromatography using a petroleum ether/Et_2O mixture as the eluant. Removal of the solvent gave 0.29 g (0.47 mmol, 70%) of pure **5a** as a white powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.35 (q, *J* = 7.04 Hz, 36H, $CH(CH_3)_2$), 2.82 (s, 3H, NCH_3), 2.89 (m, 6H, $CH(CH_3)_2$), 3.10 (s, 3H, NCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.1 ($CH(CH_3)_2$), 24.7 (t, $^2J_{PC}$ = 11.5 Hz, $CH(CH_3)_2$), 33.7 (NCH_3), 38.0 (NCH_3), 103.7 (t, $^3J_{PC}$ = 4.8 Hz, Pd−C≡*C*), 107.7 (t, $^2J_{PC}$ = 12.6 Hz, Pd−*C*≡C), 155.3 (C(O)NMe_2). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 42.1. IR (THF): ν(C≡C) 2098 cm^{-1}; ν(CO) 1605 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 251 (4.134), 288 (4.167). MS (FAB): *m*/*z* (%) 604 (19) [M$^+$], 523 (24) [(M − Br)$^+$], 362 (11) [(M − Br − P(^{i}Pr)$_3$)$^+$]. Anal. Calcd for $C_{23}H_{48}BrNOP_2Pd$ (602.91): C, 45.82; H, 8.02; N, 2.32. Found: C, 46.03; H, 7.97; N, 2.39.

***trans*-Bromobis(triisopropylphosphine)(3-*N*,*N*-tetramethyleneamino-3-oxy-1-propynyl)palladium(II) (5b).** The synthesis of **5b** from 1.23 g (1.48 mmol) of **2b** and 0.62 mL (3.25 mmol, 2.2 equiv) of P^iPr_3 in 30 mL of CH_2Cl_2 was carried out analogously to **5a**. The crude product was purified by column chromatography using

an ether/CH_2Cl_2/acetone mixture. Yield: 0.65 g (1.03 mmol; 70%) of **5b** as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (m, 36 H, CH(CH_3)$_2$), 1.87 (br, 4H, CH_2CH_2), 2.94 (m, 6 H, CH(CH_3)$_2$), 3.40 (t, J = 6.6 Hz, 2H, NCH_2), 3.53 (t, J = 6.6 Hz, 2H, NCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6 (CH(CH_3)$_2$), 24.0 (t, $^2J_{PC}$ = 11.6 Hz, CH(CH_3)$_2$), 24.3 (CH_2), 25.2 (CH_2), 44.3 (NCH_2), 47.0 (NCH_2), 103.9 (t, $^3J_{PC}$ = 4.8 Hz, Pd−C≡C), 106.0 (t, $^2J_{PC}$ = 12.4 Hz, Pd−C≡C), 153.1 (C(O)NC_4H_8). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.7. IR (CH_2Cl_2): ν(CCC) 2106 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 287 (4.224). FAB-MS: m/z (%) 629 (39) [M$^+$], 549 (18) [(M − Br)$^+$], 470 (6) [(M − P(^{i}Pr)$_3$)$^+$], 389 (9) [(M − Br − P(^{i}Pr)$_3$)$^+$], 347 (6) [(M − P(^{i}Pr)$_3$)$^+$ − C_7H_8NO], 267 (38) [(M − Br − P(^{i}Pr)$_3$ − C_7H_8NO)$^+$]. Anal. Calcd for $C_{25}H_{50}BrNOP_2Pd$ (628.95): C, 47.74; H, 8.01; N, 2,23. Found: C, 47.68; H, 7.74; N, 2.57.

