$(C_5Me_5)La(THF)[CH(SiMe_3)_2]_2$,[38] the following respective values have been reported: 84 (3)°; 76°; 86 (3)°, 85 (3)°; and 81 (5)°, 106 (8)°. In order to prove the γ-agostic interaction Ho···C13 to be sufficiently strong enough to be detected by other analytical methods (especially in solution) and to distinguish it from crystal packing effects, attempts to record ^1H NMR spectra were undertaken. Room-temperature ^1H NMR spectra show 18 equivalent protons for all six methyl groups of the $C(Si(CH_3)_3)_2$ ligand at −199.5 ppm. Four peaks are detected for the eight methyl groups of the two C_5Me_4 rings, while we find only one signal for the two methyl groups bonded to Ge (69.61 ppm). This is clearly a time-averaged spectrum, indicating that the "bond" energy of the γ-agostic Ho···C13 bond is much smaller than at room temperature. Low-temperature ^1H NMR spectra of **9**, recorded in toluene, showed a rapid decrease of the intensity of the peak for the $C(Si(CH_3)_3)_2$ group along with a high-field shift. At about 213 K this particular resonance disappeared. Unfortunately **9** becomes increasingly less soluble in toluene and forms a precipitate as one lowers the temperature to 203 K.

After submission of this paper, Marks et al.[40] reported on the synthesis and structural analysis of some Me_2Si–ring bridged dicyclopentadienyllutetium complexes. The coordination of the π-ligand in $Me_2Si(C_5Me_4)(C_5H_4)LuCH(SiMe_3)_2$ is similar to that in **7** and the overall geometry of the carbyl ligand $CH(Si(CH_3)_3)_2$ compares favorably with that of **9**.

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Supplementary Material Available: Tables of thermal parameters and hydrogen parameters for **5**, **7**, and **9** (6 pages); listings of observed and calculated structure factors for **5**, **7**, and **9** (61 pages). Ordering information is given on any current masthead page.

Convenient Synthesis of Cationic (η^3-Allyl)palladium Complexes. Preparative and Stereochemical Aspects

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The oxidative addition of allylic trifluoroacetates to $Pd(dba)_2$ (dba = dibenzylideneacetone) gives (η^3-allyl)palladium trifluoroacetates in excellent yields. The stereochemistry of the reaction is solvent dependent; i.e., predominant trans addition is observed in a THF/MeCN mixture, whereas cis addition dominates in pure THF. By addition of a neutral ligand the trifluoroacetates can be converted to cationic complexes either directly (giving trifluoroacetate salts) or by in situ ion exchange with tetrafluoroboric acid (giving tetrafluoroborate salts). The syn–anti stereochemistry of the cationic η^3-allyl complexes can be largely controlled by the use of the hindered ligand 2,9-dimethyl-1,10-phenanthroline under the appropriate preparative conditions. Cationic complexes with phenanthroline ligands can also be prepared in good yields by acid-assisted oxidative addition of allylic acetates and alcohols to $Pd(dba)_2$.

Introduction

Methods for selective preparation of (*Z*)-alkenes are of considerable interest in synthetic organic chemistry. We have recently found that a route via cationic (η^3-allyl)palladium complexes may be feasible. This is based on the ability of ligands such as 2,9-disubstituted phenanthrolines to induce an unusual thermodynamic preference for the anti configuration over the syn configuration (Scheme I).[1] Nucleophilic addition to the anti complex can then lead to the desired (*Z*)-alkene.

During our continued studies of the influence of ligands on the syn–anti equilibrium, we felt the need for a simple and general synthesis of cationic (η^3-allyl)palladium complexes. Although alternative routes have sometimes been used,[2] such complexes have been prepared from the corresponding chloride bridged dimers, generally by treatment with metal salts and the appropriate neutral ligands.[3] The chloride-bridged dimers, in turn, have been prepared by

(1) (a) Åkermark, B.; Hansson, S.; Vitagliano, A. *J. Am. Chem. Soc.* **1990**, *112*, 4587. (b) Åkermark, B.; Hansson, S.; Sjögren, M.; Vitagliano, A. Manuscript in preparation.

(2) (a) Johnson, B. F. G.; Lewis, J.; White, D. A. *Synth. Inorg. and Met.-Org. Chem.* **1971**, *1*, 235. (b) Grenouillet, P.; Neibecker, D.; Tkatchenko, J. *Inorg. Chem.* **1980**, *19*, 3189. (c) Mabbott, D. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1976**, 2156.

(3) (a) Powell, J.; Shaw, B. *J. Chem. Soc. A* **1968**, 774. (b) Paiaro, G.; Musco, A. *Tetrahedron Lett.* **1965**, 1583. (c) Deeming, A. J.; Rothwell, I. P. *Inorg. Chim. Acta* **1978**, *31*, 271. (d) Zakharova, I. A.; Gaft, Yu. L.; Kuznetsov, N. T.; Salvyn, Ya. V.; Leites, L. A.; Kurbakova, A. P.; Kagansky, M. M. *Ibid.* **1981**, *47*, 181. (e) Crociani, B.; Boschi, T.; Uguagliati, P. *Ibid.* **1981**, *48*, 9. (f) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 670.

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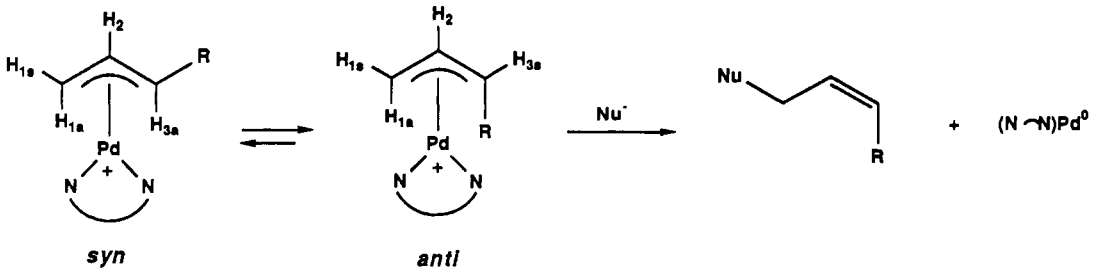
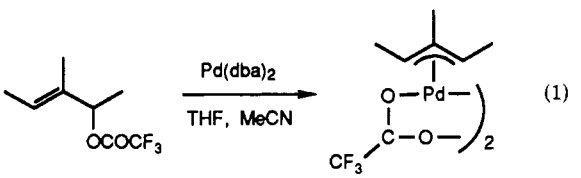
Scheme I



a number of different routes, starting from alkenes, dienes, allyl chlorides, and other allyl derivatives.[4] In the two latter cases, the reactions proceed via oxidative addition of the allyl substrate to a palladium(0) species.[4,5] This is also a crucial step in palladium-catalyzed allylic substitution, where allyl acetates are most commonly used.[5] For the preparation of isolated cationic η^3-allyl complexes, allyl trifluoroacetates should be more suitable substrates, since trifluoroacetate is less strongly coordinating than acetate and is also a superior leaving group. (η^3-Allyl)palladium trifluoroacetates have been prepared earlier,[6] but it appeared to us that a route via oxidative addition of allyl trifluoroacetates to $Pd(dba)_2$[7] should be more convenient than previous methods.

