Bis(allenylidene) Complexes of Palladium and Platinum[†]

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trans-Bis(alkynyl)palladium complexes, *trans*-[(PEt₃)₂Pd(−C≡CC(=O)NR₂)₂] (NR₂ = NMe₂ (**2a**), N(CH₂)₄ (**2b**)), were synthesized by two different methods: (a) by copper-catalyzed reaction of HC≡CC(=O)NR₂ with [PdCl₂(PEt₃)₂] under basic conditions and (b) by treating HC≡CC(=O)NR₂ with AgNO₃ followed by transmetalation of the alkynyl ligand from silver to [PdCl₂(PEt₃)₂]. The reaction of AgC≡CC(=O)NMe₂ (**3a**) with *trans*-[Br(P^tPr)₃]₂PdC≡CC(=O)N(CH₂)₄ (**5**) affords a complex containing two different alkynyl ligands, *trans*-[(P^tPr)₃]₂Pd{−C≡CC(=O)NMe₂}{−C≡CC(=O)N(CH₂)₄} (**6**). Methylation of **2a,b** and **6** with MeOTf or [Me₃O]BF₄ yields dicationic bisallenylidene complexes of palladium, *trans*-[(PEt₃)₂Pd{=C=C=C(OMe)NR₂}₂]²⁺ 2X[−] (X = OTf, BF₄; NR₂ = NMe₂, N(CH₂)₄) and *trans*-[(PEt₃)₂Pd{=C=C=C(OMe)NMe₂}{=C=C=C(OMe)N(CH₂)₄}]²⁺ 2OTf[−] (**7-OTf**). In contrast to the reaction of **3a** with [PdCl₂(PEt₃)₂], that of **3a** with the platinum complex [PtCl₂(PPh₃)₂] gives *cis*- and *trans*-[(PPh₃)₂Pt(−C≡CC(=O)NMe₂)₂] (**8a** (*cis*) and **9a** (*trans*)), depending on the reaction conditions and, upon subsequent alkylation with MeOTf, the *cis* and *trans* isomers of the first allenylidene platinum complexes, *cis*- and *trans*-[(PPh₃)₂Pt{=C=C=C(OMe)NMe₂}₂]²⁺ 2OTf[−].

Introduction

In 1976 Fischer et al.¹ and Berke² independently reported the synthesis of the first allenylidene complexes, L_nM=C=C=C(R¹)R². Since then, this new class of organometallic compounds has attracted a great deal of attention. Allenylidene complexes of most transition metals are now known, including complexes of titanium, chromium, tungsten, manganese, rhenium, iron, ruthenium, osmium, rhodium, iridium, and palladium.³ In most syntheses propargylic alcohols, HC≡CC(R¹)-(R²)OH, are used as the source of the allenylidene C₃ fragment, following a strategy originally introduced by Selegue.⁴ Coordination of the propargylic alcohol to the transition metal and tautomerization gives a hydroxyvinylidene ligand.

Subsequent elimination of water finally affords the allenylidene ligand.

We recently reported on the synthesis of the first stable palladium allenylidene complexes by a different method.⁵ Instead of propargylic alcohols, easily accessible *N,N*-dimethyl propiolamides were used as the C₃ source. Bromination of the terminal alkyne and subsequent oxidative addition to the zerovalent palladium complex [Pd(PPh₃)₄] yielded the corresponding alkynyl complex. Alkylation of these alkynyl complex at the oxygen atom of the dimethylamide substituent with either MeOTf or [Me₃O]BF₄ gave allenylidene complexes in almost quantitative yield (Scheme 1).

We now report that even dicationic bis(allenylidene) complexes are readily accessible by alkylation of suitable alkynyl complexes and on the synthesis of the first allenylidene complexes of platinum.

Results and Discussion

The bis(alkynyl)palladium complexes **2a,b**, required as starting material for the synthesis of bis(allenylidene) complexes by alkylation, were initially prepared by reaction of propiolamides **1a,b** with [PdCl₂(PEt₃)₂] in NEt₃ in the presence of a catalytic amount of copper(I) iodide (Scheme 2). In these reactions NEt₃ acts simultaneously as the solvent and the base. The same method was used by Osakada et al.⁶ for the synthesis of bis(alkynyl) complexes from methyl propiolate and [PdCl₂(PEt₃)₂]. Copper-catalyzed coupling of terminal alkynes with palladium halides was originally

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introduced by Hagihara et al.⁷ in 1970. In comparison to the method used for the synthesis of the first *mono*allenylidene complexes (see Scheme 1), this route offered two advantages: (a) the preparation of often air- and temperature-sensitive bromoalkynes by brominating terminal alkynes could be avoided and (b) instead of sensitive zerovalent tetrakis-(phosphine)palladium complexes, air-stable [PdCl₂(PET₃)₂] could be used as the precursor complex.

After recrystallization from CH₂Cl₂ the bis(alkynyl) complexes **2a,b** were obtained in only modest yields (**2a**, 45%; **2b**, 48%). In addition to **2a,b**, ca. 30% of [PdCl₂(PET₃)₂] was recovered. It was not possible to increase the yield by extending the reaction time or by using the propiolamides **1a,b** in large excess.

However, it was possible to considerably increase the yield of the bis(alkynyl) complex **2b** by transmetalation of the alkynyl ligand from silver to palladium. In addition, tedious fractional crystallization of the starting material and the product could thus be avoided. When the propiolamides **1a,b** were treated with silver nitrate, the corresponding silver acetylides **3a,b** were obtained in almost quantitative yield.⁸ Subsequent reaction of **3b** with 1/2 equiv of [PdCl₂(PET₃)₂]

gave, after column chromatography, complex **2b** in 68% isolated yield.

The observation of a triplet for the resonance of the palladium-bound carbon atom in the ¹³C NMR spectra (²J_{PC} = 16.6 Hz) indicated that the two phosphine ligands were mutually *trans*. Signals due to the corresponding *cis* isomer were not detected.