***trans*-Bromobis(triisopropylphosphine)(3-dimethylamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (6a-OTf).** The synthesis of **6a**-OTf from 0.3 g (0.50 mmol) of **5a** and 0.06 mL (0.50 mmol) of MeOTf in 30 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Complex **6a**-OTf was recrystallized from Et_2O. Yield: 0.37 g (0.49 mmol; 98%) of **6a**-OTf as a colorless powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.35 (q, J = 7.04 Hz, 36H, CH(CH_3)$_2$), 2.85 (m, 6H, CH(CH_3)$_2$), 3.25 (s, 3H, NCH_3), 3.45 (s, 3H, NCH_3), 4.20 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.0 (CH(CH_3)$_2$), 25.0 (t, $^2J_{PC}$ = 11.8 Hz, CH(CH_3)$_2$), 38.3 (NCH_3), 42.1 (NCH_3), 61.7 (OCH_3), 94.6 (t, $^3J_{PC}$ = 3.8 Hz, C_β), 121.4 (q, $^1J_{CF}$ = 320.0 Hz, CF_3), 150.3 (t, $^2J_{PC}$ = 10.6 Hz, C_α), 153.7 (C_γ). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 45.3. IR (THF): ν(CCC) 2083 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 247 (4.103), 279 (4.371). FAB-MS: m/z (%) 618 (75) [(M − OTf)$^+$], 458 (48) [(M − OTf − P(^{i}Pr)$_3$)$^+$]. Anal. Calcd for $C_{25}H_{51}BrF_3NO_4P_2PdS$ (767.01): C, 40.80; H, 6.98; N, 1.90. Found: C, 39.38; H, 6.33; N, 1.54.

***trans*-Bromobis(triisopropylphosphine)(3-*N*,*N*-tetramethyleneamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (6b-OTf).** The synthesis of **6b**-OTf from 0.18 g (0.27 mmol) of **5b** and 0.03 mL (0.27 mmol) of MeOTf in 10 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.21 g (0.26 mmol; 97%) of **6b**-OTf as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 36 H, CH(CH_3)$_2$), 2.02 (br, 4H, CH_2CH_2), 2.84 (m, 6 H, CH(CH_3)$_2$), 3.76 (t, J = 7.0 Hz, 4 H, NCH_2), 4.15 (s, 3 H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9 (CH(CH_3)$_2$), 24.7 (t, $^1J_{PC}$ = 11.1 Hz, CH(CH_3)$_2$), 24.3 (CH_2), 24.5 (CH_2), 49.3 (NCH_2), 51.8 (NCH_2), 60.7 (OCH_3), 95.3 (t, $^3J_{PC}$ = 3.8 Hz, C_β), 120.8 (q, $^1J_{CF}$ = 320.0 Hz, CF_3), 147.1 (t, $^2J_{PC}$ = 11.6 Hz, C_α), 151.1 (C_γ). ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.1. IR (CH_2Cl_2): ν(CCC) 2086 cm^{-1}; ν(CO) 1612 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 280 (4.365). FAB-MS: m/z (%) 644 (70) [(M − OTf)$^+$], 483 (65) [(M − OTf − PPh_3)$^+$], 403 (13) [(M − OTf − PPh_3 − Br)$^+$]. Anal. Calcd for $C_{27}H_{53}BrF_3NO_4P_2PdS$ (793.05): C, 40.89; H, 6.74; N, 1.77. Found: C, 40.85; H, 7.19; N, 1.54.