Results and Discussion

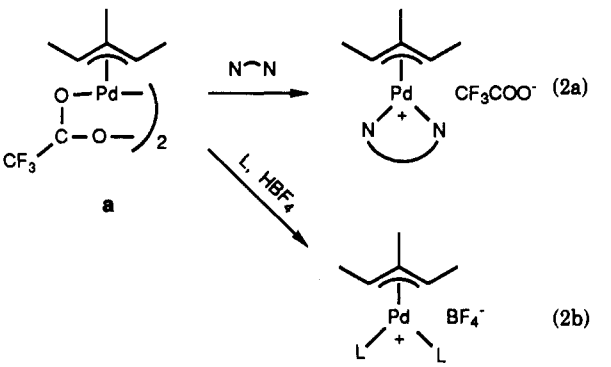
Oxidative Addition of Allyl Trifluoroacetates to $Pd(dba)_2$. Allyl trifluoroacetates were found to react smoothly with $Pd(dba)_2$ at room temperature to yield bridged trifluoroacetate complexes (eq 1). Evaporation



(1)

of the solvent, followed by extraction with water/CH_3CN (10:1) and renewed evaporation of the solvent, gave excellent yields of essentially pure (η^3-allyl)palladium trifluoroacetates (Chart I). The reaction rate was strongly dependent on the coordinating ability and/or the polarity of the solvent according to the following qualitative scale: THF/CH_3CN (4:1) > toluene/CH_3CN (4:1) > THF > toluene/acetone (4:1) > $CHCl_3$ > toluene. At the two extreme points of the scale almost quantitative yields were obtained in THF/CH_3CN solution within minutes, whereas a very sluggish reaction took place in toluene giving considerably lower yields even after 24 h.

When prepared as described above, the allylpalladium trifluoroacetates are fairly stable and most of them can be handled in air at room temperature and kept in solution (both in organic solvents and water) for days without appreciable decomposition. The complexes can be converted to cationic species simply by addition of the desired bidentate ligand (eq 2). If the ligand does not bind strongly



enough to displace the trifluoroacetate ion quantitatively (e.g. L = pyridine, cyclooctadiene, acetonitrile), the reaction may be performed with simultaneous addition of a stoichiometric amount of fluoboric acid etherate. The trifluoroacetate anion is protonated and completely exchanged for fluoroborate, and the required cationic complexes are obtained as tetrafluoroborate salts (eq 2b). This procedure is also recommended with phosphine and phosphite ligands, which yield trifluoroacetate complexes that are rapidly decomposed. In contrast, the corresponding tetrafluoroborate complexes are perfectly stable.

Stereochemistry of the Oxidative Addition. It has recently been shown that the stereochemistry of the oxidative addition of an allyl chloride to $Pd(dba)_2$ can be controlled by the choice of solvent. Trans addition was observed in a coordinating solvent such as acetonitrile or dimethyl sulfoxide, while the unusual cis addition dominated in solvents such as benzene or THF.[8] We have observed similar effects in the addition of the trifluoroacetate **16**. When compound **16** (ca. 90% isomeric purity) was reacted with $Pd(dba)_2$ in 1:2 mixture of acetonitrile and THF, one dominant product (85%) was obtained (**17a-c**) that was converted without prior isolation to the cis isomer **17c-c** by the in situ reaction with phenanthroline. Conversely, when the same reaction was performed in pure THF, the major final product was the trans isomer **17c-t**.

The ^1H NMR spectra (400 MHz) of **17c-c** and **17c-t** were completely assigned (see Experimental Section) and are consistent with the proposed structures. The assignment of the cis structure **17c-c** in a predominant pseudoboat conformation is supported by two independent pieces of evidence. First, the value of the J_{34} coupling constant (5 Hz) is as expected for an equatorial H_4 proton in such a conformation.[9] An axial H_4 proton in the same confor-

(4) For a recent review, see: (a) Maitlis, P. M.; Espinet, P.; Russel, M. J. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 6, p 385. (b) Åkermark, B.; Bäckvall, J. E.; Zetterberg, K. in *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; Verlag Chemie, in press.

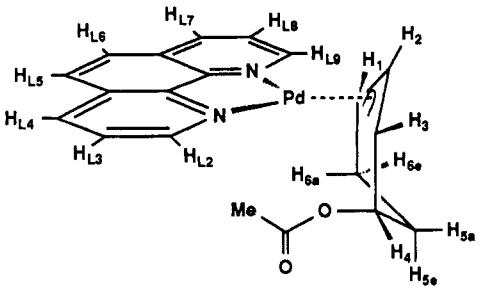
(5) For a recent review, see: Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 8, p 799.

(6) (a) Hughes, R. P.; Jack, T.; Powell, J. *J. Organomet. Chem.* **1973**, *63*, 451. (b) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (c) Trost, B.; Metzner, P. J. *Ibid.* **1980**, *102*, 3572.

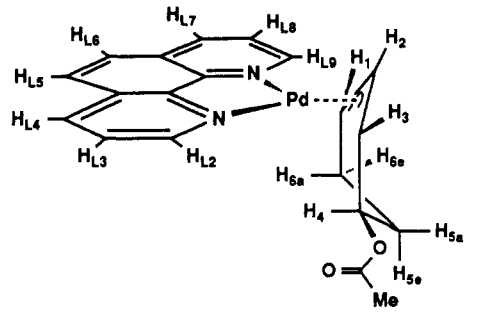
(7) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 135.

(8) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Masa-aki, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.

(9) Söderberg, B.; Åkermark, B.; Chen, Y.; Hall, S. S. *J. Org. Chem.* **1990**, *55*, 1344.



17c-c



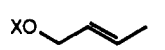
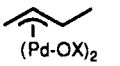
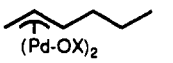
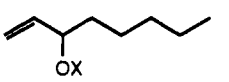
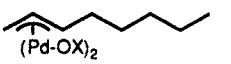
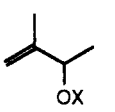
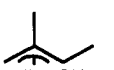
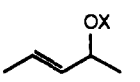
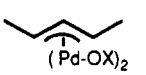
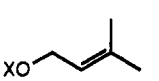
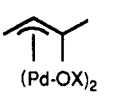
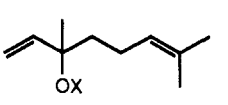
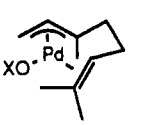
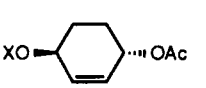
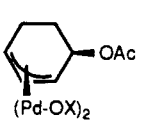
17c-t

mation would be expected to display a small J_{34} coupling constant of 1–2 Hz,[9] as is indeed observed for the isomer **17c**-t (J_{34} = 0.8 Hz), while in a pseudochair conformation both axial and equatorial H_4 protons would be expected to display a J_{34} coupling constant of 3.5 Hz.[10] Second, a substantial upfield shift of the acetate methyl group is observed in **17c**-c (1.57 ppm vs 2.29 ppm in **17c**-t), which is consistent with the methyl group being affected by the shielding of the phenanthroline aromatic electrons in **17c**-c but *not* in **17c**-t. Inspection of molecular models clearly indicates that only in the case of a cis stereochemistry the methyl group has the geometrical possibility of spending part of the time below one of the rings of the planar aromatic ligand and, thus, experiencing shielding.

The assignments by NMR spectroscopy are supported by chemical evidence. Both products **17c**-c and **17c**-t could also by obtained by alternative conditions that are expected to promote the "normal" trans addition:[11] Thus, trans **17c**-t was also prepared by reacting *cis*-1-acetoxy-4-chlorocyclohex-2-ene with $Pd(dba)_2$ in the presence of phenanthroline and silver trifluoroacetate. Similarly, the cis isomer **17c**-c could also be prepared from the *trans*-diacetate **23** in the presence of phenanthroline and trifluoroacetic acid (see below). It is finally interesting to note that the reaction was much slower (ca. 20 times) under the conditions favoring the cis addition, i.e. in absence of acetonitrile, suggesting that the main effect of the polar coordinating solvent is to stabilize the transition state of the trans addition in which charge separation is necessarily involved.