Alkylation of **2a,b** with 2.3 equiv of either MeOTf or [Me₃O]BF₄ gave dicationic allenylidene complexes. The alkylation proceeded exclusively at the oxygen atom. The addition of electrophiles to the C_β atom of (neutral or anionic) alkynyl complexes has turned out to be a convenient route to vinylidene complexes.⁹ However, in the reactions of **2a,b** with “Me⁺” there was no indication for an addition of the electrophile to the C_β atom of either one or both alkynyl ligands. The bis(allenylidene)palladium complexes **4a-X** and **4b-X** (X = OTf, BF₄) were isolated as white solids in quantitative and approximately 90% yields when MeOTf and [Me₃O]BF₄ were used as the alkylation agent, respectively. These very high yields are surprising, especially when considering that in the “second” reaction step cationic complexes are alkylated to form dicationic complexes and that only a slight excess of the alkylation agent is required. From the NMR spectroscopic data of **4a-X** and **4b-X** (e.g., ²J_{PC} = 15.6 Hz) it followed that the *trans* orientation of the ligands in the alkynyl complexes was retained in the allenylidene complexes. The synthesis of a related *trans*-bis(allenylidene)-palladium complex by a different method—transmetalation of allenylidene ligands from silver to [Pd(PPh₃)₄] accompanied by oxidation of Pd(0) to Pd(II)—has recently been reported.¹⁰

The new bis(allenylidene)palladium dications are symmetrically substituted. Therefore, we next addressed the question whether bis(allenylidene) complexes with two different allenylidene ligands are also accessible. To achieve that goal, the synthetic strategy had to be modified. Two options were conceivable: either starting from a bis(alkynyl) complex having two different alkynyl ligands or using two different alkylating agents. We choose the former option, although it required more reaction steps. First, the mono(alkynyl) complex **5** was synthesized by oxidative addition of BrC≡CC(=O)N(CH₂)₄ to [Pd(PPh₃)₄] followed by substitution of PPh₃ for the less basic PPh₃ ligand.⁵ Transmetalation of “C≡CC(=O)NMe₂” from Ag to Pd by addition of 1 equiv of the silver acetylide **3a** to a solution of **5** in CH₂Cl₂ afforded the bis(alkynyl) complex **6** in 59% yield. The bis(allenylidene) complex **7-OTf**, containing two different allenylidene ligands, was finally isolated in quantitative yield after alkylation of **6** with MeOTf as an off-white solid (Scheme 3). The observation of only one singlet in the ³¹P NMR spectra and of a triplet for the palladium-bound carbon atom in the ¹³C NMR spectra of **6** and **7-OTf** (²J_{PC} = 14.6 Hz (**6**) and 13.6 Hz (**7-OTf**)) confirmed that again the two phosphine ligands are mutually *trans*. There was no indication for the formation of a *cis* isomer.

The alkylation route to allenylidene complexes should also be applicable to the synthesis of allenylidene complexes of platinum, provided that the corresponding (alkynyl)platinum

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Scheme 3

Scheme 4

precursors are accessible. Until now, allenylidene complexes of platinum have been unknown.

Our initial attempts to synthesize (alkynyl)platinum complexes by the copper-catalyzed method met with failure. However, the complexes could be obtained in good yield by transmetalation of alkynyl ligands from silver to platinum (Scheme 4). The transmetalations proceeded smoothly, albeit significantly slower than those from silver to palladium. In contrast to bis(alkynyl)palladium complexes, the structure of the isolated bis(alkynyl)platinum complexes depended on the reaction time. When the reaction of 2 equiv of silver acetylide **3a** with a suspension of the alkynyl acceptor [PtCl₂(PPh₃)₂] in CH₂Cl₂ was terminated after 2 h, the

Scheme 5

cis-bis(alkynyl) complex **8a** was obtained, after column chromatography, in 68% isolated yield. The *cis* arrangement was deduced from the double doublet of the metal-bound carbon atoms in the ¹³C NMR spectrum (²J_{PC} = 144.7 and 20.5 Hz). When the reaction time was extended to 16 h, exclusively the *trans*-bis(alkynyl) complex **9a** was isolated in 80% yield. In contrast to the case for **8a** the resonance of the platinum-bound carbon atoms in **9a** appeared as a triplet (²J_{PC} = 14.6 Hz), thus confirming the *trans* arrangement. Since pure *cis*-**8a** was found to be stable in solution and did not isomerize to form the *trans* complex **9a**, silver acetylide must play an important role in promoting the *cis* $\rightarrow$ *trans* isomerization. Analogously to **9a**, the *trans* complex **9b** was prepared by following the same procedure.

Similarly to the related palladium complexes, the alkylation of **8a** and **9a** with MeOTf gave bis(allenylidene)platinum complexes in quantitative yield (Scheme 4), whereas the alkylation of **9a** with [Et₃O]BF₄ afforded the corresponding bis(allenylidene) complex in only 60% yield (after recrystallization). The stereochemistry at the metal center did not change on alkylation. Thus, the *cis* complex **10a**-OTf (C_α: ²J_{PC} = 140.5 and 19.1 Hz) was obtained from *cis*-**8a** and the *trans* compound **11a**-OTf (C_α: ²J_{PC} = 13.8 Hz) from *trans*-**9a**.

All new alkynyl and allenylidene complexes were characterized by spectroscopic means and by elemental analyses. The resonances of the alkynyl ligand in the ¹³C NMR spectra compared well with those of known palladium alkynyl complexes.¹¹

Two singlets for the N-bound methyl groups in the NMR spectra of the bis(alkynyl) complex **2a** and the bis(allenylidene) complex **4a**-BF₄ indicated a rather high barrier to rotation around the C(sp²)–N bond. From the coalescence of the two signals of **2a** in C₂D₂Cl₄ at 108 °C a barrier of ΔG[‡] = 76.3 ± 1.0 kJ/mol was calculated. The barrier is slightly lower than that in free propiolamides (RC≡CC(=O)NMe₂, R = H, Me, Ph: 79.6–82.1 kJ/mol)¹² and almost identical with that in the *mono*(alkynyl)palladium complex [Br(PPh₃)₂PdC≡CC(=O)NMe₂] (ΔG[‡] = 76.1 ± 0.4 kJ/mol),⁵ indicating almost negligible interaction of the metal with the C(=O)NMe₂ fragment. The barrier to rotation around the C(sp²)–N bond in the bis(allenylidene)palladium complex **4a**-BF₄ is even higher than in **2a**. No coalescence of the N–Me signals was observed up to the instrumental limit of 130 °C, indicating considerable C–N double-bond

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Figure 1. Structure of the bis(alkynyl) complex **2b** in the crystal state (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity).

character and a rather important contribution of resonance form III to the overall bond description (Scheme 5). The conclusion is supported by the appearance of the C_α resonance at rather high field. From the NMR spectra it also follows that resonance form IV can only play a minor role (if one at all).

