Selective Stabilization of the Anti Isomer of (η^3-Allyl)palladium and -platinum Complexes

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A number of 2,9-disubstituted 1,10-phenanthrolines are synthesized. These are used as ligands in different cationic (η^3-allyl)palladium and -platinum complexes. It was found that while a syn configuration was by far the most stable one with the parent 1,10-phenanthroline, 2,9-substituents such as methyl, chloro, cyano, and propynyl induced a preference for the anti configuration. Since terminal nucleophilic addition to *anti*-η^3-allyl complexes will yield (*Z*)-alkenes, this observation opens up a potentially selective route to (*Z*)-alkenes. Using molecular mechanics calculations these effects may be rationalized.

Palladium-catalyzed nucleophilic displacement of an allylic acetate has become a standard reaction in organic synthesis.[1] The reaction proceeds via (η^3-allyl)palladium complexes, and the stereochemistry of the products depends on the anti/syn configuration of the intermediate η^3-allyl complexes,[2] as illustrated in Scheme I.

The oxidative addition of palladium initially gives syn complexes from (*E*)-alkenes and anti complexes from (*Z*)-alkenes.[1,3] Nucleophilic addition gives (*E*)-alkenes from syn complexes and (*Z*)-alkenes from anti complexes. Since (η^3-allyl)palladium complexes undergo anti/syn isomerization, which may be rapid,[4] it should in principle be possible to prepare *E* or *Z* products from either *E* or *Z* acetates, provided ligands could be used to control the stereochemistry of the intermediate (η^3-allyl)palladium complexes. For some time, we have been occupied with several different approaches to solving this problem.[5] In terminally substituted η^3-allyl systems, the syn isomer dominates though exceptions are known.[6] We have recently discovered that certain bidentate planar ligands, such as 2,9-dimethyl-1,10-phenanthroline, can induce a preference for the anti isomer.[3] A reasonable explanation for this result is that the 2,9-dimethyl groups, which extend into the coordination plane, will interfere selectively with syn substituents of an η^3-allyl system. In order to explore the generality of this idea, we have prepared a series of cationic (η^3-allyl)palladium complexes with 2,9-disubstituted 1,10-phenanthroline ligands and a few analogous platinum complexes. We have also developed a molecular modeling system in order to be able to generalize the results and predict new applications.

Scheme I

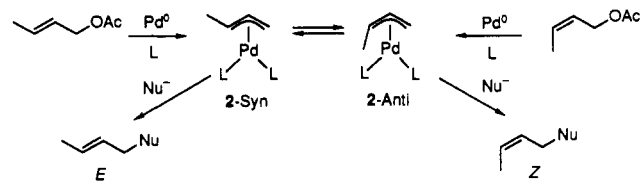
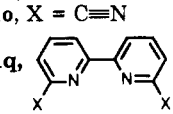
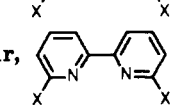
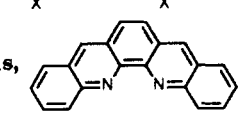


Table I. Anti/Syn Ratios for the [(1,2,3-η)-2-Butenyl]palladium Tetrafluoroborate Complexes Equilibrated in Dichloromethane

entry	L–L	[Pd(allyl)L]⁺	% anti
1	**1a**, X = H	**2a**	10
2	**1b**, X = Me	**2b**	69
3	**1c**, X = *t*-Bu	**2c**	65
4	**1d**, X = *n*-Bu	**2d**	42
5	**1e**, X = Ph	**2e**	40
6	**1f**, X = Cl	**2f**	76
7	**1g**, X = Br	**2g**	58
8	**1h**, X = CO_2Me	**2h**	10
9	**1i**, X = C≡C—Ph	**2i**	66
10	**1k**, X = C≡C—$SiMe_3$	**2k**	66
11	**1l**, X = Br, C≡C—$SiMe_3$	**2l**	58
12	**1m**, X = C≡C—C≡C—$SiMe_3$	**2m**	74
13	**1n**, X = C≡C—Me	**2n**	80
14	**1o**, X = C≡N	**2o**	81
15	**1q**,  ; X = H	**2q**	12
16	**1r**,  ; X = C≡N	**2r**	67
17	**1s**, 	**2s**	41
18	**1t**, Ph_2P—PPh_2	**2t**	6
19	**1u**, 2 PPh_3	**2u**	10

Preparation of the Ligands

Most of the ligands (1; for substituents, see Table I) were prepared according to procedures reported in the literature.

(1) (a) Tsuji, J. *Organic Syntheses with Palladium Compounds*; Springer Verlag: Heidelberg, 1980. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K. 1982; Vol. 8, pp 799–938. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Çonsiglio, G., Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257.

(3) Åkermark, B.; Hansson, S.; Vitagliano, A. *J. Am. Chem. Soc.* **1990**, *112*, 4587.

(4) For a review, see: Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 441.

(5) Åkermark, B.; Hansson, S.; Csöregh, I.; Helquist, P. To be published.

(6) (a) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642. (b) Lukas, J.; Ramakers. Blom, J. E.; Hewitt, T. G.; De Boer, J. J. U. *J. Organomet. Chem.* **1971**, *46*, 167. (c) Ohta, T.; Hosokawa, T.; Murahashi, S. I.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080.

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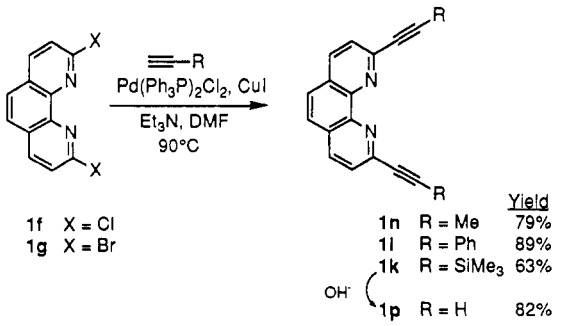
Scheme II

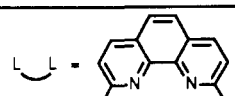
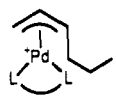
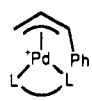
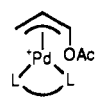
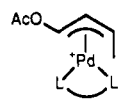
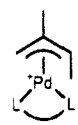
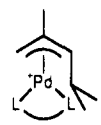
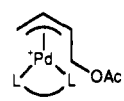


The 2,9-bis(acetylene)-substituted phenanthrolines were not known when this work was initiated, and we therefore investigated a number of routes based on palladium-catalyzed cross coupling between acetylenes and aromatic compounds. Such procedures were well established for a variety of aromatic compounds,[7] including halopyridines and haloquinolines,[8,9] but they had not been used with phenanthrolines. It was found that propyne, phenylethyne, and (trimethylsilyl)ethyne all reacted smoothly with 2,9-(dibromo or dichloro)-1,10-phenanthroline (**1f** or **1g**) in DMF solution, using bis(triphenylphosphine)palladium dichloride and copper(I) iodide in catalytic amounts and triethylamine as base. Bis(acetylene)-substituted phenanthrolines were obtained in good to excellent yields (Scheme II).

While this work was in progress, Suffert and Ziessel published a synthesis of the (trimethylsilyl)acetylene-substituted ligand **1k**.[10] However, their procedure is more complicated in that copper complexation and sonification are required to get reasonable yields. 2,9-Diethynyl-1,10-phenanthroline (**1p**) was prepared by treatment of the corresponding bis(trimethylsilyl)ethynyl-1,10-phenanthroline (**1k**) with potassium hydroxide in DMF. In our attempt to prepare dibutadiynylphenanthrolines, we first tried alkyne coupling using the Cadiot–Chodkiewicz reaction,[11] but without success. Palladium-catalyzed coupling between phenylbutadiyne[12] and dibromophenanthroline was also tried but led only to polymerization of phenylbutadiyne. However, palladium-catalyzed Stille coupling[13] using 1-(tributylstannyl)-4-(trimethylsilyl)butadiyne and dibromophenanthroline (**1g**) did produce the desired phenanthroline ligand **1m**. The isolated yield was low, ca. 10%, mainly due to decomposition during purification. The unsymmetrical 2-bromo-9-(trimethylsilyl)ethynyl-1,10-phenanthroline (**1l**) was prepared in a similar way.

The literature procedures for the preparation of 2-bromo-1,10-phenanthroline,[14,15] which is a precusor for the 2,9-dibromo-1,10-phenanthroline, did not work satisfactorily, in our hands. In these procedures 1-methyl-2-phenanthroline is treated with phosphorus pentabromide and phosphorus tribromide to give low yields of the bromophenanthroline. We have found that bromo(triphenyl)phosphonium bromide[16] is a superior reagent in this reaction and gives high yields of 2-bromophenanthroline.

Table II. Anti/Syn Ratios for (η^3-Allyl)palladium Tetrafluoroborate Complexes Equilibrated in Dichloromethane

entry	L–L = 	complex	η^3-allyl	% anti
1	**1b**, X = Me	**3b**		67
2	**1b**, X = Me	**4b**		73
3	**1b**, X = Me	**5b**		67
4	**1n**, X = C≡C—Me	**5n**		74
5	**1b**, X = Me	**6b**		3
6	**1f**, X = Cl	**6f**		3
7	**1n**, X = C≡C—Me	**6n**		36
8	**1b**, X = Me	**7b**		84
9	**1n**, X = C≡C—Me	**7n**		90
10	**1b**, X = Me	**8b**		35
11	**1b**, X = Me	**9b**		56[a]
12	**1b**, X = Me	**10b**		65
13	**1b**, X = Me	**11b**		100
14	**1b**, X = Me	**12b**		70

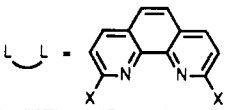
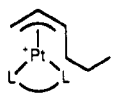
[a] *syn*-OAc-*syn*-Me = 38% and *anti*-OAc-*syn*-Me = 6%.

Preparation of the Complexes

The (trifluoroacetato)palladium complexes were conveniently prepared from allyl trifluoroacetates and palladium bis(dibenzylideneacetone) followed by addition of the appropriate ligand.[17] The fluoroborate complexes were either prepared by counterion exchange of the trifluoroacetate complexes with $NaBF_4$ or by addition of the appropriate ligand to the unligated cationic (η^3-allyl)palladium fluoroborate complexes.[18] The platinum complexes

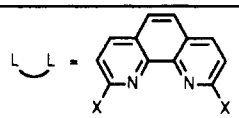
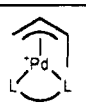
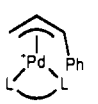
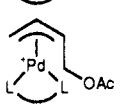
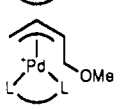
(7) Weijin, T.; Nesbitt, S.; Heck, R. F. *J. Org. Chem.* **1990**, *55*, 63.
(8) Jefferson, W. T.; Zawoiski, S. *J. Org. Chem.* **1988**, *53*, 386.
(9) Sakamoto, T.; Shiraiwa, M.; Kondo, Y.; Yamanaka, H. *Synthesis* **1983**, 312.
(10) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757.
(11) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, *2*, 819.
(12) Nye, S. A.; Potts, K. T. *Synthesis* **1988**, 375.
(13) For review: Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(14) Ogawa, S.; Yamaguchi, T.; Gotoh, N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 976.
(15) Claus, K. G.; Rund, J. V. *Inorg. Chem.* **1969**, *8*, 59.
(16) Furniss, B.; et al. *Vogel's Textbook of practical organic chemistry*, 5th ed.; Longman Scientific & Tecnical: Birmingham, AL, 1989; p 867.
(17) Vitagliano, A.; Åkermark, B.; Hansson, S. *Organometallics* **1991**, *10*, 2592.
(18) (a) Powell, J.; Shaw, B. *J. Chem. Soc. A* **1968**, 774. (b) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 670.

Table III. Anti/Syn Ratios for (η^3-Allyl)platinum Complexes

entry	L L = 	complex	η^3-allyl	solvent	% anti
1	**1a**, X = H	**16a**[a]		CD_3NO_2	23
2	**1b**, X = Me	**16b**[a]		CD_3NO_2	88
3	**1n**, X = C≡C—Me	**16n**[b]		$CDCl_3$	93
4	**1b**, X = Me	**17b**[b]		$CDCl_3$	89

[a] Counterion BF_4^-. [b] Counterion $CF_3CO_2^-$.

Table IV. Anti/Syn Ratios for (η^3-Allyl)palladium Complexes in Different Solvents

entry	L L = 	complex[a]	η^3-allyl	solvent	% anti
1	**1b**, X = Me	**2b**		CD_2Cl_2	60
2	**1b**, X = Me	**2b**[b]		$CDCl_3$	4
3	**1b**, X = Me	**2b**[b]		D_2O	70
4	**1n**, X = C≡C—Me	**2n**		CD_2Cl_2	76
5	**1n**, X = C≡C—Me	**2n**		$CDCl_3$	75
6	**1n**, X = C≡C—Me	**2n**		CD_3CN	77
7	**1n**, X = C≡C—Me	**2n**		DMF-d_7	82
8	**1n**, X = C≡C—Me	**2n**		CD_3NO_2	81
9	**1n**, X = C≡C—Me	**2n**		CD_3OD	80
10	**1n**, X = C≡C—Me	**2n**		D_2O	86
11	**1n**, X = C≡C—Me	**2n**		DMSO-d_6	45
12	**1n**, X = C≡C—Me	**6n**		D_2O	60
13	**1b**, X = Me	**12b**		CD_2Cl_2	60
14	**1b**, X = Me	**13b**		$CDCl_3$	43
15	**1b**, X = Me	**13b**		D_2O	77
16	**1n**, X = C≡C—Me	**13n**		$CDCl_3$	67

[a] Counterion $CF_3CO_2^-$. [b] Counterion Cl^-.

were prepared from the corresponding (η^3-allyl)Pt(pyridine)$_2^+$ cationic complexes[19] by addition of the appropriate ligand.