***trans*-Bromobis[tris(4-methoxyphenyl)phosphine](3-*N*,*N*-tetramethyleneamino-3-oxy-1-propynyl)palladium(II) (7b).** The synthesis of **7b** from 0.42 g (0.50 mmol) of **2b** and 0.39 g (1.10 mmol, 2.2 equiv) of P(C_6H_4OMe-4)$_3$ in 30 mL of CH_2Cl_2 was carried out analogously to **5a**. The crude product was purified by column chromatography using a petroleum ether/CH_2Cl_2/acetone mixture. Yield: 0.37 g (0.37 mmol; 74%) of **7b** as a pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 2.32 (t, J = 6.8 Hz, 2H, NCH_2), 3.06 (t, J = 6.6 Hz, 2H, NCH_2), 3.78 (s, 18H, OCH_3), 6.85−6.87 (m, 12 H, ArH), 7.57−7.61 (m, 12 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5 (CH_2), 24.9 (CH_2), 44.1 (NCH_2), 47.0 (NCH_2), 55.1 (OCH_3), 104.5 (t, $^3J_{PC}$ = 3.5 Hz, Pd−C≡C), 109.2 (t, $^3J_{PC}$ = 9.0 Hz, Pd−C≡C), 113.5 (ArC), 122.7 (t, $^2J_{PC}$ = 27.8 Hz, ArC), 136.3 (ArC), 153.1 (C(O)NC_4H_8), 161.1 (ArC). ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.2. IR (CH_2Cl_2): ν(CCC) 2114 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 317 (4.420). FAB-MS: m/z (%) 1013 (20) [M$^+$], 933 (85) [(M − Br)$^+$], 580 (27) [(M − Br − P(C_6H_4OMe-p)$_3$)$^+$]. Anal. Calcd for $C_{49}H_{50}BrNO_7P_2P$ d × 0.5 CH_2Cl_2 (1013.21): C, 56.32; H, 4.87; N, 1,33. Found: C, 55.69; H, 4.86; N, 1.02.

***trans*-Bromobis[tris(4-methoxyphenyl)phosphine](3-*N*,*N*-tetramethyleneamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (8b-OTf).** The synthesis of **8b**-OTf from 0.58 g (0.57 mmol) of **7b** and 0.07 mL (0.57 mmol) of MeOTf in 20 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.62 g (0.52 mmol; 91%) of **8b**-OTf as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 2.72 (m, 2H, NCH_2), 3.35 (m, 2H, NCH_2), 3.78 (s, 3H, OCH_3), 3.81 (s, 18 H, OCH_3), 6.92−6.95 (m, 12 H, ArH), 7.52−7.57 (m, 12 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1 (CH_2), 24.4 (CH_2), 48.7 (NCH_2), 51.3 (NCH_2), 55.4 (OCH_3), 60.5 (OCH_3), 93.9 (C_β), 114.0 (ArC), 121.6 (t, $^1J_{PC}$ = 28.7 Hz, ArC), 136,3 (t, $^2J_{PC}$ = 7.1 Hz, ArC), 151.1 (C_γ), 161.8 (ArC), 177.0 (C_α). ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.2. IR (CH_2Cl_2): ν(CCC) 2098 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 328 (4.352). FAB-MS: m/z (%) 1028 (8) [(M − OTf)$^+$], 948 (8) [(M − OTf − Br)$^+$], 595 (23) [(M − OTf − Br − P(C_6H_4OMe-p)$_3$)$^+$]. Anal. Calcd for $C_{51}H_{53}BrF_3NO_{10}P_2PdS$ (1177.32): C, 52.03; H, 4.54; N, 1.19. Found: C, 52.10; H, 4.72; N, 1.26.