The formation of dicationic (allenylidene)palladium complexes by O-alkylation of the alkynyl complexes is accompanied by a pronounced shift of the C_α resonances to lower field by about 37 ppm, a shift of the C_β resonance to higher field ($\Delta\delta \approx 8$ ppm), and a shift of the $\nu(C\equiv C)$ vibration in the IR spectra to lower energy by only 4–9 cm^{-1} . Alkylation of bis(alkynyl)platinum complexes leads to similar shifts, almost independent of the cis or trans arrangement of the ligands. On alkylation of related *mono*(alkynyl) complexes of the type *trans*-[Br(PR₃)₂PdC $\equiv$ CC(=O)NMe₂] these shifts are more pronounced by about 25%. In contrast to C_α and C_β , the resonances of the C_γ atom and of the N substituents are almost unaffected on alkylation. Similar trends have earlier been observed on alkylation of (alkynyl)pentacarbonylchromate complexes to give neutral allenylidene complexes.¹³

The ¹³C NMR spectra of the *cis*- and *trans*-bis(alkynyl)-platinum complexes are similar, the resonances of C_α and C_β of the *cis* isomers being at only slightly higher field ($\Delta\delta$ ca. 7 ppm (C_α), 4 ppm (C_β)). In general, the resonances of the alkynyl ligand in the ¹³C NMR spectra compared well with those of other known (alkynyl)platinum complexes.¹⁴

The various ¹³C resonances, the observation of two signals for the dimethylamino substituents in the ¹H and ¹³C NMR spectra, and the minor changes in the $\nu(C\equiv C)$ absorption on double alkylation of the bis(alkynyl) complexes demonstrate the importance of the resonance form III (Scheme 5) for the overall bond description of these cationic allenylidene complexes and indicate that the donor/acceptor properties of alkynyl, allenylidene, and phosphine ligands in these complexes are very similar.

The solid-state structures of the bis(alkynyl) complexes **2b** (Figure 1), **8a** (Figure 2), and **9b** (Figure 3) and the structure of the bis(allenylidene)platinum complex **12a**-BF₄ (Figure 4)

Figure 2. Structure of the bis(alkynyl) complex **8a** in the crystal state. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

Figure 3. Structure of the bis(alkynyl) complex **9b** in the crystal state. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

were additionally established by X-ray diffraction studies (Tables 1 and 2). In all four complexes the metal atom has planar coordination. As already deduced from the NMR spectra, the phosphine ligands in complex **8a** are mutually *cis* and those in the bis(alkynyl) complexes **2b** and **9b** and in the bis(allenylidene) complex **12a**-BF₄ are *trans*. In all complexes (*cis* and *trans*) the substituents at C_γ have a *transoid* orientation and occupy opposite positions with respect to the coordination plane of the metal.

In **2b** the plane formed by the atoms C(3), O, and N (C_γ plane) and the coordination plane of palladium are almost coplanar (torsion angle O(1)–C(3)–Pd(1)–P(1) = 12.9°). In contrast, in the platinum complexes **8a** (*cis*) and **9b** (*trans*) the C_γ planes are strongly tilted against the coordination plane of platinum (**8a**, 63.3 and 71.4°; **9b**, 65.4°). In the allenylidene platinum complex **12a**-BF₄ the angle between both planes is similar (69.7°) and compares well with that in the bis(allenylidene)palladium complex **13**¹⁰ (64.4°); however, it is smaller than that in the *mono*(allenylidene)palladium

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cation $\text{trans-}[\text{CF}_3\text{COO}(\text{PPh}_3)_2\text{Pd}=\text{C}=\text{C}=\text{C}(\text{OMe})\text{NMe}_2]^+$ (**14**; 90°). In all complexes the M–C $_{\beta}$ fragment only slightly

Figure 4. Structure of the bis(allenylidene) complex **12a** BF₄ in the crystal state. Ellipsoids are drawn at the 50% probability level; hydrogen atoms, anions, and two molecules of acetone are omitted for clarity.

Table 1. Important Bond Distances (Å) and Angles (deg) in 2b, 8a, 9b, and 12a-BF₄

	2b ^a	8a ^b	9b ^b	12a BF ₄ ^b
M–C $_{\alpha}$	1.9997(18)	2.001(3)/1.994(3)	2.003(3)	1.992(2)
M–P	2.3064(6)	2.3301(9)/2.3194(11)	2.3076(9)	2.3113(10)
C $_{\alpha}$ –C $_{\beta}$	1.206(2)	1.201(5)/1.203(5)	1.207(4)	1.191(3)
C $_{\beta}$ –C $_{\gamma}$	1.456(2)	1.459(5)/1.450(5)	1.456(4)	1.415(3)
C $_{\gamma}$ –N	1.348(2)	1.336(5)/1.349(5)	1.345(4)	1.306(3)
C $_{\gamma}$ –O	1.234(2)	1.252(5)/1.229(4)	1.242(4)	1.319(3)
M–C $_{\alpha}$ –C $_{\beta}$	175.85(12)	174.2(3)/176.8(3)	178.7(3)	178.64(18)
C $_{\alpha}$ –C $_{\beta}$ –C $_{\gamma}$	173.91(15)	170.9(4)/169.3(4)	174.1(3)	167.9(2)

^a M = Pd. ^b M = Pt.

deviates from linearity, C $_{\alpha}$ –C $_{\beta}$ –C $_{\gamma}$ (167.9–174.1°) being smaller than M–C $_{\alpha}$ –C $_{\beta}$ (174.2–178.7°) (Table 1).

13

The Pd–C and Pt–C (alkynyl) bond lengths are within the usually observed ranges.^{11,15,16} The Pt–C distance in the dicationic allenylidene complex **12a**-BF₄ is only marginally less than that in the neutral alkynyl complexes **8a** and **9b**. The “formal” double bond C $_{\alpha}$ –C $_{\beta}$ in **12a**-BF₄ (1.191(3) Å) compares well with the triple bond in the alkynyl complexes **8a** (1.201(5) and 1.203(5) Å) and **9b** (1.207(4) Å) and is even slightly shorter, indicating considerable triple-bond character (resonance form III in Scheme 5). The C $_{\beta}$ –C $_{\gamma}$ bond in **12a**-BF₄ (1.415(3) Å) is significantly shorter than in **8a** (1.459(5) and 1.450(5) Å) and **9b** (1.456(4) Å), corresponding to resonance forms I and II (Scheme 5). As expected, O-alkylation results in an elongation of the C $_{\gamma}$ –O bond (Table 1) and, conversely, leads to a significant shortening of the C $_{\gamma}$ –N bond (1.306(3) Å in **12a**-BF₄ compared to 1.336(5) and 1.349(5) Å in **8a** and 1.345(4) Å in **9b**). The shortening indicates a stronger π interaction of the NMe₂ substituent with the carbon chain in the allenylidene complex than in alkynyl complexes. Since the C $_{\gamma}$ –N distances in the monocationic complex **14**⁵ (1.296(4) Å) and in the dicationic complex **12a** are equal, increasing the charge of the complex does not significantly alter the extent of the Me₂N–C $_{\gamma}$ π interaction.