The equilibration between anti and syn complexes was monitored by ^1H NMR and was generally reached within hours. In some cases, when equilibration was very slow (>24 h), a catalytic amount of trifluoroacetic acid could be added to speed up the isomerization without affecting the equilibrium.

A number of selected complexes which were deemed interesting from a preparative point of view were synthesized on a larger scale, isolated, and purified. In a few cases, both the pure syn and anti forms were isolated. Some of the equilibriums were reached from both pure syn and anti complexes.

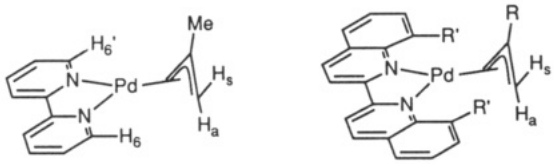
Results and Discussion

The results from the combination of the η^3-butenyl system with the different ligands are summarized in Table I, and results from a variation of the η^3-allyl system are found in Table II. In Table III, data on related (η^3-allyl)platinum complexes are presented, and in Table IV, solvent and counterion effects on the anti/syn ratio are illustrated for a few selected (η^3-allyl)palladium complexes.

The results for the simple (η^3-butenyl) system (**2**) presented in Table I clearly illustrate the potential of anti/syn control by the ligands. Simply by substituting the 1,10-phenanthroline ligand (**1a**) with 2,9-dimethyl-1,10-phenanthroline (**1b**), it was possible to increase the anti/syn ratio at equilibrium from 10/90 to ca. 70/30 (entries 1 and 2, Table I). Somewhat unexpectedly, bulkier alkyl groups in the 2- and 9-positions gave lower anti preferences, *n*-Bu (**1d**) 42% and *t*-Bu (**1c**) 65%. Lower anti preference was also observed when the 2,9-disubstituted phenyl (**1e**), bromo- (**1g**), and methoxycarbonylphenanthroline (**1h**) ligands were used. However, with the 2,9-dichloro-substituted ligand (**1f**) the anti preference was increased to 76%.

In order to fully understand the substituents effect, reliable procedures for calculating conformational equilibria for (η^3-allyl)palladium complexes are necessary. We

(19) (a) Boag, N. M.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1208. (b) *Ibid.* **1980**, 1200.



14q

14v R=CH_3, R'=H
15v R=H, R'=CH_3

Figure 1.

have therefore developed a parameter set for calculations on the (η^3-allyl)palladium moiety to be used with the MM2 force field.[20]

The calculations, using this force field, support the idea of specific steric interaction between the 2,9-substituents of phenanthroline and the syn methyl group of the square-planar (η^3-butenyl)palladium complex. A similar effect is observed for 6,6'-substituted bipyridine ligands (**2q**, 12% anti and **2r**, 67% anti) and specific steric interaction is experimentally supported by a recent study by Albinati, Pregosin, and co-workers. By X-ray analysis and NOE studies they have shown that the "reporter protons" H_6 and $H_{6'}$ of the bipyridine complex **14q** are far closer to the syn than the anti protons of the allyl group Figure 1).[21]

Calculations further suggest that selective interaction with the syn methyl of the allyl requires the ligand substituents to interfere sterically in the coordination plane. Bulk of the ligand substituents outside the coordination plane results in steric interaction with both the anti and the syn methyl of the allyl. In accordance with calculations, the anti preferences are fairly low for the *tert*-butyl- and bromo-substituted ligands (**2c**, 65%; **2g**, 58%) and also for the flexible *n*-butyl-substituted ligand (**2d**, 42%). In contrast, the anti preference is increased with substituents such as chloro or cyano (**2f**, 76%; **2o**, 81%). The disappointingly low anti preferences induced by planar 2,9-substituents such as phenyl (**2e**, 40%) and methoxycarbonyl (**2h**, 10%) suggest these substituents are rotated out of the coordination plane, precluding selective interaction with the syn methyl group.

The low anti preference observed with dibenzophenanthroline as ligand was initially surprising (**2s**, 41%). However, it has recently been shown by NMR that the ligand reporter protons, R' in complex **14v**, have essentially the same distance to the syn and anti protons of the allyl group (Figure 1).[22] Calculations show this to be due to distortion of the geometry caused by severe interaction from the ligand. The steric effects are large enough to displace the η^3-allyl system out of the coordination plane. This distortion has been experimentally observed in an X-ray crystal structure for the related complex **15v**.[23] This distortion is also observable, although in a lesser degree, in the calculated structures of complexes **2c**, **2e**, and **2b**.

These results very clearly show that general steric bulk is not sufficient for anti selectivity. The optimum geometry of the substituents on the phenanthroline ligand seems to be a narrow, rigid "cylinder". We therefore decided to examine also some acetylene substituents. The parent 2,9-diethynyl-1,10-phenanthroline (**1p**) ligand could be prepared, but on attempted synthesis of an η^3-butenyl complex, decomposition took place. The corresponding complexes with phenylethynyl- and (trimethylsilyl)-ethynyl-substituted ligands were prepared but the anti preferences were moderate (**2i** and **2k**, both 66%).[24] The best result was obtained for the complex **2n** with the propynyl-substituted ligand (80% anti), essentially the same as the nitrile substituent. The use of a very extended substituent such as (trimethylsilyl)butadiynyl (**2m**) gave a slightly lower induction (74% anti). From the results above it appears that elongation of the phenanthroline substituents from one (**2b**) to two atoms (**2o**) increases the selectivity for the anti isomer. A further elongation (**2o** → **2n**) does not have this effect but can in fact decrease the selectivity if bulky groups are introduced (cf. **2i**, **2k**).

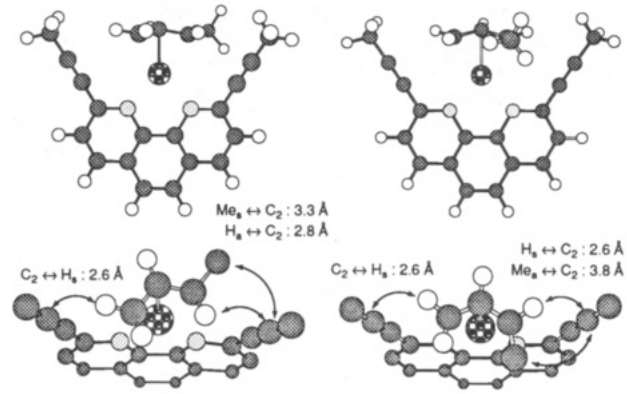


Figure 2. Calculated structures for the syn and anti isomers of complex **2n**.

The molecular modeling of the complex **2n** gives the structures *syn*-**2n** and *anti*-**2n** as presented in Figure 2. The calculated interatomic distances from the outer acetylene carbons to the methyls and some terminal hydrogens on the η^3-allyl are shown.[25]

It is clear crucial interactions take place between the outer acetylene carbon and the syn substituents, as suggested by the Chem3D model of the compound **2n**. In particular, the distance between this carbon (C_2) and the methyl group of *syn*-**2n** is far shorter (≈3.3 Å) than the corresponding distance in *anti*-**2n** (≈3.8 Å). From the calculated structure it also appears that the allyl of *syn*-**2n** is slightly rotated and pushed out of the coordination plane.

The influence of substituents other than methyl in the η^3-allyl system was also examined experimentally (Table II). A remarkable range of anti selectivity was observed with the simple 2,9-dimethyl-substituted phenanthroline ligand **1b**. Terminal alkyl groups such as ethyl, propyl, and 2-propyl all have about the same influence as the methyl group (**3b**, **4b**, and **5b**, ca. 70% anti). This is also true for an acetoxymethyl group (**12b**, 70%), while an

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(24) It is interesting to note that the unsymmetrical ligand 2-bromo-9-[(trimethylsilyl)ethynyl]-1,10-phenanthroline in the complex **2l** gives the same selectivity for the anti isomer as the 2,9-dibromo-1,10-phenanthroline (**2g**). These results suggest the less efficient substituent (2-bromo) is destabilizing the syn isomer and is determining the anti/syn ratio.

(25) The complete set of distances from terminal allyl substituents to propynyl carbons (C_1 is closest to the ring) are as follows (in Å):

	syn-**2n**				*anti*-**2n**			
	H_{1s}	H_{1a}	H_{3a}	C_{3s}	H_{1s}	H_{1a}	H_{3s}	C_{3a}
C_1	2.9	4.0	3.0	3.4	2.9	3.3	2.9	3.7
C_2	2.6	4.1	2.8	3.3	2.6	3.3	2.6	3.8
C_3	3.0	4.6	3.3	3.8	3.0	3.9	3.1	4.4

acetoxy group directly attached to the η^3-allyl has only low anti preference (**8b**, 35% anti). The phenyl substituent is exceptional and shows no anti preference (**6b**, 3% anti). A large deviation from coplanarity with the allyl system is required to accommodate the steric bulk of a phenyl ring in the anti configuration. The resulting loss of conjugation probably accounts for the high syn preference of the phenyl group. 1,2-Dimethyl substitution leads to about the same anti selectivity as 1-substitution only (**10b**, 65% anti). In contrast, a 2-methyl group in combination with a terminal 2-propyl group leads to complete anti selectivity (**11b**, 100% anti). 1,3-Dimethyl substitution does increase the selectivity and at equilibrium the complex **7b** has mainly the 1-anti-3-syn configuration (84%), the remainder being the all-syn isomer. If one of the terminal methyl groups of **7b** is exchanged for an acetoxy group, the higher syn preference for the acetoxy group is manifested by the isomeric distribution: *anti*-Me-*syn*-OAc = 56%, *anti*-OAc-*syn*-Me = 6%, *syn*-OAc-*syn*-Me = 38%.

From the results presented in Table II, it appears that the improved anti selectivity induced by the propynyl-substituted ligand **1n** also applies to η^3-allyl systems other than η^3-butenyl. By changing the ligand from **1b** to **1n**, the anti preference is raised from 67% to 74% for the 3-(2-propyl)-substituted system (**5b** → **5n**), from 3% to 36% for the 3-phenyl-substituted system (**6b** → **6n**) and from 84% to 90% for the 1,3-dimethyl system (**7b** → **7n**).

Since (η^3-butenyl)platinum complexes appear to have a higher preference for the anti configuration[26] than the corresponding palladium complexes, it seemed interesting to prepare a few (η^3-allyl)platinum complexes (Table III). Indeed, the results show a somewhat higher anti selectivity for the platinum complexes, e.g. 89% for **17b** as compared to 73% for the corresponding palladium complex **4b** (Table II, entry 2, and Table III, entry 4). The effect of substituents on phenanthroline is similar to that observed for the palladium complexes, e.g. the selectivity increases from 23% for **16a** to 88% for **16b** and 93% for **16n** (Table III, entries 1–3).

Since distortion of the square-planar arrangement around palladium and perhaps also rotation of the η^3-allyl group could contribute to low anti/syn ratios, we decided to study the effects of counter ions. It has been shown that the destabilizing effect of 2,9-disubstituted 1,10-phenanthroline ligands on the square-planar geometry can promote formation of 5-coordinate complexes.[27] In such species, which may become important when coordinating counterions are present, the specific interaction between the ligands and a syn substituent will decrease or even disappear. In CD_2Cl_2 solution, the trifluoroacetate ion, which is expected to coordinate better than the fluoroborate ion, induces slightly lower anti preferences, from 69% to 60% for the complex **2b** and from 80% to 76% for the complex **2n** (Table I, entries 2 and 13, Table IV, 1 and 4). This is reflected in a slight decrease of the molar conductivity going from the fluoroborate to the trifluoroacetate salt (39 Ω^{-1} mol^{-1} cm^2 versus 33 Ω^{-1} mol^{-1} cm^2 at the same concentration of 6.8 mmol/L in CH_2Cl_2).[28] With chloride as the counterion, which appears to give a 5-coordinate complex in dichloromethane,[29] the anti selectivity is lost (Table IV, entry 2). The above results suggest solvent polarity should also affect the anti/syn ratio by stabilizing a 4-coordinate cationic intermediate.[30] The results presented in Table IV indicate that this is correct and the relative anti configuration of complex **2n** increases from 75% in chloroform to 86% in deuterated water (entries 5 and 10), and for complex **6n** from 36% to 60% (Table II, entry 7, and Table IV, entry 12).

With increasing coordinating ability of the counterion, the solvent effect becomes dramatic. Thus, when Cl^- is the counterion, complex **2b** displays 96% syn configuration in $CDCl_3$,[31] which is changed to a 70% anti in D_2O (Table IV, entries 2 and 3). Also aprotic, polar solvents such as dimethyl formamide (DMF) and nitromethane have a favorable influence on the anti isomer population (Table IV, entries 7 and 8). Dimethyl sulfoxide (DMSO) is the exception giving only 45% *anti*-**2n** (Table IV, entry 11), but this is perhaps due to coordination to palladium[32] resulting in the formation of associated species and partial loss of the square-planar geometry.

