Highly Stereoselective Coordination of Monosubstituted η^3-Allyl Groups to Chiral (Bis(oxazoline))palladium Cations

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Stereoselectivity in coordination of various η^3-1-monosubstituted-allyl groups to chiral ((*R*,*R*)-bis(oxazoline))palladium(II) cations was investigated by ^{1}H NMR spectroscopy. When the η^3-1-phenylallyl, 1-(1-naphthyl)allyl, and 1-(silylcarbonyl)allyl groups coordinated to the palladium cation, two diastereomers arose in which the substituent occupied the syn position with respect to the η^3-allyl framework. In the major diastereomer (73–93% selectivity), the substituent at the allyl carbon was located so as to stagger the substituent at the oxazoline ring, while, in the minor diastereomer, the former eclipsed the latter. The diastereoselectivity increased in the sequence of the size of the substituent at allyl group: Ph < 1-naphthyl < $COSiMe_2Ph$. In the case of the η^3-1-(trimethylsilyl)allyl group coordination, the diastereomer in which the Me_3Si group occupied the anti position and staggered the ring substituent dominated (≥95% selectivity). A slow isomerization process between the three diastereomers of the (η^3-1-(trimethylsilyl)allyl)(bis(oxazoline))palladium complex was observed.

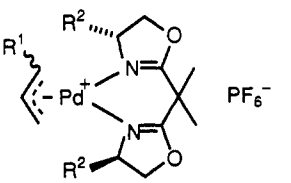
Introduction

Discrimination between enantiofaces of prochiral olefin and η^3-allyl ligands by a metal cation is an interesting and important problem. Cations having a chirality in an auxiliary[1,2] or at a metal center[3,4] have been utilized for this purpose. As for the η^3-allyl coordination, Faller developed the synthesis and application of chiral-at-metal (η^3-allyl)molybdenum cations.[3] Enantioface selection by η^3-allyl groups of the palladium cation coordinated by C_2-symmetric 2,3-bis(diphenylphosphino)butane was investigated by Bosnich and co-workers.[1a] In their study, high diastereoselectivity was attained in those complexes which contained at least two substituents on an allyl group but not in monosubstituted allyl (e.g. cinnamyl or crotyl) complexes.

Few other studies focused on highly diastereoselective coordination of the η^3-allyl group to palladium[1b-d] in spite of the great synthetic interest[5] in Pd-catalyzed asymmetric allylic alkylation and related reactions. Here we report that monosubstituted η^3-allyl groups can coordinate to chiral (bis(oxazoline))palladium cations with high diastereoselectivity. Our results may have some bearing on Pd-catalyzed asymmetric alkylation of 1,3-diphenylallyl acetate with C_2-symmetric 4,4′-disubstituted bis(oxazoline) and its analogs as chiral auxiliaries.[6,7]

Results and Discussion

Treatment of (η^3-allyl)palladium chlorides [Pd(η^3-1-RC_3H_4)Cl]$_2$ (R = Ph, 1-naphthyl, $COSiMe_2Ph$, Me, $SiMe_3$) with ammonium hexafluorophosphate in the presence of 2,2-bis(2-(4(*R*)-substituted-1,3-oxazolinyl))propane gave the cationic complexes **1**–**5** in moderate to good yields.



1a, b: R^1 = Ph **a**: R^2 = Ph
2a, b: R^1 = 1-naphthyl **b**: R^2 = *i*-Pr
3a: R^1 = $COSiMe_2Ph$
4a: R^1 = Me
5a, b: R^1 = $SiMe_3$

For these complexes, there should be four isomers in principle, $\mathbf{d_1}$–$\mathbf{d_4}$ shown in Chart I. Generally in monosubstituted η^3-allyl complexes, syn isomers are more stable than anti isomers.[8] According to the selection of ligands, however, anti configuration can be predominant over syn

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(2) (a) Erickson, L. E.; Jones, G. S.; Blanchard, J. L.; Ahmed, K. J. *Inorg. Chem.* **1991**, *30*, 3147. (b) Fulwood, R.; Parker, D.; Ferguson, G.; Kaltner, B. *J. Organomet. Chem.* **1991**, *419*, 269. (c) Uccello-Barretta, G.; Lazzaroni, R.; Bertucci, C.; Salvadori, P. *Organometallics* **1987**, *6*, 550. (d) Consiglio, G.; Pregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345.

