Asymmetric Allyl–Metal Bonding in Substituted (η^3-Allyl)palladium Complexes: X-ray Structures of *cis*- and *trans*-4-Acetoxy-[η^3-(1,2,3)-cyclohexenyl]palladium Chloride Dimers

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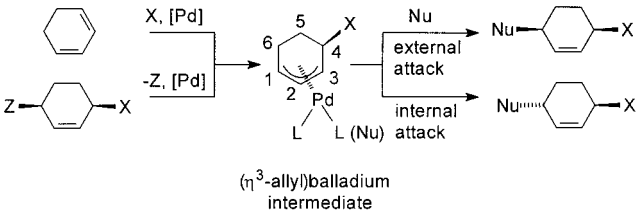
Abstract: Enantiomerically pure *cis* and *trans* isomers of 4-acetoxy-[η^3-(1,2,3)-cyclohexenyl]palladium chloride dimers (*cis*-**1** and *trans*-**1**) were prepared from enantiomerically pure *trans*-1-acetoxy-4-chloro-2-cyclohexene. X-ray analyses of these complexes show that in the *trans* complex (*trans*-**1**) the six-membered ring prefers a chair conformation, whereas in the *cis* complex (*cis*-**1**) the cyclohexenyl ring has a boat conformation. According to the X-ray structure of *trans*-**1** the Pd–C3 bond is *shorter* than the other allylic terminal palladium–carbon bond (Pd–C1). On the other hand, in *cis*-**1** the Pd–C3 and Pd–C1 bond lengths are identical within the experimental error. The calculated structures (B3PW91/LANL2DZ + P) of *trans*-**1** and *cis*-**1** also display differences in the allylpalladium bonding. The asymmetric allylpalladium bonding in *trans*-**1** is explained on the basis of $\pi-\sigma^*$ electronic interactions between the 4-acetoxy substituent and the allyl–metal moiety.

Keywords: catalysts · density functional calculations · palladium · substituent effects · structure elucidation ·

Introduction

Catalytic transformations involving (η^3-allyl)palladium intermediates have been widely applied in a number of important chemical processes including allylic substitution reactions and the oxidation of allenes, alkenes, and conjugated dienes.[1, 2] Determination of the X-ray structures of various (η^3-allyl)-palladium complexes have provided invaluable help for a deeper understanding of the mechanism of these catalytic reactions.[3, 4] However, structural data on the (η^3-allyl)palladium intermediates of the oxidative transformations is rather scarce.[5] In particular, there is a remarkable lack of available direct experimental structural data for 4-oxy-[η^3-(1,2,3)-cyclohexenyl]palladium complexes, which are the key intermediates in palladium-catalyzed regio- and stereoselective 1,4-oxidation of conjugated dienes (Scheme, X = OR, OCOR′).[2a–c, 6, 7] Theoretical studies have shown that these complexes are characterized by unusual structural features, such as asymmetric Pd–C bonding, which also explains the regioselectivity of the nucleophilic attack on the (η^3-allyl)palladium intermediates of the catalytic reactions.[8, 9]

Although, the relative configuration of certain 4-oxy-[η^3-(1,2,3)-cyclohexenyl]palladium complexes has been established by indirect methods[2a–c] and on the basis of NMR measurements, [6d–f] explicit structural evidence from X-ray crystallography is highly desirable. X-ray structural data would also be of importance for confirmation of the previously proposed electronic effect by the 4-oxy substituent on the bond lengths and reactivity.



Scheme 1. General types of palladium-catalyzed processes proceeding through 4-substituted (η^3-allyl)palladium intermediates.

In the present paper we report the X-ray crystal structure and density functional theory (DFT) geometry for *cis* and *trans* isomers of 4-acetoxy-[η^3-(1,2,3)-cyclohexenyl]palladium chloride dimers (see Figure 1) and discuss their structural features and reactivity.

