the photochemical results suggest that 1-2 CN^- ligands are prevented to escape.

The observed effects for the polyammonium macrocyclic receptors can thus be accounted for by the formation of complexes of defined geometry although, of course, one cannot exclude that such effects result from the coexistence of several adducts having various geometries.

Conclusions

The results obtained in this paper show that the photoreactivity of transition-metal complexes can be controlled by adduct formation. Furthermore, they agree with structural considerations on relative shape, size, and binding site arrangements, suggesting that the adducts formed by $Co(CN)_6^{3-}$ with polyammonium macrocyclic receptors have defined supramolecular structures. In particular, the complexes of $Co(CN)_6^{3-}$ with 32-$N_8H_8^{8+}$ and 32-C_9-$N_6H_6^{6+}$ (a and b1 in Figure 3) may be considered as complexes of complexes (or supercomplexes) since the hexacyano cobaltate anion should be contained inside the macrocyclic ligand, which substantially constitutes the second coordination sphere of the central metal. These results suggest that in favorable cases photochemistry may be a probe for supramolecular structures. Besides offering a generic protection against photodissociation, adduct formation might find interesting application in the case of complexes containing mixed ligands: on one hand it could provide information on the site of ligand release and on the other hand it can orient photosubstitution reactions toward specific products. These results and perspectives further extend the scope and applications of anion coordination chemistry.

Acknowledgment. The authors are indebted to Prof. L. G. Vanquickenborne and Dr. S. Dellonte for having made available to us emission data. Financial support by the Consiglio Nazionale delle Ricerche, the Ministero della Pubblica Istruzione, and the Centre National de la Recherche Scientifique is gratefully acknowledged.

Registry No. $\{Co(CN)_6[L\text{-}21\text{-}N_6H_6]\}^{3+}$, 98778-51-9; $\{Co(CN)_6[24\text{-}N_6H_6]\}^{3+}$, 98778-52-0; $\{Co(CN)_6[32\text{-}C_9\text{-}N_6H_6]\}^{3+}$, 98778-54-2; $\{Co(CN)_6[32\text{-}N_8H_8]\}^{5+}$, 91810-52-5; $\{Co(CN)_6[Et_2NH_2]\}^{2-}$, 98778-50-8; $Co(CN)_6^{3-}$, 14897-04-2; CN^-, 57-12-5; H_2O, 7732-18-5.

Dual Stereoselectivity in the Nucleophilic Attack on (π-Allyl)palladium Complexes

Jan-E. Bäckvall,* Ruth E. Nordberg, and Didier Wilhelm

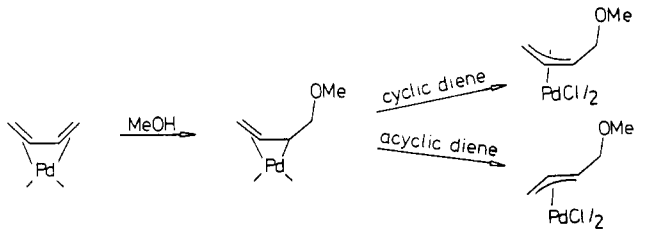
Contribution from the Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden. *Received April 9, 1985*

Abstract: Stereochemical studies of nucleophilic addition to (π-allyl)palladium complexes **1-5** and **10** show that carboxylates, e.g., acetate, can be directed toward cis or trans attack depending on the ligand environment. This dual stereoselectivity was obtained in both cyclic and acyclic systems. The acetate attack was induced by the addition of *p*-benzoquinone, which most likely coordinates to the metal. Accordingly, maleic anhydride was shown in one case to induce a cis migration of acetate in bis[(4-methoxy-η^3-1,3-cyclohexenyl)palladium acetate]. Attempts to induce a cis migration of a stabilized carbon nucleophile (acetylacetonate) in a (π-allyl)palladium complex led only to a cis/trans addition ratio of 20:80. The cis migration of carboxylates probably occurs via a (σ-allyl)palladium complex, whereas the trans attack takes place directly on the (π-allyl)palladium complex.

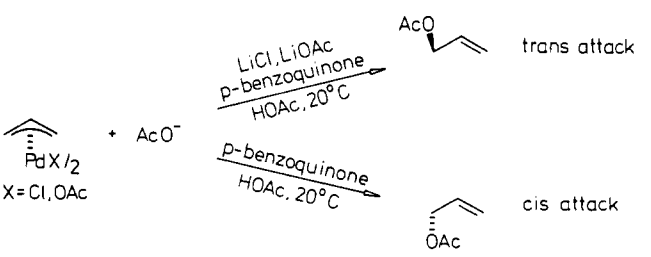
Nucleophilic addition to unsaturated hydrocarbons coordinated to a transition metal is an important type of reaction in organic synthesis. In these reactions, the question concerning the regio- and stereoselectivity plays a central role (Figure 1). Although many studies have addressed the question of altering the regioselectivity for a given nucleophile (i.e., full regiocontrol),[1-3] relatively little work has been aimed at altering the stereoselectivity (i.e., full stereocontrol).[1b,2b,c,4] A dual stereocontrol is of great importance in organic synthesis since it allows a choice in stereochemistry in the creation of new asymmetric centers.

We have recently reported palladium-catalyzed 1,4-additions to conjugated dienes involving stereo- and regioselective additions

Scheme I



Scheme II



(1) (a) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715 and references cited. (b) Birch, A. J. et al. *Tetrahedron*, **1981**, *37*, Suppl. 9, 289. (c) Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467. (d) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.* **1984**, *267*, C34.

(2) (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Trost, B. M., Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. (c) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (d) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679 and references cited. (e) Hegedus, L. S.; Darlington, W. H.; Russel, C. E. *J. Org. Chem.* **1980**, *45*, 5193. (f) Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648. (g) Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1984**, *106*, 6837.

(3) (a) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231. (b) Curtis, M. D.; Eisenstein, O. *Ibid.* **1984**, *3*, 887.

(4) (a) The usual trans addition of hydride to (cyclohexadienyl)iron complexes can be altered toward mainly cis addition by changing the hydride reagent from $NaBH_4$ to $LiEt_3BH$: See ref 1b and: Gladysz, J. A. *Aldrichim. Acta* **1979**, *12*, 13. (b) Cis hydride attack was also observed for a (cyclohexadienyl)manganese complex: Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (c) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730. (d) Trost, B. M.; Yoshida, J.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 4494.

0002-7863/85/1507-6892$01.50/0

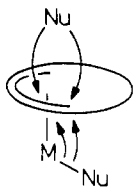
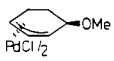
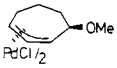
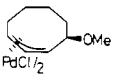
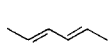
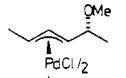
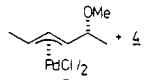


Figure 1.

Table I. Preparation of (Methoxy-η^3-alkenyl)palladium Complexes[a]

1,3-Dienes	Product[b] (% yield)	Ref.
	 (93)[c]	7,8
	1	
	 (67)[c]	8
	2	
	 (50)[c]	8
	3	
	 (96)[c]	d
	4	
	 (81)	d
	5	
	82 : 18	

[a] The diene was treated with sodium tetrachloropalladate in methanol. [b] The configuration of complex **1** has explicitly been proven by chemical transformations (ref 9). On the basis of the established trans methoxypalladation of 1,3-cyclohexadiene, the complexes **2–5** have been assigned the configuration indicated. [c] Only one diastereoisomer could be observed by ^1H and ^{13}C NMR spectroscopy. [d] Bis[(2-methoxy-η^3-3,5-hexenyl)palladium chloride] has been reported in the literature without characterization.[31]

to (π-allyl)palladium intermediates.[5,6] These catalytic reactions indicate that certain nucleophiles, e.g., carboxylates, show a dual stereoselectivity in the nucleophilic addition to the (π-allyl)palladium intermediates. Since such a dual stereoselectivity is of both mechanistic and synthetic interest, we have studied these nucleophilic addition reactions on well-defined isolated (π-allyl)palladium complexes.