(3) (a) Faller, J. W.; DiVerdi, M. J.; John, J. A. *Tetrahedron Lett.* **1991**, *32*, 1271. (b) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161. (c) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893.

(4) (a) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174 and references therein. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

(5) (a) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. (b) Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663. (c) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. (d) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327. (e) Yamaguchi, M.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049. (f) Okada, Y.; Minami, T.; Sasaki, Y.; Umezu, Y.; Yamaguchi, M. *Tetrahedron Lett.* **1990**, *31*, 3903. (g) Hiroi, K.; Abe, J. *Tetrahedron Lett.* **1990**, *31*, 3623.

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(7) For the use of C_2-symmetric bis(oxazoline) ligands as chiral auxiliaries, see: Corey, E. J.; Ishihara, K. *Tetrahedron Lett.* **1992**, *33*, 6807. Lowenthal, R. E.; Masamune, S. *Tetrahedron Lett.* **1991**, *32*, 7373. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. See also: Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 430. Onishi, M.; Isagawa, K. *Inorg. Chim. Acta* **1991**, *179*, 155.

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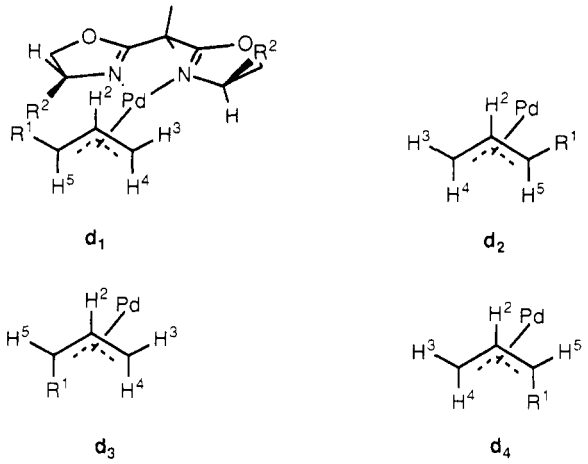
Chart I



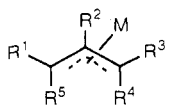
configuration.[10] Thus, it was necessary to examine the NMR spectra of each complex in detail in order to determine which is the most predominant isomer in $\mathbf{d_1}$–$\mathbf{d_4}$.

For the ^{1}H NMR spectra of **1–5**, the proton resonances for both allyl and bis(oxazoline) ligands were almost fully assigned from the peak intensities, coupling constants, ^{1}H–^{1}H COSY spectra (or homodecoupled spectra), and NOE spectra.[11] The COSY spectrum of **1a** is shown in Figure 1. ^{1}H NMR assignments for the allyl proton resonances are summarized in Table I.

All of the diastereomer ratios of the four isomers shown in Table II correspond to those of equilibrium mixtures. For complex **5a**, the isomerization between the diastereomers took place very slowly (see later).

Stereoselectivity in Coordination of the Syn-Selective Allyl Ligand. In the spectra of **1–3**, we observed the existence of only two diastereomers, which are attributable to syn isomers $\mathbf{d_1}$ and $\mathbf{d_2}$ from the coupling constants between H^2 and H^5 (Table I). Assignments of these resonances were reinforced by the observation of NOE between H^4 and H^5. We assumed that, in these complexes, the less crowded diastereomer, $\mathbf{d_1}$, was predominant, and this assumption was substantiated by examination of the resonances of the relevant bis(oxazoline) ligand protons shown in Figure 2.[12] As predicted from molecular models, the phenyl group of the allyl ligand caused large upfield shifts of one of the 4-hydrogen resonances (δ 2.83) in $\mathbf{d_1}$ and those of one of the isopropyl groups (δ 0.10, 0.35, 1.00) in $\mathbf{d_2}$.

(8) According to the accepted nomenclature for the planar allyl ligand, R^1 and R^3 are termed syn and R^4 and R^5 anti.[5a,9]



(9) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, p 385.