The picture that emerges from the results described above is fairly consistent. The basic idea of selective interference between substituents adjacent to the coordinating nitrogen atoms of bidentate planar ligands such as 1,10-phenanthroline with syn substituents of η^3-allyl square-planar complexes appears to be correct. This is supported by the data presented in Tables I–IV for Pd(II) and Pt(II) complexes of phenanthroline type ligands and also by the fact that related planar ligands such as bipyridine show similar effects. Nonplanar ligands, such as triphenylphosphine and 1,2-(diphenylphosphino)ethane generally give very low anti/syn ratios, one notable exception being a dinuclear palladium(I) complex with tricyclohexylphosphine ligands (90% anti).[33]

The combination of calculations and experimental results suggest that the anti/syn ratio of ca. 80/20 which is obtained for **2n** and **2o** is close to optimal for simple, terminally substituted (η^3-allyl)palladium systems with 2,9-disubstituted phenanthroline ligands. More sophisticated ligands are being developed, also aiming at chiral induction. However, the high anti selectivity obtained for the 1,2- and 1,3-substituted η^3-allyls **7n** and **11b** clearly demonstrates the potential of even the simple phenanthroline ligands for substituted η^3-allyl systems.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a 400-MHz NMR (Bruker Model AM400), a 250-MHz NMR (Bruker Model ACF250), or a 270-MHz NMR spectrometer (Bruker Model AC270). ^{1}H NMR chemical shifts are reported in δ (ppm) relative to Me_4Si as internal standard. ^{13}C NMR chemical shifts are given in δ values relative to the solvent ($CDCl_3$ 77.00 ppm). The following abbreviations are used in descriptions of NMR multipl-

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(28) The coordinating properties of BF_4^-, $CF_3CO_2^-$, and Cl^- are also very nicely reflected in the relative ability of the counterions to promote isomerization which is $Cl^- \gg CF_3CO_2^- > BF_4^-$.

(29) The chloride complex has a molar conductivity of 4 Ω^{-1} mol^{-1} cm^2 (C = 6.8 mmol/L in CH_2Cl_2) *versus* 39 Ω^{-1} mol^{-1} cm^2 displayed by the corresponding tetrafluoroborate salt under the same conditions. Although this indicates coordination of the chloride ion, the resulting species could contain an unsymmetrically bound phenanthroline ligand (one "normal" and one very weak Pd–N bond) and be considered as 4-coordinated with the N–N ligand acting as essentially monodentate. See, for example: Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618.

(30) This is also suggested by the effect of solvent on isomerization which is very slow in water and MeOH (days) but rapid in $CDCl_3$, DMF, and CH_3CN (half-life ≈ 15 min).

(31) The ^{1}H NMR spectrum (400 MHz) indicates that in chloroform the complex is actually in equilibrium with an appreciable amount of the chloride bridged dimer and free 2,9-dimethyl-1,10-phenanthroline (≈15% free N–N at C = 35 mmol/L).

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icities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent, br = broadened, J = coupling constant and J_{Pt} = coupling constant to ^{195}Pt, detected by satellite peaks. These subscripts are used: P = phenanthroline protons, s = proton in syn position, and a = proton in anti position relative to H_2. ^1H NMR integrations are reported as the relative number of hydrogens (H). NMR assignments were done with a homodecoupling program and were assisted with NOE experiments when necessary. Protons are identified according to the figure in ref 34.

Because of the straightforward method used in the preparation of the complexes, ^1H NMR data were generally assumed sufficient for full characterization of the compounds, but a few selected elemental analyses were also done. All phenanthroline derivatives were purified by medium-pressure liquid chromatography (MPLC) as described by Baeckström et al.[35] The gel used was Merck aluminum oxide (neutral), and the solvent gradient was a mixture of CH_2Cl_2 and hexane. TLC analysis was performed on Merck aluminum-backed F_{254} aluminum oxide (neutral) plates using UV light for visualization. Melting points were determined in open capillary tubes and are uncorrected. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany.

Synthesis of Ligands. 1,10-Phenanthroline (**1a**), 2,9-dimethyl-1,10-phenanthroline (**1b**), and 2,2'-bipyridine (**1q**) were purchased from Aldrich and used as received. 1-Methyl-1,10-phenanthrolin-2-one,[36] 2,9-di-*tert*-butyl-1,10-phenanthroline[37] (**1c**), 2,9-di-*n*-butyl-1,10-phenanthroline[37] (**1d**), 2,9-diphenyl-1,10-phenanthroline[37] (**1e**), 2,9-dichloro-1,10-phenanthroline[38] (**1f**), 2,9-dibromo-1,10-phenanthroline[14] (**1g**), 2,9-bis(methoxycarbonyl)-1,10-phenanthroline[39] (**1h**), 2,9-dicyano-1,10-phenanthroline[30] (**1o**), 6,6'-dicyano-2,2'-bipyridine[41] (**1r**), dibenzo[*b,j*]-1,10-phenanthroline[42] (**1s**), dichlorobis(triphenylphosphine)palladium(II),[43] and tetrakis(triphenylphosphine)-palladium[44] were prepared using literature procedures. 4-Methyl-1-penten-3-ol and 2,4-dimethyl-1-penten-3-ol were prepared by Grignard reactions of 2-propylmagnesium bromide with acrolein and methacrolein, respectively. The allylic trifluoroacetates were prepared by reaction of the corresponding alcohols with trifluoroacetic anhydride.[45] All other chemicals were purchased from Aldrich and purified and dried with standard methods.[46]

2-Bromo-1,10-phenanthroline. Triphenylphosphine (79 g, 301 mmol) was dissolved in dry acetonitrile (350 mL), and the mixture was cooled in an ice–water bath. Bromine (14.4 mL, 279 mmol) was added dropwise over a period of 1 h, and a light brown color was observed. 1-Methyl-1,10-phenanthrolin-2-one (45 g, 214 mmol) was added, and the mixture was refluxed for 24 h. After cooling, the solution was poured into ice water and the precipitate was removed by filtration. The filtrate was neutralized with sodium carbonate (10% in H_2O) and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. Purification of the crude product by MPLC gave 37.5 g (74%) of 2-bromo-1,10-phenanthroline: mp 157 °C (lit.[15] mp 161 °C).

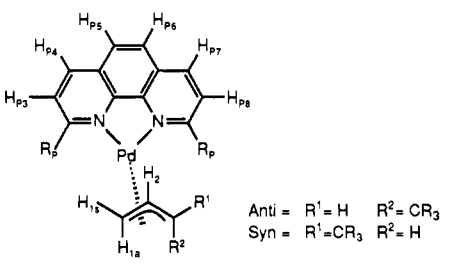
2,9-Bis(phenylethynyl)-1,10-phenanthroline (1i). 2,9-Dichloro-1,10-phenanthroline (1.5 g, 6 mmol), phenylacetylene (1.44 mL, 13 mmol), CuI (50 mg, 0.25 mmol), $Pd(Ph_3P)_2Cl_2$ (110 mg, 0.1 mmol), triethylamine (1.95 mL, 15 mmol), and DMF (5 mL) were added to a Fisher-Porter (FP) tube equipped with a magnetic stirrer. The air was pumped off, and the FP tube was flushed with nitrogen several times and then heated at 90 °C for 18 h. The black solution was cooled to room temperature and poured into H_2O (25 mL) and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. Purification of the crude product by MPLC gave 2.03 g (89%) of **1i** as a light yellow solid; mp 208 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.2 Hz, 2 H), 7.84 (d, J = 8.2 Hz, 2 H), 7.77 (s, 2 H), 7.71 (m, 4 H), 7.39 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.81, 143.94, 136.02, 132.27, 129.02, 128.38, 127.78, 126.68, 126.64, 122.53, 90.86, 90.18. Anal. Calcd for $C_{28}H_{16}N_2$: C, 88.40; H, 4.24. Found: C, 86.55: H, 4.42.

2,9-Bis((trimethylsilyl)ethynyl)-1,10-phenanthroline (1k). 2,9-Dichloro-1,10-phenanthroline (2.0 g, 8 mmol), (trimethylsilyl)acetylene (2.5 mL, 18 mmol), CuI (50 mg, 0.25 mmol), $Pd(Ph_3P)_2Cl_2$ (110 mg, 0.1 mmol), triethylamine (2.5 mL, 18 mmol), and DMF (6 mL) were added to a Fisher-Porter (FP) tube equipped with a magnetic stirrer. The air was pumped off, and the FP tube was flushed with nitrogen several times and then heated at 90 °C for 18 h. The black solution was cooled to room temperature, poured into H_2O (25 mL), and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. Purification of the crude product by MPLC gave 1.88 g (63%) of **1k** as a light yellow solid; mp 267 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 2 H), 7.75 (d, J = 8.2 Hz, 2 H), 7.73 (s, 2 H), 0.31 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.61, 143.52, 135.87, 127.86, 126.80, 126.68, 104.62, 96.71, –0.28. Anal. Calcd for $C_{22}H_{24}N_2Si_2$: C, 70.92; H, 6.49. Found: C, 71.03; H, 6.46.

2-Bromo-9-((trimethylsilyl)ethynyl)-1,10-phenanthroline (1l). 1-(Tributylstannyl)-2-(trimethylsilyl)ethyne[47] (859 mg, 2.56 mmol), 2,9-dibromo-1,10-phenanthroline (750 mg, 2.22 mmol), and tetrakis(triphenylphosphine)palladium (147 mg, 0.13 mmol) were added to toluene (20 mL). The mixture was stirred at 80 °C for 4 h under nitrogen atmosphere. The black solution was poured into H_2O (50 mL) and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. The crude product was purified by MPLC first with silica gel (hexane/EtOAc) and then a second time with aluminum oxide (neutral) (hexane/CH_2Cl_2); yield 305 mg (40%) of **1l** as a white solid, mp 192 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.3 Hz, 2 H), 8.06 (d, J = 8.4 Hz, 2 H), 7.76 (m, 2 H), 0.32 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.05, 144.97, 143.78, 142.79, 138.10, 136.00, 128.22, 127.94, 127.76, 127.03, 126.70, 126.44, 104.39, 97.13, –0.30. Anal. Calcd for $C_{17}H_{15}BrN_2Si$: C, 57.47; H, 4.26. Found: C, 57.55; H, 4.25.

2,9-Bis((trimethylsilyl)butadiynyl)-1,10-phenanthroline (1m). To a solution of (trimethylsilyl)butadiyne[47] (1.22 g, 10 mmol) dissolved in THF (20 mL) at –78 °C under N_2 was added *n*-BuLi (10 mmol) dropwise over 10 min. The mixture stirred for 10 min before Bu_3SnCl (2.44 mL, 9 mmol) was added. The temperature was slowly increased to 20 °C and kept there for 2 h. H_2O (30 mL) was added, and the mixture was extracted three times with diethyl ether (30 mL). The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. The product (1-(tributylstannyl)-4-(trimethylsilyl)butadiyne) was a liquid (3.34

(34)



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g), yield 90% with a purity of 70%.[48] No further purification was made.

1-(Tributylstannyl)-4-(trimethylsilyl)butadiyne (1.86 g, 3.25 mmol), 2,9-dichloro-1,10-phenanthroline (500 mg, 1.5 mmol), and tetrakis(triphenylphosphine)palladium (52 mg, 0.045 mmol) were added to toluene (10 mL). The mixture was stirred at 50 °C for 18 h under nitrogen atmosphere. The solution was rotary evaporated in vacuo. The crude product was purified by MPLC first with silica gel and then a second time with aluminum oxide (neutral); yield 64 mg (10%) of **1m** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H), 7.76 (s, 2 H), 0.26 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.76, 142.42, 136.06, 128.25, 127.38, 127.12, 92.86, 87.67, 76.29, 75.69, −0.48.

2,9-Dipropynyl-1,10-phenanthroline (1n). 2,9-Dichloro-1,10-phenanthroline (1.5 g, 6 mmol), triethylamine (1.95 mL, 15 mmol), CuI (50 mg, 0.25 mmol), $Pd(Ph_3P)_2Cl_2$ (110 mg, 0.1 mmol), and DMF (5 mL) were added to a Fisher-Porter (FP) tube equipped with a magnetic stirrer. The air was pumped off and the FP tube flushed with propyne gas to a pressure of 3.5 atm several times. The FP tube was then heated at 90 °C for 4 h. The black solution was cooled to room temperature and poured into H_2O (25 mL) and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. Purification of the crude product by MPLC gave 1.26 g (79%) of **1n** as a light yellow solid; mp 211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 2 H), 7.71 (s, 2 H), 7.66 (d, J = 8.2 Hz, 2 H), 2.14 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.55, 144.17, 135.75, 127.40, 126.20, 126.09, 88.27, 80.99, 4.49. Anal. Calcd for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.10; H, 4.82.

2,9-Diethynyl-1,10-phenanthroline (1p). A flask with DMF (30 mL) was cooled in an ice–water bath, KOH (5.5 mL, 1 M) and 2,9-Bis((trimethylsilyl)ethynyl)-1,10-phenanthroline (1.0 g, 2.7 mmol) was added to the flask which stirred in the ice–water bath for 1 h. H_2O (20 mL) was added, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and rotary evaporated in vacuo. Purification of the crude product by MPLC gave 0.50 g (82%) of **1p** as a light yellow solid; 235 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.2 Hz, 2 H), 7.79 (d, J = 8.2 Hz, 2 H), 7.78 (s, 2 H), 3.30 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.64, 142.86, 136.14, 128.17, 126.95, 126.89, 83.54, 78.83. Anal. Calcd for $C_{16}H_8N_2$: C, 84.19; H, 3.53. Found: C, 83.53; H, 3.84.