In summary, various types of bis(allenylidene)palladium complexes as well as the first isolable bis(allenylidene)platinum complexes are readily accessible by a straightforward two-step synthesis from silver acetylides. In contrast to the

Table 2. Crystallographic Data and Refinement Methods for 2b, 8a, 9b, and 12a-BF₄

	2b	8a	9b	12a BF ₄
empirical formula	C ₂₆ H ₄₆ N ₂ O ₂ P ₂ Pd	C ₄₇ H ₄₄ Cl ₂ N ₂ O ₂ P ₂ Pt	C ₅₂ H ₅₀ Cl ₄ N ₂ O ₂ P ₂ Pt	C ₅₆ H ₆₄ B ₂ F ₈ N ₂ O ₄ P ₂ Pt
<i>M_r</i>	586.99	996.77	1133.77	1259.74
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.226(2)	9.7026(19)	8.1772(16)	12.768(3)
<i>b</i> (Å)	7.2469(14)	24.852(5)	12.552(3)	15.817(3)
<i>c</i> (Å)	20.575(6)	18.987(6)	12.561(3)	15.353(6)
α (deg)	90	90	69.75(3)	90
β (deg)	113.33(3)	109.68(3)	83.34(3)	117.76(2)
γ (deg)	90	90	77.35(3)	90
<i>V</i> (Å ³)	1400.1(6)	4310.9(18)	1179.1(5)	2743.7(14)
<i>Z</i>	2	4	1	2
cryst size (mm ³)	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.3
ρ_{calcd} (g cm ^{−3})	1.392	1.536	1.597	1.525
μ (mm ^{−1})	0.802	3.493	3.313	2.690
<i>F</i> (000)	616	1992	568	1272
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)
max 2 θ (deg)	53.48	53.88	53.54	53.72
index ranges	−12 ≤ <i>h</i> ≤ 12 −9 ≤ <i>k</i> ≤ 9 −25 ≤ <i>l</i> ≤ 25	−11 ≤ <i>h</i> ≤ 12 −31 ≤ <i>k</i> ≤ 31 −23 ≤ <i>l</i> ≤ 24	−10 ≤ <i>h</i> ≤ 10 −15 ≤ <i>k</i> ≤ 15 −15 ≤ <i>l</i> ≤ 15	−16 ≤ <i>h</i> ≤ 16 −19 ≤ <i>k</i> ≤ 20 −19 ≤ <i>l</i> ≤ 19
no. of data	19 937	63 743	16 169	40 405
no. of unique data	2964	9171	4967	5857
<i>R</i> (int)	0.0861	0.0576	0.0578	0.0573
params	154	505	286	340
goodness of fit on <i>F</i> ²	1.045	1.105	1.038	1.048
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0266, 0.0504	0.0303, 0.0577	0.0246, 0.0573	0.0204, 0.0400
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0304, 0.0515	0.0363, 0.0593	0.0250, 0.0577	0.0284, 0.0418
largest diff peak/hole (Å ^{−3})	1.167, −0.507	1.346, −1.196	0.951, −1.965	0.466, −0.876

corresponding palladium complexes, *cis*- as well as *trans*-bis(allynylidene)platinum complexes can be obtained in pure form by choice of the reaction conditions. All new complexes are remarkably stable and exhibit all characteristic features of π -donor-substituted allenylidene complexes.

Experimental Section

All operations were performed under an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), LiAlH_4 (petroleum ether, hexane), sodium (THF, Et_2O), or KOH (NEt_3). The silica gel used for chromatography (Baker, silica for flash chromatography) was nitrogen saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra were recorded with Bruker Avance 400 and Varian Inova 400 spectrometers at ambient temperature. Chemical shifts are relative to the residual solvent peaks: tetramethylsilane (^1H , ^{13}C) and 100% H_3PO_4 (^{31}P). IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analyses: Heraeus Elemental Vario EL and Elemental Vario MICRO Cube. The compounds **1a**, **b**, **17**, **3a**, **b**, **8**, **5**, **5** and $[\text{Me}_3\text{O}]\text{BF}_4$ ¹⁸ were prepared according to literature procedures. All other chemicals were commercial products and used as supplied.

Synthesis of Bis(alkynyl)palladium Complexes. Method A. A suspension of 1 mmol of $[\text{PdCl}_2(\text{PET}_3)_2]$ in 40 mL of dry NEt_3 was treated at room temperature with 2.1 mmol of the corresponding propiolamide **1a**, **b** and 10 mg of CuI. The yellow solution turned colorless, and a white precipitate formed. The mixture was stirred for 60 min at room temperature. The precipitate was filtered off and washed with two 20 mL portions of hexane and then with 40 mL of Et_2O . The remaining residue was dissolved in 15 mL of CH_2Cl_2 and crystallized at -28°C overnight. The colorless needles (remaining $[\text{PdCl}_2(\text{PET}_3)_2]$) were filtered off, and the crude product was crystallized from 10 mL of CH_2Cl_2 at room temperature within 5 days to obtain the pure product as colorless crystalline blocks.

Method B. A suspension of 0.5 mmol of $[\text{PdCl}_2(\text{PET}_3)_2]$ in 10 mL of CH_2Cl_2 was treated with 1.0 mmol of the corresponding silver acetylide **3a**, **b** at room temperature. The mixture was stirred for 2 h. To remove AgCl, the mixture was filtered through a short plug of Celite. The resulting yellow solution was concentrated in vacuo, and the crude product was purified by column chromatography using mixtures of CH_2Cl_2 and acetone as the eluent.

***trans*-Bis(3-(dimethylamino)-3-oxy-1-propynyl)bis(triethylphosphine)palladium(II) (2a).** Colorless crystals. Yield: 45% (method A). Mp: 126°C . ^1H NMR (400 MHz, CD_2Cl_2): δ 3.09 (s, 6H, NCH₃), 2.78 (s, 6H, NCH₃), 1.89 (m, 12H, PCH_2CH_3), 1.08 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 155.9 ($\text{C}(\text{O})\text{NMe}_2$), 118.5 (t, $^2J_{\text{PC}}$ 16.6 Hz, $\text{PdC}\equiv\text{C}$), 105.5 ($\text{PdC}\equiv\text{C}$), 38.5 (NCH₃), 33.7 (NCH₃), 17.3 (t, $^1J_{\text{PC}}$ 14.6 Hz, PCH_2CH_3), 8.7 (PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 19.8 ppm. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2088 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 255 (4.313). FAB MS m/z (%): 535 (70) $[\text{M}^+]$, 417 (10) $[(\text{M} - \text{PET}_3)^+]$, 321 (12) $[(\text{M} - \text{PET}_3 - \text{CCC}(\text{O})\text{NMe}_2)^+]$. Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{N}_2\text{O}_2\text{P}_2\text{Pd}$

(534.96): C, 49.40; H, 7.91; N, 5.24. Found: C, 49.35; H, 7.58; N, 5.29.