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(11) A general procedure for assigning each resonance is as follows. COSY and/or homodecoupling experiments enabled separation of most of the peaks into those of the allyl protons and those of the oxazoline ligand protons. Then measurements of the peak intensity allowed connection of a given set of allyl resonances to a set of oxazoline resonances in one isomer, and so on, though not all the minor isomer resonances could be observed. Finally, the chemical shifts of the allyl proton resonances and the magnitude of $^3J_{H-H}$ in the allyl framework,[9] as well as NOE experiments, unambiguously enabled full assignments of the allylic syn and anti protons.

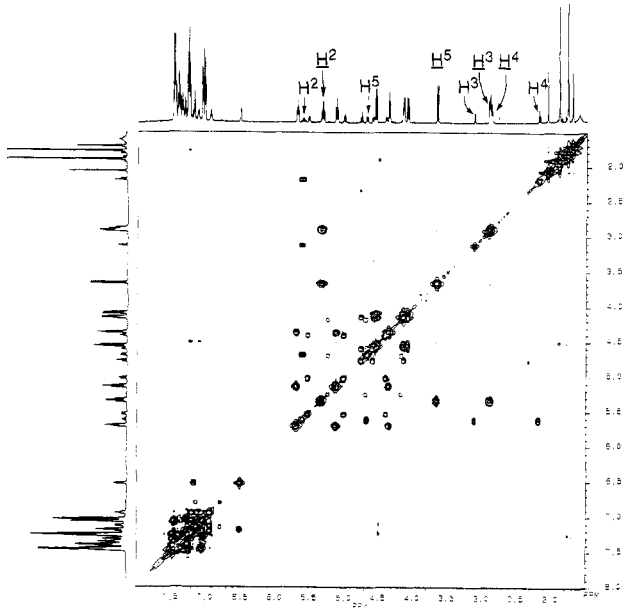


Figure 1. ^{1}H–^{1}H COSY spectrum of **1a**. Assignments of the underlined resonances belong to the major diastereomer.

In complexes **1–3**, the diastereoselectivity increased in the order R^1 = Ph < 1-naphthyl < $COSiMe_2Ph$ (see Table II), that is, in the sequence of the size of R^1. The bis(4-phenyloxazoline) complexes exhibited higher selectivity than the isopropyl derivatives.

Stereoselectivity in Coordination of the Syn and Anti Allyl Ligands. In η^3-crotyl complex **4a**, all the four diastereomers were observed (see Table I). Chemical shifts of the methyl groups (Table III) gave some important information for distinguishing between $\mathbf{d_1}$ and $\mathbf{d_2}$ (or $\mathbf{d_3}$ and $\mathbf{d_4}$). Namely, we took into account the anisotropy effect caused by the oxazoline phenyl group; of the two methyl resonance for $\mathbf{d_3}$ and $\mathbf{d_4}$, the one which appeared at the higher field (δ 0.06) was assigned to $\mathbf{d_3}$. Of the methyl resonances of the syn isomers, the one which resonated at the higher field was attributed to $\mathbf{d_2}$ for the same reason. The isomer ratio thus determined is shown in Table II. As in **1–3** discussed above, $\mathbf{d_1}$ is more stable than $\mathbf{d_2}$. Within the anti isomers, $\mathbf{d_4}$ in which the methyl group staggers the oxazoline phenyl, is more abundant than $\mathbf{d_3}$.

The trimethylsilyl-substituted η^3-allyl complexes, **5a** and **5b**, showed unusual structural features. The structural assignments shown in Tables I and III were made in a manner similar to that for the crotyl analog. However, the assignments for the anti isomers ($\mathbf{d_3}$ and $\mathbf{d_4}$) solely on the basis of $^3J_{H-H}$ values (~10 Hz) appeared somewhat ambiguous. The NOE results reinforced these assignments. Thus, in $\mathbf{d_4}$, irradiation at H^2 induced the enhancements of the resonances of H^3 and H^5 (Table IV). It was possible to distinguish between $\mathbf{d_3}$ and $\mathbf{d_4}$, because the resonances not only of H^4 and H^5 but also of the hydrogen belonging to the bis(oxazoline) ligand increased upon irradiating the Me_3Si protons (Table IV). Furthermore, in the bis(4-phenyloxazoline) complex, **5a**, the resonances attributable to $SiMe_3$ and H^3 in $\mathbf{d_3}$ that are thought to be close to the phenyl groups exhibited larger upfield shifts than the corresponding shifts in $\mathbf{d_4}$. Res-