Results and Discussion

Experimental results: Dimeric enantiomerically pure (η^3-allyl)palladium complexes *trans*-**1** and *cis*-**1** were prepared from (1*S*,4*S*)-*trans*-1-acetoxy-4-chloro-2-cyclohexene (**2**)[10] by

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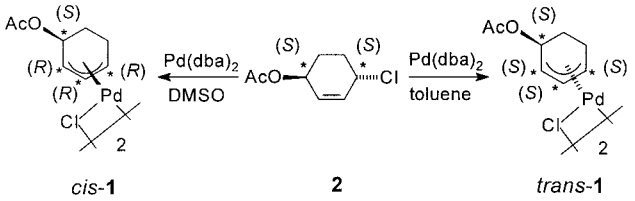
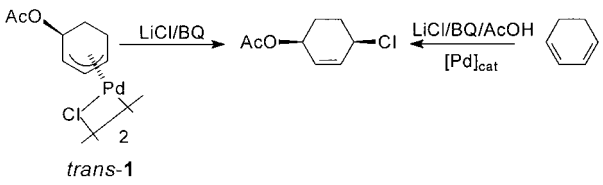
using the stereodivergent Kurosawa method[11] (Scheme 2). In this procedure palladium(0) from $Pd(dba)_2$ displaces an allylic chloride with either retention or inversion of configuration depending on the solvent. The chloroacetate precursor **2** was obtained from (1*R*,4*S*)-4-acetoxy-2-cyclohexanol as described previously.[10a]



Scheme 2. Stereochemistry of the oxidative addition of (1*S*,4*S*)-*trans*-1-acetoxy-4-chloro-2-cyclohexene to palladium as a function of the solvent polarity.

The ^1H and ^{13}C NMR spectra of our primary target compound *trans*-**1** are identical to those of the key intermediate of the palladium-catalyzed 1,4-chloroacetoxylation of 1,3-cyclohexadiene. [10b] Reaction of this complex with LiCl, in the presence of benzoquinone readily provides *cis*-1-acetoxy-4-chloro-2-cyclohexene, which is also the product obtained from catalytic 1,4-chloroacetoxylation of 1,3-cyclohexadiene (Scheme 3).[2a] Complex *cis*-**1** is not supposed to be formed as an intermediate in palladium-catalyzed 1,4-oxidation reactions, however, it may occur as an intermediate in allylic substitution reactions.[10a] The primary purpose for the preparation of *cis*-**1** is that the X-ray structure of this complex may serve as a suitable reference for analysis of the bonding features of 4-oxy-allylpalladium complexes.



Scheme 3. Formation of *cis*-**1**-acetoxy-4-chloro-2-cyclohexene by a stoichiometric reaction from *trans*-**1** and by palladium-catalyzed chloracetoxylation of 1,3-cyclohexadiene.

*X-ray studies of trans-**1** and cis-**1***: The crystals of the enantiomerically pure bis[*trans*- and *cis*-4-acetoxy-η^3-(1,2,3)-cyclohexenyl]palladium chloride dimers (**1**) were suitable for X-ray analysis (Figure 1). We believe that the failure of the previous X-ray analyses of racemic 4-substituted allylpalladium complexes is due to the presence of two diastereomers in the dimer (i.e. racemic dimer and meso dimer) causing crystal disorder, which seriously hamper the X-ray structure determination.

*Crystal data for trans-**1***: $[C_{16}H_{22}O_4Cl_2Pd_2]$:[10c] $M_r = 562.05$, monoclinic, $a = 11.842(3)$, $b = 6.509(1)$, $c = 13.023(3)$ Å, $\beta = 109.43(3)^\circ$, $U = 946.7(4)$ Å^3, space group $P2_1$ (no. 4), $Z = 2$, $T = 150(1)$ K, $\mu(Mo_{K\alpha}) = 2.20$ mm^{-1}, absolute structure: Flack parameter $= -0.09(9)$, 5679 reflections measured, 3167 unique ($R_{int} = 0.1090$), $R1 = 0.0459$, $wR2 = 0.0799$ for 1653 observed reflections [$I > 2s(I)$]. Crystal dimensions: $0.03 \times 0.05 \times 0.15$ mm^3. Average I/S 3.8 for all data.