Use of the 2,9-Dimethyl-1,10-phenanthroline Ligand To Control the Syn and Anti Stereochemistry. We have recently shown[1a] that 2,9-dimethyl-1,10-phenanthroline (and other 2,9-disubstituted phenanthrolines[1b]) is a particularly interesting ligand in η^3-allylpalladium chemistry, since it stabilizes the uncommon anti configuration. It is also comparable to phosphines in activating the complexes toward nucleophilic addition, thus opening the possibility of controlling the *E*–*Z* stereochemistry in palladium-promoted allylic substitutions.[1a] When 2,9-disubstituted phenanthrolines were used as ligands, the syn–anti isomerization of terminally monosubstituted allylic groups turned out to be far slower than with other common ligands such as phosphines or even unsubstituted phenanthroline. Moreover, the syn–anti isomerization rate of the complexes (as trifluoroacetate

Chart I. Oxidative Addition of Allylic Trifluoroacetates to $Pd(dba)_2$[a]

Substrate	Product	Yield %
 **1**	 **2a**	92
 **3**	 **4a**	93
 **5**	**4a**	91
 **6**	 **7a**	90
 **8**	 **9a**	90
 **10**	 **11a**	92
 **12**	 **13a**	90
 **14**	 **15a**	89
 **16**	 **17a**	85[b]

[a] X = CF_3CO. Reaction conditions: 30 min, 25 °C, 4:1 THF/MeCN, 0.1 mmol/mL. [b] Yield based on the phenanthroline derivative.

(10) Åkermark, B.; Söderberg, B.; Hall, S. S. *J. Org. Chem.* **1989**, *54*, 1110.

(11) (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. (b) Bäckvall, J. E. *Pure Appl. Chem.* **1983**, *55*, 1669.

salts) was found to be strongly dependent on the solvent, in the qualitative order: toluene > THF ≫ $CHCl_3$ ≫ H_2O.[12] As a consequence, it is possible to prepare the complexes with defined syn or anti stereochemistry[13] irrespective of the configuration of the starting trifluoroacetate by a simple and rational change in the preparative procedure. This is illustrated by the following points:

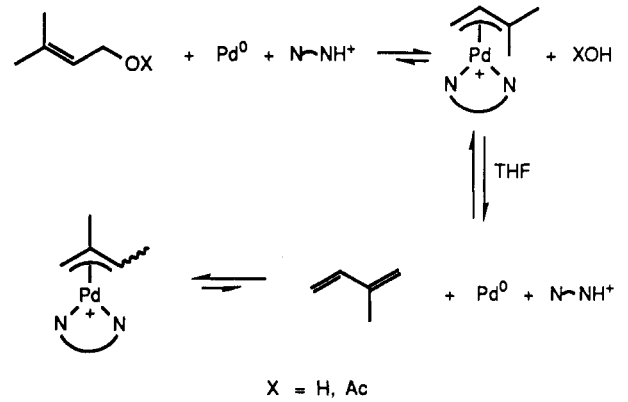
(i) Two-Step Preparation of Syn Complexes. The bridged trifluoroacetate complexes prepared as described above (Chart I, eq 1) are predominantly to exclusively the syn isomers. When the 2,9-dimethyl-10-phenanthroline ligand was added (eq 2) to an aqueous solution (slow isomerization) of the η^3-allyl trifluoroacetates, high yields of the cationic syn complexes were obtained in better than 95% isomeric purity. Thus, in the overall process reaction 1 proceeds with thermodynamic control and reaction 2 with kinetic control.

(ii) Two-Step Preparation of Anti Complexes. When the bridged trifluoroacetate complexes were reacted with the 2,9-dimethylphenanthroline ligand in toluene (fast isomerization), the anti complexes were rapidly formed in a fast equilibrium reaction. During the subsequent crystallization, the anti complexes were enriched further[14] and were finally obtained in better than 90% yields with an isomeric purity of ca. 90%. In this sequence, both reactions 1 and 2 proceed under thermodynamic control.

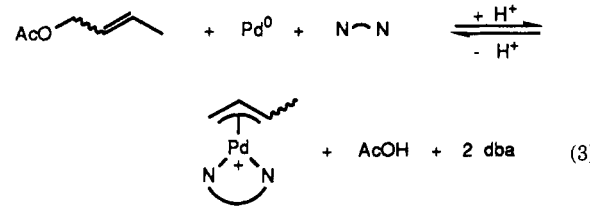
(iii) Single-Step Preparation of either Syn or Anti Complexes with Retention of Configuration of the Alkene. If, finally, the oxidative addition of the allyl trifluoroacetate to $Pd(dba)_2$ is performed in a two-phase system of toluene/water and in presence of 2,9-dimethylphenanthroline, the primary product formed in the toluene phase is extracted into the aqueous phase before it has time to isomerize. As a result, the geometry of the η^3-allyl complex is determined by the geometry of the starting allyl trifluoroacetate. By this procedure, *E* substrates gave syn complexes and *Z* substrates gave anti complexes in ca. 95% isomeric purity. Thus, the reaction proceeds completely under kinetic control.

Oxidative Addition of Allyl Acetates. The successful reaction using trifluoroacetates led us to reexamine the use of other substrates, i.e. acetates and alcohols. It has earlier been observed that stable η^3-allyl complexes are formed only from allyl acetates and palladium(0) in presence of sterically hindered phosphines.[15] It occurred to us that this could be due to the process being an equilibrium, which is controlled by the relative stabilities of the starting Pd(0) species and the final palladium(II) allyl complex. In fact, we were able to prove this in the following NMR experiment: To a solution of (*E*)-crotyl acetate in $CDCl_3$ in a NMR tube was added a solution of $Pd(dba)_2$ and 1 equiv of 2,9-dimethyl-1,10-phenanthroline. During the first few minutes, the characteristic signals of the η^3-allyl complex appeared in the ^1H NMR spectrum. However, unlike the reaction with crotyl trifluoroacetate, an equilibrium

Scheme II



was rapidly reached with the Pd(0) complex being the dominant species. Concurrently, the crotyl acetate was isomerized, perhaps via the η^3-allyl complex, to a mixture of (*E*)-crotyl acetate, (*Z*)-crotyl acetate, and 1-buten-3-yl acetate (eq 3).



(3)

In principle, by protonation of the acetate ions it should be possible to drive the equilibrium toward the η^3-allyl complex. However, the reaction of crotyl acetate with $Pd(dba)_2$ in the presence of 1 equiv of trifluoroacetic acid in either THF/CH_3CN or CH_2Cl_2/CH_3CN led only to the precipitation of metallic palladium. In order to reduce the acidity and also add a stabilizing ligand, we performed the reaction in the presence of 1 equiv of trifluoroacetic acid and slightly more than 1 equiv of 2,9-dimethyl-1,10-phenanthroline. Under these conditions, complex **2b** was formed in ca. 90% yield. The procedure appears to be general for pyridine type ligands (Chart II).

Stereochemically, the oxidative addition is a trans process, as shown by the fact that the *trans*-diacetate **23** yields the *cis*-η^3-allyl complex **17c**-c.