(12) The connectivity of the proton resonance at δ 2.83 with those at δ 0.43, 0.69, and 1.78 (as well as one at δ 4.40 with those at δ 0.77, 0.97, and 2.10) as substituents of the common carbon atom was unambiguously established by COSY experiments.

Table I. Relevant ^{1}H NMR Data for [Pd(bis(oxazoline))(η^3-$R^1C_3H_4$)](PF$_6$) Complexes[a]

			$\delta(^1H)$ ($^3J_{H-H}$ (Hz))															
			d_1				**d_2**				**d_3**				**d_4**			
complex	R^1	R^2	H^2	H^3	H^4	H^5	H^2	H^3	H^4	H^5	H^2	H^3	H^4	H^5	H^2	H^3	H^4	H^5
1a	Ph	Ph	5.33	2.94 (7.2)	2.92 (12)	3.65 (11)	5.61	3.12 (7.0)	2.19 (12)	4.70 (12)		n.d.				n.d.		
1b		*i*-Pr	6.00	4.07 (7.1)	3.56 (13)	4.53 (11)	6.14	3.96 (7.1)	3.22 (12)	4.96 (12)		n.d.				n.d.		
2a	1-naphthyl	Ph	5.38	3.04 (7.7)	3.04 (12)	4.37 (11)	5.79	3.23 (7.2)	2.32 (12)	5.28 (12)		n.d.				n.d.		
2b		*i*-Pr	6.18	4.15 (7.0)	3.80 (13)	5.32 (11)	6.42	4.12 (7.0)	3.41 (12)	5.56 (12)		n.d.				n.d.		
3a	$COSiMe_2Ph$	Ph		3.24 (7.0)	3.17 (13)	3.07 (11)	...[b]	...[b]	2.42 (12)	3.83 (12)		n.d.				n.d.		
4a	Me	Ph	4.84	2.66 (7.0)	2.46 (13)	2.76 (11)	4.84	3.01 (6.8)	1.74[c] (12)	3.78 (12)	4.84	2.73 (7.7)	2.78 (13)	4.44 (8.2)	4.69	3.38 (7.3)	1.98 (13)	3.57 (7.7)
5a	$SiMe_3$	Ph	4.77	2.84 (6.8)	2.48 (13)	2.06 (14)		n.d.			5.65	2.80 (7.2)	2.58 (12)	3.94 (10)	5.23	3.39 (7.3)	1.93 (13)	2.93 (10)
5b		*i*-Pr	5.53	4.37 (7.1)	3.44 (13)	3.15 (14)		n.d.				n.d.			6.13	3.98 (7.0)	3.04 (12)	4.05 (10)

[a] In $CDCl_3$. [b] Not assignable. [c] Overlapped with the resonance of the methyl proton of the bis(oxazoline) ligand and assigned by an NOE difference spectrum irradiating at H^3.

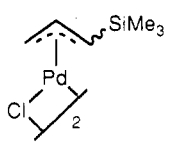
Table II. Diastereomer Ratios of [Pd(bis(oxazoline))(η^3-$R^1C_3H_4$)](PF$_6$) Complexes[a]

complex	R^1	R^2	$d_1/d_2/d_3/d_4$
1a	Ph	Ph	78/22/0/0
1b		*i*-Pr	73/27/0/0
2a	1-naphthyl	Ph	87/13/0/0
2b		*i*-Pr	81/19/0/0
3a	$COSiMe_2Ph$	Ph	93/7/0/0
4a	Me	Ph	47/17/12/24
5a	$SiMe_3$	Ph	~1/0/~1/98
5b		*i*-Pr	5/0/0/95

[a] In $CDCl_3$.

onances of H^4 and H^5 in $\mathbf{d_4}$ appeared at higher field than the corresponding shifts in $\mathbf{d_3}$ for the same reason.