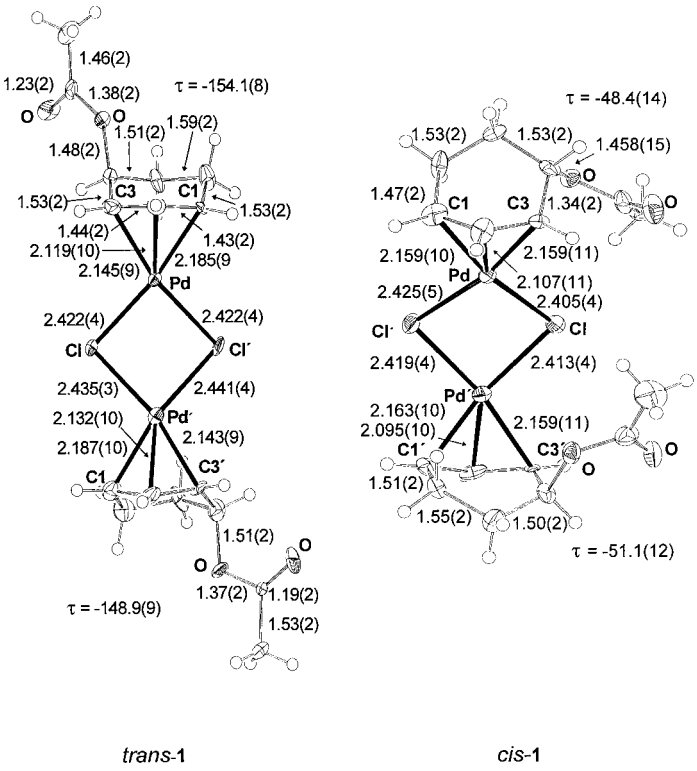


Figure 1. X-ray structure of (η^3-allyl)palladium complexes *trans*-**1** and *cis*-**1** (bond lengths in Å, angles in °). τ refers to the O-C4-C3-Pd dihedral angle.

*Crystal data for cis-**1***: $[C_{16}H_{22}O_4Cl_2Pd_2]$: $M_r = 562.05$, orthorhombic, $a = 8.3327(9)$, $b = 10.2198(14)$, $c = 21.873(3)$ Å, $U = 1862.7(4)$ Å^3, space group $P2_12_12_1$ (no. 19), $Z = 4$, $T = 150(1)$ K, $\mu(Mo_{K\alpha}) = 2.23$ mm^{-1}, absolute structure: Flack parameter $= -0.04(10)$, 14718 reflections measured, 3695 unique ($R_{int} = 0.1913$), $R1 = 0.0468$, $wR2 = 0.0718$ for 1672 observed reflections [$I > 2s(I)$]. Crystal dimensions: $0.03 \times 0.03 \times 0.22$ mm^3. Average I/S = 2.0 for all data. The data were collected on a Stoe image-plate diffractomer, and the structures was solved by direct methods and refined by full-matrix least-squares on F^2.[10d–f]

Chlorodimers *trans*-**1** and *cis*-**1** have slightly distorted C_2 symmetry (Figure 1). Analogous chloro-bridged dimers usually display clean C_2 or higher symmetries; however, in *trans*-**1** and *cis*-**1** the conformation of the acetate groups is different, which leads to minor deviations in the otherwise symmetry-equivalent geometrical parameters. The OAc group of *trans*-**1** and *cis*-**1** have *S* configuration and they occupy *trans* and *cis* positions, respectively, to the palladium atom. This confirms that the oxidative addition to palladium (Scheme 2) proceeds by a *cis* mechanism in toluene and by a *trans* mechanism in DMSO without affecting the configuration of the OAc functionality. These stereochemical pathways were previously established by Kurosawa and co-workers[11] in the oxidative addition of palladium to other allylic cyclohexenyl chlorides.

The cyclohexenyl rings in the dimeric (η^3-allyl)palladium complex *trans*-**1** possess a chair conformation rendering the

OAc groups to an axial position. However, in *cis*-**1** the six-membered rings have a boat conformation and the OAc groups are in axial position. Interestingly, alteration of the stereochemistry in analogous [η^3-(1,2,3)-cyclohexenyl]palladium complexes leads to a similar change from chair to boat conformation.[3d]

The presence of the OAc functionality does not lead to twist of the cyclohexenyl rings; the C1, C3, C4, and C6 carbons are all in the same plane. The dimer *trans*-**1** shows a bent bridge configuration[4] with a bending angle [measured as Pd-(Cl-Cl)-Pd] of 148.9(2)°, where the allyl moieties are *cis*-oriented and bent away from one another. This bridge bending angle is rather usual for analogous chlorodimers.[4] On the other hand *cis*-**1** has a bent bridge configuration with a bending angle of 148.1(2)°, in which the allyl moieties are *trans*-oriented. Although, the bent bridge configuration with *cis*-oriented allyl moieties is rather usual for chlorodimers of allylpalladium complexes, as far as we know bent bridge configuration for *trans*-oriented allyl groups has not yet been reported.