A particularly interesting extension of this methodology is the preparation of the 1-acetoxyallyl complexes **20c** and **22c** from the allylic 1,1-diacetates **19** and **21**. A few complexes of this type have been prepared before, but they represent special cases or have been prepared through more complex routes.[16] The 1-acetoxyallyl complexes should be useful synthetic intermediates, since they are the equivalent of a homoenolate.

Oxidative Addition of Allyl Alcohols. The reaction between allylic alcohols and $Pd(dba)_2$ also proceeded smoothly in the presence of 1 equiv of trifluoroacetic acid and ca. 1.1 equiv of a nitrogen bidentate ligand to give high yields of cationic complexes (Chart II). When trifluoroacetic acid was replaced by tetrafluoroboric acid etherate, even ligands such as triphenyl phosphine and triphenylphosphite could be used. Although alcohols have been used before,[4] the present method appears advantageous in terms of high yields and simplicity.

During the studies of η^3-allyl complex formation from alcohols and acetates in the presence of acid, we observed

(12) The factors affecting the syn:anti equilibrium ratio and the interconversion rate will be discussed in detail in a separate paper.[1b]

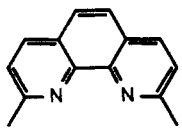
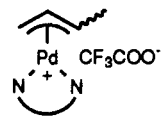
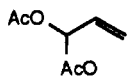
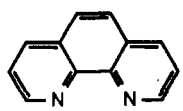
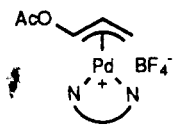
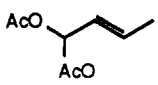
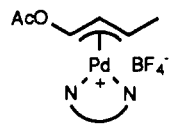
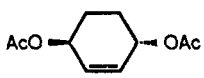
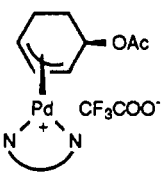
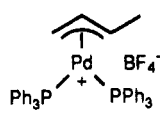
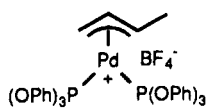
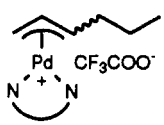
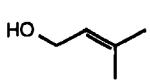
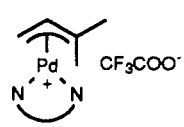
(13) The assignment of the syn or anti stereochemistry was made on the basis of the coupling constants between the η^3-allyl H_2 and H_3 protons (see Scheme I). The syn structure was assigned to the isomer displaying the large trans $^3J_{23}$ coupling constant (≈12 Hz) and the anti structure was assigned to the isomer displaying the small cis $^3J_{23}$ coupling constant (≈7 Hz), in agreement with literature.[4] The chemical shift of the H_3 proton is also of diagnostic value in the assignment of the stereochemistry, since it is found at lower field by ca. 1 ppm in the anti isomer than in the syn isomer.[4]

(14) The anti:syn equilibrium ratio for dimethylphenanthroline complexes of terminally monosubstituted allylic groups is about 7:3.[1a]

(15) (a) Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. (b) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

(16) (a) Sonoda, A.; Mann, B. E.; Maitlis, P. *J. Organomet. Chem.* **1975**, *96*, C16. (b) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890.

Chart II. Acid and Ligand-Assisted Oxidative Addition of Allylic Acetates and Alcohols to $Pd(dba)_2$[a]

Substrate	Ligand (N⌒N or L)	Product	Yield %
 **18**	 **b**	 **2b**	90
 **19**	 **c**	 **20c**	76[b]
 **21**	**c**	 **22c**	75[b]
 **23**	**c**	 **17c-c**	80
 **24**	**b**	**2b**	
24	PPh_3 **d**	 **2d**	82[c]
24	$P(OPh)_3$ **e**	 **2e**	80[c]
 **25**	**b**	 **4b**	86
 **26**	**b**	 **13b**	68

[a] Reaction conditions: 0.5–1 h, 25 °C, CH_2Cl_2 or THF, 0.05 mmol/mL, 1 equiv of CF_3COOH. [b] Trifluoroacetate ion exchanged for tetrafluoroborate prior to isolation. [c] HBF_4:Et_2O used instead of CF_3COOH.

a side reaction that may in fact be used to broaden the scope of the procedure. This is illustrated by the reactions of 3-methylbut-2-enol (**26**) that in dichloromethane solution gave a good yield of the expected product **13b**. This is also true for short reaction times in THF; however, if the reaction was allowed to proceed for 48 h, the isomeric complex **9b** was obtained, again in good yield. This reaction, which could be monitored by ^1H NMR spectroscopy in THF-d_8 solution, first gives the expected complex **13b** in a fast and reversible oxidative addition that is driven to completion by the added acid. In a second, reversible step isoprene is formed and then more slowly, in an essentially irreversible step, the isomeric 1,2-dimethylallyl complex **9b** (Scheme II). If the reaction is started with

the allyl acetate or even isoprene in place of the allyl alcohol, a similar result is obtained.

Conclusions

The oxidative addition of allyl trifluoroacetates to Pd(dba)$_2$ is a simple, selective, and essentially quantitative route to (η^3-allyl)palladium trifluoroacetates. It is anticipated that other good leaving groups such as sulfonates will work equally well. Moreover, the stereochemistry of the oxidative addition may be largely controlled by simple variation of the solvent.

The trifluoroacetate-bridged complexes are useful starting materials for the preparation of a large selection of cationic complexes, since only mixing with the stoichoimetric amount of the appropriate neutral ligand is required. If a less coordinating anion is required, anion exchange with tetrafluoroborate is very facile due to the possibility of protonating the trifluoroacetate ion and to the much lower solubility of the tetrafluoroborate salts in both water and organic solvents.

The possibility to use also alcohols and acetates after a minor modification makes the reaction a useful complement to other procedures that have been described earlier.[4] This is especially true for the direct preparation of trifluoroacetates from alkenes, which tends to give aromatic compounds when applied to substrates such as cyclohexene.[6c] For these systems, the use of allyl acetates is especially attractive, since they may be prepared by catalytic acetoxylation of cycloalkenes.[17]

Finally, the use of 2,9-disubstituted phenanthrolines as ligands in the present procedure provides a unique and simple method for the preparation of terminally substituted (η^3-allyl)palladium complexes with controlled syn or anti stereochemistry.

Experimental Section

NMR spectra were recorded on Bruker AM 400 and/or Ac 250 spectrometers. For spectra run in D_2O, sodium 3-trimethylsilylpropanesulfonate was used as the internal standard. Conventional decoupling techniques were used whenever necessary for the assignment of signals. In the reporting of ^{1}H NMR signal multiplicity, fine structure (J < 1.5 Hz) is neglected unless specified.

Materials. Tetrahydrofuran (THF) and diethyl ether were dried and distilled prior to use; other solvents were of HPLC grade and were used without further purification. Allylic alcohols were commercial compounds. Allylic trifluoroacetates **1**, **3**, **5**, **6**, **8**, **10**, **12**, and **14** were prepared by reaction of the corresponding alcohols with trifluoroacetic anhydride. **16**[18] and **23**[19] were kindly donated by Dr. S. Byström. **19** and **21** were commercial compounds. Pd(dba)$_2$ was prepared according to a published procedure.[7] All reactions involving Pd(dba)$_2$ were performed under nitrogen, while successive manipulations of the η^3-allyl complexes were performed in air.