It is of particular interest to note that the anti diastereomers, $\mathbf{d_4}$, are highly predominant in 95–98% selectivities. In (η^3-1-(trimethylsilyl)allyl)palladium chloride (**6**), i.e. the



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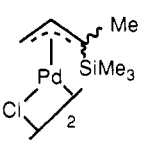

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precursor to **5**, the syn isomer was predominant over the anti (syn/anti = 73/27).[13,14] In contrast, in (η^3-1-methyl-1-(trimethylsilyl)allyl)palladium chloride (**7**), the order was reversed (syn/anti = 18/82).[15] It has been suggested that the trimethylsilyl group at the anti position does not exert a severe steric hindrance on the metal because of the long Si–C bond length.[15] Alternatively, the values of $^3J_{H-H}$ for the anti isomer (10 Hz), which are somewhat larger than normal values for coupling between H^2 and syn hydrogens, suggest occurrence of considerable distortion at the allyl carbon bearing the silyl group so as to relieve the repulsion with the metal. On the other hand, the trimethylsilyl group at the syn position would experience extremely severe hindrance by the oxazoline ligand, which would be difficult to diminish upon a distortion at the allylic carbon.

Isomerization of 5. The isomer ratio of **5a** discussed above is the thermodynamic one which was attained after the complex was allowed to stand at room temperature in $CDCl_3$ for long periods (≥2 days). Such a slow interconversion was not observed for other complexes.

Figure 3 shows the isomerization of the complex starting from a sample prepared by treatment of **6** (almost syn isomer[16]) with ammonium hexafluorophosphate in the presence of the bis(4-phenyloxazoline), followed by immediate removal of the solvent under reduced pressure and dissolution of the product in $CDCl_3$. By this method, a 46/11/44 mixture of $\mathbf{d_1}$, $\mathbf{d_3}$, and $\mathbf{d_4}$ was obtained initially. Then $\mathbf{d_4}$ increased gradually to 98% and $\mathbf{d_1}$ decreased nearly to 1%, but the behavior of the anti isomer $\mathbf{d_3}$ was somewhat irregular. Thus, the amount of $\mathbf{d_3}$ slightly increased in the early stage (~7 h) and then decreased as fast as $\mathbf{d_1}$.

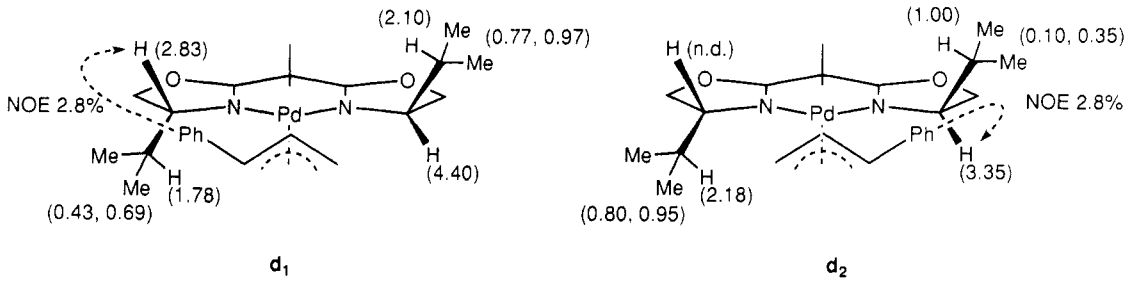
Scheme I shows the interconversion of each diastereomer proceeding via an η^1-allylic intermediate. The initial increase of $\mathbf{d_3}$ in Figure 3 cannot be ascribed to an equilibration between $\mathbf{d_3}$ and $\mathbf{d_4}$, because the stability of $\mathbf{d_3}$ at equilibrium is much lower than that of $\mathbf{d_4}$. The result is most probably due to the fast equilibration between $\mathbf{d_1}$ and $\mathbf{d_3}$ having comparable thermodynamic stability through the most unstable diastereomer $\mathbf{d_2}$, which was never detected spectrally.