Another important structural feature of *trans*-**1** is the asymmetric allyl–palladium bonding (Table 1). The palladium–carbon bond to the C3-allylic terminal position (Pd–C3 2.145(9) and Pd–C3′ 2.143(9) Å) is shorter than the other terminal palladium–carbon bond (Pd–C1 2.185(9), Pd–C1′ 2.187(10) Å). Although, the difference in bond lengths (0.042 Å) is rather small in relation to the experimental error of each bond[12] (0.009 Å) there is a significant asymmetry in the allyl–palladium bonding (Table 1), which is also displayed by the calculated DFT geometrical parameters (vide infra). In contrast to *trans*-**1**, *cis*-**1** does *not* show a contracted Pd–C3 bond compared to the Pd–C1 bond but the Pd–C3 and Pd–C1 bond lengths are identical within the experimental error. The different Pd–C bonding in *trans*-**1** and *cis*-**1** clearly indicates the stereoelectronic nature of the interactions between the acetate functionality and the allyl–palladium system.

Table 1. Selected geometrical parameters [Å] of *trans*-**1** and *cis*-**1**.

	C1–Pd	C3–Pd	Δ_{1-3}[a]	C1′–Pd′	C3′–Pd′	$\Delta_{1'-3'}$[a]
X-ray						
trans-**1**	2.185(9)	2.145(9)	0.040(13)	2.187(10)	2.143(9)	0.044(13)
cis-**1**	2.159(10)	2.159(11)	0.000(15)	2.163(10)	2.159(11)	0.004(15)
DFT						
trans-**1**	2.160	2.133	0.027	2.158	2.137	0.021
cis-**1**	2.125	2.140	−0.015	2.127	2.139	−0.012

[a] Difference between C1–Pd and C3–Pd as well as between C1′–Pd′ and C3′–Pd′.

Theoretical studies: A number of theoretical studies were published recently in which the structure and reactivity of analogues of **1** were discussed.[8, 9] However, these calculations were focused on monomeric allylpalladium chlorides in order to reduce the computational efforts required. For the first time, we publish here a theoretical calculation for a dimeric chloro complex *trans*-**1** and *cis*-**1** (Figure 2).

Computational methods: The geometries were fully optimized by employing a Becke-type[13a] three-parameter density functional model B3PW91. This so-called hybrid functional includes the exact (Hartree–Fock) exchange, the gradient-corrected exchange functional of Becke and the more recent correlation functional of Perdew and Wang.[13b] All calculations were carried out using a double-ζ(DZ) + P basis constructed from the LANL2DZ basis[13c–e] by adding one set of d-polarization functions to the heavy atoms (exponents: C 0.63, O 1.154, Cl 0.514) and one set of diffuse d-functions on palladium (exponent: 0.0628). All calculations were carried out by employing the Gaussian 94 program package.[14]