Results

A. Preparation of (π-Allyl)palladium Complexes. Cyclic (π-allyl)palladium complexes **1**, **2**, and **3** (Table I) were prepared by treatment of the corresponding dienes with Na_2PdCl_4 in methanol following a modified procedure[7] of the one reported by Robinson and Shaw.[8] A highly stereospecific trans methoxypalladation of the diene occurred which produced only one diastereoisomer of the (4-methoxy-η^3-1,3-cycloalkenyl)palladium complex (Scheme I). The exact configuration of **1** has previously been established.[9]

In the same way, methoxypalladation of (*E*,*E*)-2,4-hexadiene was stereospecific, leading to a single diastereoisomer as shown by ^1H and ^{13}C NMR spectroscopy. The NMR spectra are consistent with a syn conformation, and a trans methoxypalladation requires that this diastereoisomer is **4** (Table I). Reaction of (*E*,*Z*)-2,4-hexadiene with Na_2PdCl_4–methanol was less stereospecific and afforded an 18:82 mixture between **4** and **5** (Table I). The loss of stereospecificity is most likely due to *E*–*Z* isomerization of the diene.

B. Acetate Attack on (π-Allyl)palladium Complexes. Treatment of the (π-allyl)palladium complexes with *p*-benzoquinone in acetic acid at room temperature resulted in a nucleophilic attack by acetate on the allyl group. By altering the ligand environment of the metal, the acetate attack was directed either toward an external trans attack or toward a cis attack (Scheme II).

1. Cyclic (π-Allyl)palladium Complexes. Treatment of complex **1** with *p*-benzoquinone in acetic acid in the presence of LiCl and LiOAc (method A) afforded *cis*-**6** via an external trans attack by acetate (entry 1, Table II). However, when complex **1** was pretreated with AgOAc (to remove chloride) followed by addition of *p*-benzoquinone (method B), the acetate attack occurred exclusively from the same face as the metal (entry 2). For complex **2**, the dual stereoselectivity in the acetate attack was also obtained by using the same reaction conditions (entries 3 and 4), but in this case the cis attack was less stereoselective. For the (cyclooctenyl)palladium complex **3**, it was possible to obtain a clean cis attack to give *trans*-**8** by using the chloride-free procedure (method B). Attempts to induce a trans attack by acetate on **3** using method A failed and gave no addition product.

The configurational assignments of compounds **6**, **7**, and **8** were made by ^1H NMR spectroscopy (see Experimental Section). A common feature of cycloalk-2-ene-1,4-diols and their diacetates and dimethyl ethers is that the CH–O protons lie further downfield for the trans isomer than for the cis isomer.[6a,6b,10,11] The compounds *cis*- and *trans*-**6** were also converted to the known *cis*-and *trans*-4-methoxycyclohexanol[12] by hydrolysis and hydrogenation.

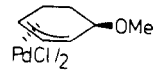
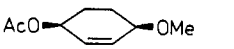
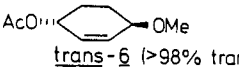
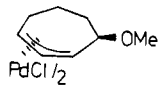
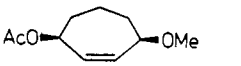
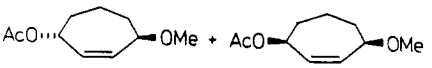
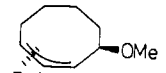
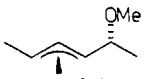
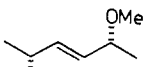
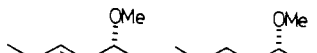
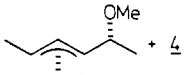
Since *p*-benzoquinone is supposed to act as a ligand (vide infra), it was of interest to investigate the effect of a related electron-withdrawing ligand, which cannot act as an oxidant. Maleic anhydride, which recently was shown to induce reductive elimination in bis(π-allyl)palladium complexes,[13] was of interest due to its apparent similarities with *p*-benzoquinone. Reaction of **1** in the presence of LiCl and LiOAc using maleic anhydride instead of *p*-benzoquinone gave mainly elimination products. Interestingly, replacement of the chloride ligand in **1** by acetate followed by treatment with maleic anhydride in acetic acid (cf. method B) induced a cis migration of the coordinated acetate to the π-allyl ligand.

2. Acyclic (π-Allyl)palladium Complexes. In order to determine whether the dual stereocontrol of the acetate attack could also be obtained in acyclic systems, we studied the reactions of (π-allyl)palladium complexes **4** and **5**. The acyclic π-allyl complexes differ from the cyclic ones in two respects. First, the conformation in the acyclic systems can change between anti and syn (but is predominantly syn), whereas the cyclic systems for steric reasons can only possess a so-called anti conformation. Second, the rotation around the C_4–C_5 bond is possible in **4** and **5**. The methoxy group can therefore appear on the same face of the π-allyl group as the metal, and hence coordination by the methoxy group is possible. These differences between the acyclic and cyclic (π-allyl)palladium complexes are probably reflected by the much lower reactivity of **4** and **5** in the nucleophilic addition reactions (Table II).

Despite the lower reactivity of the acyclic complexes **4** and **5**, it was possible to obtain the dual stereoselectivity in the nucleophilic attack by acetate. Thus, by using method A (chloride

(5) Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335.
(6) (a) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *101*, 4959. (b) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (c) Bäckvall, J. E.; Nordberg, R. E.; Nyström, J. E. *Tetrahedron Lett.* **1982**, *23*, 1617. (d) Bäckvall, J. E.; Nyström, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676. (e) Bäckvall, J. E.; Vågberg, J.; Nordberg, R. E. *Tetrahedron Lett.* **1984**, *25*, 2717.
(7) Bäckvall, J. E.; Nordberg, R. E.; Zetterberg, K., Åkermark, B. *Organometallics* **1983**, *2*, 1625.
(8) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1964**, 5002.
(9) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *J. Chem. Soc. Chem. Commun.* **1980**, 943.
(10) Nordberg, R. E. Dissertation, Royal Institute of Technology, Stockholm 1982.
(11) Barluenga, J.; Pérez-Prieto, J.; Asensio, G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 629.
(12) Eliel, E. L.; Brett, T. J. *J. Org. Chem.* **1963**, *28*, 1923.
(13) Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 5028.