In conclusion, we found that the 4,4′-disubstituted (bis(oxazoline))palladium complexes enable highly stereoselective coordination of monosubstituted η^3-allyl groups. In each complex, the major diastereomer was the less crowded syn complex, excepting the trimethylsilyl derivatives, in which the less crowded anti complexes were almost exclusively dominant.

Experimental Section

Most of commercially available reagents were used without further purification. 2,2-Bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane and its isopropyl analog were prepared by the method of Corey.[17] (η^3-1-Phenylallyl)palladium chloride, [Pd(η^3-1-PhC_3H_4)Cl]$_2$, and its 1-naphthyl and methyl analogs were

(13) Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S. *Organometallics* **1991**, *10*, 3813.
(14) Ogoshi, S.; Yoshida, W.; Ohe, K.; Chatani, N.; Murai, S. *Organometallics* **1993**, *12*, 578.
(15) Ohta, T.; Hosokawa, T.; Murahashi, S.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080.
(16) Crystallization from CH_2Cl_2–*n*-hexane gave the almost exclusively syn isomer of **6** from the syn–anti mixture.
(17) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.



d_1 d_2

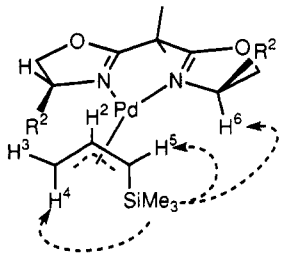
Figure 2. Conformations of **1b** with representative chemical shifts (parentheses) and NOE results.

Table III. δ(¹H) for Me and Me_3Si Groups in 4a, 5a, and 5b[a]

			δ(¹H)			
complex	R^1	R^2	d_1	d_2	d_3	d_4
4a	Me	Ph	1.16	0.79	0.06	0.74
5a	Me_3Si	Ph	0.13	n.d.	−0.32	−0.12
5b	Me_3Si	*i*-Pr	0.23	n.d.	n.d.	0.20

[a] In $CDCl_3$.

Table IV. Nuclear Overhauser Enhancement in 5



		irradiated	NOE (%)			
complex	R^2	group	H^3	H^4	H^5	H^6
5a	Ph	H^2	8.3	...[a]	11	0
		$SiMe_3$	0	...[a]	3.2	4.7
5b	*i*-Pr	H^2	6.6	0	9.5	0
		$SiMe_3$	0	3.8	3.1	4.5

[a] Not evaluated due to overlap with another resonance.

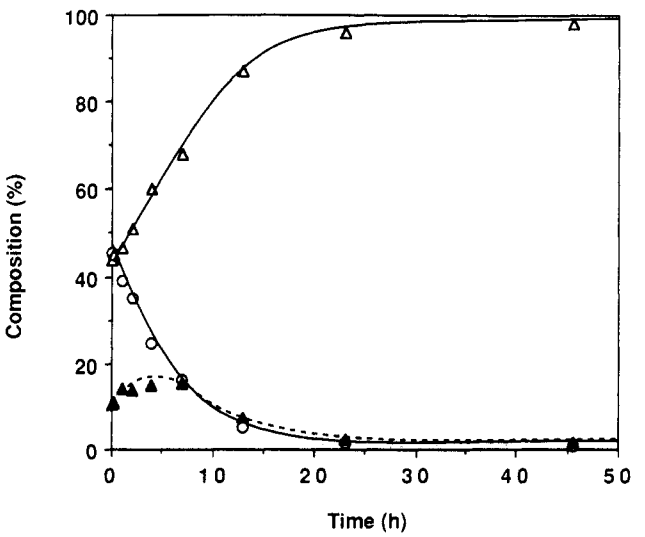
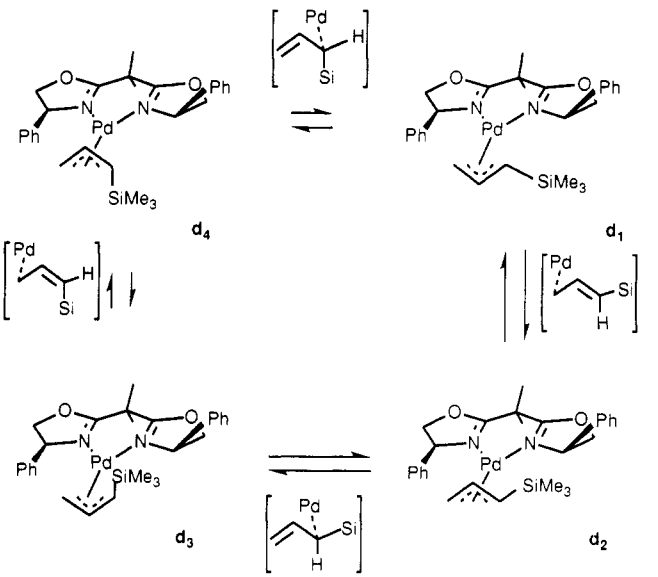