***trans*-Bis(3-(*N,N*-tetramethyleamino)-3-oxy-1-propynyl)bis(triethylphosphine)palladium(II) (2b).** Colorless crystals. Yield: 48% (method A), 68% (method B). Mp: 109°C dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 3.54 (t, J 6.0 Hz, 4H, NCH₂), 3.31 (t, J 6.0 Hz, 4H, NCH₂), 1.95 (m, 12H, PCH_2CH_3), 1.83 (m, 8H, CH₂), 1.14 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 154.2 ($\text{C}(\text{O})\text{N}(\text{CH}_2)_4$), 116.9 (t, $^2J_{\text{PC}}$ 16.6 Hz, $\text{PdC}\equiv\text{C}$), 106.9 (t, $^3J_{\text{PC}}$ 3.5 Hz, $\text{PdC}\equiv\text{C}$), 48.4 (NCH₂), 45.1 (NCH₂), 25.9 (CH₂), 25.3 (CH₂), 17.2 (t, $^1J_{\text{PC}}$ 14.6 Hz, PCH_2CH_3), 8.7 (PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 19.6 ppm. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2095 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 256 (4.293). FAB MS m/z (%): 587 (55) $[\text{M}^+]$, 515 (4) $[(\text{M} - \text{C}_4\text{H}_8\text{N})^+]$, 469 (9) $[(\text{M} - \text{PET}_3)^+]$, 371 (8) $[(\text{M} - \text{PET}_3 - \text{C}(\text{O})\text{NC}_4\text{H}_8)^+]$. Anal. Calcd for $\text{C}_{26}\text{H}_{46}\text{N}_2\text{O}_2\text{P}_2\text{Pd}$ (587.03): C, 53.20; H, 7.90; N, 4.77. Found: C, 52.92; H, 7.97; N, 4.74.

Alkylation of Bis(alkynyl)palladium Complexes. A solution of 0.11 mmol of the corresponding bis(alkynyl)palladium complex in 6 mL of CH_2Cl_2 was treated with 0.25 mmol of MeOTf or $[\text{Me}_3\text{O}]\text{BF}_4$. The mixture was stirred for 90 min at room temperature. The solvent was removed in vacuo, giving the pure product in quantitative yield.

***trans*-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienylydene)-bis(triethylphosphine)palladium(II)] Trifluoromethanesulfonate (4a-OTf).** Off white solid. Yield: 100%. Mp: 141 143°C dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.17 (s, 6H, OCH₃), 3.43 (s, 6H, NCH₃), 3.22 (s, 6H, NCH₃), 1.93 (m, 12H, PCH_2CH_3), 1.12 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 155.1 (t, $^2J_{\text{PC}}$ 15.6 Hz, C_α), 154.8 (C_γ), 121.5 (q, J_{CF} 321.3 Hz, CF_3), 97.5 (t, $^3J_{\text{PC}}$ 3.5 Hz, C_β), 62.2 (OCH₃), 42.7 (NCH₃), 38.5 (NCH₃), 17.5 (t, $^1J_{\text{PC}}$ 15.0 Hz, PCH_2CH_3), 8.8 (PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.5 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ 78.9 (SO_3CF_3) ppm. IR (CH_2Cl_2): $\nu(\text{CCC})$ 2084 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 273 (4.546). FAB MS m/z (%): 865 (5) $[(\text{M} + 2\text{H})^+]$, 712 (28) $[(\text{M} - \text{OTf} - 2\text{H})^+]$, 594 (100) $[(\text{M} - \text{OTf} - 2\text{H} - \text{PET}_3)^+]$, 446 (10) $[(\text{M} - 2\text{OTf} - 1\text{H} - \text{PET}_3)^+]$, 330 (25) $[(\text{M} - 2\text{OTf} - 2\text{PET}_3)^+]$. Anal. Calcd for $\text{C}_{26}\text{H}_{48}\text{F}_6\text{N}_2\text{O}_8\text{P}_2\text{PdS}_2$ (863.16): C, 36.18; H, 5.61; N, 3.25. Found: C, 36.28; H, 5.65; N, 3.25.

***trans*-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienylydene)-bis(triethylphosphine)palladium(II)] Tetrafluoroborate (4a-BF₄).** White solid. Yield: 100%. Mp: $125 - 127^\circ\text{C}$ dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.21 (s, 6H, OCH₃), 3.47 (s, 6H, NCH₃), 3.25 (s, 6H, NCH₃), 1.96 (m, 12H, PCH_2CH_3), 1.16 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 155.0 (t, $^2J_{\text{PC}}$ 15.6 Hz, C_α), 154.7 (C_γ), 97.5 (t, $^3J_{\text{PC}}$ 3.1 Hz, C_β), 62.2 (OCH₃), 42.6 (NCH₃), 38.3 (NCH₃), 17.4 (t, $^1J_{\text{PC}}$ 15.1 Hz, PCH_2CH_3), 8.7 (PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.4 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ 153.8 (BF_4), 153.9 (BF_4) ppm. IR (CH_2Cl_2): $\nu(\text{CCC})$ 2084 cm^{-1} . FAB MS m/z (%): 651 (3) $[(\text{M} - \text{BF}_4)^+]$, 549 (100) $[(\text{M} - 2\text{BF}_4 - \text{Me})^+]$. Anal. Calcd for $\text{C}_{24}\text{H}_{48}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{P}_2\text{Pd}$ (738.63): C, 39.03; H, 6.55; N, 3.79. Found: C, 39.16; H, 6.42; N, 4.08.