Table II. Stereocontrolled Acetate Attack on (π-Allyl)palladium Complexes

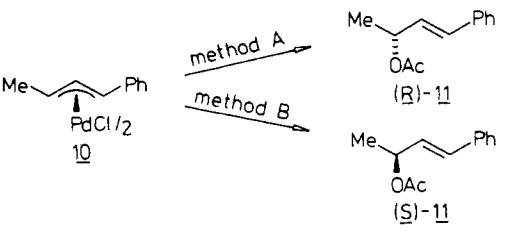
Entry	Complex	Reaction conditions[a]	Product[b]	% yield[c]
1	 1	A, 4h	 cis-6 (>95% cis)	79
2	1	B, 4h	 trans-6 (>98% trans)	75
3	 2	A, 2h	 cis-7 (>98% cis)	51[d]
4	2	B, 6h	 trans-7 72 : cis-7 28	61
5	 3	B, 4h	 trans-8 (>98% trans)	68
6	 4	A, 48	 (R^*,R^*)-9 (>87% R^*,R^*)	58[e]
7	4	B, 30h	 (R^*,S^*)-9 : (R^*,R^*)-9 78 : 22	36[e]
8	 + 4 5 82 : 18	A, 22h	(R^*,S^*)-9 + (R^*,R^*)-9 72 : 28	57[e]
9	5 + 4 82 : 18	B, 19h	(R^*,S^*)-9 + (R^*,R^*)-9 15 : 85	40[e]

[a] A, LiCl, LiOAc, *p*-benzoquinone, HOAc, 20 °C; B, (i) AgOAc (ii) *p*-benzoquinone, HOAc, 20 °C. [b] The nomenclature R^*R^* and R^*S^* denotes *RR–SS* and *RS–SR* diastereoisomers, respectively. [c] Isolated yield. [d] The yield 51% is a 2:1 mixture of *cis*-**7** and *cis*-1,4-diacetoxy-2-cycloheptene. [e] Exclusively of *E* double bond configuration. Contaminated with the regioisomer (*E*)-4-acetoxy-5-methoxy-2-hexene; entry 6, 13%; entry 7, 7%; entry 8, 14%; entry 9, <2%.

ligands), **4** afforded (R^*,R^*)-**9** as the only 1,4-diastereoisomer, which shows that the nucleophilic attack by acetate has occurred trans (entry 6). The product (R^*,R^*)-**9**, which is exclusively of *E* configuration, was contaminated with 13% of the regioisomer (*E*)-4-acetoxy-5-methoxy-2-hexene. The latter compound is most likely formed by a secondary rearrangement[14] of (R^*,R^*)-**9** due to the long reaction time. Reaction of **4** using method B (chloride free) afforded a 78:22 mixture of (R^*,S^*)-**9** and (R^*,R^*)-**9**, showing that the cis attack by acetate now predominates (entry 7). The (R^*,S^*)/(R^*,R^*) ratio was determined by ^{1}H NMR spectroscopy.

Reaction of a 82:18 mixture of complex **5** and **4** using method A and B produced a 72:28 and a 15:85 mixture, respectively, of (R^*,S^*)-**9** and (R^*,R^*)-**9** (entries 8 and 9). When these ratios are corrected for the presence of **4** (whose product pattern is known from entries 6 and 7), the stereoselectivity for trans attack on **5** is >85% (entry 8) and for cis attack >98% (entry 9). This shows that it is possible to obtain a dual stereoselectivity also for acyclic (π-allyl)palladium complexes.

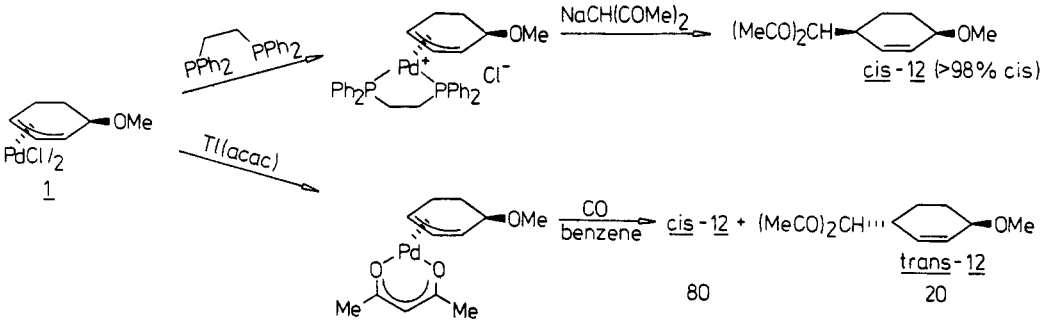
Scheme III



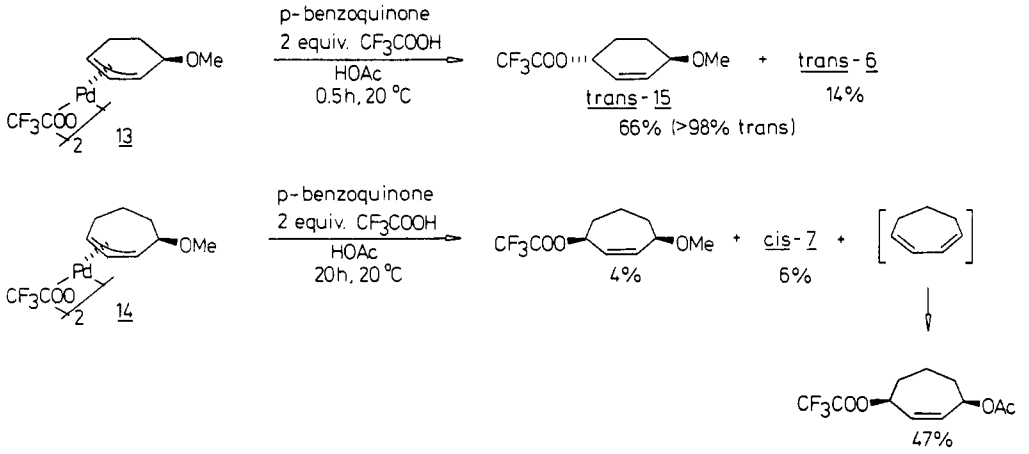
All the (π-allyl)palladium complexes in Table II, utilized for the mechanistic studies, have a methoxy group on the carbon

(14) (a) Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 5200. (b) Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321; *J. Am. Chem. Soc.* **1980**, *102*, 865. (c) Grieco, P. A.; Takigawa, T.; Bongers, S. L.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 7587.

Scheme IV



Scheme V



adjacent to the allyl unit. Such an electronegative group close to palladium may affect the reactivity of the π-allyl complex and could be of importance for the stereoselectivity. It was therefore of interest to study the nucleophilic addition reactions of an unbiased system not possessing such an electronegative substituent. We choose to use the optically active (π-allyl)palladium complex **10** recently reported by Hayashi et al.[15] Reaction of **10** using method A regioselectively produced the acetate (*R*)-**11** (>96% regioselectivity) (Scheme III). Formation of (*R*)-**11** shows that the acetate attack has occurred mainly trans (cis/trans addition = 16:84 from its specific rotation). Reaction of **10** using method B gave the acetate enriched in the isomer (*S*)-**11**. The specific rotation of (*S*)-**11** indicated that the ratio of cis/trans addition was 79:21.

C. Dual Stereoselectivity for Other Nucleophiles. It is known that (π-allyl)palladium acetates and acetylacetonates on treatment with carbon monoxide undergo attack by acetate and acetylacetonate, respectively.[16] We have previously shown that the stereochemistry of the acetate attack under these conditions occurs cis via a carbon monoxide induced migration from metal to carbon.[9] Since there was no information available concerning the stereochemistry of the attack by the acetylacetonate, we decided to study the stereochemistry of this reaction. Our aim was to find out if it is possible to obtain a dual stereoselectivity for a stabilized carbon nucleophile.

We first carried out the nucleophilic addition of sodium acetylacetonate to **1** using phosphine ligands. This led to a clean trans attack[17] by the nucleophile and formation of *cis*-**12** (Scheme IV).