Figure 3. Conversion/time plots for isomerization of **5a** at 25 °C in $CDCl_3$: d_1 (○); d_3 (▲); d_4 (△).

prepared from the corresponding allylic chlorides and $PdCl_2$ in aqueous methanol with carbon monoxide in the presence of LiCl.[18] Preparation of (η^3-1-((dimethylphenylsilyl)carbonyl)-allyl)palladium chloride was described in the literature.[14] ¹H NMR spectra were obtained on JEOL GSX-400 and Bruker

(18) Dent, W. I.; Long, R.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1585.

Scheme I



AM600 spectrometers. The chemical shifts were referenced to $CHCl_3$ (δ 7.27) in $CDCl_3$.

(η^3-1-Phenylallyl)(2,2-bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (1a). To a solution of 175 mg (0.338 mmol) of (η^3-1-phenylallyl)palladium chloride, $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)Cl]_2$, in 20 mL of CH_2Cl_2 and acetone (1/1) were added 249 mg (0.745 mmol) of 2,2-bis(2-(4(*R*)-phenyl-4,5-oxazolinyl))propane in 10 mL of the same solvent and 1.10 g (6.75 mmol) of ammonium hexafluorophosphate in 15 mL of acetone at 0 °C. The solvent was removed under reduced pressure, CH_2Cl_2 was added, and the mixture was filtered. The filtrate was evaporated, and the residual solids were recrystallized with ethanol–hexane to give 327 mg (0.465 mmol, 69%) of pale yellow microcrystals. These were washed with hexane; mp 90–97 °C dec. Anal. Calcd for $C_{30}H_{31}N_2O_2F_6PPd$: C, 51.26; H, 4.45; N, 3.96. Found: C, 51.09; H, 4.63; N, 3.96.

(η^3-1-Phenylallyl)(2,2-bis(2-(4(*R*)-isopropyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (1b) was prepared by the same procedure as described above from 0.485 mmol of $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)Cl]_2$ as pale yellow microcrystals (0.641 mmol, 66%); mp 156–159 °C dec. Anal. Calcd for $C_{24}H_{35}N_2O_2F_6PPd$: C, 45.40; H, 5.56; N, 4.41. Found: C, 45.30; H, 5.55; N, 4.35.

(η^3-1-(1-Naphthyl)allyl)(2,2-bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (2a) was prepared similarly from 0.163 mmol of $[Pd(\eta^3\text{-}1\text{-}(C_{10}H_7)C_3H_4)Cl]_2$ as pale yellow microcrystals (0.260 mmol, 80%); mp 105–111 °C dec. Anal. Calcd for $C_{34}H_{33}N_2O_2F_6PPd$: C, 54.23; H, 4.42; N, 3.72. Found: C, 54.59; H, 4.71; N, 3.76.

(η^3-1-(1-Naphthyl)allyl)(2,2-bis(2-(4(*R*)-isopropyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (2b) was prepared similarly from 0.185 mmol of $[Pd(\eta^3\text{-}1\text{-}(C_{10}H_7)C_3H_4)Cl]_2$ as pale yellow microcrystals (0.341 mmol, 93%); mp 155–160 °C dec. Anal. Calcd for $C_{28}H_{37}N_2O_2F_6PPd$: C, 49.10; H, 5.44; N, 4.09. Found: C, 49.23; H, 5.60; N, 4.11.