***trans*-[Bis(3-(*N,N*-tetramethyleamino)-3-methoxy-1,2-propadienylydene)bis(triethylphosphine)palladium(II)] Trifluoromethanesulfonate (4b-OTf).** White solid. Yield: 100%. Mp: 122°C dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.20 (s, 6H, OCH₃), 3.81 (t, J 6.0 Hz, 4H, NCH₂), 3.71 (t, J 6.0 Hz, 4H, NCH₂), 2.08 (m, 8H, CH₂), 1.98 (m, 12H, PCH_2CH_3), 1.17 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 153.9 (t, $^2J_{\text{PC}}$ 15.6 Hz, C_α), 152.3 (C_γ), 121.5 (q, J_{CF} 321.1 Hz, CF_3), 98.4 (t, $^3J_{\text{PC}}$ 3.1 Hz, C_β), 61.7 (OCH₃), 53.0 (NCH₂), 49.9 (NCH₂), 25.1 (CH₂), 25.0 (CH₂), 17.4 (t, $^1J_{\text{PC}}$ 15.1 Hz, PCH_2CH_3), 8.8 (PCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 21.3 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ 78.9 (SO_3CF_3) ppm. IR (CH_2Cl_2): $\nu(\text{CCC})$ 2086 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ): 276 (4.527). FAB MS m/z (%): 766 (4) $[(\text{M} - \text{OTf})^+]$, 648 (100) $[(\text{M} - \text{OTf} - \text{PET}_3)^+]$, 499 (8)

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[(M 2 OTf PEt₃)⁺]. Anal. Calcd for C₃₀H₅₂F₆N₂O₈P₂PdS₂ (915.23): C, 39.37; H, 5.73; N, 3.06. Found: C, 39.01; H, 5.60; N, 3.17.

trans-[Bis(3-(*N,N*-tetramethyleneamino)-3-methoxy-1,2-propadienyldiene)bis(triethylphosphine)palladium(II)] Tetrafluoroborate (4b-BF₄). White solid. Yield: 100%. Mp: 99 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 4.14 (s, 6H, OCH₃), 3.75 (br, 4H, NCH₂), 3.64 (br, 4H, NCH₂), 2.01 (m, 8H, CH₂), 1.93 (m, 12H, PCH₂CH₃), 1.12 (m, 18H, PCH₂CH₃) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 153.8 (t, ²J_{PC} 15.6 Hz, C_α), 152.2 (C_γ), 98.3 (t, ³J_{PC} 3.0 Hz, C_β), 61.6 (OCH₃), 52.8 (NCH₂), 49.6 (NCH₂), 25.0 (CH₂), 24.9 (CH₂), 17.3 (t, ¹J_{PC} 15.1 Hz, PCH₂CH₃), 8.7 (PCH₂CH₃) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 21.2 ppm. ¹⁹F NMR (376 MHz, CD₂Cl₂): δ 153.0 (BF₄), 153.1 (BF₄) ppm. IR (CH₂Cl₂): ν(CCC) 2087 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 273 (4.480). FAB MS *m/z* (%): 705 (18) [(M BF₄)⁺], 602 (54) [(M 2 BF₄ Me)⁺], 516 (100) [(M BF₄ PEt₃ N(CH₂)₄)⁺]. Anal. Calcd for C₂₈H₅₂B₂F₈N₂O₂P₂Pd·0.5CH₂Cl₂ (790.70): C, 41.09; H, 6.41; N, 3.36. Found: C, 40.83; H, 6.31; N, 3.05.

trans-(3-(Dimethylamino)-3-oxy-1-propynyl)(3'-(*N,N*-tetramethyleneamino)-3'-oxy-1'-propynyl)bis(triisopropylphosphine)palladium(II) (6). A solution of 0.8 mmol of **5** in 16 mL of dry CH₂Cl₂ was treated with 0.8 mmol of **3a** at room temperature. The mixture was stirred overnight. To remove AgCl the mixture was filtered through a short plug of Celite. The resulting brown solution was concentrated in vacuo and the crude product was purified by column chromatography using mixtures of CH₂Cl₂ and acetone as eluents. Off white solid. Yield: 59%. Mp 135 °C (dec). ¹H NMR (400 MHz, CD₂Cl₂): δ 3.44 (t, *J* 6.0 Hz, 2H, NCH₂), 3.23 (t, *J* 6.0 Hz, 2H, NCH₂), 3.04 (s, 3H, NCH₃), 2.75 (s, 3H, NCH₃), 2.72 (m, 6H, CH(CH₃)₂), 1.75 (m, 4H, CH₂), 1.29 (q, *J* 8.0 Hz, 36H, CH(CH₃)₂) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 154.6 (C(O)NMe₂), 152.9 (C(O)N(CH₂)₄), 119.7 (t, ²J_{PC} 16.1 Hz, PdC≡C), 117.9 (t, ²J_{PC} 14.6 Hz, PdC≡C), 107.6 (t, ³J_{PC} 2.0 Hz, PdC≡C), 106.3 (t, ³J_{PC} 2.0 Hz, PdC≡C), 46.9 (NCH₂), 43.8 (NCH₂), 37.0 (NCH₃), 32.5 (NCH₃), 24.7 (CH₂), 24.3 (t, ¹J_{PC} 11.6 Hz, CH(CH₃)₂), 24.0 (CH₂), 19.1 (CH(CH₃)₂) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 46.0 ppm. IR (CH₂Cl₂): ν(C≡C) 2087 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 240 (4.422). FAB MS *m/z* (%): 645 (34) [M⁺]. Anal. Calcd for C₃₀H₅₆N₂O₂P₂Pd·0.25CH₂Cl₂ (645.15): C, 54.52; H, 8.55; N, 4.20. Found: C, 54.22; H, 8.26; N, 4.18.

trans-[(3-(Dimethylamino)-3-methoxy-1,2'-propadienyldiene)-(3'-(*N,N*-tetramethyleneamino)-3'-methoxy-1'-2'-propadienyldiene)-bis(triisopropylphosphine)palladium(II)] Trifluoromethanesulfonate (7-OTf). Off white solid. Yield: 100%. Mp: 102 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 4.13 (s, 3H, OCH₃), 4.11 (s, 3H, OCH₃), 3.70 (m, 2H, NCH₂), 3.66 (m, 2H, NCH₂), 3.38 (s, 3H, NCH₃), 3.19 (s, 3H, NCH₃), 2.65 (m, 6H, CH(CH₃)₂), 1.98 (m, 4H, CH₂), 1.32 (m, 36H, CH(CH₃)₂) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 157.4 (t, ²J_{PC} 13.6 Hz, C_α), 155.8 (t, ²J_{PC} 13.6 Hz, C_α), 154.1 (C_γ), 151.7 (C_γ), 120.9 (q, *J*_{CF} 319.6 Hz, CF₃), 100.2 (C_β), 99.3 (C_β), 62.0 (OCH₃), 61.5 (OCH₃), 52.6 (NCH₂), 49.8 (NCH₂), 42.3 (NCH₃), 38.5 (NCH₃), 26.1 (t, ¹J_{PC} 11.6 Hz, CH(CH₃)₂), 24.9 (CH₂), 24.8 (CH₂), 20.2 (CH(CH₃)₂) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 50.1, 49.5 ppm. ¹⁹F NMR (376 MHz, CD₂Cl₂): δ 78.8 (SO₃CF₃) ppm. IR (CH₂Cl₂): ν(CCC) 2081 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 273 (4.546). FAB MS *m/z* (%): 822 (3) [(M OTf)⁺], 663 (100) [(M OTf P⁺Pr₃)⁺]. Anal. Calcd for C₃₄H₆₂F₆N₂O₈P₂PdS₂·1.5 CH₂Cl₂ (1100.75): C 38.74, H 5.95, N 2.54. Found: C 38.61, H 6.20, N 2.47.