***trans*-(Trifluoroacetato)bis(triphenylphosphine)(3-dimethylamino-3-oxy-1-propynyl)palladium(II) (9a).** A suspension of 0.55 g (0.68 mmol) of **2a** and 0.15 g (0.68 mmol) of CF_3COOAg in 30 mL of dry CH_2Cl_2 was stirred for 30 min. The precipitate (AgBr) that formed was filtered off. The solvent of the crude reaction mixture was removed in vacuo. Crystallization of the crude product from CH_2Cl_2/Et_2O gave 0.54 g (0.65 mmol; 96%) of **9a** as a colorless powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.93 (s, 3H, NCH_3), 2.47 (s, 3H, NCH_3), 7.41−7.51 (m, 18H, ArH), 7.71−7.79 (m, 12H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 33.2 (NCH_3), 37.2 (NCH_3), 93.8 (t, $^2J_{PC}$ = 10.7 Hz, Pd−C≡C), 107.4 (Pd−C≡C), 107.4 (CF_3COO), 128.4 (t, $^3J_{PC}$ = 5.7 Hz, m-C), 129.6 (t, $^1J_{PC}$ = 25.0 Hz, i-C), 131.2 (p-C), 134.1 (t, $^2J_{PC}$ = 5.3 Hz, o-C), 154.3 (C(O)NMe_2), 174.3 (CF_3COO). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 23.9. IR (THF): ν(C≡C) 2114 cm^{-1}; ν(CO) 1680, 1609 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 239 (4.513), 297 (4.449). FAB-MS: m/z (%) 727 (11) [(M − CF_3COO)$^+$], 631 (62) [(M − CF_3COO − C_5H_6NO)$^+$], 369 (62) [(M − CF_3COO − C_5H_6NO − PPh_3)$^+$]. Anal. Calcd for $C_{43}H_{36}F_3NO_3P_2Pd \cdot CH_2Cl_2$ (840.13): C, 57.13; H, 4.14; N, 1.51. Found: C, 57.52; H, 4.30; N, 1.81.

***trans*-(Trifluoroacetato)bis(triphenylphosphine)(3-dimethylamino-3-methoxy-1,2-propadienylidene)palladium(II) Trifluoromethanesulfonate (10a-OTf).** The synthesis of **10a**-OTf from 0.49 g (0.58 mmol) of **9a** and 0.07 mL (0.62 mmol) of MeOTf in 30 mL of CH_2Cl_2 was carried out analogously to **3a**-OTf. Recrystallization from mixtures of CH_2Cl_2 and pentane afforded 0.52 g (0.52 mmol, 90%) of pure **10a**-OTf as a colorless powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.46 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 3.03 (s, 3H, OCH_3), 7.38−7.47 (m, 18H, ArH), 7.58−7.65 (m, 12H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 38.0 (NCH_3), 41.5 (NCH_3), 61.2 (OCH_3), 95.6 (C_β), 110.9 (CF_3COO), 120.0 (SO_3CF_3), 128.3 (t, $^1J_{PC}$ = 25.8 Hz, i-C), 129.3 (t, $^3J_{PC}$ = 5.8 Hz, m-C), 132.1 (p-C), 134.7 (t, $^2J_{PC}$ = 6.7 Hz, o-C), 137.9 (t, $^3J_{PC}$ = 5.7 Hz, C_α), 153.7 (C_γ), 172.8 (CF_3COO). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 25.9. IR (THF): ν(CCC) 2102 cm^{-1}; ν(CO) 1678 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 251 (4.359), 307 (4.528). FAB-MS: m/z (%) 855 (13) [(M − OTf)$^+$], 592 (80) [(M − OTf − PPh_3)$^+$], 478 (39) [(M − OTf − PPh_3 − CF_3COO)$^+$]. Anal. Calcd for $C_{45}H_{39}F_6NO_6P_2PdS \cdot 0.5CH_2Cl_2$ (1004.23): C, 52.21; H, 3.85; N, 1.34. Found: C, 51.94; H, 4.07; N, 1.44.

***trans*-(Trifluoracetato)bis(triphenylphosphine)(3-dimethylamino-3-methoxy-1,2-propadienylidene)palladium(II) Tetrafluoroborate (10a-BF_4).** The synthesis of **10a**-BF_4 from 0.47 g (0.56 mmol) of **9a** and 99 mg (0.67 mmol, 1.2 equiv) of $[Me_3O]BF_4$ in 30 mL of