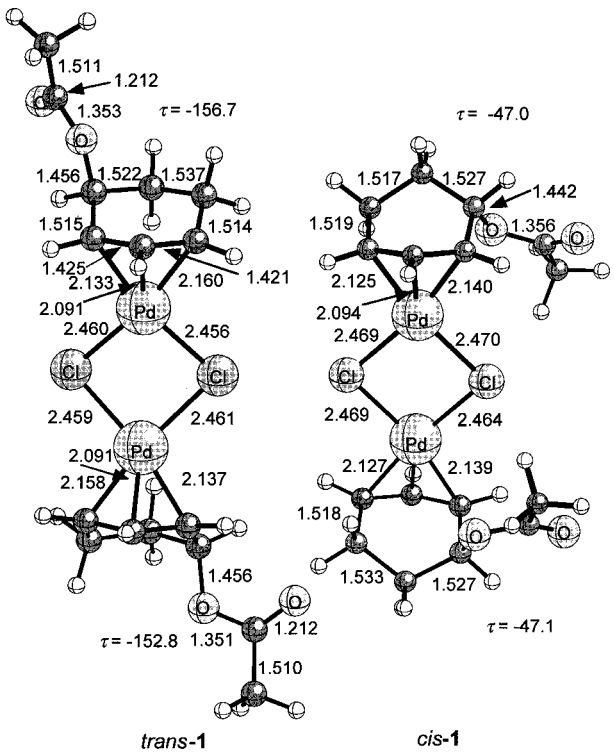


Figure 2. Calulated (B3PW91/LANL2DZ + P) structure of (η^3-allyl)palladium complexes *trans*-**1** and *cis*-**1** (bond lengths in Å, angles in °). τ refers to the O-C4-C3-Pd dihedral angle.

Because of the different conformation of the acetate groups, *trans*-**1** possesses C_1 symmetry. By rotation of the acetate groups two C_2 symmetrical structures could be obtained. However, the energy of these C_2 symmetrical complexes differ only by 0.3 kcal mol^{-1} from that of *trans*-**1**, indicating that the distortion of the acetate groups is induced by weak nonbonding interactions. The geometry calculated for *trans*-**1** and *cis*-**1** is rather similar to the analogous monomeric structure obtained at the same level of theory. Interestingly, the calculations for the monomeric forms[9] predicted a larger stability for the chair form than for the boat form in *trans*-**1**, while in case of *cis*-**1** the boat form was predicted to be more stable than the chair form. These conformational preferences are clearly verified by the above X-ray studies.

The geometrical parameters calculated for *trans*-**1** and *cis*-**1** are in good agreement with the values obtained by the X-ray studies (c.f. Figure 1 and 2). Except for the Pd–Cl bond lengths in *cis*-**1** the deviation between the measured and calculated parameters is within 0.03 Å, which is the usual

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accuracy for such DFT calculations. The calculated structure of *trans*-**1** also displays the asymmetrical allyl–palladium bonding; the Pd–C3 bond (2.13 Å) is shorter than the Pd–C1 bond (2.16 Å). The Pd–C1 and Pd–C3 bond lengths in *cis*-**1** are similar, with the Pd-C3 being slightly longer than the Pd–C1 bond. On the other hand, in the experimental structure of *cis*-**1** the Pd–C1 and Pd–C3 bond lengths are identical within the experimental error. The minor deviations between the experimental and calculated Pd–C bond lengths in *cis*-**1** can probably be ascribed to the slight overestimation of the nonbonding Pd–OAc repulsive interactions by the DFT/DZ + P theoretical model. This steric interaction does not appear in *trans*-**1**, providing a good agreement between the geometries determined by X-ray structural analysis and DFT calculations.

The asymmetric allyl–palladium bonding in *trans*-**1** is characteristic for $\pi-\sigma^*$ type MO interactions that occur between polar 4-substituents and palladium in [η^3-(1,2,3)allyl]palladium complexes. This electronic interaction was reviewed in several recent publications[8, 9] pointing out its importance on the structure and reactivity of the allylpalladium complexes. According to these studies[8, 9] the MO interactions in 4-acetoxy-substituted [η^3-(1,2,3)allyl]palladium complexes involve transfer of the electron density from the HOMO (d_π) of the allylpalladium fragment as well as from an orthogonal lone-pair orbital (n_d) of palladium into the unfilled σ*(C–O) MO of the C4–OAc bond. The electron-transfer is most efficient when the OAc functionality is in antiperiplanar conformation ($\tau = 180^\circ$, where τ denotes the O-C4-C3-Pd dihedral angle), while the electronic effects can be shut-off by rotating the OAc group by 90° ($\tau = 90^\circ$). In the case of unhindered rotation of the OAc functionality, such as in acyclic complexes, the antiperiplanar conformer is thermodynamically more stable than the $\tau = 90^\circ$ conformer, indicating that the electronic effects involve thermodynamic stabilization of the complex.[9]

Relevance of the present X-ray studies for the chemistry of the 4-substituted allylpalladium complexes