Synthesis of Bis(alkynyl)platinum Complexes. A suspension of 0.3 mmol of [PtCl₂(PPh₃)₂] in 10 mL of dry CH₂Cl₂ was treated with 0.6 mmol of the corresponding silver acetylide at room temperature. The mixture was stirred (for the reaction time, see below) at room temperature. Then the mixture was filtered through a short plug of Celite to remove AgCl. The resulting

yellow solution was concentrated in vacuo, and the crude product was purified by column chromatography using mixtures of CH₂Cl₂ and acetone as eluent.

cis-Bis(3-(dimethylamino)-3-oxy-1-propynyl)bis(triphenylphosphine)platinum(II) (8a). Reaction time: 2 h. White solid. Yield: 68%. Mp: 185 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.43 (m, 12H, *o* CH), 7.33 (m, 6H, *p* CH), 7.20 (m, 12H, *m* CH), 2.63 (s, 6H, NCH₃), 2.54 (s, 6H, NCH₃) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 155.9 (C(O)NMe₂), 135.1 (t, ²J_{PC} 6.0 Hz, *o* C), 131.0 (*p* C), 128.5 (t, ³J_{PC} 5.5 Hz, *m* C), 108.7 (dd, ²J_{PC(trans)} 144.7 Hz, ²J_{PC(cis)} 20.5 Hz, PtC≡C), 103.2 (vt, ³J_{PC} 16.1 Hz, PtC≡C), 38.2 (NCH₃), 33.6 (NCH₃) ppm, not observed: (*i* C). ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 15.0 (¹J_{Ppt} 2364 Hz) ppm. IR (CH₂Cl₂): ν(C≡C) 2117, 2108 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 227 (4.350). FAB MS *m/z* (%): 913 (11) [(M + H)⁺], 814 (2) [(M CCC(=O)NMe₂)⁺], 718 (100) [(M 2 CCC(=O)NMe₂)⁺], 650 (36) [(M PPh₃)⁺]. Anal. Calcd for C₄₆H₄₂N₂O₂P₂Pt·0.75CH₂Cl₂ (911.86): C, 57.56; H, 4.49; N, 2.87. Found: C, 57.20; H, 4.73; N, 2.82.

trans-Bis(3-(dimethylamino)-3-oxy-1-propynyl)bis(triphenylphosphine)platinum(II) (9a). Reaction time: 16 h. White solid. Yield: 80%. Mp: 263 265 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.74 7.68 (m, 12H, *o* CH), 7.46 7.37 (m, 18H, *m*, *p* CH), 2.52 (s, 6H, NCH₃), 2.24 (s, 6H, NCH₃) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 155.8 (C(O)NMe₂), 135.5 (t, ²J_{PC} 6.0 Hz, *o* C), 131.3 (*p* C), 131.1 (t, ¹J_{PC} 29.6 Hz, *i* C), 128.6 (t, ³J_{PC} 5.5 Hz, *m* C), 115.7 (t, ²J_{PC} 14.6 Hz, PtC≡C), 107.3 (PtC≡C), 37.8 (NCH₃), 33.5 (NCH₃) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 17.4 (¹J_{Ppt} 2586 Hz) ppm. IR (CH₂Cl₂): ν(C≡C) 2098 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 314 (3.873). FAB MS *m/z* (%): 913 (100) [(M + H)⁺], 867 (66) [(M NMe₂ H)⁺], 814 (9) [(M CCC(=O)NMe₂)⁺], 718 (41) [(M 2 CCC(=O)NMe₂)⁺]. Anal. Calcd for C₄₆H₄₂N₂O₂P₂Pt·0.25 CH₂Cl₂ (911.86): C, 59.53; H, 4.59; N, 3.00. Found: C, 59.75; H, 4.48; N, 3.13.

trans-Bis(3-(*N,N*-tetramethyleneamino)-3-oxy-1-propynyl)-bis(triphenylphosphine)platinum(II) (9b). Rose solid. Yield: 52%. Mp: 258 260 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.67 7.62 (m, 12H, *o* CH), 7.38 7.30 (m, 18H, *m*, *p* CH), 2.92 (t, *J* 6.0 Hz, 4H, NCH₂), 2.37 (t, *J* 6.0 Hz, 4H, NCH₂), 1.51 (m, 4H, CH₂), 1.35 (m, 4H, CH₂) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 152.8 (C(O)NMe₂), 134.2 (t, ²J_{PC} 6.5 Hz, *o* C), 129.9 (*p* C), 129.8 (t, ¹J_{PC} 29.1 Hz, *i* C), 127.2 (t, ³J_{PC} 5.0 Hz, *m* C), 113.3 (t, ²J_{PC} 14.6 Hz, PtC≡C), 107.4 (t, ³J_{PC} 2.0 Hz, PtC≡C), 46.2 (NCH₂), 43.4 (NCH₂), 24.4 (CH₂), 23.9 (CH₂) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 17.8 (¹J_{Ppt} 2590 Hz) ppm. IR (CH₂Cl₂): ν(C≡C) 2105 cm⁻¹. UV vis (CH₂Cl₂): λ_{max} (nm) (log ε) 314 (3.850). FAB MS *m/z* (%): 965 (100) [(M + H)⁺], 894 (40) [(M N(CH₂)₄)⁺], 842 (11) [(M CCC(=O)N(CH₂)₄)⁺], 718 (24) [(M 2 CCC(=O)N(CH₂)₄)⁺]. Anal. Calcd for C₅₀H₄₆N₂O₂P₂Pt·0.25CH₂Cl₂ (963.94): C, 61.26; H, 4.76; N, 2.84. Found: C, 61.10; H, 4.88; N, 2.85.