We then prepared the acetylacetonate complex of **1** and treated it with carbon monoxide in benzene. This led to a very slow reaction. ^{1}H NMR analysis of the crude product indicated a 80:20 mixture between *cis*-**12** and *trans*-**12**. Thus, only a small fraction of the acetylacetonate anion migrated from metal to carbon, and the major part dissociated and attacked the allyl group trans to the metal. This is in contrast to the acetate complex of **1**, bis-[(4-methoxy-η^3-1,3-cyclohexenyl)palladium acetate], which on treatment with CO in benzene resulted in a rapid stereospecific cis migration of acetate to give *trans*-**6**.[9]

We also studied the reactivity of coordinated trifluoroacetate toward migration in two (π-allyl)palladium complexes. Complexes **13** and **14**, readily available from **1** and **2**, respectively, by treatment with silver trifluoroacetate, were allowed to react with *p*-benzoquinone in acetic acid containing 2 equiv of trifluoroacetic acid. Interestingly, complex **13** reacted rapidly at room temperature to give the expected cis-migration product *trans*-**15** in 66% yield (Scheme V). However, the seven-membered ring complex **14** reacted very slowly, and no migration product could be detected. The main reaction path in this case was elimination, yielding 1,3-cycloheptadiene, which then underwent a palladium-catalyzed oxidation reaction in situ.[6e]

Discussion

The stereochemistry of nucleophilic attack on (π-allyl)palladium complexes has been studied for many nucleophiles.[5] It has been found that one class of nucleophiles such as hydride,[18] methyl,[19] aryl,[20] vinyl,[2c,20a] and allyl[13] add cis via a migration from the metal to the allyl group, whereas another class of nucleophiles such as stabilized carbon nucleophiles[17] amines,[7] amides,[21] alcohols (al-

(15) (a) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1983**, 736. (b) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.

(16) (a) Takahashi, Y.; Tsukiyama, K.; Sakain, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913. (b) Takahashi, Y.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1967**, 1092. (c) Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5.

(17) Trans attack by stabilized carbon nucleophiles to (π-allyl)palladium complexes is well established; for example, see ref 15b and: Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

(18) (a) Jones, D. N.; Knox, S. D. *J. Chem. Soc., Chem. Commun.* **1975**, 165. (b) Keinan, E.; Greenspoon, N. *Tetrahedron Lett.* **1982**, *23*, 241.

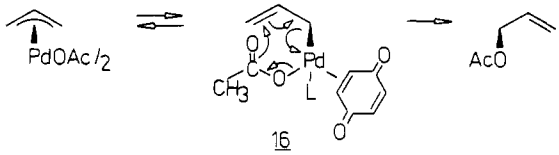
(19) Castanet, Y.; Petit, F. *Tetrahedron Lett.* **1979**, 3221.

(20) (a) Matsushita, H.; Negishi, E. I. *J. Chem. Soc., Chem. Commun.* **1982**, 160. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 107.

(21) Byström, S. E.; Aslanian, R.; Bäckvall, J. E. *Tetrahedron Lett.* **1985**, *26*, 1749.

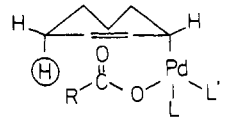
koxide),[22] chloride,[6c,6d] and phenyl sulfinate[6d,23] prefer to add trans. The general rule therefore is that a given nucleophile only adds according to one of the steric modes (cis or trans). The carboxylates, e.g., acetate, are therefore unique in the sense that they can be directed toward both steric pathways.

What is the explanation for this dual behavior of acetate? The external trans attack by acetate is the expected steric mode,[24] which is also observed with high stereospecificity (>95%) in the reactions utilizing chloride ligands. From a theoretical analysis based on a combination of ab initio–ECP calculations and frontier MO arguments, simple oxygen nucleophiles coordinated to palladium, such as CH_3O^-, HO^-, and AcO^-, are not expected to undergo migration reactions because of the low energy of the Pd–Nu bond orbital.[24] The reason why acetate can undergo a cis migration so easily in spite of being an oxygen nucleophile is probably because it is bidentate. Formation of a (σ-allyl)palladium complex **16** would lead to a favored pathway for cis migration.[25]



16

We have already provided indirect evidence for a σ-allyl intermediate, related to **16**, in the palladium-catalyzed 1,4-diacetoxylation of conjugated dienes.[6b] The reluctance of the cycloheptenyl complex **17** to undergo a cis migration can be rationalized by steric hindrance between the pseudoaxial allylic proton and the migrating nucleophile. The fact that trifluoroacetate gave



17

no cis migration whatsoever for the seven-membered ring supports this mechanism. The results from the palladium-catalyzed 1,4-acetoxy-trifluoroacetoxylation of 1,3-cycloheptadiene is in accordance with this interpretation.[6c] The role of the chloride ligands in these dual stereoselective reactions is to block the coordination of acetate to palladium,[5,6a]

Oxidation-induced acetate attack on (π-allyl)palladium complexes has been reported before.[26] Oxidants such as nitrous acid, sodium nitrite, $Hg(OAc)_2$, $Tl(OAc)_3$, and $Pb(OAc)_4$ were used, but the stereochemistry of the attack was not determined. Compared to many of these oxidants, *p*-benzoquinone with its low oxidation potential is a mild oxidant. Kinetic studies suggest that *p*-benzoquinone coordinates to palladium both in stoichiometric[27] and catalytic[6b,6d] reactions involving chloride and/or acetate attack on (π-allyl)palladium complexes.

Concluding Remarks

The present study has shown that it is possible to direct a nucleophile (e.g., a carboxylate) selectively toward either cis attack or trans attack. Such a dual stereoselectivity in the nucleophilic addition to a coordinated unsaturated hydrocarbon is previously unprecedented.[28] The dual stereoselectivity allows a *complete* stereocontrol in the creation of the new asymmetric center. It is interesting to note that the new center is created remote to the CH–OMe with full control of the relative stereochemistry.[29]

The mechanistic study of the dual nucleophilic attack on (π-allyl)palladium complexes described in this paper puts the mechanistic interpretation of the previously reported[6] palladium-catalyzed 1,4-additions to conjugated dienes on a firm basis.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^1H and ^{13}C NMR spectra were determined in chloroform-*d* (unless stated otherwise) on a Bruker WP 200 FT spectrometer at 200 and 50.3 MHz, respectively. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane. High-pressure liquid chromatography (HPLC) was run on a Waters M-45 instrument with a μ-Porasil column (silica, 10-μm packing, 0.4 × 30 cm).

1,3-Cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, and (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene were purchased from Fluka AG and were distilled before use. Analytic grade ("pro-analysi") methanol, acetone, and acetylacetone were purchased from Fluka AG and used without further purification. Palladium chloride was obtained from Engelhard Industries and converted to $Na_2PdCl_4 \cdot 3H_2O$ by stirring overnight with 2 equiv of sodium chloride in water and collecting the dark brown solid after distilling off the water under vacuum. *p*-Benzoquinone was purchased from Merck and recrystallized (ligroin) before use. LiCl (Merck), $LiOAc \cdot 2H_2O$ (BDH), AgOAc (BDH), and $AgOOCCF_3$ (Fluka AG) were commercially available and used without further purification. Tetrahydrofuran (THF) was distilled from potassium/benzophenone. Sodium acetylacetonate was prepared from equimolar amounts of acetylacetone and sodium hydride in THF. Thallium acetylacetonate was prepared according to Taylor et al.[30] from thallium ethoxide and acetylacetone. The (π-allyl)palladium complexes **1–5** were prepared according to a modified[7] method of Robinson and Shaw.[8] The (π-allyl)palladium complex **10** was a gift from Dr. T. Hayashi (Kyoto University).