Synthesis of Complexes. Pd(dibenzylideneacetone)$_2$,[49] bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-butenyl]dipalladium,[17] bis(μ-trifluoroacetato)bis[(2,3,4-η)-3-pentenyl]dipalladium,[17] bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-hexenyl]dipalladium,[17] bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-methyl-2-butenyl]dipalladium,[17] bis(μ-chloro)bis[(1,2,3-η)-2-butenyl]dipalladium,[50,51] bis(μ-chloro)bis[(1,2,3-η)-1-phenyl-2-propenyl]dipalladium,[52] bis(μ-chloro)bis[(1,2,3-η)-4-methoxy-2-butenyl]dipalladium,[53] bis(μ-chloro)bis[(1,2,3-η)-4-acetoxy-2-butenyl]dipalladium,[54] bis(μ-chloro)bis[(1,2,3-η)-2-pentenyl]dipalladium,[50] and bis(pyridine)[(1,2,3-η)-2-butenyl]platinum tetrafluoroborate[19] were prepared using literature procedures. When (η^3-allyl)palladium complexes with 2,9-disubstituted 1,10-phenanthrolines as ligands were prepared, a mixture of the syn and anti form was obtained which was recrystallized from CH_2Cl_2/diethyl ether.[55] During slow crystallization the anti form of the complex was enriched and in many cases pure anti was obtained. The ^{1}H NMR spectra, for the syn and anti form of the complexes, were recorded and assigned from the equilibrium mixture.

Anti/Syn Equilibrium of the Complexes. The anti/syn isomerization was followed by integration in ^{1}H NMR of the corresponding protons in the two isomers at regular time intervals. The equilibration time ranged from less than 2 min (e.g. complex **7b** in CD_2Cl_2) to several days (e.g. complex **2b** in D_2O). In general the trifluoroacetate complexes isomerized faster than the tetrafluoroborate complexes. To complexes with very slow isomerization was added a catalytic amount of CF_3COOH to increase the rate. With the dimethylphenanthroline complexes **2b**, **2d**, and **10b**, the equilibrium was reached both from the syn and anti complexes.

General Procedure A. The bis(μ-chloro)bis[(1,2,3-η)-allyl]dipalladium compound (0.35 mmol) was dissolved in $CHCl_3$ (3 mL) or CH_2Cl_2 (3 mL) at 0 °C. $AgBF_4$(s) (68 mg, 0.35 mmol) was added, and a white precipitate occurred immediately. After 20 min the substituted phenanthroline (0.35 mmol) was added. The reaction mixture was stirred at 20 °C for 1 h before it was filtered through a Pasteur pipet with a small piece of cotton at the bottom and a 2-cm column of Celite on top. The solvent was evaporated, and the product was recrystallized from CH_2Cl_2/diethyl ether. The total yields were about 90%.

General Procedure B.[17] The bis(μ-trifluoroacetato)bis[(1,2,3,4-η)-allyl]dipalladium compound (0.39 mmol) and the substituted phenanthroline (0.39 mmol) were added to CH_2Cl_2 (10 mL). The reaction mixture was stirred at 20 °C for 15 min. The solvent was evaporated, and the product was recrystallized in CH_2Cl_2/diethyl ether. The total yields were about 90%. Very simple variations of this procedure allow one to directly obtain better than 90% enriched samples of either syn or anti forms.[17]

General Procedure C.[17] The substituted (1,10-phenanthroline)[(1,2,3-η)-allyl]palladium trifluoroacetate (0.18 mmol) was dissolved in H_2O (10 mL). $NaBF_4$ (40 mg, 0.36 mmol) dissolved in H_2O was added dropwise to the mixture, and immediately a light yellow precipitate was formed. The product was recrystallized from CH_2Cl_2/diethyl ether. The total yields were about 90%.

General Procedure D. Bis(pyridine)[(1,2,3-η)-allyl]platinum tetrafluoroborate[19] (0.40 mmol) was suspended in diethyl ether (25 mL), and 0.40 mmol of the N-N ligand, dissolved in diethyl ether (25 mL), was added. The mixture was stirred for 24 h at room temperature and the resulting precipitate was collected, washed with diethyl ether, and dried. The yields were about 80%. The same procedure was used for trifluoroacetate salts. In the latter case the starting platinum allyl complex was prepared by oxidative addition of allyl trifluoroacetate to bis(cyclooctadiene)platinum, according to the procedure described for the chloride complexes.[19]

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2b). General Procedure A. (*anti*-**2b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.53 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.87 (d, 2 H, $H_{P3,8}$), 5.74 (dq, $J_{3s,2}$ = 6.6 Hz, 1 H, H_{3s}), 5.70 (ddd, 1 H, H_2), 4.57 (d, $J_{1s,2}$ = 6.9 Hz, 1 H, H_{1s}), 3.73 (d, $J_{1a,2}$ = 12.5, 1 H, H_{1a}), 3.05 (s, 6 H, Me_P), 1.26 (d, $J_{Me,3s}$ = 6.0 Hz, 3 H, Me). (*syn*-**2b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.50 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.97 (s, 2 H, $H_{P5,6}$), 7.83 (d, 2 H, $H_{P3,8}$), 5.52 (ddd, 1 H, H_2), 4.56 (d, $J_{1s,2}$ = 7.2 Hz, 1 H, H_{1s}), 4.44 (dq, $J_{3a,2}$ = 10.9 Hz, 1 H, H_{3a}), 3.52 (d, $J_{1a,2}$ = 12.7 Hz, 1 H, H_{1a}), 3.07 (s, 6 H, Me_P), 1.42 (d, $J_{Me,3a}$ = 6.2 Hz, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Trifluoroacetate (*anti*-2b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Trifluoroacetate (*syn*-2b). General Procedure B. (*anti*-**2b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.56 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.01 (s, 2 H, $H_{P5,6}$), 7.88 (d, 2 H, $H_{P3,8}$), 5.73 (dq, $J_{3s,2}$ = 7.2 Hz, 1 H, H_{3s}), 5.70 (ddd, 1 H, H_2), 4.58 (d, $J_{1s,2}$ = 8.6 Hz, 1 H, H_{1s}), 3.73 (d, $J_{1a,2}$ = 12.1 Hz, 1 H, H_{1a}), 3.05 (s, 6 H, Me_P), 1.25 (d, $J_{Me,3s}$ = 6.0 Hz, 3 H, Me). (*syn*-**2b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.49 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.96 (s, 2 H, $H_{P5,6}$), 7.82 (d, 2 H, $H_{P3,8}$), 5.52 (ddd, 1 H, H_2), 4.41 (d, $J_{1s,2}$ = 7.0 Hz, 1 H, H_{1s}), 4.29 (dq, $J_{3a,2}$ = 10.5 Hz, 1 H, H_{3a}), 3.36 (d, $J_{1a,2}$ = 12.2 Hz, 1 H, H_{1a}), 3.10 (s, 6 H, Me_P), 1.34 (d, $J_{Me,3a}$ = 6.1 Hz, 3 H, Me).

(48) Determined by NMR.
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(55) The crystals were dissolved in CH_2Cl_2 in a small vial which was placed in a larger vessel containing diethyl ether. The larger vessel was closed with a lid and placed in a refrigerator. The crystals appeared when the diethyl ether slowly diffused into the small container.

(2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Chloride (*syn*-2b). The compound was prepared by adding an equivalent amount of N-N ligand (1 mol/mol Pd) to a dichloromethane solution of the corresponding chloride-bridged dimer[50] and crystallizing the product by addition of diethyl ether. The resulting crystals contained both dichloromethane and ether, and the sample for NMR analysis was evaporated twice from $CDCl_3$ in order to get a spectrum free from solvent resonances. ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.77 (s, 2 H, $H_{P5,6}$), 7.60 (d, 2 H, $H_{P3,8}$), 5.40 (d app t, 1 H, H_2), 3.60 (br d, $J_{1s,2} \approx 7$ Hz, 1 H, H_{1s}), 4.26 (dq, $J_{3a,2} = 10.5$ Hz, 1 H, H_{3a}), 3.26 (s, 6 H, Me_P), 2.48 (br d, $J_{1a,2} \approx 12$ Hz, 1 H, H_{1a}), 0.96 (d, $J_{Me,3a} = 6.0$ Hz, 3 H, Me). Signals from free 2,9-dimethyl-1,10-phenanthroline and the starting chloride-bridged dimer were detectable, as well as signals from the anti isomer. The spectrum in D_2O (for both syn and anti isomers) is almost coincident with that of the trifluoroacetate salt.[17]

(2,9-Di-*tert*-butyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2c) and (2,9-Di-*tert*-butyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2c). General Procedure A. (*anti*-2c): ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.83 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.21 (s, 2 H, $H_{P5,6}$), 8.19 (d, 2 H, $H_{P3,8}$), 5.88 (dq (app quintet), $J_{3s,2} = 7.4$ Hz, 1 H, H_{3s}), 5.35 (ddd (d app t), 1 H, H_2), 4.37 (d, $J_{1s,2} = 7.5$ Hz, 1 H, H_{1s}), 3.66 (d, $J_{1a,2} = 13.5$ Hz, 1 H, H_{1a}), 1.75 (s, 18 H, Me_P), 1.00 (d, $J_{Me,3s}$ = 6.4 Hz, 3 H, Me). (*syn*-2c): ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.77 (d, 2 H, $H_{P4,7}$), 8.21 (s, 2 H, $H_{P5,6}$), 8.18 (d, 2 H, $H_{P3,8}$), 5.54 (ddd, 1 H, H_2), 4.20 (d, $J_{1s,2} = 7.4$ Hz, 1 H, H_{1s}), 4.17 (dq (app sextet), $J_{3a,2} = 11.8$ Hz, 1 H, H_{3a}), 3.26 (d, $J_{1a,2} = 13.4$ Hz, 1 H, H_{1a}), 1.78 (s, 18 H, Me_P), 1.00 (d, $J_{Me,3a} = 6.4$ Hz, 3 H, Me).

(2,9-Di-*n*-butyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2d) and (2,9-Di-*n*-butyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2d). General Procedure A. (*anti*-2d): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.63 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.02 (s, 2 H, $H_{P5,6}$), 7.91 (d, 2 H, $H_{P3,8}$), 5.77 (ddd (d app t), $J_{2,3s} = 7.4$ Hz, 1 H, H_2), 5.63 (dq (app quintet), 1 H, H_{3s}), 4.36 (d, $J_{1s,2} = 7.3$ Hz, 1 H, H_{1s}), 3.68 (d, $J_{1a,2} = 12.7$ Hz, 1 H, H_{1a}), 3.38–3.24 (m, 4 H, CH_{2P}), 1.98–1.77 (m, 4 H, CH_{2P}), 1.56–1.42 (m, 4 H, CH_{2P}), 1.22 (d, $J_{Me,3s} = 6.2$ Hz, 3 H, Me), 1.00 (t, 6 H, Me_P). (*syn*-2d): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.55 (d, $J_{P3,4} = J_{P7,8} = 8.5$ Hz, 2 H, $H_{P4,7}$), 7.96 (s, 2 H, $H_{P5,6}$), 7.86 (d, 2 H, $H_{P3,8}$), 5.52 (ddd, 1 H, H_2), 4.46 (d, $J_{1s,2} = 7.3$ Hz, 1 H, H_{1s}), 4.27 (dq (app sextet), $J_{3a,2} = 12.2$ Hz, 1 H, H_{3a}), 3.31 (d, $J_{1a,2}$ = 12.6 Hz, 1 H, H_{1a}), 3.38–3.24 (m, 4 H, CH_{2P}), 1.98–1.77 (m, 4 H, CH_{2P}), 1.56–1.42 (m, 4 H, CH_{2P}), 1.34 (d, $J_{Me,3a} = 6.2$ Hz, 3 H, Me), 1.00 (t, 6 H, Me_P).

(2,9-Diphenyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2e) and (2,9-Diphenyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2e). General Procedure A. (*anti*-2e): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.83 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.29 (d, 2 H, $H_{P3,8}$), 8.28–8.19 (br m, 4 H, Ar), 8.21 (s, 2 H, $H_{P5,6}$), 7.77–7.67 (br m, 6 H, Ar), 5.01 (ddd (d app t), 1 H, H_2), 2.89 (dq, $J_{3s,2} = 7.1$ Hz, 1 H, H_{3s}), 2.83 (d, $J_{1s,2} = 13.4$ Hz, 1 H, H_{1a}), 2.14 (d, $J_{1s,2} = 7.6$ Hz, 1 H, H_{1s}), 0.42 (d, $J_{Me,3s}$ = 6.8 Hz, 3 H, Me). (*syn*-2e): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.79 (d, $J_{P3,4} = J_{P7,8} = 8.5$ Hz, 2 H, $H_{P4,7}$), 8.24 (d, 2 H, $H_{P3,8}$), 8.16 (s, 2 H, $H_{P5,6}$), 7.99–7.91 (br m, 4 H, Ar), 7.77–7.67 (br m, 6 H, Ar), 4.87 (ddd, 1H, H_2), 3.35 (dq (app sextet), $J_{3a,2} = 11.8$ Hz, 1 H, H_{3a}), 2.69 (d, $J_{1s,2} = 7.0$ Hz, 1 H, H_{1s}), 2.42 (d, $J_{1a,2} = 13.4$ Hz, 1 H, H_{1a}), 0.21 (d, $J_{Me,3a} = 6.2$ Hz, 3 H, Me).