General Procedure for the Oxidative Addition of Allylic Trifluoroacetates to Pd(dba)$_2$. Synthesis of Bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-hexenyl]dipalladium(II) (4a). A 1.15-g (2.0-mmol) sample of Pd(dba)$_2$ was dissolved in 16 mL of anhydrous THF, and 4 mL of acetonitrile was added, together with 440 mg (2.2 mmol) of (*E*)-2-hexenyl trifluoroacetate. The mixture was stirred at room temperature until the deep purple color disappeared (15–30 min), leaving a grayish green solution containing some small amount of palladium metal. After evaporation of the solvent, the residue was extracted with a 10% solution of acetonitrile in water (4 × 5 mL), and the filtered aqueous extract was evaporated in vacuo, giving 560 mg (92% yield) of the required complex as a pale yellow microcrystalline solid. The product was pure enough to be used as such in further reactions. The analytical sample was recrystallized from diethyl ether/pentane. This compound has been reported earlier.[6b]

^{1}H NMR ($CDCl_3$): δ 5.37 (br, 1 H, H_2), 3.88 (br m, 2 H, H_{1s} and H_{3a}), 2.85 (br d, 1 H, H_{1a}), 1.4–1.7 (br m, 4 H, CH_2CH_2), 0.95 (t, 3 H, Me). Anal. Calcd for $C_8H_{11}F_3O_2Pd$: C, 31.75; H, 3.66. Found: C, 31.91; H, 3.55. The signals in the ^{1}H NMR spectrum of **4a** and of the other dimers are probably broadened by the fluxionality between different stereoisomers arising from the dimeric structure. This has been observed and investigated in detail for analogous acetato complexes.[20]

Bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-butenyl]dipalladium(II) (2a). ^{1}H NMR ($CDCl_3$): δ 5.38 (br m, 1 H, H_2), 3.95 (m, 1 H, H_{3a}), 3.90 (d, 1 H, H_{1s}), 2.86 (d, 1 H, H_{1a}), 1.19 (d, 3 H, Me). Anal. Calcd for $C_6H_7F_3O_2Pd$: C, 26.25; H, 2.57. Found: C, 26.40; H, 2.49.

Bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-octenyl]dipalladium(II) (7a). ^{1}H NMR ($CDCl_3$): δ 5.36 (br m, 1 H, H_2), 3.90 (br d, 1 H, H_{1s}), 3.85 (br, 1 H, H_{3a}), 2.85 (br d, 1 H, H_{1a}), 1.4–1.6 (br m, 4 H), 1.2–1.4 (br m, 4 H), 0.90 (br t, 3 H, Me). Anal. Calcd for $C_{10}H_{15}F_3O_2Pd$: C, 36.33; H, 4.57. Found: C, 36.49; H, 4.51.

Bis(μ-trifluoroacetato)bis[(1,2,3-η)-2-methyl-2-butenyl]dipalladium(II) (9a). ^{1}H NMR ($CDCl_3$): δ 3.82 (br, 1 H, H_{1s}), 3.72 (br, 1 H, H_{3a}), 2.67 (br, 1 H, H_{1a}), 2.20 (s, 3 H, Me), 1.11 (br d, 3 H, Me). Anal. Calcd for $C_7H_9F_3O_2Pd$: C, 29.14; H, 3.14. Found: C, 29.28; H, 3.06.

Bis(μ-trifluoroacetato)bis[(2,3,4-η)-3-pentenyl]dipalladium(II) (11a). ^{1}H NMR ($CDCl_3$): δ 5.25 (br, 1 H, H_2), 3.72 (br, 2 H, H_1 and H_3), 1.17 (d, 6 H, 2 Me). This compound has been reported earlier.[20]

Bis(μ-trifluoroacetato)bis[(1,2,3-η)-3-methyl-2-butenyl]dipalladium(II) (13a). The ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) consists of two separate sets of signals of about 5:4 intensity. As in the case of the analogous acetato complexes,[20] they are most probably due to stereoisomers arising from the dimeric structure. The subspectrum from the major species is given first: δ 5.08 (dd, 1 H, H_2), 3.80 (d, 1 H, H_{1s}), 3.20 (d, 1 H, H_{1a}), 1.25 (s, Me), 1.21 (s, Me); δ 5.20 (br dd, 1 H, H_2), 3.85 (br, 1 H, H_{1s}), 3.15 (br d, 1 H, H_{1a}), 1.28 (s, Me), 1.23 (s, Me). Anal. Calcd for $C_7H_9F_3O_2Pd$: C, 29.14; H, 3.14. Found: C, 29.32; H, 3.09.

(Trifluoroacetato)(η^5-geranyl)palladium(II) (15a). ^{1}H NMR ($CDCl_3$): δ 5.84 (dd, 1 H, H_2), 5.60 (dd, 1 H, CH=CMe_2), 4.20 (d, 1 H, H_{1s}), 3.59 (d, 1 H, H_{1a}), 3.1 (m, 1 H), 2.5 (m, 2 H), 2.0–2.1 (m, 1 H), 2.04 (s, 3 H, Me), 1.68 (s, 3 H, Me), 1.40 (s, 3 H, Me). The monomeric chelate η^5 structure with the geranyl stereochemistry (i.e. having the side chain in syn position) was assigned to **15a** on the basis of the close resemblance of its NMR spectrum with that of the analogous geranyl complex,[21] which was characterized by X-ray crystallography.[22] An open-chain trifluoroacetato-bridged dimeric complex would be expected to give rise to both the geranyl and neryl isomers in about equal amounts.[21] Intramolecular double-bond coordination in related allylic trifluoroacetates has been reported.[6a]

Cationic Complexes from (η^3-Allyl)palladium(II) Trifluoroacetates. The following procedure (A) is general for complexes with nitrogen bidentate ligands, which give stable trifluoroacetate salts.

Preparation of (2,9-Dimethyl-1,10-phenanthroline)[(1,2,3-η)-3-methyl-2-butenyl]palladium(II) Trifluoroacetate (13b). A 144-mg (0.5-mmol) sample of the trifluoroacetato complex **13a** was dissolved in diethyl ether (4 mL), and 110 mg (0.52 mmol) of 2,9-dimethyl-1,10-phenanthroline dissolved in the minimum amount of diethyl ether was added. A yellow precipitate was immediately formed, which was filtered out, washed with diethyl ether, and dried, resulting in 236 mg (95% yield) of the

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required complex. The ionic nature of the compound was established by a conductivity measurement in methylene chloride, the molar conductivity being 53 Ω^{-1} mol^{-1} cm^2, $C = 10^{-3}$ M (the analogous tetrafluoroborate salt obtained through procedure B displays a molar conductivity of 55 Ω^{-1} mol^{-1} cm^2).

^{1}H NMR (D_2O):[23] δ 8.05 (d, 2 H), 7.62 (d, 2 H), 7.36 (s, 2 H), 5.38 (dd, 1 H, H_2), 4.16 (d, 1 H, H_{1s}), 3.48 (d, 1 H, H_{1a}), 2.88 (s, 6 H, 2 Me), 1.64 (s, 3 H, Me), 1.44 (s, 3 H, Me). Anal. Calcd for $C_{21}H_{21}F_3N_2O_2Pd$: C, 50.77; H, 4.26. Found: C, 50.68; H, 4.13.

The following procedure (B) is general for preparing tetrafluoroborate salts.