Structure and conformation of the complexes: Complex *trans*-**1** represents a particularly suitable species for investigation of the structural consequences of the above electronic interactions, since the hindered rotation due to the six-membered ring framework locks the conformation of the 4-OAc group. Furthermore, in the chair form the conformation of the OAc group ($\tau = -149 - 154^\circ$) stereoelectronically favors the $\pi-\sigma^*$ type interactions.[8] The present X-ray results provide for the first time direct evidence for the presence of these type of electronic effect in *trans*-**1**. The six-membered ring framework also restricts the OAc conformation in *cis*-**1**, however in the *cis* complex $\tau = -48 - 51^\circ$, which is less favorable for the electronic interactions. This is reflected by the palladium-carbon bonding in *cis*-**1**. In contrast to *trans*-**1**, the Pd–C1 and Pd–C3 bond lengths in *cis*-**1** are similar. Interestingly, in the chair form of the *cis* complex, $\tau = -93^\circ$ (calculated value from reference [9]) and therefore in this conformation the electronic interactions between the OAc functionality and the allylpalladium moiety are completely shut-off, which is probably the reason for the low thermodynamic stability of this conformer.

Implications for the regiochemistry of the nucleophilic attack: Since the nucleophilic attack on the allyl moiety involves Pd–C bond breaking, the asymmetric bonding in *trans*-**1** also prevents the attack at the C3 terminus, for which the Pd–C bond is relatively short and therefore strong. Accordingly, a very high level of regioselectivity can be obtained in catalytic transformations proceeding by nucleophilic attack on *trans*-**1**.[2b,c, 6a–c, 7] On the contrary, in *cis*-**1** the Pd–C1 and Pd–C3 bond lengths are similar, which leads to a low level of regiodifferentiation between the C1 and C3 termini in the nucleophilic attack. Indeed, it was shown[10a] that the regioselectivity is dramatically lowered in catalytic transformations involving nucleophilic attack on *cis*-**1** as intermediate.

Conclusions

The X-ray structure of *trans*-**1** displays asymmetric allyl–palladium bonding where the Pd–C3 bond is shorter than the the Pd–C1 bond. This asymmetry, which is also found by the DFT calculations, can be ascribed to $\pi-\sigma^*$ type electronic interactions. This study provides the first direct evidence for the presence of these electronic interactions in *trans*-**1**, and, in addition, establishes the structure of the key intermediates of the palladium-catalyzed 1,4-oxidation reaction.

Experimental Section

Preparation of bis(1*S*,2*S*,3*S*,4*S*){*trans*-4-acetoxy-[η^3-(1,2,3)-cyclohexenyl]-palladium} chloride (*trans*-1): (−)-*trans*-(1*S*,4*S*)-1-Acetoxy-4-chlorocyclohex-2-ene[10a] (0.22 g, 1.26 mmol) was added to a solution of $Pd(dba)_2$ (0.66 g 1.14 mmol) in toluene (5.7 mL) at room temperature. The resulting dark red mixture was stirred for 18 h. After the evaporation of toluene, the crude reaction mixture was purified by silica gel flash chromatography (CH_2Cl_2/diethyl ether (97/3)), yielding *trans*-**1** (0.31g, 96 %) as a yellow powder. Recrystallization from diethyl ether/CH_2Cl_2 gave crystals suitable for X-ray structural analysis. Spectral data for *trans*-**1** were in accordance with those reported in reference [10b]. $[\alpha]_D^{22} = +12.1$ ($c = 1.00$, $CHCl_3$).

Preparation of bis(1*R*,2*R*,3*R*,4*S*)-{*cis*-4-acetoxy-[η^3-(1,2,3)-cyclohexenyl]-palladium} chloride (*cis*-1): (−)-*trans*-(1*S*,4*S*)-1-Acetoxy-4-chlorocyclohex-2-ene[10a] (27.5 mg, 0.16 mmol) was added to a solution of $Pd(dba)_2$ (100 mg 0.17 mmol) in dry DMSO (1.0 mL) at room temperature. The resulting dark green solution was stirred for 2 h followed by addition of water. The aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic phases were washed with water (2 × 5 mL) and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by silica gel flash chromatography (CH_2Cl_2/deithyl ether (95/5)), yielding *cis*-**1** (38.8 mg, 88 %) as a yellow powder. Recrystallization from diethyl ether/CH_2Cl_2 gave crystals suitable for X-ray structural analysis. Spectral data for *cis*-**1** were in accordance with those reported in reference [9]. $[\alpha]_D^{22} = -212.4$ ($c = 0.41$, $CHCl_3$).

Acknowledgment

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