(2,9-Dichloro-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2f) and (2,9-Dichloro-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2f). General Procedure A. (*anti*-2f): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.72 (d, $J_{P3,4} = J_{P7,8}$ = 8.6 Hz, 2 H, $H_{P4,7}$), 8.17 (s, 2 H, $H_{P5,6}$), 8.07 (d, 2 H, $H_{P3,8}$), 6.07 (dq (app quintet), $J_{3s,2} = 7.4$ Hz, 1 H, H_{3s}), 5.69 (ddd (d app t), 1 H, H_2), 4.93 (dd, $J_{1s,2} = 7.5$ Hz, $J_{1s,1a} = 1.6$ Hz, 1 H, H_{1s}), 4.07 (dd, $J_{1a,2} = 13.2$ Hz, 1 H, H_{1a}), 1.39 (d, $J_{Me,3s} = 6.6$ Hz, 3 H, Me). (*syn*-2f): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.64 (br s, 2 H, $H_{P4,7}$), 8.11 (br s, 2 H, $H_{P5,6}$), 7.97 (br s, 2 H, $H_{P3,8}$), 5.62 (ddd, 1 H, H_2), 5.09 (d, $J_{1s,2} = 7.2$ Hz, 1 H, H_{1s}), 4.72 (dq (app sextet), $J_{3a,2} = 11.3$ Hz, 1 H, H_{3a}), 3.82 (d, $J_{1a,2} = 12.9$ Hz, 1 H, H_{1a}), 1.52 (d, $J_{Me,3a}$ = 6.0 Hz, 3 H, Me). Anal. Calcd for $C_{16}H_{13}N_2Cl_2PdBF_4$: C, 38.64; H, 2.63. Found: C, 38.64; H, 2.60.

(2,9-Dibromo-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2g) and (2,9-Dibromo-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2g). General Procedure A. (*anti*-2g): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.61 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.19 (s, 2 H, $H_{P3,8}$), 8.17 (d, 2 H, $H_{P5,6}$), 6.07 (dq (app quintet), $J_{3s,2} = 7.7$ Hz, 1 H, H_{3s}), 5.72 (ddd, 1 H, H_2), 4.86 (dd, $J_{1s,2} = 7.4$ Hz, $J_{1s,1a} = 1.6$ Hz, 1 H, H_{1s}), 4.02 (dd, $J_{1a,2}$ = 12.9 Hz, 1 H, H_{1a}), 1.36 (d, $J_{Me,3s} = 6.7$ Hz, 3 H, Me). (*syn*-2g): ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, $J_{P3,4} = J_{P7,8} = 8.5$ Hz, 2 H, $H_{P4,7}$), 8.16 (d, 2 H, $H_{P3,8}$), 8.16 (s, 2 H, $H_{P5,6}$), 5.59 (ddd, 1 H, H_2), 5.08 (dd, $J_{1s,2} = 7.1$ Hz, 1 H, H_{1s}), 4.68 (dq (app sextet), $J_{3a,2}$ = 11.3 Hz, 1 H, H_{3a}), 3.80 (dd, $J_{1a,2} = 12.5$ Hz, $J_{1a,1s} = 1.0$ Hz, 1 H, H_{1a}), 1.49 (d, $J_{Me,3a} = 6.1$ Hz, 3 H, Me). Anal. Calcd for $C_{16}H_{13}N_2Br_2PdBF_4$: C, 32.78; H, 2.23. Found: C, 32.60; H, 2.15.

[2,9-Bis(methoxycarbonyl)-1,10-phenanthroline][*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2h) and (2,9-Dimethoxycarbonyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2h). General Procedure A. (*anti*-2h): ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, $J_{P3,4} = J_{P7,8} = 8.4$ Hz, 2 H, $H_{P4,7}$), 8.50 (d, 2 H, $H_{P3,8}$), 8.30 (s, 2 H, $H_{P5,6}$), 5.75 (ddd, 1 H, H_2), 5.06 (dq, $J_{3s,2} = 7.7$ Hz, 1 H, H_{3s}), 4.18 (s, 6 H, Me_P), 4.10 (d, $J_{1s,2} = 7.3$ Hz, 1 H, H_{1s}), 3.63 (d, $J_{1a,2} = 12.9$ Hz, 1 H, H_{1a}), 1.04 (d, $J_{Me,3s} = 6.7$ Hz, 3 H, Me). (*syn*-2h): ^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.58 (d, 2 H, $H_{P3,8}$), 8.29 (s, 2 H, $H_{P5,6}$), 5.44 (ddd, 1 H, H_2), 4.41 (dq, $J_{3a,2} = 11.3$ Hz, 1 H, H_{3a}), 4.18 (s, 6 H, Me_P), 4.00 (d, $J_{1s,2} = 6.7$ Hz, 1 H, H_{1s}), 3.48 (d, $J_{1a,2} = 12.8$ Hz, 1 H, H_{1a}), 1.12 (d, $J_{Me,3a} = 6.1$ Hz, 3 H, Me).

[2,9-Bis(2-phenylethynyl)-1,10-phenanthroline][*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2i) and [2,9-Bis(2-phenylethynyl)-1,10-phenanthroline][*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2i). General Procedure A. (*anti*-2i): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.68 (d, $J_{P3,4} = J_{P7,8} = 8.4$ Hz, 2 H, $H_{P4,7}$), 8.21 (d, 2 H, $H_{P3,8}$), 8.11 (s, 2 H, $H_{P5,6}$), 7.74–7.77 (m, 4 H, Ar_P), 7.50–7.58 (m, 6 H, Ar_P), 6.11 (dq (app quintet), $J_{3s,2} = 7.7$ Hz, 1 H, H_{3s}), 5.74 (ddd (d app t), 1 H, H_2), 4.94 (dd, $J_{1s,2} = 7.7$ Hz, $J_{1s,1a} = 1.6$ Hz, 1 H, H_{1s}), 4.04 (dd, $J_{1a,2} = 13.3$ Hz, 1 H, H_{1a}), 1.42 (d, $J_{Me,3s} = 6.6$ Hz, 3 H, Me). (*syn*-2i): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.66 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.17 (d, 2 H, $H_{P3,8}$), 8.08 (s, 2 H, $H_{P5,6}$), 7.77–7.74 (m, 4 H, Ar_P), 7.50–7.58 (m, 6 H, Ar_P), 5.59 (ddd, $J_{2,3a} = 11.2$ Hz, 1 H, H_2), 5.07 (d, $J_{1s,2} = 7.2$ Hz, 1 H, H_{1s}), 4.61 (dq (app sextet), 1 H, H_{3a}), 3.90 (d, $J_{1a,2} = 12.8$ Hz, 1 H, H_{1a}), 1.59 (d, $J_{Me,3a} = 6.1$ Hz, 3 H, Me).

[2,9-Bis(2-(trimethylsilyl)ethynyl)-1,10-phenanthroline][*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2k) and [2,9-Bis(2-(trimethylsilyl)ethynyl)-1,10-phenanthroline][*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2k). General Procedure A. (*anti*-2k): ^1H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, $J_{P3,4} = J_{P7,8} = 8.4$ Hz, 2 H, $H_{P4,7}$), 8.17 (s, 2 H, $H_{P5,6}$), 8.10 (d, 2 H, $H_{P3,8}$), 6.05 (dq (app quintet), $J_{3s,2} = 7.8$ Hz, 1 H, H_{3s}), 5.70 (ddd (d app t), 1 H, H_2), 4.87 (dd, $J_{1s,2} = 7.5$ Hz, $J_{1s,1a} = 1.8$ Hz, 1 H, H_{1s}), 3.89 (dd, $J_{1a,2}$ = 13.1 Hz, 1 H, H_{1a}), 1.41 (d, $J_{Me,3s} = 6.7$ Hz, 3 H, Me), 0.41 (s, 18 H, Me_P). (*syn*-2k): ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.14 (s, 2 H, $H_{P5,6}$), 8.06 (d, 2 H, $H_{P3,8}$), 5.57 (ddd, 1 H, H_2), 5.04 (d, $J_{1s,2} = 7.3$ Hz, 1 H, H_{1s}), 4.48 (dq (app sextet), $J_{3a,2} = 11.3$ Hz, 1 H, H_{3a}), 3.74 (d, $J_{1a,2} = 12.9$ Hz, 1 H, H_{1a}), 1.68 (d, $J_{Me,3a} = 6.1$ Hz, 3 H, Me), 0.39 (s, 18 H, Me_P). Anal. Calcd for $C_{26}H_{31}N_2Si_2PdBF_4$: C, 50.29; H, 5.03. Found: C, 51.61; H, 4.93.

[2-Bromo-9-((trimethylsilyl)ethynyl)-1,10-phenanthroline][*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2l) and [2-Bromo-9-((trimethylsilyl)ethynyl)-1,10-phenanthroline][*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2l). General Procedure A. (*anti*-2l): ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, $J_1 = 8.5$ Hz, 1 H), 8.56 (d, J_1 = 8.5 Hz, 1 H), 8.20 (d, $J_1 = 8.5$ Hz, 1 H), 8.12–8.06 (m, 3 H), 6.11 (dq, $J_{3s,2} = 13.2$ Hz, 1 H, H_{3s}), 5.70 (ddd, 1 H, H_2), 4.90 (d, $J_{1s,2}$ = 7.5 Hz, 1 H, H_{1s}), 3.98 (d, $J_{1a,2} = 13.1$ Hz, 1 H, H_{1a}), 1.37 (d, $J_{Me,3s} = 6.7$ Hz, 3 H, Me), 0.40 (s, 9 H, Me_P). (*syn*-2l): ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, $J_1 = 8.5$ Hz, 1 H), 8.54 (d, $J_1 = 8.5$ Hz, 1 H), 8.16 (d, $J_1 = 8.5$ Hz, 1 H), 8.12–8.06 (m, 3 H), 5.57 (ddd,

1 H, H_2), 5.08 (d, $J_{1s,2}$ = 7.1 Hz, 1 H, H_{1s}), 4.60 (dq, $J_{3a,2}$ = 10.7 Hz, 1 H, H_{3a}), 3.80 (d, $J_{1a,2}$ = 12.9 Hz, 1 H, H_{1a}), 1.54 (d, $J_{Me,3a}$ = 6.1 Hz, 3 H, Me), 0.41 (s, 9 H, Me_P).

[2,9-Bis(2-(trimethylsilyl)butadiynyl)-1,10-phenanthroline][*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2m). General Procedure A. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.11 (d, 2 H, $H_{P3,8}$), 8.10 (s, 2 H, $H_{P5,6}$), 5.93 (dq (app quintet), $J_{3s,2}$ = 7.7 Hz, 1 H, H_{3s}), 5.71 (ddd (d app t), 1 H, H_2), 4.84 (dd, $J_{1s,2}$ = 7.5 Hz, $J_{1s,1a}$ = 1.8 Hz, 1 H, H_{1s}), 4.02 (dd, $J_{1a,2}$ = 12.9 Hz, 1 H, H_{1a}), 1.47 (d, $J_{Me,3s}$ = 6.7 Hz, 3 H, Me), 0.32 (s, 18 H, Me_P).

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2n). General Procedure A. (*anti*-**2n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.56 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.02 (s, 2 H, $H_{P5,6}$), 8.01 (d, 2 H, $H_{P3,8}$), 5.89 (dq (app quintet), $J_{3s,2}$ = 7.9 Hz, 1 H, H_{3s}), 5.67 (ddd (d app t), 1 H, H_2), 4.80 (dd, $J_{1s,2}$ = 7.5 Hz, $J_{1s,1a}$ = 1.7 Hz, 1 H, H_{1s}), 3.95 (dd, $J_{1a,2}$ = 12.9 Hz, 1 H, H_{1a}), 2.34 (s, 6 H, Me_P), 1.44 (d, $J_{Me,3s}$ = 6.6 Hz, 3 H, Me). (*syn*-**2n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.97 (d, 2 H, $H_{P3,8}$), 5.57 (ddd, 1 H, H_2), 4.99 (dd, $J_{1s,2}$ = 7.1 Hz, $J_{1s,1a}$ = 0.9 Hz, 1 H, H_{1s}), 4.50 (dq (app sextet), $J_{3a,2}$ = 11.3 Hz, 1 H, H_{3a}), 3.80 (ddd, $J_{1a,2}$ = 12.6 Hz, $J_{1a,3a}$ = 1.0 Hz, 1 H, H_{1a}), 2.30 (s, 6 H, Me_P), 1.52 (d, $J_{Me,3a}$ = 6.0 Hz, 3 H, Me). Anal. Calcd for $C_{22}H_{19}N_2PdBF_4$: C, 52.37; H, 3.80. Found: C, 52.57; H, 3.81.