Preparation of Bis(ligand)[(1,2,3-η)-3-methyl-2-butenyl]palladium(II) Tetrafluoroborate (Ligand = Acetonitrile, Pyridine, Cyclooctadiene, Triphenylphosphine, Triphenyl Phosphite). A 144-mg (0.5 mmol of Pd) sample of the trifluoroacetato complex **13a** was dissolved in diethyl ether (4 mL), and 0.50 mL of the etherate of tetrafluoroboric acid (1.0 M solution in 25:1 diethyl ether/methanol) was added, immediately followed by the stoichiometric amount of the appropriate ligand (an excess in the case of acetonitrile). A colorless precipitate rapidly formed, and the suspension was evaporated to dryness. The residue was washed with diethyl ether, collected on a filter, and dried, giving the required crude complex in about 90% yield. The complexes were characterized by comparison with authentic samples obtained in previous work.[3f]

Stereochemistry of the Oxidative Addition: Reaction of 16 with Pd(dba)$_2$. A 287-mg (0.5-mmol) sample of Pd(dba)$_2$ was dissolved in 4 mL of anhydrous THF, and 2 mL of acetonitrile was added, immediately followed by 140 mg (0.55 mmol) of *trans*-1-acetoxy-4-trifluoroacetoxy-cyclohex-2-ene (**16**) (isomeric purity 90%). The mixture, initially containing some precipitated Pd(dba)$_2$, was stirred for 20 min at room temperature. The resulting grayish green solution, darkened by some small amount of palladium metal, was evaporated to dryness, and the residue was extracted with water containing 10% acetonitrile (4 × 2 mL). To the yellow aqueous solution was added 90 mg (0.5 mmol) of 1,10-phenanthroline, and the mixture evaporated to dryness, giving 232 mg of crude product **17c** (85% yield). The ^{1}H NMR analysis of the crude product indicated the presence of two isomers **17c**-c and **17c**-t in about 85:15 ratio, together with some minor unidentified inpurities. The most abundant isomer **17c**-c could be obtained essentially pure by two recrystallizations from methylene chloride/diethyl ether (colorless hygroscopic needles). Performing the reaction in the absence of acetonitrile (6 mL of anhydrous THF, reaction time 6 h) and following the same procedure enabled isolation of a crude mixture containing **17c**-c and **17c**-t in about 10:90 ratio in 84% yield.

17c-c. ^{1}H NMR (D_2O): δ 8.95 (dd, 1 H, H_{L2} or H_{L9}, J_{ortho} = 5.5 Hz, J_{meta} = 1.6 Hz), 8.83 (dd, 1 H, H_{L9} or H_{L2}), 8.60 (dd, 1 H, H_{L4} or H_{L7}, J_{ortho} = 8.2 Hz, J_{meta} = 1.6 Hz), 8.55 (dd, 1 H, H_{L7} or H_{L4}), 7.92 (dd, 1 H, H_{L3} or H_{L8}), 7.88 (dd, 1 H, H_{L8} or H_{L3}), 7.85 (AB q, 2 H, H_{L5} and H_{L6}, J_{AB} = 9 Hz), 6.26 (app t, 1 H, H_2, $J_{21} = J_{23}$ 6.8 Hz), 5.65 (dd app, t, 1 H, HJ_{12} = 6.8 Hz, J_{13} = 1.2 Hz, J_{16a} = 2 Hz, J_{16e} = 5.5 Hz), 5.45 (ddd, 1 H, H_3, J_{31} = 1.2 Hz, J_{32} = 6.8 Hz, J_{34} = 5 Hz), 5.07 (app q, 1 H, H_4, $J_{43} = J_{45a}$ = 5.0 Hz, J_{45e} = 4.5 Hz), 2.18 (d app q, 1 H, H_{6e}, $J_{6e1} = J_{6e5a} = J_{6e6e}$ = 5.5 Hz, J_{6e6a} = 18 Hz), 2.01 (dddd, 1 H, H_{6a}, J_{6a1} = 2 Hz, J_{6a5e} = 6 Hz, J_{6a5a} = 9 Hz, J_{6a6e} = 18 Hz), 1.75 (m, 1 H, H_{5e}, J_{5e4} = 4.5 Hz, J_{5e5a} = 14.5 Hz, J_{5e6a} = 6 Hz, J_{5e6e} = 5.5 Hz), 1.58 (m, 1 H, H_{5a}, J_{5a4} = 5.0 Hz, J_{5a5e} = 14.5 Hz, J_{5a6e} = 5.5 Hz, J_{5a6a} = 9 Hz), 1.57 (s, 3 H, Me). ^{13}C NMR (D_2O): δ 176.2 (MeCOO), 165.6 (q, CF_3COO^-, J_{CF} = 35 Hz), 156.5, 156.0 (C_{L2}, C_{L9}), 146.8, 146.7 (C_{L11}, C_{L12}), 142.5, 142.2 (C_{L4}, C_{L7}), 132.2 (C_{L13}, C_{L14}), 130.03, 130.00 (C_{L5}, C_{L6}), 129.1, 128.7 (C_{L3}, C_{L8}), 119.3 (q, CF_3, J_{CF} = 290 Hz), 113.5 (C_2), 83.5 (C_1), 75.4 (C_3), 74.9 (C_4), 28.8 (C_5), 28.2 (C_6), 21.1 (Me). Anal. Calcd for $C_{22}H_{19}F_3N_2O_4$: C, 49.04; H, 3.55. Found: C, 46.49; H, 3.77. The inconsistence of the formula with the analytical result can be explained by the product being hygroscopic (Calcd for $C_{22}H_{19}F_3N_2O_4 \cdot 1.5H_2O$: C, 46.70; H, 3.92.

17c-t. ^{1}H NMR (D_2O): δ 8.86 (d, 2 H, H_{L2} and H_{L9}, J_{ortho} = 5 Hz), 8.40 (d, 1 H, H_{L4} or H_{L7}, J_{ortho} = 8 Hz), 8.35 (d, 1 H, H_{L7} or H_{L4}), 7.80 (dd, 1 H, H_{L3} or H_{L8}), 7.76 (dd, 1 H, H_{L8} or H_{L3}), 7.61 (AB q, 2 H, H_{L5} and H_{L6}, J_{AB} = 8.6 Hz), 6.06 (app t, 1 H, H_2, $J_{21} = J_{23}$ = 6.5 Hz), 5.68 (app br t, 1 H, H_1, J_{12} = 6.5 Hz, J_{16a} = 1 Hz, J_{16e} = 6 Hz), 5.23 (app d, 1 H, H_3, $J_{31} = J_{34} \leq 1$ Hz, J_{32} = 6.5 Hz), 4.99 (app dd, 1 H, H_4, $J_{43} \leq 1$ Hz, J_{45e} = 6 Hz, J_{45a} = 9.5 Hz), 2.41 (dd app t, 1 H, H_{6e}, $J_{6e1} = J_{6e5a}$ = 6 Hz, J_{6e5e} = 3.2 Hz, J_{6e6a} = 18 Hz), 2.29 (s, 3 H, Me), 1.94 (dd app t, 1 H, H_{5e}, $J_{5e4} = J_{5e6a}$ = 6 Hz, J_{5e6e} = 3.2 Hz, J_{5e5a} = 12.6 Hz), 1.71 (app ddd, 1 H, H_{6a}, J_{6a1} = 1 Hz, J_{6a5e} = 6 Hz, J_{6a5a} = 11 Hz, J_{6a6e} = 18 Hz), 1.29 (m, 1 H, H_{5a}, J_{5a4} = 9.5 Hz, J_{5a5e} = 12.6 Hz, J_{5a6e} = 6 Hz, J_{5a6a} = 11 Hz). ^{13}C NMR (D_2O): δ 176.8 (MeCOO), 165.6 (q, CF_3COO^-, J_{CF} = 35 Hz), 156.3, 155.9 (C_{L2}, C_{L9}), 146.1, 145.9 (C_{L11}, C_{L12}), 142.0, 141.9 (C_{L4}, C_{L7}), 131.6, 131.5 (C_{L13}, C_{L14}), 129.8, 129.7 (C_{L5}, C_{L6}), 128.9, 128.7 (C_{L3}, C_{L8}), 119.3 (q, CF_3, J_{CF} = 290 Hz), 111.1 (C_2), 84.1 (C_1), 76.7 (C_3), 74.6 (C_4), 27.2 (C_5), 26.2 (C_6), 23.4 (Me).