(η^3-1-((Dimethylphenylsilyl)carbonyl)allyl)(2,2-bis(2-(4(*R*)-isopropyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (3a) was prepared similarly from 0.116 mmol of $[Pd(\eta^3\text{-}1\text{-}(Me_2PhSiCO)C_3H_4)Cl]_2$ as yellow microcrystals (0.167 mmol, 72%); mp 81–86 °C dec. Anal. Calcd for $C_{33}H_{37}N_2O_3F_6PPdSi$: C, 50.23; H, 4.73; N, 3.55. Found: C, 50.24; H, 4.95; N, 3.62.

(η^3-1-Methylallyl)(2,2-bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (4a). This preparation was performed in the same manner as for 1–3 from 0.300 mmol of $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)Cl]_2$. A CH_2Cl_2 extract was obtained from the reaction mixture, and removal of the solvent under reduced pressure gave the white solid **4a** (0.413 mmol, 69%); mp 76–78 °C. Anal. Calcd for $C_{25}H_{29}N_2O_2F_6PPd$: C, 46.85; H, 4.56; N, 4.37. Found: C, 46.52; H, 4.70; N, 4.52.

(η^3-1-(Trimethylsilyl)allyl)(2,2-bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (5a) was prepared similarly from 0.098 mmol of **6**.[14] Recrystallization from ethanol–hexane overnight gave white microcrystals which were composed of $\mathbf{d_1}$, $\mathbf{d_3}$, and $\mathbf{d_4}$ isomers in a ratio of 29/9/62 (0.125 mmol, 64%); mp 165–185 °C dec. Anal. Calcd for $C_{27}H_{35}N_2O_2F_6PPdSi$: C, 46.39; H, 5.05; N, 4.01. Found: C, 46.44; H, 5.04; N, 4.08.

(η^3-1-(Trimethylsilyl)allyl)(2,2-bis(2-(4(*R*)-isopropyl-1,3-oxazolinyl))propane)palladium Hexafluorophosphate (5b) was prepared similarly from 0.098 mmol of **6** as colorless prisms which were composed of $\mathbf{d_1}$ and $\mathbf{d_4}$ isomers in a ratio of 5/95 (0.082 mmol, 42%); mp 105 °C dec. Anal. Calcd for $C_{21}H_{39}N_2O_2F_6PPdSi$: C, 39.97; H, 6.23; N, 4.44. Found: C, 39.77; H, 6.29; N, 4.41. The isomer ratio did not change in $CDCl_3$ at room temperature.

Isomerization of 5a. To a solution of 15 mg (0.029 mmol) of **6** in 1.2 mL of CH_2Cl_2 and acetone (1/1) were added 20 mg (0.060 mmol) of 2,2-bis(2-(4(*R*)-phenyl-1,3-oxazolinyl))propane in 1 mL of the same solvent and 50 mg (0.31 mmol) of ammonium hexafluorophosphate in 1 mL of acetone at 0 °C. The solvent was removed under reduced pressure, and $CDCl_3$ was added to the residue. The mixture was filtered, and the filtrate was transferred into an NMR tube together with 6 μL of ethylbenzene as an internal standard. The isomer ratio ($\mathbf{d_1}/\mathbf{d_3}/\mathbf{d_4}$) was monitored by ^1H NMR spectroscopy.

NOE difference experiments were performed as sequences consisting of two spectra in which the first was obtained off-resonance and the second was obtained with irradiation at the selected resonance (32–128 scans) on a JEOL GSX-400 spectrometer at 26 °C in $CDCl_3$. The acquisition time was 2.7 s, and the pulse delay was 5.3 s. A difference FID was transformed into a frequency-domain spectrum.

For complex **1b**, irradiating at the ortho hydrogen of the phenyl group induced enhancements of the resonances of H^2 (14%), H^5 (10%), the one at δ 2.83 (2.8%), and the meta hydrogen of the phenyl group (δ 7.38, 32%) in the major diastereomer ($\mathbf{d_1}$) and of H^2 (18%), H^5 (14%), the one at δ 3.35 (2.8%), and the meta hydrogen (δ 7.35, 27%) in the minor ($\mathbf{d_2}$). For complex **5**, the selected data are listed on Table IV.

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