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Trifluoroacetate (*anti*-2n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Trifluoroacetate (*syn*-2n). General Procedure B. (*anti*-**2n**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.08 (s, 2 H, $H_{P5,6}$), 7.99 (d, 2 H, $H_{P3,8}$), 5.85 (dq (app quintet), $J_{3s,2}$ = 7.4 Hz, 1 H, H_{3s}), 5.71 (ddd (d app t), 1 H, H_2), 4.76 (dd, $J_{1s,2}$ = 7.5 Hz, 1 H, H_{1s}), 3.89 (dd, $J_{1a,2}$ = 13.2 Hz, $J_{1s,1a}$ = 1.5 Hz, 1 H, H_{1a}), 2.34 (s, 6 H, Me_P), 1.42 (d, $J_{Me,3s}$ = 6.7 Hz, 3 H, Me). (*syn*-**2n**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.06 (s, 2 H, $H_{P5,6}$), 7.96 (d, 2 H, $H_{P3,8}$), 5.57 (ddd, 1 H, H_2), 4.95 (d, $J_{1s,2}$ = 7.1 Hz, 1 H, H_{1s}), 4.48 (dq (app sextet), $J_{3a,2}$ = 11.3 Hz, 1 H, H_{3a}), 3.80 (d, $J_{1a,2}$ = 13.0 Hz, 1 H, H_{1a}), 2.31 (s, 6 H, Me_P), 1.59 (d, $J_{Me,3a}$ = 6.1 Hz, 3 H, Me).

(2,9-Dicyano-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2o) and (2,9-Dicyano-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2o). General Procedure A. (*anti*-**2o**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.05 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.45 (d, 2 H, $H_{P5,6}$), 8.38 (s, 2 H, $H_{P3,8}$), 6.23 (dq (app quintet), $J_{3s,2}$ = 7.8 Hz, 1 H, H_{3s}), 5.90 (ddd (d app t), 1 H, H_2), 5.08 (dd, $J_{1s,2}$ = 7.6, $J_{1s,1a}$ = 1.7 Hz, 1 H, H_{1s}), 4.24 (br d, $J_{1a,2}$ = 13.2 Hz, 1 H, H_{1a}), 1.48 (d, $J_{Me,3a}$ = 6.7 Hz, 3 H, Me). (*syn*-**2o**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.02 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.42 (d, 2 H, $H_{P5,6}$), 8.36 (s, 2 H, $H_{P3,8}$), 5.88 (ddd, 1 H, H_2), 5.30 (d, $J_{1s,2}$ = 7.5 Hz, 1 H, H_{1s}), 4.81 (dq (app sextet), $J_{3a,2}$ = 11.4 Hz, 1 H, H_{3a}), 4.08 (d, $J_{1a,2}$ = 14.0 Hz, 1 H, H_{1a}), 1.65 (d, $J_{Me,3a}$ = 6.1 Hz, 3 H, Me). Anal. Calcd for $C_{18}H_{13}N_4PdBF_4$: C, 45.18; H, 2.74. Found: C, 42.34; H, 2.69.

(6,6′-Dicyano-2,2′-bipyridine)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*anti*-2q) and (6,6′-Dicyano-2,2′-bipyridine)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2q). General Procedure A. (*anti*-**2q**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (dd, J_1 = 8.2 Hz, J_2 = 1.1 Hz, 2 H), 8.53 (t, J = 8.1 Hz, 2 H), 8.14 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2 H), 6.03 (dq (app quintet), $J_{3s,2}$ = 7.6 Hz, 1 H, H_{3s}), 5.80 (ddd, (d app t), 1 H, H_2), 4.94 (dd, $J_{1s,2}$ = 7.6 Hz, $J_{1s,1a}$ = 1.8 Hz, 1 H, H_{1s}), 4.04 (dd, $J_{1a,2}$ = 13.1 Hz, 1 H, H_{1a}), 1.42 (d, $J_{Me,3s}$ = 6.7 Hz, 3 H, Me). (*syn*-**2q**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.3 Hz, 2 H), 8.51 (t, J = 8.2 Hz, 2 H), 8.13 (d, J = 8.3 Hz, 2 H), 5.74 (ddd, 1 H, H_{3a}), 5.04 (d, $J_{2,3a}$ = 7.1 Hz, 1 H, H_2), 4.69 (dq (app sextet), $J_{1s,2}$ = 7.6 Hz, 1 H, H_{1s}), 3.91 (d, $J_{1a,2}$ = 13.1 Hz, 1 H, H_{1a}), 1.59 (d, $J_{Me,3a}$ = 6.1 Hz, 3 H, Me).

(Dibenzo[*b,j*]-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (anti-2s) and (Dibenzo-[*b,j*]-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium Tetrafluoroborate (*syn*-2s). General Procedure A. (*anti*-**2s**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.18 (s, 2 H), 8.51 (d, J = 8.8 Hz, 2 H), 8.31 (br d, J = 8.8 Hz, 2 H), 8.20–8.15 (m, 2 H), 7.99 (s, 2 H), 7.95–7.90 (m, 2 H), 5.88 (ddd, 1 H, H_2), 5.72 (dq, $J_{3s,2}$ = 7.7 Hz, 1 H, H_{3s}), 4.65 (d, $J_{1s,2}$ = 7.6 Hz, 1 H, H_{1s}), 3.88 (d, $J_{1a,2}$ = 13.0 Hz, 1 H, H_{1a}), 1.18 (d, $J_{Me,3s}$ = 6.7 Hz, 3 H, Me). (*syn*-**2s**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.15 (s, 2 H), 8.47 (d, J = 8.8 Hz, 2 H), 8.31 (br d, J = 8.8 Hz, 2 H), 8.20–8.15 (m, 2 H), 7.97 (s, 2 H), 7.95–7.90 (m, 2 H), 5.48 (ddd, 1 H, H_2), 4.73 (dq, $J_{3a,2}$ = 11.9 Hz, 1 H, H_{3a}), 4.47 (d, $J_{1s,2}$ = 7.1 Hz, 1 H, H_{1s}), 3.92 (d, $J_{1a,2}$ = 11.7 Hz, 1 H, H_{1a}), 1.23 (d, $J_{Me,3a}$ = 6.2 Hz, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-pentenyl]palladium Tetrafluoroborate (anti-3b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-pentenyl]palladium Tetrafluoroborate (*syn*-3b). General Procedure A. (*anti*-**3b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.87 (d, 2 H, $H_{P3,8}$), 5.70 (ddd, $J_{2,3s}$ = 7.5 Hz, 1 H, H_2), 5.68 (m, 1 H, H_{3s}), 4.56 (d, $J_{1s,2}$ = 7.5 Hz, 1 H, H_{1s}), 3.64 (d, $J_{1a,2}$ = 12.3 Hz, 1 H, H_{1a}), 3.03 (s, 6 H, Me_P), 1.56–1.66 (m, 1 H, H_4), 1.37–1.45 (m, 1 H, $H_{4'}$), 0.98 (t, $J_{5,4}$ = 7.4 Hz, 3 H, H_5). (*syn*-**3b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.50 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.97 (s, 2 H, $H_{P5,6}$), 7.83 (d, 2 H, $H_{P3,8}$), 5.52 (ddd, $J_{2,3a}$ = 11.0 Hz, 1 H, H_2), 4.59 (d, $J_{1s,2}$ = 7.2 Hz, 1 H, H_{1s}), 4.55 (m, 1 H, H_{3a}), 3.55 (d, $J_{1a,2}$ = 12.6 Hz, 1 H, H_{1a}), 3.06 (s, 6 H, Me_P), 1.74–1.84 (m, 1 H, H_4), 1.56–1.66 (m, 1 H, $H_{4'}$), 1.08 (t, $J_{5,4}$ = 7.5 Hz, 3 H, H_5).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-hexenyl]palladium Tetrafluoroborate (anti-4b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-hexenyl]palladium Tetrafluoroborate (*syn*-4b). General Procedure A. (*anti*-**4b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.88 (d, 2 H, $H_{P3,8}$), 5.72 (ddd (d app t), $J_{2,3s}$ = 7.6 Hz, 1 H, H_2), 5.64 (m, 1 H, H_{3s}), 4.56 (d, $J_{1s,2}$ = 7.6 Hz, 1 H, H_{1s}), 3.64 (d, $J_{1a,2}$ = 12.9 Hz, 1 H, H_{1a}), 3.03 (s, 6 H, Me_P), 1.71–1.61 (m, 2 H, $H_{4,4'}$), 1.49–1.33 (m, 2 H, H_5), 0.87 (t, $J_{6,5}$ = 7.2 Hz, 3 H, H_6). (*syn*-**4b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.51 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.97 (s, 2 H, $H_{P5,6}$), 7.84 (d, 2 H, $H_{P3,8}$), 5.47 (ddd, $J_{2,3a}$ = 10.9 Hz, 1 H, H_2), 4.59 (d, $J_{1s,2}$ = 7.1 Hz, 1 H, H_{1s}), 4.40 (m, 1 H, H_{3a}), 3.56 (d, $J_{1a,2}$ = 12.6 Hz, 1 H, H_{1a}), 3.06 (s, 6 H, Me_P), 1.85–1.80 (m, 1 H, H_4), 1.71–1.61 (m, 1 H, $H_{4'}$), 1.49–1.33 (m, 2 H, H_5), 0.96 (t, $J_{6,5}$ = 7.2 Hz, 3 H, H_6).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-4-methyl-2-pentenyl]palladium Tetrafluoroborate (anti-5b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-4-methyl-2-pentenyl]palladium Tetrafluoroborate (*syn*-5b). General Procedure B Then C. (*anti*-**5b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.06 (s, 2 H, $H_{P5,6}$), 7.92 (d, 2 H, $H_{P3,8}$), 5.77 (ddd (d app t), $J_{2,3s}$ = 7.8 Hz, 1 H, H_2), 5.69 (dd, $J_{3s,4}$ = 10.4 Hz, 1 H, H_{3s}), 4.52 (d, $J_{1s,2}$ = 7.6 Hz, 1 H, H_{1s}), 3.52 (d, $J_{1a,2}$ = 11.9 Hz, 1 H, H_{1a}), 3.04 (s, 6 H, Me_P), 1.63 (dqq (d app quintet), 1 H, H_4), 1.01 (d, $J_{5,4}$ = 6.6 Hz, 3 H, H_5), 0.76 (d, $J_{Me_4,4}$ = 6.6 Hz, 3 H, Me_4). (*syn*-**5b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 8.01 (s, 2 H, $H_{P5,6}$), 7.88 (d, 2 H, $H_{P3,8}$), 5.59 (ddd, 1 H, H_2), 4.64 (d, $J_{1s,2}$ = 7.2 Hz, 1 H, H_{1s}), 4.62 (dd, $J_{3a,2}$ = 11.7 Hz, $J_{3a,4}$ = 4.7 Hz, 1 H, H_{3a}), 3.62 (d, $J_{1a,2}$ = 12.4 Hz, 1 H, H_{1a}), 3.10 (s, 6 H, Me_P), 2.35 (qqd, 1 H, H_4), 1.23 (d, $J_{5,4}$ = 6.8 Hz, 3 H, H_5), 0.80 (d, $J_{Me_4,4}$ = 6.9 Hz, 3 H, Me_4). Anal. Calcd for $C_{20}H_{23}N_2PdBF_4$: C, 49.59; H, 4.78. Found: C, 49.40; H, 4.67.

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-4-methyl-2-pentenyl]palladium Tetrafluoroborate (*anti*-5n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-4-methyl-2-pentenyl]palladium Tetrafluoroborate (*syn*-5n). General Procedure B Then C.[56] (*anti*-**5n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.57 (d, $J_{P3,4}$ = $J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,P7}$), 8.04 (s, 2 H, $H_{P5,P6}$), 8.02 (d, 2 H, $H_{P3,P8}$), 6.02 (dd, $J_{3s,4}$ = 10.5 Hz, 1 H, H_{3s}), 5.71 (ddd, $J_{2,3s}$ = 7.8 Hz, 1 H, H_2), 4.64 (dd, $J_{1s,2}$ = 7.7 Hz, 1 H, H_{1s}), 3.75 (dd, $J_{1a,2}$ = 13.2 Hz, $J_{1a,1s}$ = 2.0 Hz, 1 H, H_{1a}), 2.33 (s,

(56) Bis(μ-trifluoroacetato)bis[(1,2,3-η)-4-methyl-2-pentenyl]dipalladium was made by the following procedure: 4-Methyl-3-(trifluoroacetoxy)-1-pentene (392 mg, 2 mmol) and $Pd(dba)_2$ (1.15 g, 2 mmol) were added to a mixture of anhydrous THF (16 mL) and acetonitrile (4 mL). The mixture was stirred at room temperature until a green color appeared. The same workup procedure was used as for the other bis(μ-trifluoroacetato)bis[(1,2,3-η)-allyl]dipalladium complexes.[17] The yield was 526 mg (87%).

3 H, Me_P), 2.32 (s, 3 H, Me_P), 1.79 (dqq (d app quintet), 1 H, H_4), 1.11 (d, $J_{5,4}$ = 6.6 Hz, 3 H, H_5), 1.08 (d, $J_{Me_4,4}$ = 6.6 Hz, 3 H, Me_4). (*syn*-**5n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.97 (d, 2 H, $H_{P3,8}$), 5.61 (ddd, 1 H, H_2), 5.07 (d, $J_{1s,2}$ = 7.2 Hz, 1 H, H_{1s}), 4.64 (dd, $J_{3a,2}$ = 11.7 Hz, $J_{3a,4}$ = 4.3 Hz, 1 H, H_{3a}), 3.87 (dd, $J_{1a,2}$ = 12.9 Hz, $J_{1a,1s}$ = 1.1 Hz, 1 H, H_{1a}), 2.85 (qqd, 1 H, H_4), 2.30 (s, 6 H, Me_P), 1.26 (d, $J_{5,4}$ = 6.9 Hz, 3 H, H_5), 0.84 (d, $J_{Me_4,4}$ = 6.9 Hz, 3 H, Me_4).