Complex 1.[7,8] For preparation and ^1H NMR, see ref 7: ^{13}C NMR δ 100.6, 80.8, 77.1, 76.9, 56.6, 25.6, 24.9.

Complex 2.[8] 1,3-Cycloheptadiene (800 μL, 8.1 mmol), $Na_2PdCl_4 \cdot 3H_2O$ (2.39 g, 6.8 mmol), and methanol (14 mL) were stirred at −5 °C for 0.5 h and then stored at −20 °C for 44 h. Workup as for **1** afforded 1.23 g (67%) of complex **2** as yellow crystals: ^1H NMR δ 5.15–4.85 (m, 3 H, π-system), 3.75 (m, 1 H, CH–O), 3.41 (s, 3 H, OMe), 2.2–1.4 (m, 6 H, CH_2); ^{13}C NMR δ 100.2, 87.0, 80.9, 80.6, 56.9, 33.4, 31.5, 21.5.

Complex 3.[8] 1,3-Cyclooctadiene (326 μL, 3.0 mmol), $Na_2PdCl_4 \cdot 3H_2O$ (1.77 g, 5.2 mmol), and methanol (10 mL), were stirred at −5 °C for 2 h and then stored at room temperature for 15 h. Workup as for **1** afforded 710 mg (50%) of complex **3**: ^1H NMR δ 5.34 (t, J = 8 Hz, 1 H, middle H in π-system), 4.75–4.6 (m, 2 H, π-system), 3.70 (m, 1 H, CH–O), 3.59 (s, 3 H, OMe), 2.5–2.35 (m, 1 H, one H in CH_2). 1.7–1.3 (m, 7 H); ^{13}C NMR δ 102.0, 83.1, 82.5, 77.3, 58.9, 33.3, 31.4, 24.5, 22.3.

Complex 4. (*E*,*E*)-2,4-Hexadiene (600 μL, 5.2 mmol), $Na_2PdCl_4 \cdot 3H_2O$ (1.18 g, 3.4 mmol), and methanol (6 mL) were stirred at −5 °C

(22) (a) Bäckvall, J. E.; Nordberg, R. E.; Vågberg, J. *Tetrahedron Lett.* **1983**, *24*, 411. (b) Vågberg, J., unpublished results. (c) Stanton, S. A.; Felman, S. W.; Parkhurst, C. S.; Godleski, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 1964.

(23) (a) Åkermark, B.; Nyström, J. E.; Rein, T.; Bäckvall, J. E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719. (b) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396.

(24) (a) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *104*, 4369. (b) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.*, in press.

(25) A frontier orbital controlled cis migration in the π-allyl form (η^3-coordinated) would require a direct interaction between the Pd–O bond orbital and the LUMO of the π-allyl group (cf. ref 24a). However, in the σ-allyl form, it is *not* the Pd–O bond orbital but a high-energy lone-pair orbital on the carbonyl oxygen that interacts with the LUMO of the unsaturated system. The activation barrier for the latter process is expected to be much lower according to perturbation theory arguments.[24]

(26) (a) Wolfe, S.; Campbell, P. G. C. *J. Am. Chem. Soc.* **1971**, *93*, 1499. (b) Kitching, W.; Sakakiyama, T.; Rappoport, Z.; Sleezer, P. D.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 2329. (c) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5542.

(27) Satsko, N. G.; Below, A. P.; Moiseev, I. I. *Kinet. Katal.* **1972**, *13*, 892; *Chem. Abstr.* **1973**, *78*, 83584c.

(28) (a) A few examples where a moderate dual stereoselectivity in nucleophilic additions to coordinated unsaturated hydrocarbons has been obtained are given in ref 2b, 4a, and 4c. (b) Addition of phenyllithium to (η^6-cycloheptatrienyl)manganese tricarbonyl cation has been found[28c] to proceed via a trans attack by the phenyl anion to give (*trans*-6-phenyl-η^5-1,5-cycloheptadienyl)manganese tricarbonyl. However, reaction of cycloheptatriene with phenylmanganese pentacarbonyl has been reported[28d] to give (*cis*-6-phenyl-η^5-1,5-cycloheptadienyl)manganese tricarbonyl most likely via a cis migration of phenyl to one of the coordinated double bonds in cycloheptatriene. (c) Haque, F.; Miller, J.; Pauson, P. L.; Tripathi, J. B. Pd. *J. Chem. Soc. C* **1971**, 743. (d) Burt, J. C.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1.

(29) With full control of relative stereochemistry is meant that one can create a new chiral center of either configuration in a molecule relative to a preexisting chiral center. Strategies for achieving such a stereocontrol have recently been discussed: Sharpless, K. B. *Chem. Scr.* **1985**, *25*, 71. Masamune, S.; Choy, W.; Petersen, J. S.; Lawrence, R. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

(30) Taylor, E. C.; Hawks, G. H., III; McKillop, A. *J. Am. Chem. Soc.* **1968**, *90*, 2421.

for 1 h and then stored at room temperature for 15 h and at −20 °C for 10 h. Workup as for **1** afforded 830 mg (96%) of complex **4**:[31] ^{1}H NMR δ 5.39 (t, J = 11 Hz, 1 H, middle H in π-system), 3.87 (dq, J = 6, 11 Hz, 1 H, Me–C*H*–CHCH), 3.6–3.35 (m, 2 H, MeO–C*H*–C*H*), 3.45 (s, 3 H, OMe), 1.34 (d, J = 6 Hz, 3 H, *Me*–CHOMe), 1.31 (d, J = 6 Hz, *Me*–CH); ^{13}C NMR δ 108.3, 80.9, 78.6, 75.7, 57.4, 20.5, 18.0; IR (KBr) 2970, 2920, 2870, 2820, 1450(br), 1370, 1345, 1130, 1110, 1090, 1070, 1035 cm^{-1}.

Anal. Calcd for $C_{14}H_{26}Cl_2O_2Pd_2$: C 32.95; H, 5.14. Found: C, 32.90; H, 5.02.

Complex 5. (*E*,*Z*)-2,4-Hexadiene (590 μL, 5.2 mmol), $Na_2PdCl_4 \cdot 3H_2O$ (1.18 g, 3.4 mmol), and methanol (6 mL) were stirred at −5 °C for 1 h and then stored at room temperature for 15 h and at −20 °C for 10 h. Workup as for **1** afforded 700 mg (81%) of a mixture of complexes **5** and **4** in a ratio of 82:18:[31]

Complex 5: ^{1}H NMR δ 5.33 (t, J = 11 Hz, 1 H, middle H in π-system), 3.87 (dd, J = 6, 11 Hz, 1 H, Me–C*H*–CHCH), 3.75–3.5 (m, 2 H, MeO–C*H*–C*H*), 3.39 (s, 3 H, OMe), 1.37 (d, J = 6 Hz, *Me*–CHOMe), 1.31 (d, J = 6 Hz, 3 H, *Me*–CHCH); ^{13}C NMR δ 107.7, 79.5, 79.1, 74.8, 56.5, 17.9, 17.3; IR (KBr) 2970, 2920, 2880, 2820, 1450 (br), 1370, 1100, 1080, 1040 cm^{-1}.

Acetate Attack on (π-Allyl)palladium Complexes. The reactions were carried out in acetic acid by treatment of the appropriate (π-allyl)palladium complex with *p*-benzoquinone. Two principal methods were used. Method A: the (π-allyl)palladium chloride complex was utilized together with lithium chloride and lithium acetate (described for preparation of *cis*-**6**). Method B: The (π-allyl)palladium acetate complex was used in chloride-free acetic acid. The acetate complex was generated from the chloride complex by treatment with silver acetate, either directly in acetic acid (described for *trans*-**6**) or separately in acetone followed by removal of the acetone and replacement with acetic acid (described for *trans*-**7**).