Alkylation of Bis(alkynyl)platinum Complexes. A solution of 0.11 mmol of the corresponding bis(alkynyl)platinum complex in 6 mL of dry CH₂Cl₂ was treated with 0.25 mmol of MeOTf. The mixture was stirred for 90 min at room temperature. Then the solvent was removed in vacuo, giving the pure product in quantitative yield.

cis-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienyldiene)bis(triphenylphosphine)platinum(II)] Trifluoromethanesulfonate (10a-OTf). Pale yellow solid. Yield: 100%. Mp: 207 °C dec. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.45 7.35 (m, 18H, *m*, *p* CH), 7.30 7.27 (m, 12H, *o* CH), 3.83 (s, 6H, OCH₃), 3.13 (s, 6H, NCH₃), 3.06 (s, 6H, NCH₃) ppm. ¹³C NMR (100.5 MHz, CD₂Cl₂): δ 155.6 (C_γ), 142.2 (dd, ²J_{PC(trans)} 140.5 Hz, ²J_{PC(cis)} 19.1 Hz, C_α), 134.9 (t, ²J_{PC} 6.0 Hz, *o* C), 132.2 (*p* C), 129.3 (t, ³J_{PC} 5.5 Hz, *m* C), 129.3 (t, ¹J_{PC} 29.6 Hz, *i* C), 121.6 (q, *J*_{CF} 320.6 Hz, CF₃), 93.4 (vt, ³J_{PC} 16.1 Hz, C_β), 62.4 (OCH₃), 42.6 (NCH₃), 38.2 (NCH₃) ppm. ³¹P NMR (161.8 MHz, CD₂Cl₂): δ 12.3 (¹J_{Ppt} 2407 Hz) ppm. ¹⁹F NMR

(376 MHz, CD_2Cl_2): δ 78.8 (SO_3CF_3). IR (CH_2Cl_2): $\nu(\text{CCC})$ 2127, 2106 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 227 (4.389). FAB MS m/z (%): 1091 (42) [(M OTf) $^+$], 926 (100) [(M 2 OTf CH_3) $^+$], 828 (56) [(M OTf PPh_3) $^+$], 679 (53) [(M 2 OTf PPh_3) $^+$]. Anal. Calcd for $\text{C}_{50}\text{H}_{48}\text{F}_6\text{N}_2\text{O}_8\text{P}_2\text{PtS}_2$ (1240.07): C, 48.43; H, 3.90; N, 2.26. Found: C, 48.26; H, 3.93; N, 2.15.

trans-[Bis(3-(dimethylamino)-3-methoxy-1,2-propadienyldiene)-bis(triphenylphosphine)platinum(II)] Trifluoromethanesulfonate (11a-OTf). Off white solid. Yield: 100%. Mp: 175 °C dec. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.64–7.59 (m, 12H, *o* CH), 7.51–7.45 (m, 18H, *m,p* CH), 3.24 (s, 6H, OCH_3), 2.85 (s, 6H, NCH_3), 2.60 (s, 6H, NCH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 154.7 (C_γ), 149.9 (t, $^2J_{\text{PC}}$ 13.8 Hz, C_α), 135.0 (t, $^2J_{\text{PC}}$ 6.3 Hz, *o* C), 132.8 (*p* C), 129.5 (t, $^3J_{\text{PC}}$ 5.7 Hz, *m* C), 128.9 (t, $^1J_{\text{PC}}$ 30.7 Hz, *i* C), 121.5 (q, J_{CF} 321.6 Hz, CF_3), 97.1 (t, $^3J_{\text{PC}}$ 2.0 Hz, C_β), 61.7 (OCH_3), 42.0 (NCH_3), 38.1 (NCH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 16.8 ($^1J_{\text{PPt}}$ 2370 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ 78.8 (SO_3CF_3). IR (CH_2Cl_2): $\nu(\text{CCC})$ 2093 cm^{-1} . UV vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 253 (4.583). FAB MS m/z (%): 1091 (4) [(M OTf) $^+$], 942 (7) [(M 2 OTf) $^+$], 926 (29) [(M 2 OTf CH_3) $^+$], 828 (100) [(M OTf PPh_3) $^+$], 679 (37) [(M 2 OTf PPh_3) $^+$].

trans-[Bis(3-(dimethylamino)-3-ethoxy-1,2-propadienyldiene)-bis(triphenylphosphine)platinum(II)] Tetrafluoroborate (12a-BF₄). For the alkylation $[\text{Et}_3\text{O}]\text{BF}_4$ was used instead of MeOTf . To obtain a pure compound, crystallization was necessary, resulting in a decreased yield. Colorless crystals. Yield: 60%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.63–7.58 (m, 12H, *o* CH), 7.54–7.45 (m,

18H, *m,p* CH), 3.45 (q, J 7.0 Hz, 4H, OCH_2), 2.85 (s, 6H, NCH_3), 2.60 (s, 6H, NCH_3) 0.93 (t, J 7.0 Hz, 6H, OCH_2CH_3) ppm. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 153.8 (C_γ), 148.5 (t, $^2J_{\text{PC}}$ 14.1 Hz, C_α), 135.0 (t, $^2J_{\text{PC}}$ 6.0 Hz, *o* C), 132.7 (*p* C), 129.4 (t, $^3J_{\text{PC}}$ 6.0 Hz, *m* C), 128.9 (t, $^1J_{\text{PC}}$ 30.2 Hz, *i* C), 97.3 (t, $^3J_{\text{PC}}$ 2.0 Hz, C_β), 72.1 (OCH_2), 41.7 (NCH_3), 37.9 (NCH_3), 14.4 (OCH_2CH_3) ppm. ^{31}P NMR (161.8 MHz, CD_2Cl_2): δ 16.7 ($^1J_{\text{PPt}}$ 2377 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ 152.2 (BF_4). IR (CH_2Cl_2): $\nu(\text{CCC})$ 2095 cm^{-1} . FAB MS m/z (%): 1056 (51) [(M BF_4) $^+$], 940 (100) [(M 2 BF_4 Et) $^+$], 706 (44) [(M 2 BF_4 PPh_3) $^+$].

X-ray Structural Analysis of 2b, 8a, 9b, and 12a-BF₄. Single crystals suitable for an X ray structural analysis of **2b** and **8a** were grown from CH_2Cl_2 , those of **9b** from CH_2Cl_2 /hexane, and those of **12a** BF_4 from acetone. The measurements were performed at 100(2) K with a crystal mounted on a glass fiber on a Stoe IPDS II diffractometer (graphite monochromator, $\text{Mo K}\alpha$ radiation, λ 0.710 73 Å). The structures were solved by direct methods using the SHELX 97 program package.¹⁹ 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.

Supporting Information Available: CIF files giving crystallographic data for the complexes **2b**, **8a**, **9b**, and **12a** BF_4 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

(19) Sheldrick, G. M. *SHELXTL 97, Program for Crystal Structure Analysis*; University of Gottingen, Gottingen, Germany, 1997.