(2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Tetrafluoroborate (*syn*-6b). General Procedure A. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.45 (br d, $J_{P3,4} = J_{P7,8}$ = 7.8 Hz, 2 H, $H_{P4,7}$), 7.95 (s, 2 H, $H_{P5,6}$), 7.63 (br d, 2 H, $H_{P3,8}$), 7.46–7.23 (m, 5 H, Ar), 5.94 (ddd, 1 H, H_2), 5.17 (d, $J_{1a,2}$ = 11.5 Hz, 1 H, H_{1a}), 4.63 (d, $J_{3s,2}$ = 7.1 Hz, 1 H, H_{3s}), 3.72 (d, $J_{3a,2}$ = 12.5 Hz, 1 H, H_{3a}), 2.65 (br s, 6 H, Me_P).

(2,9-Dichloro-1,10-phenanthroline)[*syn*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Tetrafluoroborate (*anti*-6f). General Procedure A. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.64 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.14 (s, 2 H, $H_{P5,6}$), 7.97 (d, 2 H, $H_{P3,8}$), 7.53–7.44 (m, 3 H, Ar), 7.25 (t, 2 H, Ar), 6.04 (ddd, 1 H, H_2), 5.38 (d, $J_{1a,2}$ = 11.5 Hz, 1 H, H_{1a}), 5.14 (dd, $J_{3s,2}$ = 6.9 Hz, $J_{3s,3a}$ = 1.1 Hz, 1 H, H_{3s}), 3.99 (dd, $J_{3a,2}$ = 12.5 Hz, 1 H, H_{3a}).

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Tetrafluoroborate (*anti*-6n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Tetrafluoroborate (*syn*-6n). General Procedure A. (*anti*-**6n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.49 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.01 (s, 2 H, $H_{P5,6}$), 7.81 (d, 2 H, $H_{P3,8}$), 7.48–7.17 (m, 5 H, Ar), 7.38 (d, $J_{3s,2}$ = 7.6 Hz, 1 H, H_{3s}), 5.97 (ddd (d app t), 1 H, H_2), 4.86 (d, $J_{1s,2}$ = 8.1 Hz, 1 H, H_{1s}), 4.12 (d, $J_{3a,2}$ = 13.7 Hz, 1 H, H_{3a}), 2.28 (s, 6 H, Me_P). (*syn*-**6n**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.49 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.99 (s, 2 H, $H_{P5,6}$), 7.81 (d, 2 H, $H_{P3,8}$), 7.48–7.17 (m, 5 H, Ar), 5.83 (dd, 1 H, H_2), 5.19 (d, $J_{1a,2}$ = 10.9 Hz, 1 H, H_{1a}), 5.02 (dd, $J_{3s,2}$ = 6.7 Hz, $J_{3s,3a}$ = 1.0 Hz, 1 H, H_{3s}), 3.96 (dd, $J_{3a,2}$ = 12.8 Hz, 1 H, H_{3a}), 2.24 (s, 6 H, Me_P). Anal. Calcd for $C_{22}H_{19}N_2PdBF_4$: C, 57.23; H, 3.74. Found: C, 57.15; H, 3.76.

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Trifluoroacetate (*anti*-6n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-1-phenyl-2-propenyl]palladium Trifluoroacetate (*syn*-6n). General Procedure B. (*anti*-**6n**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, $J_{P3,4} = J_{P7,8}$ = 8.0 Hz, 2 H, $H_{P4,7}$), 7.90 (s, 2 H, $H_{P5,6}$), 7.76 (d, 2 H, $H_{P3,8}$), 7.39–7.08 (m, 5 H, Ar), 7.12 (d, 1 H, H_{3s}), 5.97 (ddd, $J_{2,3s}$ = 7.8 Hz, 1 H, H_2), 4.63 (d, $J_{1s,2}$ = 8.0 Hz, 1 H, H_{1s}), 3.90 (d, $J_{3a,2}$ = 13.3 Hz, 1 H, H_{3a}), 2.21 (s, 6 H, Me_P). (*syn*-**6n**): ^{1}H NMR (MeOD) δ 8.46 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.90 (s, 2 H, $H_{P5,6}$), 7.75 (d, 2 H, $H_{P3,8}$), 7.39–7.08 (m, 5 H, Ar), 5.86 (ddd, 1 H, H_2), 5.19 (d, $J_{1a,2}$ = 11.1 Hz, 1 H, H_{1a}), 4.98 (d, $J_{3s,2}$ = 7.2 Hz, 1 H, H_{3s}), 3.92 (d, $J_{3a,2}$ = 12.9 Hz, 1 H, H_{3a}), 2.22 (s, 6 H, Me_P).

(2,9-Dimethyl-1,10-phenanthroline)[2-*anti*-4-*syn*-(2,3,4-η)-3-pentenyl]palladium Tetrafluoroborate (7b). General Procedure B Then C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.51 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.97 (s, 2 H, $H_{P5,6}$), 7.85 (d, 2 H, $H_{P3,8}$), 5.45 (dq, $J_{2s,3}$ = 7.5 Hz, 1 H, H_{2s}), 5.42 (dd, 1 H, H_3), 4.57 (dq, $J_{4a,3}$ = 12.4 Hz, 1 H, H_{4a}), 3.10 (s, 6 H, Me_P), 1.41 (d, $J_{5,4a}$ = 6.0 Hz, 3 H, H_5), 1.38 (d, $J_{1,2s}$ = 6.0 Hz, 3 H, H_1).

(2,9-Dipropynyl-1,10-phenanthroline)[2-*anti*-4-*syn*-(2,3,4-η)-3-pentenyl]palladium Tetrafluoroborate (7n). General Procedure B Then C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.55 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.01 (s, 2 H, $H_{P5,6}$), 7.99 (d, 2 H, $H_{P3,8}$), 5.78 (dq (app quintet), $J_{2s,3}$ = 7.8 Hz, 1 H, H_{2s}), 5.41 (dd, 1 H, H_3), 4.67 (dq (app sextet), $J_{4a,3}$ = 11.9 Hz, 1 H, H_{4a}), 2.34 (s, 6 H, Me_P), 1.59 (d, $J_{5,4a}$ = 6.0 Hz, 3 H, H_5), 1.50 (d, $J_{1,2s}$ = 6.7 Hz, 3 H, H_1).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-1-acetoxy-2-propenyl]palladium Tetrafluoroborate (*anti*-8b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-1-acetoxy-2-propenyl]palladium Tetrafluoroborate (*syn*-8b). 8b was prepared from $Pd(dba)_2$ (1 equiv) and 2,9-dimethyl-1,10-phenanthroline trifluoroacetate[57] (1.2 equiv) dissolved in THF, and 1,1-diacetoxy-2-propene (1.6 equiv) was added according to similar literature procedure.[17] (*anti*-**8b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.51 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.01 (d, $J_{1s,2}$ = 4.0 Hz, 1 H, H_{1s}), 7.98 (s, 2 H, $H_{P5,6}$), 7.76 (d, 2 H, $H_{P3,8}$), 5.56 (ddd, 1 H, H_2), 4.67 (d, $J_{3s,2}$ = 8.0 Hz, 1 H, H_{3s}), 3.94 (d, $J_{3a,2}$ = 11.8 Hz, 1 H, H_{3a}), 3.05 (s, 6 H, Me_P), 1.91 (s, 3 H, AcO). (*syn*-**8b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.52 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.99 (s, 2 H, $H_{P5,6}$), 7.83 (d, 2 H, $H_{P3,8}$), 6.97 (d, $J_{1a,2}$ = 9.0 Hz, 1 H, H_{1a}), 5.83 (ddd, 1 H, H_2), 4.51 (d, $J_{3s,2}$ = 8.0 Hz, 1 H, H_{3s}), 3.40 (d, $J_{3a,2}$ = 11.8 Hz, 1 H, H_{3a}), 2.94 (s, 6 H, Me_P), 2.24 (s, 3 H, AcO).

(2,9-Dimethyl-1,10-phenanthroline)[1-*syn*-3-*anti*-(1,2,3-η)-1-acetoxy-2-butenyl]palladium Tetrafluoroborate (1-*syn*-3-*anti*-9b) and (2,9-Dimethyl-1,10-phenanthroline)[1-*syn*-3-*syn*-(1,2,3-η)-1-acetoxy-2-butenyl]palladium Tetrafluoroborate (1-*syn*-3-*syn*-9b). 9b was prepared from $Pd(dba)_2$ (1 equiv) and 2,9-dimethyl-1,10-phenanthroline trifluoroacetate[57] (1.2 equiv) dissolved in THF, and 1,1-diacetoxy-2-butene (1.6 equiv) was added according to similar literature procedure.[17] (1-*syn*-3-*anti*-**9b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.53 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 7.99 (s, 2 H, $H_{P5,6}$), 7.85 (d, 2 H, $H_{P3,8}$), 7.05 (dd, $J_{1a,2}$ = 9.1 Hz, $J_{1a,3s}$ = 0.8 Hz, 1 H, H_{1a}), 5.76 (dd, $J_{2,3s}$ = 8.2 Hz, 1 H, H_2), 5.50 (dq, 1 H, H_{3s}), 2.98 (s, 6 H, Me_P), 2.21 (s, 3 H, OAc), 1.28 (d, $J_{Me,3s}$ = 6.9 Hz, 3 H, Me). (1-*syn*-3-*syn*-**9b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.51 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 7.98 (s, 2 H, $H_{P5,6}$), 7.83 (d, 2 H, $H_{P3,8}$), 6.89 (br s, 1 H, H_{1s}), 5.76 (dd, $J_{2,3a}$ = 11.8 Hz, $J_{2,1a}$ = 9.0 Hz, 1 H, H_2), 5.50 (br s, 1 H, H_{3s}), 2.98 (s, 6 H, Me_P), 2.16 (s, 3 H, OAc), 1.28 (br d, $J_{Me,3a}$ = 5.8 Hz, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-methyl-2-butenyl]palladium Tetrafluoroborate (*anti*-10b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-methyl-2-butenyl]palladium Tetrafluoroborate (*syn*-10b). General Procedure B Then C. (*anti*-**10b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.99 (s, 2 H, $H_{P5,6}$), 7.88 (d, 2 H, $H_{P3,8}$), 5.39 (q, 1 H, H_{3s}), 4.39 (s, 1 H, H_{1s}), 3.67 (s, 1 H, H_{1a}), 3.06 (s, 6 H, Me_P), 2.20 (s, 3 H, Me_2), 1.24 (d, $J_{Me_4,3s}$ = 6.7 Hz, 3 H, Me_4). (*syn*-**10b**): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.51 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.97 (s, 2 H, $H_{P5,6}$), 7.84 (d, 2 H, $H_{P3,8}$), 4.41 (s, 1 H, H_{1s}), 4.30 (q, 1 H, H_{3a}), 3.37 (s, 1 H, H_{1a}), 3.07 (s, 6 H, Me_P), 2.00 (s, 3 H, Me_2), 1.38 (d, $J_{Me_4,3a}$ = 6.2 Hz, 3 H, Me_4).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2,4-dimethyl-2-pentenyl]palladium Tetrafluoroborate (*anti*-11b). General Procedure B.[58] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.55 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.02 (s, 2 H, $H_{P5,6}$), 7.88 (d, 2 H, $H_{P3,8}$), 5.27 (d, $J_{3s,4}$ = 10.2 Hz, 1 H, H_{3s}), 4.33 (br s, 1 H, H_{1s}), 3.45 (d, $J_{1a,1s}$ = 1.5 Hz, 1 H, H_{1a}), 3.04 (s, 3 H, Me_P), 3.00 (s, 3 H, Me_P), 2.35 (s, 3 H, Me_2), 1.50 (dqq (d app quintet), 1 H, H_4), 0.96 (d, $J_{5,4}$ = 6.6 Hz, 3 H, H_5), 0.73 (d, $J_{Me_4,4}$ = 6.6 Hz, 3 H, Me_4). Anal. Calcd for $C_{21}H_{25}N_2PdBF_4$: C, 50.58; H, 5.05. Found: C, 50.39; H, 4.92.