***cis*-1-Acetoxy-4-methoxy-2-cyclohexene (*cis*-6).** To a stirred solution of bis[(4-methoxy-η^3-1,3-cyclohexenyl)palladium chloride] (**1**) (609 mg, 1.2 mmol) in acetic acid (4 mL) at 20 °C was added a solution of $LiOAc \cdot 2H_2O$ (2.66 g, 26 mmol), LiCl (111 mg, 216 mmol), and *p*-benzoquinone (480 mg, 4.5 mmol) in acetic acid (11 mL). The reaction was stirred at room temperature for 4 h and then diluted with 8 mL of saturated NaCl solution and extracted with 4 × 20 mL of pentane/ether (90:10). The combined extracts were washed with water (20 mL) and saturated Na_2CO_3 (3 × 10 mL) and dried $MgSO_4$. Evaporation of the solvent afforded 322 mg (79%) of *cis*-**6** (>95% cis): ^{1}H NMR δ 6.1–5.7 (m, 2 H, CH=CH), 5.19 (m, 2 H, *CH*—OAc), 3.73 (m, 2 H, *CH*—OMe), 3.39 (s, 3 H, OMe), 2.05 (s, 3 H, OAc), 1.8 (m, 4 H, CH_2CH_2); IR (CCl_4) 2945, 2815, 1735, 1370, 1230, 1210 (br), 1082, 1032 cm^{-1}. For the stereochemical assignment, see below under preparation of *trans*-**6**. Further characterization of *cis*-**6** was obtained by hydrolysis and hydrogenation (PtO_2/H_2) to the known *cis*-4-methoxycyclohexanol.[12]

***trans*-1-Acetoxy-4-methoxy-2-cyclohexene (*trans*-6).** To a stirred solution of bis[(4-methoxy-η^3-1,3-cyclohexenyl)palladium chloride] (**1**) (1.50 g, 2.96 mmol) in acetic acid (6 mL) at 20 °C was added a solution–suspension of AgOAc (1.18 g, 7.1 mmol) in acetic acid (18 mL). The mixture was stirred for 20 min, and then a solution of *p*-benzoquinone (1.27 g, 11.8 mmol) in acetic acid (10 mL) was added. The reaction mixture, which turned dark brown, was stirred at room temperature for 4 h. The reaction mixture was diluted with 15 mL of saturated NaCl solution and extracted with 4 × 50 mL of pentane/ether (90:10). The combined extracts were washed with water (50 mL), saturated Na_2CO_3 (3 × 20 mL), and dried ($MgSO_4$). Evaporation of the solvent gave 750 mg (75%) of *trans*-**6** (>98% trans): ^{1}H NMR δ 6.1–5.7 (m, 2 H, CH=CH), 5.31 (m, 1 H, *CH*—OAc), 3.83 (m, 1 H, CH—OMe) 3.38 (s, 3 H, OMe), 2.05 (s, 3 H, OAc), 2.1 (m, 2 H, CH_eCH_e, 1.6 (m, 2 H, CH_aCH_a); IR (CCl_4) 2945, 2935, 2815, 1735, 1370, 1230, 1200 (br), 1086, 1030 cm^{-1}. The stereochemical assignment is made from the ^{1}H NMR spectrum and is based on the fact that the allylic protons in 1,4-disubstituted 2-cyclohexenes lie further downfield for the trans isomer then for the cis isomer.[6a,6d,10,11] Also the spectra of the cis and trans isomers differ in the region 1.0–2.0 ppm. The signals of the CH_2–CH_2 protons appear at 2.1 and 1.7 ppm for *trans*-**6** but are concentrated at 1.8 for *cis*-**6**.[6a,10] Further characterization of *trans*-**6** was obtained by hydrolysis and hydrogenation (PtO_2/H_2) to the known *trans*-4-methoxycyclohexanol.[9,12]

***trans*-6 from 1 Using Maleic Anhydride in Place of *p*-Benzoquinone.** The reaction was carried out according to method B as described for *trans*-**7**, but *p*-benzoquinone was replaced with maleic anhydride: complex **1** (171 mg, 0.34 mmol), acetone (10 mL), AgOAc (140 mg, 0.83 mmol), acetic acid (3 mL), and maleic anhydride (73 mg, 0.74 mmol), 3 h, 20 °C, yield 52 mg (46%) of *trans*-**6** (>95% trans) contaminated with 8% of 3-acetoxy-4-methoxycyclohexene.

***cis*-1-Acetoxy-4-methoxy-2-cycloheptene (*cis*-7).** Method A was used. Complex **2** (123 mg, 0.23 mmol), $LiOAc \cdot 2H_2O$ (469 mg, 4.6 mmol), LiCl (19 mg, 0.45 mmol), and *p*-benzoquinone (100 mg, 0.93 mmol) were stirred in acetic acid (3 mL) for 2 h at room temperature. Workup as above afforded 43 mg (51%) of a mixture of *cis*-**7** (>98% cis) and *cis*-1,4-diacetoxy-2-cycloheptene[6a,b] in a ratio of 67:33. The products were separated by HPLC (ethyl acetate/hexane = 10/90) to give pure samples.

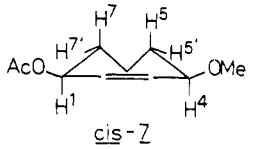
***cis*-7**: ^{1}H NMR δ 5.80 (m, J_{olefin} = 13 Hz, 1 H, HC=), 5.64 (m, J_{olefin} = 13 Hz, 1 H, HC=), 5.32 (br d, J = 10 Hz, 1 H, *H*C—OAc), 3.83 (br d, J = 11 Hz, 1 H, *H*C—OMe), 3.34 (s, 3 H, OMe), 2.06 (s, 3 H, OAc), 2.1–1.3 (m, 6 H, CH_2); IR (neat) 2930, 1738, 1372, 1245, 1030 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.07; H, 8.63.

***trans*-1-Acetoxy-4-methoxy-2-cycloheptene (*trans*-7).** To a suspension of complex **2** (150 mg, 0.28 mmol) in acetone (7 mL) under nitrogen at room temperature was added AgOAc (100 mg, 0.6 mmol). After stirring the mixture at room temperature for 20 min, the solution was filtered through a glass filter under nitrogen. The solid was washed with acetone (2 mL). The solvent was removed in vacuo, affording yellow crystals. To the (π-allyl)palladium acetate complex was added a solution of *p*-benzoquinone (121 mg, 1.1 mmol) in acetic acid (2.5 mL under nitrogen, and the mixture was stirred at room temperature for 6 h. Workup as above afforded 63 mg (61%) of a mixture of *trans*-**7** and *cis*-**7** in a ratio of 72:28.

***trans*-7**: ^{1}H NMR δ 5.88 (m, 1 H, HC=), 5.76 (m, 1 H, HC=), 5.41 (m, 1 H, *H*C—OAc), 3.92 (br d, J = 7 Hz, 1 H, *H*C—OMe), 3.34 (s, 3 H, OMe), 2.06 (s, 3 H, OAc), 2.1–1.3 (m, 6 H, CH_2).