Preparation of Syn Complexes. Synthesis of (2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-hexenyl]palladium(II) Trifluoroacetate (4b-*syn*). A 151-mg (0.5-mmol) sample of the trifluoroacetato complex **4a** was dissolved in 2 mL of methanol, and 115 mg (0.55 mmol) of 2,9-dimethyl-1,10-phenanthroline was added at 0 °C. The mixture was stirred for 5 min, and then the solvent was evaporated in vacuo at 0 °C. The residue was washed with diethyl ether (2 × 4 mL) and dried, giving 230 mg (90% yield) of the required complex in 93% isomeric purity. The corresponding tetrafluoroborate salt could be obtained in a better isomeric purity (>98%) by using the following procedure: 151 mg (0.5 mmol) of **4a** and 115 mg (0.55 mmol) of 2,9-dimethyl-1,10-phenanthroline were suspended in 8 mL of water, and the mixture was stirred until all the solid was dissolved, giving a yellow solution (5–10 min). An 80-mg (0.7-mmol) amount of $NaBF_4$ dissolved in 2 mL of water was added with stirring, and a pale yellow flocculent precipitate formed, which was filtered out and dried, giving 220 mg (91% yield) of the required compound.

^{1}H NMR (trifluoroacetate salt in D_2O):[23] δ 8.04 (d, 2 H), 7.65 (d, 2 H), 7.33 (s, 2 H), 5.53 (d app t, 1 H, H_2, $J_{21a} = J_{23a}$ = 12 Hz, J_{21s} = 7 Hz), 4.70 (d, 1 H, H_{1s}), 4.49 (ddd, 1 H, H_{3a}), 3.54 (d, 1 H, H_{1a}), 2.91 (s, 6 H, 2 Me), 1.1–1.7 (m, 1 H, CH_2CH_2), 1.03 (t, 3 H, Me). Anal. Calcd for $C_{22}H_{23}F_3N_2O_2Pd$: C, 51.73; H, 4.54. Found: C, 51.40; H, 4.45.

By use of the above described procedure, the following essentially pure syn complexes were obtained in about 90% yield:

(2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-butenyl]palladium(II) Trifluoroacetate (2b-*syn*). ^{1}H NMR (D_2O): δ 7.88 (d, 2 H), 7.47 (d, 2 H), 7.19 (s, 2 H), 5.57 (d app t, 1 H, H_2, $J_{21a} = J_{23a}$ = 12 Hz, J_{21s} = 7 Hz), 4.64 (d, 1 H, H_{1s}), 4.46 (dq, 1 H, H_{3a}), 3.39 (d, 1 H, H_{1a}), 2.74 (s, 6 H, 2 Me), 1.43 (d, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-octenyl]palladium(II) Trifluoroacetate (7b-*syn*). ^{1}H NMR ($CDCl_3$): δ 8.48 (d, 2 H), 7.92 (s, 2 H), 7.81 (d, 2 H), 5.48 (d app t, 1 H, H_2, $J_{21a} = J_{23a}$ = 12 Hz, J_{21s} = 7 Hz), 4.45 (d, 1 H, H_{1s}), 4.25 (ddd, 1 H, H_{3a}), 3.43 (d, 1 H, H_{1a}), 3.09 (s, 6 H, 2 Me), 1.1–1.7 (m, 8 H), 0.82 (t, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*syn*-(1,2,3-η)-2-methyl-2-butenyl]palladium(II) Trifluoroacetate (9b-*syn*). ^{1}H NMR (D_2O): δ 7.96 (d, 2 H), 7.54 (d, 2 H), 7.29 (s, 2 H), 4.50 (s, 1 H, H_{1s}), 4.23 (q, 1 H, H_{3a}), 3.20 (s, 1 H, H_{1a}), 2.80 (s, 6 H, 2 Me), 2.02 (s, 3 H, Me), 1.32 (d, 3 H, Me).

Preparation of Anti Complexes. Synthesis of (2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-hexenyl]palladium(II) Trifluoroacetate (4b-*anti*). A 151-mg (0.05 mmol of Pd) sample of the trifluoroacetato complex **4a** was dissolved in 25 mL of toluene, and 115 mg (0.55 mmol) of 2,9-dimethyl-1,10-phenanthroline dissolved in 25 mL of toluene was added with stirring at room temperature. A colorless flocculent precipitate formed while the suspension was kept stirring for 1 h. The precipitate was filtered out, washed with diethyl ether, and dried, giving 232 mg (91% yield) of the required complex in 90% isomeric purity. In order to maximize the abundance of the anti isomer, it is important to use a rather large volume of toluene as the solvent. Reducing the volume increases the precipitation rate relative to the isomerization rate, giving a lower content in

(23) Chemical equivalence between the two halves of the coordinated N-N ligand is observed in all the ^{1}H NMR spectra of the dimethylphenanthroline complexes. This implies a fast exchange of the two nitrogen coordination sites, as observed for other Pd(II) complexes. (a) Vrieze, K.; Van Leeuwen, P. W. N. M. *Prog. Inorg. Chem.* **1971**, *14*, 1. (b) De Renzi, A.; Morelli, G.; Panunzi, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1987**, *117*, 445. In $CDCl_3$ at −60 °C the exchange is slow enough to result in separate signals for the two methyl groups.

the anti isomer. One recrystallization from methanol/diethyl ether improved the isomeric purity to better than 97%. Molar conductivity: 53 Ω^{-1} mol^{-1} cm^2 ($C = 10^{-3}$ M in methylene chloride). ^{1}H NMR (D_2O):[23] δ 8.15 (d 2, H), 7.64 (d, 2 H), 7.51 (s, 2 H), 5.74 (m, 2 H, H_2 and H_{3a}), 4.53 (d, 1 H, H_{1s}), 3.69 (d, 1 H, H_{1a}), 2.78 (s, 6 H, 2 Me), 1.3-1.7 (m, 4 H, CH_2CH_2), 0.96 (t, 3 H, Me). Anal. Calcd for $C_{22}H_{23}F_3N_2O_2Pd$: C, 51.73; H, 4.54. Found: C, 51.43; H, 4.38.

By use of the above described procedure, the following anti complexes were obtained in about 90% yield and about 90% isomeric purity (better than 95% after one recrystallization from methanol/diethyl ether):

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-butenyl]palladium(II) Trifluoroacetate (2b-*anti*). ^{1}H NMR (D_2O): δ 7.93 (d, 2 H), 7.47 (d, 2 H), 7.26 (s, 2 H), 5.78 (app quintet, 1 H, H_{3a}), 5.61 (d app t, 1 H, H_2, $J_{21s} = J_{23a} = 7$ Hz, $J_{21a} = 12$ Hz), 4.48 (d, 1 H, H_{1s}), 3.70 (d, 1 H, H_{1a}), 2.65 (s, 6 H, 2 Me), 1.25 (d, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-octenyl]palladium(II) Trifluoroacetate (7b-*anti*). ^{1}H NMR ($CDCl_3$): δ 8.57 (d, 2 H), 7.98 (s, 2 H), 7.90 (d, 2 H), 5.75 (d app t, 1 H, H_2, $J_{21s} = J_{23a} = 7$ Hz, $J_{21a} = 12$ Hz), 5.6 (m, 1 H, H_{3a}), 4.56 (d, 1 H, H_{1s}), 3.61 (d, 1 H, H_{1a}), 3.03 (s, 6 H, 2 Me), 1.1-1.7 (m, 8 H), 0.80 (t, 3 H, Me).