CH_2Cl_2 was carried out analogously to **3a**-OTf. Yield: 0.45 g (0.48 mmol; 86%) of **10a**-BF_4 as an off-white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3 H, NCH_3), 2.89 (s, 3 H, NCH_3), 3.10 (s, 3 H, OCH_3), 7.49−7.57 (m, 18 H, ArH), 7.68−7.72 (m, 12 H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 38.0 (NCH_3), 41.7 (NCH_3), 61.3 (OCH_3), 128.4 (t, $^1J_{PC}$ = 25.9 Hz, *i*-C), 129.4 (t, $^3J_{PC}$ = 5.7 Hz, m-C), 132.2 (*p*-C), 134.9 (t, $^2J_{PC}$ = 6.4 Hz, *o*-C), 153.8 (C_γ); C_α, C_β, CF_3COO not observed. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 26.2. IR (THF): ν(CCC) 2103 cm^{-1}; ν(CO) 1678 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 307 (4.450). FAB-MS: *m*/*z* (%) 854 (33) [(M − BF_4)$^+$], 663 (100) [(M − BF_4 − CF_3COO − Ph)$^+$], 631 (49) [(M − BF_4 − CF_3COO − CCC(OMe)NMe^2)$^+$], 592 (68) [(M − BF_4 − PPh^3)$^+$], 479 (37) [(M − BF_4 − PPh_3 − CF_3COO)$^+$], 369 (82) [(M − BF_4 − PPh_3 − CF_3COO − CCC(OMe)NMe_2)$^+$]. Anal. Calcd for $C_{44}H_{39}BF_7NO_3P_2Pd$ (941.96): C, 56.10; H, 4.17; N, 1.49. Found: 56.03; H, 4.22; N, 1.42.

X-ray Structural Analysis of 5b and 10a-BF_4. Data for 5b: $C_{25}H_{50}BrNOP_2Pd\cdot CDCl_3$, M_r = 748.28, monoclinic, space group $P2_1/c$, a = 8.9048(18) Å, b = 11.445(2) Å, c = 32.830(7) Å, β = 91.24(3)°, V = 3345.1(12) Å^3, Z = 4, d_{calcd} =1.486 g cm^{-3}, F(000) = 1536, μ = 2.104 mm^{-1}, $2\theta_{max}$ = 51.3°, index ranges $-10 \le h \le 10$, $-13 \le k \le 13$, $-39 \le l \le 39$, 36 114 data (6273 unique), R(int) = 0.0931, 319 parameters, R1 ($I > 2\sigma(I)$) = 0.0343, wR2 = 0.0776, goodness of fit on F^2 1.042, $\Delta\rho_{max}$ ($\Delta\rho_{min}$) = 0.649 (−0.855) e Å^{-3}.

Data for 10a-BF_4: $C_{46}H_{43}BCl_4F_7NO_3P_2Pd$, M_r = 1111.76, monoclinic, space group $P2_1/n$, a = 11.612(2) Å, b = 23.143(5) Å, c = 18.136(4) Å, β = 90.71(3)°, V = 4873.5(17) Å^3, Z = 4, d_{calcd} = 1.515 g cm^{-3}, F(000) = 2248, μ = 0.733 mm^{-1}, $2\theta_{max}$ = 53.7°, index ranges $-14 \le h \le 14$, $-29 \le k \le 29$, $-23 \le l \le 22$, 70 118 data: (10 300 unique), R(int) = 0.0879, 586 parameters, R1 ($I > 2\sigma(I)$) = 0.0406, wR2 = 0.0959, goodness of fit on F^2 1.023, $\Delta\rho_{max}$ ($\Delta\rho_{min}$) = 1.132 (−0.975) e Å^{-3}.

Single crystals suitable for an X-ray structural analysis of **5b** were grown from $CDCl_3$ and those of **10a**-BF_4 by slow diffusion of hexane into a concentrated solution of **10a**-BF_4 in CH_2Cl_2 at 4 °C. 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.[21] The positions of the hydrogen atoms were calculated by assuming 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.

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Supporting Information Available: CIF files of the complexes **5b** and **10a**-BF_4 and tables giving the bond distances, bond angles, and torsion angles of **5b** and **10a**-BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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