The stereochemical assignment of *cis*-**7** and *trans*-**7** follows from their ^{1}H NMR spectra.[10] Compound *cis*-**7** show large J_{17} and J_{45} coupling constants due to a locked conformation in which the substituents are quasiequatorial. For *trans*-**7** two conformations are in equilibrium with



cis-7

$J_{1,7}$ = 10 Hz
$J_{4,5}$ = 11 Hz

one another, and as a result, J_{17} and J_{45} are much smaller. Also there appears to be a general trend[6b,10,11] in 1,4-dioxysubstituted cyclo-2-alkenes that the CH–O protons appear at lower field for the trans isomer than for the cis isomer.

***trans*-1-Acetoxy-4-methoxy-2-cyclooctene (*trans*-8)** was prepared according to method B as described for *trans*-**7**: complex **3** (281 mg, 0.50 mmol), acetone (15 mL), AgOAc (184 mg, 1.1 mmol), *p*-benzoquinone (216 mg, 2 mmol), acetic acid (5 mL), 4 h, 20 °C, yield 135 mg (68%) of essentially pure *trans*-**8** (>98% trans); ^{1}H NMR δ 5.72 (m, 1 H, C*H*—OAc), 5.68 (m, J = 6.0, 11 Hz, 1 H, =C*H*—CHOAc), 5.55 (m, J = 6.0, 11 Hz, 1 H, =C*H*—CHOMe), 4.27 (m, 1 H, C*H*—OMe), 3.35 (s, 3 H, OMe), 2.06 (s, 3 H, OAc), 1.9–1.4 (m, 8 H, CH_2); IR (neat) 2930, 1738, 1370, 1245, 1025 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.58; H, 9.01.

Further characterization of *trans*-**8** was obtained by hydrolysis and methylation (NaH, CH_3I, and THF) to the known[11] *trans*-1,4-dimethoxy-2-cyclooctene. Comparison of the ^{1}H NMR spectrum of the dimethyl ether obtained from *trans*-**8** with those reported for *cis*- and *trans*-1,4-dimethoxy-2-cyclooctene[11] established the trans stereochemistry (>98% trans).

(*E*)-(*R,*R**)-2-Acetoxy-5-methoxy-3-hexene ((*R**,*R**)-9) from Complex 4.** Method A was used: complex **4** (255 mg, 0.5 mmol), acetic acid (6 mL), $LiOAc \cdot 2H_2O$ (1.02 g, 10 mmol), LiCl (42 mg, 1 mmol), *p*-benzoquinone (216 mg, 2 mmol), 48 h, 20 °C, yield 100 mg (58%) of a mixture of (*R**,*R**)-**9** (>87% *R**,*R**; >95% *E* according to ^{1}H NMR) and (*E*)-4-acetoxy-5-methoxy-2-hexene in a ratio of 87:13.

(*R,*R**)-9**: ^{1}H NMR δ 5.67 (dd, J = 5, 15 Hz, 1 H, =C*H*—CHOAc), 5.56 (dd, J = 6, 15 Hz, 1 H, =C*H*—CHOMe), 5.36 (quin, J = 6 Hz, 1 H, C*H*—OAc), 3.72 (quin, J = 6 Hz, 1 H, C*H*—OMe), 3.264 (s, 3 H, OMe), 2.05 (s, 3 H, OAc), 1.318 (d, J = 6.5 Hz, 3 H, *Me*—CHOAc), 1.227 (d, J = 6.5 Hz, 3 H, *Me*—CHOMe); IR (neat) 2980, 2930, 1740, 1370, 1240 cm^{-1}.

The relative configuration of (*R**,*R**)-**9** was established by hydrolysis and methylation (CH_3I, NaH, and THF) which gave (*E*)-*dl*-2,5-dimethoxy-3-hexene. Authentic samples of (*E*)-***dl***- and (*E*)-*meso*-2,5-dimethoxy-3-hexene were prepared by methylation of (*E*)-***dl***- and (*E*)-

(31) Complexes **4** and **5** have previously been prepared from the corresponding (2-chloro-η^3-3,5-hexenyl)palladium complexes by solvolysis in methanol, but the relative configuration was not assigned: Lukas, J.; Leeuwen, P. W. N. M.; Volger, H. C.; Kouwenhoven, A. P. *J. Organomet. Chem.* **1973**, *47*, 153.

meso-3-hexene-2,5-diol, respectively, which were obtained according to ref 6b. The dimethyl ethers differ in their ^{1}H NMR spectra. **(*E*)-dl-2,5-Dimethoxy-3-hexene**: ^{1}H NMR δ 5.514 (dd, 2 H, CH=CH), 3.74 (m, 2 H, CH—O), 3.288 (s, 6 H, OMe), 1.241 (d, 6 H, CH_3). **(*E*)-*meso*-2,5-dimethoxy-3-hexene**: ^{1}H NMR δ 5.526 (dd, 2 H, CH=CH), 3.74 (m, 2 H, CH—O), 3.271 (s, 6 H, OMe), 1.257 (d, 6 H, CH_3).

(*E*)-4-Acetoxy-5-methoxy-2-hexene: ^{1}H NMR (peaks distinguishable from (*R*,R**)-**9**) δ 3.38 (s, 3 H, OMe), 2.08 (s, 3 H, OAc), 1.71 (br d, J = 6.0 Hz, 3 H, *Me*—CH=), 1.11 (d, J = 6.5 Hz, 3 H, *Me*—CHOMe).

Mixture of (*E*)-(*R*,S)- and (*E*)-(*R*,R**)-2-Acetoxy-5-methoxy-3-hexene ((*R*,S**)-9:(*R*,R**)-9 = 78:22) from Complex 4.** Method B as described for *trans*-**7** was used: complex **4** (255 mg, 0.5 mmol), acetone (14 mL), AgOAc (184 mg, 1.1 mmol), *p*-benzoquinone (216 mg, 2 mmol), acetic acid (5 mL), 30 h, 20 °C, yield 62 mg (36%) of (*R*,S**)-**9** and (*R*,R**)-**9** in a ratio of 78:22 contaminated with 7% (*E*)-4-acetoxy-5-methoxy-2-hexene. Compounds (*R*,S**)-**9** and (*R*,R**)-**9** were exclusively of *E* double bond configuration.

(*R*,S)-9**: ^{1}H NMR δ 5.67 (dd, J = 5, 15 Hz, 1 H, =C*H*—CHOAc), 5.56 (dd, J = 6, 15 Hz, 1 H, =*CH*—CHOMe), 5.36 (quin, J = 6 Hz, 1 H, *CH*—OAc), 3.72 (quin, J = 6 Hz, 1 H, CH—OMe), 3.260 (s, 3 H, OMe), 2.05 (s, 3 H, CH_3), 1.324 (d, J = 6.5 Hz, 3 H, *Me*—CHOAc), 1.234 (d, J = 6.5 Hz, 3 H, *Me*—CHOMe); IR (neat) 2980, 2930, 1740, 1370, 1240 cm^{-1}.

Mixture of (*R*,S)-9 and (*R*,R**)-9 (72:28) from a Mixture of Complexes 5 and 4 (82:18).** Method A was used: complex **5** (containing 18% of **4**) (190 mg, 0.37 mmol), acetic acid (5 mL), LiOAc·2H_2O (765 mg, 7.5 mmol), LiCl (31.5 mg, 0.75 mmol), *p*-benzoquinone (162 mg, 1.5 mmol), 22 h, 20 °C, yield 73 mg (57%) of (*R*,S**)-**9** and (*R*,R**)-**9** in a ratio of 72:28 contaminated with 14% of (*E*)-4-acetoxy-5-methoxy-2-hexene. Compounds (*R*,S**)-**9** and (*R*,R**)-**9** were exclusively of *E* double bond configuration.