(2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-methyl-2-butenyl]palladium(II) Trifluoroacetate (9b-*anti*). ^{1}H NMR (D_2O): δ 7.96 (d, 2 H), 7.54 (d, 2 H), 7.26 (s, 2 H), 5.44 (q, 1 H, H_{3a}), 4.44 (s, 1 H, H_{1s}), 3.62 (s, 1 H, H_{1a}), 2.76 9s, 6 H, 2 Me), 2.24 (s, 3 H, Me), 1.16 (d, 3 H, Me).

Preparation of Syn and Anti Complexes via Retention of Substrate Configuration. One-Step Synthesis of (2,9-Dimethyl-1,10-phenanthroline)[*anti*-(1,2,3-η)-2-hexenyl]palladium(II) Trifluoroacetate (4b-*anti*). A 287-mg (0.5-mmol) amount of $Pd(dba)_2$ and 115 mg (0.55 mmol) of 2,9-dimethyl-1,10-phenanthroline were dissolved in 10 mL of toluene. After the mixture was stirred for 5 min, 10 mL of water was added, followed by 120 mg (0.61 mmol) of (*Z*)-2-hexenyltrifluoroacetate (**5**), and the mixture was vigorously stirred for 20 min at room temperature. The aqueous layer was collected, and the toluene layer containing some precipitate and small amounts of palladium metal was again extracted with water (3 × 4 mL). The combined aqueous extracts were filtered and evaporated in vacuo at room temperature, giving 225 mg (88% yield) of the required crude product in 97% isomeric purity. The same procedure was used with (*E*)-2-hexenyl trifluoroacetate (**3**), giving the corresponding syn complex in 94% isomeric purity.

Acid-Assisted Oxidative Addition of Allylic Acetates and Alcohols to Pd(0). Synthesis of (2,9-Dimethyl-1,10-phenanthroline)[(1,2,3-η)-2-butenyl]palladium(II) Trifluoroacetate (2b). A 287-mg (0.5-mmol) amount of $Pd(dba)_2$ and 125 mg (0.6 mmol) of 2,9-dimethyl-1,10-phenanthroline were dissolved 10 mL of methylene chloride, and 78 mg (0.68 mmol) of (*E*)-crotyl acetate (**18**) was added followed by 58 mg (0.51 mmol) of trifluoroacetic acid. The mixture was stirred at room temperature until the deep purple color disappeared, leaving an orange-yellow solution darkened by small amounts of precipitated palladium metal (30–50 min). After filtration, the solution was concentrated to half-volume, and addition of diethyl ether gave the required crude product (**2b**) as a colorless microcrystalline solid (220 mg, 91% yield). The product actually consisted of a mixture of syn and anti isomers in about equal amounts. The relative amounts of the two isomers in the crude product are however poorly reproducible, since the kinetically formed syn isomer is isomerized to the more stable anti one during the reaction and subsequent workup.

Essentially the same procedure was used for preparing complexes **17b** and **17c** from the corresponding diacetate **23** and for reacting of alcohols **24-26**. Alcohol **24** was also reacted with 2 equiv of triphenylphosphine (or triphenyl phosphite) and 1 equiv of tetrafluoroboric acid of etherate in THF. The yields of the corresponding η^3-allyl complexes are given in Chart II. The triphenylphosphine and triphenyl phosphite complexes **2d** and **2e** were identified by comparison with authentic samples obtained in previous work.

Complexes **20c** and **22c** were obtained as tetrafluoroborate salts from the diacetates **19** and **21** by the following procedure:

Synthesis of (1,10-Phenanthroline)[(1,2,3-η)-3-acetoxypropenyl]palladium(II) Tetrafluoroborate (20c). A 287-mg (0.5-mmol) amount of $Pd(dba)_2$ and 147 mg (0.6 mmol) of 1,10-phenanthroline monotrifluoroacetate[24] were dissolved in 5 mL of THF, and 130 mg (0.8 mmol) of 1,1-diacethoxy-2-propene (**19**) was added. The mixture was kept stirring for 30 min at room temperature, giving a yellow-orange solution and a dark pasty precipitate. The solvent was evaporated in vacuo, and the grayish brown residue was extracted with water (3 × 2 mL). To the filtered water solution was 110 mg (1.0 mmol) of $NaBF_4$ dissolved in 2 mL of water. The resulting pale cream flocculent precipitate was filtered out, washed with water, and dried, giving 190 mg (76% yield) of the required complex **20c**, which was recrystallized from nitromethane/diethyl ether.

^{1}H NMR (15% CD_3NO_2 in $CDCl_3$): δ 9.19 (br, 1 H), 8.74 (d, 2 H), 8.60 (br, 1 H), 8.11 (s, 2 H), 8.04 (br m, 2 H), 6.89 (d, 1 H, H_{3a}), 6.14 (ddd, 1 H, H_2, $J_{21a} = 13$ Hz, $J_{23a} = 9$ Hz, $J_{21s} = 7.5$ Hz), 4.47 (d, 1 H, H_{1s}), 3.66 (d, 1 H, H_{1a}), 2.45 (s, 3 H, Me). ^{13}C NMR: δ (signals from the phenanthroline ligand are omitted) 170.2 (C=O), 108.2 (C_2), 98.1 (C_3), 58.9 (C_1), 21.6 (Me). The usual syn structure can be assigned to the complex. Small signals from the anti isomer (≈10% abundance) are also detectable in the ^{1}H NMR spectrum: δ 7.54 (d, H_{3a}), 5.65 (ddd, H_2, $J_{23a} = 4$ Hz, $J_{21s} = 8$ Hz, $J_{21a} = 13.5$ Hz), 4.72 (d, H_{1s}). Anal. Calcd for $C_{17}H_{15}BF_4N_2O_2Pd$: C, 43.21; H, 3.20. Found: C, 43.11; H, 3.07.

(1,10-Phenanthroline)[(1,2,3-η)-1-acetoxy-2-butenyl]palladium(II) Tetrafluoroborate (22c). ^{1}H NMR (15% CD_3NO_2 in $CDCl_3$): δ 8.96 (br, 1 H), 8.78 (d, 2 H), 8.66 (br, 1 H), 8.16 (s, 2 H), 8.08 (br, 2 H), 6.76 (d, 1 H, H_{1a}), 5.91 (dd, 1 H, H_2, $J_{23a} = 13$ Hz, $J_{21a} = 9$ Hz), 4.32 (dq, 1 H, H_{3a}), 2.43 (s, 3 H, MeCO), 1.83 (d, 3 H, Me). ^{13}C NMR: δ (signals from the phenanthroline ligand are omitted) 170.2 (C=O), 107.8 (C_2), 96.3 (C_1), 74.4 (C_3), 21.6 (MeCO), 17.5 (Me). The usual syn structure can be assigned to the complex. Small signals from the 1-anti-3-syn isomer and from the 1-syn-3-anti isomer (<10% abundance each) are also detectable in the ^{1}H NMR spectrum.

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