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-4-acetoxy-2-butenyl]palladium Tetrafluoroborate (*anti*-12b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-4-acetoxy-2-butenyl]palladium Tetrafluoroborate (*syn*-12b). General Procedure A. (*anti*-**12b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, $J_{P3,4} = J_{P7,8}$ = 8.3 Hz, 2 H, $H_{P4,7}$), 7.95 (s, 2 H, $H_{P5,6}$), 7.86 (d, 2 H, $H_{P3,8}$), 6.01 (ddd, $J_{2,3s}$ = 7.9 Hz, 1 H, H_2), 5.61 (m, 1 H, H_{3s}), 4.87 (dd, $J_{1s,2}$ = 7.9 Hz, 1 H, H_{1s}), 3.86 (dd, $J_{1a,2}$ = 13.3 Hz, $J_{1a,1s}$ = 1.4 Hz, 1 H, H_{1a}), 4.13 (dd, $J_{4,4'}$ = 12.6 Hz, $J_{4,3s}$ = 5.7 Hz, 1 H, H_4), 3.69 (dd, $J_{4',3s}$ = 8.9 Hz, 1 H, $H_{4'}$), 3.07 (s, 6 H, Me_P), 1.85 (s, 3 H, OAc). (*syn*-**12b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 7.92 (s, 2 H, $H_{P5,6}$), 7.81 (d, 2 H, $H_{P3,8}$), 5.73 (ddd, $J_{2,3s}$ = 10.9 Hz, 1 H, H_2), 4.85 (d, $J_{1s,2}$ = 7.3 Hz, 1 H, H_{1s}), 4.46 (m, 1 H, H_{3a}), 4.35 (dd, $J_{4,4'}$ = 13.1 Hz, $J_{4,3}$ = 3.3 Hz, 1 H, H_4), 4.25 (dd, $J_{4',3a}$ = 7.1 Hz, 1 H, $H_{4'}$), 3.99 (d, $J_{1a,2}$

(57) Obtained as a colorless crystalline precipitate by adding an equimolar amount of trifluoroacetic acid to a solution of 2,9-dimethyl-1,10-phenanthroline in a minimum amount of diethyl ether.

(58) Bis(μ-trifluoroacetato)bis[(1,2,3-η)-2,4-dimethyl-2-pentenyl]dipalladium was made by the following procedure: 2,4-Dimethyl-3-(trifluoroacetoxy)-1-pentene (420 mg, 2 mmol) and $Pd(dba)_2$ (1.15 g, 2 mmol) were added to a mixture of anhydrous THF (16 mL) and acetonitrile (4 mL). The mixture was stirred at room temperature until a green color appeared. The same workup procedure was used as for the other bis(μ-trifluoroacetato)bis[(1,2,3-η)-allyl]dipalladium complexes.[17] The yield was 523 mg (83%).

= 13.0 Hz, 1 H, H_{1s}), 3.09 (s, 6 H, Me_P), 1.87 (s, 3 H, OAc).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-4-methoxy-2-butenyl]palladium Trifluoroacetate (*anti*-13b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-4-methoxy-2-butenyl]palladium Trifluoroacetate (*syn*-13b). General Procedure A. (*anti*-13b): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.57 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.03 (s, 2 H, $H_{P5,6}$), 8.01 (d, 2 H, $H_{P3,8}$), 5.80 (ddd (d app t), 1 H, H_2), 5.70 (m, 1 H, H_{3s}), 4.97 (dd, $J_{1s,2}$ = 6.8 Hz, $J_{1s,1a}$ = 1.4 Hz, 1 H, H_{1s}), 4.04 (dd, $J_{4,4'}$ = 11.5 Hz, $J_{4,3s}$ = 3.1 Hz, 1 H, H_4), 3.98 (dd, $J_{1a,2}$ = 13.6 Hz, 1 H, H_{1a}), 3.32 (s, 3 H, OMe), 3.18 (dd, $J_{4',3s}$ = 9.7 Hz, 1 H, $H_{4'}$), 2.34 (s, 6 H, Me_P). (*syn*-13b): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.00 (s, 2 H, $H_{P5,6}$), 7.97 (d, 2 H, $H_{P3,8}$), 5.78 (ddd, 1 H, H_2), 5.14 (d, $J_{1s,2}$ = 7.4 Hz, 1 H, H_{1s}), 4.46 (m, 1 H, H_{3a}), 4.00 (d, $J_{1a,2}$ = 13.2 Hz, 1 H, H_{1a}), 3.90 (dd, $J_{4,4'}$ = 12.5 Hz, $J_{4,3a}$ = 1.2 Hz, 1 H, H_4), 3.77 (dd, $J_{4',3a}$ = 5.7 Hz, 1 H, $H_{4'}$), 3.29 (s, 3 H, OMe), 2.31 (s, 6 H, Me).

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-4-methoxy-2-butenyl]palladium Trifluoroacetate (*anti*-13n) and (2,9-Dipropynyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-4-methoxy-2-butenyl]palladium Trifluoroacetate (*syn*-13n). General Procedure B. (*anti*-13n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.07 (s, 2 H, $H_{P5,6}$), 8.07 (d, 2 H, $H_{P3,8}$), 5.83 (ddd (d app t), $J_{2,1a}$ = 13.5 Hz, $J_{2,1s}$ = 7.6 Hz, $J_{2,3s}$ = 7.6 Hz, 1 H, H_2), 5.64 (m, 1 H, H_{3s}), 4.94 (app br d, $J_{1s,1a}$ = 1.8 Hz, 1 H, H_{1s}), 4.01 (dd, $J_{4,4'}$ = 11.4 Hz, $J_{4,3s}$ = 3.1 Hz, 1 H, H_4), 3.93 (dd, 1 H, H_{1a}), 3.32 (s, 3 H, OMe), 3.16 (dd, $J_{4',3s}$ = 9.8 Hz, 1 H, $H_{4'}$), 2.33 (s, 6 H, Me_P). (*syn*-13n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, $J_{P3,4} = J_{P7,8}$ = 8.4 Hz, 2 H, $H_{P4,7}$), 8.04 (s, 2 H, $H_{P5,6}$), 7.95 (d, 2 H, $H_{P3,8}$), 5.75 (ddd, $J_{2,1a}$ = 13.1 Hz, $J_{2,3a}$ = 11.1 Hz, $J_{2,1s}$ = 7.3 Hz, 1 H, H_2), 5.07 (d, 1 H, H_{1s}), 4.43 (ddd, 1 H, H_{3a}), 3.97 (d, 1 H, H_{1a}), 3.87 (dd, $J_{4,4'}$ = 12.4 Hz, $J_{4,3a}$ = 2.7 Hz, 1 H, H_4), 3.75 (dd, $J_{4',3a}$ = 5.9 Hz, 1 H, $H_{4'}$), 3.16 (s, 3 H, OMe), 2.30 (s, 6 H, Me_P).

(1,10-Phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]platinum Tetrafluoroborate (*anti*-16a) and (1,10-Phenanthroline)-[*syn*-(1,2,3-η)-2-butenyl]platinum Tetrafluoroborate (*syn*-16a). General Procedure D. (*anti*-16a):[59] ^{1}H NMR (270 MHz, CD_3NO_2) δ 5.30 (d, app t, $J_{2,1a}$ = 12 Hz, $J_{2,1s}$ = 6.5 Hz, $J_{2,3s}$ = 6.5 Hz, 1 H, H_2), 3.27 (dd, $J_{1a,1s}$ = 2 Hz, $J_{1a,2}$ = 12 Hz, 1 H, H_{1a}), 1.33 (d, $J_{Me,3s}$ = 6 Hz, J_{Pt} = 11 Hz, 3 H, Me). (*syn*-16a): ^{1}H NMR (270 MHz, CD_3NO_2) δ 9.42 (d, $J_{P2,3}$ = 5 Hz, J_{Pt} = 33 Hz, 1 H, H_{P2}), 9.22 (d, $J_{P9,8}$ = 5 Hz, J_{Pt} = 33 Hz, 1 H, H_{P9}), 8.90 (d, $J_{P4,3}$ = 8.5 Hz, 1 H, H_{P4}), 8.85 (d, $J_{P7,8}$ = 8.5 Hz, 1 H, H_{P7}), 8.18 (s, 2 H, $H_{P5,6}$), 8.15 (dd, 1 H, H_{P3}), 8.04 (dd, 1 H, H_{P8}), 5.06 (d app t, J_{Pt} = 79 Hz, 1 H, H_2), 4.25 (dd, $J_{1s,2}$ = 7.5 Hz, $J_{1s,1a}$ = 2 Hz, 1 H, H_{1s}), 3.62 (dq, $J_{3a,2}$ = 12 Hz, J_{Pt} = 86 Hz, 1 H, H_{3a}), 3.08 (d, $J_{1a,2}$ = 12 Hz, J_{Pt} = 72 Hz, 1 H, H_{1a}), 1.72 (d, $J_{Me,3a}$ = 6 Hz, J_{Pt} = 11 Hz, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]platinum Tetrafluoroborate (*anti*-16b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]platinum Tetrafluoroborate (*syn*-16b). General Procedure D. (*anti*-16b): ^{1}H NMR (270 MHz, CD_3NO_2) δ 8.66 (d, $J_{P4,3} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.04 (s, 2 H, $H_{P5,6}$), 7.98 (d, 2 H, $H_{P3,8}$), 5.57 (app quintet, $J_{3s,2}$ = 6.5 Hz, J_{Pt} = 26 Hz, 1 H, H_{3s}), 5.14 (d app t, $J_{2,1a}$ = 12.5 Hz, J_{Pt} = 95 Hz, 1 H, H_2), 4.50 (dd, $J_{1s,1a}$ = 2.5 Hz, J_{Pt} = 20 Hz, 1 H, H_{1s}), 3.20 (d, J_{Pt} = 70 Hz, 1 H, H_{1a}), 3.15 (br s, 6 H, Me_P), 1.22 (d, $J_{Me,3s}$ = 7 Hz, J_{Pt} = 16 Hz, 3 H, Me). (*syn*-16b): ^{1}H NMR (270 MHz, CD_3NO_2) δ 8.64 (d, $J_{P3,4} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.02 (s, 2 H, $H_{P5,6}$), 7.95 (d, 2 H, $H_{P3,8}$), 4.65 (m, 1 H, H_2), 4.59 (dd, $J_{1s,1a}$ = 1.5 Hz, $J_{1s,2}$ = 6.5 Hz, 1 H, H_{1s}), 3.77 (dq, $J_{3a,2}$ = 11.5 Hz, J_{Pt} = 80 Hz, 1 H, H_{3a}), 3.20 (br s, 6 H, Me_P), 3.12 (d, $J_{1a,2}$ = 11.5 Hz, J_{Pt} = 35 Hz, 1 H, H_{1a}), 1.44 (d, $J_{Me,3a}$ = 6.5 Hz, J_{Pt} = 20 Hz, 3 H, Me). Anal. Calcd for $C_{18}H_{19}N_2PtBF_4$: C, 39.65; H, 3.51. Found: C, 39.30; H, 3.39.

(2,9-Dipropynyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]platinum Trifluoroacetate (*anti*-16n). General Procedure D. (*anti*-16n): ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.85 (d, $J_{P4,3} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.17 (s, 2 H, $H_{P5,6}$), 8.09 (d, 2 H, $H_{P3,8}$), 5.62 (app quintet, $J_{3s,2}$ = 6.5 Hz, J_{Pt} = 28 Hz, 1 H, H_{3s}), 5.06 (d app t, $J_{2,1s}$ = 7 Hz, $J_{2,1a}$ = 12 Hz, J_{Pt} = 84 Hz, 1 H, H_2), 4.64 (dd, $J_{1s,1a}$ = 3 Hz, J_{Pt} = 23 Hz, 1 H, H_{1s}), 3.27 (dd, J_{Pt} = 69 Hz, 1 H, H_{1a}), 2.36 (s, 6 H, Me_P), 1.38 (d, $J_{Me,3s}$ = 6.5 Hz, J_{Pt} = 10 Hz, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-hexenyl]platinum Trifluoroacetate (*anti*-17b) and (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-hexenyl]platinum Trifluoroacetate (*syn*-17b). General Procedure D. (*anti*-17b): ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.74 (d, $J_{P4,3} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.06 (s, 2 H, $H_{P5,6}$), 8.02 (d, 2 H, $H_{P3,8}$), 5.34 (ddd, $J_{3s,2}$ = 7 Hz, $J_{3s,4}$ = 4 Hz, $J_{3s,4'}$ = 10.5 Hz, 1 H, H_{3s}), 5.11 (d app t, $J_{2,1s}$ = 7 Hz, $J_{2,1a}$ = 12 Hz, J_{Pt} = 80 Hz, 1 H, H_2), 4.40 (dd, $J_{1s,1a}$ = 2.5 Hz, J_{Pt} = 23 Hz, 1 H, H_{1s}), 3.12 (s, J_{Pt} = 7 Hz, 6 H, Me_P), 3.00 (dd, J_{Pt} = 72 Hz, 1 H, H_{1a}), 1.6–1.1 (m, 4 H, $H_{4,4',5,5'}$), 0.88 (t, $J_{6,5}$ = 7 Hz, 3 H, Me). (*syn*-17b): ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.72 (d, $J_{P4,3} = J_{P7,8}$ = 8.5 Hz, 2 H, $H_{P4,7}$), 8.04 (s, 2 H, $H_{P5,6}$), 8.00 (d, 2 H, $H_{P3,8}$), 4.65–4.45 (m, 2 H, $H_{2,1s}$), 3.65 (d app t, $J_{3s,4}$ = 3 Hz, $J_{3a,4'} = J_{3a,2}$ = 10 Hz, J_{Pt} = 80 Hz, 1 H, H_{3s}), 3.16 (s, 6 H, Me_P), 1.9-1.3 (m, 4 H, $H_{4,4',5,5'}$), 0.96 (t, $J_{6,5}$ = 7 Hz, 3 H, Me).

(59) The spectrum was run on the equilibrium mixture. Many signals and ^{195}Pt satellite peaks were overlapped by those of the major isomer.

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