Mixture of (*R*,R)-9 and (*R*,S**)-9 (85:15) from a Mixture of Complexes 5 and 4 (82:18).** Method B as described for *trans*-**7** was used: complex **5** (containing 18% of **4**) (220 mg, 0.43 mmol), acetone (12 mL), AgOAc (150 mg, 0.9 mmol), acetic acid (4.5 mL), *p*-benzoquinone (187 mg, 1.7 mmol), 19 h, 20 °C, yield 59 mg (40%) of (*R*,R**)-**9** and (*R*,S**)-**9** in a ratio of 85:15 contaminated with 2% of (*E*)-4-acetoxy-5-methoxy-2-hexene. Compounds (*R*,R**)-**9** and (*R*,S**)-**9** were exclusively of *E* double bond configuration.

(*R*)-(*E*)-3-Acetoxy-1-phenyl-1-butene ((R)-11). Method A was used: complex **10** ([α]$^{20}_D$ −453° (*c* 0.67, $CHCl_3$), 64% ee)[15] (131 mg, 0.24 mmol), acetic acid (3 mL), LiOAc·2H_2O (530 mg, 5.2 mmol), LiCl (22.2 mg, 0.53 mmol), *p*-benzoquinone (96 mg, 0.89 mmol), 21 h, 20 °C, yield 34 mg (37%) of (*R*)-**11** ([α]$^{20}_D$ +59.0° (*c* 0.93, CCl_4), 44% ee). For the specific rotation of (*R*)-**11**, see ref 15b. ^{1}H NMR δ 7.4–7.2 (m, 5 H, Ph), 6.60 (d, J = 16.0 Hz, 1 H, =CH), 6.19 (dd, J = 6.8, 16.0 Hz, 1 H, =CH), 5.53 (quin, J = 6.5 Hz, 1 H, CH—O), 2.07 (s, 3 H, OAc), 1.41 (d, J = 6.5 Hz, 3 H, CH_3).

(*S*)-(*E*)-3-Acetoxy-1phenyl-1-butene ((*S*)-11). Method B as described for *trans*-**7** was used: complex **10** ([α]$^{20}_D$ −453°, 64% ee)[15] (131 mg, 0.24 mmol), acetone (10 mL), AgOAc (87 mg, 0.52 mmol), acetic acid (2.5 mL), *p*-benzoquinone (100 mg, 0.93 mmol), 12 h, 20 °C, yield 37 mg (41%) of (*S*)-**11** ([α]$^{20}_D$ −50.5° (*c* 0.99, CCl_4), 37% ee).

Compound *cis*-12. To a stirred solution of complex **1** (506 mg, 1 mmol) in THF (30 mL) under nitrogen at room temperature was added, 1,2-bis(diphenylphosphino)ethane (797 mg, 2.0 mmol). After 15 min of stirring, 30 mL of 0.2 M sodium acetylacetonate (6 mmol) in THF was added. The mixture was stirred at room temperature for 16 h and then filtered. Ether (10 mL) and 10 mL of 2 M $NaHCO_3$ were added, and the organic phase was separated. The aqueous phase was extracted once with ether (20 mL). The combined organic phases were washed with water and brine and then dried ($MgSO_4$). Bulb-to-bulb distillation afforded 476 mg of a fraction containing 80% *cis*-**12** (>98% cis, yield 90%). Purification by flash column chromatography (silica, ethyl acetate/hexane = 30/70) afforded a pure sample of *cis*-**12**: ^{1}H NMR δ 5.90 (m, 1 H, CH=), 5.59 (m, 1 H, CH=), 3.69 (d, J = 10.5 Hz, 1 H, *CH*-($COCH_3$)$_2$), 3.68 (m, 1 H, CH—O), 3.36 (s, 3 H, CH_3O), 2.97 (m, 1 H, CH), 2.205 (s, 3 H, CH_3), 2.201 (s, 3 H, CH_3), 1.9—1.2 (m, 4 H, CH_2CH_2); ^{13}C NMR δ 203.3, 203.0, 131.2, 129.4, 73.9, 72.7, 56.1, 35.8, 30.3, 29.7, 25.9, 22.5; IR (CCl_4) 2920, 1700, 1360, 1150, 1100, 1085, 910 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.71; H, 8.54.

Mixture of *cis*-12 and *trans*-12. To a solution of thallium acetylacetonate (439 mg, 1.45 mmol) in dry benzene (70 mL) was added a solution of complex **1** (348 mg, 0.69 mmol) in benzene (10 mL). The mixture was stirred for 20 min, and the precipitated thallium chloride was removed by filtration. The solution was concentrated to 30 mL, and carbon monoxide was bubbled through. The solution was stirred under an atmosphere of carbon monoxide for 72 h and then filtered. The solvent was removed in vacuo, and the residue which contained a lot of (4-methoxy-η^3-1,3-cyclohexenyl)palladium acetylacetonate was purified by column flash chromatography. The fractions containing addition products were collected to give 37 mg (13%) of a 4:1 mixture of *cis*-**12** and *trans*-**12**. The isomers were separated by HPLC (silica, EtOAc/hexane = 70/30).

***trans*-12**: ^{1}H NMR δ 5.85 (m, 1 H, CH=), 5.52 (m, 1 H, CH=), 3.8 (m, 1 H, CH—O), 3.56 (d, J = 10.0 Hz, 1 H, *CH*($COCH_3$)$_2$), 3.36 (s, 3 H, OMe), 3.06 (m, 1 H, CH) 2.194 (s, 3 H, CH_3), 2.186 (s, 3 H, CH_3), 2.0–1.4 (m, 4 H, CH_2CH_2).

***trans*-1-Methoxy-4-(trifluoroacetoxy)-2-cyclohexene (*trans*-15).** To a suspension of complex **1** (150 mg, 0.30 mmol) in acetic acid (0.6 mL) was added a solution–suspension of silver trifluoroacetate (154 mg, 0.70 mmol) in acetic acid (1.8 mL). After stirring the mixture at 20 °C for 20 min, trifluoroacetic acid (135 mg, 1.18 mmol) was added followed by a solution of *p*-benzoquinone (127 mg, 1.18 mmol) in acetic acid (1 mL). The reaction mixture, which darkened, was stirred at 20 °C for 30 min. Pentane (20 mL) was added under stirring, and the precipitates were separated and washed with pentane (5 mL). The combined organic phases were washed successively with 5 mL of saturated NaCl solution, 5 mL of water, 5 mL of saturated Na_2CO_3 solution, 5 mL of water, and 5 mL of saturated NaCl solution and finally dried ($MgSO_4$). Evaporation of the solvent afforded 102 mg (80%) of a 82:18 mixture of *trans*-**15** and *trans*-**6**.

***trans*-15.** ^{1}H NMR δ 6.13 (m, 1 H, CH=), 5.85 (m, 1 H, CH=), 5.49 (m, 1 H, CH—OOCCF$_3$), 3.84 (m, 1 H, CH—O), 3.39 (s, 3 H, OMe), 2.30–2.0 (m, 2 H, CH_e—CH_e), 1.82–1.50 (m, 2 H, CH_a–CH_a). Further characterization of *trans*-**15** was obtained by hydrolysis to the known *trans*-4-methoxy-2-cyclohexenol (vide supra). ^{1}H NMR analysis of the alcohol showed that it was >98% trans.

Acknowledgment. We thank the Swedish Natural Science Research Council for financial support. We are grateful to Dr. Tamio Hayashi for a gift of complex **10** and for discussions.